Properties of Aqueous Solution of a Fluorocarbon Surfactant and a Nonionic Surfactant, and Their Mixtures

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ABSTRACT

The surface tensions of aqueous solutions of lithium perfluorooctane sulfonate (LiFOS) and hexaethyleneglycol *n*-dodecylether (6ED), and of their mixtures, were measured. The effect of each surfactant additives on the adsorption and the micelle formation was discussed on the basis of the surface tension values using the Langmuir adsorption equation for the mixture of both surfactants and the modified Szyszkowski equation. From these results, in the range of low concentrations of 6ED or LiFOS, some of the 6ED molecules which had already adsorbed on the solution surface were found to be replaced by LiFOS molecules in an addition of LiFOS surfactant and vice-versa. In the ranges of higher concentration above critical micelle concentration (CMC) of each surfactant, it was concluded that the mixed micelle could be formed in the mixed system of both surfactants as well as in the mixed system of two kinds of ordinary hydrocarbon surfactants.

INTRODUCTION

Many articles (1-10) have been published on the properties of the mixture of an anionic surfactant and a nonionic one, and many workers have interpreted their results with the aid of mixed micelle formation between the surfactants.

Relatively few studies (11-14) for the effect of a fluorocarbon surfactant on the micellization of hydrocarbon surfactants have so far been reported, because all the surfactants treated in the previous works were limited to the kinds of hydrocarbon surfactants. Recently, Tiddy and coworkers (15) have investigated the effects of an addition of octanol on ammonium perfluoro octanoate/water system by nuclear magnetic resonance (NMR), and compared the obtained results with those of the corresponding hydrocarbon surfactant system consisting of sodium octanoate, octanol and water. They have assumed that each of the fluorocarbon and hydrocarbon surfactants in aqueous mixed solutions may form a separate micelle. However, mixed micelles between them will be expected to be formed under some special conditions.

In this paper, the adsorption and the micelle formation of mixture of lithium perfluorooctane sulfonate (LiFOS) and homogeneous hexaethyleneglycol *n*-dodecylether (6ED) will be discussed on the basis of the experimental data obtained by the surface tension measurement. From Gibbs' and Langmuir's equations, and from the modified Szyszkowski equation derived by Nakagaki and Handa (16), saturated adsorption amounts and the Langmuir coefficients for each surfactant are obtained by using the experimental values of the surface tension. The experimental and theoretical results are compared. Experimental results for adsorption of the single and mixed solutions up to the critical micelle concentration (CMC) are compared to theoretical values.

EXPERIMENTAL PROCEDURES

Materials

Potassium perfluorooctane sulfonate, $C_8F_{17}SO_3K$, obtained from Dai Nippon Ink and Chemical Industry Co. Ltd., Tokyo, was repeatedly washed by water to remove water-soluble impurities and then dried at 80 C. In order to exchange potassium ion into lithium ion of the salt for which the Krafft point is below 0 C, perfluorooctane sulfonic acid, $C_8F_{17}SO_3H$, was obtained by distillation of the potassium salt in the presence of 95% sulfonic acid at 150 C, 14 mm Hg (17), and was then neutralized by lithium hydroxide. Lithium perfluorooctane sulfonate, $C_8F_{17}SO_3Li$, was purified by repeated crystallization from dioxane after an extraction with ethanol. The purity of this sample was confirmed by surface tension.

Hexaethyleneglycol *n*-dodecylether used in this experiment was supplied from Nikko Chemical, Tokyo, Japan. This sample was confirmed as having homogeneous the polyethylene glycol chain length from the results of thin layer chromatography (TLC), IR spectrum, GPC and surface tension.

The water used in all experiments was purified by passing through an ion exchange column followed by distillation from an alkaline permanganate solution.

Procedures

Surface tension was measured by a modified surface tension-meter, Shimazu ST-1. The measurements were made at 25 + 0.2 C until the values agreed with each other within 0.1 dyn/cm for 15 min.

