SUBSTITUENT EFFECTS ON TRANSPORT AND THERMODYNAMIC PROPERTIES OF MOLTEN PYRIDINIUM SALTS

David S. Newman, Prasad Babu Bikkani
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

ABSTRACT

The conductivities, viscosities and densities of a series of molten dimethylpyridinium chlorides were measured as a function of temperature. The conductivity, viscosity and density of 4, t-butylpyridinium chloride were also measured as a function of temperature. The substituent effect of the bulky t-butyl group as well as the effect of a second methyl group on transport and thermodynamic properties were assessed by comparing these properties at a constant multiple of the salts' boiling point. The presence of a t-butyl group as well as the specific location of the methyl groups strongly influences the melts' properties as does the presence or absence of hydrogen bonding.

INTRODUCTION

Molten pyridinium salts, either alone or in mixtures, are useful solvents for a variety of chemical reactions including the alkylation of coal and model coal compounds (1) and various electrochemical oxidation-reductions (2,3). However, from a theoretical perspective pyridinium salts are perhaps more important because their low melting points, ease of handling, and enormous variety, allow all sorts of correlations to be made between structure, transport properties, spectra and thermodynamic properties. From these correlations of experimental results, a theoretical scaffolding to support ideas about the nature of pyridinium melts in particular, and organic melts in general, may be constructed.

In earlier studies (4,5) of molten methylpyridinium halides we found that the effect of a methyl substituent on the melts' properties depended markedly on its ring.
position. We also observed that the presence or absence of hydrogen bonding affected a melt's 1H NMR spectrum, viscosity and conductivity. The viscosity data were particularly enigmatic when viewed in context with the conductivity data because those isomeric melts with the highest conductivity also had the highest viscosity. For example, N-methylpyridinium chloride (N-mepyr-Cl) had an equivalent conductance, $\Lambda$, of 10.5 cm$^2$ (Ω eq)$^{-1}$ and an absolute viscosity, $\eta$, of 6.24 cp whereas its isomer 4-methylpyridinium chloride (4-mepyr-Cl) had a $\Lambda$ of 6.68 cm$^2$ (Ω eq)$^{-1}$ and an $\eta$ of 3.26 cp, all at a constant temperature of 425 K. Similar results were observed in the bromide and iodide melts. Strong hydrogen bonding between the 4-mepyr$^+$ ion and the Cl$^-$ ion would account for the relatively low conductivity by causing complexes to form which have long enough life times to effectively remove charge carriers from the electric field. However, 4-mepyr-Cl would seem to be more highly associated than N-mepyr-Cl (which presumably cannot hydrogen bond) and consequently would be expected to be more viscous. But 4-mepyr-Cl is considerably less viscous, which means additional factors are affecting the viscosity.

Part of the explanation for the low viscosity originated from the work of Stauge and Smith (6) who measured the dipole moments of several tri-n-butylammonium and triethylammonium salts in benzene solution at 25°C. These authors observed a substantial reduction in the measured dipole moment, $\mu_0$, of the ternary salt relative to the $\mu_0$ of the corresponding quarternary salt. They attributed this reduction in $\mu_0$ to hydrogen bonding between the trialkylammonium cation and the appropriate anion. The H-bonding forces the trialkylammonium ion to be oriented with the N-H$^+$ pointed toward the anion. The mean interionic distance would be smaller than in the tetraalkyl salt and the measured dipole moment correspondingly smaller. Shortening of the interionic distance through hydrogen bonding and stabilization of the resulting ion pairs would partially account for the relatively low viscosity and concomitant low conductivity in the hydrogen bonded pyridinium melts. However, we think an additional microscopic process is affecting these viscosities. The nitrogenic proton has been shown to be quite labile by 1H NMR measurements (7) and is most likely hopping back and forth between cation and anion. We and other authors suggested that the labile proton might be contributing to the conductivity of pyr-Cl (7,8) and we specifically presented this mechanism as a rationale for 3-mepyr-Cl and 3-mepyr-Br being better conductors than the corresponding 2-methyl salts (5). Since the 2-methyl pyridine molecule is more basic than 3-methyl pyridine (9)
and a CH₃ group in the two position partially blocks the nitrogen site, if protons were contributing they would do so less in the 2-methyl melt than in the 3-methyl melt. Alternatively, steric factors and exigencies of packing resulting from a combination of spacial orientation and electrostatic forces may be causing the conductivity differences. The labile proton may, in fact, be playing an entirely different role. Since it is not possible to separate these "hydrogen bonding effects" from substituent effects in 2,3 and 4-mepy-Cl because the two effects are intertwined, we have extended our investigation to include 1,2 and 1,3 dimethylpyridinium chloride (dimepyr-Cl) because hydrogen bonding is eliminated, but asymmetry is preserved. We have also studied the three symmetrical dimethylpyridinium chlorides, 2,4 dimepyr-Cl and 4-t-butylpyridinium chloride (4-t-bupyr-Cl) in order to reach a better understanding of substituent effects.

