Miscibility of Octyldimethylphosphine Oxide and Decyldimethylphosphine Oxide in the Adsorbed Film and Micelle

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The surface tension of the aqueous solution of octyldimethylphosphine oxide (OPO) and decyldimethylphosphine oxide (DePO) mixture was measured as a function of the total molality and the composition of the mixture at 298.15 K under atmospheric pressure. The experimental data were analyzed thermodynamically to evaluate the total surface density Γ^{H}, the composition in the adsorbed film X_2^{H}, and the composition in the micelle X_2^{M}. The relations among the compositions of bulk solution, adsorbed film, and micelle were expressed in the form of phase diagram similar to the three-dimensional one; they were compared with the phase diagrams of ideal mixed film and micelle obtained theoretically. It was concluded that the OPO and DePO molecules mix ideally in the adsorbed film while the difference in their hydrophobic chain length causes a weaker interaction in the micelle because of a spherical shape of the micelle. This conclusion was supported by the fact that the 2-(octylsulfinyl)ethanol and 2-(decylsulfinyl)ethanol mixture behaves quite analogously.

It has been insisted by many investigators that homologous surfactants mix ideally in their adsorbed films and micelles.[1—11] But the problem of the ideal mixing has not yet been solved completely because the presence of solvent and dissociation of ionic surfactants are ignored[12] and because the adsorbed film and micelle are discussed separately. It is expected that the miscibility of homologous nonionic surfactants, which do not need to take account of the dissociation, in the adsorbed film and micelle is a standard for the ideal mixing. In our previous paper, the surface tension of 2-(octylsulfinyl)ethanol (OSE) and 2-(decylsulfinyl)ethanol (DeSE) system was measured as a function of concentration and analyzed by use of our thermodynamic procedure, which makes possible to compare the adsorbed film and the micelle from the same viewpoint.[13] The experimental results suggested that the miscibility of the surfactants in the micellar state is slightly different from that in the adsorbed state. In order to confirm whether this is a general property of the homologous nonionic surfactants mixture, we adopt octyldimethylphosphine oxide (OPO) and decyldimethylphosphine oxide (DePO), of which the polar group has a simpler chemical structure, and discuss their ideal mixing in detail from the thermodynamic point of view.

Experimental

Alkyldimethylphosphine oxide was synthesized from alkyl bromide and bromomagnesium dimethylphosphinite prepared by adding diethyl phosphonate to methylmagnesium bromide in tetrahydrofuran (THF).[14] After hydrolyzing unreacted Grignard reagents with concentrated hydrochloric acid, THF was removed on a rotary evaporator. Alkyldimethylphosphine oxide was extracted with chloroform and washed with distilled water. Then it was purified by repeated recrystallization from hexane after chloroform was evaporated. The purities of OPO and DePO were confirmed by elemental analysis and by observing no minimum on the surface tension vs. concentration curves around the critical micelle concentration (CMC). Water triply distilled from alkaline permanganate solution was used to prepare solutions for measurement.

The surface tension was measured by the drop volume technique described previously[15] at 298.15 K under atmospheric pressure. The experimental error was less than ±0.05 $\mathrm{mN\,m^{-1}}$.

Results and Discussion

Useful information about the miscibility of two surfactants in their mixed adsorbed film and micelle can be obtained by measuring the surface tension as a function of the total molality m and mole fraction of surfactant 2 in the total surfactant X_2 defined, respectively, by

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

and

$$X_2 = m_2/(m_1 + m_2), \tag{2}$$

where m_i is the molality of surfactant i.[13] In this paper, the surfactants 1 and 2 denote OPO and DePO, respectively.

The surface tension γ measured at 298.15 K under atmospheric pressure is plotted against m at fixed X_2 in Fig. 1. The shape of γ vs. m curve varies regularly as X_2 increases. Each curve has a break point owing to the beginning of micelle formation and its concentration is referred to as the critical micelle concentration (CMC) C. In the concentration range above the CMC, the surface tension of mixture increases slightly with increasing m although that of pure surfactant decreases slightly.

