THE RELATIONSHIP OF THE HNMR SPECTRA OF BINARY SOLUTIONS OF METHYLPYRIDINIUM HALIDES TO THE MELT’S STRUCTURE

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ABSTRACT

The HNMR spectra of binary mixtures of 4-methylpyridinium chloride and 4-methylpyridinium iodide were measured as a function of temperature and composition over the entire composition range. Correlations were made between these spectra and thermodynamic and transport properties of the melts. The effect of hydrogen bonding on the melt’s properties was assessed and a four species model was proposed to account for these properties. A pronounced "mixed ion" effect was observed in the NMR spectra, but was barely discernible in the transport properties and completely absent in the thermodynamic properties.

INTRODUCTION

Hypotheses about ion transport mechanisms, ionic and molecular interactions, and the nature of complex species thought to exist in molten salt solutions, often have been tested by examining macroscopic properties of binary mixtures with a common ion. In effect, the common ion serves as a reference in much the same way water serves as a reference in aqueous solutions so that isothermal deviations from ideality as a function of changing composition are attributed to interactions between the components of the mixture. Although defining a reference is necessary for macroscopic measurements to be at all useful, fixing a reference 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. Moreover, since it is formally impossible to obtain molecular information from thermodynamic measurements, it is necessary to accompany the thermodynamic or transport property measurement with a microscopic measurement to establish the microscopic origin of that property unambiguously or, often enough, to avoid missing a significant interaction altogether because of the mutually canceling out of two equal but opposite macroscopic effects. Because of the comparatively long relaxation times involved and the temperature range over which the mixture is liquid, the technique of choice for many molten organic salt solutions is NMR spectroscopy.

We therefore measured the HNMR spectra of binary solutions of 4-methylpyridinium chloride (4-mepyrlCl) and 4-methylpyridinium iodide (4-mepyrlI) as a function of temperature and as a function of composition over the entire composition range. The mixtures contain identical cations, but a different anion and 4-mepyrlCl is capable of hydrogen bonding whereas 4-mepyrl is not. (1) We expected that the hydrogen bonding would cause significant deviations from ideality. We then compared these data with previously measured conductivities, viscosities and partial molar volumes (2,3,4) of the

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same solutions and constructed a detailed microscopic model of the melt. These data were also used to determine if a mixed univalent anion effect exists in these organic melts that is similar to the "mixed univalent cation effect" in inorganic melts discussed by Moynihan in 1979 (5).

EXPERIMENTAL DETAILS

The 4-mepyrCl and 4-mepyrl were each synthesized by bubbling anhydrous HCl mixed with dry nitrogen gas or anhydrous HI mixed with dry nitrogen gas through 4-methylpyridine that had been distilled over BaO. White crystalline methylpyridinium salts appeared after about one minute. Reaction vessels were wrapped with aluminum foil to exclude light so as to prevent photochemical reactions from occurring. Details of the recrystallization, washing, filtration and drying procedures can be found elsewhere (6).

The melting point of the 4-mepyrl salt was 444K and that of the 4-mepyrlCl salt was 441K. The iodide's melting point agreed exactly with our previously published value (2) and the chloride's melting point was 0.5 degrees higher than our earlier literature value. (7) Chemical analyses of the final products gave their exact stoichiometry to three significant figures. Upon melting, the 4-mepyrlCl remained water clear and after approximately 10 hrs at 473K showed no discernible decomposition. The 4-mepyrl turned yellow upon melting, but the yellow color disappeared and the salt returned to its white crystalline state upon freezing. Chemical analysis indicated the salt decomposed approximately 2% after 10 hrs at 473K. This amount of decomposition was considered negligible since no experiment lasted more than two hours and most experiments were conducted in the 430K - 460K range.

The NMR measurements of the melts were made with the variable temperature probe of a Brucker DZH 360/50 spectrometer. An external standard of DMSO was used and the temperature setting of the machine was calibrated with ethylene glycol.

