CORRELATIONS BETWEEN $^1$HNMR SPECTROSCOPY AND TRANSPORT PROPERTIES IN MOLTEN ASYMMETRIC PYRIDINIUM HALIDES

David S. Newman, Rick R. Rhinebarger and David Siconolfi

Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Abstract

The Equivalent Conductance, viscosity and $^1$HNMR spectra of 2 and 3 methylpyridinium chloride and 2 and 3 methylpyridinium bromide were measured as a function of temperature. These asymmetric salts were found to be considerably lower melting, more viscose and less mobile than their respective symmetric isomers. However, they exhibited the same chemical shift reversal of the nitrogen proton that was observed in the molten symmetrical systems. From these data details of the dynamics of motion in the melts are suggested.

Introduction

Molten pyridinium salts are of considerable practical importance and theoretical interest. In an earlier study we correlated transport properties with structure and $^1$HNMR spectra of symmetrical pyridinium halides (1,2). Here we extend this investigation to include asymmetrical salts and it will be shown that pyridinium salts naturally divide into two classes based upon their transport properties; the symmetrical salts being far more mobile than the asymmetrical salts.

The equivalent conductance, $\Lambda$, viscosity, $\eta$, and $^1$HNMR spectra of molten 2-methylpyridinium chloride (2-mepyrr/HCl) and bromide (2-mepyrr/HBr) as well as molten 3-methylpyridinium chloride (3-mepyrr/HCl) and bromide (3-mepyrr/HBr) were measured as a function of temperature over an approximately 50°C temperature range. These salts together with their melting points are shown in Fig.1.

From the substantial increase in viscosity and decrease in conductivity accompanying the changing of a methyl group from the four position to either the two or three position on the ring, inferences about the dynamics of motion in these melts can be drawn. In addition, the contribution of the labile nitrogen proton to the conductivity can be assessed.
Experimental Background

The density, conductivity and $^1$HNMR measurements as well as the general procedures for handling the compounds were similar to those described by Newman and Banjoko (1). The synthesis of the four salts can be summarized by the equation

$$\text{CH}_3\text{N} - \text{(CH}_3\text{)} + \text{HX} \rightarrow \text{CH}_3\text{N} - \text{(CH}_3\text{)}\text{HX}$$ (1)

The viscosity was measured as a function of temperature using a Cannon-Fenske Viscometer. This viscometer was easy to clean, precise enough for our purposes and much more durable than the Ostwald viscometer used in earlier studies.

Dry solid salt was introduced into a large reservoir attached to one arm of the viscometer which was then immersed in the constant temperature bath. The salt was then melted and allowed to fill the viscometer. Viscosity readings were taken at 5° intervals after letting the bath equilibrate for twenty minutes at each temperature. Three series of measurements were made with each salt.

Results and Discussion

The best least squares fit of the equivalent conductance as a function of temperature for each salt are listed in Table I and the densities as a function of temperature are listed in Table II.

Table I. Equivalent Conductance as a function of temperature for asymmetrical pyridinium halides.

\[
\ln \Lambda = a + b T^{-1}
\]

| Salt       | a   | b   | temperature range (K) |
|------------|-----|-----|-----------------------|
| 2-mepyr/HCl| 10.21| -3526| 363 - 408             |
| 2-mepyr/HBr| 12.85| -4514| 350 - 395             |
| 3-mepyr/HCl| 10.37| -3508| 369 - 419             |
| 3-mepyr/HBr| 10.27| -3449| 370 - 415             |
Table II. Density as a function of temperature

\[ \rho \ (g/cm^3) = a + bT(K) \]

| Salt        | a  | \(-b \times 10^3\) | temperature range (K) |
|-------------|----|---------------------|------------------------|
| 2 mepyr/HCl | 1.334 | 0.5657            | 363 - 408              |
| 2 mepyr/HBr | 1.711 | 0.7279            | 350 - 395              |
| 3 mepyr/HCl | 1.329 | 0.5525            | 374 - 419              |
| 3 mepyr/HBr | 1.690 | 0.6890            | 370 - 415              |

