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Heats of Solution and Viscosity *B* Coefficients for Some Cyclic Mono- and Bis(quaternary ammonium) Salts

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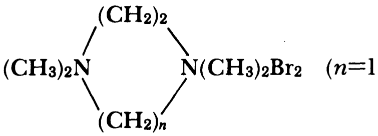
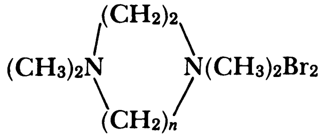
Synopsis. Heats of solution and viscosity *B* coefficients, for cyclic mono(quaternary ammonium) salts, $(CH_3)_2N(CH_2)_nBr$ (n=4—6) and cyclic bis(quaternary ammonium) salts,



(n=1—3) in water were measured, and the effect of structural changes in the solvent water upon the dissolution of both series of electrolytes is discussed.

In previous papers,[1,2] the balance of ionic hydration and hydrophobic hydration in aqueous solutions of *N,N′*-polymethylenebis(trimethylammonium) dibromides and alkyltrimethylammonium bromides was discussed on the basis of the change in the heat capacity upon dissolution in water and the temperature dependence of the viscosity *B* coefficients in aqueous solutions.

Noguchi and Rembaum[3–5] reported that, in the course of the synthetic studies of polyelectrolytes by the Menschutkin reaction between *N,N,N′,N′*-tetramethyl-α,ω-alkanediamines $(CH_3)_2N(CH_2)_xN(CH_3)_2$ (I) and α,ω-dibromoalkanes $Br(CH_2)_yBr$ (II), syntheses of polyelectrolytes were unsuccessful when the reaction systems with small values of x's and/or y's were carried out, and various linear and cyclic mono- and diammonium salts of low molecular weights were isolated. It seems that it would be of interest to study the solution properties of these low molecular weight compounds in water. We selected some cyclic mono(quaternary ammonium) salts $(CH_3)_2N(CH_2)_nBr$ (n=4—6; which will be abbreviated as NC_n[6]) and cyclic bis(quaternary ammonium) salts



(n=1—3; which will be abbreviated as NC_nC_2N[7]) from the products reported by Noguchi and Rembaum.[3–5] The experimental results will be reported on the heats of solution and the viscosity *B* coefficients of aqueous solutions of these five-, six-, and seven-membered cyclic mono- and bis(quaternary ammonium) salts in this paper.

Experimental

All the salts were prepared by the reaction of ditertiary amines (I) with dibromides (II) in acetonitrile at room temperature according to the procedure described by Noguchi and Rembaum.[3–5] After the solvent had been removed, the salts were purified several times by recrystallization from suitable solvents. The reaction system and the solvents for recrystallization are summarized in Table 1. As NC_1C_2N was obtained in poor yield by the method of Noguchi and Rembaum,[4] the iodide salt of NC_1C_2N was prepared by the reaction of *N*-methylpyrrolidine with methyl iodide in ethanol,[8] the product was then converted to the bromide salt using the anion-exchange resin. All the salts were dried in vacuo at room temperature for several days, and then analyzed for bromide ion by argentometric titration. The salts were found to have a purity greater than 99.3%. Water was triply distilled. The solutions were made by weight.

Table 1. Reaction System and the Solvents for Recrystallization

Compound	x–y Reaction	Solvent
NC_4	2-1	EtOH-water (12:1)
NC_5	1-2	EtOH-water (5:1)
NC_6	2-3	EtOH-water (7:1)
NC_1C_2N	1-4	EtOAc-EtOH (1:1)
NC_2C_2N	1-5	EtOAc-EtOH (1:1)
NC_3C_2N	1-6	EtOAc-EtOH (2:1)

The heats of solution were measured at 15, 25, and 35 °C using a twin isoperibol calorimeter, TIC-2C, of the Tokyo Riko Co., Ltd., by a method similar to that described in a previous paper.[9]

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 details of the procedure were described in a previous paper.[9] The electric conductivities were measured with an LCR meter, AG-4301B, of the Ando Electric Co., Ltd., using a frequency of 1000 Hz.

