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Viscosity *B* Coefficients for Di- and Trialkylammonium Chlorides in Aqueous Solutions

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Synopsis. The viscosity *B* coefficients of the Jones-Dole equation for di-*n*-alkylammonium chlorides (methyl to butyl) and tri-*n*-alkylammonium chlorides (methyl to propyl) in water at 25 °C were determined, and the effect of structural changes in the solvent water induced by the alkyl-substituted ammonium ions is discussed.

The behavior of electrolytes with nonpolar groups in water may be interpreted approximately by a balance of two types of interaction; hydrophobic hydration due to the nonpolar parts, and electrostrictive hydration due to the ionic parts.[1] In a previous paper,[2] the role of the alkyl groups in the coordination of the charge-bearing nitrogen atom in the series of *n*-alkylammonium salts RNH_3X, di-*n*-alkylammonium salts R_2NH_2X, tri-*n*-alkylammonium salts R_3NHX, and tetra-*n*-alkylammonium salts R_4NX was discussed on the basis of the changes in the heat capacity upon dissolution in water. The study of the viscosity of aqueous electrolyte solutions provides a useful method of obtaining information on ion-solvent interactions.[3,4] The viscosity *B* coefficients for RNH_3X[1,5] and R_4NX[6-9] are found in the literature. In this paper, we will report our experimental study of the viscosity *B* coefficients for R_2NH_2Cl (methyl to butyl) and R_3NHCl (methyl to propyl) in aqueous solutions.

Experimental

R_2NH_2Cl and R_3NHCl salts used in this work were the same samples as those described in a previous paper.[2] The viscosities were measured at 25±0.007 °C by a method similar to that described in our previous papers.[1,10]

Results and Discussion

The viscosity of aqueous electrolyte solutions is given by the Jones-Dole equation:[11]

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η and η_0 are the viscosity of the solution and the solvent respectively; *c*, the molar concentration; *A*, the constant arising from the interaction between the ions, and *B*, the viscosity *B* coefficient. Equation 1 may be converted to:

$$(\eta/\eta_0-1)/c^{1/2} = A + Bc^{1/2} \qquad (2)$$

By plotting $(\eta/\eta_0-1)/c^{1/2}$ against $c^{1/2}$, as is shown in Fig. 1, the *B* coefficient can be determined from the slope of the straight line. The values of the *B* coefficient so determined are summarized in Table 1.

The *B* value obtained in this procedure is considered to be the sum of the contributions from a cation and an anion. Taking the ionic *B* value, B_{ion}, of Cl^- ion to be −0.007 according to the separation basis of Gurney,[3] the B_{ion} values of $R_2NH_2^+$ and R_3NH^+ ions

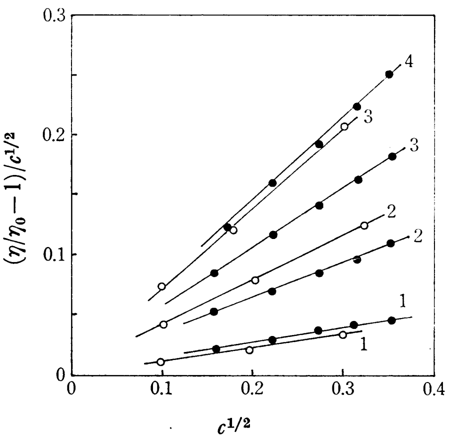

Fig. 1. Plots of $(\eta/\eta_0-1)/c^{1/2}$ against $c^{1/2}$. ● R_2NH_2Cl salts, ○ R_3NHCl salts. 1, methyl; 2, ethyl; 3, propyl; 4, butyl.

TABLE 1. ESTIMATION OF THE ION-SOLVENT INTERACTION EFFECTS

R	*B* (l/mol)	B_{ion} (l/mol)	$\bar{V}°$ (cm³/mol)	$\bar{V}°_{ion}$ (cm³/mol)	B_{solv} (l/mol)
			R_2NH_2Cl		
Me	0.105	0.112	72.5	49.3	−0.011
Et	0.286	0.293	106.7	83.5	0.084
Pr	0.490	0.497	138.7	115.5	0.208
Bu	0.687	0.694	170.7	147.5	0.325
			R_3NHCl		
Me	0.110	0.117	90.59	67.3	−0.051
Et	0.378	0.385	138.6	115.4	0.097
Pr	0.681	0.688	186.8	163.6	0.279

can be obtained; they are listed in Table 1.

