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Solution Behavior of Sodium Dodecyl Sulfate in Methanol

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The electric conductivities of sodium dodecyl sulfate (SDS) in methanol and water were measured at 298 K in a concentration range up to 10 mmol dm^{-3}. The values of the limiting molar conductivities of SDS, Λ_0, in methanol and water were estimated to be 81.5 and 74.0 S cm^2 mol^{-1}, respectively, and compared with each other. From those values and the values of NaCl in both solvents, the limiting molar conductivities of dodecyl sulfate ion in methanol and water were estimated to be 36.27 and 23.90 S cm^2 mol^{-1}, respectively. Also, the vapor-pressure depression of SDS in methanol was measured at 298 K in the concentration range up to 42 mmol kg^{-1}. From the results, and according to the theory regarding strong electrolytes, the mean ionic activity coefficient, $\gamma_\pm$, of SDS in methanol at 298 K was calculated. Further, the solubility and heat of solution of SDS in methanol at various temperatures and at 298 K, respectively, were measured. From a thermodynamic analysis of these results, the theoretical relation between ln $\gamma_\pm$ and m was obtained over the range of temperatures 285—295 K.

The behavior of amphiphilic electrolytes in non-aqueous environments is very interesting and should be further studied in the fields of material science related to biological systems, such as pharmaceutical science. As a typical amphiphilic electrolyte, sodium dodecyl sulfate (SDS) has widely been used in these fields, yielding some important results in terms of its physico-chemical properties in various media akin to biological environments.[1-6] However, the measurements and analyses so far performed have been insufficient, both quantitatively and qualitatively, for elucidating the nature of amphiphilic electrolytes in biological systems. To contribute some basic data to the above-mentioned fields of study, we have measured the physico-chemical properties of SDS in various alcohols as non-aqueous media and compared the results with those in water, some of which were previously reported.[7] In the first stage of our study, using methanol as a non-aqueous medium, we measured the electrolytic conductivity and vapor-pressure depression of a methanol solution of SDS, as well as the solubility and heat of solution of SDS in methanol, and analyzed the results according to the theories for strong electrolytes.

Experimental

Materials. SDS was purchased from Wako Pure Chemical Ind., Ltd. (biochemical use), purified by recrystallizing twice from distilled 1-butanol, washed with petroleum ether in a Soxhlet's extractor for 20 h, and dried in a vacuum for 50 h at room temperature.

Sodium chloride (NaCl) and triphenylmethane were obtained from Wako Pure Chemical Ind., Ltd. (special grade). Triphenylmethane was recrystallized twice from distilled ethanol, and dried in a vacuum.

Methanol was obtained from Wako Pure Chemical Ind., Ltd. (special grade), distilled after refluxing for 1 h on calcium (Wako Pure Chemical Ind., Ltd., assay: 99%), stored under nitrogen gas, and redistilled on calcium before use.

For expressing the composition of each solution, we generally adopted the molality of solute [mol kg^{-1}], although the solutions used in the electric conductivity measurements were prepared and expressed in terms of the molar concentration of SDS [mol dm^{-3}].

Apparatuses and Procedures. (1) Measurement of Electrolytic Conductivity: A digital conductivity meter, CM-50AT of TOA Electronics, Ltd., was used to measure the electrolytic conductivity of SDS/methanol and SDS/water systems at 298 K. As the conductivity probe, we used an immersion-type, CG-201P1 (TOA Electronics, Ltd.; 1×10^{-4}—10 S m^{-1}), which was calibrated with a 0.01 mol dm^{-3} KCl aq solution. The probe was inserted through the acrylic resin lid into a glass cell containing the solution; the cell was then sealed with paraffin to prevent any penetration of atmospheric moisture during the measurements. The electrolytic conductivity of distilled methanol and purified water were less than 2×10^{-5} S m^{-1} and 1×10^{-4} S m^{-1}, respectively.

(2) Measurement of the Vapor-Pressure Depression: An osmometer, 117-type Molecular Weight Apparatus of Corona, Ltd., was used to measure the vapor-pressure depression of SDS/methanol, NaCl/methanol, and triphenylmethane (reference)/methanol solutions at 298 K.

