2078 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2078—2082 (1971) [Vol. 44, No. 8

Studies on the Interaction between Long Chain Alcohols and Alkyl Sulfates. I.
Molecular Association between Long Chain Alcohols and Corresponding Alkyl Sulfates

Yoshikiyo Moroi, Kinshi Motomura, and Ryohei Matuura
Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka

(Received January 28, 1971)

Molecular interaction between long chain alcohols and corresponding alkyl sulfates, such as dodecyl alcohol-sodium dodecyl sulfate, tetradecyl alcohol-sodium tetradecyl sulfate and hexadecyl alcohol-sodium hexadecyl sulfate, was studied by measurement of heat of complex formation, differential thermal analysis and infrared spectroscopy. It was found that there were two kinds of complexes, I and II, differing in the composition of alcohols and corresponding sulfates. The former is stable at temperatures below the melting point of alcohol, the molar ratio of alcohol to sulfate being 0.53—0.63. The latter is stable at temperatures above the melting point of alcohol, its molar ratio being 1.0. The heat of formation of II is 7—8 kcal/mol, which suggests that the complex is formed by a force similar to hydrogen bonding between alcohols and sulfates. The peak temperature in the DTA curve due to decomposition of the complex is about 10°C lower in I than in II and the characteristic absorption bands in IR spectrum are 3480 cm^{-1} and 3520 cm^{-1} in I and II, respectively, which correspond to hydrogen bond between two components.

The properties of solutions of the alkyl sulfates have been investigated in detail, but not those of their solids. The interaction of the pure substance with other compounds has been investigated only scantily.

It is well known that a detergent such as alkyl sulfate is used as a stabilizer of the water-in-oil emulsion and its stabilizing power is increased in the presence of polar long chain compounds such as alcohol, cholesterol, *etc.* Schulman and Rideal, and Goddard and Schulman reported on the molecular interaction between polar long chain compounds studied from the monomolecular films of long chain alcohols. They concluded that the film stabilization is caused by a phenomenon called "penetration."[1,2] Maruta *et al.* and Maruta and Tokiwa investigated the adducts separated from the dilute solution of dodecyl alcohol-sodium dodecyl sulfate in the presence of polyelectrolyte and showed that the molar ratio of such adduct is 2 in terms of the ratio of alcohol to sulfate.[3–6] Kung and Goddard investigated the interaction between a long chain alcohol and an alkyl sulfate in a bulk phase and recognized the molecular complex between them, molar ratio of which is 0.5.[7–10] Epstein *et al.* made the same studies with systems, dodecyl or tetradecyl alcohol-dodecyl or tetradecyl sulfate-water and recognized two kinds of adducts whose molar ratios are 0.5 and 1 in terms of the ratio of alcohol to sulfate.[11,12]

We found the results of these studies to be unconvincing and leading to no definite conclusion. In order to obtain improved results we investigated the molecular interaction between alcohols and sulfates by thermal, spectroscopic, and statistical thermodynamical methods.

The following abbreviations are used.

DOH, TOH, HOH: Dodecyl, Tetradecyl, and Hexadecyl alcohol, respectively
SDS, STS, SHS: Sodium Dodecyl, Sodium Tetradecyl, and Sodium Hexadecyl Sulfate, respectively
DTA: Differential Thermal Analysis
IR: Infrared Spectroscopy

Experimental

Materials. DOH, TOH, and HOH were purified by fractional distillation at reduced pressure. Purity was checked by melting point measurement and DTA curves which were identical with those in literature.

SDS, STS, and SHS were prepared from the corresponding alcohols and chlorosulfonic acid and by esterification with subsequent neutralization with sodium hydroxide. They were purified by repeated crystallization from ethanol and water, and then by elimination of a small amount of alcohols by heating at about 100°C under reduced pressure for more than ten hours. The purified SDS, STS, and SHS showed only one endothermic peak at 104, 118, and 124°C on DTA curves, respectively, without any endothermic peak of the melting of alcohol. The CMC values were 8.13×10^{-3} mol/l at 25°C, 2.5×10^{-3} mol/l at 40°C, and 6.2×10^{-4} mol/l at 40°C for SDS, STS, and SHS, respectively.