The viscosity *B* coefficient is usually interpreted as consisting of two terms; the first is the effect of the ionic size, B_{size}, and the second is the contribution arising from the ion-solvent interaction, B_{solv};[4]

$$B_{ion} = B_{size} + B_{solv} \qquad (3)$$

If we assume that the Einstein equation derived for the case of spherical colloid may be applied approximately to the aqueous electrolyte solutions, B_{size} may be obtained from this equation:

$$B_{size} = 0.0025\,\bar{V}°_{ion} \qquad (4)$$

where $\bar{V}°_{ion}$ is the ionic partial molal volume expressed in cm³/mol. Thus, B_{solv} can be derived by ths use of this equation:[7]

$$B_{solv} = B_{ion} - 0.0025\bar{V}°_{ion} \qquad (5)$$

The values of the partial molal volume, $\bar{V}°$, of R_2NH_2Cl and R_3NHCl salts have been reported by Conway and

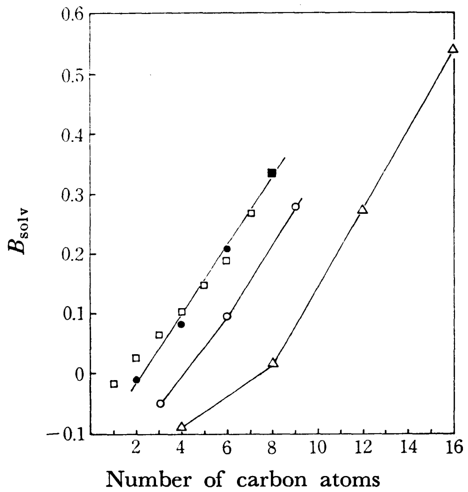

Fig. 2. Plots of B_{solv} against number of carbon atoms in the ions. □ RNH_3^+, ● $R_2NH_2^+$, ○ R_3NH^+, △R_4N^+.

his collaborators.[12,13] The $\bar{V}°_{ion}$ values of $R_2NH_2^+$ and R_3NH^+ ions may be obtained by subtracting 23.2 cm³/mol, the $\bar{V}°_{ion}$ value of Cl^- ion[14]), from the $\bar{V}°$ values of R_2NH_2Cl and R_3HNCl salts. The B_{solv} values obtained for $R_2NH_2^+$ and R_3NH^+ ions are summarized in Table 1.

As may be seen in Table 1, the B_{solv} values of $Me_2NH_2^+$ and Me_3NH^+ ions are negative; both the methyl salts are, then, to be classified as simple salts. This implies that the interaction of the charge-bearing nitrogen atom with water surpasses the hydrophobic hydration due to methyl groups; thus, the overall behavior of these methyl salts in water is governed by electrostrictive hydration.

Table 1 indicates the positive B_{solv} values for $Et_2NH_2^+$, $Pr_2NH_2^+$, $Bu_2NH_2^+$, Et_3NH^+, and Pr_3NH^+ ions; they are all classifiable as the hydrophobic structure-making ions in water.

The B_{solv} values of RNH_3^+ and R_4N^+ ions may also be obtained using the viscosity and partial molal volume data in the literature.[1,5–9,15] Thus, in the cases of RNH_3^+, $R_2NH_2^+$, R_3NH^+, and R_4N^+ series, the dependence of the B_{solv} values on the total number of carbon atoms in the ions is shown in Fig. 2. It is found that the B_{solv} values for the alkyl-substituted ammonium ions with the same number of carbon atoms will be in this order: $RNH_3^+ \fallingdotseq R_2NH_2^+ > R_3NH^+ > R_4N^+$. The Behavior of the B_{solv} values obtained in this paper for the alkyl-substituted ammonium ions is consistent with the inclination of the changes in the heat capacity upon dissolution of these salts in water reported in a previous paper.[2]

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