lower temperatures, the dipole makes a measurably larger contribution to total cohesion. Because the change is so small, however, it is impossible to say whether it is due to an increase in orientation or induction energy, or both. Except for the unlikely situation that they are changing in opposite senses, we can accept this as direct experimental evidence that temperature effects on dipolar interactions in pure liquids involving moments of 2-3 D are slight.

## Acknowledgments

Thanks are due Andy Sopcich for preparing the $C_{11}$ ketone.

## Literature Cited

(1) Beattie, J. A., et al., Proc. Am. Acad. Arts Sci., 74, 371 (1941).
(2) "CRC Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1969.
(3) Ewing, M. B., et al., J. Chem. Thermodyn., 1, 689 (1970).
(4) Finke, H. L., et al., J. Am. Chem. Soc., 78, 5469 (1956).
(5) Garbisch, E. W., Whollebe, J., J. Org. Chem., 33, 2157 (1968).
(6) Gunthard, H., Gaumann, T., Helv. Chim. Acta, 34, 39 (1951).
(7) Hanack, M., "Conformation Theory", Academic Press, New York, N.Y., 1965, p 51.
(8) Kobelt, M., et al., Helv. Chim. Acta, 32, 258 (1949).
(9) Kobelt, M., Prelog, V., Helv. Chim. Acta, 32, 1187 (1949).
(10) Meyer, E. F., Hotz, R. D., J. Chem. Eng. Data, 18, 359 (1973).
(11) Meyer, E. F., Renner, T. A., Stec, K. S., J. Phys. Chem., 75, 642 (1971).
(12) Meyer, E. F., Wagner, R. E., J. Phys. Chem., 70, 3162 (1966).
(13) Ruzicka, L., Helv. Chim. Acta, 13, 1152 (1930).
(14) Ruzicka, L., et al., Helv. Chim. Acta, 28, 613 (1945).
(15) St. Jacques, M. R., (Thesis), University Microfilms, Ann Arbor, Mich., 1967.
(16) Tarova-Pollack, M. B., Zh. Obschch. Khim., 31, 1976 (1961).
(17) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, N.Y., 1950.
(18) Vogel, A. I., J. Chem. Soc., 1323 (1938).
(19) Wagner, R. E., Meyer, E. F., J. Chem. Educ., 45, 349 (1968).
(20) Wolf, G., (Dissertation) University of Basel, Switzerland, 1971.
(21) Wolf, G., Helv. Chim. Acta, 55, 1446 (1972).

# The Density of Fused Pyridinium Salts

David S. Newman,* David P. Morgan, and Richard T. Tillack

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

The densities of seven fused pyridinium salts were measured as a function of temperature using a modified Lipkin bicapillary pycnometer. The results for each salt may be expressed by an equation of the form $\rho$ (g/cm$^3$) $= a + bT$ (°K). The experimental technique and errors involved in the measurements are discussed.

Fused pyridinium salts are useful as electrolytes in high temperature batteries and as solvents for both synthetic and structural studies. Mixtures of pyridinium salts are potentially useful as energy storage media to be used in conjunction with solar heating and air conditioning units. These salts are low melting, and in their molten state are noncorrosive to Pyrex, stable over a relatively wide temperature range, and accessible to study by NMR techniques as well as by more conventional means.

The measurement of the change in density of eight of these fused pyridinium salts as a function of temperature was undertaken to provide information for use in structural studies and those energy related applications where these salts may be important.

## Experimental Section

The salts studied were pyridinium chloride (I), N-methylpyridinium chloride (II), 4-methylpyridinium chloride (III), 4-methyl-N-methylpyridinium chloride (IV), pyridinium bromide (V), N-methylpyridinium bromide (VI), 4-methylpyridinium bromide (VII), and 4-methyl-N-methylpyridinium bromide (VIII). They are shown in Figure 1.

All of the salts were synthesized in basically the same way using a technique first described by Rozdhestvenskii and Brode (5) and modified by Newman et al. (3). The syntheses can all be summarized by eq 1.



$$\text{(1)}$$
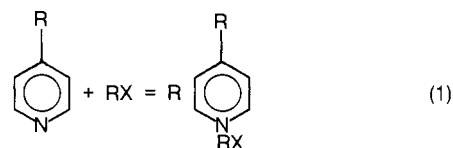
The purity of each salt was ascertained by C, H, N analyses, ir spectrum, and melting point. All salts used contained less than 1% impurities.

