

# Counterion structure and dynamics in polyelectrolyte solutions<sup>☆</sup>

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Available online 23 June 2005

## Abstract

Investigations of the counterion distribution and correlations to polyelectrolytes have seen increased activity to understand intrinsically stiff and flexible polyelectrolytes in good solvents as functions of ionic strength, charge valence, and concentration. In particular, anomalous (resonant) small-angle X-ray scattering and small-angle neutron scattering have provided new insights on counterion association/condensation. An area of expected growth is counterion dynamics studied via techniques such as electron paramagnetic resonance and neutron-spin echo spectroscopy where the counterion can be labeled along with pulsed-field gradient nuclear magnetic resonance, which can examine a wide range of time and length scales. Along with these experimental studies, theory and simulations provide important predictions and insight.

Published by Elsevier Ltd.

*Keywords:* Counterion; Counterion condensation; Poisson–Boltzmann; Polyelectrolyte; Scattering; Spectroscopy

## 1. Introduction

Applications ranging from medical technology to electronic devices have generated interest in materials synthesis for designed structure and function [1\*,2\*]. For the designed assembly of aqueous solution-based polymeric and colloidal materials, a controlled balance of the influence of long-range electrostatic interactions, directional hydrogen bonding, and solvent quality (excluded volume) is required. For electrostatics-based assembly, the counterions and ionic strength play a crucial role in determining polyelectrolyte phase diagrams, phase stability, and gel behavior. The relative acidity or basicity of functional groups in the chosen solvent controls the extent of ionization. In many cases, pure water leads to chain ionization, as in poly(styrenesulfonic acid), a model strong polyelectrolyte, whereas a change in pH tunes the extent for weak polyelectrolytes, such as poly(acrylic acid) [3\*]. Under

weak polyelectrolyte behavior, excess ions beyond the stoichiometric endpoint will contribute to the solution ionic strength and screen the long-ranged electrostatic interactions, in a manner similar to added electrolytes. Experimentalists have chosen specific counterion species that allow a host of counterion–polyion model systems [4\*]. Such approaches provide a foundation to lead the development of complex materials.

The schematic shown in Fig. 1 highlights two cases of interest; stiff polyelectrolytes that do not undergo conformational changes as function of the experimental variables noted earlier, but provide a skeleton to observe the counterion distribution. The second is an intrinsically flexible polyelectrolyte where the counterion structure is coupled to the chain conformation. A parameter central to all discussions is the chemical charge density parameter ( $\Gamma$ ) which is fixed by the polymer chemistry and is defined by the ratio of the Bjerrum length ( $l_B$ ) to the average distance between charges ( $a$ ) along the main chain,  $\Gamma = l_B/a$ . The Bjerrum length is a natural length scale that equates the thermal energy to the Coulombic potential energy and is defined by  $l_B = e^2/(4\pi\epsilon\epsilon_0 k_B T)$ , with  $e$  the elemental charge,  $\epsilon$  the solvent dielectric constant,  $\epsilon_0$  the permittivity,  $k_B$  the Boltzmann constant, and  $T$  absolute temperature. Three

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experimental methods are available to tune the charge density parameter  $a$ ,  $\epsilon$ , and  $T$ . The counterion distribution problem and its relation to  $\Gamma$  has stimulated much activity with stiff polyelectrolytes, especially in the theoretical and computer simulation community. It has been predicted that the distribution undergoes rich phase transitions [5], condensation along rod-like chains [6–8] (a topic of 40 years of interest), renormalize the chemical charge density [9], and depend of the finite size of the ions through excluded volume interactions [10]. It is anticipated that understanding the role of the counterion will help design future assembly processes by appropriately tailoring the polymer chemistry.

We highlight recent results from scattering methods that quantify the counterion structure and distribution, relative to the chain. The length scales at which strong correlations are present and their salt and polymer concentration dependencies are described. The counterion dynamics are reviewed from electron-paramagnetic resonance (EPR), nuclear magnetic resonance (NMR) and neutron-spin echo (NSE) spectroscopy to understand the time-scales of counterion–polyion correlations.