RESULTS

The HNMR spectra of the binary mixtures were obtained isothermally and, for the XCl = 0.3 and the XCl = 0.5 compositions, as a function of temperature between 425 and 440 K. The upper temperature range accessible to the instrument was only about 445 K, with 440 K being the temperature at which most of the spectra were obtained. The spectrum of the pure iodide melt was obtained at its melting point of approximately 444 K. The spectra of the XCl = 0.3 and the 0.5 melts changed their chemical shifts a negligible amount over the fairly narrow temperature range investigated. For instance, at X = 0.5, δN-H = 16.84 ppm at 430K and 16.91 ppm at 440K so that a temperature difference of ± 5 °C at any composition is insignificant as far as the chemical shift is concerned. For illustrative purposes, the spectrum obtained at 440K for XCl = 0.4 is shown in Fig. 1 relative to the external standard of DMSO. In order to correct DMSO data to TMS data, 2.49 ppm is added to the DMSO chemical shift.

Fig. 2 A shows the chemical shift, δ, as a function of composition for the nitrogenic proton and Fig. 3 shows the chemical shifts of the 4-methyl protons, the α protons, and the β protons as a function of composition at 440K. In these figures, the chemical shifts have been corrected to the more familiar TMS standard. It is obvious from these data that between XCl = 0.4 and XCl = 0.8 there is a large positive deviation from

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ideality in the chemical shifts as a function of composition, ideality being the tie line between the pure iodide and the pure chloride melts. The protons are all considerably more acidic (farther down field or more deshielded) than the weighted average of the two pure components.

DISCUSSION

Errors and Comparison With Earlier Work. The temperature of the NMR machine was controlled to ± 2 °C, but the spectra were relatively insensitive to small temperature changes so this variation was considered negligible. The chemical shifts between different samples at any nominal temperature and composition differed by about ± 0.05 ppm which is therefore considered as the random error in the chemical shift measurements. The chemical shifts of the 4-mepyri melt were within ± 0.1 ppm of those reported by Newman and Stevens (1). The present results are considered slightly more accurate because of improvements in instrumentation and technique.

Several years ago, Angell and Shuppert measured the HNMR spectra of binary mixtures of molten pyridinium chlorides and strong Lewis acids (8,9). Table I lists the chemical shifts of the nitrogenic protons taken from their work together with the chemical shifts of the nitrogenic protons in the pure 4-mepyriCl melt and the 70% 4-mepyri melt taken from our study, all corrected to TMS. It is obvious from these data that δN-H for each of the three different pyridinium chlorides are within 0.2 ppm of each other, which means the methyl group has little influence on this chemical shift, but also helps confirm the validity of the three measurements. The most striking feature of the data in Table I, is that in the four pyridinium binaries, the chemical shift is inversely proportional to the Lewis acidity of the second component; the stronger the Lewis acid, the closer the N-H proton is to the theoretical or, stating it differently, the smaller the chemical shift. The reason for this δH dependence on Lewis acidity is that the stronger the Lewis acid, the more successfully it competes with the nitrogenic proton for the deshielding Cl- ion. In a melt which is 70 mol% AlCl3, the pyridinium ion can be considered virtually "free", because nearly all of the Cl- ions are tied up in Al2Cl7- ions or AlCl4- ions. AlCl3 is a stronger Lewis acid than ZnCl2, which in turn is a stronger Lewis acid than HCl (HCl is a strong Bronsted acid, but a relatively weak Lewis acid). 4-mepyri is the weakest Lewis acid of the four and therefore, the chemical shift of its nitrogenic proton in the 70 mol% binary is the farthest down field of the four.

Mixed Ion Effect The isothermal composition dependence of the density, ρ, was used to obtain the excess molar volume, VmE. This quantity is given by the equation

\[ V_m^E = \Delta_{mix} V_m - \Delta_{mix} V_m^{ideal} \]  

where \( \Delta_{mix} V_m \) is the molar volume of mixing and \( \Delta_{mix} V_m^{ideal} \) is the ideal molar volume of mixing. The molar volume of mixing is given by the equation

\[ \Delta_{mix} V_m = \{(1-x)MC_l + xM_I \}/\rho_m - \{(1-x)MC_l/\rho_{Cl} \} - xM_I/\rho_I \]  

