The Micelle Formation of Some Alkyl Sulfates in a Dioxane-Water Mixture

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The formation of the micelles of surfactants in aqueous solutions has been known to be affected by various kinds of additives. The effect of added salts has been fully studied by many investigators. As for organic additives, Shinoda[1] and Ooshika[2] showed the decrease in the critical micelle concentration (CMC) of surfactants which resulted when some alcohols were added, correlating it with the number of carbon atoms in an alcohol molecule and in a surfactant molecule. The addition of hydrocarbons also depresses the CMC.[3] However, such substances as lower alcohols, acetone and ethylene glycol are known to increase the CMC.[3-5] Flockhart[4] suggested that the increase is due to the increasing " solvent power " of an ethanol-water mixture. Mukerjee[6] reported the increase in the CMC of dodecylpyridinium iodide in a urea-water mixture and pointed out that this probably results from the urea breaking the " iceberg " structure around the nonpolar part of the surfactant molecule. However, no quantitative explanation of any kind has yet been given of the factors that increase the CMC.

Dioxane is completely miscible with water, just as lower alcohols are, and varies the dielectric constant of its aqueous solution considerably. Therefore, it would be interesting to know how these specific characters of a dioxane-water mixture affect the solutional behavior of surfactants. In the present paper we will report the CMC's of sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS) in a dioxane-water mixture, and a theoretical consideration will be given to the change in CMC by adding dioxane to aqueous solutions of these surfactants.

Experimental

Materials.—Sodium alkyl sulfates were synthesized from corresponding pure long chain alcohols (obtained by fractional distillation) and sulfuric acid by the method reported earlier.[7] They were purified by repeated recrystallization from butanol and water, and finally extracted by ether for more than 40 hr. Their purity was checked by elementary analysis and surface tension measurements. Dioxane was distilled after refluxing it for more than 8 hr. on metallic sodium. Water was twice distilled.

Method.—The CMC's were determined by the electric conductivity method. Solubilities were determined from the weight of the solid deposited by drying up a known amount of a saturated surfactant solution obtained by the mechanical shaking of the solution in the presence of a solid phase for more than 8 hr. at a constant temperature and then filtering it through a glass filter.[8] The titration analysis using bromphenol blue was also used to check the solubilities. The results of the two methods agreed well with each other.

Results and Discussion

The CMC, determined from a break point on the equivalent conductivity vs. square root of molar concentration curves, is plotted against the concentration of dioxane in the

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[1] K. Shinoda, This Bulletin, **26**, 101 (1953).

[2] Y. Ooshika, *J. Colloid Sci.*, **9**, 254 (1954).

[3] W. D. Harkins, R. Mittelman and M. L. Corrin, *J. Phys. & Colloid Chem.*, **53**, 1350 (1949).

[4] B. D. Flockhart, *J. Colloid Sci.*, **12**, 557 (1957).

[5] A. W. Ralston and D. N. Eggenberger, *J. Phys. & Colloid Chem.*, **52**, 1494 (1948).

[6] P. Mukerjee and A. Ray, *J. Phys. Chem.*, **67**, 190 (1963).

[7] R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, This Bulletin, **31**, 532 (1958).

[8] S. Miyamoto, ibid. **33**, 371 (1960).

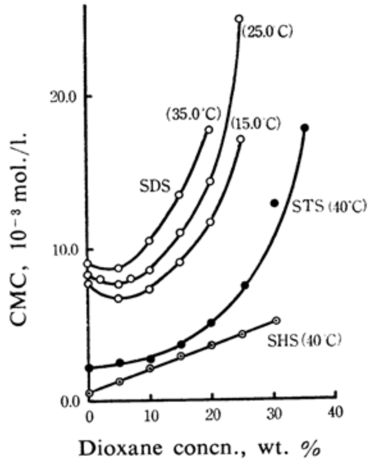

Fig. 1. The CMC of sodium alkyl sulfates (SDS, STS and SHS) as a function of dioxane concentration.

solvent in Fig. 1. No maximum was found around CMC on the conductivity curve at any dioxane concentration, but the break point became obscure as the dioxane concentration increased and eventually faded out. The CMC could not be detected in the region of dioxane more concentrated than that shown in Fig. 1. It should be noted that the CMC of SDS shows a slight minimum and then increases markedly, while that of STS and SHS increases monotonically, even linearly in the case of SHS. The CMC of SDS increases as the temperature rises at any dioxane concentration.

The results may be discussed from two points of view.