(3) Determination of the Solubility vs. Temperature Relationship: The solubility of SDS in methanol vs. the temperature relation was determined through a sort of "cloud point method" by measuring the saturation temperatures, T_c, of the SDS/methanol systems with various compositions, as follows. Certain precisely weighed amounts of SDS and methanol were together put into a glass cell (ca. 30 cm^3) with an acrylic resin lid. A conductivity probe (CG-7001PL; 1×10^{-5}—1 S m^{-1}), which was connected to the digital conductivity meter (mentioned before) and a thermometer (±0.05K) were inserted through the lid into the cell; the cell was then sealed with paraffin. After perfectly dissolving SDS by heating, we rapidly cooled the cell until SDS precipitated in fine crystals. The cell was then immersed in a bath thermostated at 278 K; the sample in the cell was continuously agitated by a magnetic stirrer at ca. 1000 rpm (tip-length; 15 mm, diameter; 5 mm). After one hour, the temperature of the system was increased at a rate of ca. 0.2—0.3 K min^{-1} by heating until the temperature became over ca. 10 K, at which point the crystals in the cell became perfectly

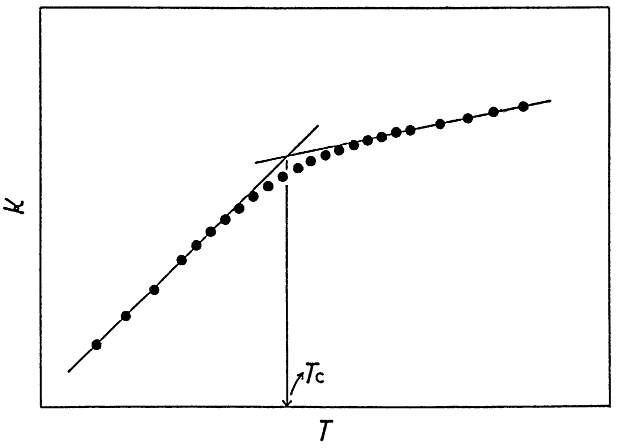

Fig. 1. Schematic electrolytic conductivity of SDS/methanol system, κ, vs. temperature, T, plot: for T_c, see text.

dissolved. During the above-mentioned heating, stirring was continued and the electrolytic conductivity, κ, of the system was measured at 0.2—0.5 K intervals. The value of T_c was estimated from the bend of a κ vs. temperature plot, as shown in Fig. 1. Often, another bend was found before reaching T_c, reflecting a change of the system from a partially solidified mass to a finely dispersed suspension. Regardless of the preceding bend, an artifact, the system was found to always be in a fine dispersion before T_c. Under continuous increasing of the temperature, a delay in the dissolution of crystals might have occurred, resulting in an error for the estimation of T_c. Therefore, measurements of κ vs. temperature under step-by-step heating, in which the isothermal state for each measurement of κ was kept for ca. 30 min after an increase of 0.2—0.5 K in temperature with 0.2—0.3 K min^{-1} heating, were carried out for a comparison of some of the same samples as those used in measurements under continuous heating. The results of both kinds of measurements were slightly different from each other and the value of T_c estimated under continuous heating was higher (although by less than ca. 0.2 K) than that under step-by-step heating, which would (in principle) be the more precise procedure. However, for the sake of simplicity, we chose a continuous-heating procedure. The values of T_c, thus obtained, were considered to be sufficiently reliable in a practical sense. From measurements of T_c for the given compositions of samples, we could determine the inverse relation, that is, the solubilities (in molality) of SDS at various temperatures.

(4) Measurement of Heat of Solution: A twin-type condution microcalorimeter (CM-204D1 of Rhesca Co., Ltd.) with an auxiliary amplifier (Micro Volt Meter AM-1001 of Okura Electric Co., Ltd.) was used to measure the endothermic heat of solution at 298 K. A given amount of SDS sealed in an ampoule was dissolved into 40 g of methanol in the calorimeter by breaking the ampoule; the endothermic heat of solution, ΔH, was then measured on a recorder (CR-101 of Rikadenki Kogyo Co., Ltd.).