RESULTS

Surface Tension of LiFOS and 6ED

Figure 1 shows the surface tension of an aqueous solution containing LiFOS and 6ED as function of the logarithm of the LiFOS concentration (C_1), while the concentration (C_2) of 6ED is kept constant. The surface tension of the single LiFOS solution showed only one break-point corresponding to the CMC (7.0×10^{-3} M) in the curve. However, an addition of small amounts of 6ED lowered the surface tension in the range of the concentration below the CMC of LiFOS and a minimum appeared near the CMC of LiFOS in the curves. When the additive concentration of 6ED exceeded the CMC of 6ED, the minimum disappeared from the curve and the surface tension indicated an almost lower value than that of the equilibrium surface tension of each component.

Figure 2 shows the surface tension of 6ED as function of LiFOS additive concentration. The surface tension of 6ED decreased with the increase of the additive concentration of LiFOS. In these cases, no minimum was observed on the curves. This is very different from each case of the curves in Figure 1. In the additive concentration of LiFOS above the CMC, the surface tension showed almost constant value at ca. 25 dyn/cm lower than the equilibrium surface tension of each surfactant and the curve showed the long plateau in most ranges of the concentration of 6ED. The concentration values of break points corresponding to the single and mixed CMC are given in Table I together with the data of Figure 1.

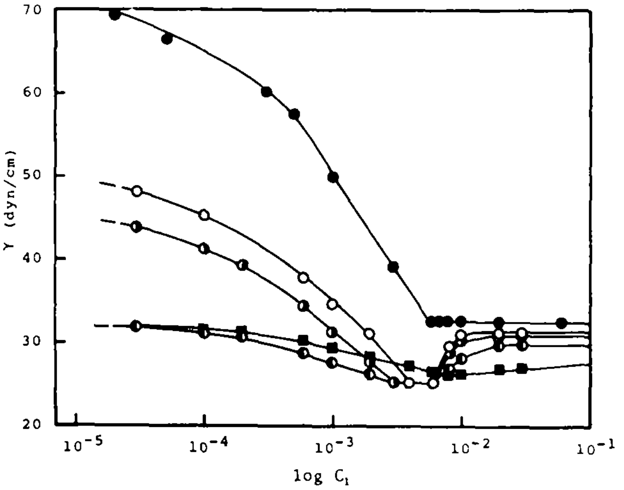

FIG. 1. The surface tension of lithium perfluorooctane sulfonate (LiFOS) in the presence and absence of hexaethyleneglycol *n*-dodecylether (6ED) vs the logarithm of LiFOS concentration (C_1). Additive concentration (C_2) of 6ED (mM): (●), 0; (◑), 0.005; (◐), 0.01; (○), 0.05; (■), 1.0.

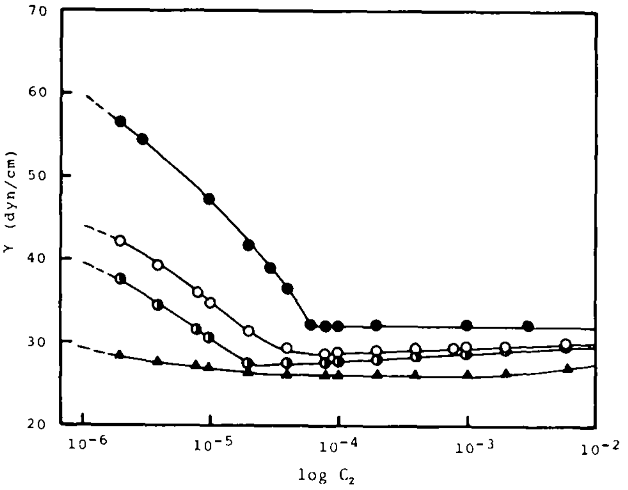

FIG. 2. The surface tension of hexaethyleneglycol *n*-dodecylether (6ED) in the presence and absence of lithium perfluorooctane sulfonate (LiFOS) vs the logarithm of 6ED concentration (C_2). Additive concentration (C_1) of LiFOS (mM): (●), 0; (○), 0.5; (◐), 1.0; (▲), 7.0.

