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Viscosity *B* Coefficients for *N,N'*-Polymethylenebis(trialkylammonium) Dibromides in Aqueous Solutions

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Synopsis. The viscosity *B* coefficients for aqueous solutions of *N,N'*-polymethylenebis(trialkylammonium) dibromides [$(C_mH_{2m+1})_3N(CH_2)_nN(C_mH_{2m+1})_3$]$Br_2$ (m=2—4, n=3—6, 8, 10, and 12) and, for comparison, of $C_nH_{2n+1}N(C_mH_{2m+1})_3Br$ (m=2, n=1—6; m=3,4, n=2—6) have been determined at 25 and 35 °C. The effect of structural changes in the solvent water upon the dissolution of these homologous electrolytes is discussed.

The physicochemical properties of aqueous solutions of tetraalkylammonium salts have been studied by many investigators in terms of the structural changes in liquid water caused by these hydrophobic solutes.[1] However, the solubilities of tetrapentylammonium salts and the higher homologs of this series are too small for precise measurements. On the other hand, bis(quaternary ammonium) salts are highly soluble in water, and it seems that bis(quaternary ammonium) salts can be expected to exhibit the characteristics of large hydrophobic solutes in water. In order to elucidate the balance of the ionic hydration and the hydrophobic hydration of *N,N'*-polymethylenebis(trialkylammonium) dibromides in water, we have extended the measurements of the viscosity *B* coefficients for these electrolytes in water. In a previous paper,[2] the results of *N,N'*-polymethylenebis(trimethylammonium)dibromides (to be abbreviated as MeC$_n$Me) and, for comparison, of alkyltrimethylammonium bromides (to be abbreviated as C$_n$Me) were reported. This paper will describe the experimental results for three homologous series of electrolytes; *N,N'*-polymethylenebis(triethylammonium) dibromides (to be abbreviated as EtC$_n$Et), *N,N'*-polymethylenebis(tripropylammonium) dibromides (to be abbreviated as PrC$_n$Pr) and *N,N'*-polymethylenebis(tributylammonium) dibromides (to be abbreviated as BuC$_n$Bu). For comparison, the viscosity *B* coefficients of the corresponding alkyl compounds with a single terminal quaternary ammonium group, alkyltriethylammonium bromides (to be abbreviated as C$_n$Et), alkyltripropylammonium bromides (to be abbreviated as C$_n$Pr) and alkyltributylammonium bromides (to be abbreviated as C$_n$Bu), have also been studied.

Experimental

Materials. EtC$_n$Et, PrC$_n$Pr, and BuC$_n$Bu were prepared by refluxing the α,ω-dibromoalkanes with an excess of the respective trialkylamines in ethanol or acetonitrile.[3,4,5] After the solvent had been removed, the salts were purified several times by recrystallization from suitable solvents: acetone–ethanol solutions for EtC$_n$Et and ethyl acetate–ethanol solutions for PrC$_n$Pr and BuC$_n$Bu. PrC$_{12}$Pr, BuC$_8$Bu, BuC$_{10}$Bu, and BuC$_{12}$Bu were found to be fairly difficult to obtain as solid samples from reaction mixtures, so they were precipitated from reaction mixtures by means of the repeated extraction of the unreacted or impure materials with dry ethyl acetate at −20 °C. C$_n$Et (except for C$_1$Et), C$_n$Pr, and C$_n$Bu were prepared by refluxing the alkyl bromides with an excess of the respective trialkylamines in ethanol. C$_1$Et was prepared by the reaction of *N,N*-diethylmethylamine with ethyl bromide in ethanol. The salts were recrystallized several times from suitable solvents: ethyl acetate–ethanol solutions for C$_n$Et, ethyl acetate–acetone solutions for C$_n$Pr and C$_2$Bu, and ethyl acetate for C$_3$Bu, and C$_4$Bu. C$_5$Bu and C$_6$Bu were found to be fairly difficult to obtain as solid samples from reaction mixtures. C$_5$Bu and C$_6$Bu were precipitated by the repeated extraction of the unreacted or impure materials with butyl acetate and isopentyl acetate respectively. All the salts were dried in vacuo at room temperature for several days and then analyzed for bromide ion by means of argentrometric titration. The salts were found to have a purity greater than 99.5%. Water was triply distilled.