Results and Discussion

1. The Value of cmc for SDS in Water.

From the molar electric conductivity vs. the square root of the concentration relationship, the value of cmc for SDS at the time of purchase was determined to be 8.0 mmol dm^{-3} in an aqueous solution at 298 K. After purification (as mentioned in the preceding section), the value of cmc became 8.23 mmol dm^{-3}. The latter value was within the range of values reported in the literature.[8—10] Also, taking into consideration our observation that the minimum, which was found in the surface tension vs. concentration plot for an intact sample, substantially disappeared after purification, we concluded that the reliability of our purification procedure was sufficient for this work.

2. Analysis of Molar Conductivity.

In order to elucidate the ionic behavior of SDS in methanol, we measured and analyzed its electric conductivity at various concentrations at 298 K. Also, the electric conductivity of SDS in water was measured for a comparison. The molar conductivity, Λ, vs. the square root of the concentration of SDS, $\sqrt{C}$, plots in methanol (solid circles) and water (empty circles) are shown in Fig. 2.

First, the results of SDS in water below cmc were analyzed in the usual way for simple electrolytes by

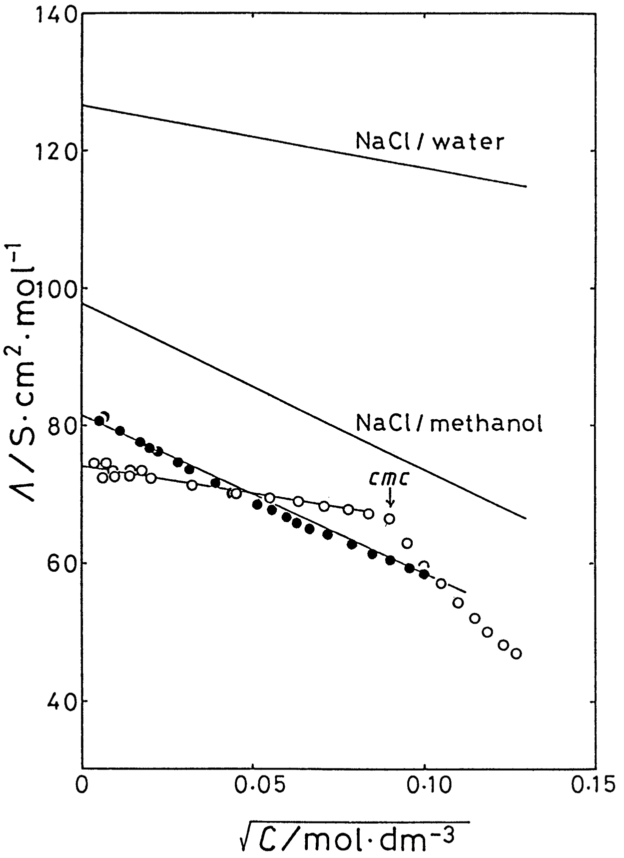

Fig. 2. Molar conductivity, Λ, vs. square root of solute concentration, $\sqrt{C}$, plots at 298 K: (●) SDS in methanol; (○) SDS in water; (——) theoretical lines drawn according to Eq. 1 with the value of Λ_0 shown in Table 1.

neglecting the hydrophobic nature of SDS, although this neglect might give a sort of apparent, or empirical, nature to the parameters adopted in the analysis. Thus, the values of Λ were approximately formulated, according to Onsager's theory:[11]

$$\Lambda=\Lambda_0-(B_1\cdot\Lambda_0+B_2)\cdot\sqrt{C}\,, \qquad (1)$$

where Λ_0 is the limiting molar conductivity of SDS in water, and B_1 and B_2 are parameters used in Debye-Hückel theory. A theoretical plot of Λ vs. $\sqrt{C}$ in water, which was drawn according to Eq. 1 in the concentration range below cmc, is shown in Fig. 2 as a solid line. The adopted value of Λ_0 was 74.0 $\mathrm{S\,cm^2\,mol^{-1}}$ (Table 1).

