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The Effect of Temperature on the Heats of Solution and Micelle Formation of Sodium Dodecyl Sulfate[1]

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For the elucidation of molecular behaviors of surfactant solutions from the view-point of thermodynamic parameters, the standard heats of solution and micelle formation per mole of sodium dodecyl sulfate (NaDS), typical anionic surfactant, or $\varDelta\bar{H}^{\circ}_{\text{sol}}$ and $\varDelta\bar{H}^{\circ}_{\text{m}}$ were determined by calorimetry in the wide range of temperature from 20° to 45°, with parallel experiments determining critical micelle concentration by conductivity measurement and degree of Na^+ ion dissociation on micelle by electromotive force measurement using Na^+ ion responsive electrode. From the values of both the standard heats, the standard enthalpies of NaDS in monomeric and micellar states, $\bar{H}^{\circ}_{\text{mono}}$ and $\bar{H}^{\circ}_{\text{mic}}$, were calculated on the relative base of standard enthalpy of solid state. The change of these values with temperature gave *ca.* 120 and 16 cal deg^{-1} mole^{-1} to the increases of the standard partial molar heat capacity of NaDS on transferring from solid state to monomeric and micellar states, *i.e.* $\varDelta\bar{C}^{\circ}_{\text{p}}$ (solid→mono, NaDS) and $\varDelta\bar{C}^{\circ}_{\text{p}}$ (solid→mic, NaDS), respectively. By applying a simple additivity rule, it was concluded that the change of heat capacity of the paraffin portion of NaDS plays an important role in the above-mentioned $\varDelta\bar{C}^{\circ}_{\text{p}}$'s, implying the formation of hydrophobic interaction between the paraffin portion and water. With other experimental data, also the systematic description of surfactant solution was done in thermodymanic terms.

After the intensive pioneering works of McBain and his co-workers on the thermodynamic properties of aqueous as well as nonaqueous solutions of soaps and other synthetic surfactants,[3] they reasoned out the existence of an association colloid, *viz.* micelle, and ascribed to its physical behaviors such a characteristic property as solubilization, anomalous viscosity or optical property in surfactant solutions.[4,5] Since then, many investigations have been carried out on the various properties of micelle: critical micelle concentration (CMC) value, micellar weight, gemoetrical shape, electric charge and so on.[6] Recently, the thermodynamics of micelle formation has become the subject of biophysics as the model system[7] containing the so-called hydrophobic bonding,[8a] which plays an important role in the denaturation and other type of reactions of proteins.[8b] Also the studies of interactions, *e.g.* solubilization-like process and molecular complex formation, of surfactants with other chemical substances of high and low molecular weights have been carried out by several authors,[9] giving a clue to the elucidation of more complicated

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[1] A part of this work was presented at the 92nd Annual Meeting of Pharmaceutical Society of Japan, Osaka, April 1972.

[2] Location: *Tanabe-dori, Mizuho-ku, Nagoya, 467, Japan.*

[3] Surface active agent is in this paper abbreviated as surfactant.

[4] *e.g.* J.W. McBain, M. Taylor, and M.E. Laing, *J. Chem. Soc.*, **121**, 621 (1922).

[5] For the earlier works of McBain, *et al.*, ref. *a*) J.W. McBain, "Colloid Science," D.C. Heath and Co., Boston, 1950; *b*) M.E.L. McBain and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press, New York, 1955.

[6] *cf.* K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants, Some Physicochemical Properties," Academic Press, New York, 1963.

[7] H. Schneider, G.C. Kresheck, and H.A. Scheraga, *J. Phys. Chem.*, **69**, 1310 (1965); D.C. Poland and H.A. Scheraga, *ibid.*, **69**, 2431 (1965); M.F. Emerson and A. Holtzer, *ibid.*, **71**, 3320 (1967).

[8] *a*) G. Nemethy and H.A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962); *b*) *Idem*, *J. Phys. Chem.*, **66**, 1773 (1962).

[9] *a*) S. Saito and K. Kitamura, *J. Colloid Interface Sci.*, **35**, 346 (1971); S. Saito, T. Taniguchi, and K. Kitamura, *ibid.*, **37**, 154 (1971); S. Saito, *Kolloid-Z. u. Z. Polymere*, **249**, 1096 (1971); *b*) W.J. Knox, Jr. and J.F. Wright, *J. Colloid Sci.*, **20**, 177 (1965); W.J. Knox, Jr. and T.O. Parshall, *J. Colloid Interface Sci.*, 33, 16 (1970).

biological systems. In the field of pharmaceutical scinces, the solubilization by surfactant micelle has become one of main topics pertaining to the drug action.[10)]

In spite of the accumulation in knowledges of surfactant micelle itself and the expansion of the field, related to the study of micelle, as were mentioned above, still are wanted the definite informations on the structure and behavior of each component species in surfactant solutions, as to make clear the very nature of micelle formation and destruction, hence of the molecular interaction between surfactant and other chemical substances. These definite informations can be expected to be supplied from either microscopic measurements or macroscopic ones. The formers consist mainly of spectrometric experiments and directly give molecular informations, though there exists scarcely more than the classic work of Hess, *et al.*[11)] using X-ray diffraction on soap solutions. The latters consist of the measurements of such properties of surfactant solutions as light-scattering, diffusion or sedimentation, electric conductivity, surface tension, vapor-pressure lowering and other thermodynamic properties. Usually the data from these measurements must be treated with thermodynamics and statistical mechanics, based on the recent progress on the theory of liquid,[8a,12)] in order to get molecular pictures of micelle.