Viscosity Measurements. The viscosities were measured at 25 and 35 °C using an automatic viscometer of the Shibayama Scientific Co., Ltd. The densities were measured using a vibrating-tube densimeter, twin-type SS-D-200 of the Shibayama Scientific Co., Ltd. The detailed procedure was described in a previous paper.[6] The electric conductivities were measured with a Yokogawa audio-frequency bridge using a frequency of 1000 Hz.

Results and Discussion

The Viscosity *B* Coefficients of Electrolytes. Jones and Dole[7] showed that the viscosity of dilute electrolyte solutions, η, can be related to the following equation:

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

where η_0 is the viscosity of the solvent, c is the molar concentration, and A and B are the characteristic constants of the solute. In a previous work[2] for MeC$_n$Me and C$_n$Me, it was found that the viscosities can be represented by Eq. 1 for concentrations up to about 0.1 mol dm^{-3}. However, successive studies of organic electrolytes with large values of viscosity *B* coefficients such as are used in this work revealed that the viscosities even in fairly dilute solutions cannot be described by Eq. 1; therefore the extended Jones-Dole equation with an extra term in c^2 was applied:

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

where D is a constant, whose significance is not completely understood. The A coefficient was interpreted theoretically by Falkenhagen and Vernon[8]; it can be calculated using the data of the limiting equivalent conductivities of the salt, the cation, and the anion. The electric conductivities of the aqueous solutions for bis(quaternary ammonium) salts as used in this work were interpreted in terms of 2-1 electrolytes by Fuoss and Chu[9] and Evans et al.[3,10] The A coefficient is fairly small numerically, and the contribution of the $Ac^{1/2}$ term to the viscosity is relatively small, in the solutions of such organic electrolytes with large B coefficients as are used in this work. The B coefficients are related to the ion-solvent interactions and to the size and shape of the ions, and are highly specific for the electrolytes and the temperature.

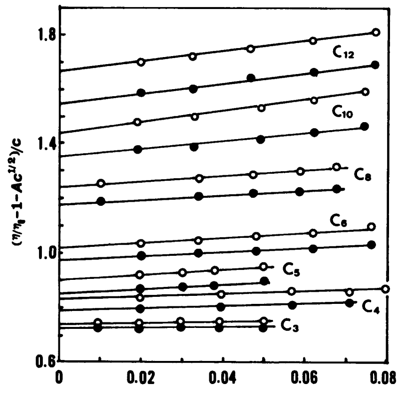

Fig. 1. Plots of $(\eta/\eta_0-1-Ac^{1/2})/c$ against c for EtC_nEt. ○: 25 °C, ●: 35 °C.

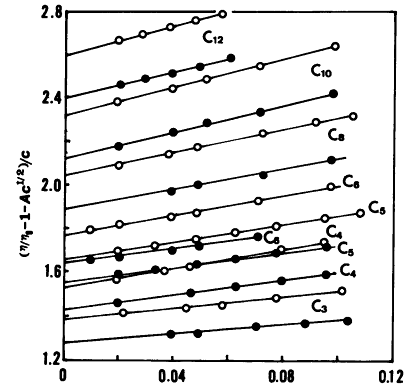

Fig. 2. Plots of $(\eta/\eta_0-1-Ac^{1/2})/c$ against c for PrC_nPr. ○: 25 °C, ●: 35 °C.

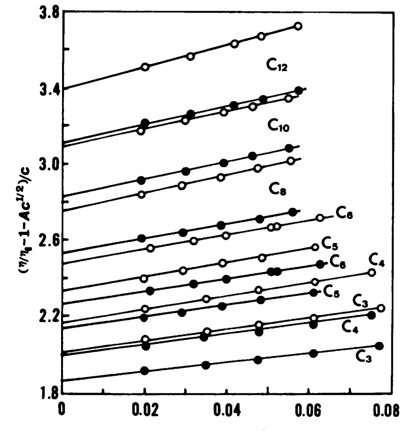

Fig. 3. Plots of $(\eta/\eta_0-1-Ac^{1/2})/c$ against c for BuC_nBu. ○: 25 °C, ●: 35 °C.

