IUPAC-NIST Solubility Data Series 70. Solubility of Gases in Glassy Polymers

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Solubility of gases in polymers is an important property of polymeric materials relevant to many practical applications. Sorption of small molecules in polymers is a fundamental concern in such areas as food packaging, beverage storage, and polymer processing. However, by far the main interest in the solubility of gases in polymers, and especially in glassy polymers, is related to development of novel advanced materials for gas separation membranes. This is because the concentration gradient of a dissolved gas is the driving force of membrane processes. Development of these novel separation methods resulted in a rapid accumulation, in the recent literature, of thermodynamic data related to the solubility of gases in polymers at different temperatures and pressures. Polymers can be regarded as special cases of media intermediate between liquids and solids. As a consequence, modeling of gas sorption in polymers is very difficult and

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presents a permanent challenge to theoreticians and experimenters. The collection and critical evaluation of solubility data for various gas–polymer systems is relevant to both practical aspects of polymer applications and to fundamental studies of polymer behavior. This volume of the IUPAC-NIST Solubility Data Series summarizes the compilations and critical evaluations of the data on solubility of gases in glassy polymers. It is implied in this edition that ''gases'' are the components that are either permanent gases (supercitical fluids) or have saturated vapor pressure more than 1 atm at ambient conditions (298 K). The polymeric components of compilations and critical evaluations are primarily high molecular mass, amorphous, linear (noncross-linked) compounds that have the glass transition temperatures above ambient temperature. The data for each gas–polymer system have been evaluated, if the results of at least three independent and reliable studies have been reported. Where the data of sufficient accuracy and reliability are available, values are recommended, and in some cases smoothing equations are given to represent variations of solubility with changes in gas pressure and temperature. Referenced works are presented in the standard IUPAC-NIST Solubility Data Series format. Depending on the gas–polymer system, reported data are given in tabular form or in the form of sorption isotherms. The data included in the volume comprise solubilities of 30 different gases in more than 80 primarily amorphous homo and copolymers. Where available, the compilation or critical evaluation sheets include enthalpies of sorption and parameters for sorption isotherms. Throughout the volume, SI conventions have been employed as the customary units in addition to the units used in original publications.

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1. Preface

The solubility of gases in polymers is an important property of polymeric materials relevant to many practical applications. In addition, information on the solubility of gases, its dependence on temperature, pressure, and pretreatment of polymer are indicative of polymer structure and mechanism of gas sorption and diffusion in polymers. The shape of solubility isotherms can indicate behavior at the molecular level. Sorption of small molecules in polymers is a fundamental concern in such areas as packaging and polymer processing. Dissolution of gases in polymers, especially at high pressure, takes place in many industrial processes and data on the solubility of gases are required in diverse and important applications. Examples include the dissolution of ethene and other gases in the process of high pressure polymerization of ethene, gas dissolution in injection molding processes, and postreactor polymer processing.

However, the main interest in the solubility of gases in polymers is due to the development of novel advanced materials for gas separation membranes. The driving force in gas transport through such nonporous polymeric membranes is the gradient of concentration of diffusing molecules across the membrane. Therefore, the solubility, the form of sorption, isotherms, and the values of their parameters are of utmost importance for understanding sorption and transport of gases and development of better gas separation processes. An interesting manifestation of this tendency is that 90% of the data available today on gas solubility in polymers and sorption thermodynamics were obtained during the last 10–15 yr, and these years were marked by important advances in the development of membrane gas separation processes.

This volume in the Solubility Data Series contains tabulated collections and critical evaluations of original data for the solubility of gases in glassy polymers. A later volume will contain compiled and evaluated data for the solubility of gases in rubbery and semicrystalline polymers as well as updated data for crystalline polymers. In some cases, the published data include the solubility at temperatures higher than the glass transition temperature of a polymer that is glassy under ambient conditions, for example polystyrene at 373–473 K. In such cases the editors preferred not to split the solubility data between two volumes and included corresponding compilation sheets in this volume.

The chemical structure of the repeat units of polymers was accepted as the basis for organizing the material within this volume. First, carbon-chain polymers are considered followed by heterochain polymers. Each polymer studied in a particular published work has been given a separate compilation sheet. Data from the same published work for the dissolution of different gases in the same polymer have been entered in the same compilation sheet. Gases are considered in sequences of increased complexity from monatomic to diatomic and so on. If several compilation sheets are available for the same polymer–gas system, the material is arranged in chronological order. Enthalpies of solution are also reported where available.

Abundant data that are available in the literature on gas solubility in polymers can be divided into two groups: the data based on direct measurements using volumetric, gravimetric, chromatographic or other methods; and the data acquired via an indirect way using the equation $S = P/D$, where S is the solubility coefficient, and P and D are the gas permeability and diffusion coefficients, respectively. Although in many cases the values obtained using both approaches are in reasonable agreement, the authors of the present volume have not compiled solubility data obtained by an indirect method because these data are less reliable.

Critical evaluations were prepared only in those cases where:

(1) two or more papers were available for the given gas–polymer system;
(2) the data corresponded to overlapping ranges of variation of pressure and/or temperature. In only a few cases, however, has there been a sufficient number of detailed studies to enable the evaluator to recommend a set of solubility values.

The data were gathered from a search of the chemical literature from the first years of this century to the first part of 1991.

The editors would like to acknowledge the help and advice from several fellow members of the IUPAC Commission on Solubility Data and in particular Professor Larry Clever (Emory University, USA) and Dr. Peter Fogg (U.K.). Enormous help of S. McFadzean and Marielle Lorusso in the final part of the preparation of the manuscript is also acknowledged and much appreciated. Professor D. R. Paul and Professor W. J. Koros, from The University of Texas at Austin, kindly provided us with the reprints and preprints of their numerous papers. This greatly facilitated our work on compilation and critical evaluation of data.

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2. Introduction to the Solubility Data Series. The Solubility of Gases in Polymers

The Solubility Data Project aims to make a comprehensive search of the literature for data on the solubility of gases, liquids, and solids in liquids. Polymers can be regarded as a special case of media intermediate by their properties between liquids and solids. The data for each system are evaluated, and where data of sufficient accuracy and reliability are available, values are recommended and in some cases a smoothing equation is suggested to represent the variation of solubility with gas pressure and/or temperature. In the case of polymers, the correlations of the solubility with some parameters of gases can also be given. A text presenting an evaluation and recommended values and the compiled data sheets are published on consecutive pages.

Definition of Gas Solubility

The distinction between solubilities of gases in liquids (polymers) and vapor–liquid equilibrium is arbitrary. It is generally accepted that the equilibrium set up between a polymer and a typical gas as argon at 298 K, i.e., above its critical temperature, is gas–liquid solubility, where as the equilibrium set up at the same temperature between the same polymer and *n*-butane is an example of vapor–liquid equilibrium. In this volume, we have taken a fairly liberal view that is in line with the general policy of all the volumes of the Solubility Data Series.

We defined gases as the compounds having vapor pressure more than 1 atm at the temperature 298 K, or having the normal boiling point of 298 K or above. So, e.g., the equilibrium solubility of 2,2-dimethylpropane (neo-pentane) was included whereas the solubility of *n*-pentane was not. The solubility of the vapor of the compounds that are liquid at 298 K will be considered in a subsequent volume of Solubility Data Series.

It is much more difficult to define adequately polymers as solvents. A transition from low molecular mass compounds to high polymers proceeds continuously, and establishing a boundary between these two kinds of chemical objects is always arbitrary. However, help in this essentially tentative choice can come if we bear in mind the fact that studies of solubility in polymers stemmed from many practical applications of high polymers found as construction, barrier, or packaging materials, membranes, etc. In all these cases polymers having molecular mass higher than 20,000–30,000 are used. Another important feature of polymers as solvents is that high molecular mass compounds in a vast majority of cases exist as mixtures of different sorts of molecules having different number of repeat units (polymer homologues), concentration of branchings, cross-links, etc. Additionally, in many cases polymer samples contain some residual solvents, traces of catalysts, curing agents, plasticizers and other additives or impurities. So in contrast to the contents of other volumes, dealing with solubility of gases in liquids, here the data reported characterize solubility in complex, sometimes poorly defined, and by no means pure chemicals. Another problem is related to the fact that glassy polymers are quasiequilibrium objects, since the relaxation processes are too slow at the temperatures below the glass transition temperature T_g. Hence, all the information obtained for solubility of gases in glassy polymers is, strictly speaking, nonequilibrium. Well known manifestations of this phenomenon are prehistory effect on solubility and the parameters of sorption isotherms, the effects of annealing, importance of the protocol of measuring the solubilities of different gases at high pressure, and so on. All this causes the difficulties in comparison of the results of independent studies and hampers the selection of the recommended values in Critical Evaluations.

Units and Quantities

The solubility of gases in polymers is of interest to different fields of polymer science and technology, as well as to other disciplines. The data have been acquired during the last 70 yr in various laboratories by means of diverse instruments. Therefore a variety of ways for reporting gas solubility has been used in the primary literature, and inevitably sometimes, because of insufficient available information, it has been necessary to use several quantities in the compiled tables and plots. Where possible, the gas solubility has been quoted as a quantity of dissolved gas reduced to standard conditions (pressure 1 atm, temperature 273.2 K) or cm^3(STP) per 1 cm^3 of polymer. Other quantities of the solubility of gases in polymers, which are in use, will be considered below. The units of pressure used are Pascals, atmospheres, bars, and millimeters or centimeters of mercury. Temperature are reported in Kelvin. Enthalpies of solution data are given in kJ mol^{-1}.

Evaluation and Compilation

The solubility of relatively few systems is known with sufficient accuracy to enable recommended values to be advanced. This is especially true for the solubility in polymers, as polymer samples studied by different authors rarely coincide (different manufacturers of the specimens, variation in molecular mass or molecular mass distribution, etc.). Although a considerable number of systems have been studied by at least two researchers, the range of pressure and/or temperature is often different, thus preventing a meaningful comparison of the data. Occasionally, one has only to guess why several groups of workers sometimes obtain very different results under the same conditions, although all the data reported seem to be flawless or, at least, plausible and internally consistent. In such cases, sometimes an incorrect assessment has been given.

Bearing in mind the mentioned peculiarities of gas–polymer systems, and especially those concerning glassy polymers, Critical Evaluations were prepared mainly for the systems where three or more sources reported solubility data. In contrast to the policy accepted by the evaluators of other volumes of Solubility Data Series, the present authors, in some cases, included the correlations of the solubility coefficients or the parameters of sorption isotherms with different characteristics of gases that allow to estimate the properties for other gas–polymer systems.

Sources and Purity of Materials

The purity of the gases has been quoted in the compiled sheets where given in the original publications. Contrary to what is usually accepted for solubility of gases in liquids, even small impurities of heavier gas components can be a source of error in reported gas solubility values. However, since a purity of gases is adequately reported in most cases, appropriate corrections can be introduced if necessary. It is much more difficult to assess (or define) the purity of polymers. In many cases, the only information available in the papers were the name of producing company and a trademark of the polymer material. The properties more often quoted in the publications are a density and a glass transition temperature. The procedure of the preparation and/or pretreatment of the films is of utmost importance, and, where possible, are also quoted in data sheets.

Apparatus and Procedures

In the compiled data sheets, some key points are made of the instruments for solubility measurement and procedure used. There are several books or papers where the experimental methods of the determination of gas solubility in polymers are considered in more length. They are given in Refs. 1–9.

Methods of Expressing Gas Solubilities

Because gas solubilities have been determined by means of different methods, they have been expressed in a variety of ways. Sometimes solubility is reported as C_{mw}(mol/g) or in number of moles of a gas dissolved in a unit of mass of polymer. When determined using a gravimetric method, solubility is given as C_{ww}(g/g) as a quantity of gas in grams per 1 g of polymer. Volumetric methods of the determination of solubility allow to measure it as C_{vw}(cm^3(STP)/g) or as a volume of gas reduced to the standard conditions dissolved in 1 g of polymer. However, the most frequently used unit for the solubility is C_{vv} or the volume of gas reduced to the standard conditions dissolved in 1 cm^3 of the polymer.

When a polymer sample is exposed to high pressure gas, its volume is decreased *n* a fraction determined by its PVT behavior. However, these effects are important only at very high pressure, and in solubility measurements have been introduced very seldom, if ever. Much more relevant are the effects of swelling or dilation of polymer samples in contact with high or even medium pressure gas. Indeed, the dilation isotherms have been reported together with sorption isotherms in many papers. Therefore, the corrections, taking into account the changes in the solubility C_{vv} owing to dilation, can be introduced. However, this was not done in most cases, mainly because a magnitude of such corrections is minor, as a rule, in comparison with the accuracy of the determination of gas solubility. Hence, in majority of the cases the C_{vv} values characterize the solubility of gas in cm^3(STP) per cm^3 of a pure polymer.

In some very rare cases solubility is expressed as the standard volume of gas per repeat unit of the polymer (expressed in g moles). All these quantities are interrelated.

$$C_{ww}=MC_{mw},$$

where M is the molecular mass of the gas

$$C_{vw}=22\,146C_{mw}=22\,416M/C_{ww}.$$

If we neglect the swelling of polymer in the process of sorption:

$$C_{vv}=C_{vw}\rho,$$

where ρ is the density of the polymer at the temperature of measurement.

Sorption Isotherms

Contrary to gas solubilities in common liquids, the solubility of gases in polymers is a nonlinear function of pressure if the latter is changed in sufficiently wide range. So a standard way of presenting solubility at a certain temperature is giving, in numerical or, more often, graphical form the dependence of solubility of pressure, or sorption isotherms. It is traditional to distinguish sorption and desorption isotherms. The former are obtained in a regime of growing pressure, the latter when a part of sorbed gas is allowed to desorb from the sample. When sorption is studied under conditions of full equilibrium, i.e., above the glass transition temperature, the sorption and desorption isotherms coincide. If the system is departed from the equilibrium, sorption hysteresis is observed at higher pressures or for highly sorbed gases. Desorption isotherms in glassy polymers lie always above sorption isotherms owing to the conditioning effect caused by high pressure gas. Usually, the model parameters are reported for sorption isotherms.

At sufficiently low pressure the isotherms of all the systems can be reduced to directly proportional dependence

$$C=Sp,$$

where C is the solubility expressed in either way discussed above, p is pressure, and S is the solubility coefficient. S is the reciprocal value of Henry's coefficient H defined by the equation of Henry's law

$$p=HC.$$

If S is expressed in cm^3(STP) per cm^3 of polymer per atm, it coincides with the Bunsen coefficient defined as the volume of gas reduced to 273.2 K and 1 atm pressure which is dissolved in a unit volume of solvent (at the temperature of measurement). In gas chromatographic determination of solubility, one obtains experimentally the mass fraction Henry's coefficient

$$H_1=p_1/(m_1/m_2),$$

where p_1 is the partial pressure of gas, m_1 is the mass of gas, and m_2 is the mass of polymer, which are in equilibrium. When passing on to the volume of gas and assuming ideal behavior of the gas one obtains

$$S=1/H_1=22\,416\rho_2/M_1,$$

where ρ_2 is the density of polymer and M_1 is the molecular mass of the gas. When p and the concentration of dissolved gas are increased, deviations from Henry's law isotherms are observed. Positive deviations, or sorption isotherms convex to the pressure axis, are characteristic for polymers at temperatures above their glass transition temperature. Under such conditions, a satisfactory description of the main part of the systems gas–high molecular weight solvent can be achieved by using Flory–Huggins equation to describe sorption isotherms[10]

$$\ln a_1=\ln f_1+f_2+c_{12}f_{22},$$

where a_1 is the activity of gas phase, f is the volume fraction, indices 1 and 2 refer to the dissolved gas and polymer, and c_{12} is the Flory–Huggins parameter characterizing the noncombinatoric contribution into the free energy of the gas–polymer system. For vapors a good approximation of the activity is the ratio p/p_0, where p is the pressure of the gas and po is its saturated vapor pressure at the temperature of measurement. In the Flory–Huggins equation the f_1 values serve as the measure of gas solubility. The volume fractions f_1 and f_2 are interrelated as $f_1+f_2=1$. An inconvenient feature of this transcendental equation is that it cannot be solved in a straightforward manner to express the solubility f_1 as a function of activity or pressure.

Negative deviations from Henry's law or the isotherms concave to the pressure axis are characteristic for sorption of gases in glassy polymers, and in the vast majority of the cases are described by the dual mode sorption (or Henry+Langmuir) model[11,12]

$$C=C_D+C_H=k_Dp+C'_Hbp/(1+bp),$$

where k_D (cm^3(STP)/cm^3 atm) is Henry's law solubility coefficient, C'_H (cm^3(STP)/cm^3) is Langmuir's sorption capacity parameter, and b (atm^{-1}) is the affinity parameter. The initial slope of an isotherm is characterized by the equation

$$C=(k_D+C'_Hb)p.$$

so the value $k_D+C'_Hb$ is often considered as an apparent solubility coefficient in glassy polymers. At higher pressure $p \gg 1/b$ the isotherm approaches the asymptote described by the linear equation

$$C=C'_H+k_Dp.$$

A transition from low pressure to high pressure range occurs at $p=1/b$, where two asymptotes intersect. However, the b value for a certain gas–polymer system is unknown in advance, whereas the experimental range of pressure is often limited. Therefore, graphical determination of three parameters of the dual mode sorption model is quite unreliable. Usually, nonlinear least squares procedures are employed in the simultaneous search for three model parameters or, otherwise, one can be obtained from an independent source, while two others are found by linear least squares method. The dual mode sorption model is not a single way to describe the isotherms concave to the pressure axis. Several other models and equations have been proposed to fit satisfactorily the experimental data. We shall consider here some of them, which contain preferably a minimum number of parameters and do not require for their use knowledge of different properties of pure polymer and the gas–polymer system. A discussion of more sophisticated models and their physical basis can be found in Ref. 13.

Freundlich isotherm might offer an equally acceptable way of analyzing the experimental data. The isotherm can be used in either this

$$C=kpn,$$

or this form

$$C=ap+kpn,$$

where $n<1$.

Other types of two terms (multiparameter) models have been discussed in the literature, among them the Langmuir1+Langmuir2 type[15]

$$C=b_1C'_{H1}p/(1+b_1p)+b_2C'_{H2}p/(1+b_2p).$$

Another model that was proposed to fit this type of sorption isotherms is the so called matrix model[16]

$$C=S_0\exp(-aC)p.$$

The extension of the gas pressure range studied resulted in finding at higher pressures a new form of the isotherm: at a certain pressure (p_g) and solute's concentration (C_g) the isotherm suffers an inflection; above pg it becomes linear or convex to the pressure axis. This was explained by plasticization induced by sorbed gas and a corresponding decrease in the glass transition temperature T_g from the T_{g0} value characteristic for pure polymer to the experimental temperature *T*. Several models were proposed to explain this behavior and describe this more complex form of the curve. Mauze–Stern isotherm:[17]

$$C=[k_D\exp(sC)]p+C'_Hbp/(1+bp).$$

Paul's *et al.* isotherm:[18]

$$C=k_Dp+C'_{H0}[(T_g-T)/(T_{g0}-T)]bp/(1+bp).$$

Here and in subsequent equations, T_g as a function of C can be estimated from the relation of Chow.[19] Kamiya's *et al.* isotherm:[20]

$$C=C_D+C_H=k_Dp+\{C'_{H0}bp/(1+bp)\}(1-C^*/C_g),$$

where $C^*=C_D+fC_H$ with $0<f<1$. All these models are based on the dual mode sorption model and differ from it by the introduction of various corrections in order to take into account plasticization and a more complex form of an isotherm. However, the same shape of the curve can be described by an entirely different form of equation. Some of the examples will be given below. Stern's *et al.* equation:[21]

$$C=S_0p\exp[AT_g(T_g-T_{g0})(T_{g0}-T)/T_{g0}^2],$$

and Laatikainen–Lindstrom's equation:[22]

$$C=Aap/\{(1-bp)[1+(a+b)p]\}.$$

Several alternative macroscopic and microscopic models having more sound physical basis have been proposed (see e.g., Refs. 23–26). However, much information (usually unavailable) about the polymer, sorbed gas, and gas–polymer interaction is required to use them in fitting or predicting the gas solubility in polymers.

In cases where nonideal behavior of gas phase is significant, all these equations can be expressed in terms of solute fagucity *f* rather than pressure. However, the model parameters obtained when using the *f* and *p* values do not differ dramatically (see, for example, Ref. 27).

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3. Critical Evaluations and Compilations of Selected Systems

3.1. Poly(4-Methylpentene-1)—Carbon Dioxide; Methane, other gases

Components:	**Evaluator:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Poly(4-methylpentene-1) (PMP); [25068-26-2] (I)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis. Russian Academy of Sciences, April, 1994

Critical Evaluation:

One two, although detailed, works have been performed on gas solubility in this semicrystalline polyolefin. Tigina[1] studied the solubility of several gases at different temperatures (280–350 K) and up to high pressure, but only for a single sample with a crystallinity of 90%. On the other hand, Puleo *et al.*[2] investigated the solubility at the narrower pressure range (0–2.0 MPa), but for several samples with crystallinity varying from 21.6% to 66.4%. This enabled the calculation of the contributions to the solubility coefficients characteristic of amorphous and crystalline phases of PMP. The solubility coefficients $S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}$ of PMP with 90% content of crystalline phase at 310 K are compared below.

		Ref. 2*	
Gas	Ref. 1	A	B
CO_2	0.51	0.346	0.28
CH_4	0.078	0.12	0.091

*A: crystallinity found by DSC method.
B: crystallinity found by X-ray diffraction.

Bearing in mind an approximate character of the calculations of S by an additive scheme,[2] the agreement can be considered as reasonable. More experimental studies are required at different temperatures and pressures for the samples with varying crystallinity before the properties of this polymer can be properly evaluated and recommended values can be advanced.

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[2] A. C. Puleo, D. R. Paul, and R. K. Wong, Polymer **30**, 1357 (1989).

Components:	**Original Measurements:**
(1) Helium; He; [7440-59-7] Hydrogen; H_2; [1333-74-0] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Poly(4-methylpentene-1) (PMP) [25068-26-2] (I)	O. N. Tigina, dissertation, GIAP, Moscow, USSR, 1983.

Variables:	**Prepared By:**
$T/\mathrm{K}=280-350$ $p/\mathrm{MPa}=0.1-15$	S. M. Shishatskii

Experimental Data

Henry's law solubility coefficients $S/\mathrm{mol/m}^3\ \mathrm{Pa}$

Gas	T/K	Pressure range, MPa	$S10^4$
N_2	300	0.1–14	0.395
	310	0.1–14	0.383
	320	0.1–14	0.365
	350	0.1–15	0.325
CO_2	300	0.1–6	2.9
	310	0.1–6	2.3
	320	0.1–6	1.8
CH_4	290	0.1–7	0.43
	300	0.1–10	0.38
	320	0.1–12	0.32
	330	0.1–14	0.29

Solubility of gases in PMP: $C/(\mathrm{mol/cm^3})$ outside the range of Henry's law

Gas	T/K	p/MPa	$C10^5$
He	293	2	1.8
		4	4.4
		6	8.8
		8	15.2
		10	24.3
	313	2	1.0
		6	4.0
		1	8.8
	333	2	0.6
		6	2.4
		10	5.3
H_2	280	2	4.0
		4	9.0
		6	14.6
		8	21.9
	290	2	3.7
		4	8.1
		6	13.4
		8	20.3
	300	2	2.9
		4	6.2
		6	10.2
		8	15.2
	350	2	2.2
		3	121
		4	176
		5	230
CH_4	290	8	35
		9	40
		10	45
		12	56
		14	70
	300	11	42
		13	53
		14	60
	320	13	43
		14	47
		4	4.4
		6	6.9
		8	9.7
N_2	290	2	8.3
		4	16.6
		5	21.0
		6	25.5
		7	30.5
		8	36.0
CO_2	290	2	74

Auxiliary Information

Method/Apparatus/Procedure

The solubility was measured by means of an apparatus of hydrostatic weighing the principle of which had been described in Ref. 1.

Source and Purity of Materials:

PMP of the grade DX-810 had a density of 0.82–0.83 g/cc and crystallinity 90%.
All the gases were ''chemically pure'' according to the Soviet Standard.

Estimated Error:

$\delta C/C = 1.5\%$.

References:

[1] I. F. Golubey and O. A. Dobrovol'skii, Gaz. Prom. **5**, 43 (1964).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(4-methylpentene-1) (PMP); [25068-26-2] (I)

Original Measurements:

A. C. Puleo, D. R. Paul, and P. K. Wong, Polymer **30**, 1357 (1989).

Variables:

T/K=308
p/MPa=0–2.2 (0–22 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms followed Henry's law, i.e., were linear.

TABLE 1. Solubility coefficients $S/\mathrm{cm^3(STP)/cm^3\ atm}$*

Sample	CH_4	CO_2
Q	0.22	0.59
S	0.20	0.52
A	0.19	0.49
H	0.18	0.52
1.0X	0.24	0.63
2.5X	0.26	0.69
10X	0.32	0.83
2.5R	0.20	0.54

*Description of samples seen at continuation sheet.

Within the validity of two-phase model and independence of phase properties of the composition the following local solubility coefficients where found.

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure for sorption measuring were similar to those described in Ref. 1.

Source and Purity of Materials:

PMP samples from Polyscience Co with different thermal history as well as the copolymers of PMP and 4-(3-butenyl) benzocyclobutane (BBC) were studied. Their properties are given in Table 3. Nothing on gas purity was indicated.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Poly(4-methylpentene-1) (PMP); [25068-26-2] (I) (2) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]	A. C. Puleo, D. R. Paul, and P. K. Wong, Polymer **30**, 1357 (1989).

Experimental Data

TABLE 2. Solubility coefficients k_D /cm^3(STP)/cm^3 atm in amorphous and crystalline phases of PMP

Method of cryst. determination	Amorphous phase		Crystalline phase	
	CH_4	CO_2	CH_4	CO_2
DSC	0.351	0.93	0.095±0.013	0.28±0.03
X-ray	0.378	0.99	0.060±0.010	0.20±0.02

TABLE 3. Description and characterization of the materials studied

Sample	Description	X-ray cryst. (%)	T_g (K)
Q	Commercial, quenched	53.6	303
S	Commercial, slow cooled	61.2	300
A	Commercial, annealed	66.4	295
H	Homopolymer	62.7	310
1.0X	Cross-linked copolymer with 1% BBC	49.7	310
2.5X	Same with 2.5% BBC	41.8	313
10X	Same with 10% BBC	21.6	326
2.5R	Control: copolymer with 2.5% 4-phenyl-1-butene unable to be cross-linked	55.8	307

3.2. Poly(Vinyl Chloride)—Nitrogen, Carbon Dioxide, Methane

Components:	**Evaluator:**
(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Poly(vinyl chloride) (PVC); [9002-86-2] (II)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis. Russian Academy of Sciences, April, 1994

Critical Evaluation:

In spite of the importance of PVC as an industrial polymeric material, only three investigations are available for the solubility of gases (nitrogen [7727-37-9], carbon dioxide [124-38-9], and methane [74-82-8]) in this polymer.[1–3] In neither case a molecular mass of the polymer studied has been indicated. The solubility has been measured in PVC containing different amount of stabilizers.[2,3] Various methods of preparation of PVC have been employed.[1] So the agreement exhibited in the apparent solubility coefficients presented below seems to be quite reasonable. Larger discrepancy is observed between the dual-mode sorption parameters reported by El-Hibri and Paul,[2] Fried *et al.*,[3] and those which can be calculated from the sorption isotherms obtained by Berens.[1] At least partly this can be a result of different pressure ranges used in these studies.

Gas	T/K	k_D	C'_H	b	$S=k_D+C'_H b$	Ref.
CO_2	298	0.184	40.3	0.0496	2.18	3
	308	0.587	8.9	0.2094	2.45	2
	298	—	—	—	2.7*	1
	298	—	—	—	2.5**	1
			Effect of heat treatment			
	298	—	—	—	1.5*	1
	298	—	—	—	1.7**	1
	308	0.643	4.85	0.361	2.38	2
N_2	302	—	—	—	0.058	1
	308	0.0169	0.4505	0.0448	0.037	2
CH_4	298	0.105	2.17	0.0491	0.21	3
	308	0.0513	2.305	0.0622	0.19	2

*The sample obtained by emulsion polymerization.
**The sample obtained by suspension polymerization.

Units: k_D /cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}.

Further experimental studies are required before this system can be properly evaluated and the parameters of sorption isotherms can be advanced.

References:

[1] A. R. Berens, Polym. Eng. Sci. **20**, 95 (1980).
[2] M. J. El-Hibri and D. R. Paul, J. Appl. Polym. Sci. **30**, 3649 (1985).
[3] J. R. Fried, E. Parker, and R. L. Ballard, Japan-US Polymer Symposium, 1985, p. 247.

Components:	**Original Measurements:**
(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] *n*-Butane; C_5H_{10}; [106-97-8] (2) Poly(vinyl chloride) (PVC); [9002-86-2] (II)	A. R. Berens, Polym. Eng. Sci **20**, 95 (1980).
Variables:	**Prepared By:**
$T/\mathrm{K}=298-303$ $p/\mathrm{kPa}=0-100$	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Concentration isotherms of CO_2 in emulsion PVC at 298 K (gravimetric data). (The original data were represented graphically)

Never-heated		Heat-treated	
Pressure/kPa	Concentration (mg_1^*/g_2^*)	Pressure/kPa	Concentration (mg_1^*/g_2^*)
7.57	0.36	7.41	0.21
13.98	0.67	15.03	0.38
28.37	1.29	28.11	0.73
41.41	1.76	41.59	1.04
55.25	2.22	54.68	1.32
68.51	2.61	68.56	1.58
81.78	2.98	82.26	1.82
94.66	3.30	94.77	2.03

TABLE 2. Sorption isotherms of CO_2 in suspension PVC (Digisorb data). (The original data were represented graphically)

CO_2 ($T=298$ K)				N_2 ($T=298$ K)			
Never-heated		Heat-treated		Never-heated		Heat-treated	
Pressure /kPa	Concentration (mg_1^*/g_2^*)	Pressure /kPa	Concentration (mg_1^*/g_2^*)	Pressure /kPa	Concentration (mg_1^*/g_2^*)	Pressure /kPa	Concentration (mg_1^*/g_2^*)
10.79	0.48	10.61	0.33	11.32	0.01	11.13	0.01
15.70	0.69	15.32	0.46	15.02	0.02	15.04	0.01
22.57	0.98	22.39	0.67	22.02	0.02	21.63	0.01
40.64	1.63	40.08	1.14	40.14	0.04	40.17	0.02
49.28	1.91	48.72	1.36	47.96	0.04	48.00	0.03
59.29	2.25	58.94	1.59	58.26	0.05	58.31	0.03
66.76	2.49	66.60	1.80	66.08	0.06	65.74	0.03
73.82	2.82	73.48	1.96	72.88	0.06	72.95	0.03
79.32	2.95	79.57	2.08	78.44	0.06	78.73	0.03
84.24	3.07	83.70	2.19	82.76	0.07	83.05	0.03
88.17	3.16	88.22	2.31	86.88	0.07	86.97	0.04
90.33	3.21	90.18	2.37	89.35	0.07	88.82	0.04
92.88	3.29	92.15	2.42	91.63	0.07	91.51	0.04
95.04	3.35	94.11	2.46	94.72	0.07	93.77	0.04
96.81	3.36	96.67	5.51	96.57	0.07	96.66	0.04
98.39	3.37	98.44	2.54	98.84	0.07	97.90	0.04
100.75	3.38	100.40	2.57	93.47	0.07	98.72	0.04
—	—	—	—	97.81	0.07	99.96	0.04
—	—	—	—	99.66	0.08	—	—

TABLE 3. Concentration isotherms of *n*-butane in emulsion PVC at 303 K; gravimetric data, sorption times >18 h (the original data were represented graphically)

Never-heated		Heat-treated	
Relative Pressure	Concentration (mg_1^*/g_2^*)	Relative Pressure	Concentration (mg_1^*/g_2^*)
0.01	0.91	0.01	0.36
0.02	1.49	0.04	1.08
0.04	2.47	0.10	2.27
0.10	5.96	—	—

Auxiliary Information

Method/Apparatus/Procedure

Gravimetric sorption experiments were carried out using a Cahn microbalance and, for highly sorbing gases like butane, a vacuum system described in Ref. 1. For nitrogen and partly for carbon dioxide a volumetric gas sorption method was used by means of Digisorb 2500 automatic surface area analyzer (Micromeritics Instruments Corp.).

Source and Purity of Materials:

Gases: research grade purity.
PVC: obtained by suspension and emulsion techniques (in the form of powder), density 1.404±0.014 g/cm^3.
''Never-heated'' samples: recovered and dried at temperature not exceeding 273 K.
''Heat-treated'' samples: heated 1 h at 373 K.

Estimated Error:

No information given.

References:

[1] A. R. Berens, Angew Makromol. Chem. **47**, 97 (1975).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(vinyl chloride) (PVC); [9002-86-2] (II)

Original Measurements:

M. J. El-Hibri and D. R. Paul, J. Appl. Polym. Sci. **31**, 2533 (1986).

Variables:

T/K=308
p/MPa=0–2.5 (0–25 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in PVC at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Ar	0.0377	1.1320	0.0410
N_2	0.0169	0.4505	0.0448
Co_2	0.5870	8.9390	0.2094
CO_2*	0.6340	4.8500	0.3610
CO_2**	0.5800	5.1600	0.2430
CH_4	0.0513	2.3050	0.0622

*No drawing, annealing at 358 K.

**Stretching to draw ratio 3 at 358 K.

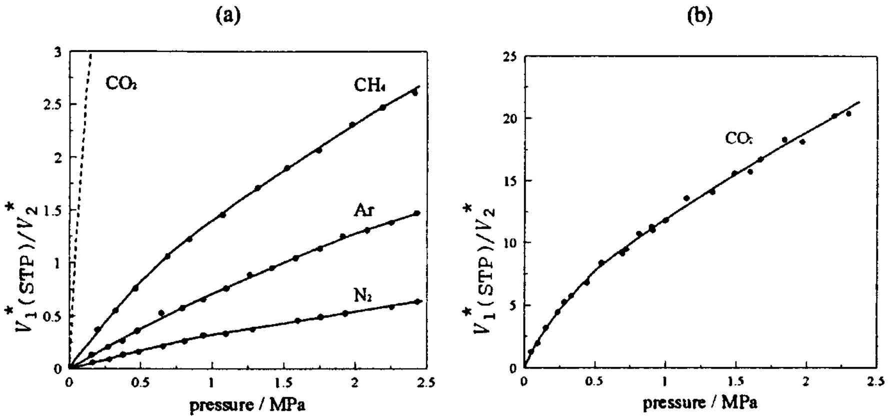

FIG. 1. Sorption isotherms of Ar, N_2, CH_4 (a) and CO_2 (b) in PVC at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The sorption measurement was carried out using the pressure decay method, Ref. 1.

Source and Purity of Materials:

CH_4: purity 99%.
Other gases: purity 99.7%.
PVC: B.F. Goodrich Co. (CS 5760); density 1.389 g/cm^3, glass transition temperature 344 K. It contained 2% of tin stabilizer.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane: CH_4; [74-82-8] (2) Poly(vinyl chloride) (PVC); [9002-86-2] (II)	J. R. Field, B. E. Parker, and R. L. Ballard, Japan-US Polymer Symposium 1985, pp. 247–248.
Variables:	**Prepared By:**
T/K=298 p/MPa=0.16–1.27	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for methane and carbon dioxide in PVC at 298 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CH_4	0.105	2.17	0.0491
CO_2	0.184	40.3	0.0496

TABLE 2. Sorption isotherms of methane and carbon dioxide in PVC at 298 K (The original data were represented graphically)

CH_4		CO_2	
Pressure/Mpa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.17	0.38	0.16	3.48
0.34	0.53	0.27	5.28
0.47	0.85	0.41	7.74
0.55	1.11	0.54	9.71
0.67	1.13	0.64	10.98
0.78	1.42	0.77	12.72
0.88	1.61	0.88	13.99
0.98	1.67	1.00	15.27
1.06	1.83	1.14	16.94
1.16	1.95	1.27	18.01

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were obtained by the pressure decay method. Ref. 1. Conditioning at 23 atm for 60 h and degassing preceded the measurements.

Source and Purity of Materials:

PVC: Samples were compression modeled at 450 K from a mixture of low molecular mass PVC resin and 3% of a stablizer (Cincinnati Milacorn (TM-692)).

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:	**Original Measurements:**
(1) Neon; Ne; [7440-01-9] Hydrogen; H_2; [1330-74-0] (2) Tricresyl phosphate: $C_{19}H_{21}O_4P$; [1330-78-5] (3) Poly(vinyl chloride) (PVC); [9002-86-2] (II)	R. M. Barrer, R. Mallinder, P.S.-L. Wong, Polymer **8**, 321 (1967).
Variables:	**Prepared By:**
T/K=283–339	Yu. P. Yampol'skii

Experimental Data

Smoothed solubility coefficients S 10^4/cm^3(STP)/cm^3 cm Hg*

Sample	Temperature/K				
	399	309	319	329	339
Unplasticized PVC			Hydrogen		
	4.6	4.4	4.0	3.8	3.7
			Neon		
	2.2	2.1	2.0	1.9	1.8
	283	291	297	307	313
Plasticized PVC			Hydrogen		
	2.8	3.0	3.2	3.4	3.5
			Neon		
	1.2	1.4	1.5	1.8	1.9

*Pressure was not indicated: presumably, $p<$atm.

Auxiliary Information

Method/Apparatus/Procedure

Volumetric method by Meares[1] was used. The sample was allowed to equilibrate with a gas, then nonsorbed gas was swipped away with mercury. The volume of gas subsequently desorbed from the sample was measured by means of McLeod gauge.

Source and Purity of Materials:

PVC from ICI (99% ''pure'') in a form of powder was studied. The plasticized sample contained 0.325 mol fraction of tricresylphosphate. Films were prepared by calendering after adding 2 parts of cadmium stearate and 0.2 parts of stearic acid per 100 parts of the polymer.

Estimated Error:
No information given.

References:
[1] P. Meares, Trans. Faraday Soc. **54**, 40 (1958).

Components:

(1) Chlorine; Cl_2; [7782-50-5]
(2) Poly(vinyl chloride) (PVC); [9002-86-2] (II)

Original Measurements:

S. Wachi, H. Morikawa, and H. Inoue, AIChE J. **34**, 1683 (1988).

Variables:

T/K=293–345
$[Cl_2]=0-35$ mol/m^3

Prepared By:

Yu. P. Yampol'skii

Experimental Data

In the subatmospheric range of pressure the concentration of dissolved chlorine C(mol/m^3) obeyed the following equation:

$$C=Sy,$$

where y is the concentration of Cl_2 in gas phase (mol/m^3). Temperature dependence of the solubility coefficient S is given below:

T/K	293	313	323	343
S	20	14	14	11

The following equation was obtained for the temperature dependence of S:

$$S=0.280\exp(\Delta H_S/RT),$$

where ΔH_s is the heat of sorption, is 10 480 kJ/mol.

Auxiliary Information

Method/Apparatus/Procedure

Physical sorption of chlorine in PVC was determined using the constant volume cell method. The pressure changes were measured by means of a sensor (Toyoda-kouki PMS-5,5H).

Source and Purity of Materials:

PVC (SC-16, DP-600) supplied by Kaneguchi Chemical Industries Co was prepared by suspension polymerization.
No information on the purity of chlorine is given.

Estimated Error:

No information given.

3.3. Poly(Vinyl Acetate)—Various Gases

Components:

(1) Helium; He; [7440-59-7] Neon; Ne; [7440-01-9]
Hydrogen; H_2; [1333-74-0]
(2) Poly(vinyl acetate) (PVA); [9003-20-7] (III)

Original Measurements:

P. Meares, Trans. Faraday Soc. **54**, 40 (1958).

Variables:

T/K=281–313
p/kPa=0.6–27

Prepared By:

Yu. P. Yampol'skii

Experimental Data

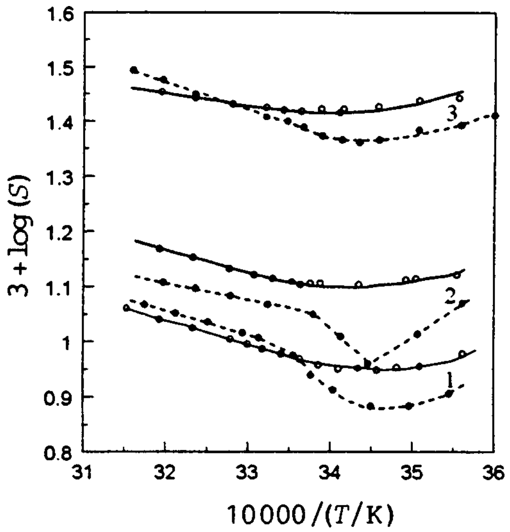

FIG. 2. Solubility coefficients $S/(\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}})$ for gases in PVA. Curves 1: Helium; curves 2: Neon; curves 3: Hydrogen. Continuous curves taken from equilibrium experiments, broken curves from diffusion experiment.

Auxiliary Information

Method/Apparatus/Procedure

After establishing equilibrium between the sample and the gas, the gas was swept away using mercury. The sorbed gas was then allowed to desorb into a known volume.

Source and Purity of Materials:

PVA: Gelva V145, $M_w=450\,000$ (determined from viscosity), $M_n=10\,000$, glass transition temperature 298.6 K.

Estimated Error:

No information given.

Components:

(1) Hydrogen; H_2; [1333-74-0]
(2) Poly(vinyl acetate) (PVA); [9003-20-7] (III)

Original Measurements:

S. Zhou and S. A. Stern, J. Membr. Sci. **50**, 19 (1990).

Variables:

T/K=268 and 278
p/MPa=0.2–2.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for hydrogen in PVA (Compiler).
(the value of b seems to be grossly overestimated)

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_h/cm^3(STP) cm^{-3}	b/atm^{-1}
268	0.0146	0.096	1.88
278	0.0173	0.027	1.84

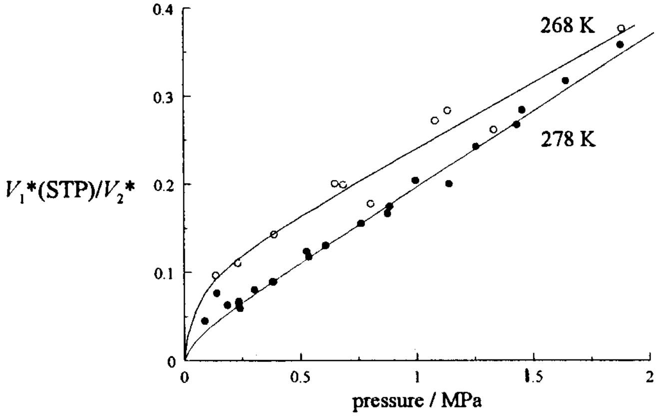

FIG. 3. Sorption isotherms for hydrogen in PVA at 268 K and 278 K.

Auxiliary Information

Method/Apparatus/Procedure

The solubility was measured by a gravimetric method. The apparatus included a Cahn microbalance, Model C 1100. Pressure was measured by a gauge (Model 901 B, Dresser Industries Inc.).

Source and Purity of Materials:

H_2: purity >99.99%.
PVA: Aldrich Chemical Co.; density 1.191 g/cm^3, glass transition temperature 296 K (via DSC).

Estimated Error:

Relative precision: solubility <16%, p<0.05%; precision in T:<0.05 K.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl acetate), (PVA); [9003-20-7] (III)

Original Measurements:

S. Takishima, K. Nakamura, M. Sasaki, and H. Masuoka, Sekiyu Gakkaishi **33**, 332 (1990).

Variables:

T/K=313.2 and 323.2
p/MPa=0.898–8.755

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility of carbon dioxide in PVA expressed as mass fractions w

p/Mpa	w	p/Mpa	w
313.2 K		323.2 K	
1.258	0.0416	0.898	0.0254
1.449	0.0532	1.819	0.0485
2.650	0.0936	1.906	0.0533
3.467	0.1264	3.309	0.0978
3.846	0.1429	4.698	0.1397
4.583	0.1723	5.655	0.1696
5.659	0.2123	6.519	0.2073
6.885	0.2786	7.861	0.2668
8.755	0.3909		

Auxiliary Information

Method/Apparatus/Procedure

Measurements of the solubility were made using a pressure decay method. The apparatus was similar to one designed by Koros.[1] Pressure was measured by a semiconductor sensor PX-1A (Tsukasu Sokken). The correction for compressibility of gas phase was introduced.

Source and Purity of Materials:

PVA (Aldrich Chemical Co) had ''viscosity'' average molecular weight 158 000 and glass transition temperature 303 K.
The purity of carbon dioxide (Chugoku Teisan) was 99.9%.

Estimated Error:

No information given.

References:

[1] W. J. Koros, Ph.D. dissertation, The University of Texas at Austin, 1977.

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Sulfur dioxide; SO_2; [7446-09-5] Ethylene; C_2H_4; [74-85-1] Chloromethane; C_2H_6; [74-84-0] Methyl chloride; CH_3Cl; [74-87-3]
(2) Poly(vinyl acetate) (PVA); [9003-20-7] (III)

Original Measurements:

D. D. Liu and J. M. Prausnitz, J. Polym. Sci., Polym. Phys. Ed., **15**, 145 (1977).

Variables:

T/K=398–473

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Mass fraction Henry's law constants/atm

	Temperature/K			
Solute	398	423	448	473
Carbon dioxide	990	1200	1500	1700
Sulfur dioxide	55	87	135	187
Ethylene	2300	2900	3300	3400
Ethane	2700	3000	3400	3700
Methyl chloride	160	220	300	410

Auxiliary Information

Method/Apparatus/Procedure

Inverse gas chromatographic method was used. Two columns were employed: hydrocarbons were studied in Chromosorb-supported column, Fluoropac-80 packed column was used for other solutes. Helium served as a carrier gas. Correction for pressure drop in the column was introduced.

Source and Purity of Materials:

PVA (Cellomer Associates) had a molecular mass 83 400.
All gases (from Matheson Gas Products) had a purity better than 99%.

Estimated Error:

No information given.

3.4. Poly(Acrylonitrile)—Carbon Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(acrylonitrile) (PAN); [25014-41-9] (IV)

Original Measurements:

G. S. Huvard, V. T. Stannett, W. J. Koros, and H. B. Hopfenberg, J. Membr. Sci. **16**, 945 (1972).

Variables:

T/K: 298–338 K
P/MPa: 0–3.0

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters of CO_2 sorption in PAN

T/K	k_D/(cm^3(STP)/cm^3 atm)	C'_H/(cm^3(STP)/cm^3)	b/(atm^{-1})
298	0.206	3.615	0.187
328	0.160	3.496	0.139
338	0.134	2.852	0.126

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the sorption experiments are the same as described in Ref. 1.

Source and Purity of Materials:

PAN from Standard Oil was used.
CO_2 (Raleing Co.) had purity 99.9%.

Estimated Error:

No information given.

References:

[1] W. R. Vieth and J. A. Eilenberg, J. Appl. Polym. Sci. **16**, 945 (1972).

3.5. Poly(Methyl Methacrylate)—Carbon Dioxide, Other Gases

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

The system PMMA–carbon dioxide has been studied in a large number of papers (Refs. 1–11). However, different temperature and pressure ranges studied and different units of the data reported prevent the comparison of all the results.

Figure 4(a) shows the temperature dependence of the solubility coefficient $S/(\mathrm{g\ g^{-1}\ atm^{-1}})$. The values obtained by pressure decay method and expressed in the standard units ($\mathrm{cm^3(STP)/cm^3\ atm}$) were recalculated by evaluator using the density 1.19 $\mathrm{g/cm^3}$ of PMMA.

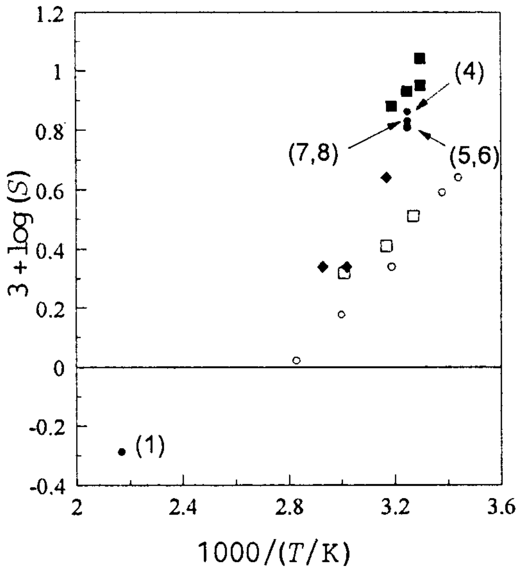

FIG. 4. (a) (●) Ref. (1), (4), (5,6), (7,8); (○) Ref. (2); (■) Ref. (3); (◆) Ref. (9); (□) Ref. (10).

Reasonable agreement can be seen between the temperature dependences reported by different authors (Refs. 2, 9, and 10). However, a significant and apparently systematic discrepancy (by a factor of 2) is observed between the values obtained at 308 K by pressure decay method (Refs. 3 and 5–8) and gravimetric method (Refs. 2 and 10). Further studies are necessary to explain this result.

TABLE 1. Dual mode sorption parameters for the system PMMA–carbon dioxide at 308 K.

$k_D/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	$C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$	$b/\mathrm{atm^{-1}}$	Ref.
1.140	14.90	0.218	4
0.916	12.59	0.236	5,6
1.068	18.00	0.186	7,8
1.200	15.60	0.172	11

Critical Evaluation:

They are in reasonable agreement. The predictions of sorption isotherms using them are presented in Table 2.

TABLE 2. Concentrations $C/(\mathrm{cm^3(STP)\ cm^{-3}})$ of CO_2 dissolved in PMMA at 308 K

	References			
p/atm	4	5,6	7,8	11
5	13.5	11.4	14.0	13.2
10	21.6	18.0	22.4	21.9
20	34.9	28.7	35.5	36.1

References:

[1] P. L. Durrill and R. G. Griskey, A. I. Ch. E. J. **12**, 1147 (1965).

[2] G. B. Okonishnikov and V. P. Skripov, Vysokomol. Soedin., Ser. B **25**, 890 (1973).

[3] J. M. H. Fechter, H. B. Hopfenberg, and W. Koros, J. Polym. Eng. Sci. **21**, 925 (1981).

[4] W. J. Koros, G. N. Smith, and V. Stannett, J. Appl. Polym. Sci. **26**, 159 (1981).

[5] E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. Stannett, J. Membr. Sci. **13**, 161 (1983).

[6] E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. Stannett, J. Membr. Sci. **18**, 53 (1984).

[7] W. J. Koros and E. S. Sanders, J. Polym. Sci., Polym. Symp. **72**, 142 (1985).

[8] E. S. Sanders and W. J. Koros, J. Polym. Sci., Polym. Phys. Ed. **24**, 175 (1986).

[9] I. S. Liau and M. A. McHugh, *Supercritical Fluid Technology*, edited by J. M. L. Penninger *et al.* (Elsevier, New York, 1985), p. 415.

[10] R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).

[11] P. C. Raymond and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **28**, 2103 (1990).

Components:

(1) Helium; He; [7440-59-7] Neon; Ne; [7440-01-9] Argon; Ar; [7440-37-1] Krypton; Kr; [7439-90-9] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

P. L. Durill, Ph.D. dissertation. Virginia Polytech. Inst., 1965.
P. L. Duriff, R. G. Griskey, AIChE J. **12**, 1147 (1965).

Variables:

T/K: 461
p/MPa: 0.26–1.9 (2.6–19 atm)

Prepared By:

A. K. Bokarev

Experimental Data

Henry's law solubility constants S for gases in PMMA

Gas	Pressure/atm	$S/(\text{cm}^3(\text{STP})/\text{g atm})$
He	3.8–7.2	0.066
Ne	2.7	0.126
Ar	3.2–7.4	0.105 ± 0.063
Kr	2.6–4.6	0.122
N_2	5.7–15.0	0.045 ± 0.028
CO_2	4.0–19.0	0.260 ± 0.024

Auxiliary Information

Method/Apparatus/Procedure

The equipment and a manometrical procedure for solubility measurements were similar to those of Lundberg *et al.*[1]

Source and Purity of Materials:

PMMA (Lucite) used is a product of du Pont de Nemours Co.: $\rho = 1.20$ g/cm^3.
Gases from Air Reduction Co., had a minimum purity: CO_2-99.5%; N_2-99.90%; Ar-99.997%. He-99.99%.
Gases (Matheson Co), included as impurities: Ne-14 ppm He, Kr-12 ppm N_2 and 23 ppm Xe.

Estimated Error:

$\delta C/C \leq 8\%$.

References:

J. L. Lundberg, M. B. Wilk, and M. J. Huyett, Appl. Phys. **31**, 1131 (1960).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

G. B. Okonishnikov and V. P. Skripov, Vysokomol. Soedin., Ser. B. **25**, 890 (1973).

Variables:

$T/\text{K} = 291-353$
$p/\text{MPa} = 0.4-6.0$

Prepared By:

S. M. Shishatskii

Experimental Data:

Linear sorption isotherms were found in the pressure range shown.

Solubility coefficients, S, for carbon dioxide in PMMA

T/K	291	295.7	313	333	353
$10^3 S/(\text{g/g atm})$	4.4	3.9	2.4	1.5	1.05

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made using a McBain spring balance described in Ref. 1. A correction for buoyancy and for sample's swelling were introduced.

Source and Purity of Materials:

ST-1-110 grade PMMA studied did not contain any plasticizers. No data are given on the purity of CO_2 taken from a cylinder.

Estimated Error:

No information given.

References:

A. I. Sakharov, *Balance in Physicochemical Studies* (in Russian), (Nauka, Moscow, 1968).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

J. M. H. Fechter, H. B. Hopfenberg, and W. J. Koros, Polym. Eng. Sci. **21**, 925 (1981).

Variables:

T/K=293–313
p/kPa=13–93

Prepared By:

Yu. P. Yampol'skii

Experimental Data:

Sorption isotherms of carbon dioxide in:
(I) ''as received'' PMMA microspheres with 14530 Å diameter at 303, 308, and 313 K,
(II) preswollen PMMA microspheres with 5436 Å diameter at 303 K.
(The original data were represented graphically)

T=303 K		T=308 K		T=313 K	
Pressure/kPa	Sorption (g_1^*/(100 g^*)$_2$)	Pressure/kPa	Sorption (g_1^*/(100 g^*)$_2$)	Pressure/kPa	Sorption (g_1^*/(100 g^*)$_2$)
(I)					
13.02	0.15	13.03	0.12	13.22	0.09
26.23	0.27	26.78	0.22	26.80	0.19
39.81	0.36	39.83	0.31	39.67	0.26
52.85	0.45	53.05	0.39	52.90	0.33
66.07	0.54	66.28	0.47	66.31	0.39
79.65	0.62	79.51	0.54	79.72	0.46
92.88	0.71	92.73	0.62	93.13	0.52
(II)					
13.17	0.17				
26.17	0.29				
39.71	0.41				
53.09	0.51				
66.46	0.60				
79.83	0.70				
93.02	0.80				

Auxiliary Information

Method/Apparatus/Procedure

Measurements were made on a Cahn RG Electrobalance. Samples of the polymer had been preswollen by exposure of methanol vapours (p/p_s=0.98). After quick removal of methanol gas sorption isotherms of carbon dioxide were obtained.

Source and Purity of Materials:

CO_2: purity 99.99%.
PMMA: microspheres of diameters 1453 Å (I) and 5436 Å (II). M_n(I)=206 000, M_n(II)=137 000, glass transition temperature (II) 393 K.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

W. J. Koros, G. N. Smith, and V. Stannett, J. Appl. Polym. Sci. **26**, 159 (1981).

Variables:

T/K=308–353
p/MPa=0–2.2

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in PMMA at various temperatures

T/K	k_D /cm^3(STP)cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
308	1.14	14.9	0.218
328	0.74	12.0	0.116
353	0.505	7.13	0.0683

Sorption enthalpies: $\Delta H_D = -3.9$ kcal mol^{-1}; -16.3 kJ mol^{-1}
$\Delta H_b = -5.6$ kcal mol^{-1}; -23.4 kJ mol^{-1}

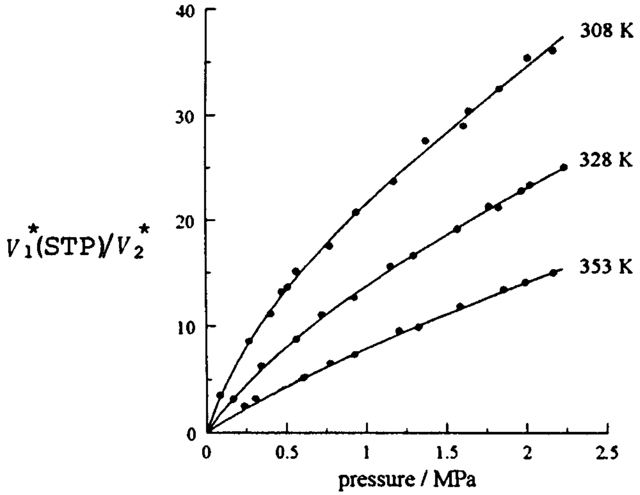

FIG. 4. (b) Sorption isotherms of carbon dioxide in PMMA.

Auxiliary Information

Method/Apparatus/Procedure

The sorption equipment described in Refs. 1 and 2 was used. The procedure involved ''interval'' sorption measurement and standard pretreatment: equilibration with carbon dioxide at 20 atm for 6 h before measurement.

Source and Purity of Materials:

CO_2: Air Products, purity >99.9%.
PMMA: Aldrich Chemical Co., M_w=599 000.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).
[2] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Ethylene; C_2H_4; [74-85-1]
(3) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. Stannett, J. Membr. Sci. **13**, 161 (1983)

Variables:

T/K=308
p/MPa=0–0.8

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Sorption isotherms of pure C_2H_4 and pure CO_2 in PMMA at 308 K. (The original data were represented graphically)

C_2H_4		CO_2		CO_2	
Pressure/MPa	Sorption $(V_1^*(STP)/V_3^*)$	Pressure/MPa	Sorption $(V_1^*(STP)/V_3^*)$	Pressure/MPa	Sorption $(V_1^*(STP)/V_3^*)$
0.09	2.03	0.06	2.37	0.53	11.90
0.16	2.92	0.11	3.58	0.55	12.13
0.19	3.36	0.12	4.03	0.56	12.30
0.22	3.81	0.15	4.64	0.59	12.46
0.27	4.29	0.20	5.85	0.63	13.25
0.32	4.90	0.21	5.97	0.65	13.56
0.34	5.13	0.24	6.79	0.67	13.72
0.39	5.62	0.27	7.39	0.70	14.05
0.43	5.99	0.30	8.05	0.70	14.19
0.47	6.46	0.34	8.80	—	—
0.53	6.92	0.39	9.66	—	—
0.56	7.04	0.42	9.92	—	—
0.64	7.83	0.45	10.45	—	—
0.73	8.29	0.45	10.64	—	—
0.75	8.85	0.48	10.92	—	—
0.80	9.06	0.50	11.34	—	—

TABLE 2. Dual mode sorption parameters for pure component sorption of CO_2 and C_2H_4 in PMMA at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.916	12.59	0.236
C_2H_4	0.531	7.09	0.259

The following figure concerns mixed gas sorption of CO_2 and C_2H_4. Points are experimental data, solid lines are predictions of DMS equation and dashed lines are prediction of DMS equation for mixed penetrants:

$$C_1=k_{D1}p_1++C'_{H1}b_1p_1/(1+b_1p_1+b_2p_2)$$

$$C_2=k_{D2}p_2+C'_{H2}b_2p_2/(1+b_1p_1+b_2p_2).$$

All the parameters for gases (1) and (2) are pure components sorption parameters from Table 2.

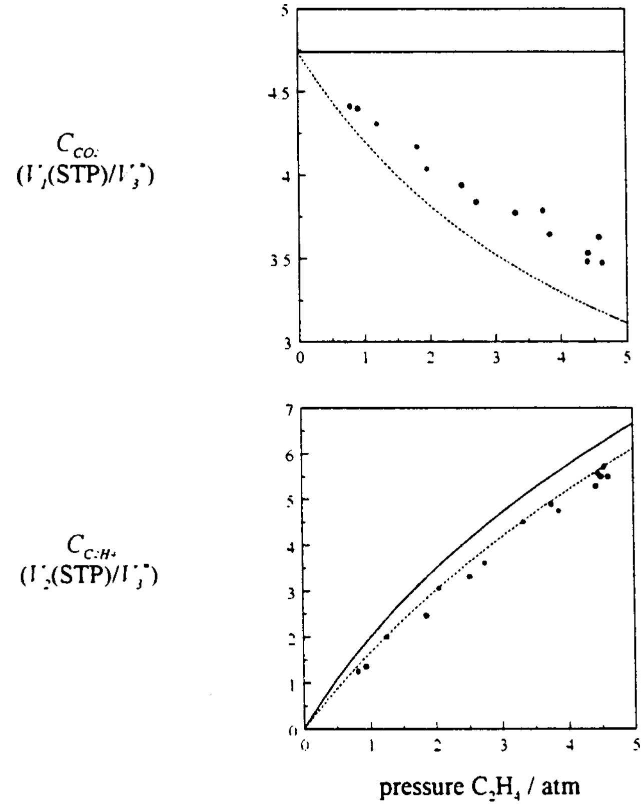

FIG. 5. Mixed gas sorption of CO_2 /C_2H_4 in PMMA at 1.53±0.05 atm CO_2.

Auxiliary Information

Method/Apparatus/Procedure

A novel apparatus to measure precisely both pure and mixed gas sorption in glassy polymers is described. A method for accurate calibration and operation of the equipment is discussed, based upon complete closure of the material balance of all gaseous components in all phases. The overall scheme of the sorption apparatus is illustrated and the details of the sorption cell are presented.

Source and Purity of Materials:

CO_2: Air Products, purity 99.99% (Coleman grade).
C_2H_4: Airco Research Triangle Park, purity 99.5% (2.5 grade).
PMMA: Aldrich Chemical Co., M_w=600 000.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Ethylene; C_2H_4; [74-85-1] (3) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)	E. S. Sanders and W. J. Koros, J. Membr. Sci. **18**, 53 (1984).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–0.81	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Sorption isotherms of pure carbon dioxide and ethylene in PMMA at 308 K (The original data were represented graphically)

Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_3^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_3^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_3^*)$
CO_2					
0.07	2.40	0.43	9.86	0.64	13.09
0.13	4.09	0.46	10.51	0.66	13.61
0.20	5.92	0.46	10.70	0.68	13.80
0.22	6.25	0.49	10.84	0.70	14.22
0.27	7.28	0.51	11.31	0.71	14.36
0.31	8.08	0.56	12.16	—	—
0.35	8.87	0.57	12.44	—	—
C_2H_4					
0.10	2.16	0.35	5.20	0.65	7.82
0.16	3.00	0.39	5.67	0.73	8.29
0.20	3.47	0.44	6.00	0.80	9.08
0.23	3.80	0.47	6.47	0.81	9.13
0.27	4.31	0.54	6.93	—	—
0.33	4.97	0.56	7.00	—	—

TABLE 2. Dual mode sorption parameters for pure carbon dioxide and ethylene in PMMA at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Pressure based parameters			
CO_2	0.916	12.59	0.236
C_2H_4	0.531	7.09	0.259
Fugacity based parameters			
CO_2	1.015	11.86	0.243
C_2H_4	0.490	8.32	0.217

The two following figures (Fig. 6 and 7) deal with mixed gas sorption of CO_2 and C_2H_4. Points are experimental data, solid lines are predictions of DMS equation and dashed lines are prediction of equation:

$$C_1 = K_{D1}p_1 + C'_1 b_1 p_1 /(1 + b_1 p_1 + b_2 p_2),$$

$$C_2 = k_{D2}p_2 + C'_{H2} b_2 p_2 /(1 + b_1 p_1 + b_2 p_2).$$

All the parameters for gases (1) and (2) are pure components sorption parameters from Table 2.

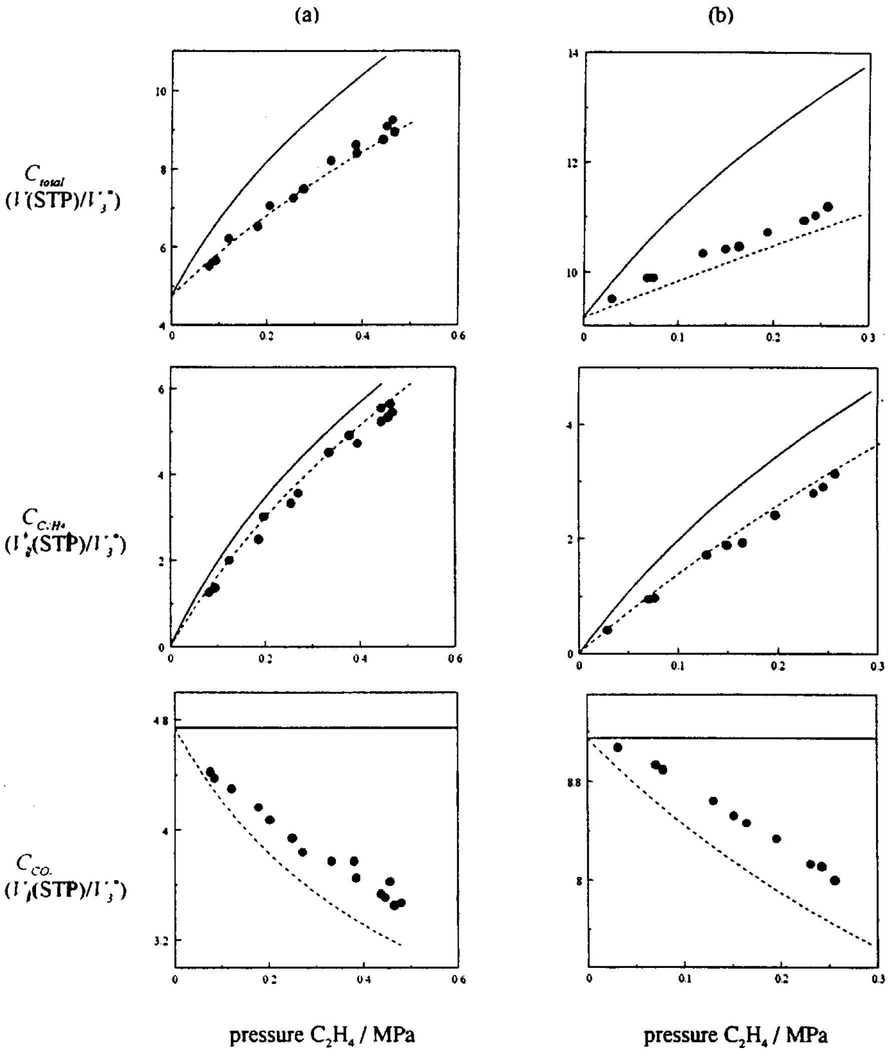

FIG. 6. Mixed gas sorption of CO_2 and C_2H_4 at 1.53 atm CO_2 (a) and 3.64 atm CO_2 (b).

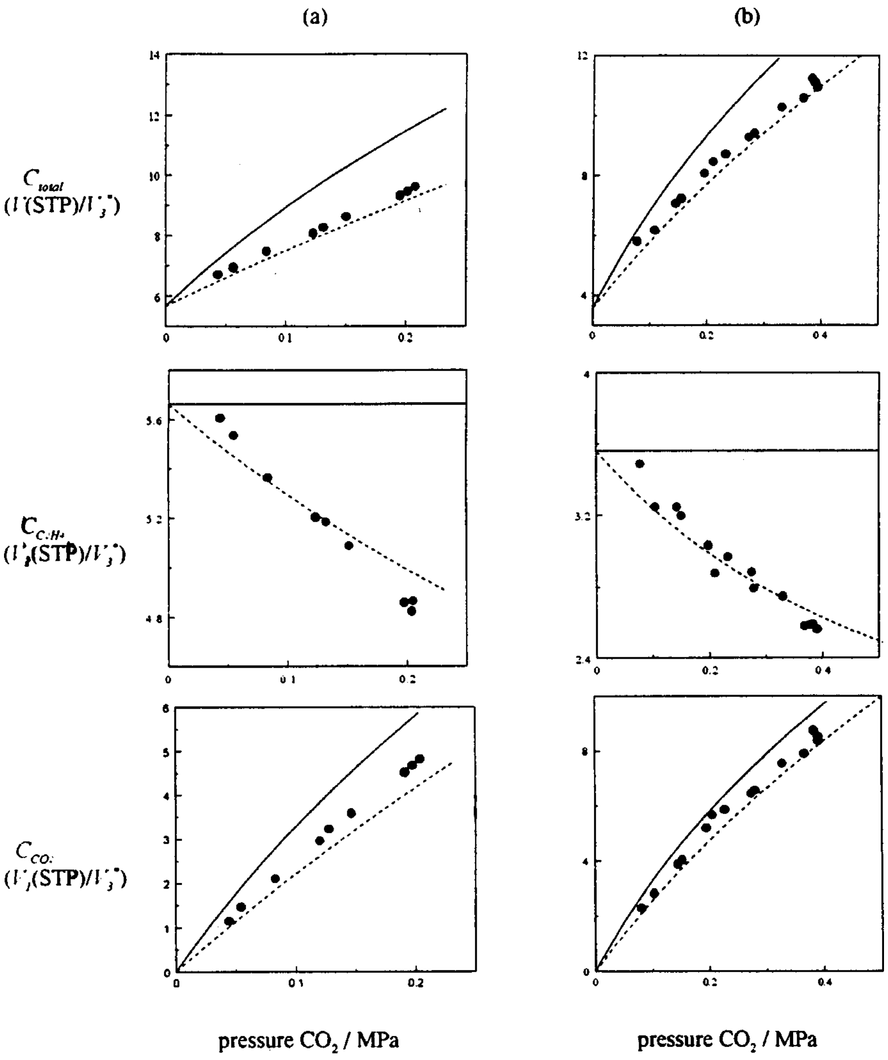

FIG. 7. Mixed gas sorption of CO_2 and C_2H_4 at 3.93 atm C_2H_4 (a) and 2.06 atm C_2H_4 (b).

Auxiliary Information

Method/Apparatus/Procedure

Apparatus specifically designed to measure mixed gas sorption was described in Ref. 1. It consisted of four chambers: one chamber contained the polymer, three others were used to meter gases accurately (individual or mixtures) into the first one or for sampling gases directly into a gas chromatograph. All chambers were provided with pressure transducers (Gould Model PA 822). The method is based on the concept of maintaining material balance. For both pure gases and mixtures. PVT behavior was taken into account.

Source and Purity of Materials:

CO_2: Air Products, purity 99.99%.
C_2H_4: Airco, purity 99.5%.
PMMA: Aldrich Chemical Co., $M_v = 600\,000$, glass transition temperature 393 K.

Estimated Error:

Relative precision of pressures: ±0.3%.
Precision in T: ±0.01 K.

References:

[1] E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Membr. Sci. **13**, 161 (1983).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Ethylene; C_2H_4; [74-85-1] Nitrous oxide; N_2O; [10024-97-2] (3) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)	W. J. Koros and E. S. Sanders, J. Polym. Sci. Polym. Symp. **72**, 142 (1985). E. S. Sanders and W. J. Koros, J. Polym. Sci., Polym. Phys. Ed. **24**, 175 (1986).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.0	A. K. Bokarev

Experimental Data

Dual mode sorption parameters for pure component sorption of CO_2, C_2H_2, and N_2O in PMMA

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C_H^*/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.944	19.68	0.158
C_2H_4	0.461	12.40	0.189
N_2O	1.068	18.00	0.186

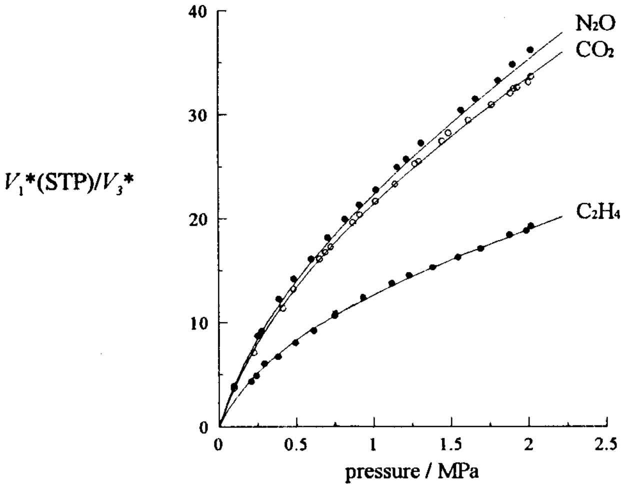

FIG. 8. Sorption isotherms for pure gases in PMMA at 308 K.

