Quaternary Ammonium Polyelectrolytes: Solution Studies of Certain Systems

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ABSTRACT

The investigation relates to density, viscosity, and conductance studies of four linear quaternary ammonium bromides with molecular weights ranging from 680 to 11,000. Of these, the two DMF-soluble compounds had their backbone quaternary centers attached to bulky substituents outside the chain and the other two, which dissolved in water, involved heterocyclic ring nitrogens carrying the positive charges in the repeating unit of the chain. Attempts have been made to comprehend the behavior of individual systems in terms of the competing solvophobic and electrostrictional interactions with the media. Concepts based on spatial disposition of the substituents and their ability to provide "pockets" for possible solvent entrapment and migration of electrostricted solvent molecules as well as formation of a "cage" of hydrogen-bonded waters around the backbone of the chain have

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been invoked to explain the characteristics of specific systems at the temperature(s) studied.
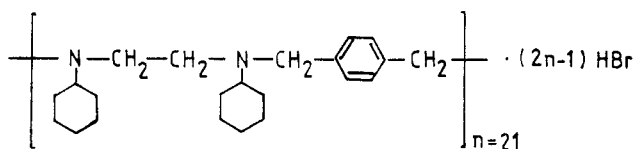
INTRODUCTION

Correlation of solvation characteristics of simple linear quaternary ammonium polyions has been surprisingly limited although solvation properties of spherically symmetrical cations including some of the simple quaternary ammonium ions in water have been systematized to a large extent [1]. For instance, consideration of the viscosity B coefficient of the Jones and Dole equation leads to two interesting classifications: the alkali metal ions are found to exhibit a decrease in B values as their radius increases, whereas the B values for the simple quaternary ammonium ions tend to increase with ion radius. The behavior of the alkali metal ions is presumably the result of electrostriction which is largely a coulombic effect arising from ion-solvent dipole interactions. On the other hand, the quaternary ammonium ions are believed to involve hydrophobic interactions of the nonpolar parts of the ions with water.

For this investigation, studies of solvation properties of polyions 1) having the backbone quaternary centers attached to bulky substituents outside the chain, and 2) those with heterocyclic ring nitrogens carrying the positive charges in the repeating unit of the chain appeared particularly interesting. The compounds on page 359 seemed relevant to us in that connection. It should be added that a recipe [2] for the preparation of C was available and the other compounds could be prepared in our laboratory. Since a large departure from the simple electrolytes was not intended, Compounds A, B, and C were considered to be of the proper molecular weight range and sufficiently large to satisfy the present requirements. Despite the fact that a higher degree of polymerization could not be achieved for D, its structural distinction from C has been the prime consideration for including it in the present study.

The actual work consisted of density, viscosity, and conductance studies of systems A, B, C, and D. Due to solubility restrictions, the first two compounds could only be studied in dimethylformamide (DMF) whereas all measurements involving C and D had to be confined to aqueous solutions. The density and viscosity measurements were carried out over a small temperature range (25 ± 5°C) while the conductance studies were made at 25°C.

The apparent molal volumes (ϕ_v) were calculated using the relation [3]

$$\phi_v = \frac{M_2}{d_0} + \frac{1000d}{C}\left(\frac{1}{d} - \frac{1}{d_0}\right) \tag{1}$$

$$\left[\!\!\begin{array}{c} N-CH_2-CH_2-N-CH_2-\!\!\bigcirc\!\!-CH_2 \end{array}\!\!\right]_{n=21} \cdot (2n-1)\ HBr$$

(A: mol. wt. = 10,248)

$$H\left[\!\!\begin{array}{c} \overset{Br^-}{\underset{+}{N}}H-CH_2-\!\!\bigcirc\!\!-CH_2 \end{array}\!\!\right]_{n=5} Br$$

(B: mol. wt. = 1490)

$$\left[\!\!\begin{array}{c} \overset{+}{N}\!\!\bigcirc\!\!\bigcirc\!\!\overset{+}{N}-CH_2-\!\!\bigcirc\!\!-CH_2 \end{array}\!\!\right]_{n=26} \cdot (2n-1)\ Br^-$$

(C: mol. wt. = 11,000)

$$\left[\!\!\begin{array}{c} \overset{+}{N}\!\!\bigcirc\!\!\bigcirc\!\!\overset{+}{N}-CH_2-CH_2 \end{array}\!\!\right]_{n=2} \cdot (2n-1)\ Br^-$$
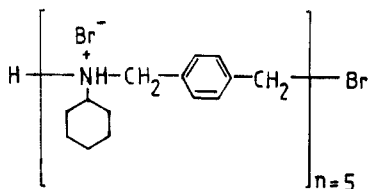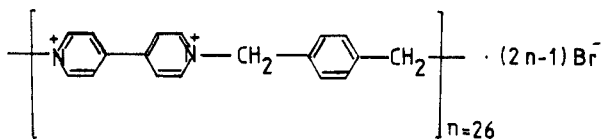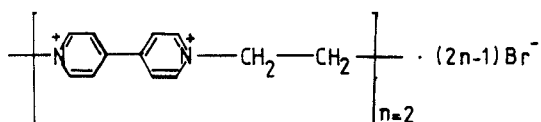
(D: mol. wt. = 680)

