Temperature Dependence of Viscosity *B* Coefficients for Disodium α,ω-Alkanedisulfonates and Disodium α,ω-Alkanediyl Disulfates in Aqueous Solutions

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Synopsis. The viscosity *B* coefficients for aqueous solutions of disodium α,ω-alkanedisulfonates $NaO_3S(CH_2)_nSO_3Na$ (n=2, 4, 6—8, 10, and 12) and disodium α,ω-alkanediyl disulfates $NaO_3SO(CH_2)_nOSO_3Na$ (n=2, 4, 6, 8, and 10) have been determined at 15, 25, and 35 °C. The effect of structural changes in the solvent water upon the dissolution of these amphiphilic electrolytes is discussed.

A series of measurements of the temperature dependence of the viscosity *B* coefficients for amphiphilic organic electrolytes in aqueous solutions has been performed in this laboratory in order to obtain information concerning the behavior of organic ions in water.[1—6] This paper is concerned with the temperature dependence of viscosity *B* coefficients for disodium α,ω-alkanedisulfonates $NaO_3S(CH_2)_nSO_3Na$ (n=2, 4, 6—8, 10, and 12) and disodium α,ω-alkanediyl disulfates $NaO_3SO(CH_2)_nOSO_3Na$ (n=2, 4, 6, 8, and 10). The main object of this paper is to compare the effect of the $-SO_3^-$ ionic parts with that of the $-OSO_3^-$ ionic parts on the ion-solvent interaction of amphiphilic organic electrolytes in water.

Experimental

Materials. $NaO_3S(CH_2)_2SO_3Na$ and $NaO_3S(CH_2)_4SO_3Na$ were commercial products of Tokyo Kasei Kogyo Co., Ltd., and were recrystallized from ethanol–water solutions. The other disodium α,ω-alkanedisulfonates were prepared by the Strecker method.[7] α,ω-Dibromoalkanes (Tokyo Kasei Kogyo Co., Ltd.) were refluxed with a saturated water solution of sodium sulfite at 100 °C for several days, after which the reaction mixtures were dried in air. The sodium salts were extracted with ethanol–water solutions (about 70% ethanol) and further purified by repeated recrystallization from ethanol–water solutions until the salts were free from the Br^- ion. All of the salts were dried in vacuo at 100 °C for several days. Disodium α,ω-alkanediyl disulfates were the same samples as described in a previous paper.[8] Water was triply distilled.

Viscosity Measurements. The viscosities were measured at 15, 25, and 35 °C using an automatic viscosimeter (SS-290S, 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.[1] The electric conductivities were measured with an LCR meter (AG-4301B, of the Ando Electric Co., Ltd.) at a frequency of 1000 Hz.

Results and Discussion

The viscosity of dilute electrolyte solutions (η) can be related to the extended Jones–Dole[9] equation,

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

where η_0 is the viscosity of the solvent, c is the molar concentration, and A, B, and D are constants. The A coefficient was theoretically interpreted by Falkanhagen and Vernon;[10] it can be calculated using the data of the limiting equivalent conductivities of the salt, cation, and anion. The B coefficients are related to the ion–solvent interactions and to the size and shape of the ions; they are highly specific for the electrolytes and temperature. The significance of the D coefficient is not completely understood.

Equation 1 may be converted to

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

When the left-hand side of Eq. 2 is plotted against c, the viscosity B coefficient is obtained as the intercept of a straight line. The limiting molar conductivities required for the calculation of the A values in Eq. 2 were obtained from measurements of the electric conductivities for aqueous solutions of these salts. The $Ac^{1/2}$ factor in Eq. 2 is relatively small, and the A values are insensitive to the variation in the temperature in the range of 15—35 °C; therefore, the values of A calculated using the limiting molar conductivities at 25 °C were also used for the A values at 15 and 35 °C. For example, Figs. 1 and 2 show the results of plotting Eq. 2 at 25 °C for $NaO_3S(CH_2)_nSO_3Na$ and $NaO_3SO(CH_2)_nOSO_3Na$, respectively. The values of A and B for both series of electrolytes are summarized in Table 1. The B values for these homologous series of compounds are all positive, and increase approximately linearly with the number of carbon atoms in the polymethylene group (n), respectively.

