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Effect of Counter-ions on the Thermodynamic Properties of Alkali Dodecyl Sulfates in Monomeric and Micellar Dispersions

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In order to elucidate the behavior of ionic portion as well as hydrophobic one of surfactant at solution and micelle formation with the view-point of enthalpy and heat capacity changes, the molar standard enthalpies of solution and micelle formation of lithium, sodium and potassium dodecyl sulfates (generically abr. as DMS), $\Delta_{sol}\bar{H}^{\circ}_{MDS}$ and $\Delta_{m}\bar{H}^{\circ}_{MDS}$, were determined by calorimetry at various temperatures from 20° to 50°, and also their critical micelle concentrations, CMC's by electric conductivity measurement. The molar standard Gibbs free energy and entropy of micelle formation as well as the degree of counter-ion dissociation in micelle were calculated using thermodynamic relations from the values of CMC at various temperatures and $\Delta_{m}\bar{H}^{\circ}_{MDS}$. On the basis of Born's theory, $\Delta_{sol}\bar{H}^{\circ}_{MDS}$ was expressed in the terms, explicitly containing the ionic radii of both dodecylsulfate anion and counter-cation, Li^+, Na^+, and K^+, in MDS crystal and in water, and the terms, representing the hydrophobic contributions of MDS to lattice and hydration energies. The substitution of experimental and literary values into the above-mentioned expression gives, *e.g.* 2.2 Å and 2.0 Å as ionic radii of dodecylsulfate ion in crystal and in water, respectively. Also, $\Delta_{m}\bar{H}^{\circ}_{MDS}$ and its corresponding heat capacity, $\Delta_{m}\bar{C}^{\circ}_{p,\,MDS}$, were analyzed with respect to the hydrophobic and ionic contributions to micelle formation.

Precedingly,[2] the authors showed that the effect of temperature on the enthalpy changes of solution and micelle formation of sodium dodecyl sulfate depends mainly upon the heat capacity changes of its non-polar part, indicating a significant role of hydrophobic interaction played in the behavior of surfactant in water. Although the contribution of ionic part to the above-mentioned temperature effect was found relatively small, the possibility of substantial participation of ionic portion into the enthalpy changes themselves can be expected from the rather great variations of solvation enthalpies among different ionic species.[3] Moreover, the complicated behavior of ions involving water-structures[4] must be taken into consideration on the discussion of hydrophobic interaction. In order to settle such matters and elucidate the nature of other thermodynamic parameters of ionic surfactant, we have carried out the following experiments on lithium, sodium and potassium dodecyl sulfates (abr. as LiDS, NaDS and KDS, respectively) and discussed the results with special interest in the effect of counter-ions.

Experimental

Materials——Dodecyl Sulfates: Conc. sulfuric acid (240 ml: *ca.* twice equivalent amount) was mixed to 500 ml of 1-dodecanol dropwise for 1 hr at 25—30°. After 1 hr of further mixing, a sufficient quantity of conc. respective alkali hydroxide aq. solution was added to neutralize the dodecylsulfuric acid produced. From the resulting paste, LiDS, NaDS, or KDS was separated out by three recrystallizations in isopropanol for LiDS in *n*-butanol for NaDS or in ethanol for KDS. Each dodecyl sulfate was then purified by repeated petroleum-ether extractions for 30 hr in total. After dried, these samples were stored in a vacuum desiccator. The crystals thus obtained are anhydrous powder (LiDS), lustrous thin crystals of eighth hydrate (NaDS) and quarterhydrate (KDS), respectively.[5] The water content of each crystal was determined by gravimetry

1) Location: *Tanabe-dori, 3-1, Mizuho-ku, Nagoya, 467, Japan.*
2) H. Kishimoto and K. Sumida, *Chem. Pharm. Bull.* (Tokyo), **22**, 1108 (1974).
3) E.A. Moelwyn-Hughes, "Physical Chemistry," 2nd rev. ed., Pergamon Press, Oxford, 1965, Chapts. 13, 18.
4) H.S. Frank and M.W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).
5) With respect to NaDS, these three states of crystal correspond to ξ-phase, α-phase, and κ-phase, respectively, F.F. Rawlings, Jr., and E.C. Lingafelter, *J. Am. Chem. Soc.*, **77**, 870 (1955).

with successive heatings and vacuum dryings. The purity of these substances was considered to suffice for our experiments, since their critical micelle concentrations (CMC's) came in the range of reliable values in literatures, as seen in Fig. 1.

The purity of 1-dodecanol (G.R. from Tokyo Kasei Kogyo Co., Ltd.) was certified by gas chromatography to be over 99.5%. Hydroxides, sulfuric acid and solvents used were obtained from Wako Pure Chemical Ind., Ltd. (S.G.). Solvents were distilled before use. Distilled and deionized water was used throughout.

Apparatuses and Procedures——For the determination of CMC, the electric conductivity of surfactant solution was measured at various concentrations using a conductivity cell of dipping type and a universal bridge. For enthalpy changes of surfactant on solution and micelle formation, the heats of solution and dilution were measured with a twin-type conduction calorimeter, generally giving mean errors of ca. 0.5 and 0.1 kcal mole^{-1}, respectively. Details of apparatuses, procedures and thermodynamic analyses of the above-mentioned experiments were described in the preceding paper.[2)]

Result

CMC

The CMC values of LiDS, NaDS and KDS were obtained at various temperatures and are shown in Fig. 1 and Table I. Although the CMC of NaDS was measured also in the preceding work,[2)] we adopted the data of newly prepared NaDS in this work, because of the conformity on the preparative method of dodecyl sulfates. The latter CMC, adopted in this work, is higher than the former by 0.3—0.4$\times 10^{-3}$ mole kg^{-1} in molality over the temperature range of our experiments. This difference in CMC corresponds, however, to the deviation of only 0.03 kcal mole^{-1} on the evaluation of free energy of micelle formation, based on eqn. (3), showing the availability of both samples to the measurements for thermodynamic parameters, such as free energy or enthalpy.

