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# The Thermodynamics of the Micelle Formation of Sodium $\alpha,\omega$-Alkanediyl Disulfate

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**Synopsis.** The critical micelle concentrations of a $\alpha,\omega$-type surfactant: (sodium $\alpha,\omega$-alkanediyl disulfate: $n$=12, 14, 16) in an aqueous solution have been determined by studying the electrical conductivity, and the free energies of the micelle formation have then been estimated from these data. The free energy of micelle formation of a $\alpha,\omega$-type surfactant was smaller than that of a normal-type surfactant with the same alkyl chain length as the $\alpha,\omega$-type one. The free-energy changes per -($CH_2$)- segment was also calculated from these data. It is found that the free-energy change per -($CH_2$)- segment of the $\alpha,\omega$-type surfactant is $-11.1$ [kJ mol$^{-1}$].

A $\alpha,\omega$-type (bola form) surfactant has two head groups, are at each end of the hydrocarbon chain.[1—14] Interest in this surfactant has increased steadily in recent years from the standpoint of fundamental studies and applications. Studies of $\alpha,\omega$-type surfactant in aqueous solutions can be made from three points of view. First is how the $\alpha,\omega$-type surfactants are built up at the air–water interface. Second is how the micelle of the $\alpha,\omega$-type surfactants is formed in aqueous solutions and what kind of conformation the $\alpha,\omega$-type surfactants form in the micelle. Third is how the liquid crystalline phase of the $\alpha,\omega$-type surfactants is made up in a surfactant-water system. The critical micelle concentration and molecular areas have been determined by measuring the surface tension as a step in studying the carbon chain conformation in the air-water interface.[6,8] It has been suggested that the $\alpha,\omega$-type surfactant forms vertical "wicket-like" loops at the air-water interface. With regard to the micelle formation of $\alpha,\omega$-type surfactants, Zana et al.[10] have investigated the micelle properties of $C_nMe_6$ (*N,N′*-polymethylenebis(triethylammonium) dibromide: $n$= 12, 16, 22) by means of the P-jump and the ultrasonic absorption; they have concluded that the $C_{22}Me_6$ alkyl chain is probably folded in micelles, as the properties of $C_{22}Me_6$ are the same as those of normal alkyl-chain surfactant whose chain length is half that of $C_{22}Me_6$. We ourselves have investigated the micelle properties of $C_{20}Et_6$ in aqueous solutions by means of the $^1$H NMR (FT PGSE technique)[12] and $^{13}$C, $^{14}$N NMR relaxation methods.[13] From the water, surfactant, and micelle self-diffusion coefficients, the length of alkyl carbon chain is obtained to be close to the micelle diameter. $^{13}$C and $^{14}$N NMR relaxation and NOE measurements indicate that the alkyl-carbon chain of $C_{20}Et_6$ is stretched out rather than folded.

The determination of the thermodynamic parameter of micelle formation has been studied by measuring the cmc at various temperatures. This kind of study is important in discussing the micelle property. In this study, several $\alpha,\omega$-type surfactants such as sodium $\alpha,\omega$-alkanediyl disulfate ($n$=12, 14, 16) were synthesized, and the cmc values at different temperatures were compared with that of a normal type surfactant, sodium alkyl sulfate.[16,17]

## Experimental

**Materials.** The $C_{12}Na_2$ (sodium $\alpha,\omega$-dodecane disulfate) was prepared as has been described previously.[8] The $C_{14}Na_2$ and $C_{16}Na_2$ were synthesized via $\alpha,\omega$-alkanediol by using $\alpha,\omega$-alkanedioic acid ($n$=14, 16) (Tokyo Kasei Co.) as the starting material via $\alpha,\omega$-alkanediol. Normal alkanedioic acids were reduced to $\alpha,\omega$-alkanediol by using the borane-THF complex (Aldrich Chem. Co.). After the product has been recrystallized twice with benzene, the complete reduction to $\alpha,\omega$-alkanediol was confirmed by measuring the IR spectrum. The diol thus prepared was reacted with chlorosulfuric acid to give $\alpha,\omega$-alkane disulfate. Then, this disulfate was neutralized with sodium hydroxide. After the product has been recrystallized three times with an acetone-ethanol mixture and three times with an ethyl acetate-ethanol mixture, it was washed twice with diethyl ether and then dried more than 72 h under a vacuum. The purity of the white crystalline product was confirmed to be above 99% by means of elemental analysis, isotachophoresis (IP-3A: Shimadzu Co., Ltd.), NMR, and the surface tension.

**Measurement.** The electroconductivity of the solution was measured by means of a conductivity meter (Model CM-30ET Toa Denpa Co.) at 20, 25, 30, 40, 50, and 60 ±0.1 °C.