On the approach just mentioned, it will easily be understood from the view-point of statistical thermodynamics[8a,12)] that the determination of such a partial molar parameter as Gibbs free energy, enthalpy, entropy or heat capacity of surfactant in the standard state of micelle as well as monomeric forms is of great importance and necessity to connect the observed properties and processes of surfactant with its molecular nature. Although the change in the first mentioned parameter during micelle formation can be determined with relatively high precision from the measurements of CMC value and a few other properties of micelle and from some thermodynamic treatments,[13)] the other parameters, especially the partial molar heat capacity, cannot be determined precisely without the direct calorimetric measurements over the wide range of temperature. Recently, several workers[14)] carried out the calorimetric measurements on various surfactants. However, these experiments were still limited, especially in the range of temperature. Therefore, we have carried out the following experiments on the aqueous solution of a typical anionic surfactant, sodium dodecyl sulfate, laying emphasis on the wide temperature range for the determination of the most urgently needed parameter, *i.e.* the partial molar heat capacity, which may describe clearly the molecular behavior of surfactant.

Theoretical

Thermodynamic Parameters from CMC Measurement

In an aqueous solution of alkali salt of anionic surfactant without other electrolyte, the equilibrium between the single ions and partially charged micelles may be represented by eqn. (1),[13)] in the case of sodium salt of uni-uni-valent anionic surfactant,

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[10)] *cf.* L. Sjöblom, "Solvent Properties of Surfactant Solutions," ed. by K. Shinoda, Marcel Dekker, Inc., New York, 1967, pp. 189—262; W.V. Valkenburg, *ibid.*, pp. 263—283.

[11)] K. Hess, H. Kiessig, and W. Philippoff, *Naturwissenshaften*, **26**, 184 (1938).

[12)] H. Eyring and R.P. Marchi, *J. Chem. Educ.*, **40**, 562 (1963).

[13)] J.N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).

[14)] *a*) E.D. Goddard and G.C. Benson, *Trans. Faraday Soc.*, **52**, 409 (1956); *b*) E.D. Goddard, C.A. Hoeve, and G.C. Benson, *J. Phys. Chem.*, **61**, 593 (1957); P. White and G.C. Benson, *J. Colloid Sci.*, **13**, 584 (1958); *c*) J.M. Corkill, J.F. Goodman, and J.R. Tate, *Trans. Faraday Soc.*, **60**, 996 (1964); J.M. Corkill, J.F. Goodman, P. Robson, and J.R. Tate, *ibid.*, **62**, 987 (1966); J.M. Corkill. J.F. Goodman, S.P. Harrold, and J.R. Tate, *ibid.*, **62**, 994 (1966); *d*) G. Pilcher, M.N. Jones, L. Espada, and H.A. Skinner, *J. Chem. Thermodyn.*, **1**, 381 (1969); L. Espada, M.N. Jones, and G. Pilcher, *ibid.*, **2**, 1 (1970); M.N. Jones, G. Pilcher, and L. Espada, *ibid.*, **2**, 333 (1970).

$$\nu S^- + (\nu - z)Na^+ \rightleftarrows M^{z-}, \qquad (1)$$

where S^-, Na^+ and M^{z-} represent the single surfactant ion, free sodium ion and the micelle, which is composed of ν surfactant anions and $(\nu - z)$ bound sodium ions, resulting in net charge z-, respectively. The values of ν and z depend upon temperature as well as composition and are usually averaged ones, taking into consideration the poly-dispersity of micelles.

In the case of large ν, the standard Gibbs free energy of micelle formation per mole of S^- in eqn. (1), $\Delta\bar{G}^\circ_m$, can be approximately given as follows,

$$\Delta\bar{G}^\circ_m = (2 - p/\nu)RT\ln(\text{CMC}), \qquad (2)$$

where p/ν and CMC represent the degree of dissociation of counter-ions in micelle and the critical micelle concentration at a given temperature, T, respectively. From the thermodynamic treatment of eqn. (2), the corresponding standard enthalpy of micelle formation per mole of surfactant ions, $\Delta\bar{H}^\circ_m$, can be obtained by the following equation,

$$\Delta\bar{H}^\circ_m = \frac{d(\Delta\bar{G}^\circ_m/T)}{d(1/T)} \qquad (3)$$

The estimation of standard enthalpy from the analysis of equilibrium constants or $\Delta\bar{G}^\circ_m$ at a few different temperatures, however, is open to argument, as these estimated parameters in micelle formation are sensitive to temperature change. They may be rather directly obtained from the determination of heat of micelle formation by calorimetric measurements as follows.

$\Delta\bar{H}^\circ_m$ from Heat of Solution

Goddard and Benson[14a)] proposed the method of estimating $\Delta\bar{H}^\circ_m$ from the heats of solution of surfactants in various amounts. The schematic presentation of the method is shown in Fig. 1.

The values of $\bar{H}_2$ on the ordinate can be calculated, using the following equation.

$$\bar{H}_2 = \bar{H}_2(\text{solid state}) + \Delta H + m\cdot d\Delta H/dm, \qquad (4)$$

where $\bar{H}_2$ and $\bar{H}_2$ (solid state) mean the partial molar heat contents of solute in solution and solid state, respectively and ΔH is the heat of solution per mole of solute of final concentration, m. From the various ΔH's at different m's, the curve can be obtained, as shown in Fig. 1, thereby taking into consideration the constancy of $\bar{H}_2$ (solid state) value in eqn. (4).

$\Delta\bar{H}^\circ_m$ from Heat of Dilution

An alternative method for the heat of micelle formation consists in a series of the heat-of-dilution measurements of surfactant. Although various modifications[14b,c,d)] are possible

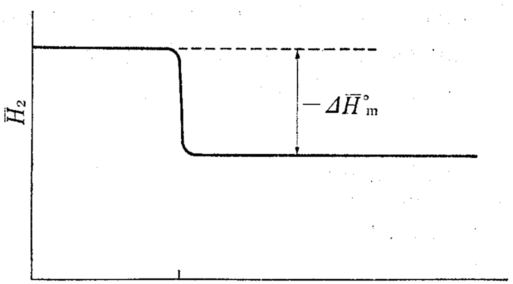

Fig. 1. Partial Molar Heat Content of Solute, $\bar{H}_2$, against Concentration (Ideal Case, Diagrammatic)

The descension of curve at CMC as seen in this diagram occurs in exothermic micelle formation, viz. $\Delta\bar{H}^\circ_m < 0$. In the case of endothermic micelle formation, the curve ascends upwards instead.[14a)]