## 2. Structure

In solution, the pair correlations between molecules are measured by a scattering experiment in which the intensity is measured as a function of the scattering wave vector ( $\mathbf{Q}$ ) defined by  $\mathbf{Q} = 4\pi\lambda^{-1} \sin \theta/2$ , where  $\lambda$  is the radiation wavelength and  $\theta$  the scattering angle. The inverse of  $\mathbf{Q}$  is proportional to the length scale of the correlations, hence small-angle neutron or X-ray scattering (SANS, SAXS) measures the local structure of polymers over length scales of (10 to 1000) Å. In the limit of coherent scattering, the amplitude of the scattered intensity,  $I(\mathbf{Q})$ , has contributions from all pair-wise correlations between components  $i$  and  $j$  and is quantified by the partial structure factors ( $S_{ij}$ ) that are weighted by the difference in scattering lengths ( $b_i$ ) between components, the scattering contrast. For example the case

where  $m$  represents the monomer repeat unit,  $c$  the counterion and  $o$  the solvent,

$$I(\mathbf{Q}) = (b_m - b_o)^2 S_{mm}(\mathbf{Q}) + (b_c - b_o)^2 S_{cc}(\mathbf{Q}) + 2(b_m - b_o)(b_c - b_o) S_{mc}(\mathbf{Q}). \quad (1)$$

Polyelectrolyte solution scattering [11\*] as studied by SANS typically measures the polyion contribution to the fluctuations and shows a scattering peak at low ionic strength solutions. The peak intensity follows well-defined concentration scaling relationships in dilute, semidilute, and concentrated solutions. The SANS technique has low sensitivity (or ‘visibility’) to inorganic counterions because the scattered intensity is dominated by the high contrast between hydrogen and deuterium. However, the influence of charge valence on the conformational and collective behavior of the polymer has been studied [12,13]. Recently, the counterion–counterion correlations were measured by SANS for semidilute solutions of tetramethylammonium poly(styrene sulfonate) (TMA-PSS) [14\*\*] (Fig. 2a) by eliminating the polymer contribution to the scattering. Measurements of the counterion–counterion partial structure factor allows quantification of the correlation length ( $\xi$ ); consider the main result from [14\*\*]  $\xi = (75.2 \pm 5.6) C_p^{-0.45 \pm 0.02}$  versus the counterion ‘invisible’ experiment [12] where  $\xi = (73 \pm 9) C_p^{-0.48 \pm 0.03}$  (Na-PSS), with concentration in  $[\text{gL}^{-1}]$ , and  $\xi = 1/\mathbf{Q}_{\max}$  in [Å]. These results show that high-charge density polyelectrolytes ( $\Gamma \geq 1$ ) exhibit a strong coupling, even for the flexible chain case, at the no-added salt level; the counterions dress or associate with the chains in semidilute solution. As salt is added, the polyion–‘visible’ experiments of Nishida et al. [15] show that the long-range electrostatic interactions are screened recovering the scattering behavior typical of neutral polymer solutions. For the counterion ‘visible’ experiment [14\*\*], the addition of NaCl (a neutron ‘invisible salt’) leads to an elimination of small-angle scattering as shown in Fig. 2b, implying that the monovalent TMA<sup>+</sup> and Na<sup>+</sup> cations have equilibrated. Such an ion exchange was concluded by Lachenmayer and Oppermann using electric birefringence and conductivity measurements for a model stiff polyelectrolyte [16]. This leads to an interesting question regarding the counterion structure in the presence of multivalent ions [17,18\*], for instance ion exchange, or competition between monovalent and divalent ions to more complex polyion–polyion complexation utilized by polyelectrolyte layer-by-layer assembly [19].

Anomalous small-angle X-ray scattering (ASAXS) with synchrotron radiation, was used to study double stranded (ds) deoxyribonucleic acid (DNA) [20\*,21\*\*], rod-like synthetic polyelectrolytes [22\*\*,23\*,24\*], and colloidal polyelectrolytes [25]. These experiments utilize two scattering measurements with incident x-ray energies away and near the absorption-edge of the element of interest. The near-edge absorption exploits the change in the atomic

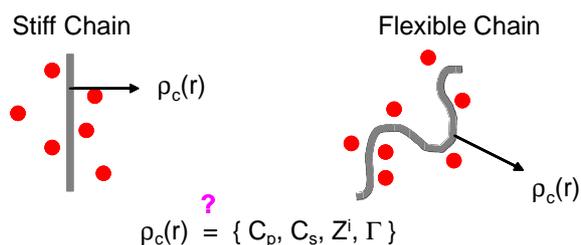


Fig. 1. Schematic of intrinsically stiff versus flexible polyelectrolyte with neutralizing counterions (●) in the chain vicinity. The fundamental goal is to quantify this counterion distribution  $\rho_c(r)$  near the chain as well as the counterion dynamics as a function of polymer concentration ( $C_p$ ), added salt concentration ( $C_s$ ), charge valence ( $Z^l$ ), and charge density ( $\Gamma$ ).

