Relative Volatilities of Ionic Liquids by Vacuum Distillation of Mixtures

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The relative volatilities of a variety of common ionic liquids have been determined for the first time. Equimolar mixtures of ionic liquids were vacuum-distilled in a glass sublimation apparatus at approximately 473 K. The composition of the initial distillate, determined by NMR spectroscopy, was used to establish the relative volatility of each ionic liquid in the mixture. The effect of alkyl chain length was studied by distilling mixtures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids, or mixtures of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids, with different alkyl chain lengths. For both classes of salts, the volatility is highest when the alkyl side chain is a butyl group. The effect of cation structure on volatility has been determined by distilling mixtures containing different types of cations. Generally speaking, ionic liquids based on imidazolium and pyridinium cations are more volatile than ionic liquids based on ammonium and pyrrolidinium cations, regardless of the types of counterions present. Similarly, ionic liquids based on the anions $[(C_2F_5SO_2)_2N]^-$, $[(C_4F_9SO_2)(CF_3SO_2)N]^-$, and $[(CF_3SO_2)_2N]^-$ are more volatile than ionic liquids based on $[(CF_3SO_2)_3C]^-$ and $[CF_3SO_3]^-$, and are much more volatile than ionic liquids based on $[PF_6]^-$.

Introduction

Ionic liquids (ILs) are molten salts with melting temperatures of <373 K.[1] Because of their ionic nature, ILs are uniquely suited for certain applications in electrochemistry, separations, synthesis, and engineering.[2] The conventional wisdom about ILs has been that they have no observable vapor pressure. Primarily for this reason, ILs are often referred to as "green" solvents because they do not create atmospheric pollution in the way that volatile molecular solvents do. Indeed, there is excellent evidence that the vapor pressures of ILs are extremely low near room temperature. For example, the ideal gas vapor pressure of 1-butyl-3-methylimidazolium hexafluorophosphate has been estimated to be 10^{-10} Pa at 298 K.[3] Other ILs have been studied by X-ray photoelectron spectroscopy in an ultra-high-vacuum chamber ($p \approx 10^{-7}$ Pa) at room temperature.[4] By simulation[5] and experiment,[6] the cohesive energy densities for a variety of ILs are found to be very large near room temperature, which explains the low volatility of these liquids.[5a]

Recently, however, there have been reports indicating that the vapor pressures of some ILs become significant at higher temperatures. In 2005 Rebelo et al.[7] used surface tension and density data to predict the normal boiling temperatures of salts of 1-alkyl-3-methylimidazolium (abbreviated $[C_n\text{mim}]^+$, where *n* is the number of carbons in the alkyl group) with the anions $[BF_4]^-$, $[PF_6]^-$, and $[(CF_3SO_2)_2N]^-$ (abbreviated as $[Tf_2N]^-$). They predicted that salts of $[Tf_2N]^-$ would have the lowest boiling temperatures (around 525 K for $[C_{10}\text{mim}][Tf_2N]$).[7] Soon after this prediction was made, vapor pressure measurements

by Knudsen effusion on $[C_2\text{mim}][Tf_2N]$, $[C_4\text{mim}][Tf_2N]$, $[C_6\text{-}\text{mim}][Tf_2N]$, and $[C_8\text{mim}][Tf_2N]$ were reported.[8] Vapor pressures for $[C_4\text{mim}][Tf_2N]$ were determined over the widest temperature range, and reported to be 0.0036 Pa at 437.84 K (the lowest temperature) and 0.515 Pa at 517.45 K (the highest temperature).[8] It is worth noting that the Knudsen effusion apparatus could not detect a vapor pressure for $[C_4\text{mim}][PF_6]$ at temperatures up to 473 K.[3] In early 2006 Earle et al.[9] reported vacuum distillations of ILs using both a Kugelrohr apparatus (at 573 K and 600 Pa) and a sublimation apparatus (at 473 K and 0.1 Pa). Several classes of pure ILs were evaporated and condensed without decomposition. Additionally, distillations of a few binary mixtures of ILs showed that the initial distillate was enriched in one of the ILs, as would be expected for the separative distillation of compounds with different vapor pressures.[9]
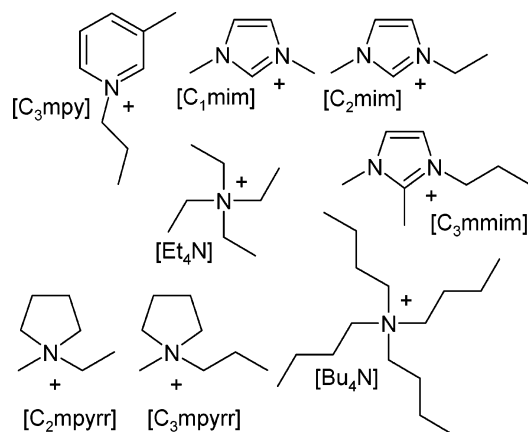
We realized that a relative volatility series for ILs could be established by analyzing the initial distillate from mixtures to see which salts distill preferentially.[10] This straightforward approach avoids the difficulties and pitfalls of absolute vapor pressure measurements in the low-pressure regime. Herein we report the results of more than 30 distillations of IL mixtures. In this way we determined the relative volatilities of ILs containing the following ions: 1-alkyl-3-methylimidazolium, $[C_n\text{mim}]^+$; 1-alkyl-2,3-dimethylimidazolium, $[C_n\text{mmim}]^+$; *N*-alkyl-*N*-methylpyrrolidinium, $[C_n\text{mpyrr}]^+$; *N*-propyl-3-methylpyridinium, $[C_3\text{mpy}]^+$; tetraalkylammonium, $[R_4N]^+$; tetrafluoroborate, $[BF_4]^-$; hexafluorophosphate, $[PF_6]^-$; trifluoromethanesulfonate, $[CF_3SO_3]^-$ (abbreviated as $[TfO]^-$); bis(trifluoromethylsulfonyl)imide, $[(CF_3SO_2)_2N]^-$ (abbreviated as $[Tf_2N]^-$); bis(pentafluoroethylsulfonyl)imide, $[(C_2F_5SO_2)_2N]^-$; (nonafluorobutylsulfonyl)(trifluoromethylsulfonyl)imide, $[(C_4F_9SO_2)(CF_3SO_2)N]^-$ (abbreviated as $[(C_4F_9SO_2)(Tf)N]^-$); and tris(trifluoromethylsulfonyl)methanide, $[(CF_3SO_2)_3C]^-$ (abbreviated