The solute–solvent interaction of amphiphilic organic electrolytes in water is determined by the balance of the two different modes of hydration (ionic hydration and hydrophobic hydration). In our previous paper,[11] it was found that both the $-SO_3^-$ and $-OSO_3^-$ ionic parts may be classified as water-structure-breakers. The temperature dependence of the B values is a factor of the solute–solvent interaction; the B values increase with the temperature for a water-structure-breaking salt, and decrease with the temperature for a water-structure-making solute.[12] The viscosity B coefficients listed in Table 1 are naturally made up of the sum of

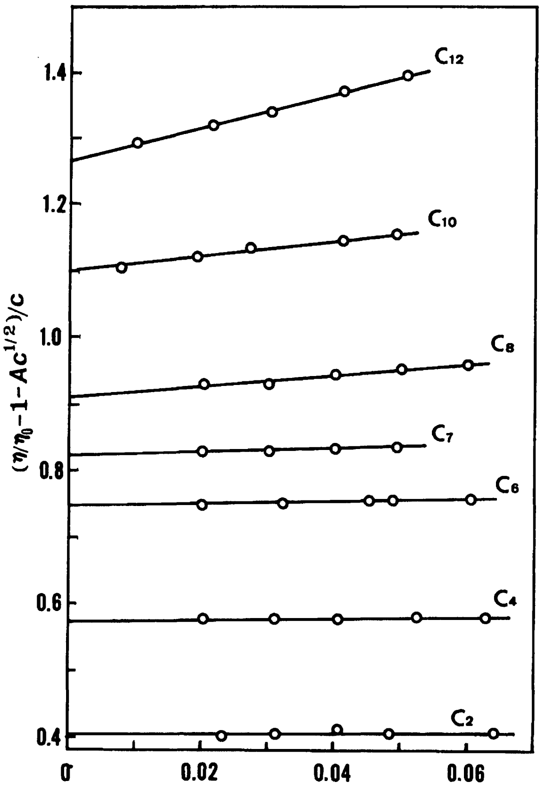

Fig. 1. Plots of $(\eta/\eta_0-1-Ac^{1/2})/c$ against c at 25 °C for $NaO_3S(CH_2)_nSO_3Na$.

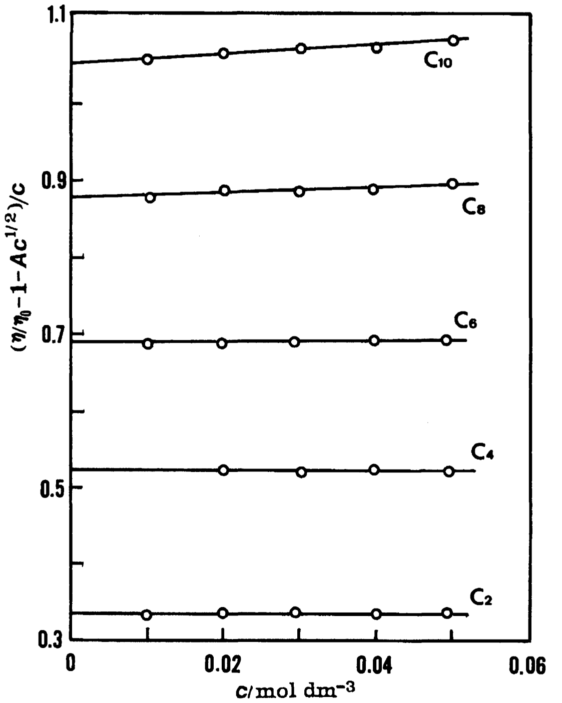

Fig. 2. Plots of $(\eta/\eta_0-1-Ac^{1/2})/c$ against c at 25 °C for $NaO_3SO(CH_2)_nOSO_3Na$.