The specimens of mixtures of alcohols and sulfates used for DTA and IR measurements were prepared by the following two methods. a) Melt method. Weighed amounts of alcohols and sulfates were ground in a mortar and then kept at about 30, 45, and 55°C for dodecyl, tetradecyl, and hexadecyl compounds, respectively. b) Crystallization method. Weighed amounts of alcohols and sulfates were dissolved in ethanol and the solvent was eliminated by vaporization at temperatures 0—5°C. In both methods, the speci-

---

[1] J. H. Schulamn and E. K. Rideal, *Proc. Roy. Soc.* (London), **B122**, 29 (1937).

[2] E. D. Goddard and J. H. Schulman, *J. Colloid Sci.*, **8**, 309, 329 (1953).

[3] I. Maruta, T. Sakai, F. Tokiwa, and T. Saito, *Nippon Kagaku Zasshi*, **82**, 1512 (1961).

[4] I. Maruta and F. Tokiwa, *ibid.*, **82**, 1658 (1961).

[5] I. Maruta and F. Tokiwa, *ibid.*, **82**, 1660 (1961).

[6] I. Maruta and F. Tokiwa, *ibid.*, **83**, 732 (1962).

[7] H. C. Kung and E. D. Goddard, *J. Phys. Chem.*, **67**, 1965 (1963).

[8] H. C. Kung and E. D. Goddard, *ibid.*, **68**, 3465 (1964).

[9] H. C. Kung and E. D. Goddard, *Proc. IVth Intern. Congr. Surface Active Substances, Brussels*, 751 (1964).

[10] H. C. Kung and E. D. Goddard, *J. Colloid Sci.*, **20**, 766 (1965).

[11] M. B. Epstein, A. Wilson, C. W. Jakob, L. E. Conroy, and J. Ross, *J. Phys. Chem.*, **58**, 860 (1954).

[12] M. B. Epstein, A. Wilson, J. Gershman, and J. Ross, *ibid.*, **60**, 1051 (1956).

mens were kept above or below the melting points of alcohols.

Methods. The apparatus for the measurement of the heat of complex formation is shown in Fig. 1. Weighed amounts of ground sulfates were dropped into alcohols in a Dewer bottle which was inserted in a thermally controlled water bath at 35, 45, and 55°C for SDS, STS, and SHS, respectively. The heat evolved was estimated from the temperature rise of the system due to mixing, using a thermocouple. Each measurement was performed at least three times.

The DTA apparatus is characterized by a copper block and two pen recorders, one indicating the temperature of the specimen and the other the temperature difference between specimen and reference substance (Al_2O_3). The heating rate was about 3°C/min. The sample weight was about 25 mg. The specimen was cooled to 0, 12, and 25°C for SDS, STS, and SHS, respectively, before heating.

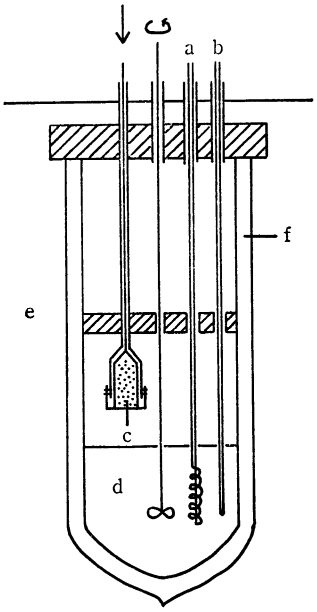

Fig. 1. Apparatus used for measurement of heat of complex formation.
(a) heater, (b) thermocouple, (c) sulfate,
(d) alcohol, (e) water bath, (f) Dewar bottle

The ratio of alcohol to sulfate in the complex was determined as follows. Since the thermal conductivity and packing of a specimen had a large effect on the DTA curve, a definite condition was necessary to calculate the amount of alcohol and complex from the peak area of the DTA curve. Only a specimen with a 1.5 ratio of alcohol to sulfate was used for determining the composition of the complex. The specific area of the alcohol of the above system was determined by subtracting the peak area of a weighed amount of specimen from the peak area of a weighed amount of specimen containing some extra alcohol, and then dividing the area difference by the amount of the added alcohol. The sulfate in the specimen should be completely changed to a complex on account of the large amount of peak area of excess alcohol. Under these conditions, the ratio of alcohol to sulfate in a complex could be determined.

