CONDUCTIVITY, VISCOSITY, HNMR SPECTRA AND DENSITY OF MIXTURES OF 2-METHYLPYRIDINIUM CHLORIDE AND \(\mu\)-HYDROGENBIS(2-METHYLPYRIDINIUM) IODIDE.

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ABSTRACT

The viscosity, electrical conductivity, and density of binary solutions of 2-methylpyridinium chloride and \(\mu\)-hydrogenbis(2-methylpyridinium) iodide were measured as a function of composition and as a function of temperature. It was found that the transport properties showed an Arrhenius temperature dependence and that the densities were linear in temperature. However, the isothermal variation of density with composition showed a fairly sharp maximum at \(X_1 = 0.9\) which is accounted for by a model in which the \(\mu\)-hydrogen bond breaks as the Cl\(^{-}\) ion concentration increases.

INTRODUCTION

Correlating transport properties of binary molten organic salt solutions with thermodynamic properties and molecular structure allow inferences to be drawn regarding the interionic forces extant in the liquid and the microscopic changes in melt structure that cause these transport and thermodynamic phenomena (1). A particularly interesting system in this respect is the binary solution of 2-methylpyridinium chloride (2-MPCl) and \(\mu\)-hydrogenbis(2-methylpyridinium) iodide (\(\mu\)-H-I). \(\mu\)-H-I is shown in Fig. 1.

In an earlier study, it was found that the reaction between 2-methylpyridine and HI(g) produced \(\mu\)-H-I rather than the expected 2-methylpyridinium iodide (2-MPI) (2). The \(\mu\)-H-I melt has unusual transport properties as well as an exceptionally low liquid density compared to the other methylpyridinium iodides. This low density is attributed to the \(\mu\) compound's inability to pack tightly in the liquid state so that if the \(\mu\)-hydrogen bond were to break, the liquid structure might "collapse", causing a precipitous
increase in melt density accompanied by changes in transport properties. This bond might be cleaved by adding 2-MPC1 to the μ-H-I because the Cl⁻ ion would compete with the ring nitrogen for the hydrogen and is also capable of forming strong hydrogen bonds. Therefore, it was decided to vary the composition of a binary mixture of 2-MPC1 and μ-H-I and observe the changes in density and transport properties that resulted. In addition, the low liquidus temperatures of these binary solutions make them easily accessible to NMR measurements so that structural properties might be correlated with transport properties.

EXPERIMENTAL DETAILS

2-MPC1 was synthesized by passing HCl(g) through 2-methylpyridine that had been dried over CaO and distilled at 128-129 °C. The reaction is

\[
\text{HCl}(g) + 2\text{-CH}_3\text{C}_5\text{H}_5\text{N}(1) \rightarrow 2\text{-CH}_3\text{C}_5\text{H}_6\text{NCl}(s) \quad [1]
\]

The melting point of 2-MPC1 was 88-89°C which is in exact agreement with literature values (1,3). The μ-H-I was synthesized by a reaction similar to Eq. [1] except that gaseous HI was bubbled through 2-methyl pyridine and the reaction vessel was covered with aluminum foil so as to prevent light from reaching the μ-H-I. The final recrystallized product had a melting point of 93-94°C, which is in agreement with our earlier result (2).

A capillary cell with cylindrical platinum electrodes and a Jones bridge were used to measure the ac conductivity at 1000 Hz. The variable temperature probe of a Varian XL-200 NMR machine was used to obtain the NMR spectra. DMSO was used as an external standard. A Lipkin bicapillary arm pycnometer was used to measure melt densities and a Cannon-Fenske viscometer was used to measure viscosity. All transfer operations were done in a controlled atmosphere dry box in which the "boil off" from liquid nitrogen was circulated.

RESULTS

Figure 2 shows a plot of the natural log of the equivalent conductance (\(\Lambda\)) vs. 1000/T for various compositions, and Fig. 3 shows a graph of the natural log of the melt viscosity (\(\eta\)) vs. 1000/T for the same compositions. Figure 4 shows a graph of density vs T for...
the different melt compositions. It is clear that, within experimental error, these curves are all linear. It is also obvious from Fig. 4 that the pure µ-H-I is not the most dense melt. Figure 5 is a plot of density vs composition at three different temperatures: 373 K, 393 K, and 408 K. The dashed curve is the "measured" density vs composition behavior at 408 K if our proposed model were correct (vide infra). Figure 6 is a plot of the specific conductance vs mole fraction at three different temperatures and it is clear there are two maxima in each of the curves. Figure 7 shows the equivalent conductance vs composition at the same three temperatures and, at least at the two lower temperatures, there seems to be an inflection point. To calculate the \( /\) values in Fig. 7, the equivalent weight of the u-H-I was used. Figure 8 is the HNMR spectrum of pure 2-MPC1 at 102°C. The HNMR spectrum for the pure µ-H-I is given elsewhere (2). Figure 9 is a graph of the nitrogenic and u-proton chemical shifts as a function of composition at 102°C. The lower curve in this figure shows the chemical shifts of the gamma proton as a function of composition. At 200 MHz, the machine could not resolve the two gamma peaks. Figure 10 shows the isothermal changes in viscosity as a function of composition.