Values of $\overline{V}_2{}^0$ were obtained by extrapolating the ϕ_v- concentration plots to zero concentration. The viscosity data for A, B, and C were fitted to the reciprocal form of the Fuoss-Strauss equation [4]. The intrinsic viscosities of the three systems were evaluated from the intercepts of the corresponding plots. Compound D, however, showed a linear increase of reduced viscosity with concentration. The value of the reduced viscosity extrapolated to zero concentration was taken as the intrinsic viscosity in this case.

The results of conductance measurements were treated according to the Lattey equation [5]. Plots of $\sqrt{c}/(\Lambda_0 - \Lambda_c)$ vs $\sqrt{c}$ for different

trial values of the limiting conductance (Λ_0) were inspected, and the macroion mobilities were ascertained on the basis of the minimum value of Λ_0 which gave a linear plot in the individual cases.

EXPERIMENTAL

Chemicals

Demineralized water distilled twice from a Pyrex glass still was used in making all aqueous solutions. The specific conductivity of the water varied between 1×10^{-6} and 5×10^{-6} mho/cm. The solvent dimethylformamide was a Sarabhai-Merck reagent-grade product (specific conductivity = 1.5×10^{-6} mho/cm). All other chemicals were either high purity materials originally or were purified before use.

Preparation of Quaternary Ammonium Bromides A, B, C, and D

Compound A is a condensation product of α,α'-dibromo-p-xylene (I) and N,N'-dicyclohexylethylenediamine (II) which was first prepared by the reaction of 1,2-dibromoethane and cyclohexylamine. Solutions of I (20 g/100 mL) and II (17 g/100 mL) were prepared separately in rectified spirit by slight heating. The solution of II was then added to that of I and the mixture was refluxed at ~80° with continuous stirring for 2 h. It was stirred intermittently until a light yellow solid separated out. It was filtered, washed several times with hot ethanol, and dried in vacuo at room temperature. The compound did not seem to have a sharp melting point. However, thermogravimetric analysis indicated some distortion above 140°C. [Analysis (%): C = 49.60, H = 7.24, N = 5.66.] The IR spectrum revealed C–H stretching (2700–2800 cm^{-1} nujol; 2800–2900 cm^{-1} KBr), C–H bending (1448 cm^{-1} nujol; 1424-56 cm^{-1} KBr), and C–Br stretching (560 cm^{-1} nujol, KBr) frequencies as characteristic of the terminal–CH$_2$Br group. The N–H stretching at 3153 cm^{-1} and N–H bending vibrations near 1575 and 1640 cm^{-1} together with some absorptions between 1800 and 2500 cm^{-1} (in both nujol and KBr) are typically suggestive of the amine-salt structure of the nitrogens. Also, the N–H stretching vibration for the secondary amine (3483 cm^{-1} nujol, KBr) and the C–N vibrations at ~1345 cm^{-1} nujol and 1375 cm^{-1} KBr, provided strong evidence for the terminal cyclohexylamino group in the chain. Determination of ionic bromine in a DMF-water mixture indicated 4.00 mol Br$^-$ per 1000 g of the sample. The indicated structure conforms to the theoretical percentages (C = 54.09, H = 7.37, N = 5.73) and a total of 41 quaternary centers with the calculated nonionic terminal bromine of 0.0984 mol per 1000 g of the sample.

For the preparation of B a mixture of I and cyclohexylamine dissolved in DMF was heated for 3-4 h at 60-70°C and then kept at room temperature for several days. On evaporating the solvent at 160°C a brown syrupy material resulted. Upon addition of water, a sticky solid separated out which was washed with ethanol several times and dried in vacuo at 50°C to obtain a brown crystalline hygroscopic product in 25% yield. [Analysis (%): C = 56.40, H = 5.57, N = 4.17.] Determination of ionic bromine in the DMF-water mixture indicated 3.50 mol Br⁻ per 1000 g of the sample. The infrared spectrum (nujol) of the polymer revealed absorptions at 2568-2738 cm^{-1} (C–H stretching), 1456 cm^{-1} (C–H bending), and 584 cm^{-1} (C–Br stretching) due to the end –CH_2 group. The N–H stretching at 3153 cm^{-1} and the N–H bending vibrations near 1567 and ~1648 cm^{-1}, in addition to some absorptions between 1800 and 2500 cm^{-1}, suggested the amine-salt structure for all the nitrogens in this system.