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SCHEME 1:   Representative IL Cations along with Their Abbreviations

Figure 1. Schematic drawing of the sublimation apparatus used to distill the IL mixtures. The drawing shows the inlet (A) and outlet (B) connections to the circulating bath, the connection to the vacuum line (C), the cold finger condenser (D), and the sublimator flask (E).

as [Tf$_3$C]$^-$). The structures and abbreviations of representative IL cations are shown in Scheme 1. Most of the distillations are of equimolar binary mixtures of ILs that have a common cation or a common anion. We also distilled equimolar ternary mixtures of ILs with a common cation, and equimolar binary mixtures of ILs without a common ion.

We believe that the information garnered from these distillations will be useful in guiding the selection of ILs for high-temperature applications. Additionally, we hope that this work will provide an impetus for absolute vapor pressure measurements on ILs, for computational studies of IL volatility, and for further studies of the vapor phase of ILs,[11] all of which are badly needed. We also hope that this work will spur the search for ILs with especially high and especially low vapor pressures, both of which would be useful in certain types of applications.

Experimental Section

Materials. The pyrrolidinium salts and the [C$_1$mim][Tf$_2$N] were synthesized at the United States Naval Academy (see the Supporting Information for a description of their synthesis). They were found to be ≥99% pure by ^{1}H and ^{19}F NMR. The [C$_6$mim][Tf$_2$N] is from the high purity batch[12] of material that was synthesized for IUPAC Project 2002-005-1-100.[13] The remaining ILs were purchased from commercial sources (see the Supporting Information for a table listing the purity of each). HPLC-grade acetone was used to make the IL mixtures (see below) and to wash all of the glassware.

Distillation Procedure. The vacuum line used to degas and distill the ILs consisted of a vacuum manifold, a liquid nitrogen trap, and a mechanical pump. Prior to each distillation, the ILs were degassed under vacuum with stirring, but without heating, until the vacuum in the system was ≤0.1 Pa. The degassed ILs were transferred into a nitrogen atmosphere glove box with an atmospheric moisture content of less than 10 ppm. In the glove box a binary mixture with a 1:1 mol ratio (or ternary mixture with a 1:1:1 mol ratio) was prepared by weighing the ILs into the flask of a small glass sublimator (Figure 1). The total mass of each mixture was approximately 1 g, enough to form a 1−2 mm layer of liquid at the bottom of the sublimator flask. Then the sublimator flask was taken out of the glove box and, any IL clinging to its inner wall was washed to the bottom with acetone. Next, most of the acetone was driven off by heating in air at about 50 °C. The remaining acetone was removed by connecting the sublimator to the vacuum line and heating to 60−70 °C until a vacuum of ≤0.1 Pa was reached. At this point the vacuum was released and a drop of the mixture was removed
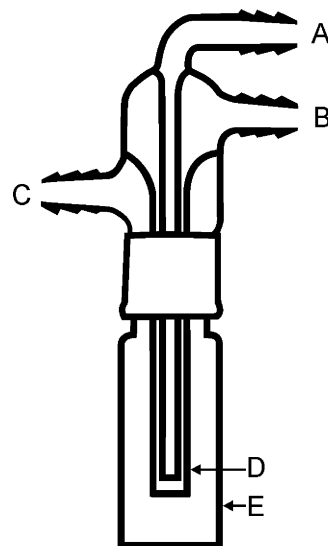
with a glass pipet for NMR analysis. After re-establishing a vacuum of ≤0.1 Pa, the sublimator was placed on a hotplate and the cold finger condenser was connected to a liquid circulating bath maintained at 25 °C. The distillation was started by turning on the hotplate. During a typical distillation, the temperature of the hotplate surface increased from ambient to 200 °C over 40−50 min, and was then maintained at 200−215 °C for an additional 10−200 min, depending on the rate of distillation. At this point, 5−30 mg of distillate had collected on the cold finger condenser. The distillation was stopped by removing the hotplate. Then the sublimator was taken apart and the distillate on the cold finger condenser was washed off with CD$_3$CN and analyzed by NMR. The undistilled liquid remaining in the flask was also analyzed by NMR.

