

## Ionic Liquids by Proton Transfer: Vapor Pressure, Conductivity, and the Relevance of $\Delta pK_a$ from Aqueous Solutions

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**Abstract:** We describe the behavior of the conductivity, viscosity, and vapor pressure of various binary liquid systems in which proton transfer occurs between neat Brønsted acids and bases to form salts with melting points below ambient. Such liquids form an important subgroup of the ionic liquid (IL) class of reaction media and electrolytes on which so much attention is currently being focused. Such “protic ionic liquids” exhibit a wide range of thermal stabilities. We find a simple relation between the limit set by boiling, when the total vapor pressure reaches one atm, and the difference in  $pK_a$  value for the acid and base determined in dilute aqueous solutions. For  $\Delta pK_a$  values above 10, the boiling point elevation becomes so high (>300 °C) that preemptive decomposition prevents its measurement. The completeness of proton transfer in such cases is suggested by the molten salt-like values of the Walden product, which is used to distinguish good from poor ionic liquids. For the good ionic liquids, the hydrogen bonding of acid molecules to the proton-transfer anion is strong enough that boiling points, but not melting points, may maximize at the hydrogen-bonded dianion composition. High boiling liquids of this type constitute an interesting class of high-temperature protic acid that may have high-temperature fuel cell applications.

### Introduction

Liquid salts, formed by transfer of protons from Brønsted acids to Brønsted bases, form a “protic” subgroup of the class of ambient temperature fluid systems now referred to as “ionic liquids”. Research activity in ionic liquids has been increasing exponentially over the past decade as new applications for these vaporless phases continue to be discovered.<sup>1–8</sup> Most of the ionic liquid systems under study have been of the “aprotic” class, meaning that the cation is formed by transferring any group other than a proton to a basic site on the parent base molecule. Though the first ionic liquid ever reported, ethylammonium nitrate in 1914,<sup>9</sup> was of the protic variety, and though protic ionic liquids featured heavily in early studies by molten salt chemists,<sup>10–15</sup> the main developments of the ionic liquid field

have tended to exclude protic salts, except where protonating ability was specifically sought.<sup>16,17</sup> An outstanding example is that of ref 17, which appeared in print after submission of this article. In ref 17, Susan et al. showed for the first time that protic ionic liquids can serve as the electrolytes of fuel cells, and this is also the finding of studies in this own lab that were motivated by the present paper.<sup>18</sup> This promises a large new field of application for ionic liquids.

Although protic ionic liquids are very easy to form,<sup>19</sup> and although they may have great thermal stability<sup>19</sup> and high fluidity,<sup>20</sup> they may also be quite inferior with respect to the

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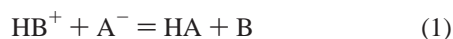
properties for which ionic liquids are most valued. We have earlier described a classification scheme by means of which certain protic ionic liquids are shown to provide examples of “poor” ionic liquids, in which low conductivity is found in concert with increased vapor pressures.<sup>21</sup> It is the purpose of this paper to clarify the issues involved.

The possibility of obtaining liquids with low vapor pressures by the proton-transfer mechanism has been utilized in military programs for some time.<sup>22,23</sup> In these applications, the combination of oxidizing anions with reducing cations in mobile liquids such as hydroxylammonium nitrate (HAN) (containing small, controlled, amounts of water) makes possible the controlled redox energy release appropriate for artillery propellants. The ionic liquids formed in these systems seem to have low viscosities, judging by military report data<sup>23</sup> for the partially hydrated practical formulations (that have been included in certain journal publications<sup>24</sup>), but no reports of viscosity or conductivity values for the anhydrous ionic liquids have been found.

Recently, the proton transfer from strong acid to base has been advanced as a general preparative technique for formation of ionic liquids but the issue of vapor pressures was left unaddressed. Examples reported have had in common the very weakly basic anion bis(trifluoromethanesulfonyl)imide, TFSI<sup>-</sup>.<sup>19</sup> The relation between the protic and aprotic versions of the ionic liquid, and in particular the relation between their relative vapor pressures, awaits systematic attention. It will be seen from the following considerations that the ionic liquids reported by Ohno and co-workers probably satisfy the conditions for very low vapor pressure, though the existence of controversy concerning the acidity of HTFSI means that direct measurements of the type we report in this paper will be needed to remove residual ambiguities.

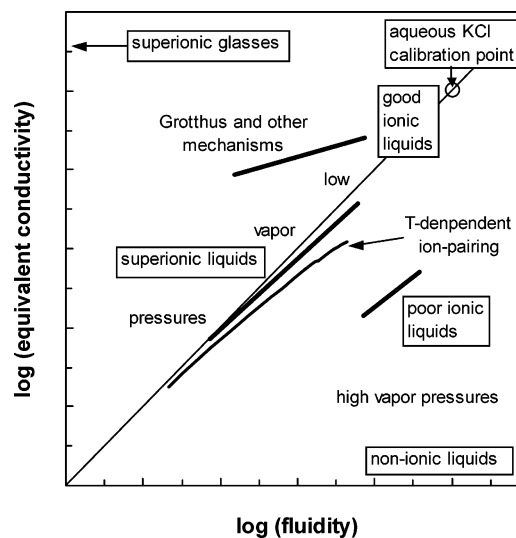
Low vapor pressures are the consequence of the dramatic lowering of the partial pressures characteristic of the pure acid and pure base due to the free energy lowering associated with proton transfer. In any liquid, it is the arrival of the vapor pressure at 1 atm during heating that determines the “normal” boiling point. A mixture of acid and base in which there is no energy decrease obtained by transferring the proton, would boil at a temperature between the boiling points of the components at the temperature at which the sum of their partial pressures is one atm.