The preparation and characterization of C have been given in an earlier article [6].

Compound D was obtained by refluxing an equimolar mixture of 4,4'-bipyridine and 1,2-dibromoethane at ~80°C in dry acetonitrile for 48 h. The resulting yellowish brown product was washed twice with hot acetonitrile and then dried in vacuo at 40°C. As in the case of C, the material was found to respond to Zn-HCl reduction, giving a violet-colored radical cation which could be reoxidized by air oxygen. [Analysis (%): C = 41.46, H = 3.29, N = 8.32.] The observed infrared frequencies (KBr) are ~2960 cm^{-1} (C–H stretching), 810 cm^{-1} (C–H bending), 1460 cm^{-1} (C=C stretching), 1630 cm^{-1} (>C=N–C substituted imine vibration) correspond to the terminal bipyridine ring, and 3100 cm^{-1} (C–H stretching), 1490 cm^{-1} (C–H bending), 570 cm^{-1} (C–Br stretching) to the end –CH_2Br group in the system. The thermogravimetric curve showed that the compound started decomposing above 200°C and that a sharp loss in weight occurred at 300°C. Determination of ionic bromine by conductometric titration indicated 3.80 mol Br⁻ per 1000 g of the sample. Moreover, differential vapor pressure measurements with 13.83 and 17.03 mg/mL solutions in water gave molarities of 0.08156 and 0.10037$_5$, respectively, and an average molecular weight of 680 for the compound on the consideration that 4 ions (3 Br⁻ ions and 1 cation) per molecule would become available according to the proposed structure.

Density and Viscosity Measurements

Known amounts of the compounds were transferred to volumetric flasks, dissolved in limited quantities of the solvents, and diluted up to the mark at 25°C. In density measurements, concentrations were expressed in monomol/L, using 488 (for A), 298 (for B), 423 (for C), and 340 (for D) as the corresponding gram monomolecular weights obtained by simply dividing the molecular weights by the

degrees of polymerization. The gram monomolecular weights for A, C, and D calculated in this manner correspond to those for the respective monomeric units. However, the value for a monomeric unit of B with terminal H and Br is 363; the gram monomolecular weight selected for the present purpose represents a value averaged over the weight of the entire molecule. For viscosity measurements, concentrations were expressed in grams/deciliter.

The solution densities were determined by using a bicapillary pycnometer of approximately 20 mL capacity with the arms graduated in 0.01 mL. The pycnometer was first calibrated with a known quantity of water, and buoyancy corrections were applied to all weights.

The viscosity measurements were carried out using a Ubbelohde-Cannon-Fenske type of viscometer. Generally, for both aqueous as well as DMF solutions, a particular viscometer giving efflux times of 192.6 s for water and 184.3 s for DMF at 25°C was used. However, for some aqueous solutions of very low viscosities, such as those of D, another viscometer of the same type but yielding efflux time of 500.6 s for water was found more convenient.

For all density and viscosity measurements the solvents and the solutions were temperature-equilibrated in advance for a sufficiently long time in a thermostat, the temperature of which could be maintained constant within ±0.1°C at 20, 25, and 30°C as desired. For almost all the solutions, both density and viscosity measurements were made the same day, one after the other. Viscosity measurements were always accompanied initially by blank runs with the solvents in question. The measured efflux times are considered accurate to ±0.1 s. The values used in viscosity calculations were the averages of 3-4 observations in each case. In view of any possible surface activity of the present quaternary ammonium compounds, special care was taken during measurements and in cleaning the glassware used. The reported viscosities are considered accurate to better than ±0.1%.

Conductance Measurements

All conductances were measured at $25 \pm 0.05°C$ in the conventional way using a dip-type cell (cell constant = 0.6055 cm^{-1}) with lightly platinized electrodes. An RC 18A Beckman conductance bridge and a WTW (model LBR/R) instrument have been used in the measurements; no significant differences in the resistances were observed at 50, 1000, and 3000 Hz. The reported equivalent conductances have been calculated on the basis of equivalents of ionic bromine available per mole of the different compounds used, and are corrected for the solvent conductance.