The IR apparatus used was a 225-Hitachi grating infrared spectrophotometer. The specimens for IR were the same as those for DTA and were dispersed as a mull in chlorohexabutadiene. When IR measurements were carried out below melting point of alcohols, the cell holder was cooled by dry ice to a temperature just above dew point.

Results and Discussion

Heat of Complex Formation. The heat of complex formation is shown in Table 1. For comparison, ΔH of $C_{10}H_{21}OH$-SDS was measured and it was found to be nearly equal to 0, which indicates that the heat of mixing of alcohol and sulfate is negligible. Hence it can be said that ΔH's for the other three systems are heat of reaction. We assume that alcohols and sulfates make a complex in a solid state and that lattice sites in a complex are occupied by molecules of alcohol and sulfate.

Table 1. Heat of complex formation

System	Temp. (°C)	ΔH (kcal/mol-sulfate)
DOH-SDS	35.0	-7.35 ± 0.3
TOH-STS	45.0	-7.83 ± 0.4
HOH-SHS	55.0	-8.23 ± 0.4
$C_{10}H_{21}OH$-SDS	35.0	0

DTA and IR. Many kinds of specimens were investigated by DTA and IR technique. Typical examples are shown in Figs. 2—4. The difference between results obtained by the melt and crystallization methods is almost negligible. DTA curves are composed of four endothermic peaks, which can be as-

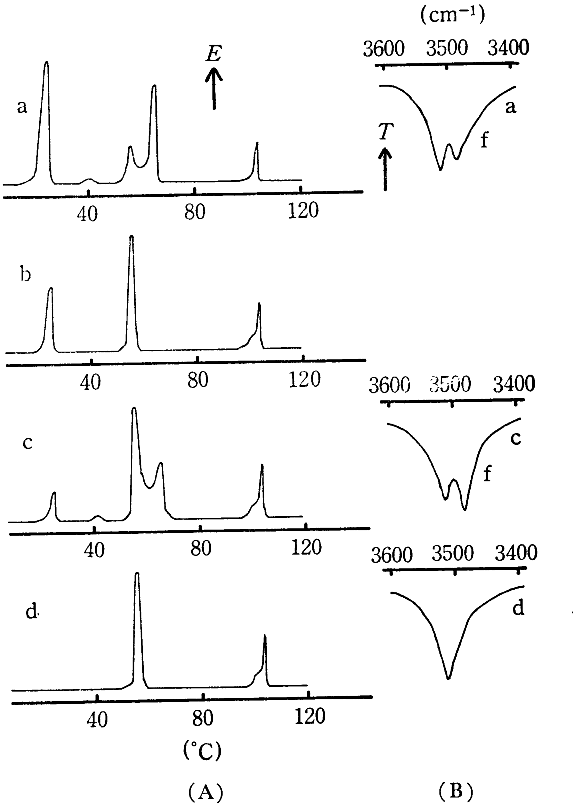

Fig. 2. DTA curves (A) and infrared spectra (B) of DOH-SDS system. Molar ratio of DOH to SDS:
(a), 1.5; (b), 1.0: (c), 0.67; (d), 0.5.
E : endothermic
T : transmittance
f : below melting point of DOH