Making the initial IL mixture by rinsing the walls of the sublimator flask with acetone has two advantages. First, it assures that all of the IL weighed into the sublimator is transferred into the bottom of the flask (this is important because the sublimator is heated only from the bottom). Second, it facilitates the formation of a homogeneous mixture by temporarily forming a low viscosity solution. However, control experiments in which no acetone was used to make the mixture showed no significant change in the distillate composition (and, qualitatively, no change in the rate of distillation). For example, one of the data points for [C$_6$mim][Tf$_2$N] + [C$_2$mim][Tf$_2$N] (Figure 2), was collected without using acetone, as was one of the data points for [C$_6$mpyrr][Tf$_2$N] + [C$_3$mpyrr][Tf$_2$N] (Figure 3).

The distillation temperatures were determined by measuring the temperature of the hotplate surface with an infrared thermometer. At 473 K, the standard uncertainty of the thermometer reading is ±6 K. Additionally, there is an undetermined difference in temperature between the surface of the hotplate and the IL mixture in the sublimator. The pressures were determined with a thermocouple vacuum gauge located about halfway between the sublimator and the cold trap. Consequently, the reported pressures are intended only to indicate the quality of the vacuum, not the absolute pressure inside the sublimator.

By using a thin layer of IL and heating it slowly, we were able to degas and distill the mixtures without bubble formation
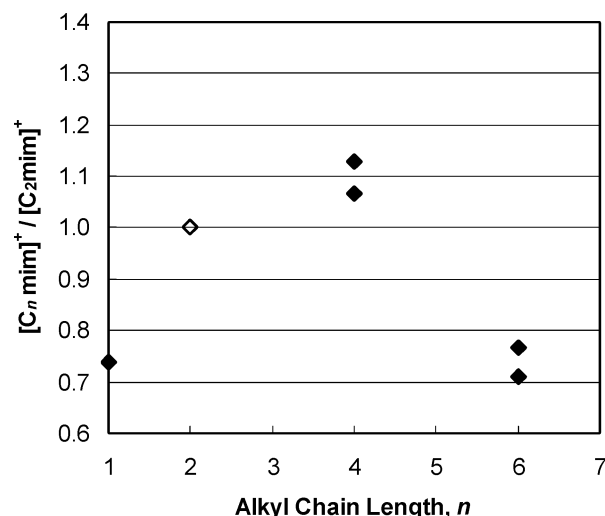
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Figure 2. Plot of the molar ratios of cations in the initial distillate from a series of equimolar binary mixtures of the type ([$C_n$mim][Tf$_2$N] + [C_2mim][Tf$_2$N]). There is a peak in the ratio at $n = 4$ (i.e., when the alkyl side chain of [$C_n$mim]$^+$ is a butyl group), which corresponds to a peak in volatility. The value of the ratio is defined to be 1.0 at $n = 2$ because [C_2mim][Tf$_2$N] is the comparison point for all the mixtures. Replicate distillations give an indication of the scatter in the data.
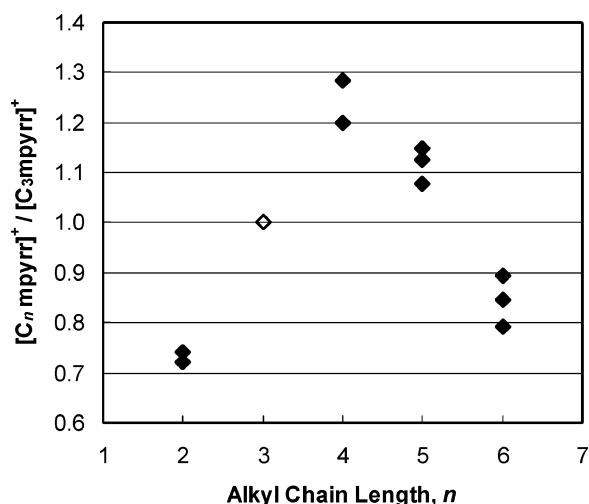

Figure 3. Plot of the molar ratios of cations in the initial distillate from a series of equimolar binary mixtures of the type ([$C_n$mpyrr][Tf$_2$N] + [C_3mpyrr][Tf$_2$N]). There is a peak in the ratio at $n = 4$ (i.e., when the alkyl side chain of [$C_n$mpyrr]$^+$ is a butyl group), which corresponds to a peak in volatility. The value of the ratio is defined to be 1.0 at $n = 3$ because [C_3mpyrr][Tf$_2$N] is the comparison point for all the mixtures. Replicate distillations give an indication of the scatter in the data.