Since the dielectric constant of methanol (2.88×10^{-10} $\mathrm{F\,m^{-1}}$ at 298.15 K) is of the same order as that of water (6.93×10^{-10} $\mathrm{F\,m^{-1}}$ at 298.15 K), the property of methanol as the medium for SDS would be regarded as the same as that of water, although a hydrophobic interaction in methanol is considered to be less significant than in water from a comparison of solvent structure between both media. Thus, we analyzed the electric conductivity of SDS in methanol in a similar manner as water, according to Eq. 1. The theoretical line for methanol is shown by the solid line in Fig. 2. The value of Λ_0 was 81.5 $\mathrm{S\,cm^2\,mol^{-1}}$ (Table 1).

We next analyzed the values of Λ_0 for SDS in water and methanol on based on the knowledge of the values for NaCl. In Fig. 2 we show theoretical plots of Λ vs. $\sqrt{C}$ for NaCl in water and methanol, which were obtained on the basis of published data,[12] as can be seen in Table 1. The variation of Λ_0 with a different medium in Table 1 can be attributed to the difference of medium viscosity, η, and Stokes' ionic radius, $r_{\mathrm{s,i}}$,[11] since Λ_0 is the sum of the limiting molar conductivities of ions, $\lambda_{\mathrm{o,i}}$, and the value of $\lambda_{\mathrm{o,i}}$ for each ionic species is related to η and $r_{\mathrm{s,i}}$, as follows:

$$\lambda_{\mathrm{o,i}}=F\cdot e/6\pi\cdot r_{\mathrm{s,i}}\cdot\eta, \qquad (2)$$

where F is the Faraday constant and e is the protonic charge. The case for water was then examined. For NaCl, the literature values[11] of $\lambda_{\mathrm{o,Na^+}}$ and $\lambda_{\mathrm{o,Cl^-}}$ are known, as shown in Table 1. Since the value of $\lambda_{\mathrm{o,Na^+}}$ for SDS must be the same as that for NaCl, the value of $\lambda_{\mathrm{o,DS^-}}$ was obtained by subtracting $\lambda_{\mathrm{o,Na^+}}$ for NaCl (Table 1) from Λ_0 of SDS. By using Eq. 2 we obtained the value of $r_{\mathrm{s,DS^-}}$ in water, which is of apparent nature owing to the non-spherical structure with a non-polar moiety of the $\mathrm{DS^{-1}}$ ion. Similarly, the values of $\lambda_{\mathrm{o,DS^-}}$ and $r_{\mathrm{s,DS^-}}$ in methanol were calculated. It was reasoned from a comparison of the values in Table 1 that a significant decrease of Λ_0 for NaCl on substituting methanol for water as solvent can mainly be attributed to an increase in $r_{\mathrm{s,Cl^-}}$, while the increase of Λ_0 for SDS on the same substitution can be attributed to a decrease of the medium viscosity from 0.890 to 0.541 mPa s at 298.15 K.

3. Solution Behavior of SDS in Methanol from the Vapor-Pressure Depression Measurements. The results of vapor-pressure depression measurements at 298 K are shown in Fig. 3. In the concentration range up to 42 $\mathrm{mmol\,kg^{-1}}$, where our measurements were carried out without much error, a plot of ΔV (reading of vapor-pressure depression) vs. the molality of SDS, m, overlapped a plot for NaCl without any

