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Heats of Solutions of Bolaform Electrolytes in Water

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Synopsis. The heats of solutions of polymethylenediammonium dichlorides $[H_3N(CH_2)_nNH_3]Cl_2$ (n=2—8, 10, and 12) and disodium polymethylene disulfates $Na_2[O_3SO(CH_2)_nOSO_3]$ (n=2—6, 8, and 10) in water were measured at 15, 25, and 35 °C. The changes in the heat capacity for dissolution, $\Delta C_p°$, were obtained from the relation between the heats of soultion and the temperature, and the results were compared with the $\Delta C_p°$ values for alkylammonium chlorides and sodium alkyl sulfates previously reported.

The physical properties of amphiphilic electrolytes in water have been discussed in terms of the resultant change in the water structure upon the introduction of ions into water. Nonpolar groups, such as alkyl groups and polymethylene groups, act as water-structure makers in water; that is, the water molecules form an icelike structure around the nonpolar groups. The study of the heat capacities of aqueous electrolyte solutions provides a useful method of obtaining information about the influence of ions on the structure of solvent water. In previous papers,[1,2] the results on the changes in the heat capacity for the dissolution in water, $\Delta C_p°$ for a series of alkylammonium chlorides (C_nH_{2n+1} NH_3Cl, which will be abbreviated as C_nCl) and sodium alkyl sulfates ($C_nH_{2n+1}OSO_3Na$, which will be abbreviated as, NaC_n) were reported. In this paper, the experimental results regarding the heats of solution and the $\Delta C_p°$ values for polymethylenediammonium dichlorides ($[H_3N(CH_2)_nNH_3]Cl_2$, which will be abbreviated as, C_nCl_2) and disodium polymethylene disulfated ($Na_2[O_3SO(CH_2)_nOSO_3]$, which will be abbreviated as, Na_2C_n) will be reported. This type of electrolyte, in which an ionic part is attached at each end of the chain, is called a bolaform eletrolyte. The main object of this paper is to compare the hydrophobic character of the polymethylene group in a bolaform electrolyte with that of the alkyl group for a monovalent electrolyte.

Experimental

Materials. The organic chemicals used were obtained from the Tokyo Kasei Kogyo Co., Ltd. C_7Cl_2, C_8Cl_2, $C_{10}Cl_2$, and $C_{12}Cl_2$ were prepared by the neutralization of the corresponding diamines in methanol with hydrochloric acid, and the solvents were evaporated to dryness. All the C_nCl_2 salts were recrystallizaed twice from ethanol–water solutions and dried *in vacuo* at room temperature. Na_2C_n salts were synthesized by the esterification of the corresponding alcohols by the use of concentrated sulfuric acid in cabon tetrachloride or chloroform below 15 °C. After removing the carbon tetrachloride or chloroform, the solutuions were neutralized with a concentrated solution of sodium hydroxide. The reaction mixtures were dried in air and extracted with ethanol–water solutions (about 60% ethanol). The products were further purified several times by recrystallizing them from ethanol–water solutions (about 80% ethanol) and then dried *in vacuo* at 100 °C. Water was triply distilled.

TABLE 1. HEATS OF SOLUTION AND HEAT-CAPACITY CHANGES

n	$\Delta H_s°$/kJ mol^{-1} 15 °C	25 °C	35 °C	$\Delta C_p°$/J K^{-1} mol^{-1} 25 °C
		$[H_3N(CH_2)_nNH_3]Cl_2$		
2	31.21	28.24	25.48	−287
3	27.53	25.19	22.97	−228
4	26.69	24.98	23.30	−170
5	9.62	8.45	7.53	−105
6	22.84	22.51	22.26	−29
7	20.63	20.84	21.17	27
8	22.89	23.89	24.89	100
10	29.58	32.01	34.31	237
12	40.88	44.31	47.91	352
		$Na_2[O_3SO(CH_2)_nOSO_3]$		
2	27.93	25.69	23.60	−217
3	10.70	8.87	7.35	−167
4	30.49	29.51	28.63	−93
5	22.36	21.92	21.50	−43
6	20.60	20.94	21.08	24
8	23.36	24.80	25.99	132
10	37.09	39.76	42.61	276

Calorimetry. The heats of solution in water were measured at 15, 25, and 35 °C with a twin isoperibol calorimeter TIC-2C, manufactured by the Tokyo Riko Co., Ltd. The sample and blank ampoules were, respectively, set in the measuring and reference Dewar vessels, each containing 200 cm^3 of water, resting in depressions in an aluminum block controlled to ±0.01 °C. After thermal equilibrium had been attained, the sample and blank ampoules were broken simultaneously. The difference in temperature measured by a pair of thermistors was recorded on a chart recorder. The calorimeter was checked by measuring the heat of solution of potassium chloride at 25 °C. The value obtained was within 1% of that reported in the literature.[3]

Results and Discussion

Heat-of-solution measurements have been carried out in the concentration range of 6×10^{-4}—2.5×10^{-3} mol dm^{-3}. In this concentration range, any dependence of the heat of solution on the concentration is within the limits of experimental error, so the average of three or more measurements has been taken as the heat of solution at an infinite dilution, $\Delta H_s°$. The $\Delta H_s°$ values of C_nCl_2 and Na_2C_n are listed in Table 1. Results from the $\Delta H_s°$ values were used to calculate the change in the heat capacity in going from the pure compounds to an aqueous solution at an infinite