## Results and Discussion

The cmc values were determined from plots of the specific conductance, $\kappa$, against the molar concentration, $C$, at several temperatures. These values are tabulated in Table 1. The cmc values decreased with the increase in the carbon chain lengths of the surfactant, while the cmc values of each surfactant increased with the increasing the temperature. Some cmc data taken from the literature[16] for hydrocarbon surfactants, sodium alkyl sulfates, are also shown in Fig. 1 for comparison with those for the $\alpha,\omega$-type surfactants. As the change in the cmc is small between 25 °C and 40 °C, the data for monoalkyl sulfate are used at 40 °C.[20] The $C_nNa_2$'s cmc change against the carbon-chain length was smaller than that of the normal-type surfactant. From these results, it can be said that the

Table 1. cmc's Against the Temperature ($\times10^{-3}$ mol kg$^{-1}$)

| Temp/°C | $C_{12}Na_2$ | $C_{14}Na_2$ | $C_{16}Na_2$ | $C_{18}Na_2$ |
|---|---|---|---|---|
| 20 | 60 | — | — | — |
| 25 | 61 | — | — | — |
| 30 | 63 | — | — | — |
| 40 | 64 | 38 | — | — |
| 50 | 65 | 41 | — | — |
| 60 | 68 | 46 | 11.8 | — |
| 70 | | | | 7.6a) |

a) This value is taken from Ref. 7.

chain length of a α,ω-type surfactant is smaller than half the length of a normal-type surfactant.[19] Zana et al. reported that the $C_nMe_6$'s cmc's change against the carbon-chain length was smaller than those of the $C_nMe_3$. This also suggests that the α,ω-type surfactant may be regarded as shorter than half the length of the normal-type surfactant. The micelle formation free energies of sodium α,ω-alkanediyl disulfate were calculated[15] from cmc measurements at different temperatures. These free energy values are shown in Table 2. A phase separation model was used for these calculations.[16] The following equation was used for the calculation of the micelle formation free energy:

$$\Delta G^\circ = (3-2\alpha)\,RT \ln \mathrm{cmc} \tag{1}$$

where $\alpha$ is the counterion binding of the micelle, $R$, the gas constant, and $T$, the absolute temperature. Each $\alpha$ value was also obtained by conductivity measurement. The micelle-formation free energies of $C_nNa_2$ were slightly decreased with increase in the temperature. The micelle-formation entropy changes in $C_nNa_2$ were also calculated from the cmc's at different temperatures, but the entropy changes of $C_nNa_2$ ($n$=12, 14) were negligibly small. These results show that the entropy change is not very important in forming the micelle in the case of $n$=12 or 14. In other words, the "iceberg" structure of water is not much destroyed when the $C_nNa_2$ ($n$=12, 14) micelle forms.[18] However, any further discussion of entropy change would be meaningless because these calculations of entropy changes contain many errors. Figure 2 shows the micelle formation free energy changes against the alkyl chain length at 60 °C. The free energy decreases with the increase in the alkyl carbon chain length. Increasing the alkyl carbon chain serves to increase in the hydrophobic effect and further to make micelle formation easier. The free energy change against the -($CH_2$)- segment of $C_nNa_2$ was $-11.1$ [kJ mol$^{-1}$].

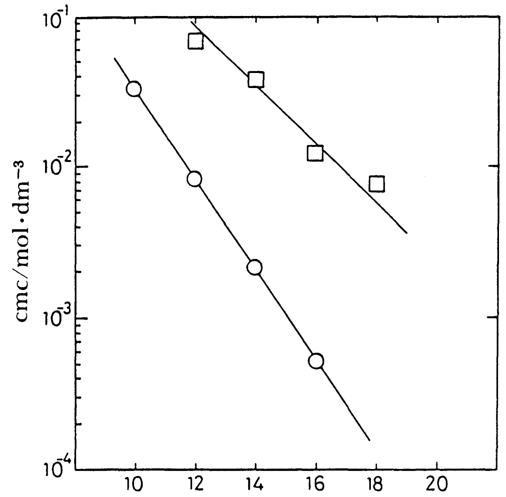

Fig. 1. cmc's of sodium $n$-alkyl sulfate and sodium α,ω-alkanediyl disulfate as a function of hydrocarbon chain length.
(□): $C_nNa_2$, (○): $C_nNa$.

Table 2. The Free-Energy Change of Micelle Formation

| | Temp/°C | $G_m$/kJ mol$^{-1}$ |
|---|---|---|
| $C_{12}Na_2$ | 20 | −10.7 |
| | 30 | −11.2 |
| | 40 | −11.2 |
| | 50 | −11.4 |
| | 60 | −11.6 |
| $C_{14}Na_2$ | 40 | −11.4 |
| | 50 | −11.5 |
| | 60 | −12.1 |
| $C_{16}Na_2$ | 60 | −15.7 |
| $C_{18}Na_2$ | 70 | −17.8 |

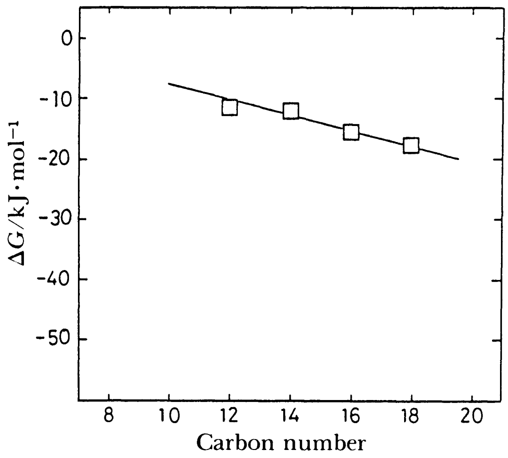

Fig. 2. Standard free energy of sodium α,ω-alkanediyl disulfate as a function of hydrocarbon chain length.
(□): $C_nNa_2$.

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