(all of the distillations were performed below the boiling temperature). It was necessary to avoid such bubbling to ensure that any IL on the cold finger condenser was transferred as a vapor, and not by splashing.

NMR Analysis. All NMR spectra were collected on a 400 MHz NMR spectrometer with CD$_3$CN as the solvent. The mole fraction (x) of each cation was determined by ^{1}H NMR, and the mole fraction of each anion was determined by ^{19}F NMR. The initial mixture was analyzed by NMR in order to check its preparation by mass; the agreement was always good, with $|x_{NMR} - x_{mass}| \leq 0.013$ for all the initial mixtures. The initial distillate was analyzed by NMR in order to determine the mole fraction of each ion, and to check for decomposition. The undistilled liquid was analyzed by NMR in order to check for decomposi-

tion. For all of the distillations reported, less than 1% decomposition was observed by both ^{1}H and ^{19}F NMR.

The mole fraction of an ion (x_{ion}) in the initial distillate has two primary sources of uncertainty. First, the standard uncertainty in x_{ion} that results from the preparation of the initial mixture is estimated to be $u_{mixture} = 0.02 \cdot x_{ion}$ (i.e., $\pm 2\%$). Second, the standard uncertainty in x_{ion} resulting from the scatter in the data for repeated distillations is estimated to be $u_{scatter} = 0.03 \cdot x_{ion}$ (i.e., $\pm 3\%$). Assuming that these two sources of uncertainty are independent, the expanded ($k = 2$) uncertainty in x_{ion} in the initial distillate is $U = 0.07 \cdot x_{ion}$ (i.e., $\pm 7\%$). It follows that the expanded ($k = 2$) uncertainty in the ratios of ions shown in Figures 2 and 3 is $U_{ratio} = 0.10 \cdot ratio$ (i.e., $\pm 10\%$).[14]

Results

The Effect of Alkyl Chain Length on the Volatility of [$C_n$mim][Tf$_2$N] Salts. Equimolar mixtures of ([C_1mim][Tf$_2$N] + [C_2mim][Tf$_2$N]), ([C_4mim][Tf$_2$N] + [C_2mim][Tf$_2$N]), and ([C_6mim][Tf$_2$N] + [C_2mim][Tf$_2$N]) were vacuum-distilled at approximately 473 K in a glass sublimation apparatus. The initial distillate on the cold finger condenser was analyzed by NMR spectroscopy. For the mixture of ([C_1mim][Tf$_2$N] + [C_2mim]-[Tf$_2$N]), the initial distillate contained 0.425 mole fraction [C_1-mim]$^+$ and 0.575 mole fraction [C_2mim]$^+$; therefore, the molar ratio of [C_1mim]$^+$/[C_2mim]$^+$ in the initial distillate was 0.74. That is, [C_1mim][Tf$_2$N] is found to be less volatile than [C_2-mim][Tf$_2$N] in this distillation. Similarly, [C_4mim][Tf$_2$N] was found to be more volatile than [C_2mim][Tf$_2$N], and [C_6mim]-[Tf$_2$N] was found to be less volatile than [C_2mim][Tf$_2$N]. Figure 2 shows how the molar ratios of cations in the initial distillate depend on alkyl chain length. From Figure 2 it is seen that the volatility series for [$C_n$mim][Tf$_2$N] salts at 473 K is [C_4mim]-[Tf$_2$N] > [C_2mim][Tf$_2$N] > [C_1mim][Tf$_2$N] $\approx$ [C_6mim][Tf$_2$N].

The Effect of Alkyl Chain Length on the Volatility of [$C_n$mpyrr][Tf$_2$N] Salts. Equimolar mixtures of ([C_2mpyrr]-[Tf$_2$N] + [C_3mpyrr][Tf$_2$N]), ([C_4mpyrr][Tf$_2$N] + [C_3mpyrr]-[Tf$_2$N]), ([C_5mpyrr][Tf$_2$N] + [C_3mpyrr][Tf$_2$N]), and ([C_6mpyrr]-[Tf$_2$N] + [C_3mpyrr][Tf$_2$N]) were vacuum distilled in a manner analogous to the [$C_n$mim][Tf$_2$N] mixtures. For each mixture, the molar ratio of cations in the initial distillate was determined by NMR spectroscopy and is plotted in Figure 3. Several replicate experiments give an indication of the scatter in the data. For the [$C_n$mpyrr][Tf$_2$N] series, we again see an initial increase in volatility with increasing alkyl chain length, followed by a peak in volatility when the alkyl side chain is a butyl group. From Figure 3, one can quickly see that the volatility series for the [$C_n$mpyrr][Tf$_2$N] salts at 473 K is [C_4mpyrr][Tf$_2$N] > [C_5mpyrr][Tf$_2$N] > [C_3mpyrr][Tf$_2$N] > [C_6mpyrr][Tf$_2$N] > [C_2mpyrr][Tf$_2$N].

