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The Surface Adsorption of Sodium Alkyl Sulfates from Dioxane-Water Mixtures

By Keishiro SHIRAHAMA, Kiyoshi NAKAO, Hiroko ENDO and Ryohei MATUURA

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki

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The surface adsorptions of three sodium alkyl sulfates (C_{12}, C_{14}, C_{16}) from dioxane-water mixtures have been measured by using ^{35}S-labeled surfactants; it has been found to decrease with an increase in the dioxane concentration. This decrease has been explained in terms of the following factors; (1) the variation in the standard chemical potential of the surfactant in the bulk phase, or the free energy of transfer, (2) the surface tension of the solution, and (3) the dielectric constant of the solvent. In a solvent containing more dioxane than 40 wt.%, it has been shown, both by experiment and by theory, that these alkyl sulfates lose their surface activities.

The air/solution interface reflects the properties of the bulk phase. Thus, in the case of a surfactant solution, the surface excess may be correlated to the chemical potential of the surfactant in the solution by Gibbs' equation.

If the nature of a solvent in the bulk phase is changed by adding to it a third substance, the surface properties should correspondingly be altered; therefore, it is informative to study the surface phenomena in relation to the nature of the solvent in the bulk phase.

The surface adsorption of an ionic surfactant from an aqueous solution has been shown to be affected very much by the addition of extraneous salts, and this has been explained by considering only the electrical double layer produced just below the surface.1)

In a previous paper, such properties as the micelle formation and solubility of sodium alkyl sulfates in the dioxane-water mixed solvent were discussed in detail.2)

The present work will describe the surface adsorption of sodium hexadecyl (SHS), tetradecyl (STS) and dodecyl (SDS) sulfates from their solution in a dioxane-water mixture, and will attempt to explain the decrease in the surface adsorption in terms of the variation, with the dioxane concentration, of the standard chemical potential of the surfactant, of the dielectric constant of the solvent, and of the surface tension of the solution.

Experimental

The surfactants used, i. e., SHS, STS and SDS, were synthesized and purified as described in the previous work.2) The surface adsorption measured by the radiotracer method in the same way as has already been reported.3) The surface tension of the solutions was measured by the drop-weight method with the Harkins-Brown corrections applied.4) The solvents used were the same as were used in the previous work.2) The experiments were carried out at 25°C.

Results and Discussion

The surface adsorption of the three alkyl sulfates is shown in Fig. 1 as a function of the dioxane concentration. The general feature is the decrease in the adsorption with the increase in the dioxane concentration; the adsorption becomes undetectable when the dioxane concentration increases beyond 30 wt.% for SDS and STS, and 45 wt.% for SHS. This trend may be explained in the following manner.

The chemical potential of the surfactant ion in the surface phase is expressed as:

$$\mu^{s} = \mu^{os} + \boldsymbol{k}T \ln a^{s} - \gamma A + e\psi \qquad (1)$$

and that in the bulk phase as:

$$\mu = \mu^{o} + \boldsymbol{k}T \ln a \qquad (2)$$

where the superscript s refers to the surface, μ^{o} and a are the standard chemical potential and the activity, respectively, of the surfactant ion; γ is the surface tension of the solution; A is the surface area of a surfactant molecule; e is a unit charge, and ψ is the surface potential. The other notations have the ordinary meanings. According to Gouy's theory,

$$\psi = (2\boldsymbol{k}T/e)\sinh^{-1}\{(\sigma/C^{1/2})(500\pi/D\boldsymbol{R}T)^{1/2}\} \qquad (3)$$

In this equation, C is the total electrolyte concentration in mol./1.; D is the dielectric constant of the solvent, and $\sigma = e\Gamma$, where Γ is the surface excess of a surfactant in mol./cm^2.

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1) R. Matuura, H. Kimizuka and K. Yatsunami, This Bulletin, **32**, 646 (1959); R. Matuura, H. Kimizuka and A. Matsubara, ibid., **34**, 1512 (1961); R. Matuura, H. Kimizuka, A. Matsubara, K. Matsunobu and T. Matsuda, ibid., **35**, 552 (1962).

2) K. Shirahama and M. Matuura, ibid., **38**, 373 (1965).

3) R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, ibid., **31**, 532 (1958).

4) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **38**, 288 (1916); **41**, 499 (1919).

When $\psi \geqq 100$ mV., Eq. 3 reduces to:

$$\psi = (2\boldsymbol{k}T/e)\ln\{(2e\Gamma/C^{1/2})(500\pi/D\boldsymbol{R}T)^{1/2}\} \quad (4)$$

The activities a^s and a in Eqs. 1 and 2 can be replaced by concentrations when the solutions are sufficiently dilute. Using Eq. 4 and the relation $C^s = 1000\Gamma/d$, where C^s is the surface concentration expressed in mol./l., and d, the surface thickness,[5] we obtain from equating Eqs. 1 and 2, after rearrangment:

$$3\boldsymbol{k}T\ln\Gamma = \mu^{\circ} - \mu^{\circ s} + \gamma A + \boldsymbol{k}T\ln D + K \quad (5)$$

where $K = 2\boldsymbol{k}T\ln C - \boldsymbol{k}T\ln(10^6 e^2\pi/2d\boldsymbol{R}T)$. Here, we are primarily interested in the relative adsorption, Γ_x/Γ_0, where the subscripts 0 and x refer to the water and dioxane-water mixtures, respectively. Hence at a constant surfactant concentration in the bulk phase, we have:

$$\log(\Gamma_x/\Gamma_0) = \frac{1}{3}\{(\mu_x{}^{\circ} - \mu_0{}^{\circ})/2.3\boldsymbol{R}T + (\gamma_x - \gamma_0)A/2.3\boldsymbol{R}T + \log(D_x/D_0)\} \quad (6)$$

