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Studies on the Interaction between Long Chain Alcohols and Alkyl Sulfates. II. Molecular Association between Dodecyl Alcohol and Dodecyl Sulfate of Divalent Metals

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Molecular interaction between dodecyl alcohol and dodecyl sulfate of divalent metal cations such as Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} was studied by measurement of heat of complex formation, differential thermal analysis and infrared spectroscopy. It was found that magnesium, manganese, cobalt, nickel, and copper dodecyl sulfates formed two or three kinds of complexes with dodecyl alcohol, differing in composition depending on temperature. On the other hand, no evidence of complex formation could be found by these experimental techniques for calcium, strontium and barium dodecyl sulfates, all of which are very small in solubility into water. For the former class of metal dodecyl sulfates the composition of complex was 3.5—4.0 in molar ratio of alcohol to sulfate at temperature below the melting point of alcohol, while it was 5.0—6.0 at temperature above it. The heat of complex formation above the melting point of alcohol was −40—−44 kcal/mol-sulfate. Two or three characteristic absorption bands could be found over the range 3200—3500 cm^{-1}, suggesting that the complex formation is due to hydrogen bonding between two components.

Many papers concerning the interaction between long chain alcohols and alkyl sulfates have been published with viewpoints of emulsion and film stabilization due to complex formation and penetration. The results, however, have not been coincident with one another. Recently, Friberg has attempted to interrelate the molecular complexes as emulsion and foam stabilizer with phase diagram of the components;[1-3] in his papers the materials have not been confined to long chain compounds.

In our previous paper, it has been shown that there are two kinds of complexes, I and II, between dodecyl alcohol and sodium dodecyl sulfate, tetradecyl alcohol and sodium tetradecyl sulfate, hexadecyl alcohol and sodium hexadecyl sulfate, differing in the composition ratio of alcohol to sulfate.[4] The complex I was stable at temperature below the melting point of alcohol, the molar ratio of alcohol to sulfate being 0.55—0.63. The complex II was stable at temperature above the melting point of alcohol, its molar ratio being 1.0.

The object of this paper is to extend the previous work to divalent alkyl sulfates and to see the difference between monovalent and divalent cation complexes by the same methods as in the previous paper. Also it is our aim to investigate whether the mechanism of the complex formation could be elucidated by statistical thermodynamics.

The following abbreviations are used.

DOH: Dodecyl Alcohol
$Mg(DS)_2$, $Ca(DS)_2$, $Sr(DS)_2$, $Ba(DS)_2$, $Mn(DS)_2$, $Co(DS)_2$, $Ni(DS)_2$, $Cu(DS)_2$: Magnesium, Calcium, Strontium, Barium, Manganese, Cobalt, Nickel, and Copper Dodecyl Sulfate, respectively.

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[1] St. Friberg and L. Rydhag, *Kolloid-Z. Z. Polym.*, **244**, 233 (1971).

[2] St. Friberg and S. I. Ahmad, *J. Colloid Interfac. Sci.*, **35**, 175 (1971).

[3] St. Friberg, *Kolloid-Z. Z. Polym.*, **244**, 333 (1971).

[4] Y. Moroi, K. Motomura, and R. Matuura, This Bulletin, **44**, 2078 (1971).

These are often represented as $M(DS)_2$.
DTA: Differential Thermal Analysis
IR: Infrared Spectroscopy

Experimental

Materials. DOH was the same as described in the previous paper.[4] $M(DS)_2$ was prepared by a double decomposition from divalent metal cation chloride or sulfate and purified sodium dodecyl sulfate (SDS) in aqueous media. The CMC value was 8.13×10^{-3} mol/*l* at 25°C. The precipitate of $M(DS)_2$ formed was purified by repeated recrystallizations from water, and was dried at 125°C for fifteen minutes under a reduced pressure. The purified $M(DS)_2$ did not show any characteristic endothermic peak of SDS at 104°C on a DTA curve. The absorption bands of water could hardly be found in their IR spectra.

The specimens of complexes of DOH and $M(DS)_2$ used for measurements of DTA, IR and heat of complex formation were prepared by the two methods, *i.e.*, the melt method and the crystallization method. These were quite the same as described in the previous paper. Most of these metal dodecyl sulfates were so hygroscopic that all operations were performed in an atmosphere of dried nitrogen gas.

