Binary Mixed Systems of Anionic/Nonionic Surfactants : Synergistically Enhanced Surface Activity and Relationship among Compositions of Monomers in Bulk(X_2), Micelles(Y_2) and Adsorbed Film at Air/Water Interface(Z_2)

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Abstract : Micelle formation in water and adsorbed film formation at air/water interface were studied by surface tension measurement for two mixed surfactant systems : combinations of sodium salts of α -sulfonatomyristic acid methyl ester (α -SM y ·Me) and the propyl ester (α -SM y ·Pr) with n-decanoyl-N-methyl glucamide (MEGA-10). The α -SM y ·Pr/MEGA-10 and the α -SM y ·Me/MEGA-10 mixed systems were found to synergistically enhance surface activity and form well-mixed micelles with the aid of strong interaction between head groups.

Critical micellization concentration (CMC) as a function of mole fraction of MEGA-10 in the surfactant mixture ($X_{\text{MEGA-10}}$) for both mixed systems was noted to deviate negatively from ideal mixing. Micellar phase (CMC vs $Y_{\text{MEGA-10}}$ relation) curves were simulated through use of the interaction parameter, $\omega_R = -2.1$ for α -SM y ·Me/MEGA-10 and $\omega_R = -2.0$ for α -SM y ·Pr/MEGA-10 and indicated the presence of azeotropes. Based on equations for estimating composition (Z_i) and the interaction parameter (ω_A) in adsorbed film equilibrated with monomers in bulk solution, phase diagrams were constructed that included the two relations of CMC vs $X_{\text{MEGA-10}}$ and CMC vs $Z_{\text{MEGA-10}}$. Adsorbed film of the respective mixed systems was formed through stronger interactions between anionic and nonionic surfactants compared to those of mixed micelles ($-\omega_A > -\omega_R$). The diagrams demonstrated that composition in micelles (Y_i) differs from that in the adsorbed film (Z_i).

From the slope of surface tension (γ) vs logarithmic molality ($\ln m_i$) curve, just below CMC, surface excess (Γ) was determined and mean molecular area (A_m) was computed as a function of $X_{\text{MEGA-10}}$ or $Z_{\text{MEGA-10}}$. From A_m data, partial molecular area (PMA) of each component was determined as a function of $Z_{\text{MEGA-10}}$; a large deviation from ideal mixing (the additivity rule) was observed for the respective mixed systems. Effects of differences in head group moiety, *i.e.*, either methyl or propyl, were clearly evident with respect to hydrophobicity difference, but physicochemical behavior appeared essentially the same.

Key words : mixed surfactant systems, surface tension, adsorbed film formation, surface excess (adsorption), partial molecular area (PMA)

1 Introduction

For the mixture of two surfactants undergoing micelle formation above a critical micellization

concentration (CMC), the solution properties fall either between or outside the solution properties of the two-single surfactant solutions. This is also the case for the CMC of a binary surfactant solution. Clint¹⁾ has given us the relation between mole fraction and CMC of the i th component ($i=1, 2$) for ideal mixtures, and Rubingh²⁾ has made a comprehensive theoretical attempt to deal with non-ideal mixture on the basis of the regular solution theory.

Amongst various combinations of non-ideal mixed systems, some mixtures such as those composed of fluorocarbon and hydrocarbon surfactants have been found to deviate positively from ideal mixing (as predicted by Raoult's law or Clint's equation)^{1)~6)}. Recently, a series of novel polymerizable hydrocarbon and fluorocarbon cationic surfactants (N-alkoxycarbonylmethyl-N-[Z-(N'-alkylacrylamido)-ethyl]-N,N-dimethyl ammonium bromide) were found to form mixed micelles whose interaction parameter (based on the regular solution theory²⁾) is 1.25, indicating the formation of one type of mixed micelles (Candau *et al.*⁷⁾). In contrast, even for a mixed system of fluorocarbon-hydrocarbon surfactants, a negative deviation has been observed. For the mixture of n-methyl-N-octanoyl and n-methyl-N-nonanoyl glucamides (MEGA-8 and MEGA-9, respectively) with sodium perfluorooctanoate (SPFO), the negative deviation is likely to come from a synergistically enhanced interaction between different head groups^{6),8)}. Lange and Beck⁹⁾ have shown such negative deviations in mixtures of sodium dodecyl sulfate (SDS) and dodecyl octaoxyethylene.

Moroi *et al.*¹⁰⁾ and others^{11)~13)} have investigated the mixtures of ionic/nonionic surfactants to evaluate CMC since as early as the 1960's. Showing decreased CMC of Triton X-100 resulting from the addition of sodium dodecylsulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB), Moulik *et al.*¹⁴⁾ have concluded that the incorporation of the hydrophobic tails of the ionic surfactants into the interior of Triton X-100 micelles is thermodynamically favored whereas the reverse process is not. Further, they have performed a thermodynamic study on the micelle formation of ternary mixed systems of SDS, Tween-20 and Brij-35¹⁵⁾. Very recently, Shiloach and Blankshtein have investigated synergism in mixed micelle

formation and micellar growth in ionic/nonionic surfactant mixtures by applying surface tension and static light scattering measurements: one is dodecyl hexa (ethylene oxide) ($C_{12}E_{16}$) with SDS and the other is $C_{12}E_{16}$ with sodium dodecyl hexa (ethylene oxide) sulfate (SDE 6 S). It is noteworthy that the experimental mixed CMC and mixed micelle aggregation numbers compare well with those predicted by molecular-thermodynamic theory of mixed micellization¹⁶⁾. From their work plenty of insights can be deduced.

In the mixed system of a nonionic surfactant (n-decanoyl-N-methylglucamide, MEGA-10) with a bile salt, sodium deoxycholate, the analysis of CMC data indicated that the properties of mixed micelles are different between the ranges below and above the composition of MEGA-10 ($X_{\text{MEGA-10}}$) congruent to 0.2 where an azeotropic exists and that the composition of mixed micelles is very similar to that of monomeric species in bulk solution¹⁷⁾. In addition to the previous temperature study on MEGA series¹⁸⁾, micelle and adsorbed film formation of MEGA-10 have been thermodynamically studied by means of surface tension measurements (drop volume method), for comparison with n-nonyl- β -D-thiomaltoside (NTM) being used as a protein-solubilizer¹⁹⁾. As briefly introduced above, primary concerns are furthermore being concentrated on such ionic/nonionic surfactant mixtures by various methodologies and theories. Mixed systems of nonionic surfactants with anionic surfactants seem, in general, to show unique behavior differing from those of ionic/ionic surfactants mixtures. In addition, nonionic surfactants, having sugar-type hydrophilic groups are different from those with polyoxyethylene head groups. Considering that a binary mixed system of an anionic surfactant (sodium salt of α -sulfonylmyristic acid methyl ester, α -SMy·Me) and MEGA-10 must give us some fresh information, we studied micelle formation in water and adsorbed film formation at air/water interface for the α -SMy·Me/MEGA-10 mixed system²⁰⁾. The former (α -SMy·Me), a top-heavy type surfactant assigned to the so called α -SF series, is known to be biodegradable, high in detergency and have tolerance against hard water^{21)~24)}, while the latter (MEGA-10), which has 5 hydroxy groups with an amide bond, has been also used as a membrane-protein solubilizer²⁵⁾.

