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Why Are Ionic Liquids Liquid? A Simple Explanation Based on Lattice and Solvation Energies

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Abstract: We have developed a simple and quantitative explanation for the relatively low melting temperatures of ionic liquids (ILs). The basic concept was to assess the Gibbs free energy of fusion ($\Delta_{fus}G$) for the process $IL_{(s)} \rightarrow IL_{(l)}$, which relates to the melting point of the IL. This was done using a suitable Born−Fajans−Haber cycle that was closed by the lattice (i.e., $IL_{(s)} \rightarrow IL_{(g)}$) Gibbs energy and the solvation (i.e., $IL_{(g)} \rightarrow IL_{(l)}$) Gibbs energies of the constituent ions in the molten salt. As part of this project we synthesized and determined accurate melting points (by DSC) and dielectric constants (by dielectric spectroscopy) for 14 ionic liquids based on four common anions and nine common cations. Lattice free energies ($\Delta_{latt}G$) were estimated using a combination of Volume Based Thermodynamics (VBT) and quantum chemical calculations. Free energies of solvation ($\Delta_{solv}G$) of each ion in the bulk molten salt were calculated using the COSMO solvation model and the experimental dielectric constants. Under standard ambient conditions (298.15 K and 10^5 Pa) $\Delta_{fus}G°$ was found to be negative for all the ILs studied, as expected for liquid samples. Thus, these ILs are liquid under standard ambient conditions because the liquid state is thermodynamically favorable, due to the large size and conformational flexibility of the ions involved, which leads to small lattice enthalpies and large entropy changes that favor melting. This model can be used to predict the melting temperatures and dielectric constants of ILs with good accuracy. A comparison of the predicted vs experimental melting points for nine of the ILs (excluding those where no melting transition was observed and two outliers that were not well described by the model) gave a standard error of the estimate (s_{est}) of 8 °C. A similar comparison for dielectric constant predictions gave s_{est} as 2.5 units. Thus, from very little experimental and computational data it is possible to predict fundamental properties such as melting points and dielectric constants of ionic liquids.

Introduction

Ionic liquids (ILs) are receiving an ever-increasing amount of interest due to their wide and diverse potential to serve as novel reaction media,[1,2] as electrolytes in batteries,[3−5] solar cells, and fuel cells,[6−9] as lubricants and heat-transfer fluids,[10,11] as stationary phases in gas chromatography, and as matrixes for MALDI-TOF mass spectrometry and in nanoscience.[12−16] A milestone in ionic liquid technology has recently been reached, as there are now large scale industrial applications involving ILs (the BASIL process of BASF being the most widely publicized).[17−19] The replacement of classical materials with ILs can have many benefits and has been shown to enhance catalytic reactions, simplify product or catalyst separation, and reduce the risks associated with using volatile and highly flammable organic compounds. Ionic liquids also have environmental benefits, as the negligible vapor pressure of these materials under

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(1) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(2) Wasserscheid, P.; Welton, T. *Ionic Liquids in synthesis*; Wiley-VCH: 2003.

(3) Shobukawa, H.; Tokuda, H.; Susan, A. B. H.; Watanabe, M. *Electrochim. Acta* **2005**, *50*, 3872−3877.

(4) Shobukawa, H.; Tokuda, H.; Tabata, S.-i.; Watanabe, M. *Electrochim. Acta* **2004**, *50*, 1−5.

(5) Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Watanabe, M.; Terada, N. *Chem. Commun.* **2006**, 544−545.

(6) Wang, P.; Zakeeruddin, S. M.; Shaik, M.; Humphry-Baker, R.; Grätzel, M. *Chem. Mater.* **2004**, *16*, 2694−2696.

(7) Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.-E.; Teuscher, J.; Kantlehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 6850−6856.

(8) Mazille, F.; Fei, Z.; Kuang, D.; Zhao, D.; Zakeeruddin, S. M.; Grätzel, M.; Dyson, P. J. *Inorg. Chem.* **2006**, *45*, 1585−1590.

(9) Angell, C. A.; Xu, W. *Science* **2003**, *302*, 422−425.

(10) Valkenburg, M. E. V.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. *Thermochim. Acta* **2005**, *425*, 181−188.

(11) Ye, C.; Liu, W.; Chen, Y.; Yu, L. *Chem. Commun.* **2001**, 2244−2245.

(12) Armstrong, D. W.; Zhang, L.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679−3686.

(13) Armstrong, A.; He, L.; Liu, Y. S. *Anal. Chem.* **1999**, *71*, 3873−3876.

(14) Berthod, A.; He, L.; Armstrong, A. *Chromatographia* **2001**, *53*, 63−68.

(15) Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3026−3027.

(16) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S.-g. *J. Am. Chem. Soc.* **2004**, *126*, 480−481.

(17) Freemantle, M. *Chem. Eng. News* **2003**, *81*, 9.

(18) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792−793.

(19) Seddon, K. R. *Nature Mat.* **2003**, *2*, 363−365.

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normal reaction conditions reduces their potential to escape into the environment.[20]

However, while the applications of ILs develop, the origins of their fundamental physical properties are still relatively poorly understood. There are also very few predictive tools that allow the rational design of new ionic liquids.[21−30] Since it has been estimated that there may be up to 10^{18} salts that form ILs,[21,31] and it would be impossible to systematically survey even a fraction of these, the ability to predict the physical properties of unknown salts is an important goal in this field.

Quantitative Structure−Property Relationship (QSPR) methods have been used in recent studies to correlate the melting points of ILs based on several cation types with “molecular descriptors” derived from quantum chemical calculations.[21−24,26,27] These studies suggest that it is possible to predict the melting points for some salt types with reasonable accuracy based on empirically derived equations. However, the derivation of these correlations requires relatively large experimental data sets of known melting points. Thus, it is not possible to use this technique for IL compositions where few or no examples are known. In addition, the statistical methods used to derive these correlations are rather complex and require specialist software, which restricts the use of this method to experienced laboratories.

Alavi and Thompson have also studied the melting behavior of ILs using molecular dynamics simulations.[28] In this work [EMIM][PF_6] was studied over a range of temperatures, which included points either side of the experimentally determined melting point (331−333 K), and several features of the simulations were taken to indicate the onset of melting. This allowed a melting point prediction of 375 K to be made, which compares reasonably well with the observed melting temperature. However, the relatively large error (∼40 °C) and computationally very intensive method may limit the applicability of this technique for screening large numbers of unknown salts for potential new ILs.