The following figures (Figs. 9–11) refer to mixed gas sorption of CO_2 /C_2H_4 and CO_2 /N_2O. Points are experimental data, solid lines are predictions of DMS equation and dashed lines are prediction of equation:

$$C_1=k_{D1}p_1+C'_{H1}b_1p_1\ /(1+b_1p_1+b_2p_2),$$

$$C_2=k_{D2}p_2+C'_{H2}b_2p_2\ /(1+b_1p_1+b_2p_2).$$

All the parameters for gases (1) and (2) are pure components sorption parameters from Table 1.

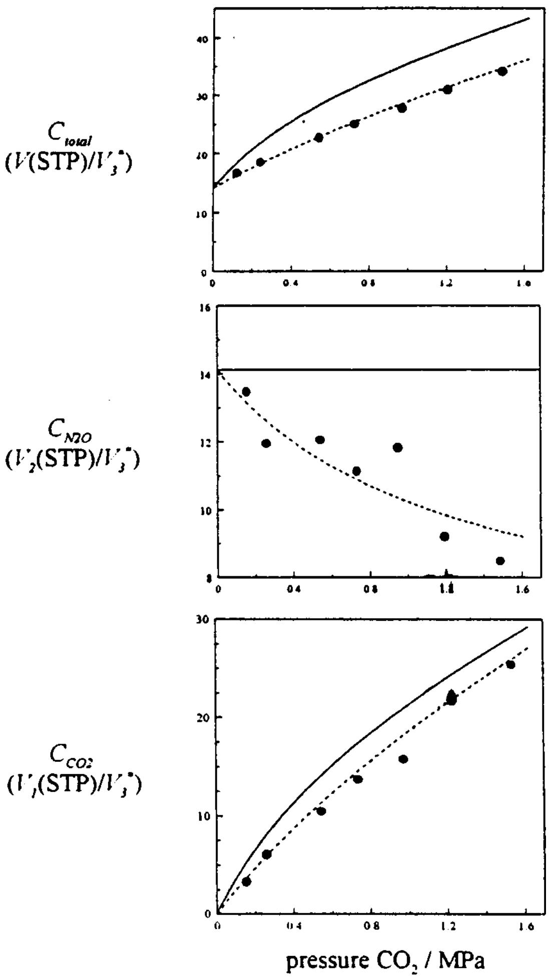

FIG. 9. High-pressure mixed-gas sorption of CO_2 /NO_2 at 5.00 atm N_2O.

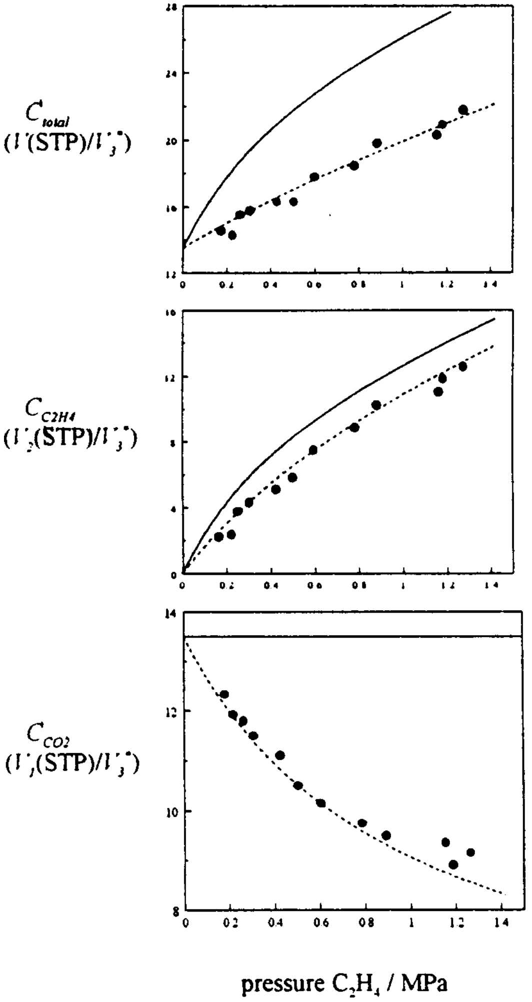

FIG. 10. High-pressure mixed-gas sorption of CO_2 /C_2H_4 at 5.05 atm CO_2.

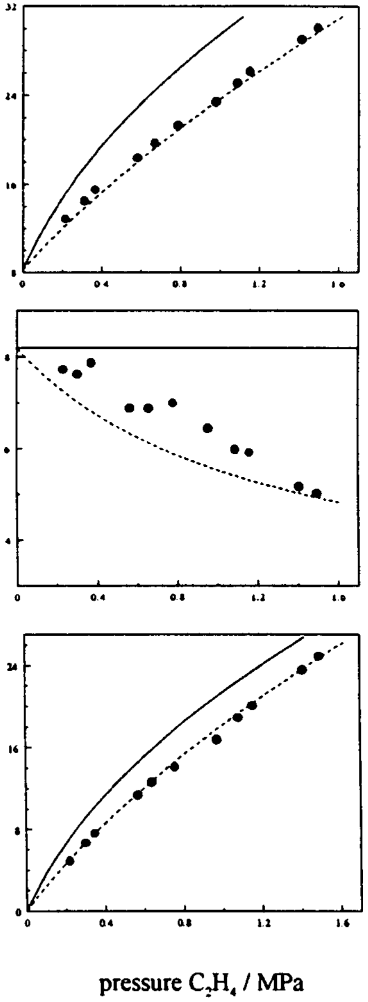

FIG. 11. High-pressure mixed-gas sorption of CO_2 /C_2H_4 at 4.87 atm C_2H_4.

Auxiliary Information

Method/Apparatus/Procedure

An apparatus for precise measurement of both pure and mixed gas sorption in glassy polymers was used. Details in Ref. 1.

Source and Purity of Materials:

CO_2: Air Products; purity 99.99% (Coleman grade).
C_2H_4: Airco Research Triangle Park; purity 99.5% (2.5 grade).
N_2O: Airco Research Triangle Park; purity 99.5% (4.5 grade).
PMMA: Aldrich Chemical Co.; $M_w = 600\ 000$.

Estimated Error:

No information given.

References:

[1] E. S. Sanders, W. J. Koros, B. Hopfenberg, and V. Stannett, J. Membr. Sci. **13**, 161 (1983).
[2] W. J. Koros, J. Polym. Sci., Polym. Phys. Ed. **18**, 981 (1980).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)

Original Measurements:

I. S. Liau and M. A. McHugh, *Supercritical Fluid Technology*. edited by J. M. L. Penninger, M. Radosz, M. A. McHugh, and V. J. Krukonis (Elsevier, Amsterdam, 1985), pp. 415–434.

Variables:

$T/\mathrm{K} = 315–341.2$
$p/\mathrm{MPa} = 0–26.2$

Prepared By:

A. K. Bokarev

Experimental Data

Sorption isotherms of carbon dioxide in poly(methyl methacrylate).

$T = 315$ K		$T = 331.2$ K		$T = 341.2$ K	
Weight fraction	Pressure/MPa	Weight fraction	Pressure/MPa	Weight fraction	Pressure/MPa
2.78	0.67	2.94	1.36	3.99	1.96
4.52	1.23	8.67	4.12	14.06	7.40
5.52	1.66	12.51	6.12	15.50	8.12
7.71	2.38	12.67	7.13	18.11	11.23
9.16	3.10	18.29	9.28	20.76	12.79
10.21	4.71	18.81	11.59	24.30	15.36
14.74	5.78	22.01	14.28	26.51	17.86
17.57	6.89	23.98	17.83	30.16	20.67
17.73	7.30	24.30	19.57	30.62	22.37
19.13	8.87	25.41	21.88	32.74	26.16
23.77	11.63	26.78	24.91	—	—
25.03	13.41	—	—	—	—
25.94	14.86	—	—	—	—
26.89	15.91	—	—	—	—
27.45	17.97	—	—	—	—
27.94	21.74	—	—	—	—
28.40	23.48	—	—	—	—
28.77	25.95	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

An apparatus similar to that described in Ref. 1 was used for pressure equilibrium sorption of supercritical fluid solvent into solid polymers up to 300 atm. Experimental apparatus included: gas/liquid compressor (Superpressure Inc., Model 46-14025-1), pressure gauges (Dresser Industries, Models Z15R, Z15T), holding tank (316 stainless steel, volume of $123.33 \pm 0.28\ \mathrm{cm}^3$), and high pressure view cell. The temperature was measured using a platinum resistance element (Degussa, Inc.).

Source and Purity of Materials:

CO_2: Linde Co.
PMMA: $M_w = 60\ 600$, $M_n = 33\ 200$, glass transition temperature 378 K.

Estimated Error:

Relative precision of solubilities $< 3\%$.
Precision in T: ± 0.2 K.

References:

[1] S. Ozava, S. Kusumi, and Y. Ogino, Proceeding of the Fourth Int. Conference on High Pressure, Kyoto, Japan, 1974.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)	R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).
Variables:	**Prepared By:**
T/K=305.9–332.0 p/MPa=0–10.4	Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide in PMMA at elevated pressures. Sorption=vol. of gas at STP/mass of unswollen polymer (cm^3(STP) g^{-1}). (The original data were represented graphically)

T=305.9 K		T=315.2 K		T=332.0 K	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/g_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/g_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/g_2^*)$
0.60	11.13	0.64	7.79	1.30	13.78
1.30	21.51	1.34	18.42	2.12	22.88
2.10	33.43	2.16	28.55	3.00	29.40
2.92	46.65	2.92	36.86	3.83	37.99
3.76	58.32	3.74	47.25	4.69	44.25
4.61	70.00	4.50	54.53	5.57	50.78
5.49	83.73	5.38	65.70	6.28	58.06
6.47	103.41	6.23	77.37	7.31	70.27
7.41	119.47	7.25	93.18	8.08	83.22
8.35	119.56	8.12	107.44	8.88	94.89
9.39	119.67	8.89	113.18	9.67	105.79
10.40	121.57	9.66	120.21	10.37	113.33
—	—	10.38	135.99	—	—

Auxiliary Information

Method/Apparatus/Procedure

A gravimetric method was used. The polymer samples were suspended from a quartz spring. Correction for buoyancy were introduced using CO_2 densities up to higher pressures.

Source and Purity of Materials:

CO_2: Linde Co., purity 99.99%.
PMMA: Scientific Polymer Products, M_w=90 000, glass transition temp. 378 K.

Estimated Error:

No information given.

Components:	**Evaluator:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)	Yu. P. Y. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Three independent studies[1–3] have been reported on sorption of carbon dioxide in PEMA. In all three cases, a high molecular weight polymer was used. Koros *et al.*[1] observed, in the pressure range 0–2 MPa, a dual mode sorption shapes of the isotherms concave to the pressure axis. However, at higher pressures, the isotherms change to linear or even nonlinear form convex to the pressure axis[2,3] that was explained in terms of the effect of plastisization exerted by carbon dioxide.

Figure 12 shows the temperature dependence of the pressure p_g at which the glass transition in the polymer takes place, as well as the corresponding concentration C_g of carbon dioxide. It is seen that the data of Refs. 2 and 3 are in a good agreement. The both curves reach the temperature axis as it can be anticipated, in the vicinity of the glass transition temperature for the pure PEMA.

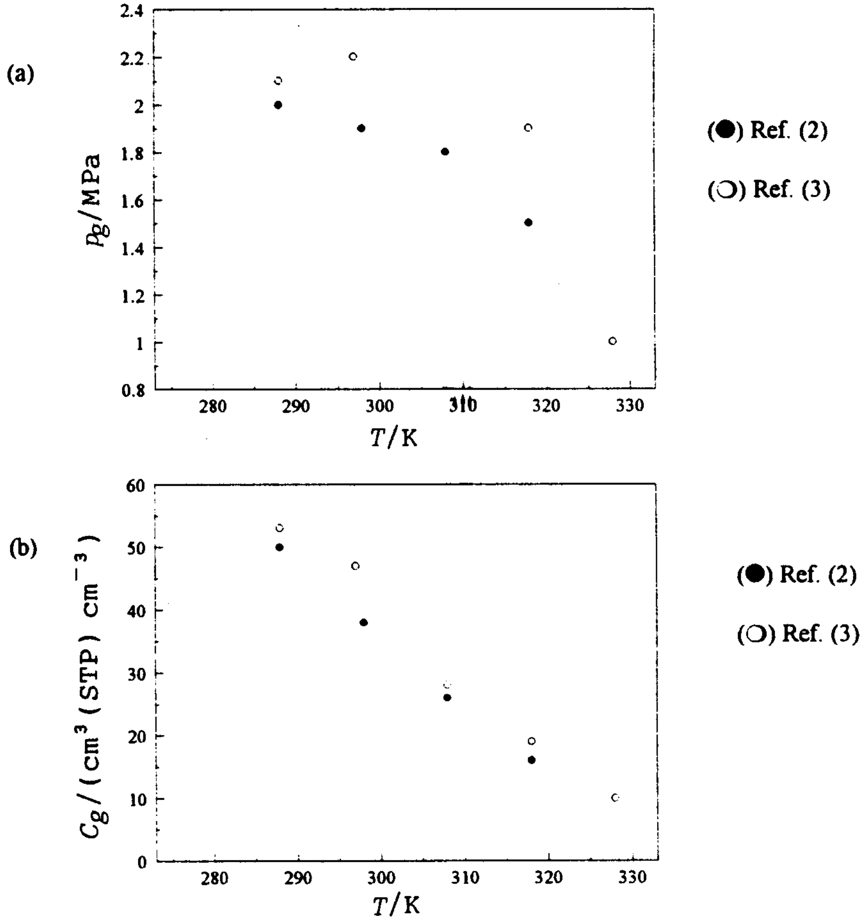

FIG. 12. Temperature dependence of (a) p_g /MPa and (b) C_g /(cm^3(STP) cm^{-3}).

Figure 13 shows Van't Hoff plot for the solubility coefficients taken from the graphs[2,3] or calculated by the dual mode sorption parameters. The values reported in all three works are in good agreement.

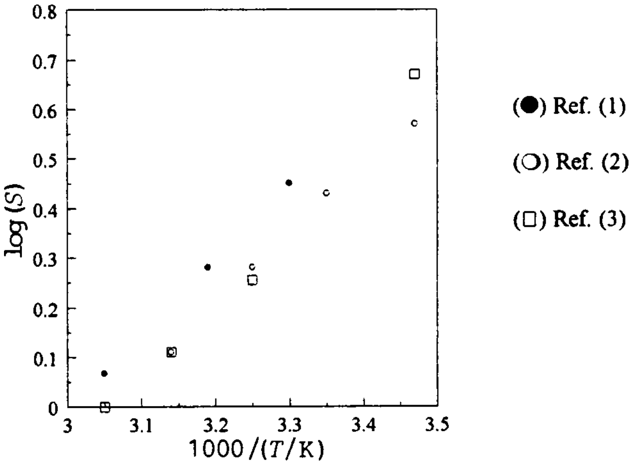

FIG. 13. Temperature dependence of the solubility coefficients.

The least squares treatment of the data gave the following equation:

$$\log(S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}) = -4.353 + 1.433/(T/\mathrm{K}).$$

The corresponding enthalpy of sorption $\Delta H_s = -27.5$ kJ/mol.

It can be recommended for the prediction of the initial slope of the isotherms. For the pressure of carbon dioxide up to 2 MPa the dual mode sorption parameters reported by Koros *et al.*[1] can be used. For the higher pressure, the works of Chiou and Paul[2] and Kamiya *et al.*[3] give rather close values of solubility, but the sorption isotherm obtained in Ref. 3 should be, tentatively, recommended since they cover the wider range of pressure and temperature.

References:

[1] W. J. Koros, G. N. Smith, and V. Stannett, J. Appl. Polym. Sci. **26**,159 (1981).

[2] J. S. Chiou and D. R. Paul, J. Membr. Sci. **45**, 167 (1989).

[3] Y. Kamiya, K. Mizoguchi, T. Hirose, and Y. Naito, J. Polym. Sci., Part B: Polym. Phys. **27**, 879 (1989).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)	W. J. Koros, G. N. Smith, and V. Stannett, J. Appl. Polym. Sci. **26**, 159 (1981).
Variables:	**Prepared By:**
T/K=303–328 p/MPa=0–2.1	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in PEMA

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
303	1.28	8.14	0.193
313	1.14	3.78	0.204
328	0.932	0.996	0.246

Sorption enthalpies: $\Delta H_D = -2.6$ kcal mol^{-1}; -10.9 kJ mol^{-1}; $\Delta H_b = +2.0$ kcal mol^{-1}; $+8.4$ kJ mol^{-1}

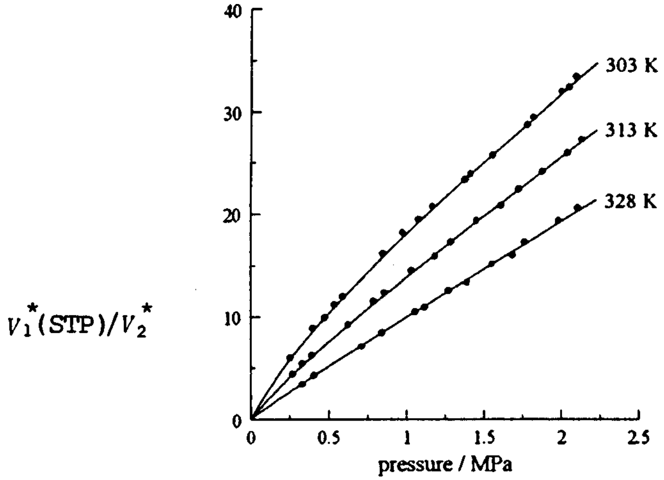

FIG. 14. Sorption isotherms of carbon dioxide in PEMA.

Auxiliary Information

Method/Apparatus/Procedure

The sorption equipment described in Refs. 1 and 2 was used. The procedure involved ''interval'' sorption measurement and standard pretreatment: equilibration with carbon dioxide at 20 atm for 6 h before measurement.

Source and Purity of Materials:

CO_2: Air Products; purity >99.9%.
PEMA: Aldrich Chemical Co., M_w=309 000.

Estimated Error:

No information given.

References

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

[2] W. J. Koros, and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976)

Components:	**Original Measurements:**
(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)	J. S. Chiou and D. R. Paul, J. Membr. Sci. **45**. 167 (1989).
Variables:	**Prepared By:**
T/K = 298–318 p/MPa = 0–3.8	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for methane and argon in PEMA

Gas	T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CH_4	298	0.183	2.87	0.0677
	308	0.165	2.24	0.0536
	313	0.144	1.87	0.0422
Ar	308	0.0902	1.20	0.0405

Solubility coefficient for N_2 at 308 K: 0.058 cm^3(STP) cm^{-3} atm^{-1} (calculated by compiler).

TABLE 2. Sorption isotherms of methane in PEMA at 298 K (a) and 318 K (b) (The original data were represented graphically)

	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
(a)	0.20	0.73	1.43	4.11	2.71	6.85
	0.42	1.41	1.63	4.50	2.90	7.18
	0.64	2.02	1.85	5.05	3.33	8.10
	0.82	2.55	2.06	5.62	3.39	8.27
	1.02	3.03	2.28	5.95	—	—
	1.25	3.62	2.47	6.19	—	—
(b)	0.26	0.55	1.37	2.65	2.67	4.89
	0.27	0.59	1.43	2.81	2.76	4.99
	0.55	1.12	1.74	3.29	3.00	5.39
	0.66	1.40	1.96	3.62	3.29	5.83
	0.81	1.60	2.19	4.16	3.30	5.89
	0.97	1.91	2.29	4.14	3.37	6.42
	1.24	2.45	2.50	4.51	3.67	6.42

TABLE 3. Sorption isotherms of various gases in PEMA at 308 K (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
Ar					
0.27	0.33	1.40	1.68	2.79	3.21
0.39	0.48	1.61	1.94	2.85	3.21
0.50	0.61	1.75	2.05	3.29	3.69
0.77	0.94	1.98	2.25	3.43	3.82
0.85	1.07	2.04	2.42	3.68	4.08
1.04	1.22	2.27	2.66	—	—
1.26	1.51	2.45	2.77	—	—
CH_4					
0.25	0.70	1.52	3.44	2.83	6.01
0.51	1.29	1.82	4.15	3.09	6.42
0.75	1.89	2.14	4.63	3.20	6.71
1.02	2.44	2.23	5.00	3.54	7.34
1.34	3.20	2.60	5.57	—	—
CH_4 (films conditioned in 30 atm of CO_2)					
0.33	0.90	1.03	2.70	2.07	4.69
0.52	1.38	1.28	3.09	2.33	5.2
0.61	1.62	1.42	3.47	2.53	5.28
0.77	2.02	1.62	3.75	2.73	5.66
0.92	2.30	2.00	4.47	2.76	5.90
N_2					
0.28	0.17	1.56	0.95	2.83	1.62
0.34	0.26	1.62	0.95	2.91	1.73
0.62	0.41	1.89	1.10	3.16	1.86
0.68	0.46	2.11	1.23	3.39	2.03
0.90	0.59	2.25	1.34	3.53	1.99
1.05	0.61	2.32	1.39	3.67	2.21
1.45	0.87	2.63	1.54	3.78	2.21

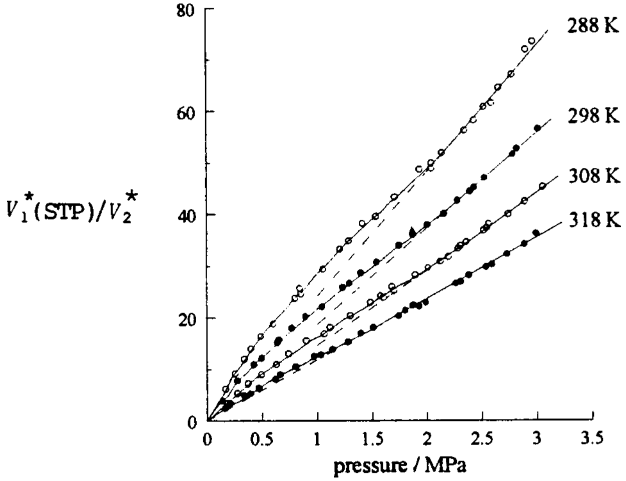

FIG. 15. Sorption isotherms of carbon dioxide in PEMA at 288, 298, 308, and 318 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured by the pressure decay method using a dual-volume sorption cell.

Source and Purity of Materials:

PEMA: DuPont Co. (Elvacite 2042).
$M_w = 438\,000$, glass transition temp. 342 K (DSC method).

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)

Original Measurements:

Y. Kamiya, K. Mizoguchi, T. Hirose, and Y. Naito, J. Polym. Sci., Part B: Polym. Phys. **27**, 879 (1989).

Variables:

$T/\mathrm{K} = 288$
$p/\mathrm{MPa} = 0-5.1$ (50 atm)

Prepared By:

A. K. Bokarev

Experimental Data

The isotherms were treated by the equation:

$$C = C_D + C_H = [k_D \exp(sC^*)]p + C'_{H0}bp[(1 - C^*/C_g)/(1+bp)],$$

where the parameters k_D, C'_{H0}, and b have the usual meaning; s is the parameter characterizing the concentration dependence of the ordinary dissolution, that is, $s=0$ and $s>0$ correspond to Henry's law and Flory–Huggins dissolution, respectively. C_g is the solute concentration corresponding to the glass transition and

$$C^* = C_D + fC_H = [k_D p + fC'_{H0}bp/(1+bp)]/[1 + fC'_{H0}bp/C_g(1+bp)],$$

where f is the ratio of the plastisizing ability of a Langmuir species (H) to that of an ordinary dissolved species (D).

TABLE 1. Parameters for ordinary dissolution (Flory–Huggins's) and for Langmuir isotherms

T/K	k_D/cm^3(STP) cm^{-3} atm^{-1}	C'_{H0}/cm^3(STP) cm^{-3}	b/atm^{-1}	10^3 S/cm^3(STP) cm^{-3}	C_g/cm^3(STP) cm^{-3}
288	2.11	28.9	0.097	3.0	−0.17
297	1.90	22.5	0.065	2.3	−0.34
308	1.42	15.8	0.055	2.6	−0.28
318	1.15	9.5	0.045	2.8	−0.27
328	0.97	3.5	0.022	3.1	−0.22
338(T_g)	0.84	0	0	2.4	−0.40
348	0.76	0	0	1.9	−0.51
358	0.67	0	0	3.1	−0.19

TABLE 2. Sorption and desorption isotherms of carbon dioxide in PEMA at (a) 288 K, (b) 297 K, (c) 308 K, and (d) 318 K (The original data were represented graphically)

Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$
(a) Sorption					
0.11	3.96	1.58	42.26	3.04	79.99
0.21	7.92	2.06	50.19	3.54	99.79
0.61	19.99	2.23	54.91	3.77	109.59
1.10	30.75	2.56	64.90	—	—
Desorption					
0.21	9.24	1.08	32.07	2.82	71.88
0.36	13.76	1.34	36.97	3.29	90.17
0.61	21.12	1.82	46.79	—	—
0.82	26.97	2.32	59.05	—	—
(b) Sorption					
0.21	6.04	2.23	46.62	5.02	122.46
0.69	16.79	4.21	99.07	—	—
1.47	31.33	4.90	129.61	—	—
Desorption					
0.11	3.40	1.10	26.23	2.60	54.55
0.29	9.24	1.29	27.37	3.46	77.19
0.49	13.58	1.71	35.67	3.98	88.89
0.91	20.76	2.03	44.73	—	—
(c) Sorption					
0.21	4.34	1.29	20.21	3.21	50.24
0.50	9.06	1.68	25.69	3.67	59.68
0.71	10.58	1.88	28.52	4.92	87.61
0.89	14.54	2.64	40.80	4.97	88.56
Desorption					
0.31	6.23	1.47	22.86	3.38	55.34
0.43	7.18	2.05	31.36	4.03	66.85
0.71	12.65	2.36	35.89	4.38	75.34
1.06	17.56	2.93	45.52	—	—
(d) Sorption					
0.36	5.10	1.58	18.91	3.55	45.74
0.86	10.21	2.56	31.76	5.02	69.54
Desorption					
0.61	8.31	2.07	25.33	4.27	57.26
1.09	13.42	3.06	38.56	—	—

TABLE 3. Sorption and desorption isotherms of carbon dioxide in PEMA at (a) 328 K, (b) 338 K, (c) 348 K, and (d) 358 K (The original data were represented graphically)

Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\text{STP})/V_2^*)$
(a) Sorption					
0.30	3.59	1.49	14.38	4.03	43.88
0.70	7.00	2.26	23.27	4.98	55.79
1.08	10.97	3.01	31.59	—	—
Desorption					
0.14	2.08	1.28	12.49	4.40	48.42
0.51	5.30	2.05	21.19	—	—
0.90	8.89	3.21	34.24	—	—
(b) Sorption					
1.23	10.04	3.43	30.29	—	—
2.23	19.50	5.01	46.56	—	—
Desorption					
0.31	2.65	1.75	15.34	4.26	38.99
0.70	5.68	2.84	25.37	—	—
(c) Sorption					
0.37	2.65	2.08	16.10	4.02	32.20
1.09	8.34	2.57	19.70	4.16	33.34
1.58	11.37	3.06	23.68	5.01	41.29
1.83	13.64	3.53	28.22	—	—
(d) Sorption					
0.15	1.51	1.58	10.43	3.27	22.94
0.60	3.61	2.08	14.22	3.77	26.54
0.62	4.55	2.56	17.63	4.26	30.14
1.10	7.02	3.04	21.23	5.02	36.20

Auxiliary Information

Method/Apparatus/Procedure

Sorption and desorption isotherms were measured with an electronic microbalance (Cahn model 2000) placed in a high-pressure chamber in Ref. 1

Source and Purity of Materials:

CO_2: purity 99.99%.
PEMA: prepared by radical polymerization; density 1.120 g/cm^3 at 298 K (flotation method), glass transition temperature of penetrant-free PEMA 334 K.

Estimated Error

No information given.

References:

[1] Y. Kamiya, K. Mizoguchi, T. Hirose, and Y. Naito. J. Polym. Sci., Polym. Phys. Ed. **24**, 535 (1986).

Components:
(1) Propane; C_3H_8; [74-98-6]
(2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)

Original Measurements:
U. B. Goradia and H. G. Spencer, J. Appl. Polym. Sci. **33**, 1525 (1987).

Variables:
T/K: 288–353
p/kPa: 0–79.74

Prepared By:
A. K. Bokarev

Experimental Data

TABLE 1. Apparent Henry's law solubility coefficient

T/K	$k_D\ 10^2$/cm^3(STP) cm^{-3} cm Hg^{-1}
333	2.10(+3%)
333*	2.06(+3%)
342	2.44(+6%)
348	2.27(+7%)
353	1.96(+9%)

*Sorption experiment with annealed samples.

TABLE 2. Dual mode sorption model parameters

T/K	$k_D 10^2$/cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	$b\ 10^2$/cm Hg^{-1}
288	3.02(±7%)	4.83(±10%)	2.10(±11%)
303	2.73(±10%)	3.10(±14%)	1.20(±17%)
318	2.24(±9%)	1.77(±15%)	1.05(±19%)

Auxiliary Information

Method/Apparatus/Procedure

A low pressure, finite volume, sorption apparatus previously described[1] was used at pressures up to 60 cm Hg.

Source and Purity of Materials:

Atactic PEMA obtained from Polyscience, Inc., as a primary standard, had an M_w of 350 000 with $M_w/M_n = 2.2$; $T_g = 338$ K.

Estimated Error:

References:

[1] J. A. Yavorsky and H. G. Spencer, J. Appl. Polym. Sci. **31**, 501 (1986).

Components:
(1) Argon: Ar; [7440-37-1]
(2) Poly(ethyl methacrylate) (PEMA); [9003-42-3] (VII)

Original Measurements:
Y. Kamiya, K. Mizoguchi, Y. Naito, and D. Bourbon, Int. Congress on Membranes (ICOM-90), Chicago, 1990, pp. 1382–1384.

Variables:
T/K = 278.2–358.2
p/MPa = 0–5.0 (0–50 atm)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for argon in PEMA

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
278.4	—	5.23	0.024
283.2	—	4.21	0.023
288.2	—	3.55	0.023
298.2	—	2.75	0.020
308.2	—	2.23	0.019
318.2	—	2.36	0.014
328.2	0.104	3.49	0.006
338.2	0.094	1.40	0.006
343.2	0.091	0.21	0.020
348.2	0.088	—	—
353.2	0.089	—	—

Table 2. Sorption isotherms of argon in PEMA (The original data were represented graphically)

$T=278.4$ K		$T=298.2$ K		$T=328.2$ K		$T=358.2$ K	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.51	1.01	0.34	0.28	0.51	0.54	0.51	0.74
0.54	0.99	0.39	0.33	0.52	0.49	0.52	0.67
0.56	1.05	0.85	0.76	0.10	1.07	1.00	1.43
0.99	1.86	1.10	0.92	1.01	1.05	1.01	1.35
1.02	1.81	1.10	0.99	1.50	1.58	0.99	1.29
1.04	1.85	2.08	1.81	1.49	1.54	1.50	2.08
1.51	2.61	2.08	1.85	1.99	2.10	1.50	1.92
2.01	3.47	3.07	2.67	2.00	2.06	1.99	2.75
2.01	3.39	3.07	2.71	2.96	3.12	2.00	2.69
2.01	3.37	3.32	2.91	2.96	3.05	1.98	2.60
2.51	4.16	4.05	3.49	3.95	4.06	1.99	2.52
3.01	4.78	4.11	3.56	3.97	4.02	2.48	3.23
3.02	4.70	5.04	4.33	4.95	5.07	2.48	3.08
3.98	6.01	5.03	4.39	4.95	5.02	2.99	3.85
3.98	5.94	—	—	—	—	3.02	3.85
3.98	5.89	—	—	—	—	2.98	3.74
4.90	7.13	—	—	—	—	2.99	3.67
4.90	7.10	—	—	—	—	2.97	3.61
—	—	—	—	—	—	3.47	4.33
—	—	—	—	—	—	3.49	4.17
—	—	—	—	—	—	3.95	4.90
—	—	—	—	—	—	3.96	4.81
—	—	—	—	—	—	3.97	4.69
—	—	—	—	—	—	4.37	5.28
—	—	—	—	—	—	4.49	5.22
—	—	—	—	—	—	4.90	5.84
—	—	—	—	—	—	4.96	5.87
—	—	—	—	—	—	4.95	5.72

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were determined gravimetrically with an electronic microbalance Cahn 2000.

Source and Purity of Materials:

Ar: purity 99.999%.
PEMA: glass transition temperature 334 K.

Estimated Error:

No information given.

Components:

(1) Ethane; C_2H_6; [74-84-0] *n*-butane; C_4H_{10}; [106-97-8]
(2) Poly(*n*-butyl methacrylate) (PBMA); [9003-63-8] (VIII)

Original Measurements:

S. A. Stern, U. M. Vakil, and G. R. Mauze, J. Polym. Sci., Part B: Polym. Phys. **27**, 405 (1989).

Variables:

T/K: 259.4–315.4
p/kPa: 0–67

Prepared By:

A. K. Bokarev

Experimental Data

Sorption isotherms of ethane are linear in the range 259–315 K. Solubility coefficients can be described by van't Hoff equation

$$S=5.25\times10^{-5}-\exp(-\Delta H_s/RT)\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3\ \mathrm{cm\ Hg},$$

where $\Delta H_s=-14.9$ kJ/mol.

Sorption isotherms of butane are linear in the range 283–313 K: at lower temperatures they are convex to the pressure axis. The isotherms were represented by exponential relation

$$C=S(0)p-\exp(\sigma\cdot c),$$

where $S(0)$ is the Henry's law solubility coefficient and σ is a constant which depends on temperature. The parameters of this equation are given below:

T/K	$S(0)/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ (\mathrm{cm\ Hg})^{-1}$	$\sigma/\mathrm{cm}^{-3}\ \mathrm{cm}^{-3}(\mathrm{STP})$
273	0.432	0.0128
283	0.336	0.0051
293	0.252	0
303	0.176	0
313	0.179	0

S(0) can be described by the van't Hoff equation

$$S(0)=5.24\times10^{-4}\ \exp(-\Delta H_g/RT)\mathrm{cm}^{-3}(\mathrm{STP})\ \mathrm{cm}^{-3}\ (\mathrm{cm\ Hg})^{-1},\ \ \text{where } \Delta H_s=-20.6\ \text{kJ/mol}.$$

Auxiliary Information

Method/Apparatus/Procedure

The solubility was measured by a gravimetric method. The apparatus included a Cahn microbalance, Model 2000 RG.

Source and Purity of Materials:

PBMA (Scientific Polymer Products of Ontario, NY) had a density of 1.06 g/cm^3 at 299 K and glass transition temperature (DSC) in the temperature range from 295 to 308 K.
The minimum purity of ethane and *n*-butane (Linde Division of Union Carbide Corp.) were 99.0%.

Estimated Error:

No information given.

3.7. Polystyrene—Various Gases

Components:	**Evaluator:**
(1) Argon; Ar; [7440-37-1] (2) Polystyrene (PS); [9003-53-6] (IX)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Only three papers[1–3] have been published for the system PS–argon. The work of Schulz and Gerrens[1] is inconsistent and should be excluded from further consideration. Vieth *et al.*[3] reported sorption isotherms and dual mode sorption parameters for the solubility in oriented and unoriented PS at the ambient temperature, whereas Durrill[2] studied the solubility in PS above its glass transition temperature.

Pressure dependence of solubility is given below based on the parameters of sorption isotherms obtained by Vieth *et al.*[3]

p/MPa	C/cm^3(STP) cm^{-3}
0.5	1.2
1.0	2.2
1.5	3.2
2.0	4.0

Combined consideration of the results from Refs. 2 and 3 results in the enthalpy of sorption of argon in PS equal to −7.1 kJ/mol.

References:

[1] G. V. Schulz and H. Gerrens, Z. Phys. Chem. **7**, 182 (1956).

[2] P. L. Durrill, dissertation, Virginia Polytechnic Institute, 1965.

[3] W. R. Vieth, P. M. Tam, and A. S. Michaels, J. Colloid Interface Sci. **22**, 360 (1996).

Components:	**Evaluator:**
(1) Nitrogen; N_2; [7727-37-9] (2) Polystyrene (PS); [9003-53-6] (IX)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Four investigations[1–4] have been reported for the solubility of nitrogen in PS. The work by Scultz and Gerrens[2] seems to be unreliable: the pressure of the measurement is not indicated, besides there is some inconsistency among the solubility coefficients for various gases (N_2,He, H_2). The only paper reported the solubility for the ambient temperature is the paper of Vieth *et al.*,[4] and its results can be, tentatively, recommended for this most important range of temperature.

Two papers[1,3] deal with solubility at higher temperature above T_g of PS and at higher pressure. The results of them are in disagreement. Tentatively, one can give the preference to the results of Durrill.[3] Further careful work is needed before really reliable values can be advanced as recommended for this system.

The values of solubility at different pressures and 298 K given below are based on dual mode sorption parameters reported in Ref. 4.

p/MPa	C/cm^3(STP) cm^{-3}
0.5	0.6
1.0	1.2
1.5	1.7
2.0	2.3

References:

[11] D. M. Newitt and K. E. Weale, J. Chem. Soc. 1541 (1948).

[2] V. Schulz and H. Gerrens, Z. Phys. Chem. **7**, 182 (1956).

[3] P. L. Durrill, dissertation, Virginia Polytechnic Institute, 1965.

[4] W. R. Vieth, P. M. Tam, and A. S. Michaels, J. Colloid Interface Sci. **22**, 360 (1966).

Components:	**Evaluator:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polystyrene (PS); [9003-53-6] (IX)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994.

Critical Evaluation:

Nine experimental studies are available for the solubility of carbon dioxide in PS. In several papers this system was studied in the range of glassy state of this polymer and at pressures as high as 7.0 MPa.[3,4,6–9] Newitt *et al.*[1] and Durrill[2] have studied the solubility at higher temperatures and pressures. Chiou, Maeda, and Paul[5] have investigated sorption in plasticized PS.

Different samples of PS having molecular mass in the range 36 000–850 000 were studied in the range of temperature 293–393 K. Up to 333 K sorption isotherms are concave to the pressure axis, i.e., agree with the dual mode sorption model, above this temperature they are linear possibly due to the plasticization effect exerted by carbon dioxide on PS.

A summary of the dual mode sorption parameters as well as the apparent solubility coefficients *S* are given in Table 1.

TABLE 1. The dual mode sorption parameters at different temperatures

T/K	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
293	0.801	13.0	0.184	3.19	7
303	0.713	11.0	0.134	2.19	7
308	0.535	8.6	0.194	2.20	9
308	0.50	9.2	0.16	1.97	4
313	0.586	8.8	0.092	1.40	7
313	0.80	8.3	0.14	1.96	6
323	0.70	6.0	0.15	1.60	6
333	0.66	5.0	0.11	1.21	6

Units: k_D and S/cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}.

The parameters k_D and b decrease with temperature but do not form an overall smooth dependence. Accordingly, it is not included into this critical evaluation and, for the temperatures 293–313 K, the results of Sada *et al.*[7] and, for the range 313–333 K, the results of Carfagna *et al.*[6] should be recommended.

The values of C'_H and S found by different authors[4,6,7,9] are in good agreement and form, within experimental scatter, a smooth temperature dependence (Figs. 16 and 17). The results of Vieth *et al.*[3] reveal a deflection from these and were excluded from the group of recommended values.

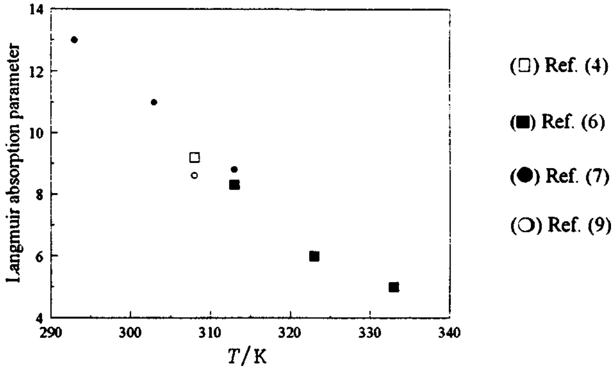

FIG. 16. Temperature dependence of Langmuir adsorption parameter C'_H/(cm^3(STP) cm^{-3}).

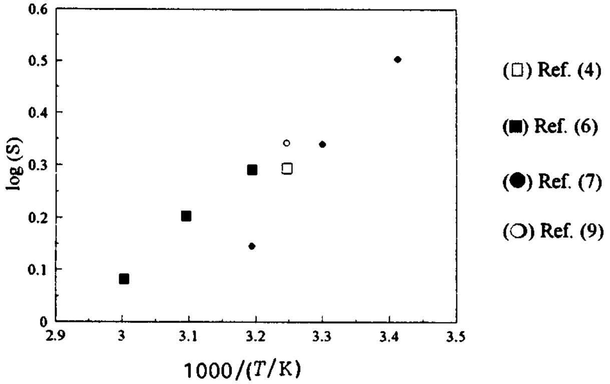

FIG. 17. Temperature dependence of apparent solubility coefficient S/(cm^3(STP) cm^{-3} atm^{-1}).

Temperature dependence of C'_H intersects the horizontal axis at about 360 K, i.e., somewhat lower than accepted glass transition temperature of PS (about 373 K).

Temperature dependence of the apparent solubility coefficient can be given by the equation

$$\log(S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}) = -2.840 + 970.0/(T/\mathrm{K}).$$

Enthalpy of sorption is equal to −18.6 kJ/mol.

The interval of higher pressures has been investigated by Wissinger and Paulaitis.[8] They found nearly linear sorption isotherms, probably, owing to the plasticization effects. The solubilities found in Ref. 6 and 8 for 3.0 MPa, where the pressure ranges of two works overlap, are in good agreement. So for higher pressure the results of Ref. 8 may be recommended.

All the results considered above concern high molecular mass PS (M_M about 105). Toi and Paul[4] studied the effects of the molecular mass of PS on the solubility and the parameters of the dual mode sorption isotherms. The increase in molecular mass from 3 600 to 850 000 results in the increase in the solubility at any given pressure as well as in the values of C'_H, while two other parameters remain intact.

The solubility in PS stretched or biaxially oriented was studied by Vieth *et al.*[3] and Carfagna *et al.*[6] It was shown that the deformation tends to decrease the solubility. Meanwhile, no quantitative recommendation can be made basing on the results of these papers.

The range of rubbery state of PS was investigated much less thoroughly.[1,2] The results of Newitt and Weale[1] and of Durrill[2] do not agree with each other. The results of Ref. 2 may be preferred at least tentatively. Further studies are needed to resolve this range of conditions.

References:

[1] D. M. Newitt and K. E. Weale, J. Chem. Soc. 1541 (1948).
[2] P. L. Durrill, dissertation, Virginia Polytechnic Institute, 1965.
[3] W. R. Veith, P. M. Tam, and A. S. Michaels, J. Colloid Interface Sci. **22**, 360 (1966).
[4] K. Toi and D. R. Paul, Macromolecules **15**, 1104 (1982).
[5] J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **30**, 4019 (1985).
[6] C. Carfagna, L. Nicodemo, L. Nicolais, and G. Campanile, J. Polym. Sci., Part B: Polym. Phys. **24**, 1805 (1986).
[7] E. Sada, H. Kumazawa, H. Yakushji, Y. Bamba, K. Sakata, and S-T. Wang, Ind. Eng. Chem., Res. **26**, 433 (1987).
[8] R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).
[9] P. C. Raymond and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **28**, 2079 (1990).

Components:	**Evaluator:**
(1) Methane; CH_4; [74-82-8] (2) Polystyrene (PS); [9003-53-6] (IX)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

A number of studies[1–8] have been published for the system PS–methane. Sorption isotherms in the range of pressure 0–3 MPa at the temperatures 293–323 K, i.e., in the glassy state have been reported by several authors.[3,4,6–8] Lundberg *et al.*[1,2,5] have studied this system at much higher pressures and at temperatures above the glass transition of this polymer. These two sets of data should be considered separately.

A summary of the parameters of the dual mode sorption model for this system are presented in Table 1 at different temperatures. The apparent solubility coefficients S are shown as well. It is seen that the C'_H and S values decrease with temperature monotonously while temperature dependence for two other parameters k_D and b is not evident. The linear extrapolation of the temperature dependence of C'_H indicates that Langmuir capacity parameter vanishes at the temperature somewhat lower than the glass transition temperature of PS.

TABLE 1. Dual mode sorption parameters at different temperatures

T/K	k_D	C'_H	b	$S=k_D+C'_H b$	Ref.
293	0.305	5.00	0.0811	0.7105	7
298	0.193	3.25	0.164	0.726	4
298	0.16	7.4	0.108	0.9592	3
303	0.277	4.93	0.0623	0.584	7
303	—	—	—	0.5244	6
308	0.175	2.53	0.146	0.5444	4
308	0.135	3.28	0.061	0.335	8
313	0.244	3.63	0.0439	0.4034	7
318	0.165	1.98	0.112	0.3868	4
323	—	—	—	0.3344	6

Units: k_D and $S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$; $C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$; $b/\mathrm{atm^{-1}}$.

Smoothed concentration of methane dissolved at different temperatures and pressures are shown in Table 2. The solubility coefficients obtained in high pressure (0–3.0 MPa)[4,7,8] and low pressure (up to 7 kPa)[6] ranges are in reasonable agreement.

TABLE 2. Smoothed data for solubility $C/(\mathrm{cm^3(STP)cm^{-3}})$ of methane in PS

	Pressure/MPa			
T/K	1.0	2.0	3.0	Ref.
293	5.3	9.2	12.7	7
298	3.9	6.3	8.5	4
308	3.0	5.0	6.8	4, 8
318	2.7	4.7	6.5	4

The results of Vieth *et al.*[3] show that biaxial orientation leads to the decrease in solubility. All three model parameters (k_D, C'_H, b) go down as well.

For the range of higher pressures and temperatures the earlier results[1,2] have been proved later[5] to be somewhat erroneous. Recalculated data are presented in Ref. 5 and can be recommended.

Smoothed values of solubility are presented below for different pressures and temperatures.

TABLE 3. Solubility of methane in PS at high pressure and temperature

p/atm	$C/\mathrm{cm^3(STP)\ g^{-1}}$	p/atm	$C/\mathrm{cm^3(STP)\ g^{-1}}$
	$T=398.6$ K		$T=428.6$ K
100	8.3	100	
200	16	200	
300	20		$T=461.6$ K
400	24	100	12
500	26	200	21
600	28	300	30

References:

[1] J. L. Lundberg, B. M. Wilk, M. J. Huyett, J. Polym. Sci. **57**, 165, 275 (1962).

[2] J. L. Lundberg, B. M. Wilk, and M. J. Huyett, Ind. Eng. Chem., Fundam. **2**, 37 (1963).

[3] W. R. Vieth, P. M. Tam, and A. S. Michaels, J. Colloid Interface Sci. **22**, 360 (1966).

[4] W. R. Vieth, C. S. Frangoulis, and J. A. Rionda, J. Colloid Interface Sci. **22**, 454 (1966).

[5] J. L. Lundberg, E. J. Mooney, and C. E. Rogers, J. Polym. Sci.: Part A **7**, 947 (1969).

[6] J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).

[7] E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, K. Sakata, and S-T. Wang, Ind. Eng. Chem., Res. **26**, 433 (1987).

[8] P. C. Raymond and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **28**, 2079 (1990).

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

The papers where solubility data have been reported for the system PS–propane can be partitioned into two groups. Barrie *et al.*,[2] Yavorsky,[4] and Stewart *et al.*[6] have studied sorption isotherms by gravimetric or volumetric methods at the temperatures 293–353 K and in the pressure range 0–5 kPa. Inverse gas chromatography was employed in measurement solubility at higher temperatures.[4–6] So these two groups of works cover the different intervals of conditions and should be considered separately.

In the lower temperature range, the dual mode sorption parameters for the sorption in glass PS have been reported only in Refs. 2 and 4 Barrie *et al.* found much higher values of b and the smaller C'_H values than those reported by Yavorsky.[4] There are some regular discrepancies in the apparent solubility coefficients $S=k_D+C'_H b$. On the other hand, the data of Barrie *et al.*[2] agree reasonably with the sorption isotherms reported in Ref. 6. Bearing in mind this, and the greater scatter of the points in the sorption isotherms obtained by Yavorsky[4] the results of Barrie *et al.* should be tentatively recommended for the temperature range 293–333 K.

The values of Langmuir capacity constant C'_H reported in Ref. 2 go down with temperature and vanish at about 360 K, i.e., below the glass transition temperature of PS.

In the high temperature range, the data of Iwai *et al.*[3,5] and Stiel and Harnish[1] agree quite reasonably. Average solubility coefficients $S/(\mathrm{g\ Mpa^{-1}\ g^{-1}})$ based on these results are given below:

T/K	408	423	448	473	498
$S10^2$	1.56	1.33	1.06	0.88	0.76

References:

[1] L. I. Stiel and D. F. Harnish, AIChE J. **22**, 117 (1976).
[2] J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).
[3] M. Ohzono, Y. Iwai, and Y. Arai, Kagaku Kogaku Ronbunshu **10**, 536 (1984).
[4] J. A. Yavorsky, dissertation, Clemson University, 1984.
[5] Y. Iwai, M. Ohzono, and Y. Arai, Chem. Eng. Commun. **34**, 225 (1985).
[6] M. E. Stewart, H. B. Hopfenberg, W. J. Koros, and N. R. McCoy, J. Appl. Polym. Sci. **34**, 721 (1987).

Components:

(1) 2-Methylpropane; C_4H_{10}; [75-28-5]
(2) Polystyrene (PS); [9003-53-6] (IX)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Three experimental studies[1–3] are available for the solubility of 2-methylpropane in PS. The results have been obtained by means of inverse gas chromatography.

Solubility coefficients $S/(\mathrm{cm^3(STP)\ g^{-1}\ atm^{-1}})$ from these papers are compared below:

	T/K			
Ref.	423	448	473	498
1	1.20	0.86	0.65	0.52
2, 3	0.77	0.66	0.58	0.50

It is evident that there is a reasonable agreement between the data at higher temperatures, but at the lower temperature the discrepancy becomes significant. Further research is desirable to resolve this system.

References:

[1] L. I. Suel and D. F. Harnish, AIChE. J. **22**, 117 (1976).
[2] M. Ohzono, Y. Iwai, and Y. Arai, Kagaku Kogaku Ronbunshu **10**, 536 (1984).
[3] Y. Iwai, M. Ohzono, and Y. Arai, Chem. Eng. Commun. **34**, 225 (1985).

Components:

(1) Chlorodifluoromethane; $CHClF_2$; [75-45-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

The solubility coefficients measured at higher temperatures[2] were recalculated to convert them into the same units as in Ref. 3, i.e., (cm^3(STP)/cm^3 atm). Volumetric thermal expansion coefficients[4] 2×10^{-4} K^{-1} at $T<T_g$ (●) and 6×10^{-4} K^{-1} at $T>T_g$ (○) were used in the calculation. It is seen that the slopes of the linear dependences and, hence, the enthalpies of sorption change when passing from glassy to rubbery state of PS. The point reported by Durrill and Griskey was not included, tentatively, into the calculation. The enthalpies of sorption corresponding the glassy and rubbery states are equal to −34.2 and −15.4 kJ/mol, respectively.

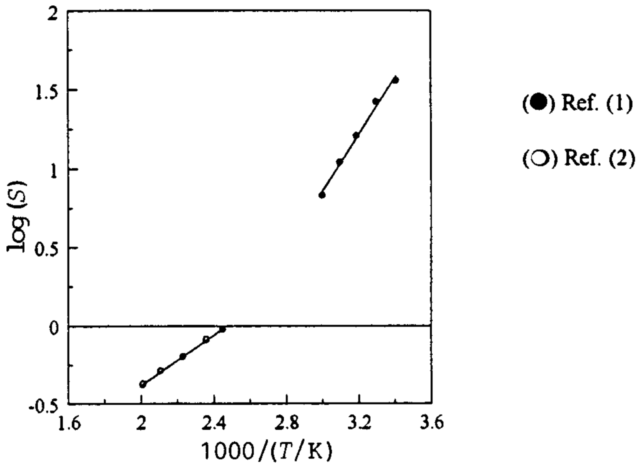

FIG. 18. The solubility of chlorodifluoromethane (Freone 22) in PS was measured only in three papers.[1–3] Barrie *et al.*[3] studied this system using a gravimetric technique in the temperature range 293–333 K. At much higher temperatures, this system was investigated by means of inverse gas chromatography.[2] The figure shows the temperature dependence T/K of the solubility coefficient S/(cm^3(STP) g^{-1} atm^{-1}).

References:

[1] P. L. Durrill and R. G. Griskey, AIChE J. **12**, 1147 (1966).
[2] L. I. Stiel and D. F. Harnish, AIChE J. **22**, 117 (1976).
[3] J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).
[4] *Polymer Encyclopaedia* (in Russian) (Sov. Encycl. Publishers, Moscow, 1977), Vol. 3, p. 534.

Components:

(1) Nitrogen; N_2; [7727-37-9]
Ethyne; C_2H_2; [74-86-2] Hydrogen; H_2; [1333-74-0] Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene; (PS); [9003-53-6] (IX)

Original Measurements:

D. M. Newitt and K. E. Weale, J. Chem. Soc. 1541 (1948).

Variables:

T/K: 347–464
p/MPa: 8.0–30.0

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Solubility C/cm^3(STP)/cm^3 of gases in PS at 443 K

Gas	p/atm	C	Gas	p/atm	C
H_2	80	2.89	N_2	118	2.95
	142	5.35		182	5.02
	224.5	8.48		187	5.57
	233	9.42		232	6.15
	243	9.66		282.5	7.93
	306.5	11.95		287	7.77
CO_2	50	3.04	C_2H_2	49	5.27
	51	2.82		77.55	8.05
				92.5	9.75

TABLE 2. Temperature dependence of solubility coefficient S/cm^3(STP)/cm^3 atm

Gas	T/K	S	Gas	T/K	S
N_2	347	0.035	H_2	290	0.065
	409	0.033		322	0.061
	422	0.031		345	0.060
	443	0.0275		399	0.047
	464	0.026		415	0.042
				443	0.037
				459.5	0.034

The data fitted the following van't Hoff equations:

$$\log(S/\mathrm{cm^3(STP)/cm^3\ atm}) = -2.4 + 1900/4.58\ (T/\mathrm{K}) \quad \text{for } H_2:$$

$$\log(S/\mathrm{cm^3(STP)/cm^3\ atm}) = -2.4 + 1700/4.58\ (T/\mathrm{K}) \quad \text{for } N_2.$$

Auxiliary Information

Method/Apparatus/Procedure

Manometric method of measurement of solubility was used.

Source and Purity of Materials:

PS from B. X. Plastics Ltd. was studied. No characteristics of the polymer given.

Estimated Error:

Nothing specified.

Components:

(1) Helium; He; [7440-59-7] Nitrogen; N_2; [7727-37-9] Argon; Ar; [7440-37-1] Carbon dioxide; CO_2; [124-38-9] Chlorodifluoromethane (R22); $CHFCl_2$; [75-45-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

P. L. Durill, Ph.D. dissertation, Virginia Polytech. Inst., 1965.
P. L. Durill and R. G. Griskey, AIChE J. **12**, 1147 (1965).

Variables:

T/K: 461
p/MPa: 0.3–1.9 (3–19 atm)

Prepared By:

A. K. Bokarev

Experimental Data

Henry's law solubility coefficients S of gases in PS

Gas	Pressure/atm	$S/(\text{cm}^3(\text{STP})/\text{g atm})$
He	2–13.6	0.029 ± 0.020
N_2	3.1–7.0	0.0488
Ar	3.3–7.4	0.093 ± 0.004
CO_2	7.4–19.1	0.223 ± 0.015
$CHFCl_2$	5.8–8.1	0.388

Auxiliary Information

Method/Apparatus/Procedure

The equipment and a manometrical procedure for solubility measurements were similar to those of Lundberg *et al.*[1]

Source and Purity of Materials:

PS used is a product of Monsanto Co. $M_w=450\,000$; $T_g=354$ K; $\rho=1.05$ g/cm^3.
Gases from Air Reduction Co., had a minimum purity:
CO_2-99.5%;
N_2-99.90%;
Ar-99.997%;
He-99.99%;
R22 (Allied Chemical Co.)-99.9%.

Estimated Error:

$\delta C/C\leq 8\%$.

References:

[1] J. L. Lundberg, M. B. Wilk, and M. J. Huyett, Appl. Phys. **31**, 1131 (1960).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

W. R. Vieth, P. M. Tam, and A. S. Michaels, J. Colloid Interface Sci. **22**, 360 (1966).

Variables:

T/K=298
p/MPa=0–2.1 (0–20 atm)

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for various gases in polystyrene at 298 K

	k_D /cm^3(STP) cm^{-3} atm^{-1}		C'_H/cm^3(STP) cm^{-3}		b/atm^{-1}	
Gas	Oriented	Unoriented	Oriented	Unoriented	Oriented	Unoriented
N_2	0.02	0.025	6.65	8.3	0.015	0.013
Ar	0.06	0.065	7.55	9.1	0.021	0.021
CH_4	0.13	0.160	5.58	7.4	0.080	0.108
CO_2	0.57	0.650	6.05	7.7	0.400	0.370

TABLE 2. Solubility isotherms of various gases in polystyrene at 298 K (The original data were represented graphically)

First runs				Second runs			
Oriented		Unoriented		Oriented		Unoriented	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
Ar							
0.42	0.98	0.54	1.23	0.56	1.60	0.43	1.23
0.79	1.68	0.99	1.97	1.05	2.42	1.01	2.34
1.12	2.17	1.50	2.71	1.42	3.20	1.70	3.57
1.43	2.75	1.84	3.20	1.77	3.73	2.09	4.10
1.78	3.25	2.06	3.48	2.10	4.30	—	—
2.04	3.32	—	—	—	—	—	—
CO_2							
0.14	3.07	0.17	3.36	0.35	6.35	0.29	5.82
0.27	4.63	0.34	5.57	0.69	9.88	0.83	11.39
0.41	6.19	0.51	7.42	1.04	13.12	1.39	15.70
0.55	7.54	0.68	8.89	1.35	15.04	1.89	18.89
0.69	8.77	0.88	10.29	1.75	18.40	—	—
0.86	9.84	1.08	11.56	1.98	19.88	—	—
1.02	10.86	1.32	12.91	—	—	—	—
1.17	11.97	1.54	14.47	—	—	—	—
1.37	13.12	1.77	15.53	—	—	—	—
1.55	14.39	—	—	—	—	—	—
1.73	15.33	—	—	—	—	—	—
CH_4							
0.34	1.80	0.43	2.38	0.48	3.40	0.48	3.40
0.51	2.54	0.85	3.57	0.93	5.16	0.97	5.25
0.78	3.36	1.26	4.67	1.36	6.60	1.59	7.21
1.05	4.14	1.77	5.78	1.79	7.87	2.03	8.24
1.34	4.88	2.02	6.27	2.06	8.44	—	—
1.63	5.49	—	—	—	—	—	—
1.90	6.19	—	—	—	—	—	—
N_2							
0.47	0.66	0.60	0.82	0.58	0.98	0.49	0.78
0.99	1.07	1.08	1.15	1.09	1.48	0.86	1.19
1.53	1.56	1.57	1.64	1.55	1.89	1.33	1.64
1.99	1.93	2.06	1.97	2.09	2.42	1.85	2.21

Auxiliary Information

Method/Apparatus/Procedure

A direct measurement of the solubility was made with a volumetric apparatus. With the film sample placed in the sorption bomb, the sorption system is evacuated and flushed with gas several times. The system is then evacuated to 0.02 mm Hg. Gas is then introduced rapidly, and the initial pressure recorded. Sorption takes place instantaneously and proceeds until the equilibrium pressure is established.

Source and Purity of Materials:

Gases: minimum purity 99.99%.

Biaxially oriented PS film: Dow Chemical Co., density 1.0490 g/cm^3.

Cast annealed PS film: prepared from a solution of about 20% by weight of oriented PS in methylene dichloride, density 1.0474 g/cm^3.

Estimated Error:

Relative precision of solubilities: CO_2 8.1%; CH_4 6.3%; Ar 10.5%; N_2 15%.

Components:

(1) Various gases (He, Ar, Kr, Xe, N_2)
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

H. Odani, K. Taira, N. Nemoto, and M. Kurata, Bull. Inst. Chem. Res., Kyoto Univ. **57**, 4, 226 (1979).

Variables:

T/K: 298–348
p/kPa: 0–26

Prepared By:

A. K. Bokarev

Experimental Data

Equilibrium solubility coefficient at 298 K and heats of solution of gases in polystyrene

Gas	S 10^3/cm^3(STP) cm^{-3} cm Hg^{-1}	ΔH_s /kJ mol^{-1}
Helium; He; [7440-59-7]	0.17	—
Argon; Ar; [7440-37-1]	5.03	−13.6
Krypton; Kr; [7439-90-9]	17.8	−17.5
Xenon; Xe; [7440-63-3]	89.0	−23.2
Nitrogen; N_2; [7727-37-9]	2.29	−13.8

Auxiliary Information

Method/Apparatus/Procedure

The solubility has been measured by a volumetric method. Measurements were performed using an apparatus similar to that employed by Meares.[1]

Source and Purity of Materials:

Anionically polymerized PS sample having $M_w = 106\,000$ was used.

He, Ar, Kr, Xe and N_2 were obtained from Takachiho Kagaku Kogyo, Co. Ltd., and the purity of each gas exceeded 99.995% by volume.

Estimated Error:

No information.

References:

[1] P. Meares, Trans. Faraday Soc. **54**, 40 (1958).

Components:

(1) Methane; CH_4; [74-82-8]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

J. L. Lundberg, B. M. Wilk, and M. J. Huyett, Ind. Eng. Chem., Fundam. **2**, 37 (1963).
J. L. Lundberg, E. J. Mooney, and C. E. Rogers, J. Polym. Sci. Part A-2 **7**, 947 (1969).

Variables:

T/K=373–461
p/MPa=4.9–67

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility of methane in PS

T/K	p/atm	C/cm^3(STP) cm^{-3}
373.35	320	22.5
398.55	50	4.5
	217	16.5
	300	22
	333	21
	347	24
	433	24
	467	25
	537	27
	590	28
	667	29
428.57	50	5
	163	14
	243	23
461.55	67	8
	120	14
	200	21
	250	25
	313	30

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Auxiliary Information

Method/Apparatus/Procedure

The method of ''interval'' sorption was used. Pressure decrease due to sorption in a closed system of known volume was measured with a pressure transducer. Polymer samples were put between two disks of sintered glass. No correction for the swelling of the sample was introduced.

Source and Purity of Materials:

PS had M_w=500 000.
Purity of methane was >99.0%.

Estimated Error:

$\delta T = \pm 0.02$ K
$\delta p = \pm 0.5$ atm
$\delta C/C < 5\%$

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

K. Toi and D. R. Paul, Macromolecules **15**, 1104 (1982).

Variables:

T/K=308–328
p/MPa=0–2.3 (0–22 atm)
M_v=3600–850 000

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Molecular masses and polydispersity of PS studied

Type	MM	M_w/M_n
PS-I	M_v=3600	<1.06
PS-I	M_v=9100	<1.06
PS-I	M_v=17 400	<1.06
PS-I	M_v=850 000	<1.06
PS-II	M_n=90 000	2.8

TABLE 2. Dual mode sorption parameters for carbon dioxide at 308 K (Read off the plots by the compiler)

MM	T_g/K	k_D/cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
3600	345	0.38	5.0	0.17
9100	359	0.46	7.5	0.20
17 400	371	0.45	8.0	0.17
850 000	374	0.50	9.2	0.16
90 000	374	0.51	9.5	0.17

TABLE 3. Effect of temperature on sorption of CO_2 in monodisperse polystyrenes with $M_v = 3600$ (The original data were represented graphically)

$T=308$ K		$T=318$ K		$T=328$ K	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.08	0.92	0.08	0.63	0.10	0.42
0.13	1.42	0.13	0.92	0.14	0.71
0.17	1.72	0.18	1.17	0.24	1.13
0.22	2.18	0.20	1.38	0.31	1.43
0.28	2.76	0.33	2.14	0.38	1.60
0.36	3.18	0.37	2.27	0.43	1.85
0.40	3.56	0.41	2.48	0.52	2.40
0.52	4.27	0.46	2.94	0.63	2.73
0.60	4.73	0.53	3.31	0.74	3.16
0.72	5.45	0.63	3.65	0.82	3.45
0.80	5.78	0.73	3.90	1.01	4.25
0.89	6.70	0.81	4.37	1.21	5.01
0.99	7.17	0.91	4.91	1.40	5.64
1.18	7.92	1.01	5.54	1.60	6.44
1.36	8.89	1.22	6.26	1.75	7.07
1.55	9.56	1.41	7.06	1.93	7.75
1.76	10.74	1.56	7.73	2.02	8.21
1.91	11.41	1.76	8.53	2.11	8.67
2.01	11.75	1.96	9.25	2.18	8.80
2.09	12.21	2.03	9.79	—	—
2.17	12.51	2.13	10.09	—	—
2.29	13.01	2.20	10.34	—	—
—	—	2.29	10.93	—	—

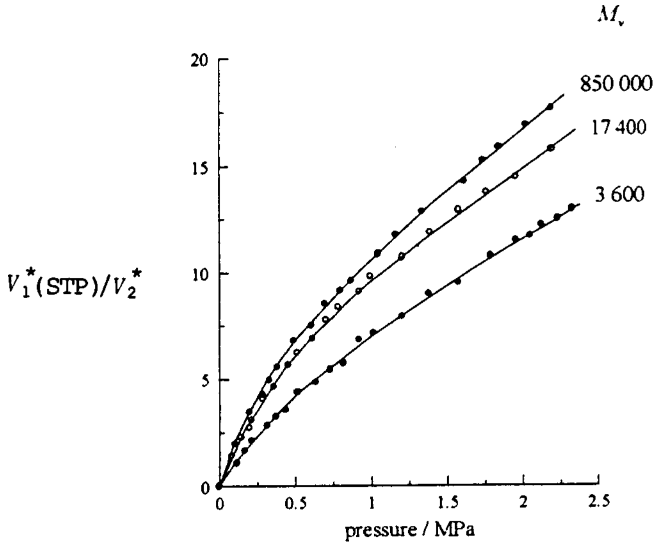


FIG. 19. Sorption isotherms of carbon dioxide in various monodisperse polystyrenes at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The method of sorptions measurement was the same as described in Refs. [1] and [2]. Prior to determination of the sorption isotherms the films cast from trichloroethylene solution and free from the solvent were conditioned for 1 d at 24 atm of CO_2.

Source and Purity of Materials:

Monodispersed PS-I: Pressure Chemical Co., Polydispersed PS-II: Cosden Oil and Chemical Co.

Their viscosity molecular masses, M_w/M_n ratios and T_g values are given above.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

[2] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene (PS); [9003-53-6] (IX)
(3) Mineral oil Phosphoric acid, tri(methyl phenyl) ester (tricresyl phosphate, TCP); $(CH_3C_6H_4)_3PO$; [1330-78-5]

Original Measurements:

J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **30**, 4019 (1985).

Variables:

T/K=298–338
p/MPa=0–3.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

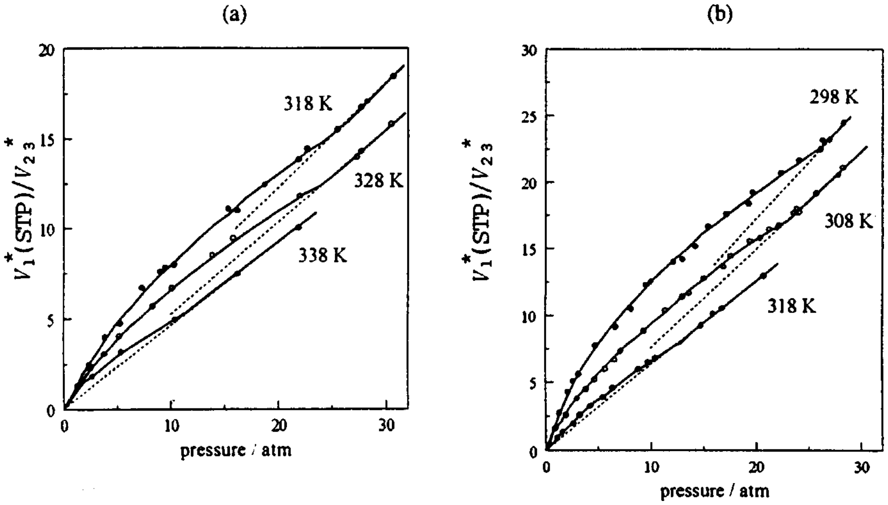


FIG. 20. Effect of temperature on sorption isotherms of carbon dioxide in PS containing 3% by mass of mineral oil (a) and 10% by mass of TCP (b).

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were obtained using dual-volume dual-transducer cell design based on the pressure decay principle.

Source and Purity of Materials:

PS: M_n=90 000, M_w/M_n=2.8.
PS containing 3% of mineral oil: T_g=360 K.
PS containing 10% of TCP: T_g=343 K.
The samples were conditioned at the highest CO_2 pressure before measurement.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).

Variables:

T/K=308.2–338.2
p/MPa=0–7.3 (0–70 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide in polystyrene at different temperatures. (The original data were represented graphically)

T=308.2 K		T=323.2 K		T=338.2 K	
Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)	Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)	Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)
0.51	6.04	0.52	4.86	0.42	4.19
1.02	9.38	1.05	6.94	0.80	5.94
1.57	13.31	1.57	10.03	1.24	7.60
2.06	15.98	2.17	14.88	1.65	10.61
2.92	23.44	2.68	17.46	2.04	11.35
3.78	31.73	3.19	20.89	2.47	14.53
4.55	36.32	3.68	23.64	2.87	16.44
5.52	42.67	4.22	25.64	3.33	18.01
6.38	48.36	4.71	29.23	3.69	19.51
7.29	57.32	5.17	31.31	4.01	21.68
—	—	5.57	35.67	4.32	24.11

Auxiliary Information

Method/Apparatus/Procedure

A gravimetric method was used. The polymer samples were suspended from a quartz spring. A correction for buoyancy was introduced using the densities of carbon dioxide up to high pressures.

Source and Purity of Materials:

CO_2: Linde, purity 99.99%.
Polystyrene: Scientific Polymer Products, M_w=250 000, glass transition temp. 373 K.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

C. Carfagna, L. Nicodemo, L. Nicolais, and G. Campanile, J. Polym. Sci., Part B: Polym. Phys. **24**, 1805 (1986).

Variables:

T/K=300–393
p/MPa=0–3.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Table 1. Dual mode sorption parameters for CO_2 in polystyrene at various temperatures

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Oriented film			
300.8	0.698	8.132	0.388
313	0.463	6.839	0.298
323	0.296	5.273	0.227
333	0.307	2.956	0.157
352	0.453	—	—
373	0.425	—	—
Unoriented film			
313	0.744	8.341	0.131
323	0.712	5.990	0.151
333	0.659	5.004	0.112
353	0.577	—	—
373	0.477	—	—
393	0.417	—	—

Table 2. Sorption isotherms of carbon dioxide in oriented PS films at various temperatures (The original data were represented graphically)

Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
T=300.8 K							
0.04	1.44	0.96	13.63	1.43	16.08	2.28	22.04
0.31	6.10	1.02	13.85	1.84	19.72	2.37	23.60
0.46	7.84	1.20	15.62	1.93	20.56	2.92	26.67
0.45	8.70	1.37	16.59	2.16	21.61	—	—
T=313 K							
0.13	2.06	0.43	5.54	1.15	10.88	2.15	15.59
0.17	2.87	0.49	6.38	1.23	11.27	2.34	16.51
0.30	4.29	0.61	7.31	1.61	13.29	2.89	18.49
0.33	4.78	0.82	9.04	1.80	13.71	—	—
0.39	5.18	0.93	9.83	2.06	15.29	—	—
T=323 K							
0.11	1.29	1.01	7.01	1.82	9.54	2.33	10.90
0.28	2.62	1.22	7.16	1.92	9.43	2.55	11.22
0.33	3.06	1.37	8.17	2.03	10.23	2.64	11.79
0.55	4.29	1.51	8.64	2.14	9.84	2.89	12.61
0.71	5.48	1.74	8.79	2.22	10.65	—	—
T=333 K							
0.10	0.57	0.58	2.97	1.15	4.50	2.02	7.78
0.16	0.79	0.67	3.50	1.23	5.44	2.34	8.68
0.21	1.19	0.80	3.57	1.35	6.05	2.53	9.23
0.31	1.62	0.95	4.54	1.43	6.13	2.93	10.25
0.40	2.24	1.04	4.79	1.53	6.38	—	—
0.48	2.63	1.10	4.65	1.72	6.93	—	—
T=353 K							
0.13	0.34	1.15	4.68	1.80	6.78	2.74	11.59
0.27	1.31	1.41	5.54	1.88	8.08	—	—
0.59	2.34	1.62	6.09	2.01	8.19	—	—
0.82	3.25	1.56	6.69	2.31	9.32	—	—
T=373 K							
0.30	0.99	0.72	2.54	0.88	3.19	2.43	9.39
0.41	1.29	0.79	3.16	1.70	6.57	—	—

Table 3. Sorption isotherms of carbon dioxide in unoriented PS films at various temperatures (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
$T=313$ K							
0.15	2.78	1.00	12.46	1.96	19.72	3.01	26.35
0.30	4.02	1.27	14.49	2.19	22.44	—	—
0.60	8.10	1.52	16.06	2.30	22.14	—	—
0.76	9.34	1.78	19.46	2.89	26.59	—	—
$T=323$ K							
0.29	3.40	0.893	10.13	1.52	14.46	2.63	22.73
0.40	5.10	1.204	11.92	1.78	16.66	2.87	23.56
0.61	6.73	1.386	13.50	2.40	20.19	—	—
$T=333$ K							
0.17	1.81	0.47	4.86	1.10	10.05	2.16	17.41
0.23	2.15	0.71	6.72	1.36	12.48	2.51	20.23
0.31	2.94	0.70	7.35	1.48	13.15	3.03	23.26
0.44	4.24	0.89	8.01	1.78	14.77	—	—
$T=353$ K							
0.18	1.18	1.17	7.07	2.24	13.41	2.85	16.54
0.61	3.70	1.48	9.09	2.30	13.11	—	—
0.89	5.56	1.82	10.88	2.65	15.19	—	—
$T=373$ K							
0.17	0.78	0.90	4.36	1.44	7.15	2.24	10.49
0.29	1.17	0.99	4.35	1.56	7.48	2.47	11.15
0.60	2.79	1.08	5.19	1.85	8.19	2.92	13.39
0.83	3.74	1.10	5.02	2.15	9.76	3.07	14.05
$T=393$ K							
0.22	0.60	0.46	1.49	1.50	6.23	2.38	9.45
0.27	0.83	0.60	2.28	1.91	7.39	2.93	11.73
0.30	0.94	0.91	3.78	2.17	9.07	3.05	12.40

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus used was similar to that described in Ref. 1. Experiments were performed on uniaxially drawn samples. Unoriented samples were obtained by annealing the extruded film at 453 K for 20 min.