Developing a Volatility Series for Different Classes of Cations. In addition to testing the effect of alkyl chain length on IL volatility, we also determined the effect of different types of cations on IL volatility. That is, do certain classes of cations form more volatile salts? One difficulty in answering this question is that, as we have just seen for [$C_n$mim][Tf$_2$N] and [$C_n$mpyrr][Tf$_2$N] salts, there is significant variability in volatility within each class of ILs due to the size of the alkyl side chains. In order to minimize this size effect, cations with similar masses (except for [Bu$_4$N][Tf$_2$N]) were deliberately chosen for comparison (Table 1). For this set of experiments, equimolar mixtures of the type ([cation][Tf$_2$N] + [C_4mpyrr][Tf$_2$N]) were distilled. Among other reasons, [C_4mpyrr][Tf$_2$N] was chosen as the comparison IL for these distillations because it has

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TABLE 1: Ratio of Cations in the Initial Distillate from Equimolar Binary Mixtures of ILs with a Common Anion

mixture ([A][B] + [C][B])	A:C in distillate
[C$_4$mim][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.944:0.056
[C$_4$mim][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.933:0.067
[C$_3$mmim][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.884:0.116
[C$_3$mpy][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.845:0.155
[Bu$_4$N][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.809:0.191
[Et$_4$N][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.467:0.533

TABLE 2: Ratio of Anions in the Initial Distillate from Equimolar Binary Mixtures of ILs with a Common Cation

mixture ([A][B] + [A][D])	B:D in distillate
[C$_4$mpyrr][(C$_2$F$_5$SO$_2$)$_2$N] + [C$_4$mpyrr][Tf$_2$N]	0.676:0.324
[C$_3$mmim][(C$_2$F$_5$SO$_2$)$_2$N] + [C$_3$mmim][Tf$_2$N]	0.663:0.337
[C$_4$mpyrr][(C$_4$F$_9$SO$_2$)(Tf)N] + [C$_4$mpyrr][Tf$_2$N]	0.613:0.387
[C$_3$mmim][Tf$_3$C] + [C$_3$mmim][Tf$_2$N]	0.126:0.874
[C$_4$mim][TfO] + [C$_4$mim][Tf$_2$N]	0.087:0.913
[C$_4$mim][PF$_6$] + [C$_4$mim][Tf$_2$N]	0.020:0.980

excellent thermal stabililty and it does not have an acidic proton. Table 1 shows the mole fractions of cations in the initial distillate for each mixture. [C$_4$mim][Tf$_2$N] was found to be about 15 times as volatile as [C$_4$mpyrr][Tf$_2$N], and is the most volatile of these salts (the two experiments listed in Table 1 for [C$_4$mim][Tf$_2$N] were performed by two different researchers at NIST). [C$_3$mmim][Tf$_2$N] is also relatively volatile (about 8 times as volatile as [C$_4$mpyrr][Tf$_2$N]), excellent evidence that proton transfer from the C-2 carbon is not necessary for the vaporization of imidazolium salts under these conditions.[9] [C$_3$mpy][Tf$_2$N] was found to about 5 times as volatile as [C$_4$mpyrr][Tf$_2$N]. [Et$_4$N]-[Tf$_2$N] and [C$_4$mpyrr][Tf$_2$N] have similar volatilities. From these experiments it would seem that the salts of flat aromatic cations (imidazolium and pyridinium) are generally more volatile than the salts of tetrahedral, nonaromatic cations (pyrrolidinium and ammonium). However, a comparison of the experiments with [Et$_4$N][Tf$_2$N] and [Bu$_4$N][Tf$_2$N] (Table 1) demonstrates an important point: a small change in the length of the cation's alkyl side chains can have an effect that is as large as changing to a different type of cation. To summarize, the volatility series for different classes of cations at 473 K is [C$_4$mim]$^+$ > [C$_3$mmim]$^+$ > [C$_3$mpy]$^+$ > [Bu$_4$N]$^+$ ≫ [C$_4$mpyrr]$^+$ ≈ [Et$_4$N]$^+$.

Developing a Volatility Series for Different Classes of Anions. We have also explored the effect of different types of anions on IL volatility. For this set of experiments, equimolar mixtures of the type ([cation][anion] + [cation][Tf$_2$N]) were distilled. Table 2 shows the mole fractions of anions in the initial distillate from each mixture. For the mixture ([C$_4$mpyrr][(C$_2$F$_5$-SO$_2$)$_2$N] + [C$_4$mpyrr][Tf$_2$N]), the [(C$_2$F$_5$SO$_2$)$_2$N]$^-$ salt is about twice as volatile as the [Tf$_2$N]$^-$ salt (Table 2). We also checked the effect of changing the counter cation by distilling the mixture ([C$_3$mmim][(C$_2$F$_5$SO$_2$)$_2$N] + [C$_3$mmim][Tf$_2$N]); once again, the [(C$_2$F$_5$SO$_2$)$_2$N]$^-$ salt is about twice as volatile as the [Tf$_2$N]$^-$ salt. The results in Table 2 also show that [C$_4$mpyrr][(C$_4$F$_9$-SO$_2$)(Tf)N] is 1.6 times as volatile as [C$_4$mpyrr][Tf$_2$N], that [C$_3$mmim][Tf$_2$N] is about 7 times as volatile as [C$_3$mmim]-[Tf$_3$C], that [C$_4$mim][Tf$_2$N] is about 10 times as volatile as [C$_4$mim][TfO], and that [C$_4$mim][Tf$_2$N] is about 50 times as volatile as [C$_4$mim][PF$_6$]. Distillations of mixtures containing [BF$_4$]$^-$ salts always showed some decomposition by ^{19}F NMR; for this reason, no results for [BF$_4$]$^-$ salts are reported in Table 2. Nevertheless, it appears that [BF$_4$]$^-$ salts have a relatively low volatility (similar to [PF$_6$]$^-$ salts). To summarize, the volatility series for different classes of anions at 473 K is [(C$_2$F$_5$SO$_2$)$_2$N]$^-$ > [(C$_4$F$_9$SO$_2$)(Tf)N]$^-$ > [Tf$_2$N]$^-$ ≫ [Tf$_3$C]$^-$ > [TfO]$^-$ ≫ [PF$_6$]$^-$.