In the present paper, following the temperature studies on micelle formation of α -SM y ·alkyl series surfactants^{26,27)} and MEGA- n ($n=8, 9, 10$) series surfactants¹⁸⁾ in addition to the mixed system of α -SM y ·Me/MEGA-10²⁰⁾, we have performed a surface tension study on micelle formation and surface adsorption of mixed systems of α -SM y ·Pr with MEGA-10. We paid special attention to the composition of micelles and adsorbed films at equilibria with monomeric surfactant mixture in bulk solution as well as comparison with α -SM y ·Me/MEGA-10. In this study is shown the extent to which the estimated composition of adsorbed film differs not only from that of singly dispersed species but also from that of micelles and to what extent the intermolecular interaction acts in the phases of adsorbed film and micelles.

2 Experimental

2.1 Materials

Sodium salts of α -sulfonatomyristic acid methyl ester, α -SM y ·Me and propyl ester, α -SM y ·Pr (from Lion Co., Tokyo) were synthesized and purified in the same manner as reported in previous papers^{26,27)}. The purity was chromatographically confirmed to be greater than 99%, and when checked by surface tension measurement, the plot of surface tension (γ) vs logarithmic

concentration gave no minimum (See Fig. 1). n -Decanoyl- N -methylglucamide, MEGA-10 (from Doujindo Laboratories, Kumamoto) which was highly purified by repeated recrystallization from ethanol and diethyl ether (1:9) was used as received.

2.2 Surface tension measurements

The surface tension (γ) measurements were performed on the basis of essentially the same drop volume method as reported previously¹⁹⁾, but an automated surface tensiometer (Yamashita Giken YDS 94) was used for α -SM y ·Me/MEGA-10 mixed system²⁰⁾, while for α -SM y ·Pr/MEGA-10, a Wilhelmy type tensiometer was used: FASE surface tensiometer (CBVP-A 3, Kyowa Kagaku Interface Science Co., Tokyo) the temperature of which was controlled by circulating thermostated water at $30 \pm 0.02^\circ\text{C}$. The room temperature was regulated at $23 \pm 3^\circ\text{C}$.

3 Results and discussion

Figure 1 shows two sets of the plot of surface tension against logarithmic concentration ($\ln m_t$) for each pure system together with a mixed system as an example in the respective frames (a) and (b). The accuracy of the surface tension measurements has been described elsewhere²⁰⁾. The concentration giving a break in the curve is assumed as CMC for

Fig. 1 Surface tension (γ) vs logarithmic concentration plots for (a) α -SM y ·Me or (b) α -SM y ·Pr (○), MEGA-10 (●) and examples of the mixed systems [the mole fractions ($X_{\text{MEGA-10}}$) are indicated in the inset]. The logarithmic value was calculated from the total concentration of the surfactant mixture (m_t) in molality.

both single systems, while the CMC for the mixed system is taken as the concentration giving the minimum surface tension. Comparing α -SM γ ·Me and MEGA-10, α -SM γ ·Me with a longer hydrocarbon chain as the hydrophobic group has a CMC of 2.8 mM, and MEGA-10 with a shorter hydrophobic chain has its CMC of 4.7 mM, indicating that the former has a higher ability of micelle formation than the latter. In comparison of α -SM γ ·Me and α -SM γ ·Pr, the higher total hydrophobicity of the latter is clearly reflected in the CMC value (CMC=1.2 mM). On the other hand, if in terms of the surface activity (surface tension lowering ability) the three single systems are compared, MEGA-10 is superior to α -SM γ ·Me and α -SM γ ·Pr. These antagonistic properties observed for both surfactant combinations arose greatly our interest in examining the mixing effect. Looking at the γ vs $\ln m_i$ curves of mixed systems given in Fig. 1 (a) and (b), the γ is lowered more rapidly than for the respective single systems by synergistically enhanced surface activity at the very low concentration. After reaching the minimum, the γ gradually increases and seems to reach a certain constant value within the curves of the single systems above their CMCs.

All the γ vs $\ln m_i$ plots of the other mixed systems, at every 0.1 in mole fraction of MEGA-10 in the surfactant mixture ($X_{\text{MEGA-10}}$), also demonstrated possession of a minimum in addition to their synergistically enhanced surface activity (not shown here). This suggests that those surfactants possessing a higher surface activity have a trend of faster adsorption (in dynamics) or more preferential adsorption (in energetics) compared to those having a lower surface activity and that even above CMC the increased surface tension accompanies a composition change in micelles as well as surface film phase. The determination of CMC for mixed systems was made at the concentration giving a minimum as mentioned above, because surfactant molecules are considered to start micelle formation at the minimum.

Next, CMCs thus determined were plotted against mole fraction of MEGA-10 ($X_{\text{MEGA-10}}$) as is shown in Fig. 2. The open and closed circles are points measured for α -SM γ ·Me and α -SM γ ·Pr, respectively. In the figure are shown theoretical curves (dotted lines) of ideal mixing estimated from Raoult's law or Clint's equation¹⁾ for the

Fig. 2 The CMC vs $X_{\text{MEGA-10}}$ curves. The open and closed circles indicate measured CMC of α -SM γ ·Me/MEGA-10 and of α -SM γ ·Pr/MEGA-10 mixed systems, respectively. Dotted lines are projections of ideal mixing.

respective mixed systems. The CMC-composition curves for the present mixed systems are known to deviate negatively much from those of ideal mixing.

(a) Mixed Micelle Formation.