The Solubilization of Dioxane.—In spite of a strong affinity with water, dioxane is considered to be solubilized partly in the micelle of the surfactant, as in the case of alcohols, resulting in a lowering of the CMC. Shinoda[1] derived an equation which expresses the lowering of the CMC of soap solutions resulting from the solubilization of alcohols. The equation is as follows:

$$\ln(-\mathrm{dCMC}/\mathrm{d}x) = -0.64\, mw/kT + m'w/kT + \text{const.} \qquad (1)$$

where x is the concentration of alcohols, m and m' are the number of carbon atoms in soap and alcohol molecules respectively, and w is the free energy change per methylene group when transferred from water into the micelle phase. Judging from the assumptions included in Eq. 1, it is not unreasonable to apply the same type of equation to the alkyl sulfates-water-dioxane system, which may be expressed as:

$$\ln(-\mathrm{dCMC}/\mathrm{d}x) = -gmw/kT + \text{const.} \qquad (2)$$

where g is a constant (calculated as 0.68) for homologues of sodium alkyl sulfates. Equation 2 means that $-\mathrm{dCMC}/\mathrm{d}x$ decreases as m increases. This effect of lowering the CMC probably competes with a solvent effect, i. e., the effect of raising the CMC, which increases with an increase in the dioxane concentration. The details of this solven effect will be referred to later. It is because of these two compensating effects that the CMC vs. dioxane concentration curve for SDS passes through a minimum. In the case of STS and SHS, the value of $-\mathrm{dCMC}/\mathrm{d}x$ is not so large as to show a minimum on the CMC vs. dioxane concentration curve, even at the lower concentration of dioxane. Indeed, we could determine the unknown constant by substituting the value of $-\mathrm{dCMC}/\mathrm{d}x$ for SDS into Eq. 2 and in turn obtain the values for STS and SHS of 0.386×10^{-3} and 0.089×10^{-3} respectively. These are quite small compared with the 1.72 $\times 10^{-3}$ for SDS.

In order to compare the CMC-lowering effect of dioxane on SDS with that of some lower alcohols, $\log(-\mathrm{dCMC}/\mathrm{d}x)$ is plotted against the number of carbon atoms in an alcohol molecule, and the value of $\log(-\mathrm{dCMC}/\mathrm{d}x)$ for dioxane is placed on this plot, as Fig. 2* shows. We see from this figure that dioxane corresponds, with regard to the CMC-lowering effect, to "an alcohol with one and a half carbon atoms."

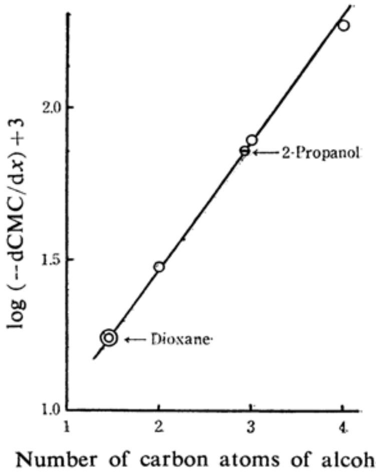

Fig. 2. $\log(-\mathrm{dCMC}/\mathrm{d}x)$ vs. number of carbon atoms in an alcohol molecule. The points for dioxane and 2-propanol were placed in order to obtain corresponding number of carbon atoms of straight chain alcohols.

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* The data in Fig. 2 for ethanol and propanol were taken from Flockhart's paper (Ref. 4 and B. D. Flockhart and A. R. Ubbelohde, *J. Colloid Sci.*, **8**, 428 (1953)) and those for butanol, from Tomoto's (unpublished).

The Solvent Power of the Dioxane-Water Mixture.—In the micellar solution the chemical potential of surfactant molecules in the bulk solution is equal to that in the micelle phase. Therefore,

$$\mu_s^\circ + 2RT\ln C = \mu_m^\circ + RT\ln Xf \qquad (3)$$

where μ_s° and μ_m° are the standard chemical potential of the surfactant in the bulk solution and that in the micelle phase respectively; C is the CMC, and X and f are, respectively, the mole fraction and the activity coefficient of surfactant in the mixed micelle, both of which become unity when the solvent is pure water. Hereafter, the subscript x refers to the dioxane concentration in the solvent and 0, to pure water.