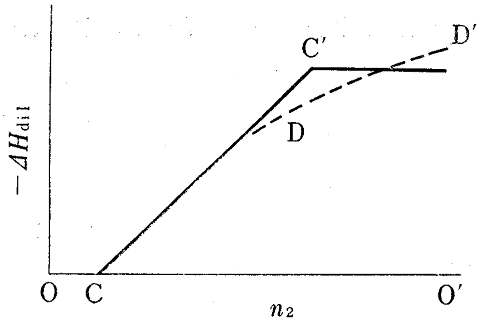

Fig. 2. Schematic Presentation of Heat of Dilution, $-\Delta H_{dil}$, against the Number of Moles of Solute, n_2, in the Case of Exothermic Micelle Formation

C and C′ correspond to n_2's in the systems, where the concentrations of the initial solution to be diluted and the final resulting solution are CMC, respectively. D corresponds to C′ in the case of actural deviated behavior of solution.

with regard to the analysis of data, we took a simple procedure based upon the following approximations: i) upon mixing the solution to be diluted with water, the partial molar enthalpy of each species present remains constant and can be replaced by the respective standard value, ii) in our preliminary treatment, only two species, *i.e.* monomeric surfactant and mono-disperse micellar one, can represent the solute species of system and iii) both below and at CMC, the system consists of monomer and solvent, while above CMC the rest of surfactant being in micellar form.

Upon dilution of the surfactant solution below CMC with solvent, the following relation can easily be deduced and will later be experimentally verified;

$$-\Delta H_{\text{dil}} = 0 \tag{5}$$

where $-\Delta H_{\text{dil}}$ gives the exothermic heat of dilution and in this case of dilution experiment, no heat is expected to be observed.

Upon dilution of the surfactant solution above CMC with solvent, the heat of dilution can easily be deduced and given in the following simple equation relating to $\Delta\bar{H}^\circ_{\text{m}}$.

$$-\Delta H_{\text{dil}} = n_{\text{destroyed}}\Delta\bar{H}^\circ_{\text{m}}, \tag{6}$$

where $n_{\text{destroyed}}$ stands for mole numbers of the surfactant in micellar form, which is destroyed into monomeric form by dilution. When the concentration of resulting solution drops below CMC, $n_{\text{destroyed}}$ can be replaced by $(n_2-n_{\text{mono,i}})$, where n_2 and $n_{\text{mono,i}}$ denote moles of total and monomeric surfactant in the initial solution to be diluted, respectively. Since the amount of initial solution was nearly kept constant with the value of *ca.* 2 g. in our dilution experiments, $n_{\text{mono,i}}$ became constant and the slope of $-\Delta H_{\text{dil}}$ against n_2 as shown by $\angle$C′CO′ in Fig. 2 gives $\Delta\bar{H}^\circ_{\text{m}}$. In the dilution experiments, where the concentration of resulting solution remains above CMC, $n_{\text{destroyed}}$ cannot be represented by $(n_2-n_{\text{mono,i}})$, but has a constant value against further increase of n_2 and $-\Delta H_{\text{dil}}$ remains also constant as shown by the horizontal line drawn from the inflexion point C′. However, the real relation between $-\Delta H_{\text{dil}}$ and n_2 based upon experimental values may deviate from the above-mentioned simplified one owing to the possible deviation of actual $\Delta\bar{H}_{\text{m}}$ from its standard value, $\Delta\bar{H}^\circ_{\text{m}}$, especially in the high concentration of micelles in the initial solution to be diluted. In such a case as shown, *e.g.* by the broken line CDD′, which represent the experimental deviated tendency, $\Delta\bar{H}^\circ_{\text{m}}$ should be calculated from the slope of the straight line, CC′, obtained by extrapolation to the rising point, C.

Determinations of $\bar{H}^\circ_{\text{mono}}$ and $\bar{H}^\circ_{\text{mic}}$ on the Basis of $\bar{H}^\circ_{\text{solid}}$

$\Delta\bar{H}^\circ_{\text{m}}$, thus obtained, gives the partial molar standard enthalpy of surfactant in micellar state, $\bar{H}^\circ_{\text{mic}}$, on the basis of its corresponding value in monomer state, $\bar{H}^\circ_{\text{mono}}$. This latter quantity, however, had better be considered on the more fundamental basis of the quantity of surfactant in pure solid state, $\bar{H}^\circ_{\text{solid}}$, the determination of which depends solely upon the measurement of heat capacity from very low temperature to the required temperature. Measuring the heat of solution per mole of solute, $-\Delta H_{\text{sol,C}}$, at various final concentration, C, the extrapolated value at infinite dilution, $-\Delta H_{\text{sol,o}}$ or $-\Delta\bar{H}^\circ_{\text{sol}}$ can be determined, although $\Delta H_{\text{sol,C}}$ at low concentrations can be approximately treated as $\Delta\bar{H}^\circ_{\text{sol}}$. Clearly, from this $\Delta\bar{H}^\circ_{\text{sol}}$ as well as $\Delta\bar{H}^\circ_{\text{m}}$, the following relations can be obtained on the basis of $\bar{H}^\circ_{\text{solid}}$.

$$\bar{H}^\circ_{\text{mono}} = \bar{H}^\circ_{\text{solid}} + \Delta\bar{H}^\circ_{\text{sol}} \tag{7}$$

$$\bar{H}^\circ_{\text{mic}} = \bar{H}^\circ_{\text{mono}} + \Delta\bar{H}^\circ_{\text{m}} = \bar{H}^\circ_{\text{solid}} + \bar{H}^\circ_{\text{sol}} + \Delta\bar{H}^\circ_{\text{m}} \tag{8}$$

Experimental

Materials The NaDS (sodium dodecyl sulfate) used was obtained from Henkel International GmbH. Düsseldorf (Texapon L 100), and recrystallized twice from distilled normal butanol, followed by repeated