Source and Purity of Materials:

PS atactic: Montedison Co., $M_w=290\,000$, glass transition temperature 371 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, K. Sakata, and S.-T. Wang, Ind. Eng. Chem., Res. **26**, 433 (1987).

Variables:

T/K=293–313
p/MPa=0.2–3.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	T/K	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	293	0.801	13.0	0.184
	303	0.713	11.0	0.134
	313	0.586	8.81	0.0918
CH_4	293	0.305	5.00	0.0811
	303	0.277	4.93	0.0623
	313	0.244	3.63	0.0439

Auxiliary Information

Method/Apparatus/Procedure

Equilibrium sorption was measured by the pressure decay method in the cell similar to that described in Ref. 1. The pressure in the cell was continuously measured by a pressure transducer.

Source and Purity of Materials:

PS films provided by Mitzubishi–Monsanto Chemical Co were studied.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed., **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polystyrene (PS); [9003-53-6] (IX)	P. C. Raymond and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **28**, 2079 (1990).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.5 (0–25 atm)	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Sorption C/cm^3(STP)/cm^3 of methane and carbon dioxide in PS*

p/atm	CH_4	CO_2
5	1.5	6.7
10	2.6	11.1
15	3.6	14.6
20	4.4	17.6
25	5.3	20.0

*Smoothed data taken from the plot by the compiler.

TABLE 2. Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CH_4	0.135	3.28	0.061
CO_2	0.535	8.63	0.194

Auxiliary Information

Method/Apparatus/Procedure

Gas sorption measurement was performed using the same equipment and procedure as in Ref. 1. Sorption isotherm for methane were obtained using polymer samples which had never been exposed to CO_2. The CO_2 isotherm was obtained using the sample that had been conditioned in CO_2 at 25 atm for 24 h.

Source and Purity of Materials:

PS (Cosden Oil 550) had a density 1.052 g/cc and the glass transition temperature 373 K. No information on gas purity given.

Estimated Error:

No information given.

References:

[1] Y. Maeda and D. R. Paul, Polymer **26**, 2055 (1985).

Components:	**Original Measurements:**
(1) Propane; C_3H_8; [74-98-6] (2) Polystyrene (PS); [9003-53-6] (IX)	H. G. Spencer and J. A. Yavorsky, J. Appl. Polym. Sci. **28**, 2937 (1983).
Variables:	**Prepared By:**
T/K=345–370 p/kPa=0–40	A. K. Bokarev

Experimental Data

Temperature dependence for the solubility coefficient S of propane in polystyrene is given by the equation: $S = S_0 \exp(-\Delta H/RT)$.

At 353 K, the parameters are:

ΔH/kJ mol^{-1}	ln(S_0 /(cm^3(STP)/cm^3 cm Hg))	ln(S/cm^3(STP)/(cm^3 cm Hg))
−8	−7.15	−4.49

Temperature dependence for solubility coefficient S of propane in polystyrene.

T/K	ln(S/cm^3(STP)/(cm^3 cm Hg))
343.6	−4.44
348.4	−4.52
357.1	−4.48
370.3	−4.59

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out in a low pressure, constant-volume cell previously described, Ref. 1.
A correction for the buoyancy was introduced.

Source and Purity of Materials:

C_3H_8: Matheson, purity 99.99%.
PS: Polysciences Inc., M_w=23 000, glass transition temperature 334 K, density (303 K) 1.06 g/cm^3.

Estimated Error:

No information given.

References:

[1] J. A. Yavorsky and H. G. Spencer, J. Appl. Polym. Sci. **25**, 2109 (1980).

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

J. A. Yavorsky, Ph.D. dissertation, Department of Chemistry and Geology, Clemson University, 1984.

Variables:

T/K=313–353
p/kPa=0–580

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for propane in polystyrene

T/K	$10^2 k_D$ /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	$10^2 b$/cm Hg^{-1}
313	2.49	3.7	1.33
333	1.98	4.2	0.25
353	1.62	3.7	0.06

TABLE 2. Sorption isotherms of propane in polystyrene (The original data were represented graphically)

$T=313$ K		$T=333$ K		$T=353$ K	
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
32.64	1.32	36.97	0.40	23.76	0.33
41.20	1.74	36.44	0.69	71.27	0.99
51.07	2.03	131.88	2.73	111.78	1.52
238.32	7.02	141.62	2.78	153.75	2.18
—	—	144.81	3.51	280.14	3.79
—	—	248.83	6.02	309.51	4.24
—	—	313.34	6.08	542.21	7.50
—	—	493.11	11.34	577.30	8.25
—	—	550.73	10.27	—	—

Auxiliary Information

Method/Apparatus/Procedure

The equilibrium solubility of gases in the polymer was measured by a manometric technique. High pressure apparatus (up to 930 kPa) with pressure transducers was employed.

Source and Purity of Materials:

C_3H_8: Matheson, minimum purity 99.98%.
PS: Polyscience, Inc., $M_w=190\,000$.

Estimated Error:

Relative precision of DMS parameters: $k_D \pm 21\%$; $C'_H \pm 29\%$; $b \pm 55\%$.

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

M. E. Stewart, H. B. Hopfenberg, W. J. Koros, and N. R. McCoy, J. Appl. Polym. Sci. **34**, 721 (1987).

Variables:

T/K: 303
p/kPa: 6.1–93.1

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility C (g per 100 g polymer) of propane in PS*

Sample	p/mm Hg	C	Sample	p/mm Hg	C
PS as	46	0.20	PS preswollen	46	0.30
received	149	0.38	in C_3H_8	144	0.56
	357	0.56	(700 mm Hg, 30 min)	448	0.85
	558	0.79			
	700	1.05			

*Taken from the graph by compiler.

Auxiliary Information

Method/Apparatus/Procedure

Gas sorption measurements were performed using a Cahn RG microbalance. The sorption apparatus and procedure are discussed in Ref. 1

Source and Purity of Materials:

Emulsion polymerized PS (B.F. Goodrich Co R/D center) had $M_n=440\,000$ and glass transition temperature 381 K. Instrument grade propane was 99.99% pure.

Estimated Error:

No information given.

References:

[1] J. M. H. Fechter, H. B. Hopfenberger, and W. J. Koros, Polym. Eng. Sci. **21**, 925 (1981).

Components:

(1) *n*-Butane; C_4H_{10}; [106-97-8] 2-Methylpropane; C_4H_{10}; [75-28-5] Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

Y. Iwai, M. Ohzono, and Y. Arai, Chem. Eng. Commun. **34**, 225 (1985).

Variables:

T/K=423–498

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Values of weight fraction Henry's constants/MPa for hydrocarbons in molten polystyrene. The experienced data follow the curves calculated by the UNIFAC-FV model. (The original data were represented graphically)

T/K	*n*-Butane	2-Methylpropane	Propane
423.2	35.96	47.49	78.79
448.2	42.33	56.46	100.53
473.2	51.81	62.58	123.04
498.2	61.53	74.33	137.76

Auxiliary Information

Method/Apparatus/Procedure

A gas chromatographic method used for the determination of weight fraction Henry's constants and was similar to those described in Refs. 1 and 2. PS was coated on Chromosorb W (AW DMSC 60/80). Helium was used as a carrier gas.

Source and Purity of Materials:

Estimated Error:

No information given.

References:

[1] D. D. Liu and J. M. Prausnitz, Ind. Eng. Chem. Fundam. **15**, 330 (1976).

[2] M. Ohzono, Y. Iwai, and Y. Arai, Kagaku Kogaku Ronbunshu **10**, 536 (1984).

Components:

(1) Various organic gases
(2) Polystyrene (PS); [9003-53-6] (IX)

Original Measurements:

L. I. Stiel and D. F. Harnish, AIChE J. **22**, 117 (1976).

Variables:

T/K=408–503

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Infinite dilution solubility coefficients S_r/(cm^3(STP)/g atm)

	Temperature				
Gas	408	423	448	473	498
Trichlorofluoromethane; CCl_3F [75-69-4]	3.85	3.02	2.09	1.55	1.17
Dichlorodifluoromethane; CCl_2F_2 [75-71-8]	1.12	0.94	0.70	0.56	0.45
Chlorodifluoromethane; $CHClF_2$ [75-45-6]	0.94	0.81	0.64	0.53	0.44
Chlorofluoromethane; CH_2ClF [593-70-4]	2.01	1.65	1.20	—	—
Chloromethane; CH_3Cl [74-87-3]	—	1.70	1.30	—	—
Propane; C_3H_8 [74-98-6]	0.90	0.78	0.62	0.51	0.43
2-Methylpropane; C_4H_{10} [75-28-5]	—	1.20	0.86	0.65	0.52

Auxiliary Information

Method/Apparatus/Procedure

Solubility in the limit of infinite dilution ($p \rightarrow 0$) was determined by means of inverse gas chromatography PS was coated on Fluoropak-80 support. Polymer content was in the range 4.8%–13.1% in the columns having the length 24–71 m. The correction for pressure drop in a column was introduced.

Source and Purity of Materials:

Molecular mass, M_n, of PS=110 000–115 000.

Estimated Error:

$\delta T = 1$ K
$\delta S/S = 10\%$

Components:	**Original Measurements:**
(1) Methane; CH_4; [74-82-8] Propane; C_3H_8; [74-98-6] Chlorodifluoromethane; $CHClF_2$; [75-45-6] (2) Polystyrene (PS); [9003-53-6] (IX)	J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).
Variables:	**Prepared By:**
T/K=293–333 p/kPa=0–65.6	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters and solubility coefficients ($S=k_D+C'_H b$)

Gas	T/K	$k_D 10^2$/ cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/cm Hg^{-1}	S/cm^3(STP) cm^{-3} cm Hg^{-1}
CH_4	303	—	—	—	0.0069
	323	—	—	—	0.0044
	303*	4.69	1.01	0.18	0.229
	323*	2.82	0.735	0.071	0.0804
	293	4.39(±5%)	1.32(±9%)	0.209(±18%)	0.32(±9%)
C_3H_8	303	3.30(±11%)	1.36(±17%)	0.136(±28%)	0.218(±11%)
	313	2.93(±6%)	0.90(±12%)	0.127(±20%)	0.143(±8%)
	323	2.46(±6%)	0.70(±16%)	0.106(±23%)	0.0984(±7%)
	333	2.29(±14%)	0.51(±45%)	0.108(±62%)	0.0776(±17%)
	293*	7.34(±8%)	2.16(±15%)	0.18(±28%)	0.471(±13%)
	303*	5.42(±9%)	1.95(±14%)	0.15(±25%)	0.347(±11%)
$CHClF_2$	313	4.49(±7%)	1.50(±13%)	0.11(±20%)	0.210(±7%)
	323	3.81(±7%)	1.20(±15%)	0.089(±20%)	0.145(±6%)
	333	3.18(±18%)	0.80(±59%)	0.071(±63%)	0.089(±9%)

*PS films, other data refer to PS powder.

(For Tables 2, 3, and 4, the original data were represented graphically.)

TABLE 2. Sorption isotherms of chlorodifluoromethane in polystyrene powder

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
T=293 K							
2.10	0.61	12.93	2.03	28.67	3.30	46.78	4.51
4.89	1.13	16.80	2.49	32.64	3.65	54.80	5.02
6.38	1.30	20.66	2.70	36.89	3.82	—	—
8.57	1.65	25.01	3.08	39.76	4.07	—	—
T=303 K							
2.00	0.41	12.61	1.63	29.43	2.75	49.50	3.69
4.08	0.75	16.77	1.90	33.88	2.89	56.81	3.99
6.17	1.02	20.73	2.20	37.24	3.15	—	—
8.55	1.23	25.87	2.47	40.90	3.28	—	—
T=313 K							
2.19	0.28	13.28	1.22	29.10	2.07	49.55	2.90
4.77	0.60	17.13	1.41	33.64	2.26	55.97	3.15
6.75	0.77	21.19	1.66	36.91	2.43	—	—
8.82	0.91	25.04	1.83	40.76	2.56	—	—
T=323 K							
2.48	0.23	12.87	0.92	29.66	1.63	48.83	2.32
4.16	0.36	18.80	1.21	33.02	1.78	56.24	2.58
7.73	0.64	21.37	1.29	37.17	1.92	—	—
9.41	0.73	25.72	1.53	41.91	2.11	—	—
T=333 K							
2.37	0.15	12.75	0.65	28.85	1.19	49.98	1.80
4.65	0.28	17.10	0.80	32.90	1.34	58.18	2.04
6.43	0.37	21.74	0.94	37.04	1.40	—	—
8.70	0.48	25.49	1.09	41.59	1.55	—	—

TABLE 3. Sorption isotherms of methane and propane in polystyrene film

CH_4				C_3H_8			
T=303 K		T=323 K		T=303 K		T=323 K	
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
5.53	0.03	3.50	0.01	2.43	0.33	2.65	0.15
7.87	0.04	8.72	0.03	3.37	0.44	3.75	0.20
9.89	0.05	11.53	0.04	5.72	0.67	7.26	0.36
10.52	0.06	13.47	0.04	7.43	0.77	10.22	0.44
11.92	0.06	21.10	0.07	15.63	1.22	14.12	0.62
15.43	0.08	28.81	0.10	23.20	1.58	19.89	0.84
18.00	0.10	30.45	0.11	28.34	1.81	26.74	1.01
24.31	0.13	45.17	0.15	44.80	2.49	38.04	1.32
28.05	0.15	—	—	—	—	48.25	1.57
33.97	0.18	—	—	—	—	—	—
38.80	0.20	—	—	—	—	—	—
46.66	0.24	—	—	—	—	—	—

TABLE 4. Sorption isotherms of propane in polystyrene powder

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
$T=293$ K							
1.37	0.32	6.59	0.88	16.78	1.48	42.50	2.57
2.54	0.49	8.51	0.98	24.75	1.88	52.10	2.91
4.37	0.64	12.36	1.29	33.20	2.19	65.23	3.34
$T=303$ K							
1.36	0.24	6.66	0.68	17.43	1.26	41.22	2.11
2.62	0.36	8.88	0.84	24.82	1.59	52.33	2.42
4.35	0.51	12.63	1.04	32.97	1.87	65.56	2.78
$T=313$ K							
1.64	0.19	6.64	0.48	16.72	0.90	41.84	1.63
2.99	0.26	8.37	0.58	24.97	1.17	54.48	1.94
4.34	0.35	12.88	0.76	33.21	1.41	65.40	2.20
$T=323$ K							
1.45	0.13	6.82	0.35	16.7	0.70	42.76	1.32
2.79	0.19	8.45	0.43	24.94	0.90	52.43	1.54
4.33	0.27	12.39	0.55	33.08	1.10	65.55	1.79
$T=333$ K							
1.44	0.10	6.53	0.28	16.78	0.56	41.11	1.11
2.50	0.16	8.45	0.35	25.60	0.78	52.99	1.32
4.49	0.22	12.47	0.47	33.26	0.93	63.23	1.51

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured using an electronic vacuum microbalance (Sartorius, Model 4102) as described in Ref. 1.

Source and Purity of Materials:

$CHClF_2$: purity >99.5%.
Hydrocarbon gases: purity >99.9 mol %.
Emulsion polymerized PS: B. F. Goodrich Research Center; dispersed form (particles size 0.53 μm) or film cast from methylene chloride.
PS: glass transition temperature 374 K.

Estimated Error:

Indicated in Table 1.

References:

[1] J. A. Barrie and D. Machin, J. Macromol. Sci.-Phys. B. **3**, 645 (1969).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(*p*-methoxystyrene); [24936-44-5] (X)

Original Measurements:

A. C. Puleo, N. Muruganandam, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **27**, 2385 (1989).

Variables:

T/K=308
p/MPa=0.2–2.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide at 308 K

	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
1st cycle	0.873	3.03	0.502
2nd cycle	0.536	14.08	0.123

TABLE 2. Sorption isotherms of carbon dioxide at 308 K (The original data were represented graphically)

1st cycle		2nd cycle	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)
0.27	4.09	0.21	3.96
0.54	7.04	0.66	9.55
0.87	9.95	1.06	13.53
1.28	13.61	1.44	16.56
1.63	16.63	1.79	19.02
1.96	19.41	1.96	20.54

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure in sorption measurements were the same as those described in Ref. 1.

Source and Purity of Materials:

Polymer: prepared according to Ref. 2; glass transition temperature 378 K, M_w=980 000, density 1.118 g/cm^3.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).
[2] H. K. Hall and M. A. Howey, Polym. Bull. **12**, 427 (1984).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(*p*-acetoxystyrene); [24979-78-0] (XI)

Original Measurements:

A. C. Puleo, N. Muruganandam, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **27**, 2385 (1989).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0.2-2.0$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide at 308 K

	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
1st cycle	1.24	5.65	0.431
2nd cycle	0.769	16.82	0.221

TABLE 2. Sorption isotherms of carbon dioxide at 308 K (The original data were represented graphically)

1st cycle		2nd cycle	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.35	7.15	0.17	5.38
0.67	11.15	0.38	9.20
0.95	14.71	0.65	13.13
1.19	18.03	0.93	16.82
1.41	20.92	1.24	20.07
1.56	22.89	1.50	23.08
1.94	27.00	1.90	26.19

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure in sorption measurements were the same as those described in Ref. 1.

Source and Purity of Materials:

Polymer: Celanese Chemical Co., glass transition temperature 399 K, $M_w=250\,000$, density 1.168 g/cm^3.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

3.8. Poly(Vinyl Cyclohexane Carboxylate)—Carbon Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl cyclohexane carboxylate) (PVCH); [29316-32-3] (XII)

Original Measurements:

T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **34**, 1657 (1987).

Variables:

$T/\mathrm{K}=278-358$
$p/\mathrm{kPa}=0-100$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide in PVCH

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
278	2.19	1.150	1.87
283	1.97	0.830	2.11
288	1.77	0.684	1.85
293	1.60	0.559	1.57
298	1.46	0.373	1.69
303	1.32	0.230	1.57
308	1.22	0.227	1.04

TABLE 2. Henry's law parameters for carbon dioxide in rubbery PVCH

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}
318	1.020
328	0.866
338	0.752
348	0.653
358	0.560

TABLE 3. Sorption isotherms of carbon dioxide in PVCH in the range 278–358 K (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
$T=278$ K		$T=293$ K		$T=318$ K	
6.89	0.24	54.69	1.14	13.44	0.13
13.77	0.50	64.22	1.30	26.88	0.27
20.19	0.73	79.69	1.59	40.81	0.42
26.61	0.97	93.12	1.80	54.23	0.53
38.03	1.34	$T=298$ K		66.12	0.68
38.81	1.31	6.72	0.12	79.24	0.81
53.04	1.78	13.91	0.26	92.68	0.95
65.71	2.11	22.97	0.43	$T=328$ K	
76.18	2.38	32.97	0.62	14.20	0.10
77.90	2.36	45.62	0.82	27.32	0.21
85.24	2.54	53.12	0.96	41.56	0.37
93.22	2.73	66.39	1.16	54.49	0.44
$T=283$ K		81.07	1.40	67.32	0.60
6.73	0.22	93.72	1.57	79.48	0.69
13.14	0.42	$T=303$ K		92.44	0.82
20.18	0.63	4.84	0.09	$T=338$ K	
26.59	0.81	13.59	0.21	26.52	0.20
39.57	1.17	20.62	0.31	40.75	0.32
43.95	1.26	26.87	0.46	53.84	0.40
53.48	1.49	33.26	0.49	67.89	0.51
66.14	1.76	41.08	0.64	79.74	0.61
75.21	2.01	46.54	0.70	93.48	0.72
85.68	2.20	54.19	0.84	$T=348$ K	
97.71	2.46	59.97	0.92	14.07	0.06
$T=288$ K		66.84	1.01	27.28	0.15
7.19	0.20	72.47	1.10	40.72	0.28
13.45	0.37	79.49	1.17	53.97	0.36
27.52	0.73	89.95	1.30	66.61	0.46
41.11	1.01	96.98	1.40	79.52	0.50
52.99	1.26	$T=308$ K		93.11	0.62
67.53	1.59	5.46	0.05	$T=358$ K	
79.24	1.80	13.59	0.18	20.18	0.10
92.68	2.06	27.02	0.38	34.07	0.19
$T=293$ K		39.82	0.56	40.86	0.25
8.75	0.19	54.81	0.75	53.96	0.33
15.32	0.34	67.15	0.92	67.96	0.36
22.04	0.48	84.63	1.12	79.96	0.46
34.23	0.75	93.53	1.24	93.04	0.50
40.95	0.89	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

Cahn RG electromicrobalance was used. The procedure is described in Refs. 1 and 2. Two types of experiments were performed: sorption in fully preevacuated sample and ''interval'' sorption experiments. No difference between the data obtained is observed.

Source and Purity of Materials:

CO_2: purity 99.99%.

PVCH: prepared from polyvinyl alcohol (polymerization degree $n=2000$) and cyclohexane carboxylic acid chloride in anhydrous pyridine: Degree of esterification >97%, $M_w=270\,000$ (GPC), density 1.119 g/cm^3, $T_g=328$ K.

Estimated Error:

No information given.

References:

[1] Y. Kamiya, K. Mizoguchi, Y. Naito, and J. Hirose, J. Polym. Sci., Part B: Polym. Phys. **24**, 535 (1986).

[2] Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, J. Polym. Sci.: Part B: Polym. Phys. **24**, 1525 (1986).

3.9. Poly(Vinyl Benzoate)—Various Gases

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl benzoate) (PVB); [24991-32-0] (XIII)

Original Measurements:

Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, J. Pol. Sci., Polym. Phys. Ed. **24**, 535 (1986).

Variables:

T/K=298–343
p/MPa=0–5.0

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Sorption and desorption isotherms of nitrogen in PVB (The original data were represented graphically)

T=308.2 K		T=323.2 K		T=338.2 K	
Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)	Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)	Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)
Sorption					
0.20	0.09	0.22	0.05	0.22	0.02
0.61	0.26	0.61	0.17	0.61	0.10
1.10	0.44	1.09	0.31	1.09	0.21
2.08	0.79	2.07	0.58	2.07	0.42
3.05	1.11	3.06	0.82	3.05	0.62
4.03	1.39	4.04	1.07	4.04	0.81
5.01	1.68	5.02	1.29	5.02	0.99
Desorption					
0.36	0.15	0.36	0.10	0.35	0.07
0.85	0.37	0.85	0.25	0.84	0.19
1.33	0.55	1.59	0.47	1.35	0.30
2.56	0.98	2.57	0.73	2.32	0.50
3.54	1.26	3.31	0.92	3.31	0.70
4.52	1.58	4.28	1.14	4.29	0.87

TABLE 2. Sorption and desorotion isotherms of argon in PVB (The original data were represented graphically)

T=298.2 K		T=308.2 K		T=338.2 K		T=343.2 K	
Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)	Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)	Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)	Pressure/MPa	Solubility (V_1^*(STP)/V_2^*)
Sorption							
0.11	0.15	0.07	0.06	0.22	0.15	0.11	0.09
0.60	0.77	0.60	0.63	0.60	0.41	0.36	0.18
1.09	1.29	1.08	1.09	1.09	0.70	1.08	0.50
2.12	2.25	2.07	1.92	2.07	1.29	2.06	0.92
3.09	3.09	3.04	2.71	3.09	1.83	3.05	1.34
4.13	3.87	4.04	3.33	4.03	2.32	4.27	1.80
4.52	4.14	5.02	3.96	5.01	2.82	5.02	2.10
5.02	4.47	—	—	—	—	—	—
Desorption							
0.35	0.49	0.22	0.24	0.35	0.26	0.60	0.27
0.85	1.01	0.86	0.89	0.84	0.60	1.82	0.84
1.58	1.80	1.58	1.54	1.57	1.05	3.78	1.65
2.55	2.71	2.57	2.34	2.55	1.63	—	—
3.78	3.68	3.54	3.03	3.54	2.13	—	—
—	—	4.23	3.47	4.52	2.61	—	—

TABLE 3. Dual mode sorption parameters of gases in PVB at various temperatures

Gas	T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
N_2	308	0.0230	1.07	0.0222
	323	0.0217	0.44	0.0222
	338	0.0207	—	—
Ar	298	0.0597	2.30	0.0398
	308	0.0563	1.80	0.0387
	318	0.0510	1.30	0.0382
	328	0.0458	0.91	0.0358
	338	0.0510	—	—
	343	0.0444	—	—

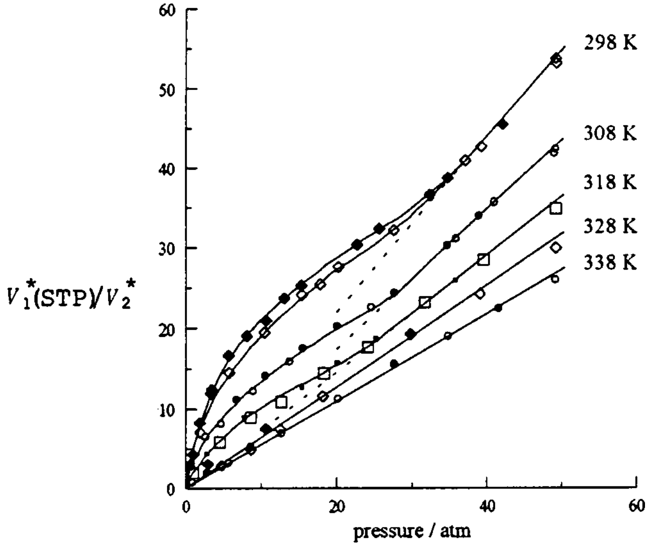


FIG. 21. Sorption and desorption isotherms of carbon dioxide in PVB. Open and filled symbols represent sorption and desorption, respectively.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured gravimetrically with a Cahn model 2000 electrobalance.

Source and Purity of Materials:

Ar: purity 99.999%.
N_2: purity 99.999%.
CO_2: purity 99.99%.
PVB: reaction of poly(vinyl alcohol) and benzoyl chloride (see Ref. 1).

Estimated Error:

No information given.

References:

[1]T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **30**, 401 (1985).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl benzoate) (PVB); [24991-32-0] (XIII)

Original Measurements:

Y. Kamiya, T. Hirose, K. Mizoguchi, and K. Terada., J. Polym. Sci., Part B: Polym. Phys. **26**, 1409 (1988).

Variables:

T/K=298
p/MPa=0–5.0

Prepared By:

A. K. Bokarev

Experimental Data

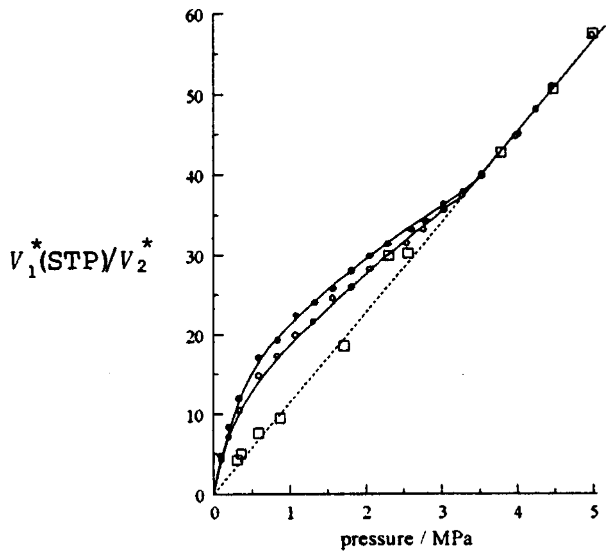


FIG. 22. Sorption and desorption isotherms of carbon dioxide in PVB at 298 K: (□) first sorption run; (○)(●) subsequent sorption and desorption runs.

The isotherm was treated by the Kamiya's *et al.* equation. The following values of the parameterrs were found at 298 K:
k_D=1.15 cm^3(STP)/cm^3 atm b=0.167 atm^{-1}
C'_{H0}=22.0 cm^{-3}(STP)/cm^3(sorption); C'_{H0}=30.2 cm^3(STP)/cm^3(desorption)
C_g=38.5 cm^3(STP)/cm^3 f=0.8 (dimensionless)

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured gravimetrically with a Cahn model 2000 electrobalance. A correction for the buoyancy was introduced.

Source and Purity of Materials:

CO_2: purity 99.99%.
PVB: reaction of poly(vinyl alcohol) and benzoyl chloride (see Ref. 1). Density (298 K)=1.214 g/cm^3.

Estimated Error:

No information given.

References:

[1]T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **30**, 401 (1985).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl benzoate) (PVB); [24991-32-0] (XIII)

Original Measurements:

T. Hirose, K. Mizoguchi, Y. Naito, and Y. Kamiya, J. Appl. Polym. Sci. **35**, 1715 (1988).

Variables:

T/K=278–358
p/kPa=0–100

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 3. Dual mode sorption parameters for carbon dioxide in PVB

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
278	1.78	4.69	1.60
288	1.45	3.59	1.35
298	1.18	3.52	0.821
308	1.00	3.05	0.623
318	0.851	1.78	0.547
328	0.730	0.666	0.760
338	0.641	—	—
343	0.577	—	—
348	0.545	—	—
353	0.511	—	—
358	0.472	—	—

TABLE 2. Dual mode sorption parameters for carbon dioxide in PVB after annealing at 358 K

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
288	1.45	1.71	1.338
298	1.55	1.73	0.739
308	1.00	0.890	0.828
318	0.851	0.477	0.760

Table 3. Sorption isotherms of carbon dioxide in PVB. Sorption isotherms are linear above 338 K (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
$T=278$ K					
6.72	0.51	40.08	2.53	79.84	4.03
16.17	1.27	53.44	3.05	94.13	4.46
26.85	1.86	66.96	3.59	—	—
$T=288$ K					
6.70	0.40	41.07	1.83	80.78	3.02
13.55	0.74	54.11	2.28	93.63	3.29
27.09	1.34	67.13	2.63	—	—
$T=298$ K					
6.84	0.26	40.84	1.34	82.26	2.35
13.36	0.51	54.17	1.67	94.95	2.63
26.23	0.94	67.03	2.00	—	—
$T=308$ K					
10.48	0.27	43.64	1.07	80.11	1.78
19.53	0.52	54.27	1.28	89.78	1.91
33.97	0.87	66.96	1.59	94.23	2.07
$T=318$ K					
6.66	0.11	40.89	0.67	80.97	1.21
13.47	0.23	54.99	0.85	99.03	1.44
26.63	0.46	68.14	1.06	—	—
$T=328$ K					
10.93	0.12	42.60	0.47	78.86	0.81
12.66	0.10	47.04	0.55	86.77	0.89
20.59	0.24	60.96	0.63	98.48	0.98
24.70	0.24	63.34	0.67	99.59	0.98
32.78	0.38	73.63	0.76	—	—
$T=338$ K					
14.39	0.07	53.72	0.35	79.64	0.51
26.40	0.14	66.84	0.43	93.38	0.59
34.13	0.21	66.67	0.44	97.65	0.61
40.76	0.26	66.99	0.44	—	—
$T=348$ K					
20.09	0.07	54.69	0.31	80.46	0.43
41.57	0.23	68.13	0.37	93.74	0.49
$T=358$ K					
33.68	0.16	62.45	0.29	81.27	0.38
38.42	0.17	68.62	0.32	89.02	0.42
53.13	0.24	68.94	0.32	95.03	0.44
54.23	0.27	78.58	0.37	98.67	0.45

Table 4. Sorption isotherms of carbon dioxide in PVB after annealing at 358 K (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
$T=288$ K					
7.04	0.21	34.24	1.04	80.89	2.02
13.77	0.44	41.41	1.20	89.18	2.21
20.65	0.64	54.47	1.48	99.66	2.39
27.20	0.82	65.95	1.76	—	—
$T=298$ K					
6.83	0.11	40.13	0.85	93.35	1.76
13.70	0.30	53.47	1.08	98.78	1.90
27.07	0.57	66.68	1.35	99.52	1.82
28.04	0.62	80.04	1.60	—	—
$T=308$ K					
13.49	0.20	53.33	0.81	82.82	1.19
26.82	0.40	67.44	0.98	90.58	1.27
41.12	0.64	75.85	1.11	98.66	1.36
$T=318$ K					
13.77	0.13	53.85	0.61	89.45	0.93
27.40	0.30	66.85	0.76	98.79	1.01
41.01	0.44	80.44	0.86	—	—

Table 5. Dual mode sorption parameters for CO_2 in PVB at 298 K after exposure to 50 atm of CO_2

	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Just after exposure	1.18	6.88	0.889
Next day	1.18	5.74	0.990
7 days later	1.18	5.00	0.942
11 months later	1.18	3.54	1.008
After measurements at 298 K in Table 3	1.18	3.52	0.827
After annealing at 358 K	1.18	1.73	0.739

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made using facilities and procedures described in Ref. 1.

Source and Purity of Materials:

CO_2: purity >99.99%.

PVB films: preparation and its properties reported in Ref. 2. The sample films were exposed to CO_2 of 50 atm at 308 K before measurements.

Estimated Error:

No information given.

References:

[1]T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **34**, 1657 (1987).

[2]T. Hirose, K. Mizoguchi, and Y. Kamiya, *ibid.* **30**, 401 (1985).

3.10. Poly(Vinyl Butyral)—Carbon Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(vinyl butyral) (PVBu) (XIV)

Original Measurements:

Y. Kamiya, T. Hirose, K. Mizoguchi, and K. Terada, J. Polym. Sci., Part B: Polym. Phys. **26**, 1409 (1988).

Variables:

$T/\mathrm{K}=298$
$p/\mathrm{MPa}=0-5.0$

Prepared By:

A. K. Bokarev

Experimental Data

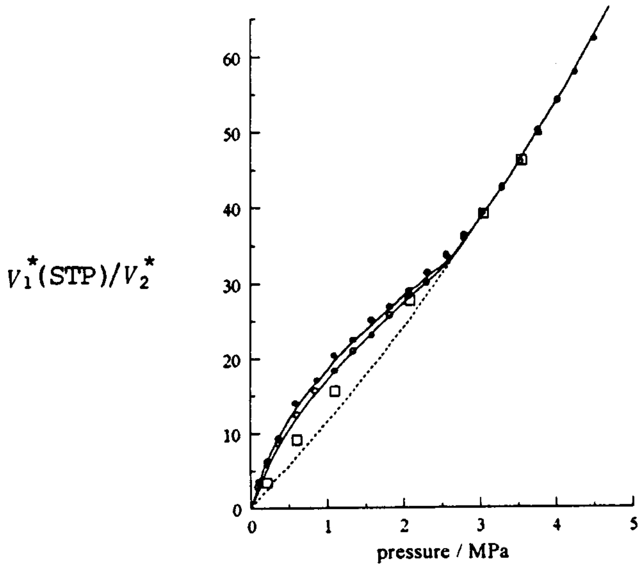


FIG. 23. Sorption and desorption isotherms of carbon dioxide in PVBu at 298 K: (□) first sorption run; (○)(●) subsequent sorption and desorption runs.

The isotherm was treated by the equation:

$$C=C_D+C_H=[k_D\exp(sC^*)]p+C'_{H0}bp(-C^*C_g)/(1+bp),$$

where the parameters k_D, C'_{H0}, and b have the usual meaning, C_g is the solute concentration corresponding to the glass transition and

$$C^*=C_D+fC_H=[k_Dp+fC'_{H0}bp/(1+bp)]/[1+fC'_{H0}bp/C_g(1+bp)],$$

where f is an adjustable parameter, characterizing the plastisizing ability of a solute.

Parameters for ordinary dissolution (Flory–Huggins's) and for Langmuir isotherms at 298 K.

f	k_D/ $\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	C'_{H0}/ $\mathrm{cm^3(STP)\ cm^{-3}}$	b/ $\mathrm{atm^{-1}}$	10^3S/ $\mathrm{cm^3(STP)\ cm^{-3}}$	C_g/ $\mathrm{cm^3(STP)\ cm^{-3}}$
0.8	1.13	20.7 (sorption) 28.6 (desorption)	0.096	3.5	34.0

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured gravimetrically with a Cahn model 2000 electrobalance. A correction for the buoyancy was introduced.

Source and Purity of Materials:

CO_2: purity 99.99%.
PVBu Mitsubishi Monsanto Chemical Co., density at 308 K 1.087 g/cm^3, M_w between 34 000 and 38 000, butyral content 88%.

Estimated Error:

No information given.

References:

[1] T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **30**, 401 (1985).

3.11. Poly(Vinylmethylether)—Propane

Components:

(1) Propane; C_3H_8; [74-82-8]
(2) Poly(vinylmethyl ether) (PVME); [9003-09-2]

Original Measurements:

H. G. Spencer and J. A. Yavorsky, J. Appl. Polym. Sci., **28**, 2937 (1983).

Variables:

T/K: 317–357
p/kPa: 0–40

Prepared By:

A. K. Bokarev

Experimental Data

In the pressure range indicated above, solubility obeys Henry's law.

Temperature dependence for solubility coefficient, S, is given by equation:

$$S=S_0\exp(-\Delta H/RT)$$

Parameter	Data
$\Delta H/(\mathrm{kJ/mol})$	−10.0
$\ln(S_0/(\mathrm{cm^3(STP)/cm^3\ cm\ Hg}))$	−7.57
$\ln S(353\ \mathrm{K})/(\mathrm{cm^3(STP)/cm^3\ cm\ Hg})$	−4.05

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out in a low pressure, constant-volume cell previously described.[1] The correction for the buoyancy was introduced.

Source and Purity of Materials:

The polymer investigated was supplied by Polysciences, Inc.
It had $M_w=34\,000$; $T_g=247$ K.
A density at 303 K was 1.04 g/cm^3.
Propane of 99.99% purity (Matheson) was used.

Estimated Error:

No estimates.

References:

[1] J. A. Yavorsky and H. G. Spencer, J. Appl. Polym. Sci. **25**, 2109 (1980).

3.12. Poly(Vinyltrimethyl Silane)—Various Gases

Components:

(1) Hydrocarbon gases C_1–C_4
(2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

The solubility of gaseous hydrocarbons in PVTMS has been measured using three different techniques: volumetric,[1] gravimetric,[2–4] and inverse gas chromatography.[5–8] The data for the following gases are available: methane [74-82-8],[1] acetylene [74-86-2],[2–4,8,9] ethylene [74-85-1],[2–5,7–9] ethane [74-84-0],[2–5,7–9] propadiene [463-49-0],[2–4,8,9] propyne [74-99-7],[2–4,8,9] propene [115-07-1],[2–5,7–9] propane [74-98-6],[2,9] n-butane [106-97-8].[5,7] Except propane and butane for which the dual mode sorption isotherms have been obtained,[4,6] the solubility of all other gases was measured in the range of pressure corresponding to the linear part of the sorption isotherm, i.e., the solubility coefficients have been reported. There is a general tendency for the solubility to increase with the critical temperature of gases, the variation of solubility with critical temperature is shown below. Values of critical temperature were taken from Ref. 10.

Correlation of the solubility coefficients S with critical temperature T_c/K of hydrocarbons

Hydrocarbons	T_c/K	$\log(S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}})$	Ref.
CH_4	190.5	−1.86	1
C_2H_2	309	−1.48	2–4
	309	−1.6	7, 8
C_2H_4	282.6	−1.33	2–4
	282.6	−1.44	5, 6
	282.6	−1.44	7, 8
C_2H_6	305.4	−1.15	2–4
	305.4	−1.14	5, 6
	305.4	−1.14	7, 8
CH_2CCH_2	393	−0.5	7, 8
	393	−0.5	2–4
CH_3CCH	401	−0.5	7, 8
	401	−0.5	2–4
C_3H_6	364.9	−0.5	2–4
	364.9	−0.6	7, 8
	364.9	−0.6	5, 6
C_3H_8	379.9	−0.6	5, 6
	379.9	−0.4	7, 8
	379.9	−0.4	2–4
n-C_4H_{10}	427.1	−0.05	5, 6

Critical Evaluation:

The solubility coefficients obtained by means of a gravimetric method (McBain balance) are, in majority of cases, higher than those measured using inverse gas chromatography method. However, the differences are well within the limits of scatter.

References:

[1] V. V. Volkov, S. G. Durgaryan, E. G. Novitskii, and N. S. Namctkin, Dokl. Akad. Nauk SSSR **232**, 838 (1977).

[2] V. V. Volkov, N. S. Nametkin, E. G. Novitskii, and S. G. Durgaryan, Vysokomol. Soedin. Ser A **21**, 920 (1979).

[3] V. V. Volkov, N. S. Nametkin, E. G. Novitskii, and S. G. Durgaryan, Vysokomol. Soedin. Ser. A **21**, 927 (1979).

[4] V. V. Volkov, dissertation, Moscow, TIPS, 1979.

[5] N. E. Kaliuzhnyi, Yu. P. Yampol'skii, S. G. Durgaryan, and N. S. Nametkin, Dokl. Akad. Nauk SSSR **265**, 1170 (1982).

[6] V. V. Volkov, A. K. Bokarev, S. G. Durgaryan, and N. S. Nametkin, Dokl. Akad. Nauk SSSR **282**, 641 (1985).

[7] Yu. P. Yampol'skii, N. E. Kaliuzhnyi, and S. G. Durgaryan, Macromolecules **19**, 846 (1986).

[8] M. B. Davydova, Yu. P. Yampol'skii, N. K. Gladkova, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **30**, 554 (1988).

[9] M. B. Davydova, Yu. P. Yampol'skii, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **30**, 1430 (1988).

[10] D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969).

Components:	**Original Measurements:**
(1) Different gases (2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)	V. V. Volkov, S. G. Durgaryan, E. G. Novitskii, and N. S. Nametkin, Dokl. Akad. Nauk SSSR **232**, 838 (1977); Vysokomol. Soedin., Ser. A **21**, 927 (1979).
Variables:	**Prepared By:**
$T/\mathrm{K}=283-323$ $p/\mathrm{kPa}=0-93$	Yu. P. Yampol'skii

Experimental Data

Solubility coefficients $S/\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3$ atm at 298 K and enthalpies of sorption ΔH kcal/mol

Gas	$S10^2$	$-\Delta H$
Helium; He; [7440-59-7]	0.11	1.45
Argon; Ar; [7440-37-1]	0.63	2.83
Hydrogen; H_2; [1333-74-0]	0.12	1.66
Nitrogen; N_2; [7727-37-9]	0.40	2.62
Oxygen; O_2; [7782-44-7]	0.56	2.69
Methane; CH_4; [74-82-8]	1.37	3.82
Carbon dioxide; CO_2; [124-38-9]	3.52	4.93

Auxiliary Information

Method/Apparatus/Procedure

A McBain quartz spring microbalance and a volumetric apparatus were used for sorption measurements.

Source and Purity of Materials:

PVTMS synthesized by BuLi initiated anionic polymerization had: $M_w=608\,000$, $M_n=416\,000$. All the gases were ‘‘chromatographically’’ pure.

Estimated Error:

$\delta S/S=10\%$.
$\delta(\Delta H)/\Delta H=20\%$.

Components:

(1) Xenon; Xe; [7440-63-3] and hydrocarbons
(2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)

Original Measurements:

V. V. Volkov, N. S. Nametkin, E. G. Novitskii, and S. G. Durgaryan, Vysokomol. Soedin, Ser. A. **21**, 920 (1979).

Variables:

$T/\mathrm{K}=293-313$
$p/\mathrm{kPa}=0-93$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficients $S/\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3$ atm at 298 K and enthalpies of sorption $\Delta H/\mathrm{kcal/mol}$

Gas	$S10^2$	$-\Delta H$
Xenon	7.1	4.20
Acetylene; C_2H_2; [74-86-2]	3.3	—
Ethylene; C_2H_4; [74-85-1]	4.7	4.02
Ethane; C_2H_6; [74-84-0]	7.0	3.58
Propadiene; C_3H_4; [463-49-0]	31.5	5.47
Propyne; C_3H_4; [74-99-7]	30.0	5.64
Propene; C_3H_6; [115-07-1]	31	5.96
Propane; C_3H_8; [74-98-6]	40	6.20
n-Butane; C_4H_{10}; [106-97-8]	272	—

Auxiliary Information

Method/Apparatus/Procedure

A McBain balance with a quartz spring was used in sorption measurement.

Source and Purity of Materials:

PVTMS synthesized in the presence of BuLi had $M_w=608\,000$ and $M_n=416\,000$.
All the gases were chromatographically pure.

Estimated Error:

$\delta S/S=10\%$.

Components:

(1) Various hydrocarbons C_2–C_4
(2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)

Original Measurements:

N. E. Kaliuzhnyi, Yu. P. Yampol'skii, S. G. Durgaryan, and N. S. Nametkin, Dokl. Akad. Nauk SSSR **265**, 1170 (1982).

Variables:

$T/\mathrm{K}=298-383$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficients $S/\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3$ atm of hydrocarbons

			S		
Gas	S (at 298 K)	Gas	298 K	333 K	373 K
Ethylene; C_2H_4; [74-85-1]	3.6	Propane; C_3H_8; [74-98-6]	27	8.05	—
Ethane; C_2H_6; [74-84-0]	7.2	*n*-Butane; C_4H_{10}; [106-97-8]	90	22.2	5.62
Propene; C_3H_6; [115-07-1]	23				

Enthalpies of sorption $\Delta H/\mathrm{kcal/mol}$

Gas	ΔH
C_2H_6	5.4
C_3H_8	6.42 ± 0.15
C_4H_{10}	8.02 ± 0.06

Auxiliary Information

Method/Apparatus/Procedure

Inverse gas chromatography was used for the determination of solubility coefficients. By the measurements correction for the pressure drop in a column was introduced.

Source and Purity of Materials:

PVTMS was prepared by anionic polymerization (sec. BuLi as a catalyst) and had molecular mass about 500 000 and a density 0.898 g/cc.

Components:

(1) Various hydrocarbons
(2) Poly(vinyltrimethyl silane); (PVTMS); [25036-32-2] (XV)

Original Measurements:

M. B. Davydova, Yu. P. Yampol'skii, N. K. Gladkova, and S. G. Durgarvan, Vysokomol. Soedin. Ser. A **30**, 554 (1988);
M. B. Davydova, Yu. P. Yampol'skii, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **30**, 1430 (1988).

Variables:

T/K = 295 – 345

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficients $S/(\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3\ \mathrm{atm})$ at 295 K

Gas	S	Gas	S
Ethyne; C_2H_2; [74-86-2]	2.5	Propyne; C_3H_4; [74-99-7]	29.5
Ethylene; C_2H_4; [74-85-1]	3.6	Propene; C_3H_6; [115-107-1]	24
Ethane; C_2H_6; [74-84-0]	7.2	Propane; C_3H_8; [74-98-6]	38
1,2-Propadiene; C_3H_4; [463-49-0]	31		

Heats of sorption, ΔH/kJ/mol, $= -R\mathrm{d}(\ln S)/\mathrm{d}(1/T)$

Gas	$-\Delta H$/kJ/mol	Gas	$-\Delta H$/kJ/mol
Ethyne	24.0	Propyne	30.6
1,2-Propadiene	30.6	Propene	31.8
Propane	34.8		

Auxiliary Information

Method/Apparatus/Procedure

Inverse gas chromatographic method of measurement of solubility was described in Ref. 1. The determination was performed in the condition of infinite dilution and in the absence of diffusion limitation.

Source and Purity of Materials:

PVTMS studied had molecular mass 600 000.

Estimated Error:

$\delta(\Delta H)/\Delta H < 5.3\%$

References:

[1] Yu. P. Yampol'skii, S. G. Durgaryan, and N. E. Kaliuzhnyi, J. Chrom. **286**, 97 (1984).

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)

Original Measurements:

V. V. Volkov, A. K. Bokarev, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **26**, 1294 (1984).

Variables:

T/K = 298
p/MPa = 0 – 0.4

Prepared By:

S. M. Shishatskii

Experimental Data

TABLE 1. Sorption isotherm of sulfur dioxide in PVTMS at 298 K. Thickness of the film: 64 μm (The original data were represented graphically)

Relative pressure	Sorption (V_1^*(STP)/V_2^*)
0.24	12.14
0.34	15.00
0.40	17.03
0.47	19.89
0.54	22.00
0.70	27.81
0.80	31.27

Relative pressure (p/p_s) = ratio of partial pressure and its saturted vapor pressure at the temperature of the experiment.

TABLE 2. Sorption and desorption isotherms of sulfur dioxide in PVTMS at 298 K. Thickness of the film: 160 μm (The original data were represented graphically)

Relative pressure	Sorption (V_1^*(STP)/V_2^*)	Relative pressure	Desorption (V_1^*(STP)/V_2^*)
0.18	10.04	0.14	8.94
0.24	13.16	0.18	10.88
0.27	14.25	0.20	12.65
0.33	15.34	0.25	14.25
0.38	17.96	0.33	18.22
0.40	17.96	0.40	22.35
0.51	21.49	0.46	25.55
0.60	23.94	0.55	29.09
0.72	28.40	0.68	32.71
0.83	32.45	0.75	34.57
0.96	40.63	0.85	38.02
0.98	43.16	0.90	40.04
1.00	46.62	0.94	42.32

Relative pressure (p/p_s) = ratio of partial pressure and its saturated vapor pressure at the temperature of the experiment.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured gravimetrically using a McBain balance.

Source and Purity of Materials:

PVTMS: Kuskovo Chemical Plant.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Sulfur dioxide; SO_2; [7446-09-5] (2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)	Yu. P. Yampol'skii, V. V. Volkov, N. E. Kaliuzhnyi, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **26**, 1640 (1984).

Variables:	**Prepared By:**
T/K=298 p/kPa=0–100	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for SO_2 in PVTMS at 298 K

k_D /mol cm^{-3}(STP) Pa^{-1}	C'_H/mmol cm^{-3}	b/(kPa)$^{-1}$
2.0109	0.45	0.01

Sorption isotherm of sulfur dioxide in PVTMS at 298 K. (The original data were represented graphically)

Pressure/kPa	Sorption (mmol/cm^3)
8.68	0.06
13.28	0.09
19.41	0.12
26.39	0.16
44.28	0.24
57.40	0.28
58.25	0.29
67.79	0.33
72.90	0.35
81.25	0.38
91.31	0.42

Auxiliary Information

Method/Apparatus/Procedure

Sorption was studied using a McBain balance with quartz spring. The procedure has been described in Ref. 1.

Source and Purity of Materials:

SO_2: traces of air were removed from the gas prior to use. PVTMS films: recast after dissolving gas separation PVTMS membrane (NPO Plastmassy) in methylbenzene.

Estimated Error:

No information given.

References:

[1] V. V. Volkov, N. S. Nametkin, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **21**, 920 (1979).

Components:	**Original Measurements:**
(1) Xenon; Xe; [7440-63-3] Carbon dioxide; CO_2; [124-38-9] Nitrous oxide; N_2O; [10024-97-2] Propane; C_3H_8; [74-98-6] (2) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)	V. V. Volkov, A. K. Bokarev, S. G. Durgaryan, and N. S. Nametkin, Doklady Akad. Nauk., SSSR. **282**, 641 (1985). N. A. Plate, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, and Yu. P. Yampol'skii J. Membr. Sci. **60**, 13 (1991).

Variables:	**Prepared By:**
T/K=298 p/MPa=0–0.7	S. M. Shishatskii

Experimental Data

Dual mode sorption parameters for PVTMS at 298 K

Gas	$k_D\times10^2$/(cm^3(STP)/cm^3 cm Hg)	C'_H/(cm^3(STP)/cm^3)	$b\times10^2$/(cm Hg)$^{-1}$
Xe	1.20	18.5	0.41
CO_2	0.46	28.7	0.11
N_2O	1.4	13.1	0.29
C_3H_8	0.113	5.2	19.1

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using a gravimetric technique described in Ref. 1.

Source and Purity of Materials:

No information given.

Estimated Error:

No information given.

References:

[1] V. V. Volkov, A. K. Bokarev, and S. G. Durgaryan, Vysokomol. Soedin., Ser A. **26**, 1295 (1984).

3.13. Poly(Trimethylsilyl Propyne)—Various Gases

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

PTMSP is known as the most permeable among polymers, both glassy and rubbery. So its sorption drew attention of several groups of investigators.[1–5] The dual mode sorption parameters as well as the apparent solubility coefficients S obtained by different researchers at temperatures 298–328 K are compared below.

TABLE 1. Dual mode sorption parameters and apparent solubility coefficients

T/K	p/atm	k_D	C'_H	b	$S=k_D+C'_H b$	Ref.
298	0–65	3.6	47.7	0.107	8.7	2, 3
298	0–60	1.3	139	0.064	10.2	5
303	0–40	1.53	151	0.0403	6.6	4
308	0–25	1.50	113	0.058	8.0	1
328	0–25	0.98	71.9	0.059	5.2	1

Units: k_D and $S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$; $C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$; $b/\mathrm{atm^{-1}}$.

A significant scatter of the values of the sorption model parameters is seen, which is related to the substantial time dependence of transport and thermodynamic properties of this polymer (for more details see Ref. 6). The scatter of the S values is not very large, and better agreement is observed between the data from different papers.

An essential feature of the sorption in PTMSP is the large values of Langmuir capacity parameter C'_H, much higher than in other polymers. The minimal value reported in Refs. 2 and 3 is presumably underestimated owing to the narrow pressure range studied in these works. It is intriguing and as yet unexplained fact that Henry's law solubility coefficients k_D in PTMSP are significantly higher than in other polymers. This is true not only for carbon dioxide but for other gases as well.[1–3]

Referring to the data given in Table 1 one can tentatively recommend the sorption parameters measured in Refs. 5 and 1 since they form a plausible temperature dependence for all three parameters and for S.

The enthalpy of sorption calculated from Van't Hoff plot for S is equal to -14.7 ± 4.9 kJ/mol. The scatter in the temperature dependences of the k_D and b values prevents the calculation of the corresponding enthalpies of Henry's law dissolution and Langmuir adsorption.

References:

[1] Y. Ichiraku, S. A. Stern, and T. Nakagawa, J. Membr. Sci. **34**, 5 (1987).

[2] A. K. Bokarev, V. V. Volkov, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, and Yu. P. Yampol'skii, Dokl. Akad. Nauk. SSSR **305**, 117 (1989).

[3] N. A. Plate, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, and Yu. P. Yampol'skii, J. Membr. Sci. **60**, 13 (1991).

[4] T. Nakagawa, M. Sekiguchi, K. Nagai, and A. Higuchi, Intern. Congress on Membranes (ICOM-90), Chicago, 1990, p. 824.

[5] V. I. Bondar, Yu. M. Kukharskii, and V. V. Volkov, Abstracts, 5th Intern. Symp. on Solubility Phenomena, Moscow, 1992, p. 227.

[6] D. R. Paul and Yu. P. Yampol'skii, Eds., *Polymeric Gas Separating Membranes* (CRC, Boca Raton, 1994), p. 192.

Components:

(1) Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7]
Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)

Original Measurements:

Y. Ichiraku, S. A. Stern, and T. Nakagawa, J. Membr. Sci. **34**, 5 (1987).

Variables:

T/K=308 and 328
p/MPa=0–2.7 (0–27 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in PTMSP at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	1.497	112.9	0.058
	0.978*	71.9*	0.059*
CH_4	0.667	87.8	0.035
N_2	0.431	15.4	0.042
O_2	0.656	16.8	0.036

*At 328 K.

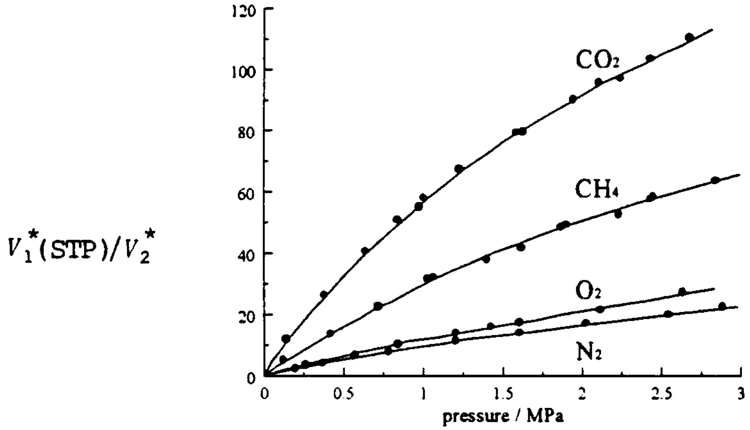


FIG. 24. Sorption isotherms of various gases in PTMSP at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The solubility was measured by a volumetric method. The apparatus and the procedure are described in detail in Ref. 1.

Source and Purity of Materials:

Gases: purity >99.5%.
PTMSP: Sanyo Chemical Industries, density 0.938 g/cm^3, M_w =700 000, no glass transition observed below 473 K.

Estimated Error:

Relative precision of solubilities: from $\pm 6.6\%(CO_2)$ to $\pm 54\%(N_2)$.

References:

[1] V. M. Shah, B. J. Hardy, and S. A. Stern, J. Polym. Sci., Part B: Polym. Phys. **24**, 2033 (1986).

Components:	Original Measurements:
(1) 2-Methylpropane; C_4H_{10}; [75-28-5] (2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)	H. Odani, H. Shimomura, K. Nakanishi, T. Masuda, and T. Higashimura, Japan—US Polymer Symposium 1985, pp. 251–252.

Variables:	Prepared By:
T/K=298 p/kPa=0–100	Yu. P. Yampol'skii

Experimental Data

Sorption isotherm of 2-methylpropane in PTMSP at 298 K. (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
4.22	14.74
9.03	20.59
12.78	23.79
24.40	30.22
27.09	30.65
41.94	35.56
67.73	43.01
93.33	50.19

Auxiliary Information

Method/Apparatus/Procedure

Sorption was studied by a gravimetric method.

Source and Purity of Materials:

PTMSP: synthesized according to Ref. 1 and stored in methanol until used.

Estimated Error:

No information given.

References:

[1] K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, J. Appl. Polym. Sci. **30**, 1605 (1985).

Components:	Original Measurements:
(1) Xenon; Xe; [7440-63-3] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] (2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)	S. Asakawa, Y. Saitoh, K. Waragai, and T. Nakagawa, Gas Separation Purification, **3**, 117 (1989).

Variables:	Prepared By:
T/K=307.8 p/kPa=0–93	V. I. Bondar

Experimental Data

Linear sorption isotherms were observed for all three gases.

Solubility coefficients S

Gas	$10^2 S$/cm^3(STP)/cm^3 cm Hg
Xe	19.71
O_2	2.4
CO_2	8.83

Auxiliary Information

Method/Apparatus/Procedure

A gravimetric method of the measurement was employed (the McBain balance with a quartz spring). The correction allowing for buoyancy was made.

Source and Purity of Materials:

PTMSP was prepared according to Ref. 1. It had M_w =2 500 000.

Estimated Error:

No information given.

References:

[1] T. Masuda, E. Isobe, T. Higashimura, and K. Takada, J. Am. Chem. Soc. **105**, 74 (1983).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] Ethane; C_2H_6; [74-84-0]
(2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)

Original Measurements:

V. I. Bondar, Yu. M. Kukharskii, and V. V. Volkov, Abstracts, 5th Intern. Symposium on Solubility Phenomena, Moscow, 1992, p. 227.

Variables:

T/K=298
p/MPa=0–11

Prepared By:

V. I. Bondar

Experimental Data

Dual mode sorption parameters for various gases in PTMSP at 298 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Ar	0.096	90.9	0.015
N_2	0.062	60.0	0.017
CO_2	1.300	139.0	0.064
CH_4	0.200	88.3	0.041
C_2H_6	2.830	75.1	0.473

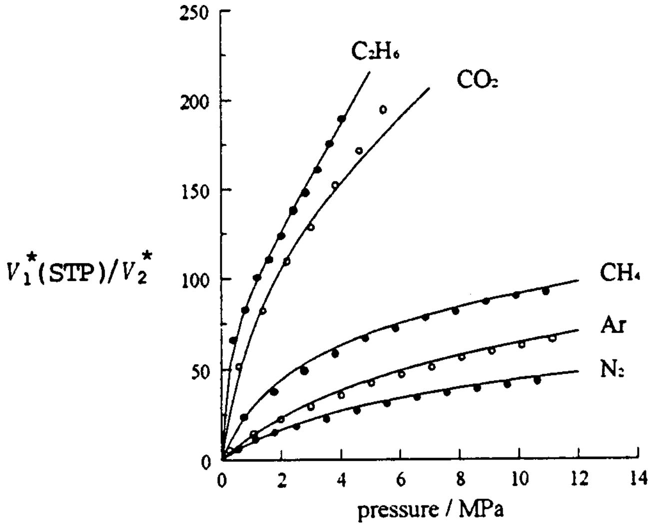


FIG. 25. Sorption isotherms of various gases in PTMSP at 298 K.

Auxiliary Information

Method/Apparatus/Procedure

Solubility was measured by means of gravimetric method using Sartorius 4436 microbalance.

Source and Purity of Materials:

PTMSP: prepared according the method of Masuda *et al.*[1]

Estimated Error:

No information given.

References:

[1] T. Masuda, E. Isobe, and T. Higashimura, J. Am. Chem. Soc. **105**, 7473 (1983).

Components:

(1) Argon; Ar; [7440-37-1] Krypton; Kr; [7439-90-9] Xenon; Xe; [7440-63-3] Carbon dioxide; CO_2; [124-38-9] Nitrous oxide; N_2O; [10024-97-2] Methane; CH_4; [74-82-8]
(2) Poly(trimethylsilyl propyne) (PTMSP); [87842-32-8] (XVI)

Original Measurements:

A. K. Bokarev, V. V. Volkov, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, and Yu. P. Yampol'skii, Dokl. Akad. Nauk SSSR **305**, 117 (1989).
N. A. Plate, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, and Yu. P. Yampol'skii, J. Membr. Sci. **60**, 13 (1991).

Variables:

T/K=298
p/kPa=0–665

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in PTMSP at 298 K

Gas	10^2k_D/cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	10^2b/cm Hg^{-1}
CO_2	4.70	47.70	0.141
N_2O	6.15	42.88	0.329
Xe	4.84	61.73	0.399

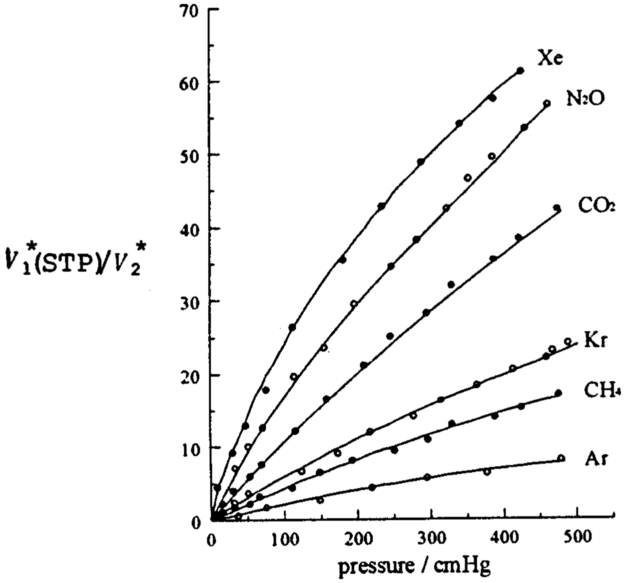


FIG. 26. Sorption isotherms of various gases in PTMSP at 298 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were performed using McBain balance as is described in Ref. 1

Source and Purity of Materials:

PTMSP: prepared by polymerization in the presence of $TaCl_5$ as a catalyst: density 0.964 g/cm^3 (measured in a gradient column). $M_w=590\,000$, $M_n=125\,000$, glass transition temperature 503 K.

Estimated Error:
No information given.

References:
[1] V. V. Volkov, A. K. Bokarev, and S. G. Durgaryan, Vysokomol. Soedin., Ser. A **26**, 1294 (1984).

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Poly(trimethylsilyl propyne) (PMSP); [87842-32-8] (XVI)

Original Measurements:

L. C. Withchey-Lakshmanan, H. B. Hopfenberg, and R. T. Chern, J. Membr. Sci. **48**, 321 (1990).

Variables:

T/K=308
p/kPa=0–120

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for propane at 308 K*

k_D	C'_H	b
3.6 10^{-4} mol/g atm	2.16×10^{-3} mol/g	4.4 (atm)$^{-1}$
6.3 cm^3(STP)/cm^3 atm	37.7 cm^3(STP)/cm^3	4.4 (atm)$^{-1}$

*The first line gives the values as reported by the authors, the second line recalculated by the compiler.

Auxiliary Information

Method/Apparatus/Procedure

The sorption measurements were performed with a McBain quartz spring balance following a procedure described in Ref. 1

Source and Purity of Materials:

PMSP had $M_w=600\,000$, a density 0.78 g/cm^3. Purity of propane 99.5%.

Estimated Error:
No information given.

References:
[1] R. M. Felder, C. J. Patton, and W. J. Koros, J. Polym. Sci., Polym. Prep. **19**, 1895 (1981).

Components:
(1) Carbon dioxide; CO_2; [124-38-9] Propane; C_3H_8; [74-98-6]
(2) Poly(trimethylsilyl propyne) (PTMSP) [87842-32-8] (XVI)

Original Measurements:
T. Nakagawa, M. Sekiguchi, K. Nagai, and A. Higuchi, Int. Congress on Membranes (ICOM-90) Chicago, 1990, pp. 824–26.
T. Nakagawa, H. Nahano, and A. Higuchi, Membrane Symposium N1 ''Control in Membrane Transport,'' Kvoto, 1989, pp. 36–39.

Variables:
$T/\mathrm{K}=303$ and 308
$p/\mathrm{MPa}=0-0.1$ (for C_3H_8) and 0–4.0 (for CO_2)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Dual-mode sorption parameters

Gas	T/K	k_D ,/cm^3(STP)/cm^3 atm	C'_H ,/cm^3(STP)/cm^3	b, atm^{-1}
CO_2	303	0.534	151.2	0.0403
	308	1.497	112.9	0.058
C_3H_8	303	6.93	50.14	2.15

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were done by means of Cahn electrobalance, model 2000.

Source and Purity of Materials:

PTMSP was synthesized according to Masuda *et al.*[1] It did not reveal any glass transition up to 620 K.

References:

[1] K. Takada, H. Mitiuta, T. Masuda, and T. Higashimura, J. Appl. Polym. Sci. **30**, 1605 (1983).

Components:
(1) Carbon dioxide; CO_2; [124-38-9] Propane; C_3H_8; [74-98-6]
(2) Brominated poly(1-trimethylsilyl-1-propyne)

Original Measurements:
T. Nakagawa, M. Sekiguchi, K. Nagai, and A. Higuchi, Int. Congress on Membranes (ICOM-90), Chicago, 1990, pp. 824–26.

Variables:
$T/\mathrm{K}=303$
$p/\mathrm{MPa}=0-4.0$

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Dual-mode sorption parameters

Gas	[Br],%	p/MPa	k_D ,/cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	2.6	0–4.0	1.77	48.8	0.0701
C_3H_8	11.9	0–0.1	9.65	19.6	5.96

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made by means of Cahn electrobalance model 2000.

Source and Purity of Materials:

Poly(trimethylsilylpropyne was synthesized according to Ref. 1. Bromination was carried out by dipping samples into bromine water. The polymer revealed a glass transition at 323 K.

Estimated Error:
No information given.

References:

[1] K. Takada, H. Mitiuta, T. Masuda, and T. Higashimura, J. Appl. Polym. Sci. **30**, 1605 (1983).

3.14. Poly(Phenylene Oxides)—Various Gases

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(2,6-dimethylphenylene oxide) (PPO); [24938-67-8] (XVIII)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Four investigations are available on solubility of carbon dioxide and methane in PPO.[1–4] PPO is a semicrystalline polymer with high glass transition temperature of amorphous phase. However, no author reported the content of amorphous and crystalline phases of polymer studied and other important characteristics like molecular mass. All this should result in predicaments in comparison of the data obtained in different papers.

Table 1 shows the dual mode sorption parameters and apparent solubility coefficients *S* calculated from them or from the initial slope of the experimental isotherms.

TABLE 1. Dual mode sorption parameters and apparent solubility coefficients

Gas	T/K	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
CO_2	308	0.788	32.6	0.216	7.8	1
	308	0.849	25.9	0.239	7.0	3
	308	—	—	—	6*	2
CH_4	293	—	—	—	4.7	4
	308	—	—	—	2.2*	2
	308	0.267	19.1	0.1077	2.3	3

Units: k_D and $S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}$; $C'_H/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$; b/atm^{-1}.
*Calculated from the plots by evaluator.

In spite of the difficulties mentioned above, the dual mode sorption parameters found by different authors agree reasonably, as well as the solubility coefficients at constant temperature.

Enthalpy of sorption of methane in PPO found from the *S* values measured at two different temperatures is shown to be equal to −35.6 kJ/mol.

References:

[1] Y. Maeda and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **25**, 981 (1987).
[2] R. T. Chern, L. Jia, S. Shimoda, and H. B. Hopfenberg, J. Membr. Sci. **48**, 333 (1990).
[3] B. J. Story and W. J. Koros, J. Appl. Polym. Sci. **42**, 2613 (1991).
[4] O. M. Ilinitch, G. L. Semin, M. V. Chertova, and K. I. Zamaraev, J. Membr. Sci. **66**, 1 (1992).

3.15. Poly(2,3 Dimethylphenylene Oxide)—Carbon Dioxide, Methane

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(2, 6-dimethylphenylene oxide) (PPO); [24938-67-8] (XVIII)

Original Measurements:

K. Toi, G. Morel, and D. R. Paul, J. Appl. Polym. Sci. **27**, 2997 (1982).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.5$

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for various gases in PPO at 308 K

Gas	$k_D/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}$	$C'_H/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$	b/atm^{-1}
Ar	0.21	9.4	0.058
CO_2	0.95	27.5	0.250
CH_4	0.33	18.1	0.110
N_2	0.12	7.1	0.040

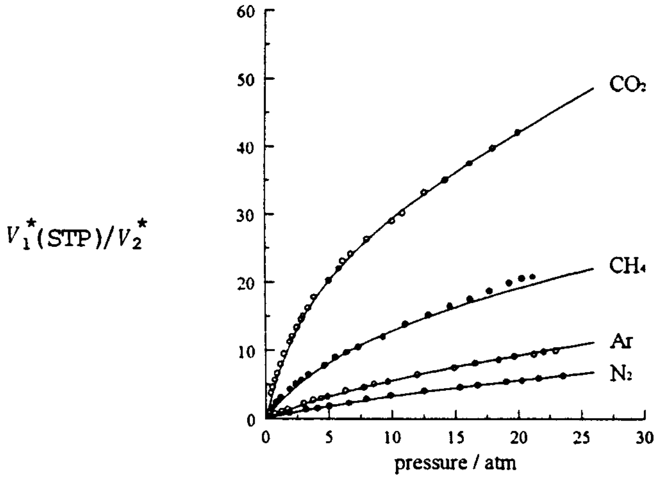


FIG. 27. Sorption isotherms of various gases in PPO at 298 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made using facilities and procedures described previously, Ref. 1

Source and Purity of Materials:

PPO: General Electric Co., $M_w=34\ 000$. $M_n=22\ 600$.