DISCUSSION

Adsorption of LiFOS and 6ED

In order to obtain more information about some adsorption states of both surfactants up to the CMC, saturated adsorption amounts (Γs) and the Langmuir coefficient (k) for each surfactant are calculated from Figures 1 and 2 using Gibbs' and Langmuir's equations (I) and (II) as follows:

$$\Gamma = \Gamma skC / (1 + kC) \qquad [I]$$

$$\Gamma = (-1/nRT)\, d\gamma / d\ln C, \qquad [II]$$

where γ is the surface tension, Γ, adsorption amount and C, the concentration of the surfactants. Here, C can be used instead of the activity because of the very diluted solution. The relevant form of Gibbs' equation for LiFOS will depend on the concentrations of Li^+ and $C_8F_{17}SO_3^-$ in the solution. When no electrolyte is added in the solutions as pointed out by Matijevic and Pethica (18) and Lange (19), the factor n in Equation II should be 1 for 6ED and 2 for LiFOS, respectively. The k values were 5.0×10^6 and 4.7×10^8 for LiFOS and 6ED, respectively. On the other hand, the values of Γ for each surfactant were 2.1×10^{-10} mol/cm^2 for LiFOS and 3.4×10^{-10} mol/cm^2 for 6ED, respectively, and corresponded to 79.1 Å^2 and 48.8 Å^2, the surface areas (Å^2/molecule) occupied by one molecule for each component.

TABLE I

Values of the Langmuir Coefficient, k_1, k_2, and the Values of the Break Point on the Surface Tension Curves at the Additive Concentration

	k_1 and k_2	Additive concentration (mmol/L)	Break point (mmol/L)
LiFOS (C_1)	5.0×10^6	$C_2 = 0$	7.0
		$C_2 = 0.005$	4.2
		$C_2 = 0.01$	3.1
		$C_2 = 0.05$	2.7
6ED (C_2)	4.7×10^8	$C_1 = 0$	6.8×10^{-2}
		$C_1 = 0.5$	4.4×10^{-2}
		$C_1 = 1.0$	2.3×10^{-2}

Effect of Additive Surfactant on Adsorption

Assuming that the mixing of both surfactants in the adsorption layer is ideal, as proposed by Nakagaki and Handa (16), the modified Langmuir adsorption equation for a mixed solution may be given as:

$$\Gamma_1 = \Gamma s_1 k_1 C_1 / (1 + k_1 C_1 + k_2 C_2) \qquad [III]$$

$$\Gamma_2 = \Gamma s_2 k_2 C_2 / (1 + k_1 C_1 + k_2 C_2), \qquad [IV]$$

where Γ_1 and Γ_2 are the adsorption amounts for each surfactant and Γs_1 is the saturated adsorption amount for LiFOS in the presence of 6ED, Γs_2 is the saturated adsorption amount for 6ED in the presence of LiFOS. Here, Gibbs' adsorption equation of a mixed solution is:

$$-d\gamma = \Gamma_1 2RT\, d\ln C_1 + \Gamma_2 RT\, d\ln C_2 \qquad [V]$$

If one component in both surfactants is kept constant, then Equation V reduces to:

$$-d\gamma = \Gamma_1 2RT\, d\ln C_1 \qquad [VI]$$

$$-d\gamma = \Gamma_2 RT\, d\ln C_2 \qquad [VII]$$

In Figure 3(a), the adsorption amount, Γ_1, is calculated from Equation VI by the direct differentiation of the experimental curves and is compared with the theoretical values calculated from Equation III.