Methods. A Shimadzu X-ray diffractometer (DV-1) with a Geiger counter was employed with a beam exit slit of 0.7 mm. The nickel filtered copper radiation was used in all cases. The apparatus was standardized at angles 28.44° of silicon. The scanning speed was 1 deg/min., and the chart speed was 20 mm/min.

The DTA apparatus and operational condition were the same as those in the preceeding paper.[4] In the present case, two or three endothermic peaks appeared in DTA curves of the complexes even after a long time. As a result, the ratio of alcohol to sulfate in the complex above the melting point of DOH was determined from the composition at which the exothermic peak due to freezing of excess free alcohol disappeared on cooling curve. On the other hand, below the melting point the ratio was determined from the composition at which the endothermic peak due to melting of excess free alcohol disappeared on heating curve. This method is different from the previous one,[4] and the reason will be made clear in the next section.

The IR apparatus and operational condition were the same as those in the preceeding paper[4] except replacing hexachlorobutadiene by Nujol.

The heat of complex formation was measured at 35°C with an Applied Electric Laboratory calorimeter, Model CM-204S1. The samples were so hygroscopic that they were sealed into a glass ampule. On mixing them with DOH the ampule was held in DOH and crushed in it by a small hammer, after having been thermally equilibriated. The sample weight was about 100 mg and DOH used was 50 ml. Sodium dodecyl sulfate, sodium tetradecyl sulfate, and sodium hexadecyl sulfate formed the complexes with their corresponding alcohols which are insoluble in the alcohols, while complexes of $M(DS)_2$ with DOH were very soluble in DOH. Consequently $M(DS)_2$ with DOH were very soluble in DOH. Consequently, the heat of complex formation could not be measured only through mixing the sulfate with the alcohol. Therefore, it was determined by subtracting the heat (ΔHs) evolved by solubilizing the complex into DOH from the heat (ΔHt) evolved by mixing the dried sulfate with DOH with subsequent solubilization of complex.

Results and Discussion

X-ray Diffraction. The characteristic data of $M(DS)_2$ are collected in Table 1. As $Co(DS)_2$, $Ni(DS)_2$, and $Cu(DS)_2$ are so hygroscopic that their characteristics change during operation, the values for these sulfates are those for the compounds with water of crystallization, *i.e.*, $M(DS)_2\cdot nH_2O$. The amounts of water of crystallization for hygroscopic $M(DS)_2$ determined by elementary analysis were identical with those in literature,[5] and the agreement between the calculated and observed values of elementary analysis was good.

TABLE 1. RESULTS OF DTA AND X-RAY DIFFRACTION FOR $M(DS)_2$

$M(DS)_2$	DTA (°C) Dehydration	Transition	X-ray (Å) Long spacing
$Mg(DS)_2$		120	34.0
$Ca(DS)_2$		83	30.0
$Sr(DS)_2$			36.0
$Ba(DS)_2$		121	33.8
$Mn(DS)_2$		132	32.1
$Co(DS)_2\cdot 6H_2O$	56, 85, 110		20.6
$Ni(DS)_2\cdot 6H_2O$	57, 72, 85, 101		29.2
$Cu(DS)_2\cdot 4H_2O$	44, 118		25.0
NaDS		104	31.6, 39.0

It can be said from this result that the X-ray long spacing of metal sulfates with water of crystallization are shorter than those without water. This fact indicates that the carbon chain axis of sulfates with water is more tilted than those without water.

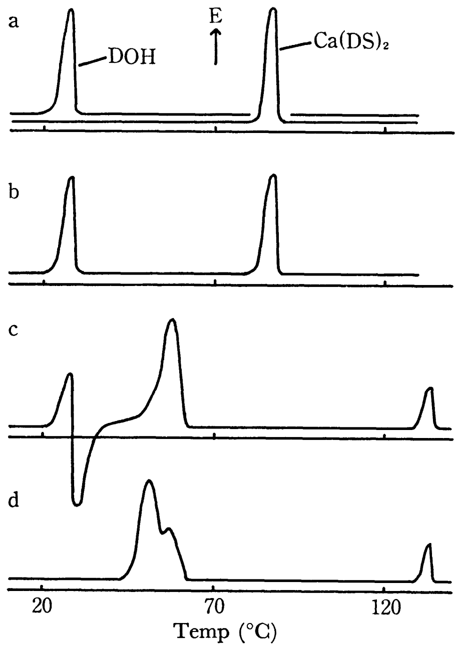

Fig. 1. DTA curves for detecting a complex formation. a: DOH and $Ca(DS)_2$ b: mixture of DOH and $Ca(DS)_2$, c: mixture of DOH and $Mn(DS)_2$, d: $Mn(DS)_2$-DOH complex, E: endothermic

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[5] R. Matuura and I. Satake, *Yushi*, **16**, 94 (1963).

