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ORIGINAL CONTRIBUTION

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Miscibility of sodium dodecyl sulfate and sodium decyl sulfate in the adsorbed film and micelle

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Abstract The interfacial tension of the aqueous solution of sodium dodecyl sulfate (SDS) and sodium decyl sulfate (SDeS) mixture against hexane was measured as a function of the total molality and composition of the surfactant mixture at 298.15 K under atmospheric pressure. The compositions of adsorbed film and micelle were evaluated numerically by applying the thermodynamic relations to the experimental results. These results were shown in the form of the phase diagrams of adsorption and micelle formation and compared with those of the aqueous solution of sodium perfluorooctanoate (SPFO) and SDeS mixture. It was found that the diagrams of SDS and SDeS system have swollen cigar shapes and are quite different from those of SPFO and SDeS system which show non-ideal mixing both in the adsorbed film and micelle. This finding was attributed to the fact that the interaction between fluorocarbon and hydrocarbon chains is weaker than that between hydrocarbon chains.

Key words Miscibility – adsorbed film – micelle – phase diagram – ideal mixing

Introduction

The miscibility of surfactants in the adsorbed film and micelle has been investigated by many workers with great interest from the theoretical and technological viewpoints [1–3]. Among others, we have innovated the thermodynamic theory for evaluating the compositions of adsorbed film and micelle and then clarifying the miscibility of surfactants by means of phase diagrams of adsorption and micelle formation [4–6]. So far, we have applied the theory to the aqueous solutions of various surfactant mixtures in contact with air and proposed a criterion for the ideal mixing of surfactants in the adsorbed film and micelle [7–14].

Furthermore, in our latest paper on the aqueous solution of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS) in contact with hexane [15], it was concluded that SPFO and SDeS molecules mix non-ideally in the adsorbed film and do not mix over a rather wide range of composition in the micellar state because of weak interaction between SPFO and SDeS molecules. Now it is quite necessary to obtain the phase diagrams of adsorption and micelle formation of a surfactant mixture which is expected to mix ideally in the adsorbed film at the aqueous solution/hexane interface and micelle.

For this purpose the sodium dodecyl sulfate (SDS) and SDeS system [16] was employed because it contains SDeS in common with our previous system and the hydrocarbon chain of SDS molecules is longer only by two carbons than that of SDeS. The interfacial tension of the aqueous solution against hexane was measured as a function of the total molality and composition at 298.15 K under atmospheric pressure. The results were analyzed according to our theory and the phase diagrams were compared with those of the SPFO–SDeS system.

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Experimental

Sodium decyl sulfate was synthesized by sulfonation of decanol with chlorosulfonic acid in diethyl ether. After neutralization with sodium hydroxide, the product was freeze-dried and recrystallized twice from ethanol. Sodium dodecyl sulfate purchased from Nakarai Co., Ltd. was recrystallized once from water and twice from ethanol. Their purities were checked by observing no minimum on the surface tension vs. concentration curves around the CMC. Water was triply distilled from dilute alkaline permanganate solution and hexane once in the presence of metallic sodium particles. They were saturated with each other before the measurements.

The equilibrium interfacial tension γ was measured with an accuracy of $0.05\,\mathrm{mN\,m^{-1}}$ at 298.15 K under atmospheric pressure by the pendant drop method [17]. Temperature was kept constant within 0.01 K.

Results and discussion

The total molality m of the surfactants and the mole fraction X_2 of SDeS in the surfactant mixture were adopted as the experimental variables. They are defined by

$$m = m_1 + m_2 \tag{1}$$

and

$$X_2 = m_2/m\,, \tag{2}$$

where m_1 and m_2 are the molalities of SDS and SDeS, respectively [4–9]. The interfacial tension γ of the aqueous solution of SDS–SDeS mixture against hexane is shown as a function of m at constant X_2 in Fig. 1. It is seen that the interfacial tension decreases monotonously with increasing m and the γ vs. m curve has a distinct break at the critical micelle concentration (CMC).