Because there is less peak overlap in the ^{19}F NMR spectra, it is feasible to distill mixtures containing more than two types of anions.[15] This approach is demonstrated by the distillation of equimolar ternary mixtures of ILs with a common cation. In the first experiment, the initial distillate from the mixture ([C$_3$mmim][Tf$_2$N] + [C$_3$mmim][(C$_2$F$_5$SO$_2$)$_2$N] + [C$_3$mmim]-[Tf$_3$C]) had mole fractions of 0.322:0.632:0.045 for [Tf$_2$N]$^-$:[(C$_2$F$_5$SO$_2$)$_2$N]$^-$:[Tf$_3$C]$^-$. In the second experiment, the initial distillate from the mixture ([C$_4$mpyrr][Tf$_2$N] + [C$_4$mpyrr][(C$_2$F$_5$-

SO$_2$)$_2$N] + [C$_4$mpyrr][(C$_4$F$_9$SO$_2$)(Tf)N]) had mole fractions of 0.223:0.450:0.328 for [Tf$_2$N]$^-$:[(C$_2$F$_5$SO$_2$)$_2$N]$^-$:[(C$_4$F$_9$SO$_2$)-(Tf)N]$^-$. The same ordering of volatilities is obtained from these ternary mixtures as for the binary mixture experiments listed in Table 2. In fact, the ratio of any two anions in the distillate from the ternary mixtures is essentially identical to the corresponding ratio found in Table 2.

The Effect of Multiple Counterions on the Volatility Series. All of the distillations that have been described to this point are for mixtures in which there is a common counterion. For example, [Tf$_2$N]$^-$ was the only anion present in distillations for the [C$_n$mim][Tf$_2$N] series, the [C$_n$mpyrr][Tf$_2$N] series, and the "cation series". What would happen to the composition of the initial distillate if multiple counter anions were present? To further probe the effect of counterions on relative volatility, several distillations were done with binary mixtures in which there was no common ion (Table 3). In this type of experiment four types of ions are present—two cations and two anions. A ratio of cations in the initial distillate was obtained by ^{1}H NMR analysis, and a ratio of anions was obtained by ^{19}F NMR analysis. In this way, each distillation yields a comparison with the "cation series" (Table 1) and the "anion series" (Table 2).

Remarkably, for all of the experiments shown in Table 3, the ratios of cations or anions that appear in the initial distillate are essentially identical to the corresponding ratios from Table 1 or Table 2. For example, for the mixture ([C$_4$mim][PF$_6$] + [C$_4$mpyrr][Tf$_2$N]), the ratio of [C$_4$mim]$^+$:[C$_4$mpyrr]$^+$ in the initial distillate was 0.932:0.068, and the ratio of [PF$_6$]$^-$:[Tf$_2$N]$^-$ in the initial distillate was 0.017:0.983 (Table 3). These ratios are very similar to the ratios found for [C$_4$mim]$^+$:[C$_4$mpyrr]$^+$ in Table 1 (0.944:0.056 and 0.933:0.067), and for [PF$_6$]$^-$:[Tf$_2$N]$^-$ in Table 2 (0.020:0.980). As a second example, for the mixture ([Et$_4$N][Tf$_2$N] + [C$_4$mim][TfO]), the ratio of [Et$_4$N]$^+$:[C$_4$mim]$^+$ in the initial distillate was 0.067:0.933, and the ratio of [Tf$_2$N]$^-$:[TfO]$^-$ in the initial distillate was 0.886:0.114 (Table 3). The ILs [Et$_4$N][Tf$_2$N] and [C$_4$mim][Tf$_2$N] were never directly compared in the "cation series", but each was compared to [C$_4$mpyrr][Tf$_2$N]. Using the cation ratios from Table 1 for the distillations of ([C$_4$mim][Tf$_2$N] + [C$_4$mpyrr]-[Tf$_2$N]) and ([Et$_4$N][Tf$_2$N] + [C$_4$mpyrr][Tf$_2$N]), one can predict a ratio of about 0.05:0.95 for [Et$_4$N]$^+$:[C$_4$mim]$^+$, which is very close to the observed ratio of 0.067:0.933. Additionally, the ratio of [Tf$_2$N]$^-$:[TfO]$^-$ (0.886:0.114) for this distillation is quite similar to the ratio of [Tf$_2$N]$^-$:[TfO]$^-$ in Table 2 (0.913:0.087).