Equation 2 may be converted to:

$$(\eta/\eta_0-1-Ac^{1/2})/c = B + Dc. \tag{3}$$

When the left-hand side of Eq. 3 is plotted against c, the viscosity B coefficient is obtained as the intercept

Table 1. The Values of A and B

n		A		B	
		dm$^{3/2}$ mol$^{-1/2}$		dm^3 mol^{-1}	
	T/°C	25	35	25	35
		EtC_nEt			
3		0.0162	0.0167	0.740	0.728
4		0.0165	0.0170	0.826	0.794
5		0.0168	0.0173	0.905	0.857
6		0.0171	0.0176	1.018	0.968
8		0.0174	0.0178	1.242	1.168
10		0.0176	0.0180	1.440	1.348
12		0.0178	0.0183	1.660	1.542
		PrC_nPr			
3		0.0177	0.0179	1.347	1.273
4		0.0181	0.0186	1.530	1.433
5		0.0187	0.0191	1.652	1.541
6		0.0190	0.0193	1.770	1.636
8		0.0194	0.0197	2.045	1.890
10		0.0196	0.0199	2.313	2.120
12		0.0198	0.0200	2.602	2.398
		BuC_nBu			
3		0.0183	0.0191	2.015	1.860
4		0.0188	0.0195	2.162	1.998
5		0.0192	0.0199	2.330	2.142
6		0.0197	0.0203	2.472	2.272
8		0.0205	0.0212	2.770	2.538
10		0.0208	0.0217	3.090	2.827
12		0.0212	0.0221	3.410	3.107
		C_nEt			
1		0.0070	0.0072	0.275	0.261
2		0.0072	0.0073	0.337 0.333[12] 0.339[11]	0.316 0.322[12]
3		0.0074	0.0075	0.426	0.393
4		0.0075	0.0077	0.518	0.472
5		0.0077	0.0078	0.608	0.553
6		0.0079	0.0080	0.698	0.622
		C_nPr			
2		0.0079	0.0080	0.643	0.594
3		0.0082	0.0084	0.745 0.760[11]	0.675
4		0.0085	0.0086	0.837	0.761
5		0.0087	0.0089	0.938	0.845
6		0.0088	0.0090	1.055	0.938
		C_nBu			
2		0.0083	0.0085	0.955	0.864
3		0.0086	0.0088	1.066	0.971
4		0.0088	0.0090	1.162 1.148[11]	1.057
5		0.0090	0.0091	1.280	1.148
6		0.0092	0.0092	1.378	1.240

of a straight line. For example, Figs. 1—3 show the results of plotting Eq. 3 for EtC_nEt, PrC_nPr, and BuC_nBu respectively. The values of A and B for the electrolytes are summarized in Table 1. The B values for C_2Et, C_3Pr, and C_4Bu are in reasonable agreement with the literature values.[11,12] The B values for six homologous series of compounds increase approximately linearly with the number of carbon atoms in the polymethylene or alkyl group, n, respectively.

The Solute-Solvent Interaction. The temperature dependence of the B values is a factor of the solute-solvent interaction; the B values increase with the temperature for a solvent-structure-breaking salt, and decrease with the temperature for a solvent-structure-making solute.[13] For all the organic electrolytes used in this work, it may be seen in Table 1 that the B values decrease as the temperature is raised from 25 to 35 °C; therefore they may be considered to behave as structure-making salts in water.