Estimated Error:

No information given.

References:

[1] D. R. Paul, Ber. Bunsenges Phys. Chem. **83**, 294 (1979).

Components:
(1) Carbon dioxide; CO_2; [124-38-9]
(2) Methane; CH_4; [74-82-8]
(3) Poly(2, 6-dimethylphenylene oxide) (PPO); [24938-67-8] (XVIII)

Original Measurements:
B. J. Story and W. J. Koros, J. Appl. Polym. Sci. **42**, 2613 (1991).

Variables:
$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.0$ (0–20 atm)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Dual mode sorption model parameters for pure gases in PPO at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.8490	25.86	0.2395
CH_4	0.2674	19.10	0.1077

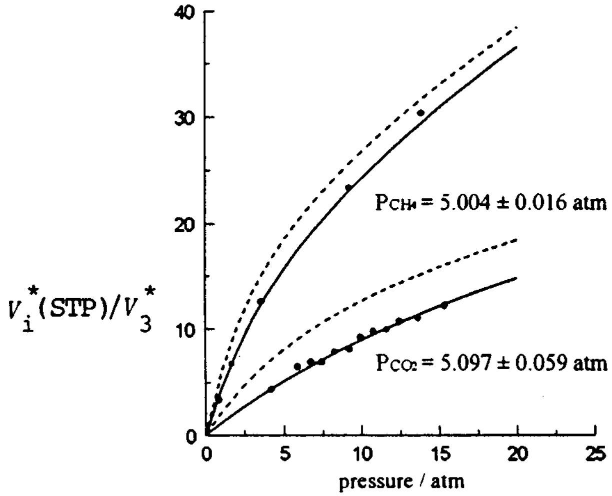


FIG. 28. Mixed gas sorption CO_2 /CH_4 in poly(phenylene oxide) at 308 K. Solid lines: sorption model for mixed gas sorption $C_i = k_{Di}p_i + C'_{Hi}b_ip_i/(1+b_jp_j+bp_i)$, (Dotted lines) sorption model for pure gases.

Auxiliary Information

Method/Apparatus/Procedure

Standard pressure decay system (Ref. 1) was used in pure gas sorption. Mixed gas sorption experiments were performed using a special apparatus having additional chambers for preparation and chromatographic sampling of gas mixtures.

Source and Purity of Materials:
No information given.

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:
(1) Xenon; Xe, [7440-63-3] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(phenylene oxide) (PPO) [24938-67-8] (XVIII)

Original Measurements:
S. Asakawa, Y. Saitoh, K. Waragai, and T. Nakagawa, Gas Separation Purification **3**, 117 (1989).

Variables:
$T/\mathrm{K}=307.8$
$p/\mathrm{kPa}=0-93$

Prepared By:
V. I. Bondar

Experimental Data

Solubility coefficients, S

Gas	10^2S/cm^3(STP)/cm^3 cm Hg
Xe	18.81
CO_2	8.56

Auxiliary Information

Method/Apparatus/Procedure

A McBain balance with a quartz spiral was used in the solubility measurements, the correction for buoyancy was introduced.

Source and Purity of Materials:
PPO was obtained by oxidative coupling method according to Ref. 1. Nothing specified on molecular mass or crystallinity.

Estimated Error:
No information given.

References:
[1] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, J. Am. Chem. Soc. **81**, 6335 (1959).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Decanedioic acid, dioctyl ester (dioctyl sebacate, DOS); $C_{26}H_{50}O_4$; [2432-87-3] Phosphoric acid, tri(methyl phenyl) ester (tricresyl phosphate, TCP); $C_{21}H_{21}O_4P$; [1330-78-5]
(3) Poly(2, 6-dimethylphenylene oxide) (PPO); [24938-67-8] (XVIII)

Original Measurements:

Y. Maeda and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **25**, 981 (1987).

Variables:

T/K = 308–328
p/MPa = 0–2.2 (0–22 atm)

Prepared By:

A. K. Bokarev

Experimental Data

Table 1. Dual mode sorption parameters for CO_2 in PPO at different temperatures and its mixtures with plasticizers at 308 K

System	T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}	T_g /K
PPO	308	0.788	32.6	0.216	481.8
	318	0.586	30.0	0.164	481.8
	328	0.463	28.4	0.128	481.8
TCP (mass %)					
10%	308	0.543	21.6	0.181	427.1
20%	318	0.654	14.2	0.132	380.9
30%	328	0.821	3.8	0.251	345.0
DOS (mass %)					
10%	308	0.532	20.5	0.141	408.8
20%	318	0.763	7.3	0.172	354.1
30%	328	1.090	—	—	312.3

Table 2. Sorption isotherms of carbon dioxide in pure PPO (The original data were represented graphically)

Pressure/MPa	Sorption/ (V_1^*(STP)/V_3^*)	Pressure/MPa	Sorption/ (V_1^*(STP)/V_3^*)	Pressure/MPa	Sorption/ (V_1^*(STP)/V_3^*)	Pressure/MPa	Sorption/ (V_1^*(STP)/V_3^*)
T = 308 K							
0.04	4.24	0.28	14.92	0.83	27.13	1.61	38.02
0.06	4.92	0.37	17.64	0.84	27.92	1.89	41.15
0.08	5.94	0.41	18.09	1.02	30.16	1.91	40.80
0.10	7.08	0.42	19.34	1.11	31.86	2.00	41.70
0.12	8.33	0.46	20.02	1.18	32.41	2.03	42.38
0.17	10.60	0.55	21.82	1.30	34.55	—	—
0.19	11.17	0.65	24.08	1.37	35.45	—	—
T = 318 K							
0.09	4.80	0.41	14.77	0.91	23.45	1.74	32.51
0.18	7.98	0.55	17.60	1.14	25.91	1.76	32.16
0.19	8.66	0.70	20.07	1.34	28.38	2.08	35.28
0.28	11.38	0.79	21.54	1.43	29.38	2.16	35.60
0.32	12.28	0.84	22.21	1.50	30.51	—	—
T = 328 K							
0.13	4.79	0.44	12.48	1.08	21.13	1.74	27.37
0.19	6.38	0.57	14.62	1.27	23.48	1.82	28.15
0.30	9.55	0.79	17.88	1.30	23.93	1.98	29.25
0.38	11.13	0.95	19.56	1.68	26.70	2.09	30.02

Table 3. Effect of the content of DOS (mass %) on CO_2 sorption isotherms for PPO at 308 K (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})
DOS 0 mass %							
0.06	4.91	0.28	14.94	0.65	23.94	1.36	35.39
0.08	5.85	0.38	17.82	0.83	27.17	1.61	37.94
0.10	7.10	0.41	18.07	0.84	27.87	1.87	41.03
0.12	8.29	0.43	19.31	1.01	30.01	1.89	40.63
0.17	10.82	0.45	19.66	1.11	31.95	1.98	41.38
0.19	11.27	0.47	19.91	1.17	32.35	2.01	42.38
DOS 10 mass %							
0.18	5.02	0.60	12.63	1.48	21.72	2.14	26.38
0.23	6.36	0.84	15.48	1.53	21.97	—	—
0.30	7.90	0.94	16.48	1.78	24.02	—	—
0.46	10.44	1.15	18.77	2.09	26.32	—	—
DOS 20 mass %							
0.13	2.44	0.50	7.27	0.97	12.22	2.09	21.52
0.22	3.78	0.65	8.72	1.34	15.22	—	—
0.27	4.28	0.72	9.52	1.43	15.82	—	—
0.38	5.78	0.83	10.67	1.76	18.67	—	—
DOS 30 mass %							
0.20	2.59	0.65	7.53	1.37	14.62	2.14	23.16
0.28	3.44	0.95	10.43	1.53	16.32	—	—
0.37	4.39	0.99	10.98	1.81	19.32	—	—
0.48	5.69	1.19	12.83	2.09	22.51	—	—

Table 4. Effect of the content of TCP (mass %) on CO_2 sorption isotherms for PPO at 308 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})
TCP 0 mass %							
0.04	3.19	0.30	14.77	0.83	27.21	1.62	37.90
0.06	4.67	0.39	17.83	0.84	27.89	1.87	41.27
0.08	5.81	0.42	18.05	1.01	30.14	1.89	40.58
0.11	7.17	0.44	19.30	1.11	31.83	1.99	41.48
0.14	8.19	0.48	19.98	1.18	32.39	2.02	42.38
0.18	10.69	0.56	21.79	1.29	34.42	—	—
0.20	11.03	0.66	23.94	1.36	35.21	—	—
TCP 10 mass %							
0.13	4.54	0.44	11.44	0.83	17.18	1.46	23.68
0.18	6.13	0.58	13.81	0.91	18.20	1.71	25.46
0.23	7.15	0.70	15.61	1.11	20.21	1.88	26.69
0.27	8.28	0.73	16.29	1.27	21.78	1.95	27.13
0.35	9.75	0.78	16.62	1.35	22.33	—	—
TCP 20 mass %							
0.16	3.17	0.41	7.00	0.86	12.17	1.43	17.08
0.21	4.08	0.51	8.12	1.14	14.74	1.89	20.53
0.29	5.09	0.67	10.15	1.20	15.30	1.95	20.98
0.34	6.10	0.81	11.83	1.40	17.20	—	—
TCP 30 mass %							
0.20	2.48	0.43	5.18	0.93	10.10	1.48	14.91
0.26	3.16	0.49	5.73	1.00	10.66	1.57	15.46
0.31	3.94	0.55	6.29	1.06	11.22	1.77	17.59
0.40	4.73	0.67	7.76	1.18	12.34	2.14	20.49

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure for measuring sorption isotherms are described in Ref. 1.

Source and Purity of Materials:

PPO: General Electric Co., $M_n = 22\,600$. $M_w = 34\,000$, $M_z = 57\,200$, glass transition temperature 482 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9] Methane; CH_4; [74-82-8]
(2) Poly(2, 6-dimethyl-1, 4-phenyleneoxide) (PPO); [24938-67-8] (XVIII) Aryl-brominated PPO (Br content 36% and 91%)

Original Measurements:

R. T. Chern, F. R. Sheu, L. Jia, V. T. Stannett, and H. B. Hopfenberg, J. Membr. Sci. **35**, 103 (1987).

Variables:

T/K: 308
p/MPa: 0–3.0 (1–3 atm)

Prepared By:

A. K. Bokarev

Experimental Data

Dual-mode sorption parameters for gases in PPO and PPOBr at 308 K

Polymer	Gas	k_D/cm^{-3}(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/(atm^{-1})
PPO	CO_2	0.921	32.74	0.195
	CH_4	0.321	22.19	0.107
	N_2	0.153	9.95	0.048
PPOBr	CO_2	0.941	35.42	0.244
(36%)	CH_4	0.344	24.93	0.113
	N_2	0.162	11.83	0.053
PPOBr	CO_2	0.969	37.54	0.292
(91%)	CH_4	0.379	26.90	0.120
	N_2	0.169	15.06	0.057

Auxiliary Information

Method/Apparatus/Procedure

A dual-transducer pressure-decay cell, was used for the solubility measurements. For details see Refs. 1 and 2.

Source and Purity of Materials:

PPO in powder form was obtained from General Electric Co. Bromination of PPO resulted in only aryl-substituted polymer. The ratio of mono- to di-substituted PPO was 2.6 for PPOBr (36%) and 8.6 for PPO (91%).
The purity of gases (Air Products and Chemicals) used: Coleman grade CO_2 (99.999%), instrument grade CH_4 (99.7%), N_2 ($>$99.99%).

Estimated Error:

Not specified.

References:

[1] R. T. Chern, W. J. Koros, R. Yui, H. B. Hopfenberg, and V. T. Stannett, J. Polym. Sci., Polym. Phys. Ed. **22**, 1061 (1984).
[2] E. S. Sanders, W. J. Koros, V. T. Stannett, and H. B. Hopfenberg, J. Membr. Sci. **13**, 161 (1983).

Components:	**Original Measurements:**
(1) Hydrocarbons C_1–C_3 (2) Poly(phenylene oxide) (PPO); [25134-01-4]	O. M. Ilinitch, G. L. Semin, M. V. Chertova, and K. I. Zamaraev, J. Membr. Sci. **66**, 1 (1992).
Variables:	**Prepared By:**
T/K=293.2 p/kPa=0–100	O. M. Ilinitch

Experimental Data

Solubility $C/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$ of hydrocarbons in PPO

Gas	p/kPa	C	Gas	p/kPa	C
Methane;	21.3	1.0	Propane;	6.9	9.7
CH_4;	34.0	1.4	C_3H_8;	13.7	12.6
[74-82-8]	46.7	1.8	[74-98-6]	20.3	14.4
	60.0	2.3		30.0	16.1
	72.6	2.8		34.7	16.9
	84.0	3.4			
Ethane;	6.0	3.3	Propylene;	4.4	6.6
C_2H_6;	7.6	4.5	C_3H_6;	8.1	9.3
[74-84-0]	20.0	7.0	[115-07-1]	13.6	11.6
	25.6	8.2		20.0	13.7
	34.7	9.8		26.7	15.4
				34.7	17.1
Ethylene;	4.7	2.6			
C_2H_4;	8.0	3.5			
[74-85-1]	10.0	4.3			
	14.2	5.1			
	23.3	6.9			
	34.3	8.6			
	36.0	9.2			

Auxiliary Information

Method/Apparatus/Procedure

The conventional McBain balance was used.

Source and Purity of Materials:

PPO was prepared via oxidative polycondensation of 2,6-dimethylphenol. Major possible impurity: phenoquinone and copper. Purity >99.9%; a density 1.17 g/cm^3, T_g=482 K.
All the gases had a purity 99.9%.

Estimated Error:

$\delta T=\pm 0.1$ K; $\delta p=\pm 0.2$ kPa.
$\delta C/C=\pm 0.1$ (compiler).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Poly(2, 6-dimethylphenylene oxide) (PPO); [24938-67-8] (XVIII) Brominated PPO	R. T. Cher, L. Jia, S. Shimoda, and H. B. Hopfenberg, J. Membr. Sci. **48**, 333 (1990).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.5	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Properties of PPO and brominated PPO

Characteristics	PPO	PPOBr (0.36)	PPOBr (0.91)	PPOBr (1.06)
% Repeat unit				
Mono-Br	0	20.4	73.9	60.0
Di-Br	0	7.8	8.5	24.0
Unmodified	100	71.8	17.6	16.0
Density/g cm^{-3}	1.061	1.203	1.380	1.390
T_g /K	483	506	535	542

TABLE 2. Sorption isotherms of carbon dioxide in the various polymers at 308 K (The original data were represented graphically)

PPO		PPOBr (0.36)		PPOBr (0.91)		PPOBr (1.06)	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.13	8.79	0.13	10.19	0.14	12.50	0.12	10.42
0.17	9.93	0.20	13.39	0.22	17.33	0.36	22.35
0.24	12.90	0.24	15.69	0.40	23.48	0.38	21.41
0.30	14.95	0.32	18.43	0.45	24.85	0.24	15.93
0.36	16.31	0.49	23.43	0.63	29.61	0.55	26.41
0.45	18.57	0.53	24.79	0.88	35.25	0.70	32.35
0.72	24.90	0.61	26.37	0.97	36.59	0.74	30.93
0.81	27.17	0.76	29.52	1.08	38.60	0.96	35.20
0.88	28.05	0.86	31.78	1.33	42.16	0.90	36.86
1.02	30.28	0.95	33.11	1.52	44.82	1.11	40.91
1.17	33.20	1.02	34.00	1.65	45.9	1.27	41.97
1.37	35.16	1.28	38.47	1.73	46.77	1.41	46.29
1.36	36.56	1.34	38.90	2.06	51.20	1.53	48.07
1.50	36.70	1.41	40.01	2.13	51.86	1.63	48.93
1.73	40.27	1.46	40.45	2.22	53.89	1.85	52.27
1.76	41.18	1.75	44.20	2.32	54.52	2.06	55.85
1.94	42.91	1.88	45.75	2.65	58.25	2.22	57.61
2.16	45.10	1.93	46.64	—	—	2.53	61.35
2.38	47.27	2.14	48.83	—	—	—	—
2.63	51.06	2.32	51.03	—	—	—	—
2.80	52.81	—	—	—	—	—	—

TABLE 3. Sorption isotherms of methane in the various polymers at 308 K (The original data were represented graphically)

PPO		PPOBr (0.36)		PPOBr (0.91)		PPOBr (1.06)	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.10	2.85	0.03	2.08	0.11	4.02	0.04	2.17
0.19	4.50	0.18	4.89	0.20	6.46	0.18	7.05
0.47	8.56	0.23	6.06	0.48	11.51	0.45	12.40
0.51	9.24	0.29	7.32	0.53	12.18	0.61	14.13
0.57	10.11	0.37	8.58	0.69	14.51	0.80	17.53
0.70	11.36	0.43	9.75	0.93	17.10	1.03	19.83
0.99	14.34	0.52	10.91	0.96	17.88	1.22	22.25
1.10	15.30	0.66	12.65	1.04	18.06	1.45	24.16
1.17	15.77	0.72	13.32	1.17	20.20	1.65	25.98
1.28	16.53	0.80	14.38	1.26	19.68	1.88	27.30
1.67	19.10	0.88	15.15	1.50	21.30	2.07	29.23
1.73	19.28	0.99	16.11	1.40	22.70	2.27	30.36
1.79	19.95	1.08	16.97	1.61	24.12	2.44	31.79
2.03	20.98	1.13	17.35	1.74	24.19	2.57	31.96
2.21	22.22	1.19	18.03	1.80	25.06	—	—
2.26	22.40	1.27	18.79	2.02	26.39	—	—
2.46	23.04	1.50	20.51	2.10	26.86	—	—
2.63	24.48	1.56	20.60	2.29	27.90	—	—
2.67	24.47	1.69	21.75	2.50	28.73	—	—
—	—	1.80	22.31	2.57	29.11	—	—
—	—	2.00	23.74	—	—	—	—
—	—	2.07	23.72	—	—	—	—
—	—	2.18	24.58	—	—	—	—
—	—	2.26	25.35	—	—	—	—
—	—	2.36	25.82	—	—	—	—
—	—	2.41	25.81	—	—	—	—
—	—	2.46	26.09	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured with a dual transducer barometric device described in Ref. 1.

Source and Purity of Materials:

Bromination was conducted at 273 K in dilute solution of PPO in chloroform (<5%). According to NMR none of the methyl groups were brominated. Aromatic rings were brominated mainly in three and five positions.

Estimated Error:
No information given

References:
[1] E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Membr. Sci. **13**, 16 (1983).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Methane; CH_4; [74-28-8]
(3) Carboxylated poly(phenylene oxide) (CPPO)

Original Measurements:

B. J. Story and W. J. Koros, J. Appl. Polym. Sci. **42**, 2613 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in CCPO at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.7918	26.28	0.2852
CH_4	0.2981	15.53	0.1254

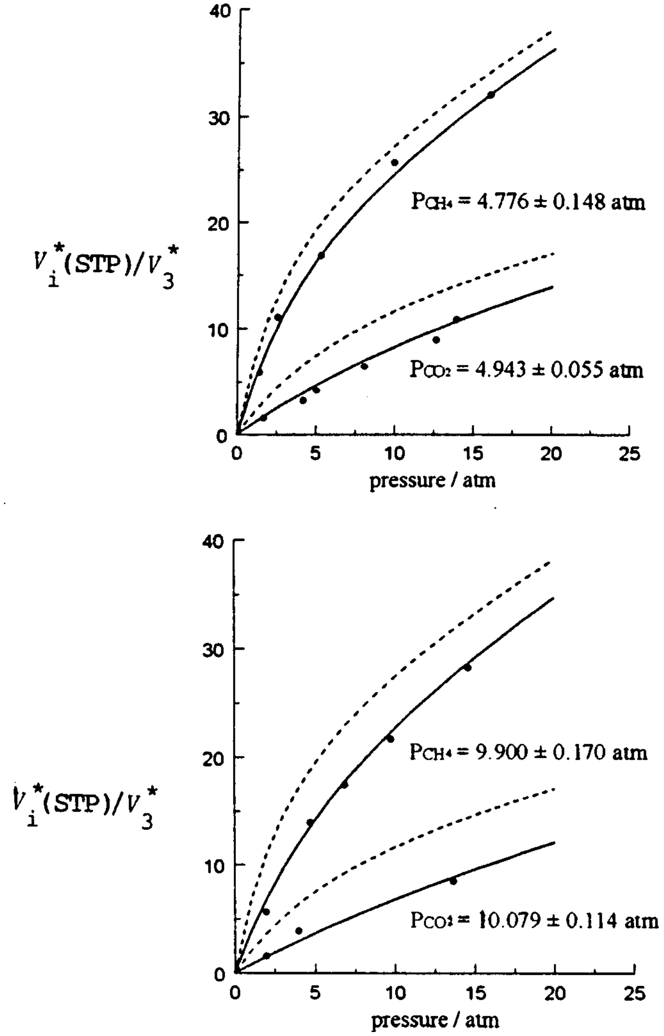


FIG. 29. Mixed gas sorption CO_2/CH_4 in CPPO at 308 K and two different pressures. (Solid lines) sorption model for mixed gas sorption $C_i = k_{Di}p_i + C'_{Hi}b_ip_i/(1+b_ip_i+b_jp_j)$. (Dotted lines) sorption model for pure gases.

Auxiliary Information

Method/Apparatus/Procedure

A standard pressure decay system (Ref. 1) was used in pure gas sorption. Mixed gas sorption experiments were performed using a special apparatus having additional chambers for preparation and chromatographic sampling of gas mixtures.

Source and Purity of Materials:

CPPO: prepared via lithiation into methyl groups with BuLi/THF with subsequent carboxylation and acidification. The average content of COOH groups per repeat unit was 0.22.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

3.16. Poly(Ethylene Terephthalate)—Carbon Dioxide and Other Gases

Components:	**Evaluator:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

This system has been studied thoroughly by a number of investigators.[1–9] However, the variation in crystallinity of polymer samples, as well as different temperature and pressure ranges studied preclude an accurate comparison of all the results.

Table 1 summarizes the dual mode sorption parameters at 298 K for the samples having different degrees of crystallinity. It is seen that other factors beside crystallinity determine the parameters of sorption isotherms. Moreover, depending on the method of crystallization, different values of model parameters can be observed for the same crystallinity.[9] Perhaps, this is caused by the effects of quenching or swelling in high pressure gas. The same is true for the solubility coefficient.

TABLE 1. The dual mode sorption parameters and apparent solubility coefficients S at 298 K

Crystallinity/%	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
0	0.38	5.3	0.44	2.7	1
25*	0.77	2.6	1.5	4.7	9
27**	0.73	7.0	1.3	9.8	9
43	0.21	4.2	0.45	2.1	1
46	0.37	5.7	0.52	3.3	2
59	0.36	7.9	0.35	3.1	5

*Crystallization by heating.

**Crystallzation by exposing to high pressure carbon dioxide.

Units: k_D and $S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$; $C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$; $b/\mathrm{atm^{-1}}$.

For the given samples of PETP, very good temperature dependences of the parameters of sorption isotherms have been obtained (see e.g., Refs. 5 and 9). Figure 30 shows temperature dependence of the C'_H parameter determined by different authors and for the samples with different pretreatment. It indicates that the differences in crystallization methods cause larger alterations in the C'_H values than those obtained in independent sorption studies.

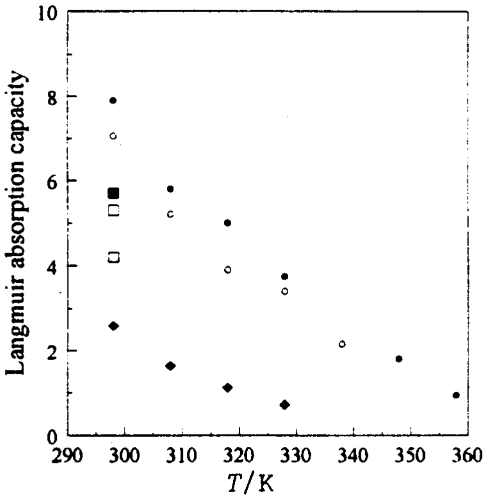


FIG. 30. Temperature dependence of Langmuir adsorption capacity $C'_H/(\mathrm{cm^3(STP)\ cm^{-3}})$. (□) Ref. 1; (■) Ref. 2; (●) Ref. 5: (○) Ref. 9 (crystallization by exposure to CO_2); (♦) Ref. 9 (crystallization by heating).

It can be seen too that the C'_H values vanish in the vicinity of T_g of PETP, in fact, one of the best documented cases of such a behavior. Table 2 presents the temperature dependence of the solubility coefficients. In spite of the substantial scatter, a decrease in the S values with temperature can be observed.

TABLE 2. Solubility coefficients S in semicrystalline samples of PETP (if not stated otherwise)

T/K	$S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	Ref.
290	3.1	6a
298	2.7	1b,c
	3.3	2b
	3.1	5b
308	4.6	7a
	2.2	5b
	5.0	8a,c
	3.8	8a
	1.7	4a
318	1.7	5b
	2.3	7a
338	0.6	8a,c
	1.1	8a
358	0.35	5b

[a] Found by evaluator from the initial slope of sorption isotherms.

[b] Calculated using the dual mode sorption parameters.

[c] Amorphous sample.

Further experimental studies with well characterized polymer samples are required in order to properly evaluate this system.

References:

[1] A. S. Michaels, W. R. Vieth, and J. A. Barrie, J. Appl. Polym. Sci. **34**, 1 (1963).

[2] W. R. Vieth, H. H. Alcalay, and A. J. Frabetti, J. Appl. Polym. Sci. **8**, 2125 (1964).

[3] K. Toi, J. Polym. Sci., Polym. Phys. Ed. **11**, 1829 (1973).

[4] W. J. Koros, D. R. Paul, M. Fujii, and H. B. Hopfenberg, J. Appl. Polym. Sci. **21**, 2899 (1977).

[5] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **16**, 1947 (1978).

[6] O. N. Tigina, Dissertation, GIAP, Moscow, USSR, 1983.

[7] M. D. Sefcik, H. K. Yuen, and D. D. Chan, Polymer **26**, 2043 (1985).

[8] Y. Kamiya, T. Hirose, Y. Naito, and K. Mizoguchi, J. Polym. Sci., Part B: Polym. Phys. **26**, 159 (1988).

[9] T. Hirose, K. Mizoguchi, Y. Kamiya, and Y. Terada, J. Appl. Polym. Sci. **37**, 1513 (1989).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

W. R. Vieth and K. J. Sladek, J. Colloid Sci. **20**, 1014 (1965).

Variables:

T/K=313
p/MPa=0–1.8

Prepared By:

A. K. Bokarev

Experimental Data

Sorption isotherm of carbon dioxide in a PETP Mylar film at 313 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.15	2.10	0.93	5.81
0.19	2.35	1.07	6.37
0.21	2.61	1.07	5.96
0.32	3.27	1.23	6.88
0.42	3.57	1.41	7.69
0.46	3.98	1.43	7.23
0.61	4.85	1.54	8.15
0.72	5.46	1.75	8.65
0.75	5.31	1.76	8.34
0.90	5.97	—	—

Auxiliary Information

Method/Apparatus/Procedure

The experimental technique used to obtain the gas solubility data was identical to that reported by Michaels *et al.*[1] The details of the apparatus and procedure had been described in Ref. 2.

Source and Purity of Materials:

PETP: commercial grade biaxally oriented Mylar film described in Ref. 2.
M_w=from 15 000 to 20 000, amorphous volume fraction $\alpha=0.54$.

Estimated Error:

No information given.

References:

[1] A. S. Michaels, W. R. Vieth, and J. A. Barrie, J. Appl. Phys. **31**, 1 (1963).
[2] W. R. Vieth, H. H. Alcalay, and A. J. Frabetti, J. Appl. Polym. Sci. **8**, 2125 (1964).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

K. Toi, J. Polym. Sci., Polym. Phys. Ed. **11**, 1829 (1973).

Variables:

T/K: 288–315
p/kPa: 0–101.3

Prepared By:

A. K. Bokarev

Experimental Data

Henry's law is obeyed by O_2, Ar, and N_2, in all samples of PETP at pressure up to 1 atm. The deviations from Henry's law were observed for CO_2. The dual mode sorption model equation was follow $C=[1.89p/(1+0.45p)]+0.38pa$, where a is volume fraction of amorphous phase, for CO_2 /PETP systems.

The solubility coefficients S/cm^3(STP)cm^{-3} atm^{-1} of gases in PETP-50 at 303 K

N_2	0.084
O_2	0.092
Ar	0.105
CO_2[a]	1.353

[a] PETP-75.

Heats of sorption for CO_2 in PETP-75 at 70 cm Hg gas pressure was equal to −5.37 kcal/mol.

Auxiliary Information

Method/Apparatus/Procedure

Manometric method was used for the measurement of solubility.
The pressure changes due to sorption were measured with a cathetometer.

Source and Purity of Materials:

Four samples of commercial PETP (Diafoil, Mitsubishi Plastics Ltd.) were studied: one having amorphous structure (PETP-75) and three having the degree of crystallinity of 48.0% (PETP-50, 75, and 100, where figures are the thickness of the samples). Completely amorphous PETP-75 had density 1.331 g/cc. Other samples had $\rho=1.400$ g/cc. Commercial gases were used. CO_2 was purified by the sublimation method by means of liquid nitrogen.

Estimated Error:

$\delta S/S=+3\%$.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate) (PETP);
[25038-59-9] (XIX)

Original Measurements:

W. J. Koros, D. R. Paul, M. Fujii, H. B. Hopfenberg, and V. Stannett, J. Appl. Polym. Sci. **21**, 2899 (1977).

Variables:

T/K=308–338
p/MPa=0–2.1

Prepared By:

A. K. Bokarev

Experimental Data

Sorption isotherms of carbon dioxide in poly(ethylene terephthalate) at 308 and 338 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
T=308 K					
0.08	1.64	0.94	7.39	1.79	10.36
0.18	2.88	1.01	7.73	1.85	10.87
0.19	2.71	1.08	7.84	1.88	10.93
0.27	3.50	1.26	8.79	1.94	11.15
0.41	4.63	1.52	9.75	2.03	11.60
0.60	5.87	1.57	9.63	2.07	11.77
0.63	5.87	1.66	10.09	—	—
0.76	6.66	1.76	10.65	—	—
T=338 K					
0.18	1.13	0.82	3.49	1.69	5.50
0.22	1.35	0.96	3.60	1.81	6.12
0.42	2.25	1.18	4.50	1.92	6.29
0.55	2.65	1.25	4.61	1.95	6.23
0.59	2.76	1.26	4.44	1.97	6.23
0.73	2.92	1.52	5.45	—	—

Auxiliary Information

Method/Apparatus/Procedure

Design and operation of the sorption cell have been described in the literature.[1,2]

Source and Purity of Materials:

PETP: commercially available transparent and highly crystalline sample.[3]

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym Phys. Ed. **14**, 1903 (1976).
[2] W. J. Koros, D. R. Paul, and A. A. Rocha, *ibid.* **14**, 687 (1976).
[3] W. J. Koros, Ph.D. dissertation, The University of Texas at Austin, 1977.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate); (PETP); [25038-59-9] (XIX)

Original Measurements:

W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **16**, 1947 (1978).

Variables:

T/K: 298–388
p/MPa: $0-2.0$ $(0-20\ atm)$

Prepared By:

A. K. Bokarev

Experimental Data

Dual-mode sorption parameters for CO_2 in PETP

T/K	k_D /cm^3(STP)cm^{-3} atm^{-1}	C_H'/cm^3(STP) cm^{-3}	b/atm^{-1}
298	0.362	7.913	0.351
308	0.330	5.760	0.322
318	0.260	4.960	0.282
328	0.234	3.753	0.252
338	0.214	2.735	0.197
348	0.210	1.814	0.165
358	0.196	0.936	0.167
368	0.194		
378	0.184		
388	0.167		

Below 358 K, sorption isotherms of CO_2 in PETP show a nonlinear character typical for glassy polymers. Above 358 K, the isotherms are completely linear at pressures at high as 20 atm.

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and experimental procedure used for sorption measuring have been described elsewhere.[1]

Source and Purity of Materials:

PETP (Kinmar) from Commercial Plastics Co had the weight average molecular mass of 54 000, T_g=358 K, and the degree of crystallinity near 60%. A density of amorphous PETP was 1.331 g/cc, those of semicrystalline samples were in the range 1.4±0.003 g/cc.
The CO_2 used was >99% pure.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed., **14**, 687 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

O. N. Tigina, dissertation, GIAP, Moscow, USSR, 1983.

Variables:

T/K=290 and 320
p/MPa=0.4–4.0

Prepared By:

S. M. Shishatskii

Experimental Data

Solubility of carbon dioxide (g/g polymer) in PETP

T/K	p/MPa	C 10^2	T/K	p/MPa	C 10^2
290	0.4	1.73	320	0.4	0.8
	0.5	2.2		0.6	1.1
	0.6	2.3		0.8	1.3
	0.8	2.9		1.0	1.5
	1.0	3.2		1.2	1.8
	1.2	3.8		1.4	1.9
	1.4	4.2		1.6	2.1
	1.6	4.5		1.8	2.2
	1.8	4.8		2.0	2.3
	2.0	5.1		2.2	2.4
	2.2	5.3		2.4	2.5
	2.4	5.5		2.6	2.6
	2.6	5.7		2.8	2.6
	2.8	5.8		3.0	2.7
	3.0	5.9		3.2	2.8
	3.2	6.0		3.4	2.8
	3.4	6.1		3.6	2.9
	3.6	6.2		3.8	2.9
	3.8	6.3			
	4.0	6.3			

Auxiliary Information

Method/Apparatus/Procedure

The solubility was measured by means of an apparatus of hydro-static weighing, the principle of which had been described in Ref. 1.

Source and Purity of Materials:

PETP (specification TU-29-02-367-71) was studied. It had a density 1.34 g/cc and a degree of crystallinity 25%.

Estimated Error:

$\delta C/C=1.5\%$

References:

[1] I. F. Golubev and O. A. Dobrovol'skii, Gaz. Prom. **N5**, 43 (1964).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

M. D. Sefcik, H. K. Yuen, and D. D. Chan, Polymer **26**, 2043 (1985).

Variables:

T/K=308–328
p/kPa=0–100 (0–1 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide in PETP (the original data were represented graphically)

$T=308$ K		$T=318$ K		$T=328$ K		$T=308$ K*	
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
2.03	0.06	5.07	0.12	4.05	0.06	3.04	0.11
2.03	0.09	8.11	0.19	8.11	0.14	13.17	0.42
3.04	0.16	12.16	0.28	12.16	0.22	33.44	0.86
5.07	0.27	20.27	0.48	20.27	0.33	101.33	2.17
8.11	0.36	27.36	0.62	27.36	0.44	—	—
12.16	0.53	33.44	0.74	33.44	0.54	—	—
17.23	0.71	43.57	0.92	43.57	0.70	—	—
24.32	0.94	53.70	1.09	53.70	0.85	—	—
33.44	1.14	62.82	1.25	62.82	0.95	—	—
48.64	1.48	73.97	1.42	73.97	1.11	—	—
66.87	1.87	84.10	1.59	84.10	1.24	—	—
85.11	2.24	93.22	1.73	94.23	1.36	—	—
102.34	2.53	101.33	1.88	103.35	1.48	—	—

*Repeated after all the measurements.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were determined gravimetrically using a Mettler Thermoanalyzer-1.

Source and Purity of Materials:

PETP: B. F. Goodrich Co., glass transition temperature 340 K, amorphous phase content 66%.

A powdered sample of PETP was prepared by dissolving the polymer in a mixed solvent (67% of $C_2H_2Cl_4$ and 33% of C_6H_5OH) with subsequent precipitation in excess methanol.

Surface area of the powder: 7.5 m^2/g.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)	Y. Kamiya, T. Hirose, Y. Naito, and K. Mizoguchi, J. Polym. Sci., Part B: Polym. Phys. **24**, 159 (1988).
Variables:	**Prepared By:**
$T/\mathrm{K}=308-338$ $p/\mathrm{MPa}=0-5.0$	A. K. Bokarev

Experimental Data

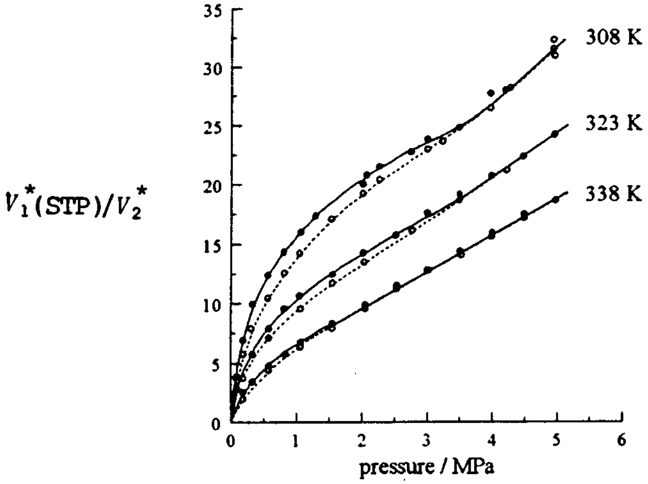


FIG. 31. Sorption isotherms of carbon dioxide in CO_2-conditioned crystalline PETP, measured after CO_2 sorption experiment at 308 K. Open and filled symbols represent sorption and desorption, respectively.

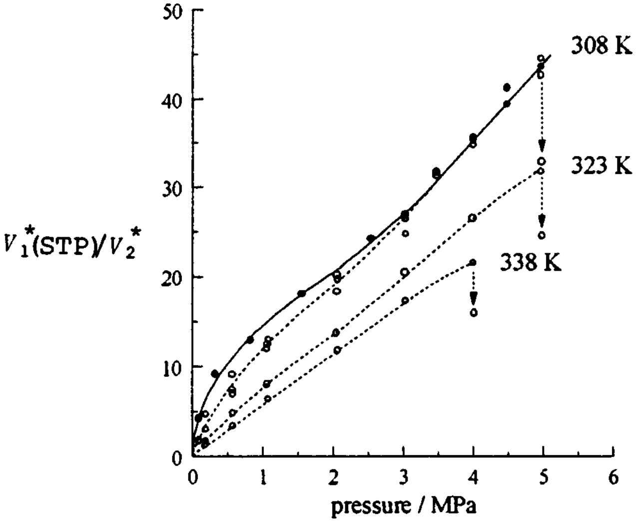


FIG. 32. Sorption isotherms of carbon dioxide in amorphous PETP. The dotted arrows show the decreases in concentration accompanying crystallization. Open and filled symbols represent sorption and desorption, respectively.

Auxiliary Information

Method/Apparatus/Procedure

The isotherms of gases in the polymer were obtained gravimetrically using a Cahn model 2000 electrobalance. Details of this apparatus were described previously.[1]

Source and Purity of Materials:

CO_2: purity 99.99%.
Amorphous PETP: Diafoil Ltd., density 1.336 g/cm^3.
PETP after thermal crystallization for about 5 h at 393 K in an air: density 1.37–1.38 g/cm^3.
PETP after CO_2 exposure crystalline film to 50 atm at 308 K for 24 h or more: density 1.367 g/cm^3.

Estimated Error:

No information given.

References:

[1] Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, J. Pol. Sci., Polym. Phys. Ed. **24**, 535 (1986).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)	T. Hirose, K. Mizoguchi, Y. Kamiya, and K. Terada, J. Appl. Polym. Sci. **37**, 1513 (1989).
Variables:	**Prepared By:**
T/K=298–338 p/kPa=0–100 (0–1 atm) amorphous volume fraction α=0.73–0.96	A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for CO_2 in *c*-PETP

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
298	0.733	7.05	1.30
308	0.633	5.22	1.36
318	0.522	3.94	1.30
328	0.485	3.45	0.739
338	0.429	2.15	0.668
308[a]	0.633	3.19	1.50

[a] After annealing of *c*-PETP at 338 K.

TABLE 2. Dual mode sorption parameters for CO_2 in *h*-PETP

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
298	0.770	2.59	1.52
308	0.665	1.64	1.79
318	0.579	1.12	1.59
328	0.509	0.72	1.33

TABLE 3. Comparison of solubilities of CO_2 in *c*-PETP before and after thermal annealing at 338 K (The original data were represented graphically)

Before annealing				After annealing at 338 K			
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
13.51	0.99	67.61	2.73	13.79	0.67	68.15	2.01
27.34	1.51	83.71	3.21	27.18	1.01	69.27	1.97
40.80	2.03	87.94	3.34	41.00	1.43	80.35	2.17
54.60	2.40	97.87	3.54	41.74	1.39	87.62	2.33
—	—	—	—	55.52	1.68	88.75	2.31
—	—	—	—	60.52	1.91	97.93	2.48

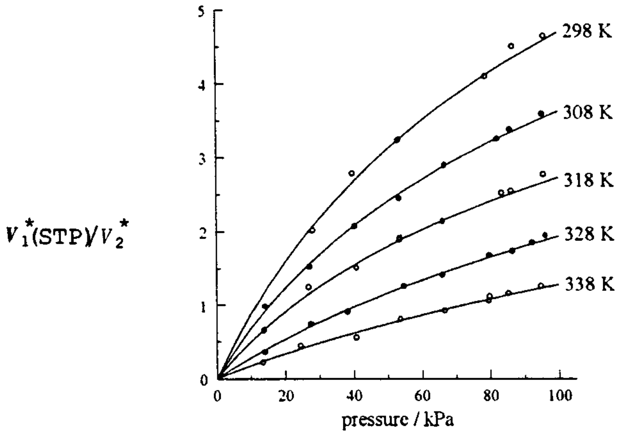


FIG. 33. Sorption isotherms of carbon dioxide in *c*-PETP.

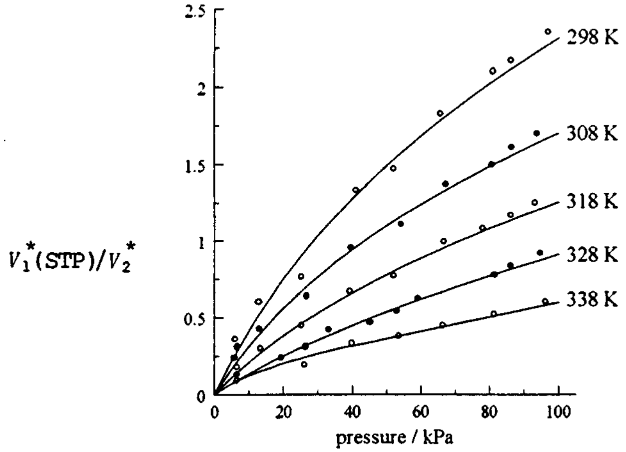


FIG. 34. Sorption isotherms of carbon dioxide in *h*-PETP.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms for gases in the polymer were obtained gravimetrically using a Cahn model 2000 electrobalance. Details of this apparatus were described in Ref. 1

Source and Purity of Materials:

Amorphous PETP (*a*-PETP): Mitsubihi Diafoil Co., erystallization by exposing to CO_2 (50 atm, 308 K) (*c*-PETP) or thermal (398 K, 5.3 h) (*h*-PETP)
a-PETP: density 1.336 g/cm^3, $\alpha=0.96$.
c-PETP: density 1.362 g/cm^3, $\alpha=0.73$.
h-PETP: density 1.362 g/cm^3, $\alpha=0.70$.

Estimated Error:
No information given.

References:
[1] T. Hirose, K. Mizoguchi, and Y. Kamiya, J. Appl. Polym. Sci. **34**, 1657 (1987).

Components:
(1) Hydrogen; H_2; [1333-74-0] Nitrogen; N_2; [7727-37-9]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:
H.-C. Draisbach, D. Jeschke, and H. A. Stuart, Z. Naturforschung **17a**, 447 (1962).

Variables:
T/K=293–373
p/MPa=6.65–66.5

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Solubility coefficients S 10^2/cm^3(STP)/cm^3 atm of hydrogen*

	Temperature/K								
Sample	293	303	313	323	333	343	353	363	373
Amorphous	2.68	2.47	2.29	2.12	2.01	2.00	2.09	2.27	2.45
Cryst., 30.6%	2.39	2.21	2.00	1.82	1.71	1.62	1.56	1.59	1.65
Cryst., 43.0%	2.21	2.00	1.83	1.68	1.62	1.56	1.50	1.53	1.53

*Smoothed values from the plot, taken by compiler.

Enthalpies of sorption ΔH/(cal/mol of hydrogen)

Sample	$T<T_g$	$T>T_g$
Amorphous	1700	1900
Cryst., 30.6%	1900	—
Cryst., 43.0%	2000	—

Solubility coefficients S/cm^3(STP)/cm^3 atm of nitrogen at 338 K

Amorphous	Cryst., 30.6%	Cryst., 43.0%
0.0238	0.0231	0.0226

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurement was employed using a high vacuum glass apparatus with McLeod gauge.

Source and Purity of Materials:

Three samples of commercial PETP (Terylen) were studied: one having amorphous structure and two having the degrees of crystallinity of 30.6 and 43.0%. PETP had $T_g=343$ K.
Nothing specified on the purity of gases.

Estimated Error:
No information given.

Components:

(1) Helium; He; [7440-59-7] Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] Ethane; C_2H_6; [74-84-0]

(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

A. S. Michaels, W. R. Vieth, and J. A. Barrie, J. Appl. Phys. **34**, 1 (1963).

Variables:

T/K=298–338

p/MPa=0–1.26

Prepared By:

S. M. Shishatskii

Experimental Data

Henry's law is obeyed by He, O_2, Ar, N_2, and CH_4 in amorphous PETP at subatmospheric pressure. Deviations from Henry's law were observed for CO_2 and C_2H_6 even below 1 atm and at higher pressures.

Table 1. Solubility coefficients of various gases in amorphous PETP at 298 K

Sorption	He	Ar	N_2	O_2	CO_2	CH_4	C_2H_6
$cm^3(STP)/cm^3$ atm	0.0078	0.082	0.058	0.100	2.71	0.240	0.99

α=amorphous volume fraction

Tabel 2. Temperature dependence of the solubility coefficients $S(cm^3(STP)/cm^3$ atm)

Gas	T/K	Sample	
		Amorphous	Crystalline ($\alpha=0.58$)
CH_4	308	0.175	—
	318	0.116	—
	337	0.065	—
	308	—	0.155
	322	—	0.100
	338	—	0.073
CO_2	298	—	2.00
	312	—	1.20
	328	—	0.64
	338	—	0.50
	348	—	0.34

Table 3. Sorption isotherms of ethane in PETP at 298 K (The original data were represented graphically)

$\alpha=0.54$		$\alpha=1.0$	
Pressure/kPa	Sorption $(V_1^*(STP)/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(STP)/V_2^*)$
19.09	0.13	20.54	0.20
31.29	0.24	43.08	0.38
43.39	0.33	62.01	0.51
57.63	0.41	75.77	0.60
73.57	0.49	89.41	0.67
85.53	0.55	107.63	0.76
102.61	0.64	125.24	0.84
124.64	0.72	140.59	0.92
143.81	0.78	—	—

Tabel 4. Sorption isotherms of carbon dioxide in PETP at 298 K (I) and 313 K (II) and at subatmospheric pressure (The original data were represented graphically)

Pressure/kPa	Sorption $(V_1^*(STP)/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(STP)/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(STP)/V_2^*)$
(I)					
$\alpha=0.57$					
6.73	0.16	52.14	0.91	112.39	1.61
17.02	0.38	60.11	1.00	115.05	1.63
21.00	0.42	69.87	1.13	131.02	1.83
28.12	0.54	83.99	1.23	149.57	2.00
30.35	0.58	86.62	1.23	161.07	2.11
38.36	0.70	99.99	1.47	170.80	2.21
41.04	0.76	103.1	1.51	—	—
$\alpha=1.0$					
12.62	0.36	50.16	1.13	109.34	2.07
21.14	0.57	54.63	1.23	111.56	2.11
23.34	0.57	58.20	1.29	124.44	2.28
35.39	0.81	72.94	1.58	137.31	2.46
34.99	0.85	85.33	1.71	145.76	2.59
39.44	0.92	87.14	1.77	156.39	2.71
41.22	0.94	100.03	1.95	—	—
(II)					
$\alpha=0.65$					
4.01	0.05	47.96	0.55	85.91	0.89
11.47	0.15	48.38	0.60	95.27	0.99
11.46	0.17	51.23	0.59	100.9	1.03
17.11	0.19	53.08	0.64	101.36	1.05
17.09	0.21	58.71	0.67	111.21	1.12
22.21	0.29	64.81	0.72	122.00	1.20
39.03	0.50	69.97	0.76	125.26	1.26
42.82	0.49	71.85	0.77	132.79	1.28
43.28	0.51	76.53	0.81	—	—
$\alpha=1.0$					
7.23	0.15	29.60	0.48	68.88	0.93
14.21	0.26	33.82	0.52	73.56	0.98
16.09	0.27	38.52	0.54	82.45	1.07
22.63	0.36	48.33	0.66	100.23	1.26
30.10	0.45	50.65	0.71	—	—
31.50	0.47	63.75	0.86	—	—

TABLE 5. Sorption isotherms of carbon dioxide in PETP at elevated pressure and 298 K (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
$\alpha = 1.0$, run I		$\alpha = 1.0$, run II	
0.17	2.89	0.14	2.71
0.25	4.08	0.20	3.41
0.33	4.70	0.28	3.89
0.44	5.22	0.31	4.48
0.48	5.55	0.36	4.70
0.57	6.14	0.41	5.07
0.69	6.77	0.48	5.74
0.78	7.21	0.61	6.40
0.85	7.31	0.73	6.95
0.95	7.68	0.81	7.24
1.04	8.08	0.91	7.61
1.12	8.38	1.00	7.98
1.19	8.60	1.07	8.27
—	—	1.16	8.60
—	—	1.24	9.08
$\alpha = 0.57$, run III		$\alpha = 0.57$, run IV	
0.12	1.78	0.28	2.55
0.15	1.89	0.41	3.66
0.24	2.48	0.55	4.65
0.34	3.18	—	—
0.47	3.69	—	—
0.55	4.25	—	—

Auxiliary Information

Method/Apparatus/Procedure

A manometric procedure of sorption measurement was used either in glass apparatus (low pressure sorption measurement) or in a steel bomb equipped with high pressure gauge (0–2.5 MPa).

Source and Purity of Materials:

Gases (except CH_4): purity>99.5%. CH_4; purity 99%.
Amorphous PETP (Mylar): DuPont Co., $M_w = 15\,000 - 20\,000$, density 1.331 g/cm^3. Semicrystalline samples: density in the range 1.37–1.39 g/cm^3.
Crystalline samples: prepared by annealing for 1 h at 390–420 K; degree of crystallinity from 35% to 46%.

Estimated Error:

Relative precision of solubilities: 3.5% and 6% at 95% confidence level for CO_2 in low and high pressure measurement. 10% for O_2, N_2, and CH_4 at the the same level of confidence.

Components:

(1) Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7]
Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(ethylene terephthalate) (PETP); [25038-59-9] (XIX)

Original Measurements:

W. R. Vieth, H. H. Alcalay, and A. J. Frabetti, J. Appl. Polym. Sci. **8**, 2125 (1964).

Variables:

T/K=298–328
p/MPa=0–1.7 (17 atm)

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Solubility constants for oriented poly(ethylene terephtpalate), $\alpha = 0.49$

	N_2	O_2	CH_4	CH_4	CH_4
Temperature T/K	298	298	298	313	328
Solubility constant* S/cm^3(STP) cm^{-3} atm^{-1}	0.044	0.076	0.200	0.130	0.087

*Value found from Van't Hoff plot.

TABLE 2. Sorption isotherms of carbon dioxide in PETP, $\alpha = 0.49$ (The original data were represented graphically)

$T = 298$ K		$T = 313$ K	
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
5.5	0.12	9.7	0.15
12.5	0.27	19.3	0.28
17.3	0.38	34.9	0.43
36.0	0.76	55.3	0.64
52.5	0.99	75.7	0.82
76.8	1.34	93.3	0.98
105.1	1.67	116.4	1.16
119.2	1.83	130.0	1.27

TABLE 3. Sorption isotherms of carbon dioxide in oriented PETP at 298 K (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.16	3.19	0.51	6.11	1.06	8.74
0.17	3.42	0.58	6.71	1.14	9.11
0.18	3.46	0.63	6.89	1.15	9.15
0.21	3.92	0.64	6.93	1.24	9.47
0.27	4.24	0.73	7.53	1.36	9.87
0.27	4.52	0.73	7.66	1.44	10.01
0.31	4.70	0.74	7.25	1.60	10.87
0.33	4.88	0.81	7.80	1.64	10.59
0.35	4.97	0.96	8.29	1.76	11.13
0.40	5.34	0.97	8.52	—	—
0.45	5.61	0.98	8.29	—	—
0.46	5.70	1.02	8.75	—	—

The isotherms fitted the equations:

$$C = C_D + C_H = k_D^* p\alpha + C_H' bp/(1+bp),$$

where the parameters C_H', and b have the usual meaning, k_D^* is Henry's law dissolution constant, and α is the amorphous volume fraction.

The following dual mode sorption parameters are reported for CO_2 sorption at 298 K and 0–17 atm pressure range in PETP ($\alpha = 0.54$):

k_D /cm^3(STP) cm^{-3} atm^{-1}	C_H'/cm^3(STP) cm^{-3}	b/atm^{-1}
0.37	5.7	0.52

Heats of sorption, found from Vant'Hoff for $S(CO_2)$ in PETP ($\alpha = 0.49$):

$$\Delta H\ (CO_2) = -7.4\ \text{kcal/mol};\quad -31.0\ \text{kJ/mol}$$

$$\Delta H\ (CH_4) = -5.4\ \text{kcal/mol};\quad -22.6\ \text{kJ/mol}.$$

Auxiliary Information

Method/Apparatus/Procedure

The procedure for low pressure measurements was described in Ref. 1.
High pressure experiments were performed in a stainless steel bomb equipped with a pressure gauge.

Source and Purity of Materials:

CO_2,N_2,O_2: minimum purity 99.5%.
CH_4: purity 99%.
PETP (oriented Mylar): Du Pont Co., $M_w = 15\,000–20\,000$, density 1.39 g/cm^3, amorphous volume fraction $\alpha = 0.49$ and 0.54.

Estimated Error:

Relative precision of solubility constants: ±8%.

References:

[1] A. J. Michaels and W. R. Vieth, J. Appl. Phys. **34**, 1 (1963).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(butylene terephthalate) (PBTP) (XX)	L. Thuy and J. Springer, Colloid Polym. Sci. **266**, 614 (1988).
Variables:	**Prepared By:**
T/K = 298–338 p/MPa = 0.1–3.0	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in PBTP

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C_H'/cm^3(STP) cm^{-3}	b/atm^{-1}
298	0.48	7.70	0.18
308	0.42	5.55	0.17
318	0.37	3.70	0.16
328	0.34	1.67	0.15
338	0.29	—	—

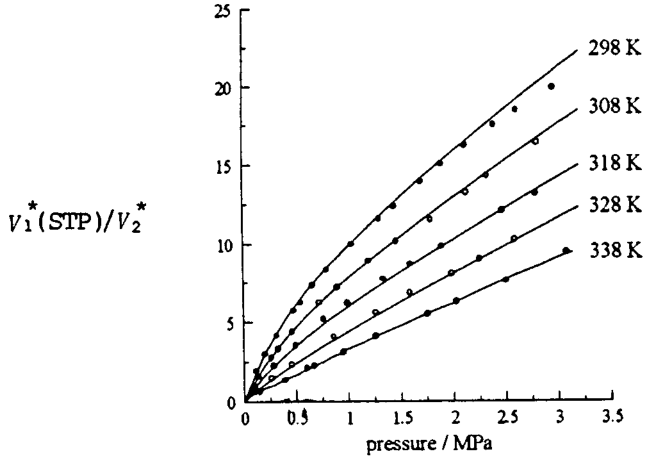


FIG. 35. Sorption isotherms of carbon dioxide in PBTP.

Auxiliary Information

Method/Apparatus/Procedure

High pressure apparatus was employed including Sartorius microbalance (model 4436).

Source and Purity of Materials:

PBTP: BASF (Ultradur B 255O). The granular degassed polymer was pressed into thin foil at 528 K and then quickly quenched in a mixture of ice, salt, and water.
Density 1.283 g/cm^3, degree of crystallinity about 19%, glass transition temperature 316 K.

Estimated Error:

No information given.

3.17. Polycarbonate—Carbon Dioxide

Components:	**Evaluator:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate (PC); [24936-68-3] (XXI)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Bisphenol A polycarbonate (for brevity here and further, *polycarbonate*) is a well known and widely used industrial plastic produced by General Electric Co. under a tradename Lexan. Many authors dealt with the system PC–carbon dioxide.[1–11] The polymer samples studied were nearly identical in majority of the cases. The data have been obtained in the temperature range 293–373 K and at pressures up to 10 MPa. It was the system PC–CO_2, which was used as an example for the demonstration of the effects of annealing and conditioning on the sorption parameters,[4,9,11] which are generally characteristic of other glassy polymers. Exposing a polymer sample to high pressure gas, results in an increase in the concentration of dissolved gas the larger the higher is the pressure of such conditioning.[4] The annealing of polymer samples at sub-T_g temperatures leads to a decrease in the concentration of the dissolved gas.

The table shows the pressure dependence of the concentration, C, of carbon dioxide dissolved in the polymer samples unconditioned (''as received'') and exposed to 2 MPa of carbon dioxide prior to solubility measurement. It is seen that the difference between the individual ''sorption isotherms'' is not dramatic. The last line presents average values of C at different pressures.

Pressure dependence of the concentration $C/(\text{cm}^3(\text{STP})\ \text{cm}^{-3})$ of dissolved CO_2 at 308 K

Pressure/MPa					
0.5	1.0	1.5	2.0	Type of sample	Ref.
12.2	16.6	20.6	24.5	**	2
12.8	18.5	23.0	27.2	*	4
13.2	19.0	23.6	27.6	**	5
—	17	—	27	**	6
11.7	18.6	24.0	28.7	**	8
—	16	—	26	**	10
13.2	19.3	24.0	28.1	*	11
12.6	17.9	23.0	27.0	—	Av.

*Conditioned at 2.0 MPa of CO_2.
**''As received.''

References:

[1] F. J. Norton, J. Appl. Polym. Sci. **7**, 1649 (1963).
[2] W. R. Vieth and J. A. Eilenberg, J. Appl. Polym. Sci. **16**, 945 (1972).
[3] W. J. Koros, D. R. Paul, and A. Rocha, J. Polym. Sci., Polym. Sci. Ed. **14**, 687 (1976).
[4] A. J. Wonders and D. R. Paul, J. Membr. Sci. **5**, 63 (1979).
[5] A. H. Chan and D. R. Paul, Polym. Eng. Sci. **20**, 87 (1980).
[6] G. K. Fleming and W. J. Koros, Macromolecles **19**, 2285 (1986).
[7] Y. Kamiya, T. Hirose, K. Mizogchi, and K. Terada, J. Polym. Sci., Part B: Polym. Phys. **24**, 1525 (1986).
[8] E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, and K. Sakata, Ind. Eng. Chem., Res. **26**, 433 (1987).
[9] N. Muruganandam, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **25**, 1999 (1987).
[10] R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).
[11] G. K. Fleming and W. J. Koros, Macromolecules **23**, 1353 (1990).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate Lexan (PC); [24936-68-3] (XXI)	F. J. Norton, J. Appl. Polym. Sci. **7**, 1649 (1963).
Variables:	**Prepared By:**
T/K: 273–333 p/kPa: 101.3	A. K. Bokarev

Experimental Data

TABLE 1. Solubility C of CO_2 in Lexan at 1 atm*

T/K	C/cm^3 gas (STP)/cm^3
273	4.43
298	12.76
323	25.10

*Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure	**Source and Purity of Materials:**
Manometric method.	Lexan PC from General Electric Co. was studied. No more information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate (PC); [24936-68-3] (XXI)	W. R. Vieth and J. A. Eilenberg. J. Appl. Polym. Sci. **16**, 945 (1972).
Variables:	**Prepared By:**
T/K=308–338 p/MPa=0–2.2	A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide in polycarbonate

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
308	0.765	9.53	1.50
318	0.708	7.20	1.16
338	0.346	7.09	0.94

TABLE 2. Sorption isotherms of carbon dioxide in polycarbonate (The original data were represented graphically)

T=308 K		T=318 K		T=338 K	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.33	7.72	0.25	5.93	0.20	3.50
0.41	9.09	0.40	8.12	0.36	5.27
0.56	11.36	0.53	9.32	0.50	6.88
0.68	13.54	0.66	11.26	0.72	8.41
0.91	15.31	0.8	12.14	0.87	9.37
1.20	17.64	1.10	14.55	1.01	9.76
1.36	19.08	1.49	17.03	1.25	10.62
1.51	20.13	1.69	18.64	1.45	11.09
1.88	22.85	2.16	21.52	1.83	12.84
—	—	—	—	2.16	13.37

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used. Other details are given in Ref. 1.

Source and Purity of Materials:

PC: preparation described in Ref. 2, amorphous film, thickness 0.5 mm.

Estimated Error:

Relative precision: $C'_H < 8.7\%$.

References:

[1] W. R. Vieth, C. S. Frangoulis, and J. A. Rionda, J. Colloid Interface Sci. **22**, 454 (1966).

[2] P. J. Eloranta, thesis, B. S. Department of Chemical Eng., M.I.T., Cambridge, MA, 1968.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate; (PC); [24936-68-3] (XXI)	W. J. Koros, D. R. Paul, and A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).
Variables:	**Prepared By:**
T/K: 308 K P/MPa: 0.1–2.5	A. K. Bokarev

Experimental Data

Solubility of carbon dioxide in PC at 308 K*

p/atm	5	10	15	21	25	30
C^*/cm^3(STP) cm^{-3}	14.2	20.5	26.7	32.0	37.4	42.3

*Smooth values taken from the graph by compiler.

TABLE 1. Dual mode sorption parameters for CO_2 in polycarbonate at 308 K

Method	$k_D$cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Graphical	0.992	13.7	0.392
Nonlinear	0.933	15.3	0.338
Least squares			

Auxiliary Information

Method/Apparatus/Procedure

Measurements of gas solubility in polymer performed using a pressure decay method of dual-volume dual transducer type.

Source and Purity of Materials:

Bisphenol A polycarbonate (PC) (Lexan) was obtained from the General Electric Co. M_W=35 800. The CO_2 used in experiment was >99% pure.

Estimated Error:

δC=0.45 cm^3(STP)/cm^3(polymer).

Components:
(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:
A. J. Wonders and D. R. Paul, J. Member. Sci. **5**, 63 (1979).

Variables:
$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.02$ (0–20 atm)

Prepared By:
A. K. Bokarev

Experimental Data

Sorption isotherms of carbon dioxide in polycarbonate at 308 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
Series on initial exposure film					
0.08	3.12	0.83	15.13	1.55	22.34
0.11	3.88	1.02	17.47	1.63	23.21
0.22	5.92	1.06	17.91	1.71	24.50
0.33	7.76	1.09	18.34	1.81	25.37
0.43	9.70	1.12	18.34	1.96	26.66
0.51	10.78	1.20	19.31	2.02	27.53
0.72	13.69	1.29	20.07	—	—
0.79	14.88	1.40	21.15	—	—
Series after CO_2 exposure at 20 atm					
0.09	4.20	0.80	16.39	1.49	22.98
0.20	7.00	0.89	17.47	1.60	24.39
0.31	9.26	1.00	18.33	1.69	25.14
0.42	11.20	1.12	19.74	1.74	25.79
0.51	12.61	1.21	20.49	1.95	26.99
0.58	13.58	1.30	21.36	2.02	27.85
0.70	15.20	1.39	22.12	—	—

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedure used in the present sorption experiments are the same as described earlier.[1] Results labeled ''initial'' were obtained by beginning with ''as-received'' polymer and simply conducting a sorption experiment by increasing experimental pressure. ''Uniform'' samples were also prepared in a separate bomb using CO_2 pressures of 20, 40, and 60 atm for 24 h.

Source and Purity of Materials:

CO_2: purity 99%.
PC (Bisphenol A polycarbonate): Lexan, General Electric Co., $M_w=35\,800$.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:
(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:
A. H. Chan and D. R. Paul, Polym. Eng. Sci. **20**, 87 (1980).

Variables:
$T/\mathrm{K}=308-348$
$p/\mathrm{MPa}=0-2.0$ (0–20 atm)

Prepared By:
A. K. Bokarev

Experimental Data

TABLE 1. Temperature dependence of sorption parameters for carbon dioxide in PC. Sorption measurements were made after conditioning at 20 atm of CO_2

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
333	0.64	18.00	0.234
353	0.46	12.78	0.156
373	0.30	11.16	0.098
Van't Hoff parameters/(kcal/mol^{-1})	−4.0	—	−4.8

TABLE 2. Dual mode sorption parameters for carbon dioxide in annealed PC. Sorption measurements were made at 308 K after conditioning at 20 atm of CO_2

PC sample history	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
As received	0.642	18.00	0.234
Annealed at 398 K for			
2 h	0.618	15.49	0.230
10 h	0.609	14.66	0.220
1 day	0.601	14.17	0.231
2 day	0.587	13.89	0.228
8.5 day	0.611	12.89	0.238
14 day	0.532	13.71	0.238
Annealed at 408 K for			
0.5 h	0.574	17.05	0.220
5h	0.570	15.43	0.226
10 h	0.550	15.20	0.227
2 day	0.560	14.80	0.230

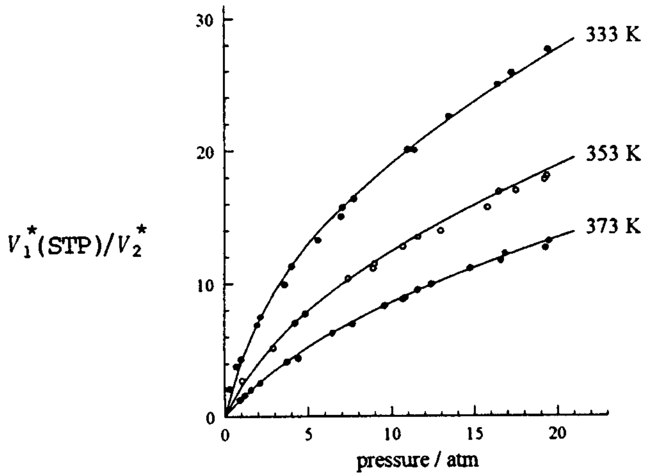


FIG. 36. Effect of temperature on carbon dioxide sorption in PC for ''as-received'' material conditioned at 20 atm of CO_2.

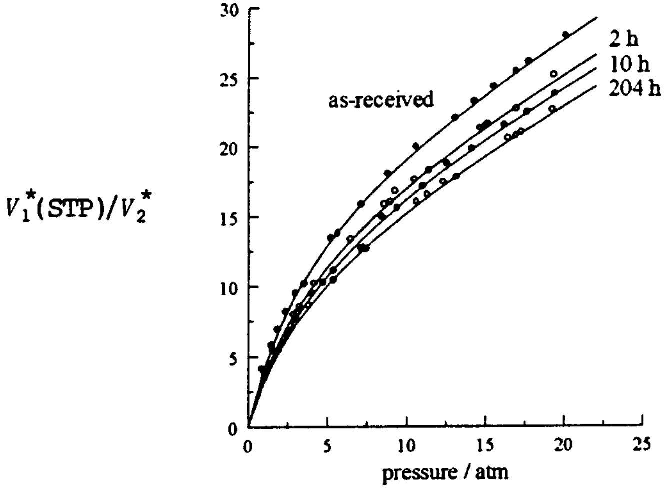


FIG. 37. Equilibrium sorption of carbon dioxide in PC samples annealed at 398 K. Sorption measurements were made at 308 K after conditioning at 20 atm of CO_2.

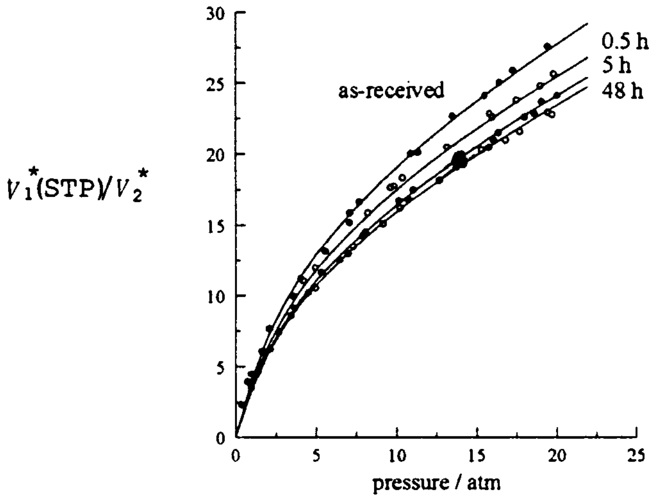


FIG. 38. Same as for Fig. 37 except that the annealing temperature was equal to 408 K.

Auxiliary Information

Method/Apparatus/Procedure

The equilibrium solubility of CO_2 in the polymer was measured by a pressure decay technique described earlier, Ref. 1.

Source and Purity of Materials:

PC (Lexan): General Electric Co., $M_w = 35\ 800$, glass transition temperature 418 K.

Estimated Error:

No information given

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate (PC); [24936-68-3] (XXI)	G. K. Fleming and W. J. Koros, Macromolecules **19**, 2285 (1986).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–6.2	A. K. Bokarev

Experimental Data

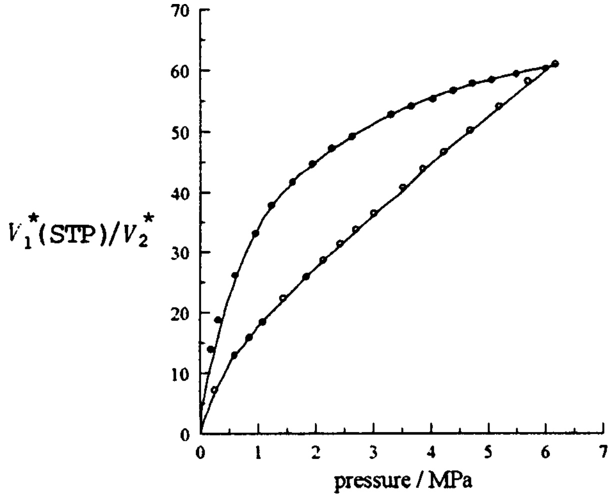


FIG. 39. Sorption and desorption isotherms of carbon dioxide in polycarbonate at 308 K. Open and filled symbols represent sorption and desorption, respectively.

Auxiliary Information

Method/Apparatus/Procedure

Gas sorption measurements were made with a pressure decay cell that has been used at pressures up to 30 atm.[1,2] With slight modification, this design was used to make sorption measurements up to 68 atm.

Source and Purity of Materials:

CO_2: Linde, Inc., purity 99.99%.
PC: General Electric Co. (commercial grade film), density 1.200±0.001 g/cm^3.

Estimated Error:

No information given.

References:

[1] W. J. Koros, Ph.D. dissertation, University of Texas of Austin, Austin, TX, 1977.