To interpret the negative deviation shown in Fig. 2, we employed Rubingh²⁾ equations which are widely used. At the CMC, the composition of surfactant i ($i=1, 2$) in the micelle, Y_i is related to the monomeric concentration of surfactant i , C_{im} and to the CMC of pure i , C_i^0 as $Y_i = C_{im}/C_i^0$. In the system of surfactants 1 and 2, the Rubingh's equations are expressed as :

$$\frac{Y_1^2 \ln(C_m X_1 / C_1^0 Y_1)}{(1 - Y_1)^2 \ln\{C_m(1 - X_1) / C_2^0(1 - Y_1)\}} = 1 \quad (1)$$

where, C_m is the CMC of the mixed system. Rubingh²⁾ has introduced an interaction parameter, ω_R in the mixed micelle on the basis of the regular solution approximation :

$$\omega_R = \ln(C_m X_1 / Y_1 C_1^0) / (1 - Y_1)^2 \quad (2)$$

The substitution of the Y_1 value calculated from Eq. 1 into Eq. 2 produces the ω_R value at each X_1 . In Fig. 3 (a) and (b), the solid lines along open and closed circles were calculated by applying Eqs. 1 and 2, where the interaction parameter ω_R values were taken as -2.1 for α -SM γ ·Me/MEGA-10 and

Fig. 3 Phase diagrams of α -SMy·Me/MEGA-10 (a) and α -SMy·Pr/MEGA-10 (b) mixed surfactant systems at 30°C and 1 atm. Open and closed circles indicate the measured CMC values as a function of mole fraction of MEGA-10 in the surfactant mixtures ($X_{\text{MEGA-10}}$). The solid lines and broken lines were simulated using Rubingh's equations, and the broken lines along with open squares correspond to the respective micellar composition curves.

-2.0 for α -SMy·Pr/MEGA-10.

The simulated curves completely satisfy the experimental results. In the figure the broken lines correspond to the correlation between micellar composition Y_1 (in this case $Y_{\text{MEGA-10}}$) and CMC. In other words, each micellar phase curve is equivalent to the CMC vs $Y_{\text{MEGA-10}}$ curve, and the singly dispersed (monomeric) phase curve is equivalent to the CMC vs $X_{\text{MEGA-10}}$ curve. The figure indicates that the α -SMy·Me/MEGA-10 mixed system has an azeotropic point at $X_{\text{MEGA-10}} = \text{ca. } 0.4$ while α -SMy·Pr/MEGA-10 seems to have one at $\text{ca. } 0.3$, and also at these mole fractions the most stabilization in free energy is attained by the respective mixtures. The negative interaction parameters and its absolute values (-2.1 and -2.0) suggest a special interaction between N-methyl glucamine and α -alkyl sulfonic groups, which is much superior to the hydrophobic interaction between hydrocarbon chains. All the data related to micelle formation such as CMC, $Y_{\text{MEGA-10}}$, ω_R and activity coefficients f_1 and f_2 are listed in Table 1.

A similar negative deviation has been observed even for a mixed system of nonyl-N-methyl glucamine (MEGA-9) with sodium perfluorooctanoate (SPFO)^(6,8). Since fluorocarbon surfac-

tants possess not only hydrophobicity but also oleophobicity, the interaction between fluorocarbon and hydrocarbon chains in micelle is mutually phobic (repulsive) causing a positive deviation from ideal mixing. This phenomenon has been observed for various ionic-ionic surfactant mixtures^{(3,28)~(34)}, and from the aspects of chemical structure the mixed micelle formation has been examined⁽³⁴⁾. Nevertheless, the combination of MEGA-9 with SPFO shows the lower CMC and the higher surface activity than those of its components. The negative deviation was interpreted as evidence that SPFO and MEGA-9 are miscible in micelles with the aid of a reduction in the repulsive forces between head groups probably resulting from the penetration of the nonionic surfactant into the space between the ionic head groups^(6,8,34). This is the case not only for α -SMy·Me/MEGA-10 but also α -SMy·Pr/MEGA-10 mixed systems.

(b) The Composition of Mixed Adsorbed Film.

Next, turning our attention to the composition of the adsorbed film phase comprising surfactants 1 and 2, we suppose an equilibrium between the mixed adsorbed film and the bulk, the concentration of which is CMC (denoted as $m_1 + m_2 = m_t$). And it is assumed that the amount of adsorbed

Table 1 Values of CMC, Y_2 , ω_R , f_1 and f_2 for Mixed Micelles of Anionic/Nonionic Binary Combinations at 30°C.

※ Subscript 2 corresponds to MEGA-10.

α -SMY·Me/MEGA-10 Systems					
$X_{\text{MAGA-10}}$	CMC (mmol·kg ⁻¹)	Y_2	ω_R	f_1	f_2
0	2.8				
0.1	2.4	0.18	- 2.0	0.93	0.24
0.2	2.2	0.28	- 2.1	0.85	0.33
0.3	2.0	0.35	- 2.3	0.78	0.40
0.4	2.0	0.39	- 2.3	0.72	0.46
0.5	2.0	0.44	- 2.3	0.66	0.51
0.6	2.1	0.49	- 2.3	0.60	0.57
0.7	2.4	0.54	- 2.1	0.54	0.64
0.8	2.6	0.61	- 2.0	0.45	0.72
0.9	3.2	0.71	- 1.9	0.34	0.84
1	4.7				
			average		
			- 2.1		
α -SMY·Pr/MEGA-10 Systems					
$X_{\text{MAGA-10}}$	CMC (mmol·kg ⁻¹)	Y_2	ω_R	f_1	f_2
0	1.2				
0.1	1.2	0.09	- 1.5	0.98	0.19
0.2	1.2	0.16	- 1.7	0.95	0.25
0.3	1.2	0.23	- 1.8	0.90	0.30
0.4	1.2	0.29	- 2.1	0.85	0.36
0.5	1.3	0.33	- 2.0	0.80	0.41
0.6	1.4	0.38	- 2.0	0.75	0.46
0.7	1.5	0.44	- 2.1	0.68	0.53
0.8	1.7	0.50	- 2.2	0.60	0.61
0.9	2.0	0.59	- 2.6	0.50	0.71
1	4.7				
			average		
			- 2.0		

species (in the adsorbed phase) is negligible compared with that in the bulk phase.

In the beginning we consider an equilibrium between the bulk phase (b) and the adsorbed film phase (a) not only at the given temperature (T) and pressure (p) but also at a constant surface tension (γ) based on the literature by Aratono *et al.*³⁵⁾. The chemical potential of pure system of surfactant i ($i=1$ or 2) in bulk solution phase is expressed as :

$$\mu_{i(b)}^0 = \mu_{i(b)}^* + RT \ln m_i^0 \quad (3)$$

where m_i corresponds to either molarity or molality as a concentration chosen and the circle of superscript indicates the pure system. The chemi-

cal potential of species i in the mixed system is as follows.

$$\mu_{i(b)} = \mu_{i(b)}^* + RT \ln m_i \quad (4)$$

Here, $\mu_{i(b)}^*$ is the standard chemical potential. From these two equations the next expression is given for the mixed system.

