INTRODUCTION:

Hypotheses about the nature of ion transport mechanisms, ionic interactions, and complex species in molten salts have often been tested by examining the macroscopic properties of binary mixtures of inorganic salts with a common cation or common anion. The common ion serves as a reference in much the same way that water serves as a reference in aqueous electrolyte solutions. A fixed reference is necessary for microscopic measurements to be useful, but it masks molecular contributions to the observed phenomenon. It is therefore desirable to have a microscopic measurement accompany the thermodynamic or transport measurement to unmask the microscopic details. The most powerful microscopic technique is, in principle, neutron diffraction, but adequate neutron sources are not generally available and neutron diffraction patterns are very difficult to interpret. The high temperatures necessary for most inorganic molten salt studies make optical spectroscopic measurements difficult to make and NMR measurements impossible. Moreover, optical spectra do not give information about radial distribution functions as do diffraction patterns, so their applicability to the microscopic interpretation of transport properties is limited. This limitation is further exacerbated because no one has defined a complex to everyone's satisfaction. As a result, there are no specific criteria for differentiating between "quasi-lattice vibrations" and "species vibrations" (1) so that even when optical spectra are available, their interpretations are often ambiguous.

By investigating binary mixtures of pyridinium salts with a common ion, much of the same sort of information can be obtained as can be obtained with inorganic salts, but many more subtle questions can be answered because of the great structural variability of these systems, and many of the experimental difficulties of high temperature chemistry are avoided. Since these mixtures are liquid at low enough temperatures for their HNMR spectra to be obtained, one additional microscopic measurement is available that is unavailable for most inorganic mixtures. Since the pyridinium mixtures are also potentially useful as solvents and as electrolytes for batteries, the properties of these melts can be of practical importance as well.
In previous studies we have observed correlations between transport properties, structure, and HNMR spectra of molten 4-methyl pyridinium iodide (4-mepyrl) and molten 4-methyl pyridinium chloride (4-mepyrcI) (2,3). These two salts have similar melting points and liquid ranges, and consequently make a particularly suitable system upon which to test a variety of ideas about binary mixtures with a common ion. In this case the anion is mixed and the cation is common to both salts.

The primary purpose for our investigation is to demonstrate the usefulness of pyridinium binaries as sources of general information about molten salts. This we do by answering a fundamental question as to whether or not there is a "mixed univalent anion effect" in these organic melts that is similar to the mixed univalent cation effect described by Moynihan for inorganic salts (4). A mixed univalent ion effect is the deviation from additivity of a physical property as a function of composition, as one ion is isothermally substituted for the other. The second question we will attempt to answer is whether or not there are correlations between HNMR spectra and transport properties. The third question is what is the role of hydrogen bonding in a binary mixture when one of the components hydrogen bonds and the other does not. In order to answer these questions, the conductivity, viscosity, density and HNMR spectra were measured as a function of composition and as a function of temperature. From the isothermal measurements of density vs. composition, the excess partial molar volumes were calculated.

EXPERIMENTAL PROCEDURE

The methyl pyridinium salts were synthesized and analyzed by methods already described in the literature (5,6). The 4-mepyrl melted at 171°C and turned yellow upon melting. The yellow color disappeared upon freezing. The 4-mepyrcI melted at 167°C and remained water clear. Analysis of the single salt before and after an experiment showed that there was no discernable decomposition of the chloride and about 2% decomposition of the iodide over the course of about ten hours at temperatures approaching 200°C. This was considered negligible. All transfer operations and preparation of salt mixtures were done in a Kewaunee dry box under nitrogen atmosphere.

Density measurements were made with a modified Lipkin bicapillary arm pycnometer (7). The precision of these measurements was ± 0.1%. Conductivity measurements were made with a Jones bridge at a frequency of 1000 Hz using a capillary cell with cylindrical platinum electrodes. The cell constant was 199.53 cm⁻¹, a Cannon – Fenske viscometer was used to measure the melt's viscosity. The HNMR spectra were obtained using the variable temperature probe of a Varian CFT 20 NMR machine and an external standard of DMSO.
RESULTS

The measured density, \( \rho \), in g/cm\(^3\), is given by an equation of the form

\[
\rho = A - B \times 10^{-4} \ T (K)
\]  

(1)

The values of \( A \), \( B \), and the temperature range for each of the pure melts and the mixtures are given in Table I.