[2] W. J. Koros and D. R. Paul, J. Membr. Sci. **5**, 63 (1978).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polycarbonate (PC); [24936-68-3] (XXI)	Y. Kamiya, T. Hirose, K. Mizoguchi, and K. Terada, J. Polym. Sci., Part B: Polym. Phys. **24**, 1525 (1986).
Variables:	**Prepared By:**
T/K=308–328 p/MPa=0–5.0	A. K. Bokarev

Experimental Data

(For all the following tables, the original data were represented graphically)

TABLE 1. Sorption and desorption isotherms of carbon dioxide in PC at 308 K, first series of experiments

''As received'' film				Rod specimens			
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.10	3.31	0.04	4.32	0.32	7.94	0.36	15.16
0.41	9.10	0.09	6.63	1.41	21.13	0.58	20.94
0.70	13.16	0.17	9.38	2.98	34.91	1.00	27.74
0.98	16.78	0.22	11.11	4.86	49.14	1.93	38.47
1.37	21.41	0.29	13.86	—	—	3.41	45.61
1.87	26.63	0.43	18.19	—	—	4.78	47.55
2.39	32.14	0.68	23.69	—	—	—	—
4.86	47.85	0.97	28.61	—	—	—	—
—	—	1.26	32.08	—	—	—	—
—	—	1.58	35.42	—	—	—	—
—	—	1.92	37.89	—	—	—	—
—	—	2.02	38.18	—	—	—	—
—	—	2.27	39.93	—	—	—	—
—	—	2.65	41.96	—	—	—	—
—	—	2.99	43.28	—	—	—	—
—	—	3.49	44.60	—	—	—	—
—	—	3.91	46.21	—	—	—	—

TABLE 2. Sorption and desorption isotherms of carbon dioxide in polycarbonate film at 308 K, second and third series

Second series				Third series			
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Desorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Desorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.17	6.64	0.17	5.63	0.04	3.74	0.12	5.77
0.29	9.96	0.23	10.25	0.25	8.66	0.13	7.50
0.36	11.55	0.27	12.27	0.43	11.99	0.16	8.51
0.49	14.44	0.39	16.17	0.65	15.75	0.30	12.85
0.57	15.46	0.59	20.22	0.87	19.22	0.43	16.89
0.78	18.50	0.77	24.41	1.21	22.99	0.75	23.83
0.96	20.96	1.04	28.47	1.54	26.76	1.06	27.89
1.15	22.99	1.32	32.23	1.91	30.38	1.92	38.46
1.44	26.18	1.76	36.58	2.42	34.16	2.43	41.52
1.78	29.37	2.23	39.49	2.90	37.36	3.47	46.05
2.05	31.83	2.87	42.55	3.43	40.42	—	—
2.35	33.87	3.34	44.31	3.90	43.33	—	—
2.67	35.76	3.90	45.63	4.32	45.37	—	—
2.98	37.36	4.37	47.10	4.79	49.72	—	—
3.49	40.42	—	—	4.76	47.99	—	—
3.96	43.33	—	—	—	—	—	—
4.40	45.95	—	—	—	—	—	—
4.82	47.99	—	—	—	—	—	—

TABLE 3. Sorption and desorption isotherms of carbon dioxide in polycarbonate film at 328 K, measured after experiments at 298 K

Sorption		Desorption		Intermediate sorption*	
Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$
0.24	4.41	0.13	2.56	0.91	16.25
0.33	6.13	0.14	3.70	1.88	23.40
0.48	7.84	0.15	4.70	3.01	28.56
0.87	12.12	0.22	5.98	4.00	31.57
1.30	15.69	0.30	7.69	—	—
1.97	21.12	0.51	11.54	—	—
2.98	26.99	0.81	15.96	—	—
3.70	30.14	1.11	19.25	—	—
4.34	32.87	1.87	24.96	—	—
4.94	35.16	2.59	28.69	—	—
—	—	3.37	31.7	—	—
—	—	4.17	34.00	—	—

TABLE 4. Sorption and desorption isotherms of carbon dioxide in polycarbonate film at 318 K

First series**		Second series		Intermediate sorption***	
Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$
Sorption		Sorption			
0.79	11.62	0.14	4.98	0.56	15.58
1.53	18.35	0.38	9.52	1.06	20.44
2.95	28.96	0.57	12.83	1.61	24.93
5.00	40.32	0.92	15.84	2.41	29.52
		1.12	18.84	3.36	34.05
Desorption		1.54	22.71	4.47	37.82
0.44	13.12	2.03	25.66	4.91	40.08
1.16	23.67	2.98	30.49	—	—
2.20	32.10	3.95	34.94	—	—
3.51	37.35	4.91	38.86	—	—
—	—			—	—
—	—	Desorption		—	—
—	—	0.09	3.99	—	—
—	—	0.26	9.81	—	—
—	—	0.56	15.58	—	—
—	—	0.80	19.65	—	—
—	—	1.71	28.99	—	—
—	—	2.93	34.92	—	—
—	—	4.08	38.17	—	—

*Experiments for decending scanning isotherm.
**Series of experiments on ''as received'' film.
***Experiments for ascending scanning isotherm.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms for gases in the polymer were obtained gravimetrically using a Cahn model 2000 electrobalance. Details of this apparatus are described in Ref. 1.

Source and Purity of Materials:

CO_2: purity 99.99%.
PC (Bisphenol A polycarbonate): film (thickness 75 μm), rod (diameter 3 mm); densities at 298 K 1.194 g/cm^3 (''as received'') and 1.192 g/cm^3 (after CO_2 exposure); glass transition temperature 417 K.

Estimated Error:

No information given.

References:

[1] Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, J. Polym. Sci., Polym. Phys. Ed. **24**, 535 (1986).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

R. G. Wissinger and M. E. Paulaitis, J. Polym. Sci., Part B: Polym. Phys. **25**, 2497 (1987).

Variables:

T/K=308.2
p/MPa=0–10.2

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility of carbon dioxide C

p/atm	C/cm^3(STP)/g polymer*
9.8	13
18	21
27	27
35	34
43	40
51	47
69	59
88	63
102	65

*Taken from a graph by the compiler.

Auxiliary Information

Method/Apparatus/Procedure

The gravimetric method was used. The polymer samples were suspended from a quartz spring. The corrections for buoyancy were introduced using CO_2 densities up to higher pressure.

Source and Purity of Materials:

PC (General Electric Co) had glass transition temperature 420 K. The purity of CO_2 (Linde Co) was 99.99%.

Estimated Error:

$\delta C/C = \pm 1$ cm^3(STP)/g polymer.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

G. K. Fleming and W. J. Koros, Macromolecules **23**, 1353 (1990).

Variables:

T/K=308
p/MPa=0–6.3 (0–900 psia)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

The effects of conditioning (pretreatment) of the polymer by exposing it prior to sorption experiments to high pressure carbon dioxide atmosphere was studied.

TABLE 1. Dual mode sorption parameters for carbon dioxide sorption in PC at 308 K (p: conditioning pressure)

p/psia	p/MPa	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Pressure-based model				
300	2.07	0.681	17.30	0.261
600	4.14	0.587	29.61	0.194
900	6.21	0.542	29.21	0.167
Fugacity-based model				
300	2.07	0.844	15.16	0.303
600	4.14	0.843	19.42	0.265
900	6.21	0.868	21.24	0.257

TABLE 2. Dual mode desorption parameters for carbon dioxide in PC at 308 K (p: conditioning pressure)

Fugacity-based model				
p/psia	p/MPa	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
300	2.07	0.617	21.00	0.285
600	4.14	0.254	46.59	0.125
900	6.21	0.261	59.50	0.117

The differences between sorption and desorption parameters are indicative for hysteresis phenomena.

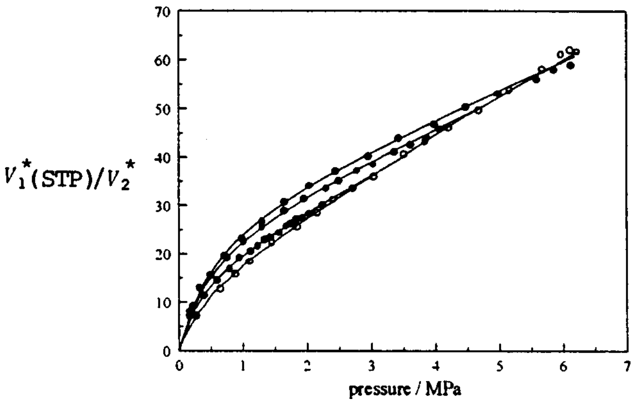


FIG. 40. Sorption isotherms of CO_2 in PC at 308 K for conditioning pressures of 300, 600, and 900 psia. (○) ''as-received;'' (●) CO_2-conditioned.

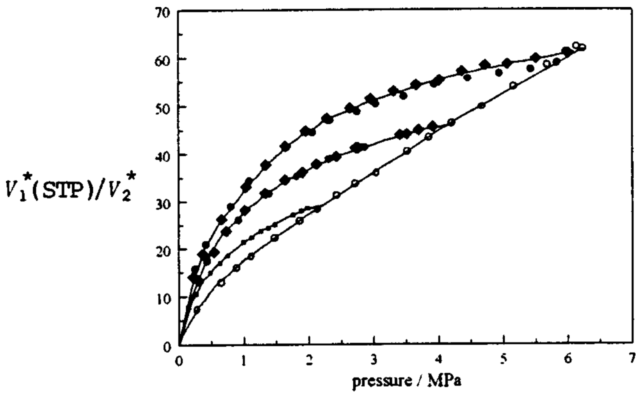


FIG. 41. Initial CO_2 sorption and desorption in PC at 308 K after conditioning pressures of 300, 600, and 900 psia. (○) ''as-received;'' (●) desorption.

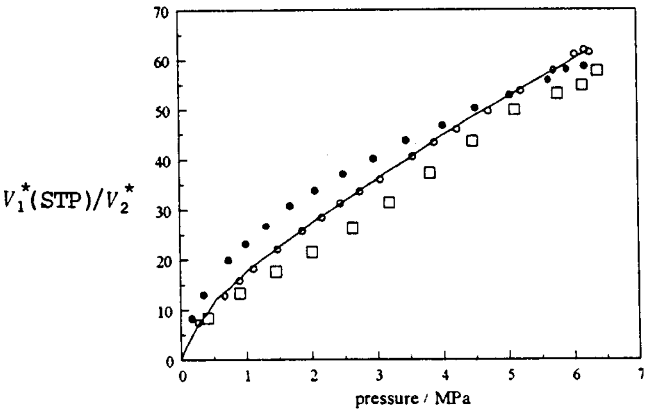


FIG. 42. Sorption isotherms of CO_2 at 308 K in CO_2-conditioned, ''as-received,'' and annealed PC. The annealed sample was first CO_2-conditioned at 900 psia and then annealed at 408 K for 500 h under vacuum. (○) ''as-received;'' (●) 900 psia conditioned; (□) annealed.

Auxiliary Information

Method/Apparatus/Procedure

The procedures and apparatus for sorption measurements were identical with those described in Ref. 1.

Source and Purity of Materials:

CO_2: purity 99.99%.

PC (Bisphenol A polycarbonate): General Electric, density 1.200 g/cm^3.

Estimated Error:

No information given.

References:

[1]G. K. Fleming and W. J. Koros, Macromolecules **19**, 2285 (1986).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-828] (2) Polycarbonate (PC); [24936-68-3] (XXI)	E. Sada, H. Kumszawa, H. Yakushji, Y. Bamba, K. Sakata, and S.-T. Wang, Ind. Eng. Chem., Res. **26**, 433 (1987).
Variables:	**Prepared By:**
T/K=293–313 p/MPa=0.2–3.0	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	T/K	k_D /(cm^3(STP)/cm^3 atm)	C'_H/(cm^3(STP)/cm^3)	b/atm^{-1}
CO_2	293	0.911	23.1	0.264
	303	0.804	19.9	0.197
	313	0.702	16.0	0.124
CH_4	293	0.335	6.40	0.157
	303	0.308	5.62	0.120
	313	0.280	4.72	0.0872

Auxiliary Information

Method/Apparatus/Procedure

Equilibrium sorption was measured by the pressure decay method in the cell similar to one described in Ref. 1. The pressure changes in the cell were continuously measured by a pressure transducer.

Source and Purity of Materials:

PC films were provided by Teijin Co.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

3.18. Polycarbonate—Sulfur Dioxide

Components:	**Evaluator:**
(1) Sulfur dioxide; SO_2; [7446-09-5] (2) Polycarbonate (PC); [24936-68-3] (XXI)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

The system sulfur dioxide–polycarbonate has been studied by Davis and Rooney[1,2] and by Frimpong *et al.*[3] In all the papers, the same commercial material Lexan (General Electric Co.) was investigated.

The parameters of the dual mode sorption isotherm reported in Refs. 1 and 3 are fairly close, so the following pressure dependence of the solubility at 298 K can be recommended.

p/kPa	10	30	50	101
C/cm^3(STP) cm^{-3}	11.6 ± 1.1	22.0 ± 1.6	31.2 ± 1.2	51.4 ± 2.0

References:

[1] E. G. Davis and M. L. Rooney, Kolloid Z.-Z. Polym. **249**, 1043 (1971)

[2] E. G. Davis and M. L. Rooney, J. Polym. Sci., Polym. Phys. Ed. **10**, 2325 (1972).

[3] S. Frimpong, C. A. Plank, and W. L. S. Laukhauf, Chem. Eng. J. **42**, 25 (1989)

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

E. G. Davis, M. L. Rooney, and Z.-Z. Kolloid Polym. **249**, 1043 (1971).

Variables:

T/K=298
p/kPa=0–100

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for sulfur dioxide in polycarbonate at 298 K

k_D /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/cm Hg^{-1}
0.522	10	0.241

Sorption isotherm of sulfur dioxide in polycarbonate at 298 K. (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
3.20	5.27	49.53	27.05
6.52	8.15	56.7	30.32
12.01	11.48	62.33	31.87
17.72	14.27	67.71	33.44
23.65	16.88	74.37	36.02
28.12	19.01	81.25	38.41
33.53	21.11	88.11	40.63
39.41	22.83	95.75	43.71
45.56	25.08	99.97	45.67

Auxiliary Information

Method/Apparatus/Procedure

A modified McBain balance technique described in Ref. 1 was used to measure the solubility of sulfur dioxide in the polymer.

Source and Purity of Materials:

SO_2: purity 99.95%.
PC: Lexan, General Electric Co., density 1.119 g/cm^3, glass transition temperature 422 K.

Estimated Error:

No information given.

References:

[1] S. Prager and A. F. Long, J. Am. Chem. Soc. **73**, 4072 (1951).

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Polycarbonate; (PC); [24936-68-3] (XXI)

Original Measurements:

E. G. Davis and M. L. Rooney, J. Polym. Sci., Polym. Phys. Ed. **10**, 2325 (1972).

Variables:

T/K: 298
p/kPa: 13.87; 79.46

Prepared By:

A. K. Bokarev

Experimental Data

Solubility of sulfur dioxide in polycarbonate

p/kPa	C/cm^3(STP) cm^{-3}
13.87	12.8
79.46	40.6

Auxiliary Information

Method/Apparatus/Procedure

A modified McBain balance technique was used to measure the solubility of sulfur dioxide in the polymer.

Source and Purity of Materials:

PC (''Lexan'') with ρ=1.119 g/cm^3, provided by General Electric Co. (USA). M_w=45 000; T_g=422 K. Sulfur dioxide of 99.95% purity was used.

Estimated Error:

dT/K: ±0.5.

Components:	**Original Measurements:**
(1) Sulfur dioxide; SO_2; [7446-09-5] (2) Polycarbonate (PC); [24936-68-3] (XXI)	S. Frimpong, C. A. Plank, and W. L. S. Laukhauf, Chem. Eng. J. (Lausanne) **42**, 25 (1989).
Variables:	**Prepared By:**
$T/\mathrm{K}=283.2-343.2$ $p/\mathrm{kPa}=0-100$	Yu. P. Yampol'skii

Experimental Data

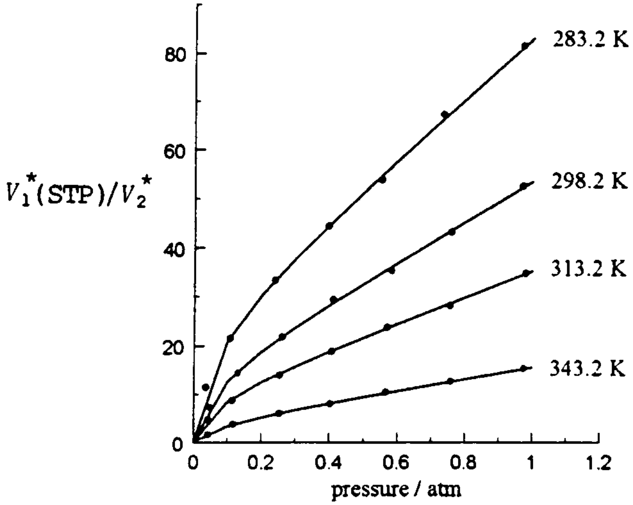


FIG. 43. Sorption isotherms of sulfur dioxide in polycarbonate.

Dual mode sorption parameters for sulfur dioxide in polycarbonate

T/K	$k_D\ /\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	$C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$	$b/\mathrm{atm^{-1}}$
283.2	61.66	22.45	19.39
298.2	40.26	13.93	16.33
313.2	26.27	9.52	15.57
343.2	11.72	4.08	12.13

The experiment data for 298.2 and 313.2 K were correlated by the equation

$$C=123.212\ \exp[1.0772\times10^{-3}(RT/\mathrm{cal\ mol^{-1}})(\ln(p/\mathrm{atm})+(2355/((T/\mathrm{K})-33))-10.24)]$$

based on adsorption potential theory in Ref. 1.

Auxiliary Information

Method/Apparatus/Procedure

A McBain quartz spring balance was employed for sorption measurement. The apparatus is described in Ref. 2.

Source and Purity of Materials:

PC (Lexan 101): General Electric Co., glass transition temperature 421 K (DSC), melting point 496.8 K.

Estimated Error:

Relative precision in T: ±0.1 K.

References:

[1] C. A. Plank, W. L. S. Laukauf, and G. R. Ranade, J. Appl. Polym. Sci. **30**, 2695 (1985).
[2] G. R. Ranade, V. M. Nadgir, C. A. Plank, and W. L. S. Laukauf, J. Appl. Polym. Sci. **28**, 201 (1983).

3.19 Polycarbonate—Methane

Components:

(1) Methane; CH_4; [74-82-8]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Four papers are available for the system polycarbonate–methane. Pope *et al.*[4] studied history effects on sorption isotherms (unconditioned film, the film conditioned by exposure to high pressure carbon dioxide gas and exchange-conditioned by subsequent sweeping CO_2 by methane) and showed the significant changes in the isotherm's shape caused by the pretreatment of a sample. On the other hand, the other papers[1–3] reported the dual mode sorption parameters but did not study the effects of different pretreatment of the films on the parameters of the sorption model.

Below the solubility coefficients at 308 K are shown based on the dual mode sorption parameters[1–3] and by the initial slope of the isotherms.[4]

$S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	0.85	0.84	0.99	0.54	1.0
Ref.	1	2	3	4*	4**

*Unconditioned film.
**Exchange-conditioned film.

In spite of possible different film history, the solubility coefficients lie within fairly narrow limits. Accordingly, sorption isotherms are given for the samples with different pretreatment.

Solubility of methane $C/(\mathrm{cm^3(STP)\ cm^{-3}})$ in PC at 308 K and different pressure

			Ref. 4	
p/MPa	Ref. 1	Ref. 2	A	B
0.5	3.2	3.3	2.5	5.0
1.0	5.3	5.6	4.3	8.2
2.0	8.2	9.5	6.8	13.0
3.0	10.4	12.9	8.2	15.7

A Unconditioned film.
B Exchange-conditioned film.

These data indicate a possible range of variation of the solubility of CH_4 in polycarbonate at different pressures.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).
[2] E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, K. Sakata, and S-T. Wang, Ind. Eng. Chem., Res. **26**, 433 (1987).
[3] T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).
[4] D. S. Pope, G. K. Fleming, and W. J. Koros, Macromolecules **23**, 2988 (1990).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] Nitrogen; N_2; [7727-37-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).
W. J. Koros, Ph.D. dissertation, The University of Texas at Austin, 1977.

Variables:

T/K: 308 p/MPa: 0–2.33

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for polycarbonate at 308 K

Parameter	CO_2	CH_4	N_2
$k_D\ /(\mathrm{cm^3(STP)/cm^3\ atm})$	0.685	0.147	0.0909
$C'_H/(\mathrm{cm^3(STP)/cm^3})$	18.81	8.38	2.11
$b/(\mathrm{atm^{-1}})$	0.215	0.100	0.074

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

Bisphenol A polycarbonate (Lexan) was obtained from the General Electric Co. $M_w = 35\ 800$.
Each gas was of chromatographic quality (purity >99.99%).

Estimated Error:

Nothing specified.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Methane; CH_4; [74-82-8] (2) Polycarbonate (PC); [24936-68-3] (XXI)	D. S. Pope, G. K. Fleming, and W. J. Koros, Macromolecules **23**, 2988 (1990).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–6.89	Yu. P. Yampol'skii

Experimental Data

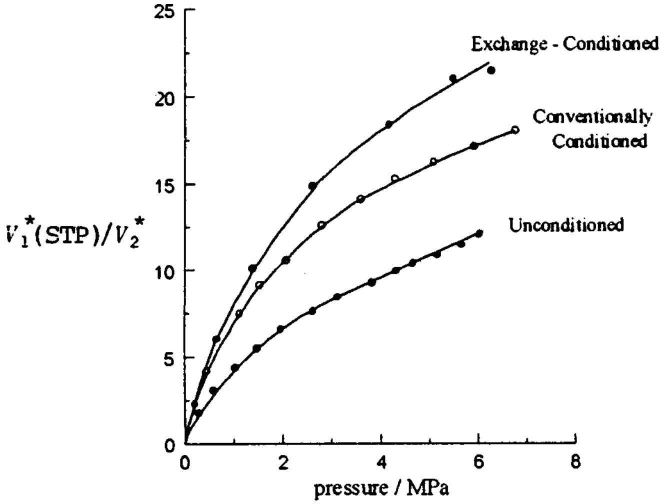


FIG. 44. Sorption isotherms of methane in polycarbonate for unconditioned, carbon dioxide conditioned and exchange conditioned samples.

Auxiliary Information

Method/Apparatus/Procedure

Two methods of conditioning were studied. Conventionally conditioned isotherms were obtained with the samples which had been previously in contact with CO_2 gas under pressure of 6.21 MPa for 2–3 h with consequent pumping for 2 days. Both isotherms were obtained by pressure decay method.[1] Exchange conditioning involved exposing the samples to CO_2 gas and then sweeping it by a CH_4 flux with the subsequent gravimetric determination of sorption.

Source and Purity of Materials:

CH_4: purity >99.99%.
PC: General Electric Co., density 1.200 g/cm^3, glass transition temperature 423 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci.: Polym. Phys. Ed. **14**, 1903 (1976).

3.20. Polycarbonates—Propane and Other Gases

Components:	**Original Measurements:**
(1) Propane; C_3H_8; [74-98-6] (2) Polycarbonate (PC); [24936-68-3] (XXI)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Only two papers are available for this system.[1,2] However, they cover the same temperature (303–333 K) and pressure (0–0.1 MPa) ranges. In both cases, the polymer is probably Lexan from General Electric Co. recast from methylene dichloride. This enables a meaningful comparison of the data to be done. The parameters of sorption isotherms at 323 K reported in Refs. 1 and 2 agree within the estimated error. Hence, the following pressure dependence was calculated for propane solubility in polycarbonate.

p/kPa	10	30	50	101
C/cm^3(STP) cm^{-3}	0.83±0.03	1.67±0.05	2.37±0.02	4.03±0.05

References:

[1] J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).

[2] J. A. Yavorsky and H. J. Spencer, J. Appl. Polym. Sci. **25**, 2109 (1980).

Components:	**Original Measurements:**
(1) Propane; C_3H_8; [74-98-6] (2) Polycarbonate (PC); [24936-68-3] (XXI)	J. A. Yavorsky and H. J. Spencer, J. Appl. Polym. Sci. **25**, 2109 (1980).
Variables:	**Prepared By:**
T/K: 321.7; 323 p/kPa; Not stated	A. K. Bokarev

Experimental Data

Table 1. Thermal treatment of films

Sample	Thermal treatment
PC-1	3 days in vacuum at 313–323 K
PC-A1	Treatment of PC-1 plus 49 h at 408 K in vacuum
PC-A2	Treatment of PC-A1 plus 51 h at 408 K in vacuum
PC-10	3 days in vacuum at 353 K

Table 2. Dual mode sorption parameters for the propane–polycarbonate system

Sample	T/K	k_D 10^2/cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/(cm Hg)$^{-1}$
		Unannealed films		
PC-1	323.0	4.5	0.72	0.23
PC-10	321.7	3.0	1.5	0.08
		Annealed films		
PC-A1	323.0	4.5	0.53	0.22
PC-A2	323.0	4.5	0.48	0.22

Auxiliary Information

Method/Apparatus/Procedure

The volumetric sorption procedure was used to determine the sorption equilibrium properties.

Source and Purity of Materials:

The bisphenol-A polycarbonate. Lexan, was supplied by the General Electric Co. $M_n = 12\,500$; $M_w = 35\,300$. Films were cast on mercury at about 307–309 K from 5% to 10% solutions in methylene chloride. The thermal treatment of the films is summarized in Table 1. The T_g for these films were in the range 421–428 K.

Propane used was 99.5% pure and was subjected to freeze–pump–thaw cycles.

Estimated Error:

No estimates possible.

Components:	**Original Measurements:**
(1) Propane; C_3H_8; [74-98-6] (2) Polycarbonate (PC); [24936-68-3] (XXI)	J. A. Barrie, M. J. L. Williams, and K. Munday, Polym. Eng. Sci. **20**, 21 (1980).
Variables:	**Prepared By:**
T/K=303–333 p/kPa=0–8.0	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters, solubility coefficients S, $(S = k_D + C'_H b)$, and errors (%) for propane in polycarbonate

T/K	10^2 k_D/ cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/ cm^3(STP) cm^{-3}	b/cm Hg^{-1}	S/ cm^3(STP) cm^{-3} cm Hg^{-1}
303	6.07 (±7%)	1.67 (±11%)	0.311 (±30%)	0.579 (±18%)
313	5.01 (±2%)	1.25 (±4%)	0.254 (±9%)	0.368 (±5%)
323	4.01 (±8%)	1.02 (±21%)	0.167 (±43%)	0.210 (±19%)
333	2.55 (±17%)	1.22 (±31%)	0.094 (±50%)	0.140 (±19%)

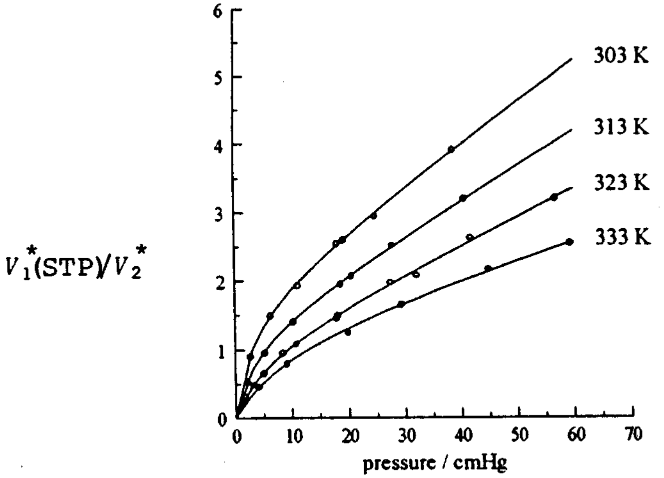


FIG. 45. Sorption isotherms for propane in PC.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms were measured using an electronic vacuum microbalance Sartorius, model 4102 as described in Ref. 1.

Source and Purity of Materials:

PC films: cast from methylene chloride; glass transition temperature 420 K.

Estimated Error:

See table.

References:

[1] J. A. Barrie and D. Machin, J. Makromol. Sci.-Phys. B. **3**, 645 (1969).

Components:

(1) Helium; He; [7440-59-7] Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Methane; CH_4; [74-82-8]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Variables:

T/K=308
p/MPa=0–2.53

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for various gases in polycarbonate at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Ar	0.1534	3.093	0.063
He	0.0145	0.313	0.0121
CH_4	0.1473	8.382	0.0841
N_2	0.0909	2.109	0.0564

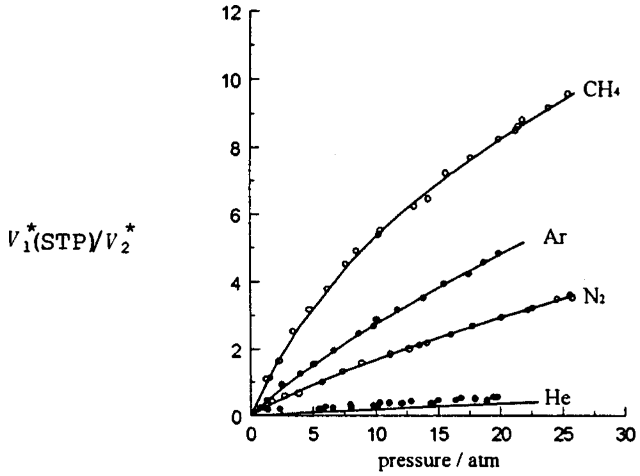


FIG. 46. Sorption isotherms of various gases in polycarbonate at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedure used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

Gases; purity >99%.
PC (Bisphenol A polycarbonate, Lexan); General Electric Co., M_w=35 800.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)

Original Measurements:

W. J. Koros, and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Variables:

T/K=308
p/MPa=0.1–2.6

Prepared By:

A. K. Bokarev

Experimental Data

Sorption isotherm of nitrogen in polycarbonate at 308 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.08	0.18	1.37	2.14
0.11	0.21	1.44	2.21
0.14	0.27	1.63	2.47
0.19	0.42	1.82	2.72
0.30	0.58	2.03	2.96
0.40	0.69	2.25	3.18
0.60	1.03	2.29	3.24
0.75	1.34	2.49	3.50
0.90	1.58	2.60	3.57
1.14	1.85	2.59	3.63
1.29	2.01	—	—

Auxiliary Information

Method/Apparatus/Procedure

Measurement of gas solubility was performed using a pressure decay method with a dual-volume dual transducers system (see also Ref. 1). In order to achieve superior precision the ratio of the two working volumes should be close to 1. It was shown that the reduction of this ratio from 9.7 to 1.45 resulted in much less scatter.

Source and Purity of Materials:

N_2: purity>99%.
PC (Bisphenol A polycarbonate): Lexan, General Electric Co., M_w=35 800.

Estimated Error:

Relative precision of solubilities: ±0.07 cm^3(STP)/cm^3 polymer.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polycarbonate (PC); [24936-68-3] (XXI)
Tetramethylpolycarbonate (TMPC); [38797-88-5] (XXII)
Tetrachloropolycarbonate (TCPC); [26913-25-7] (XXIV)
Tetrabromopolycarbonate (TBPC); [28774-93-8] (XXV)

Original Measurements:

N. Muruganandam, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **25**, 1999 (1987).

Variables:

T/K=308–358
p/MPa=0.1–2.0 (1–20 atm)

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for various gases in the polycarbonates at 308 K

Polymer	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}	Conditions
CO_2				
PC	0.685	18.81	0.262	Conditioned
TMPC	1.011	27.66	0.283	Conditioned
TCPC	0.860	26.35	0.316	Conditioned
TBPC	0.840	24.59	0.395	Conditioned
TBPC*	0.179	17.77	0.128	Conditioned
CH_4				
TMPC	0.281	12.29	0.106	Unconditioned
TCPC	0.289	12.22	0.128	Unconditioned
TBPC	0.275	12.37	0.141	Unconditioned
PC	0.147	8.38	0.084	Conditioned
TMPC	0.244	15.34	0.100	Conditioned
TCPC	0.340	11.26	0.150	Conditioned
TBPC	0.209	15.05	0.120	Conditioned
N_2				
PC	0.091	2.11	0.056	Unconditioned
TMPC	0.102	8.43	0.032	Unconditioned
TCPC	0.145	6.22	0.046	Unconditioned
TBPC	0.148	4.63	0.061	Unconditioned

*At 358 K.

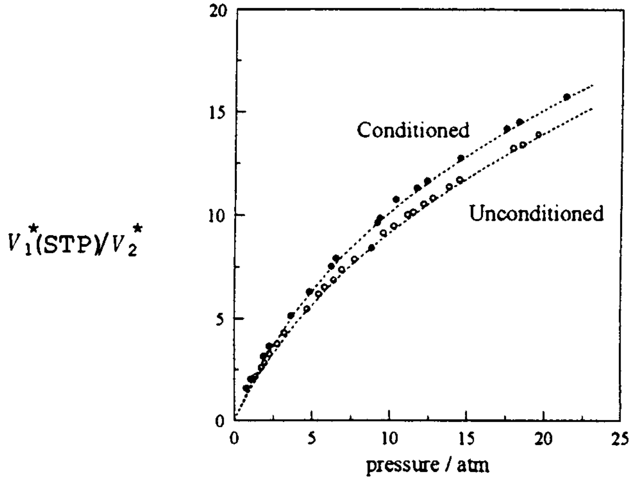


FIG. 47. Comparison of sorption isotherms of methane at 308 K in TMPC for unconditioned and conditioned films.

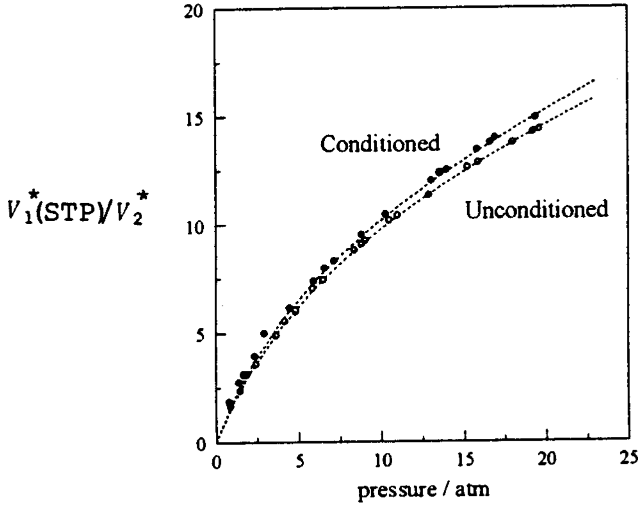


FIG. 48. Comparison of sorption isotherms of methane at 308 K in TCPC for unconditioned and conditioned films.

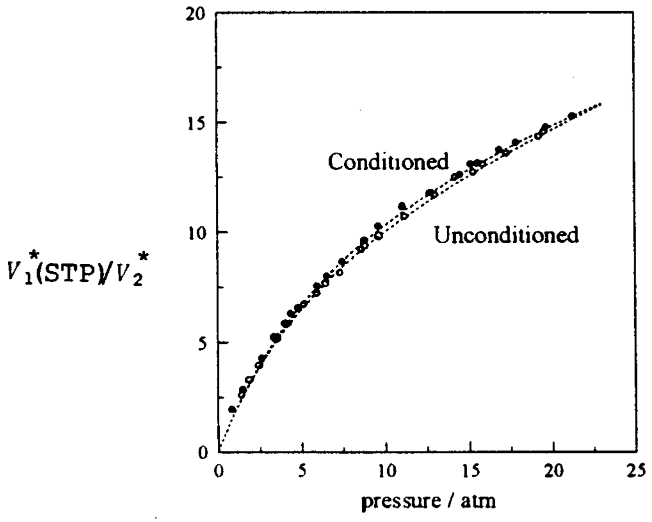


FIG. 49. Comparison of sorption isotherms of methane at 308 K in TBPC for unconditioned and conditioned films.

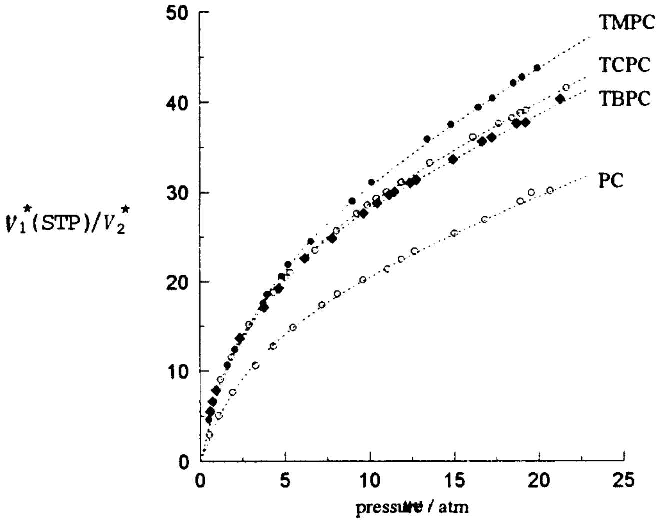


FIG. 50. Sorption isotherms of carbon dioxide at 308 K in polycarbonates conditioned by prior CO_2 exposure.

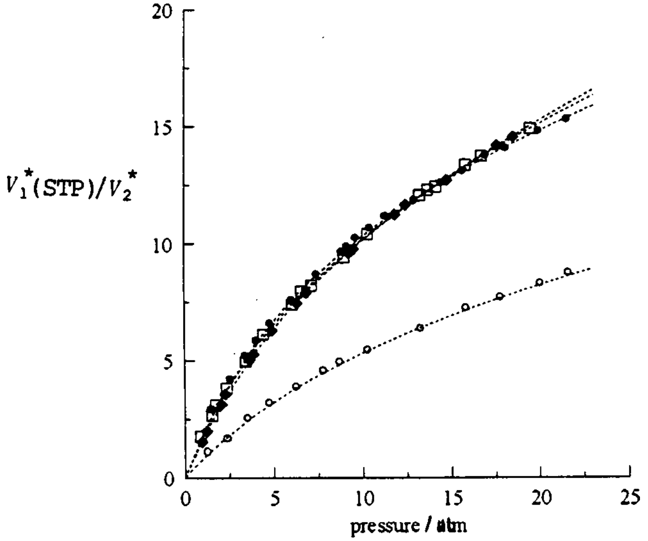


FIG. 51. Sorption isotherms of methane at 308 K in polycarbonates conditioned by prior CO_2 exposure. (○) PC; (◆) TMPC; (□) TCPC; (●) TBPC.

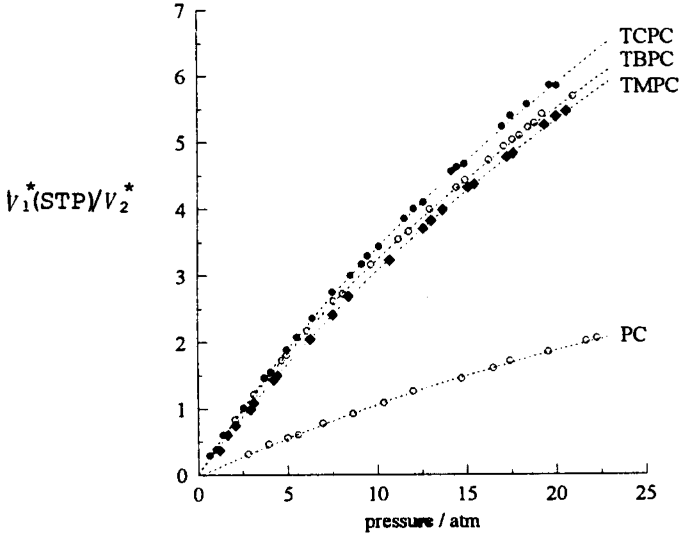


FIG. 52. Sorption isotherms of nitrogen at 308 K in polycarbonates without prior CO_2 exposure.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using the method described in Ref. 1 Sorption data were collected using films never exposed to CO_2 (unconditioned films) and films that had been exposed to CO_2 at 20 atm for 24 h.

Source and Purity of Materials:

Gases: purity 99%.
PC: General Electric Co., density 1.200 g/cm^3.
TMPC: Bayer AG, density 1.083 g/cm^3.
TBPC: Dow Chemical Co., density 1.953 g/cm^3.

Polymer	M_w	h/(dl/g)	T_g/K
PC	35 800	—	423
TMPC	—	0.530	466
TCPC	—	0.534	503
TBPC	—	0.417	536

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Components:

(1) Methane; CH_4; [74-82-8]
(2) Tetramethylpolycarbonate (TMPC); [38797-88-5] (XXII)

Original Measurements:

D. S. Pope, G. K. Fleming, and W. J. Koros, Macromolecules **23**, 2988 (1990).

Variables:

T/K=308
p/MPa=0–5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of methane at 308 K in unconditioned, conventionally conditioned, and exchange-conditioned samples of TMPC. (The original data were represented graphically)

Unconditioned		Conventionally conditioned		Exchange-conditioned	
Pressure/MPa	Sorption/ (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption/ (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption/ (V_1^*(STP)/V_2^*)
0.42	4.82	0.72	9.44	0.52	9.25
0.93	8.25	1.77	15.67	1.07	14.90
1.49	11.04	2.89	20.73	1.77	20.21
2.05	13.20	3.83	24.11	2.47	24.26
2.60	15.15	4.87	27.17	3.06	26.84
3.12	16.79	—	—	3.80	29.83
3.72	18.52	—	—	4.48	32.29
4.31	20.04	—	—	—	—
4.94	21.45	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

Two methods of conditioning were studied. Conventionally conditioned isotherms were obtained with the samples which had been previously in contact with CO_2 gas under pressure of 6.21 MPa for 2–3 h with consequent pumping for 2 days. Exchange conditioning involves exposing samples to CO_2 gas and then sweeping it with methane flux. For exchange conditioning runs a gravimetric technique was used, in two other types of experiments a pressure decay method was applied.[1]

Source and Purity of Materials:

CH_4: purity 99.99%.
TMPC: Dow Chemical Co., density 1.08 g/cm^3, glass transition temperature 476 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Tetramethylpolycarbonate (TMPC); [38797-88-5] (XXII)	G. K. Fleming and W. J. Koros, J. Polym. Sci., Part B: Polym. Phys. **28**, 1137 (1990).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–6.2 (0–62 atm)	Yu. P. Yampol'skii

Experimental Data

Sorption isotherm of carbon dioxide in TMPC on a fugacity basis at 308 K. (The original data were represented graphically)

Fugacity/MPa	Sorption (V_1^*(STP)/V_2^*)	Fugacity/MPa	Sorption (V_1^*(STP)/V_2^*)
0.21	13.53	3.03	68.80
0.60	26.09	3.27	71.90
0.98	35.48	3.47	75.91
1.33	42.17	3.72	80.36
1.65	48.41	3.91	84.60
1.95	52.61	4.13	88.39
2.26	57.50	4.30	92.86
2.51	61.95	4.47	93.49
2.77	64.81	—	—

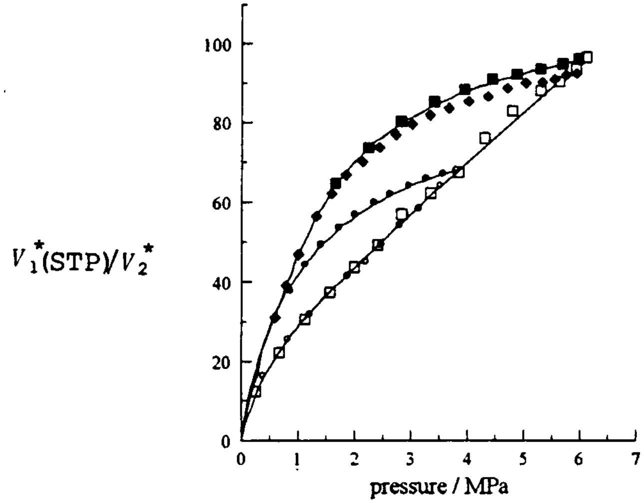


FIG. 53. Sorption (open points) and desorption (filled points) isotherms of carbon dioxide in TMPC for maximum conditioning pressures of 37.95 (○) (●) and 62.1 (□) (■) atm. (♦) second desorption

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay sorption cell and procedure used are described in Ref. 1.

Source and Purity of Materials:

CO_2: Linde Inc., purity 99.99%.
TMPC: Bayer AG, density 1.083 g/cm^3, glass transition temperature 475 K, d spacing 6.0 Å (WAXD).

Estimated Error:

No information given.

References:

[1] G. K. Fleming and W. J. Koros, Macromolecules **19**, 2285 (1986).

Components:	**Original Measurements:**
(1) Helium; He; [7440-59-7] Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Tetrabromopolycarbonate (TBPC); [28774-93-8] (XXV)	M. W. Hellums, W. J. Koros, G. R. Husk, and D. R. Paul, J. Membr. Sci. **46**, 93 (1989).

Variables:	**Prepared By:**
T/K=308 p/MPa=0–6.06	Yu. P. Yampol'skii

Experimental Data

Solubility of gases $C/(cm^3(STP)/cm^3)$ in TBPC at different pressures*

Gas	p/atm	C	Gas	p/atm	C
He	7.2	0.40	CH_4	3.0	4.4
	12.6	0.55		7.2	7.6
	18.4	0.80		12.0	10.6
	25.5	1.05		17.3	12.8
				23.0	14.7
N_2	3.6	1.4			
	7.4	2.6	CO_2	5.4	19
	11.7	3.6		9.5	25
	17.3	4.8		15.0	32
	20.0	5.4		20.7	37.5
O_2	1.0	0.6			
	2.35	1.2			
	5.0	2.6			
	8.2	3.95			
	12.5	5.5			

*Taken from the graphs by compiler.

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay apparatus was used in sorption measurement (see Ref. 1).

Source and Purity of Materials:

TBPC was prepared from tetrabromo-bisphenol A using standard interfacial polymerization technique. It had the following characteristics:
ρ=1.083 g/cc, T_g=466 K

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul. J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Hexafluoropolycarbonate (HFPC); [32291-26-2] (XXVI)	G. K. Fleming and W. J. Koros, J. Polym. Sci., Part B: Polym. Phys. **28**, 1137 (1990).

Variables:	**Prepared By:**
T/K=308 p/MPa=0.3–3.3	V. I. Bondar

Experimental Data

TABLE 1. Sorption and desorption isotherms of carbon dioxide in HFPC at 308 K. (The original data were represented graphically)

Sorption		Desorption	
Pressure/MPa	Solubility $(V_1^*(STP)/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(STP)/V_2^*)$
0.59	30.19	0.32	13.48
0.88	36.46	0.69	20.83
1.20	42.07	1.03	26.23
1.54	46.17	1.37	30.76
1.83	49.61	1.63	36.60
2.08	52.41	1.91	40.70
2.23	53.70	2.11	43.72
2.39	54.99	2.37	47.82
2.63	57.14	2.60	51.28
2.89	59.07	2.77	53.43
3.12	60.57	2.94	56.24
3.29	61.42	3.09	58.40
—	—	3.29	61.42

Experimental Data

TABLE 2. Sorption isotherms of carbon dioxide in HFPC at 308 K on fugacity basis. (The original data were represented graphically)

Fugacity/MPa	Sorption $(V_1^*(STP)/V_2^*)$
0.36	16.40
0.72	26.28
1.08	33.42
1.36	38.05
1.63	42.04
1.85	45.62
2.11	49.40
2.32	52.97
2.52	55.92
2.68	58.65
2.82	61.38

TABLE 3. Dual mode sorption parameters for carbon dioxide in HFPC at 308 K

Type	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Pressure	1.09	28.05	0.255
Fugacity	1.33	25.48	0.275

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay sorption cell and procedure were described in Ref. 1.

Source and Purity of Materials:

HFPC: Dow Chemical Co., density 1.478 g/cm^3, glass transition temperature 445 K, *d* spacing 5.8 A (WAXD method).
The polymer was conditioned before measurement of sorption isotherms by exposing to CO_2 at 33 atm.

Estimated Error:

No information given.

References:

[1] G. K. Fleming and W. J. Koros, Macromolecules **19**, 2285 (1986).

Components:	**Original Measurements:**
(1) Methane; CH_4; [74-82-8] Tetramethylhexafuropolycarbonate (TMHFPC); [125431-72-3] (XXIII)	D. S. Pope, G. K. Fleming, and W. J. Koros, Macromolecules **23**, 2988 (1990).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–3	Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of methane at 308 K in unconditioned, conventionally conditioned, and exchange-conditioned samples of TMHFPC. (The original data were represented graphically)

Unconditioned		Conventionally conditioned		Exchange-conditioned	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.20	3.51	0.70	11.09	0.34	7.02
0.60	8.50	1.41	17.75	0.71	12.18
1.05	12.66	2.12	22.64	1.23	17.93
1.61	16.39	2.72	26.45	1.75	22.42
2.23	20.03	—	—	2.23	25.65
2.94	23.33	—	—	2.69	28.38

Auxiliary Information

Method/Apparatus/Procedure

Two methods of conditioning were studied. Conventionally conditioned isotherms were obtained with the samples which had been previously in contact with CO_2 gas under pressure of 6.2 MPa for 2–3 h with consequent pumping for 2 days. Exchange conditioning involves exposing samples to CO_2 gas and then sweeping it with a methane flux. For exchange conditioning runs a gravimetric technique was used. In two other types of experiments a pressure decay method was applied.[1]

Source and Purity of Materials:

CH_4: purity >99.99%.
TMHFPC: synthesized, density 1.200 g/cm^3, glass transition temperature 481 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Helium; He; [7440-59-7] Nitrogen; N_2; [7727-37-9]
Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9]
Methane; CH_4; [74-82-8]
(2) Tetrabromohexafluoropolycarbonate (TBHFPC);
[126430-95-3] (XXVII)

Original Measurements:

M. W. Hellums, W. J. Koros, G. R. Husk, and D. R. Paul, J. Membr. Sci. **46**, 93 (1989).

Variables:

T/K=308
p/MPa=0–6.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility of gases C/cm^3(STP)/cm^3 in TBPC at different pressures*

Gas	p/atm	C	Gas	p/atm	C
He	2.4	0.2	CH_4	3.0	5.3
	8.7	0.6		9.0	11.5
	15.6	1.05		13.5	14.8
	23.0	1.5		18	17.3
	35.0	2.35		22	19
				26.5	21.5
				32.5	23.5
N_2	1.0	0.6	CO_2	3.5	22
	3.0	2.0		8.0	36
	6.0	3.4		15.5	47
	9.0	4.9		22	60
	14.0	6.8		28	74
				39	100
				52	116
O_2	0.6	0.4			
	1.6	1.3			
	2.4	1.9			
	4.1	3.1			
	6.3	4.65			

*Taken from the graphs by compiler.

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay apparatus was used in sorption measurement (see Ref. 1).

Source and Purity of Materials:

TBHFPC was prepared from tetrabromohexafluorobisphenol A using standard interfacial polymerization technique. It had the following characteristics: $\rho=1.987$ g/cc, $T_g=528$ K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2;
[124-38-9] Methane; CH_4; [74-82-8]
(2) Bisphenol norbornene polycarbonate (NBPC) (XXVIII)

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **29**, 731 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters at 308 K

Gas	k_D /cm^3(STP)/cm^3 atm	$C'_{H,}$/cm^3(STP)/cm^3	b/atm^{-1}
N_2	0.166	3.15	0.071
CO_2	0.978	19.8	0.306

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay sorption cell as described in Ref. 1. The films were cast from methylene dichloride solution.

Source and Purity of Materials:

NBPC (Eastman Kodak Co) had a density 1.20 g/cc, the glass transition temperature of 508 K. The intrinsic viscosity in methylene dichloride solution was 0.55 dl/g.
Purity of gases not indicated.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Bisphenol-*Z*-polycarbonate (PCZ); [25135-52-8] (XXIX)

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym Phys. **29**, 731 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters at 308 K

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	0.545	18.5	0.172
CH_4	0.223	5.65	0.106

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay apparatus (see Ref. 1). The films were cast from methylene dichloride solution.

Source and Purity of Materials:

PCZ (Mitsubishi Gas Chemical Co) had a density 1.20 g/cc and glass transition temperature of 458 K. Its intrinsic viscosity in chloroform was 0.49 dl/g. Purity of gases not indicated.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Bisphenol chloral polycarbonate (BCPC); [31546-39-1] (XXX)

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **29**, 731 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters at 308 K

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	0.718	14.9	0.271
CH_4	0.130	6.64	0.088

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay apparatus (see Ref. 1). The films were cast from methylene dichloride solution.

Source and Purity of Materials:

PCPC from General Electric Co had a density 1.39 g/cc and glass transition temperature of 437 K. Its intrinsic viscosity in chloroform was 0.66 dl/g. Purity of gases not indicated.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

3.21. Poly(Aryl-*bis*-isopropylidene Ether Ketone)—Carbon Dioxide and Methane

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(aryl-bis-isopropylidene ether ketone) (PAEK-12H); [122165-94-0] (XXXI)

Original Measurements:

J. M. Mohr and D. R. Paul, Polymer **32**, 2387 (1991)

Variables:

T/K=308
p/MPa=0–2.0

Prepared By:

V. I. Bondar

Experimental Data

Dual mode sorption parameters for carbon dioxide in PAEK-12H at 308 K

k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0.700	9.22	0.305

Sorption isotherms of carbon dioxide and methane in PAEK-12H at 308 K. (The original data were represented graphically)

CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.13	3.19	0.17	0.95
0.26	5.51	0.34	1.76
0.42	7.71	0.50	2.37
0.55	9.38	0.68	2.94
0.70	11.13	0.86	3.47
0.87	12.31	1.04	4.19
1.01	14.46	1.21	4.98
1.19	15.51	1.38	5.49
1.36	16.79	1.57	5.94
1.54	17.96	1.75	6.46
1.74	19.31	2.02	6.92
1.97	21.38	—	—
2.07	22.33	—	—

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used described in Ref. 1.

Source and Purity of Materials:

PAEK-12H: synthesized (Ref. 2), density 1.166 g/cm^3, glass transition temperature 444 K.

Estimated Error

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] G. L. Tullos, P. E. Cassidy, and A. K. St. Clair, Proc. ACS. Div. Polym. Materials **60**, 310 (1989).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(aryl-isopropylidene-hexafluoro-isopropylidene ether ketone) (PAEK-6H6F); [122165-96-2] (XXXII)
Poly(aryl-hexafluoroisopropylidene-isopropylidene ether ketone) (PAEK-6F6H); [122165-95-1] (XXXIII)

Original Measurements:

J. M. Mohr and D. R. Paul, Polymer **32**, 2387 (1991).

Variables:

T/K=308
p/MPa=0–2.0

Prepared By:

V. I. Bondar

Experimental Data

Dual mode sorption parameters for carbon dioxide in polymers at 308 K

Polymer	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
6H6F	0.840	10.90	0.373
6F6H	0.756	12.70	0.331

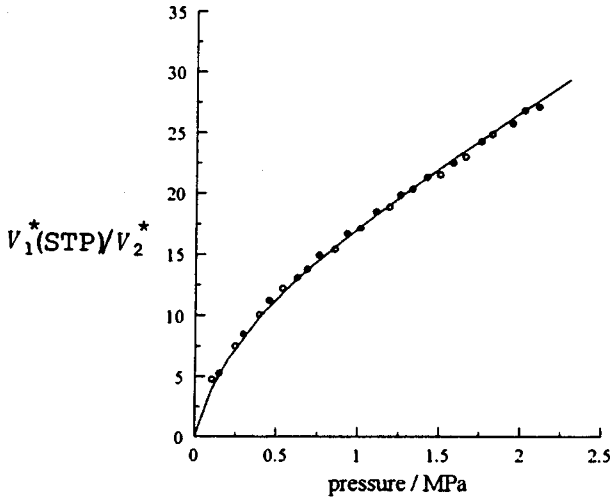


FIG. 54. Sorption isotherms of carbon dioxide in PAEK-6H6F (○) and PAEK-6F6H (●).

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used as described in Ref. 1.

Source and Purity of Materials:

PAEK-6H6F, PAEK-6F6H: synthesized by the procedure described in Ref. 2. 6H6F: density 1.287 g/cm^3, T_g=452 K. 6F6H: density 1.284 g/cm^3, T_g=454 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] G. L. Tullos, P. E. Cassidy, and A. K. St. Clair, Proc. ACS, Div. Polym. Materials **60**, 310 (1989).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(aryl-bis-hexafluoroisopropylidene ether ketone) (PAEK-12F); [122165-97-3] (XXXIV)

Original Measurements:

J. M. Mohr and D. R. Paul, Polymer **32**, 2387 (1991).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.0$

Prepared By:

V. I. Bondar

Experimental Data

Dual mode sorption parameters for carbon dioxide in PAEK-12F at 308 K

k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0.970	14.32	0.381

Sorption isotherms of carbon dioxide and methane in PAEK-12F at 308 K. (The original data were represented graphically)

CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.14	6.00	0.16	1.81
0.31	10.48	0.23	2.55
0.47	13.37	0.34	3.19
0.63	15.47	0.50	3.93
0.77	18.01	0.65	4.70
0.93	20.20	0.84	5.40
1.09	22.30	1.01	5.95
1.27	23.68	1.18	6.63
1.41	25.70	1.33	7.23
1.58	27.35	1.49	7.63
1.76	29.36	1.67	8.12
1.90	30.93	1.83	8.47
2.05	32.32	2.00	8.82

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used described in Ref. 1.

Source and Purity of Materials:

PAEK-12F synthesized (Ref. 2), density 1.401 g/cm^3, glass transition temperature 458 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] G. L. Tullos, P. E. Cassidy, and A. K. St. Clair, Proc. ACS, Div. Polym. Materials **60**, 310 (1989).

3.22. Polyarylate—Various Gases

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyarylate Ardel (PA); [25639-68-3](LXX)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.33$

Prepared By:

A. K. Bokarev

Experimental Data

Table 1. Dual mode sorption parameters for gases in polyarlyate at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.631	22.69	0.215
CH_4	0.181	6.45	0.100
N_2	0.081	1.22	0.074

Table 2. Sorption isotherms of various gases in polyarylate at 308 K (The original data were represented graphically)

CO_2		CH_4		N_2	
Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)	Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)	Pressure/MPa	Sorption ($V_1^*(STP)/V_2^*$)
0.21	7.30	0.26	1.65	0.19	0.30
0.27	9.17	0.32	1.98	0.23	0.37
0.31	10.11	0.36	2.22	0.30	0.44
0.35	11.14	0.42	2.53	0.33	0.54
0.60	15.81	0.62	3.39	0.40	0.54
0.65	16.74	0.70	3.82	0.44	0.63
0.73	18.33	0.78	4.09	0.59	0.78
0.97	21.03	0.85	4.44	0.68	0.89
1.04	21.96	1.04	4.97	0.70	0.98
1.13	23.27	1.13	5.40	0.85	1.13
1.38	25.49	1.21	5.66	0.92	1.20
1.46	26.52	1.29	5.95	1.03	1.30
1.58	27.72	1.48	6.38	1.11	1.39
1.84	29.38	1.56	6.71	1.19	1.52
1.91	29.94	1.65	6.97	1.29	1.61
2.30	33.08	1.74	7.23	1.40	1.70
2.33	33.36	1.92	7.66	1.49	1.74
—	—	2.02	7.92	1.57	1.87
—	—	2.12	8.16	1.64	1.98
—	—	2.18	8.31	1.75	2.04
—	—	—	—	1.82	2.15
—	—	—	—	1.94	2.19
—	—	—	—	2.04	2.26
—	—	—	—	2.22	2.46

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

CO_2, CH_4, N_2: purity >99.99%.
PA (Ardel D-100): Union Carbide Co., density 1.21 g/cm^3, glass transition temperature 457 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74082-8]
(2) Polyarylate Ardel (PA); [25639-68-3] (LXX)

Original Measurements:

F. R. Sheu, R. T. Chern, V. T. Stannett, and H. B. Hopfenberg, J. Polym. Sci., Part B: Polym. Phys. **26**, 883 (1988).

Variables:

$T/\text{K}=308$
$p/\text{MPa}=1-2.3$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	k_D, /cm^3(STP) cm^{-3} atm^{-1}	C'_H, /cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.98	19.8	0.30
CH_4	0.27	9.0	0.12

Auxiliary Information

Method/Apparatus/Procedure

Sorption apparatus and procedure were described in Ref. 1.

Source and Purity of Materials:

Polymer from Union Carbide had a density of 1.204 g/cm^3 and glass transition temperature 463 K.

Estimated Error:

No information given.

References:

[1] E. S. Sanders, W. J. Koros, H. B. Hopfenberger, and V. T. Stannett, J. Membr. Sci. **13**, 61 (1982)

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyarylate Ardel (PA); [25639-68-3] (LXX)

Original Measurements

F. R. Sheu, R. T. Chern, V. T. Stannett, and H. B. Hopfenberg, J. Pol. Sci., Part B: Polym. Phys. **26**, 883 (1988).

Variables:

T/K=308
p/MPa=0.1–2.3

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for gases in polyarylate at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	1.98	19.8	0.30
CH_4	0.27	9.0	0.12

TABLE 2. Sorption isotherms of carbon dioxide and methane in polyarylate at 308 K (The original data were represented graphically)

CO_2		CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.09	4.55	0.78	21.18	0.12	1.41
0.12	5.87	0.97	23.88	0.33	3.15
0.13	6.75	1.09	25.44	0.53	4.62
0.17	7.91	1.14	26.30	0.72	5.79
0.29	11.10	1.21	26.85	0.96	7.21
0.32	12.26	1.44	29.83	1.11	8.03
0.39	13.70	1.63	31.79	1.31	9.06
0.48	15.87	1.73	32.92	1.59	10.21
0.58	17.44	1.77	33.64	1.85	11.19
0.63	18.45	1.92	35.04	2.21	12.42
0.68	19.31	2.19	37.85	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption apparatus and procedure were the same as in Ref. 1.

Source and Purity of Materials:

PA: Union Carbide Co., density 1.204 g/cm^3, glass transition temperature 463 K.

Estimated Error:

No information given.

References:

[1] E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Membr. Sci. **13**, 61 (1983).

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Polyarylate (Ardel-D 100); [25639-68-3] (LXX)

Original Measurements:

G. R. Ranade, R. Chandler, C. A. Plank, and W. L. S. Laukhauf, Polym. Eng. Sci. **25**, 164 (1985).

Variables:

T/K=298–336
p/kPa=0–90

Prepared By:

S. M. Shishatskii

Experimental Data

Dual mode sorption parameters for sulfur dioxide in polyarylate

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
278	1.78	4.69	1.60
298	32.47	16.06	16.03
313	14.99	25.07	5.02
328	5.01	20.01	2.77
336	3.50	24.04	1.26

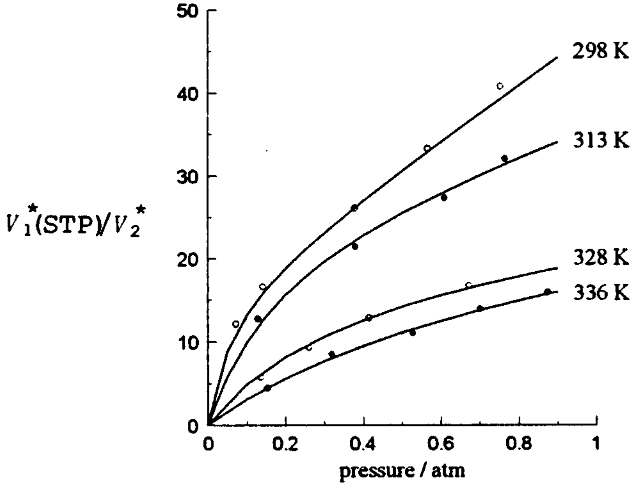


FIG. 55. Sorption isotherms of sulfur dioxide in polyarylate.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using a gravimetric technique (a McBain quartz spring balance). For detailed description of the experimental procedure see Ref. 1.

Source and Purity of Materials:

Polyarylate (Ardel-D 100): Union Carbide, copolyester of bisphenol A with 50/50 mixture of iso- and terephthalic acid. Density 1.21 g/cm^3, M_n=12 300, M_w=29 800.

Estimated Error:

Precision in T: ±0.1 K

References:

[1] G. R. Ranade, V. M. Nadgir, C. A. Plank, and W. L. S. Laukhuf, J. Appl. Polym. Sci. **28**, 201 (1983).

3.23. Polyhydroxyether—Carbon Dioxide, Methane, Nitrogen

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyhydroxyether (PHE); [26402-79-9] (LXIX)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).

Variables:

T/K: 308
p/MPa: 0–2.33

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for PHE at 308 K

Parameters	CO_2	CH_4
k_D /cm^3(STP) cm^{-3} atm^{-1}	0.289	0.051
C'_H/cm^3(STP) cm^{-3}	10.01	2.70
b/atm^{-1}	0.184	0.067

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

PHE (Union Carbide) had a tradename Phenoxy PKHH.
Density: 1.18 g/cm^3; $T_g = 376$ K.
Each gas was of chromatographic quality (purity>99.99%).

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyhydroxyether (PHE); [26402-79-9] (LXIX)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0$–2.5

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for various gases in polyhydroxyether at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.289	10.01	0.184
CH_4	0.051	2.70	0.067

TABLE 2. Sorption isotherms of various gases in polyhydroxyether at 308 K (The original data were represented graphically)

CO_2		CH_4		N_2	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.30	3.52	0.30	0.57	0.27	0.11
0.35	4.26	0.36	0.62	0.32	0.13
0.39	4.82	0.41	0.74	0.37	0.17
0.44	5.38	0.47	0.81	0.42	0.19
0.66	6.76	0.52	0.90	0.49	0.26
0.75	7.41	0.69	1.19	0.55	0.19
0.83	8.06	0.76	1.21	0.66	0.19
0.90	8.71	0.86	1.36	0.74	0.26
1.09	9.34	0.92	1.45	0.81	0.30
1.19	9.89	1.00	1.52	0.89	0.33
1.26	10.44	1.13	1.69	0.97	0.39
1.36	10.90	1.20	1.76	1.04	0.33
1.54	11.63	1.30	1.93	1.11	0.31
1.65	11.90	1.38	1.92	1.19	0.37
1.73	12.26	1.45	2.07	1.26	0.39
1.82	12.72	1.55	2.16	1.34	0.43
2.01	13.63	1.64	2.21	1.44	0.48
2.11	13.81	1.73	2.30	1.53	0.46
2.19	14.08	1.83	2.35	1.55	0.41
2.28	14.44	1.90	2.49	1.64	0.54
—	—	2.01	2.54	1.73	0.52
—	—	2.09	2.66	1.81	0.57
—	—	2.18	2.68	1.92	0.61
—	—	2.28	2.78	2.00	0.59
—	—	—	—	2.08	0.63
—	—	—	—	2.18	0.65
—	—	—	—	2.27	0.69
—	—	—	—	2.35	0.72
—	—	—	—	2.46	0.74

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

CO_2,CH_4,N_2: purity>99.99%.
PHE (Phenoxy PKHH): Union Carbide, density 1.18 g/cm^3, glass transition temperature 376 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

3.24. Poly(Phenolphthalein Phthalate)—Various Gases

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(phenolphthalein phthalate) (PPhPh); [24938-86-1] (XXXVI)

Original Measurements

F. R. Sheu and R. T. Chern, J. Polym. Sci., Part B: Polym. Phys. **27**, 1121 (1989).
F. R. Sheu, R. T. Chern, V. Stannett, and H. B. Hopfenberg, J. Polym. Sci., Part B: Polym. Phys. **26**, 883 (1988).

Variables:

T/K=308.2
p/MPa=0–2.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for CO_2, CH_4, and N_2 in different polymers at 308.2 K

Polymer	Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
PPhPh-tere	CO_2	1.312	36.37	0.413
	CH_4	0.321	13.76	0.160
	N_2	0.155	4.67	0.065
PPhPh-50:50	CO_2	1.230	34.66	0.413
	CH_4	0.324	13.74	0.154
	N_2	0.151	4.39	0.077
PPhPh-iso	CO_2	1.229	31.54	0.452
	CH_4	0.329	13.00	0.154
	N_2	0.157	4.12	0.067

TABLE 2. Sorption isotherms of carbon dioxide in poly(phenolphthalein phthalate)s at 308.2 K (The original data were represented graphically)

PPha-tere		PPha-50:50		PPha-iso	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.07	10.09	0.07	9.22	0.20	16.71
0.09	12.10	0.10	12.25	0.24	19.60
0.13	15.42	0.16	15.71	0.31	22.05
0.16	17.15	0.30	22.91	0.42	26.08
0.25	21.47	0.38	25.07	0.51	27.67
0.31	24.35	0.43	27.23	0.59	30.69
0.34	25.22	0.51	29.25	0.74	32.71
0.41	27.67	0.64	32.71	0.79	34.29
0.44	29.54	0.80	36.17	0.90	35.88
0.59	32.85	0.83	37.03	1.02	38.62
0.64	34.58	0.89	38.04	1.15	40.20
0.74	37.03	1.02	40.06	1.21	40.92
0.78	38.04	1.25	44.24	1.34	42.94
0.86	40.06	1.29	44.96	1.44	45.10
0.94	40.63	1.31	44.96	1.55	46.54
1.04	42.80	1.41	46.40	1.62	46.40
1.21	46.11	1.64	50.29	1.76	48.41
1.28	47.98	1.66	50.58	1.84	50.58
1.32	47.12	1.74	51.87	1.91	51.59
1.43	49.28	1.78	52.02	—	—
1.57	51.73	1.93	53.46	—	—
1.59	52.45	1.97	54.61	—	—
1.67	54.32	—	—	—	—
1.81	54.61	—	—	—	—
1.85	55.04	—	—	—	—
1.92	56.63	—	—	—	—

TABLE 3. Sorption isotherms of methane in poly(phenolphthalein phthalate)s at 308.2 K (The original data were represented graphically)

PPha-tere		PPha-50:50		PPha-iso	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.16	3.06	0.16	2.96	0.09	1.82
0.20	3.94	0.19	3.63	0.14	2.65
0.27	4.82	0.29	4.77	0.23	3.94
0.34	5.55	0.31	5.18	0.34	5.23
0.43	6.58	0.41	6.32	0.29	4.56
0.52	7.67	0.50	7.20	0.47	6.68
0.62	8.49	0.57	7.87	0.49	6.89
0.72	9.37	0.61	8.23	0.56	7.56
0.77	9.68	0.69	9.11	0.68	8.39
0.86	10.61	0.74	9.32	0.70	8.70
0.98	11.02	0.83	10.09	0.84	9.78
1.03	11.59	0.98	11.07	0.89	10.14
1.13	12.26	1.11	11.95	0.97	10.60
1.14	12.10	1.21	12.62	1.08	11.37
1.24	13.08	1.32	13.23	1.12	11.63
1.34	13.23	1.42	13.80	1.25	12.46
1.39	13.70	1.48	13.95	1.32	12.87
1.51	14.31	1.60	14.67	1.40	13.28
1.61	15.24	1.74	15.07	1.51	13.69
1.72	15.02	1.87	15.84	1.58	14.10
1.73	15.49	1.94	16.41	1.69	14.71
1.85	16.16	1.98	16.72	1.79	15.17
1.86	15.85	—	—	1.90	15.63
1.95	16.15	—	—	—	—
1.99	16.88	—	—	—	—

TABLE 4. Sorption isotherms of nitrogen in poly(phenolphthalein phthalate)s at 308.2 K (The original data were represented graphically)

PPha-tere		PPha-50:50		PPha-iso	
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.08	0.34	0.08	0.36	0.11	0.44
0.11	0.50	0.22	0.85	0.15	0.63
0.16	0.68	0.28	0.11	0.20	0.78
0.21	0.87	0.35	1.40	0.28	1.06
0.28	1.13	0.42	1.64	0.39	1.36
0.32	1.25	0.50	1.94	0.46	1.65
0.37	1.47	0.59	2.28	0.53	1.88
0.42	1.60	0.65	2.43	0.61	2.07
0.50	1.87	0.78	2.78	0.71	2.50
0.58	2.12	0.82	2.94	0.83	2.74
0.68	2.47	0.93	3.23	0.93	3.03
0.72	2.70	0.98	3.40	1.02	3.24
0.81	2.85	1.13	3.73	1.17	3.66
0.92	3.15	1.19	3.87	1.26	3.91
0.99	3.36	1.34	4.28	1.38	4.18
1.11	3.65	1.56	4.74	1.46	4.27
1.13	3.73	1.65	4.92	1.62	4.66
1.19	3.89	1.73	5.09	1.73	4.94
1.28	4.07	1.90	5.48	1.82	5.11
1.32	4.21	1.95	5.58	1.89	5.21
1.47	4.69	—	—	—	—
1.49	4.74	—	—	—	—
1.64	4.79	—	—	—	—
1.67	4.95	—	—	—	—
1.83	5.28	—	—	—	—
1.88	5.44	—	—	—	—
1.84	5.53	—	—	—	—
1.93	5.52	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay sorption cell was used in the measurements.

Source and Purity of Materials:

Gas purity: CO_2 99.99%; CH_4 99.7%; N_2 99.999%.
PPhPh: synthesized by interfacial polycondensation from phthaloyl chlorides and phenolphthalein.
PPhPh-50:50: synthesized by reacting phenolphthalein with a mixture of 50:50 terephthaloyl and isophthaloyl chlorides.
Iso-: $T_g = 522$ K, density 1.304 g/cm^3
50:50 isomers: $T_g = 552$ K, density 1.298 g/cm^3
Tere-: $T_g = 572$ K, density 1.297 g/cm^3.