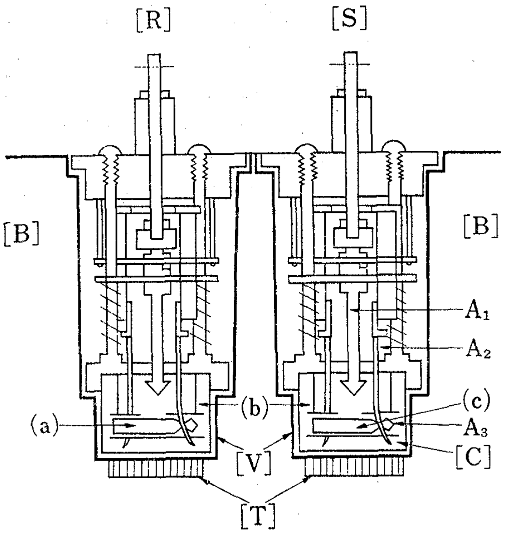

Fig. 3. Principal Diagrams of Twin-type Conduction Calorimeter

Reference and sample subcalorimeters, [R] and [S], are set in the aluminum block or standard bed, [B]. The out-side part of each subcalorimeter consists of an vessel-holder, [V], which is briefly drawn by bold solid lines as well as a ladder, [T]. The latter indicates heat-sensing thermometers. The in-side part of each subcalorimeter, *i.e.* reaction-vessel, consists of a stanless-steel bottom cell, [C], and a top mechanism, main devices of which are as follows. A_1: breaking device for the sample holder; A_2: liquid-stirring device; A_3: sample-holder. Contents in each cell or holder are as follows. (a): blank or *ca.* 2 g of water; (b): *ca.* 40 g of water; (*c*): *ca.* 2 g of NaDS aq. solution or a certain amount of well-dried NaDS sample (crystals). Between [C] and [V], *ca.* 3.5 ml of heat conducting liquid is filled.

petroleum-ether extractions for 30 hr, in total.[15] The purity of this substance seems to suffice for our experiments, since its CMC, measured and to be mentioned later, coincided well with the values cited in literatures.[15,16]

KCl (potassium chloride) was obtained from Katayama Kagaku Kogyo (Polarographic Reagent), and heated at 105° for 3 hr, just before use. Distilled and deionized water was used throughout.

Apparatuses and Procedures

1) **Electric Conductivity Measurement**——For the determination of CMC, the electric conductivity of surfactant aqueous solutions was measured in a conductivity cell of dipping type, CG 2001 PL of TOA Electronics, using as the measureing apparatus a universal bridge, Type 4255A of Yokogawa-Hewlett-Packard Ltd., Japan, with a hand-made variable capacitor (C=*ca.* 100 pF max). The sample solution was contained in a glass-vessel, *ca.* 20 minutes before each measurement. For keeping the temperature of the solution constant during experiment, the above-mentioned glass-vessel was dipped in a bath with the jacket, through which thermostatted water was circulated. The temperature of the sample solution was thus kept constant within the variation of 0.02°, which was confirmed with a Beckmann-type thermometer. The cell constant in conductivity computation was $0.995 \times 10^{-1}\text{cm}^{-1}$ at 25.0°, for example. Successive measurements for the various concentrations of surfactant were carried out, using a multiple dilution method, after sufficient blending of newly produced mixture.

2) **Measurements of Heats of Solution and Dilution**——For the determination of heat of solution or dilution, a twin-type conduction calorimeter, CM 204D1 of Ôyodenki Kenkyujo, similar to the calorimeter described by Koishi,[17] was used. This apparatus consists of a common heat-reservoir with thermostat and a pair of twin subcalorimeters, each of which is composed of a reaction-vessel and a vessel-holder with thermoelements for heat-sensing. The difference between the electromotive forces (EMF) of thermoelements owing to the difference of temperatures of reaction-vessels was amplified by an auxiliary outside amplifier, Micro Volt Meter AM-1001 of Ohkura Electric and finally plotted as thermograms, *i.e.* the differential EMF *vs.* elapsed time diagram, on an electronic recorder, CR-101 of Rikadenki Kogyo. From the principle of the twin-type conduction calorimeter,[17] the difference between heats liberated or absorbed in each reaction-vessel is represented as the area under the curve of diagram from the beginning of reaction to the final stage of approach to the base-line, usually attained after about two hr.

Meanwhile, some descriptions of the construction and procedure in regard to the reaction-vessels will be made as follows. The main experiments on the heat of solution and all the ones on the heat of dilution were carried out with the reaction-vessels using sealed glass ampoules for sample-holding, as seen in Fig. 3, although the preliminary experiments on the heat of solution were carried out with the reaction-vessels using synthetic resin tubes for sample-holding, as in Koishi's work.[17]

For the measurement of heat of solution, a well dried sample (NaDS) was put in the tube or ampoule of sample system and the tube or ampoule was set on the top mechanism of sample reaction-vessel, which consists of a liquid-stirring device and a breaking device for the sample-holder. Usually, the gravimetric measurement of sample was done on the enclosed state of sample in the sample-holder. The top mechanism, thus prepared, was then joined carefully with the stainless steel cell, in which a given amount of water as solvent had been put beforehand. On the other hand, the similar top mechanism of reference system, which have the similar sample-holder but no material in it, was joined with the bottom cell, which contained the similar amount of water as in the case of sample system. After the construction of both reaction-vessels, as mentioned above, and the setting of these vessels on the respective vessel-holders in the calorimeter,

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[15] Modification of the method by K. Shirahama and T. Kashiwabara, *J. Colloid Interface Sci.*, **36**, 65 (1971).
[16] *a*) M.J. Schick, *J. Phys. Chem.*, **68**, 3585 (1964); *b*) P. Mukerjee, K.J.M ysels, and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967).
[17] M. Koishi, *Bull. Chem. Soc. Japan*, **39**, 2406 (1966).

followed by the remaining supplementary procedures, it took about 12 hr to attain the thermal stationary state, which can be indicated by the constant EMF or base-line on the electronic recorder. Moreover, we had kept for more than two days the calorimeter at a given temperature, when the alteration of experimental temperature had been done. After several hours of constant base-line, both sample-holders were broken and the sample was mixed with water by the stirring device of sample system, which was set in continuous motion before and after the breaking as that of reference system was. From this time on, the differential heat liberated or absorbed in the sample reaction-vessel, relative to that in the reference reaction-vessel, was plotted as the integrated value on the recorder as mentioned before. The heat thus obtained was always calibrated by the use of electric heater inside the calorimeter and sometimes by the measurement of the heat of solution of a given amount of KCl (*ca.* 20 to 50 mg) into a given amount of water (*ca.* 50 g).18) The relative experimental errors could remain within 1% under normal conditions.