where the \( M_j \) are the molecular weights and the \( \rho_j \) are the densities of the mixture, chloride, and iodide melts, respectively.(2,4)
Since $\Delta_{\text{mix}} v_m^{\text{ideal}} = 0$, $v_m = v_m^E = \Delta_{\text{mix}} v_m$. At all temperatures investigated, within experimental error, $v_m^E = 0$. This means that the solutions appear to be behaving ideally with regard to this mixing function and no mixed ion effect is observed. Fig. 4 shows the molar conductance of several binary mixtures as a function of composition and Fig. 5 shows the viscosity as a function of composition for the same melts. Here it is clear that there is a small, but distinct, negative deviation from additivity at the lower temperatures which diminishes as the temperature is raised. With respect to the transport properties then, there does seem to be a small mixed ion effect at the lower temperatures. There is also a large positive deviation from additivity in the chemical shift isotherms which means that at the molecular level the mixtures are anything but ideal.

This implies there is a mixed univalent anion effect in this binary mixture of organic salts which is similar to the mixed univalent cation effect bound in binary mixtures of inorganic salts (5) and what appears to be a mixed divalent cation effect bound in binary mixtures of inorganic salts (5) and what appears to be a mixed divalent cation effect found by Kim and Sadoway (10) in several alkaline earth fluoride mixtures. We therefore suggest the mixed ion effect may be quite general. It is certainly not limited to univalent cations. The mixed ion effect can now be generalized to include deviations from additivity in isotherms of various properties as a function of composition as one ion is substituted for another ion in a glass or melt. Macroscopically, whether or not a mixed ion effect is observed depends on the magnitude of the effect, the precision of the experiment, and whether or not there are mutually canceling out effects. On a microscopic level, e.g. $^1$HNMR spectrometry or FTIR spectroscopy, the effect can always be observed, in principle.

The reasons why the mixed ion effect on the transport properties diminishes with increasing temperature at all compositions are that the configurational entropy increases with increasing temperature, which means, among other things, that the local relaxation times are shorter relative to the site to site jump times. This results in a more idealized fluid in which the transport isotherms are linear functions of the composition. In other words, as thermal energy increases relative to the chemical potential, concentrations of weakly associated species are reduced and since it is these weakly associated complexes that causes the deviations from additivity in the transport property, the magnitude of the mixed ion effect necessarily diminishes. With regard to the thermodynamic property, the apparent ideality of the mixing function, $v_m^E = 0$, is caused by compensating forces, or phenomena that cancel each other, because complexation is certainly occurring, as indicated by the $^1$HNMR spectra. What must be happening then, is that the reduction in volume caused by increased ion pair formation is accompanied by just enough expansion due to local relaxation for $v_m^E$ to be zero, within experimental error.

**Modeling The 4-MepyrCl - 4-MepyrI Binary Mixtures**. In order to explain the large deviation from ideality in the chemical shifts of the N-H proton and the ring protons as a function of composition, while simultaneously accounting for the ideality in the mixing function and the small, but distinct, mixed ion effect in the transport properties, we propose the following model. We assume there are four possible species in the mixture and that at any composition but the pure 4-mepyrI, there is an equilibrium between at least two of them. The four species are shown in Fig. 6.

The species present in the neat chloride melt are A in equilibrium with B. The reasons for postulating the existence of a neutral species in this melt are that the $\Lambda_m$ of 4-mepyrCl is $6.61 \text{ cm}^2\Omega^{-1}\text{mol}^{-1}$ at 425K whereas the $\Lambda_m$ for N-methylpyridinium chloride (N-mepyrCl) is $10.5 \text{ cm}^2\Omega^{-1}\text{mol}^{-1}$ at the same temperature (11,12). Since both molecules
have virtually the same dimensions, but N-mepyrCl cannot hydrogen bond, the lower equivalent conductance must be attributed almost exclusively to hydrogen bonding between the 4-mepyr$^+$ ion and the Cl$^-$ ion to form an associated species. To sharpen this argument, the equivalent conductance of 4-mepyrI is 7.97 cm$^2$Ω$^{-1}$mol$^{-1}$ and the equivalent conductance of N-mepyrI is 8.16 cm$^2$Ω$^{-1}$mol$^{-1}$, a difference just barely exceeding the experimental error in the measurement(2). In neither of these two melts does hydrogen bonding occur.