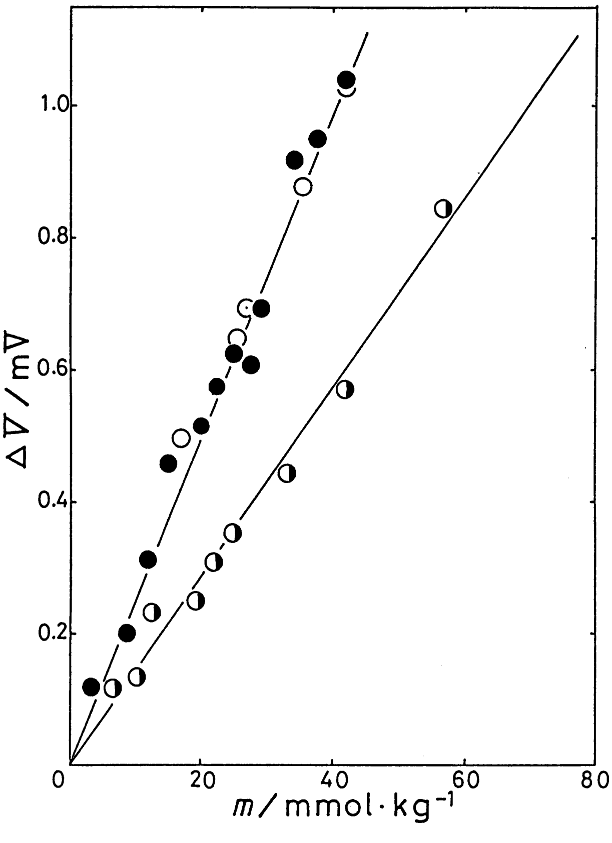

Fig. 3. Reading of vapor-pressure depression, ΔV, at various molalities of solute, m, in methanol at 298 K: (●) SDS; (○) NaCl; (◑) triphenylmethane.

Table 1. The Parameters Concerned with Electric Conductivities of Electrolytes at 298 K

	Λ_0 a)	$\lambda_{0,\ a^+}$ a)	$\lambda_{0,\mathrm{Cl^-}}$ a)	$\lambda_{0,\mathrm{DS^-}}$ a)	$\gamma_{\mathrm{s,Na^+}}$ b)	$\gamma_{\mathrm{s,Cl^-}}$ b)	$\gamma_{\mathrm{s,DS^-}}$ b)
NaCl/Water	126.45 c)	50.10 c)	76.35 c)	—	0.18	0.12	—
SDS/Water	74.0	50.10	—	23.90	0.18	—	0.39
NaCl/Methanol	97.61 d)	45.23 d)	52.38 d)	—	0.34	0.29	—
SDS/Methanol	81.5	45.23	—	36.27	0.34	—	0.42

a) Unit: $\mathrm{S\,cm^2\,mol^{-1}}$. b) Unit: nm. c) Ref. 12-a. d) Ref. 12-b.

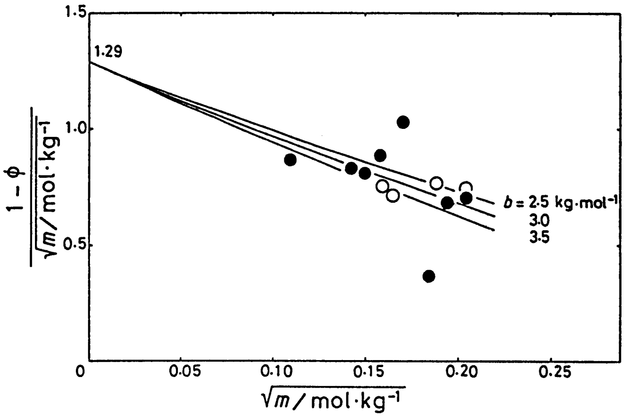

Fig. 4. Relation between the osmotic coefficient of methanol solution, ϕ, and the solute molality, m, at 298 K: (●) SDS; (○) NaCl; (——) theoretical lines drawn according to Eq. 6 when the values of b are 2.5, 3.0, and 3.5 $\mathrm{mol^{-1}\,kg}$, respectively.

significant distinction; its slope was about twice that for triphenylmethane (reference). The osmotic coefficient of SDS in methanol, ϕ, at various m was calculated through an analysis of ΔV vs. m based on an isopiestic method.[13] We thereby adopted 2 as the stoichiometric coefficient, ν, of SDS in methanol (similar to NaCl) and 1 for that of triphenylmethane, respectively. From a plot of $(1-\phi)/\sqrt{m}$ vs. $\sqrt{m}$ (Fig. 4), the mean activity coefficient, $\gamma_\pm$, of SDS in methanol was estimated according to the following equation using a graphical integration method:

$$-\ln\gamma_\pm = 1-\phi+2\cdot\int_0^m\{(1-\phi)/\sqrt{m}\}\cdot \mathrm{d}\sqrt{m}. \tag{3}$$