In order to visualize the X_2 dependence of m at fixed γ, the m vs. X_2 curves obtained from Fig. 1 are shown together with the C vs. X_2 curve in Fig. 2. Similarly the γ vs. X_2 curves at fixed m are drawn with the surface tension at the CMC γ^{C} vs. X_2 curve in Fig. 3. It is seen that the total molality decreases steeply with

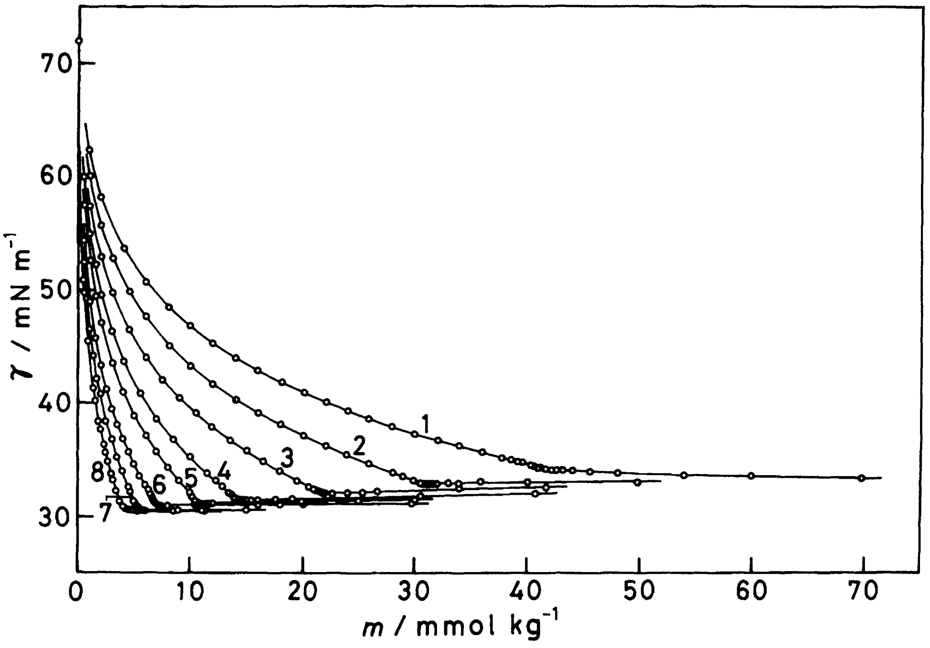

Fig. 1. Surface tension vs. total molality curves at fixed composition: (1) $X_2=0$, (2) 0.0400, (3) 0.100, (4) 0.200, (5) 0.300, (6) 0.500, (7) 0.700, (8) 1.

increasing X_2 at small X_2 and gradually at large X_2 and the shape of C vs. X_2 curve resembles that of m vs. X_2 curve at low γ. Both values of γ at fixed m and of γ^{C} decrease with increasing X_2, but the variation of γ^{C} is slight compared with that of γ at fixed m. Let us analyze these experimental results by use of thermodynamic procedure developed previously.[13)]

First we consider the adsorbed film free from the micelle on the basis of the concept of surface excess quantity. Introducing the surface excess number of moles of surfactant i per unit area Γ_i^{H} with reference to the two dividing planes that make those of water and air zero simultaneously,[16)] we define the total surface density Γ^{H} and the composition of surfactant 2 in the adsorbed film X_2^{H} by

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

and

$$X_2^{\mathrm{H}} = \Gamma_2^{\mathrm{H}}/(\Gamma_1^{\mathrm{H}} + \Gamma_2^{\mathrm{H}}), \tag{4}$$

respectively.

The value of Γ^{H} can be calculated by applying the next equation to the γ vs. m curve in Fig. 1:

$$\Gamma^{\mathrm{H}} = -(m/RT)(\partial\gamma/\partial m)_{T,p,X_2}, \tag{5}$$

where the solution is assumed ideal. The Γ^{H} vs. m curve at fixed X_2 is drawn in Fig. 4. It is seen that Γ^{H} value increases steeply with increasing m at relatively low concentration and approaches the saturated one at a concentration near the CMC. The curve varies in shape gradually from OPO to DePO.