The reason for postulating the existence of the associated monomer in this melt rather than the charged dimeric chloride similar to that proposed by Shuppert and Angell (8) (similar to species C in Fig. 7) is that while this species would also be expected to lower the conductivity relative to that of N-mepyrCl, it would be expected to raise the viscosity. However, the viscosity of 4-mepyrCl is considerably less than the viscosity of N-mepyrCl (3.05 cp vs 6.42 cp at 425K) (11). Therefore, the dimeric species cannot be a major contributor to the structure of the neat melt. The fact that the relative viscosity difference, \(\frac{\eta_{N\text{mepyrCl}} - \eta_{4\text{mepyrCl}}}{\eta_{N\text{mepyrCl}}} = 0.52\), and the relative conductance difference \(\frac{\Lambda_{N\text{mepyrCl}} - \Lambda_{4\text{mepyrCl}}}{\Lambda_{N\text{mepyrCl}}} = 0.37\), differ in the same "anti-Walden's rule" sense is also the expected consequence of our model because a neutral species acts as a kind of "lubricant" causing a breakdown, or relaxation, in the symmetry of Coulombic forces. This relaxation caused by molecular contraction along the line of centers during the formation of the neutral ion pair causes a concomitant local expansion which would be expected to reduce the viscosity while at the same time reducing the conductivity since there are fewer charges per unit volume. Therefore, the argument for postulating the eventual formation of a dimeric species as \(X_f\) increases, is that it is necessary to account for the fact that the maximum chemical shift deviation occurs at \(X_f = 0.6\) rather than at \(X_f = 0.5\) or lower, where it would occur if only the associated monomer, B, were forming.

The relative molar conductance is, to a good first approximation, a direct measure of the fraction of the 4-mepyrCl melt that is dissociated at any instant. For example, if the relative molar conductance was unity, the 4-mepyrCl melt would be completely dissociated. Therefore, the percent associated is given by the equation:

\[
\%4\text{-mepyrCl associated} = \left(1 - \frac{\Lambda_{4\text{-mepyr}}}{\Lambda_{N\text{-mepyrCl}}}\right) \times 100 = 37\% \quad [3]
\]

which means that in the pure chloride melt, the mole fraction of associated species, B, is 0.37 and the mole fraction of dissociated species, A, is 0.63.

As the formal mole fraction of 4-mepyr (\(X_f\)) increases from 0 to 1, there is an initial increase in the concentration of 4-mepyr$^+$ ions because 4-mepyrI does not hydrogen bond. According to Le Chatelier's Principle, an increase in [4-mepyr$^+$] has the effect of driving the equilibrium between A and B to the right, thereby increasing [B] and ultimately decreasing [A]. A third species, D, is, of course, being added which has the additional consequence that I$^-$ ions are becoming more numerous while inherently more mobile Cl$^-$ ions are having their motion restricted by being associated with 4-mepyr$^+$ ions in neutral complexes. This would be expected to initially cause a small negative deviation from additivity in conductivity because slower I$^-$ ions are not simply being substituted for faster Cl$^-$ ions, neutral species are also being formed. The mole fraction of D then, is always equal to the formal mole fraction, \(X_f\). As \(X_f\) continues to increase, [A] decreases and [B] increases until all of A is gone. At this mole fraction, a new dimeric species, C, begins to

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form again because of LeChatelier’s principle and because the Lewis acid, 4-mepyrt+ considers B to be a stronger Lewis base than I".

The mole fractions of each species present in the melt are listed in Table I. The calculations were made by assuming that in the pure chloride melt, \( X_I = 0 \)
\[ X_B = 0.37 \text{ and } X_A = 0.63 \]  \( \text{(Eq [4])} \), and then simply increasing \( X_I \) from 0 to 1. For example, at \( X_I = X_D = 0.2 \), \( X_C = 0.8 \), \( X_B = (0.37 \times 0.8) + 0.2 = 0.496 \), \( X_A = 0.8 - 0.496 = 0.304 \). \( X_{\text{total}} = X_D + X_B + X_A = 1 \). The largest mole fraction of B, 0.613, appears at \( X_D = 0.387 \). At this mole fraction, all of the dissociated 4-mepyrtCl is gone and C is just beginning to form.