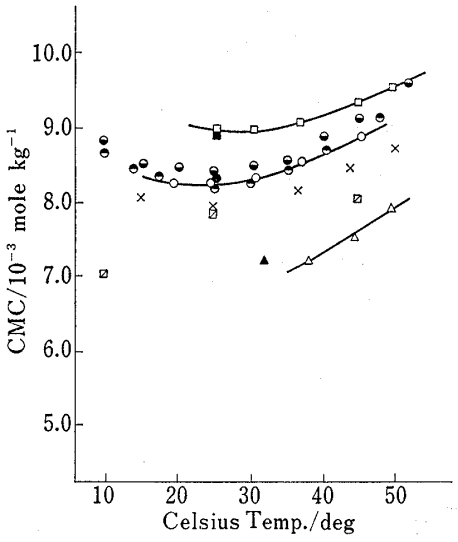

Fig. 1. CMC *vs.* Temperature Relationship of MDS

—□—: LiDS, —○—: NaDS, —△—: KDS

Previous and other workers' values are cited by the following symbols with the reference number in parentheses.

LiDS ■: 7*a*), ◪: *a*)

NaDS ●: 7*a*), ◒: *b*), ◓: *c*), ×: (previous work, 2)

KDS ▲: 7*a*)

a) M.J. Schick, *J. Phys. Chem.*, **68**, 3585 (1964)

b) E.D. Goddard and G.C. Benson, *Can. J. Chem.*, **35**, 986 (1957)

c) B.D. Flockhart, *J. Colloid Sci.*, **16**, 484 (1961)

Partial Molar Standard Enthalpy of Solution from Heat of Solution

The molar heats of solution of LiDS, NaDS and KDS at various temperatures were measured and plotted in Fig. 2, jointly with the data of NaDS in the preceding work, indicating a good agreement between the data on our samples (NaDS) prepared in different manners, as was anticipated in the preceding paragraph. As already mentioned,[2)] the endothermic

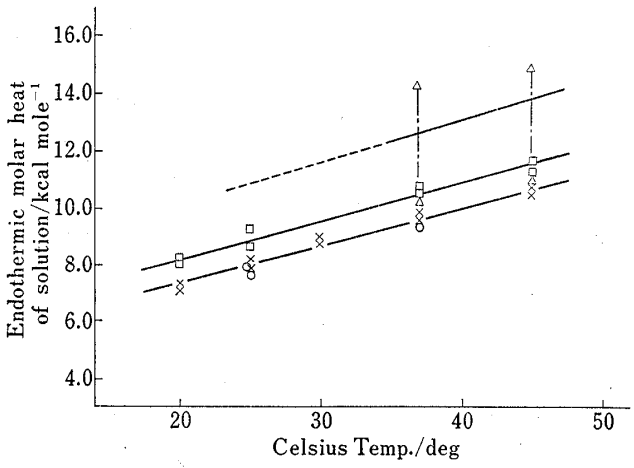

Fig. 2. Endothermic Molar Heat of Solution of MDS at Various Temperatures

□: LiDS, ○: NaDS, △: KDS, ×: NaDS (previous work, 2)

TABLE I. Various Parameters of MDS at Micelle Formation and Solution

Temp. (°C)	CMC/10^{-3} mole kg^{-1}			$\Delta_m\overline{G}°$/kcal mole^{-1} from CMC in mole fraction[a]			$\Delta_m\overline{H}°$/kcal mole^{-1} from calorimetry		
	LiDS	NaDS	KDS	LiDS	NaDS	KDS	LiDS	NaDS	KDS
20		8.24			−9.24			0.30	
25	8.90	8.23		−9.06	−9.40		0.20	−0.30	
30	8.93	8.29		−9.21	−9.55		−0.34	−0.80	
35	9.00	8.43	7.12	−9.35	−9.69	−10.10	−0.85	−1.35	−1.95
40	9.15	8.61	7.34	−9.49	−9.82	−10.23	−1.36	−1.85	−2.50
45	9.35	8.84	7.60	−9.62	−9.96	−10.35	−1.88	−2.30	−3.05
50	9.60		7.95	−9.73		−10.46	−2.40	−2.80	−3.60

	$\Delta_m\overline{S}°$/cal deg^{-1} mole^{-1}			$\Delta_{sol}\overline{H}°$/kcal mole^{-1}			α			
	LiDS	NaDS	KDS	LiDS	NaDS	KDS	LiDS	NaDS		KDS
20		32.47		8.20	7.30					
25	31.06	30.52		8.80	7.90	10.60[b]	0.303[c] 0.17[f]	0.275[c] 0.229[f]	0.21[d] 0.228[g]	0.245[e]
30	29.26	28.86		9.45	8.60			0.242[g]		
35	27.58	27.06	26.45	10.15	9.20	12.05		0.258[g]		
40	25.96	25.45	24.68	10.80	9.85	12.90				
45	24.33	24.08	22.94	11.50	10.50	13.75				
50	22.68		21.23							
mean							0.25[h]	0.20[h]		0.16[h]

a) For the unitary expression to thermodynamic functions, "mole fraction" was used as concentration unit.[2]
b) ref. 10
c) ref. 7*a*
d) ref. 2
e) An extrapolated value by us from the data on LiDS, NaDS with respect to Stoke's law hydrated radius.[7a]
f) ref. 7*b*
g) ref. 7*c*
h) Mean value used by us for experimental temperature-region. (see context)

molar heat of solution into sufficiently low concentration can give approximately the partial molar standard enthalpy of solution, $\Delta_{sol}\overline{H}°$, which is defined by the following equation.[6]

$$\Delta_{sol}\overline{H}° = \overline{H}°_{mono} - \overline{H}°_{solid}, \quad (1)$$

where $\overline{H}°_{mono}$ and $\overline{H}°_{solid}$ are the partial molar standard enthalpy of surfactant in monomer state and that in solid state, respectively. The values of $\Delta_{sol}\overline{H}°$ in Table I are corrected ones corresponding to the smoothed lines through original data as seen in Fig. 2.