| Salt                  | A    | B    | Temperature Range (K) | Correlation Coefficient |
|-----------------------|------|------|-----------------------|-------------------------|
| 4-mepyrCl             | 1.3655 | 6.590 | 443-468               | 0.998                   |
| 4-mepyrl              | 1.9513 | 7.420 | 438-463               | 0.999                   |
| 74.63\% 4-mepyrCl/4-mepyrl | 1.5368 | 6.743 |                        | 0.9953                  |
| 51.19\% 4-mepyrl/4-mepyrCl | 1.6994 | 7.571 | 423-463               | 0.9997                  |
| 48.81\% 4-mepyrCl/4-mepyrl | 1.5202 | 6.134 | 432-452               | 0.9973                  |
| 71.53\% 4-mepyrCl/4-mepyrl | 1.6506 | 6.985 | 429-460               | 0.9994                  |
| 43.51\% 4-mepyrCl/4-mepyrl | 1.8065 | 6.817 | 423-458               | 0.9994                  |
| 25.53\% 4-mepyrCl/4-mepyrl | 1.5202 | 6.134 | 432-452               | 0.9997                  |
| 74.47\% 4-mepyrCl/4-mepyrl | 1.6506 | 6.985 | 429-460               | 0.9994                  |

The specific conductances of the melts followed Arrhenius behavior over the temperature range studied and are given by an equation of the form

\[
\ln \chi (\Omega \ cm)^{-1} = P - Q/T(K)
\]  

(2)

The values of \( P \) and \( Q \) for the melts are listed in Table II.

| Salt                  | P    | Q    | Correlation coeff. |
|-----------------------|------|------|--------------------|
| 4-mepyrl(18.32\%)/4-mepyrCl(81.79\%) | 3.341 | 2564 | 0.999              |
| 4-mepyrl(34.58\%)/4-mepyrCl(65.42\%) | 3.285 | 2557 | 0.999              |
| 4-mepyrl(49.16\%)/4-mepyrCl(50.84\%) | 3.161 | 2507 | 0.999              |
| 4-mepyrl(76.08\%)/4-mepyrCl23.92\% | 2.978 | 2451 | 0.999              |

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The equivalent conductance, $\Lambda$, was calculated from the density and specific conductance using the equation

$$\Lambda = \frac{x^4}{\rho}$$

(3)

where $M$ is the equivalent weight of the salt mixture and is calculated from the equation:

$$M = x(M_{\text{4-mepyrCl}}) + (1-x) (M_{\text{4-mepyrI}})$$

and $\rho$ is the density of the corresponding mixture. Figure 1 shows plots of $\Lambda$ vs. $x$ for the binary mixture at several different temperatures. It is clear that there is a negative deviation from additivity and that this negative deviation becomes less pronounced as temperature increases.

Viscosity also followed Arrhenius behavior over the temperature range studied and can be described by an equation of the form:

$$\ln \eta = -Y + \frac{Z}{T}$$

(4)

where $\eta$ is given in centipoise. The values of $Y$ and $Z$ are listed in Table III for the pure melts and several binary mixtures. Fig. 2 shows several viscosity vs composition isotherms and again there is a negative deviation from additivity which diminishes with increasing temperature.

**TABLE III VISCOSITY**

| Salt              | $Y$  | $Z$  | Correlation Coeff. |
|------------------|------|------|---------------------|
| 4-mepyrI         | 11.46| 3493 | 0.997               |
| 4-mepyrCl        | 11.58| 3464 | 0.999               |
| 67.8%4-mepyrI/32.2%4-mepyrCl | 11.29| 3382 | 0.999               |
| 49.2%4-mepyrI/50.8%4-mepyrCl | 11.36| 3396 | 0.999               |
| 29.7%4-mepyrI/70.3%4-mepyrCl | 11.52| 3453 | 0.999               |

Figure III shows the HNMR spectrum of a binary mixture at 175°C. The essential features of the spectrum were the same at each composition and were relatively insensitive to temperature. Figure IV is a graph of the $\text{>N-H}$ chemical shift vs composition at 175°C.
DISCUSSION

The molar volume of mixing, $\Delta_{\text{mix}} V_m$, is given by the equation

$$\Delta_{\text{mix}} V_m = [(1-x)M_{\text{Cl}} + xM_i]/\rho_m - (1-x)M_{\text{Cl}}/\rho_{\text{Cl}}^i - xM_i/\rho_i^e$$  \hspace{1cm} (5)

where the $\rho_i$ are the densities and the $M_i$ are the molecular weights.

The excess molar volume, $V_m^{E}$, is defined by the equation:

$$V_m^{E} = \Delta_{\text{mix}} V_m^{\text{ideal}} - \Delta_{\text{mix}} V_m$$ \hspace{1cm} (6)

Since $\Delta_{\text{mix}} V_m^{\text{ideal}}$ is zero, $V_m^{E} = \Delta_{\text{mix}} V_m$. Figure 5 shows a graph of $V_m^{E}$ vs. composition for two selected temperatures and, within experimental error, $V_m^{E}$ is zero indicating ideality in the mixing function. Since the Coulombic attraction between $I^-$ and 4-mepyr$H^+$ must differ from the Coulombic attraction between $Cl^-$ and 4-mepyr$H^+$, the apparent ideal behavior must be caused by compensating factors rather than uniformity of forces.