Several groups have tried to develop methods to predict the other fundamental physical properties of ILs. Seddon et al. have explored the correlation between the density and surface tension of several imidazolium based ILs.[25] It was possible for this group to predict the density of a particular salt from its surface tension and vice versa with good accuracy using a parameter called the parachor. The parachor is a relatively old concept that relates the surface tension (γ) and density (ρ) of a substance using eq 1.[32,33]

$$P = \frac{(M_w)\gamma^{1/4}}{\rho} \tag{1}$$

where M_w is the molecular weight of the salt. The parachor could be calculated with good accuracy for the ILs in this study, directly from their structural compositions, without the need for experimental data. It was also possible for this group to study the relationships between the surface tension, density, and refractive index and make predictions based on these relationships. However, all of these calculations require at least some experimental data from the IL under study in order to calculate the desired physical property, which precludes the use of such methods for predicting the properties of unknown salts.

Recent work by Abbott has shown that the concept of “hole theory”, which was developed to explain the mobilities of ions in high-temperature molten salts, can be applied to ILs.[29,30] This modified hole theory says that in order for ions in an IL to move they must find themselves next to a hole of sufficient size for them to move into. Abbott found that the probability of finding large enough holes to permit movement is very low in ILs, which is consistent with the relatively high viscosities of many salts. It was possible using this theory to predict the viscosities and conductivities of a range of ILs with some success. The accuracy of viscosity predictions was rather low, $s_{est} = 419$ cP. However, conductivities could be predicted with much greater accuracy ($s_{est} = 0.2$ mS cm^{-1}). As with the work of Seddon, these calculations required experimental data (such as densities, viscosities, and surface tensions) from the IL under study in order to make predictions of the other physical properties of the salt. As such, their application is currently limited to salts that have already been synthesized and at least partially characterized.

The above studies show that quantitative relationships between IL structures and their physical properties can be exploited to give powerful predictive tools. However, further work is needed to develop simple theoretical models that explain and can predict the fundamental properties of ILs, such as melting points, viscosities, conductivities, dielectric constants, etc. particularly for previously unknown salts.

In this publication, we attempt to answer the question “why are *Ionic Liquids* liquid?”. We have used a simple approach, based on lattice and solvation energies, to answer this question using simple quantum chemical calculations in combination with a minimum of experimental data. We also show that this method allows the prediction of melting points and dielectric constants of ionic liquids.

Methodology

When a solid melts to form a liquid (the thermodynamic process known as fusion), the enthalpy (H) and entropy (S) of the substance change. These changes, combined with a temperature term (T), give the well-known equation for the Gibbs free energy change for a process or reaction (eq 2), in this case the Gibbs free energy of fusion ($\Delta_{fus}G$):

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

At the melting temperature $\Delta_{fus}G$ is zero. At other temperatures the sign of $\Delta_{fus}G$ denotes whether the solid (positive $\Delta_{fus}G$) or liquid state

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(20) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 831−834.

(21) Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 225−231.

(22) Katritzky, A. R.; Lomaka, A.; Petrukhin, R.; Jain, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 71−74.

(23) Eike, D. M.; Brennecke, J. F.; Maginn, E. J. *Green Chem.* **2003**, *5*, 323−328.

(24) Trohalaki, S.; Pachter, R. *QSAR Comb. Sci.* **2005**, *24*, 485−490.

(25) Seddon, K. R.; Deetlefs, M.; Shara, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 642−649.

(26) Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. *J. Chem. Inf. Comput. Sci.* **2005**, *45*, 533−534.

(27) Trohalaki, S.; Pachter, R.; Drake, S. R.; Hawkins, T. *Energy Fuels* **2005**, *19*, 279−284.

(28) Alavi, S.; Thompson, D. L. *J. Chem. Phys.* **2005**, *122*, 154704−154712.

(29) Abbott, A. P. *ChemPhysChem* **2004**, *5*, 1242−1246.

(30) Abbott, A. P. *ChemPhysChem* **2005**, *6*, 2502−2505.

(31) Seddon, K. R. In *The International George Papatheodorou Symposium*; Boghosian, S., Ed.; Institute of Chemical Engineering and High Temperature Chemical Processes: Patras, Greece, 1999; pp 131−135.

(32) Macleod, D. B. *Trans. Faraday Soc.* **1923**, *19*, 38−41.

(33) Sugden, S. J. *J. Chem. Soc., Trans.* **1924**, *125*, 32−41.

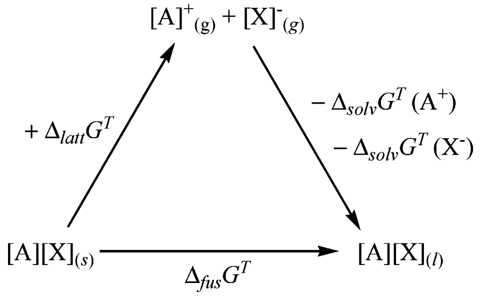

Figure 1. Born−Fajans−Haber cycle for the assessment of the melting (fusion) of a binary salt composed of complex ions ([A][X]), at temperature *T*, from lattice and solvation energies.

(negative $\Delta_{fus}G$) is favored at that temperature. In the context of ionic liquids this means that a salt should be liquid at temperature *T* if the $\Delta_{fus}G$ is negative at that temperature. Thus, room-temperature ionic liquids should have negative values of $\Delta_{fus}G°$ under standard ambient conditions (298.15 K and 10^5 Pa).

It is not possible to calculate $\Delta_{fus}G$ directly using simple methods, but using an appropriate Born−Fajans−Haber cycle (Figure 1), $\Delta_{fus}G$ can be estimated using the recently developed principles of Volume-Based Thermodynamics (VBT) and simple quantum chemical calculations in combination with available experimental data.[34]

The following sections explain how the lattice and solvation Gibbs energies were assessed and what assumptions were made. It should be noted though that the underlying Born−Fajans−Haber cycle in Figure 1 is exact and the prediction of $\Delta_{fus}G$ only relies on the quality of the assessed quantities $\Delta_{latt}G$ and $\Delta_{solv}G$.

