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Viscosity *B* Coefficients for Polymethylenebis(trimethylammonium) Dibromides in Aqueous Solutions

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Synopsis. The viscosity *B* coefficients of the Jones-Dole equation for *N,N'*-polymethylenebis(trimethylammonium) dibromides [$(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$ (n=3—8, 10, and 12) and for comparison for alkyltrimethylammonium bromides $C_nH_{2n+1}N(CH_3)_3Br$ (n=2—6) in aqueous solutions at 25 and 35 ° have been determined, and the effect of structural changes in the solvent water upon the dissolution of both series of electrolytes is discussed.

In a previous paper,[1] the balance of ionic hydration and hydrophobic hydration in aqueous solutions of *N,N'*-polymethylenebis(trimethylammonium) dibromides ([$(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$, which will be abbreviated as, MeC_nMe) were discussed on the basis of the changes in the heat capacity upon dissolution in water. In this paper, an experimental study of the viscosity *B* coefficients for a series of MeC_nMe and, for comparison, for a series of alkyltrimethylammonium bromides ($C_nH_{2n+1}N(CH_3)_3Br$, which will be abbreviated as C_nMe) in aqueous solutions will be reported.

Experimental

MeC_nMe except for MeC_7Me and C_nMe were the same samples as those described in a previous paper.[1] MeC_7Me was prepared by the reaction of 1,7-dibromoheptane with an excess of trimethylamine in ethanol, and was purified several times by recrytallization from ethanol. Water was triply distilled.

The viscosities were measured at 25 and 35 °C with 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.[2] The electrical conductivities were measured with a Yokogawa audio-frequency bridge using a frequency of 1000 Hz.

Results and Discussion

The Viscosity B *Coefficients of Electrolytes.* The viscosity of an aqueous solution of an electrolyte, η, can be represented by the Jones-Dole equation:

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

where η_0 is the viscosity of water, c is the molar concentration, A is a constant related to the ion-ion interaction, and B is the viscosity *B* coefficient. The constant A was interpreted theoretically by Falkenhagen and Vernon,[3] and can be calculated using the data of the limiting equivalent conductivities of the salt, cation, and anion. Equation 1 may be converted to,

$$\eta/\eta_0-1-Ac^{1/2}=Bc \tag{2}$$

When the left-hand side of Eq. 1, using the calculated values of A, is plotted against c, the viscosity B coefficient is obtained as the slope of a linear line. Figures 1 and 2 show the results of plotting Eq. 2 for MeC_nMe and C_nMe respectively. The values of A and B for both series of compounds are summarized in Table 1. The B values for C_2Me, C_4Me, and C_6Me are in reasonable agreement with the values reported by Tanaka *et al.*[4] The B values for both series of compounds increase approximately linearly with the number of carbon atoms in the polymethylene or alkyl group, n.

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 temperature for a solvent-structure-making solute.[5] For the MeC_nMe series, it may be seen in Table 1 that the B values for MeC_3Me and MeC_4Me increase as the temperature is

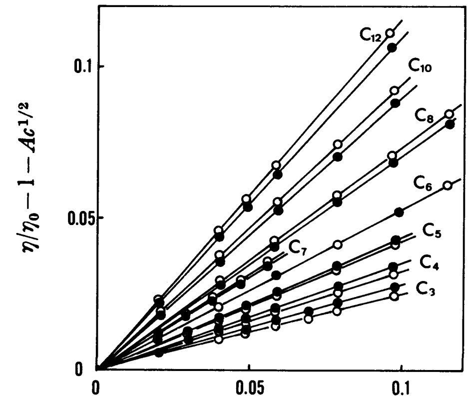

Fig. 1. Plots of $\eta/\eta_0-1-Ac^{1/2}$ against c for MeC_nMe. ○, 25 °C; ●, 35 °C.

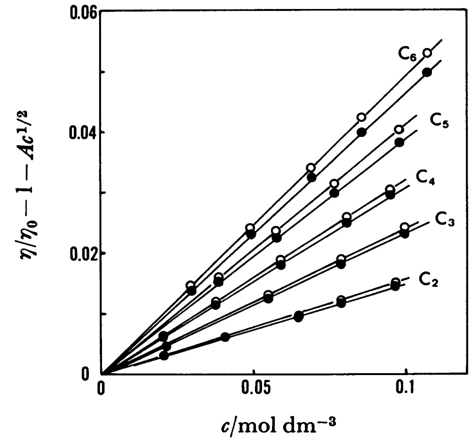

Fig. 2. Plots of $\eta/\eta_0-1-Ac^{1/2}$ against c for C_nMe. ○, 25 °C; ●, 35 °C.

