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The Physicochemical Properties of Aqueous Solutions of Sodium Alkanesulfonates. Apparent Molar Volumes, Viscosity *B* Coefficients, Heats of Solution, and Surface Tensions

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The apparent molar volumes, viscosity *B* coefficients, heats of solution, and surface activity of sodium alkanesulfonates (RSO_3Na, methyl to hexyl) in water were measured. The limiting apparent molar volumes at 25 °C increase with the number of carbon atoms in the alkyl chain; the increment per methylene group is about 16 $cm^3\,mol^{-1}$. The viscosity *B* coefficients of $MeSO_3Na$ and $EtSO_3Na$ increase with the temperature, while those of *n*-$BuSO_3Na$ decrease with an increase in the temperature. The changes in heat capacity for dissolution in water, ΔC_p°, as calculated from the heats of solution at 15, 25, and 35 °C, were negative for $MeSO_3Na$ and $EtSO_3Na$, while the ΔC_p° values for *n*-$PrSO_3Na$ and higher homologs were positive. $MeSO_3Na$ raises the surface tension of water, while $EtSO_3Na$ and higher homologs reduce it. The structural changes in the solvent water upon the dissolution of sodium alkanesulfonates are discussed in comparison with those of sodium alkyl sulfates previously reported.

The behavior of amphiphilic organic ions in water may be interpreted approximately in terms of a balance of two types of interaction: hydrophobic hydration due to the nonpolar parts, and electrostrictive hydration due to the ionic parts.[1] Both sodium alkanesulfonates (RSO_3Na) and sodium alkyl sulfates ($ROSO_3Na$) are typical amphiphilic organic electrolytes. The temperature dependence of the heats of solution and the viscosity *B* coefficients for a homologous series of $ROSO_3Na$ were reported in previous papers.[2,3] In this paper, experimental results will be reported on the apparent molar volumes, viscosity *B* coefficients, heats of solution, and surface activity of a series of RSO_3Na in water. The main object of this work is to compare the role of the alkyl group of RSO_3Na in the structural influence in water with that of $ROSO_3Na$ previously reported.

Experimental

Materials. The organic chemicals used were commercial products from the Tokyo Kasei Kogyo Co., Ltd. Sodium methane- and ethanesulfonates were prepared by the neutralization of the corresponding sulfonic acids with a solution of sodium hydroxide, after which the water was evaporated to dryness. The sodium salts were twice recrystallized from ethanol–water solutions. The other sodium alkanesulfanates were synthesized by the Strecker method.[4] Alkyl bromides were refluxed with a saturated water solution of sodium sulfite for several days, after which the mixtures were dried in air. The sodium salts were extracted with ethanol and then further purified by repeated recrystallization from ethanol–water solutions until the salts obtained were free from Br^- ion. All the products of sodium alkanesulfonates were subjected to air-drying under a relative humidity of 50%. Analysis using an electrobalance showed that sodium methanesulfonate was anhydrous, while the other ethane-, 1-propane-, 1-butane-, 1-pentane-, and 1-hexanesulfonates were exactly monohydrates. The monohydrate samples were very stable in air. The conversion from monohydrate salts to anhydrous salts was found to be very troublesome, especially for $EtSO_3Na$; therefore, the monohydrate samples were used for the measurements for density, viscosity, and surface tension. Sodium alkyl sulfates used for the measurements of the surface tension were the same samples as were employed in previous studies.[2,3] Water was triply distilled.

Density Measurement. The densities were measured using a vibrating-tube densimeter, twin-type SS-D-200, manufactured by the Shibayama Scientific Co., Ltd. Two measuring vessels were immersed in a water bath with a capacity of about 40 dm^3 controlled to ±0.002 °C. One of the measuring vessels was used for the density measurement of a solution; the other measuring vessel was used for monitoring the density of water. The apparatus constant of the meter was determined using water and dry air as standard substances; their densities were taken from the literature.[5]

Viscosity Measurement. The viscosities were measured with an automatic viscometer manufactured by the Shibayama Scientific Co., Ltd. The flow times of Ubbelohde-type viscometers were about 250 s at 25 °C for water, measuring to 0.01 s. The viscosity, η, was calculated from the average flow time, t, and the density, ρ, based on the equation:

$$\eta = \rho k_1(t-k_2/t). \tag{1}$$

The k_1 and k_2 constants were determined from the measurements for water at 25 and 40 °C. The viscosity values of water at these temperature were taken from the literature.[6]