The mole fractions in Table I, together with the assumption that each species' contribution to the melt's measured chemical shift of the nitrogenic proton is additive, can be used to calculate these shifts. That is, for the purpose of modeling the system, the simplifying assumption that at any instant each species present in the melt exists independently of the others so that the product of the chemical shift of this species and its mole fraction equals the chemical shift of the mixture:

\[
\delta_{\text{mixt}} = \Sigma(\delta_i X_i) \]  \[ \text{[4]} \]

These calculated shifts will then be compared to the measured shifts in order to further support the four species model. Using Eq. [4], two equations for two different mole fractions of 4-mepyrtCl were solved simultaneously to calculate the chemical shifts of the nitrogenic protons of A and B. For example, at \( X_I = 0, 0.376(\delta_B) + 0.630(\delta_A) = 17.31 \text{ ppm} \) and at \( X_I = 0.3, 0.559(\delta_B) + 0.141(\delta_A) + 0.3(14.51 \text{ ppm}) = 16.85 \text{ ppm} \). Solving these two equations simultaneously yields a value of 16.9 ppm for the chemical shift of pure A, were it to exist independently and a value of 18.08 for the chemical shift of pure B if it were to exist independently. The chemical shift of the pure dimer, C, has a value of 17.49 ppm which is obtained by making the simple assumption that the nitrogenic proton of the dimer is half way between the chemical shift of A's nitrogenic proton and B's nitrogenic proton. The chemical shift of the nitrogenic proton in D is 14.51 ppm. Using these chemical shifts and Eq. [4], the chemical shifts of the nitrogenic proton were calculated for each formal \( X_I \) and plotted against the formal mole fraction, \( X_I \), in Fig. 2B. The rather remarkable coincidence of the two curves, one empirically measured and the other calculated, lends some measure of confidence to our model and lends additional support for the existence of C. At \( X_I = 0.7, X_B \) is calculated to be zero and \( \delta_C \) multiplied by its mole fraction plus \( \delta_D \) times its mole fraction gives the measured chemical shift of the binary within experimental error.

**Effect of Hydrogen Bonding.** Based on our discussion of the mixed ion effect and our model of the binary mixture, we can say with some degree of assurance that H-bonding between the pyridinium ion and the Cl- actually reduces the mixed ion effect on the transport properties and molar volumes in the binary melts, but increases the mixed ion effect on the proton chemical shifts of the melts. That is, a larger deviation from ideality would be expected in the thermodynamic and transport properties in a mixture of N-mepyrtCl and N-mepyrtI where no H-bonding can occur, but a smaller deviation in the proton chemical shifts. In addition, H-bonding reduces the melt's viscosity, an effect exactly opposite to what is generally observed in molecular liquids, such as water or ammonia, where H-bonding increases the viscosity. We suggest that this too may be general: namely that in molten salts H-bonding decreases viscosity where as in molecular
liquids H-bonding increases viscosity. A decrease in bulk volume due to contraction of a molecule along its line of centers, >N-H-Cl, which might have been expected to accompany the viscosity decrease, was not observed. We think this is due to the introduction of an element of asymmetry into the Coulombic field by the neutral species which has a long enough life time for the melt to locally expand just enough to offset the contraction.