Assessment of $\Delta_{latt}G$. $\Delta_{latt}G$ can be calculated from the lattice enthalpy ($\Delta_{latt}H$) of the salt and the entropy change on forming gaseous ions from the solid ($\Delta_{latt}S$) using eq 2. We used the VBT method developd by Jenkins, Glaser, and Passmore to estimate the lattice potential energy (U_{POT}) and, from this, $\Delta_{latt}H$, for the ILs in this study.[35] Jenkins et al. found that U_{POT} is proportional to the inverse cube root of the molecular volume of the formula unit (V_m) for a range of inorganic salts. From a large sample of experimental data they were able to derive empirical equations that can be used to estimate U_{POT}. For AX salts, with one cation and one anion, U_{POT} (in kJ mol^{-1}) is given by

$$U_{POT} = 2\left(\frac{\alpha}{\sqrt[3]{V_m}} + \beta\right) \tag{3}$$

where α and β are empirical coefficients (117.3 and 51.9 kJ mol^{-1}, respectively, for simple AX salts) and V_m is the molecular volume in nm^3. $\Delta_{latt}H$ is determined from U_{POT} for these salts by adding 2*RT*, where *R* is the gas constant.[36]

$\Delta_{latt}S$ is the difference between the entropy of the solid salt S_{solid}(AX) and the sum of the gas-phase entropies of the individual ions (which can be calculated using standard quantum chemical software—TURBOMOLE in this case).[37−40] Jenkins et al. have also developed the empirical eq 4 for calculating the standard entropy ($S°_{298}$ in J mol^{-1} K^{-1} at 298.15 K and 10^5 Pa) of a solid AX salt from its molecular volume (V_m) in nm^3[41]

$$S°_{298} = kV_m + c \tag{4}$$

Table 1. Ion Volumes of Ions Found in ILs Investigated During This Study

cations	V_{ion} (nm^3)	anions	V_{ion} (nm^3)
$[EMIM]^+$	0.156 ± 0.018	$[BF_4]^-$	0.073 ± 0.009
$[C_3MIM]^+$	0.178 ± 0.028	$[PF_6]^-$	0.109 ± 0.008
$[BMIM]^+$	0.196 ± 0.021	$[TfO]^-$	0.131 ± 0.015
$[C_5MIM]^+$	0.219 ± 0.015	$[Tf_2N]^-$	0.232 ± 0.015
$[BMMIM]^+$	0.229 ± 0.012		
$[BPy]^+$	0.198 ± 0.013		
$[BMPyr]^+$	0.221 ± 0.015		
$[C_5MPyr]^+$	0.238 ± 0.018		
$[C_5NEt_3]^+$	0.268 ± 0.016		

where *k* and *c* are empirical constants (1360 J K^{-1} mol^{-1} nm^{-3} and 15 J K^{-1} mol^{-1}, respectively). This equation was used to determine the standard entropy of the solid ILs in this study, which we then used as an estimate of S_{solid}(AX). Although Glaser has suggested alternative empirical constants for ILs, these are not based on experimental data, and so we decided to use those constants derived for inorganic salts until experimental data and thus correlations are derived specifically for ionic liquids.[42]

Assessment of the Molecular Volume (V_m). The VBT methods described above require the molecular volume of the formula unit (V_m) for each IL in the study. This is the sum of the ion volumes (V_{ion}) of the individual ions, which can be determined for solid-state ions from X-ray crystal structures. It is not necessary to have determined the crystal structure of the IL under study, as V_{ion} can be determined from a crystal structure containing one of the ions of interest in combination with a reference ion, for which the ion volume has previously been established. The ion volumes of such reference ions can be found in large databases compiled during previous work in this area.[35,43]

For example, the ion volumes of the $[BF_4]^-$ anion (0.073 ± 0.009 nm^3) and many other anions commonly found in ILs have already been determined.[35,43] The ion volume of an unknown cation $V_{ion}(A^+)$ can be calculated from the crystal structure of $[A]^+[X]^-$ by dividing the unit cell volume (V_{cell}) by the number of formula units per unit cell (*Z*) and subtracting the ion volume of the reference anion $V_{ion}(X^-)$ (eq 5). We note that the unit cell parameters of X-ray crystal structures are usually reported in Å^3 (1 Å^3 = 0.001 nm^3). However, VBT methods use the molecular volume in nm^3, so it is necessary to make a conversion before the calculation.

$$V_{ion}(A^+) = \frac{V_{cell}(A^+\,X^-)}{Z} - V_{ion}(X^-) \tag{5}$$

Thus, if V_{ion} of one of the ions of a salt $[A]^+[X]^-$ is known, and the solid-state structure of $[A]^+[X]^-$ has been determined, it is possible to establish the missing V_{ion} of the other ion. Good accuracy can be achieved by taking the average ion volume determined from several crystal structures containing different reference ions. Once the ion volume of an unknown ion has been determined, it can be used as the reference value for another calculation. Details of the structures used to determine the volumes of ILs in this study are provided in the Supporting Information.

Even if there is no reported crystal structure containing a particular ion, the volume of that ion can be estimated from the volumes of a given homologous series. For example, the volumes of $[MMIM]^+$, $[EMIM]^+$, $[C_3MIM]^+$, and $[BMIM]^+$ can be determined from X-ray structures. Thus, it is possible to estimate the volume of $[C_5MIM]^+$ based on the average volume change of 0.023 nm^3 that occurs when adding or subtracting a "$-CH_2-$" group from a member of the above series. The ion volumes of the anions and cations found in the ILs in this study are given in Table 1.

A final method for the determination of ion volumes comes from the work of Hofmann, who has determined the average atomic volumes

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(34) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *34*, 866−874.
(35) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glaser, L. *Inorg. Chem.* **1999**, *38*, 3609−3620.
(36) Jenkins, H. D. B. *J. Chem. Ed.* **2005**, *82*, 950−952.
(37) Arnim, M. v.; Ahlrichs, R. *J. Chem. Phys.* **1999**, *111*, 9183−9190.
(38) Császár, P.; Pulay, P. *J. Mol. Struct.* **1984**, *114*, 31−34.
(39) Koga, T.; Kobayashi, H. *J. Chem. Phys.* **1985**, *82*, 1437−1439.
(40) Pulay, P. *Chem. Phys. Lett.* **1980**, *23*, 393−398.
(41) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2003**, *42*, 8702−8708.
(42) Glasser, L. *Thermochim. Acta* **2004**, *421*, 87−93.
(43) Jenkins, H. D. B.; Liebman, J. F. *Inorg. Chem.* **2005**, *44*, 6359−6372.

for a large number of elements.[44] These atomic volumes can be used to determine the volume of an ion or salt simply by summing the volume contributions from each atom in the molecular formula. This is a very simple method and extends the VBT calculations, and thus the work described herein, to include ion types that have not been previously observed in X-ray crystal structures and in theory to any imaginable ion or salt. Our experience is that the calculation of $\Delta_{\mathrm{latt}}G$, and thus $\Delta_{\mathrm{fus}}G$, using V_{m} derived from Hofmann's atomic volumes gives very similar results compared to calculations using V_{m} derived from X-ray crystal structures (standard difference between the two methods (s_{est}): for $\Delta_{\mathrm{fus}}G°$ calculations = 4 kJ mol^{-1}, for melting point predictions = 2 °C). A comparison of the ion volumes, thermodynamic calculations, and melting point predictions using these two volume determination methods is given in the Supporting Information. However, we have also found that a volume-based approach may be used to predict some of the other fundamental properties of ILs.[45] In this case volumes derived from X-ray structures give better results. Thus, we have tried to enlarge the database of ion volumes for ions commonly found in ILs (Table 1) and have used the volumes given in Table 1 for the calculations herein.