Then, from Eq. 3;

$$2RT\ln C_x = -(\mu_{sx}^\circ - \mu_m^\circ) + RT\ln X + RT\ln f \qquad (4)$$

Equation 4 becomes simpler, when no solubilized substance is present, as follows:

$$2RT\ln C_0 = -(\mu_{s0}^\circ - \mu_m^\circ) \qquad (5)$$

Subtracting Eq. 5 from Eq. 4 we obtain:

$$2RT\ln (C_x/C_0) = -(\mu_{sx}^\circ - \mu_{s0}^\circ) + RT\ln X + RT\ln f \qquad (6)$$

Equation 6 is quite a general expression for the solvent effect on the micelle formation. Shinoda[1] and Ooshika[2] explained the CMC-lowering effect of alcohols in terms of the entropy of mixing and the reduction of charge density of micelles on adding alcohols, factors which correspond to the second and the third term of the right hand side of Eq. 6 respectively. Namely, in their theory the effect due to the first term is neglected.

In order to evaluate $\mu_{sx}^\circ - \mu_{s0}^\circ$, which is often called the free energy of transfer, solubility measurements are employed. For a 1 : 1 electrolyte the free energy of transfer, ΔF_{tr}, is correlated with the solubility as:

$$\Delta F_{tr} = \mu_{sx}^\circ - \mu_{s0}^\circ = -2RT\ln (a_x/a_0) \qquad (7)$$

where a_x and a_0 are activities of the saturated solution of the electrolyte in mixed and pure solvents respectively. Here, in the case of a micellar solution, we assume that a single surfactant ion in the presence of micelle behaves very much like a surfactant ion in the presence of a solid phase just below the Krafft point. For SHS we see, as has already been stated, that the CMC-lowering effect, and accordingly, the solubilization of dioxane in surfactant micelles, is so small as to be neglected and that only the solvent effect should be considered. We are concerned primarily with this case. Then, combining Eq. 6 with Eq. 7:

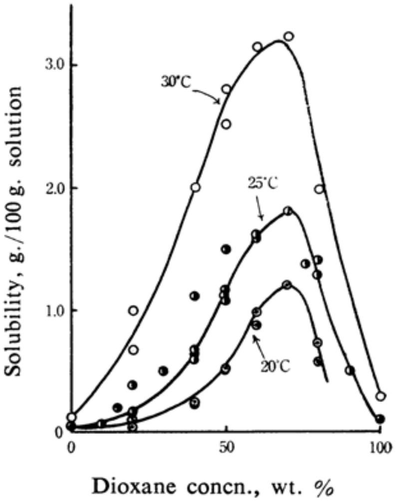

Fig. 3. Solubility of SHS in dioxane-water mixture at 20.0, 25.0 and 30.0°C.

$$\Delta F_{tr} = -2RT\ln (a_x/a_0) = -2RT\ln (C_x/C_0) \qquad (8)$$

Taking the accuracy of measurement into account, we can safely use the solubility in place of the activity. The solubility of SHS in a dioxane-water mixture is plotted against the concentration of dioxane at 20, 25 and 30°C in Fig. 3. The result of the numerical calculations of the free energy of transfer from pure water to 20% dioxane-water using (a) solubility data and (b) CMC data is shown in Table I as an example. The rather good agreement between the values from (a) and (b) suggests that the assumptions made above are correct.

TABLE I. THE FREE ENERGY OF TRANSFER FOR SHS FROM PURE WATER TO A 20% DIOXANE-WATER MIXTURE

Dioxane %	(a) Solubility g./100g. solvent 25°C	30°C	(b) CMC mmol./l. 40°C
0.0	0.027	0.117	0.52
20.0	0.15	0.672	3.54
$-\Delta F_{tr}$ kcal./mol.	2.23	2.30	2.58

Now let us try to represent ΔF_{tr} as an explicit function of the dioxane concentration. In the process of solution an electrolyte experiences various kinds of energy changes, among which the factors that affect the unitary term are given by:

$$\mu_{sx}^\circ = K_1/D + K_2 \qquad (9)$$

where K_1 and K_2 are constants, and D is the dielectric constant of the solvent.[9] Equation 9 means that the unitary term can be divided into two parts, i. e., one dependent on, and one independent of, the dielectric constant of the solvent. In fact, for simple inorganic electrolytes the logarithm of solubility is nearly linear against $1/D$ (Born's equation). However, in the case of an amphipathic compound like SHS, the solubility increases at first and then decreases with the dioxane concentration, as is shown in Fig. 3. This suggests that an appreciable hydrophobic contribution must be included in the K_2 in Eq. 9. Thus, we should rewrite Eq. 9 as:

$$\mu_{sx}^{\circ}=K/D+L+M \tag{10}$$

where K is a constant, dependent on the geometry of ions; L is a term representing hydrophobic contributions, and M is a constant independent of the nature of the solvent.