Solutions were prepared according to the procedure mentioned in the case of density and viscosity measurements.
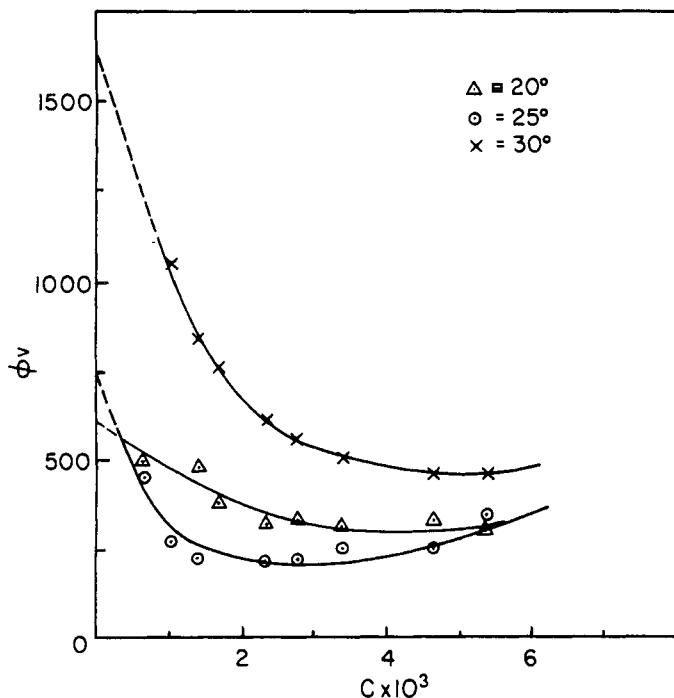
FIG. 1. Plots of apparent molal volume vs concentration for Compound A at 20, 25, and 30°C.

RESULTS AND DISCUSSIONS

As shown in Fig. 1, the apparent molal volume of Compound A at any temperature decreases with an increase in concentration with a tendency to level off beyond ~0.002 monomol/L. This may suggest that, overall, the system is experiencing a larger degree of solvophobicity in DMF in comparison with the competing electrostrictional effects. For a given concentration the actual value of ϕ_v at any temperature apparently represents the net result of these two opposing effects [3]. The sharp decrease of the apparent molal volume with concentration at 30°C would seemingly reflect the existence of overwhelmingly strong solvophobic interactions even at this temperature. In contrast, however, a moderation of the behavior is observed at 20°C with the apparent molal volumes assuming intermediate values. Thus it may be reasonable to assume that the solvophobicity of the system is chiefly due to "locking up" [7] of the solvent molecules in
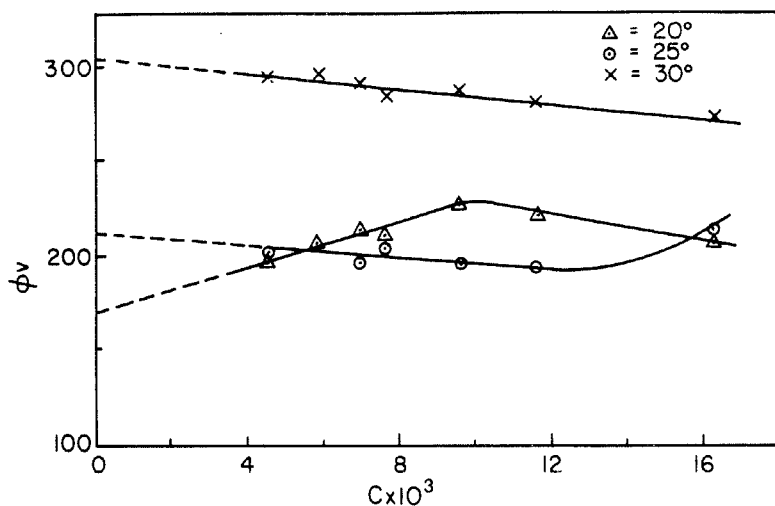
FIG. 2. Plots of apparent molal volume vs concentration for Compound B at 20, 25, and 30°C.

the void spaces provided by the ethylene and xylyl groups on the backbone of the polyion in cooperation with the spatial disposition of the outside cyclohexyl groups. As the temperature is lowered, the volume of the void space(s) is likely to contract; accordingly, accommodation of the large DMF molecules will become relatively difficult at 20°C with the result that the solvophobicity may be reduced to an extent barely sufficient to overcome the electrostrictional contribution of solvation at the temperature. The extrapolated values of apparent molal volumes ($\bar{V}_2^0$) for A are 620 (20°C), 750 (25°C), and 1650 mL/monomole (30°C). This observed increase in volume with temperature may indicate a general expansion of the polyion and its counterions due simply to thermal agitation.