It is very likely that the reduction of molecular volume caused by hydrogen bonding is compensated for by expansion due to local relaxation (8). Therefore, as $I^-$ is substituted for $Cl^-$ the reduction in volume caused by ion pair formation between $\text{N-H}^+$ and $Cl^-$ is accompanied by just enough expansion, caused by local relaxation, for the excess partial molar volume to be zero.

Despite the fact that within experimental error $V_m^{E}$ is zero, there is a distinct negative deviation from additivity in both the conductance and viscosity isotherms. Moreover, this deviation diminishes with increasing temperature. There is therefore a definite mixed univalent ion effect in the binary pyridinium salt system with all of the attributes of the mixed univalent cation effect in inorganic salts that were described by Moynihan (4). However, in the pyridinium melts it is the anion that is mixed and not the cation. Since the more mobile species is the anion (9, 10), and not the cation, as it is in most of the inorganic salts studied, we suggest that this effect is general and should be called the mixed mobile ion effect.

Claes and Glibert have recently found what appears to be a very pronounced mixed univalent anion effect in $\text{LiNO}_3 - \text{Li(OK)}$, $\text{NaNO}_3 - \text{Na(OK)}$, and $\text{KNO}_3 - \text{K(OK)}$ binary melts (11). However, the explanation for their results remains somewhat obscure because of the obvious difference in transport mechanism between the $\text{NO}_3^-$ ion and the $\text{OH}^-$ ion.
In the pure 4-mepyrCl melt hydrogen bonding is an important factor, (12,13), but in the iodide melt hydrogen bonding does not occur (14). As I⁻ is substituted for Cl⁻, complexes like

\[(\text{Me}^- \text{PyrH} \cdots \text{Cl}^- \cdots \text{HPyr-Me}^+)\]

will form, thus immobilizing the inherently more mobile Cl⁻ species and freeing the inherently less mobile I⁻ species. Complexes of this sort will continue to form until a mole fraction of 0.5 is reached and then any added 4-mepyrI will result in a reduction of the complex ion concentration. The conductance and viscosity should be at the minimum at a mole fraction of 0.5 which is close to the observed result. The reason why the viscosity of the melt also goes through a minimum (the fluidity goes through a maximum) is that there is a contraction of the ions along the >N-H-Cl-H-N< bond and a concommitant local expansion due to the positive charge being spread over a much greater volume than before (8). Hydrogen bonding in ionic systems tends to reduce viscosity whereas hydrogen bonding in molecular systems (water, ammonia, etc.) tends to increase viscosity.

Because the transport measurements give no specific information about the species present, we look to the HNMR spectra of the melts for help in this respect and these spectra corroborate our conjectures. If there is complex formation arising from hydrogen bonding between the >N-H⁺ and Cl⁻ then the magnetic environment around the nitrogenic proton should reflect this hydrogen bonding. That it does reflect it is pointed out in in Fig. 4. Here the chemical shift deviates from linearity in a positive sense. That is, the nitrogenic proton is further down field (more acidic) and closer to the pure Cl⁻ melt value. Again, at around a mole fraction of 0.5 the chemical shift begins to move upfield (proton becomes more shielded) more sharply until the pure I⁻ value is reached. The δ's of the ring protons and methyl groups showed no deviation from linearity.

There are many reasons why the mixed mobile species effect tends to vanish with increasing temperature, but the simplest way to summarize them is to say that the configurational entropy is greater, and the local relaxation times are shorter relative to the site to site jump times. Thus the system approaches a more "ideal" fluid state.

The estimated errors in this experiment are ± 0.2% in the density, ± 1% in the composition, ± 2% in the viscosity and HNMR spectra measurements yielding an overall accuracy of about ± 3%. Of some concern is the fact that we were unable to obtain a temperature dependent proton chemical shift which would correlate with the vanishing of the mixed mobile species effect. However, the temperature range available to us was only about 25°C and at the higher temperatures the iodide melt was beginning to decompose so that it may simply have been lost in experimental error.
CONCLUSION

Binary mixtures of molten pyridinium salts have been shown to exhibit a mixed univalent anion effect similar to the mixed univalent cation effect found in many molten inorganic salts, and we suggest it be called the mixed mobile species effect. Moreover, we have correlated the NMR spectra with both viscosity and conductivity data to elucidate the effect of structure on transport properties of molten salts. Finally, we have shown that mixtures of molten pyridinium salts are viable systems for studying properties of molten salts in general.

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Fig. 1  Equivalent Conductance vs. Mole Fraction

Fig. 2  Viscosity vs. Mole Fraction

Fig. 3  HNMR Spectrum of a Binary Mixture of Molten Salts at 175°C
Fig. 4  N-H Chemical Shift vs. Composition at 175°C

Fig. 5  $V_m$ vs. Composition at Two Different Temperature