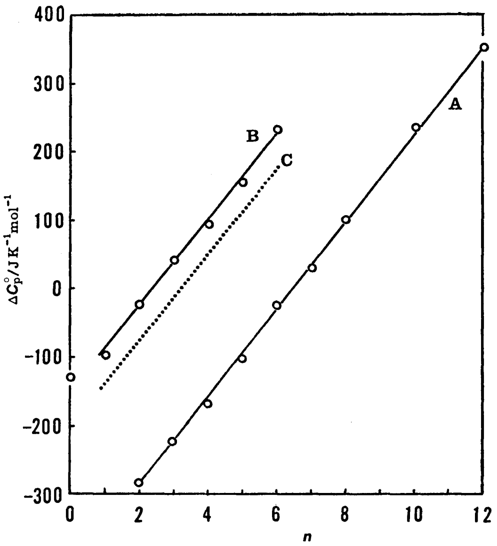

Fig. 1. Plot of ΔC_p° against n. A, $[H_3N(CH_2)_nNH_3]Cl_2$; B, $C_nH_{2n+1}NH_3Cl$; C, $-(CH_2)_nNH_3Cl$.

dilution, ΔC_p°;

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

where T is the temperature. The ΔC_p° values obtained at 25 °C are also listed in Table 1. The magnitude and sign of ΔC_p° can be taken as relative measures of the structural effect upon the solvent water.[1,4,5] The ΔC_p° values of simple salts indicate negative values, whereas the ΔC_p° values of hydrophobic solutes indicate positive values.

As may be seen in Table 1, the ΔC_p° values for C_2Cl_2, C_3Cl_2, C_4Cl_2, C_5Cl_2, and C_6Cl_2 are negative, while the ΔC_p° values become positive in the case of C_7Cl_2 and higher homologs. In an earlier work[1] on C_nCl series, C_1Cl and C_2Cl showed negative values of ΔC_p°, while C_3Cl and higher homologs showed positive values of ΔC_p°. Figure 1 shows the ΔC_p° values as a function of the number of carbon atoms, n, in the polymethylene or alkyl group for C_nCl_2 and C_nCl. If we take one-half the ΔC_p° values for C_nCl_2, the ΔC_p° values for a series of $-(CH_2)_nNH_3Cl$ 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 carbon atoms, the ΔC_p° values for $-(CH_2)_nNH_3Cl$ are lower than those for C_nCl. With the same ΔC_p° values, the difference in n between the two ΔC_p°-*vs.-n* lines for C_nCl and $-(CH_2)_nNH_3Cl$ corresponds to about 0.8.

Table 1 indicates that the ΔC_p° values for Na_2C_2, Na_2C_3, Na_2C_4, and Na_2C_5 are negative, while the ΔC_p° values for Na_2C_6 and higher homologs are positive. In a previous paper[2] on a NaC_n series, NaC_1 showed a negative value of ΔC_p°, while NaC_3 and higher homologs showed positive ΔC_p° values. Figure 2 shows the ΔC_p° values as a function of n for Na_2C_n and NaC_n. The dotted line in Fig. 2 represents the data for a $-(CH_2)_nOSO_3Na$ series. With the same ΔC_p° values, the differnce in n between the two ΔC_p°-*vs.-n* relations for NaC_n and $-(CH_2)_nOSO_3Na$ corresponds to about 0.7.

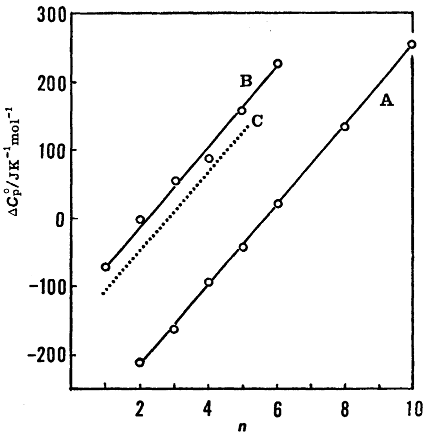

Fig. 2. Plot of ΔC_p° against n. A, $Na_2[O_3SO(CH_2)_nOSO_3]$; B, $C_nH_{2n+1}OSO_3Na$; C, $-(CH_2)_nOSO_3Na$.

With bolaform electrolytes, the electrostrictive hydration due to the two ionic parts situated at opposite ends of a chain may interfere with the interaction of the hydrophobic polymethylene chain with water, and the smaller members of both series of C_nCl_2 and Na_2C_n are water-structure-breaking ions. When the charged groups are sufficiently far apart, the solvent-structuring effect of the hydrophobic polymethyene chain becomes important. However, the hydrophobic character of the polymethylene chain in bolaform electrolytes is considerably diminished as compared with that of the alkyl chain in monovalent electrolytes.

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References

1) K. Tamaki, S. Yoshikawa, and M. Kushida, *Bull. Chem.Soc.Jpn.*, **48**, 3018 (1975).

2) K. Tamaki, Y. Isomura, and Y. Ōhara, *Bull. Chem. Soc. Jpn.*, **45**, 2939 (1972).

3) G. Somsen, J. Coops, and M. W. Tolk, *Recl. Trav. Chim. Pays-Bas*, **82**, 231 (1963).

4) E. M. Arnett and J. J. Campion, *J. Am. Chem. Soc.*, **92**, 7097 (1970).

5) B. Chawla and J. C. Ahluwalia, *J. Solution Chem.*, **4**, 383 (1975).