The general nature of the ϕ_v-C plots for Compound B (Fig. 2) at 25 and 30°C resembles that of A. The slight upward trend visible at 25°C beyond ~0.0130 monomol/L may be attributed to large electrostrictional contributions. The sharp maximum at 0.0101 monomol/L shown by the 20°C plot further indicates that the solvophobic interactions for this system are also primarily determined by solvent incorporation into the available void spaces of the polyion (between the xylyl and the cyclohexyl groups linked to the quaternary centers). At 20°C the solvophobic interactions would be rather limited due to the contraction of the void spaces, and the contributions of these interactions may be inappreciable in comparison with the electrostrictional contributions until a concentration of ~0.010 monomol/L corresponding to the maximum is attained. At higher temperatures,
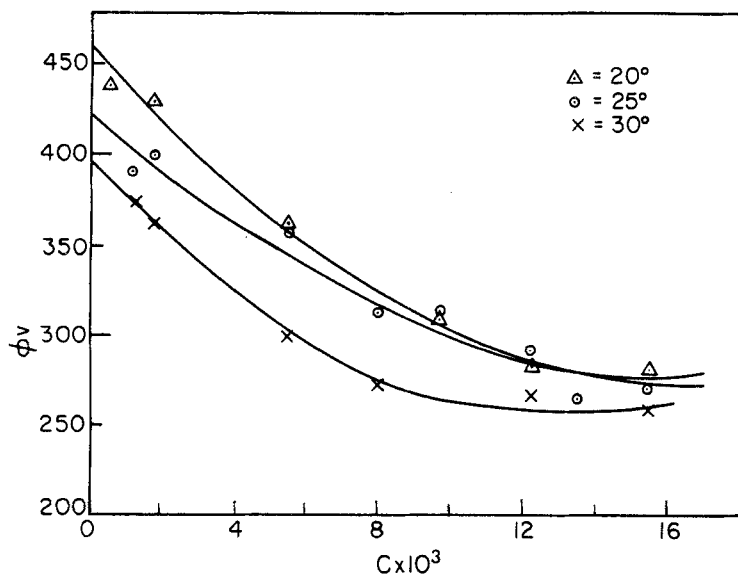
FIG. 3. Plots of apparent molal volume vs concentration for Compound C at 20, 25, and 30°C.

i.e., 25 and 30°C, more void spaces are likely to become available due to the opening of the two ring systems, viz., the xylyl and cyclohexyl groups and, therefore, the chances for the solvophobic interactions to exceed the effects of electrostriction will increase over the same range of concentrations. At concentrations beyond the 20°C maximum the higher population of polyions may lead to an overall increase of the available void space, so the latter may cause solvophobicity to overcome the competition of the electrostrictional contributions and ultimately manifest itself as the predominant effect. An additional reason for solvophobicity at higher concentrations may also be visualized by considering that the short and somewhat rigid polyions in this case are drawn closer to each other in a common pool of counterions which may suitably orient themselves to provide an appropriate geometry favoring solvent entrapment within the empty spaces of the arrangements so produced. The $\bar{V}_2^0$ values obtained for B at the different temperatures are 171 (20°C), 214 (25°C), and 306 mL/monomol (30°C).

The density behavior of the aqueous solutions of the 4,4'-bipyridine systems C and D are represented in Figs. 3 and 4 in the form of ϕv-C plots. As is evident, a dominant hydrophobic effect is exhibited by C at all temperatures. The values of $\bar{V}_2^0$ at different temperatures, however, indicate a reversal of the trend observed in the case of the two DMF-soluble compounds: viz., A and B. This behavior may be
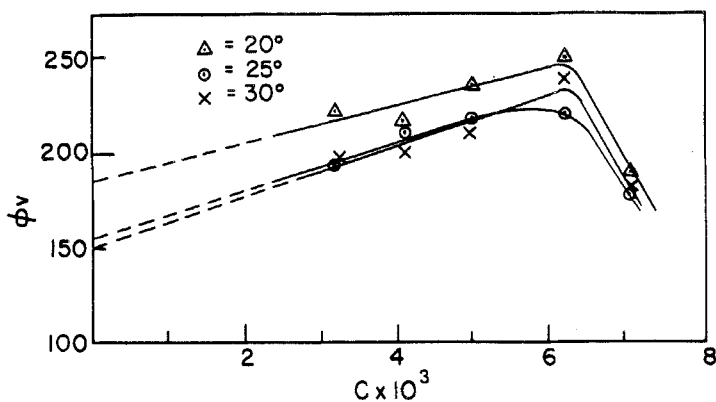
FIG. 4. Plots of apparent molal volume vs concentration for Compound D at 20, 25, and 30°C.

associated with the existence of a "cage" of hydrogen-bonded water [8] around the polyion of C. The exact structure and the equilibrium dimension of the "cage" is perhaps determined by the blocking effect of the bulky substituents of the polyion and the reduced positive charge density on the quaternized centers due to the presence of the adjacent electron-rich xylyl moiety. The observed lowering of $\overline{V}_2^0$ with temperature may thus be a result of the reduction of the hydrogen-bonded solvent envelope. In addition, if one bears in mind that the bipyridine system is noncoplanar [9] in the solution phase, the reduction of volume with temperature may be considered to be related with entrapment or packing of water molecules from the cage structure into the void spaces provided by the opening up of the bipyridine rings.