DTA. The complex formation could easily be detected by DTA technique. The typical examples are shown in Fig. 1. When the mixture of M(DS)$_2$ and DOH in a solid phase is heated in a DTA cell from the temperature below the melting point of DOH to higher temperature, the DTA curve results merely in the superposition of their own DTA curves, unless they form a complex. On the other hand, the mixture which forms a complex shows a sharp exothermic peak in the heating curve just beyond the endothermic peak due to melting of DOH. This exothermic peak is followed by a new endothermic peak which corresponds to the characteristic peak of the complex. This phenomenon indicates that the mixture in solid state cannot undergo a reaction, while the melt of DOH can react with solid M(DS)$_2$ to form a complex accompanying heat evolution.

The sodium sulfate complexes were so stable that they kept up their own state during the operation without showing any peak in a DTA curve due to transition. On the contrary, divalent cation complexes are not so stable and have two or three more endothermic peaks even after being kept at a fixed temperature for a long time. Therefore, it was difficult to assign each endothermic peak to a complex. When the complexes formed above the melting point of DOH are cooled below it, they release the extra DOH at freezing state and transform to the other complexes. These complexes formed below the melting point of DOH are so unstable that they react again with the extra molten DOH on being heated above the melting point of DOH and show the exothermic peak due to complex formation in addition to the characteristic endothermic peak of the complex. However, it was possible, in some cases, to assign the peak to complex L or complex H, with the aid of the measurement of peak area on DTA curve, depending on the temperature at which the complex was kept. Complex L and complex H are complexes which formed below and above the melting point of DOH, respectively. The results of differential thermograms of these complexes are summarized in Table 2. Consequently, differing from the method in the previous paper, the following method was used in this study to determine the composition of the complex. The composition of complex L was determined from the ratio of DOH to M(DS)$_2$ in the state where the endothermic peak due to melting of extra free DOH disappears, and the composition of complex H was determined from the ratio in the state where the exothermic peak due to freezing of extra free DOH disappears. The typical DTA curves of manganese complex are shown in Fig. 1.

Table 2. Characteristic endothermic temperatures of complexes in DTA curves

Metal	Complex L (°C)	Complex H (°C)
Mg	40—43	53—55
Ca	—	—
Sr	—	—
Ba	—	—
Mn	40—41, 46—47	57—58
Co	38—40, 47—50	57—59
Ni	30—33, 38—40	
Cu	40—42, 48—50	

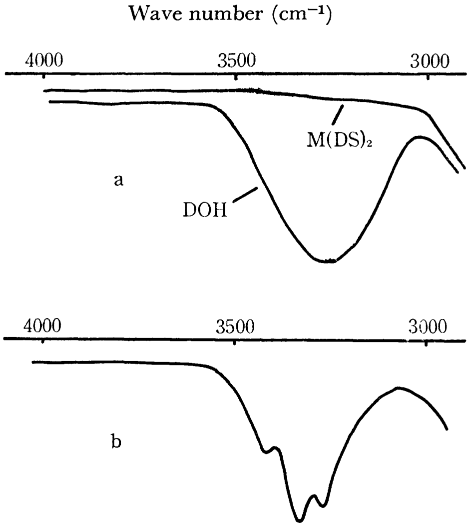

Fig. 2. IR spectra of complex formation. a: DOH and M(DS)$_3$, b: Mn(DS)$_2$-DOH complex

Infrared. Infrared spectroscopy as well as DTA are useful technique for detecting the complex formation. It is shown in Fig. 2 that the spectrum in the hydroxyl stretching region has sharper bands than those of DOH and is composed of two or three absorption bands. These bands, however, are broader in comparison with those of sodium sulfate complex. This might suggest that there are two or three kinds of (slightly diffused) bonding states between M(DS)$_2$ and DOH. The characteristic band region of complexes is the same as that of DOH, indicating that complexes are formed by the hydrogen bonding between two components in a manner similar to DOH. As will be mentioned later, it can also be confirmed from the magnitude of heat of complex formation that the complex formation is mainly due to the hydrogen bonding. The characteristic bands are summarized in Table 3.