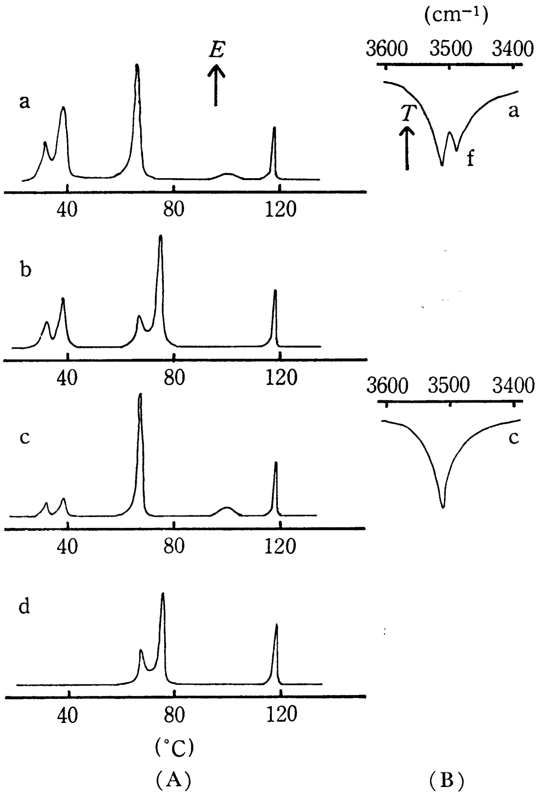

Fig. 3. DTA curves (A) and infrared spectra (B) of TOH-STS system. Molar ratio of TOH to STS:
(a), 1.5; (b), 1.0; (c), 0.67; (d), 0.5.
E : endothermic
T : transmittance
f : below melting point of TOH

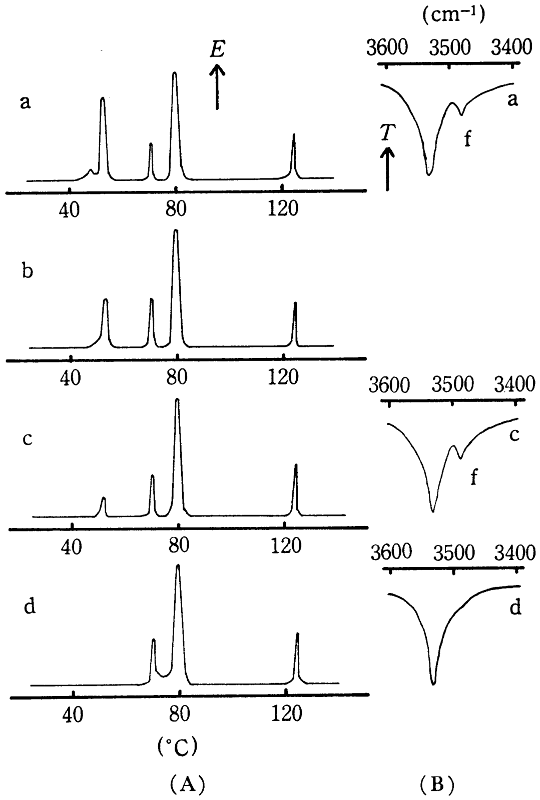

Fig. 4. DTA curves (A) and infrared spectra (B) of HOH-SHS system. Molar ratio of HOH to SHS:
(a), 1.5; (b), 1.0; (c), 0.67; (d), 0.5.
E : endothermic
T : transmittance
f : below melting point of HOH

signed to melting of alcohol, decomposition of complex I, decomposition of complex II, and transformation of sulfate from a low temperature to a high temperature type. An endothermic peak due to the melting of alcohol decreases with the decrease of the ratio of alcohol to sulfate. There are two kinds of endothermic peaks due to the decomposition of the complex. One is due to the decomposition of complex I which is obtained by keeping specimens below melting point of alcohol for more than ten days. The other is due to the decomposition of complex II which is obtained by keeping the specimens above melting point of alcohol. There should be an endothermic peak due to transition of complex I to complex II in a DTA curve, but no such peak appeared. This can be attributed to the very long time required for the transition. Specimens often show two endothermic peaks, which indicates that II has not completely been transformed into I. The molar peak area of alcohol on decomposition is a little larger in I than in II. This means that alcohol is more strongly bonded to sulfate in I than in II.

TABLE 2. RESULTS OF DTA AND IR

System	Complex	Decomposition temp. (°C)	Absorption band (cm^{-1})	Molar ratio of alcohol to sulfate
DOH-SDS	I	56—57	3479—3485	0.53—0.63
	II	65—66	3510—3515	1
TOH-STS	I	66—67	3479—3485	0.53—0.63
	II	74—75	3515—3520	1
HOH-SHS	I	69—70	3479—3485	0.53—0.63
	II	79—80	3530—3533	1

The ratio of alcohol to sulfate were 0.53—0.63 and 1.0 for I and II, respectively, according to the method of composition determination mentioned above. Kung and Goddard determined the composition of this complex from the ratio at which the endothermic peak of alcohol disappeared.[7,8] This seems to be wrong, since a part of II whose molar ratio of alcohol to sulfate is 1.0 releases alcohol to turn into I whose molar ratio is 0.53—0.63, when II is cooled below the melting point of alcohol, as is shown by DTA measurement. Details of differential thermograms of three kinds of systems are summarized in Table 2.