Chemical Shifts of the Ring and Methyl Protons. The hydrogen bonding between the Cl\(^-\) ion and the 4-mepyr\(^+\) ion affects the ring and methyl protons as well as the N-H. These protons become more acidic or deshielded with increasing 4-mepyr\(^+\)-Cl\(^-\) association because this association reduces the polarization of the \(\pi\) electrons (2, 9). The less polarized, or the more "benzene-like", the ring current, the more it deshields. In addition to our results confirming those of Shuppert and Angell with regard to ring protons, they lend additional support to our model. The associated species B and the dimeric ion, C, have much less polarized, or distorted, ring currents than do dissociated species A and D. Consequently, the ring and methyl protons in B and C will be more acidic or down field than in A or D. In particular, the greater the relative concentration of B, the greater the deviation from ideality. In our model, the total mole fraction of B is 0.496 at \(X_J = 0.2\), 0.559 at \(X_J = 0.3\), 0.613 at \(X_J = 0.387\), 0.6 at \(X_J = 0.4\), 0.436 at \(X_J = 0.5\), and 0.292 at \(X_J = 0.6\). It then drops sharply to 0 at \(X_J = 0.7\) which very much parallels the chemical shift vs. composition behavior of the ring and methyl protons.

Additional evidence that our suggestions with regard to the ring protons are probably correct is that the least acidic or most shielded ring protons are in pure D where no association occurs and the ring current is the most distorted.

CONCLUSION

We have used HNMR spectroscopy to discover intermolecular interactions in binary melts that would have gone unnoticed had molar volumes or transport properties been used exclusively. We have correlated these HNMR spectra with equivalent conductance, viscosity and molar volume and constructed a model of these binary melts in which a completely neutral monomeric chloride species (Fig. 6, B) and a dimeric chloride ion, (Fig.6, C) form in the melt. Both of these species have a long enough lifetime to affect the HNMR spectrum. We have found that the phenomenon referred to as the mixed univalent ion effect is neither restricted to cations nor to univalent ions, but is probably quite general in nature. We further suggest that hydrogen bonding generally reduces the mixed ion effect on macroscopic properties and that hydrogen bonding generally reduces viscosity in ionic melts.

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### Table I

Chemical Shifts of the N-H proton in melts containing pyridinium salts, all corrected to TMS.

| Species                          | $\delta_{N-H}$ |
|----------------------------------|----------------|
| pyridinium chloride              | 17.2           |
| 2-methylpyridinium chloride      | 17.1           |
| 4-methylpyridinium chloride      | 17.3           |
| 4-meprCl in 70 mol% 4-mepryl     | 15.5           |
| pyrCl in 70 mol% HCl             | 15.3           |
| pyrCl in 70 mol% ZnCl$_2$        | 13.3           |
| pyrCl in 70 mol% AlCl$_3$        | 12.8           |
| pyrH$^+$, theoretical            | 12.7           |

### Table II

The Mole Fraction of each model species present in binary mixtures of 4-methylpyridinium chloride and 4-methylpyridinium iodide

| XCl | XA | XB | XC | XD |
|-----|----|----|----|----|
| 1.00| 0.630 | 0.370 | 0.00 | 0.00 |
| 0.900 | 0.467 | 0.433 | 0.00 | 0.10 |
| 0.800 | 0.304 | 0.496 | 0.00 | 0.20 |
| 0.700 | 0.141 | 0.559 | 0.00 | 0.30 |
| 0.613 | 0.00 | 0.613 | 0.00 | 0.387 |
| 0.600 | 0.00 | 0.587 | 0.013 | 0.400 |
| 0.50 | 0.00 | 0.430 | 0.127 | 0.436 |
| 0.400 | 0.00 | 0.292 | 0.217 | 0.492 |
| 0.300 | 0.00 | 0.00 | 0.30 | 0.70 |
| 0.20 | 0.00 | 0.00 | 0.20 | 0.80 |
| 0.100 | 0.00 | 0.00 | 0.10 | 0.90 |
| 0.00 | 0.00 | 0.00 | 0.00 | 1.00 |
Fig. 1  HNMR spectrum of $X_{Cl} = 0.4$ vs DMSO

Fig. 2  A. Measured N-H chemical shifts as a function of composition  
B. Theoretical N-H chemical shifts as a function of composition

Fig. 3  △ = proton chemical shifts  
△ □ proton chemical shifts  
○ CH3 proton chemical shifts
Fig. 4  Molar conductivities of binary mixtures

Fig. 5  Viscosities of binary mixtures

Fig. 6, Four species present in the Binary Mixtures