Figure 2 shows a graph of ln\( \rho \) vs T\(^{-1} \) for the four melts and it should be noted that there is a slight, but distinct curvature in the plots which is reminiscent of the behavior of partially associated liquids like molten silicates. Figure 3 shows the \(^1\)HNMR spectrum of 2-mepyr/HCl at 100°C relative to an external standard of DMSO and Fig. 4 shows the spectrum of 3-mepyr/HCl at the same temperature relative to the same external standard. There was no change in chemical shift or peak narrowing greater than 0.02 ppm which is at the limit of experimental error. Comparing our proton chemical shifts in the 2-mepyr/HCl melt with the chemical shifts in the same melt reported by Angell and Shuppert (3) we agree within experimental error on the location of the \( \alpha, \beta, \gamma \) and methyl peaks, but differ by 1 ppm on the \( >N-H \) chemical shift, theirs being further down field than ours. One possible reason for this discrepancy is that a trace of water may still be present in our melts, but not in theirs. This water molecule would tend to lie on or at the \( >N-H \) proton and shield it from the magnetic field. On the other hand, they used an internal standard of (NH\(_4\))\(_4\)HCl which both exchanges with the \( >N-H \) and supplies Cl\(^-\) ions. These factors could tend to deshield the \( >N-H \) and cause it to resonate in the more acidic region of the spectrum. There does not seem to be any other melt spectra in the literature to compare our data with. Our melting point of 89°C for the 2-methyl salt is exactly the same as that reported by Angell, Hodge and Cheeseman (4) and our specific conductances also agree within experimental error with theirs. Table III lists the chemical shifts for the four asymmetric pyridinium salts corrected to TMS.

Table III. \( \delta \) in ppm vs TMS

| Salt        | \(-CH_3\) | \( \alpha \) | \( \beta \) | \( \gamma \) | \( >N-H \) |
|-------------|-----------|-------------|-------------|-------------|-----------|
| 2 mepyr/HCl | 2.92      | 8.93        | 8.08        | 8.71        | 16.12     |
| 2 mepyr/HBr | 3.13      | 9.01        | 8.26        | 8.93        | 15.78     |
| 3 mepyr/HCl | 2.59      | 9.04        | 8.18        | 8.65        | 16.37     |
| 3 mepyr/HBr | 2.78      | 9.21        | 8.40        | 8.84        | 15.80     |
The $\delta$s in Table III exhibit the same $\geq-N-H^+$ shift reversal shown by the symmetric melts (1). The $\geq-N-H^+$ is more deshielded in the chlorides than in the bromides, but the ring protons and $CH_3$ group are further downfield in the bromide melts than in the chloride melts. We again think this shift reversal is due to the formation of complexes between the pyridinium ion and the halide ion in the melts. The $\geq-N-H^+$ forms a stronger bond to the $Cl^-$ than it does to the $Br^-$ and this overcomes the deshielding due to crowding that affects the ring protons and methyl groups.

In Table IV we list the equivalent conductance, viscosity, and energies of activation for each salt in a standard state of 1:1 times the melting point in degrees Kelvin. The $E_a$ is obtained from the best least squares fit of the ln$\gamma$ vs $T^{-1}$ curves and is therefore only an approximation. There are several striking features of these data. The $\Lambda$ for 3-mepy/HBr is slightly greater than the $\Lambda$ for 3-mepy/HCl at 1.1 $T_M$ and as far as we know this is the only molten salt system in which a bromide is more mobile, albeit slightly, than the corresponding chloride. An explanation for this peculiar behavior will be suggested shortly. A second interesting observation is that the asymmetric salts are considerably poorer conductors and are considerably more viscose than their symmetrical isomers. A third observation is that the 3-methyl salts are better conductors than the corresponding 2-methyl salts.

Assuming the same sort of complex is forming in the asymmetric salts as in the symmetric salts (1), the most reasonable explanation for the higher conductivity of the 3-methyl salt than the corresponding 2-methyl salt is that the labile nitrogen proton is contributing to the conductivity (4), but this contribution is a larger fraction of the 3-methyl salt's conductivity than it is of the 2-methyl salt's conductivity. This happens because the 2-methylpyridine is more basic than the 3-methylpyridine (5) and therefore attracts the labile proton more strongly and reduces its concentration. A second reason is that

| Salt       | $\Lambda$(cm$^2$Ω$^{-1}$eq$^{-1}$) | $\gamma$(c p.) | $E_a$(kJ/mole) | $E_A$(kJ/mole) |
|------------|----------------------------------|----------------|----------------|----------------|
| 2 pyr/HCl  | 3.88                             | 7.06           | 36.2           | 29.3           |
| 2 pyr/HBr  | 3.19                             | 10.87          | 44.7           | 37.5           |
| 3 pyr/HCl  | 5.63                             | 6.33           | 34.2           | 29.2           |
| 3 pyr/HBr  | 5.89                             | 8.26           | 32.9           | 28.6           |

Table IV. Transport properties at 1:1 $T_M$ (K)
the methyl group on the two position of the ring partially, if not totally, blocks the $>\text{N-H}^+$ and prevents it from readily transferring to the halide ion. Since the densities of the 2 and 3 mepar/HCl is are virtually identical (Table II), as are the densities of the 2 and 3 mepar/HBr, and the molecular dimensions are so similar, a difference in liquid free volume by itself would be unable to account for the substantial differences in conductance between the two pairs of salts. To a rough approximation then, the difference between the $\Lambda_s$ of the 2-mepyr/HCl and 3-mepyr/HCl or the 2-mepyr/HBr and the 3-mepyr/HBr is equal to the contribution of the proton to the conductance. At 1.1 $T_M$ $\Lambda_{H^+}$ is 1.75 (Q eq)$^{-1}$ cm$^2$ in the chloride system while in the bromide system $\Lambda_{H^+}$ is 2.70 (Q eq)$^{-1}$ cm$^2$. Whether or not an actual Grotthuss mechanism, in which there is a transfer of charge or virtual movement without an actual proton diffusion, as is thought to be present in, say, aqueous HCl solutions occurs, or a hopping mechanism in which a given proton is "hopping" from site to site and during one of its excursions reaches an electrode, occurs cannot be ascertained with confidence at this time. Nevertheless, some protonic contribution to the conductance must be taking place.