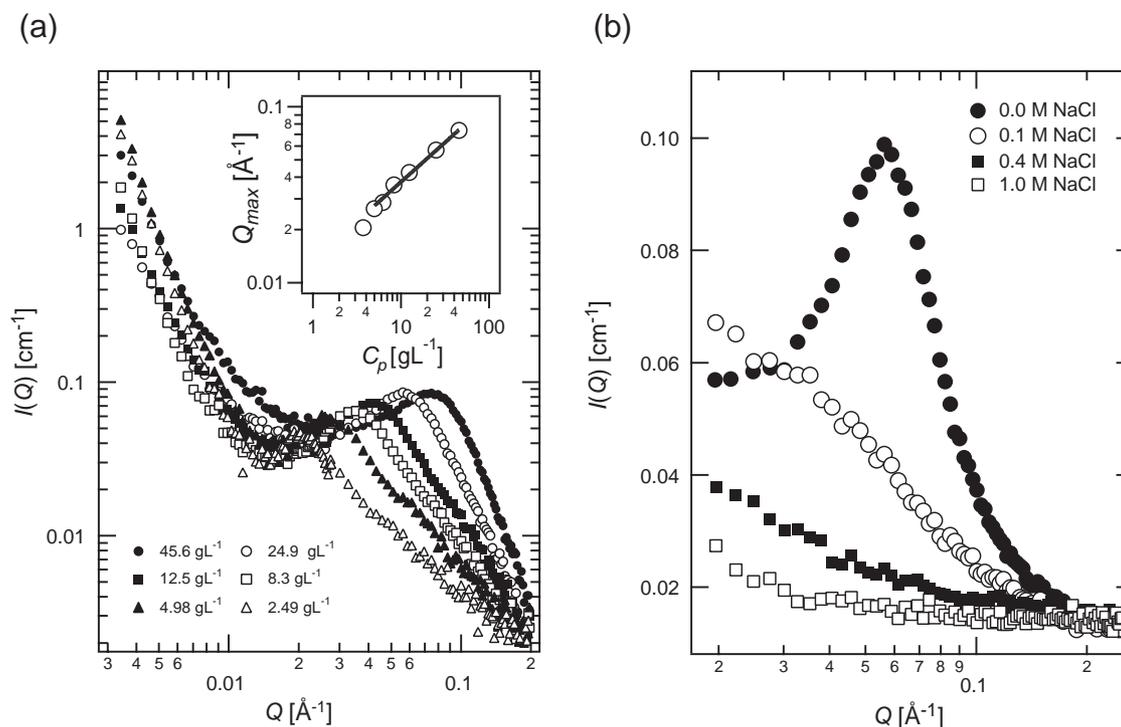


Fig. 2. (a) Small-angle neutron scattering from protonated TMA deuterated PSS in  $D_2O$  as a function of polymer concentration. The inset provides the scaling of the peak position as a function of polymer concentration. (b) 'Visible' organic counterions associate with the negatively charged chain at low salt and are displaced by added SANS 'invisible' sodium ions for fixed polymer concentration of  $24.9 \text{ gL}^{-1}$ . Reprinted from Ref. [14] V.M. Prabhu, E.J. Amis, D.P. Bossev, and N. Rosov, *Journal of Chemical Physics*, 121, 4424 (2004).