Table 3. Characteristic absorption bands of complexes in IR spectra

Metal	Absorption band (cm^{-1})		
Mg	~3310	~3370	~3450
Mn	~3290	~3320	~(3460)
Co	~3280	~3320	~(3480)
Ni	~3290	~3340	~(3420)
Cu	~3200	~3300	

Heat of Complex Formation. As shown in Fig. 3, M(DS)$_2$ reacts with molten DOH to form a complex with heat evolution and then resolves in molten DOH with heat absorption. When particles of larger size, of M(DS)$_2$ were dropped into molten DOH, the rate of resolution is larger than that of complex formation, accompanying net heat absorption. The heat of complex H formation (ΔH_H) is shown in Table 4 together with the results of complex H composition. Complex H used to measure ΔH_S had the composition of M(DS)$_2$·6DOH. Even if the ratio of alcohol to sulfate is less than six, the effect of excess DOH on ΔH_S should be

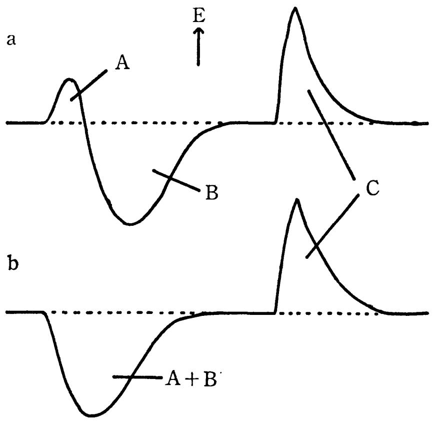

Fig. 3. Diagram of heat of complex formation and dissolution into DOH. a: $M(DS)_2$ in small size, b: $M(DS)_2$ in larger size, A: heat of complex formation, B: heat of dissolution of complex, C: standard heat, E: exothermic

Table 4. Heat of complex formation and composition of complex

Metal	ΔH_H (kcal/mol-sulfate)	Molar ratio of DOH to $M(DS)_2$ complex L	Molar ratio of DOH to $M(DS)_2$ complex H
Mg	−41.0±2	3.8—4.0	5.8—6.0
Mn	−40.1±2	3.8—4.0	5.8—6.0
Co	−41.2±2	3.8—4.0	5.0—6.0
Ni	−41.5±2	3.8—4.0	5.0—6.0
Cu	−44.0±2	3.8—4.0	5.5—6.0

negligible because of very little solubilization of complex H in excess DOH. The values of ΔH_H are about −40 kcal/mol-sulfate. These values are five or six times as large as those of sodium sulfate complex formation (7—8 kcal/mol-sulfate). This is consistent with the fact that the ratio of alcohol to sulfate in complex H is 5 to 6, while that of complex II of sodium sulfate is 1.0.

Statistical Thermodynamical Consideration

It seems to be instructive in a further investigation to discuss the complex formation with the viewpoint of statistical thermodynamics. In analogy with the previous paper,[4] this discussion is intended to explain the composition of complexes, namely the molar ratio of alcohol to sulfate in a complex, which is nearly 4 below the melting point of alcohol and nearly 6 above it. As mentioned above, there are two or three complexes in total, differing from the case of sodium sulfates. Furthermore, a divalent metal sulfate has two radicals of alkyl sulfate in a molecule, and then the theoretical treatment comes to be a little more difficult.