Discussion

The most interesting feature in Figures 2 and 3 is the peak in volatility at intermediate alkyl chain lengths.[16] The initial increase in volatility with increasing alkyl chain length is larger than the expanded uncertainties in the data, so the peaks are statistically significant. It appears that a peak in volatility at intermediate alkyl chain lengths will be observed for the [R$_4$N]-[Tf$_2$N] series also, since we find that [Bu$_4$N][Tf$_2$N] is more volatile than [Et$_4$N][Tf$_2$N] (Table 1). Additionally, it appears that the same type of behavior is observed for side chains on

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TABLE 3: Ratio of Cations and the Ratio of Anions in the Initial Distillate for Equimolar Binary Mixtures of ILs without a Common Ion

mixture ([A][B] + [C][D])	A:C in distillate	B:D in distillate
$[C_4mim][PF_6]$ + $[C_4mpyrr][Tf_2N]$	0.932:0.068	0.017:0.983
$[Et_4N][Tf_2N]$ + $[C_4mim][TfO]$	0.067:0.933	0.886:0.114
$[C_3mpy][Tf_2N]$ + $[C_3mmim][Tf_3C]$	0.440:0.560	0.885:0.115
$[C_3mmim][(C_2F_5SO_2)_2N]$ + $[C_2mim][Tf_2N]$	0.380:0.620	0.666:0.334

the anion since salts of $[(C_2F_5SO_2)_2N]^-$ and $[(C_4F_9SO_2)(Tf)N]^-$ are more volatile than salts of $[Tf_2N]^-$ (Tables 2 and 3). The initial increase in volatility with an increase in alkyl chain length would be very unusual for a series of molecular compounds, so it is reasonable to look for an explanation that involves the ionic nature of these liquids. A variety of intermolecular forces exist between the ions in the liquid phase including ion–ion, hydrogen bonding, and van der Waals forces. The strongest of these are the ion–ion Coulombic forces which are largely determined by the shape of the ions and the charge delocalization, which in turn influences how the ions may approach one another. As the cations increase in size, the centers of charge are held farther apart on average, which decreases Coulombic interactions and concomitantly increases volatility.[11a,17] The eventual decrease in volatility with longer alkyl side chains can be explained by van der Waals interactions, which increase in strength with more efficient packing of the chains and with increasing molecular weight due to the greater electron density available for polarization. As the alkyl side chain lengthens, increases in the van der Waals interactions eventually become large enough to outweigh decreases in the Coulombic interactions, causing a decline in volatility (see the Supporting Information for further discussion of this point). If the peaks in these volatility series are "real" (i.e., not the result of some type of nonideal behavior of the mixtures), then they could serve as a useful test of computer models of IL behavior, and of the reliability of absolute vapor pressure measurements on ionic liquids.

The absolute vapor pressure measurements[8] that were mentioned in the Introduction give a different volatility series for $[C_nmim][Tf_2N]$ from the one shown in Figure 2. Over the temperature range studied (which included 473 K), the order of vapor pressures at each temperature by Knudsen effusion is $[C_2mim][Tf_2N] > [C_6mim][Tf_2N] > [C_4mim][Tf_2N] > [C_8mim]-[Tf_2N]$.[8,18] It is not clear why the relative volatilities obtained from the effusion measurements disagree with the relative volatilities obtained from the distillation experiments. One possible explanation is that there was an undetected problem with volatile impurities or with decomposition for some of the effusion experiments (which could also account for the difficult-to-explain order of the vapor pressures). Another possible explanation is that evaporation from the IL mixtures is not ideal, so that the ratio of ILs in the initial distillate does not always reflect the relative vapor pressures of the pure ILs. Studies of whether or not IL mixtures behave ideally would be very interesting.

The volatility series for $[C_nmim][Tf_2N]$ that is shown in Figure 2 is partially consistent with the predictions made by Rebelo et al.[7] that were mentioned in the Introduction. They used surface tension and density data to predict the normal boiling temperatures for $[C_nmim][Tf_2N]$ salts with $n = 2, 4, 6$, and 10. They predict that boiling temperatures will decrease steadily as the alkyl chain lengthens, which is consistent with our observation of increasing volatility up to $n = 4$, but not with the decrease in volatility at $n = 6$.