Partial Molar Standard Enthalpy of Micelle Formation from Heat of Dilution

The heats of dilution of LiDS, NaDS and KDS at various temperatures were measured, where the dilution ratio, diluent/solution to be diluted, was always 20/1. The heats obtained with various final concentrations are shown in Fig. 3. From these data, the partial molar standard enthalpies of micelle formation of LiDS, NaDS and KDS, $\Delta_m\overline{H}°$'s, were calculated according to the following equation[2] and shown in Fig. 4 and Table I.

$$\Delta_m\overline{H}° = -\Delta_{dil}H/n_{destroyed}, \quad (2)$$

where $\Delta_{dil}H$ and $n_{destroyed}$ denote the endothermic heat of dilution and moles of the surfactant in micellar form, which is destroyed into monomeric form by dilution, respectively. Similarly

6) $\Delta_{sol}\overline{H}°$, $\Delta^{mic}_{mono}\overline{C}^{\circ}_{p,\,NaDS}$ and so on are used here in place of $\Delta\overline{H}^{\circ}_{sol}$, $\Delta\overline{C}^{\circ}_{p}$(mono→mic, NaDS) and so on in a previous paper, according to M.L. McGlashan, "Physicochemical Quantities and Units," 2nd ed., Royal Institute of Chemistry, London, 1971.

as in the case of $\Delta_{sol}\bar{H}^\circ$, $\Delta_m\bar{H}^\circ$ of NaDS in the preceding work was added to the above-mentioned data.

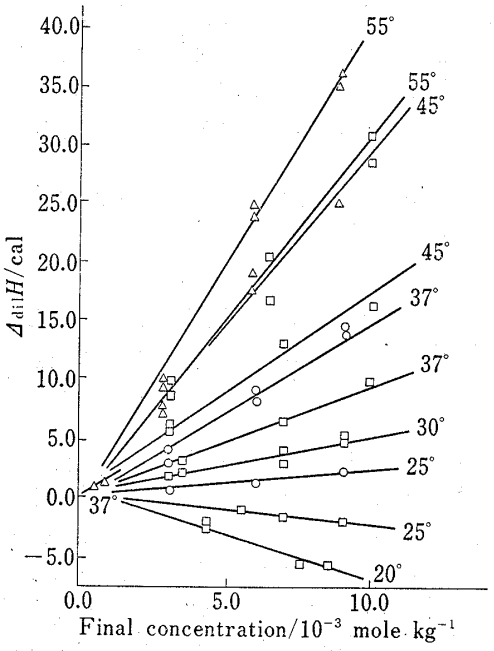

Fig. 3. Heat of Dilution of MDS, $\Delta_{dil}H$, at Various Temperatures

In this figure, experimental values are converted to the system containing 1 kg of water as solvent.
□: LiDS, ○: NaDS, △: KDS

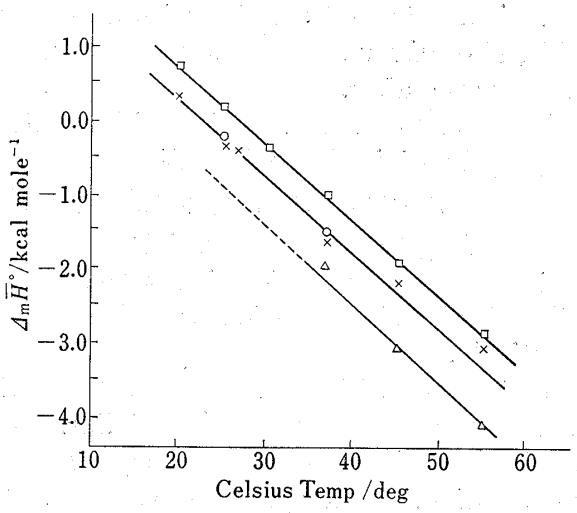

Fig. 4. Partial Molar Standard Enthalpy of Micelle Formation of MDS, $\Delta_m\bar{H}^\circ$, at Various Temperatures

□: LiDS, ○: NaDS, △: KDS, ×: NaDS (previous work, 2)

Partial Molar Standard Gibbs Free Energy and Entropy of Micelle Formation from CMC Value and Heat of Dilution

Partial molar standard Gibbs free energy of micelle formation, $\Delta_m\bar{G}^\circ$, can be obtained from CMC value, according to the following equation,[2]

$$\Delta_m\bar{G}^\circ = (2-\alpha)\boldsymbol{R}T \ln (\text{CMC}), \tag{3}$$

where α means the degree of dissociation of counter-ions in micelle. From $\Delta_m\bar{G}^\circ$'s, $\Delta_m\bar{H}^\circ$ can be computed using the following thermodynamic equation.

$$\Delta_m\bar{H}^\circ = \frac{d(\Delta_m\bar{G}^\circ/T)}{d(1/T)} \tag{4}$$

Using above relations with the values of CMC and α on NaDS, we have obtained $\Delta_m\bar{H}^\circ$, which agrees well with the $\Delta_m\bar{H}^\circ$ from heat-of-dilution measurement.[2] Taking into consideration this fact and the unsatisfying accuracy of α determination with the present technical level, reversely we chose appropriate values as α's for our samples including NaDS to make conform the $\Delta_m\bar{H}^\circ$ obtained from CMC to the $\Delta_m\bar{H}^\circ$ from heats of dilution. These α values were brought into the range of distribution of reported values,[7] as shown in Table I.