$$\mu_{i(b)} = \mu_{i(b)}^0 + RT \ln \left(\frac{m_i}{m_i^0} \right) \quad (5)$$

On the other hand, the chemical potential of species i in the film phase at a surface tension γ is presented as the following, when the composition of i in the adsorbed film phase and the activity coefficient are denoted as Z_i and f_i , respectively,

$$\mu_{i(a)} = \mu_{i(a)}^0(T, p, \gamma) + RT \ln f_i Z_i \quad (6)$$

Note that the standard chemical potential as function of temperature, T , pressure, p , and surface tension, γ is equivalent to that of the pure system. Therefore, at equilibrium two relations should simultaneously hold : $\mu_{i(b)} = \mu_{i(a)}$ as well as $\mu_{i(b)}^0 = \mu_{i(a)}^0$, this brings about the following relations which have been given in the literature³⁵⁾.

$$m_i = f_i Z_i m_i^0 \quad (7)$$

In the previous paper²⁰⁾ we were wrong with respect to defining the standard chemical potentials for both phases, and the relation corresponding to Eq. 7 which was given as $m_i = Z_i f_i \Gamma_i^0$ (Γ_i^0 is the surface excess of pure i). The mass balance in bulk solution gives the following relations for the mixed system of surfactants 1 and 2 when the mole fractions in the mixture and concentrations are denoted as X_1 and X_2 ($X_1 + X_2 = 1$) and m_1 and m_2 , respectively.

$$m_1 + m_2 = X_1 m_t = (1 - X_2) m_t + X_2 m_t = m_t \quad (8)$$

where m_t is the total concentration of the surfactants at the given surface tension. Thus, when an equilibrium is attained between the bulk and the adsorbed film phases, the relations are expressed as follows :

$$\begin{aligned} m_1 &= f_1 Z_1 m_1^0 = f_1 (1 - Z_2) m_t^0 = (1 - X_2) m_t \\ m_2 &= f_2 Z_2 m_2^0 = X_2 m_t \end{aligned} \quad (9)$$

It is noted that in this study m_i^0 is the CMC of α -SMY·Me or α -SMY·Pr and the surface tension fixed was taken at the CMC of α -SMY·Me or α -SMY·Pr, so that m_t^0 and each m_t were read from the γ vs $\ln m_t$ curves of MEGA-10 pure system and

mixed systems at $\gamma = 40.1 \text{ mNm}^{-1}$ in $\alpha\text{-SMY} \cdot \text{Me/MEGA10}$ and $\gamma = 37.9 \text{ mNm}^{-1}$ in $\alpha\text{-SMY} \cdot \text{Pr/MEGA 10}$ mixed systems. The mole fraction of 2 in bulk solution is expressed by using Eq. 10,

$$X_2 = \frac{m_2}{m_1 + m_2} = \frac{f_2 Z_2 m_2^0}{f_1 (1 - Z_2) m_1^0 + f_2 Z_2 m_2^0} \quad (10)$$

The concentrations in bulk are the same as those prepared, since the amount forming the film is negligible compared with those in bulk. Equation 10 tells us that if m_1^0 , m_2^0 , f_1 , and f_2 are known, the composition in the film can be estimated. Based on the regular solution theory, the activity coefficients f_1 and f_2 are given as:

$$\begin{aligned} f_1 &= \exp[\omega_A Z_2^2] \\ f_2 &= \exp[\omega_A (1 - Z_2)^2] \end{aligned} \quad (11)$$

where ω_A corresponds to the interaction parameter. From analogy with the derivation of Rubingh's equations²⁾, we obtained the following equations²⁰⁾.

$$\frac{(1 - Z_2)^2 \ln [(1 - X_2) m_1 / (1 - Z_2) m_1^0]}{Z_2^2 \ln (X_2 m_t / Z_2 m_2^0)} = 1 \quad (12)$$

$$\omega_A = [\ln (X_2 m_t / Z_2 m_2^0)] / (1 - Z_2)^2 \quad (13)$$

Eqs. 12 and 13 simultaneously tell us that if the m_1^0 , m_2^0 and m_t at the given γ are determined against the net mole fraction X_2 , then the adsorbed film composition Z_1 is given by Eq. 12, and ω_A can be evaluated from Eq. 13 by using the Z_2 value. As was done for ω_R in Eqs. 1 and 2, and as was pointed out by Moroi³⁶⁾, the single parameter was determined by averaging the ω_A values against each Z_2 value over the entire composition range.

Here it should be noted that the above two equations were derived without taking into consideration that ionic surfactants dissociate in water. In order to strictly treat with ionic surfactant mixture or nonionic/ionic surfactant mixtures, Motomura *et al.*³⁷⁾ have employed the following variables for such a mixed system as composed of a 1-1 type ionic surfactant (1) with a nonionic surfactant (2):

$$\begin{aligned} \bar{m}_t &= 2m_1 + m_2, \quad \bar{X}_1 = 2m_1 / (2m_1 + m_2) = 1 - \bar{X}_2 \\ \bar{X}_2 &= m_2 / (2m_1 + m_2), \quad \bar{X}_{2,c} \text{ etc.} \end{aligned}$$

According to their treatment, the following expressions are given:

$$\frac{(1 - \bar{Z}_2)^2 \ln [(1 - \bar{X}_2) \bar{m}_t / (1 - \bar{Z}_2) \bar{m}_1^0]}{\bar{Z}_2^2 \ln (\bar{X}_2 \bar{m}_t / \bar{Z}_2 \bar{m}_2^0)} = 1 \quad (14)$$

A similar procedure to the above results in:

$\bar{X}_{1,b} = 1 - \bar{X}_{2,b} = 2m_{1,b} / (2m_{1,b} + m_{2,b})$ in bulk solution at a given surface tension,

$\bar{Z}_1 = 1 - \bar{Z}_2 = 2n_{1,a} / (2n_{1,a} + n_{2,a})$ in adsorbed film (n_i denotes mole number),

$\bar{m}_1^0 = 2m_1^0$, and $\bar{m}_2^0 = m_2^0$

and

$$\omega_A = \frac{\ln (\bar{X}_2 \bar{m}_t / \bar{Z}_2 \bar{m}_2^0)}{(1 - \bar{Z}_2)^2} \quad (15)$$

Eq. 14 can be rewritten as:

$$\frac{(1 - \bar{Z}_2)^2 \ln [m_{1,b} / (1 - \bar{Z}_2) m_1^0]}{\bar{Z}_2^2 \ln (m_{2,b} / \bar{Z}_2 m_2^0)} = 1 \quad (14')$$

Recalling that the relations $m_{1,b} = (1 - X_2) m_t$ and $m_{2,b} = X_2 m_t$ had originally been given, we can further rewrite Eq. 14' and Eq. 15 as follows.

$$\frac{(1 - \bar{Z}_2)^2 \ln [(1 - X_2) m_t / (1 - \bar{Z}_2) m_1^0]}{\bar{Z}_2^2 \ln (X_2 m_t / \bar{Z}_2 m_2^0)} = 1 \quad (16)$$

and

$$\omega_A = \frac{\ln (X_2 m_t / \bar{Z}_2 m_2^0)}{(1 - \bar{Z}_2)^2} \quad (17)$$

From comparison of Eqs. 12 and 13 with Eqs. 16 and 17, it is known that $\bar{Z}_2$ corresponds to Z_2 . Therefore, Eqs. 12 and 13, which had not been considered for 1-1 ionic/nonionic mixtures, are applicable not only to nonionic/nonionic but also to ionic/nonionic mixed systems.