The values of $\overline{V}_2^0$ [186 (20°C); 154 (25°C); 150 mL/monomol (30°C)] of D exhibit the same trend as C while the patterns of concentration dependence of the apparent molal volume of the system (Fig. 4) are similar to those of B at 20°C, indicating a net electrostrictional effect at lower concentrations, attainment of a maximum (at 0.0062 monomol/L), and then a decrease reflecting hydrophobicity. The absence of the xylyl moiety in the backbone would enable the quaternized center in this relatively small ion to exert high positive charge density and to be more accessible to the solvent molecules for electrostrictional interactions. The observed hydrophobicity at higher concentrations may be due to the entrapment of solvent molecules by suitable geometrical structures consisting of several dimeric cations held together in the pool of counterions as has been proposed in the case of B. Or, more possibly, the effect arises from packing of electrostricted water molecules into the void space between the two pyridine rings of the bipyridine system; as the temperature is raised, the electrostricted waters conceivably enjoy greater freedom to move

into any of the empty spaces provided in the backbone of the dimeric cation and a net contraction in volume results. The actual value of ϕ_v at any temperature would be determined by the volume of the available empty space and the degree of freedom of the electrostricted waters to migrate into it.

Assuming an average value of 28.1 (DMF) [10] and the value 31.6 (water) [11] mL/g for $\overline{V}_2^0$ for Br^- ion, the partial molal volumes of the cations of A, B, C, and D are calculated to be 693.8, 185.9, 360.8, and 90.8 mL/g ion, respectively, at 25°C. Although the uncertainty in the apparent molal volumes is estimated to be $\sim 1\%$, larger uncertainties could be involved in the graphical extrapolation of the ϕ_V-C plots in obtaining the partial molal volumes of the present systems. However, the systematic order in which the $\overline{V}_2^0$ values appear to depend on temperature in the individual cases is considered interesting and meaningful.

The results of viscosity measurements at 20, 25, and 30°C for Systems A, B, C, and D are presented in Tables 1 and 2. The intrinsic viscosities for A, B, and C in the particular solvents studied were calculated from the intercepts of the corresponding reciprocal plots ($\eta_{sp}/C = A/(1 + B\sqrt{C})$) based on the Fuoss-Strauss equation [4]. The actual values of $[\eta]$ obtained for the DMF-soluble systems are 0.070 (20°C), 0.252 (25°C), and 0.359 dL/g (30°C) for A and 0.282_4 (20°C), 0.561 (25°C), and 1.14 dL/g (30°C) for B, while the aqueous solutions of C yielded values of 0.840 (20°C), 0.605 (25°C), and 0.568_5 dL/g (30°C), indicative of a decrease in size with temperature. Although the intrinsic viscosities for both A and B reveal an increase with temperature, the large values of $[\eta]$ for B probably suggests that the system conforms to a "free-draining" model. In contrast, A–a more flexible system—may have a tendency to curl together with its associated solvent molecules and behave as an "impermeable coil"; the solvent DMF in this case perhaps acts as a poor solvent promoting polymer-polymer contacts [12]. The high temperature sensitivity observed for both A and B may further indicate the presence of van der Waals' attraction among the proximate cyclohexyl groups outside the chain in or between individual segments of the polyion. Such interactions in the present instances are likely to induce contraction of the systems as the temperature is lowered. The decrease of $[\eta]$ for A with a reduction of temperature may be further aided by the progressively greater curling tendency of the system. Besides these possibilities, it is also conceivable that intermolecular interactions leading to aggregate formation could occur at higher concentrations. Accordingly, any increase in reduced viscosity with temperature may represent a corresponding increase in size (that is, expansion) of the aggregates. As is evident, the data for B at high concentrations seem to be in order in this respect and corroborate our earlier assumption of aggregate formation in explaining the 20°C behavior of the ϕ_v-concentration dependence for the system (Fig. 2).