Ion volumes determined in the above ways are usually relatively consistent between different crystal structures or estimations, and standard errors for the volumes are usually less than 0.02 nm^3 for cations and around 0.01 nm^3 for anions.[35] This uncertainty does not have a large effect on lattice potential energy estimations using the VBT model. For example, if we estimate the lattice potential energy (U_{POT}) for [BMIM][Tf$_2$N] using an average volume of 0.196 nm^3 for the cation and 0.232 nm^3 for the anion, we obtain a U_{POT} value of 415 kJ mol^{-1}. Even if both the cation and anion volumes have a large deviation in the same direction, i.e., the molecular volume (V_{m}) deviates by $\pm$0.03 nm^3 from the average, then the range of estimated U_{POT} values is relatively small, from 423 to 408 kJ mol^{-1}, and similar to that estimated using the average volume. Thus, it is relatively easy to establish the ion volumes of unknown ions, and the errors associated with such a procedure are relatively small (typically less than 5−10 kJ mol^{-1} for the estimation of U_{POT}). This can be attributed to the relatively large ions and accordingly low lattice potential energies.

Assessment of $\Delta_{\mathrm{solv}}G$. Herein we consider that the free energy change associated with the formation of a liquid salt from its gaseous ions can be approximated by the sum of the Gibbs free energies of solvation ($\Delta_{\mathrm{solv}}G$) of each ion in a medium with the dielectric constant of the bulk molten salt. This approximation should be accurate if there are only relatively weak interactions between ions in the liquid, which is likely to be a reasonable approximation for most ionic liquids involving complex and weakly coordinating ions. The presence of long-lived ion pairs in the IL would weaken this approximation. However, a recent study on the basis of dielectric spectroscopy showed no evidence of ion pairing in the [Tf$_2$N]$^-$ salts of imidazolium cations on the picosecond to nanosecond time scale.[46] Thus, at least in these ILs, there is strong experimental evidence that any ion pairing interactions are short-lived and for the purposes of this study can be considered to form part of the time-averaged ion−ion interactions in the IL.

In order to calculate $\Delta_{\mathrm{solv}}G$, the gas-phase geometry of each individual ion was optimized at the (RI)-BP86/SV(P) level using TURBOMOLE.[37−40] $\Delta_{\mathrm{solv}}G$ values for each ion were then calculated, at the dielectric constant of the IL under study, using the COSMO solvation model implemented in TURBOMOLE.[47] The total $\Delta_{\mathrm{solv}}G$ for the salt was then calculated as the sum of the $\Delta_{\mathrm{solv}}G$ energies for each ion. The COSMO model simulates the effects of a dielectric medium, with a specific dielectric constant, around the gas-phase structure of a molecule or ion and then refines the total energy of the species within this medium. The difference in SCF energies between the gas phase and "solvated" species is taken to be the solvation free energy of the species in the medium. For these COSMO calculations it was necessary to know, or have a reasonable estimate of, the static dielectric constant of the IL being studied. This is a very difficult property to measure directly due to the high conductivity of ILs, and until recently it has only been possible to investigate the polarity of ILs, and in some cases estimate their dielectric constants, using solvatochromic dyes and the solvent-dependent behavior of other probe molecules.[48−59] However, it has recently been shown that it is possible to extrapolate the static dielectric constant of an IL from dielectric spectroscopy.[46,60] As part of our experimental study we determined the dielectric constants of 11 ambient temperature ionic liquids using dielectric spectroscopy. These dielectric constants and those previously determined from dielectric spectroscopy were used as input parameters for the COSMO calculations above. This allowed the calculation of $\Delta_{\mathrm{solv}}G$ for each ion at the dielectric constant of the IL under study. The use of a single, global dielectric constant for the calculation of $\Delta_{\mathrm{solv}}G$ for each ion is a simplification, since the local dielectric environment of each ion will be different due to differences in the solvation environments of anions and cations in the medium. However, this approximation greatly simplifies these calculations, since the local dielectric environment of each ion in an IL is very difficult to measure (or estimate for unknown salts). Moreover, using $\Delta_{\mathrm{solv}}G$ values calculated in this way in the thermodynamic cycle shown in Figure 1 gives very good results for the calculation of $\Delta_{\mathrm{fus}}G$, although error cancellation may be involved in the calculations.

Computational Details. The gas-phase geometry of each individual ion was optimized at the (RI)-BP86/SV(P) level using the TURBOMOLE program.[37−40] Stationary points were confirmed as minima by frequency analysis. In some cases several minima with different conformations were calculated to find the global minimum. Gas-phase entropies were calculated using the FREEH module of TURBOMOLE. Computational details including SCF energies, atomic coordinates, and vibrational frequencies are provided in the Supporting Information.

Ionic Liquid Synthesis and Characterization. As the calculations above require the dielectric constant of the IL to be known and interpretation of the results requires accurate melting points, we undertook an experimental study to determine these physical properties for the 14 ILs that are included in Table 2. Their constituent ions, with abbreviated names, are shown in Scheme 1.