There are two kinds of equations to evaluate X_2^{H}:

$$X_2^{\mathrm{H}} = X_2 - (X_1X_2/m)(\partial m/\partial X_2)_{T,p,\gamma} \tag{6}$$

and

$$X_2^{\mathrm{H}} = X_2 - (X_1X_2/RT\Gamma^{\mathrm{H}})(\partial\gamma/\partial X_2)_{T,p,m}. \tag{7}$$

Figure 5 shows the m vs. X_2^{H} curve, obtained from the m vs. X_2 curve in Fig. 2 by use of Eq. 6, together with it. We call this type of figure the phase diagram of adsorption since it has an analogy to the three-dimensional phase diagram.[17)] It is found that the adsorbed film is richer in DePO than the bulk solution over the whole range of X_2. Note that the m vs. X_2^{H} curve is actually identical with the straight line that connects the m values of pure OPO and DePO at a given γ. On the other hand, the γ vs. X_2 curve and γ vs. X_2^{H} curve obtained from Fig. 3 by use of Eq. 7 are shown in Fig. 6. It is important to notice that this diagram has a cigar shape. The X_2^{H} value in Fig. 6 was in agreement with that in Fig. 5 within experimental error.

Next, we proceed to the analysis of micellar solution. In a similar manner as the adsorbed film, introducing the excess number of molecules of surfactant i in one mixed micelle particle N_i^{M} with reference to the spherical dividing surface that makes the corresponding quantity of water zero,[18)] we define the composition of surfactant 2 in the micelle X_2^{M} by

$$X_2^{\mathrm{M}} = N_2^{\mathrm{M}}/(N_1^{\mathrm{M}} + N_2^{\mathrm{M}}). \tag{8}$$

The value of X_2^{M} at the CMC is evaluated by applying the next relation to the C vs. X_2 curve in Fig. 2:

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

The C vs. X_2^{M} and C vs. X_2 curves are depicted in Fig. 7 and we call it the phase diagram of micelle

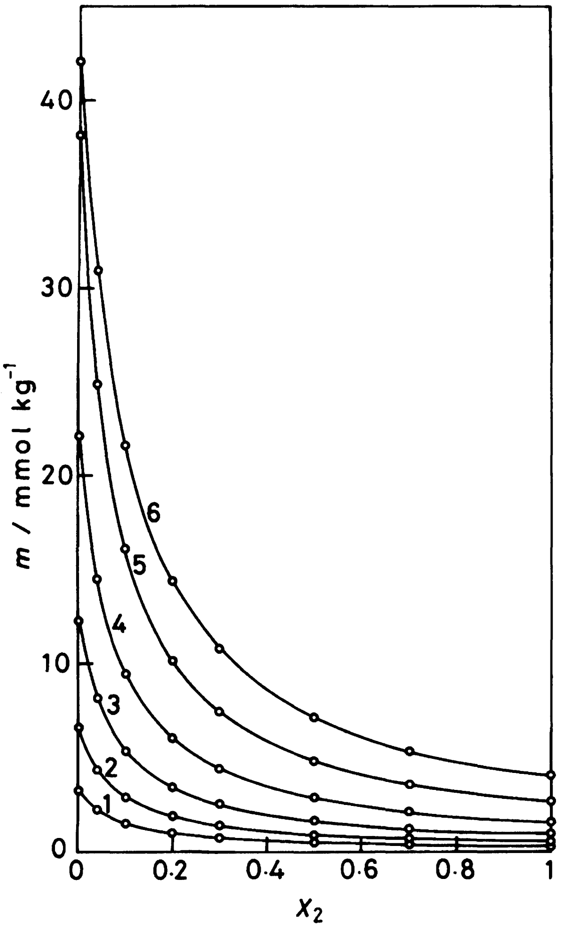

Fig. 2. Total molality vs. composition curves at fixed surface tension: (1) γ=55 mN m^{-1}, (2) 50, (3) 45, (4) 40, (5) 35; (6) C vs. X_2.

formation.[17] It is found that although the micelle is richer in DePO than the bulk solution, the C vs. X_2^M curve is not straight but slightly convex upward and is different from the m vs. X_2^H curve.

From Figs. 3 and 7, the γ^C vs. X_2 and γ^C vs. X_2^M curves are obtained and shown in Fig. 8. This figure explains the experimental result that the surface tension of mixed micellar solution increases with an increase in m at fixed X_2.