Substituting the data of m_t 's and m_1^0 and m_2^0 into Eqs. 12 and 13, the composition of surfactant 2 (corresponding to MEGA-10) in the adsorbed film phase, Z_2 was calculated as a function of the net mole fraction, X_2 . The results are demonstrated in **Fig. 4(a)** and **(b)** for the respective mixed systems. **Figure 4** shows phase diagrams indicating the composition of the adsorbed film, in other words, the curves of the phase equilibrium between the adsorbed film and monomeric species. To obtain the m_t vs Z_2 curve along with simultaneous satisfaction of the relation of m_t vs X_2 , the ω_A value was given -3.7 for $\alpha\text{-SMY} \cdot \text{Me/MEGA-10}$ and -8.3 for $\alpha\text{-SMY} \cdot \text{Pr/MEGA-10}$ mixed systems. In **Table 2**, the data in regard to the surface film are summarized together with those of $\alpha\text{-SMY} \cdot \text{Me/MEGA-10}$ mixed systems.

Fig. 4(a) and **(b)** show that m_t vs $Z_{\text{MEGA-10}}$ curve

Fig. 4 Phase diagrams of monomers in bulk solution (m_t vs $X_{\text{MEGA-10}}$) and adsorbed film at air/water interface (m_t vs $Z_{\text{MEGA-10}}$) the surface tension of which is fixed (a) at $\gamma=40.1 \text{ mNm}^{-1}$ for $\alpha\text{-SMy} \cdot \text{Me} / \text{MEGA-10}$ and (b) at $\gamma=37.9$ for $\alpha\text{-SMy} \cdot \text{Pr} / \text{MEGA-10}$ mixed systems, at 30°C and 1 atm. m_t vs $Z_{\text{MEGA-10}}$ curves were simulated from our theory. The error margin is $\pm 7\%$.

differs from m_t vs $X_{\text{MEGA-10}}$ curve, but both mixed systems have similarly an azeotrope point at *ca.* $Z_{\text{MEGA-10}}=0.5$. In the previous paper²⁰⁾, we reported abnormally large value of ω_A (-44) and an azeotropic point at $X_{\text{MEGA-10}}=Z_{\text{MEGA-10}}=0.5$, suggesting that a paired form of $\alpha\text{-SMy} \cdot \text{Me}$ with MEGA-10 acts like a unit surfactant. However, it must be noted here that the huge ω_A value came from ill-considered equations.

Examining Fig. 3(b) and Fig. 4(b) for $\alpha\text{-SMy} \cdot \text{Pr} / \text{MEGA-10}$ mixed system, the interaction parameter of the adsorbed film was estimated as $\omega_A=-8.3$ while that of mixed micelle was $\omega_R=-2.0$. In regard to ω_R values both surfactant mixed systems are included within common combinations, since it has been known that the value of micelle formation ranges -1 to -18.5 for almost all combinations of binary mixed surfactant systems²⁾ (p.188 in Ref. No.36). It is not yet possible to explain why the large absolute value (-8.3) was obtained compared with ω_A of $\alpha\text{-SMy} \cdot \text{Me} / \text{MEGA-10}$ and even with ω_R of the present mixture. Anyway the more surface active MEGA-10 shows a higher density in the adsorbed film than in bulk as well as micelles (compare CMC vs $Y_{\text{MEGA-10}}$ curve and m_t vs $Z_{\text{MEGA-10}}$ curve below $X=0.5$), while at the range above $X=0.5$, instead of MEGA-10, $\alpha\text{-SMy} \cdot \text{Me}$ and $\cdot\text{Pr}$ are denser than

MEGA-10. Both curves of m_t vs $Z_{\text{MEGA-10}}$ suggest that pairing of MEGA-10 with $\alpha\text{-SMy} \cdot \text{Me}$ or $\cdot\text{Pr}$ is favored when the adsorption takes place. The pair formation (like a dimeric unit of MEGA-10 with $\alpha\text{-SMy} \cdot \text{Me}$ or $\cdot\text{Pr}$) seems to accompany a contraction due to closely contacting. Synergism in enhancement of surface activity as well as CMC appears more prominently for $\alpha\text{-SMy} \cdot \text{Pr} / \text{MEGA-10}$ than for $\alpha\text{-SMy} \cdot \text{Me} / \text{MEGA-10}$. It is interesting to note that the longer side alkyl chain (propyl) leads to the stronger interaction between head groups of $\alpha\text{-SMy} \cdot \text{Pr}$ and MEGA-10.

Finally, comparing the compositions between the micelles ($Y_{\text{MEGA-10}}$) at CMC and the adsorbed film ($Z_{\text{MEGA-10}}$) at a given constant surface tension, $Y_{\text{MEGA-10}}$ is not the same as $Z_{\text{MEGA-10}}$, as shown in Fig. 5(a) and (b). The respective $Y_{\text{MEGA-10}}$ and $Z_{\text{MEGA-10}}$ values in Fig. 5(a) and (b) were determined by reading them at respectively corresponding $X_{\text{MEGA-10}}$ values in Fig. 3(a) and (b) (X_2 - Y_2 curves) and in Fig. 4(a) and (b) (X_2 - Z_2 curves). These figures exhibit that MEGA-10 has a trend gather more easily to form the adsorbed film than to form mixed micelles, and simultaneously it has a trend to make pairing with $\alpha\text{-SMy} \cdot \text{Me}$ or $\cdot\text{Pr}$ when MEGA-10 adsorbs at the air/water interface. That is, the more surface active MEGA-10 molecules, come up to the surface taking $\alpha\text{-SMy} \cdot$

Table 2 Values of m_t , Z_2 , Γ , $\bar{A}_m$, $\bar{A}_1$ and $\bar{A}_2$ for Mixed Micelles of Anionic/Nonionic Binary Combinations at 30°C.

※ Subscript 2 corresponds to MEGA-10.

