THE HNMR SPECTRA OF MOLTEN ASYMMETRIC PYRIDINIUM SALTS

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ABSTRACT

The HNMR spectrum of molten 2-methylpyridinium tetrafluoroborate was measured as a function of temperature from −15 °C to 105 °C. DMSO was the external standard. The N-H peak, initially at 11.08 ppm, broadened monotonically with increasing temperature until at approximately 85 °C, it became so broad that it was no longer discernable. This temperature dependence was in marked contrast to the temperature dependence of the N-H proton in 2-methylpyridinium chloride melts. In the chloride melt, the N-H peak is narrow and its chemical shift is temperature independent. Its width narrows slightly with increasing temperature, indicating that the proton is likely in the rapid exchange region with respect to HNMR relaxation time and is hopping back and forth between the 2-methylpyridine ring and the chloride ion. In contrast, in 2-mepyBF₄, the N-H proton does not leave the 2-mepyririne ring, but becomes increasingly delocalized with increasing temperature.

INTRODUCTION

In recent years there has been a veritable explosion of interest in both single component low melting salts and solutions of low melting salts. This explosion was triggered primarily by the fact that these solutions are not only potentially useful in a wide variety of engineering applications, but have been actually patented and incorporated into many commercial processes and devices. Possibly most intriguing among the potential commercial applications is the notion of “clean chemistry” in which low temperature molten salt solutions replace traditional organic solvents thereby removing these solvents from the planet’s pollution stream (1). In order to tailor a melt’s properties to fit a particular application, the thermodynamics (reversible and irreversible) transport properties, and microscopic structure of the melt must be well understood and correlated. In the past, hypotheses about the relationship between a melt’s structure and its properties have often been formulated and tested by studying binary mixtures with a common ion such as MX and M X or M X and M X', the common ion serving, in effect, as a reference in much the same way that water serves as a reference in aqueous solutions. In these melts, isothermal deviations from additivity as a function of changing composition are attributed to changing interactions largely caused by the uncommon ion. For example, properties of a mixture of 4-methylpyridinium iodide (4-mepyrI) and 4-methylpyridinium chloride (4-mepyrCl) that changed as a function of composition were attributed largely to the differences between the Cl⁻ and the I⁻ (2). However, this picture is
inherently somewhat simplistic even though concepts such as the “mixed ion effect” (2,3), which can be defined as deviations from additivity in the isotherms of various properties as one cation or one anion is substituted for another in a glass or melt, derive from these studies. Although defining a reference is necessary for macroscopic measurements to be at all useful, fixing a reference that is not naturally fixed may inherently mask microscopic or molecular contributions to the property measured. This is especially true in the case of partial molar volumes where the reference is the molar volume of each of the pure components.

Historically, the anions of most of the low melting organic cation containing salts studied were the halides and the haloaluminates. Virtually all of these melts were very hygroscopic, necessitating the use of glove boxes, or other means, to scrupulously avoid contact of the salt with water. In recent years BF₄⁻, PF₆⁻, and N(SO₂CF₃)₂⁻ have been extensively used as the anions, ostensibly because their interactions with the organic cation seems to be considerably weaker than that of the halide or chloroaluminate ion, thereby increasing the conductivity of the melt. However, other properties of the melts changed as well, most noticeable of which were the melt’s interaction with water and its melting point. For example, 2-methylpyridinium chloride is very hygroscopic and melts at 89.5 °C, but 2-mepyridinium iodide does not readily form when HI reacts with 2-methylpyridine (4) and the μ-compound that does form is very hygroscopic and melts at 92.5 °C. 2-methylpyridinium tetrafluoroborate (2-mepyBF₄), melts at 6 °C, but can readily be supercooled to approximately −45 °C, and can be left exposed to the atmosphere for hours with little, if any, water being taken up by the salt. Considering that the BF₄⁻ ion has a lower molecular weight and is probably smaller than, for example, the I⁻ ion, the origin of these differences in melt properties is not clear. Because all of the melt’s strong interaction with water cannot be caused by the halide ion alone, but must be shared by both ions, it is not obvious why changing the Cl⁻ or I⁻ for a BF₄⁻ ion causes the 2-mepyridinium ions to stop interacting with water.