EXPERIMENTAL DETAILS

All salts were synthesized by bubbling HCl or CH₃Cl through a solution of the substituted pyridine in pet. ether. The synthetic details are described elsewhere (10).

Conductivity measurements were made at 1 kHz using a Pyrex capillary cell fitted with cylindrical platinum electrodes. A Canon-Fenske viscometer was used for viscosity measurements and a modified Lipkin bicapillary arm pycnometer was used to measure density. All of the experimental details have been described earlier (8,11).

Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN.

All transfer operations were performed in a dry box through which nitrogen gas circulated.

RESULTS

The normal boiling and melting points of the six dimethylpyridinium chlorides and 4-t-bupyr-Cl are listed in Table I. Also listed are the melting and boiling points of pyridinium chloride to serve as references.
TABLE I
Normal Melting and Boiling Points of Pyridinium Chloride

| Salt                  | Tm(°C) | Tb(°C) |
|-----------------------|--------|--------|
| 1,2-dimethylpyr-Cl    | 102    | 163    |
| 1,3-dimethylpyr-Cl    | 148    | 185    |
| 1,4-dimethylpyr-Cl    | 216±2* | 218±2* |
| 3,5-dimethylpyr-Cl    | 232    | 239*   |
| 2,6-dimethylpyr-Cl    | 239*   | 239*   |
| 2,4-dimethylpyr-Cl    | 230    | 242*   |
| 4-t-butylpyr-Cl       | 154    | 240*   |
| pyridinium-Cl         | 144    | 219    |

*slight decomposition

It is evident that the three symmetrical dimethylpyridinium chlorides have no appreciable liquid range at atmospheric pressure. Therefore their transport properties could not be measured. It is also evident that the hydrogen bonded liquids have substantially higher boiling points than liquids without hydrogen bonds.

Carbon, H and Cl analysis of the salts whose transport properties were measured were within 0.1% of theoretical for t-butylpyr-Cl and 2,4-dimethylpyr-Cl and within 2% of theoretical for 1,2 and 1,3 dimethylpyr-Cl.

Figure 1 shows the density of each of the four salts plotted as a function of temperature. Included in the figure for reference are the densities of pyr-Cl and 2-methyl-pyridinium chloride (2-mepyr-Cl) taken from earlier studies (5,11). It can be seen from these curves that steric effects determine the relative densities to a greater extent than do molecular weights or electrostatic effects. The bulky 4-t-butylpyr-Cl is the least dense liquid, even though it has the highest molecular weight, while pyr-Cl is the most dense, but has the lowest molecular weight. The ionic radius seems to be the principal factor that governs the relative densities.

The logarithms of the equivalent conductances of the four salts plotted as a function of T⁻¹ are shown in Fig. 2 and Fig. 3 shows the logarithms of their absolute viscosities plotted as a function of T⁻¹. The ʌ's for pyr-Cl and the viscosities for 2-mepyr-Cl are included for reference.
DISCUSSION

To validly assess substituent effects each substituted molecule must be in the same thermodynamic state. The "practical" standard state is, of course, a common temperature at which the salts being compared are liquids. The "natural" standard state for liquids seems to be the ideal glass transition state, \( T_0 \), or the normal boiling point, \( T_b \) (12). \( T_0 \) is the temperature where the configurational entropy vanishes and \( T_b \) is the temperature at which it is maximized for the liquid state. We have chosen to use \( T_b \) as the reference state.

Referring first to the conductivity data in Fig. 2 it is evident that 4-t-butpyr-Cl, 1,2-dimepyr-Cl and 2,4-dimepyr-Cl all have similar \( \Lambda \)'s at their respective \( T_b \)'s. The \( \Lambda \) for 1,3-dimepyr-Cl is considerably higher at its \( T_b \) and also higher at any "common" temperature. This means 1,3-dimepyr-Cl is a better conductor than 1,2 dimepyr-Cl and a CH\(_3\) group in the 3 position enhances conductivity relative to a CH\(_3\) group in the 2-position. Comparing \( \Lambda \)'s at 425 K, which was the common temperature used in earlier studies when neither \( T_0 \) nor \( T_b \) data were available (5), gives the results shown in Table II.

TABLE II
Equivalent Conductances at 425 K

| Salt             | \( \Lambda \) cm\(^2\) (\( \Omega \) eq\(^{-1}\)) | % difference | actual difference |
|------------------|---------------------------------|--------------|------------------|
| 3-mepyr-Cl       | 8.58                            | 22           | 1.9              |
| 2-mepyr-Cl       | 6.68                            |              |                  |
| 1,3-dimepyr-Cl   | 10.91                           | 14           | 1.52             |
| 1,2-dimepyr-Cl   | 9.32                            |              |                  |
| 4-t-butpyr-Cl    | 2.92                            |              |                  |

These data indicate that protonic contribution to the conductivity in the 3-mepyr-Cl is probably very small or nonexistent.