The consideration is based on the concept of chapter XI in "mixture" by Guggenheim.[6] We denote alcohol and sulfate by A and B, respectively, and consider a binary mixture containing Nr molecules of alcohol and N molecules of sulfate on a lattice of $N(r+2)$ sites with a coordination number Z, where $M(DS)_2$ is regarded as a dimer and occupies two lattice sites. Since A and B molecules have ZNr and $(2Z-2)N$ contact number, respectively, the total number of intermolecular contact (Q) is given by

$$Q=\frac{ZN}{2}(r+q), \tag{1}$$

where q is defined so that the open chain r-mer containing r elements may have Zq contacts, and then q is in this case equal to $2-2/Z$. The ratios of Q from A and B are denoted by U and V, respectively.

$$U=\frac{r}{r+q} \tag{2}$$

$$V=\frac{q}{r+q} \tag{3}$$

There are four kinds of contacts, A-A, A-B, B-A, and B-B. We denote by $-2X/Z$ the energy for a pair of the same kind of molecules and further define W such that the contribution of A-B contact of configurational energy is

$$-\frac{X'_{\mathrm{A-A}}+X'_{\mathrm{B-B}}+W}{Z}. \tag{4}$$

What must be emphasized at this point is that the energy for a longitudinal pair should be different from that for a lateral one. Nevertheless, we used $-2X/Z$ as the mean value of them. Consequently, the discussion cannot be given in terms of individual item, but may be limited to the mean values as a whole.

From these definitions, we can construct Table 5 for a complete random distribution. The prime in Table 5 refers to the newly obtained complex, E_c being the total configurational energy.

Table 5. Number of pairs and certain related quantities

Kind of contact	Number of contacts	Energy of all such contacts
A-A	QU^2	$-\frac{2}{Z}\ QU^2X'_{\mathrm{A-A}}$
A-B	QUV	$-\frac{1}{Z}\ QUV(X'_{\mathrm{A-A}}+X'_{\mathrm{B-B}}+W)$
B-A	QVU	$-\frac{1}{Z}\ QVU(X'_{\mathrm{B-B}}+X'_{\mathrm{A-B}}+W)$
B-B	QV^2	$-\frac{2}{Z}\ QU^2X'_{\mathrm{B-B}}$
All	Q	$-\frac{2Q}{Z}\ (UX'_{\mathrm{A-A}}+VX'_{\mathrm{B-B}}+UVW)=E_C$

E_c can be rewritten as follows;

$$E_c=-N\left(rX'_{\mathrm{A-A}}+qX'_{\mathrm{B-B}}+\frac{rq}{r+q}W\right) \tag{5}$$

According to definition, the configurational partition function Ω is given by

$$\Omega=\sum\exp(-E_c/kT), \tag{6}$$

where the summation extends over the $g(Nr,\ N)$ distinguishable configurations. $g(Nr,\ N)$ is given by

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[6] E. A. Guggenheim, "Mixtures", ed. by R. H. Fowler, P. Kapitza, N. F. Mott, and E. C. Bullard, Oxford at the Clarendon Press (1952).

$$g(Nr, N) = \left(\frac{Z}{2}\right)^N \frac{(Nr+2N)!}{(Nr)!N!}\left\{\frac{(Nr+Nq)!}{(Nr+2N)!}\right\}^{1/(2-q)}. \qquad (7)$$

As the configurational free energies of pure substances containing the same number of molecules are $-NrX_{\text{A-A}}$ and $-NqX_{\text{B-B}}$, the molar free energy of mixing of the sulfate is given by

$$\begin{aligned}\Delta F_{\text{m}} = &-Nr(X'_{\text{A-A}}-X_{\text{A-A}}) - Nq(X'_{\text{B-B}}-X_{\text{B-B}}) - \frac{Nrq}{r+q}W \\ &- RT\Bigg[\ln 2Z - r\ln\frac{r}{r+2} - 2\ln\frac{2}{r+2} + \frac{1}{2-q} \\ &\times\left\{r\ln\frac{r+q}{r+2} + q\ln(r+q) - 2\ln(r+2)\right\}\Bigg], \qquad (8)\end{aligned}$$

where N is Avogadro's number. Concerning a liquid or solid phase, we can, without serious error, replace internal energy and Helmholtz free energy by enthalpy and Gibbs free energy, respectively. Consequently the molar enthalpy of mixing of sulfate is given by

$$\begin{aligned}\Delta H = &-Nr(X'_{\text{A-A}}-X_{\text{A-A}}) \\ &- Nq(X'_{\text{B-B}}-X_{\text{B-B}}) - \frac{Nrq}{r+q}W, \qquad (9)\end{aligned}$$

where we assume that the temperature changes of $X'_{\text{B-B}}$, $X_{\text{B-B}}$, and W are negligible, because of very limited temperature range 20—35°C in this case.