According to eqn. (3) with CMC and above-mentioned α, $\Delta_m\bar{G}^\circ$ was calculated and tabulated in Table I. Also, the corresponding value of partial molar standard entropy of micelle formation, $\Delta_m\bar{S}^\circ$, defined as $(\Delta_m\bar{H}^\circ-\Delta_m\bar{G}^\circ)/T$, was obtained, where the value of Δ_mH° from heat of dilution was used.

7) *a*) P. Mukerjee, K.J. Mysels, and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967); *b*) T. Ingram and M.N. Jones, *Trans. Faraday Soc.*, **65**, 297 (1969); *c*) J. Piercy, M.N. Jones, and G. Ibbotson, *J. Colloid Interface Sci.*, **37**, 165 (1971).

Discussion

Ionic Radii on the Enthalpy of Solution

As is evident from Fig. 2, the magnitude of $\Delta_{sol}\overline{H}^{\circ}$ of each dodecyl sulfate followed the order, KDS>LiDS>NaDS, with respect to the kind of counter-ion over experimental temperature region. Its contradiction with a usually conceivable sequence for alkali metal, such as Li, Na, K or *vice versa*, was found to be not of fundamental, but of apparent nature, as will be shown soon after.

The $\Delta_{sol}\overline{H}^{\circ}$ of dodecyl sulfate with counter-ion, M^+, which stands for Li^+, Na^+ or K^+ in our case, may be divided as follows.[8]

$$\Delta_{sol}\bar{H}^{\circ}_{MDS} = \Delta_{sub}\bar{H}^{\circ}_{MDS} + \Delta_{h}\bar{H}^{\circ}_{M^+} + \Delta_{h}\bar{H}^{\circ}_{DS^-}, \quad (5)$$

where $\Delta_{sub}\overline{H}^{\circ}_{MDS}$ denotes the partial molar standard enthalpy change of MDS from solid to ions in vacuum by sublimation accompanied with ionization and $\Delta_{h}\overline{H}^{\circ}_{M^+}$ or $\Delta_{h}\overline{H}^{\circ}_{DS^-}$ the similar change of counter-ion or dodecyl sulfate ion from vacuum into water by hydration, respectively.

Of these terms in eqn. (5), the value of l.h.s. term was obtained, as in Table I, from our heat measurements and the second r.h.s. term can be evaluated from the heats of solution of various salts including M^+, although the values depend upon the choice of theoretical basis for evaluation. Thereby, we adopted -269.8 kcal mole^{-1} as reference to $\Delta_{h}H^{\circ}_{H^+}$ at 25°, following Conway's citation,[9] where -132.1, -106.0 and -85.8 kcal mole^{-1} are assigned to $\Delta_{h}\overline{H}^{\circ}_{M^+}$ values for Li^+, Na^+ and K^+, respectively. Substituting these values and the $\Delta_{sol}\overline{H}^{\circ}_{MDS}$ values at 25°, *i.e.* 8.8, 7.9 and 10.6 kcal mole^{-1} for LiDS, NaDS and KDS,[10] respectively, into eqn. (5), its remainder, $\Delta_{sub}\overline{H}^{\circ}_{MDS}+\Delta_{h}\overline{H}^{\circ}_{DS^-}$, can be obtained as 140.9, 113.9 and 96.4 kcal mole^{-1} for LiDS, NaDS and KDS, respectively.

According to Born's theory,[3] the lattice energy, $\Delta_{lat}U$, of the inorganic crystal may be formulated as follows,

$$\Delta_{lat}U = \frac{NC_{M}e^2}{s}(1-1/n), \quad (6)$$

where N, C_M,[11] e, s and n are the Avogadro's number, the Madelung constant, the electronic charge in e.s.u. the equilibrium nearest neighbor separation in crystal and the index for the inverse power describing the dispersion repulsive force, respectively. Taking into consideration the circumstances that NaDS and probably LiDS as well as KDS are estimated[12] to have their ionic parts gathering together in pseudo-crystalline arrangement and also the hydrophobic parts in similar but separate group, and neglecting the possible differences of crystal state[5] and number of hydrated water among samples, we approximately modified eqn. (6) for the lattice energy of ionic surfactant, $\Delta_{lat}U'$, to the following equation.

$$\Delta_{lat}U' = \frac{NC_{M}'e^2}{s}\Delta_{lat}U_{H\phi}, \quad (7)$$

where the first and second r.h.s. terms represent the contributions of ionic and hydrophobic parts to the total lattice energy, respectively, and C_M' have the nature of two-dimensional Madelung constant,[13] containing implicitly the factor, $(1-1/n)$, in eqn. (6). Since the difference