α -SMY-Me/MEGA-10 Systems						
$X_{\text{MEGA-10}}$	m_t (mmol·kg ⁻¹) at $\gamma=40.1\text{mNm}^{-1}$	Z_2	Γ ($\times 10^{-6}\text{mol}\cdot\text{m}^{-2}$)	$\bar{A}_m$ (Å ²)	$\bar{A}_1$ (Å ²)	$\bar{A}_2$ (Å ²)
0	2.83		3.78	43.9	43.9	
(0.05)	1.90	0.25	3.99	41.6	45.8	29.4
0.1	1.52	0.33	4.18	39.7	48.4	22.6
0.2	1.29	0.41	4.42	37.6	46.0	25.5
0.3	1.02	0.47	4.54	36.6	43.7	28.5
0.4	0.81	0.51	4.61	36.0	40.4	32.0
0.5	0.78	0.54	4.63	35.9	33.6	37.7
0.6	0.81	0.58	4.58	36.3	30.0	40.7
0.7	0.94	0.63	4.50	36.9	23.4	44.7
0.8	1.02	0.68	4.34	38.2	18.8	48.2
0.9	1.13	0.75	4.11	40.4	23.1	46.3
(0.95)	1.29	0.81	3.97	41.8	31.9	44.0
1	1.68		3.86	43.0		43.0
α -SMY-Pr/MEGA-10 Systems						
$X_{\text{MEGA-10}}$	m_t (mmol·kg ⁻¹) at $\gamma=37.9\text{mNm}^{-1}$	Z_2	Γ ($\times 10^{-6}\text{mol}\cdot\text{m}^{-2}$)	$\bar{A}_m$ (Å ²)	$\bar{A}_1$ (Å ²)	$\bar{A}_2$ (Å ²)
0	1.20		3.61	46.0	46.0	
(0.05)	0.72	0.24	3.70	44.8	48.3	36.4
0.1	0.55	0.31	3.83	43.4	51.6	24.7
0.2	0.46	0.36	3.95	41.8	56.6	15.1
0.3	0.44	0.40	4.11	39.5	54.5	17.4
0.4	0.44	0.43	4.20	38.5	46.8	28.2
0.5	0.42	0.45	4.34	38.2	40.2	36.4
0.6	0.43	0.48	4.35	38.2	33.4	43.8
0.7	0.44	0.51	4.26	39.0	27.6	49.8
0.8	0.44	0.54	4.18	39.8	27.3	50.6
0.9	0.60	0.59	4.06	40.9	30.4	48.2
(0.95)	1.07	0.67	3.94	42.1	36.7	44.8
1	2.41		3.86	43.0		43.0

(): indicates intrapolated values.

Me or ·Pr with themselves (especially at the lower ranges of $X_{\text{MEGA-10}}$ or $Z_{\text{MEGA-10}}$). Here it may be noted, for comparison with the present work, that Paulin and Bibett recently investigated the adsorption of mixed surfactant systems onto isolated oil/water interface according to the Gibbs equation (although the details are not introduced here) ³⁸⁾.

(c) *The Surface Excess and Partial Molecular Area.*

The amount of adsorbate per unit area (e.g. mol·m⁻²) is called surface excess or surface concentration or surface adsorbed amount depending on the defined model of surface, i.e., either the surface

phase or the Gibbs dividing surface ³⁹⁾. If the Gibbs approach is to be used, the usual convention is to place the dividing surface such that $\Gamma_{(\text{solvent})}=0$, and then the excess of adsorbate is written as $\Gamma_{(\text{adsorbate})}$, to denote this choice. This term $\Gamma_{(\text{adsorbate})}$ may be called the relative adsorption ³⁹⁾. In the above section the adsorbed film is sometimes called the surface phase as if it had a certain thickness, however, from our concept the solvent was excluded for conciseness. So, the relative adsorption or the surface excess is, hereafter, employed.

Fig. 5 The comparison of compositions in micelles ($Y_{\text{MEGA-10}}$) and in adsorbed films ($Z_{\text{MEGA-10}}$) of the surfactant mixtures estimated for (a) $\alpha\text{-SMy}\cdot\text{Me}/\text{MEGA-10}$ and (b) $\alpha\text{-SMy}\cdot\text{Pr}/\text{MEGA-10}$.

Fig. 6 The surface excess, Γ , curves as functions of $X_{\text{MEGA-10}}$ and $Z_{\text{MEGA-10}}$ obtained for (a) $\alpha\text{-SMy}\cdot\text{Me}/\text{MEGA-10}$ and (b) $\alpha\text{-SMy}\cdot\text{Pr}/\text{MEGA-10}$ mixed systems.

Here, let us consider how the surface excess of such a system consisting of ionic and nonionic mixtures is represented. When the combination of surfactants 1 and 2 is composed of 1-1 type of ionic and nonionic ones, respectively, the surface phase formulation, neglecting the amount of water at air/water interface, is given at constant temperature and pressure as³⁹⁾:

$$-\frac{d\gamma}{RT} = 2\Gamma_1 d\ln m_1 + \Gamma_2 d\ln m_2 \quad (18)$$

Referring to the treatment by Motomura *et al.*³⁷⁾, we have shown the Gibbs adsorption isotherm is given for the 1-1 ionic/nonionic surfactant mixture at constant temperature, pressure and mole fraction, as follows²⁰⁾.

$$\Gamma_{\text{mix}} = -\frac{1}{RT} \frac{d\gamma}{d\ln \bar{m}_t} = \frac{1}{RT} \frac{d\gamma}{d\ln m_t} = 2\Gamma_1 + \Gamma_2 \quad (19)$$

where $\bar{m}_t$ is defined as being equal to $m_t(2-X_2)$. This tells us that from the slopes below CMC of the

curves, γ vs $\ln m_i$, can be used to determine the surface excess at the respective mole fractions.

The Γ_{mix} thus determined was plotted as functions of net mole fraction of MEGA-10, $X_{MEGA-10}$, and simultaneously $Z_{MEGA-10}$ for the two mixed systems as shown in Fig. 6(a) and (b). In Fig. 6(a) the maximum surface excess was attained at $X_{MEGA-10}=0.5$, when the formed film shows an azeotropic behavior at $X_{MEGA-10}=Z_{MEGA-10}=ca. 0.5$. This diagram seems to correspond well to Fig. 4(a). Compared with the pure α -SMY·Me system, the mixed systems at maximum surface excess is higher by a factor of 1.2 ($4.6/3.8 \approx 1.2$. See Fig. 6(a)) than the pure α -SMY·Me. On the other hand, in the α -SMY·Pr/MEGA-10 mixed system (Fig. 6(b)), too, the maxim Γ_{mix} is likely to have an azeotropic point at $X_{MEGA-10}=Z_{MEGA-10} \approx 0.4 \sim 0.6$ and it is also *ca.* 1.2 times higher than that of the pure α -SMY·Pr system. In regard to Γ_{mix} vs $Z_{MEGA-10}$ relation, it may be allowed to say that both the mixed systems exhibit an azeotropic behavior. In general, the increase of Γ_{mix} with increase in mixing extent, *i.e.*, with approaching 1 : 1 mixture, might reflect the strong interaction between head groups and this is in parallel with synergistically enhanced surface activity. This interaction can be seen from the behavior of the partial molecular surface area in the adsorbed film.