When the free energy change in the proton transfer process is large, the proton may become so firmly localized on the Brønsted base that the probability of reforming an acid molecule HA becomes negligible at ambient temperatures. This probability is measured by the Boltzmann function  $\exp(-\epsilon/kT)$ , where  $\epsilon = \Delta G^\circ/N_{Av}$  and  $\Delta G^\circ$  is the molar free energy change in the process that reverses the original proton transfer



Here, pure liquid (Raoult's law) standard states for reactants

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**Figure 1.** Classification diagram for ionic liquids, based on the classical Walden rule, and deviations therefrom.

and products are used. Due to the strong coulomb interaction between ions, and the long range of the interaction, the vapor pressure over the liquid is very low.

In some cases to be clarified below, the probability of reforming the acid and base remains negligible even at temperatures as high as 300 °C. The salt is then, by most measures, as true a salt as the aprotic ionic liquids formed by, e.g.,  $-\text{CH}_3^+$  transfer, rather than by proton transfer, to the same basic site<sup>25–31</sup> (example:  $\alpha$ -methyl pyridinium nitrate as opposed to simple pyridinium nitrate). Indeed, we will see that protic ionic liquids formed from combinations of superacids such as trifluoromethanesulfonic acid and even moderately strong base (to give e.g., imidazolium triflate) can be more ideally ionic than some aprotic cases.<sup>32</sup>

One way of assessing the ionicity of ionic liquids is to use the classification diagram shown in Figure 1<sup>21,32</sup> which is based on the classical Walden rule.<sup>33</sup> The Walden rule relates the ionic mobilities (represented by the equivalent conductivity  $\Lambda$  ( $\Lambda = F\sum u_i z_i$ )) to the fluidity  $\phi$  ( $\phi = \eta^{-1}$ ) of the medium through which the ions move. If the liquid can be well represented as an ensemble of independent ions then the Walden plot will correspond closely with the ideal line. Ideally, which means in the absence of any ion–ion interactions, the slope should be unity. The position of the ideal line is established using aqueous KCl solutions at high dilution.

As argued elsewhere,<sup>21,32,34</sup> a liquid system in which the ions are uniformly distributed with respect to ions of the opposite

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charge develops a Madelung energy comparable to that of the corresponding crystal. This is demonstrated by the absence of anything unusual about the heats and entropies of fusion of classical ionic systems, as would be the case if the Madelung energy were lost on fusion. The vapor pressure of the “good” ionic liquid is then necessarily very low because the Madelung energy as well as the dipole–dipole interaction between ion pairs must be overcome before an ion pair can pass into the vapor state.

Salts formed by proton transfers that are weak will not form liquids with uniform charge distributions hence their Walden plots will fall below the ideal line, and their vapor pressures will not be very low. In such cases, the boiling that must occur when the total vapor pressure reaches the external pressure will fall below decomposition temperatures, and the vapor will tend to contain molecular species rather than ion pairs. In this work, we will provide experimental data on a number of binary, solvent-free, Brønsted acid–base systems that will help test these notions.

Not only does presentation of data in the Figure 1 form allow us to detect the existence of different forms of association of cations with anions, but it also serves to display the presence of abnormally high mobilities of one or other of the charge-carrying species. Excess mobility on the part of protons is a classical subject, and mechanisms that permit its understanding date from the original work of Grothaus, as invoked by Bernal and Fowler.<sup>35</sup> Not so commonly discussed, but phenomenologically indistinguishable, is the excess conductivity which is found when species that are much larger than protons can slip through the structure via channels that present lower energy barriers than those characterizing the viscous flow process. For these, the motion is described by the “fractional Walden rule”

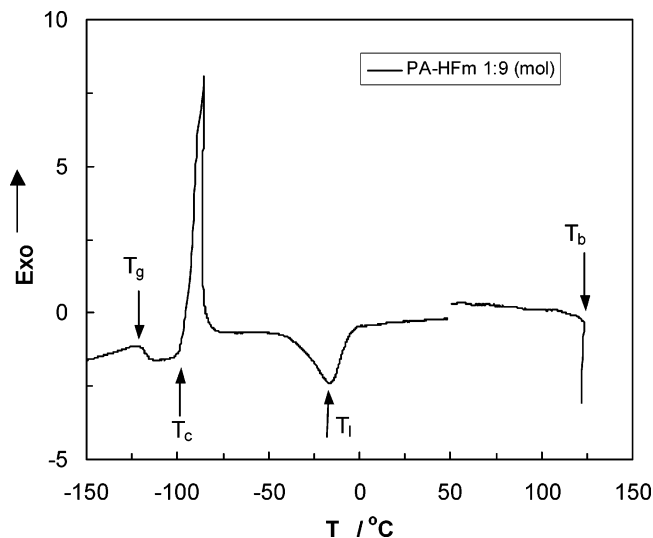
$$\Lambda\eta^\alpha = \text{constant} \quad (2)$$

where  $\alpha < 1$ .

In the log–log plot of Figure 1, data for systems featuring this sort of “decoupling”<sup>36</sup> appear as straight lines of slope  $\alpha$ . In the case of solutions of strong mineral acid in aqueous protic solvents, this decoupling appears to commence at a higher fluidity than in the case of silver ions in liquid halides.<sup>37,38</sup> In less well-known cases, such as mineral acids in glycerol, the departure occurs at lower fluidities. There is need for additional empirical information on this decoupling phenomenon. The identification of conditions needed for decoupled proton motion in solvent-free systems, is very desirable.

## Experimental Section

The liquid protonic acids, trifluoroacetic acid (HTFA, 99%), dichloroacetic acid (HDCA, 99+%) and nitric acid (70%), the bases ethylamine EA (99+%), propylamine PA (99+%),  $\alpha$ -picoline ( $\alpha$ Pic, i.e., 2-methylpyridine, 98%), and 1-methylimidazole (MIm, 99%) were obtained from Aldrich Chemical Co. Anhydrous acetic acid (HAc, 99+%) was obtained from Mallinckrodt, and anhydrous formic acid (HFm, 98%) was obtained from Fluka. Anhydrous trifluoromethanesulfonic acid (or triflic acid, HTf, purity unspecified) was obtained from Matrix Scientific. All chemicals were used as received.