TABLE 1. Results of Viscosity Measurements on Solutions of A and B in Dimethylformamide[a]

| | A | | | | B | | |
| Conc, C (g/dL) | Viscosity, η (cP) | | | Conc, C (g/dL) | Viscosity, η (cP) | | |
	20°C	25°C	30°C		20°C	25°C	30°C
0.0696	0.8927	0.8140	0.7621	0.1370_4	0.9030	0.8161	0.7740
0.1160	0.8940_5	0.8162	0.7631	0.1748	-	0.8191	0.7716
0.1364	0.8953	0.8172	0.7643	0.2088	0.9074_4	0.8192	0.7721
0.1660	0.8964_5	0.8214	0.7644	0.2284	0.9078	0.8194	0.7738
0.2268	0.8185	0.8263	0.7679	0.2872	0.9118	0.8218	0.7762
0.2624	0.8981	0.8275_5	0.7692	0.3480	0.9134	0.8255_5	0.7790_5
				0.4868	0.9221	0.8301	0.7847

[a]Viscosity of dimethylformamide (η_0): 0.88975 (20°C), 0.80322 (25°C), 0.75464 (30°C) cP.

TABLE 2. Results of Viscosity Measurements on Solutions of C and D in Water[a]

	C				D			
Conc, C (g/dL)	Viscosity, η (cP)			Conc, C (g/dL)	Viscosity, η (cP)		
	20°C	25°C	30°C		20°C	25°C	30°C
0.0360	–	0.9096	–	0.1096	1.0105	0.8968	0.8024_4
0.0504	–	0.9096	0.8142	0.1404	1.0137	0.8979_5	0.8037
0.0760	1.0301	0.9160	0.8193	0.1704	1.0159_4	0.9016_5	0.8042_4
0.1367	–	0.9329_5	–	0.2120	1.0191	0.9037	0.8064
0.2312	1.0712	0.9426	0.8472	0.2412	1.0239	0.9064	0.8091
0.3376	1.0886	0.9519	0.8533	0.2808	–	0.9096	–
0.4100	1.0953	0.9671	0.8624				
0.5164	1.0984_5	0.9695	0.8657				
0.5696	–	0.9833	–				
0.6516	1.1191	0.9839	0.8946				

[a]Viscosity of water (η_0): 1.0050 (25°C), 0.8937 (25°C), 0.8007 (30°C) cP.

System C, for which a hydrogen-bonded water cage around the polymer backbone has been assumed in explaining its partial molal volume characteristics, is found to yield appreciably high values of $[\eta]$ [0.840 (20°C), 0.605 (25°C), 0.568$_5$ (30°C)], especially in comparison with A which has a molecular weight of the same order of magnitude. It is also to be noted that the $[\eta]$ values show a relatively gradual decrease with temperature unlike A and B. The root-mean-square and end-to-end distances (R in Å) as calculated from the Flory-Fox equation [13] are found to be 70 (20°C), 107 (25°C), and 121 (30°C) for A and 164 (20°C), 147 (25°C), and 144 (30°C) for C. From a comparison of these estimates with the plane projection distances* (221.9 Å for A, 395.7 Å for C) based on bond lengths for the two cases, the extent of coiling is determined to be nearly the same for both systems. The low values of $[\eta]$ for A, however, have been attributed to its behavior as an impermeable coil. Thus it may not be unreasonable to assume that C conforms to the free-draining model as does B. The temperature effect on $[\eta]$ and the reduced viscosities over finite concentrations may accordingly be related to contraction of the coil with its surrounding water-cage. Apparently, as a solvent, water tends to prevent polymer-polymer contacts and, therefore, reduces any possibility for curling in this case. The decrease of $[\eta]$ with temperature may thus be a combined result of the reduction of the size of the water-cage and a decrease of the total frictional resistance due to the immobilized waters of the cage.

The aqueous solutions of the dimeric Compound D yielded the smallest viscosities of all the systems studied (Table 2), exhibiting a linear relationship between the reduced viscosity and concentration. Treatment of the data according to the Fuoss-Strauss equation through the reciprocal plot resulted in a negative value of B. Therefore a straightforward free-hand extrapolation of η_{sp}/C vs C plot to zero concentration was used for obtaining $[\eta]$. The intrinsic viscosities [0.0350 (20°C), 0.0120 (25°C), 0.0006 (30°C)] thus derived are found to be considerably low and indicate a gradual decrease with temperature. The latter may signify an accompanying contraction of the system due to any possible migration of the electrostricted waters into the void spaces offered by the bipyridine ring as has been proposed in interpreting the concentration dependence of ϕ_v in this case.

The average values of energies of activation calculated on the basis of viscosity data obtained at intermediate ranges of concentration are found to be 2.84 (A), 3.05 (B), 4.20 (C), and 4.13 (D) kcal/mol. The similarity of the orders of magnitude of these activation energies with those of the smaller quaternary ammonium salts [14] is interesting.

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*These distances were calculated as follows: (end-to-end length of the monomer unit) × (degree of polymerization) + (additional contributions of the terminal bonds).