First, when $r=0$, we obtain the equation

$$\Delta H = -Nq(X'_{\text{B-B}}-X_{\text{B-B}}) \equiv \Delta H_0 \qquad (10)$$

The new parameter ΔH_0 is hypothetically equivalent to the heat evolved when a sulfate is transformed into a complex whose lattice sites are all occupied by sulfate molecules.

Second, when $r=r_H$, which is the ratio of DOH to M(DS)_2 in complex H, ΔH_H is given by

$$\Delta H_{\text{H}} = -r_{\text{H}}(NX'^{\text{H}}_{\text{A-A}} - NX^{1}_{\text{A-A}}) + \Delta H_0 - \frac{Nr_{\text{H}}q}{r_{\text{H}}+q}W, \qquad (11)$$

where $X^1_{\text{A-A}}$ is the $X_{\text{A-A}}$ of liquid alcohol and ΔH_H is equal to the heat of complex H formation measured above the melting point of alcohol.

We may obtain unknown parameters from the ratios of DOH to M(DS)_2 in complex L and complex H, imposing conditions consistent with the results on ΔG_m.

For complex L,

$$\begin{aligned}&\frac{\partial\Delta G_{m\text{L}}}{\partial r} < 0 \text{ at } r = r_{\text{L1}}, \\ &\frac{\partial\Delta G_{m\text{L}}}{\partial r} > 0 \text{ at } r = r_{\text{L2}}, \qquad (12)\\ \text{and}\quad &\Delta G_{m\text{H}} < 0 \quad \text{at } r_{\text{L1}} < r < r_{\text{L2}},\end{aligned}$$

where r_{L1} and r_{L2} are lower and upper limit of r_{L}, respectively.

For complex H,

$$\begin{aligned}&\frac{\partial\Delta G_{m\text{H}}}{\partial r} < 0 \text{ at } r = r_{\text{H1}}, \\ &\frac{\partial\Delta G_{m\text{H}}}{\partial r} > 0 \text{ at } r = r_{\text{H2}}, \qquad (13)\\ \text{and}\quad &\partial\Delta G_{m\text{H}} < 0 \quad \text{at } r_{\text{H1}} < r < r_{\text{H2}},\end{aligned}$$

where r_{H1} and r_{H2} are lower and upper limit of r_{H}, respectively.

We employed 1, 2, and 3 kcal/mol -M(DS)_2 as a reasonable value for ΔH_0, and 22.8 and 15.1 kcal/mol for $NX_{\text{A-A}}$ and $NX^1_{\text{A-A}}$, respectively, according to the previous paper.[4] Thus NW and $NX'_{\text{A-A}}$ can be obtained from Eqs. (11), (12), and (13), with Z to be an unknown parameter. A typical example for calculation is shown in Fig. 4 for Mg(DS)_2-DOH complex. The results obtained are summarized in Table 6. This shows that the values of $NX'_{\text{A-A}}$ are 17—19 and 11—13 kcal/mol for $NX'^{\text{L}}_{\text{A-A}}$ and $NX'^{\text{H}}_{\text{A-A}}$ respectively.

In the previous paper, $NX'_{\text{A-A}}$ was the average of those of complex I and II. On the other hand, in