Ionic liquids were synthesized and dried using established methods that gave materials with minimal halide and water impurities.[61−64] It was particularly important for this study to prepare highly pure ionic liquids, as impurities can have a large effect on the melting point of

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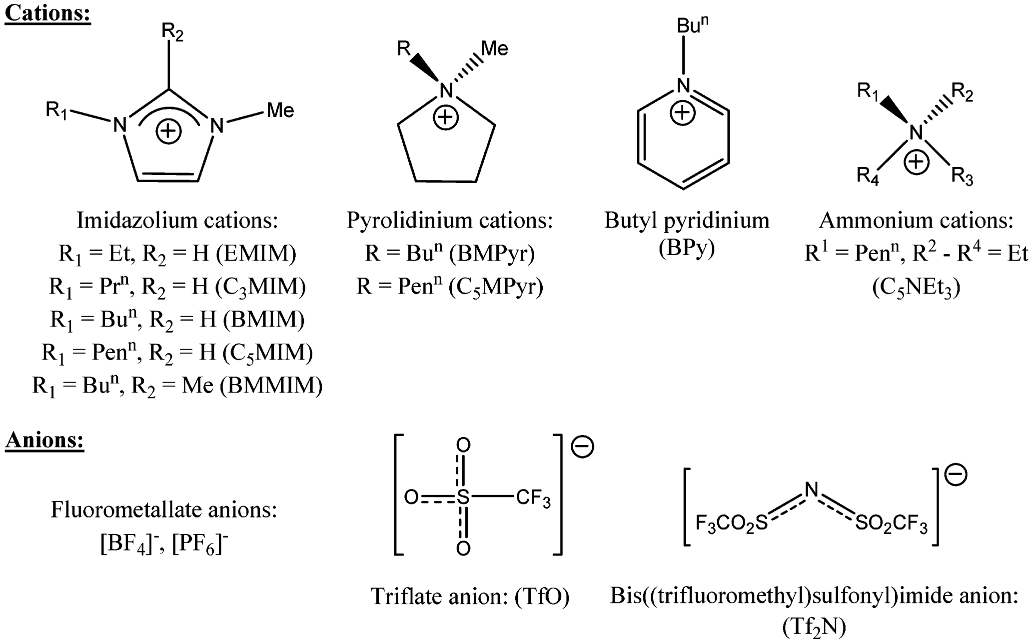
(44) Hofmann, D. W. M. *Acta. Crystallogr.* **2002**, *B58*, 489−493.
(45) Daguenet, C.; Krossing, I.; Schubert, T.; Slattery, J. M. Unpublished work.
(46) Weingärtner, H.; Oleinikova, A.; Wakai, C.; Daguenet, C.; Dyson, P. J.; Krossing, I.; Slattery, J. M. *J. Phys. Chem. B* **2006**, *110*, 12682−12688.
(47) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799−805.
(48) Earle, M. J.; Engel, B. S.; Seddon, K. R. *Aust. J. Chem.* **2004**, *57*, 149−150.
(49) Kawai, A.; Hidemori, T.; Kazuhiko, S. *Chem. Lett.* **2004**, *11*, 1464−1465.
(50) Angelini, G.; Chiappe, C.; De Maria, P.; Fontana, A.; Gasparrini, F.; Pieraccini, D.; Pierini, M.; Siani, G. *J. Org. Chem.* **2005**, *70*, 8193−8196.
(51) Tao, G.-h.; Zou, M.; Wang, X.-h.; Chen, Z.-y.; Evans, D. G.; Kou, Y. *Aust. J. Chem.* **2005**, *58*, 327−331.
(52) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319−2358.
(53) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591−595.
(54) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commun.* **2001**, 413−414.
(55) Baker, S. N.; Baker, G. A.; Bright, F. V. *Green Chem.* **2002**, *4*, 165−169.
(56) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2003**, *107*, 7340−7346.
(57) Dzyuba, S. V.; Bartsch, R. A. *Tetahedron Lett.* **2002**, *43*, 4657−4659.
(58) Fletcher, K. A.; Storey, I. A.; Hendricks, A. E.; Pandey, S. *Green Chem.* **2001**, *3*, 210−215.
(59) Poole, C. F. *J. Chromatogr. A* **2004**, *1037*, 49−82.
(60) Wakai, C.; Oleinikova, A.; Ott, M.; Weingärtner, H. *J. Phys. Chem. B* **2005**, *109*, 17028−17030.
(61) Wasserscheid, P.; Sesing, M.; Korth, W. *Green Chem.* **2002**, *4*, 134−138.
(62) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103−6110.
(63) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim. Acta* **2000**, *357−358*, 97−102.
(64) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

Table 2. Summary of Experimental and Thermodynamic Data

salt name	melting point (°*C*, ± 0.3)	dielectric constant (±0.3)	molecular volume (V_m/nm^3)	$\Delta_{latt}H°$ (kJ mol^{-1})	$\Delta_{latt}S°$ (kJ K^{-1} mol^{-1})	$\Delta_{latt}G°$ (kJ mol^{-1})	$\Delta_{solv}G°$ (kJ mol^{-1})	$\Delta_{fus}G°$ (kJ mol^{-1})
[EMIM][BF$_4$][2,69]	15 to −1[a]	12.9	0.229 ± 0.027	492	0.324	395	−418	**−23**
[EMIM][TfO][2,64,70]	−9 to −15[a]	15.1	0.265 ± 0.033	464	0.339	363	−404	**−41**
[EMIM][Tf$_2$N]	−19	12.3	0.388 ± 0.033	425	0.370	320	−364	**−44**
[C$_3$MIM][Tf$_2$N]	not observed	11.8	0.410 ± 0.043	420	0.372	314	−359	**−45**
[BMIM][BF$_4$][60]	not observed	11.7[a]	0.269 ± 0.030	472	0.331	373	−409	**−37**
[BMIM][PF$_6$][60]	9	11.4[a]	0.305 ± 0.029	457	0.325	360	−385	**−25**
[BMIM][TfO]	13	13.2	0.327 ± 0.036	449	0.346	346	−395	**−49**
[BMIM][Tf$_2$N]	−5	11.6	0.428 ± 0.036	420	0.377	308	−358	**−50**
[BMMIM][Tf$_2$N]	not observed	11.5	0.461 ± 0.027	412	0.387	297	−349	**−52**
[C$_5$MIM][Tf$_2$N]	−10	11.4	0.451 ± 0.033	415	0.380	302	−357	**−55**
[BPy][Tf$_2$N]	23	11.5	0.430 ± 0.028	420	0.353	315	−358	**−43**
[BMPyr][Tf$_2$N]	−9	11.9	0.453 ± 0.030	414	0.345	311	−356	**−45**
[C$_5$MPyr][Tf$_2$N]	8	11.1	0.470 ± 0.033	411	0.352	306	−351	**−45**
[C$_5$NEt$_3$][Tf$_2$N]	0	10.0	0.500 ± 0.031	404	0.367	295	−337	**−43**

[a] Values not determined during this study; relevant references are indicated next to compound names.