In the case of single LiFOS solution, the experimental result for the adsorption amount, Γ_1, agreed well with the theoretical value calculated from Equation III as shown in curve-1 in Figure 3(a), but the others deviated from the theoretical value and were found to be larger than the theoretical values in the ranges of the lower concentration of LiFOS. On the other hand, these Γ_1 values in higher concentration of LiFOS showed smaller experimental values than the theoretical ones. These results suggest that adsorption amounts of LiFOS decrease with the increase of additive concentration of 6ED, and instead of the adsorption of LiFOS, some of 6ED molecules adsorb on the solution surface.

In the case of LiFOS addition, Γ_2 curves in Figure 3(b) showed the same tendency as the case of Γ_1 curves in Figure 3(a). Equation V can be integrated with Equations III and IV to give:

$$F = \gamma_0 - \gamma = (\Gamma s_1 + \Gamma s_2) RT \ln(1 + k_1 C_1 + k_2 C_2), \qquad [VIII]$$

where $\ln(1 + k_1C_1 + k_2C_2)$ can be calculated using the values of the k_1 and k_2, which have previously been obtained for each single solute solution. The value (Γs_1 +

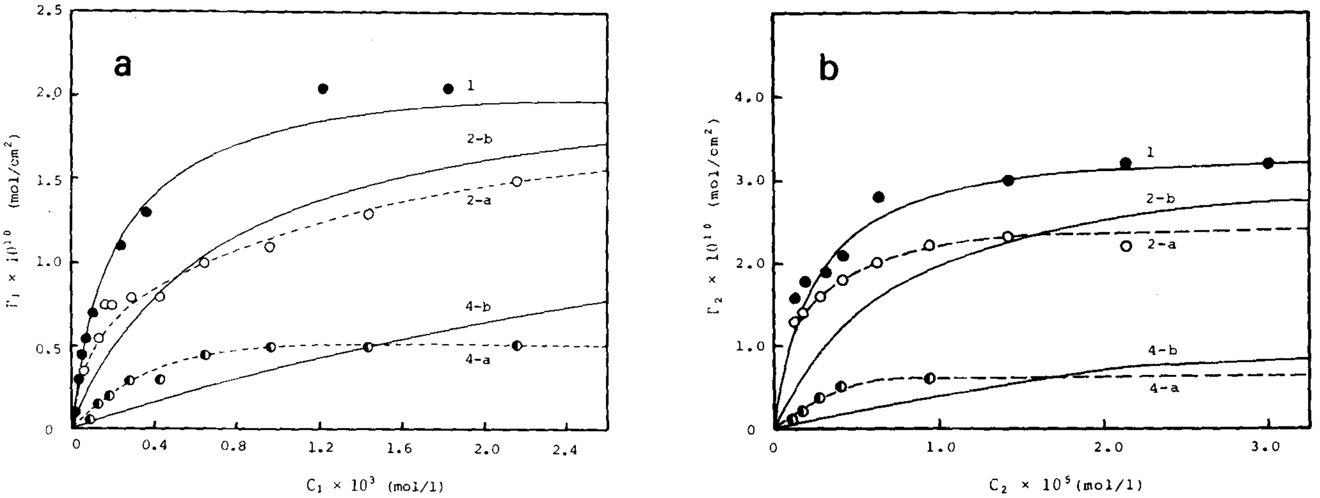

FIG. 3(a). The experimental values (Γ_1) of adsorption amount for lithium perfluorooctane sulfonate (LiFOS) calculated from Equation III and the calculated theoretical values (Γ_1) from Equation III in the presence and absence of hexaethyleneglycol *n*-dodecylether (6ED) vs the concentration (C_1) of LiFOS. Additive concentration (C_2) of 6ED (mM): experimental curves (curve 1), 0; (curve 2-a), 0.005; (curve 4-a), 0.05. Calculated curves (curve 2-b), 0.005; (curve 4-b), 0.05. (b). The experimental values (Γ_2) of adsorption amount for hexaethyleneglycol *n*-dodecylether (6ED) calculated from Equation IV and the calculated theoretical values (Γ_2) from Equation IV in the presence and absence of lithium perfluorooctane (LiFOS) vs the concentration (C_2) of 6ED. Additive concentration (C_1) of LiFOS (mM): experimental curves (curve 1), 0; (curve 2-a), 0.5; (curve 4-a), 7.0. Calculated curves (curve 2-b), 0.5; (curve 4-b), 7.0.