**Figure 2.** Differential thermal analysis scans for characterization of glass temperature ( $T_g$ ), devitrification temperature ( $T_c$ ) and liquidus temperature ( $T_l$ ) (left scan), and boiling temperature ( $T_b$ ) (right scan). The DTA range extends up to 500 °C.

The thermal transitions of interest to this work were determined using a simple home-built differential thermal analysis DTA unit utilizing the three-terminal system described elsewhere.<sup>11b,39</sup> Although extensively used for glass transition and melting point determinations in the past, its utility for the boiling point determinations of primary importance to the present work, has previously not been given much attention. DTA has special advantages for the study of corrosive systems because of its use of glass sample tubes, and the absence of expensive components in proximity to the samples. In addition, the use of unsealed sample containers makes possible the determination of boiling points which are not investigable in standard differential scanning calorimetry DSC instruments. Our DTA setup, based on Al heater blocks and Pyrex glass sample tubes, has temperature range of  $-180$  to  $+500$  °C.

The determination of boiling points of liquids and solutions by DTA is very simple.<sup>40,41</sup> The boiling point has its own distinct signal in DTA. When boiling occurs, the rapid growth of bubbles in the slightly superheated liquid, combined with the large value of the heat of vaporization, causes a sudden absorption of energy. This gives rise to a sharp pen displacement (see Figure 2). The error due to superheating is minimized by adding a small amount of inert alumina powder to the sample container to promote bubble nucleation.

In pure liquids, bubble growth is very rapid. In solutions in which only one component is volatile, bubble growth can be much slower due to the need for diffusion of the volatile component to the bubble surface. The need for diffusion, coupled with the higher viscosity of the solutions in which ionic species provide electrostatic constriction, leads to less striking, though still obvious, signals in the binary solutions. Weaker signals, particularly near stoichiometric compositions, lead to an increased uncertainty in the boiling point assignment in the intermediate ranges, as will be seen in the scatter of binary solution data presented in the next section.

In the case of  $\alpha$ -picoline + triflic acid, the proton-transfer energy is very large (see discussion section). Due to the large negative  $\Delta G^\circ$  the formation process (reverse of eq 1), the activity of the more volatile component (excess acid or excess base) is so reduced that a chemical decomposition point is reached before boiling (which only involves the reversible endothermic proton transfer) can be observed. In fact, it

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is estimated below that, in the absence of chemical decomposition, the boiling point for the stoichiometric composition in this case would lie near 450 °C!

When decomposition occurs, the direction of the thermal effect changes from endothermic to exothermic, at least for the substances of this study. The source of the energy release cannot be ascertained without a detailed study of the (irreversible) decomposition process.

Reproducibility (precision) of boiling points is better than 1 K for the single components. The accuracy and precision can be judged from the results for  $\alpha$ -picoline (127 and 127 °C in successive runs, vs 128 °C (literature value)), and acetic acid 116 °C (literature 117–118 °C). The increased difference in the second case is attributable to the fact that the reagent was only 98–99% pure.

A DTA trace, showing the sequence of transitions observed in a formic acid + propylamine solution is given in Figure 2. It shows how the boiling point of the acid is raised from the normal value (101 °C) to 124 °C by incorporation of 10mol % of the strong base, the boiling point of which is only 53 °C. The glass transition is seen at  $-123$  °C, increased from that estimated for the pure base, ca.  $-133$  °C. The system then crystallizes at  $-98$  °C to yield a solid, the salt propylammonium formate which subsequently redissolves at  $-17$  °C. The liquid range (liquidus to boiling) is thus 141 °C.

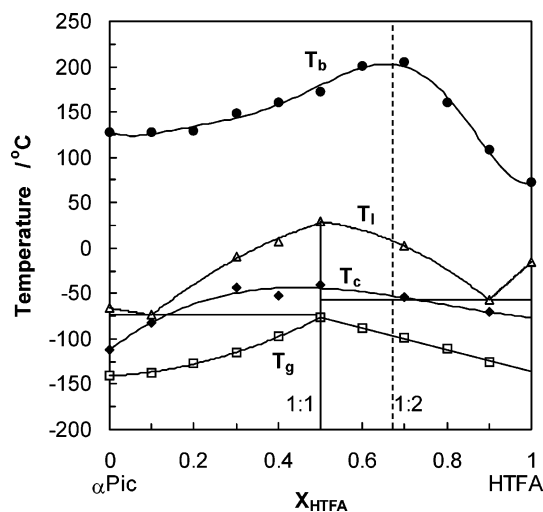
It would be quite simple to repeat the boiling point measurement using an apparatus in which the external pressure is reduced to known values well below ambient, and thereby to obtain the liquid/vapor coexistence line (and the heats of vaporization), but this has not been done so far.

Conductivities were measured using dip type cells of cell constant about  $0.1 \text{ cm}^{-1}$  calibrated with a 0.1M KCl solution. The cell conductance was determined in the frequency range from 10 Hz to 1 MHz using an automated HP4192 LF frequency analyzer, as described many times before [e.g., ref 32]. The conductivity was determined from the initial part of the almost frequency-independent plateau ( $\log \sigma$  vs  $\log f$  plot). Values obtained were checked against the data obtained by short extrapolation to the real axis of the usual complex impedance plot.