scattering factor allowing the pair correlations from heavy atomic element counterions as described by Patel et al. [23<sup>\*</sup>]. Das et al. [21<sup>\*\*</sup>] differentiated the counterion cloud structure associated with a dilute 25 base pair (bp) DNA solution as a function of charge valence using  $Rb^+$  and  $Sr^{2+}$  ions. This model short cylinder polyelectrolyte<sup>1</sup> scattering behavior was compared to a non-linear Poisson–Boltzmann model quantifying the ionic excess radial distribution from the double helix. Such comparison is possible for stiff (or short strands) polyelectrolytes since the conformation of the polyion is not expected to change. Andresen et al. extended these results to quantify the  $Rb^+$  and  $Sr^{2+}$  concentration at the DNA surface [20<sup>\*</sup>]. They found that the ion distribution for a 24 bp DNA, in dilute solution, was invariant to the competing mixture of monovalent and divalent counterions and the concentration of each charge valence scaled in proportion to the equilibrium solution concentration. These results validated several key assumptions in the Poisson–Boltzmann model. However, it was observed that the absolute surface concentrations were lower than predicted, suggesting that the finite size of ions or excluded volume effects, which were not considered, may play an important role very close to the chain. Recent computer simulations

have probed the distribution of monovalent and divalent ions around DNA taking into account the double helix and finite size of ions [26<sup>\*\*</sup>,27]. The extension of ASAXS measurements to higher relative molecular mass DNA with varying persistence lengths and to semidilute solutions should provide an interesting test for current models as correlations between DNA strands become important. Morfin et al. [28] combined SAXS and SANS to understand semidilute solutions of high relative molecular mass DNA with a mixture of monovalent and divalent salts and found that the modeled cross sectional radius was independent of the divalent ion concentration.

The correlations of counterions to the chains are also directly quantified via the osmotic properties, or osmotic coefficient [22<sup>\*\*</sup>]. Hansen et al. [29<sup>\*\*</sup>] indicated the importance of finite-size of the stiff polyelectrolyte in comparing osmotic pressure data to the non-linear Poisson–Boltzmann cell model for DNA solutions. Several approaches to calculate the osmotic properties of polyelectrolytes are available [30–34]. Since double stranded DNA is a highly charged polyelectrolyte ( $\Gamma > 4$ , using one elementary charge distributed every  $1.7 \text{ \AA}$  along the axis) [29<sup>\*\*</sup>], a charge-renormalization mechanism is expected [6,9]. However, interpreting the ion distribution about a polyelectrolyte alone cannot verify the mechanism. Popov and Hoagland utilized capillary electrophoresis to understand the counterion condensation mechanism from electro-

<sup>1</sup> B-DNA, the bp–bp distance through the axis of the double helix is  $3.4 \text{ \AA}$  suggesting a cylinder length of  $85 \text{ \AA}$ .

phoretic mobility measurements on ionene cationic polyelectrolytes [35\*\*]. They examined a wide-range of charge-density parameters by varying the solvent dielectric constant and distance between charges covering  $\Gamma$  values below and above the theoretical Manning condensation limit,  $\Gamma \geq (Z_p Z_c)^{-1}$ , where  $Z_p$  and  $Z_c$  represent the charge valence of the polymer segment and counterion, respectively. The general features of counterion condensation were observed, however, the notion of a critical charge density was not universal and appeared to depend on a constant Bjerrum length.

The importance of the coupled conformational properties to salt, or counterion, was observed in recent examinations by Horkay and Bassar [36\*\*] with cross-linked DNA gels that exhibit a volume transition. They observed using osmotic and mechanical measurements that the ion exchange between  $\text{Na}^+$  for  $\text{Ca}^{2+}$  led to a reduced counterion contribution to the osmotic pressure within the gel, but shear modulus data do not support  $\text{Ca}^{2+}$  ion induced cross-linking as the origin of the volume transition. Even though the structure of polyelectrolyte gels is heterogeneous [37], comparisons between thermodynamics and structure have been made by Horkay et al. [38,39]. The counterion structure near the chains may help understand the complex phase transitions in these gels and semidilute solutions. Recently Muthukumar considered the additional influence of chain flexibility, ion-pairing and translational entropy of adsorbed and free counterions via a variational method at the Debye–Hückel level of electrostatics [40].