The mean surface (occupation) area per molecule, A_m can be calculated from the relation, $A_m = 1/\Gamma L$, where L denotes the Avogadro's number. By the use of surface excess data, Fig. 7 was constructed for the respective mixed systems. Both figures (a) and (b) similarly demonstrate a deep minimum at $Z_{MEGA-10} = ca. 0.5$, deviating negatively from the additivity rule (dotted lines). This reflects Γ vs $Z_{MEGA-10}$ relations shown in Fig. 5(a) and (b), and also suggests that as the mixing ratio approaches 1 : 1, the number of MEGA-10/ α -SMY·Me or ·Pr pairs increases accompanied by contraction due to a strong interaction.

Here, from analogy of the partial molar volume of a solute in solution, the partial molecular area (PMA) for each component is evaluated using the following equation^{20,39)}.

$$A_m = \bar{A}_1 + Z_2 \left(\frac{\partial A_m}{\partial Z_2} \right)_{T,V,T,n_1} \quad (20)$$

$\bar{A}_1$ is here, the PMA of component 1 and defined as :

$$\bar{A}_1 = \left(\frac{\partial A_t}{\partial n_1} \right)_{T,V,T,n_2} \quad (21)$$

when n_1 plus n_2 moles form a surface area A_t ($n_1 \bar{A}_1 + n_2 \bar{A}_2 = A_t$). It should be noted here that if the mixing was ideal, the PMA should have been linear with Z_2 (the additivity rule).

Equation 20 means that $\bar{A}_1$ and $\bar{A}_2$ are determin-

Fig. 7 The changes in mean molecular area (A_m) with mole fraction in the surfactant mixtures ($Z_{MEGA-10}$) and an example of determination of partial molecular area (PMA) at point P. The error margin is $\pm 1.5 \text{ \AA}^2$. Dotted lines correspond to the additivity rule.

(a) : α -SMY·Me/MEGA-10, (b) : α -SMY·Pr/MEGA-10.

Fig. 8 The changes in partial molecular areas (a) of $\alpha\text{-SMy}\cdot\text{Me}$ and MEGA-10 and (b) of $\alpha\text{-SMy}\cdot\text{Pr}$ and MEGA-10 as a function of mole fraction of MEGA-10 in the adsorbed film phase.

able from the respective intercepts on A_m -axis at $Z_2=0$ and $Z_2=1$ under the conditions of constant temperature and volume or pressure, and fixed surface tension. The A_m curves obtained from Γ_{mix} data satisfy the required conditions and allow us to evaluate PMA of the respective components as a function of Z_2 . A tangential line drawn at any given point on the A_m vs Z_2 curve gives two intercepts on the A_m -axes; the respective intercepts themselves are $\bar{A}_1$ and $\bar{A}_2$ (See Fig. 7(a) and (b)). The estimated PMA values are listed together with the mean molecular surface area, A_m and Γ_{mix} at every 0.1 increment in $X_{\text{MEGA-10}}$ in Table 2.

Further, the PMA is plotted against $Z_{\text{MEGA-10}}$ for each component of the two mixed systems (See Fig. 8(a) and (b)). In both mixed systems, the PMA vs $Z_{\text{MEGA-10}}$ curves demonstrate that as $Z_{\text{MEGA-10}}$ approaches 0.5, the PMA of every surfactant as major component (more than 50% content) slightly increases and via maximum suddenly decreases. The PMA curves of the two surfactants in the respective mixed systems intersect the other's at $Z_{\text{MEGA-10}}=0.5$, meaning that PMA attains the same as that of the other. Interestingly, the minor component in any case has a less PMA. Accompanied by pairing, the respective two surfactants' PMAs in both mixed systems decrease due to a strong interaction, in particular the molecule of the minor component shrinks more than that of the major one.

Comparing the two mixed systems (Fig. 8(a) and (b)), the difference of the esterified alcohol, *i.e.*, either methyl or propyl, is reflected, but it may be said that $\alpha\text{-SMy}\cdot\text{Me}$ and $\alpha\text{-SMy}\cdot\text{Pr}$ behave somewhat similarly against MEGA-10.

Apart from our study using classical surface tension measurements, very recently, there appeared few notable papers on binary mixed systems performed using such modernized techniques as the following. By means of small-angle neutron scattering measurements, Penfold *et al.* studied the structure and composition of two surfactants mixtures, *i.e.*, SDS with hexaethylene glycol monododecyl ether (C_{12}EO_6) and hexadecyltrimethylammonium bromide (C_{16}TAB) with C_{12}EO_6 . They found that for the SDS/ C_{12}EO_6 mixture, the micellar aggregation number is essentially constant with composition and concentration whereas for the $\text{C}_{16}\text{TAB}/\text{C}_{12}\text{EO}_6$ mixture there is a marked micellar growth with increasing concentration and mole fraction of C_{12}EO_6 ^{(40),(41)}. Pulsed-field-gradient NMR methods have also been shown to be useful for determining the partitioning of surfactants between monomeric and micellar forms in mixed systems by Eads and Robosky. They reported that the observed behavior is not consistent with expectations from the regular solution model, but the use of the van Laar expression accounts well for the composition dependence of the activity coefficients⁽⁴²⁾. These studies have motivated us to measure the aggrega-

tion number as a function of $X_{\text{MEGA-10}}$, so we are performing our study using the fluorescence method (to be reported elsewhere).

4 Conclusions

A surface tension study was performed on two mixed surfactant systems composed of an anionic surfactant, either one of α -sulfonato myristic acid methyl or propyl ester sodium salt (α -SM $\cdot$ Me or α -SM $\cdot$ Pr), and a nonionic surfactant, n-decanoyl-N-methyl glucamide (MEGA-10) in water. Based on the data obtained from the plots of the surface tension (γ) vs logarithmic total molality ($\ln m_t$) of the surfactant mixtures at every 0.1 mole fraction of MEGA-10 in the mixture ($X_{\text{MEGA-10}}$ or X_2), CMC's and the surface excesses for the mixed systems (C_m and Γ_{mix} , respectively) together with those for the respective single systems (C_1^0 , C_2^0 and Γ_1^0 , Γ_2^0) were determined at 30°C.