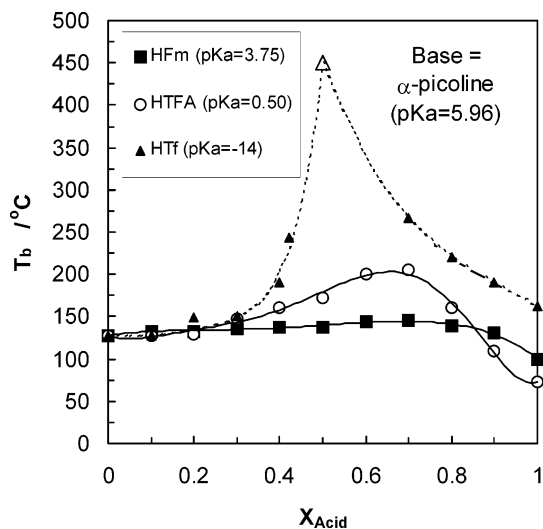
Kinematic viscosities of ionic liquids were measured using Cannon–Ubbelohde viscometers of appropriate viscometer constants, in the temperature range between ambient and 130 °C.  $\text{CaCl}_2$  drying-tubes were used to protect the samples from moisture in the air. A uniform temperature environment was provided by a tall, cartridge-heated aluminum temperature-smoothing block with slots to permit meniscus observation. The temperature of the sample was maintained for half an hour before measurement. The precision of measurement with Cannon–Ubbelohde viscometers is controlled by the reproducibility of flow times, and accuracy is controlled by accuracy of calibration constants and by temperature measurement. Precision was limited at the highest temperatures (above 100 °C) by the short flow times ( $<10$  s) consequent on our using only a single viscometer for each sample. The flow times were reproducible: the standard deviation was  $\pm 0.2$  s. For temperatures below 40 °C, the run times are often 200 s or longer hence the reading error is only 0.1% of the efflux time. Data were converted to normal viscosities, here reported in poise ( $10 \text{ p} = 1 \text{ Pa}\cdot\text{s}$ ), to maintain the simplicity of the Walden plot (Figure 1, and the more detailed version given below).

## Results

The temperatures of the various transition points ( $T_g$ ,  $T_c$ ,  $T_l$ , and  $T_b$ ) obtained from scans such as those in Figure 2, are shown for the case of the system  $\alpha$ -picoline + trifluoroacetic acid in Figure 3. We note that the glass temperature and liquidus temperature both reach maximum values at the stoichiometry of the simple proton-transfer compound  $\alpha$ -picolinium trifluoroacetate. On the other hand, the boiling point continues to rise with excess acid until the composition 67% acid, corresponding to



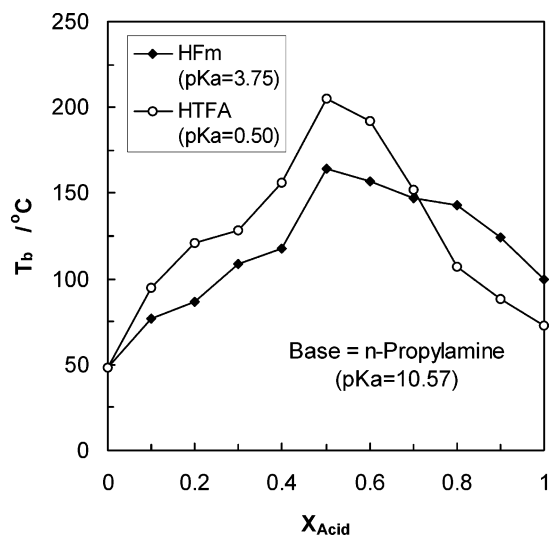
**Figure 3.** System  $\alpha$ -picoline + trifluoroacetic acid, showing glass temperatures (open squares), devitrification temperatures (filled diamonds), liquidus temperatures or freezing points (open triangles), and boiling points at 1 atm pressure (solid circles). Note that the maximum boiling point (at which the combined vapor pressures of acid and base components equals 1 atm) occurs at the dianion composition, whereas the congruently melting salt has the 1:1 single proton-transfer stoichiometry.



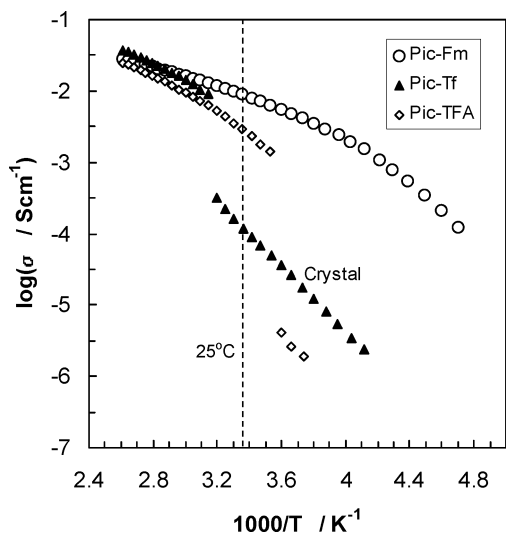
**Figure 4.** Boiling points (see Figure 3 caption) in binary systems of the same base  $\alpha$ -picoline, with protic acids of different strengths as indicated by  $\text{p}K_a$  values determined in aqueous solutions (see legend). The open triangle at the 1:1 stoichiometry is the value predicted using the correlation obtained in a later figure. Prior chemical decomposition prevents direct measurements. The extrapolation is drawn sharply peaked, for the same reason that, in binary phase diagrams, stoichiometric compounds at which there are very rapid changes of chemical activity show sharply peaked liquidus temperatures (see ref 1, Chapter 3, Figure 3.1–3).

the formation of the dianion  $\text{H}(\text{TFA})_2^-$ , is reached. Evidently this hydrogen-bonded species has a very high stability in this system.

In Figure 4, we show the boiling points of several binary systems in which the strength of the acid is increased while the base,  $\alpha$ -picoline, is kept common to each. In the case of the strongest acid of the study, trifluoromethanesulfonic acid, the boiling point lies above the decomposition temperature of the aromatic base. An extrapolation of the data obtained for compositions where boiling occurred before decomposition (solid symbols), suggests near the 1:1 composition, the vapor



**Figure 5.** Boiling point maxima in systems of strong base (*n*-propylamine) with different acids.

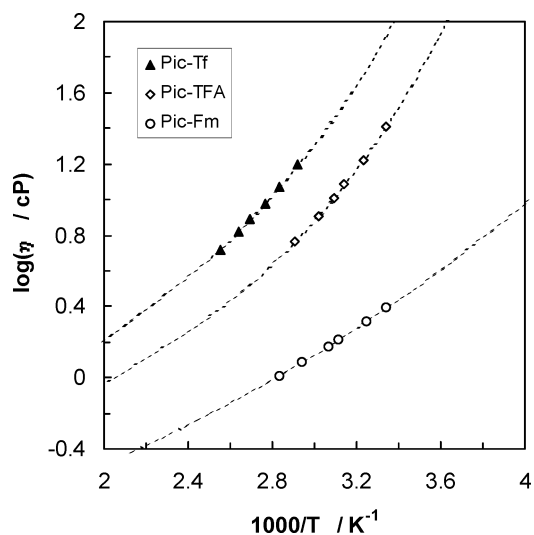


**Figure 6.** Arrhenius plot of specific conductivities of different proton transfer ionic liquids (stoichiometric 1:1 compositions). Note that the conductivity behavior contrasts strongly with the viscosity behavior seen in the next figure. (In the legend, Pic =  $\alpha$ -picolinium.)

pressures of acid or base species would be very low, even at 250 °C.