Scheme 1. Schematic Representations of the Constituent Ions of ILs in This Study and Their Abbreviated Names



the salt.[65−68] For hydrophobic [Tf$_2$N]$^-$ and [PF$_6$]$^-$ salts, halide metathesis reactions in water were used to synthesize the IL. Halide impurities were then removed by several washes with water, and the material was dried under high vacuum at 70 °C. For the hydrophilic [BMIM][TfO] salt a halide-free synthesis based on the methylation of 1-butylimidazole was used, as halide impurities are difficult to remove from [TfO]$^-$ salts. For the hydrophilic [BMIM][BF$_4$] salt a conventional halide metathesis method in dichloromethane was used. [BMIM][BF$_4$] was purified by washing the dichloromethane solution of the salt with several aliquots of water, followed by drying under a high vacuum at 70 °C. Experimental details, NMR spectroscopic data, and DSC graphs are provided in the Supporting Information.

As mentioned above, the dielectric constants of the salts synthesized during this study were measured using dielectric spectroscopy, and the data presented here represents the largest hitherto reported collection of static dielectric constants of ionic liquids. Because the applied technique is currently limited to liquids close to room temperature, materials that melt above room temperature were not included in the present study. A summary of the experimental data can be found in Table 2.

Literature data were used in one case in order to a give more complete homologous series. The melting points of [EMIM][BF$_4$] and [EMIM][TfO] were taken from literature sources.[2,64,69,70] For these salts the range of reported melting points is quoted, as it is difficult to judge which data are the most accurate. The dielectric constants of [BMIM][BF$_4$] and [BMIM][PF$_6$] have previously been determined using dielectric spectroscopy, and these values were used in this study.[60]

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(65) Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.
(66) Widegren, J. A.; Laesecke, A.; Magee, J. W. *Chem. Commun.* **2005**, 1610−1612.
(67) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156−164.
(68) Poole, C. F.; Kersten, B. R.; Ho, S. S. J.; Coddens, M. E.; Furton, K. G. *J. Chromatogr.* **1986**, *352*, 407−425.
(69) Choudhury, A. R.; Winterton, N.; Steiner, A.; Cooper, A. I.; Johnson, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 16792−16793.
(70) Every, H.; Bishop, A. G.; Forsyth, M.; MacFarlane, D. R. *Electrochim. Acta* **2000**, *45*, 1279−1284.

Results and Discussion

Dielectric Constants. Interestingly, the range of dielectric constants displayed by the ILs investigated (see Table 2) is relatively small (10.0−15.1), even though the compositions of the ILs are very different. The trends in the dielectric constant are consistent with those seen previously.[60] Larger dielectric constants are observed for $[TfO]^-$ salts, which may be related to the larger dipole moment of the triflate anion. Lower dielectric constants are observed as the alkyl chain length of the cation increases, in the same way as in alcohols.

Melting Points. The data in Table 2 show how difficult it is to determine qualitative correlations between the composition and the melting point of an IL. The melting points of the $[EMIM]^+$ and $[BMIM]^+$ salts in general increase with increasing anion size, although [BMIM][TfO] does not fit with this trend. There is not a good correlation between the alkyl chain length and melting point for $[Tf_2N]^-$ salts of the imidazolium cations. The melting point of $[EMIM][Tf_2N]$ is lower than expected if we consider that the melting points of ILs often decrease with increasing alkyl chain length (up to around C_6 to C_8, where liquid crystalline phases that lead to higher melting points may be seen).[2] Similarly, the melting points of the pyridinium salts increase as a butyl chain is replaced by a pentyl chain, which is also counterintuitive based on the observation above.

No melting points were observed during this study for three of the salts that were synthesized $[C_3MIM][Tf_2N]$, $[BMIM][BF_4]$, and $[BMMIM][Tf_2N]$. This behavior has previously been observed for $[BMIM][BF_4]$.[71] At present we do not have an explanation for why some salts do not exhibit defined melting temperatures, as there does not appear to be any common features that separate these salts from those that show defined melting points. It may be that there are kinetic reasons for this, for example, high viscosities near the crystallization temperature, which prevent the formation of ordered solids on the time scale of the DSC experiments. It is also possible that even very small amounts of impurities prevent the observation of melting points in these samples.

Assessment of $\Delta_{fus}G°$. To answer the question of why ionic liquids melt at relatively low temperatures, we needed to calculate $\Delta_{fus}G°$ for each salt using the methods described above. A summary of the individual components of the Born−Fajans−Haber cycle (at 298.15 K and 10^5 Pa) is given in Table 2.

Under standard ambient conditions (298.15 K and 10^5 Pa) the value of $\Delta_{fus}G°$ was negative for all salts. This supports the hypothesis that ionic liquids are liquid at relatively low temperatures because the liquid state is more thermodynamically favorable. This is the case because the relatively large size and weakly coordinating nature of the ions involved lead to a small lattice enthalpy (411 to 492 kJ mol^{-1}). Also, the large size and conformational flexibility of the ions (particularly the cations) lead to a large difference in entropy between the solid and gaseous state (0.324 to 0.387 kJ mol^{-1} K^{-1}). The combination of these two parameters gives $\Delta_{latt}G$ values that are relatively small and can be overcome by the solvation free energy of the individual ions in the bulk molten salt ($\Delta_{solv}G$). In classical salts such as NaCl the large $\Delta_{latt}H$ (800 kJ mol^{-1}) and small $\Delta_{latt}S$ (0.158 kJ mol^{-1} K^{-1}) give a $\Delta_{latt}G$ that is too large to be overcome by forming a molten salt, and thus the solid state is thermodynamically favorable.

It is not possible to directly compare the $\Delta_{fus}G°$ values with the melting points for different salts to explain trends in the experimental data, as we do not know the rate at which $\Delta_{fus}G$ changes with temperature for each salt. This is dependent on the entropy changes that occur in the Born−Fajans−Haber cycle and as such is affected by the structure of both the anion and the cation. However, a preliminary assessment of the data in Table 2, for example, within the $[EMIM]^+$ and $[BMIM]^+$ cation series, suggests that the model is working well, as more negative $\Delta_{fus}G$ values are found as the melting point of the salt decreases, except in the case of [BMIM][TfO].

In the case of [BMIM][TfO] and $[BPy][Tf_2N]$ the model gives rather negative $\Delta_{fus}G°$ values, even though these salts melt at temperatures close to 298.15 K. These salts appear to be problematic for the method, possibly due to stronger or more covalent interactions in the solid state, which lead to larger lattice enthalpies than predicted using the VBT model. Since $\Delta_{latt}G$ calculations using VBT methods strictly only account for Coulombic interactions, a greater degree of covalent character of the interactions in the solid state may lead to errors in these calculations. The recently reported X-ray crystal structure of [BMIM][TfO] supports this suggestion.[69] In this salt the triflate anion makes a short contact from one oxygen atom to the acidic proton of the imidazolium ring (2.25 Å) and sits with all three oxygen atoms directly above the π-system of another imidazolium ring. The additional energy that these interactions would add to the lattice enthalpy, which is not taken into account in our calculations, could account for the underestimation of $\Delta_{fus}G°$. In $[BPy][Tf_2N]$ π-stacking interactions between the cations could lead to an additional attractive interaction that leads to a larger $\Delta_{latt}H$ than estimated using the VBT approach. Unfortunately, there is no reported crystal structure of $[BPy][Tf_2N]$ so the influence of π-stacking remains to be proven.