Results and Discussion

Heats of Solution. Heat-of-solution measurements were carried out in the concentration range of $(1.5—2.8)\times10^{-3}$ mol dm^{-3}. In this concentration range, any dependence of the heat of solution on the concentration is within the limit of experimental error, so the average of three or more measurements has been taken as the heat of solution at infinite dilution, ΔH_s^0. The ΔH_s^0 values of NC_n and NC_nC_2N in water are listed in Table 2. The ΔH_s^0 values were all endothermic, and the results from the ΔH_s^0 values were used to calculate the change in the heat capacity for dissolution at infinite dilution, ΔC_p^0:

$$\Delta C_p^0 = d\Delta H_s^0/dT, \qquad (1)$$

where T is the temperature. The ΔC_p^0 values obtained at 25 °C are also listed in Table 2.

The sign and magnitude of ΔC_p^0 can be taken as a relative measure of the structural effect upon the solvent water.[10,11] The ΔC_p^0 values of common salts

Table 2. Heats of Solution and Heat-Capacity Changes

n		ΔH_s^0/kJ mol^{-1}			ΔC_p^0/J K^{-1} mol^{-1}
	T/°C	15	25	35	25
			NC$_n$		
4		17.79±0.08	17.61±0.04	17.73±0.08	−3±6
5		18.80±0.09	19.03±0.03	19.20±0.10	20±7
6		14.92±0.10	15.47±0.05	16.18±0.07	63±6
			NC$_n$C$_2$N		
1		32.60±0.15	29.19±0.07	26.52±0.08	−304±9
2		52.42±0.21	49.52±0.25	47.10±0.28	−266±18
3		37.04±0.07	34.86±0.11	32.41±0.10	−231±6

indicate negative values, whereas the ΔC_p^0 values of hydrophobic solutes indicate positive values.

As may be seen in Table 2, the values of ΔH_s^0 of NC$_4$ are insensitive to the temperature, this means that ionic and hydrophobic hydration balance each other. In the case of NC$_5$ and NC$_6$, the ΔC_p^0 values become positive, and they are hydrophobic structure-makers. With the NC$_n$C$_2$N series, three salts showed the negative ΔC_p^0 values, though the magnitude of ΔC_p^0 become less negative as the number of carbon atoms in the methylene groups increases; they are water-structure-breakers. On comparing of the ΔC_p^0 values of NC$_n$ and NC$_n$C$_2$N in Table 2 with those of alkyltrimethylammonium bromides and *N,N′*-polymethylenebis(trimethylammonium) dibromides reported in a previous paper,[1] it is found that, for the same number of carbon atoms, the hydrophobicity of the cyclic mono- and bis(quaternary ammonium) salts is weaker than that of the linear mono- and bis(quaternary ammonium) salts respectively.

The Viscosity *B* Coefficients. The viscosity of an aqueous solution of an electrolyte, η, for concentrations up to about 0.1 mol dm^{-3} can be represented by the Jones-Dole equation:[12]

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

where η_0 is the viscosity of water, and A and B, the characteristic constants of the solutes. The A coefficient was interpreted theoretically by Falkenhagen and Vernon;[13] it can be calculated using the data of the limiting equivalent conductivities of the salt, the cation, and the anion. The B coefficient is related to the ion-solvent interaction and to the size and shape of the ion, and it is highly specific for the electrolyte and the temperature. Equation 2 may be converted to:

$$\eta/\eta_0 - 1 - Ac^{1/2} = Bc. \tag{3}$$

When the left-hand side of Eq. 3, using the calculated values of A, is plotted against c, the viscosity B coefficient is obtained as the slope of a straight line. Figures 1 and 2 show the results of plotting Eq. 3. The values of A and B are listed in Table 3. It is noted that the B values of cyclic mono- and bis(quaternary ammonium) salts studied in this work are smaller than those of respective mono- and bis(quaternary ammonium) salts with the same number of carbon atoms reported in a previous paper.[2] Previous experimental results of viscosity B coefficients at 25 °C are available for iodide salts of NC$_4$ (0.142 dm^3 mol^{-1})[14] and NC$_5$ (0.208 dm^3 mol^{-1}).[14]

The temperature dependence of the B values may be regarded as an index of the solute-solvent interaction;