In order to express L as a function of the dioxane concentration, we may tentatively utilize the regular solution theory of Hildebrand.[10] In a regular ternary solution the partial molar heat of mixing for component 1 (here the surfactant), $\overline{E}_m$, is expressed as:

$$\overline{E}_m=V_1(\delta_1-\delta_0)^2\phi_0^2 \tag{11}$$

where V_1 is the molar volume and δ_1 is the solubility parameter, each for component 1. ϕ_0 and δ_0 are given by:

$$\phi_0=\phi_2+\phi_3, \quad \delta_0=\frac{\delta_2\phi_2+\delta_3\phi_3}{\phi_2+\phi_3}$$

where the ϕ's and δ's are the volume fractions and solubility parameters respectively, each for the subscript component. When component 1 is extremely dilute, Eq. 11 becomes:

$$\overline{E}_m=V_1\{(\delta_1-\delta_2)-(\delta_3-\delta_2)\phi_3\}^2 \tag{12}$$

Neglecting a slight volume contraction on mixing, we can substitute ϕ_3 for x, since the specific gravity of dioxane is about 1.03 at 25°C. Then Eq. 12 may be put into the following form:

$$L(x)=L_0(1-rx)^2 \tag{13}$$

where L_0 is a hydrophobic contribution in pure water and r is a constant correlating with the solubility parameters. L_0 may be approximated by the free energy of transfer for hexadecane from water to pure hexadecane, which can be obtained by extrapolating published data for some lower alkanes[11] (Fig. 4). The value is 14.5 kcal./mol.

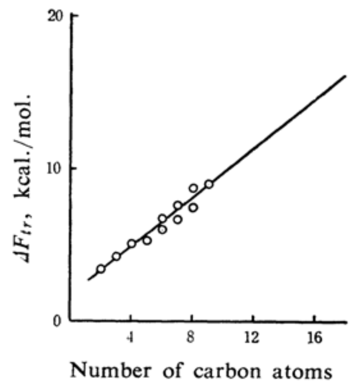

Fig. 4. Free energy of transfer (ΔF_{tr}) for some alkanes from pure liquid to water.

The dielectric constant of a dioxane-water mixture is a nearly linear function of the weight fraction of dioxane, which is expressed empirically as follows:[12]

$$D(x)=78.6(1-0.975\,x) \tag{14}$$

Combining Eqs. 13 and 14 with Eq. 10, we obtain:

$$\mu_{sx}^{\circ}=K/78.6(1-0.975\,x)+14.5(1-rx)^2+M \tag{15}$$

Then we have:

$$\Delta F_{tr}=\mu_{sx}^{\circ}-\mu_{s0}^{\circ}=(K/78.6)\{1/(1-0.975x)-1\} + 14.5\{(1-r\,x)^2-1\} \tag{16}$$

The unknown parameters, K and r, could be determined by using the data of ΔF_{tr} from pure water to 20% and 40% dioxane-water mixtures. The values found were $K=2.1\times10^2$ kcal. and $r=0.61$. Thus, finally we obtain:

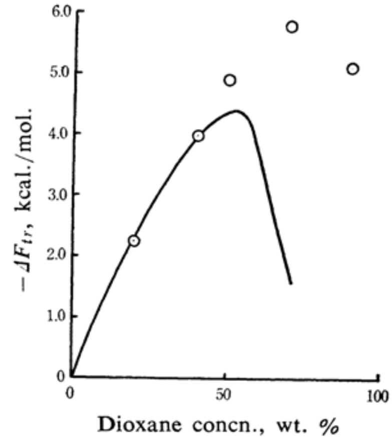

Fig. 5. Comparison of ΔF_{tr} from solubility data with that from Eq. 17 (solid line) at 25°C.

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[9] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York (1953).

[10] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," Reinhold, New York (1950), p. 198.

[11] G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

[12] J. B. Hasted, G. H. Haggis and P. Hutton, *Trans. Faraday Soc.*, **47**, 577 (1951).