Γs_2) of the slope denoted by Γsmix can be regarded as variables, as the (Γs_1 + Γs_2) of values depend on each additive concentrations of the surfactants.

In Figures 4(a) and (b), the values of F are plotted against the $\ln(1 + k_1C_1 + k_2C_2)$ for each value of the additive concentration of 6ED and LiFOS, respectively.

The apparent values of the Γsmix obtained from the slopes of the straight, dashed lines in Figures 4(a) and (b) are listed in Table II. Here, the theoretical values of the surface pressure (F) calculated from Equation VIII are indicated by the straight lines-(A) and (B) in Figures 4(a) and (b), respectively, and then the value of the slope obtained from the straight lines is equal to the sum (Γs_1 + Γs_2) of the saturated adsorption amounts of each surfactant. The surface pressure (F) of 6ED indicated by the dashed lines increased more than that of theoretical value (straight line) with the increase of the additional concentrations of LiFOS as shown in Figure 4(a). Accordingly, the apparent values of the Γsmix for dashed, straight lines in Figure 4(a) indicated larger values than that of (Γs_1 + Γs_2) given by the slope of line-A. The surface pressure (F) of LiFOS as shown by the dashed lines in Figure 4(b) indicated a tendency similar to the case of 6ED in Figure 4(a).

These results suggest that when LiFOS is added in the solution, some of 6ED molecules adsorbed on the solution surface are replaced by some of the LiFOS molecules, and vice-versa. These are supported by the fact that their surface tensions are lowered with the increase of the additive concentration of 6ED and LiFOS, respectively, as shown in Figures 1 and 2.

Property of Mixed Solution above the CMC of LiFOS

Figure 5 shows the effect of 6ED additive on the equilibrium surface tension of LiFOS above the CMC. The surface tension decreases with the increase of 6ED additive concentration and indicates a lower value of ca. 25 dyn/cm than that of each component, ca. 33.0 dyn/cm for LiFOS and 32.0 dyn/cm for 6ED, respectively. This phenomenon is very different from that observed in the mixed system between two kinds of ordinary hydrocarbon surfactants (7). This finding suggests that at some higher concentrations of LiFOS, 6ED molecules in the mixed system adsorb on the solution surface in more excess than in the single system. By adding the small amount of 6ED, as has been stated previously, the surface tensions in Figure 1 were lowered remarkably and showed a minimum in the curve