Spectra in the hydroxyl band stretching region are shown in Figs. 2—4. There are two kinds of absorption bands which belong to I and II, namely the bands near 3480 and 3520 cm^{-1} due to I and II, respectively. However, when the specimen is not cooled to a temperature below melting point of alcohol, only one absorption band near 3520 cm^{-1} appears. This indicates that I is completely transformed into II by the heat of IR ray. On the other hand, specimens kept below melting point of alcohol showed two kinds of absorption bands. In the case of system HOH-SHS whose complex II can not be easily transformed into complex I due to high melting point of alcohol, the band of I appeared only as a shoulder in a absorption band of II. Goddard *et al.* could find only one absorption band near 3520 cm^{-1} due to II and insisted on the presence of only one kind of complex.[8] Details of infrared spectra of three systems of alcohol and sulfate are shown in Table 2.

Statistical Thermodynamical Consideration. It is enlightening to consider complex formation from the viewpoint of statistical thermodynamics. The main object of this consideration is to show why the molar ratio of alcohol to sulfate in a complex below melting point of alcohol is 0.53—0.63 and that above melting point of alcohol is 1.0. 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 $N(1+r)$ sites with a coordination number Z. Since each molecule has Z closest neighbours, there are in all $NZ(1+r)/2$ pairs of closest neighbours, the pairs being three kinds such as A–A, B–B, and A–B. We denote the energy per pair by $-2X/Z$ and assume complete randomness in placing the molecules on sites. It is also assumed that alcohol and sulfate are so similar in size and shape that they are interchangeable on a lattice. Then we can construct Table 3 for the number of pairs and related quantities. The prime in Table 3 refers to the newly obtained complex, E_c being the configurational energy. According to definition, the configurational partition function Ω is given by

TABLE 3. NUMBER OF PAIRS AND CERTAIN RELATED QUANTITIES

Kind of pair	Number of pairs	Energy per pair	Energy of all such pairs
A–A	$NZ\frac{r^2}{2(1+r)}$	$-2X'_{\mathrm{A-A}}/Z$	$-NX'_{\mathrm{A-A}}\frac{r^2}{1+r}$
A–B	$NZ\frac{r}{1+r}$	$-2X'_{\mathrm{A-B}}/Z$	$-NX'_{\mathrm{A-B}}\frac{2r}{1+r}$
B–B	$NZ\frac{1}{2(1+r)}$	$-2X'_{\mathrm{B-B}}/Z$	$-NX'_{\mathrm{B-B}}\frac{1}{1+r}$
All	$NZ\frac{1+r}{2}$		$-\frac{N}{1+r}(r^2X'_{\mathrm{A-A}}$ $+2rX'_{\mathrm{A-B}}+X'_{\mathrm{B-B}})=E_c$

$$\Omega = \sum \exp(-E_c/\boldsymbol{k}T)\,, \tag{1}$$

where the summation extends over the $\{N(1+r)\}!/N!(Nr)!$ distinguishable configurations. Thus we have

$$\Omega = \frac{\{N(1+r)\}!}{N!(Nr)!}\exp(-E_c/\boldsymbol{k}T)\,. \tag{2}$$

Hence the configurational free energy F_c is given by

$$\begin{aligned} F_c &= -\boldsymbol{k}T\ln\Omega \\ &= -\frac{N}{1+r}(r^2X'_{\mathrm{A-A}}+2rX'_{\mathrm{A-B}}+X'_{\mathrm{B-B}}) \\ &\quad + N\boldsymbol{k}T\{r\ln r-(1+r)\ln(1+r)\}\,. \end{aligned} \tag{3}$$

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

$$\begin{aligned} \varDelta F_m = &-\frac{\boldsymbol{N}}{1+r}(r^2X'_{\mathrm{A-A}}+2rX'_{\mathrm{A-B}}+X'_{\mathrm{B-B}}) + \boldsymbol{N}rX_{\mathrm{A-A}} \\ &+ \boldsymbol{N}X_{\mathrm{B-B}} + \boldsymbol{R}T\{r\ln r-(1+r)\ln(1+r)\}\,, \end{aligned} \tag{4}$$

where $\boldsymbol{N}$ is Avogadro's number.