The approximations made when calculating $\Delta_{fus}G°$ values in the above way give some sources of error that we have, as yet, been unable to correct. As mentioned above, the VBT approximation may underestimate the lattice enthalpy when interactions such as π-stacking, hydrogen bonding, or other more directional interactions are present in the solid state. Also, dispersive forces, which would add to the lattice enthalpy for these salts, are not taken into account in the VBT method, and neither are the changes in zero-point energy that may occur in the cycle.

Prediction of Melting Points and Dielectric Constants. Despite the above-mentioned sources of error, it was possible to use the method described herein to predict the melting points and dielectric constants of the ILs in this study with good accuracy in most cases. We can make these predictions, since $\Delta_{fus}G$ is zero at the melting temperature. Thus, if we calculate $\Delta_{fus}G$ over a range of temperatures, using the correct dielectric constant, and plot $\Delta_{fus}G$ vs temperature, the melting point is found where $\Delta_{fus}G = 0$. Conversely, if we know the melting point of the salt and calculate $\Delta_{fus}G$ for a range of dielectric constants, the dielectric constant of the salt at the melting point can be obtained from a plot of $\Delta_{fus}G$ vs the dielectric constant at the point where $\Delta_{fus}G = 0$.

Two approximations must be made for these calculations. First, the dielectric constant of the salt is independent of

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(71) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954−964.

Table 3. Effect of Temperature on the Static Dielectric Constants of Two Imidazolium Salts

salt	temperature (°C)	dielectric constant (±0.3)
[EMIM][Tf_2N]	15	12.5
	25	12.3
	35	11.8
	45	11.7
[BMIM][Tf_2N]	15	11.6
	25	11.6
	35	11.5
	45	11.7

temperature. To investigate this, we determined the dielectric constants of two salts ([EMIM][Tf_2N] and [BMIM][Tf_2N]) between 15 and 45 °C. The results are shown in Table 3.[72]

These measurements showed no significant change in the dielectric constant for [BMIM][Tf_2N] (given the experimental error of approximately ±0.3) and only a relatively small change in dielectric constant for [EMIM][Tf_2N]. Thus, the approximation is not unreasonable for these calculations.

The second assumption is that the calculated $\Delta_{\mathrm{solv}}G$ is independent of temperature. Unfortunately, this is not the case, as $\Delta_{\mathrm{solv}}G$ contains a temperature-dependent entropy term. However, we can approximately correct for errors caused by this assumption by considering another Born−Fajans−Haber cycle (Figure 2).

$$\begin{tikzcd}
{[A]^+_{(g)}}^{298} + {[X]^-_{(g)}}^{298} \arrow[r, "+\Delta_{corr}G^{T}"] \arrow[dr, "-\Delta_{solv}G^{298}"] & {[A]^+_{(g)}}^{T} + {[X]^-_{(g)}}^{T} \arrow[d, "-\Delta_{solv}G^{T}"] \\
{[A][X]_{(s)}} \arrow[u, "+\Delta_{latt}G^{298}"] \arrow[ur, "+\Delta_{latt}G^{T}"'] \arrow[r, "\Delta_{fus}G"'] & {[A][X]_{(l)}}
\end{tikzcd}$$

Figure 2. Born−Fajans−Haber cycle for the melting (fusion) of a binary salt composed of complex ions ([A][X]) at different temperatures (298.15 K and *T*).

Under standard conditions $\Delta_{\mathrm{fus}}G°$ is calculated from the lattice free energy and the solvation free energy at 298.15 K using eq 6:

$$\Delta_{\mathrm{fus}}G^{298} = \Delta_{\mathrm{latt}}G^{298} - \Delta_{\mathrm{solv}}G^{298} \tag{6}$$

At a different temperature (T), $\Delta_{\mathrm{fus}}G^{T}$ is calculated using the lattice free energy and solvation free energy at that temperature:

$$\Delta_{\mathrm{fus}}G^{T} = \Delta_{\mathrm{latt}}G^{T} - \Delta_{\mathrm{solv}}G^{T} \tag{7}$$

However, we can only calculate the solvation free energy at 298.15 K using the COSMO model, which would lead to an overestimation of the magnitude of $\Delta_{\mathrm{solv}}G$ at temperatures below 298.15 K and an underestimation of this value at higher temperatures. Using the Born−Fajans−Haber cycle shown in Figure 2, it is possible to calculate $\Delta_{\mathrm{solv}}G^{T}$ from the value generated by COSMO ($\Delta_{\mathrm{solv}}G^{298}$) and a correction factor ($\Delta_{\mathrm{corr}}G$):

Table 4. Melting Point and Dielectric Constant Predictions for the ILs in This Study

salt	exptl melting point (°C)	predicted melting point (°C)	exptl dielectric constant	predicted dielectric constant
[EMIM][BF_4][2,69]	15 to −1[a]	3	12.9	13.5
[EMIM][TfO][2,64,70]	−9 to −15[a]	−13	15.1	16.0
[EMIM][Tf_2N]	−19	−7	12.3	17.5
[C_3MIM][Tf_2N]	not observed (liquid at rt)	−7	11.8	*b*
[BMIM][BF_4][47]	not observed (liquid at rt)	−9	11.7[a]	*b*
[BMIM][PF_6][47]	9	3	11.4[a]	9.5
[BMIM][TfO]	13	−17	13.2	7.5
[BMIM][Tf_2N]	−5	−10	11.6	10.5
[BMMIM][Tf_2N]	not observed (liquid at rt)	−9	11.5	*b*
[C_5MIM][Tf_2N]	−10	−12	11.4	11.0
[BPy][Tf_2N]	23	−6	11.5	6.5
[BMPyr][Tf_2N]	−9	−6	11.9	13.0
[C_5MPyr][Tf_2N]	8	−6	11.1	8.0
[C_5NEt_3][Tf_2N]	0	−1	10.0	9.5

[a] Values not determined during this study; relevant references are indicated next to compound names. [b] It is not possible to make dielectric constant predictions, if the melting point is not known, so no predictions are made for salts where no melting point was observed.