The density of the molten salts was measured using a modified Lipkin bicapillary arm pyconometer shown in Figure 2 (2). The pycnometer was calibrated with water at 25 °C in such a way that the volume of the liquid could be given by an equation of the form $V_{liq} = a + b$ (capillary reading).

To measure density as a function of temperature, the solid salts were each placed in the large reservoir on the left side of the pycnometer which was closed with a one-hole Teflon stopper connected to a filled drying tube. The filled pycnometer was placed in a constant temperature bath slightly above the melting point of the salt and as the salt melted a slight vacuum was applied to the right side of the pycnometer through another filled drying tube. This technique facilitated the filling of the capillary region of the pycnometer with molten salt. The temperature was increased in 10° increments and allowed to equilibrate for 10 min at each temperature before a volume reading was made. This procedure was followed until a predetermined upper temperature limit was reached. The temperature was then decreased first 5° and then in 10° increments until the salt froze. A volume reading was taken at each temperature after the system had equilibrated. The weight of the salt was determined as follows. Excess salt that adhered to the reservoirs was removed and the pycnometer together with the remaining frozen salt weighed. Next the salt was remelted and poured from the pycnometer. The pycnometer was then thoroughly cleaned and reweighed.
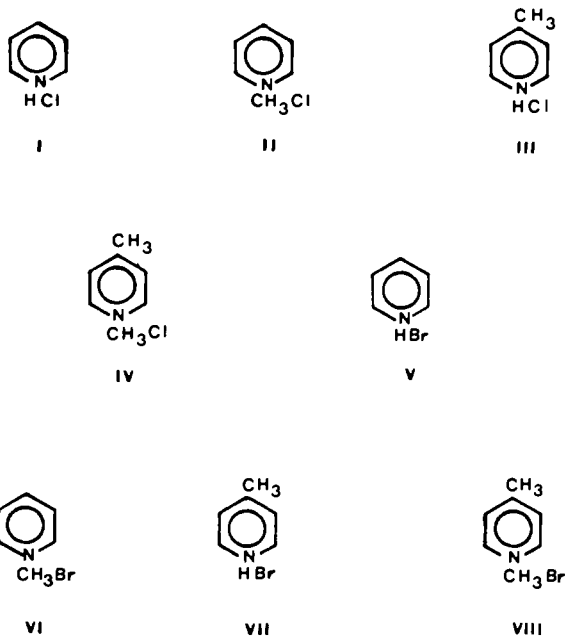
**Figure 1.** Pyridinium chloride (I), N-methylpyridinium chloride (II), 4-methylpyridinium chloride (III), 4-methyl-N-methylpyridinium chloride (IV), pyridinium bromide (V), N-methylpyridinium bromide (VI), 4-methylpyridinium bromide (VII), 4-methyl-N-methylpyridinium bromide (VIII).
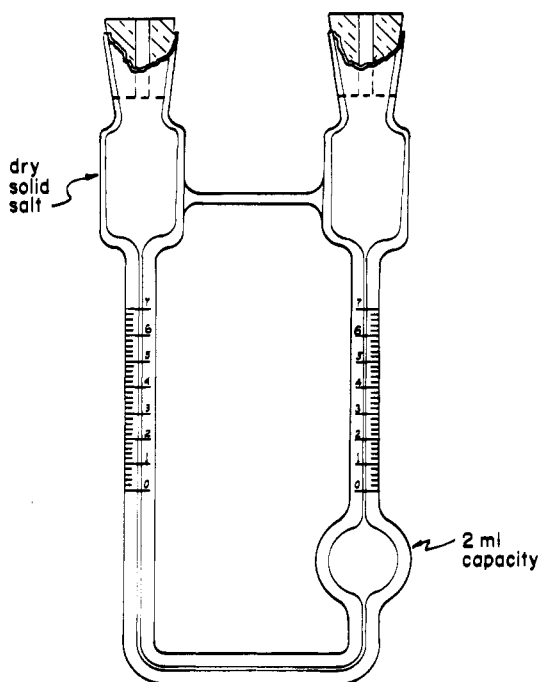


**Figure 2.** Modified Lipkin bicapillary arm pycnometer.

All transfer operations were done in a drybox because the salts are hygroscopic.

The constant temperature bath was Dow Corning 710 Oil (flash point 300 °C) regulated to ±0.1° and fitted with a lamp which allowed the meniscus of the capillary to be easily read.