However, the estimated value of $\ln\gamma_\pm$ is considered to be more or less unreliable, since the value of $(1-\phi)/\sqrt{m}$ in the lower concentration region was determined only from an extrapolation of its measured value in the higher concentration region. Therefore, we first assumed a theoretical relation[13] between $\gamma_\pm$ and m, i.e., Eq. 4:

$$\ln\gamma_\pm = -A_\gamma\cdot\sqrt{m}/(1+\sqrt{m/m^\ominus})+b\cdot m, \tag{4}$$

where A_γ is a theoretical constant, which was calculated using to Eq. 5, and is 3.873 $\mathrm{mol^{-1/2}\,kg^{1/2}}$ at 298 K for methanol as a solvent; $m^\ominus$ is the unit molality and b is a constant to be estimated from experiments. Also,

$$A_\gamma = [\{(2L)^{1/2}\cdot e^3\}/\{8\pi\cdot(\varepsilon_0\cdot k)^{3/2}\}]\cdot(\rho_1)^{1/2}\cdot(\varepsilon_\mathrm{r}\cdot T)^{-3/2}, \tag{5}$$

where L is Avogadro's number, k Boltzmann's constant, e the protonic charge, ρ_1 the density of the solvent, ε_0 the dielectric constant of the vacuum, and ε_r the relative dielectric constant of the solvent.

From a combination of Eqs. 3 and 4, we have

$$(1-\phi)/\sqrt{m} = (A_\gamma/m^{3/2})\cdot \{(1+\sqrt{m})-2\cdot\ln(1+\sqrt{m})-(1+\sqrt{m})^{-1}\}-(1/2)\cdot b\cdot\sqrt{m}. \tag{6}$$

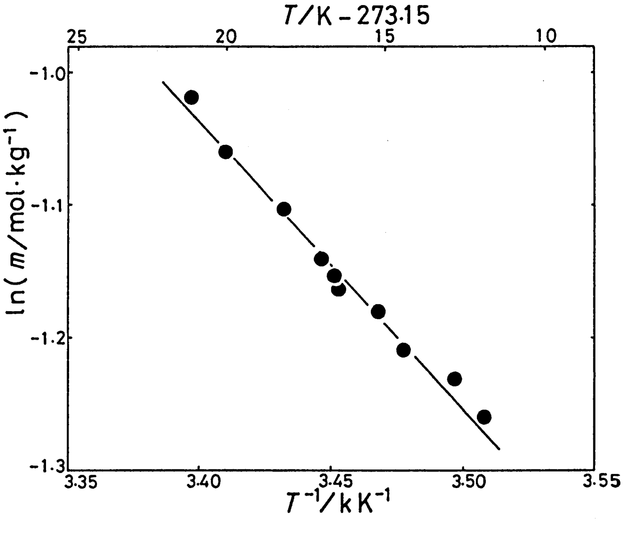

Fig. 5. Logarithm of SDS solubility in methanol on molality basis, $\ln m$, vs. reciprocal temperature, $1/T$, plot: (——) straight line by the least-squares method.

We then adopted Eq. 6 as the theoretical equation for simulating the experimental plot $(1-\phi)/\sqrt{m}$ vs. $\sqrt{m}$. In Fig. 5, we show theoretical curves of $(1-\phi)/\sqrt{m}$ vs. $\sqrt{m}$. The optimal value of b for SDS in methanol at 298 K was estimated to be 3.0±0.5 $\mathrm{mol^{-1}\,kg}$. Similarly, the value of b for NaCl was roughly estimated to be 3.0±1.0 $\mathrm{mol^{-1}\,kg}$. However, in order to make the estimation of b for SDS, as well as for NaCl, more reliable, further experiments are considered to be necessary with respect to improvements in the precision and expansion of the solute concentration range.