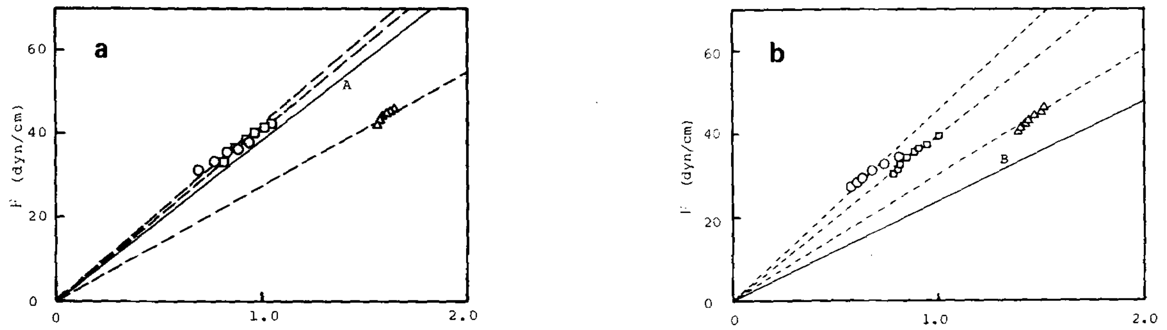

FIG. 4(a). The surface pressure (F) of mixed solution in the presence of a given concentration of lithium perfluorooctane sulfonate (LiFOS) vs $\ln(1 + k_1C_1 + k_2C_2)$. LiFOS concentration (C_1) (mM): (○), 0.5; (□), 1.0; (△), 7.0. Straight line-A: theory (2 x Γs_2 = 6.8 x 10^{-10} mol/cm^2). (b). The surface pressure (F) of mixed solution in the presence of a given concentration of hexaethyleneglycol *n*-dodecylether (6ED) vs $\ln(1 + k_1C_1 + k_2C_2)$. 6ED concentration (C_2) (mM): (○), 0.005; (□), 0.01; (△), 0.05. Straight line-B: theory (2 x Γs_1 = 4.3 x 10^{-10} mol/cm^2).

TABLE II

Experimental Values of Saturated Adsorption Amount and the Theoretical Values from Equation VIII at Each Additive Concentration

Surfactant	Additive concentration C_1 or C_2 (mmol/L)	Saturated adsorption amount (Γsmix) (mol/cm^2)
6ED (C_2)	$C_1 = 0$	6.8×10^{-10} ($2 \times \Gamma s_2$)
	$C_1 = 0.5$	7.4×10^{-10}
	$C_1 = 1.0$	7.2×10^{-10}
	$C_1 = 7.0$	4.9×10^{-10}
LiFOS (C_1)	$C_2 = 0$	4.3×10^{-10} ($2 \times \Gamma s_1$)
	$C_2 = 0.005$	8.0×10^{-10}
	$C_2 = 0.01$	6.9×10^{-10}
	$C_2 = 0.05$	5.3×10^{-10}

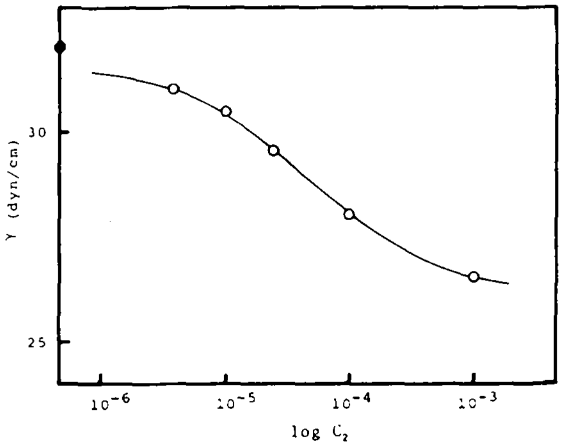

FIG. 5. The surface tension of lithium perfluorooctane sulfonate (LiFOS) above the CMC in the presence of hexaethyleneglycol *n*-dodecylether (6ED) vs the logarithm of 6ED concentration (C_2).

suggesting the existence of the mixed micelle. In this region, mixed micelles have some possibility of being formed in the solution, because the minimum corresponding to the CMC of mixed micelles is located at just lower concentration than that of single LiFOS. This also suggests that the mixed micelle begins to be formed from this minimal point in the mixed solution, as Schick and Manning (8), Lange and Beck (9), and Clint (10) have pointed out that the CMC of a mixed micelle is lowered more than that of single surfactants.

Moreover, the existence of the plateau in the surface tension curves in Figures 1 and 2 suggests that some mixed micelles will be formed in this region as described previously in our works about the sodium dodecyl sulfate-nonionic surfactant mixture (20). Consequently, it is concluded that the mixed micelle could exist even in the mixed system of 6ED and LiFOS as well as in the mixture between sodium dodecyl sulfate and nonionic surfactants (7,20).

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