For the measurement of heat of dilution, the experimental procedures were the same as that of heat of solution, except that nearly equal amounts of the aqueous solution of sample and the solvent (*ca.* 2 g, weighted by balance) were sealed in ampoules for sample-holding of sample reaction-vessel and reference reaction-vessel, respectively.

3) **Measurement of Na^+ Ion Activity by Na^+ Ion Responsive Electrode**——For the determination of the micellar charge, which is prerequisite to the calculation of $\Delta \bar{G}_m{}^\circ$ or other parameters using eqn. (2) or its derived eqn., the measurements of Na^+ ion activities in various concentrations of NaDS aq. solution were carried out using a sodium ion responsive electrode, Type 39278 of Beckman Instruments Inc., U.S.A., and a liquid-bridge calomel reference electrode, double-sleeve type, of TOA Electronics. The EMF between these electrodes dipped in sample solution was measured with a high precision pH-meter, Expandomatic SS-2 of Beckman Instruments Inc. For the calibration of Na^+ ion activity, various concentrations of NaCl aq. solution were used. Taking account of the precipitation by the contact of NaDS aq. solution with KCl aq. solution, normal NaCl aq. solution was filled in the outer section of bridge of reference electrode. Similar precautions and procedures were made as in the case of conductivity measurement.

Result and Discussion

CMC Values

From the definition of CMC by Phillips,13) the curve of electric conductivity *vs.* concentration of a surfactant solution can give the CMC of the surfactant. The CMC of NaDS was thus obtained in the temperature region of 15.4° to 50.0° as shown in Fig. 4. The interpolated values of CMC at several temperatures in round degrees were presented in Table I. The

TABLE I. Various Parameters of NaDS at Micelle Formation

Temp. (°C)	CMC					P/ν		
	Our value		Literary values in molality $\times 10^3$					
	Molality $\times 10^3$	Mole fraction $\times 10^4$	Ref. 19	Ref. 20	Other value	Our value	Ref. 22f	Other value
10			8.80	8.64	7.4a)			
15	8.05	1.450	8.50	8.41			0.242	
20	7.96	1.434	8.47	8.26				
25	7.93	1.429	8.40	8.16	7.2a) 8.27b) 8.10c) 8.33c)	0.21	0.228	0.25d) 0.29e) 0.18f) 0.16g) 0.229h) 0.22i)
30	7.96	1.434	8.45	8.25			0.242	
35	8.07	1.454	8.55	8.41			0.258	0.28d)
40	8.23	1.483	8.90	8.66	7.6a)			
45	8.45	1.522	9.10	8.94				
50	8.70	1.567	9.61	9.27				

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18) J. Coops, G. Somsen, and M.W. Tolks, *Rec. Trav. Chim.*, **82**, 231 (1963).

Temp. (°C)	$\Delta\bar{G}^\circ_m$ (kcal/mole) from CMC in mole fraction	$\Delta\bar{H}^\circ_m$ (kcal/mole) from CMC Our value	Ref. 14*d*	Ref. 19	Ref. 20	$\Delta\bar{H}^\circ_m$ (kcal/mole) from calorimetry Our value	Ref. 14*d*	Ref. 19	Ref. 23
10			1.95	1.1	1.2				
15	−9.06		1.30	0.7					
20	−9.23	0.4	0.80	0.4	0.4	0.3			
25	−9.38	0.0		0.0		−0.3	0.09	0.1	−0.4
30	−9.54	−0.5		−0.5	−0.3	−0.9	−0.61		−1.0
35	−9.67	−1.2	−1.70	−1.0		−1.5			−1.6
40	−9.81	−1.9	−2.0	−1.2	−1.1	−1.9			−2.2
45	−9.94	−2.3	−2.6	−1.5		−2.2			
50	−10.05	−2.7		−1.7	−1.8	−2.7			

a) ref. 16*a*, *b*) ref. 15. *c*) ref. 16*b*. *d*) ref. 22*e*. *e*) ref. 22*a*. *f*) ref. 22*b*. *g*) ref. 22*c*. *h*) ref. 21. *i*) ref. 22*d*.

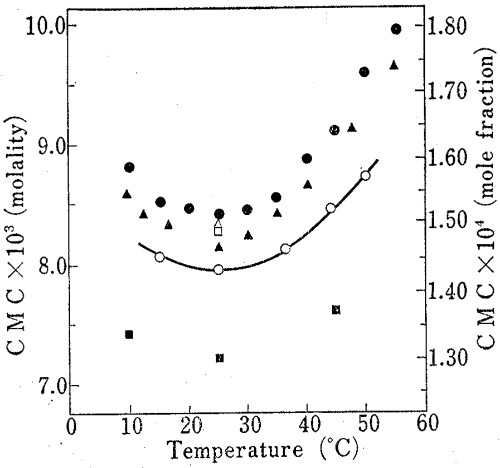

Fig. 4. CMC *vs*. Temperature Relationship of NaDS

Left and right ordinates represent CMC or NaDS in molality and mole-fraction scale, respectively. —○—: our experimental value; other workers' values are indicated by the following marks with the reference number in parentheses.
●: (19), ▲: (20), ■: (16-*a*), △: (16-*b*), □: (15).

relatively good agreement between our result and recent values in literatures[15,16,19,20] showed the sufficient purity of our sample.