DISCUSSION

The conductivity and viscosity at each melt composition shows strict Arrhenius behavior over the relatively narrow temperature range investigated. However, isothermal measurements of /\ and \( /\) show a negative deviation from ideality as a function of composition, the deviation decreasing with increasing temperature. Moreover, the negative deviation is considerably more pronounced for viscosity than it is for conductivity. Although the density at each composition is a linear function of temperature, the isothermal changes in density as a function of composition go through a sharp maximum at around \( X_I = 0.9 \). This maximum becomes less pronounced as the temperature increases.

The model we propose to account for these results is one in which the µ-H-I dissociates into 2-MPI and 2-methylpyridine as \( X_I \) varies from 1 to 0. In other words, at all concentrations other than \( X_I = 1 \) and \( X_I = 0 \) there is some 2-methylpyridine in the solution, and there are four constituents in the mixture: 2-MPC1, 2-MPI, µ-H-I and 2-methylpyridine. Therefore, the densities of the 2-MPI and 2-methylpyridine have to be considered when calculating the
density of the mixture at all intermediate compositions between \(X_i = 1\) and \(X_i = 0\). The density of 2-MPI is not known, but the density of 3-MPI is known (2), and it is expected to be within +/- 1% of the density of 2-MPI because this is the case with 2-MPC1 and 3-MPC1 as well as with 2-MPBr and 3-MPBr (1). The density of 2-methylpyridine is easily measured as a function of temperature. Using these data and the additional assumption that \(\Delta V_{\text{mix}} = 0\), the dashed curve in Fig. 5 was calculated. It is obvious that the measured density vs mole fraction curves exhibit a sharper and more complex maximum than the model density vs mole fraction curve does. But, considering that the actual \(\Delta V_{\text{mix}}\) is almost certainly not zero and that hydrogen bonded species like \(\text{[>N-H..Cl..HN<]}^+\) form between two 2-methylpyridinium ions and a Cl- ion (3), the fact that the calculated maximum is near the measured maximum and the calculated curve has the same general shape as the measured curve is very reassuring.

This simple model also predicts one broad maximum in the specific conductance vs composition curves. Since the total number of charges is constant, as the density increases the number of charge carriers per unit volume must increase. In addition, the mobility of these charge carriers would be expected to increase at first because the 2-methylpyridine molecules formed by the dissociation of the \(\mu\text{-H-I}\) acts as a sort of lubricant and reduces the viscosity. The combination of these two phenomena increases the specific conductance. As the melt becomes richer in Cl-, hydrogen bonding between Cl- and 2-MP+ ions begins to control the transport mechanism (that is why the pure 2-MPC1 is a poorer conductor than the pure \(\mu\text{-H-I}\)) and the specific conductance would be expected to decrease monotonically until the pure 2-MPC1 conductance is reached. Although the measured specific conductance vs composition roughly approximates this behavior, the observed shallow minimum or second maximum cannot be explained by this simple model alone. In a future study we will offer a more detailed explanation for the "second maximum" in these curves.

A further indication that this model is essentially correct arises from the equivalent conductance vs. composition curves. In Fig. 7, if the equivalent weight of \(\mu\text{-H-I}\) (314 amu) is used to compute the equivalent conductances from the specific conductances (which is correct way to proceed if the \(\mu\text{-H-I}\) did not dissociate) an inflection point arises in the /\ vs composition curve (Fig.6). If, on the other hand, the equivalent weight of 2-MPI (221 amu) is used with the appropriate mole
fractions of 2-MPC1 and μ-H-I, e.g., at a nominal X₁ = 0.5 only the equivalent weight of 2-MPI and 2-MPC1 were used to compute the equivalent conductance from the specific conductance because there is no longer any μ-H-I present, the typical smooth /\ vs composition curves shown in Fig. 11 are obtained and the inflection point vanishes.

Our preliminary HNMR curves indicate that some μ-H-I persists at X₁ = 0.4 whereas our model predicts it should all be gone at X₁ = 0.5. This small discrepancy is almost certainly due to the fact that some of the Cl⁻ ions are hydrogen bonded to the 2-MP⁺ ions and are not free to compete for the μ-hydrogen.

CONCLUSION

The binary mixture of 2-MPC1 and μ-H-I exhibited unusual density vs. mole fraction behavior at each of three different temperatures. This unusual behavior is explained to a first approximation by a model in which the μ-H-I dissociates into 2-MPI and 2-picoline as the system becomes richer in 2-MPC1. In a future study, this model will be refined to include nonideal mixing and hydrogen bonding between the Cl⁻ ions and the 2-MP⁺ ions.

REFERENCES

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Figure 1. Structure of μ- hydrogenbis (2 - methylpyridinium) iodide
Figure 2.
\( \ln \Lambda \) vs. \( 1/T \)

Figure 3.
\( \ln \Pi \) vs. \( 1/T \)
Figure 4.
Densities as a function of temperature

Figure 5.
Densities as a function of mole fraction
Figure 6.
Specific conductances as a function of mole fraction

Figure 7.
Equivalent conductances as a function of a mole fraction
Fig. 8. $^1$HNMR spectrum of $\mu$-hydrogenbis(2-methylpyridinium) iodide. 102°C

Figure 9.
Chemical shift $\delta$

Chemical shift $\delta$(ppm)

$I$: $N\cdot H$  $\Delta$: $N\cdot H\cdot N$  $\bigcirc$: $Y\cdot H$

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Viscosities as a function of mole fraction

Figure 10.

Revised equivalent conductances as a function of mole fraction

Figure 11.