Figure 5 contains data analogous to those of Figure 4 for the case in which the stronger, nonaromatic base *n*-propylamine is used as the common component. In this case, even formic acid yields a proton-transfer salt with a boiling point elevation of some 100 K above the additive value.

Data on the conductivities of the systems of Figure 4 are shown in Figure 6, and viscosity data are shown in Figure 7. Conductivity and viscosity data for the remaining systems are available, but are subsumed into the more economic form of Figure 1, and presented in the Discussion section. The data have been reduced to Vogel–Fulcher–Tammann (VFT) equation parameters, presented in Table 1. These are valid only in the range of the data, but the dashed lines of Figure 7 show what they predict for the extended range. Finally, data for the densities that are needed to convert specific conductivities into equivalent conductivities, are summarized in Table 2 by the linear equations.



**Figure 7.** Arrhenius plot of the viscosities of the ionic liquids of Figure 5, showing that the IL formed from the strongest acid (triflic acid) is much the most viscous. Dashed lines are extrapolations based on Vogel–Fulcher–Tammann equation fitting, see text. (In the legend, Pic =  $\alpha$ -picolinium.)

**Table 1.** VFT Equation Parameters of Viscosity Data for  $\alpha$ -Picolinium Salt<sup>a</sup>

	$\eta_0/cP$	D	$T_0/K$	$T_g/K$	$R^2$
$\alpha$ Pic-Fm	0.04	7.66	103	154	0.999
$\alpha$ Pic-TFA	0.14	3.11	187	196	0.999
$\alpha$ Pic-Tf	0.16	4.09	181	186 <sup>b</sup>	0.999

<sup>a</sup> VFT equation  $\eta = \eta_0 \exp[DT_0/(T-T_0)]$  <sup>b</sup> Interpolated from data on the HTf/ $\alpha$ -Picoline system.

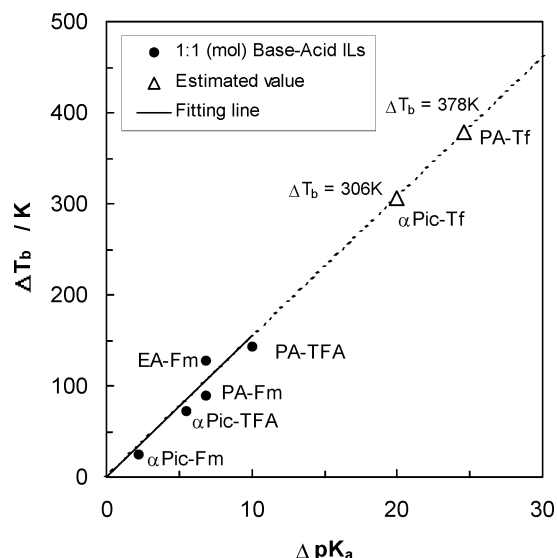
**Table 2.** Linear Density Equations for  $\alpha$ -Picolinium Salts

	$\rho/gcm^{-3}$ (t in °C)
$\alpha$ Pic-Fm	$1.05-4.39 \times 10^{-4} t$
$\alpha$ Pic-TFA	$1.31-5.26 \times 10^{-4} t$
$\alpha$ Pic-Tf	$1.46-7.16 \times 10^{-4} t$

## Discussion

**1. Proton-Transfer Salts.** The data of Figures 4 and 5 provide an opportunity to quantify what would be expected from the concept of acid–base processes. We expect that the activities of the individual components will be lowered from the ideal solution values very strongly when there is a large driving force to transfer the proton from acid to base, thereby forming the salt. In aqueous solutions, the free energy driving the transfer may be obtained from data on the work of transfer of protons from acid to water, and from water to base, respectively. These are extensively catalogued in terms of the  $pK_a$  values and  $pK_b$  values. For a given substance acting alternatively as an acid or as a base, these are related by  $pK_a + pK_b = 14$ . The value 14 is determined by the properties of the solvent water and is the base 10 logarithm of its auto-dissociation constant,  $pK_w$ . The  $pK_w$  is related to the work ( $-RT \ln K_w$ ) of transferring a proton from one water molecule to a distant one within the solution medium provided by water itself, as has been described in great detail in the book by Gurney.<sup>42</sup> The sum of  $pK_a$  and  $pK_b$  for the acid and base that form the anion and cation of a given salt, allow us to obtain a measure of the free energy of formation of

(42) Gurney, R. W. *Ionic Processes in Solution*; Dover Scientific Pub. Co.: New York, N. Y., 1962.



**Figure 8.** Correlation of the excess boiling point (determined at the 1:1 composition) with the difference in aqueous solution  $pK_a$  values for the component Brønsted acids and bases of the respective ionic liquids. The  $\Delta T_b$  value is determined as the difference between the measured boiling point and the value, at 1:1, of the linear connection between pure acid and pure base boiling points. Note the very large excess boiling points extrapolated for the ionic liquids formed from the superacid HTf (open triangles). These values could not be determined experimentally because of prior decomposition.

the salt from its ions in the 1.0 molar aqueous solution,  $\Delta G = -RT \ln(\Delta pK_a)$ .<sup>42</sup>

It is of interest to see if the wealth of information available for these interactions in aqueous solutions has any relevance to the behavior of the same acids and bases interacting in the absence of water, or of any other solvent. The dielectric constant of water, through which the transfer of the proton in aqueous systems occurs, is very large, about 80. The work of transfer to restore the original molecular acid and base components from the salt should therefore be much greater in the absence of any dielectric, particularly a medium with the dielectric constant of water. Thus, the driving force for salt formation in the systems we have studied could be very different from that measured in water. Whether any correlations can survive such a drastic change of proton transfer environment can only be determined by experiment.