Calorimetry. The heats of solution of the anhydrous salts in water were measured at 15, 25, and 35 °C with a twin isoperibol calorimeter TIC-2C, manufactured by the Tokyo Riko Co., Ltd. To obtain anhydrous samples, all the salts were dried *in vacuo* at 100 °C for several days. The glass ampoules filled with samples were further dried *in vacuo* at 100 °C for about 6 h and then sealed. 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, as 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.[7]

Surface-tension Measurement. The surface tensions were measured at 25±0.01 °C by means of the drop-volume method using a micrometer syringe, similar to that described in a previous paper.[8]

Results and Discussion

Apparent Molar Volumes. The apparent molar volumes, ϕ_v, in $cm^3 mol^{-1}$ were calculated from the densities using the following equation:

$$\phi_v = \frac{1}{m}\left(\frac{1000+mM}{\rho} - \frac{1000}{\rho_0}\right), \tag{2}$$

where m is the molal concentration in $mol\,kg^{-1}$; M, the molar mass in $g\,mol^{-1}$, and ρ_0 and ρ, the densities in $g\,cm^{-3}$ of water and of a solution respectively. The solutions were made by weight. When the sample of $RSO_3Na \cdot H_2O$ was dissolved in water, the quantity of the water was made equal to the total of the weighed quantity of water in a weighing bottle plus the liberated water from the weighed quantity of solid $RSO_3Na \cdot H_2O$; the quantity of the latter was calculated from the chemical formula. The apparent molar volume of electrolytes is given by the equation:9)

$$\phi_v = \phi_v{}^\circ + A_v c^{1/2} + B_v c, \tag{3}$$

where $\phi_v{}^\circ$ is the limiting value, which is identical with the partial molar volume at an infinite dilution; A_v and B_v, the constants, and c, the molar concentration in $mol\,dm^{-3}$. The value of constant A_v is 1.868 $cm^3\,dm^{3/2}\,mol^{-3/2}$ for water at 25 °C;9) the relation $\phi_v - 1.868\,c^{1/2}$ *versus* c for a series of RSO_3Na is shown in Fig. 1. The values of $\phi_v{}^\circ$ and B_v are given in Table 1. It is found that the $\phi_v{}^\circ$ values increase as the alkyl-chain length increases and that the increments in the $\phi_v{}^\circ$ values per methylene group from $EtSO_3Na$ to higher homologs are about 16 $cm^3\,mol^{-1}$; this value corresponds approximately to the value of other homologous compounds, such as alkanoates and alkylammonium salts.10–13) The B_v values of RSO_3Na are found to decrease with an increase in the number of carbon atoms, as is shown in Table 1; this fact is in accord with the results for other homologous compounds.10–13)

Table 1. Limiting apparent molar volumes of RSO_3Na at 25 °C

RSO_3Na	$\phi_v{}^\circ/cm^3\,mol^{-1}$	$B_v/dm\,cm^3\,mol^{-2}$
Methyl	53.99 53.88a)	0
Ethyl	69.31 71.56a)	−1.15
Propyl	85.08	−1.9
Butyl	101.08	−2.25
Pentyl	117.02	−2.7
Hexyl	132.98	−2.8

a) Ref. 11.

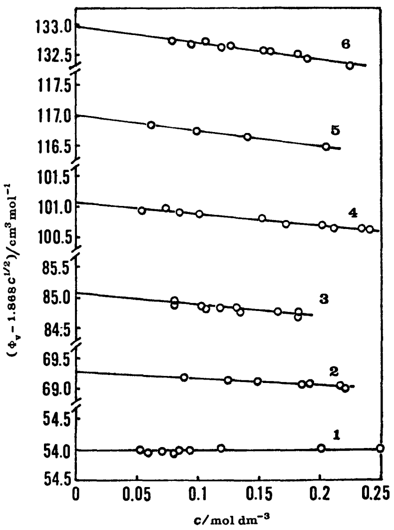

Fig. 1. Apparent molar volumes of RSO_3Na at 25 °C. 1, methyl; 2, ethyl; 3, propyl; 4, butyl; 5, pentyl; 6, hexyl.