Concerning 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

$$\begin{aligned} \varDelta H_m = &-\frac{\boldsymbol{N}}{1+r}(r^2X'_{\mathrm{A-A}}+2rX'_{\mathrm{A-B}}+X'_{\mathrm{B-B}}) \\ &+ \boldsymbol{N}rX_{\mathrm{A-A}} + \boldsymbol{N}X_{\mathrm{B-B}}\,, \end{aligned} \tag{5}$$

where we assume that the temperature changes of $X'_{\mathrm{A-A}}$, $X'_{\mathrm{A-B}}$, $X'_{\mathrm{B-B}}$, and $X_{\mathrm{B-B}}$ are negligible, which is permissible over the temperature range 20—60°C, *i.e.*, our experimental temperature range.

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

$$\varDelta H_m = -\boldsymbol{N}X'_{\mathrm{B-B}} + \boldsymbol{N}X_{\mathrm{B-B}} \equiv \varDelta H_0\,. \tag{6}$$

The new parameter $\varDelta H_0$ is hypothetically equivalent to the transition enthalpy evolved when a sulfate is transformed into complex whose lattice sites are all occupied by sulfate molecules.

Second, when $r=1$, $\varDelta H$ is given by

$$\begin{aligned} \varDelta H = &-\frac{\boldsymbol{N}}{2}(X'_{\mathrm{A-A}}+2X'_{\mathrm{A-B}}+X'_{\mathrm{B-B}}) \\ &+ \boldsymbol{N}X^1_{\mathrm{A-A}} + \boldsymbol{N}X_{\mathrm{B-B}} \end{aligned} \tag{7}$$

where $X^1_{\mathrm{A-A}}$ is the $X_{\mathrm{A-A}}$ of liquid alcohol and $\varDelta H$ is equal to the heat of complex formation measured above melting point of alcohol, because the molar ratio of alcohol to sulfate in the complex is 1.0.

Substituting Eqs. (6) and (7) into Eq. (4) we obtain for the temperature below melting point of alcohol

$$\begin{aligned} \varDelta G_m = &\frac{r-r^2}{1+r}\boldsymbol{N}X'_{\mathrm{A-A}} + \frac{1-r}{1+r}\varDelta H_0 \\ &+ (2\varDelta H-2\boldsymbol{N}X^1_{\mathrm{A-A}})\frac{r}{1+r} + \boldsymbol{N}rX_{\mathrm{A-A}} \\ &+ \boldsymbol{R}T\{r\ln r-(1+r)\ln(1+r)\}\,, \end{aligned} \tag{8}$$

and for the temperature above melting point of alcohol

$$\begin{aligned} \varDelta G^1_m = &\frac{r-r^2}{1+r}\boldsymbol{N}X'_{\mathrm{A-A}} + \frac{1-r}{1+r}\varDelta H_0 \\ &+ (2\varDelta H-2\boldsymbol{N}X^1_{\mathrm{A-A}})\frac{r}{1+r} + \boldsymbol{N}rX^1_{\mathrm{A-A}} \\ &+ \boldsymbol{R}T\{r\ln r-(1+r)\ln(1+r)\}\,. \end{aligned} \tag{9}$$

It is reasonable for $\boldsymbol{N}X^1_{\mathrm{A-A}}$ to be replaced by molar heat of vaporization, since X is the energy for a molecule to part from the lattice site to an infinite separation. Similarly we can calculate $\boldsymbol{N}X_{\mathrm{A-A}}$, using the specific heat capacity of alcohol equal to 0.36 cal/g measured for three kinds of alcohols and assuming that alcohol gas is ideal.

Thus, we get Table 4 for the three kinds of systems.