8) R.W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, 1953.
9) B.E. Conway, "Physical Chemistry, An Advanced Treatise," ed. by H. Eyring, D. Henderson, and W. Jost, Vol. IXA, Academic Press, New York, 1970, Chapt. I, Tables VI and VIII.
10) 10.6 kcal mole^{-1} for KDS at 25° was an extrapolated value from the data at high temperatures.
11) Conventionally, the symbol of Madelung Constant is α, but we already used it for the degree of dissociation of counter-ions in micelle.
12) L.H. Jensen and E.C. Lingafelter, *J. Am. Chem. Soc.*, **68**, 1729 (1946).
13) B.A. Pethica, In "Symp. Surface Activity and the Microbial Cell," Soc. of Chem. Ind., London, 1965, Monograph 19, p. 85.

between $\Delta_{lat}U'$ and $\Delta_{sub}\bar{H}^{\circ}_{MDS}$ is of order RT (R: gas constant), which can be roughly neglected, $\Delta_{sub}\bar{H}^{\circ}_{MDS}$ in eqn. (5) will be replaced by the terms of eqn. (7), where s must be substituted by the sum of the ionic radius of M^+ in crystal, which is defined as usual,[14] r_{c,M^+}, and the effective ionic radius of dodecyl sulfate ion in crystal, r_{c,DS^-}. The meaning of the last-mentioned ionic radius will be understood in terms of its evaluation to be made in the subsequent paragraphs. With these modifications, eqn. (5) can be transformed as follows.

$$\Delta_{sol}\bar{H}^{\circ}_{MDS} - \Delta_h\bar{H}^{\circ}_{M^+} = \frac{NC_{M'}e^2}{r_{c,M^+}+r_{c,DS^-}} + \Delta_{lat}U_{H\phi} + \Delta_h\bar{H}^{\circ}_{DS^-}. \quad (8)$$

Giving various arbitrary values to r_{c,DS^-}, we plotted the l.h.s. value at 25°, which was already mentioned as $(\Delta_{sub}\bar{H}^{\circ}_{MDS}+\Delta_h\bar{H}^{\circ}_{DS^-})$ in the preceding paragraph, against the inverse value of $(r_{c,M^+}+r_{c,DS^+})$ for LiDS, NaDS and KDS, as seen in Fig. 5.

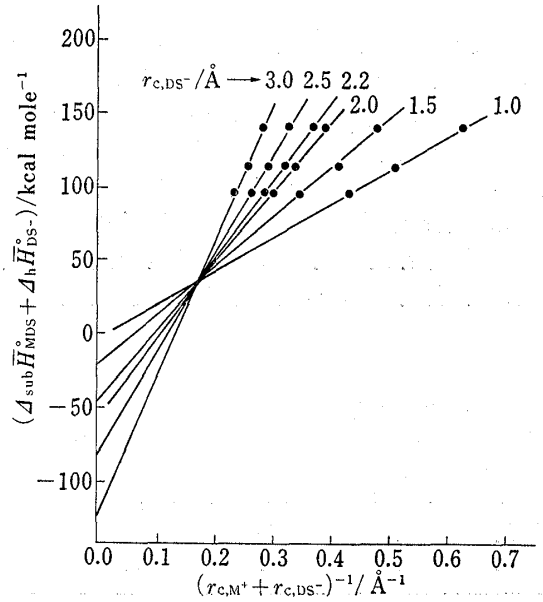

Fig. 5. The Relation between $(\Delta_{sub}\bar{H}^{\circ}_{MDS}+\Delta_h\bar{H}^{\circ}_{DS^-})$ and $(r_{c,M^+}+r_{c,DS^-})^{-1}$ for Various Arbitrary Values of r_{c,DS^-} at 25°

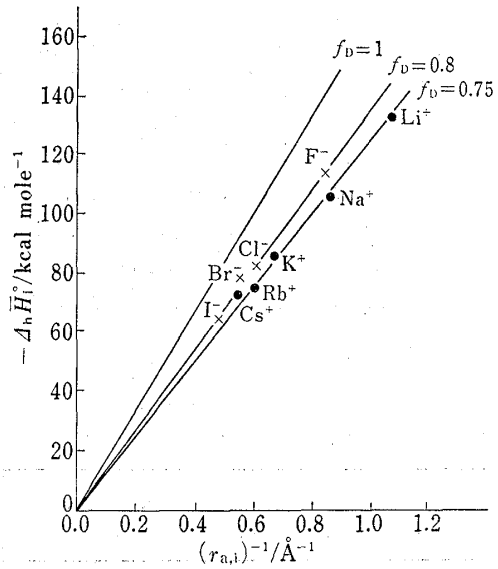

Fig. 6. The Relation between $-\Delta_h\bar{H}^{\circ}_i$ and $(r_{a,i})^{-1}$ of Various Cations and Anions at 25°

The plots of co-ordinate with *ca.* 2.2 Å as common r_{c,DS^-} value for three dodecylsulfates could satisfy the linear relationship demanded by eqn. (8) and also the slope calculated on the assumption that $C_{M'}$ has the value of *ca.* 1.6 which is in the range expected from the values for ordinary inorganic salts,[3,15] *e.g.* 1.5 (as $C_M(1-1/n)$) for NaCl, and the two-dimensional Madelung constant for square-lattice phospholipid monolayer, *i.e.* 1.6.[13] From the intercept of this line on the ordinate axis, the value of $(\Delta_{lat}U_{H\phi}+\Delta_h\bar{H}^{\circ}_{DS^-})$ in eqn. (8) was evaluated to be *ca.* −55 kcal mole^{-1}. Calculated as the sum of enthalpies of melting and vaporization,[16] the sublimation enthalpy of normal hydrocarbon was found to be roughly expressed in linear form, assigning about 1.70 and 1.76 kcal mole^{-1} to each CH_2– and CH_3–groups of hydrocarbon, respectively. Therefrom, the value of sublimation enthalpy of $C_{12}H_{25}$-group or approximately the $\Delta_{lat}U_{H\phi}$ of MDS was estimated to be *ca.* 20.5 kcal mole^{-1}. Then, to $\Delta_h\bar{H}^{\circ}_{DS^-}$, *ca.* −75 kcal mole^{-1} could be allotted. Since the hydration of ions can be, in the sense of energetics, attributed to the change of state of water, which surrounds them, and the change itself