The purpose of the present study was to examine the interaction between the two surfactants not only in micelles but also in adsorbed film phase. In the two combinations of mixed systems, the relation between monomeric species and micelles was observed from the plot of CMC vs $X_{\text{MEGA-10}}$. This plot gave a curve which negatively deviated from ideal mixing. Applying Rubingh's equations (derived from the regular solution theory) to a simulation of the CMC vs $X_{\text{MEGA-10}}$ curve, simultaneously resulted in the interaction parameter value of $\omega_R = -2.1$ (for α -SM $\cdot$ Me) or -2.0 (for α -SM $\cdot$ Pr) and the corresponding micellar composition values, or curves of CMC vs mole fraction of MEGA-10 in micelles $Y_{\text{MEGA-10}}$. The curves indicated the existence of an azeotrope for both systems.

In order to estimate the composition of adsorbed film phase ($Z_{\text{MEGA-10}}$), we derived equations using the γ vs $\ln m_t$ data as a function of $X_{\text{MEGA-10}}$, which was also based on the regular solution theory. That is, the equations are related to the composition in the adsorbed film, $Z_{\text{MEGA-10}}$, equilibrated with monomers in bulk and also to the interaction parameter (ω_A). Then, a phase diagram including the relations of m_t vs $X_{\text{MEGA-10}}$ (singly dispersed phase curve) and m_t vs $Z_{\text{MEGA-10}}$ (adsorbed film phase curve) was constructed for each mixed system. From the diagram an azeotrope was found to be formed by the 1 : 1 mixture (at $X_{\text{MEGA-10}} = Z_{\text{MEGA-10}} = 0.5$), indicating that the

composition in micelles (Y_i) differs from that in the adsorbed film (Z_i).

In addition, the γ vs $\ln m_t$ curve was found to show synergistically enhanced surface activity, probably coming from effectively enhanced hydrophobicity by pairing through a strong interaction between the head groups of both surfactants. This speculation may be supported by the following PMA behavior, as well as by the azeotrope found at $Z_{\text{MEGA-10}} = 0.5$.

Calculating the mean molecular area (A_m) from Γ_{mix} data, the partial molecular area (PMA) of each component was determined as a function of $Z_{\text{MEGA-10}}$. The plot of PMA against $Z_{\text{MEGA-10}}$ for each surfactant demonstrated that both curves intersect at $Z_{\text{MEGA-10}} \approx 0.5$ (the Γ_{mix} vs $X_{\text{MEGA-10}}$ curve, accordingly, has a maximum of $X_{\text{MEGA-10}} \approx 0.5$), suggesting that a paired form of α -SM $\cdot$ Me with MEGA-10 or that of α -SM $\cdot$ Pr with MEGA-10 acts like a unit surfactant. Anyway, all the data obtained demonstrated that the two surfactants, α -sulfonatoalkyl ester sodium salts and MEGA-10 strongly interact with each other, showing a synergism in surface activity and micellization.

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[報文] イオン性／非イオン性界面活性剤二成分混合系： 相乗的に強められる界面活性および単分散組成(X_2)、ミセル 組成(Y_2)、ならびに気／水界面の吸着膜組成(Z_2)の関係

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表面張力測定法により、陰イオン性と非イオン性界面活性剤二成分の混合系 2 種の組合せ (α -SM y ・Me/MEGA-10 及び α -SM y ・Pr/MEGA-10) の水溶液中におけるミセル形成と気／液界面における吸着膜の形成について研究した。本研究は、前者の α -SM y ・Me/MEGA-10 について既に報告済み (Langmuir, 2000, 16 (4) 1508-1514) のものと、加えて、側鎖の炭素数が二つ多い α -SM y ・Pr/MEGA-10 について得た結果とを比較しながら、一つの論文としたものである。

表面張力対対数濃度の曲線を仕込みの組成 (X_i , $i = 1, 2$) ごと求め、これより臨界ミセル濃度 (CMC) と表面過剰量 (Γ) の基礎データを X_i の関数として決定した。Rubingh の式を用いて、ミセル内の Interaction Parameter (ω_s) と、単分散種 (組成 X_i) と平衡にあるミセル形成種の組成 (Y_i) とを見積った。また理論を展開して単分散種と平衡にある吸着膜の組成 (Z_i) と吸着膜内の Interaction Parameter (ω_a) を見積ることが出来た。両組合せの混合系とも、陰イオン性／非イオン性界面活性剤の親水基間の強い相互作用によって、界面活性およびミセル形成能が相乗的に高められていることを明らかにした。吸着膜内における各分子の部分分子面積 (PMA) を見積って、異種分子間の強い相互作用の様子を示すことが出来た。

(連絡者：杉原剛介) Vol.49, No.9, 915 (2000)

[報文] 2, 3 本のアルキル鎖を持ったコンプレキサン型 界面活性剤の合成と界面化学的性質

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2 及び 3 本のアルキル鎖を有するコンプレキサン系多鎖多親水基型界面活性剤 (2R $_n$ ida, 2R $_n$ edda, 2R $_n$ dtdda, 3R $_n$ dtdda ; n はアルキル鎖長を意味する) を各種アミン類と臭化物より合成し、それらの界面化学的性質について検討した。2, 3 鎖型コンプレキサンの臨界ミセル濃度 (cmc) は、アルキル鎖長、鎖数の増加及びスパーサーの長さの減少とともに低濃度側へ移行した。3R $_8$ dtdda, 3R $_{12}$ dtdda の cmc は 1 鎖型界面活性剤 2-アミノドデカン酸よりも 2~3 桁小さくなった。2, 3 鎖型コンプレキサンの cmc における表面張力は、アルキル鎖長、鎖数及びスパーサーの長さによって著しく異なり、3R $_8$ dtdda が 24 mN m⁻¹ の最も優れた値を示した。3R $_n$ dtdda の分子占有面積は、R $_{12}$ NAC の面積の 3 倍あるいは 2R $_n$ ida, 2R $_n$ edda, 2R $_n$ dtdda の面積よりも小さくなった。2, 3 鎖型コンプレキサン水溶液は、トルエンと振り混ぜることによりエマルションを形成した。2R $_{12}$ ida は安定な water-in-oil 型エマルション、鎖長 10~12 の 2R $_n$ edda, 2R $_n$ dtdda 及び 3R $_8$ dtdda は安定な oil-in-water 型エマルションを形成した。鎖長 12 のトルエン-コンプレキサン水溶液の界面張力は、いずれも 1~2 mN m⁻¹ であった。各多鎖多親水基型コンプレキサンは、親水性-疎水性バランス (HLB 値) が約 22 のときに高い界面活性能を示し、3R $_8$ dtdda が気-液及び液-液界面において最も効率的な界面活性剤であった。

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