Watanabe and co-workers[19] have suggested that the more ion pairing there is in the liquid phase the higher the vapor pressure of the IL. This is consistent with a recent mass spectrometry study of IL vapors,[11a] and is consistent with the behavior of high-temperature molten salts (e.g., alkali halides), which are known to vaporize as tight ion-pairs.[20] Watanabe and co-workers have determined experimentally the amount of ion pairing in a variety of ILs in the temperature range 263–353 K. For salts of $[C_nmim][Tf_2N]$ with $n = 1, 2, 4, 6$, and 8, the extent of ion pairing increases as the alkyl chain lengthens.[21] For $[Tf_2N]^-$ salts with a variety of cationic structures, the amount of ion pairing follows the trend $[C_4mim]^+ \approx N$-butylpyridinium $> [(Bu)(CH_3)_3N]^+ > [C_4mpyrr]^+$.[22] For $[C_4mim]^+$ salts with a variety of anionic structures, the amount of ion pairing follows the trend $[TfO]^- > [Tf_2N]^- \approx [(C_2F_5SO_2)_2N]^- \approx [BF_4]^- > [PF_6]^-$.[23] The trends in the ion-pairing data show some dependence on temperature, and all of the ion-pairing data are for temperatures much lower than the distillations described herein. Nevertheless, there is enough agreement between the ion-pairing data and the distillations to give credence to the idea that ion pairing in the liquid is important for volatility. For example, the ion-pairing data correctly predict the relatively high volatility of $[C_4mim]^+$ salts and the relatively low volatility of $[C_4mpyrr]^+$ and $[PF_6]^-$ salts.

For the distillations described herein, the ratio of any two particular ions in the distillate had little dependence on the other ions present. The most compelling example of this is for the ions $[(C_2F_5SO_2)_2N]^-$ and $[Tf_2N]^-$. The distillations of five different mixtures containing the anions $[(C_2F_5SO_2)_2N]^-$ and $[Tf_2N]^-$ have been described (including the two ternary mixtures), and for all five mixtures the ratio of $[(C_2F_5SO_2)_2N]^-$: $[Tf_2N]^-$ in the distillate was very close to 2:1. In general, it appears that $[(C_2F_5SO_2)_2N]^-$ salts are simply more volatile than $[Tf_2N]^-$ salts. Similarly, it appears that $[PF_6]^-$ salts are simply less volatile than $[Tf_2N]^-$ salts. It will be interesting to see if exceptions to either of these cases can be found. Further discussion about why some ions form more volatile salts can be found in the Supporting Information.

Conclusions

In addition to determining the relative volatilities of a number of ionic liquids, we believe that this work has uncovered two general features of IL volatility. First, a peak in volatility is observed when the alkyl side chains on the ions are of intermediate length. Second, certain classes of salts (e.g., $[(C_2F_5SO_2)_2N]^-$ salts) are more volatile than others (e.g., $[PF_6]^-$ salts), regardless of the counterions present. We hope that this work will encourage others to study IL volatility. In particular, computational studies would be of great value.

Supporting Information Available: Synthetic procedure for the ILs made at the United States Naval Academy; table showing the source and purity of each of the ILs used in the distillation experiments; tables showing the mole fractions of cations in the initial distillate for the experiments plotted in Figures 2 and 3; further discussion of the peak in volatility at intermediate alkyl chain lengths; further discussion about why some ions form more volatile salts. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) This approach for determining relative volatility could also be used for mixtures of molecular substances with low vapor pressures (e.g., polycyclic aromatic compounds). However, the mixture would have to form a homogeneous liquid phase at the distillation temperature in order to work properly.

(11) Throughout this paper we make the tacit assumption that the IL vapor phase consists of ion pairs. This makes physical sense and is consistent with the behavior of high-temperature molten salts. Although we have no direct evidence for ion pairs in the vapor phase of the distillations, recent mass spectrometry studies of IL vapors provide some insight. In the first paper, which is probably the most relevant in terms of experimental conditions, it is concluded that ILs evaporate as (uncharged) ion pairs. (a) Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982−990. (b) Chen, H.; Ouyang, Z.; Cooks, R. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3656−3660. (c) DaSilveira Neto, B. A.; Santos, L. S.; Nachtigall, F. M.; Eberlin, M. N.; Dupont, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7251−7254.

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(15) In principle, we could have determined the entire anion series in a single experiment. Our reasons for not doing so are that we could not easily obtain all the appropriate salts with the same counter cation, and that in the glove box it is difficult to prepare properly such a complicated mixture.

(16) The existence of the peak in volatility in the [$C_n$mim][Tf_2N] series was missed in our earlier work[9] on IL distillation because [C_2mim][Tf_2N] was compared only to [C_6mim][Tf_2N], [C_{10}mim][Tf_2N], and [C_{16}mim]-[Tf_2N].

(17) It must be noted that simulations for the [$C_n$mim][Tf_2N] series (with $n = 2−8$) showed no obvious change in Coulombic interactions with increasing alkyl chain length.[6c] However, it is quite possible that such simulations cannot detect sufficiently small changes in Coulombic interactions to observe the type of trend shown in Figure 2.

(18) Even though the ordering of vapor pressures at 473 K obtained from Knudsen effusion does not agree with the relative volatilities from the distillation of IL mixtures, the actual values of vapor pressure reported in reference 8 are generally consistent with the temperature and pressure needed to distill mixtures of [$C_n$mim][Tf_2N] salts.

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