We test the possibility of correlation first by comparing the increases in boiling point, over the additive values, for each acid/base pair studied (Figures 4 and 5) as a function of the difference in  $pK_a$  values of the acid and base components in water.<sup>43</sup> We use  $pK_a = 14 - pK_b$  values for the base, when only  $pK_b$  values have been tabulated. The  $pK_a$  values for the individual components are given in the figure legends.

This correlation is shown in Figure 8. It uses data for all acid/base combinations studied in this work for which the boiling points at 1:1 acid: base fall below any decomposition temperature. It is seen that four points fall precisely on the same line, within the uncertainty of determination, whereas a fifth falls close to the line. (The fifth case, EA-Fm, is the one in which the difference in pure acid and pure base boiling points is the largest, hence that in which the additive baseline for assessing the  $\Delta T_0$  value is the most dubious). As noted already, for the case in which the value of  $\Delta pK_a$  is largest, involving the strongest acid of all (Figure 4), the boiling point falls above

the decomposition temperature, as indeed the correlation plot Figure 8 would predict. If we use the plot to estimate the (immeasurable) boiling point, then it seems compatible with the extrapolations in Figure 4 of the two arms of the solution boiling points measured on either side of the stoichiometric ratio. These suggest that in the absence of decomposition, boiling would not occur before 450 °C. Clearly, the salt of  $\alpha$ -picolinium triflate should be regarded unequivocally as an ionic liquid.

Turning to another measure, we examine the conductivity of the ionic liquid formed by the proton transfer, relative to its fluidity, as in Figure 1. We recall that the ideal line is obtained on the basis that ions have mobilities that are determined only by the viscosity of the medium, and that the number of ions present in the equivalent volume is that indicated by salt composition (i.e., all ions contribute equally).<sup>33,44</sup> The ideal line position is fixed from dilute solution data where the ions are remote from one another and the Stokes–Einstein and Nernst–Einstein relations are well obeyed.<sup>44,45</sup> Due to the inevitability of inter-ionic friction in an ionic liquid some degree of departure must be expected. The deviations from the Nernst–Einstein equation predicted by theory<sup>46</sup> will cause experimental points to fall below the dilute solution limit. The closer to the ideal line the data for a given salt are found to lie, the more ideal it may be considered.

After conversion of the specific conductivity  $\sigma$  data of Figure 4 to equivalent conductivities  $\Lambda$ , and the kinematic viscosity  $\nu$  data (in centistokes) of Figure 5 to dynamic viscosity  $\eta$  data (in centipoises), using

$$\Lambda = V_e \sigma \quad (3)$$

and

$$\eta = \nu \rho \quad (4)$$

where  $V_e$  is the equivalent volume and  $\rho$  is the density, the data for the two series of salts (formed at 1:1 stoichiometry) are plotted in Figure 9.

Again we see that, in a given series with common base, the salts with the largest difference in aqueous solution  $pK_a$  values, propylammonium trifluoroacetate and  $\alpha$ -picolinium triflate, are the ones that conform most closely to the Walden rule with ideal  $\Lambda/\eta^{-1}$  value. Indeed, they lie significantly closer to the ideal line than those data for one member of the collection of aprotic salts we recently described.<sup>32</sup> This is the tetrafluoroborate salt of a quaternary ammonium salt<sup>47</sup> typical of more recent ionic liquid studies.<sup>48,49</sup> On the basis of its aprotic character, such salts would be expected to yield more ideal ionic liquids than the proton transfer salts, yet this evidently not always the case.

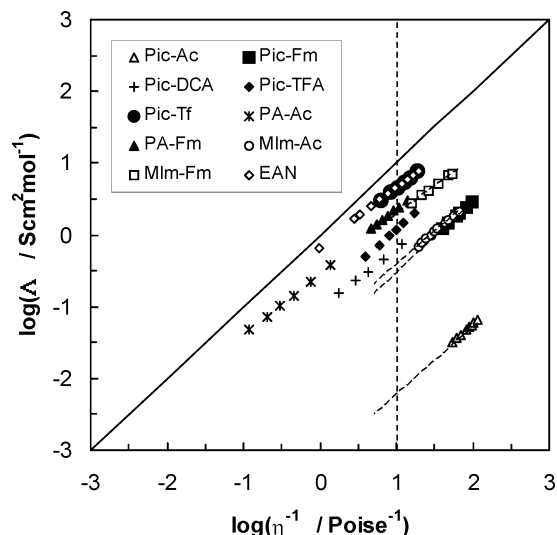
We test the Walden ideality relation more quantitatively in Figure 10. There we plot the interval between the experimental Walden plot for each liquid and the ideal line,  $\Delta W$ , measured at a fixed value of  $\log \eta^{-1}$ , against the differences in aqueous

(43) The  $pK_a$  values were taken from (a) Covington, A. K.; Davison, W. *CRC Handbook of Chemistry and Physics*, 75<sup>th</sup> ed.; Lide, D. R., Editor-in-chief; Chemical Rubber Co. Press: Boston, p 8–43; and (b) *Lange's Handbook of Chemistry*, 13<sup>th</sup> ed.; Dean, J. A., Ed.; McGraw-Hill, Inc.: New York, p 5–18. For the case of triflic acid, we adopted the  $pK_a$  value –14 suggested by Ripin, D.; Evans, D. (see <http://daecr1.harvard.edu/pK<sub>a</sub>/pK<sub>a</sub>.html>).