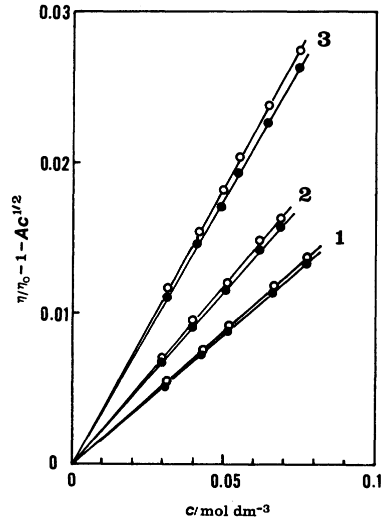


Fig. 1. Plots of $\eta/\eta_0-1-Ac^{1/2}$ against c for NC$_n$. 1, NC$_4$, 2, NC$_5$; 3, NC$_6$. ○, 25 °C; ●, 35 °C.

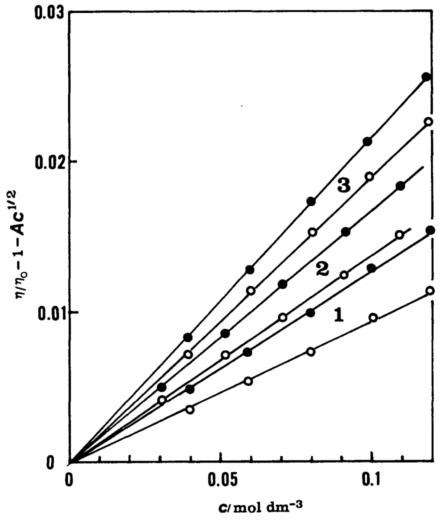


Fig. 2. Plots of $\eta/\eta_0-1-Ac^{1/2}$ against c for NC$_n$C$_2$N. 1, NC$_1$C$_2$N; 2, NC$_2$C$_2$N; 3, NC$_3$C$_2$N. ○, 25 °C; ●, 35 °C

Table 3. The Values of A, B, and B_{ion}

n		$A/\text{dm}^{3/2}\,\text{mol}^{-1/2}$		$B/\text{dm}^3\,\text{mol}^{-1}$		$B_{\text{ion}}/\text{dm}^3\,\text{mol}^{-1}$	
	$T/°\text{C}$	25	35	25	35	25	35
				NC_n			
4		0.0066	0.0068	0.177	0.175	0.217	0.201
5		0.0067	0.0070	0.238	0.230	0.278	0.256
6		0.0069	0.0071	0.368	0.354	0.408	0.380
				NC_nC_2N			
1		0.0131	0.0136	0.094	0.128	0.174	0.180
2		0.0132	0.0137	0.137	0.168	0.217	0.220
3		0.0135	0.0140	0.189	0.216	0.269	0.268

the B values increase with the temperature for a solvent-structure-breaking salt, while they decrease with temperature for a solvent-structure-making solute.[15] For the NC_n series, it may be seen in Table 3 that the B values decrease as the temperature is raised from 25 to 35 °C; these salts may be considered to behave as structure-making salts in the water phase. However, as the difference in the B values of NC_4 between 25 and 35 °C is small, NC_4 may therefore be considered to behave as a borderline salt. For all the salts of NC_nC_2N used, the B values increase as the temperature is raised from 25 to 35 °C; these salts may be classified as structure-breaking salts in the water phase.

The B values of electrolytes are determined by adding the individual contributions of the ions. Out and Los[16] reported the ionic B values, B_{ion}, of the Br^- ion as a function of temperature according to the convention of Gurney[17] that the B_{ion} values for K^+ and Cl^- ion are equal. The B_{ion} values of Br^- ion[16] are -0.040 and $-0.026\,\text{dm}^3\,\text{mol}^{-1}$ at 25 and 35 °C, respectively. The B_{ion} values of organic ions obtained are included in Table 3. With the NC_n^+ series, the B_{ion} values decrease with the temperature, so they are classified as structure-making ions. With the $NC_nC_2N^{2+}$ series, the B_{ion} values vary little with temperature. In this case the ionic hydration due to the two charge-bearing$>N(CH_3)_2^+$-groups may interfere with the interaction of hydrophobic-$(CH_2)_n$-groups with water. For both series of NC_n^+ and $NC_nC_2N^{2+}$ ions, the changes in the B_{ion} values, which occur as the temperature is raised from 25 to 35 °C, decrease with n; this indicates that hydrophobic hydration gradually increases with the number of methylene groups.

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