The value of γ at a given m and that at the CMC γ^{C} read from Fig. 1 are plotted against X_2 in Fig. 2. It is seen that the interfacial tension at a given m increases greatly, while the one at the CMC slightly, with increasing X_2. Furthermore, the molalities at a given γ and at the CMC (C) obtained from Fig. 1 are plotted against X_2 in Fig. 3. It is seen that the m and C values increase monotonously with increasing X_2.

To elucidate the miscibility of SDS and SDeS molecules in the adsorbed film and micelle, it is useful to analyze the experimental results by using the thermodynamic equations developed previously [4–6]. The total interfacial density of surfactants is defined by

$$\Gamma^{\mathrm{H}} = \Gamma_1^{\mathrm{H}} + \Gamma_2^{\mathrm{H}}\,, \tag{3}$$

where Γ_i^{H} is the interfacial excess number of moles of surfactant i per unit area with reference to the two dividing planes which makes the excess numbers of moles of water and hexane zero. The values of Γ^{H} are calculated by applying the equation

$$\Gamma^{\mathrm{H}} = -(m/2RT)(\partial\gamma/\partial m)_{T,p,X_2}\,, \quad m < C\,, \tag{4}$$

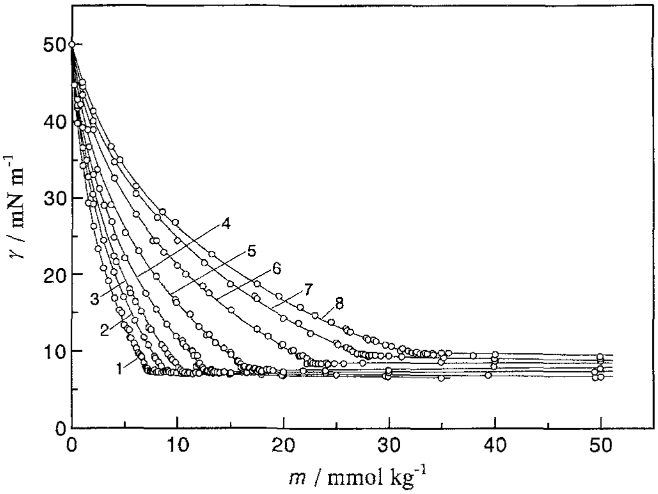
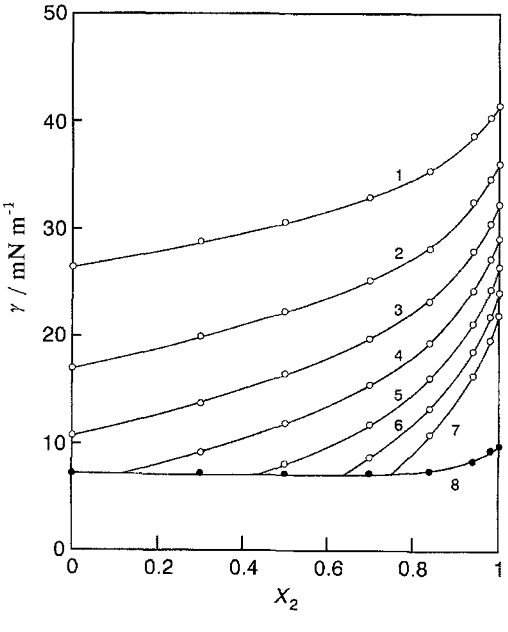


Fig. 1 Interfacial tension vs. total molality curves at constant composition: (1) $X_2 = 0$, (2) 0.300, (3) 0.500, (4) 0.700, (5) 0.840, (6) 0.940, (7) 0.980, (8) 1

Fig. 2 Interfacial tension vs. composition curves at constant total molality: (1) $m = 2\,\mathrm{mmol\,kg^{-1}}$, (2) 4, (3) 6, (4) 8, (5) 10, (6) 12, (7) 14, (8) γ^{C} vs. X_2



to the curves in Fig. 1 and plotted against m in Fig. 4; the Γ^{H} value increases gradually with increasing m and decreases regularly with increasing X_2. These findings suggest that SDS and SDeS are miscible with each other in all proportions in the adsorbed film.

