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Heats of Solution of Bolaform Electrolytes in Water. II. Polymethylenebis(trimethylammonium) Dibromides

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Synopsis. The heats of solution of polymethylenebis(trimethylammonium) dibromides $[(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$ (n=3—6, 8, 10, and 12) and alkyltrimethylammonium bromides $C_nH_{2n+1}N(CH_3)_3Br$ (n=2—6) in water were measured at 15, 25, and 35 °C. The hydrophobic character of the polymethylene groups was compared with that of alkyl groups on the basis of the changes in the heat capacity for dissolution, which were obtained from the relation between the heats of solution and the temperature.

In a previous paper,[1] the heats of solution for two series of bolaform electrolytes, polymethylenediammonium dichlorides and disodium polymethylene disulfates, in water were reported, and hydrophobic character of polymethylene groups in bolaform electrolytes was compared with that of alkyl groups for corresponding monovalent electrolytes, alkylammonium chlorides and sodium alkyl sulfates, respectively. The present paper is the extension of the previous work, and the heats of solution for a series of polymethylenebis(trimethylammonium) dibromides ($[(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$, which will be abbreviated as, MeC$_n$Me) and for comparison for a series of alkyltrimethylammonium bromides ($C_nH_{2n+1}N(CH_3)_3Br$, which will be abbreviated as, C$_n$Me) in water will be reported. The changes in the heat capacity for dissolution in water, $\Delta C_p°$, for MeC$_n$Me and C$_n$Me were obtained from the relation between the heats of solution and the temperature, and the hydrophobic character of the polymethylene groups in MeC$_n$Me was compared with that of the alkyl group in C$_n$Me.

Experimental

Materials. MeC$_n$Me were prepared by the reactions of the α,ω-dibromoalkane with an excess of trimethylamine in ethanol.[3] The salts, except for MeC$_{12}$Me, were purified several times by recrystallization from ethanol. MeC$_{12}$Me was recrystallized from an ethyl acetate–ethanol solution. C$_n$Me were prepared by the reactions of alkyl bromides with an excess of trimethylamine in ethanol. The salts were recrystallized several times from ethanol. All the salts were dried *in vacuo* at room temperature for several days, and were analyzed for bromide ion by argentometric titration. All the salts were found to have a purity greater than 99.6%. Water was triply distilled.

Calorimetry. The heats of solution were measured by a method similar to that described in previous papers.[1,2]

Results and Discussion

Heat-of-solution measurements have been carried out over the concentration range of 8×10^{-4}—3×10^{-3} mol dm^{-3}. In this concentration range, any dependence of the heats of solution on the concentration is within the limit of experimental error, so the average of three or more measurements was taken as the heats of solution at infinite dilution, $\Delta H_s°$. The $\Delta H_s°$ values of MeC$_n$Me and C$_n$Me are listed in Table 1. The $\Delta H_s°$ values were used to calculate the changes in the heat capacity, $\Delta C_p°$, in going from the pure compounds to an aqueous solution at infinite dilution:

Table 1. Heats of solution and heat-capacity change

n	$\Delta H_s°$/kJ mol^{-1} 15 °C	25 °C	35 °C	$\Delta C_p°$/J K^{-1} mol^{-1} 25 °C
	$C_nH_{2n+1}N(CH_3)_3Br$			
2	17.11	17.15	16.95	0
3	9.43	10.12	10.77	67
4	9.65	10.54	11.49	92
5	18.44	20.47	22.40	198
6	11.06	13.59	16.31	262
	$[(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$			
3	21.70	19.97	18.47	−162
4	25.84	24.87	24.00	−92
5	27.05	26.77	26.76	−14
6	31.01	31.56	32.07	53
8	27.14	28.94	30.58	172
10	24.87	27.91	30.80	297
12	38.04	42.15	46.69	433

$$\Delta C_p° = \mathrm{d}\Delta H_s°/\mathrm{d}T,$$

where T is the temperature. The magnitude and sign of $\Delta C_p°$ can be taken as relative measure of the solute-solvent interaction.[4—6] The $\Delta C_p°$ values of simple salts indicate negative values, whereas the $\Delta C_p°$ values of hydrophobic solutes indicate positive values.