Because it is formally impossible to obtain molecular information from thermodynamic measurements, it is necessary to accompany the macroscopic measurement with a microscopic measurement in order to establish unambiguously the molecular origin of the measured macroscopic property or, often enough, to avoid missing a significant interaction altogether because of the mutually canceling out of two equal but opposite effects. The comparatively long relaxation times involved, and the temperature range over which the mixture is liquid, suggest that the microscopic technique of choice for many low melting molten organic salt solutions is NMR spectroscopy. In this study we will measure the temperature dependence of the HNMR spectra of 2-mepyBF₄ and compare it to the temperature dependence of the HNMR spectra of 2-mepyCl.
EXPERIMENTAL

Synthesis of 2-Methylpyridinium Tetrafluoroborate

The 2-mepyrBF₄ was prepared as follows (5). A solution of 22 mmol of Ag₂O (Aldrich) in 30 ml H₂O by volume was treated with 44 mmol of 48% HBF₄ (Aldrich). The resulting mixture was stirred at 20 °C, for 45 minutes and the colored solution turned gray. 5.72 g of 2-mepyrCl, prepared by the procedure described by Elias and Angell (6) was weighed under dry-nitrogen in a glove box, dissolved in a small volume of water and added to the gray solution. The heterogeneous mixture was then stirred for two hours, filtered, and rotoevaporated in a 45°C bath. The resulting material was stored between 3-5 days at -15°C and a white solid was obtained. If the solid compound did not form, dry-nitrogen was passed through the heterogeneous mixture for two hours at 75 °C, and the last procedure was repeated. The final white product was subsequently dried under vacuum, giving a yield of approximately 78%.

HNMR Spectra

The ¹H NMR measurements of the melts were made with the variable temperature probe of a Varian UnityPlus 400 MHz spectrometer using an external standard of DMSO.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the entire HNMR spectrum of 2-mepyrBF₄ relative to the virtually temperature independent external DMSO reference that appears at approximately 2.49 ppm relative to a TMS zero point. The temperature range over which measurements were made was from -15 °C to 105 °C and the spectra were taken at ten degree intervals. Figure 2 shows a greatly expanded N-H peak from approximately 10.5 ppm to 11.8 ppm over the same temperature range. It is obvious that all of the protons are resonating at lower frequencies as the temperature increases, which means that they are all becoming more deshielded as a function of temperature. More significantly however, is the broadening and ultimately “vanishing” of the N-H peak as T increases so that by approximately 85 °C this peak is not visible on the scale shown in Figure 1.

This temperature dependence is in marked contrast to the temperature dependence of 2-mepyrCl (2) that at 95 °C shows a similar spectrum to that of the 2-mepyrBF₄ at -15 °C; the principal difference between the two spectra being that in the chloride system, the N-H proton resonates around 16.5 ppm and not around 11 ppm. This is, of course, expected because of the strong hydrogen bonding between the N-H and the Cl⁻ ion. The spectra of the ring and methyl protons are practically identical in the two melts. In the chloride melt, the chemical shift is virtually temperature independent, but more importantly, the N-H peak sharpens with increasing temperature indicating that the proton is most likely in the rapid exchange region with respect to HNMR relaxation time and is rapidly hopping back and forth between the 2-methylpyridine ring and the chloride ion. Although Tiers and Bovey found that narrow N-H absorption bands were obtained in several asymmetric N-substituted amides in the absence of proton exchange, other authors have found that rapid exchange of the N-H proton removed fine structure caused