Further we have the following equation to evaluate the value of X_2^H at the CMC $X_2^{H,C}$, when the adsorbed film is in equilibrium with the micelle, from the γ^C vs. X_2 curve and X_2^M value given in Fig. 8;

$$X_2^{H,C} = X_2^M - (X_1X_2/RT\Gamma^{H,C})(\partial\gamma^C/\partial X_2)_{T,p}, \quad (10)$$

where $\Gamma^{H,C}$ is the value of Γ^H at the CMC estimated from Fig. 4. Figure 9 shows the γ^C vs. $X_2^{H,C}$ curve together with the γ^C vs. X_2^M curve and this phase diagram clearly represents the relation between the adsorbed film and micelle. The micelle is richer in OPO, which has a shorter hydrophobic chain, than the adsorbed film. It was reported previously that the micelle is richer in the component having the bigger hydrophilic group than the adsorbed film.[19] The bulky hydrophilic group and short hydrophobic chain of surfactant seem to be geometrically favorable for its micelle formation because the micelle is spherical in shape at the CMC. It should be also noted that the component that prefers the micelle to the adsorbed film has a higher γ^C value.

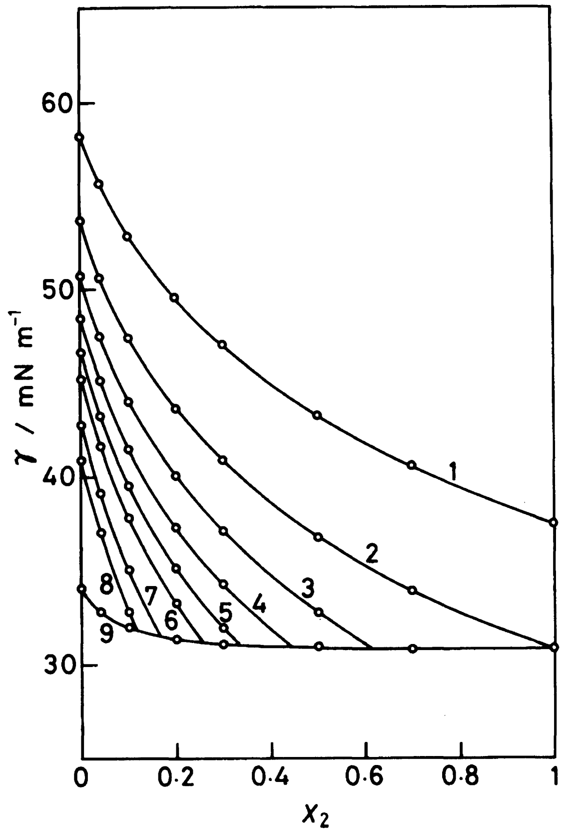

Fig. 3. Surface tension vs. composition curves at fixed total molality: (1) m=2 mmol kg^{-1}, (2) 4, (3) 6, (4) 8, (5) 10, (6) 12, (7) 16, (8) 20; (9) γ^C vs. X_2.

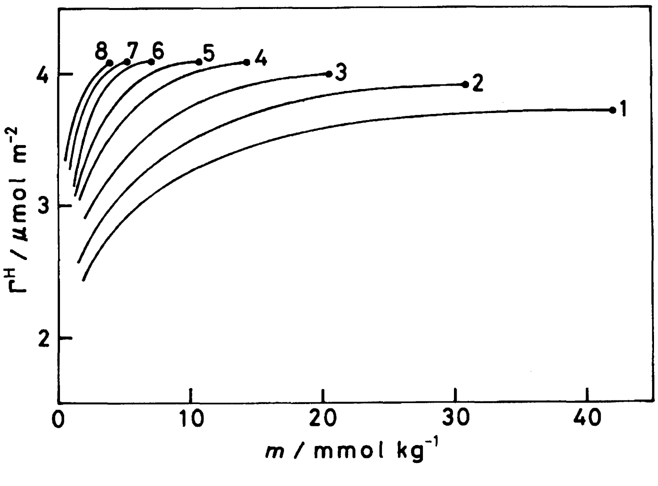

Fig. 4. Total surface density vs. total molality curves at fixed composition: (1) X_2=0, (2) 0.0400, (3) 0.100, (4) 0.200, (5) 0.300, (6) 0.500, (7) 0.700, (8) 1; (•) $\Gamma^{H,C}$.