$\Delta\bar{G}^\circ_m$ and $\Delta\bar{H}^\circ_m$ from CMC Values and Degrees of Dissociation of Micelle

By measuring Na^+ ion activity in various concentrations of NaDS aq. solution at 25° and following the treatments of Ingram and Jones,[21] *et al.*[22] on the activity data, the degree of dissociation of micelle at this temperature was obtained and presented in Table I. This value coincided well with other workers' ones, although there is a slight discrepancy among cited values owing to the difficulty of EMF measurement. The degrees of dissociation of micelle at other temperatures were estimated to be practically not different from that at 25°, as was shown in the data of Satake, *et al.*[22e] and of Piercy, *et al.*[22f] Therefore, we adopted that value as the approximately admissible values at other temperatures for the calculation of $\Delta\bar{G}^\circ_m$ and $\Delta\bar{H}^\circ_m$, as will be mentioned below.

From equations (2) and (3) with the above-mentioned parameters, *i.e.* CMC values and degrees of dissociation at various temperatures, the $\Delta\bar{G}^\circ_m$'s and $\Delta\bar{H}^\circ_m$'s were calculated and presented in Table I. These values of $\Delta\bar{H}^\circ_m$ were plotted for comparison in Fig. 5, showing a good concordance with those from the calorimetric measurements, which will be presented in the subsequent section, in the region throughout of our experiments. This concordance shows the adequacy of both methods for the determination of $\Delta\bar{H}^\circ_m$, *viz.* CMC *vs.* temperature

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21) T. Ingram and M.N. Jones, *Trans. Faraday. Soc.*, **65**, 297 (1969).
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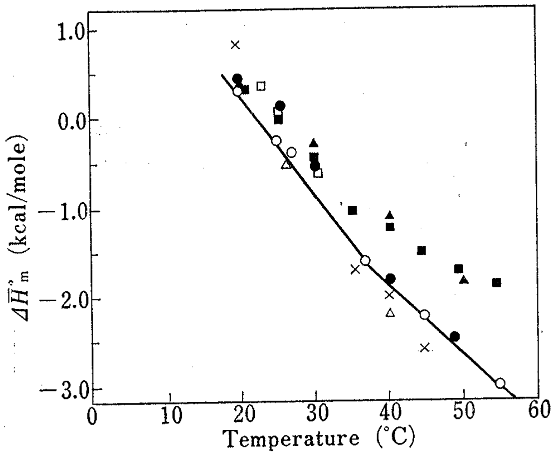

Fig. 5. The Increments of Partial Molar Standard Enthalpy of NaDS by Micelle Formation, $\Delta\bar{H}^\circ_m$'s, at Various Temperatures

Open circles represent the values obtained from our heat-of-dilution experiments and solid circles represent the values calculated from CMC *vs.* temperature method, using our experimental results. The other workers' values by heat-of-dilution experiments are indicated as follows: □ (14-*d*), ◑ (14-*a*), △ (23). Also the other workers's values based on CMC measurements are indicated as follows: × (14-*d*), ■ (19), ▲ (20). The numerals in parentheses after marks denote the reference number of data sources.

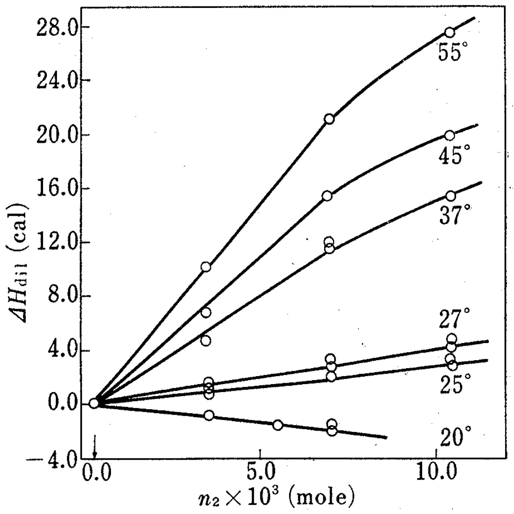

Fig. 6. The Heats of Dilution of NaDS, $-\Delta H_{dil}$'s, at Various Temperatures

In the figure, ΔH_{dil} in place of $-\Delta H_{dil}$ is plotted on ordinate. The total system consists of 1000 g of water and n_2 mole of NaDS, which is indicated by abscissa. The arrow on abscissa shows the point corresponding to C in Fig. 2.

method and heat-of-dilution method. Our results show also good agreements with other workers' values by the former method at various temperatures and by the latter method, although in different modifications, near the room temperature.

$\Delta\bar{H}^\circ_m$ from Heat of Dilution

The heats of dilution of NaDS at various temperatures were measured and plotted in Fig. 6, where we adopted the values converted to the system consisting of 1000 g of water as total amount of solvent. Since the experimental system consists of nearly constant amounts of water in spite of various amounts of solute, n_2, in the course of heat-of-dilution measurement using the twin subcalorimeters, which were presented in Fig. 3. In the case of the converted system, which was shown in Fig. 6, n_2 equals m_2, that is the molality of solute in the final diluted solution. For the sake of brevity, the system in converted unit only will be subjected to our treatment hereafter, if not otherwise specified.

With the initial surfactant concentration below CMC, the heat of dilution was not detected within the experimental error, thus confirming the assumption, which had preceded the relation (5). With the initial surfactant concentration above CMC, the heat increases or decreases linearly against n_2. Then clearly, eqn. (6) can be applied to our result of heat of dilution to determine $\Delta\bar{H}^\circ_m$. The values thus obtained were plotted in Fig. 5. The nearly straight trend of $\Delta\bar{H}^\circ_m$ *vs.* temperature relationship in our experimental range will be explained in terms of the constant heat capacities, as will be mentioned in the subsequent section after next. The values cited in Table I are interpolated ones at round degrees of temperature.