The first term of the right hand side of Eq. 6 can be estimated from the solubility data shown in the previous paper,[2] while the other terms can easily be calculated from the data of the surface tension and the dielectric constant of the solution and the solvent (Table I). The calculated values are shown by the solid lines in Fig. 1. The rather good agreement with experimental values may show the validity of Eq. 6. In order to see what term of the three in the R.H.S. of Eq. 6 is the most effective in effecting the decrease in the surface adsorption with the dioxane concentration, the magnitude of each term is shown in Table II.

TABLE I. VARIOUS PROPERTIES OF THE SOLUTION

Dioxane wt. fraction	Surface tension (dyne/cm)			Dielectric constant*
	SHS	STS	SDS	
0.0	66.0	71.6	70.8	78.5
0.1	54.5	54.1	56.5	70.0
0.2	52.0	49.0	49.0	61.6
0.4	48.9	43.0	48.0	42.8
Surfactant concn. (mol./l.)	10^{-5}	5×10^{-5}	10^{-4}	

* Dielectric constant was quoted from Ref. 6.

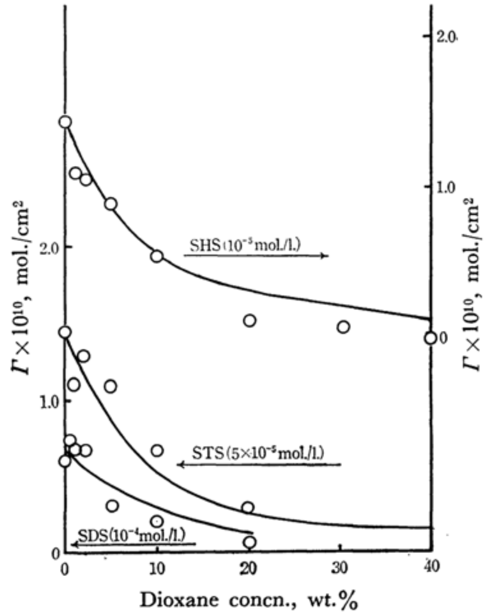

Fig. 1. Surface adsorption vs. dioxane concentration.
Circles are the measured points at 25°C.

TABLE II. THE CALCULATION OF EACH TERM OF Eq. 6

Dioxane wt. fr.	$-(\mu_x{}^{\circ}-\mu_0{}^{\circ})/2.3\boldsymbol{R}T$*	$-(\gamma_x-\gamma_0)A/2.3\boldsymbol{R}T$**	$-\log(D_x/D_0)$
	SHS	$C=10^{-5}$ mol./l.	
0.1	0.974	0.238	0.0496
0.2	1.59	0.292	0.106
0.4	2.58	0.356	0.263
	STS	$C=5\times10^{-5}$ mol./l.	
0.1	0.898	0.364	
0.2	1.45	0.468	
0.4	2.01	0.594	
	SDS	$C=10^{-4}$ mol./l.	
0.1	0.800	0.300	
0.2	1.31	0.468	

* Calculated on the molar concentration basis, while in the previous paper the free energy of transfer was calculated on the mole fraction basis.

** γA was calculated in kcal. with A taken as 20Å².

It is evident that the free energy of transfer term, $(\mu_x{}^{\circ}-\mu_0{}^{\circ})$, is the major factor. This means that the surfactant becomes more solvophilic as the dioxane concentration increases, and that it is pulled down from the surface to the bulk phase. As to the surface tension term, it also contributes, although not dominantly, to the decrease in the surface adsorption. Finally, the low dielectric constant of the mixed solvent affects the surface adsorption so as to strengthen the electric field due to the ions in the diffuse layer, and in turn, to increase the surface electrical energy. Thus, the bulk phase becomes more favorable for the surfactant to escape from the surface, and, in the region of dioxane concentration greater than 40 wt.%, the surfactant is no longer "surface-active."

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[5] J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, London (1961), p. 154.

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

This corresponds to the fact that no micelle formation was detected in this region.⁽²⁾ In spite of the larger bulk concentration in the case of SDS and STS, the surface adsorptions disappear at a dioxane concentration smaller than that in the case of SHS. This, however, may easily be understood. The shorter hydrocarbon chain would become readily solvophilic upon the addition of a smaller amount of dioxane.

The approximation made in the derivation of Eq. 4 from Eq. 3 was checked; it was found to be satisfied at all points measured. The other assumption is the complete dissociation of the adsorbed surfactant. In an aqueous medium, an almost complete dissociation has been suggested by a comparison of the surface excess measured by the radiotracer method with the one calculated from the surface tension measurement.⁽³⁾ In a dioxane-rich solvent, there should be an appreciable ionic association, but such a solvent is outside our present area of interest.