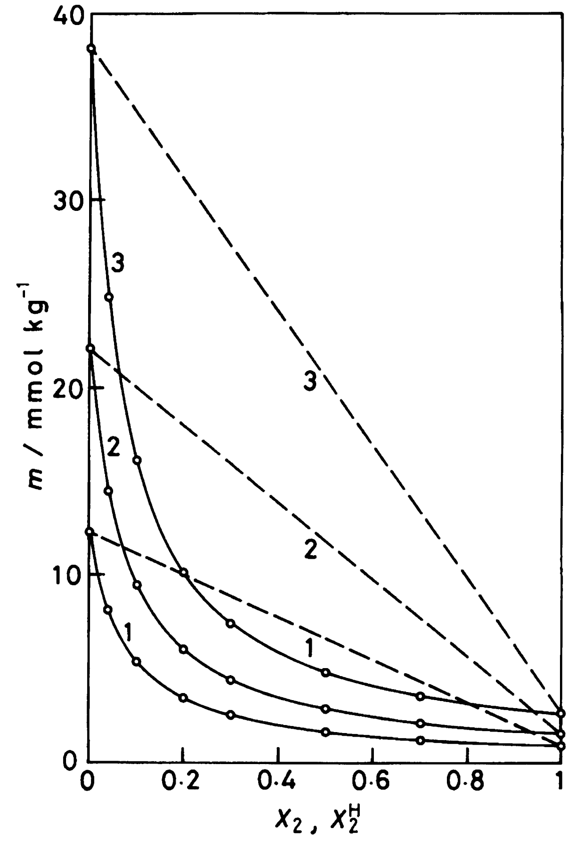

Fig. 5. Total molality vs. composition curves at fixed surface tension: (1) $\gamma=45$ mN m^{-1}, (2) 40, (3) 35; (—) X_2, (---) X_2^H.

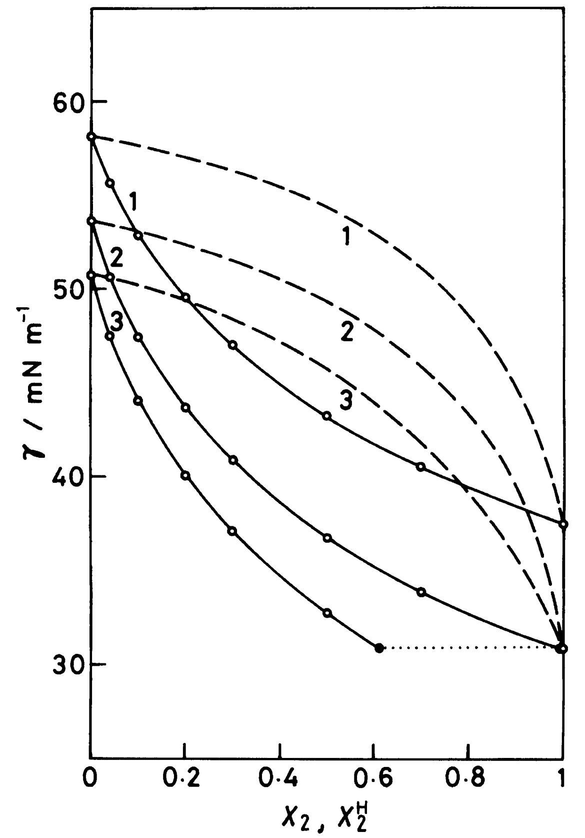

Fig. 6. Surface tension vs. composition curves at fixed total molality: (1) m=2 mmol kg^{-1}, (2) 4, (3) 6; (—) X_2, (---) X_2^H; (●) γ^C.

Therefore, we can say that the γ^C value is correlated to the difference between the ability of the micelle formation and that of the surface adsorption.