TABLE 3. Results of Conductance Measurements at 25°C

| Compound	Conc, $C \times 10^3$ (g equiv/L)	Equiv conductance, Λ_c
A[a]	2.13	42.43
	4.29	32.77
	5.44	29.37_5
	6.66	27.01
	8.06	25.46
	9.92	22.44
B[a]	0.87	92.74
	1.46	82.55_5
	2.20	72.70
	2.97	67.82
	3.63	62.46_5
	4.61	59.14
C[b]	1.01	90.22
	1.47	81.61
	1.66	88.29
	2.32	87.56
	6.44	80.89
	10.75	75.79
	15.16	73.39
	18.86	71.79
	25.35_5	69.12
	30.01	68.31
D[b]	1.67	94.24
	3.23	93.37
	4.26	95.09
	5.67	90.22
	6.48	89.59
	9.16_5	87.26
	9.61	85.97
	10.64	88.97
	11.45	85.32_5
	15.19	86.07
	19.20	85.48

[a]In DMF.
[b]In water.
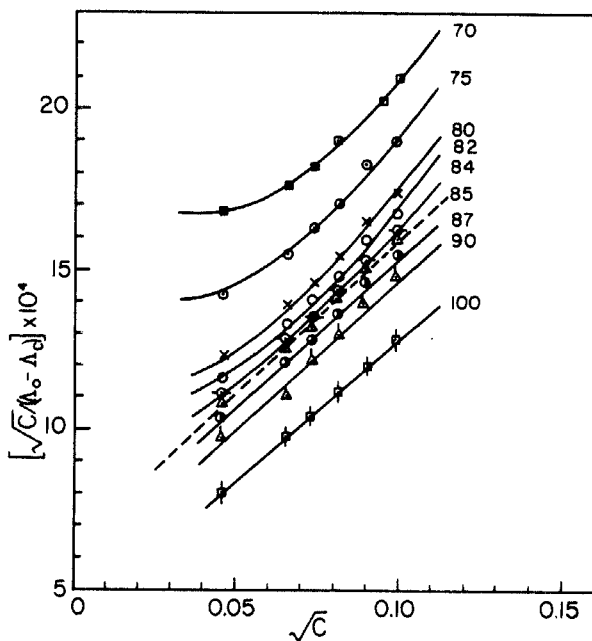
FIG. 5. Lattey equation plots for Compound A. The plot shown
for $\Lambda_0 = 85$ represents the least-squares line.

The results of conductance measurements on all four systems are
presented in Table 3. A typical Lattey equation plot is shown in
Fig. 5, using different trial values of Λ_0 for the case of Compound A.
In any instance the minimum value of Λ_0 which yielded a linear plot
was chosen as the limiting equivalent conductance of the system
concerned. The values of the limiting conductances thus obtained are
85 (A), 140 (B), 100 (C), and 122 (D). The least-squares values of
D and G obtained for the minimum Λ_0 line are given below. Subtracting
the value of $\lambda^0_{Br^-}$ for 25°C in DMF (53.6) [15] and water (78.3) as the
case may be, the following values of λ_+^0 were obtained for the differ-
ent cations involved in the present study: 31.4 (A), 86.4 (B), 21.7
(C) and 43.7 (D).

	A	B	C	D
D	0.00063	0.00045	0.00301	0.00073
G	0.00962	0.00553	0.01363	0.02180

Excluding the case of B for which the mobility of the cation (86.4) appears to be somewhat inconsistently large, the values derived for the other three systems follow the sequence D (MW 680) > A (MW 10,248) > C (MW 11,000). This seems to agree with the observed trend of the intrinsic viscosities (0.012, 0.252, and 0.605 dL/g at 25°C) and, in all possibility, may reflect the effect of an increase in size of the respective cations in that order. The curling tendency of A may be a specifically helpful factor in determining its position in the mobility sequence in spite of the large molecular weight of the system. It is interesting to note, however, that the ratio of the mobilities of C and A is close to that of the reciprocals of the end-to-end plane projection distances (221.9 Å for A and 395.7 Å for C) of the molecules concerned [16]. The comparatively large mobility of the B cation may apparently be due to the rigidity of its structure. As is evident, it is difficult to obtain any direct correlation among the present limiting cation conductances as obtained from the Lattey equation when assuming the simple additivity rule. Furthermore, it seems plausible that the individual values will be drastically modified if one introduces corrections based on Manning's self-diffusion coefficient ratio [17] of the Br^- ion or Eisenberg's ϕ [18] in the derived results. In the absence of estimates on these corrections, no critical appraisal of the present values thus seems possible. Both DMF and water fortuitously have nearly the same viscosities, but the lower dielectric constant [38 (DMF); 78 (water)] of the former solvent would certainly warrant greater consideration for correction due to counterion association.

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