### 3. Dynamics

The dynamics of the counterions and polyelectrolyte solutions is a topic that is of great interest, but has not been extensively explored. Previous methods including dynamic

light scattering have led the field in understanding the coupled diffusion. However, advanced experimental methods to study counterions with specificity are emerging. Ionic spin probe counterions were studied with electron paramagnetic resonance (EPR) spectroscopy by Hinderberger et al. [41\*\*,42\*\*]. The dynamics of model divalent organic counterion Fremy's salt (FS) and trianion triarylmethyl radical, were observed in model flexible and stiff polyelectrolyte solutions. The spin probe method allows an independent measurement of the influence of the medium on counterion relaxation; hence retaining specificity regarding the ions near the chain, counterion valence and exchange, and timescale of association, or condensation. The dynamic electrostatic attachment of the counterions near the chain was classified into site-binding, territorial, and free ions in complement to the true equilibrium profile. These experiments refuted the static viewpoint of divalent counterions immobilized upon the polyion because the timescale of site binding and equilibration with territorial binding was estimated less than 1 ns. Hence, the fast-moving counterions relax in the vicinity of the chain, a notion that was not in question. The concept of counterion exchange between monovalent and divalent was verified under all conditions supporting the argument that entropy increases with the release of two monovalent counterions from a local site, or territorially bound divalent ions.

Since the counterions were observed to exhibit strong correlations to the chain; the ratio of the FS spin probe to poly(diallyldimethylammonium chloride) (PDADMAC) polymer ( $R$ ) was varied by changing the polymer concentration, allowing a test of the FS distribution as a function of polyion sites. The EPR technique distinguishes between spin probes that appear to be homogeneously distributed versus distributed along the chain contour for the system shown in Fig. 3a, reproduced from reference [41\*\*]. In the high polymer concentration limit (semidilute solution) the spin

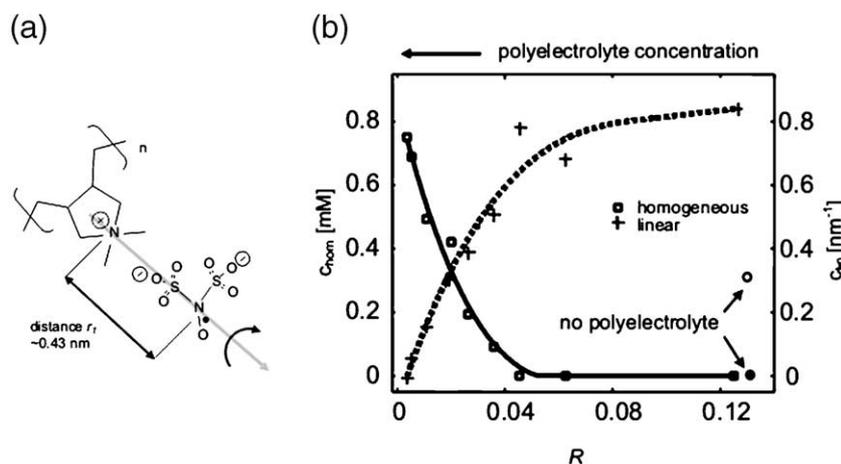


Fig. 3. (a) Local geometry of Fremy's salt spin probe that is site bound to a PDADMAC ammonium group. (b) Extracted contributions of three-dimensional ( $C_{\text{hom}}$ , homogeneous) and one-dimensional ( $C_{\text{lin}}$  linear) Fremy's salt distributions with PDADMAC over the whole range of  $R$  (FS/PDADMAC concentrations) in glycerol/water mixtures. Solid and dotted black lines are meant as a guide to the eye. Reproduced with permission from Ref. [41] D. Hinderberger, H.W. Spiess, G. Jeschke, Journal of Physical Chemistry B, 108, 3698 (2004). Copyright 2004 American Chemical Society.

probes are distributed among all polymer chains and modeled as a homogeneous distribution shown in Fig. 3b. In the dilute limit, where many spin probes occur for each chain, a linear distribution of FS along the chain is recovered.