Estimated Error:

Precision in T: ±0.1 K.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
Methane; CH_4; [74-82-8]
Ethane; C_2H_6; [74-84-0]
(2) Poly(tetrabromophenolphthalein-terephthalate) (XXXVII)

Original Measurements:

R. T. Chern and C. N. Provan, Macromolecules **24**, 2203 (1991).

Variables:

T/K=308
p/MPa=0–2.1

Prepared By:

Yu. P. Yampol'skii

Experimental Data

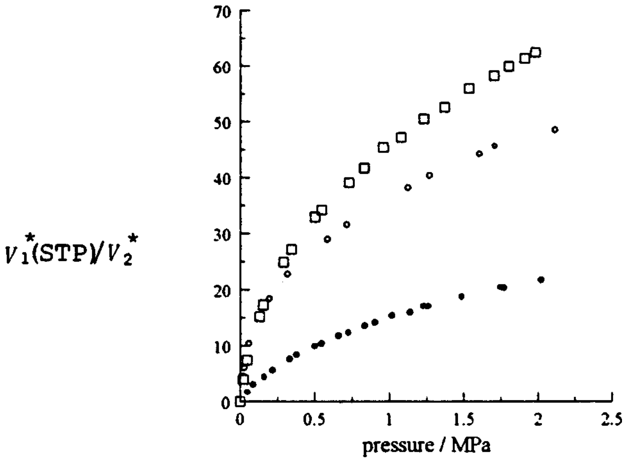


FIG. 56. Sorption isotherms of carbon dioxide (□), methane (●), and ethane (○) in the polymer at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used.

Source and Purity of Materials:

Poly(tetrabromophenolphthaleinterephthalate): density 1.750 g/cm^3, $M_w = 26\,000$,
$M_w/M_n = 2.0$, glass transition temp. 592 K.

Estimated Error:

No information given.

Components:

(1) Argon; Ar; [7440-37-1]
Nitrogen; N_2; [7727-37-9]
Methane; CH_4; [74-82-8]
(2) Copolyester (Kodar A-150)

Original Measurements:

P. Masi, D. R. Paul, and J. W. Barlow, J. Polym. Sci., Polym. Phys. Ed. **20**, 15 (1982).

Variables:

T/K=308
p/MPa=0–3.5

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters for various gases in copolyester at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Ar	0.117	2.09	0.050
CH_4	0.174	2.76	0.094
N_2	0.078	1.40	0.034

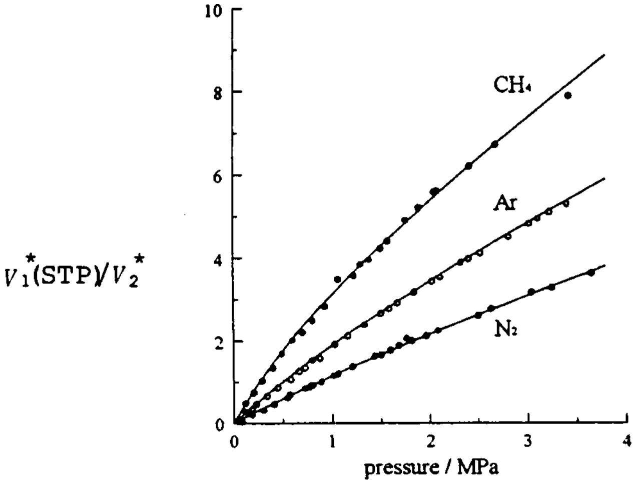


FIG. 57. Sorption isotherms of various gases in Kodar A-150 at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using a pressure decay method described in Ref. 1. The specimens before measurement were exposed to CO_2 at 20 atm for 1 day.

Source and Purity of Materials:

Copolyester (Kodar A-150): Eastman Chemical Products, Inc., film completely amorphous, ratio of units of isophthalic and terephthalic acids 20/80, M_n=22 000, glass transition temperature 360 K (thermal analysis).

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

3.25. Polysulfone—Carbon Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Several investigations have been carried out for this system.[1–6] In most cases PSF from Union Carbide has been studied, except the paper by Sada *et al.*[5] where Toray Co. provided the sample and the work by McHattie *et al.*[6] where the polymer was synthesized in the laboratory. A comparison of the dual mode sorption parameters as well as the apparent solubility coefficients $S=k_D+C'_H b$ at different temperatures is shown in Fig. 58. A fairly good agreement between the values of k_D and C'_H can be observed. However, systematic discrepancies in the affinity parameter b can be noted between those reported by Japanese authors[5] and found for PSF from Union Carbide. These differences are also reflected in the temperature dependence of S. Since the pressure range studies and the scatter of the experimental points are similar in two groups of the data, one is tempted to attribute this disagreement to some differences of the polymer sample.

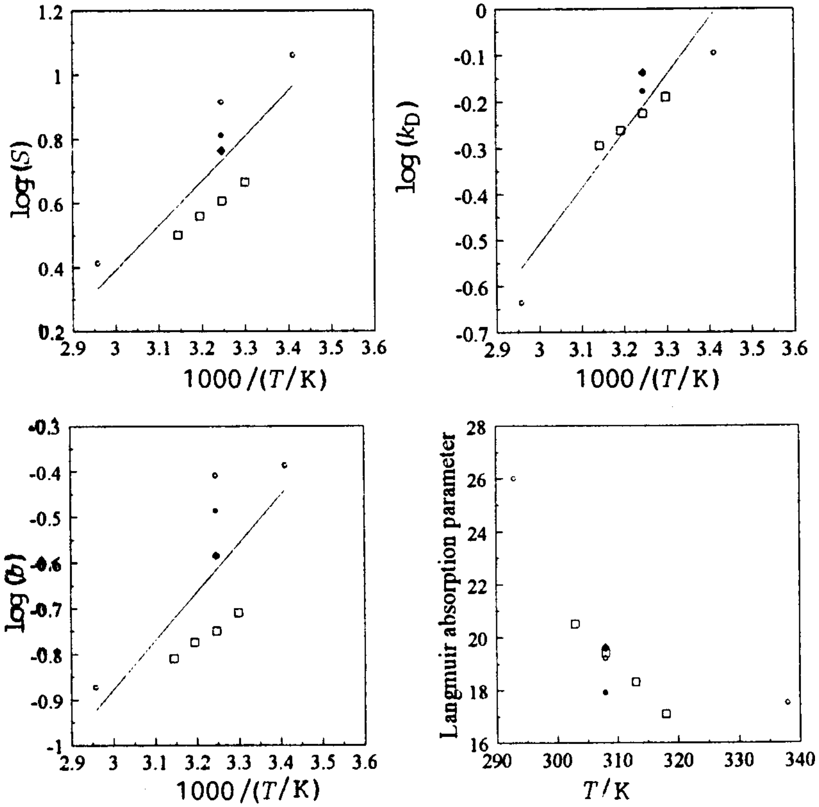


FIG. 58. (a) log S vs 1/(T/K); (b) log k_D vs 1/(T/K); (c) log b vs 1/(T/K); (d) C'_H vs T/K

Units: k_D and S/cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}. (●) Ref. 1; (○) Ref. 4; (□) Ref. 5; (◆) Ref. 6.

Critical Evaluation:

The following dual mode sorption parameters as a function of temperature can be recommended for sorption of carbon dioxide in PSF from Union Carbide at the pressure range 0–2.0 MPa.

T/K	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
293	0.801	26.0	0.410	11.5	3,4
308	0.705	18.9	0.325	6.8	1,3
338	0.231	17.5	0.134	2.6	3,4

Units: k_D and S/cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}.

References:

[1] A. J. Erb and D. R. Paul, J. Membr. Sci. **8**, 11 (1981).

[2] J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **30**, 4019 (1985).

[3] J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **33**, 1823 (1987).

[4] Y. Maeda and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **25**, 957 (1987).

[5] E. Sada, H. Kumazawa, P. Xu, and M. Nishigaki, J. Membr. Sci. **37**, 165 (1988).

[6] J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

3.26. Polysulfone—Methane and Other Gases

Components:

(1) Methane; CH_4; [74-82-8]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Only three papers are available for the solubility of methane in PSF at the pressure range 0–2.0 or 0–3.0 MPa.[1–3] The polymer specimens were provided by Union Carbide Co.,[1] Toray Co.,[2] or synthesized in the laboratory.[3] The summary of the dual mode sorption parameters and the apparent solubility coefficients S are presented below.

T/K	k_D	C'_H	b	$S=k_D-C'_Hb$	Ref.
303	0.441	9.26	0.116	1.5	2
308	0.161	9.86	0.0698	0.84	1
308	0.257	6.58	0.0901	0.85	3
313	0.413	7.63	0.0886	1.08	2
323	0.376	6.07	0.0748	0.83	2

Units: k_D and $S/\text{cm}^3(\text{STP})\ \text{cm}^{-3}\ \text{atm}^{-1}$; $C'_H/\text{cm}^3(\text{STP})\ \text{cm}^{-3}$; b/atm^{-1}.

A rather poor agreement between the data of different authors is observed. One may assume that this is the result of different samples studied as it is true for the system PSE–carbon dioxide. Another possible source of errors can be caused by too narrow pressure range for methane sorption. Indeed, the affinity constants b reported in Ref. 1–3 are equal to 0.07–0.12 atm^{-1}. So the point of intersection of the initial slope and the high pressure (Langmuir) asymptote should be close to pressure 8.6–14.3 atm, which is not too far from the maximum pressure of the isotherms. Hence, the limiting slope of the Langmuir part of isotherms has not been probably reached. Further experimental studies of well characterized sample are required before this system can be properly evaluated, and recommended values can be advanced.

References:

[1] A. J. Erb and D. R. Paul, J. Membr. Sci. **8**, 11 (1981).
[2] E. Sada, H. Kumazawa, P. Xu, and M. Nishigaki, J. Membr. Sci. **37**, 165 (1988).
[3] J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] Ethane; C_2H_6; [74-84-0]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Original Measurements:

Y. Kamiya, T. Hirose, K. Mizoguchi and K. Terada, J. Polym. Sci., Part B: Polym. Phys. **24**, 1525 (1986).

Variables:

$T/\text{K}=308-338$
$p/\text{MPa}=0-5.0$

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Sorption and desorption isotherms of carbon dioxide in polysulfone at 308 K (The original data were represented graphically)

First series (''as received'' film)				Second series			
Pressure/MPa	Sorption ($V_1^*(\text{STP})/V_2^*$)	Pressure/MPa	Desorption ($V_1^*(\text{STP})/V_2^*$)	Pressure/MPa	Sorption ($V_1^*(\text{STP})/V_2^*$)	Pressure/MPa	Desorption ($V_1^*(\text{STP})/V_2^*$)
0.11	3.66	0.14	7.09	0.14	5.98	0.24	11.4
0.33	8.07	0.39	16.48	0.32	11.73	1.60	33.99
0.69	13.24	0.67	22.44	0.58	16.13	3.58	42.33
1.16	17.85	1.18	29.92	0.99	21.52	4.93	44.65
2.03	25.64	2.00	36.94	1.50	26.46	—	—
3.50	34.70	3.00	41.39	2.04	30.73	—	—
4.96	43.54	3.94	43.52	2.83	35.65	—	—
—	—	—	—	3.69	39.67	—	—
—	—	—	—	4.31	42.49	—	—

TABLE 2. Sorption and desorption isotherms of carbon dioxide in polysulfone measured after CO_2 sorption experiment at 308 K (The original data were represented graphically)

$T=318$ K		$T=328$ K		$T=338$ K	
Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$
Sorption					
0.34	9.93	0.33	8.00	0.10	2.81
0.85	16.91	0.52	9.93	0.31	6.37
1.19	20.18	0.81	13.05	0.60	9.64
1.58	22.42	1.06	15.43	0.82	11.87
1.87	25.09	1.54	18.71	1.15	14.70
2.47	28.07	1.86	20.94	1.54	17.08
3.07	30.46	2.47	23.78	1.87	19.16
3.63	32.70	3.10	26.46	2.37	21.40
4.33	34.80	3.57	28.26	2.91	23.35
5.04	37.20	4.03	29.90	3.28	24.69
—	—	4.53	31.25	3.85	26.49
—	—	5.00	32.90	4.40	27.84
—	—	—	—	4.92	29.49
Desorption					
0.12	6.96	0.15	5.92	0.18	6.22
0.37	13.78	0.39	11.56	0.40	10.52
0.64	18.38	0.65	15.87	0.70	14.09
1.16	24.33	1.07	20.18	0.88	16.02
1.60	27.75	1.52	23.15	1.27	19.15
2.06	30.43	2.03	25.99	1.59	20.93
2.47	32.37	2.55	27.93	1.95	22.72
3.04	34.17	3.06	29.43	2.53	24.96
3.54	35.67	3.63	30.78	2.98	26.16
4.14	36.57	4.32	32.13	3.49	27.66
4.95	37.19	—	—	4.00	28.57
—	—	—	—	4.47	29.32
—	—	—	—	4.83	29.78

TABLE 3. Sorption and desorption isotherms of ethane in polysulfone at 308 K, measured after CO_2 sorption experiments (The original data were represented graphically)

Sorption		Desorption	
Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Solubility $(V_1^*(\mathrm{STP})/V_2^*)$
0.12	5.65	0.10	7.39
0.30	9.12	0.30	12.16
0.52	11.80	0.55	15.53
0.84	14.65	1.05	18.63
1.09	15.50	1.97	21.27
1.14	16.37	—	—
2.03	19.53	—	—
3.04	21.98	—	—

TABLE 4. Sorption and desorption isotherms of CH_4 and N_2 in polysulfone at 308 K, measured after CO_2 sorption experiments (The original data were represented graphically)

CH_4				N_2			
Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Desorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/MPa	Desorption $(V_1^*(\mathrm{STP})/V_2^*)$
0.11	1.39	0.11	1.64	0.12	0.29	0.12	0.44
0.31	3.14	0.29	3.54	0.23	0.48	0.31	0.84
0.60	5.35	0.58	5.68	0.45	1.06	0.41	1.12
1.07	7.24	1.11	8.04	0.62	1.47	1.09	2.46
1.55	9.30	2.04	11.17	1.14	2.37	1.59	3.18
2.53	11.91	3.02	13.15	2.05	3.80	2.60	4.63
3.05	12.59	4.00	14.61	2.74	4.69	3.52	5.52
4.03	14.37	5.03	15.68	3.50	5.43	4.36	6.30
5.00	15.53	—	—	4.19	6.06	—	—
—	—	—	—	4.88	6.61	—	—
—	—	—	—	4.97	6.63	—	—

TABLE 5. Dual mode sorption parameters for nitrogen in polysulfone at 308 K

k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0.043	7.5	0.031

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherms for gases in the polymer were obtained gravimetrically using a Cahn Model 2000 electrobalance. Details of this apparatus were described previously.[1]

Source and Purity of Materials:

Gas purity: CO_2 99.99%, CH_4 99.9%, C_2H_6 99.7%.

PSF (Udel Polysulfone): Nissan Chemical Industries Ltd., densities (at 298 K) 1.240 g/cm^3 (''as received'') and 1.238 g/cm^3 (after CO_2 exposure), glass transition temperature 455 K.

Estimated Error:

No information given.

References:

[1] Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, J. Polym. Sci., Polym. Phys. Ed. **24**, 535 (1986).

Components: (1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polysulfone (PSF); [25135-51-7] (XXXVIII)	**Original Measurements:** A. J. Erb and D. R. Paul, J. Membr. Sci. **8**, 11 (1981). J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **33**, 1823 (1987).
Variables: T/K=308 p/MPa=0–3.0	**Prepared By:** Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in ''as-received'' polysulfone films at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Ar	0.150	6.72	0.0317
N_2	0.0753	9.98	0.0156
CO_2	0.664	17.90	0.3260
CH_4	0.161	9.86	0.0698

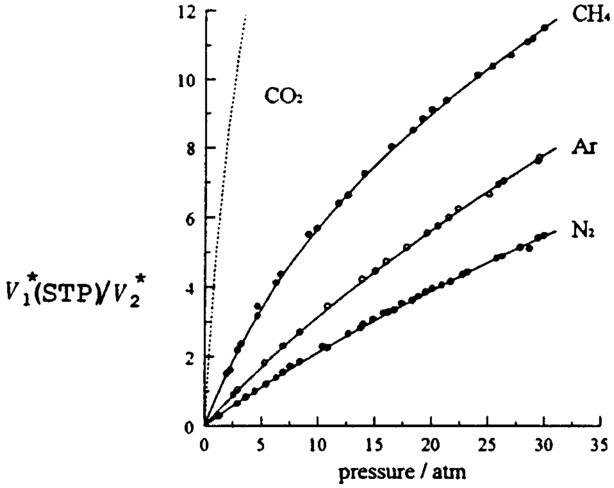


FIG. 59. Sorption isotherms of various gases in ''as-received'' polysulfone films.

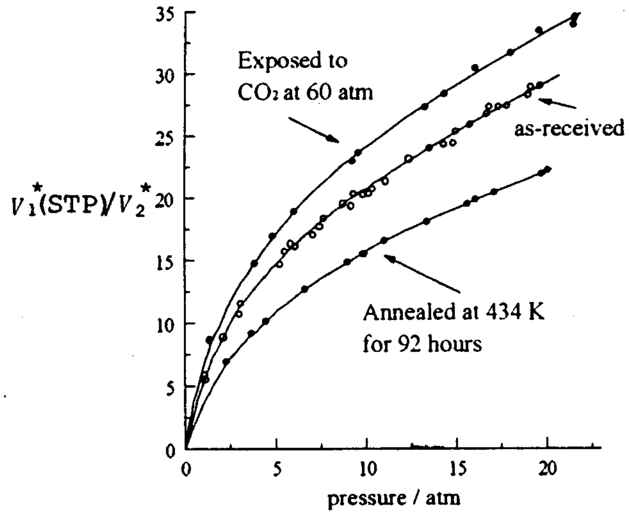


FIG. 60. Effects of history of sample treatment on sorption isotherms: CO_2 sorption at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption apparatus and procedure are described in Ref. 1.

Source and Purity of Materials:

Commercial PSF: Union Carbide Corp., studied in the form of melt extruded film; glass transition temperature 455 K (DSC).

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polysulfone (PSF); [25135-51-7] (XXXVIII)	J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **30**, 4019 (1985).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.2 (0–22 atm)	S. M. Shishatskii

Experimental Data

Sorption isotherm of carbon dioxide in polysulfone at 308 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.12	5.95	1.10	21.58
0.17	7.97	1.20	22.68
0.28	11.07	1.39	24.11
0.32	11.49	1.46	24.70
0.45	14.10	1.61	25.54
0.61	16.37	1.79	27.14
0.68	17.29	1.83	27.14
0.81	18.89	2.02	28.41
0.85	18.97	2.07	28.66
1.04	21.08	2.12	29.17

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherm was obtained using a dual-volume dual-transducer cell design based on the pressure decay principle.

Source and Purity of Materials:

PSF: conditioned at the highest CO_2 pressure before measurement; glass transition temperature 455 K.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polysulfone (PSF); [25135-51-7] (XXXVIII) (3) 4,4′-Dichlorodiphenyl sulfone (DDS); $(C_{12}H_8)_2C_{12}S$; [38980-51-7] (4) *N*-phenyl-2-naphtylamine (PNA); $C_{16}H_{13}N$; [135-88-6] (5) Tricresyl phosphate (TCP); $C_{21}H_{21}O_4P$; [1330-78-5]	Y. Maeda and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **25**, 957 (1987). J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **33**, 1823 (1987).
Variables:	**Prepared By:**
T/K=293–338 p/MPa=0–2.2 (0–22 atm)	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in polysulfone at different temperatures and its mixtures with plasticizers at 308 K

System	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
PSF			
293 K	0.801	26.0	0.410
308 K	0.725	19.2	0.390
338 K	0.231	17.5	0.134
DDS (mass %)			
10%	0.563	13.6	0.394
20%	0.296	10.2	0.226
30%	0.458	8.8	0.312
PNA (mass %)			
10%	0.392	13.9	0.159
20%	0.363	8.1	0.278
TCP (mass %)			
5%	0.503	13.9	0.280
10%	0.426	12.2	0.259
15%	0.476	9.7	0.248
20%	0.443	7.4	0.271

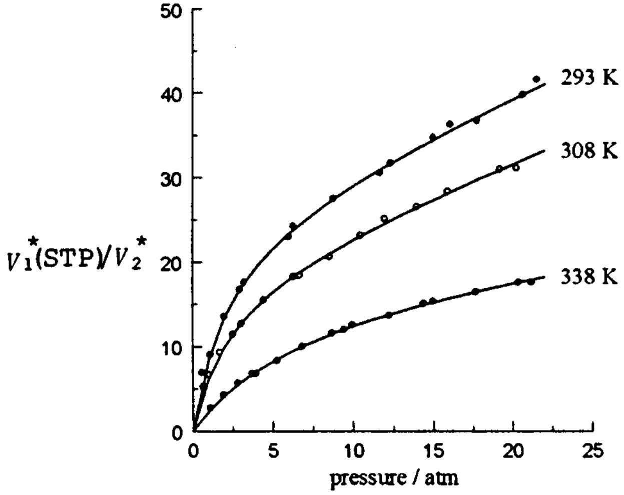


FIG. 61. Effect of temperature on CO_2 sorption isotherms in pure polysulfone.

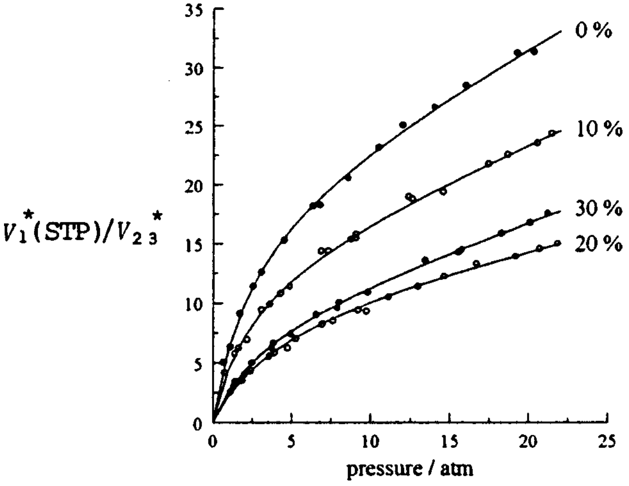


FIG. 62. Effect of the content of DDS (mass %) on CO_2 sorption isotherms for polysulfone at 308 K.

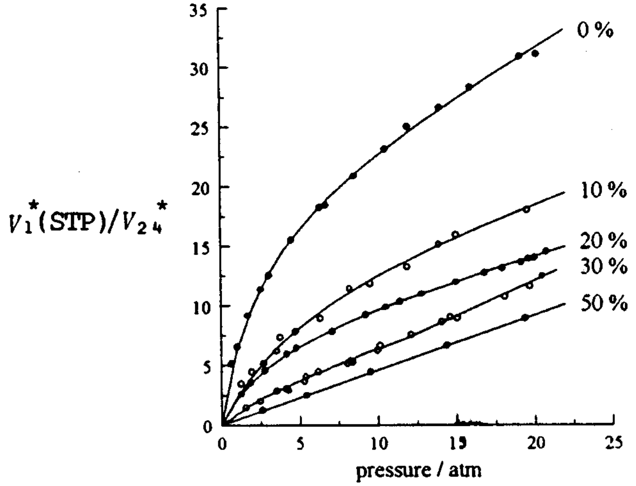


FIG. 63. Effect of the content of PNA (mass %) on CO_2 sorption isotherms for polysulfone at 308 K.

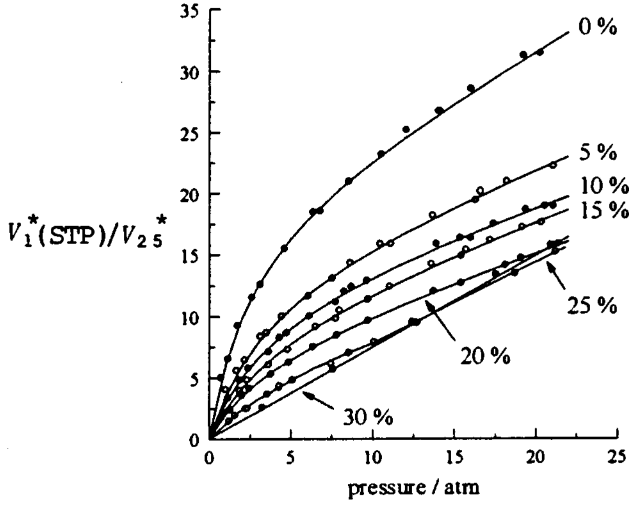


FIG. 64. Effect of the content of TCP (mass %) on CO_2 sorption isotherms for polysulfone at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure for measuring sorption isotherms were described in Ref. 1.

Source and Purity of Materials:

PSF: Union Carbide Corp., glass transition temperature 459 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] Nitrogen; N_2; [7727-37-9]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **26**, 729 (1988).
A. J. Erb, M.S. thesis, The University of Texas at Austin, 1977.

Variables:

T/K: 308
p/MPa: 0–2.33

Prepared By:

A. K. Bokarev

Experimental Data

Dual mode sorption parameters fro PSF at 308 K

Parameters	CO_2	CH_4	N_2
k_D /cm^3(STP)/cm^3 atm	0.664	0.161	0.0753
C'_H/(cm^3(STP)/cm^3)	17.91	9.86	9.98
b/(atm^{-1})	0.326	0.070	0.0156

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

PSF: no information given.
Each gas was of chromatographic quality (purity >99.99%).

Estimated Error:

Nothing specified.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polysulfone (PSF); [25135-51-7] (XXXVIII)	E. Sada, H. Kumazawa, P. Xu, and M. Nishigaki, J. Membr. Sci. **37**, 165 (1988).
Variables:	**Prepared By:**
T/K=303–323 p/MPa=0–2.0	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide and methane in polysulfone

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2			
Pressure			
303	0.646	20.5	0.195
308	0.595	19.4	0.178
313	0.547	18.3	0.168
318	0.508	17.1	0.155
Fugacity			
303	0.737	19.6	0.199
308	0.677	18.5	0.183
313	0.630	17.4	0.168
318	0.595	16.2	0.155
CH_4			
Pressure			
303	0.441	9.26	0.1160
313	0.413	7.63	0.0886
323	0.376	6.07	0.0748
Fugacity			
303	0.489	8.37	0.1210
313	0.445	6.60	0.0976
323	0.415	5.12	0.0785

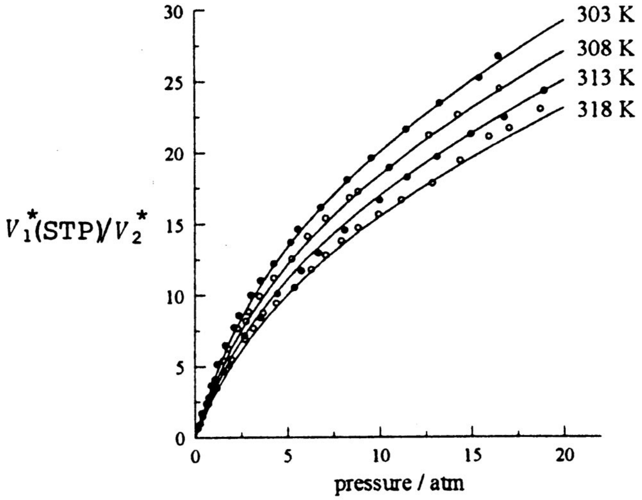


FIG. 65. Sorption isotherms of carbon dioxide in polysulfone.

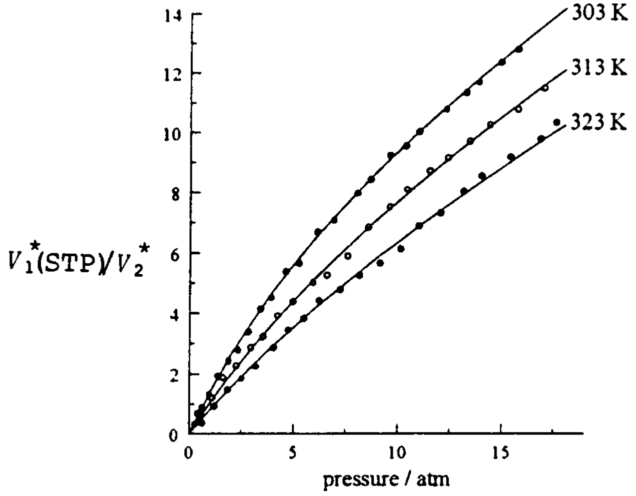


FIG. 66. Sorption isotherms of methane in polysulfone.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using a pressure decay method.

Source and Purity of Materials:

PSF (Torayslon-PSF): Toray Co., film samples; glass transition temperature 463 K.

Estimated Error:

No information given.

Components:
(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Original Measurements:
E. Sada, H. Kumazawa, and P. Xu, J. Polym. Sci., Part B: Polym. Phys. **27**, 919 (1989).

Variables:
T/K=313
p/MPa=0–1.8 (0–18 atm)

Prepared By:
A. K. Bokarev

Experimental Data

Solubility of carbon dioxide C,/cm^3(STP)/cm^3 in PSF membranes at 313 K*

	Pressure, atm									
Sample	2	4	6	8	10	12	14	16	18	20
As cast	3.0	5.7	7.9	10.2	12.1	14.0	15.9	17.7	19.5	21.2
Commercial	5.6	9.5	12.4	14.9	16.8	18.9	20.5	22.5	23.6	25.2

*Smooth values taken from the graph by compiler.

Dual-mode sorption parameters for CO_2 in PSF films at 313 K

Sample	k_D/cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
Cast PSF	0.813	6.61	0.155
Commercial PSF (Torayslon-PS)	0.547	18.3	0.168

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure for measuring sorption isotherms were described in Ref. 1.

Source and Purity of Materials:

The commercial polysulfone samples Torayslon-PS (Toray Co. Ltd.) and P-1700 (Union Carbide) were used. P-1700 had the glass transition temperature 459 K. A dense PSF (P-1700) membrane was prepared by casting a mixed solution of 25.5% PSF, 55.5% *N*,*N*-dimethylacetamide, and 19.0% acetone by weight. Purity of CO_2 not specified.

Estimated Error:
No information given.

References:
[1] E. Sada, H. Kumazawa, and Y. Yoshio, J. Polym. Sci., Polym. Phys. Ed. **26**, 1035 (1989).

Components:
(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polysulfone (PSF); [25135-51-7] (XXXVIII)

Original Measurements:
J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

Variables:
T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

TABLE 1. Solubility of gases C/cm^3(STP)/cm^3 in PSF*

	Pressure/atm			
Gas	5	10	15	20
N_2	1.2	2.2	3.1	3.9
CO_2	15.0	21.7	26.6	30.5
CH_4	3.6	6.0	8.0	9.9

*Smoothed values taken from the plot by compiler.

TABLE 2. Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
N_2	0.166	0.957	0.104
CO_2	0.728	19.6	0.260
CH_4	0.257	6.58	0.0901

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:

PSF was synthesized according to Ref. 2. It had a density 1.240 g/cc and the glass transition temperature 459 K.

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriam, J. Polym. Sci.: Part A-1 **5**, 2375 (1967).

Components:

(1) Nitrogen; N_2; [7727-37-9]
Carbon dioxide; CO_2; [124-38-9]
Methane; CH_4; [74-82-8]
(2) Dimethyl bisphenol A polysulfone (DMPSF); [58978-16-8]

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Solubility of gases C/cm^3(STP)/cm^3 in DMPSF*

	Pressure/atm			
Gas	5	10	15	20
N_2	1.05	1.8	2.5	3.05
CO_2	11.8	17.2	21.3	25.0
CH_4	3.1	5.0	6.3	7.4

*Smoothed values taken from the plot by compiler.

TABLE 2. Dual mode sorption parameters*

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm/^{3}	b/atm^{-1}
CO_2	0.505	17.8	0.235
CH_4	0.135	8.64	0.0564

*Fit for nitrogen did not converge.

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:

DMPSF was synthesized according to Ref. 2. It had a density 1.213 g/cc and the glass transition temperature 453 K.

Estimated Error:
No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriam, J. Polym. Sci.: Part A-1 **5**, 2375 (1967).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Tetramethyl bisphenol A polysulfone (TMPSF); [32034-67-6]

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
N_2	0.225	3.74	0.0461
CO_2	0.597	26.0	0.261
CH_4	0.460	7.26	0.233

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:

TMPSF was synthesized according to Ref. 2. It had a density 1.151 g/cc and the glass transition temperature 515 K.

Estimated Error:
No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] D. K. Mohanty, Y. Sachdeva, J. L. Hedrick, J. F. Wolfe, and J. E. McGrath, Polymer Preprints, ACS, Div. Polym. Chem. **25**, 2, 19 (1984).

Components:
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Hexafluorobisphenol A polysulfone (HFPSF); [31694-07-2]

Original Measurements:
J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 2618 (1991).

Variables:
$T/\text{K}=308$
$p/\text{MPa}=0\text{–}2.0$ (0–20 atm)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	0.785	21.0	0.285
CH_4	0.180	7.32	0.146

Auxiliary Information

Method/Apparatus/Procedure
The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:
HFPSF was synthesized according to Ref. 2. It had a density 1.427 g/cc and the glass transition temperature 465 K.

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] R. N. Johnson, A. G. Farnham, R. A. Glendinning, W. F. Hale, and C. N. Merriam, J. Polym. Sci.: Part A-1 **5**, 2375 (1967).

Components:
(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9]
(2) Bisphenol F polysulfone (PSF-F); [31694-05-0]

Original Measurements:
J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 2618 (1991).

Variables:
$T/\text{K}=308$
$p/\text{MPa}=0\text{–}2.0$ (0–20 atm)

Prepared By:
Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
CO_2	0.505	22.6	0.162
CH_4	0.246	8.84	0.0571

Auxiliary Information

Method/Apparatus/Procedure
The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:
PSF-F was synthesized according to Ref. 2. It had a density 1.282 g/cc and the glass transition temperature 452 K.

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] D. K. Mohanty, Y. Sachdeva, J. L. Hedrick, J. E. Wolfe, and J. E. McGrath, Polymer Preprints, ACS, Div. Polym. Chem. **25**, 2, 19 (1984).

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Dimethyl bisphenol Z polysulfone (DMPSF-Z); [134140-27-5] (XLIII)

Original Measurements:

J. S. McHattie, W. J. Koros, and D. R. Paul, Polymer **32**, 840 (1991).

Variables:

T/K=308
p/MPa=0–2.0 (0–20 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters

Gas	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
N_2	0.153	0.694	0.196
CO_2	0.560	18.6	0.252
CH_4	0.330	5.21	0.0907

Auxiliary Information

Method/Apparatus/Procedure

The measurement of sorption was carried out using a pressure decay method.[1]

Source and Purity of Materials:

DMPSF-Z was synthesized according to Ref. 2. It had a density 1.227 g/cc and the glass transition temperature 470 K.

Estimated Error:
No information given.

References:
[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).
[2] D. K. Mohanty, Y. Sachdeva, J. L. Hedrick, J. E. Wolfe, and J. E. McGrath, Polymer Preprints, ACS, Div. Polym. Chem. **25**, 2, 19 (1984).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyethersulfone (PES) Victrex 600 P; [25667-42-9] (XLIV)

Original Measurements:

E. S. Sanders, J. Membr. Sci. **37**, 63 (1988).

Variables:

T/K=308
p/MPa=0–4.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for various gases in polyethersulphone at 308 K

Gas	k_D /cm^3(STP)/cm^3 atm^{-1}	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
Ar	0.147	7.23	0.054
CO_2	0.631	29.78	0.313
CH_4	0.168	10.80	0.123
N_2	0.086	5.98	0.047

TABLE 2. Sorption isotherms of various gases in polyethersulphone at 308 K. (The original data were represented graphically)

Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
Ar					
0.20	1.00	1.35	5.00	2.52	7.90
0.32	1.48	1.47	5.26	2.67	8.10
0.51	2.32	1.83	6.32	3.06	9.03
0.89	3.68	1.87	6.39	3.32	9.52
1.02	4.06	2.12	6.84	—	—
CO_2					
0.15	11.38	0.77	25.76	2.15	39.89
0.18	12.79	1.07	29.37	2.21	39.89
0.27	14.60	1.21	31.58	2.23	41.10
0.27	15.91	1.27	31.47	2.40	41.39
0.30	15.90	1.45	34.19	2.49	41.89
0.40	18.02	1.74	36.89	2.61	43.80
0.46	20.63	1.78	36.79	2.62	42.89
0.58	23.04	1.83	37.49	2.61	42.29
0.69	24.75	2.09	39.90	2.86	44.79
CH_4					
0.32	3.81	1.72	10.39	2.66	12.87
0.51	5.21	1.79	10.69	2.88	13.56
0.93	7.51	1.89	10.89	2.91	13.26
0.97	7.71	2.35	12.28	3.31	14.34
1.18	8.61	2.37	12.17	3.65	15.13
N_2					
0.22	0.77	1.17	3.10	2.33	5.16
0.35	1.13	1.27	3.26	2.57	5.58
0.45	1.35	1.41	3.58	3.02	5.90
0.49	1.52	1.47	3.68	3.24	6.45
0.62	1.94	1.84	4.29	3.41	6.48
0.77	2.23	1.98	4.55	3.69	6.97
0.89	2.52	2.23	4.87	3.91	7.26
1.03	2.81	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

A high pressure sorption apparatus used was very similar to equipment described in Ref. 1.

Source and Purity of Materials:

Amorphous PES (grade 600 P, VICTREX): ICI, glass transition temperature 508 K.

Estimated Error:

No information given.

References:

[1] E. S. Sanders, W. I. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Membr. Sci. **13**, 161 (1983).

3.27. Cellulose—Sulfur Dioxide

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Cellulose; [9004-34-6] (XLV)

Original Measurements:

G. M. Eaton, dissertation: The University of Tennessee, Knoxville, 1986.

Variables:

T/K=298–323

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Four types of cellulosic fibers were studied: native cellulose (ethanol extracted cotton), modified cellulose (NaOH mercerized cotton and liquid ammonia treated cotton), and regenerated cellulose (viscose rayon).

Sorption of sulfur dioxide by cellulose fibers (mg/g fiber)

	Dried fiber Temperature/K				Conditioned fiber*
Fiber type	298	303	308	323	298
Extracted cotton	9.23	8.56	11.85	7.05	72.08
Mercerized cotton	26.28	16.19	15.15	13.29	74.27
Ammonia treated cotton	18.89	10.49	5.16	1.10	63.03
Viscose rayou	3.06	0.51	0.53	—	4.19

*The tabular data for this fiber in the dissertation appear to be inconsistent with the graphical data while the graphical data appear to be consistent with those for the dried fiber. The compiler concludes that typographical errors were made in the data table and the solubility values for the conditioned fiber were therefore taken directly from the graph by digitization. These data should therefore be considered as *highly tentative*.

Auxiliary Information

Method/Apparatus/Procedure

An exposure chamber was developed which would simulate ambient conditions. Fiber samples were dried or conditioned to 69% rel. humidity and exposed to 3 ppm sulfur dioxide for 5 h at 170 cc/min. Then the samples were exposed to a stream of dry air at the same flow rate for 4 h. The concentration of gas exiting the chamber was monitored and compared with the known concentration of gas introduced into the chamber to evaluate the amount of gas sorbed.

Source and Purity of Materials:

Native cotton (Starlab, Knoxville) and unfinished rayon staple (American Enka) were studied. The cotton was extracted in a Soxhlet for 4 h. with ethanol. Mercerization was carried out in 18% solution of NaOH for 15 min at ambient temperature. The duration of ammonia treatment was 30 s 3 ppm certified standard sulfur dioxide in dry air (Matheson Co) was used.

Estimated Error:

No information given.

3.28. Nitrocellulose—Various Gases

Components:	Original Measurements:
(1) He; Ar; N_2; O_2; CO_2; SO_2; NH_3; C_2H_6; C_3H_8; n-C_4H_{10}. (2) Nitrocellulose; (NC); [9004-70-0] (XLVI)	P. Y. Hsieh, J. Appl. Polym. Sci. **7**, 1743 (1963).
Variables:	**Prepared By:**
T/K: 298 p/kPa: 5.3–6.9	A. K. Bokarev

Experimental Data

Solubility coefficients of gases for nitrocellulose films at 298 K

Gas	Solubility coefficient; cm^3(STP) cm^{-3} cm Hg^{-1}; Volumetric	Gravimetric
(2) Helium; [7440-59-7]	—	0.0016
(3) Nitrogen; [7727-37-9]	0.0009	0.0006
(4) Oxygen; [7782-44-7]	0.0019	0.0013
(5) Argon; [7440-37-1]	0.0016	0.0014
(6) Carbon dioxide; [124-38-9]	0.0131	0.0096
(7) Sulfur dioxide; [7446-09-5]	0.2215	0.0977
(8) Ammonia; [7664-41-7]	1.2359	0.7265
(9) Ethane; [115-07-1]	0.0533	0.0483
(10) Propane; [74-98-6]	0.0534	0.0394
(11) *n*-Butane; [106-97-8]	0.0248	0.0147

Auxiliary Information

Method/Apparatus/Procedure

Both gravimetric and volumetric methods were used. In gravimetric one, sorption isotherms were determined with a quartz helix microbalance. The change in elongation of the quartz helix was detected by a linear variable differential transformer, Type 060 SLB and was amplified and read by means of a linear variable differential transformer indicator, Model 300B.

No details on volumetric method were given.

Source and Purity of Materials:

NC from the Hercules Powder Co. had a density of 1.46 g/cm^3. Gases from the Matheson Co. had the minimum purity of 99.5%, except ethane for which the purity was 99%.

Estimated Error:

No information given.

3.29. Ethyl Cellulose—Various Gases

Components:	Original Measurements:
(1) He; Ar; N_2; O_2; CO_2; SO_2; NH_3; C_2H_6; C_3H_8; n-C_4H_{10}. (2) Ethyl Cellulose (EC); [9004-57-3] (XLVII)	P. Y. Hsieh, J. Appl. Polym. Sci. **7**, 1743 (1963).
Variables:	**Prepared By:**
T/K: 298 p/kPa: 6–8	A. K. Bokarev

Experimental Data

Solubility coefficients of gases for ethyl cellulose films at 298 K

Gas	Solubility coefficient/cm^3(STP) cm^{-3} cm Hg^{-1}; Volumetric	Gravimetric
(2) Helium; [7440-59-7]	—	0.0024
(3) Nitrogen; [7727-37-9]	0.0021	0.0019
(4) Oxygen; [7782-44-7]	0.0024	0.0023
(5) Argon; [7440-37-1]	0.0026	0.0025
(6) Carbon dioxide; [124-38-9]	0.0207	0.0200
(7) Sulfur dioxide; [7446-09-5]	0.4978	0.3596
(8) Ammonia; [7664-41-7]	0.605	0.484
(9) Ethane; [115-07-1]	0.0748	0.0484
(10) Propane; [74-98-6]	0.1534	0.1263
(11) *n*-Butane; [106-97-8]	0.3887	0.2655

Auxiliary Information

Method/Apparatus/Procedure

Both gravimetric and volumetric methods were used. In gravimetric one sorption isotherms were determined with a quartz helix microbalance. The change in elongation of the quartz helix was detected by a linear variable differential transformer, Type 060 SLB and was amplified and read by means of a linear variable differential transformer indicator, Model 300B. No details on volumetric method were given.

Source and Purity of Materials:

EC (T50, content ethoxy groups 49.5%) was obtained from the Hercules Powder Company. The density was 1.10 g cm^{-3}. Gases from the Matheson Co. had the minimum purity of 99.5%, except ethane for which the purity was 99%.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Ethyl Cellulose (EC); [9004-57-3] (XLVII)

Original Measurements:

A. H. Chan, W. J. Koros, and D. R. Paul, J. Membr. Sci. **3**, 117 (1978).

Variables:

T/K=308
p/MPa=0–2.6

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in ethyl cellulose at 308 K

k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
1.189	4.847	0.365

Sorption isotherm of carbon dioxide in ethyl cellulose at 308 K. (The original data were represented graphycally)

Pressure/MPa	Sorption V_1^*(STP)/V_2^*
0.15	3.44
0.24	5.09
0.37	7.44
0.66	11.50
1.32	19.76
1.97	27.19
2.35	32.29
2.62	35.59

Auxiliary Information

Method/Apparatus/Procedure

Sorption apparartus used was described in Ref. 1.

Source and Purity of Materials:

EC: Dow Chemical Co., presumed ethoxy groups content 48.6%, glass transition temperature in the region 393–398 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) *n*-Butane; C_4H_{10}; [106-97-8] 2-Methylpropane; C_4H_{10}; [75-28-5] 2.2-Dimethylpropane C_5H_{12}; [463-82-1]
(2) Ethyl Cellulose (EC); [9004-57-3] (XLVII)

Original Measurements:

R. M. Barrer, J. A. Barrie, and J. Slater, J. Polym. Sci. **27**, N 115, 177 (1958).
A. H. Chan, W. J. Koros, and D. R. Paul, J. Membr. Sci. **3**, 117 (1978).

Variables:

T/K=303.7–353
p/kPa=0–24

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Enthalpies of sorption of hydrocarbon gases in ethyl cellulose

	$-\Delta H_D$		$-\Delta H_H$	
Gas	/kcal mol^{-1}	/kJ mol^{-1}	/kcal mol^{-1}	/kJ mol^{-1}
n-Butane	4.33	18.12	3.28	13.72
2-Methylpropane	2.01	8.41	2.25	9.41
2,2-Dimethylpropane	9.10	38.07	9.36	39.16

Table 2. Sorption isotherms of various gases in ethyl cellulose measured by Barrer *et al.* (The original data were represented graphically)

n-C_4H_{10}		iso-C_4H_{10}		neo-C_5H_{12}	
Pressure/cm Hg	Sorption, 10^5 s/ (mol_1 cm_2^{-3})	Pressure/cm Hg	Sorption, 10^5 s/ (mol_1 cm_2^{-3})	Pressure/cm Hg	Sorption, 10^5 s/ (mol_1 cm_2^{-3})
$T = 303.7$ K		$T = 303.7$ K		$T = 323.3$ K	
1.78	5.86	1.93	4.38	2.80	4.00
3.57	9.75	5.20	8.79	4.91	5.70
5.69	13.27	7.06	10.87	7.23	7.61
8.82	17.26	10.86	13.70	11.23	9.65
11.71	20.58	14.80	16.35	13.62	11.19
14.53	23.22	—	—	15.40	12.52
$T = 313.5$ K		$T = 313.5$ K		$T = 338.6$ K	
2.56	5.34	2.77	3.83	2.12	1.77
5.18	8.81	4.59	5.81	4.10	3.20
7.81	11.87	6.85	7.65	6.65	4.63
11.61	15.34	11.59	10.82	9.68	5.99
15.14	17.88	14.52	12.42	14.34	7.52
$T = 323.3$ K		$T = 323.3$ K		$T = 348$ K	
3.60	4.82	3.54	3.38	4.87	2.69
6.70	7.78	5.79	4.98	7.86	3.81
9.99	10.47	8.39	6.61	11.15	5.13
11.51	11.30	11.15	8.04	16.15	6.38
14.50	13.17	14.04	9.30	—	—
—	—	16.16	10.01	—	—
$T = 333$ K		$T = 333$ K		$T = 353$ K	
2.93	2.85	2.02	1.40	2.65	1.33
4.61	4.20	4.28	2.83	5.27	2.41
8.38	6.58	7.00	4.19	8.49	3.39
12.15	8.81	10.06	5.61	11.95	4.61
14.03	9.69	13.16	6.8	15.67	5.52
—	—	15.64	7.44	—	—
$T = 343$ K		$T = 343$ K			
3.57	2.33	2.39	1.12		
5.62	3.42	5.11	2.34		
9.99	5.49	8.24	3.53		
11.57	6.12	11.67	4.62		
14.43	7.36	14.93	5.66		

Table 3. Dual mode sorption parameters for gases in EC calculated by Chan *et al.* by treatment o sorption isotherms (The original data were represented graphically)

T/K	k_D /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/cm Hg^{-1}
n-C_4H_{10}			
303	0.1656	3.71	0.2173
313	0.1161	3.73	0.1232
323	0.1020	2.30	0.1297
333	0.1007	1.28	0.1395
343	0.0610	1.30	0.1005
iso-C_4H_{10}			
303	0.0909	3.34	0.1810
313	0.0614	2.94	0.0087
323	0.0978	0.75	0.4587
333	0.0552	2.03	0.0688
343	0.0698	0.51	0.1362
neo-C_5H_{12}			
323	0.1023	1.68	0.2074
338	0.0699	1.45	0.1149
348	0.0390	2.37	0.0638
353	0.0346	1.26	0.0894

Auxiliary Information

Method/Apparatus/Procedure

A glass volumetric apparatus was employed. The sorption system was immersed in a thermostat and the pressure was read by a cathetometer.

A nonlinear least squares program was used to calculate sorption parameters as in Ref. 1

Source and Purity of Materials:

EC: Standard Ethocel, density 1.13 g/cm^3, $M_n = 35\,000$.

Estimated Error:

Relative precision: $p \pm 6.6\%$.

Precision in T: ± 0.05 K.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:	**Original Measurements:**
(1) Ethane; C_2H_6; [115-07-1] Propane: C_3H_8; [74-98-6] *n*-Butane; C_4H_{10}; [106-97-8] (2) Ethyl Cellulose (EC); [9004-57-3] (XLVII)	E. Casur and T. G. Smith, J. Appl. Polym. Sci. **31**, 1425 (1986).

Variables:	**Prepared By:**
T/K=303–343 p/kPa=0–26	A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parrameters for various gases in ethyl cellulose

Gas	T/K	k_D /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/cm Hg^{-1}
C_2H_6	303	0.0476	0.348	0.0349
	313	0.0378	0.300	0.0307
	323	0.0295	0.299	0.0225
	333	0.0248	0.280	0.0179
	343	0.0199	0.250	0.0169
	349	0.1181	0.303	0.4251
C_3H_8	303	0.1319	0.479	0.2914
	313	0.1012	0.295	0.2601
	323	0.0769	0.217	0.2347
	333	0.0613	0.096	0.3280
	343	0.0493	0.089	0.3267
C_4H_{10}	303	0.2282	3.718	0.3128
	313	0.1884	2.650	0.2684
	323	0.1635	1.577	0.2645
	333	0.1439	0.809	0.3043
	343	0.1181	0.303	0.4251

TABLE 2. Heats of sorption in ethyl cellulose/(kcal/mol). Values obtained from van't Hoff plots for k_D, b and the solubility coefficient S ($S=k_D-C'_Hb$), respectively

Gas	ΔH_D	ΔH_H	ΔH_S
Ethane	−4.46	−4.12	−4.68
Propane	−5.10	−2.10	−7.13
n-Butane	−3.27	−1.65	−8.46

(For Tables 3, 4 and 5, the orriginal data were represented graphically.)

TABLE 3. Sorption isotherms of *n*-butane in ethyl cellulose

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
T=303 K		T=313 K		T=323 K	
1.81	1.43	1.76	0.93	1.76	0.61
3.11	1.99	3.10	1.36	2.96	0.91
4.36	2.46	4.44	1.78	4.44	1.20
5.75	2.97	5.79	2.15	5.73	1.48
7.09	3.42	7.08	2.48	7.07	1.71
9.86	4.19	9.81	3.05	9.75	2.19
12.55	4.87	12.44	3.61	12.39	2.59
15.27	5.48	15.21	4.09	15.16	2.99
18.00	6.03	17.94	4.60	17.79	3.34
21.93	6.83	21.91	5.24	21.86	3.93
26.09	7.63	25.93	5.83	25.97	4.46
T=333 K		T=343 K			
1.71	0.38	1.66	0.26		
3.05	0.63	2.96	0.42		
4.21	0.82	4.25	0.57		
5.59	1.03	5.77	0.71		
6.93	1.22	6.97	0.81		
9.61	1.55	9.70	1.09		
12.38	1.87	12.38	1.35		
15.20	2.19	15.15	1.61		
17.83	2.51	17.78	1.85		
21.80	2.98	21.89	2.19		
25.87	3.45	25.90	2.57		

TABLE 4. Sorption isotherms of ethane in EC at various temperatures

Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)V_2^*)
T=303 K		T=313 K		T=323 K	
2.99	0.11	2.88	0.09	2.80	0.08
5.67	0.23	5.60	0.19	5.64	0.15
8.33	0.36	8.40	0.29	8.30	0.22
11.02	0.47	11.02	0.38	10.99	0.29
13.63	0.58	13.68	0.46	13.65	0.36
17.65	0.74	17.66	0.59	17.63	0.46
25.87	1.08	25.84	0.85	25.82	0.66
T=333 K		T=343 K			
2.99	0.07	2.95	0.06		
5.61	0.12	5.57	0.10		
8.26	0.18	8.26	0.14		
10.92	0.24	11.03	0.20		
13.50	0.29	13.50	0.23		
17.56	0.38	17.60	0.30		
25.82	0.55	25.72	0.44		

TABLE 5. Sorption isotherms of propane in EC at various temperatures

Pressure/kPa	Sorption $(V_1^*(\text{STP})/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(\text{STP})/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(\text{STP})/V_2^*)$
$T=303$ K		$T=313$ K		$T=323$ K	
4.40	0.60	4.37	0.44	5.74	0.42
5.77	0.81	5.62	0.57	8.37	0.60
7.10	0.99	7.07	0.72	11.07	0.78
9.80	1.31	9.81	0.92	13.81	0.97
12.51	1.61	12.43	1.20	17.80	1.20
15.17	1.92	15.14	1.39	21.80	1.44
17.83	2.17	17.80	1.60	25.99	1.68
21.94	2.56	21.84	1.92	—	—
25.94	2.92	25.98	2.22	—	—
$T=333$ K		$T=343$ K			
5.70	0.30	5.66	0.25		
8.33	0.45	8.33	0.34		
11.03	0.58	10.92	0.46		
13.73	0.71	13.70	0.57		
17.73	0.91	17.66	0.73		
21.88	1.09	21.84	0.88		
25.95	1.28	25.95	1.05		

Auxiliary Information

Method/Apparatus/Procedure

Sorption was determined by a gravimetric method using a Cahn microbalance (Model KG). Corrections were made for buoyancy effects.

Source and Purity of Materials:

Gases: purity 99.99%.

EC (Ethocel 10 cp): Dow Chemical Co., contained 48%–49.5% ethoxy groups, density 1.13 g/cm^3, glass transition temperature 396 K.

Estimated Error:

No information given.

3.30. Cellulose Acetate—Carbon Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Cellulose acetate (CA); [9004-35-7] (XLVIII)

Evaluator:

Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Three papers are available on the system cellulose acetate–carbon dioxide.[1–3] In all the cases the degree of esterification and the origin of the samples were the same: CA obtained from Eastman Kodak Co. contained 39.8% of acetyl groups. Stern and De Meringo[1] studied sorption of CO_2 in CA at 273–343 K and reported the dual mode sorption parameters for somewhat narrower range of temperature. In a subsequent paper[2] of the same group the reported isotherm at 303 K was confirmed, but no sorption parameters were given. Sada *et al.*[3] studied the sorption in the temperature range 293–313 K. The table summarizes the sorption parameters found in Refs. 1 and 3 for this system. It can be seen that there is a reasonable agreement for Henry's law solubility coefficient k_D, but not for other two model parameters. The C'_H and b values reported in both papers monotonously decrease with temperature, but there is a significant discrepancy between two sets of values.

Dual mode sorption parameters at different temperatures

T/K	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
273.2	3.4	44.57	0.511	26.2	1
283.2	2.9	35.26	0.441	18.5	1
293.2	1.83	22.7	0.500	13.2	3
302.9	1.24	20.3	0.437	10.1	3
303.2	1.24	42.6	0.134	6.9	1
313.2	1.10	17.7	0.280	6.0	3
318.2	0.79	36.5	0.107	4.7	1

Units: k_D and $S/\text{cm}^3(\text{STP})\ \text{cm}^{-3}\ \text{atm}^{-1}$; $C'_H/\text{cm}^3(\text{STP})\ \text{cm}^{-3}$; b/atm^{-1}

The temperature dependencies of S and k_D are shown in Figs. 67 and 68.

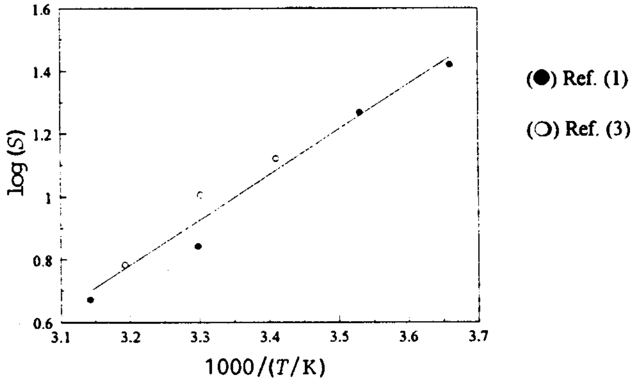


FIG. 67. Temperature dependence of apparent solubility coefficient $S/(\text{cm}^3(\text{STP})\ \text{cm}^{-3}\ \text{atm}^{-1})$.

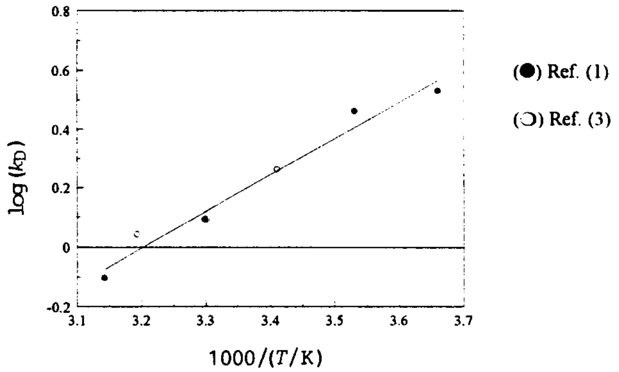


FIG. 68. Temperature dependence of Henry's law solubility coefficient k_D /(cm^3(STP) cm^{-3} atm^{-1}).

From the temperature dependence of k_D and S it was found, respectively,

$$\log(S/(\mathrm{cm^3(STP)cm^3\ atm^{-1}}))=-3.8226+1438.7/(T/\mathrm{K})$$

$$\log(k_D/(\mathrm{cm^3(STP)cm^3\ atm^{-1}}))=-3.9595+1236.3/(T/\mathrm{K})$$

$$\Delta H_D=-23.7\pm1.8\ \mathrm{kJ/mol}$$

$$\Delta H_S=-27.5\pm2.3\ \mathrm{kJ/mol.}$$

It is difficult to give much credit to the parameters reported in any of these works. Nevertheless, as one may tentatively suspect the effects of exposing the polymer to high pressure of CO_2 as a main reason for these differences, the data of Sada *et al.*[3] should be regarded as describing the sample ''as received,'' while those of Stern and De Meringo[1] as characterizing the polymer swollen in high pressure gas. Much larger values of the Langmuir capacity parameter C'_H are typical for such samples.

References:

[1] S. A. Stern and A. H. De Meringo, J. Polym. Sci., Polym. Phys. Ed. **16**, 735 (1978).
[2] S. A. Stern and S. S. Kulkarni, J. Membr. Sci. **10**, 235 (1982).
[3] E. Sada, H. Kumazawa, Y. Yoshio, S.-T. Wang, and P. Xu, J. Polym. Sci., Part B: Polym. Phys. **26**, 1035 (1988).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Cellulose 2,4-acetate (CA); [9004-35-7] (XLVIII)	S. A. Stern and A. H. De Meringo, J. Polym. Sci., Polym. Phys. Ed. **16**, 735 (1978).
Variables:	**Prepared By:**
T/K=273.0–343.0 p/MPa=0–4.0	A. K. Bokarev

Experimental Data

Dual mode sorption parameters for carbon dioxide in cellulose 2,4-acetate

T/K	k_D /cm^3(STP) g^{-1} atm^{-1}	C'_H/cm^3(STP) g^{-1}	b/atm^{-1}
273.0	2.50	32.77	0.511
283.0	2.13	25.93	0.441
303.0	0.911	31.31	0.134
318.0	0.580	26.81	0.107

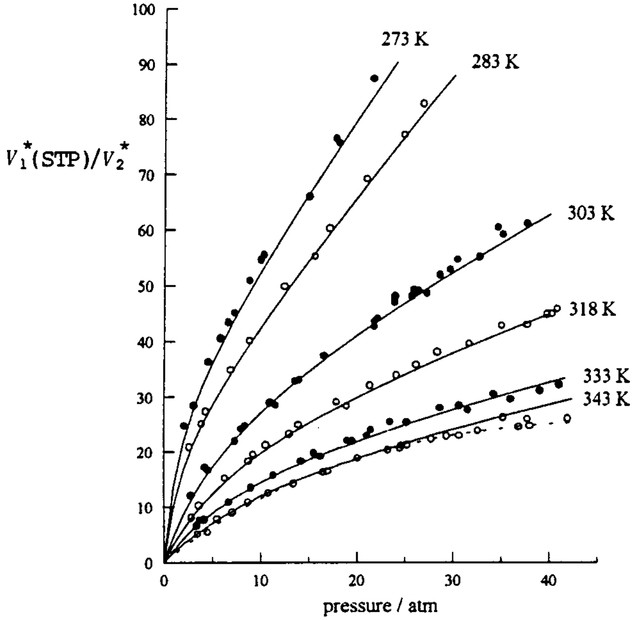


FIG. 69. Sorption isotherms of carbon dioxide. Continuous curves: Gas solubilities calculated from the dual mode sorption model. Dotted curve: Gas solubility at 343 K calculated from the empirical relation $C=1.4p\ \exp(-0.02p)$.

Auxiliary Information

Method/Apparatus/Procedure

A volumetric method was used in measurement of the solubility. The gas pressure decay with time was followed by means of a gauge. Corrections for the equation of state of CO_2 were made according to Ref. 1.

Source and Purity of Materials:

CO_2: purity 99.9%.
CA: Eastman Kodak, Trademark Edukit; content of acetyl groups 39.8%, density 1.36 g/cm^3.

Estimated Error:

Standard error of estimate of CO_2 concentration: from 5.5% at 273 K to 14% at 343 K.

References:

[1] N. E. Van Huff, G. Houghton, and J. Coull, J. Chem. Eng. Data **8**, 336 (1963).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Cellulose 2,4-acetate (CA); [9004-35-7] (XLVIII)

Original Measurements:

S. A. Stern and S. S. Kulkarni, J. Membr. Sci. **10**, 235 (1982).

Variables:

T/K=263–303
p/MPa=0–4 (0–40 atm)

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for methane in cellulose 2.4-aceteate (sample I)

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
303	0.024±0.035	10.03±2.99	0.052±0.016
293	0.067±0.018	8.32±1.21	0.076±0.013
288	0.083±0.061	8.35±3.54	0.087±0.043
283	0.099±0.019	8.22±1.14	0.109±0.022
273	0.101±0.043	10.22±2.71	0.104±0.040
263	0.119±0.028	11.48±1.61	0.117±0.024

Heats of solution of CH_4 in cellulose 2,4-acetate (sample I)

Apparent heat of ordinary dissolution: $\Delta H_D = -5.4$ kcal/mol; -22.6 kJ/mol.

Apparent heat of ‘‘hole-filling’’: $\Delta H_H = -2.9$ kcal/mol; -12.1 kJ/mol.

Solubility=(vol. of gas at STP/cm^3)/(mass of unswollen polymer /g)

TABLE 2. Solubility isotherm of carbon dioxide in cellulose 2,4-acetate (sample II) at 303 K (The original data were represented graphically)

Time sequence	Pressure/MPa	Solubility (V_1^*(STP)/m$_2^*$)	Time sequence	Pressure/MPa	Solubility (V_1^*(STP)/m$_2^*$)
1	2.07	38.80	5	2.61	43.70
2	0.97	25.63	6	2.53	42.21
3	0.57	18.13	7		
4	2.67	44.60	—	—	—

TABLE 3. Effect of CO_2 exposure on the solubility isotherm of CH_4 in cellulose 2,4-acetate at 293 K (The original data were represented graphically)

Sample I, after exposure to CO_2		Sample III, prior to exposure to CO_2		
Pressure/MPa	Solubility (V_1^*(STP)/m$_2^*$)	Time sequence	Pressure/MPa	Solubility (V_1^*(STP/m$_2^*$)
0.47	2.56	1	1.80	3.73
0.68	3.41	2	2.50	4.12
1.03	4.39	3	0.83	2.65
1.51	5.45	4	0.30	1.43
1.68	5.84	5	2.13	4.00
2.15	6.59	6	0.58	2.28
2.48	7.04	7	2.81	4.34
2.83	7.56	8	1.28	3.25
3.12	7.93	9	1.43	3.26
3.59	8.43	10	3.22	4.71
—	—	11	3.79	4.89
—	—	12	2.55	4.22

TABLE 4. Effect of exposure to CO_2 at high pressures on the dual mode sorption parameters for CH_4 in cellulose 2,4-acetate at 293 K

Polymer sample	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Sample I after CO_2 exposure	0.067±0.018	8.32±1.21	0.076±0.013
Sample II prior CO_2 exposure	0.046±0.033	3.09±2.92	0.159±0.070
Sample II after CO_2 exposure	0.082±0.019	6.23±2.27	0.120±0.059
Sample III prior CO_2 exposure	0.038±0.019	4.12±1.62	0.151±0.031

The fact that the Henry's law dissolution was found to be more exothermic than Langmuir ''hole-filling'' process lead the authors to test a different type of sorption isotherm-''two Langmuir sorption model'' proposed by Vieth *et al.*[2]

$$C=C'_H(1)b(1)p/[1+b(1)p]+C'_H(2)b(2)p/[1+b(2)p].$$

The parameters of this model are presented in Table 5.

TABLE 5. ''Two Langmuir sorption model'' parameters

T/K	$C'_H(1)$/cm^3(STP) g^{-1}	$C'_H(2)$/cm^3(STP) cm^{-3}	$b(1)$/atm^{-1}	$b(2)$/atm^{-1}
303	12.09	2.76	0.021	0.126
293	14.14	3.18	0.020	0.146
288	15.11	3.56	0.020	0.158
283	16.26	4.39	0.018	0.165
273	17.21	5.01	0.021	0.177
263	20.61	6.03	0.018	0.220

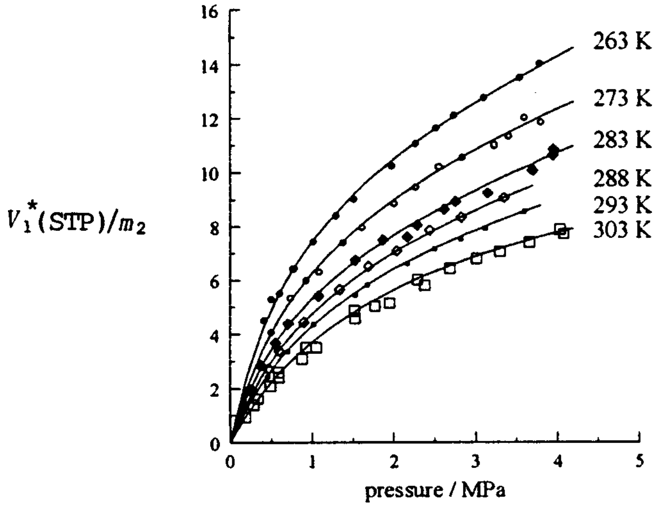


FIG. 70. Solubility isotherms of methane in cellulose 2.4-acetate (sample I). Solubility=(vol. of gas at STP/cm^3)/(mass of unswollen polymer/g).

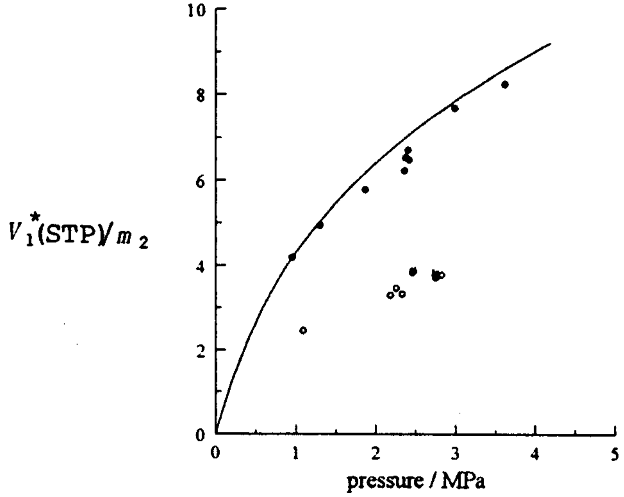


FIG. 71. Reproducibility of solubility isotherms of methane in cellulose 2,4-acetate at 293 K. Solubility=(vol. of gas at STP/cm^3)/(mass of unswollen polymer/g). (Solid line) calculated from the dual mode sorption model with sample I, after exposure to CO_2. (○) measurements with sample II prior to CO_2 exposure. (●) measurements with sample II after exposure to high-pressure CO_2.

Auxiliary Information

Method/Apparatus/Procedure

The solubility of CO_2 and CH_4 in cellulose 2.4-acetate was measured by a volumetric method. The apparatus and experimental procedure used have been described in Ref. 1.

Source and Purity of Materials:

CO_2: Matheson, purity 99.99%. CH_4: Matheson, purity 99.97%. CA: Eastman Kodak Co., density 1.36 g/cm^3. Sample I: previously exposed to carbon dioxide in the temperature range from 273 to 343 K and at pressure up to 45 atm.

Estimated Error:

Relative precision of solubilities: CO_2 10%, CH_4 between 16% and 20%.

References:

[1] S. A. Stern and A. H. De Meringo, J. Polym. Sci., Polym. Phys. Ed. **16**, 735 (1978).
[2] W. R. Vieth and M. A. Amini, Ind. Eng. Chem. Fundam. **16**, 82 (1977).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Cellulose Acetate (CA); [9004-35-7] (XLVIII)

Original Measurements:

E. Sada, H. Kumazawa, Y. Yoshio, S.-T. Wang, and P. Xu, J. Polym. Sci., Part B: Polym. Phys. **26**, 1035 (1988).

Variables:

T/K=293–313
p/MPa=0–1.5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide in cellulose acetate

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
293	1.83	22.7	0.500
302	1.24	20.3	0.437
313	1.10	17.7	0.280

$\Delta H_H = -22.7$ kJ/mol; $\Delta H_D = -17.8$ kJ/mol.

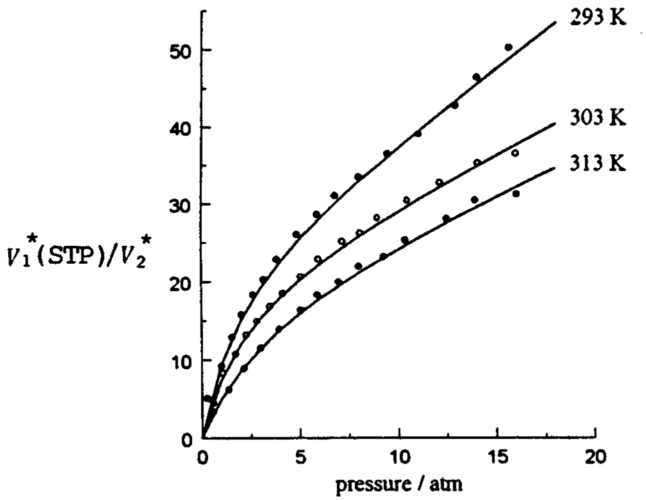


FIG. 72. Sorption isotherms of carbon dioxide in cellulose acetate.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured by the pressure decay method. The procedure and apparatus were similar to those described in Ref. 1.

Source and Purity of Materials:

CA: Eastman Kodak (E 398-3); content of acetyl groups 39.8%. The film cast from acetone solution was annealed in a water bath at 363 K for 10 min. The film was dried in vacuum for 24 h before measurement of sorption.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 667 (1976).

3.31. Poly(γ-Methyl Glutamate)—Carbon Dioxide

Components:

(1) Xenon; Xe; [7440-63-3] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(γ-methyl-*L*-glutamate) (PMG); [25086-16-2] (XLIX)

Original Measurements:

T. Yoshida, A. Takizawa, and Y. Tsujita. J. Appl. Polym. Sci. **22**, 279 (1978).

Variables:

T/K=293–308
p/kPa=6.6–52.5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

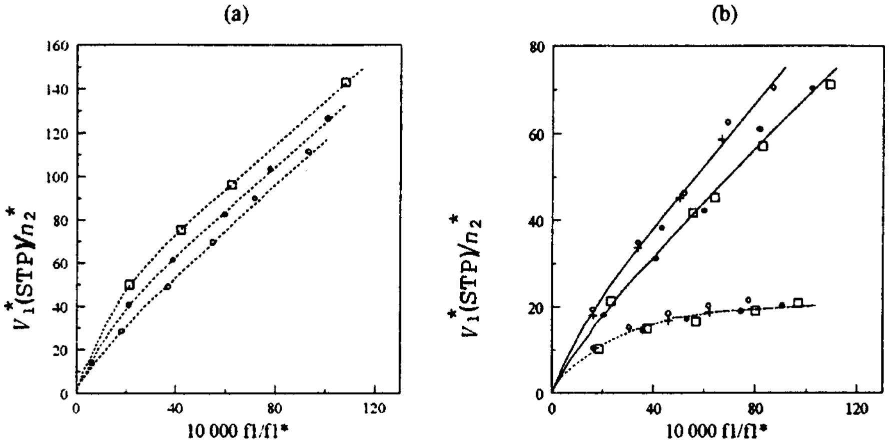


FIG. 73. Sorption isotherms of carbon dioxide (a) and xenon (b) in PMG. Sorption=(vol. of gas at STP/cm^3)/mol of residue. (□) 293 K, (●) 298 K, (○) 303 K, (+) 308 K. Broken line is heat treated sample.