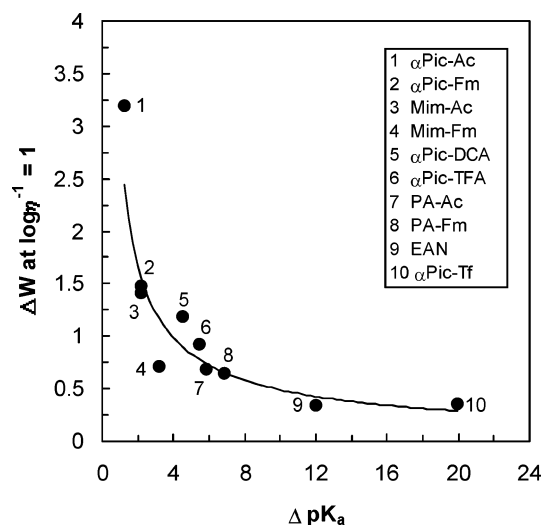
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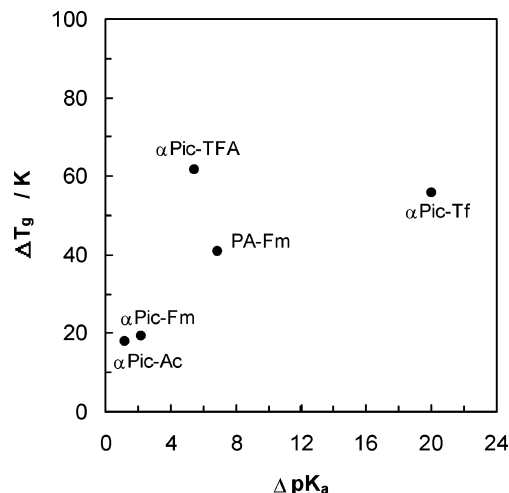
**Figure 9.** Walden plots for the various ionic liquids obtained by in this work, as indicated in the legend. The vertical line at  $\log(1/\eta) = 1$ , is used to define the deviations from “ideal” Walden behavior used to construct the next figure. EAN is ethylammonium nitrate.



**Figure 10.** Deviations from the “ideal” Walden behavior for ionic liquids plotted against  $\Delta pK_a$  values for the component Brønsted acids and bases of the respective ionic liquids. Clearly case with small  $pK_a$  values cannot be classed as ionic liquids. When  $\Delta pK_a$  is greater than ca. 10, no difference can be observed between proton-transfer ionic liquids and aprotic ionic liquids by their transport behavior.

solution acid and base  $\Delta pK_a$  values, as used in Figure 8. Here again, we find a surprisingly good (inverse) correlation. Figure 9 and Figure 10 together tell us that, when the aqueous  $\Delta pK_a$  value is greater than about 10, the difference between the positions of the Walden plot for the proton-transfer salt and for salts where proton transfer is not a possibility, has vanished.

Above, we have made successful correlations of the salt-like character of proton-transfer salts at two rather different temperatures—the boiling point in the first instance (in Figure 8) and a midrange isoviscous point, in the second (Figure 10). There remains the evaluation at low temperatures that can be made tentatively in terms of the excess glass temperatures  $\Delta T_g$ .  $\Delta T_g$ , like  $\Delta T_b$ , is assessed as the difference between the measured  $T_g$  at the stoichiometric salt composition, and the additive value at the same composition. The excess  $T_g$  is shown as a function of  $\Delta pK_a$  in Figure 11. It is subject to much larger



**Figure 11.** Poor correlation of excess glass transition temperatures  $T_g$  (determined at the 1:1 composition) with the  $\Delta pK_a$  values for the acid base combination. The  $\Delta T_g$  value is determined as the difference between the measured  $T_g$  and the value at 1:1 of the linear connection between pure acid and pure base glass temperatures. The  $\Delta T_g$  value for  $\alpha$ Pic-Tf is obtained by interpolations.

scatter than the others, implying that other important factors enter into the determination of the glass temperature, as is known from earlier work.<sup>32</sup>

Comparable increases in  $T_g$  due to proton transfer, 57 K, were reported long ago for the case of hydrazine (8.1) + formic acid (3.75)<sup>11a</sup> for which  $\Delta pK_a$  is 4.35. The conductivity of the 1:1 solution in this system (which is liquid at 35 °C, indeed it does not exist as a distinct crystalline solid), was until very recently<sup>20</sup> the highest ever measured for an ionic liquid,<sup>50</sup> probably due to the very low value of  $T_g$  for this case (−115 °C).<sup>11a</sup>

**2. Thermodynamics of Ionic Liquid Formation.** From the comparisons in Figures 8 and 9, it can be seen that the Walden rule criterion is less discriminating between ionic liquids formed by proton transfer, than the vapor pressure criterion. Two liquids that appear equally ionic by the Walden rule criterion can be distinguished one from the other by the boiling point elevation criterion. In this section, we discuss briefly the thermodynamic reason for this distinction, and note that it also provides a basis for distinguishing aprotic from protic salts.

The ionic liquid can be thought of as the result of a proton “falling” from a quantized energy level on the acid molecule (called an “occupied” level, after Gurney<sup>42</sup>) into a previously unoccupied, or “vacant”, level (also quantized) on the base, to form the protonated cationic species, as illustrated in Figure 12.

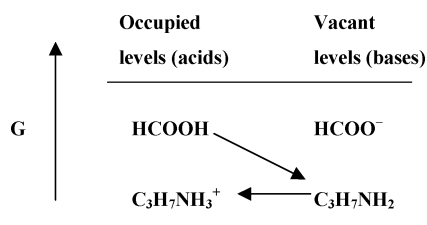
The fact that the reverse proton transfer can yield two new species within the ionic liquid provides a thermodynamic (entropic) drive to generate vapor. This must ultimately win out as temperature increases because of the  $T\Delta S$  component of the total free energy change. The question is only whether the boiling point (at which the sum of the two molecular partial pressures reaches 1 atm.) will be reached before chemical decomposition, as opposed to reformation of the molecular acid and base reactants by eq 1, renders it irrelevant. The equilibrium