14) L. Pauling, "General Chemistry," 3rd ed., W.H. Freeman & Co., San Francisco, 1970.
15) C. Kittel, "Introduction to Solid State Physics," 2nd ed., John Wiley & Sons, Inc., New York, 1956.
16) Chem. Soc. Japan (ed.), "Kagaku Binran," Maruzen Co. Ltd., Tokyo, 1966, pp. 782—785.

can be approximately divided to the electrostatic and hydrophobic parts, if ions contain hydrophobic groups, $\Delta_h\bar{H}^\circ_{DS^-}$ may be separated as follows.

$$\Delta_h\bar{H}^\circ_{DS^-} = \Delta_h\bar{H}^\circ_{S^-} + \Delta_h\bar{H}^\circ_D, \quad (9)$$

where $\Delta_h H^\circ_{S^-}$ and $\Delta_h\bar{H}^\circ_D$ represent the ionic and hydrophobic contributions of dodecylsulfate ion to $\Delta_h\bar{H}_{DS^-}$, respectively. From the heats of solution of various hydrocarbon gases in water[17] and their simple algebra, the heats of solution of CH_2–, CH_3– and ultimately $C_{12}H_{25}$–groups could be approximately estimated to be −0.85, −2.1 and −11 kcal mole^{-1}, respectively. Substitution of the last-mentioned value as $\Delta_h\bar{H}^\circ_D$ into eqn. (9) gives the value of *ca.* −65 kcal mole^{-1} to $\Delta_h\bar{H}^\circ_{S^-}$.

It was also expected from Born's theory[3] that a linear relationship exists between the hydration energy of ion, such as $\Delta_h\bar{H}^\circ_i$, and the ionic radius in aqueous solution, $r_{a,i}$, as follows.

$$\Delta_h\bar{H}^\circ_i = -\frac{f_D N e^2}{2r_{a,i}}, \quad (10)$$

where f_D means the correction factor containing dielectric constant, which is approximately equal to unity in aqueous media, and the meanings of N and e are the same with those in eqn. (6). Although the significant deviation of the line based on eqn. (10) from the $\Delta_h\bar{H}^\circ_i$ *vs.* $r_{a,i}$ plots in Fig. 6 suggests the rather rough premises for the above equation, it will be still used as an empirical relation, if f_D is substituted with a suitable number, *i.e.* 0.8 for mono-valent anion and 0.75 for mono-valent cation. Then, the effective ionic radius of the ionic part proper in dodecylsulfate ion in water, r_{a,DS^-}, was calculated to be *ca.* 2.0 Å. Both this value and 2.2 Å as r_{c,DS^-} would be acceptable in the sence of effective value. For comparison, they are listed in Table II with the values of other ions.

Table II. Ionic Radii (Å) in Water and Crystal[a]

	DS^-	F^-	Cl^-	Br^-	I^-	Li^+	Na^+	K^+
r_a	2.0	1.16	1.64—1.63	1.80	2.04	0.93	1.17—1.18	1.49
r_c	2.2	1.36	1.81	1.95	2.16	0.60	0.95	1.33

a) ref. 9 except DS^-

After all, the enthalpy of solution of MDS can be written in physically definable terms as follows.

$$\Delta_{sol}\bar{H}^\circ_{MDS} = \frac{NC_M' e^2}{r_{c,M^+}+r_{c,DS^-}} - \frac{0.75Ne^2}{2r_{a,M^+}} - \frac{0.8Ne^2}{2r_{a,DS^-}} + \Delta_{lat}U_{H\phi} + \Delta_h\bar{H}^\circ_D, \quad (11)$$

With respect to the quantitative reliability of this equation, it is to be noted that the first and third r.h.s. terms might change in the order of 10 kcal mole^{-1} owing to the slight revaluation of r_{c,DS^-} and consequently of r_{a,DS^-} in the order of 0.1 Å, which can be anticipated as seen in Fig. 5.

Analysis of the Enthalpy of Micelle Formation

For the analysis of the enthalpy change of MDS at micelle formation, $\Delta_m\bar{H}^\circ_{MDS}$, we adopted an analogous method to the previously reported for the analysis of the heat capacity changes of NaDS[2] and Aerosol OT,[18] since only the values of α for each surfactant and the hydration enthalpy of liquid hydrocarbon, *e.g.* $\Delta^{mono}_{liq}\bar{H}^\circ_D$ for dodecyl-radical of MDS, will suffice there and also a unified description of both the enthalpies of solution and micelle formation can be possible, although it lacks the explicit relation to ionic radii in the preceding treatment on $\Delta_{sol}\bar{H}^\circ_{MDS}$. Since the process of micelle formation in terms of enthalpy change consists mainly of (I) the destruction of water structure surrounding the hydrophobic portion of surfactant

17) G. Némethy and H.A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).
18) Y. Sato, M. Ueno, and H. Kishimoto, *Yakugaku Zasshi*, **95**, 1286 (1975).

due to its escape from water and aggregation to liquid state inside the micelle and (II) the dehydration of the polar portion and its electrostatic interaction due to aggregation around the micelle, $\Delta_m\bar{H}^\circ_{MDS}$ can be approximately divided into the two r.h.s. terms in eqn. (12), where the first corresponds to (I) and the second to (II).