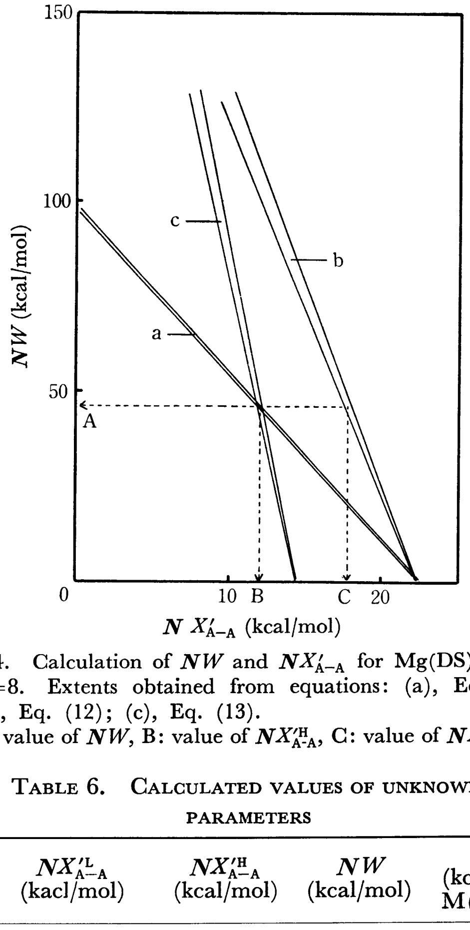

Fig. 4. Calculation of NW and $NX'_{\text{A-A}}$ for Mg(DS)_2-DOH, $Z=8$. Extents obtained from equations: (a), Eq. (11); (b), Eq. (12); (c), Eq. (13).
A: value of NW, B: value of $NX'^{\text{H}}_{\text{A-A}}$, C: value of $NX'^{\text{L}}_{\text{A-A}}$

Table 6. Calculated values of unknown parameters

Metal	$NX'^{\text{L}}_{\text{A-A}}$ (kacl/mol)	$NX'^{\text{H}}_{\text{A-A}}$ (kcal/mol)	NW (kcal/mol)	H_{L} (kcal/mol-M(DS)_2)
		$Z=6$		
Mg	18.0±0.6	12.0±0.2	46±2	−35.0±10
Mn	18.0±0.6	12.0±0.2	46±2	−35.0±10
Co	18.6±0.6	12.2±0.6	47±2	−36.1±10
Ni	18.6±0.6	12.2±0.6	47±2	−36.1±10
Cu	18.4±0.6	12.2±0.3	49±2	−38.4±10
		$Z=8$		
Mg	18.0±0.3	12.2±0.2	46±2	−35.0± 9
Mn	18.0±0.3	12.2±0.2	46±2	−35.0± 9
Co	18.1±0.3	11.8±0.6	47±2	−36.6± 9
Ni	18.1±0.3	11.8±0.6	47±2	−36.6± 9
Cu	17.1±0.3	11.9±0.3	49±2	−37.4± 9
		$Z=12$		
Mg	17.4±0.3	11.9±0.2	45±2	−33.0± 9
Mn	17.4±0.3	11.9±0.2	45±2	−33.0± 9
Co	17.0±0.3	11.5±0.6	48±2	−35.4± 9
Ni	17.0±0.3	11.5±0.6	48±2	−35.4± 9
Cu	17.5±0.3	11.8±0.3	44±2	−32.3± 9

the present treatment the $NX'_{\mathrm{A-A}}$ is separated into $NX'^{\mathrm{L}}_{\mathrm{A-A}}$ and $NX'^{\mathrm{H}}_{\mathrm{A-A}}$ for complex L and complex H, respectively. Comparing these values with the previous ones, 14—16 kcal/mol, which is almost equal to the mean value of $NX'^{\mathrm{L}}_{\mathrm{A-A}}$ and $NX'^{\mathrm{H}}_{\mathrm{A-A}}$, we arrive at the conclusion that the state of alcohol in monovalent cation complex is almost equal to that in divalent one.

Using the values of $NX'^{\mathrm{L}}_{\mathrm{A-A}}$, the heat of complex L formation can also be calculated with W in complex H also shown in Table 6. Thus, it is found that the absolute value of ΔH_{L} is smaller than that of ΔH_{H} and the effect of the alterations of ΔH_0 and Z on unknown parameters is rather small.

What is evident from these results is as follows; $\mathrm{M(DS)_2}$ of divalent ion whose sulfate ($\mathrm{MSO_4}$) is rather soluble in water is apt to form a complex with DOH, and *vice versa*.

For Ca, Sr, and Ba dodecyl sulfate, the intermolecular force in a crystal state is so strong that the complex cannot be formed. In other words, their own intermolecular force is stronger than that between $\mathrm{M(DS)_2}$ and DOH in a complex state. On the other hand, the intermolecular force of dodecyl sulfate of such metals as Mg, Mn, Co, Ni, and Cu is weaker than that between $\mathrm{M(DS)_2}$ and DOH in a complex state and leads to a negative enthalpy change on the complex formation that has a main effect on negative free energy change.

According to the above discussion, the dodecyl sulfate of divalent metals having larger solubility into a water must form a complex with DOH. The composition of it should depend on the metal ion and the temperature.