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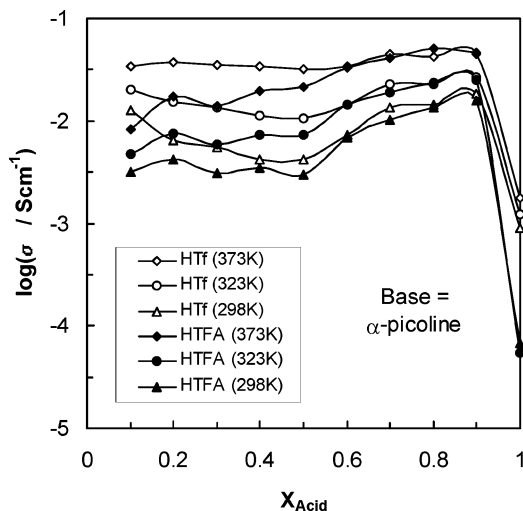
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**Figure 12.** Free energy levels  $G$  for protons on acid/conjugate base pairs, following Gurney.<sup>42</sup> The gap between levels measures the free energy of proton transfer at the stoichiometric composition. The larger the gap the smaller the Boltzmann probability of reformation of the original molecular pair at any given temperature, hence the smaller the vapor pressure over the ionic liquid at ambient pressure. At the boiling point the sum of the two molecular partial pressures, and whatever paired species might form in the vapor, reaches 1 atm.



**Figure 13.** Conductivity isotherms for binary solutions of the two acid–base pairs showing conductivity minima at the stoichiometric compositions at which the glass temperatures maximize (see Figure 3). High conductivities are realized in acid and base-rich compositions until decreasing ionic concentrations become dominant.

involved in the boiling is of the simple “two-state” variety, and should be preceded by a rise in heat capacity. The excess heat capacity of a two-state system is given by

$$\Delta C_p = R(\Delta H/RT)^2 X(1 - X) \quad (5)$$

where  $X$  is the fraction of protons that have been excited into high energy sites at temperature  $T$  and  $\Delta H$  is the enthalpic component of the free energy gap  $\Delta G = \Delta H - T\Delta S$ .  $X$  itself depends on both the enthalpy and entropy terms in the free energy of proton transfer represented in Figure 12 by the free energy gap between the two levels. Whether or not the rise in heat capacity will be easily detected will depend on the value of the  $\Delta S$  component of the free energy of proton transfer. The value of  $\Delta S$  determines the temperature interval over which the system passes from the ionic liquid to the molecular state.  $\Delta S$  itself is determined largely by differences in vibration frequencies in the molecules and ions, and in the liquid quasi-lattice, when the proton transfer occurs. Generally, the heat capacity increase will occur over too wide a temperature range to be detected without quantitative heat capacity measurements, and may be swamped by other effects.

For aprotic ionic liquids, the corresponding exchange between anion and cation species would involve the transfer of alkyl

groups such as  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$ , rather than protons. Because this is a much more energetic process, involving the rupture of covalent bonds, it will not be observed. Rather it will be preempted by, or combined with, other irreversible chemical decomposition modes.

**3. High-Temperature Protonic Acids.** A potentially important aspect of this study concerns the demonstrated general existence of high-temperature-stable, proton-rich, ionic liquids. First, we note that the stabilization of proton-carrying dianions in the presence of weak field cations has been reported before. The existence of  $\text{HCl}_2^-$  as a stable anionic species with lifetime long with respect to the NMR time scale was demonstrated spectroscopically in some of the early ionic liquid work.<sup>51</sup> More recently, the difluoride anion which is well-known in inorganic chemistry, has been the subject of several ionic liquid studies.<sup>52,53</sup> In principle, such anions could serve as the proton-transporting media in high-temperature fuel cells. The stability of dianion stoichiometries is best seen in Figure 4 in which the maximum boiling point is exhibited not at the 1:1 composition but at the 2:1 acid: base composition. The stability of the  $\text{AHA}^-$  anion derives from the existence of a strong hydrogen bond between the anion and the additional molecule of acid. This bond is strong enough in the case of  $\text{HF}_2^-$  that the anion forms even in the presence of alkali cations. With anions less electronegative than  $\text{F}^-$ , the bond can form only when the cation exerts too weak an electric field to control the anion orientation, as in ionic liquids.

In future work, we will characterize these species by their proton NMR spectra and their O–H vibration frequencies. For the moment, we wish only to comment on the properties of the solutions containing them, and the properties they exhibit relative to those of the stoichiometric salt compositions.

In Figure 13 we show the conductivities of the solutions of two of these systems. Both have the same base,  $\alpha$ -picoline, but the acids differ greatly in strength. In one case, trifluoroacetic acid, the  $\Delta pK_a$  value is 7.3 units and the boiling point at the 1:1 stoichiometry is easily measured, 175 °C. In the second case, triflic acid, the  $\Delta pK_a$  value is ca. 20 and the boiling point cannot be observed. The conductivities however are not so different because, although the ionicity of the triflate salt is high in consequence of its stronger proton transfer, the concomitantly higher  $T_g$  renders the ion mobilities smaller. The former is evidently the more important because the triflate salt has the higher conductivity. Because it also has the lower vapor pressure it is, of the two, the ionic liquid of preference if conductivity is an important consideration. However, if fluidity should be an important consideration, then the trifluoroacetate IL may be the more desirable medium.

Passing to the acid-rich compositions, it is noted that the conductivity has increased strongly because of the decreasing  $T_g$  value (Figure 3). The conductivity of the involatile proton-rich liquid reaches 11  $\text{mScm}^{-1}$  at ambient temperature, which is higher than that of most 1M solutions of salts in molecular solvents. The conductivities of more favorable solutions, published in ref 20 since this paper was submitted, reach values characteristic of aqueous solutions, and prove to have valuable

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applications in fuel cells of a novel type.<sup>54</sup> Despite their high proton contents, these liquids are not as aggressive as might be expected. For instance, their action on zinc to release hydrogen proceeds very slowly at ambient temperature and requires heating to 100 °C to proceed rapidly. So long as water is excluded such ambient temperature acids should not be considered difficult to handle.

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