$$\Delta_m\bar{H}^\circ_{MDS} = \Delta^{mic}_{mono}\bar{H}^\circ_{MDS} = \Delta^{liq}_{mono}\bar{H}^\circ_{D} + (1-\beta')\Delta^{liq}_{mono}\bar{H}^\circ_{M\text{-}S}, \quad (12)$$

where "mono" and "mic" represent monomeric and micellar dispersions in water, respectively; "liq" represents a hypothetically liquid state, the concept of which was introduced to account for the hypothetical aggregation of surfactant with micelle-like structure, but no interaction with solvent; "M-S" and "D" mean the polar and hydrophobic portions of MDS; and β' denotes the factor, in terms of enthalpy change, accounting for the incomplete interaction of polar portion in micelle with water in comparison with the case of monomeric dispersion and approximately can be considered to equal the analogous factor in terms of heat capacity change, β, which could be assumed to be 0.5 α.[2,18] The value of $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$ is $-\Delta^{mono}_{liq}\bar{H}^\circ_{M-S}$ by definition.[6] With respect to the magnitudes of each term of factor, $\Delta_m\bar{H}^\circ_{MDS}$ and α for LiDS and NaDS at 25° were obtained as shown in Table I, these for KDS can be estimated to be -0.9 kcal mole^{-1} and 0.16 from the extrapolation of values at higher temperatures, and also the value of $\Delta^{liq}_{mono}\bar{H}^\circ_D$ can be estimated to be -5.3 kcal mole^{-1} from the formula,[2] $\Delta^{liq}_{mono}H^\circ_D = \Delta^{liq}_{mono}\bar{H}^\circ_{C_{18}H_{38}} - 1/2\Delta^{liq}_{mono}\bar{H}^\circ_{C_2H_6}$, where each r.h.s. term was evaluated to be -4.2 and 1.1 kcal mole^{-1} as extrapolated or directly observed one,[17] respectively. Then, $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$ for each surfactant can be evaluated as shown in Table III with the substitution of 0.5 α into β'.

TABLE III. Transfer Enthalpies (kcal mole^{-1}) of MDS and Its Portions

	β'	$\Delta^{liq}_{solid}\bar{H}^\circ_{MDS}$	$\Delta^{mic}_{mono}\bar{H}^\circ_{MDS}$	$\Delta^{liq}_{mono}\bar{H}^\circ_{D}$	$\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$	$\Delta_h\bar{H}^\circ_{M^+}$	$\Delta_h\bar{H}^\circ_{S^-}$
LiDS	0.125	9.8	0.20	−5.3	6.3	−132.1	−65
NaDS	0.10	8.2	−0.30	−5.3	5.6	−106.0	−65
KDS	0.08	10.1	−0.90	−5.3	4.8	−85.8	−65

From the inspection of the data in Table III, it is evident that the hydrophobic contribution, represented by $\Delta^{liq}_{mono}\bar{H}^\circ_D$, and the polar one, $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$, to micelle formation nearly compensate with each other, giving small net enthalpy change of micelle formation, and also, the two kinds of energy, which can be considered to constitute $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$ unitedly, *i.e.* the large dehydration energy, which are related to $-\Delta_h\bar{H}^\circ_{M^+}$ and $-\Delta_h\bar{H}^\circ_{S^-}$, and the aggregation energy of polar portions at micelle formation, have nearly the same magnitudes of value, but with opposite signs, as each other, producing relatively small value of $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$. The positive and decreasing value of $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$ with the order of LiDS, NaDS and KDS can infer that the dehydration energy predominates over the aggregation energy in over-all magnitude and the effect of ionic radius on the former exceeds that on the latter, since both kinds of energy can be considered to decrease with the increase of ionic radius, *i.e.* with the order of Li^+, Na^+ and K^+.

Alternative Analysis of the Enthalpy of Solution

Also, $\Delta_{sol}\bar{H}^\circ_{MDS}$, which was analyzed in the form of eqn. (5) and so on, can be expressed in the following alternative form on the same principle as mentioned above.

$$\Delta_{sol}\bar{H}^\circ_{MDS} = \Delta^{mono}_{solid}\bar{H}^\circ_{MDS} = \Delta^{liq}_{solid}\bar{H}^\circ_{MDS} + \Delta^{mono}_{liq}\bar{H}^\circ_{D} + \Delta^{mono}_{liq}\bar{H}^\circ_{M\text{-}S}, \quad (13)$$

where "solid" means the solid state of MDS. The first r.*h*.s. term corresponds to the transformation of MDS from solid state to hypothetically liquid one. The second and third terms are complements with each other for $\Delta^{mono}_{liq}\bar{H}^\circ_{MDS}$, corresponding to the non-polar and polar contributions, respectively. By substituting into eqn. (13) the values of $\Delta_{sol}H^\circ_{MDS}$, $\Delta^{mono}_{liq}\bar{H}^\circ_D$ and $\Delta^{mono}_{liq}\bar{H}^\circ_{M-S}$, which were obtained before and the last two of which were presented as $\Delta^{liq}_{mono}\bar{H}^\circ_D$ and $\Delta^{liq}_{mono}\bar{H}^\circ_{M-S}$ with opposite signs, we can evaluate $\Delta^{liq}_{solid}\bar{H}^\circ_{MDS}$ as shown in Table III. The

value of $\Delta^{liq}_{solid}\bar{H}^{\circ}_{MDS}$ shows no regularity on the order of cationic radius, notwithstanding that the lattice energy of MDS, *i.e.* $\Delta_{lat}U'$, depends strongly upon ionic radius of cation as seen, *e.g.* in the first term of eqn. (11). This means that in the process for $\Delta^{liq}_{solid}\bar{H}^{\circ}_{MDS}$, the separation of ionic parts does not occur, but only the liquefaction occurrs, leaving the main effect of ionic radius to the enthalpy of vaporization of MDS into ionized gaseous state, $\Delta^{gas}_{liq}\bar{H}^{\circ}_{MDS}$, which approximately makes up $\Delta_{lat}U'$ together with $\Delta^{liq}_{solid}\bar{H}^{\circ}_{MDS}$. The difference among the values of $\Delta^{liq}_{solid}\bar{H}^{\circ}_{MDS}$ for three surfactants, therefore, seems to result from rather the possible differences of crystal state and number of hydrated water, which were neglected before on the discussion of eqn. (7), than the difference of ionic radius of counter-cation.