**Results**

The densities of seven of the salts proved to be linear functions of the temperature over the temperature range studied. The data have been fitted to the equation

$$\rho \ (g/cm^3) = a + bT \ (°K) \tag{2}$$

**Table I. Density Parameters $(\rho(g/cm^3) = a + bT)$**

| Salt | $a$ | $-(b \times 10^3)$ | $\sigma \times 10^3$ | Temp range, °K | Melting point, °C |
|------|-----|--------------------|--------------------|---------|-------------------|
| I | 1.395 | 0.5716 | 0.1 | 398–458 | 144 ± 0.5 |
| II | 1.349 | 0.4964 | 1.1 | 382–433 | 149.5 ± 0.5 |
| III | 1.339 | 0.5755 | 1.42 | 410–473 | 167 ± 0.5 |
| V | 1.810 | 0.7055 | 2.1 | 497–537 | 220 ± 0.5 |
| VI | 1.723 | 0.6528 | 1.0 | 398–468 | 151.5 ± 0.5 |
| VII | 1.703 | 0.7004 | 0.54 | 410–518 | 162 ± 0.5 |
| VIII | 1.610 | 0.5701 | 0.42 | 418–498 | 156 ± 0.5 |

and are summarized in Table I. Also included in the table are the temperature ranges over which each salt was studied, the root mean square deviation, $\sigma$, of the experimental points from the calculated straight line, and the melting point of each salt.

**Discussion**

The error in the density vs. temperature data reported in Table I is estimated to be approximately ±1%. This combined error arises largely from uncertainty in the level of the liquid in the pycnometer, from small amounts of decomposition of the salts and from small quantities of impurities in the melts. Initially, corrections were made for thermal expansion of the Pyrex pycnometer, but the error arising from this source is negligible relative to the other errors mentioned.

Our density measurements for pyridinium chloride (I) agreed to within 0.6% of those of Easteal and Angell ( 1) for this salt. We could find no other pyridinium salt densities to compare our other data with.

We were able to find literature values for the melting points of salts I, II, V, and VI only. Melting points for the other salts do not seem to have been previously reported. Our value of 144 ± 0.5 °C for the melting point of salt I is the same as that listed in the ref 6 and within 0.5° of the value found by Easteal and Angell ( 1). Two values for the melting point of salt V are listed in ref 7. These are 206 and 225 °C. Our value of 220 °C falls within this range. Wallace and Bruins ( 8) report a melting point of 150–151 °C for salt VI, which is in excellent agreement with our value. However, they report a melting point of 138 °C for salt II. We consider their value much too low, probably because they did not dry this extremely hygroscopic salt sufficiently.

Comparing the densities of the bromide salts with those of the chloride salts it is obvious that the bromide salts are more dense. This is because the bromide ion is more massive than the chloride ion.

A less obvious structural feature of the melts that can be obtained from the density data is that methyl groups substituted at either the 1 or 4 positions decrease the density of the respective melt. For example, N-methylpyridinium chloride is less dense than pyridinium chloride despite the fact that the N-methylpyridinium ion is heavier than the pyridinium ion. Two factors are likely to be contributing to the observed decrease in density with increasing methyl substitution. Since it is likely the positive charge of a pyridinium ion is located on the nitrogen (3, 4) the electron donating methyl group decreases this charge. This in turn decreases the Coulombic attraction for the halide ion resulting in greater separation in the liquid state. The second contributing factor is steric. The bulky methyl groups do not allow the cations to come close together thus introducing more "holes" in the melt.

An attempt was made to study the density of salt IV (mp 220 ± 0.5 °C), but because it decomposed within a few degrees of its melting point, accurate measurements could not be made. A possible explanation for this odd behavior is that salt IV may form a plastic crystal in the solid state.

**Literature Cited**

(1) Easteal, A. J., Angell, C. A., *J. Phys. Chem.*, **74**, 3987 (1970).
(2) Morgan, D. P., MS Thesis, Bowling Green State University, Bowling Green, Ohio, 1972.
(3) Newman, D. S., Rohr, W., Kirklin, D., Frame, H. D., *J. Electrochem. Soc.*, **119**, 797 (1972).
(4) Rerat, P. C., *Acta Crystallogr.*, **15**, 427 (1962).
(5) Rozdhestvenskii, M. S., Brode, L. M., *J. Appl. Chem. USSR*, **10**, 722 (1937).

(6) "Handbook of Chemistry and Physics", 47th ed, Chemical Rubber Company, Cleveland, Ohio, 1966, p C-517.
(7) "Handbuch der Organischen Chemie", *Beilstein*, **20**, Suppl II, p 103.
(8) Wallace, R. A., Bruins, P. F., *J. Electrochem. Soc.*, **114**, 209 (1967).