Now, let us discuss the ideal mixing of nonionic surfactants in the adsorbed film. If the ideal mixing is assumed, the chemical potential of surfactant i in the adsorbed film μ_i^H should be defined by

$$\mu_i^H = \mu_i^{H,0}(T,p,\gamma) + RT \ln X_i^H, \tag{11}$$

where $\mu_i^{H,0}(T,p,\gamma)$ is that of pure surfactant i.[20] When the bulk solution is free from micelle and in equilibrium with the ideal adsorbed film at fixed γ, μ_i^H equals the chemical potential of surfactant i in the bulk solution which is supposed an ideal dilute one, μ_i, expressed as

$$\mu_i = \mu_i^{\ominus}(T,p) + RT \ln mX_i. \tag{12}$$

We have the next equation for the pure surfactant i;

$$\mu_i^{H,0} = \mu_i^{\ominus}(T,p) + RT \ln m_i^0, \tag{13}$$

where m_i^0 is the molality of pure surfactant i at a given γ. Substituting Eqs. 11, 12, and 13 into $\mu_i=\mu_i^H$, we obtain

$$mX_i = m_i^0 X_i^H. \tag{14}$$

It is important to note that Eq. 14 is similar to Raoult's law. Eliminating X_i from Eq. 14 leads us to the equation

$$m = m_1^0 - (m_1^0 - m_2^0)X_2^H, \tag{15}$$

which indicates that the relation between m and X_2^H is linear at fixed γ. This is in accord with the experimental result as seen in Fig. 5. Therefore, the linearity of m vs. X_2^H curve is considered to be a standard for the ideal mixing of surfactants in the adsorbed film. Further Eq. 14 gives us the equation

$$m = m_1^0 m_2^0/[m_2^0 + (m_1^0 - m_2^0)X_2], \tag{16}$$

which is in good agreement with the m vs. X_2 curve drawn in Fig. 5. In Table 1, comparison is made between observed and calculated values of m at $\gamma=35$ mN m^{-1}. The agreement of the theoretical equations with the experimental results shows that Eq. 11 is useful in examining the miscibility of nonionic surfactants in the film state.

In the similar manner, we can consider the miscibility of nonionic surfactants in the micellar state when the ideal mixing of the surfactants is described by the analog of Eq. 11:

$$\mu_i^M = \mu_i^{M,0}(T,p) + RT \ln X_i^M, \tag{17}$$

where $\mu_i^{M,0}(T,p)$ is the chemical potential of pure sur-

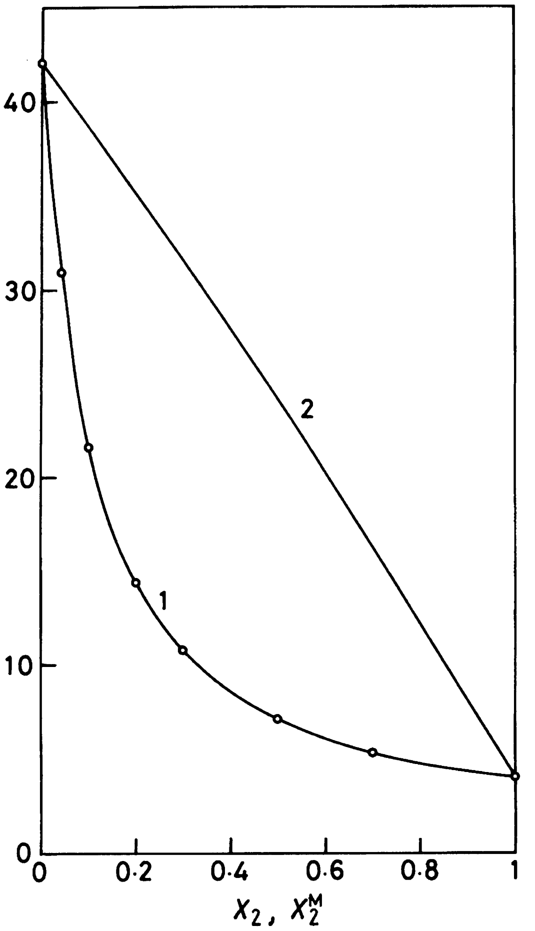

Fig. 7. CMC vs. composition curves: (1) C vs. X_2, (2) C vs. X_2^{M}.