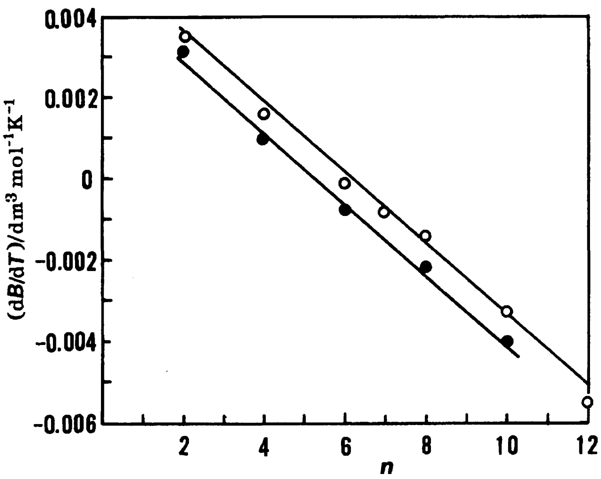

Fig. 3. Plots of dB/dT against n. ○, $NaO_3S(CH_2)_nSO_3Na$; ●, $NaO_3SO(CH_2)_nOSO_3Na$.

Table 1. The Values of A, B, and dB/dT

n	A	B			dB/dT
	$dm^{3/2}$ $mol^{-1/2}$	dm^3 mol^{-1}			dm^3 mol^{-1} K^{-1}
T/°C		15	25	35	25
		$NaO_3S(CH_2)_nSO_3Na$			
2	0.0160	0.375	0.405	0.445	0.0035
4	0.0187	0.558	0.574	0.590	0.0016
6	0.0202	0.760	0.748	0.750	−0.0001
7	0.0209	0.830	0.825	0.815	−0.0008
8	0.0213	0.928	0.910	0.900	−0.0014
10	0.0217	1.140	1.100	1.075	−0.0033
12	0.0219	1.320	1.265	1.210	−0.0055
		$NaO_3SO(CH_2)_nOSO_3Na$			
2	0.0170	0.298	0.336	0.361	0.0032
4	0.0179	0.514	0.526	0.534	0.0010
6	0.0191	0.700	0.692	0.685	−0.0008
8	0.0202	0.905	0.878	0.862	−0.0022
10	0.0216	1.105	1.056	1.025	−0.0040

the contributions from sodium and organic ions. Fortunately, the B values of sodium ion are insensitive to the temperature.[13] Therefore, the temperature dependences of the viscosity B coefficients of the sodium salts conveniently reflect the nature of the organic ions.

For the disulfonate series, $NaO_3S(CH_2)_nSO_3Na$, it may be seen in Table 1 that the B values for the salts with n=2 and 4 increase as the temperature is raised from 15 to 35 °C. This implies that the interaction of the $-SO_3^-$ ionic part with water surpasses hydrophobic hydration due to the ethylene or tetramethylene group; thus, the overall behavior of these electrolytes in water is governed by ionic hydration. The B values of the n=6 salt are insensitive to the temperature. With this salt, the contributions of the two types of hydration (ionic and hydrophobic) seem to cancel each other out. With the n=7 salt and higher homologs, the B values decrease with an increase in the temperature. In this case, conversely, the interaction of the polymethylene group with water surpasses the ionic hydration due to the ionic parts; consequently, these salts exhibit water-structure-making solutes. On the other hand, for the disulfate series, $NaO_3SO(CH_2)_nOSO_3Na$, the B values for the salts with n=2 and 4 increase with the temperature; these salts may be considered to act as structure-breaking salts. The B values for the n=6 salt and the higher homologs decrease with the temperature, and should be classified as hydrophobic structure-makers.

The facts discussed above indicate that the $-SO_3^-$ ionic part is considerably more hydrophilic than the $-OSO_3^-$ ionic part. The temperature dependence of the viscosity B coefficients at 25 °C (dB/dT) are also listed in Table 1. In Fig. 3 the dB/dT values are plotted against n for both series. It is found that, for the same number of n, the dB/dT values for the disulfonate series are higher than those for the disulfates series; the hydrophobic character of the disulfonates is diminished compared with that of disulfates with the same number of n. It is interesting to note that the dB/dT value of $NaO_3SO(CH_2)_6OSO_3Na$ corresponds to that of $NaO_3S(CH_2)_7SO_3Na$, as shown in Table 1.

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