In all likelihood, if the more valid \( T_b \) reference state were used it would increase the difference between a CH\(_3\) on the 2 position and one on the 3-position (as it does in the 1,2 and 1,3 dimethylpyr-Cl melts) and there would no longer be a need for a "protonic contribution" to explain the conductivity differences. Comparing the \( \Lambda \)'s of pyr-Cl with those of 1,3-dimepyr-Cl (23 vs 18 cm\(^2\) (\( \Omega \))

---

210
at the respective boiling points, again shows that a protonic contribution seems to be unnecessary. The difference in $\Lambda$ would be expected from differences in mass and ionic radius alone. In fact, if $\ln \Lambda$ vs $T^{-1}$ for 1,3 dimepyr-Cl is extrapolated to 219°C the $\Lambda$'s are virtually indistinguishable. The principal role of a nitrogenic proton is to hydrogen bond and by so doing form neutral species (ion pairs or molecules) that do not contribute to the conductivity. This is almost certainly the reason why the 1,2 and 1,3 dimethyl chlorides are respectively better conductors than the 2 and 3 methyl chlorides despite their greater molecular weights.

Focusing attention on the viscosity data in Fig. 3 it can be seen that the viscosities of the two dimethylpyridinium isomers are, within experimental error, the same at their respective boiling points. This is especially reassuring since it is expected that at $T_b$, where $\Delta S$ is a maximum and the interionic attractive forces are approximately equal to the thermal forces, the viscosities would be equal for isomers with nearly the same radii. Furthermore, these results support the contention that, at least for viscosity, $T_b$ is a valid standard state.

It is also evident that for 1,2-dimepyr-Cl and for 1,3 dimepyr-Cl the $\Gamma$'s are about equal at lower temperatures. For example, at 0.95 $T_b$ (a temperature in common to both melts and hence a valid standard state) corresponding to 435 K for 1,3-dimepyr-Cl and 415 for 1,2-dimepyr-Cl, the $\Gamma$'s are 3.06 cp and 3.00 respectively. As the temperature drops, the viscosities diverge a bit. A much larger difference, but in the same direction, is obtained if a practical constant temperature standard state is used. In any case, the sizeable difference in conductivity between the isomers cannot be attributed to viscosity differences nor to protonic contributions and therefore must arise out of a distinctive charge transfer mechanism.

Extrapolating $\Gamma$ of t-butpyr-Cl to its $T_b$, a value of 0.9 cp is obtained. This is clearly much lower than the viscosities of either di-methyl isomer at its $T_b$. At 0.95 $T_b$, a more reasonable standard state since no decomposition is occurring, $\Gamma$ is only 1.04 cp. What is perhaps more striking is that at 425 K 4-t-butpyr-Cl has an $\Gamma$ of 5.52 cp while N-mepyrr-Cl has an $\Gamma$ of 5.24 cp. The large 4-t-butyl ion is actually less viscous than the smaller N-mepyrr-ion despite the fact that the t-butyl moiety is about the same size as the pyridinium moiety and the molecular weight of 4-t-butpyr-Cl is greater than that of either the dimethyl isomer or the methyl isomer.
Since it bears on the discussion that follows, the relevant dipole moment data of Bauge and Smith are reproduced in Table III. It is evident from these data

**TABLE III**

Measured Dipole Moments of Alkyl Ammonium Salts in Benzene Solution at 25°C

| Salt                        | $\mu_D$ | $\mu_0$ (corresponding quaternary salt) |
|-----------------------------|---------|----------------------------------------|
| Tri-n-butylammonium bromide | 8.50    | 12.2                                   |
| Tri-n-butylammonium picate  | 11.79   | 15.3                                   |
| Tri-n-butylammonium chloroacetate | 6.41 | 14.8                                   |
| Tri-n-butylammonium benzoate| 4.27    | 12.1                                   |

that a shortening of the principal interionic axis will not completely explain the reduction of $\mu_D$ in the chloroacetate and benzoate solutions even though it is adequate to explain much of the reduction of $\mu_D$ in the bromide and picate solutions.