$\Delta\bar{H}^\circ_{sol}$ from Heats of Solution below CMC

The heats of solution of NaDS into various concentrations of aqueous solution were measured at temperatures from 20° to 45°. Although the heat of solution per mole of NaDS, $\Delta H_{sol,C}$ or simply ΔH_{sol}, was nearly constant, always endothermic, below CMC in final concentration, there was a little trend of inclination in the ΔH_{sol} *vs.* final concentration, C, relation. There-

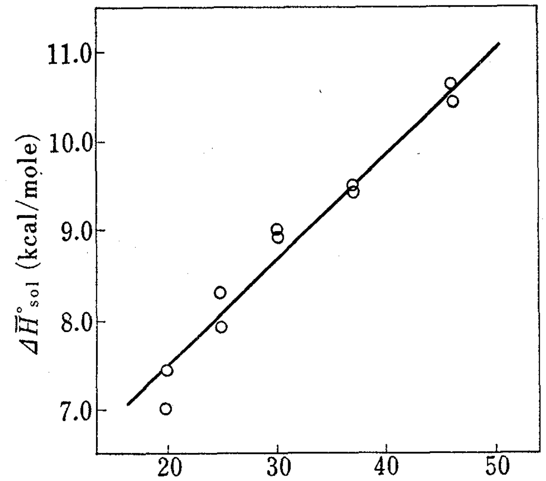

Fig. 7. The Increments of Partial Molar Standard Enthalpy of NaDS by Solution from Solid State of Monomeric State, $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$'s, at Various Temperatures

Open circles represent the values from our heat-of-solution experiments. The solid line is drawn to represent the linear relationship of $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$ with tempe rature by root-mean-square (r.m.s.) method.

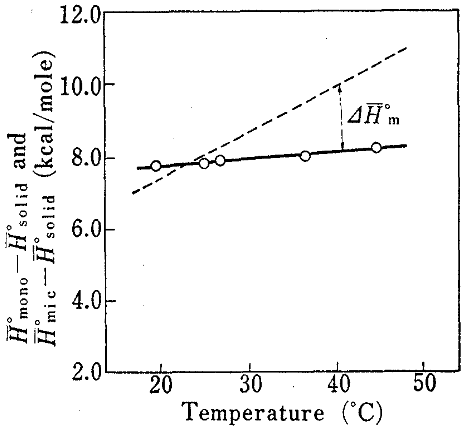

Fig. 8. Partial Molar Standard Enthalpies of NaDS in Monomeric and Micellar States Relative to That of Solid State, $(\bar{H}^{\circ}_{\mathrm{mono}}-\bar{H}^{\circ}_{\mathrm{solid}})$ and $(\bar{H}^{\circ}_{\mathrm{mic}}-\bar{H}^{\circ}_{\mathrm{solid}})$, against Temperature

The value of $(\bar{H}^{\circ}_{\mathrm{mono}}-\bar{H}^{\circ}_{\mathrm{solid}})$ is represented by the dotted line, which was derived from the data of heat-of-solution and in a linear form as shown in Fig. 7. Open circles represent the values of $(\bar{H}^{\circ}_{\mathrm{mic}}-\bar{H}^{\circ}_{\mathrm{solid}})$ and the solid line represents the r.m.s. line of them. The difference between the above-mentioned values is $\Delta\bar{H}^{\circ}_{\mathrm{m}}$.

fore, as the $\Delta H_{\mathrm{sol},0}$ or simply $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$, mentioned in eqn. (7), the extrapolated value of ΔH_{sol} to infinte dilution was adopted. The $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$'s thus obtained were plotted against temperature in Fig. 7. Similar to the tendency of $\Delta\bar{H}^{\circ}_{\mathrm{m}}$, $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$ is nearly in linear relation to temperature. This implies the constant heat capacity of surfactant in monomeric, especially in diluted, state, which will be discussed in the following section in detail.

Standard Enthalpies of NaDS in Monomeric and Micellar States relative to That of Solid State

Clearly from eqns. (7) and (8) with above-determined $\Delta\bar{H}^{\circ}_{\mathrm{m}}$ and $\Delta\bar{H}^{\circ}_{\mathrm{sol}}$, the standard enthalpies of NaDS in monomeric and micellar states, $\bar{H}^{\circ}_{\mathrm{mono}}$ and $\bar{H}^{\circ}_{\mathrm{mic}}$, can be calculated on the relative base of standard enthalpy of solid state. Such relative values of $\bar{H}^{\circ}_{\mathrm{mono}}$ and $\bar{H}^{\circ}_{\mathrm{mic}}$ are shown in Fig. 8 against temperature, where the individual values of $\bar{H}^{\circ}_{\mathrm{mic}}$ were plotted on the basis of r.m.s. line of $\bar{H}^{\circ}_{\mathrm{mono}}$.

What is evident from the figure is the nearly constant value of $\bar{H}^{\circ}_{\mathrm{mic}}$ with the increase of temperature, and not of $\bar{H}^{\circ}_{\mathrm{mono}}$ on the value of $\bar{H}^{\circ}_{\mathrm{solid}}$ as reference. Large positive values of both $\bar{H}^{\circ}_{\mathrm{mono}}$ and $\bar{H}^{\circ}_{\mathrm{mic}}$ to $\bar{H}^{\circ}_{\mathrm{solid}}$ show the high predominance of the lattice, mostly coulombic, energy of solid state NaDS over the hydration energy of ionic parts of NaDS in solution.

To develope the discussion further more and in a quantitative way, the temperature-derivative of enthalpy, *i.e.* heat capacity, would be better to be treated concerning to each state of NaDS. The increase of the standard partial molar heat capacity of NaDS on transferring from solid state to monomeric state in solution, abridged in symbol as $\Delta\bar{C}_{\mathrm{p}}^{\circ}$ (solid→mono, NaDS), can be estimated from the inclination of $\bar{H}^{\circ}_{\mathrm{mono}}$ -plot in Fig. 8, giving *ca.* 120 cal deg^{-1} mole^{-1} in the temperature range of 20° to 45°. Similarly, $\Delta\bar{C}_{\mathrm{p}}^{\circ}$ (solid→mic, NaDS), where "mic" denotes micellar state in solution, was estimated to be *ca.* 16 cal deg^{-1} mole^{-1} in the same temperature region. These increments, thus obtained, may be analysed into a few elementary portions as follows.