Pulsed-field gradient nuclear magnetic resonance (PFG NMR) experiments by Schipper et al. [43\*\*] and Schipper and Leyte [44\*\*] examined the self diffusion of polyion, counterion and solvent spanning the dilute to concentrated solutions with a TMA-neutralized poly(methacrylic acid), a model flexible polyelectrolyte. One main result reproduced in Fig. 4a clearly shows the reduced counterion self diffusion coefficient dependence on the polyelectrolyte concentration. The three regimes of dynamics were quantified using a Poisson–Boltzmann cell model as shown in Fig. 4b with the dotted line for the reduced counterion diffusion coefficient corrected by the reduced solvent diffusion. Simulation and theoretical results are now available that include the effects of coil dimensions with polymer concentration [45\*] that may allow experimentalists to quantify data beyond geometric models. In a related study, Sasaki and Schipper [46] examined the self diffusion of  $\text{Li}^+$  counterions in poly(acrylic acid) gels and solutions as a function of neutralization degree by PFG NMR. They observed the coupled diffusion of the counterions behaved similarly for the gels and semidilute solutions at equal concentrations. Neutron-spin echo spectroscopy provides the dynamic structure factor on the length scales of a SANS experiment, with relaxation time scales between 45 ps and 100 ns. Using NSE with a labeling technique, Prabhu et al. [14\*\*] observed a slowing-down of the counterion dynamics at length scales slightly shorter than the static correlation length. The  $Q$ -dependent diffusion coefficient is expected

from coupled diffusion and comparable to predictions by Chang and Yethiraj [45\*].

#### 4. Summary

It was the intention of this review to focus on recent developments in understanding the distribution and dynamics of counterion species. It appears that a fundamental problem in quantifying scattering data is that conclusions are highly model dependent. The well developed Poisson–Boltzmann geometric models, in most cases are quantitatively compared to experiment, but are speculative as correlations between chains appear. Hence, in the limit of intrinsically flexible polyelectrolytes, comparisons to analytical or simulation results are now available. New materials with non-covalent interactions will allow polymer and colloidal science to tailor complex materials and design charged, self-assembling systems. The model behavior of polyelectrolytes with hydrogen bonding effects and the specific role of ion-pairing will emerge as this field continues to develop.

#### Acknowledgements

The author thanks Eric Lin (Polymers Division, NIST) for many helpful comments and Dariush Hinderberger (Laboratory of Physical Chemistry, ETH Zürich) for fruitful discussions and introducing him to the EPR methods at the 5th International Symposia on Polyelectrolytes 2004, Amherst, MA.

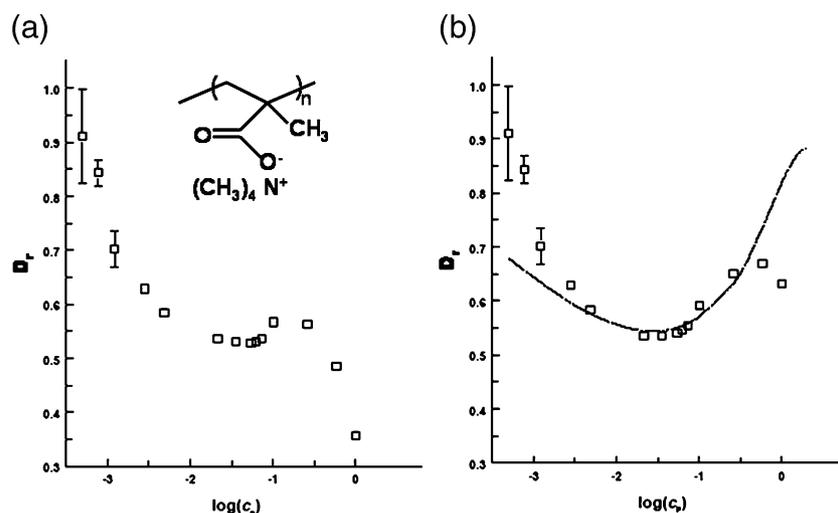


Fig. 4. (a) The relative  $\text{TMA}^+$  self-diffusion coefficient,  $D_r$ , versus the logarithm of the poly(methacrylic acid) (PMA) concentration,  $\log(C_p)$ , for salt-free, completely neutralized solutions of PMA consisting of 90 monomers in  $\text{D}_2\text{O}$ . (b) The relative  $\text{TMA}^+$  self-diffusion coefficient,  $D_r$ , corrected for the self-diffusion coefficient for the solvent versus  $\log(C_p)$ . The dashed-dotted curve represents the relative counterion self-diffusion coefficient calculated using the Poisson–Boltzmann model for spherical symmetry ( $R_s=1$  nm,  $N_q=20$ ). Reproduced with permission from Ref. [44]. Copyright 1999 Institute of Physics Publishing.

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