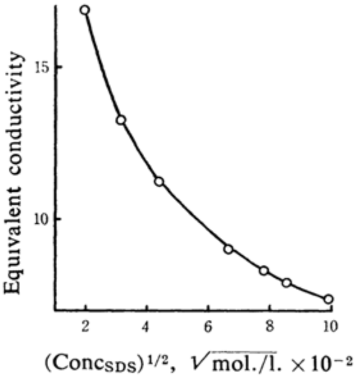

Fig. 6. Equivalent conductivity of SDS in an 80% dioxane-water mixture at 25.0°C.

$$\Delta F_{tr}=(2.1\times10^2/78.6)\{1/(1-0.975x)-1\} \\ +14.5\{(1-0.61x)^2-1\} \qquad (17)$$

In Fig. 5 the experimental value of ΔF_{tr} obtained from the solubility data is compared with the value calculated by using Eq. 17. The agreement is as expected in the dioxane concentration region of less than 50 per cent. Over 50 per cent the experimental values are higher than the theoretical. This may be caused by several factors, one of which is the imperfect dissociation effect. For example, as is shown in Fig. 6, the equivalent conductivity vs. the square root of concentration for SDS in an 80% dioxane-water mixed solvent gives a curved line, while there should be a straight line in a solvent with a higher dielectric constant. The same behavior is expected for SHS. This is probably caused by the imperfect dissociation of the surfactant molecules in a solvent with a low dielectric constant, leading to the diminution of coefficient 2 of Eq. 8 towards unity. Therefore, the effect of imperfect dissociation should reduce the experimental value of $-\Delta F_{tr}$ leading to a better agreement with the predicted value. Another factor which is considered to cause the discrepancy between the theoretical and the experimental values of ΔF_{tr} in the higher concentration region of dioxane is the effect of selective solvation.

The values of CMC can now be calculated from ΔF_{tr} of Eq. 17 for each dioxane concentration by using Eq. 8. In Fig. 7 the calculated values of CMC are compared with the observed. For SHS solutions the agreement is satisfactory. For STS, especially for SDS solutions, the same result can not be expected, since in these cases the CMC-lowering effect of dioxane, i. e., the solubilization of dioxane by the surfactant micelles, is not negligible. When the dioxane concentration is large, the formation of the micelles of sodium alkyl sulfates is not observable, so the comparison of the theoretical with the experimental values of CMC becomes impossible. However, from the standpoint of the hydrophobic contribution of Eq. 13, we can confirm that the present theory of the solvent power of a dioxane-water mixture is reasonable. For example, in the 50% dioxane solution the calculated value of the hydrophobic contribution is 7.0 kcal., which corresponds to the value of hexane on the plot in Fig. 4. The micelle formation of polar-nonpolar compounds with six carbon atoms has not been believed to be appreciable in an aqueous solution. This corresponds to the fact that the surfactants used in the present study do not seem to form micelles in 50% or more concentrated dioxane-water mixtures, as has been shown in these experiments.

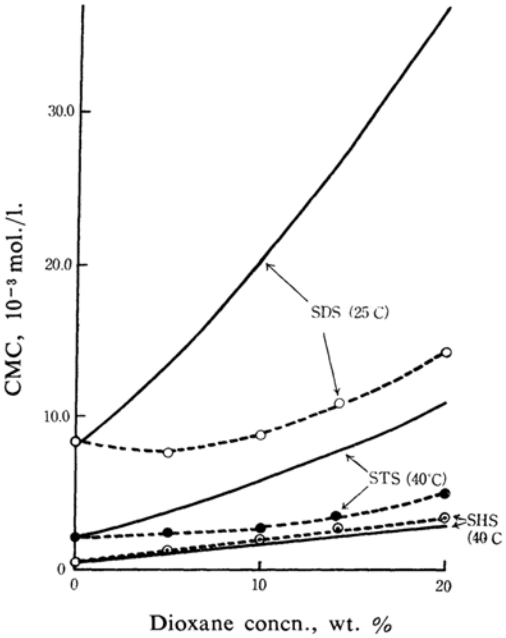

Fig. 7. Comparison of CMC values of sodium alkyl sulfates (SDS, STS and SHS) in dioxane-water mixture with those calculated by using Eq. 17 (solid line).

Summary

The CMC values of three sodium alkyl sulfates with the number of carbon atoms 12, 14 and 16 in a dioxane-water mixture have been measured. The CMC-lowering effect of dioxane, especially appreciable in the case of sodium dodecyl sulfate, has been explained in terms of Shinoda's equation. The CMC-raising effect of dioxane, which is the main effect in the case of sodium hexadecyl sulfate, has been explained by the decrease in the standard chemical potential, i. e., the free energy

of transfer, ΔF_{tr}, of the surfactant. An equation has been derived which expresses ΔF_{tr} as a function of the dioxane concentration by applying Born's equation and Hildebrand's regular solution theory.

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