Electrochemical Society Proceedings Volume 2002-19

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by quadrupole broadening, and narrowed the hydrogen absorption peaks (7,8). To cite several examples, Shuppert and Angell measured the HNMR spectra of binary mixtures of molten pyridinium chlorides and strong Lewis acids (9,10) and were able to clearly observe the nitrogen broadened N-H peak in the 70 mole percent AlCl3/pyrCl solution. In this solution, the pyridinium ion can be considered to be virtually “free” because nearly all of the Cl" is tied up in Al2Cl7" or AlCl4" ions and both of these ions are very weak Lewis bases. In both pure pyrCl and 2-mepyrCl, where rapid proton exchange is presumed to occur, the N-H peak was extremely narrow and showed no evidence of nitrogen broadening. Moreover, these authors attributed a portion of the unusually high electrical conductivity of these melts to a protonic contribution that could only occur if protons were exchanging. Newman, et.al. (2) measured the HNMR spectra of binary mixtures of 4-mepyrcI and 4-mepyrI. In this study, it was found that the N-H peak was extremely sharp and the proton resonated within 0.2 ppm of the N-H protons in both the pyrCl and 2-mepyrCl melts. This indicated that the methyl group has little influence on this chemical shift and makes it virtually impossible for the asymmetry, per se, to cause a narrowing of the N-H peak in the 2-mepyrCl melts spectrum. Moreover, these authors found that their 70 m% 4-mepyrI/4-mepyrCl solution had virtually the same N-H chemical shift as Shuppert and Angell’s pyrCl in 70m% HCl and in the latter system, proton exchange must be occurring. Therefore, it is extremely unlikely, if not impossible, that proton exchange is not occurring in our 2-mepyrCl melt.

We suggest that in the 2-mepyrBF4 melt, the N-H proton may not be hopping back and forth between the nitrogen and the BF4" ion, but is confined to the ring. Moreover, at the lowest temperatures, the measured N-H chemical shift is closer to the theoretical chemical shift of 12.7 ppm, calculated for a free pyrH+, than it is to the measured N-H chemical shift in 2-mepyrCl that further indicates that the proton is confined to the nitrogen and is not “feeling” the presence of the BF4" (9,10,2). As the temperature increases, the N-H proton becomes more and more delocalized around the ring, thus increasing the melt’s entropy with increasing temperature. At the higher temperatures, the H+ spends perhaps half its time on the nitrogen and the rest of its time elsewhere on the ring or methyl group. Because the N-H peak in 2-mepyrBF4 is considerably broader than it is in the 2-mepyrCl, even at the lowest temperatures studied, the N-H proton probably remains on the nitrogen long enough for its peak to be slightly broadened by the nitrogen’s quadrupole. That this proton is not simply being shielded more by the sp2 electrons of the ring nitrogen as the temperature rises, is indicated by the fact that it is resonating at lower energies rather than higher that would be the case if the proton was getting closer to the nitrogen.

Figure 3 shows the relative intensity of the N-H proton peak and the ring proton peaks at -15 °C and at 105 °C. At the lower temperature there is a near perfect 1:2:2 ratio as expected, but at the higher temperature the ratio changes to 0.5:2.25:2.25. This is quite consistent with the proton being 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:

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

(1)
\[ C_6H_5NH^+BF_4^- = C_6H_5NH^+ + BF_4^- \]  

(2)

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

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  

(3)

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

\[ \Delta G^o = -RT\ln K \]  

(4)

K, the equilibrium constant increases. The existence of this high entropic salt is also consistent with the fact that it does not interact strongly with water.

A reaction such as

\[ C_6H_5NH^+ + BF_4^- + H_2O \rightarrow HBF_4 + C_6H_5NH^+OH^- \]  

(5)

would be expected to lose this entropy of delocalization, possibly in a hydrogen bond between the N-H^+ and an OH^-, and would be thermodynamically highly unfavorable. A plausible reason why the BF_4^- ion behaves so differently than the Cl^- ion, or for that matter, the I^- ion, is that when the H^+ leaves the HBF_4 molecule, the extra electron in the resulting BF_4^- ion somehow gets buried in the ion's interior, leaving the surface somewhat more positive.

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Figure 1. Temperature Dependence of the HNMR spectrum of 2-methylpyridinium tetrafluoroborate from \(-15^\circ C\) to \(105^\circ C\).
Figure 2. Change of the N-H peak as a function of temperature.
Figure 3. Relative intensities of the N-H peak and the ring proton peaks at −15 °C and at 105 °C respectively.