This conjecture is further supported by the fact that the 3-mepyr/HBr is a slightly better conductor than the 3-mepyr/HCl at 1.1 $T_M$. Hydrogen bonding is considerably stronger in the chloride melt than in the bromide melt which reduces the contribution of both H$^+$ and Cl$^-$ to the conductivity in the chloride melt relative to the contribution of H$^+$ and Br$^-$ to the bromide melt's conductivity. In addition, the greater size of the Br$^-$ increases the stringency of the packing requirements and allows the melt fewer degrees of freedom so that if a concerted Grotthusslike mechanism consisting of the partial "in plane" rotation of the pyridinium ring accompanied by the passing of its proton to a Br$^-$ which in turn collides with another proton, etc. were to occur, it would be favored in the Br$^-$ melt. This possible mechanism contributing to the high bromide conductivity is illustrated in Fig. 5 and is consistent with the suggestion that the dominant associated species is the (3-mepyr-H...X..H-pyr me-3)$^-$ ion (1,3). Two predictions based on this mechanism are that the viscosity of the 3-mepyr/HBr melt is also greater than the viscosity of the 3-mepyr/HCl melt, and the $E_A$ for 3-mepyr/HCl is greater than $E_A$ for 3-mepyr/HBr. Both of these predictions are borne out if the salts are compared in the same standard state of 1.1 $T_M$ (Table IV). The bromide melt has the greater viscosity because the packing is tighter and the liquid layers cannot pass over each other easily. On the other hand, the chloride melt has the greater $E_A$ because part of this energy must go toward the breaking of stronger hydrogen bonds.
Finally, the extraordinarily large difference in conductance and viscosity between the symmetric and asymmetric salts which results from very slight differences in molecular size and melt density probably arises because there is very little free volume and molecular motion must be highly correlated. In all likelihood there are at least three contributions to the mobility, besides the protonic contribution, and each one requires an energy of activation. The first, and most obvious mode of motion is one salt layer passing by another "in plane", as it were. The second mode is an inplane rotation of the pyridinium ion and the third is an out of plane rotation of the pyridinium ion. Both the in and out of plane rotations share the primary responsibility for the large difference in transport properties between the symmetrical and asymmetrical melts. It is during these rotations, coupled with the translational motion that the asymmetric pyridinium ions interfere with each other and also block the passage of the halide ions.

Conclusions

By changing the structure of the pyridinium melts in a systematic way and correlating these changes with transport properties and "HNMR spectra, inferences about the dynamics of mass transfer in these melts may be made. As an example we are able to conclude there are at least four distinct contributions to the conductance. These are an in and out of plane rotation, an inplane translation of one layer past another and a hopping or Grotthusslike movement of the acidic proton.

List of References

1. D. S. Newman, O. Banjoko, Proceedings of the Second International Symposium on Molten Salts, p. J. Braunstein, Editor (Electrochemical Society 1979).
2. D. S. Newman, R. T. Tillack, D. P. Morgan, W. C. Wan, J. Electrochem. Soc. 124, 856 (1977).
3. C. A. Angell, J. W. Shuppert, J. Chem. Phys. (in press).
4. C. A. Angell, I. M. Hodge, P.A. Cheeseman, "Proceedings of the International Symposium on Molten Salts", Edited by J. P. Pemsl, J. Braunstein, D. R. Morris, K. Nobe and N. E. Richards. (Electrochemical Society 1976) p 138.
5. A. Albert, E. P. Serjeant, "Ionization Constants of Acids and Bases" (Methuen and Co.Ltd., London 1962) p. 145.
Figure 1. Asymmetric pyridinium halides

Figure 2. Lnγ vs T⁻¹ for the four asymmetric pyridinium halides
- ● - 2mepy/HBr; ○ - 2mepy/HCl;
- x - 3mepy/HCl; □ - 3mepy/HBr

Figure 3. ¹HNMR spectrum of 2-mepy/HCl at 100°C vs DMSO
Figure 4. $^1$HNMR spectrum of 3-mepyrm/HCl at 100°C vs DMSO

Figure 5. Possible mechanism for proton transfer in pyridinium halide melts