Figure 4 shows the changes in the viscosity B coefficients which occur as the temperature is raised from 25 to 35 °C, ΔB, as a function of n for all the homologous series used in this work. The results for the MeC_nMe and C_nMe series reported in a previous paper[2] are also included in Fig. 4. It is found that the ΔB values generally decrease with n for each homologous series of electrolytes, and that the ΔB values for both bis(quaternary ammonium) compounds and the corresponding terminal mono(quaternary ammonium) compounds with the same number of n are in these orders: $BuC_nBu<PrC_nPr<EtC_nEt<MeC_nMe$ and $C_nBu<C_nPr<C_nEt<C_nMe$ respectively. If we take one-half the ΔB values for $[(C_mH_{2m+1})_3N(CH_2)_nN(C_mH_{2m+1})_3]Br_2$, the ΔB values for a series of $\text{-}(CH_2)_nN(C_mH_{2m+1})_3Br$ can be estimated. The ΔB vs. n relations thus obtained are plotted as dotted lines in Fig. 4. It may be seen that, for the same number of n, the ΔB values for $\text{-}(CH_2)_nN(CH_3)_3Br$ are larger than those of ΔB for C_nMe. This fact indicates the hydrophobic character of the polymethylene chain in MeC_nMe is considerably diminished as compared with that of the alkyl chain in C_nMe with the same number of n. Analogous results are still observed by a comparison of the ΔB values for the EtC_nEt and C_nEt series; the ΔB values for $\text{-}(CH_2)_nN(C_2H_5)_3Br$ are larger than those of C_nEt. It seems that two terminal $(C_2H_5)_3N^+$- groups situated at opposite ends of a chain may interfere with the interaction of a polymethylene group with water.

On the other hand, it may be seen from Fig. 4 that, for the same number of n, the ΔB values of $\text{-}(CH_2)_nN(C_3H_7)_3Br$ and $\text{-}(CH_2)_nN(C_4H_9)_3Br$ are nearly the same as those of C_nPr and C_nBu, respectively. In these cases, the hydrophobic hydration of propyl or butyl groups attached to the charge-bearing nitrogen atoms surpass the ionic hydration due to the ionic parts. Therefore, it seems that the hydrophobic characteristics of the polymethylene groups of the PrC_nPr and BuC_nBu series are comparable to those of the alkyl group of the corresponding mono(quaternary ammonium) salts.

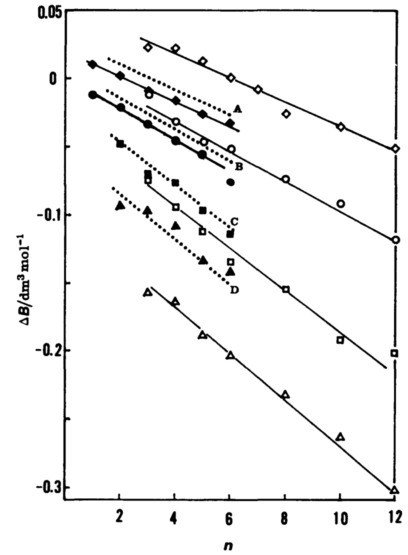

Fig. 4. Plots of ΔB against n.
◇: MeC_nMe, ◆: C_nMe, ○: EtC_nEt, ●: C_nEt, □ PrC_nPr, ■: C_nPr, △: BuC_nBu, ▲: C_nBu.
A: $\text{-}(CH_2)_nN(CH_3)_3Br$, B: $\text{-}(CH_2)_nN(C_2H_5)_3Br$, C: $\text{-}(CH_2)_nN(C_3H_7)_3Br$, D: $\text{-}(CH_2)_nN(C_4H_9)_3Br$.

The Viscosity *B* Coefficients of Ions. The viscosity B coefficients of electrolytes are considered to be determined by adding the individual contribution of the solute constituent ions. The ionic B values for the Br^- ion, derived according to the convention of Gurney[14] that the ionic B values for K^+ and Cl^- ions are equal, are -0.40 and $-0.26\ dm^3\ mol^{-1}$ at 25 and 35 °C respectively.[12] Therefore, the values of ΔB for all the organic ions used in this work become more negative than those of the corresponding salts, and the organic ions may also be classified as structure-making ions.

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