The mechanism we propose to account for the unusual viscosities of the H-bonded pyridinium melts (and possibly for some of the data of Bauge and Smith) assumes that the equilibrium shown below persists in the H-bonded melts but not in the H-methyl melts.

$$\text{Cl}^- + \text{R}^+ \text{pyr}^- \rightarrow \text{R}^- \text{pyr}^+ \text{Cl}^- = \text{R}^- \text{pyr} + \text{R}^- \text{Cl}$$

When $\text{R}^+$ is a proton this "mobile equilibrium" (7) lies considerably further to the right (favoring a higher ion pair and neutral molecule concentration) than when $\text{R}^+$ is a CH$_3$ group. The labile proton jumps back and forth between pyridine and Cl$^-$ and may remain at the bottom of a potential well for perhaps 10$^{-6}$ or 10$^{-7}$ sec. This is too short a time span to be detected by IHNNMR, but represents perhaps 10,000 translational or rotational movements of the molecule. The model is shown schematically in Fig. 4. The cation and anion are initially drawn together via H-bonding along the principal interionic axis. The proton hops from pyridine to Cl$^-$ creating two neutral species and a modicum of empty space. The neutral species rotate and translate relatively freely thus lowering the viscosity, but not increasing the
conductivity. The extra free space increases the probability of an appropriate density fluctuation and thereby decreases the absolute viscosity. In other words, charge neutralization causes local liquid relaxation and local liquid expansion. Without this sort of microscopic process it is very difficult to account for the fact that 4-t-butpyr-Cl is less viscous than N-mepyrCl. The extremely low viscosity of 4-t-butpyr-Cl at T_b is not unreasonable if, on a fast time scale, a high enough concentration of HCl and 4-t-butylpyridine persists.

The energies of activation for viscosity and equivalent conductance are listed in Table IV.

| Salt           | E_\gamma (kJ/mole) | E_\lambda (kJ/mole) | E_\gamma / E_\lambda |
|----------------|--------------------|---------------------|-----------------------|
| t-butpyr-HCl   | 47.4               | 33.2                | 1.42                  |
| 1,3 dimetpyr-Cl| 37.6               | 26.7                | 1.40                  |
| 1,2 dimetpyr-Cl| 33.6               | 24.5                | 1.36                  |
| 2,4 dimetpyr-Cl| (66.4)             | 27.6                | 2.4                   |

With the exception of E_\gamma for 2,4-dimepyr-Cl which is probably unreliable because of the small liquid range and partial decomposition, the values are not, especially remarkable. The large E_\gamma for 4-t-butpyr-Cl is expected because of the cations' size and the H-bonding in the melt. The ratios are lower than those for inorganic melts which generally range between 2 and 5 and are a bit higher than the values for typical methylpyridinium halides and alkylammonium salts which range between 1.09 and 1.4, with the bulk of the ratios clustering around 1.1. The dominance of attractive forces, coupled with the need for cooperative movement for large ions to move past one another in an environment containing relatively little free space, ensures that neither viscosity nor conductance will require substantially different amounts of energy.

REFERENCES

1. D.S. Newman, R.E. Winans, R.L. McBeth, Reactions of Coal and Model Coal Compounds in Room Temperature Molten Salt Mixtures, "Proceedings of the Third International Symposium on Molten Salts," G. Mamantov, Editor, The Electrochemical Society, Softbound Proceedings Series, Princeton, N.J. 1981, pp 425-438.
2. C. Nanjundiah, K. Shimizu, R.A. Osteryoung, J. Electrochem. Soc. 129 2474 (1982).
3. G.T. Cheek, R.A. Osteryoung; J. Electrochem. Soc 129 2489 (1982).
4. D.S. Newman, R.T. Tillack, D.P. Morgan, Wai-Ching Wan, Correlations Between $^1$HNMR Spectroscopy and Transport Properties in Molten Pyridinium Salts, J. Electrochem. Soc. 124 856 (1977).
5. D.S. Newman, R.R. Rhinebarger, D. Siconolfi, O.A. Banjoko, The Relationship of Transport Properties and $^1$HNMR Spectra to the Structure of Molten Methyldipyridinium Halides, J. Electrochem. Soc. 128 2336 (1981).
6. K. Bauge, J.W. Smith; J. Chem. Soc. (A) 616 (1966).
7. J.W. Shuppert, C.A. Angell, J. Chem. Phys. 67 3050 (1977).
8. D.S. Newman, W. Rohr, D. Kirklin, H.D. Frame, J. Electrochem. Soc. 119 797 (1972).
9. A. Albert, E.P. Sergeant, "Ionization Constants of Acids and Bases" p. 145, Methuen and Co. Ltd. London (1962).
10. M.S. Rozhdestvenskii, L.M. Brode; J. Appl. Chem. USSR 10 722 (1937).
11. D.S. Newman, D.P. Morgan, R.T. Tillack, J. Chem. Eng. Data 21 279 (1976).
12. J. Wong, C.A. Angell, "Glass Structure by Spectroscopy," Chpt. 1 Marcel Dekker Inc., New York (1976).
Fig. 1 Density as a function of temperature

Fig. 2 Equivalent conductance as a function of temperature
Fig. 3  Viscosity as a function of temperature

Fig. 4  Model of hydrogen bonded pyridinium melts