$$\begin{aligned}\Delta\bar{C}^{\circ}_{p}(\text{solid}\rightarrow\text{mono, NaDS}) &= \Delta\bar{C}^{\circ}_{p}(\text{solid}\rightarrow\text{liq, NaDS}) + \Delta\bar{C}^{\circ}_{p}(\text{liq}\rightarrow\text{mono, D}) \\ &\quad + \Delta\bar{C}^{\circ}_{p}(\text{liq}\rightarrow\text{mono, Na–S}) \qquad (9)\end{aligned}$$

and

$$\Delta\bar{C}_p^\circ(\text{solid}\rightarrow\text{mic, NaDS}) = \Delta\bar{C}_p^\circ(\text{solid}\rightarrow\text{liq, NaDS}) + \beta\cdot\Delta\bar{C}_p^\circ(\text{liq}\rightarrow\text{mono, Na–S}) \qquad (10)$$

The first terms of the r.h.s. of both equations are the quantities on transferring from solid state to a hypothetical liquid state of NaDS. The second and third terms of the r.h.s. of eqn. (9) are the constitutional portions of the increments of $\bar{C}_p^\circ$ of NaDS on transferring from the hypothetical liquid state to monomeric state in solution with regard to the non-polar part (D: $C_{12}H_{25}$) and polar part (Na-S: OSO_3Na) of NaDS, respectively. On solution of NaDS from the hypothetical liquid state to micellar state, the non-polar portion of NaDS is considered to be unchanged and gives no contribution in eqn. (10). The contribution of the polar part on transferring from the hypothetical liquid state to micellar state may be approximately treated as the form of the last term in eqn. (10), by introducing a factor, β. This factor represents the dissociation and hydration of every ionic species and will be unity in the limiting case of perfect dissociation of counter ions and smallest aggregation of micelle with regard to polar heads only of surfactant ions. Roughly speaking, with the micelle of large aggregation and perfect counter-ion dissociation, the factor may be supposed to be 0.5. With α as the degree of counter-ion dissociation, the factor will be 0.5 α. Meanwhile, $\Delta\bar{C}_p^\circ$ of lower *n*-paraffin on transferring from pure liquid to aqueous solution have been obtained as 45, 60, 69 and 80 cal deg^{-1} mole^{-1} for CH_4, C_2H_6, C_3H_8, and C_4H_{10}, respectively.[8a)] From these values, $C_{13}H_{28}$ will have approximately 170 cal deg^{-1} mole^{-1} by extrapolation. Provided that the contribution of CH_3-radical is considered to be half of that of C_2H_6, $C_{12}H_{25}$-radical, hydrophobic part of NaDS, will have 140 cal deg^{-1} mole^{-1} as $\Delta\bar{C}_p^\circ$ (liq→mono, D). With this value and 0.2 as α, or 0.1 as β, the solution of the simultaneous equations (9) and (10) gives 20 and -40 cal deg^{-1} mole^{-1} as $\Delta\bar{C}_p^\circ$ (solid→liq, NaDS) and $\Delta\bar{C}_p^\circ$ (liq→mono, Na-S), respectively. Taking account of the general tendency[24)] that the $\bar{C}_p^\circ$ of an organic compound in liquid state is higher than that in solid state by the amount, which varies from nearly zero cal deg^{-1} mole^{-1} in the case of the compound with non-polarity to about 20 cal deg^{-1} mole^{-1} in the case of the compound with strong polarity, 20 cal deg^{-1} mole^{-1} for $\Delta\bar{C}_p^\circ$ (solid→liq, NaDS) seems to have a sound basis, implying the validity of our analysis as in equations (9) and (10). According to White and Benson,[25)] 69 cal deg^{-1} mole^{-1} was assigned to potassium octanoate for $\Delta\bar{C}_p^\circ$ (solid→ mono). If 20 and 90 cal deg^{-1} mole^{-1} are assigned to $\Delta\bar{C}_p^\circ$ (solid→liq, K octanoate) and $\Delta\bar{C}_p^\circ$ (liq→mono, C_7H_{15}) following the example of NaDS, the similar equation as eqn. (9) gives -41 cal deg^{-1} mole^{-1} for $\Delta\bar{C}_p^\circ$ (liq→mono, ionic part of K octanoate). This coincidence does not seem to be unexpected, since the main parts of these $\Delta\bar{C}_p^\circ$'s consist in the dissociation and hydration of ionic portions, which have no great discrepancy between both surfactants.

From equations (9) and (10), $\Delta\bar{C}_p^\circ$ on micelle formation, $\bar{C}_{p,\text{mic}}^\circ - \bar{C}_{p,\text{mono}}^\circ$, can be given as follows.

$$\begin{aligned}\Delta\bar{C}_p^\circ(\text{mono}\rightarrow\text{mic, NaDS}) &= \Delta\bar{C}_p^\circ(\text{solid}\rightarrow\text{mic, NaDS}) - \Delta\bar{C}_p^\circ(\text{solid}\rightarrow\text{mono, NaDS})\\ &= -\Delta\bar{C}_p^\circ(\text{liq}\rightarrow\text{mono, D}) + (\beta-1)\cdot\Delta\bar{C}_p^\circ(\text{liq}\rightarrow\text{mono, Na–S}) \qquad (11)\end{aligned}$$

It will be appropriately concluded therefore that the $\Delta\bar{C}_p^\circ$ or temperature-dependence of heat of micelle formation consists mainly in $\Delta\bar{C}_p^\circ$ (liq→mono, D) or the change of heat capacity owing to the formation of hydrophobic interaction between the paraffin portion of surfactant and water, since the second term of r.h.s. of eqn. (11) is small compared with the first term.

For the further study of the contribution of ionic portions, which was shown in the last terms of equations. (9), (10) and (11), now the experiments on dodecylsulfates with other

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25) P. White and G.C. Benson, *J. Phys. Chem.*, **64**, 599 (1960).

cations are being carried out.

Also, the discussions on other thermodynamic parameters than enthalpy and heat capacity, *i.e.* entropy and Gibbs free energy of micelle as well as monomeric species will be done at the report of the above-mentioned work, although the experimentally derived results without detailed discussions were reported on this paper as in Table I.

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