We calculated the minimum values of $\varDelta G_m$ and r which made $\varDelta G_m$ minimum, substituting seven values of −1, 0, 1, 2, 3, 4, 5 kcal/mol and 12, 13, 14, 15, 16,

TABLE 4. VALUES OF NX_{A-A} AND NX^1_{A-A}

System	Temp. (°C)	NX_{A-A} (kcal/mol)	NX^1_{A-A} (kcal/mol)
DOH-SDS	20	22.8	
	35		15.1
TOH-STS	30	22.8	
	45		14.9
HOH-SHS	40	22.2	
	55		14.7

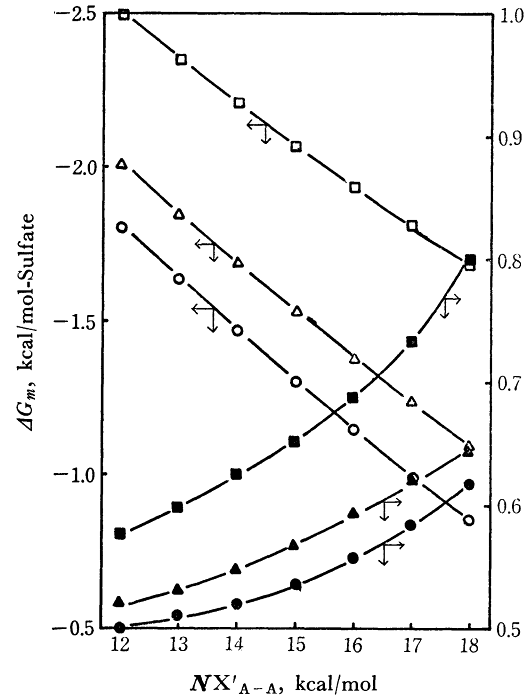

Fig. 5. Minimum of ΔG_m and r against X'_{A-A} at ΔH_0 equal to 1.0.

● ○: DOH-SDS

▲ △: TOH-STS

■ □: HOH-STS

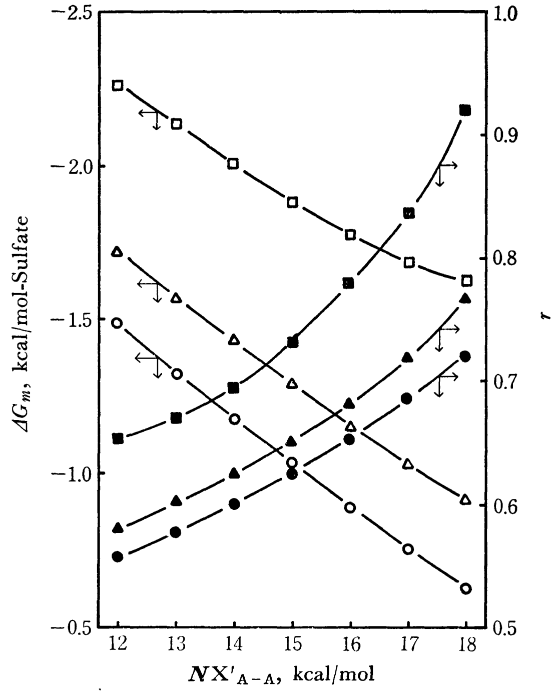

Fig. 6. Minimum of ΔG_m and r against X'_{A-A} at ΔH_0 equal to 2.0.

● ○: DOH-SDS

▲ △: TOH-STS

■ □: HOH-SHS

17, 18 kcal/mol into ΔH_0 and NX'_{A-A}, respectively. As a result we could obtain, as the values consistent with experimental results, only two values of ΔH_0 equal to 1 and 2 kcal/mol which we can accept as a reasonable values for a transition enthalpy of long chain compounds. The calculated results are shown in Figs. 5 and 6 for complex I only. The results of complex II always showed that the molar ratio of alcohol to sulfate equal to 1.0 made ΔG^1_m minimum. From Figs. 5 and 6, we see that the values of NX'_{A-A} 14—16, 13—15, and 12—13 kcal/mol for DOH-SDS, TOH-STS and HOH-SHS, are consistent with experimental results.