4. Analysis of Solubility. (1) The Coexisting Phase of SDS in Equilibrium with its Methanol Solution: Generally speaking, the solubility of the material in a solvent depends upon the state of the phase which coexists with its solution in equilibrium. It was therefore necessary to examine the nature of the coexisting phase or precipitate as to whether the phase is unique or a type of polymorphic phase, we also had to determine whether the phase consisted of only pure SDS or both SDS and solvent, together. First, it was found from its appearance that the coexisting phase was crystalline over the range of temperatures from 278 to 305 K. As discussed later regarding a thermodynamic analysis of solubility data, the existence of a polymorphism would be almost excluded for the coexisting phase over the temperature region 285—295 K. We next examined the posibility of whether the phase contains solvent molecules or not. By heating, we dissolved a sufficiently large amount of SDS in methanol; we then cooled the resultant solution to the room temperature (ca. 293 K) in order to precipitate out SDS crystals. The precipitate was separated by filtration and put into a weighing bottle. The weight decrease of the precipitate, which occluded some amount of the solvent, was measured at regular time intervals, during which the sample was at first desiccated under decreased pressure by means of a water-jet-pump to evaporate the occluded methanol in the space between the crystals, and finally in vacuo to remove any methanol inside each crystal, if present. From an analysis of the time course of the weight decrease, it was estimated that the coexisting SDS crystal did not contain any solvent molecules.

(2) Thermodynamic Analysis of Solubility Data: A plot of the solubility, ln m vs. the reciprocal temperature, $1/T$, for SDS in methanol is shown in Fig. 5. The results were analyzed thermodynamically regarding a previously examined assumption that pure SDS in the crystal phase coexists in equilibrium with the dissociated ions of SDS in methanol, i.e., Na^+ and DS^- ions. Then, we have the relation between the standard enthalpy of SDS at the transfer from crystal to dissociated ions, $\Delta_c^i H^\ominus$, and the temperature dependency of solubility, m, as follows:

$$\Delta_c^i H^\ominus = -2R\cdot[\partial\{\ln(\gamma_\pm\cdot m/m^\ominus)\}/\partial(1/T)]. \qquad (7)$$

The significance of the presence of $\gamma_\pm$ in Eq. 7 can easily be ascertained. When the value of $\Delta_c^i H^\ominus$ is calculated from the results, as shown in Fig. 5, by assuming the value of $\gamma_\pm$ to be either unity or constant, the value of $\Delta_c^i H^\ominus$ becomes 34.2 kJ mol^{-1}, which is very different from the value estimated calorimetrically, 19.5±2.0 kJ mol^{-1} (mentioned later). When Eq. 4 is substituted into Eq. 7, we have

$$\Delta_c^i H^\ominus = -2R\cdot [\partial\{-A_\gamma\cdot\sqrt{m}/(1+\sqrt{m/m^\ominus})+b\cdot m+\ln(m/m^\ominus)\}/\partial(1/T)]. \qquad (8)$$

While the values of m (solubility) and A_γ were measured and calculated at various temperatures, respectively, the value of b was estimated only at 298 K (as mentioned before). In order to complete Eq. 8 in terms of the actual values, it is necessary to know the values of $\Delta_c^i H^\ominus$ and b at various temperatures. Over a narrow range of temperatures, i.e., 285—298 K, the value of $\Delta_c^i H^\ominus$ can be approximately assumed to be constant. Since the value of $\Delta_c^i H^\ominus$ can be measured directly, the values of b at various temperatures can be estimated.

(3) Heat of Solution by Calorimetry and Estimation of *b* at Various Temperatures: In Fig. 6 we show the endothermic heat of solution, ΔH, vs. the amount of SDS, n_2, which was dissolved into 40 g of methanol. The final concentrations of SDS in methanol after dilution were in the range 1—10 mmol kg^{-1}. From the slope of ΔH vs. n_2 (a linear plot at infinite dilution), the standard solution enthalpy of SDS in methanol, i.e., $\Delta_c^i H^\ominus$, was estimated to be 19.5±2.0 kJ mol^{-1}.

