ABSTRACT

The HNMR spectrum of 1-butyl-3-methylimidazoliumBF4 (BmimBF4), 1-hexyl-3-methylpyridiniumPF6 (HmpyrPF6), and 1,3-dibutylimidazolium PF6 (diBimPF6) were each measured as a function of temperature over most of their liquid ranges. The HNMR spectrum of a 1:1 mixture of the two PF6 salts was also measured as a function of temperature over much of the mixture’s liquid range. The 19FNMR spectrum of PF6 was also measured as a function of temperature in each of the PF6 salts. From the lack of a discernable temperature dependency of any of the chemical shifts, it was concluded that the ionic interactions were all likely to be enthalpic and that the entropy of each liquid may have been maximized, thus suggesting that mixtures of these salts may well be described as “regular” solutions. In addition, an unusual species may exist in the diBimPF6 melt.

INTRODUCTION

Many years ago, Joel Hildebrand introduced the concept of “regular solutions” to describe solutions in which the excess molar entropy of mixing, \( S_m^E = 0 \), but \( H_m^E \) and \( V_m^E \), etc., were not equal to zero (1). This required the solutions’ entropy to be essentially the same as that of an ideal gas mixture at the same temperature and pressure. In other words, the molecules or ions were distributed randomly, but interacted with each other strongly and nonrandomly. This concept, along with its associated “solubility parameter” theory, turned out to be almost completely useless as a quantitative predictor of solution behavior except for iodine in several nonpolar solvents, but it did serve from time to time as an interesting model (2,3,4) to qualitatively and in a few cases quantitatively, explain deviations from ideality in binary liquid mixtures. We revisit this concept and suggest that the ionic liquids NaAlCl4, (5), 1-butyl-3-
methylimidazolium$\text{BF}_4$, (Bmim$\text{BF}_4$) 1-hexyl-3-methylpyridinium$\text{PF}_6$, (Hmpyr$\text{PF}_6$) and 1,3 dibutylimidazolium$\text{PF}_6$, (diBim$\text{PF}_6$) as well as many other similar ionic liquids, may form regular solutions. For these solutions, a useful energy of interaction parameter, $w$, in the equation:

$$G^E_m = x(1-x)Lw \tag{1}$$

where $G^E_m$ = the excess molar free energy of mixing, $x$ is the mole fraction and $L$ is Avogadro’s number, may be calculated. Alternatively, estimates of $w$ would allow the calculation of the excess free energy of mixing. This is something that has eluded us in the past.

In an earlier study of the temperature dependence of the HNMR spectrum of 2-methylpyridinium tetrafluoroborate (2-mepyr$\text{BF}_4$) from $-15^\circ\text{C}$ to $105^\circ\text{C}$ (6), there was a near perfect 1:2:2 proton ratio, as expected at the lower temperature, but at the higher temperature the ratio changed to 0.5:2.25:2.25. This suggested rather strongly that the proton was delocalized and moving about the ring.

The increased delocalization of the nitrogenic proton would be expected to increase the entropy of the salt with increasing temperature so that if the enthalpy of the reaction:

$$\text{C}_6\text{H}_8\text{N} + \text{HBF}_4 = \text{C}_6\text{H}_8\text{NH}^+\text{BF}_4^- \tag{2}$$

were small and negative, the large, increasingly positive entropy would be expected to drive the reaction to the right because according to the equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{3}$$

as $T \Delta S^\circ$ gets larger, $\Delta G^\circ$ gets more negative and because

$$\Delta G^\circ = -RT \ln K \tag{4}$$

$K$, the equilibrium constant, increases. However, the increasing delocalization of the proton meant that the entropy of this system could not be maximized despite the very weak interactions between the $\text{BF}_4^-$ and the pyridinium ring. This prompted us to consider the Bmim$\text{BF}_4$ ionic liquid in which the interactions between the $\text{BF}_4^-$ ion and the Bmim$^+$ ion would still be weak, but the question of a mobile or delocalized proton was moot. The complete lack of any discernable temperature dependence of the HNMR spectrum in this melt, despite the sensitivity of pulsed NMR measurements, led us to consider the concept of a regular solution as a possible model for many of these salts and also to consider the possibility that pulsed NMR experiments together with relatively straight forward statistical mechanics could replace the much more tedious and difficult Raoult’s Law measurements of molten salt solutions.
EXPERIMENTAL

Synthesis

The BmimBF₄ and the HmpyrPF₆ were prepared following literature procedures that are based on the metathesis of the corresponding imidazolium chlorides with appropriate salts (7). The water-immiscible ionic liquid, diBimPF₆, was prepared based on a process known as “one-pot synthesis of ionic liquids” (Scheme 1). By mixing aqueous formaldehyde with two equivalents of 1-butylamine, hexafluorophosphoric acid, or bis(trifluoromethane-sulfonyl)imide and aqueous glyoxal solution, the hydrophobic ionic liquid (lower layer) thus formed can be separated directly from the reaction mixture (8,9).