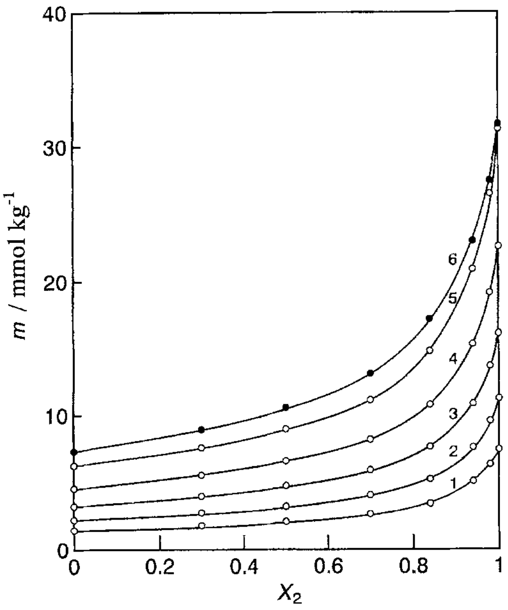
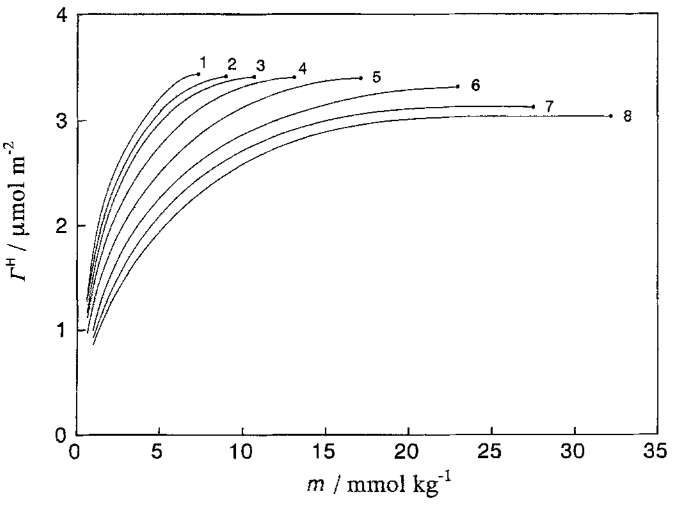


Fig. 3 Total molality vs. composition curves at constant interfacial tension: (1) $\gamma = 30\,\mathrm{mN\,m^{-1}}$, (2) 25, (3) 20, (4) 15, (5) 10, (6) C vs. X_2

Fig. 4 Total interfacial density vs. total molality curves at constant composition: (1) $X_2 = 0$, (2) 0.300, (3) 0.500, (4) 0.700, (5) 0.840, (6) 0.940, (7) 0.980, (8) 1: (●) Γ^{H} at the CMC $\Gamma^{\mathrm{H,C}}$



Now let us introduce the mole fraction of SDeS in the adsorbed film defined by

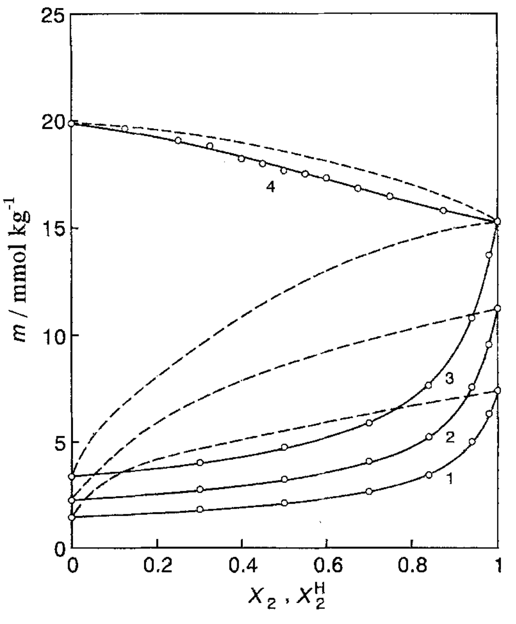
$$X_2^{\mathrm{H}} = \Gamma_2^{\mathrm{H}} / \Gamma^{\mathrm{H}} \tag{5}$$