In order to estimate the values of b in Eq. 8 at various temperatures, we used the relation $-A_\gamma\cdot\sqrt{m}/(1+\sqrt{m/m^\ominus})+b\cdot m+\ln(m/m^\ominus)$ vs. $1/T$, which can be represented as a straight line, when $\Delta_c^i H^\ominus$ is constant. The slope of this line must be the value of $\Delta_c^i H^\ominus$ divided by $2R$. The ordinates at 298 K were calculated by using the solubility, m, and the value of b (estimated before). Then, the values of b at other temperatures were calculated (Fig. 7). It was found that there was a linear dependency of b on T:

$$b \doteqdot 3.0\ \mathrm{mol^{-1}\,kg} + 0.069\ \mathrm{mol^{-1}\,kg\,K^{-1}}\times(298\ \mathrm{K}-T). \qquad (9)$$

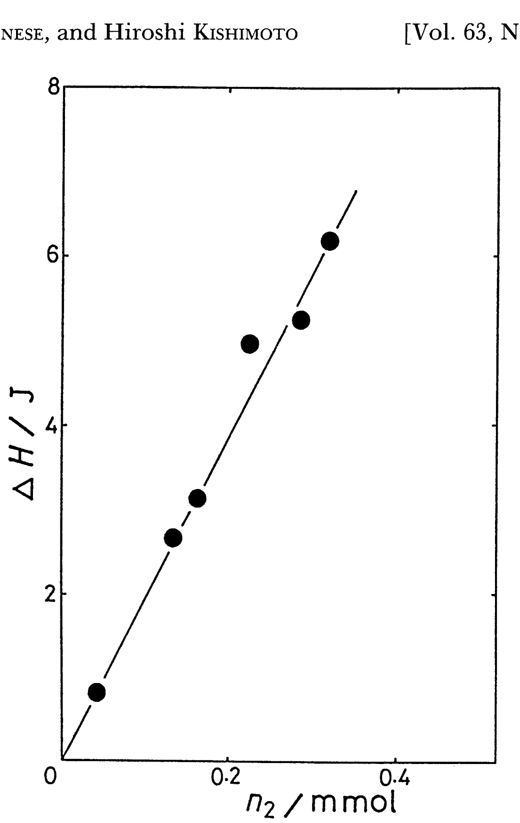

Fig. 6. Solution enthalpy, ΔH, of SDS in methanol at 298 K against the dissolved amount of SDS, n_2.

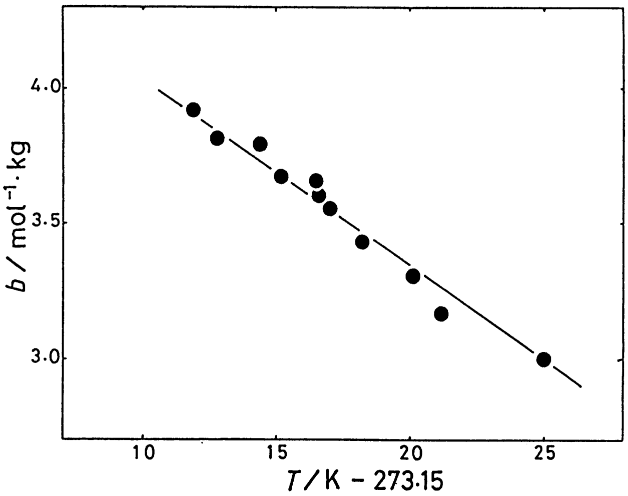

Fig. 7. Estimated values of b at various temperatures: (——) straight line by the least-squares method.

By substituting Eq. 9 into Eq. 4, we have obtained an empirical relation between ln $\gamma_\pm$ and T, at least over the range 285 to 298 K for T.

This relation might have to be modified, since it could hardly disclose the different natures between SDS and NaCl, in spite of the fact that very different parameters were found in conductivity measurements for SDS and NaCl. In other words, there remains a question as to whether SDS and NaCl significantly differ or not with each other concerning the thermodynamic solution behavior in methanol. In order to answer the above-mentioned question, and also to examine several assumptions used in this work, we are now studying systems which consist of non-polar solvents other than methanol.

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