\[
\text{In ice-bath, then rt-50^\circ C} \quad \text{overnight} \quad \text{(yields typically ~99\%)}
\]

\[
1 \text{ eq. HCHO (aq.)} \quad 2 \text{ eq. } n\text{-BuNH}_2 \quad \text{overnight}
\]

\[
1 \text{ eq. HPF}_6 \text{ (aq.) or (CF}_3\text{SO}_2\text{)NHNH} \quad \text{n-Bu}
\]

\[
1 \text{ eq. Glyoxal (aq.)}
\]

\[X=\text{PF}_6^-, \quad "\text{biPF}_6^-", \quad X=\text{(CF}_3\text{SO}_2\text{)N}: \quad "\text{biNTf}_6^-", \quad \text{n-Bu}
\]

Scheme 1.

NMR Spectra

The \(^1\)HNMR and the \(^19\)FNMR measurements of the melts were made with the variable temperature probe of a Varian UNITYplus 400 MHz spectrometer using an external standard of DMSO so that the reference could not interfere with the ionic interactions of the liquid. The two-dimensional NMR spectra were obtained by using a standard phase-sensitive correlation spectroscopy (COSYPS) pulse sequence. This sequence consists of a preparation period (d1), a 90° RF pulse (pw), an evolution period (d2) during which the nuclear spins precess, a second 90° pulse (p1) during which the spins mix and transfer information, and a detection period (at) during which the free induction decay (FID) is observed.

RESULTS AND DISCUSSION

Figure 1 shows the BmimBF₄ spectrum at each of five different temperatures and except for an increase in resolution at the higher temperatures, there is absolutely no change in the chemical shifts of any of the protons. Moreover, the room temperature spectrum is in substantial agreement with the spectrum of the same compound obtained by Xiao and Johnson (10). The lack of any temperature dependence strongly suggests the ions are randomly distributed throughout the melt.

Figure 2 shows the 1 and 2-dimension spectra of diBimPF₆ while Figure 3 shows the 1-d spectrum at each of five different temperatures. Again, except for an increase in resolution that can be attributed to a decrease in viscosity, there is no discernable temperature dependence of the spectra. Each peak has been identified and the integrations are exact for the 1,3 dibutylimidazolium ion structure, except for the feature at 7.356-7.456 ppm. The area under this series of peaks integrates within experimental error to one so it’s a single proton. Again, like the other peaks, it does not shift at all as a function of temperature, which indicates it is part of the system, not an impurity. We tentatively
suggest that the species is HPF$_6$ trapped by the “arms” of the imidazolium ring, and bonded to it coulombically so that it is not free to move about the melt. Again, the lack of temperature dependence of any chemical shift strongly suggests random distribution of the positive and negative ions.

Figure 4 shows the 1 and 2-dimension spectra of HmpyrPF$_6$ while Figure 5 shows the 1-d spectrum at each of five different temperatures. Again, except for an increase in resolution that can be attributed to a decrease in viscosity, there is no discernable temperature dependence of the spectra of any systemic peak. Each peak has been identified and the integrations are exact for the known Hmpyr$^+$ ion structure.

Figure 6 shows the $^{19}$FNMR of the PF$_6^-$ ion in the HmpyrPF$_6$ melt with two sharp temperature independent peaks at −73.362 and −71.478 ppm respectively. Two peaks are expected because of the spin $\frac{5}{2}$ of phosphorus. The $^{19}$FNMR spectrum of the PF$_6^-$ ion in the diBimPF$_6$ melt is nearly identical, with peaks at −71.358 and −73.252 ppm. The fact that the chemical shifts are so similar, despite the difference in cation structure, indicates that the proton cannot be chemically coupled to the PF$_6^-$ ion and further substantiates both the randomness of the distribution of positive and negative ions and the weakness of the PF$_6^-$ - cation interactions. Why we do not detect the H$^+$ ion in the HmpyrPF$_6$ melt is not clear yet.

We next measured the HNMR spectra of a 1:1 mixture of diBimPF$_6$ and HmpyrPF$_6$ at temperatures between 25 °C to 105 °C and then again at 25 °C after the sample stayed sealed at 105 °C for an hour. This system has different cations, but the same anion. The results of these experiments are shown in Table 1 in which we list the chemical shifts of each of the protons, first in the neat melts and then in the 1:1 mixture at 25 °C because there were no measurable temperature dependent chemical shifts in the mixture and, what is even more surprising, each of the peaks experienced exactly the same chemical shift that it did in the neat melt. We have not seen any other binary molten salt mixture exhibit this behavior. This means that, in anthropomorphic terms, none of the ions felt the presence of any of the other ions. This implies that the ions are again distributed randomly, meaning that the entropy of mixing was maximized and again leading us to explore further the notion of regular solutions as a model for these molten salt mixtures.