Viscosity. The viscosities of RSO_3Na at 25 °C were reported in a previous paper.1) In this work, the temperature dependence of the viscosity B coefficients for RSO_3Na (methyl to butyl) were reinvestigated by means of a more elaborate apparatus. The viscosity of aqueous electrolyte solution is given by the Jones-Dole equation:13)

$$\eta/\eta_0 = 1 + A_\eta c^{1/2} + B_\eta c, \tag{4}$$

where η_0 and η are the viscosity of water and the solution respectively; A_η, the constant arising from the interaction between the ions, and B_η, the viscosity B coefficient, which is interpreted in terms of a specific solute-solvent interaction. Equation 4 may be converted to:

$$(\eta/\eta_0 - 1)/c^{1/2} = A_\eta + B_\eta c^{1/2}. \tag{5}$$

For example, Fig. 2 shows the results of the plotting

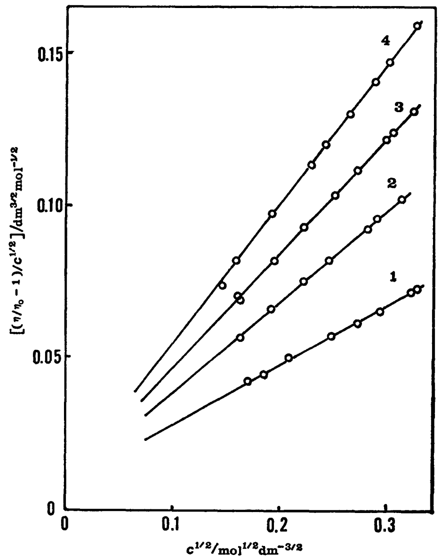

Fig. 2. Plot of $(\eta/\eta_0 - 1)/c^{1/2}$ against $c^{1/2}$ for RSO_3Na at 25 °C. 1, methyl; 2, ethyl; 3, propyl; 4, butyl.

Table 2. Viscosity $B/dm^3\,mol^{-1}$ coefficients of RSO_3Na

RSO_3Na	25 °C	40 °C
Methyl	0.198	0.208
Ethyl	0.304	0.310
Propyl	0.383	0.383
Butyl	0.468	0.436

of Eq. 5 at 25 °C. The B_η values obtained at 25 and 40 °C are summarized in Table 2. It may be seen in Table 2 that the B_η values for $MeSO_3Na$ and $EtSO_3Na$ increase with the temperature and that the B_η values of n-$PrSO_3Na$ are insensitive to the temperature. With n-$BuSO_3Na$, the B_η values decrease with an increase in the temperature. In a previous work[3] on the viscosity of $ROSO_3Na$ solutions, it was found that $MeOSO_3Na$ showed a slight increase in the B_η values with the temperature and that the B_η values of n-$PrOSO_3Na$ decreased slightly with an increase in the temperature. Kay *et al.*,[14] reported an increase in the B_η values with the temperature for a solvent-structure-breaking salt such as tetramethylammonium salt and a decrease in the B_η values with an increase in the temperature for a solvent-structure-making salt such as tetrapropyl- and tetrabutylammonium salts. On comparing the viscosity B coefficients of RSO_3Na with those of $ROSO_3Na$, it is found that the hydrophobicity of RSO_3Na is weaker than that of $ROSO_3Na$.

Heat of Solution. Heat-of-solution measurements were carried out in the concentration range of (1—5) × 10^{-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 an infinite dilution, ΔH_s°. The ΔH_s° values of anhydrous RSO_3Na in water are listed in Table 3. The ΔH_s° values at 25 °C reported in the literature[15,16] are also included in Table 3. The ΔH_s° values obtained in this work are slightly more positive than those reported by Krishnan and Friedman.[16] Results from the ΔH_s° values were used to calculate the change in the heat capacity for dissolution at an infinite dilution, ΔC_p°:

$$\Delta C_p^\circ = d\Delta H_s^\circ/dT, \tag{6}$$

where T is the temperature. The results for ΔH_s° were represented by the equation:

$$\Delta H_s^\circ = a + bT + cT^2, \tag{7}$$

and by:

$$\Delta C_p^\circ = b + 2cT, \tag{8}$$

where a, b, and c are the experimental constants; the ΔC_p° values obtained at 25 °C are also listed in Table 3. As may be seen in Table 3, $MeSO_3Na$ and $EtSO_3Na$ show negative ΔC_p° values, while n-$PrSO_3Na$ and higher homologs show the positive ΔC_p° values, which increase with the number of carbon atoms in the alkyl chain. In an earlier work[2] on a series of $ROSO_3Na$, $MeOSO_3Na$ showed only the negative value of ΔC_p° and $EtOSO_3Na$ showed insensitive ΔH_s° values with an increase in the temperature. Further, n-$PrOSO_3Na$ and higher homologs showed positive ΔC_p° values. Figure 3 shows the ΔC_p° values as a function of the number of carbon atoms in the alkyl chain of both the RSO_3Na and $ROSO_3Na$ series. The magnitude and sign of ΔC_p° can be taken as a relative measure of the structural effect upon the solvent water.[17,18] The ΔC_p° values of simple salts indicate negative values, whereas the ΔC_p° values of hydrophobic solutes indicate positive values.[18] Therefore, the results (Table 3 and Fig. 3) indicate that the hydrophobic effect of RSO_3Na is weaker than that of $ROSO_3Na$.

TABLE 3. HEATS OF SOLUTION AND HEAT-CAPACITY CHANGES OF RSO_3Na

RSO_3Na	ΔH_s°/kJ mol^{-1}			ΔC_p°/J K^{-1} mol^{-1}
	15 °C	25 °C	35 °C	25 °C
Methyl	7.87	6.92 6.95[a] 6.40[b]	6.17	−85
Ethyl	−2.82	−3.16 −3.60[b]	−3.48	−33
Propyl	−6.13	−5.84 −6.19[b]	−5.63	25
Butyl	0.08	0.93 0.84[b]	1.77	85
Pentyl	−3.59	−2.24 −2.68[b]	−0.97	131
Hexyl	−0.96	0.62 0.25[b]	2.53	175

a) Ref. 15. b) Ref. 16.

Surface Tension. In this paper, the change in the surface tension, $\Delta\sigma$, is defined as:

$$\Delta\sigma = \sigma_0 - \sigma, \tag{9}$$

where σ_0 and σ are the surface tension of water and a solution respectively. Figure 4 shows the change in the surface tension of aqueous solutions of RSO_3Na as a function of the logarithmus of the molar concentration. It may be seen that $MeSO_3Na$ raises the surface tension of pure water, whereas $EtSO_3Na$ and higher homologs reduce the surface tension of water. For comparison, the results[19] for $ROSO_3Na$ presented earlier are shown in Fig. 5. In this case, all the salts represent the surface-active property. The shape of the surface tension-*versus*-concentration curve for an organic salt in aqueous solutions is considered to give a rough criterion of the behavior of the salt in water; simple salt raises the surface tension of water, whereas hydrophobic salts reduce it.[21] In a previous paper[21] on the surface tension of a series of alkylammonium chlorides in aqueous solutions, ethylammonium chloride

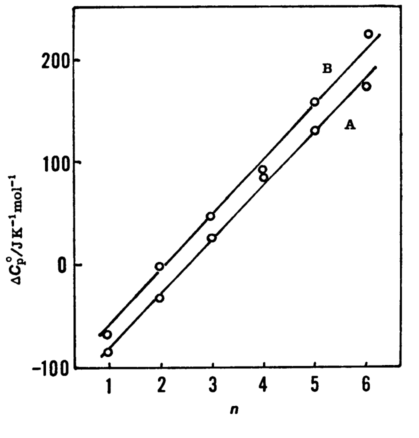

Fig. 3. Plot of ΔC_p° against number of carbon atoms in the alkyl chain, n. A, RSO_3Na; B, $ROSO_3Na$.

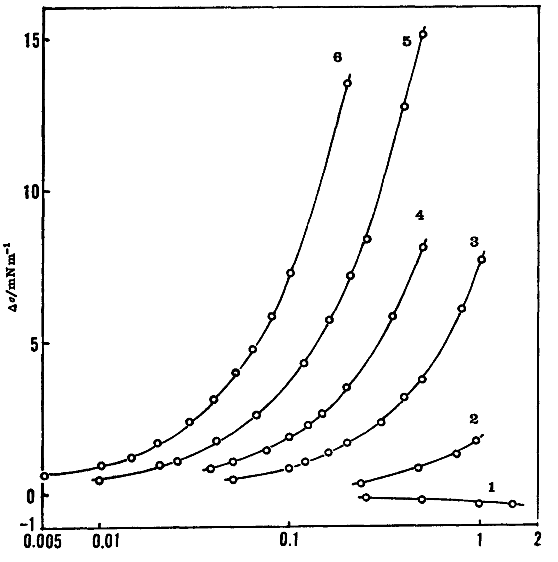

Fig. 4. Change in surface tension as a function of log *c* for RSO_3Na. 1, methyl; 2, ethyl; 3, propyl; 4, butyl; 5, pentyl; 6, hexyl.