The $\Delta C_p°$ values obtained at 25 °C are listed in Table 1. As may be seen in Table 1, for the MeC$_n$Me series, MeC$_3$Me, MeC$_4$Me, and MeC$_5$Me show the negative $\Delta C_p°$ values. Therefore, the electrostrictive hydration due to the charge-bearing groups $-N(CH_3)_3^+$ may interfere with the interaction of the hydrophobic $-(CH_2)_n-$ group of the lower homologs with water. In the case of MeC$_6$Me and larger MeC$_n$Me homologs, the $\Delta C_p°$ values become positive and they increase with an increase in the chain length. They are classified as hydrophobic structure-makers.

With the C$_n$Me series, the $\Delta C_p°$ value for tetramethylammonium bromide ($(CH_3)_4NBr$, abbreviated as C$_1$Me in this paper) was reported to be −42 J K^{-1} mol^{-1} by Sarma, Mohanty, and Ahluwalia[7] and −47 J K^{-1} mol^{-1} by Arnett and Campion.[4] Table 1 indicates that the $\Delta H_s°$ values of C$_2$Me are virtually independent of the temperature, for which electro-

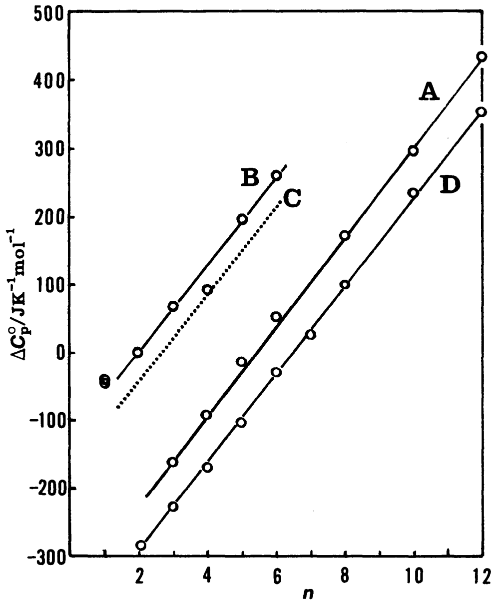

Fig. 1. Plot of ΔC_p° against n. A: $[(CH_3)_3N(CH_2)_nN(CH_3)_3]Br_2$, B: $C_nH_{2n+1}N(CH_3)_3Br$, C: $-(CH_2)_nN(CH_3)_3Br$, D: $[H_3N(CH_2)_nNH_3]Cl_2$.

strictive and hydrophobic hydration balance each other. In the case of C3Me and higher homologs, the ΔC_p° values become positive, and they are hydrophobic structure-makers.

The ΔC_p° values are plotted against the number of carbon atoms, n, in the polymethylene or alkyl group for MeC$_n$Me and C$_n$Me in Fig. 1. If we take one-half the ΔC_p° values for MeC$_n$Me, the ΔC_p° values for a series of $-(CH_2)_nN(CH_3)_3Br$ can be estimated. The ΔC_p° *vs.* n relation thus obtained is plotted as a dotted line in Fig. 1. It is found that for the same number of n, the ΔC_p° values for $-(CH_2)_nN(CH_3)_3Br$ are lower than those for C$_n$Me. With the same ΔC_p° values, the difference in n between the two ΔC_p°-*vs.*-n lines for C$_n$Me and $-(CH_2)_nN(CH_3)_3Br$ corresponds to about 0.8. Therefore, the hydrophobic character of the polymethylene chain in MeC$_n$Me is considerably diminished below that of alkyl chain in monovalent C$_n$Me salts with the same number of n.

In Fig. 1, a plot of the ΔC_p° values against n for polymethylenediammonium dichlorides reported in a previous paper[1)] is also included. For the same number of n, the ΔC_p° values for MeC$_n$Me are larger by about 75 J K^{-1} mol^{-1} than those for polymethylenediammonium dichlorides. This may be mainly attributed to the hydrophobic effect of the methyl groups attached to the two terminal nitrogen atoms, because the difference in ΔC_p° values due to the variation in halide ions for the same cations is very small.[6)]

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