Table 1. The values of A, B, and B_{ion}

n	A		B		B_{ion}	
	$dm^{3/2}\ mol^{-1/2}$		$dm^3\ mol^{-1}$		$dm^3\ mol^{-1}$	
T/°C	25	35	25	35	25	35
			$[(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$			
3	0.0143	0.0147	0.260	0.284	0.340	0.336
4	0.0146	0.0151	0.330	0.353	0.410	0.405
5	0.0150	0.0154	0.426	0.440	0.506	0.492
6	0.0154	0.0159	0.536	0.537	0.616	0.589
7	0.0158	0.0163	0.643	0.635	0.723	0.687
8	0.0162	0.0167	0.733	0.708	0.813	0.760
10	0.0167	0.0172	0.945	0.909	1.024	0.961
12	0.0170	0.0176	1.165	1.115	1.245	1.167
			$C_nH_{2n+1}N(CH_3)_3Br$			
1			0.076[a)]	0.087[a)]	0.116	0.113
2	0.0065	0.0067	0.151 0.16[b)]	0.148	0.191	0.174
3	0.0068	0.0070	0.239	0.229	0.279	0.255
4	0.0071	0.0073	0.326 0.31[b)]	0.310	0.366	0.336
5	0.0073	0.0075	0.414	0.388	0.454	0.414
6	0.0075	0.0077	0.494 0.45[b)]	0.461	0.534	0.487

a) Ref. 6; b) Ref. 4.

raised from 25 to 35 °C, and these salts may therefore be considered to behave as structure-breaking salts in the water phase. The B values of MeC$_6$Me are insensitive to the temperature. With MeC$_7$Me and higher homologs, the B values decrease with an increase in the temperature, therefore these salts exhibit a water-structure-making-effect. It was noted in previous work[1)] on the change of heat capacity upon dissolution that MeC$_6$Me exhibited a slight tendency to behave as a structure-making solute. The classification of the behavior of a salt in water is somewhat dependent on the experimental method adopted.

With the C$_n$Me series, viscometric studies of tetramethylammonium bromide $(CH_3)_4NBr$, abbreviated as C$_1$Me in this paper, have been reported by several investigators, and the results by Out and Los[6)] are included in Table 1. The B values for C$_1$Me increase with the temperature; this salt may be considered to act as a structure-breaking salt. The B values of C$_2$Me are insensitive to the temperature, and it seems to be a borderline salt. The B values for C$_3$Me and the higher homologs decrease with the temperature, and they are to be classified as hydrophobic structure-makers.

Figure 3 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 MeC$_n$Me and C$_n$Me. If we take one-half the values of ΔB for MeC$_n$Me, the values of ΔB for a series of $-(CH_2)_nN(CH_3)_3Br$ can be estimated. The ΔB *vs.* n relation thus obtained is plotted as a dotted line in Fig. 3. It is found that, for the same number of n, the values of ΔB for $-(CH_2)_nN(CH_3)_3Br$ are higher than those of ΔB for C$_n$Me. This fact indicates that the hydrophobic character of the polymethylene chain in MeC$_n$Me is considerably diminished as compared with that of the alkyl chain in C$_n$Me with the same number of n.

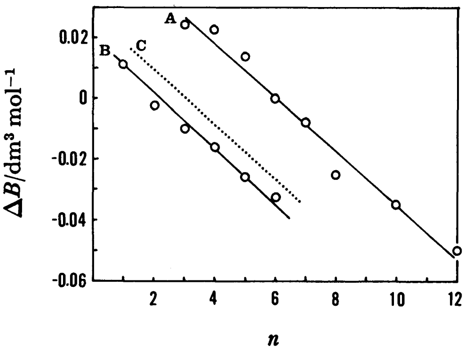

Fig. 3. Plots of ΔB aganist n. A, MeC$_n$Me; B, C$_n$Me; C, $-(CH_2)_nN(CH_3)_3Br$.

The Viscosity B *Coefficients of Ions.* The B values of electrolytes are determined by adding the individual contributions of the ions. Out and Los[6)] reported the ionic B values of the Br$^-$ ion as a function of temperature according to the convention of Gurney[7)] that the ionic B values for K$^+$ and Cl$^-$ ions are equal. The ionic B values of Br$^-$ ion[6)] are -0.040 and $-0.026\ dm^3\ mol^{-1}$ at 25 and 35 °C, respectively. The B values of organic ions obtained are included in Table 1. With the MeC$_n$Me^{2+} series, the ionic B values of MeC$_3$Me^{2+} and MeC$_4$Me^{2+} ions vary little with temperature. The ionic B values of MeC$_5$Me^{2+} and the higher homologous ions decrease with the temperature, so they are classified as structure-making ions. With the C$_n$Me series, the ionic B values of C$_1$Me$^+$ are practically constant between 25 and 35 °C. The B values of C$_2$Me$^+$ and the higher homologous ions decrease with the temperature, so they are classified as structure-making ions.

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