and evaluate it numerically by applying the relation

$$X_2^{\mathrm{H}} = X_2 - 2(X_1 X_2 / m)(\partial m / \partial X_2)_{T,p,\gamma} \tag{6}$$

to the m vs. X_2 curves shown in Fig. 3 [6]. In Fig. 5, the m vs. X_2^{H} curves are shown together with the m vs. X_2 curves at 20, 25, and $30\,\mathrm{mN\,m^{-1}}$. These are analogues of diagrams of phase equilibrium and called the phase diagram of adsorption [6]. It is observed that X_2^{H} has a smaller value than X_2 over the whole composition range, i.e., the adsorbed film at the water/hexane interface is richer in more surface-active SDS molecules than the aqueous solution. For comparison, the corresponding diagram of the SPFO–SDeS mixture at $20\,\mathrm{mN\,m^{-1}}$ [15] is also shown in Fig. 5. It is seen that the shapes of these diagrams are fairly different from each other. Since it is expected that molecular interaction between different species is not so different from that between same species in the SDS–SDeS system and very different in the SPFO–SDeS system, a swollen cigar shape in the former suggests probably an almost ideal mixing in the adsorbed film at the interface. In the next paper, the phase diagram of an ideal mixing in the adsorbed film is

Fig. 5 Total molality vs. composition curves at constant interfacial tension: SDS–SDeS system (1) $\gamma = 30\,\mathrm{mN\,m^{-1}}$, (2) 25, (3) 20; SPFO–SDeS system (4) $20\,\mathrm{mN\,m^{-1}}$; (——) m vs. X_2, (– – –) m vs. X_2^{H}



derived theoretically and this point will be examined quantitatively [18].

Next, let us turn our attention to the miscibility of SDS and SDeS molecules in the micellar state. The mole fraction X_2^M of SDeS in the micelle is defined by

$$X_2^M = N_2^M/(N_1^M + N_2^M) , \tag{7}$$

where N_i^M is the excess number of molecules of surfactant i in one mixed micelle particle with respect to the spherical dividing surface chosen so as to make the excess number of molecules of water zero [6]. Here the existence of hexane molecules in a mixed micelle is not taken into account on the basis of our previous finding that only one or two hydrocarbon molecules are solubilized into a micelle particle [19]. The X_2^M value was estimated by applying the equation

$$X_2^M = X_2 - 2(X_1X_2/C)(\partial C/\partial X_2)_{T,p} \tag{8}$$

to the C vs. X_2 curve in Fig. 3. The result is shown in the form of the C vs. X_2^M curve together with the C vs. X_2 curve in Fig. 6, which is called the phase diagram of micelle formation [6]. It is found that X_2^M is smaller than X_2 over the whole composition range; the micelle is enriched in SDS molecules than the bulk solution, and SDS and SDeS molecules mix homogeneously in the micelle as well as in the adsorbed film. In Fig. 6, it is noted that the diagram of SPFO–SDeS system is strikingly different in shape from that of the SDS–SDeS system; the latter has a swollen cigar shape and the former has a hetero-azeotropic point at which the two kinds of micelles having different compositions coexist [15]. This difference is explained by the weaker interaction between hydrocarbon and fluorocarbon chains.

In our previous studies, we have shown that two nonionic surfactants mix ideally in the adsorbed film and almost ideally in the micelle when they have the same hydrophilic group and their hydrocarbon chains are two carbons apart [11, 12]. Therefore it is expected that the diagrams of the SDS–SDeS system in Figs. 5 and 6 show an almost ideal mixing in the adsorbed film and micelle. This idea is confirmed by comparing these diagrams with the theoretical ones in our next paper [18]. We only point out here that the ideal mixing is given theoretically by the straight line connecting the m or C values at $X_2 = 0$ and $X_2 = 1$ in nonionic mixtures [12] and by the positively deviated curve from the straight line in ionic surfactant mixtures having common counter ion [18].