|                  | diBimPF$_6$ | HmpyrPF$_6$ | 1:1Mixture | diBimPF$_6$ | HmpyrPF$_6$ | 1:1Mixture |
|------------------|-------------|-------------|------------|-------------|-------------|------------|
|                  | 8.76        | 8.44        | 8.84       | 8.77        | 8.51        | 8.44       |
|                  | 7.67        | 8.64        | 8.04       | 7.65        | 7.30 m      | 7.65       |
|                  | 7.38 m      | 4.7         | 7.05       | 1.52        | 1.05        |
|                  |             |             | 1.49/1.40  | 0.94        |             |
|                 |             |             | 1.47       | 1.05 0.96   |             |

A prediction about solution behavior that is a requirement of the regular solution model is that if $w$ in Eq [1] is positive (heat of mixing is endothermic), then it must be the case that there is a $T_c$ below which the two components of the mixture are immiscible.
This is exactly what occurs in the HmipyPF$_6$ - water system and is probably the reason the two components are essentially immiscible at all temperatures measured, with the immiscibility increasing as the temperature decreases - in perfect qualitative agreement with theory. This occurs because the system prefers to form AA and BB pairs rather than AB pairs. On the other hand, we noted that upon mixing of HmipyPF$_6$ and diBimPF$_6$ the components were completely miscible in all proportions at 25 °C despite the high viscosity of both liquids. This means that the mixing is exothermic (w in Eq [1] is negative) and the mixture prefers AB pairs to AA or BB pairs (or does not care in which case Raoult’s Law would be followed exactly). The regular solution model also predicts this behavior.

In order to make a rough estimate of w without calorimetric measurements of the heat of mixing and concomitant measurements of vapor pressures and gaseous composition, we use the energy of activation for viscosity. $E_h$ as our interaction parameter because the energy of activation for viscosity is the closest measurement we have for the enthalpy needed to move one component past another in a melt and reflects closely the forces of attraction between AA molecules or BB or AB molecules in the liquid. Unfortunately, as far as we can tell, no one has measured the change in viscosity as a function of temperature for either the neat melts or the mixture so we use the $E_h$ for a similar melt, BmimPF$_6$, measured by Carper et al (11) that at 25 °C, as near as we can estimate from their plot, is ranged from approximately 35 kJ/mol to 22 kJ/mol. This range of values is quite similar to the $E_h$ for many viscous low temperature and room temperature melts and since we would be expected to be a bit more viscous, we will estimate our $E_h$ to be approximately 36 kJ/mol. Using this value and assuming the excess free energy of mixing in Eq.[1] to be entirely enthalpic we estimate the enthalpy of mixing of our 1:1 melt to be approximately −9 kJ/mol based on $L_w$ being taken as -36 kJ/mol for both components of the ionic liquid.

CONCLUSIONS

We have measured the 1-d and 2-d HNMR spectra of BmimBF$_4$, HmipyPF$_6$ and diBimPF$_6$ as well as the HNMR spectrum of a 1:1 binary mixture of binary HmipyPF$_6$ and diBimPF$_6$ at several different temperatures and found that within experimental error there is no temperature dependence of the chemical shifts of any of the protons or the fluorine in PF$_6^*$. We have also found that these melts seem to have all of the attributes of “regular solutions” and have made a very rough estimate of the excess molar free energy of mixing for our binary mixture. Finally, we may have discovered an unusual species extant in the diBimPF$_6$ ionic liquid that persists in the mixture.

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Figure 1. The HNMR spectra of BmimBF$_4$ at 25°C, 45°C, 65°C, 85°C, and 105°C relative to an external standard of DMSO at 2.49 ppm.

Figure 2. The 1 and 2-d HNMR spectra of diBimPF$_6$ relative to an external standard of DMSO at 2.49 ppm that is not part of the system.
Figure 3. The HNMR spectra of diBimPF$_6$ at 25°C, 45°C, 65°C, 85°C, and 105°C Relative to an external standard of DMSO at 2.49 ppm

Figure 4. The 1 and 2-d HNMR spectra of HmpyrPF$_6$ relative to an external standard of DMSO at 2.49 ppm that is not part of the system
Figure S. The HNMR spectra of HmpyrPF$_6$ at 25°C, 45°C, 65°C, 85°C, and 105°C Relative to an external standard of DMSO at 2.49 ppm

Figure 6: The $^{19}$FNMR of the PF$_6^-$ ion in the HmpyrPF$_6$ melt with two sharp temperature independent peaks at -73.362 and -71.478 ppm respectively. The $^{19}$FNMR spectrum of the PF$_6^-$ ion in the diBimPF$_6$ melt is nearly identical, with peaks at -71.358 and -73.252.