# Characterization of the Drag Reducing Properties of Poly(ethylene oxide) and Poly(acrylamide) Solutions in External Flows

**Ralph C. Little, Robert L. Patterson, and Robert Y. Ting\***

*Naval Research Laboratory, Washington, D.C. 20375*

**The drag reduction characteristics of aqueous solutions of high molecular weight poly(ethylene oxide) and poly(acrylamide) and its related polymers were studied in a rotating disk apparatus. Intrinsic viscosity measurements were also made in a multibulb capillary viscometer. The concentration dependence of the percent drag reduction was found to obey the universal drag reduction relationship. The drag reduction efficiency for each compound was determined and compared with those obtained from two pipe flow systems. The data show that characterizations in the three different apparatus are consistent in rating the drag reduction efficiency. It also demonstrated the usefulness of the universal drag reduction equation in laboratory characterization of the drag reducing properties of dilute polymer solutions in both internal and external flows.**

The ability of very high molecular weight polymeric additives to reduce frictional drag in the turbulent flow of Newtonian fluids is well known. Many investigators have verified this drag reduction phenomenon, in pipe flows as well as in rotating disk flows, using various combinations of polymer–solvent systems ( *1* ). Extensive research in recent years has indicated that the factors contributing to the effectiveness of drag reducing polymers include molecular flexibility, high molecular weight, and good solubility, but little has been achieved in the development of techniques for quantitative characterization of polymer drag reduction effectiveness. Different graphic presentations or proposed slope parameters by different authors seemed to have so far caused more confusion than leading to a unified basic understanding of the phenomenon. Therefore, it is highly desirable to develop even an empirical function to relate drag reduction to relevant solution properties, particularly one which would quantitatively characterize the drag reduction effectiveness and greatly reduce the amount of time spent in evaluation procedures.

The most striking feature of the drag reduction phenomenon is the low concentration involved in causing a substantial effect. For instance, a 60% drag reduction can easily be achieved in a turbulent pipe flow by the addition of as little as 5 ppm of polymers such as poly(ethylene oxide). A compound may be considered more effective than a given reference sample if it produces a higher percent drag reduction for a fixed concentration. Alternatively, a more effective agent may be considered

as one which requires a lower concentration to achieve a certain percent drag reduction. Therefore, it seems reasonable to relate the effectiveness of a compound to its concentration dependence of the drag reduction effect.

Little ( *5* ) recently modified Virk's universal drag reduction equation ( *3* ) to account for the concentration dependence of drag reduction in capillary tubes. The equation, for a given Reynolds number or flow rate, takes the form

$$\frac{DR}{DR_m} = \frac{c}{c + [c]} \tag{1}$$

where DR is the percent drag reduction, $c$ is the polymer concentration, $DR_m$ is the maximum drag reduction, and $[c]$ is the intrinsic concentration. It has been shown that the parameter $[c]$ was useful in superposing all the experimental data onto a single universal drag reduction curve ( *5, 10* ). The drag reduction equation, empirical in nature, involves two adjustable constants $[c]$ and $DR_m$. These parameters, being constants characteristic of a given polymer compound, may serve as a measure of the drag reduction effectiveness and thus be useful tools for laboratory characterization of drag-reducing polymers. The physical significance of these parameters becomes very clear if the limit of (DR/$c$) at zero concentration is examined. According to eq 1,

$$\lim_{c \to 0} \frac{DR}{c} = \lim_{c \to 0} \frac{DR_m}{c + [c]} = \frac{DR_m}{[c]} \tag{2}$$

The parameter, $DR_m/[c]$, therefore is a measure of the "efficiency" of the polymer additives on a unit concentration basis at infinite dilution. It may be obtained by plotting the drag reduction data in terms of $c/DR$ vs. $c$. Equation 1 may be rearranged as

$$\frac{c}{DR} = \frac{c}{DR_m} + \frac{[c]}{DR_m} \tag{3}$$

i.e., a linear relationship exists between $c/DR$ and $c$. Such a plot, if linear, shows the validity of eq 1. The intercept at $c = 0$ yields the value of $[c]/DR_m$, the inverse of which is the drag reduction efficiency. The intercept at $c/DR = 0$ gives the intrinsic concentration $[c]$, which is the concentration required to reach half of $DR_m$ at the given flow rate.

The validity of the drag reduction equation has been established for data obtained in internal flows of different tube diameters ( *5, 9* ) using many different polymer–solvent combinations