Auxiliary Information

Method/Apparatus/Procedure

Cahn microbalance was used to determine sorption. Fugacity ratio was calculated by means of corresponding state principle.[1,2]

Source and Purity of Materials:

PMG: Kyowa Hakko K. K; viscosity average degree of polymerization about 1150.

Estimated Error:

Weight determination accuracy: ±10 mg for 50–100 mg samples. Precision in T: ±0.5 K.

References:

[1] T. H. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes* (New York, 1964).
[2] T. M. Prausnitz. J. Phys. Chem. **66**, 640 (1962).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(γ-methyl-*L*-glutamate) (PMG); [25086-16-2] (XLIX)	Y. Tsujita, T. Sumitomo, M. Nomura, and A. Takizawa, J. Appl. Polym. Sci. **30**, 2723 (1985).
Variables:	**Prepared By:**
T/K=298–308 p/kPa=0–40	Yu. P. Yampol'skii

Experimental Data

Different forms of PMG:PMG cast from chloroform (C), dimethyl-formamide (D), mixture of methylene chloride–dimethylformamide (D-D), and β-form of PMG (β).

Sorption=(vol. of gas at STP/cm^3)/mol of residue.

TABLE 1. Parameters of Langmuir equation $p/n = 1/ab + p/b$

Sample	$a/(\text{cm Hg})^{-1}$	$b/\text{cm}^3(\text{STP})\ \text{mol}^{-1}$
C	0.036	660
D	0.022	370
D-D	0.035	480
β	0.018	371

TABLE 2. Sorption isotherms of carbon dioxide in the different forms of PMG at (a) 298 K and (b) 308 K (The original data were represented graphically)

Fugacity ratio $10^4 f_1/f_1^0$	Sorption $(V_1^*(\text{STP})/n_2^*)$	Fugacity ratio $10^4 f_1/f_1^0$	Sorption $(V_1^*(\text{STP})/n_2^*)$	Fugacity ratio $10^4 f_1/f_1^0$	Sorption $(V_1^*(\text{STP})/n_2^*)$
(a)					
Form C					
12.25	106.36	46.00	219.72	70.69	286.40
21.64	145.08	54.17	242.58	84.52	319.70
38.96	198.34	63.06	260.50	—	—
Form D-D					
22.01	115.18	—	—	—	—
39.50	165.03	—	—	—	—
59.01	210.67	—	—	—	—
Form D					
7.44	25.15	29.91	66.93	61.01	116.04
11.64	40.93	38.41	82.59	72.12	132.77
21.07	56.57	48.98	101.98	83.78	146.08
Form β					
13.50	38.99	39.25	69.33	70.51	113.90
23.29	52.73	51.88	89.04	83.85	129.05
30.99	60.47	62.23	102.39	—	—
(b)					
Form C					
22.53	138.62	56.05	244.8	73.47	283.30
39.48	191.14	65.70	265.73	84.10	312.15
Form D-D					
18.18	100.53	53.91	172.97	92.31	254.05
36.17	140.91	71.55	217.15	—	—
Form D					
19.94	54.33	39.92	85.58	64.36	115.19
29.74	70.33	52.90	102.26	—	—

Auxiliary Information

Method/Apparatus/Procedure

Method of sorption measurement was described in Ref. 1.

Source and Purity of Materials:

PMG: Ajimoto Co.; M_w=100 000. Films were cast from $CHCl_3$, DMFA, mixture of DMFA and CH_2Cl_2.

PMG in β-form was cast from CH_2Cl_2, then treated by 80% water solution of HCOOH and dried.

Estimated Error:

No information given.

References:

[1] H. Kodama, Y. Tsujita, and A. Takizawa, J. Macromol. Sci. Phys. **17**, 57 (1980).

Components:	**Original Measurements:**
(1) Xenon; Xe; [7440-63-3] (2) Poly(γ-ethyl-*L*-glutamate) (PELG); [25189-52-0] (LI)	T. Yoshida, A. Takizawa and Y. Tsujita, J. Appl. Polym. Sci. **22**, 279 (1978).
Variables:	**Prepared By:**
T/K=293–308 p/kPa=6.6–52.5	Yu. P. Yampol'skii

Experimental Data

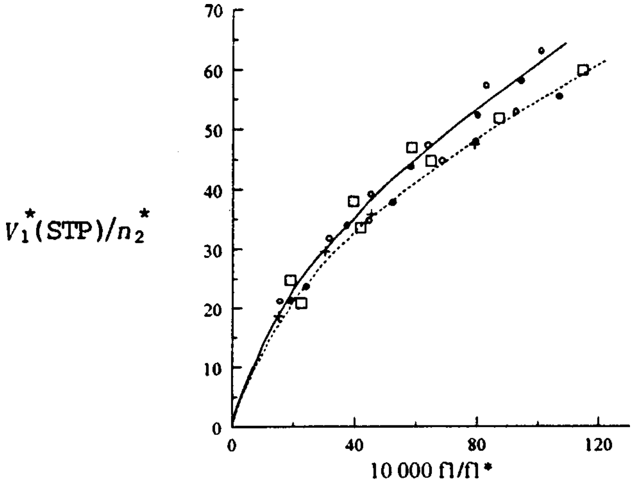


FIG. 74. Sorption isotherms of xenon in PELG. Sorption=(vol. of gas at STP/cm^3)/mol of residue. (☐) 293 K, (●) 298 K, (○) 303 K, (+) 308 K. Broken line is heat treated sample.

Auxiliary Information

Method/Apparatus/Procedure

Cahn electrobalance was used to measure sorption. Corresponding state principle was applied for calculation of fugacity ratio.[1,2]

Source and Purity of Materials:

Xe: purity 99.99%.

PELG: Ajinimoto K. K.; viscosity average degree of polymerization about 1150.

Estimated Error:

Weight determination accuracy: ±10 mg for 50–100 mg samples.

Precision in T: ±0.5 K.

References:

[1] T. H. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes* (New York, 1964).

[2] T. M. Prausnitz, J. Phys. Chem. **66**, 640 (1962).

Components:	**Original Measurements:**
(1) Xenon; Xe; [7440-63-3] (2) Poly(n-alkyl-*L*-glutamates) (LI)	T. Yoshida, A. Takizawa, and Y. Tsujita, J. Appl. Polym. Sci. **22**, 279 (1978).
Variables:	**Prepared By:**
T/K=293 p/kPa=6.6–52.5	Yu. P. Yampol'skii

Experimental Data

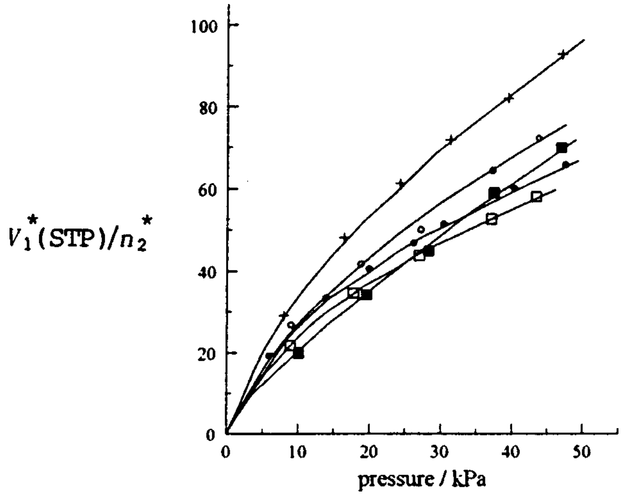


FIG. 75. Sorption isotherms of xenon in poly(n-alkyl-*L*-glutamates) at 298 K. Sorption=(vol. of gas at STP/cm^3)/mol of residue. (■)Me, (☐) Et, (●) Pr, (○) Bu, (+) Amyl.

Auxiliary Information

Method/Apparatus/Procedure

Cahn electrobalance was used to measure sorption. Corresponding state principle was applied for calculation of fugacity ratio.[1,2]

Source and Purity of Materials:

Xe: purity 99.999%.

Poly(n-alkyl-*L*-glutamates) and alkyls C_3–C_5: prepared according to Ref. 3 by ester exchange method.

Other alkyl derivatives: Kyuowa Hakko K. K. and Ajimoto Co.; degree of polymerization 1150.

Estimated Error:

Weight determination accuracy: ±10 mg for 50–100 mg samples.

Precision in T: ±0.5 K.

References:

[1] T. H. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes* (New York, 1964).

[2] T. M. Prausnitz, J. Phys. Chem. **66**, 640 (1962).

[3] A. Takizawa, H. Okada, S. Kadota, and H. Nonovama, J. Appl. Polym. Sci. **18**, 1443 (1974).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(γ-octyl-*L*-glutamate)

Original Measurements:

T. Yoshida, A. Takizawa, and Y. Tsujita, J. Appl. Polym. Sci. **22**, 279 (1978).

Variables:

T/K=293–303
p/kPa=6.6–52.5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide in poly(γ-octyl-*L*-glutamate) based on fugacity. (The original data were represented graphically.) Sorption=vol. of gas at STP/mol of polymer (cm^3 (STP)/n polymer)

T=293 K		T=298 K		T=303 K	
Fugacity ratio $10^4f_1/f_1^0$	Sorption (cm^3 mol^{-1})	Fugacity ratio $10^4f_r/f_1^0$	Sorption (cm^3 mol^{-1})	Fugacity ratio $10^4f_1/f_1^0$	Sorption (cm^3 mol^{-1})
15.38	89.52	13.27	78.75	11.52	68.72
32.19	119.68	27.16	114.45	21.48	96.98
52.59	153.57	44.05	131.26	39.73	127.89
73.39	181.53	60.92	150.66	54.42	150.62
—	—	78.14	173.40	68.76	170.74

Auxiliary Information

Method/Apparatus/Procedure

A Cahn electrobalance was used to measure the sorption.

Source and Purity of Materials:

CO_2: purity 99.999%.
Poly(γ-octyl-*L*-glutamate): prepared according to Ref. 1 by a ester exchange method.

Estimated Error:

Weight determination accuracy: ±10 mg for 50–100 mg sample.
Relative precision in T: ±0.5 K.

References:

[1] A. Takizawa, H. Okada, S. Kadota, and H. Nonovama, J. Appl. Polym. Sci. **18**, 1443 (1974).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(γ-benzyl-*L*-glutamate) (PBLG); [25014-27-1] (LII)

Original Measurements:

Y. Oohachi, H. Hamano, T. Yoshida, Y. Tsujita, and A. Takizawa, J. Appl. Polym. Sci. **22**, 1469 (1978).
T. Yoshida, A. Takizawa, and Y. Tsujita, J. Appl. Polym. Sci. **22**, 279 (1978).

Variables:

T/K=293–308
p/kPa=6.6–52.5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

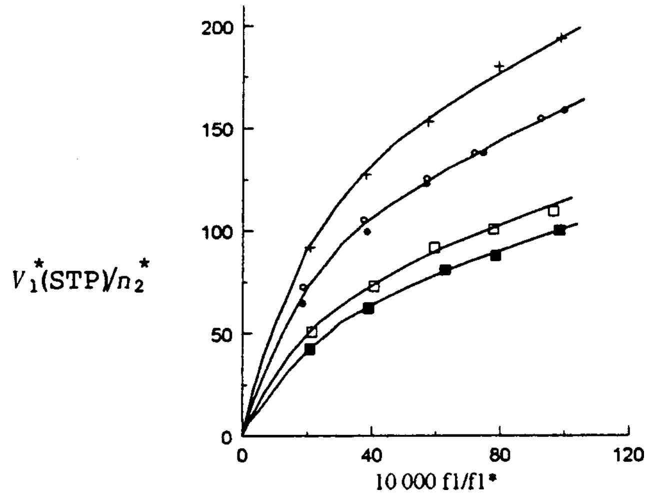


FIG. 76. Fugacity ratio calculated by corresponding state principle, Refs. 1,2. Sorption=(vol. of gas at STP/cm^3)/mol of residue. Sorption isotherms of carbon dioxide in PBLG. (■) PBLG cast from benzene at 318 K, (□) same film heat treated, (●) PBLG cast from benzene at 333 K, (○) same film heat treated, (+) cast from ethylene dichloride at 298 K.

Auxiliary Information

Method/Apparatus/Procedure

Cahn electrobalance was used to measure sorption.

Source and Purity of Materials:

PBLG: prepared by benzylation of *L*-glutamic acid with subsequent polymerization. The degree of polymerization was always 1200, except the sample cast from ethylene dichloride where it was equal to 550. Heat treatment was performed at 413 K for several hours.

Estimated Error:

Weight determination accuracy: ±10 mg for 50–100 mg samples.
Precision in T: ± 0.5 K.

References:

[1] T. H. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes* (New York, 1964).
[2] T. M. Prausnitz, J. Phys. Chem. **66**, 640 (1962).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(γ-benzyl-*L*-glutamate) (PBG); [25014-27-1] (LII)

Original Measurements:

S. Vivatpanachart, Y. Tsujita, and A. Takizawa, Makromol. Chem. **182**, 1197 (1981).

Variables:

T/K=283
p/kPa=6.5–46

Prepared By:

S. M. Shishatskii

Experimental Data

The sorption isotherms can be presented by the Langmuir equation:

$$p/n = 1/ab + p/b,$$

where p is pressure and n is the volume of carbon dioxide in cm^3(STP)/mol of residue. The parameters have the following values:

$$b = 0.065\ \mathrm{cm^3(STP)/residue},\quad a = 250\ \mathrm{cm\ Hg^{-1}}.$$

Auxiliary Information

Method/Apparatus/Procedure

The method of sorption determination was the same as described in Ref. 1.

Source and Purity of Materials:

Racemic PBG was obtained by dissolution of equal amounts of *L* and *D* forms of the polymer. Both forms were prepared by polymerization of corresponding *N*-carboxyanhyrides.

Estimated Error:

No information given.

References:

[1] H. Kodama, Y. Tsujita, and A. Takizawa, J. Macromol. Sci. Phys. **17**, 57 (1980).

3.32. Poly(β-Benzyl-*L*-Aspartate)—Carbon-Dioxide

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(β-benzyl-*L*-aspartate) (PBLA) (LIII)

Original Measurements:

H. Kodama, Y. Tsujita, and A. Takizawa, J. Macromol. Sci. Phys. B **17**, 57 (1980).

Variables:

T/K=303–313
p/kPa=9.3–43.9

Prepared By:

Yu. P. Yampol'skii

Experimental Data

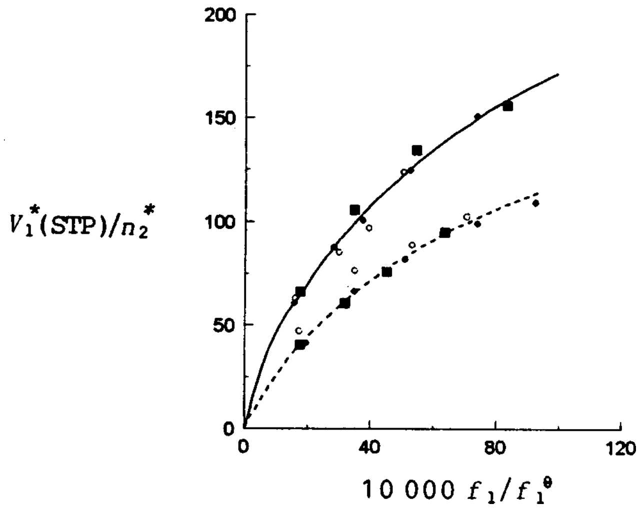


FIG. 77. Sorption isotherms of carbon dioxide in the α and ω forms of PBLA. Sorption=(vol. of gas at STP/cm^3)/mol of residue. (□) 303 K, (●) 308 K, (○) 313 K. Continuous line: α form; broken line: ω form.

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were performed by means of electrobalance Cahn RG.

Source and Purity of Materials:

PBLA: M_w=12 000.
Hexagonal or α-form: prepared by casting from 4 mass % $CHCl_4$ solution.
Tetragonal or ω-form: prepared by annealing of α-form films at 423 K.

Estimated Error:

No information given.

3.33. Polyamides (Nylons)—Various Gases

Components:

(1) Hydrogen chloride; HCl; [7647-01-0] Ammonia; NH_3; [7664-41-7]
(2) Poly(hexamethylene adipinamide) (Nylon 66); [32131-17-2] (LIV)

Original Measurements:

L. H. Reverson and L. E. Peterson, J. Phys. Chem. **60**, 1172 (1956).

Variables:

T/K=194.3–303.6
p/kPa=0–120

Prepared By:

Yu. P. Yampol'skii

Experimental Data

(For the following tables the original data were represented graphically.)

Relative pressure=ratio of partial pressure and its saturated vapor pressure at the temperature of the experiment.

TABLE 1. Sorption and desorption isotherms of ammonia in nylon at 241.9 and 303.6 K

T=241.9 K				T=303.6 K			
Sorption		Desorption		Sorption		Desorption	
Relative pressure	Solubility ($10^3 m_1/m_2$)	Relative pressure	Solubility ($10^3 m_1/m_2$)	Relative pressure	Solubility ($10^3 m_1/m_2$)	Relative pressure	Solubility ($10^3 m_1/m_2$)
0.004	0.85	0.004	1.37	0.07	7.65	0.06	16.62
0.010	1.36	0.047	3.82	0.22	15.58	0.55	42.34
0.016	1.80	0.069	4.45	0.43	26.39	0.78	48.31
0.021	2.06	0.092	5.10	0.65	37.94	0.89	52.50
0.027	2.45	0.111	5.64	0.81	46.65	—	—
0.034	2.74	—	—	0.89	52.50	—	—
0.046	3.19	—	—	—	—	—	—
0.057	3.64	—	—	—	—	—	—
0.076	4.31	—	—	—	—	—	—
0.089	4.96	—	—	—	—	—	—
0.111	5.64	—	—	—	—	—	—

TABLE 2. Sorption and desorption isotherms of hydrogen chloride in nylon at 194.3 K

Sorption		Desorption	
Pressure/kPa	Solubility ($10^3 m_1/m_2$)	Pressure/kPa	Solubility ($10^3 m_1/m_2$)
0.13	484	0	610
1.77	718	7.49	1022
4.19	789	32.29	1160
11.84	915	81.65	1376
26.19	1072	121.75	1633
51.66	1217	—	—
71.08	1306	—	—
98.89	1453	—	—
121.75	1633	—	—

TABLE 3. Sorption and desorption isotherms of hydrogen chloride in nylon at 273 and 293 K

T=273 K				T=293 K			
Sorption		Desorption		Sorption		Desorption	
Pressure/kPa	Solubility ($10^3 m_1/m_2$)	Pressure/kPa	Solubility ($10^3 m_1/m_2$)	Pressure/kPa	Solubility 1000 m_1/m_2	Pressure/kPa	Solubility ($10^3 m_1/m_2$)
0	81.7	0	289.2	0	142.4	0.34	307.9
0	183.8	7.23	400.1	0	257.2	2.93	347.1
4.13	395.1	—	—	5.17	360.4	—	—
12.57	445.4	—	—	14.3	392.9	—	—
26.35	480.7	—	—	33.42	416.1	—	—
54.09	505.0	—	—	66.83	442.6	—	—
91.29	524.3	—	—	108.00	464.7	—	—
111.45	530.9	—	—	—	—	—	—

Sorption isotherms of ammonia and hydrogen chloride at lower temperature exhibit hysteresis (sorption curves are below desorption curves). It vanishes for the sorption of hydrogen chloride at 273 and 293 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made using a McBain type microbalance described in Ref. 1.

Source and Purity of Materials:

NH_3: purity 99.9%, traces of water removed by melted sodium. HCl: liberated by dropping hydrochloric acid into sulfuric acid; water vapor removed by P_2O_5 trap, redistilled using dry CO_2/acetone bath. Nylon 6,6: undrawn bright yarn contained 0.02% of TiO_2.

Estimated Error:

No information given.

References:

[1] L. H. Ryerson and J. H. Honig, J. Amer. Chem. Soc. **75**, 3925 (1953).

Components:

(1) Neon; Ne; [7440-01-9] Argon; Ar; [7440-37-1] Hydrogen; H_2; [1333-74-0] Carbon dioxide; CO_2; [124-38-9]
(2) Polyundecaneamide; Nylon 11; [25035-04-5] (LV)

Original Measurements:

R. Ash, R. M. Barrer, and D. G. Palmer, Polymer **11**, 421 (1970).

Variables:

T/K=293.2–333.2
p/kPa=6.65–33.25

Prepared by:

Yu. P. Yampol'skii

Experimental Data

Solubility isotherms obeyed Henry's law; the solubility coefficients $S/(\mathrm{cm}^3/\mathrm{cm}^3\ \mathrm{atm})$ determined from their slopes are given below, as well as the enthalpies of solution $\Delta H/(\mathrm{kcal/mol})$

Gas	T/K	$S\ 10^2$	ΔH	Gas	T/K	$S\ 10^2$	ΔH
Ne	293.2	0.54	1.0	H_2	293.2	1.45	0.5
	303.2	0.56			303.2	1.48	
	313.2	0.62			313.2	1.50	
	323.2	0.65			323.2	1.58	
	333.2	0.66			333.2	1.63	
Ar	313.2	3.91	−0.4	CO_2	313.2	36.8	−3.2
	323.2	3.88			323.2	31.4	
	333.2	3.77			333.2	28.0	

Auxiliary Information

Method/Apparatus/Procedure

After the equilibrium was attained the remaining gas was swept by mercury. The measurement of the pressure of gas desorbed was performed by means of McLeod type gauge. Corrections for loss of gas by desorption during flushing process were introduced.

Source and Purity of Materials:

Nylon 11 was obtained from Griflex Ltd.
Gases (British Oxygen Co) were spectrally pure.

Estimated Error:

$\delta T = \pm 0.1$ K.
$\delta S/S = \pm 0.02$.

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Polyamide (Nylon 11); [25035-04-5] (LV)

Original Measurements:

E. G. Davis and M. L. Rooney, Kolloid Z.-Z. Polym. **249**, 1043 (1991).

Variables:

T/K: 298
p/kPa: 0–101.3

Prepared By:

A. K. Bokarev

Experimental Data

p/kPa	13.3	26.6	39.9	53.2	66.5	79.8	93.1
$C^*\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$	6.6	9.8	12.3	14.8	17.3	20.1	22.2

*Smoothed values taken from the graph by compiler.

Dual-mode sorption parameters for SO_2 in PA at 298 K

$k_D/\mathrm{cm}^3\ \mathrm{cm}^{-3}\ \mathrm{cm\ Hg}^{-1}$	$C'_H/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$	$b/(\mathrm{cm\ Hg})^{-1}$
0.248	5.8	0.169

Auxiliary Information

Method/Apparatus/Procedure

A modified McBain balance technique described in Ref. 1 was used to measure the solubility coefficient of sulfur dioxide in Nylon 11.

Source and Purity of Materials:

PA (Nylon 11): density 1.030 g/cm^3; from Societe Organico (France). $T_g = 319$ K.
Sulfur dioxide of 99.95% purity was used.

Estimated Error:

No estimates possible.

References:

[1] S. Prager and A. F. Long, J. Am. Chem. Soc. **73**, 4072 (1951).

3.34. Polyimide Kapton H—Carbon Dioxide, Methane, Sulfur Dioxide

Components:	Evaluator:
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polyimide Kapton H; [25036-53-7] (LVI)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April. 1994

Critical Evaluation:

Sorption of carbon dioxide in poly(4,4′-oxydiphenylene pyromellitimide) known under trademark Kapton H was studied in a number of works.[1–6] The majority of researchers dealt with commercial samples of this material. Only Okamoto *et al.*[5] investigated the specimens of this polymer prepared in the laboratory by imidization at different temperatures. The parameters of sorption isotherms obtained for this material differ from those measured for Kapton H. The table shows the selected dual mode sorption parameters for the system Kapton H–CO_2. It is seen that smooth temperature dependence is observed for all three model parameters and for the apparent solubility coefficient *S*.

Dual mode sorption parameters for the system Kapton H–CO_2

T/K	k_D	C'_H	b	$S=k_D-C'_Hb$	Ref.
308	0.594	23.5	0.300	7.6	3
323	0.630	13.3	0.394	5.9	5
323	0.650	12.8	0.42	6.0	2
353	0.436	8.5	0.239	2.5	5
353	0.40	8.9	0.23	2.4	2
383	0.28	6.1	0.16	1.3	2
383	0.292	5.7	0.153	1.2	5

Units: k_D and S/cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}.

A larger scatter is observed for the affinity parameter *b* especially at lower temperatures. The enthalpies corresponding to van't Hoff plots of k_D, b, and S are as follows:

$$\Delta H_D = -11.3 \text{ kJ/mol}$$

$$\Delta H_H = -11.9 \text{ kJ/mol}$$

$$\Delta H_S = -25.1 \text{ kJ/mol.}$$

The Langmuir capacity parameters decrease with temperature. It is noteworthy that temperature dependence is strongly nonlinear. so it is difficult to determine the temperature at which C'_H vanishes. However, it is probably lower than the glass transition temperature of this polymer for which the values higher than 600 K[2,3] and even 780 K [1] have been reported.

References:

[1] R. T. Chern, W. J. Koros, B. Yui, H. B. Hopfenberg, and V. T. Stannett, J. Polym. Sci., Plym. Phys. Ed. **22**, 1061 (1984).

[2] K. Tanaka, H. Kita, and K. Okamoto, Japan-US Polymer Symposium, 1985, p. 249.

[3] T. Uragami, H. B. Hopfenberg, W. J. Koros, D. K. Yang, V. T. Stannett, and R. T. Chern, J. Polym. Sci., Part B: Polym. Phys. **24**, 779 (1986).

[4] K. C. O'Brien, W. J. Koros, and G. R. Husk, Polym. Eng. Sci. **27**, 211 (1987).

[5] K. Okamoto, K. Tanaka, O. Yokoshi, and H. Kita, J. Polym. Sci., Part B: Polym. Phys. **27**, 643 (1989).

[6] H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, Polym. J. **21**, 681 (1989).

Components:	Original Measurements:
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polyimide Kapton H; [25036-53-7] (LVI)	R. Y. Chern, W. J. Koros, B. Yui, H. B. Hopfenberger, and V. T. Stannett, J. Polym. Sci., Polym. Phys Ed. **22**, 1061 (1984).

Variables:	Prepared By:
T/K=333 p/MPa=0–2.0 (0–20 atm)	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for carbon dioxide and methane in Kapton H at 333 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Based on pressure			
CO_2	0.380±0.054	12.280±1.48	0.296±0.023
CH_4	0.700±0.011	2.684±0.376	0.174±0.032
Based on fugacity			
CO_2	0.439±0.058	11.817±1.486	0.316±0.069
CH_4	0.073±0.011	2.653±0.384	0.175±0.034

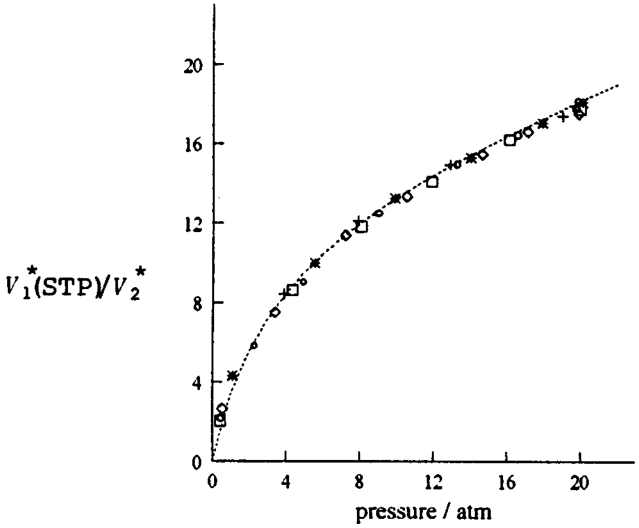


FIG. 78. Sorption isotherms of carbon dioxide in Kapton H at 333 K. Different symbols stand for different runs.

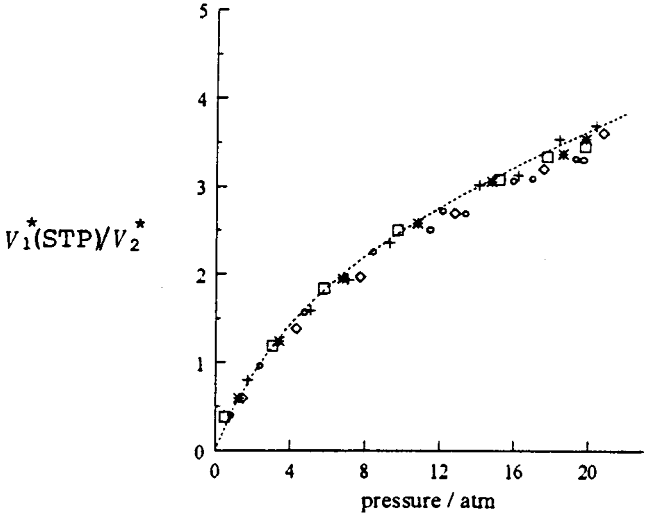


FIG. 79. Sorption isotherms of methane in Kapton H at 333 K. Different symbols stand for different runs.

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method of sorption measurement used was described in detail in Ref. 1. Each isotherm included several consecutive series of runs with stepwise pressure increase. The virgin films were degassed at 333 K for 120 h before measurement.

Source and Purity of Materials:

CO_2: Coleman-grade 99.999%.
CH_4: instrument-grade 99.7%.
Kapton H: E. I. DuPont Co.; no glass transition temperature revealed in DSC measurement up to 777 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polyimide Kapton H; [2536-53-7] (LVI)

Original Measurements:

K. Tanaka, H. Kita, and K. Okamoto, Japan–US Polymer Symposium, 1985, pp. 249–250.

Variables:

T/K = 323–383
p/MPa = 0–2.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters*

T/K	k_D /(cm^3(STP)/cm^3 atm)	C'_H/(cm^3(STP)/cm^3)	b/(atm^{-1})
323	0.65	12.8	0.42
353	0.4	8.9	0.23
383	0.28	6.1	0.16

(Sorption enthalpies: $\Delta H_D = -14.4$ kJ/mol. $\Delta H_H = -18.9$ kJ/mol.)
*Taken from a graph by the compiler.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured by the pressure decay method. The same isotherms were obtained for "as received" samples and the specimens preliminary exposed to 50 atm of carbon dioxide at 323 K for 24 h.

Source and Purity of Materials:

Polyimide Kapton H (Du Pont Co) had glass transition temperature >573 K. No other information given.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polyimide Kapton H; [25036-53-7] (LVI)	T. Uragami, H. B. Hopfenberg, W. J. Koros, D. K. Yang, V. T. Stannett, and R. T. Chern, J. Polym. Sci., Part B: Plym. Phys. **24**, 779 (1986).
Variables:	**Prepared By:**
T/K=308–328 p/kPa=0–78	A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide in Kapton Film at 308 and 318 K

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
308	0.461	18.19	0.287
318	0.389	13.29	0.275

TABLE 2. Equilibrium sorption isotherms of carbon dioxide in Kapton film (The original data were represented graphically)

T=308 K		T=318 K		T=328 K	
Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_2^*)
2.61	0.20	3.18	0.17	3.53	0.12
3.75	0.26	4.89	0.26	4.78	0.18
5.68	0.39	7.39	0.39	6.03	0.20
7.50	0.55	10.01	0.50	7.40	0.26
10.01	0.70	13.53	0.72	9.44	0.34
11.60	0.83	17.06	0.88	11.38	0.40
13.98	0.98	21.61	1.14	14.45	0.52
17.51	1.24	27.07	1.41	17.63	0.65
22.28	1.58	35.15	1.78	22.87	0.83
28.42	1.99	42.20	2.12	28.33	1.02
35.82	2.46	47.66	2.36	35.61	1.27
44.91	2.98	58.24	2.82	44.37	1.55
51.62	3.34	66.65	3.14	56.20	1.94
57.76	3.72	72.80	3.39	63.14	2.16
64.59	4.13	77.46	3.57	70.77	2.41
72.78	4.56	—	—	76.34	2.57
76.98	4.75	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

A quartz spring balance and experimental procedure similar to that reported in Ref. 1 were used to measure the sorption of CO_2 in Kapton.

Source and Purity of Materials:

CO_2: Air Products and Chemical Inc., purity 99.999%. Polyimide Kapton: E. I. du Pont de Nemours & Co., film density 1.42 g/cm^3, glass transition temperature in the range 620–720 K.[2]

Estimated Error:
No information given.

References:

[1] C. H. M. Jaques and H. B. Hopfenberg, Polym. Eng. Sci. **14**, 441 (1974).
[2] W. J. Wrasidlo, Macromol. Sci. Phys. **B6**, 559 (1972).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polyimide Kapton H; [25036-53-7] (LVI)	K. C. O'Brien, W. J. Koros, and G. R. Husk, Polym. Eng. Sci. **27**, 211 (1987).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–1.1	Yu. P. Yampol'skii

Experimental Data

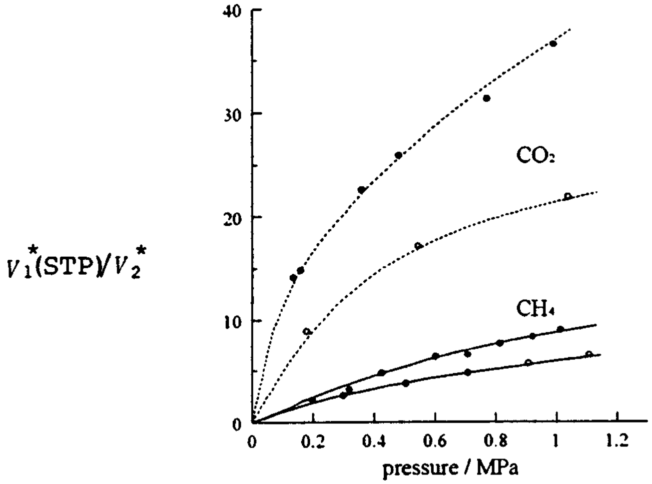


FIG. 80. Sorption isotherms in commercial Kapton H (○) and synthesized samples of polyimide (●) obtained by reaction of pyromellitic dianhydride and oxydianiline PMDA-ODA.

Auxiliary Information

Method/Apparatus/Procedure

A method based on the principle of material balance for all gas introduced into the cell was employed.[1,2]

Source and Purity of Materials:

Kapton H: density 1.430 g/cm^3, M_w=39 200. PMDA-ODA: density 1.402 g/cm^3.
M_w=36 900; structure confirmed by IR spectroscopy.

Estimated Error:
No information given.

References:

[1] E. S. Sanders, Ph.D. dissertation, N. C. State University, 1983.
[2] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Copoly(pyromellitic dianhydride-oxydianiline);
PMDA-ODA (polyimide Kapton H); [25036-53-7] (LVI)

Original Measurements:

K. C. O'Brien, W. J. Koros, and G. R. Husk, J. Membr. Sci. **35**, 217 (1988).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0.1-1.4$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide and methane in PMDA-ODA at 308 K. (The original data were represented graphically)

CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.16	14.36	0.21	3.21
0.36	22.17	0.31	4.46
0.52	26.96	0.47	5.84
0.76	32.12	0.71	7.36
0.98	36.22	0.91	8.61
1.37	42.11	1.00	9.07
—	—	1.12	9.80

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out using a single transducer apparatus described in Ref. 1.

Source and Purity of Materials:

PMDA-ODA: polymerization performed in dimethylacetamide at 288–293 K to form polyamic acid precursor according to standard procedure.[2] The polyamic acid solution was wet cast on a glass substrate heated for 1 h at 353 K under Ar to remove the solvent and then imidized by a two-step cure under vacuum (24 h at 483 K and 4 h at 553 K). The polymer studied did not reveal a glass transition temperature at temperatures up to 750 K. Density was 1.402 g/cm^3.

Estimated Error:

Relative precision of solubilities: 5%.

References:

[1] S. E. Sanders, Ph.D. dissertation, NC State University, 1983.
[2] C. E. Scroog, A. L. Endrey, S. V. Abravio, C. E. Berro, W. M. Edwards, and K. L. Olivier, J. Pol. Sci., Part A **3**, 1373 (1965).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polyimide (PMDA-ODA) (Kapton H); [25036-53-7] (LVI)

Original Measurements:

K. Okamoto, K. Tanaka, O. Yokoshi, and H. Kita, J. Polym. Sci., Part B: Polym. Phys. **27**, 643 (1989).

Variables:

$T/\mathrm{K}=323-383$
$p/\mathrm{MPa}=0-2.7$

Prepared By:

S. M. Shishatskii

Experimental Data

Dual mode sorption parameters for carbon dioxide in polyimide films

Sample	T/K	k_D /cm^{-3}(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Imidization at 473 K	323	0.900	24.2	0.375
	353	0.599	17.7	0.206
	383	0.424	12.0	0.133
Imidization at 673 K	353	0.444	10.6	0.226
Kapton-H	323	0.630	13.3	0.394
	353	0.436	8.5	0.239
	383	0.292	5.7	0.153

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay method was used for sorption measurements. The cell employed was similar to the one described in Ref. 1.

Source and Purity of Materials:

Polyimide was obtained by condensation of pyromellitic acid dianhidride and oxydiphenylenediamine with subsequent thermal imidization at 473 and 673 K. These samples and commercial polyimide Kapton H (Toray-DuPont Inc.) had the following densities: 1.405, 1.429, and 1.431 g/cm^3, respectively. No information given on carbon dioxide purity.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed., **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Copoly(pyromellitic dianhydride-oxydianiline)
PMDA-ODA (polyimide Kapton H); [25036-53-7] (LVI)

Original Measurements:

H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, Polymer J. **21**, 681 (1989).

Variables:

$T/\mathrm{K}=298$
$p/\mathrm{kPa}=0-1.200$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Table 1. Dual mode sorption parameters as a function of imide content (%) for CO_2 in polyimide films. (The original data were represented graphically.

%	k_D /cm^3(STP) cm^{-3} cm Hg^{-1}	C_H'/cm^3(STP) cm^{-3}	b/cm Hg^{-1}
3.62	0.0596	2.14	0.0047
34.76	0.0810	72.84	0.0061
40.61	0.0872	273.54	0.0072
51.28	0.0956	211.76	0.0073
57.93	0.0922	175.26	0.0075
100	0.0720	34.44	0.0084

Table 2. Sorption isotherms of CO_2 in the films imidized for various periods at 423 K (The original data were represented graphically)

Pressure/kPa	Sorption (V_1^*/(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*/(STP)/V_2^*)	Pressure/kPa	Sorption (V_1^*/(STP)/V_2^*)
Film not imidized					
49	3.08	400	15.97	800	25.54
97	5.32	501	18.67	900	27.33
199	9.37	596	20.97	—	—
301	12.67	696	23.17	—	—
Film imidized for 50 h					
68	6.47	534	21.43	1052	30.45
135	9.91	665	24.03	1191	32.60
268	14.91	799	26.50	—	—
398	18.20	906	28.36	—	—
Film imidized for 100 h					
134	12.62	533	25.97	910	34.09
295	19.18	665	29.01	1056	36.68
399	22.55	782	31.74	1174	38.47
Film imidized for 200 h					
64	9.94	553	27.85	1044	37.44
135	13.88	667	30.46	1178	39.54
264	19.82	800	33.25	—	—
400	23.87	924	35.41	—	—
Film imized for 400 h					
132	14.89	519	28.62	936	37.48
266	20.83	660	31.72	1048	39.46
395	24.94	791	34.89	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption weasurement was carried out by Cahn 2000 electromicro-balance.

Source and Purity of Materials:

CO_2: purity 99.9%.
Polyimide: prepared by imidization of the polyamide produced by the reaction of pyromellitic acid dianhydride with 4,4′ diaminodiphenyl ether in *N*-methylpyrrolidone solution. Imidization was carried out at 423 K for 50–400 h *in vacuo*.
An additional sample with 100% imide content was also studied. For the thermally treated samples, the imide content lay in the range 35%–58%.
T_g of unimidized polymer and polyimide were equal to 428 and 683 K, respectively.

Estimated Error:

No information given.

Components:

(1) Sulfur dioxide; SH$_2$; [7446-09-5]
(2) Polyimide Kapton; [25036-53-7] (LVI)

Original Measurements:

W. J. Koros, C. J. Patton, R. M. Felder, and S. J. Fincher, J. Polym. Sci., Polym. Phys. Ed. **18**, 1485 (1980).

Variables:

T/K: 298
p/kPa: 0–75

Prepared By:

A. K. Bokarev

Experimental Data

Solubility of SO$_2$ in Kapton at 298 K*

p/atm	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
C/cm^3(STP) cm^{-3}	18.1	24.2	28.1	32.3	35.6	39.3	42.8	46.0

* Smooth values taken from the graph by compiler.

Dual mode sorption parameters of SO$_2$ sorption in Kapton film at 298 K

k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0.389	13.29	0.275

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments was described earlier.[1]

Source and Purity of Materials:

The polyimide Kapton (E.I. du Pont de Nemours Co.) had density 1.42 g/cm^3, and the glass transition temperature 600 K. The SO$_2$ was obtained from Air Products and Chemical, Inc., at purity of 99.9%.

Estimated Error:

No information given.

References:

[1] C. H. M. Jaques and H. B. Hopfenberg, Polym. Eng. Sci. **14**, 441 (1974).

Components:

(1) Sulfur dioxide; SO$_2$; [7446-09-5]
(2) Polyimide Kapton H; [25036-53-7] (LVI)

Original Measurements:

R. M. Felder, C. J. Patton, and W. J. Koros, J. Polym. Sci., Polym. Phys. Ed. **19**, 1895 (1981).

Variables:

T/K=298–308
p/kPa=0–80

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for sulfur dioxide in polymide Kapton H

T/K	k_D /cm^3(STP) cm^3 atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
298	32.51	21.29	20.40
308	28.48	16.78	18.06
318	21.94	14.22	16.31
328	18.71	11.11	16.02

The following parameters of temperature dependence of k_D and b are reported:

$$k_D = k_{D_0}\ \exp[3.7(\text{kcal mol}^{-1})/RT]$$

$$b = b_0\ \exp[1.6(\text{kcal mol}^{-1})/RT].$$

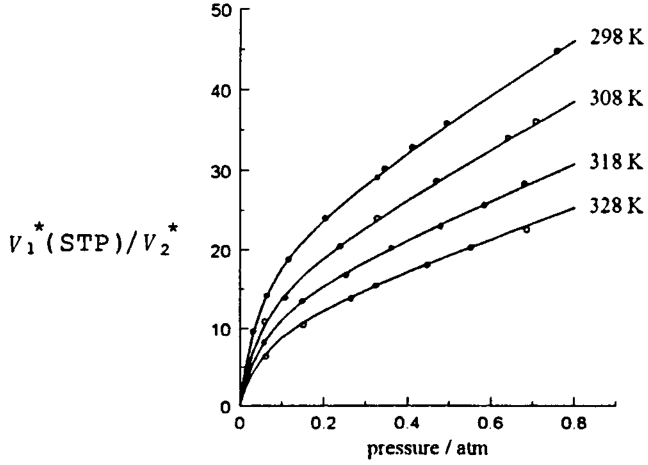


FIG. 81. Sorption isotherms of sulfur dioxide in polyimide Kapton H.

Auxiliary Information

Method/Apparatus/Procedure

A quartz spring balance was used to measure the sorption.

Source and Purity of Materials:

Kapton H: DuPont Co, density 1.42 g/cm^3.

Estimated Error:

No information given.

3.35. Polimide Upilex R—Carbon Dioxide

Components:	Evaluator:
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polyimide Upilex R; [26615-45-2] (LVII)	Yu. P. Yampol'skii, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, April, 1994

Critical Evaluation:

Three investigations are available on sorption of CO_2 in the polyimide obtained from 3.3′, 4,4′-biphenyltetracarboxydianhydride and 4.4′-oxydianiline known under the tradename Upilex R.[1–3] The authors studied commercial samples of Upilex R, but in one case specimens synthesized and pretreated under different conditions were investigated as well.[3] For the temperature range 308–383 K and at pressures up to 3 MPa, the sorption isotherms can be described by parameters shown in the table which are based on data reported in two papers[1,3] by the same group. The results of Sada *et al.*[2] are somewhat different, particularly at lower temperatures.

Selected dual mode sorption parameters for the system Upilex R–CO_2

T/K	k_D	C'_H	b	$S=k_D+C'_Hb$	Ref.
308	0.596	12.0	0.478	6.3	3
323	0.50	8.6	0.44	4.3	1
323	0.456	10.3	0.348	4.0	3
353	0.335	5.9	0.252	1.8	3
353	0.35	5.0	0.30	1.8	1
383	0.254	3.4	0.162	0.8	3
383	0.25	3.0	0.19	0.8	1

Units: k_D and S/cm^3(STP) cm^{-3} atm^{-1}; C'_H/cm^3(STP) cm^{-3}; b/atm^{-1}.

Figures 82–84 show the temperature dependences of S, b, and k_D, respectively.

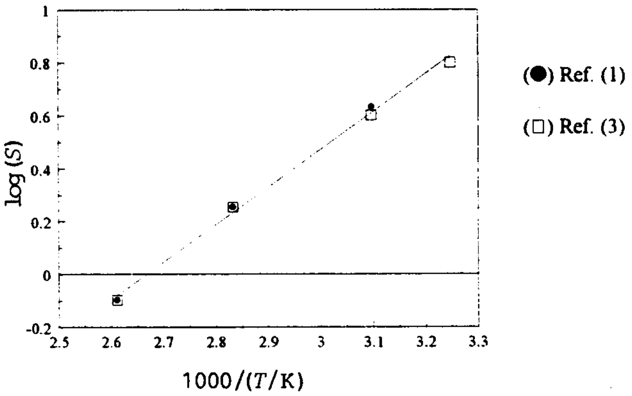


FIG. 82. Temperature dependence of apparent solubility coefficient S/(cm^3(STP) cm^{-3} atm^{-1}).

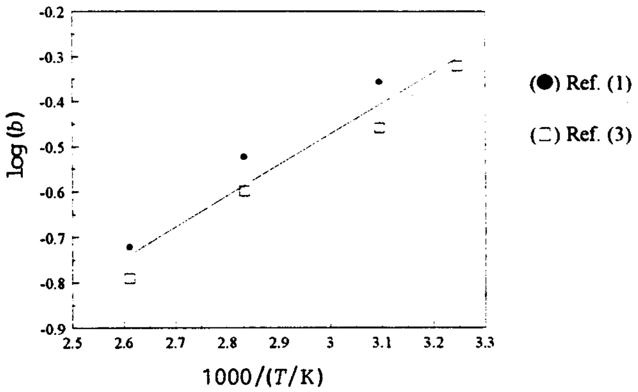


FIG. 83. Temperature dependence of the affinity parameter b/(atm^{-1}).

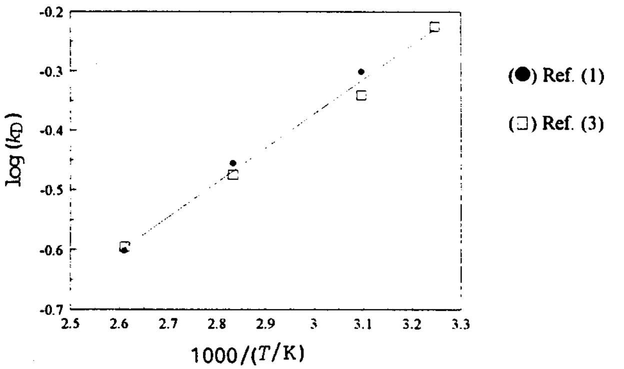


FIG. 84. Temperature dependence of Henry's law solubility coefficient k_D /(cm^3(STP) cm^{-3} atm^{-1}).

A least squares treatment of the temperature dependence of k_D , b, and S resulted in the following values of enthalpies:

$$\Delta H_D = -11.10 \text{ kJ/mol}$$

$$\Delta H_H = -13.13 \text{ kJ/mol}$$

$$\Delta H_S = -27.35 \text{ kJ/mol.}$$

The temperature dependence of Langmuir capacity adsorption parameter C'_H shows that it vanishes in the vicinity of 450 K or at temperatures much lower than the glass transition temperature of this polymer. The dual mode sorption parameters can be found based on fugacity instead of pressure.[2] The values calculated in two cases do not differ greater than by 10%, although the enthalpies ΔH_D and ΔH_H are greater when the parameters are found via fugacity.

A study of the effects of pretreatment of the films indicated[3] that the presence of the solvent led to the increase in the apparent solubility coefficient, while the annealing resulted in the opposite effect.

References:

[1] K. Tanaka, H. Kita, and K. Okamoto, Japan–US Polymer Symposium, 1985, p. 249.

[2] E. Sada, H. Kumazawa, and P. Xu, J. Appl. Polym. Sci. **35**, 1497 (1988).

[3] K. Okamoto, K. Tanaka, H. Kita, A. Nakamura, and Y. Kusuki, J. Polym. Sci., Part B: Polym. Phys. **27**, 1221 (1989).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polyimide Upilex R; [26615-45-2] (LVII)	K. Tanaka, H. Kita, and K. Okamoto. Japan–US Polymer Symposium, 1985, pp. 249–250.
Variables:	**Prepared By:**
T/K=323–383 p/MPa=0–2.0	Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters*

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
323	0.50	8.6	0.44
353	0.35	5.0	0.30
383	0.25	3.0	0.19

*Read by the compiler from the plot.

Sorption enthalpies: $\Delta H_D = -12.3$ kJ/mol, $\Delta H_H = -15.7$ kJ/mol.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured by the pressure decay method. The same isotherms were obtained for ''as received'' samples and the specimens preliminary exposed to 50 atm of carbon dioxide at 323 K for 24 h.

Source and Purity of Materials:

Polyimide Upilex R (Ube Industries) had the glass transition temperature 558 K.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Polyimide Upilex R; [26615-45-2] (LVII)	E. Sada, H. Kumazawa, and P. Xu, J. Appl. Polym. Sci. **35**, 1497 (1988).
Variables:	**Prepared By:**
T/K=303–333 p/MPa=0–1.7	Yu. P. Yampol'skii

Experimental Data

Dual sorption parameters for carbon dioxide in Upilex polymide

T/K	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Based on pressure			
303	1.24	7.39	1.70
313	1.04	5.67	1.23
323	0.817	4.27	0.865
333	0.692	3.34	0.635
Based on fugacity			
303	1.35	6.93	1.91
313	1.12	5.28	1.35
323	0.875	3.95	0.954
333	0.736	3.09	0.683

Van't Hoff parameterrs ΔH_D from $k_D(T)$ and ΔH_H from $b(T)$ plots

Parameter	Pressure	Fugacity
ΔH_D /kJ. mol^{-1}	−16.6	−15.9
ΔH_H /kJ. mol^{-1}	−27.9	−29.0

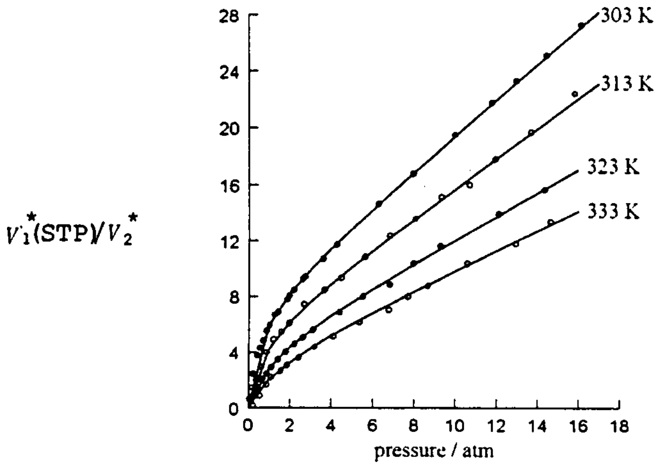


FIG. 85. Sorption isotherms of carbon dioxide in polyimide Upilex R.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured by pressure decay method. The apparatus was similar to that described in Ref. 1.

Source and Purity of Materials:

Polyimide Upilex R: Ube Industries; glass transition temperature 558 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polyimide from 3.3′, 4,4′-Biphenyltetracaboxylic dianhydride (BPDA) and 4.4′-Oxydianiline (ODA) (Upilex-R); [26615-45-2] (LVII)

Original Measurements:

K. Okamoto, K. Tanaka, H. Kita, A. Nakamura, and Y. Kusuki, J. Poly. Sci.: Part B: Polym. Phys. **27**, 1221 (1989).
K. Okamoto, K. Tanaka, K. Yokoshi, K. Hidetoshi, and A. Nakamura.

Variables:

T/K=308–383
p/MPa=0–3.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameterrs for CO_2 in commercial and laboratory samples of BPDA-ODA polyimides

Sample	T/K	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
Upilex-R	308	0.596	12.0	0.478
	323	0.456	10.3	0.348
	353	0.335	5.9	0.252
	383	0.254	3.4	0.162
1	323	0.609	17.9	0.392
	353	0.449	10.6	0.236
	353	0.316	11.0	0.167
	383	0.327	7.0	0.140
2	353	0.267	4.7	0.216

Auxiliary Information

Method/Apparatus/Procedure

Apparatus and procedure of sorption measurement was similar to one described in Ref. 1

Source and Purity of Materials:

Films of the polymer prepared from BPDA and ODA in p-chlorphenol were cast from the same solvent, dried (373 K, 3 h), immersed in ethanol, dried once more at 443 K for 20 h (sample 1). Sample 2 was prepared by annealing it at 543 K, 3 h. Commercial Upilex-R (Ube Industries) had T_g=558 K, ρ =1.402 g/cc. Sample 1 had the same T_g .

Estimated Error:

No information given.

References:

[1] W. J. Koros, and D. R. Paul J. Polym. Phys., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2)Copoly(pyromellitic dianhydride-methylene dianiline); PMDA-MDA (LVIII)

Original Measurements:

K. C. O'Brien, W. J. Koros, and G. R. Husk, J. Membr. Sci, **35**, 217 (1988).

Variables:

T/K=308
p/MPa=0.2–1.3

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption of carbon dioxide and methane in PMDA-MDA at 308 K. (The original data were represented graphically)

CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.20	16.66	0.22	3.48
0.27	19.32	0.49	5.84
0.57	28.03	0.80	8.24
0.85	32.67	1.12	10.08
0.99	34.27	—	—
1.31	38.56	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out using a single transducer apparatus described in Ref. 1.

Source and Purity of Materials:

PMDA-MDA: polymerization performed in dimethylacetamide at 288–293 K to form polyamic acid precursor according to standard procedure.[2] The polyamic acid solution was wet cast on a glass substrate heated for 1 h at 353 K under Ar to remove the solvent and then imidized by a two-step cure under vacuum (24 h at 483 K and 4 h at 553 K).
T_g was not reached even though the polymer was heated to 750 K.
Density was 1.352 g/cm^3.

Estimated Error:

Relative precision of solubilities: ±5%.

References

[1] S. E. Sanders, Ph.D. dissertation, NC State University, 1983.
[2] C. E. Scroog, A. L. Endrey, S. V. Abravio, C. E. Berro, W. M. Edwards, and K. L. Olivier, J. Pol. Sci., Part A **3**, 1373 (1965).

3.36. Other Polyamides—Various Gases

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Copoly(pyromellitic dianhydride-isopropylidene dianiline); PMDA-IPDA (LIX)

Original Measurements:

K. C. O'Brien, W. J. Koros, and G. R. Husk, J. Membr. Sci. **35**, 217 (1988).

Variables:

T/K=308
p/MPa=0.1–1.7

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of carbon dioxide and methane in PMDA-IPDA at 308 K. (The original data were represented graphically)

CO_2		CH_4	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.15	14.35	0.22	3.86
0.46	35.63	0.59	9.90
0.88	47.54	1.03	13.46
1.31	55.91	1.50	16.26
1.63	63.02	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out using a single transducer apparatus described in Ref. 1.

Source and Purity of Materials:

PMDA-IPDA: polymerization performed in dimethylacetamide at 288–293 K to form polyamic acid precursor according to standard procedure.[2] The polyamic acid solution was wet cast on a glass substrate heated for 1 h at 353 K under Ar to remove the solvent and then imidized by a two-step cure under vacuum (24 h at 483 K and 4 h at 553 K).
T_g was not reached even through the polymer was heated to 750 K.
Density was 1.285 g/cm^3.

Estimated Error:

Relative precision of solubilities: ±5%.

References:

[1] S. E. Sanders, Ph.D. dissertation, NC State University, 1983.
[2] C. E. Scroog, A. L. Endrey, S. V. Abravio, C. E. Berro, W. M. Edwards, and K. L. Olivier, J. Pol. Sci., Part A **3**, 1373 (1965).

Components:

(1) Nitrogen; N_2; [7727-37-9] Methane; CH_4; [74-82-8]
(2) Copoly(pyromellitic dianhydride-isopropylidene dianiline); PMDA-IPDA (LIX)

Original Measurements:

T. H. Kim, W. J. Koros, G. R. Husk, and K. C. O'Brien, J. Appl. Polym. Sci. **34**, 1767 (1987).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.1$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms of methane and nitrogen in PMDA-IPDA at 308 K. (The original data were represented graphically)

CH_4		N_2	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*STP)/V_2^*)
0.60	10.01	0.29	1.55
1.05	13.62	0.47	2.29
1.53	16.44	0.55	2.54
2.02	18.47	0.76	3.36
—	—	0.83	3.70
—	—	1.17	4.84
—	—	1.51	5.99
—	—	1.81	6.84
—	—	2.09	7.51

Auxiliary Information

Method/Apparatus/Procedure

The pressure decay method of measurement of sorption was described in Ref. 1.

Source and Purity of Materials:

PMDA-IPDA: prepared by reaction of pyromellitic dianhydride with isopropylidene diamine. No details on synthesis or properties of the polymer are given.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyimides derived from hexafluoroisopropylidene dianhydrides and diamines (see formulas)

Original Measurements:

M. R. Coleman and W. J. Koros, J. Membr. Sci. **50**, 285 (1990).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=1.013$ (10 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficients $S/\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3$ atm of gases in polyimides

	Gases			
Polymer	O_2	N_2	CO_2	CH_4
6FDA-ODA	1.03	0.54	4.89	1.32
6FDA-MDA	0.82	0.46	3.96	1.18
6FDA-IPDA	0.90	0.50	4.24	1.20
6FDA-6FpDA	0.99	0.67	4.72	1.44
6FDA-6FmDA	0.61	0.35	2.89	0.81

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were made with a pressure decay cell described in Ref. 1

Source and Purity of Materials:

Polyimides from Hoechst-Celanesc Co. had the following characteristics:

Polymer	T_g K	ρ, g/cc
6FDA-ODA	577	1.432
6FDA-MDA	577	1.400
6FDA-IPDA	583	1.352
6FDA-6FpDA	593	1.466
6FDA-6FmDA	527	1.493

The gases had purity >99.97%.

Estimated Error:

No information given.

References:

[1] W. J. Koros and D. R. Paul, J. Polym. Sci., Polym. Phys. Ed. **14**, 1903 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polyimide Ultem; [61128-24-3] (LXVIII)

Original Measurements:

K. Okamoto, K. Tanaka, O. Yokoshi, K. Hidetoshi, and A. Nakamura, Intern. Congress on Membranes ICOM-87 1987, 9-P15, pp. 542–543.

Variables:

T/K: 353
p/MPa: 0–3.0

Prepared By:

Yu.P. Yampol'skii

Experimental Data

Dual-mode sorption parameters for carbon dioxide

k_D,/cm^3(STP)cm^{-3} atm^{-1}	C'_H,/cm^3(STP) cm^{-3}	b/atm^{-1}
0.527	6.1	0.286

Auxiliary Information

Method/Apparatus/Procedure

Equilibrium sorption was measured by the pressure decay method using a dual-volume sorption cell.

Source and Purity of Materials:

Commercial sample of Ultem-1000 (General Electric Co) had a density 1.289 g/cm^3, glass transition temperature 488 K, and had an amorphous structure.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polyimide: product of biphenyltetracarboxylic dianhidride and sulfonodianiline; (BPDA-SDA)

Original Measurements:

K. Okamoto, K. Tanaka, O. Yokoshi, K. Hidetoshi, and A. Nakamura, Intern. Congress on Membranes ICOM-87, 1987, 9-P15, pp. 542–543.

Variables:

T/K: 353
p/MPa: 0–2.5

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual-mode sorption parameters for carbon dioxide

k_D ,/cm^{-3}(STP) cm^{-3} atm^{-1}	C'_H,/cm^3(STP) cm^{-3}	b/atm^{-1}
0.647	19.8	0.279

Auxiliary Information

Method/Apparatus/Procedure

Equilibrium sorption was measured by the pressure decay method using a dual-volume sorption cell.

Source and Purity of Materials:

Polyimide BS-1 had the following characteristics: density 1.417 g/cm^3, glass transition temperature 623 K.

Estimated Error:

No information given.

Components:

(1) Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polyetherimide (PEI); [61128-24-3] (LXXI)

Original Measurements:

T. A. Barbari, W. J. Koros, and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **26**, 729 (1988).

Variables:

T/K=308
p/MPa=0–2.3

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual-mode sorption parameters for various gases in polyetherimide at 308 K

Gas	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
CO_2	0.758	25.02	0.366
CH_4	0.207	7.31	0.136
N_2	0.063	4.15	0.045

TABLE 2. Sorption isothems of various gases in polyetherimide at 308 K (The original data were represented graphically)

CO_2		CH_4		N_2	
Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)	Pressure/MPa	Sorption (V_1^*(STP)/V_2^*)
0.19	10.88	0.12	1.12	0.27	0.65
0.24	12.85	0.24	2.10	0.34	0.81
0.27	14.26	0.29	2.51	0.40	0.83
0.33	15.38	0.37	3.08	0.45	0.98
0.56	20.05	0.45	3.59	0.71	1.44
0.64	21.83	0.67	4.78	0.77	1.59
0.70	23.23	0.81	5.35	0.88	1.65
0.78	23.79	0.90	5.81	0.94	1.78
0.98	26.96	1.07	6.55	1.14	2.11
1.08	28.17	1.14	6.59	1.25	2.24
1.16	29.10	1.25	7.29	1.34	2.26
1.25	29.75	1.29	7.17	1.42	2.35
1.45	32.17	1.48	7.98	1.59	2.70
1.55	33.10	1.57	8.15	1.75	2.93
1.64	33.93	1.66	8.53	1.79	2.85
1.72	34.39	1.79	8.69	1.89	2.94
1.93	36.43	1.89	9.15	2.26	3.39
2.02	37.36	2.06	9.60	2.35	3.52
2.20	38.37	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

The sorption apparatus and procedures used in the present sorption experiments are the same as described earlier.[1]

Source and Purity of Materials:

Gas: purity>99.99% (chromatographic quality).
PEI (Ultem): General Electric Co., density 1.28 g/cm^3, glass transition temperature 488 K.

Estimated Error:

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Helium; He; [7440-59-7] Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(amide aminoacid) 6FDA-TADPO; [132634-94-7] (LXVII)

Original Measurements:

D. R. B. Walker and W. J. Koros, J. Membr. Sci. **55**, 99 (1991).

Variables:

T/K=308
p/MPa=0.3–1.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficient S/cm^3(STP)/cm^3 atm

He	N_2	O_2	CO_2	CH_4
0.058	0.33	0.56	3.05	0.8

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay method and apparatus was used.

Source and Purity of Materials:

The polymer was synthesized according to Ref. 1. It had a density 1.413 g/cc.
All the gases were Linde UHP (purity more than 99.97%).

Estimated Error:

No information given.

References:

[1] R. T. Foster and C. S. Marvel, J. Polym. Sci., A **3**, 417 (1965).

3.37. Polypyrrolone—Various Gases

Components:

(1) Helium; He; [7440-59-7] Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Polypyrrolone; [12634-94-7]

Original Measurements:

D. R. B. Walken and W. J. Koros, J. Membr. Sci. **55**, 99 (1991).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0.3-1.0$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility coefficient $S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^3\ \mathrm{atm}$

He	N_2	O_2	CO_2	CH_2
0.091	0.72±0.08	1.04	4.41	1.7

Auxiliary Information

Method/Apparatus/Procedure

Pressure decay method and apparatus was used.

Source and Purity of Materials:

The polymer was synthesized according to Ref. 1. It had a density 1.405 g/cc.
All the gases were Linde UHP (purity more than 99.97%).

Estimated Error:

No information given.

References:

[1] R. T. Foster and C.S. Marvel, J. Polym. Sci., A. **3**, 417 (1965).

3.38. Block Copolymers and Polymer Blends—Various Gases

Components:

(1) Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7] Carbon dioxide; CO_2; [124-38-9]
(2) Poly(4-vinylpyridine-co-acrylonitrile); [25232-41-1]

Original Measurements:

M. Yoshikawa, T. Ezaki, K. Sanui, and N. Ogata, J. Appl. Polym. Sci. **35**, 145 (1988).

Variables:

$T/\mathrm{K}=303$
$p/\mathrm{kPa}=0-80$ (0–0.8 atm)

Prepared By:

S. M. Shishatskii

Experimental Data

The solubility of gases in two statistical copolymers having a mole fraction of 4-vinylpyridine equal to 0.038 (copolymers I) and 0.098 (copolymer II) was studied.

TABLE 1. Dual mode sorption parameters and solubility coefficient, S, for various gases in the copolymers (I) and (II) at 303 K

Gas		$S/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}$	$k_D\ /\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}\ \mathrm{atm}^{-1}$	$C'_H/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$	b/atm^{-1}
N_2	(I)	6.92	—	—	—
	(II)	8.54	—	—	—
O_2	(I)	16.8	—	—	—
	(II)	18.2	—	—	—
CO_2	(I)	—	46.5	10.2	25.3
	(II)	—	52.6	7.5	44.9

TABLE 2. Sorption isotherms of various gases in the copolymers (I) and (II) at 303 K (The original data were represented graphically)

CO_2		N_2		O_2	
Pressure/kPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$	Pressure/kPa	Sorption $(V_1^*(\mathrm{STP})/V_2^*)$
(I)					
3.89	6.91	30.10	2.18	40.84	6.68
12.31	13.66	58.23	4.69	61.26	9.79
27.18	21.47	73.74	5.31	75.66	12.79
40.13	27.81	—	—	—	—
57.57	35.79	—	—	—	—
(II)					
4.26	7.31	24.98	2.17	35.71	6.55
11.63	11.77	40.52	3.12	53.18	9.95
26.37	21.16	63.97	5.27	65.95	11.94
40.85	28.74	—	—	—	—
57.11	38.52	—	—	—	—

Auxiliary Information

Method/Apparatus/Procedure

Solubility measurement was performed in a gravimetric sorption apparatus with a quartz spring. The films were cast from DMF solutions.

Source and Purity of Materials:

Poly(4-vinylpyridine-co-acrylonitrile): synthesized by the radical polymerization according to Ref. 1.
Copolymer I: glass transition temp. 407 K.
Copolymer II: glass transition temp. 377 K.

Estimated Error:

No information given.

References:

[1] M. Yoshikawa, S. Shudo, K. Sanui, and N. Ogata, J. Membr. Sci. **26**, 51 (1986).

Components:

(1) Nitrogen; N_2; [7727-37-9] Oxygen; O_2; [7782-44-7]
(2) Copoly(vinylidene cyanide-vinyl acetate) (CVC-VA); [9003-24-1]

Original Measurements:

H. Hachisuka, H. Kito, Y. Tsujita, A. Takizawa, and T. Kinoshita, J. Appl. Polym. Sci. **35**, 1333 (1988).

Variables:

$T/\mathrm{K}=298$
$p/\mathrm{MPa}=0.13-1.3$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters for nitrogen and oxygen in CVC-VA memberances at 298 K for different times of annealing at 433 K

Time of annealing		$10^4 k_D$ /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	$10^3 b$/cm Hg^{-1}
N_2	''as cast''	2.0	1.74	0.8
	5 h	2.0	1.70	0.8
	15 h	2.0	1.66	0.8
O_2	''as cast''	2.6	2.18	1.1
	5 h	2.6	2.12	1.1
	15 h	2.6	2.06	1.1

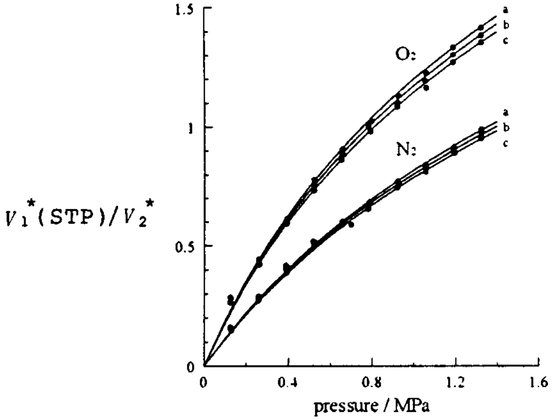


FIG. 86. Sorption isotherms of nitrogen and oxygen in CVC-VA at 298 K for different times of annealing at 433 K: (a) as cast; (b) 5 h annealing; (c) 15 h annealing.

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out by means of Cahn Electrobalance 2000 instrument. A correction for a buoyancy contribution was introduced. The films were cast from DMF.

Source and Purity of Materials:

Gases: purity>99.9%.
Alternating coplymer of VC and VA: Mitsubishi Petrochemical Co., amorphous polymer, glass transition temp. 449 K, density of as cast film, and ones anneled for 5 and 15 h equal to 1.212, 1.217, and 1.220 g/cm, respectively (at 433 K).

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Copoly(vinylidene cyanide-vinyl acetate) (CVC-VA); [9003-24-1]

Original Measurements:

H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, Polymer **29**, 2050 (1988).

Variables:

T/K=298
p/MPa=0–1.33

Prepared By:

Yu. P. Yampol'skii

Experimental Data

The effects of annealing time at 433 K on dual mode sorption parameters for carbon dioxide in CVC-VA at 298 K (taken from the plot by compiler)

Time of annealing/h	$10^2 k_D$ /cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	$10^3 b$/cm Hg^{-1}
0	1.65	17.3	3.65
1	1.50	16.4	3.65
5	1.50	15.0	3.65
10	1.48	14.3	3.65
15	1.48	14.2	3.65

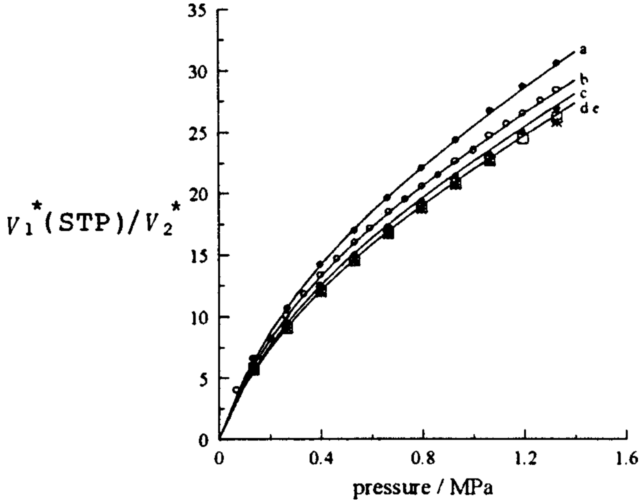


FIG. 87. Sorption isotherms of carbon dioxide in CVC–VA at 298 K for different times of annealing at 433 K: (a) as cast; (b) 1 h; (c) 5 h; (d) 10 h; (e) 15 h.

Auxiliary Information

Method/Apparatus/Procedure

Sorption was determined using gravimetric apparatus with Cahn Electrobalance 2000 instrument. A buoyancy correction was made.

Source and Purity of Materials:

Alternating copolymer VC-VA: amorphous polymer, intrinsic viscosity 4.9 dl/g, glass transition temperature of the films ''as cast'' 449 K.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Random copolymers styrene/methyl methacrylate (SMMA)

Original Measurements:

P. C. Raymond and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **28**, 2079 (1990).

Variables:

T/K=308
p/MPa=0–2.5 (0–25 atm)
Weight % MMA=20.5–88.0

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption parameters in SMMA coplymers

N	Weight % MMA	k_D /cm^3(STP)/cm^3 atm	C'_H/cm^3(STP)/cm^3	b/atm^{-1}
		Methane*		
1	20.5	0.132	3.06	0.085
2	58.5	0.145	2.03	0.156
3	88.0	0.181	1.72	0.152
		Carbon dioxide**		
1	20.5	0.539	10.7	0.182
2	58.5	0.812	10.5	0.249
3	88.0	1.07	13.8	0.193

*Unconditioned film never exposed to CO_2.
**The isotherms obtained after exposing to CO_2 at 25 atm for 24 h.