$$\Delta_{\mathrm{solv}}G^{T} = \Delta_{\mathrm{solv}}G^{298} + \Delta_{\mathrm{corr}}G^{T} \tag{8}$$

Again, the Born−Fajans−Harber cycle provides the solution, allowing this correction factor to be calculated from other parts of the cycle:

$$\Delta_{\mathrm{corr}}G^{T} = \Delta_{\mathrm{latt}}G^{T} - \Delta_{\mathrm{latt}}G^{298} \tag{9}$$

Finally, substitution of eq 8 into eq 7 gives eq 10 with which we can calculate the Gibbs free energy of fusion for a binary salt composed of complex ions ([A][X]) at different temperatures:

$$\Delta_{\mathrm{fus}}G^{T} = \Delta_{\mathrm{latt}}G^{T} - \Delta_{\mathrm{solv}}G^{298} + \Delta_{\mathrm{corr}}G^{T} \tag{10}$$

This is still an approximation, as we use the standard entropy of the salt (at 298.15 K), estimated using the VBT formula, to calculate $\Delta_{\mathrm{latt}}G^{T}$ at the temperature (T). However, the error involved with this approximation is expected to be relatively small and is difficult to overcome using VBT or simple quantum chemical calculations. It should be noted here that $\Delta_{\mathrm{corr}}G^{T}$ can also be calculated directly from the gas phase calculations at 298.15K and temperature T. Full details of these calculations, including plots of $\Delta_{\mathrm{fus}}G$ vs T and $\Delta_{\mathrm{fus}}G$ vs dielectric constant are given in the Supporting Information. Melting point and dielectric constant predictions are given in Table 4.

Considering the potential problems discussed above and the sensitivity of the predicted melting point to small changes in $\Delta_{\mathrm{fus}}G$ (a 10 kJ mol^{-1} change in $\Delta_{\mathrm{fus}}G$ leads to a 10−15 °C change in predicted melting point), the predicted melting points are in good agreement with the experimental values ($s_{\mathrm{est}} = 8$

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(72) Determination of the dielectric spectra over an extended temperature range required some changes in the experimental procedure. When remeasuring the samples at 25 °C with the modified procedure, this led to a systematic difference in the dielectric constant of +0.3 compared to the values in Table 1. These differences are within the experimental uncertainty, but for internal consistency of the two data sets, the data in Table 3 were corrected for this effect.

°C) for the 9 ILs where melting transitions were observed experimentally, excluding [BMIM][TfO] and [BPy][Tf_2N], which proved problematic for this method (v.s.).

Interestingly, the predicted dielectric constants are of a similar order of magnitude to the values obtained using dielectric spectroscopy. This is rather different from the IL polarities estimated using solvatochromic dyes or other chemical probes. These methods usually give solvent polarities similar to that of acetonitrile ($\epsilon = 25.3$) for imidazolium-based ILs, and estimates as high as 55 have been made for the dielectric constant of ILs based on $[BMIM]^+$.[48−59] This highlights the difference between the static dielectric constant and the solvent behavior of an IL. The dielectric constant is a physical property of the pure material, whereas solvent behavior is strongly dependent on the nature of interactions between the solvent and the solute. In the case of ILs it seems that dielectric spectroscopy and probe-based polarity methods are measuring different properties and care should be taken to use the correct value. For the COSMO calculations herein, the static dielectric constant (derived from dielectric spectroscopy) is clearly more appropriate for modeling the solvation of gaseous ions in the bulk liquid.

Conclusions

We have shown that it is possible using a simple model to explain the low melting points of ILs compared to classical inorganic salts. The lattice free energies ($\Delta_{latt}G$) of 14 salts were estimated using a combination of Volume Based Thermodynamics (VBT) and quantum chemical calculations. The free energies of solvation ($\Delta_{solv}G$) of each ion in the bulk molten salt were also calculated using the COSMO solvation model and experimentally determined dielectric constants. This allowed the free energy of fusion ($\Delta_{fus}G$) to be calculated for each salt under standard ambient conditions. The negative $\Delta_{fus}G°$ values obtained for all ILs indicate that these salts are liquid at ambient temperatures because the liquid state is thermodynamically favorable under these conditions. This is due to the large size and conformational flexibility of the ions, which leads to small lattice enthalpies and large entropy changes that favor the liquid state.

This method can also be used to predict the melting points and dielectric constants of ILs with good accuracy in most cases. Thus, we anticipate that this approach may be used to estimate the melting temperatures of hitherto unknown salts based on simple VBT and quantum chemical calculations and an estimate of the dielectric constant of the salt. It is also possible to predict the potential melting temperatures of ILs for which no melting point has been observed, e.g., [C_3MIM][Tf_2N], [BMIM][BF_4], and [BMMIM][Tf_2N] (see Table 4). In these cases the estimated melting point could help to pinpoint the true melting temperature potentially facilitating their experimental determination.

In addition to melting point predictions for unknown salts, this model could be used to predict the dielectric constant of an ionic liquid, if the melting point is already known. This may be very useful, as the melting point of a new salt is relatively easy to measure, whereas the dielectric constants of ILs are rather difficult to measure. We are currently working on methods to further refine the theoretical model to improve the accuracy of predictions and to account for problem cases such as [BMIM]-[TfO] and [BPy][Tf_2N].

Finally, it is possible to use the above model to make some suggestions for the design of new ionic liquids. If a low melting temperature is desired in a salt then $\Delta_{latt}G$ must be minimized and $\Delta_{solv}G$ must be maximized. It has been known for some time, based on a qualitative assessment of the melting points of ILs, that this can be achieved by using large ions with high conformational flexibility. Additionally, nonsymmetrical ions should be used in order to avoid efficient packing in the solid state and the larger lattice enthalpy that will result. However, in contrast to the trial and error approach hitherto used, one can now assess the potential of a desired ion pair to act as an IL based on straightforward and simple calculations. When confident with the model it is possible to obtain a clear indication whether a given ion pair is suitable as an IL within 2 to 4 h. Moreover, as the database of ion volumes and quantum chemical ion calculations increases, and by the availability of Hofmann's atomic volumes, the time required to make a prediction is greatly reduced.

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Supporting Information Available: Experimental details, DSC graphs, XYZ coordinates, SCF energies and vibrational frequencies of all quantum chemical calculations, details of $\Delta_{fus}G°$ calculations, details of melting point and dielectric constant prediction calculations, details of X-ray crystal structures used to determine the ion volumes herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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