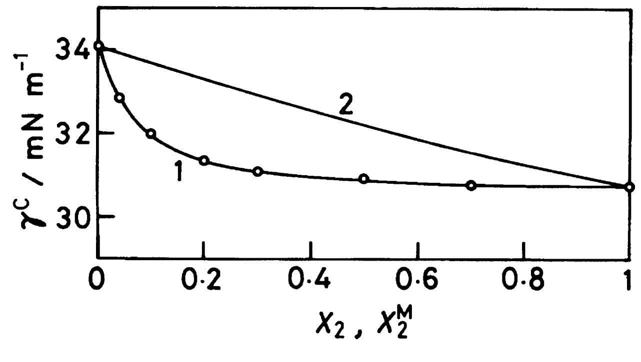

Fig. 8. Surface tension at CMC vs. composition curves: (1) γ^{C} vs. X_2, (2) γ^{C} vs. X_2^{M}.

factant i. Now the analog of Eq. 14 is derived as

$$CX_i = C_i^0 X_i^{\mathrm{M}}, \tag{18}$$

where C_i^0 is the CMC of the pure surfactant i. This equation is also similar to Raoult's law. Therefore, we obtain

$$C = C_1^0 - (C_1^0 - C_2^0)X_2^{\mathrm{M}} \tag{19}$$

and

$$C = C_1^0 C_2^0/[C_2^0 + (C_1^0 - C_2^0)X_2], \tag{20}$$

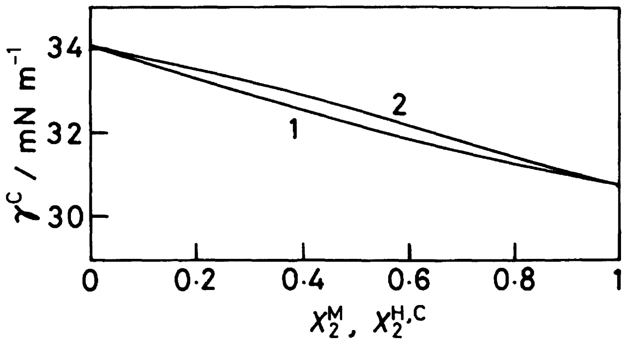

Fig. 9. Surface tension at CMC vs. composition curves: (1) γ^{C} vs. X_2^{M}, (2) γ^{C} vs. $X_2^{\mathrm{H,C}}$.

Table 1. Values of Total Molality at 35 mN m^{-1} and CMC

X_2	m/mmol kg^{-1} Obsd	m/mmol kg^{-1} Eq.16	C/mmol kg^{-1} Obsd	C/mmol kg^{-1} Eq.20
0	38.2	—	42.1	—
0.0400	24.9	24.9	31.0	30.6
0.100	16.1	16.3	21.6	21.6
0.200	10.1	10.4	14.4	14.6
0.300	7.44	7.60	10.8	11.0
0.500	4.81	4.96	7.15	7.36
0.700	3.58	3.68	5.35	5.53
1	2.65	—	4.03	—

which correspond to Eqs. 15 and 16, respectively. Equation 19 suggests that the C vs. X_2^{M} curve is linear if the surfactants mix ideally in the micelle. The C vs. X_2^{M} curve given in Fig. 7 deviates appreciably from the straight line, although the C vs. X_2 plot roughly fits the line traced by Eq. 20 (Table 1). It is assured that the deviation of the C vs. X_2^{M} curve from the straight line reveals the nonideal behavior of surfactants in the mixed micelle, because a straight line is of greater advantage than a curved line when the fit between observed and calculated values is examined. It may be said that the mixing of OPO and DePO molecules in the micelle is disturbed a little by a difference of two carbon atoms between their hydrocarbon chains. The nonideal mixing of OPO and DePO in the micelle is also expected from the fact that they differ greatly in the micelle aggregation number.$^{21)}$ The above results indicate that Eq. 17 also holds approximately.

Here, it is noteworthy that the ideal phase diagrams of adsorption and micelle formation are analogous to the ideal phase diagram that represents the equilibrium between the mixed gas and liquid solution. It is presumed therefore that the positive deviation of the C vs. X_2^{M} curve is attributed to a weaker interaction between different kinds of surfactant molecules in the micelle.

In the OSE–DeSE system were observed the phase diagrams of adsorption and micelle formation similar to those of the OPO–DePO system.$^{13)}$ So we can conclude that homologous nonionic surfactants mix ideally in the adsorbed film but the difference in their hydrophobic chain length gives rise to a weaker interaction in the micelle. This is because the adsorbed film and the micelle have distinct geometrical structure; the difference in hydrophobic chain length considerably affects the miscibility of surfactants in the micelle because of the spherical shape of micelle.

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