Auxiliary Information

Method/Apparatus/Procedure

The equipment and procedure for sorption measurement were the same as in Ref. 1.

Source and Purity of Materials:

For the copolymers 1, 2, and 3 the glass transition temperatures were 371, 375, and 378 K, respectively, and the densities 1.075, 1.132, and 1.168 g/cc.

Estimated Error:

No information given.

References:

[1] Y. Maeda and D. R. Paul, Polymer **26**, 2055 (1985).

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Copoly(trimethylsilylpropyne-phenylpropyne)
Poly(trimethylsilylpropyne) (PTMSP);
[87842-32-8]
Poly(1-phenyl-1-propyne) (PPHP)

Original Measurements:

T. Nakagawa, M. Sekiguchi, K. Nagai, and A. Higuchi, Int. Congress on Membranes (ICOM-90), Chicago, 1990, pp. 824–826.

Variables:

T/K=303
p/kPa=0–100
Copolymer composition: [TMSP]=90%; [PHP]=10%

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Sorption isotherms for three propyne polymers were reported. Their parameters are given below

Polymer	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP)/cm^{-3}	b/atm^{-1}
PTMSP	6.93	50.14	2.15
Compolymer	8.35	43.59	2.77
PPHP	5.84	12.47	5.48

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were done by means of Cahn electrobalance, model 2000.

Source and Purity of Materials:

The copolymer and PPHP were synthesized in the presence of a catalyst $TaCl_5-Ph_3Bi-H_2O$. The synthesis of PTMSP was described in Ref. 1.

References:

[1] K. Takada, H. Mituta, T. Masuda, and T. Higashimura, J. Appl. Polym. Sci. **30**, 1605 (1983).

Components:

(1) Hydrocarbons C_1-C_3
(2) Statistical copolymer of 2,6-dimethyl-1,4-phenylene oxide (97.5 mol %) and 2,6-diphenyl-1,4-phenylene oxide (2.5 mol %)

Original Measurements:

O. M. Ilinitch, G. L. Semin, M. V. Chertova, and K. I. Zamaraev, J. Membr. Sci. **66**, 1 (1992).

Variables:

T/K=293.2
p/MPa=0–100

Prepared By:

O. M. Ilinitch

Experimental Data

Solubility C/cm^3(STP) cm^{-3} of hydrocarbonds in the copolymer

Gas	p/kPa	C	Gas	p/kPa	C
Methane	28.0	0.6	Ethane	2.7	0.9
CH_4	34.7	0.4	C_2H_6	5.3	1.6
[74-82-8]	50.0	0.7	[74-84-0]	8.0	2.2
	66.6	1.2		10.7	2.6
	86.6	1.4		13.3	2.9
	96.0	1.5		17.3	3.4
				21.3	3.8
Propane	3.3	2.8		25.3	4.4
C_3H_8	6.3	3.6			
[74-98-6]	9.6	4.3	Propene	1.6	2.0
	13.3	5.1	C_3H_6	4.0	2.9
	18.7	5.8	[115-07-1]	6.7	4.0
	24.0	6.6		10.6	4.9
	29.3	7.3		14.0	5.6
	29.3	4.9		20.0	6.8
	33.3	5.5		26.7	7.6
	34.4	7.9		33.3	9.0
	40.0	8.4		38.7	9.6
	46.7	9.4		53.3	11.5
	53.3	10.2			
	61.3	11.2			

Auxiliary Information

Method/Apparatus/Procedure

The conventional McBain sorption spring balance was used.

Source and Purity of Materials:

The copolymer was prepared via oxidative copolycondensation of two monomers.
The purity of product 99.9%, it had density 1.10 g/cm^3 and T_g =754 K.
All the gases had a purity >99.9%.

Estimated Error:

$\delta T = \pm 0.1$ K; $\delta p = \pm 0.2$ kPa.
$\delta C/C = 0.1$ (compiler).

Components:

(1) Hydrocarbons C_1–C_3
(2) Statistical copolymer of 2,6-dimethyl-1,4-phenylene oxide (75 mol %) and 2,6-diphenyl-1,4-phenylene oxide (25 mol %)

Original Measurements:

O. M. Ilinitch, G. L. Semin, M. V. Chertova, and K. I. Zamaraev, J. Membr. Sci. **66**, 1 (1992).

Variables:

$T/\mathrm{K}=293.2$
$p/\mathrm{MPa}=0–100$

Prepared By:

O. M. Ilinitch

Experimental Data

Solubility $C/\mathrm{cm}^3(\mathrm{STP})\ \mathrm{cm}^{-3}$ of hydrocarbons in the copolymer

Gas	p/kPa	C	Gas	p/kPa	C
Methane	34.0	0.4	Propane	5.1	3.1
CH_4	53.3	0.8	C_3H_8	10.0	4.4
[74-82-8]	66.7	1.2	[74-98-6]	14.0	5.1
	82.6	1.5		20.0	5.9
				24.0	6.6
Ethane	7.3	1.1		29.3	7.2
C_2H_6	14.0	1.4		34.4	7.8
[74-84-0]	21.3	2.1		40.0	8.4
	26.9	2.5		46.6	9.4
	34.4	3.6		53.3	10.2
				61.3	11.2
Ethylene	8.0	1.0			
C_2H_4	12.0	1.3	Propylene	1.6	2.0
[74-85-1]	14.3	1.6	C_3H_6	4.0	2.9
	18.7	1.8	[115-07-1]	6.7	4.0
	22.0	2.1		10.6	4.9
	26.0	2.6		14.0	5.6
	34.7	3.2		20.0	6.8
				26.7	7.6
				33.3	9.0
				38.7	9.6
				53.3	11.5

Auxiliary Information

Method/Apparatus/Procedure

The conventional McBain sorption spring balance was used.

Source and Purity of Materials:

The copolymer was prepared via oxidative copolycondensation of two monomers.
The purity of product 99.9%, it had density 1.10 g/cm^3 and $T_g=483$ K.
All the gases had a purity >99.9%.

Estimated Error:

$\delta T=\pm 0.1$ K; $\delta p=\pm 0.2$ kPa.
$\delta C/C=0.1$ (compiler).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Copolyimide

Original Measurements:

K. Okamoto, K. Tanaka, O. Yokoshi, K. Hidetoshi, and A. Nakamura, Intern. Congress on Membranes ICOM-87, 9-P15, pp. 542–543.

Variables:

$T/\mathrm{K}=353$
$p/\mathrm{MPa}=0-2.5$

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual-mode sorption parameters for carbon dioxide

Sample	k_D /(cm^3(STP)/cm^3 atm)	C'_H/(cm^3(STP)/cm^3)	b/atm^{-1}
Cast	0.588	20.9	0.281
Annealed	0.573	18.5	0.249

Auxiliary Information

Method/Apparatus/Procedure

Equilibrium sorption was measured by the pressure decay method using a dual-volume sorption cell.

Source and Purity of Materials:

The polymers films (both cast and annealed at 603 K for 5 h) had the following characteristics: density 1.357 g/cm^3, glass transition temperature 623 K. Cast and annealed films had amorphous structure.

Estimated Error:

No information given.

Components:

(1) Sulfur dioxide; SO_2; [7446-09-5]
(2) Poly(dimethylsiloxane) (PDMS);
[9016-00-6]
(3) Poly(vinyltrimethyl silane) (PVTMS); [25036-32-2] (XV)

Original Measurements:

V. V. Volkov, A. K. Bokarev, and S. G. Durgaryan, Vyoskomol. Soedin, Ser. B **26**, 107 (1985).

Variables:

T/K=298
p/MPa=0–0.4

Prepared By:

S. M. Shishatskii

Experimental Data

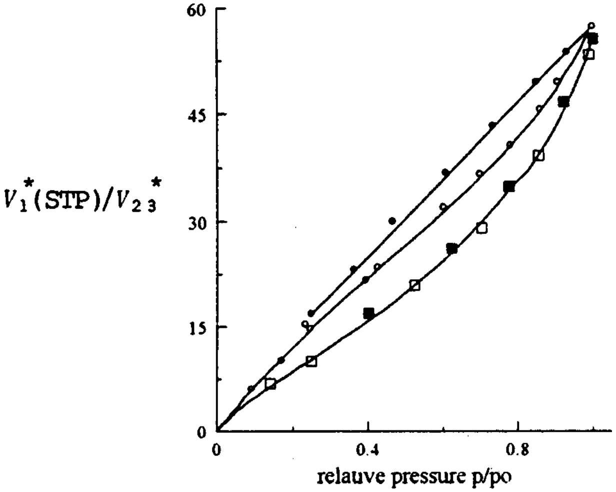


FIG. 88. Sorption (open symbols) and desorption (closed symbols) isotherms of sulfur dioxide in block-copolymers with mass % siloxane content of 13% (circles) and 42% (squares).

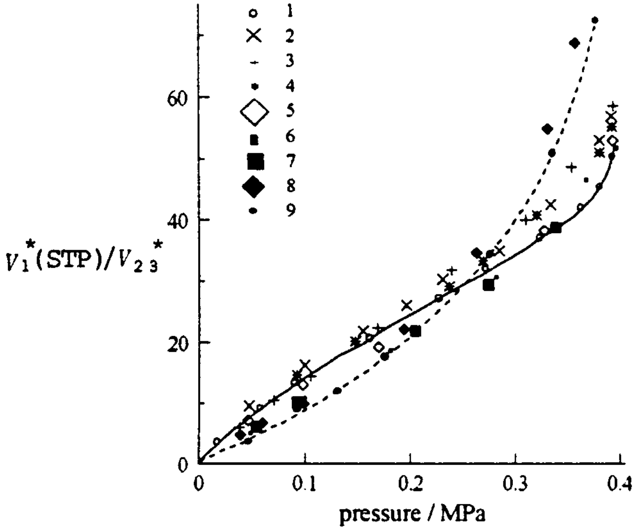


FIG. 89. Sorption isotherms of sulfur dioxide in silane-siloxane copolymers with mass % siloxane content of: 0% (1), 4% (2), 13% (3), 22% (4), 34% (5), 38% (6), 42% (7), 62% (8), 100% (9).

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured by means of a McBain balance using the technique described in Ref. 1.

Source and Purity of Materials:

PVTMS: M_n=200 000.
PDMS: M_n=150 000.
Silane-siloxane block-copolymers of the A-B type: prepared by anionic polymerization; M_n(silane block)=200 000, weight contents of siloxane block indicated in Fig. 89.

Estimated Error:

No information given.

References:

[1] V. V. Volkov, A. K. Bokarev, and S. G. Durgaryan, Vysokomol, Soedin., Ser. A. **26**, 1294 (1984).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Copolymer of ethylene-vinyl acetate (CEVA); [24937-78-8]
(3) Chlorosulphonated polyethylene Hypalon-48 (CPE)

Original Measurements:

J. A. Barrie and W. D. Webb, Polymer **30**, 327 (1989).

Variables:

T/K = 303–323 p/kPa = 0–33.25
CEVA conc. in blends, wt. %: 0–100

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Solubility in miscible blends of CEVA and CPE obeys Henry's law.

Solubility coefficients S $10^2/(cm^3(STP)/cm^3\ cm\ Hg)$ of CO_2 in the blends

	Temperature K				
CEVA, wt %	303	313	323	T_g /K	$\rho/(g/cm^3)$
100	2.00	1.73	1.48	257	0.98
90	1.87	1.59	1.38		
80	1.81	1.57	1.37		
70	1.71	1.44	1.26		
60	1.56	1.35	1.18		
50	1.52	1.32	1.17		
40	1.42	1.22	1.08		
30	1.33	1.15	1.00		
20	1.27	1.10	0.98		
0	1.10	0.96	0.85	293	1.27

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were performed using a vacuum electronic microbalance (Sartorius Instruments).

Source and Purity of Materials:

CEVA containing 45 wt % of vinyl acetate with $M_w = 37\ 700$ from Bayer Co and CPE (Hypalon 48) from DuPont, UK obtained by sulphochlorination of PE having $M_n = 23\ 900$ Cl content 44 wt % were studied. A small but not specified content of SO_2Cl groups in CPE is possible. Both polymers were shown by x-ray diffraction to be amorphous. Some phase separation is reported for the blends with CEVA content lower than 50% (DSC data).

Estimated Error:

No information given.

Components:

(1) Helium; He; [7440-59-7] Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(methyl acrylate) (PMA); [9003-21-8] (V)
(3) Poly(epichlorohydrin) (PECH); [24969-06-0]

Original Measurements:

J. S. Chiou, J. W. Barlow, and D. R. Paul, J. Appl. Polym. Sci. **30**, 1137 (1985).

Variables:

T/K: 308
p/MPa: 0–2.0

Prepared By:

A. K. Bokarev

Experimental Data

At 308 K sorption isotherms of simple gases in PMA/PECH blends are completely linear at pressures as high as 2 MPa, and sorption can be described by Henry's law.

Solubility coefficients $k_D \cdot 10^4/(cm^3(STP)/cm^3\ cm\ Hg)$

Gases	PMA	75 PMA/25 PECH	50 PMA/50 PECH	25 PMA/75 PECH	PECH
He	1.35	1.26	1.14	—	0.990
Ar	9.96	9.19	8.73	8.33	7.73
N_2	4.86	4.34	4.17	3.98	3.66
CH_4	19.4	17.6	16.6	16.4	15.6
CO_2	261.0	225.0	181.0	152.0	124.0

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and experimental procedure used for sorption measuring have been described elsewhere.[1]

Source and Purity of Materials:

The PMA (from Celanese Chemical Co.) had $M_w = 576\ 000$; $T_g = 291$ K; $\rho = 1.21$ g/cm^3.
The PECH (Hydrin 100) was obtained from B. F. Goodrich Co. $T_g = 251$ K; $\rho = 1.37$ g/cm^3.
Gases: no information.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)
(3) Styrene/acrylonitrile copolymer (CPSAN)

Original Measurements:

J. S. Chiou and D. R. Paul, J. Appl. Polym. Sci. **34**, 1037 (1987).

Variables:

T/K=308
p/MPa=0.2–2.6 (2–26 atm)

Prepared By:

S. M. Shishatskii

Experimental Data

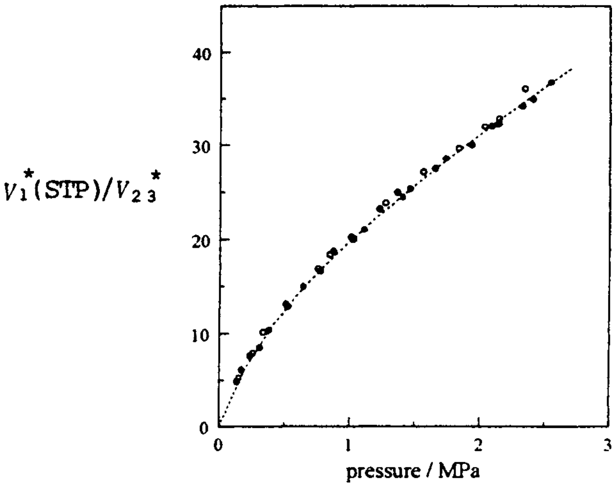


FIG. 90. Sorption of carbon dioxide was studied in homogeneous and phase separated blends PMMA/CPSAN (50/50 by mass). The composition of CPSAN is 28 mass % of acrylonitrile. The parameters of dual mode sorption isotherm for carbon dioxide in the blends at 308 K are $k_D=0.89$ $cm^3(STP)/cm^3$ atm; $C'_H=16.6$ $cm^3(STP)/cm^3$; $b=0.183$ atm^{-1}. Sorption isotherm of carbon dioxide in homogeneous (●) and phase-separated (○) PMMA/CPSAN blends.

Auxiliary Information

Method/Apparatus/Procedure

A pressure decay method was used but no details are given. The films cast from tetrahydrofuran had a morphology of homogeneous blends. Subsequent heating at 488 K resulted in phase separated blends.

Source and Purity of Materials:

PMMA: Rohm and Haas Plexiglas V(811). $M_w=105\,400$, $M_n=52\,400$, density 1.188 g/cm^3, glass transition temperature 379 K.
CPSAN: Union Carbide RMD-4511. $M_w=223\,000$, $M_n=88\,600$, density 1.080 g/cm^3, glass transition temperature 377 K.

Estimated Error:

No information given.

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)
(3) Poly(vinylidene fluoride) (PVF_2); [24937-79-9]

Original Measurements:

J. S. Chiou, Y. Maeda, and D. R. Paul, J. Appl. Polym. Sci. **30**, 4019 (1985).

Variables:

T/K=308
p/MPa=0–2.53 (0–25 atm)

Prepared By:

Yu. P. Yampol'skii

Experimental Data

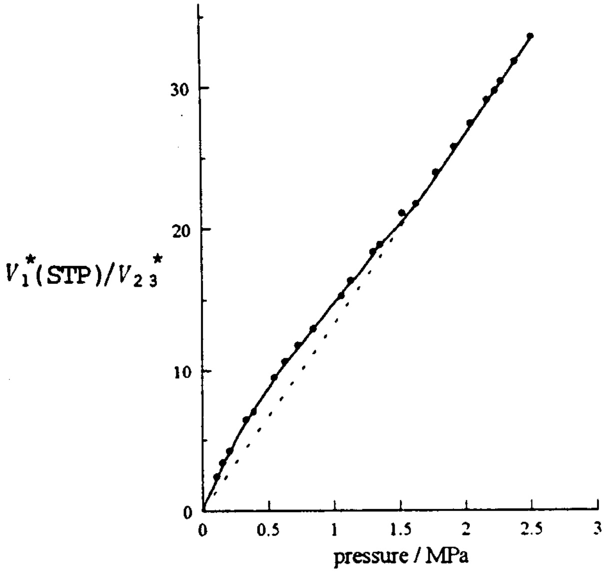


FIG. 91. Sorption isotherm of carbon dioxide in an amorphous blend containing 65% PMMA and 35% PVF_2 at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

Sorption isotherm was obtained using the dual-transducer cell design based on the pressure decay principle.

Source and Purity of Materials:

Polymers: conditioned at highest pressure of carbon dioxide before measurement, completely amorphous and miscible blend, glass transition temperature 335 K.

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI) (3) Poly(vinylidene fluoride) (PVF_2); [24937-79-9]	J. S. Chiou and D. R. Paul, J. Appl. Polym. Sci. **32**, 2897 (1986).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.5 (0–25 atm) mass % PVF=0–100	Yu. P. Yampol'skii

Experimental Data

The sorption isotherms for some blends (PVF_2 content in the range 35–60 mass %) showed an unusual form and could not be described by dual mode sorption model. A modified DMS model was proposed where for the Langmuir capacity parameter C'_H from the DMS model an equation was suggested:

$$C'_H = C'_{H0}(T_g - T)/(T_{g0} - T),$$

where C'_{H0} is initial Langmuir capacity parameter prior to any reduction in T_g due to CO_2 plastisization, T_{g0} is the glass transition temperature for the pure polymer. T_g is the glass transition temperature in the presence of sorbed gas, and T is the temperature of measurement, i.e., 308 K.

Sorption parameters for carbon dioxide in PMMA/PVF_2 blends*

PVF_2 mass %	Volume fraction of amorph phase α	From isotherm slope		From regression analysis		
		k_D	k_D/α	k_D	C'_{H0}/α	b
100	0.426	0.664	1.559	—	—	—
80	0.621	0.865	1.394	—	—	—
60	0.812	1.105	1.362	1.494	7.26	0.0859
50	0.886	1.215	1.371	—	—	—
40	0.953	1.283	1.346	1.403	8.15	0.101
35	0.971	1.319	1.358	1.417	10.9	0.126
20	1.0	—	—	1.352	16.3	0.103
0	1.0	—	—	1.409	25.6	0.0993

Units: α, dimensionless; k_D, $cm^3(STP)/cm^3$ atm; C'_{H0}, $cm^3(STP)/cm^3$; b, atm^{-1}.

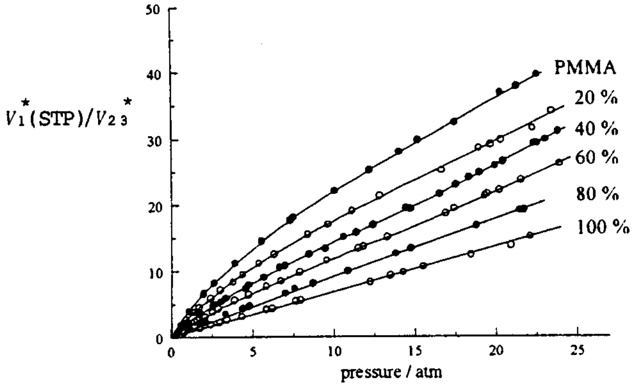


FIG. 92. Sorption isotherms of carbon dioxide in PMMA/PVF_2 blends at 308 K (mass % PVF_2).

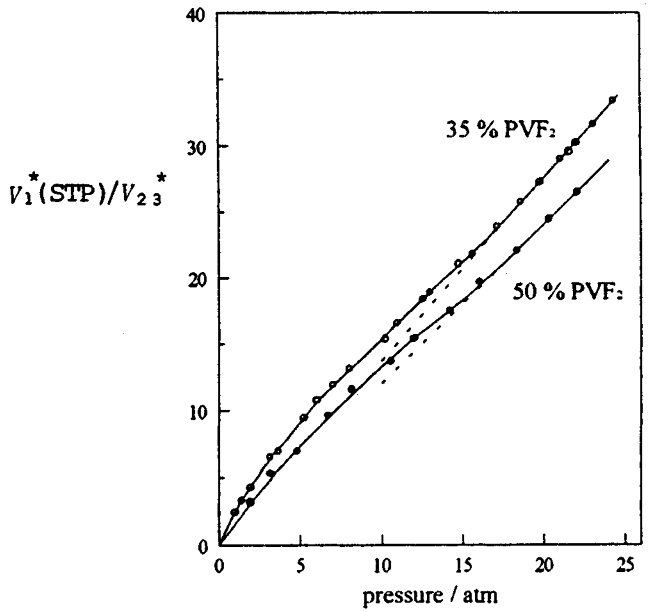


FIG. 93. Sorption isotherms of carbon dioxide in PMMA/PVF_2 blends at 308 K for 35 and 50 mass % of PVF_2.

Auxiliary Information

Method/Apparatus/Procedure

No details of the experimental procedure are given. Apparently, sorption is measured by pressure decay method.[1]

Source and Purity of Materials:

PMMA Rohm and Haas Co. (Plexiglas V(811)), fully amorphous, glass transition temp. 378 K.

PVF_2: Pennwalt Co. (Kynar 460 N), crystallinity 60%, melting point 433 K.

Blends: prepared as described in Ref. 2. Miscible blends were studied.

Estimated Error:

No information given.

References:3

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976)
[2] J. S. Chiou, J. W. Barlow, and D. R. Paul, J. Appl. Polym. Sci. **30**, 2633 (1985).

Components:

(1) Argon; Ar; [7440-37-1] Nitrogen; N_2; [7727-37-9] Carbon dioxide; CO_2; [124-38-9] Methane CH_4; [74-82-8]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)
(3) Poly(vinylidene fluoride) (PVF_2); [24937-79-9]

Original Measurements:

J. S. Chiou and D. R. Paul, J. Appl. Polym. Sci. **32**, 4793 (1986).

Variables:

$T/\mathrm{K}=308$
$p/\mathrm{MPa}=0-2.7$ (0–27 atm)
mass % PVF=0–100

Prepared By:

Yu. P. Yampol'skii

Experimental Data

TABLE 1. Solubility coefficients of various gases in PVF_2 at 308 K

Gas	Ar	N_2	CH_4
$S/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	0.0350	0.0206	0.0488

TABLE 2. Dual mode sorption parameters for various gases in PMMA at 308 K

Gas	$k_D\ /\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	$C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$	$b/\mathrm{atm^{-1}}$
Ar	0.1150	1.450	0.0480
N_2	0.0737	0.814	0.0301
CH_4	0.1820	3.620	0.0560

TABLE 3. Dual mode sorption parameters for argon in extruded PMMA/PVF_2 blends at 308 K.

PVF_2 mass %	$k_D\ /\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$	$C'_H/\mathrm{cm^3(STP)\ cm^{-3}}$	$b/\mathrm{atm^{-1}}$	$(k_D/\alpha)/\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-1}}$
100	0.0350	—	—	0.0779
90	0.0480	—	—	0.0857
80	0.0568	—	—	0.0849
60	0.0742	—	—	0.0817
40	0.0893	—	—	0.0893
20	0.1040	0.982	0.0345	0.1040
0	0.1150	1.450	0.0480	0.1150

α is the crystallinity of PVF_2 in the blend.

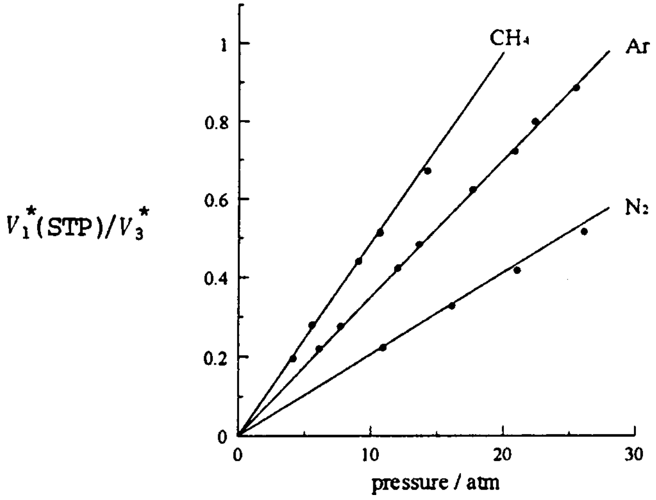


FIG. 94. Sorption isotherms of Ar, CH_4, and N_2 in PVF_2 at 308 K.

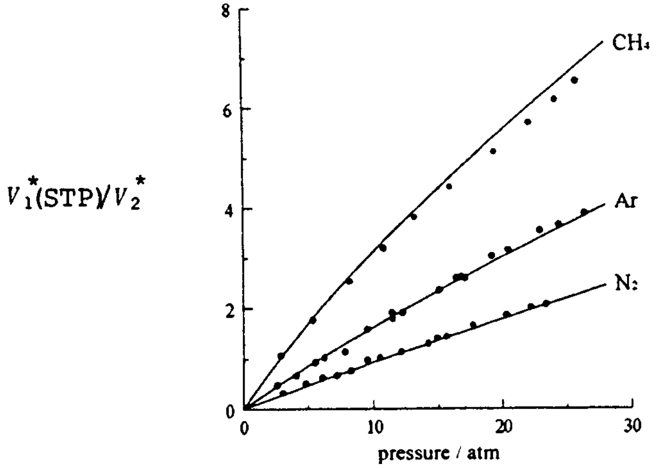


FIG. 95. Sorption isotherms of Ar, CH_4, and N_2 in PMMA at 308 K.

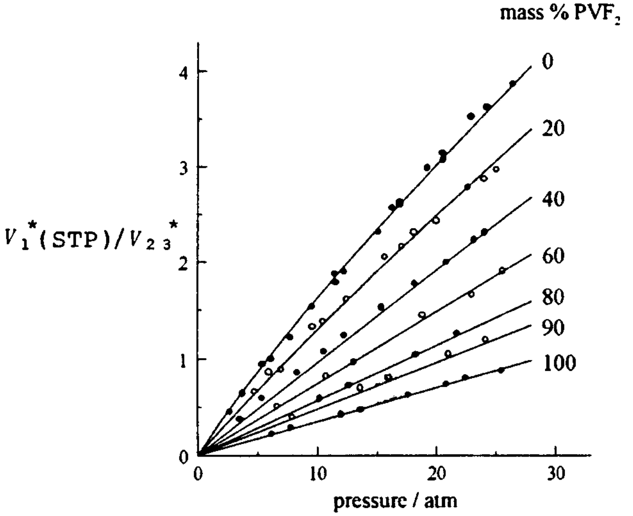


FIG. 96. Sorption isotherms of argon in PMMA/PVF$_2$ blends at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure were the same as described in Ref. 1.

Source and Purity of Materials:

PMMA: Rohm and Haas (Plexiglas V(811)), glass transition temp. 378 K, completely amorphous.

PVF$_2$: Pennwalt (Kynar 460N), crystallinity 60%, melting point 433 K.

Blends: films prepared by extrusion. Miscible blends were studied.

Estimated Error

No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **30**, 2633 (1985).

Components:

(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8]
(2) Poly(methyl methacrylate) (PMMA); [9011-14-7] (VI)
(3) Bisphenol chloral polycarbonate (BCPC); [31546-39-1] (XXX)

Original Measurements:

P. C. Raymond and D. R. Paul, J. Polym. Sci.: Part B: Polym. Phys. **28**, 2103 (1990).

Variables:

T/K=308
p/MPa=0–2.5

Prepared By:

V. I. Bondar

Experimental Data

Dual mode sorption parameters for carbon dioxide and methane in polymers at 308 K

PMMA Vol.%	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
Carbon dioxide (in conditioned polymers)			
0	0.718	14.9	0.271
28.0	0.736	14.8	0.240
53.9	0.778	15.7	0.190
77.8	1.03	11.9	0.245
100	1.20	15.6	0.172
Methane (in unconditioned polymers)			
0	0.130	6.64	0.088
28.0	0.116	6.92	0.069
53.9	0.144	4.58	0.077
77.8	0.133	4.60	0.061
100	0.199	1.53	0.153

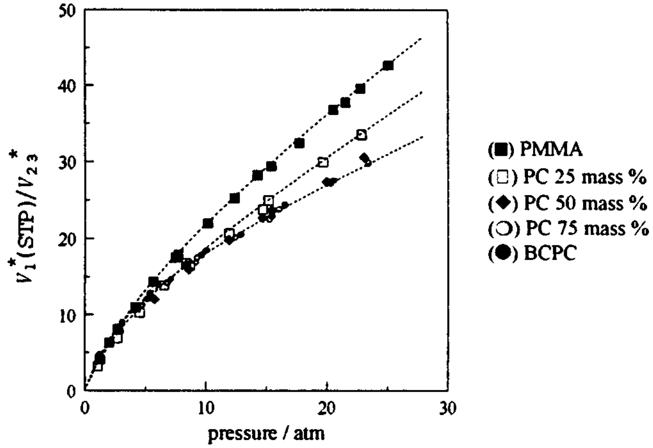


FIG. 97. Sorption isotherms of carbon dioxide in conditioned blends and homopolymers at 308 K.

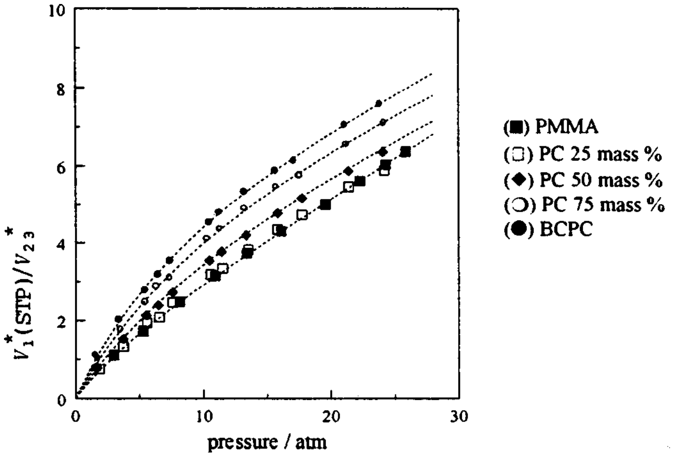


FIG. 98. Sorption isotherms of methane in unconditioned blends and homopolymers at 308 K.

Auxiliary Information

Method/Apparatus/Procedure:

A pressure decay method was used. Methane sorption was measured on samples that had not previously been exposed to CO_2. For CO_2 these measurements were preceded by conditioning the films at 25 atm of CO_2 for 24 h.

Source and Purity of Materials:

BCPC: General Electric Co.
PMMA: Rohm and Haas Co.

PMMAmass %	T_g /K	density/g cm^{-3}
0	437	1.392
25	413	1.336
50	401	1.285
75	386	1.235
100	379	1.188

Estimated Error:

No information given.

Components:

(1) Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-62] (IX)
(3) Poly(vinylmethyl ether) (PVME); [9003-09-2]

Original Measurements:

H. G. Spencer and J. A. Yavorsky, J. Appl. Polym. Sci. **28**, 2937 (1983).

Variables:

T/K=312–370
p/kPa=0–40
PS mass content/%=25–75

Prepared By:

A. K. Bokarev

Experimental Data

In the pressure range indicated above solubility obeys Henry's law. Temperature dependence for the solubility coefficient S of propane in PS/PVME blends is given by the equation:

$$S=S_0\ \exp(-\Delta H/RT).$$

TABLE 1. Mass content dependence for the solubility coefficient S of propane in PS/PVME blends at 353 K

PS content mass %	$-\Delta H$/(kJ/mol)	ln(S_0 /(cm^3(STP)/cm^3 cm Hg))	ln(S/(cm^3(STP)/cm^3 cm Hg))
25	10	−7.49	−3.99
50	7	−6.61	−4.36
75	5	−6.15	−4.54

TABLE 2. Temperature dependence of the solubility coeficient S of propane in PS/PVME blends

T/K	ln(S/(cm^3(STP)/cm^3 cm Hg))
PS 25 mass %	
328.3	−3.82
333.7	−3.73
346.4	−3.79
350.4	−4.08
358.7	−4.17
364	−4.06
PS 50 mass %	
324.9	−4.19
337.2	−4.29
361.3	−4.48
370.9	−4.46
PS 75 mass %	
313.6	−4.35
323.8	−4.49
333.2	−4.35
353.5	−4.59

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurements were carried out in a low pressure, constant-volume cell previously described.[1]

Source and Purity of Materials:

C_3H_8: Matheson, purity 99.99%.
PS, PVME: Polysciences, Inc.
PS: $M_w = 23\,000$; PVME: $M_w = 34\,000$.

PS/%	T_g /K	ρ/g, cm−3
25	253	—
50	275	1.052
75	303	1.060

Estimated Error:
No information given.

References:
[1] J. A. Yavorsky and H. G. Spencer, J. Appl. Polym. Sci. **25**, 2109 (1980).

Components:
(1) Propane; C_3H_8; [74-98-6]
(2) Polystyrene (PS); [9003-53-62] (IX)
(3) Poly(vinylmethyl ether) (PVME); [9003-09-2]

Original Measurements:
J. A. Yavorsky, Ph.D. dissertation, 1984.

Variables:
T/K = 278–374
p/kPa = 0–798

Prepared By:
A. K. Bokarev

Experimental Data

The PS/PVME blends studied contained 90.0% and 75.0% by weight PS. $M_s = 0.90$ and $M_s = 0.75$, respectively.

TABLE 1. Sorption isotherms of propane below 350 K in the copolymer blend for which $M_s = 0.90$ (The original data were represented graphically)

$T = 283$ K		$T = 303.5$ K		$T = 322$ K	
Pressure/kPa	Sorption (V_1^*(STP)/V_{23}^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_{23}^*)	Pressure/kPa	Sorption (V_1^*(STP)/V_{23})
28.83	0.80	31.97	0.47	32.66	0.28
70.22	1.30	75.92	0.98	78.92	0.50
79.17	2.81	185.78	2.75	172.72	1.44
167.26	3.06	353.37	5.19	172.07	1.67
239.05	6.22	378.07	7.15	306.54	2.28
299.18	5.68	710.15	11.39	368.64	4.08
—	—	791.00	12.15	745.61	5.89

Sorption isotherms above 350 K show a linear relationship, and the solubility coefficient is independent of pressure.

TABLE 2. Dual mode sorption parameters and solubility coefficient, S, for propane in the copolymer blend for which $M_s = 0.90$ (pressure range 0–798 kPa)

T/K	k_D 10^2/cm^3(STP) cm^{-3} cm Hg^{-1}	C_H'/cm^3(STP) cm^{-3}	b/cm Hg^{-1}	S/cm^3(STP) cm^{-3} cm Hg^{-1}
283	2.29% ± 9%	10.9% ± 15%	0.50% ± 35%	2.84% ± 10%
303.5	1.15% ± 19%	10.8% ± 35%	1.30% ± 53%	2.55% ± 9%
322	0.86% ± 12%	11.4% ± 22%	0.70% ± 44%	1.66% ± 12%
353	0.90% ± 6%	4.5% ± 50%	0.15% ± 100%	0.97% ± 10%
364	0.82% ± 12%	—	—	0.82% ± 12%
369	1.11% ± 9%	—	—	1.11% ± 9%

TABLE 3. Sorption isotherms of propane below 323 K in the co-polymer blend for which $M_s=0.75$ (The original data were represented graphically)

$T=278$ K		$T=293$ K		$T=308$ K	
Pressure/kPa	Sorption (V_1^*(STP)/V_{23})	Pressure/kPa	Sorption (V_1^*(STP)/V_{23})	Pressure/kPa	Sorption (V_1^*(STP)/V_{23})
14.2	1.07	6.45	0.38	6.04	0.13
31.83	2.24	10.30	0.58	6.86	0.24
62.01	5.20	22.19	1.16	10.47	0.42
—	—	26.45	1.06	13.37	0.41
—	—	46.51	2.46	15.44	0.29
—	—	57.04	2.64	16.86	0.50
—	—	—	—	18.81	0.59
—	—	—	—	22.72	0.94
—	—	—	—	31.42	1.06
—	—	—	—	55.68	2.21

Sorption isotherms above 323 K are linear in the pressure range studied, and the solubility coefficients are independent of pressure.

TABLE 4. Dual mode sorption parameters and solubility coefficient, S, for propane in the copolymer blend for which $M_s=0.75$ (pressure range 0–66 kPa)

T/K	k_D 10^2/ cm^3(STP) cm^{-3} cm Hg^{-1}	C'_H/cm^3(STP) cm^{-3}	b/cm Hg^{-1}	S/ cm^3(STP) cm^{-3} cm Hg^{-1}
278	6.40% ± 11%	3.2% ± 20%	2.15% ± 50%	13.29% ± 16%
293	4.00% ± 12%	2.2% ± 22%	1.80% ± 44%	7.99% ± 44%
308	3.50% ± 11%	2.1% ± 19%	0.55% ± 40%	6.79% ± 12%
323	2.40% ± 12%	1.4% ± 32%	0.35% ± 55%	4.33% ± 51%
323	2.40% ± 12%	1.4% ± 32%	0.35% ± 55%	4.33% ± 51%
333	3.06% ± 4%	—	—	3.06% ± 4%
343	2.49% ± 4%	—	—	2.49% ± 4%
353	1.99% ± 4%	—	—	1.99% ± 4%
364	1.89% ± 4%	—	—	1.89% ± 4%
374	1.65% ± 4%	—	—	1.65% ± 4%

The isotherms when $M_s=0.75$ Q and $M_s=0.75$ QA were linear.

TABLE 5. Solubility coefficient when $M_s=0.75$ Q

T/K	k_D 10^2/cm^3(STP) cm^{-3} cm Hg^{-1}
323	3.19% ± 8%
328	3.67% ± 4%
333	2.96% ± 4%
343	2.21% ± 4%
358	1.99% ± 4%

TABLE 6. Solubility coefficient when $M_s=0.75$ QA

T/K	k_D 10^2/cm^3(STP) cm^{-3} cm Hg^{-1}
323	2.45% ± 4%
327	3.14% ± 4%
338	2.71% ± 4%
358	2.00% ± 4%

Auxiliary Information

Method/Apparatus/Procedure

The equilibrium solubility of gases in the polymer was measured by a manometric technique. High pressure apparatus (up to 930 kPa) and low pressure apparatus (up to 100 kPa) with pressure transducers were employed. One sample with $M_s=0.75$ was quenched in cold vapor produced by placing a piece of metal in liquid nitrogen. The sample was cooled in this manner to below room temperature but well above the temperature of liquid nitrogen. This sample was coded as $M_s=0.75$ Q. Another sample for which $M_s=0.75$ was brought to 358 K and then cooled at an average rate of 0.05 K/min to 323 K. This sample was coded as $M_s=0.75$ QA.

Source and Purity of Materials:

C_3H_8: Matheson Co., purity >99.98%.
PS: Polyscience, Inc., $M_w=190\,000$.
PVME: Polyscience, Inc., $M_w=34\,000$.

Estimated Error:

No information given.

Components:

(1) Propane; C_3H_8; [74-98-6] Miscible blend (75/25% w/w) of
(2) Polystyrene (PS); [9003-53-6] and
(3) Poly (vinylmethyl ether) (PVME); [9003-09-2]

Original Measurements:

J. A. Yavorsky and H. J. Spencer, J. Appl. Polym. Sci. **31**, 501 (1986).

Variables:

T/K: 308–374
p/kPa: 0–80

Prepared By:

A. K. Bokarev

Experimental Data

Soprtion parameters for the 75/25° (w/w) PS/PVME blends

Series	T/K/ $cm^3(STP)\ cm^{-3}\ cm\ Hg^{-1}$	$10^2\ k_D/cm^3(STP)\ cm^{-3}$	$C'_H/cm\ Hg^{-1}$	$10^2\ b/cm^3(STP)\ cm^{-3}\ cm\ Hg^{-1}$	k^*
C-1	308	3.5(±11%)	2.1(±19%)	1.6(±40%)	6.79(±12%)
	293	4.0(±12%)	2.2(±22%)	1.8(±44%)	7.99(±13%)
	278	6.4(±11%)	3.2(±20%)	2.2(±50%)	13.3(±16%)
	323	2.4(±12%)[a]	1.4(±32%)	1.4(±55%)	4.33(±51%)[b]
	333				3.06(±4%)
	343				2.49(±4%)
	353				1.99(±4%)
	364				1.89(±4%)
	374				1.65(±4%)
Q	323				3.19(±8%)
	328				3.67(±4%)
	333				2.96(±4%)
	343				2.21(±4%)
	358				1.99(±4%)
SC-2	323				2.45(±4%)[c]
	327				3.14(±4%)
	338				2.71(±4%)
	356				2.00(±4%)

$k^* = k_D + C'_H b$.
[a] k^*, after extended annealing in vacuum at 323 K.
[b] k^*, initial sorption isotherm.
[c] k^*, after annealing.

Auxiliary Information

Method/Apparatus/Procedure

A dual volume–single transducer manometric system similar to that previously described[1] was used.

Source and Purity of Materials:

PS and PVME (Poly Sciences, Inc.) had M_w 190 000 and 34 000, respectively.
Two 75:25% PS/PVME blends were prepared and three thermal histories developed. Sample SC-1 was cooled slowly, a rate of 0.75 K/min, from 358 K to room temperature. Q was rapidly quenched from 358 K to room temperature. After investigating sample Q up to 358 K, it was very slowly cooled, a rate of 0.05 K/min, to 333 K. This sample is designated SC-2.
Propane (Matheson Co) 99.98% purity.

References:

[1] H. J. Spencer and J. A. Yavorsky, J. Appl. Polym. Sci. **28**, 2937 (1983).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polystyrene (PS); [9003-53-6]
(3) Poly(vinylmethyl ether) (PVME); [9003-09-2] (polymer blends)

Original Measurements:

H. Hachisuka, T. Sato, Y. Tsujita, A. Takizawa, and T. Kinoshita, Polym. J. **21**, 417 (1989).

Variables:

T/K=298
p/MPa=0–1.33

Prepared By:

Yu. P. Yampol'skii

Experimental Data

Dual mode sorption paramters for CO_2 in PS/PVME blends

Composition total	PS/PVME phase	$k_D\ 10^2/cm^3(STP)/cm^3\ cm\ Hg$	$C'_H/(cm^3(STP)/cm^3)$	$b\ 10^3/(cm\ Hg)^{-1}$
100/0	—	1.12	4.1	2.36
		Single phase blends		
75/25	—	1.41	1.5	1.45
50/50	—	2.01	—	—
20/80	—	2.62	—	—
		Phase separated blends		
75/25	(83/17)/(21/79)	1.49	2.4	2.76
50/50	(73/27)/(31/69)	2.05	0.4	4.73
20/80	(74/26)/(19/81)	2.93	1.1	3.95
0/100	—	4.00	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption measurement was carried out using electromicrobalance Cahn 2000. The correction for buoyancy was introduced.

Source and Purity of Materials:

Type	PS, %	PVME, %	T_g, K
Single phase	75	25	315.0
same	50	50	262.9
same	20	80	248.6
Phase separated	83	17	321.2
(75/25)	21	79	249.2
Phase separated	73	27	301.2
(50/50)	31	69	253.2
Phase separated	74	26	308.6
(20/80)	19	81	248.0

CO_2 purity >99.99%

Estimated Error:

No information given.

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] (2) Poly(phenylene oxide) (PPO); [25134-01-4] and (3) Polystyrene (PS); [9003-34-6] (IX) miscible blends	G. Morel and D. R. Paul, J. Membr. Sci. **10**, 273 (1982).
Variables:	**Prepared By:**
T/K: 308 p/MPa: 0–2.3	A. K. Bokarev

Experimental Data

Dual mode sorption parameters for CO_2 in miscible blends PPO and PS*

% PPO in blends	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0	0.550	9.28	0.133
10	0.488	12.22	0.126
25	0.482	14.72	0.124
50	0.494	20.56	0.155
75	0.589	22.78	0.165
90	0.683	25.00	0.175
100	0.754	29.00	0.198

*Taken from the plot by compiler.

Auxiliary Information

Method/Apparatus/Procedure

The experimental equipment and procedures for sorption measurements have been described previously.[1]

Source and Purity of Materials:

The PPO used was supplied by General Electric Co.; $M_n = 22\,600$; $M_w = 34\,000$.

The PS used was a commercial product. Costen Polystyrene 550. Films containing different proportions of these polymers were cast from 10% trichloroethylene solutions on mercury surface.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci **2**, 165 (1977).

Components:	**Original Measurements:**
(1) Carbon dioxide; CO_2; [124-38-9] Methane; CH_4; [74-82-8] (2) Polystyrene (PS); [9003-53-6] (IX) (3) Tetramethyl bisphenol A Polycarbonate (TMPC)	N. Muruganandam and D. R. Paul, J. Polym. Sci., Part B: Polym. Phys. **25**, 2315 (1987).
Variables:	**Prepared By:**
T/K=308 p/MPa=0–2.0	Yu. P. Yampol'skii

Experimental Data

TABLE 1. Dual mode sorption parameters for carbon dioxide in TMPC/PS blends at 308 K

TMPC mass %	k_D/cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0	0.550	9.44	0.177
20	0.604	11.53	0.198
40	0.579	15.37	0.186
60	0.667	19.05	0.207
81	0.879	20.49	0.275
100	1.011	27.66	0.283

TABLE 2. Dual mode sorption parameters for methane in TMPC/PS blends at 308 K

TMPC mass %	k_D/cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0	0.109	6.99	0.068
20	0.252	3.85	0.126
40	0.192	6.80	0.094
60	0.230	8.90	0.090
81	0.237	12.72	0.086
100	0.244	15.34	0.100

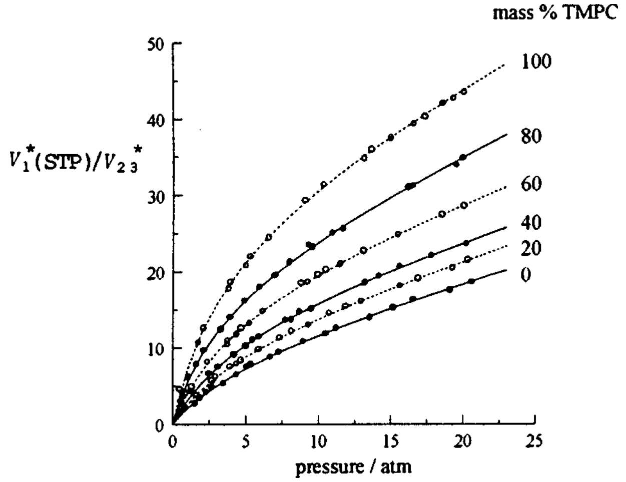


FIG. 99. Sorption isotherms of carbon dioxide in TMPC/PS blends at 308 K.

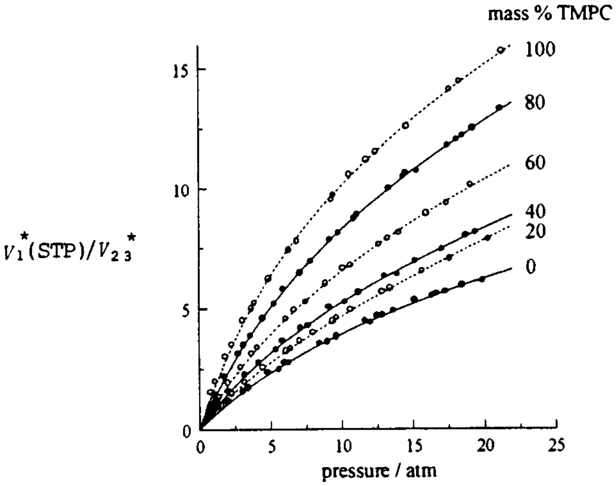


FIG. 100. Sorption isotherms of methane in TMPC/PS blends at 308 K.

Auxiliary Information

Method/Apparatus/Procedure

The apparatus and procedure are described in Ref. 1. The films previously had been exposed to carbon dioxide at 20 atm for 24 h.

Source and Purity of Materials:

PS: Cosden Oil and Chemical Co., $M_n = 100\,000$, $M_w = 350\,000$, glass transition temp. 375 K.
TMPC: Bayer AG, glass transition temp. 466 K.
Blends: glass transition temperatures varied monotonously in the range of the values characteristic for pure components.

Estimated Error:

No information given.

References:

[1] W. J. Koros, A. H. Chan, and D. R. Paul, J. Membr. Sci. **2**, 165 (1977).

Components:

(1) Carbon dioxide; CO_2; [124-38-9]
(2) Polycarbonate (PC); [24936-68-3] (XXI)
(3) Copolyester (Kodar A-150)

Original Measurements:

P. Masi, D. R. Paul, and J. W. Barlow, J. Polym. Sci., Polym. Phys. Ed. **20**, 15 (1982).

Variables:

T/K=308
p/MPa=0–2.1

Prepared By:

A. K. Bokarev

Experimental Data

TABLE 1. Dual mode sorption parameters for CO_2 in polycarbonate–copolyester blends at 308 K (taken from the plot by the compiler)

PC mass %	k_D /cm^3(STP) cm^{-3} atm^{-1}	C'_H/cm^3(STP) cm^{-3}	b/atm^{-1}
0	0.644	9.4	0.29
25	0.613	13.1	0.23
50	0.613	13.8	0.28
75	0.655	18.0	0.23
100	0.686	19.2	0.26

TABLE 2. Sorption isotherms of carbon dioxide in polycarbonate–copolyester blends at 308 K

Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})	Pressure/MPa	Sorption (V_1^*(STP)/V_{23})
PC 0 mass %					
0.09	2.57	0.71	10.75	1.47	17.39
0.13	3.34	0.92	12.86	1.67	18.47
0.17	4.05	0.94	12.49	1.74	19.29
0.21	4.88	1.05	13.78	1.75	18.68
0.31	6.18	1.25	15.28	1.86	19.67
0.43	8.01	1.28	15.76	2.08	21.11
0.59	9.71	1.35	16.16	—	—
PC 25 mass %					
0.42	8.50	1.11	16.42	1.58	19.46
0.51	9.73	1.21	17.29	1.66	20.40
0.56	10.99	1.36	17.66	1.79	21.75
0.60	11.03	1.34	18.09	1.90	22.13
0.73	12.68	1.48	19.01	1.96	22.35
1.01	15.61	1.51	19.73	—	—
PC 50 mass %					
0.32	8.53	1.07	16.97	1.58	20.97
0.42	10.06	1.17	17.79	1.72	22.01
0.49	11.13	1.26	18.66	1.79	22.29
0.73	13.94	1.43	19.93	1.91	23.10
0.84	14.94	1.46	19.99	2.02	24.15
PC 75 mass %					
0.29	9.26	1.23	20.97	1.76	25.68
0.40	11.22	1.24	21.45	1.80	26.09
0.53	13.23	1.29	21.73	1.83	26.14
0.72	15.52	1.31	21.96	1.90	26.72
0.84	16.99	1.41	22.60	2.03	27.28
1.02	19.10	1.47	23.54	2.06	28.36
1.08	19.87	1.57	24.36	2.12	28.76
PC 100 mass %					
0.11	5.22	0.97	20.33	1.71	27.21
0.18	7.49	1.12	21.61	1.84	28.19
0.44	12.89	1.21	22.66	1.93	29.61
0.54	14.97	1.29	23.42	2.00	29.10
0.74	17.38	1.49	24.68	2.09	30.16
0.80	18.69	1.52	25.40	—	—

Auxiliary Information

Method/Apparatus/Procedure

Sorption was measured using a pressure decay method described in Ref. 1. The specimens were exposed to CO_2 at 20 atm for 1 day.

Source and Purity of Materials:

Copolyester (Kodar A-150): Products, Inc. contained the units of isophthalic and terephthalic acid in a ratio 20/80; $M_n = 22\,000$, glass transition temperature 360 K.

PC (Bisphenol A Polycarbonate): Lexan 131-111 General Electric Co., $M_n = 13\,300$, $M_w = 34\,200$, glass transition temperature 421 K. The blends were produced by extrusion at 293 K (above T_m of the copolyester).

Estimated Error:

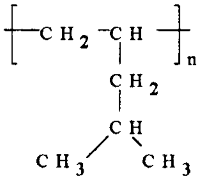
No information given.

References:

[1] W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed. **14**, 687 (1976).

4. Structure Formulas of Polymers

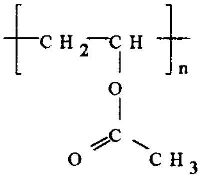
I Poly(4-methylpentene-1)



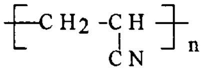
II Poly(vinyl chloride) (PVC)

$-\!\left[CH_2-CHCl\right]_n\!-$

III Poly(vinyl acetate) (PVA)

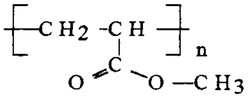


IV Polyacrylonitrile

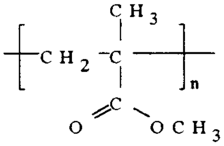


$-\!\left[CH_2-\underset{CN}{CH}\right]_n\!-$

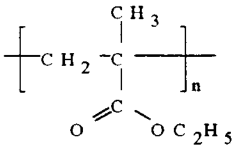
V Poly(methyl acrylate) (PMA)



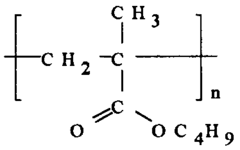
VI Poly(methyl methacrylate) (PMMA)



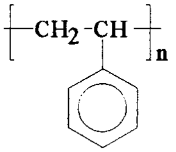
VII Poly(ethyl methacrylate) (PEMA)



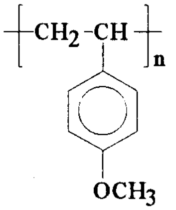
VIII Poly(butyl methacrylate)



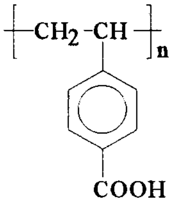
IX Polystyrene (PS)



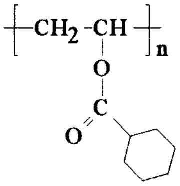
X Poly(p-methoxystyrene)



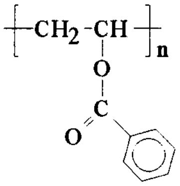
XI Poly(p-acetoxystyrene)



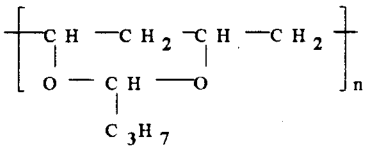
XII Poly(vinyl cyclohexanecarboxylate)



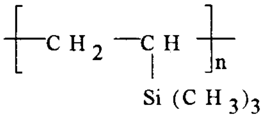
XIII Poly(vinyl benzoate) (PVB)



XIV Poly(vinyl butyral) (PVBu)

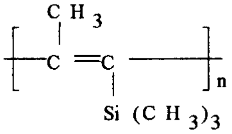


XV Poly(vinyltrimethyl silane) (PVTMS)



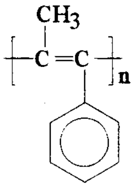
$\left[CH_2-CH(Si(CH_3)_3) \right]_n$

XVI Poly(trimethylsilyl propyne) (OTMSP)

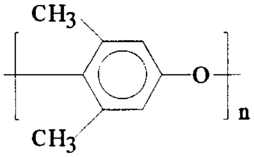


$\left[C(CH_3)=C(Si(CH_3)_3) \right]_n$

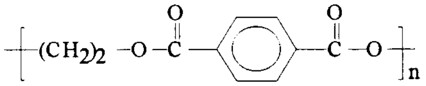
XVII Poly(phenyl propyne)



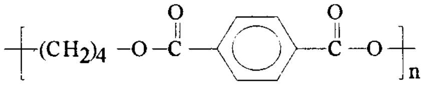
XVIII Poly(2,6-dimethylphenylene oxide)



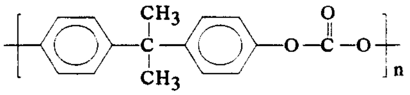
XIX Poly(ethylene terephthalate) (PETP)



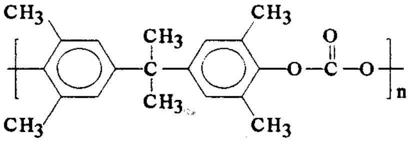
XX Poly(butylene terephthalate) (PBTP)



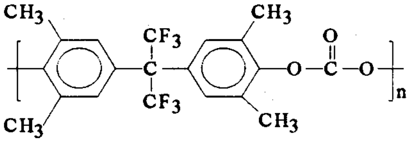
XXI Polycarbonate (PC)



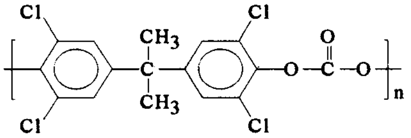
XXII Tetramethylpolycarbonate (TMPC)



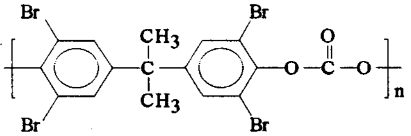
XXIII Tetramethylhexafluoropolycarbonate



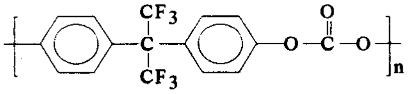
XXIV Tetrachloropolycarbonate (TCPC)



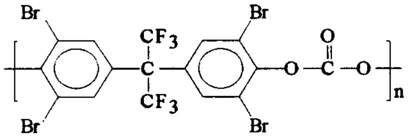
XXV Tetrabromopolycarbonate (TBPC)



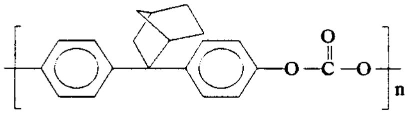
XXVI Hexafluoropolycarbonate



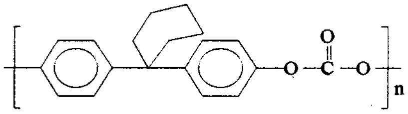
XXVII Tetrabromohexafluoropolycarbonate



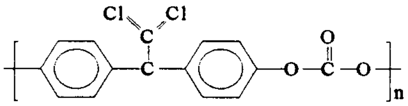
XXVIII Bisphenol norbornene polycarbonate



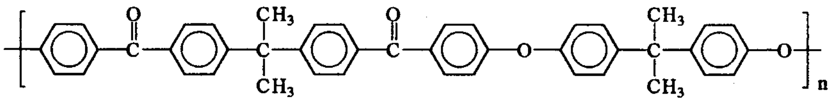
XXIX Bisphenol Z polycarbonate



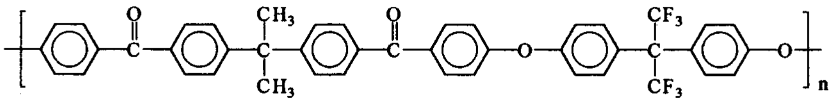
XXX Bisphenol chloral polycarbonate



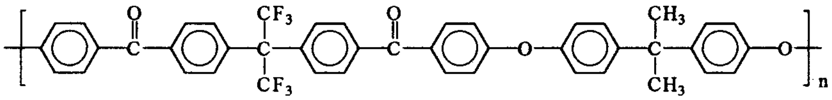
XXXI Poly(aryl-bis-isopropylidene etherketone)



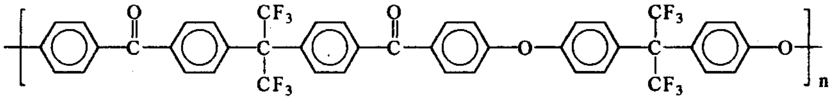
XXXII Poly(aryl-isopropylidene-hexafluoroisopropylidene etherketone) (PAEK-6H6F)



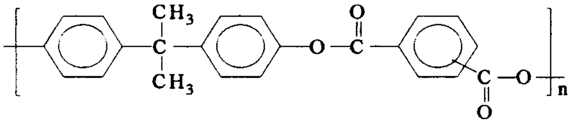
XXXIII Poly(aryl-hexafluoroisopropylidene-isopropylidene etherketone) (PAEK-6F6H)



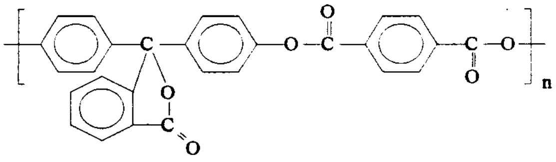
XXXIV Poly(aryl-bis hexafluoroisopropylidene etherketone)



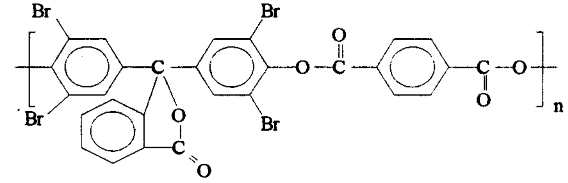
XXXV Polyarylate



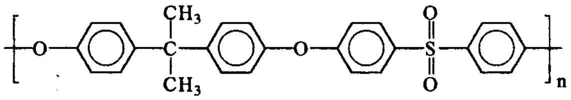
XXXVI Poly(phenolphthaleine phthalate)



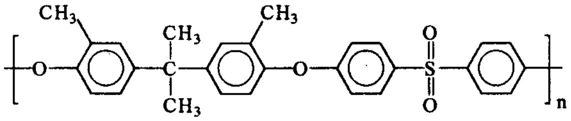
XXXVII Tetrabromo poly(phenol phthaleine phthalate)



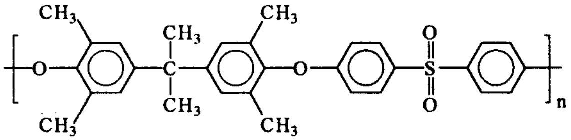
XXXVIII Polysulfone (PSF)



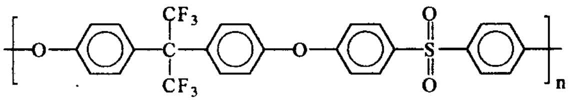
XXXIX Dimethyl polysulfone



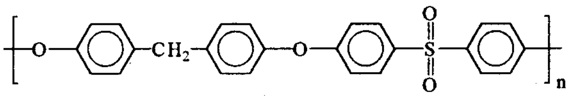
XL Tetramethyl polysulfone



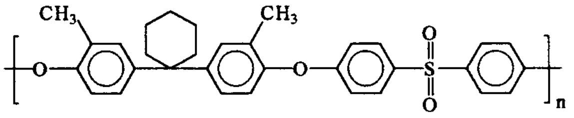
XLI Hexafluoro polysulfone



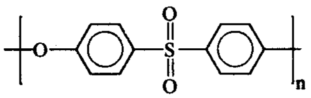
XLII Polysulfone-F



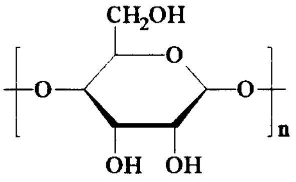
XLIII Dimethyl bisphenol Z polysulfone



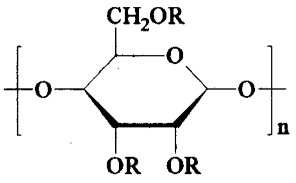
XLIV Polyethersulfone



XLV Cellulose

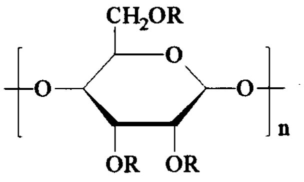


XLVI Nitrocellulose



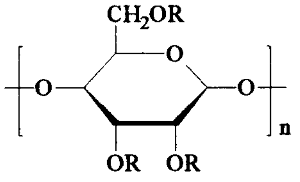
R = H or NO_2

XLVII Ethyl Cellulose (EC)



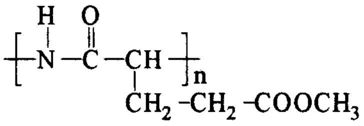
R=H or C_2H_5

XLVIII Cellulose Acetate (CA)



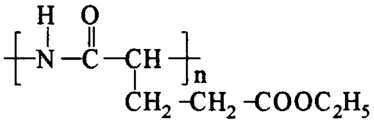
R=H or $C(O)OCH_3$

XLIX Poly(γ-methyl glutamate) (PMG)



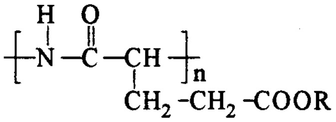
$$\left[-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{CH_2-CH_2-COOCH_3}{\underset{|}{CH}}- \right]_n$$

L Poly(γ-ethyl glutamate)



$$\left[-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{CH_2-CH_2-COOC_2H_5}{\underset{|}{CH}}- \right]_n$$

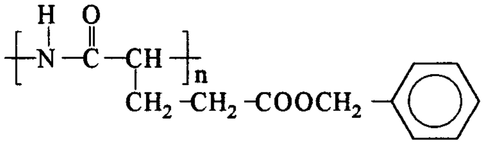
LI Poly(γ-alkyl-*L*-glutamates)



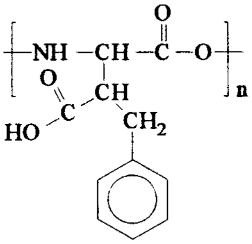
$$\left[-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{CH_2-CH_2-COOR}{\underset{|}{CH}}- \right]_n$$

R = n-C3H $_7$, n-C_4H_9,
n-C_5H_{11}, n-C_8H_{17}

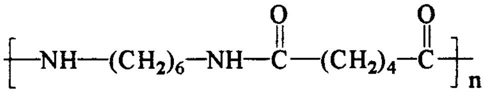
LII Poly(γ-benzyl-*L*-glutamate) (PBLG)



LIII Poly(β-benzyl-*L*-aspartate) (PBLA)

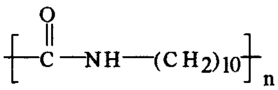


LIV Poly(hexamethylene adipinamide) (Nylon 6.6)



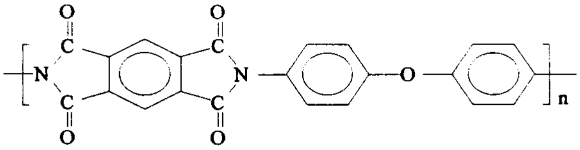
$$\left[-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}- \right]_n$$

LV Nylon 11

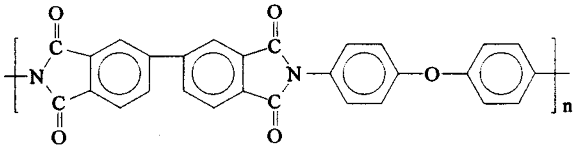


$$\left[-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_{10}- \right]_n$$

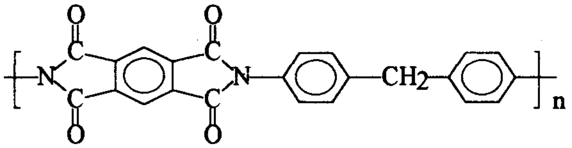
LVI Polyimide Kapton H (PMDA-ODA)



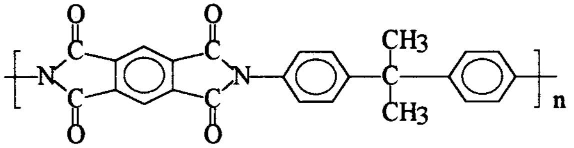
LVII Polyimide Upilex R



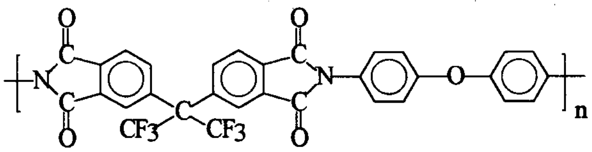
LVIII Copoly(pyromellitic dianhydride-methylene dianiline) (PMDA-MDA)



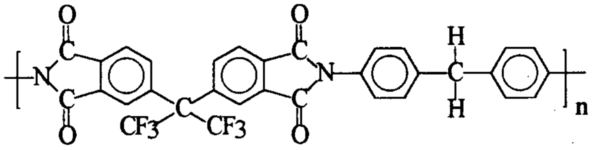
LIX Copoly(pyromellitic dianhydride - isopropylidene diamine) (PMDA-IPDA)



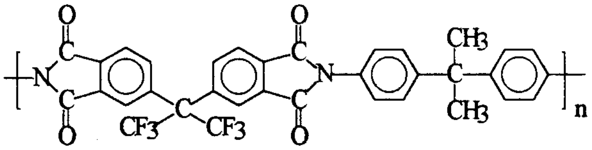
LX 6FDA-ODA



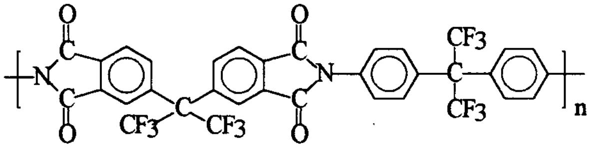
LXI 6FDA-MDA



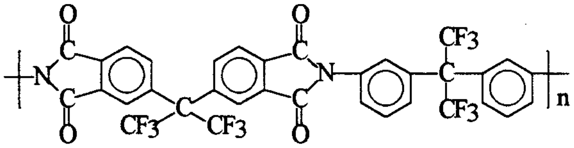
LXII 6FDA-IPDA



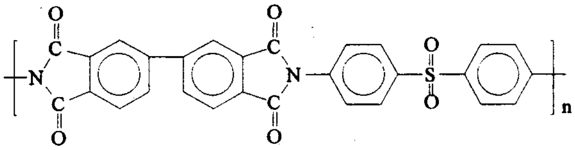
LXIII 6FDA-6FpDA



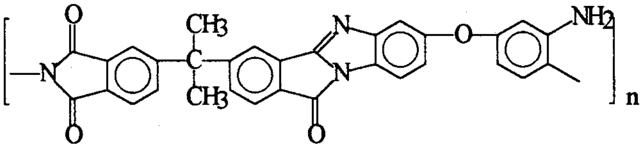
LXIV 6FDA-6FmDA



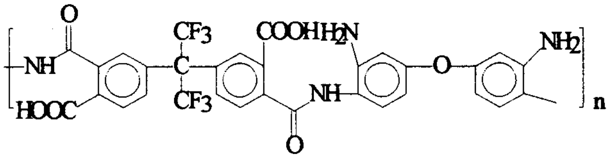
LXV Polyimide BS-1



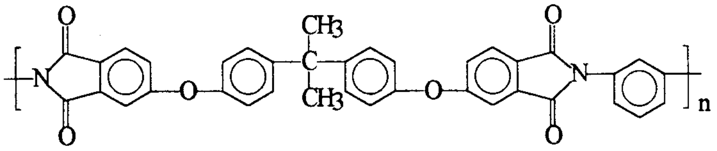
LXVI Polypyrrolone



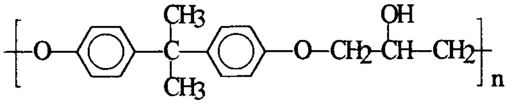
LXVII 6FDA-TADPO Poly(amide amino acid)



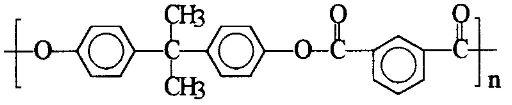
LXVIII Ultem 1000



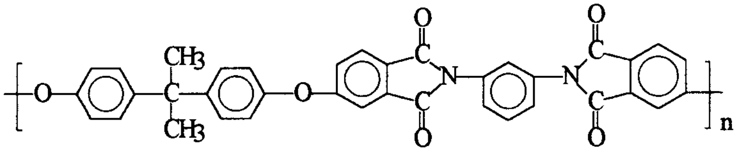
LXIX Polyhydroxyether



LXX Polyarylate (Ardel)



LXXI Polyetherimide (Ultem)



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5. Polymer Index

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.

6. Gas Index

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compilation tables.

7. Registry Number Index

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