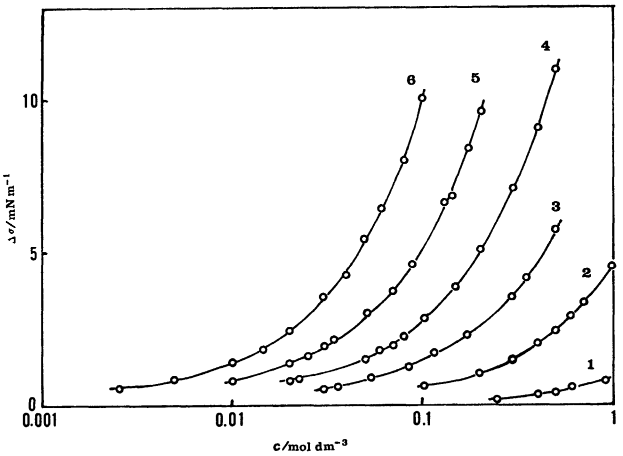

Fig. 5. Change in surface tension as a function of log *c* for $ROSO_3Na$. 1, methyl; 2, ethyl; 3, propyl; 4, butyl; 5, pentyl; 6, hexyl.

exhibited a weak surface-active property, while this salt was classified as a weak structure-breaker from the measurement of ΔC_p°.[18] This inclination must be kept in mind when one makes any remark about the behavior of salts in water on the basis of the surface-tension data alone. Nevertheless, as may be seen in Figs. 4 and 5 it is obvious that the surface activity of RSO_3Na in water is rather weaker than that of $ROSO_3Na$.

In order to compare the strength of the surface activity for homologous compounds, the Traube factors are obtained using the $\Delta\sigma$ values *versus* the molar concentration curves shown in Figs. 4 and 5. The Traube factor means the ratio of the molar concentrations of equal $\Delta\sigma$ values when the chain of an aliphatic compound is lengthened by one methylene group. The Traube factors are found to be about 2 for the homologous compounds from n-$PrSO_3Na$ to n-$C_6H_{13}SO_3Na$ as well as for those from n-$PrOSO_3Na$ to n-$C_6H_{13}OSO_3Na$ inclusive. This is a characteristic feature of a homologous series of surface-active electrolytes with one alkyl chain.[22]

General Considerations. The classification of the behavior of amphiphilic electrolytes in water is dependent on the experimental method adopted and its interpretation. One should be particularly cautious about the classification when the absolute values of the structural measure are rather small. In general, from the experimental results obtained in this work it may be concluded that the hydrophobic character of RSO_3Na is slightly reduced compared with that of $ROSO_3Na$. In the case of $ROSO_3Na$ studied earlier, $MeOSO_3Na$ is a simple salt, $EtOSO_3Na$ is a borderline solute, and n-$PrOSO_3Na$ and higher homologs are hydrophobic structure-makers. On the other hand, in the case of RSO_3Na studied in this work, $MeSO_3Na$ and $EtSO_3Na$ may be classified as simple salts; n-$PrSO_3Na$, as a borderline or a weak hydrophobic structure-maker, and n-$BuSO_3Na$ and higher homologs, as excellent hydrophobic structure-makers. In this connection, Klevens[23] pointed out that all straight-chain saturated surface-active agents of equal chain length have approximately the same critical micelle concentrations, and that C_{12} sulfonate and C_{11} sulfate belong to the same C_{12} family. In this case, the chain length was measured from the hydrogen of the ultimate carbon to the charged atom at the hydrophilic end of the alkyl chain. From the results of experiments with ΔC_p°, shown in Fig. 3, it is found that the solvent-structure-making effect of the extra –O– group in $ROSO_3Na$ is comparable to about a half of that of a methylene group.

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