Entropy of Micelle Formation

From the large gain of entropy at micelle formation, as seen in Table I, it can be qualitatively concluded that the sum of entropy increases due to the destruction of water structure around the hydrophobic portion and to the dehydration of ions constituting surfactant greatly exceeds in magnitude the entropy decrease due to the association of surfactant ions with themselves and with counter-ions. The difference among MDS's, although slight, seems perhaps to result from that of the magnitude of dehydration, which follows the order, $Li^+ > Na^+ > K^+$ with respect to cations.

The magnitudes and differences among MDS's of CMC and $\Delta_m\bar{G}^{\circ}_{MDS}$ depend clearly on these of $\Delta_m\bar{H}^{\circ}_{MDS}$, $\Delta_m\bar{S}^{\circ}_{MDS}$ and slightly α, which have been almost discussed except the last.

Effects of Temperature on the Enthalpies of Solution and Micelle Formation

According to the previous work[2] and corresponding to eqns. (12) and (13), the temperature coeffecients of the above-mentioned enthalpies, *i.e.* the heat capacities of solution and micelle formation of MDS, $\Delta_{sol}\bar{C}^{\circ}_{p.\,MDS}$ and $\Delta_m\bar{C}^{\circ}_{p.\,MDS}$, can be written in the following forms.

$$\Delta_{sol}\bar{C}^{\circ}_{p,MDS} = \Delta^{mono}_{solid}\bar{C}^{\circ}_{p,MDS} = \Delta^{liq}_{solid}\bar{C}^{\circ}_{p,MDS} + \Delta^{mono}_{liq}\bar{C}^{\circ}_{p,D} + \Delta^{mono}_{liq}\bar{C}^{\circ}_{p,M\text{-}S}, \quad (14)$$

and

$$\Delta_m\bar{C}^{\circ}_{p,MDS} = \Delta^{mic}_{mono}\bar{C}^{\circ}_{p,MDS} = \Delta^{liq}_{solid}\bar{C}^{\circ}_{p,D} + (1-\beta)\Delta^{liq}_{mono}\bar{C}^{\circ}_{p,M\text{-}S}. \quad (15)$$

From the direct analysis of experimental data, $\Delta^{mono}_{solid}\bar{C}^{\circ}_{p.\,MDS}$ and $\Delta^{mic}_{mono}\bar{C}^{\circ}_{p.\,MDS}$ were obtained as shown in Table IV. Using these data and eqns. (14) and (15) as well as the value of $\Delta^{mono}_{liq}\bar{C}^{\circ}_{p.D}$, which was estimated as 140 cal deg^{-1} $mole^{-1}$ in the previous work,[2] we calculated the values of $\Delta^{liq}_{solid}\bar{C}^{\circ}_{p.\,MDS}$ and $\Delta^{mono}_{liq}\bar{C}^{\circ}_{p.\,M-S}$, as shown in Table IV.

Table IV. Transfer Heat Capacities (cal deg^{-1} $mole^{-1}$) of MDS and Its Portions

	$\Delta^{liq}_{solid}\bar{C}^{\circ}_{p,MDS}$	$\Delta^{mono}_{solid}\bar{C}^{\circ}_{p,MDS}$	$\Delta^{mic}_{mono}\bar{C}^{\circ}_{p,MDS}$	$\Delta^{mono}_{liq}\bar{C}^{\circ}_{p,D}$	$\Delta^{mono}_{liq}\bar{C}^{\circ}_{p,M-S}$
LiDS	25	125	−105	140	−40
NaDS	20	120	−104	140	−40
KDS	60	168	−110	140	−32

Taking into consideration generally the larger error in heat capacity than in enthalpy and specifically the scatter in experimental values of KDS from the beginning of heat-of-solution measurement, we may conclude that the greater parts of $\Delta_{sol}\bar{C}^{\circ}_{p.MDS}$ and $\Delta_m\bar{C}^{\circ}_{p.MDS}$ consist in the heat capacity change due to the solution of liquid hydrophobic portion of MDS into water or its reverse process, *i.e.* $\Delta^{mono}_{liq}\bar{C}^{\circ}_{p.D}$ or $\Delta^{liq}_{mono}\bar{C}^{\circ}_{p.D}$, although the term accompanying the hydration or dehydration of polar portion, *i.e.* $\Delta^{mono}_{liq}\bar{C}^{\circ}_{p.M-S}$ or $\Delta^{liq}_{mono}\bar{C}^{\circ}_{p.M-S}$, cannot be disregarded. On the circumstances mentioned above, the effect of counter-cation would not be examined properly,

which will be expected in the succeeding analysis of the works carried out in the urea-water-surfactant system.[19]

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19) K. Sumida and H. Kishimoto, The 95th Annual Meeting of Pharmaceutical Society of Japan, Nishinomiya, Apr. 1975.