By comparing the diagram 2 in Fig. 6 with that the diagram 4 in Fig. 5, we notice that the miscibility of surfactants is more strongly influenced by the difference of molecular interaction in the spherical micelle than in the plane interface. Therefore it is useful to examine the relationship between the compositions of adsorbed film and micelle at the CMC by use of the equation [6]

$$X_2^{H,C} = X_2^M - (X_1X_2/RT\Gamma^{H,C})(\partial \gamma^C/\partial X_2)_{T,p} . \tag{9}$$

Fig. 6 Critical micelle concentration vs. composition curves: (1) SDS–SDeS system, (2) SPFO–SDeS system; (——) C vs. X_2, (– – –) C vs. X_2^M

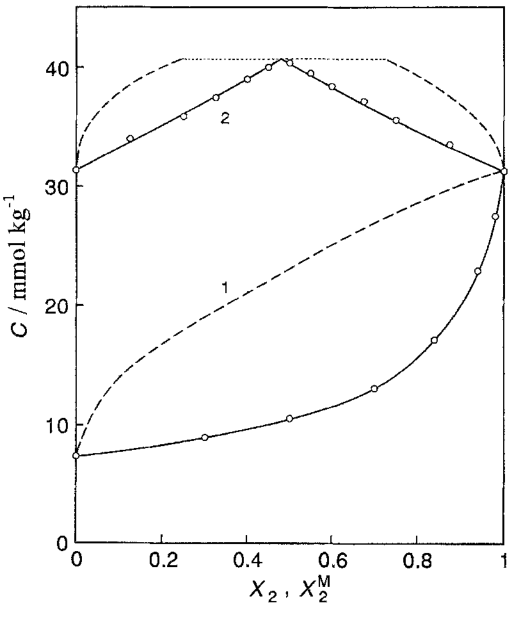
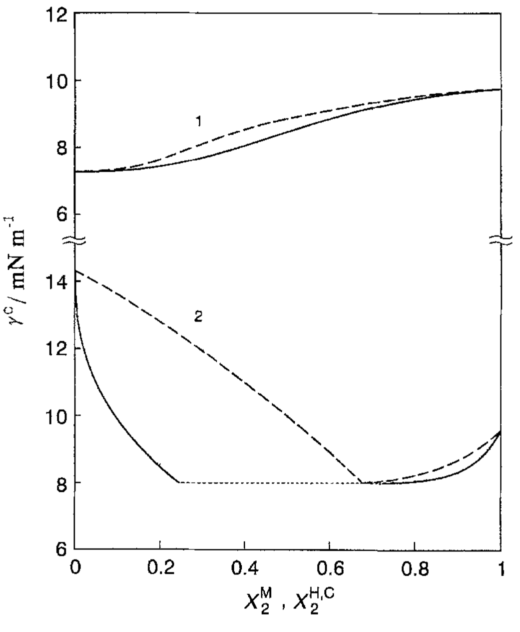


Fig. 7 Interfacial tension at the CMC vs. composition curves: (1) SDS–SDeS system, (2) SPFO–SDeS system; (——) γ^C vs. X_2^M, (– – –) γ^C vs. $X_2^{H,C}$



Here $X_2^{\mathrm{H,C}}$ and $\Gamma^{\mathrm{H,C}}$ are the values of X_2^{H} and Γ^{H} at the CMC. The $X_2^{\mathrm{H,C}}$ value, which was estimated by using the γ^{C} vs. X_2^{M} curve drawn in Fig. 7 and the γ^{C} vs. X_2 curve in Fig. 2, are plotted in the form of γ^{C} vs. $X_2^{\mathrm{H,C}}$ curve in Fig. 7. It is seen that the adsorbed film is richer in SDS than the micelle. Therefore it is said that the difference in geometry between the plane interface and spherical micelle affects the compositions in them even when surfactants mix substantially ideally in the respective states.

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