Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. I. a Combination of Top-heavy Type Anionic Surfactants

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Abstract: The micellization and adsorbed film formation for an aqueous binary mixed system of anionic top-heavy type surfactants: sodium salt of α-sulfonatomyristic acid isopropyl ester (α-SMy·iPr) and sodium 1-oxo-1 [4-(tridecafluorohexyl) phenyl]-2-hexanesulfonate (FC6-HC4), were studied by means of surface tension measurement (drop volume method). The surface tension (γ) was precisely measured for the solutions of the respective single and eleven mixed systems at 30.00 ± 0.03°C in order to determine critical micellization concentrations (CMC) and surface excesses (Γ) as a function of net mole fraction of FC6-HC4 (X_{FC6-HC4}). The effect of added NaCl on CMC was examined for each single system to determine the degree of counterion binding (βi) from the Corrin-Harkins plot. Using the data of CMC and βi, we estimated the micellar composition (Y_{FC6-HC4}), activity coefficients (fi) of the two surfactants in mixed micelles, and the interaction parameter (ω0), the calculation of which was made on the basis of our own theoretical equations taking into account of mutual counterion effect in binary ionic surfactant mixtures. From the CMC-Y_{FC6-HC4} curve, markedly positive and slightly negative deviations from ideal mixing micelle formation were found, i.e. the positive deviation at the range of 0 < X_{FC6-HC4} < ca. 0.3 and the slightly negative deviation at the range of ca. 0.3 < X_{FC6-HC4} < 1. On the other hand, the composition of adsorbed film (Z_{FC6-HC4}) was also estimated as a function of X_{FC6-HC4} using the surface tension data from below CMCs. In addition, Γ was determined as functions of X_{FC6-HC4} and Z_{FC6-HC4} and the partial molecular area (PMA) was evaluated from the plot of mean molecular surface area (A_m) vs. Z_{FC6-HC4}. All the data obtained showed without exception that an addition of 10 to 20% α-SMy·iPr to FC6-HC4 results in a marked enhancement of surface activity and micelle formation ability, accompanying a favorable packing in two-dimensional or three dimensional structuring by the two top-heavy type surfactants, and that the two or three dimensional structures are thermodynamically more stable due to higher FC6-HC4 content.

Key words: adsorbed film, mixed surfactant system, micellization, critical micellization concentration (CMC), surface tension, surface excess, partial molecular area, degree of counterion binding

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1 Introduction

While surface active substances called surfactants or in some cases called detergents had been widely applied to various fields in daily life as well as in industries since the dawn of human history, scientific studies on their physicochemical properties were not started until the 20th Century. In the last several decades, however, extensive efforts have been concentrated and in parallel with it we could have a few leading monographs (1-3) in addition to ones by Sihinoda et al. (4) and by Mukerjee and Mysels (5) which have been cited world wide. On the other hand, as mixing of different species of surfactants results in more useful performance caused by synergism, studies on mixed surfactant systems have also been systematically performed (6, 7). Of these, the mixed systems of fluorocarbon and hydrocarbon surfactants are in general expected to show a certain unique behavior, since fluorocarbon surfactants exhibit not only hydrophobicity but also lipophobicity. Various types of fluorocarbon/hydrocarbon surfactant mixtures or respective single components have been revealed in regard to their physicochemical properties in media (8-16). Further, the so-called hybrid type surfactants consisting of hydrocarbon and fluorocarbon chains in a molecule were also synthesized, and their behavior of micelle and adsorbed film formation was investigated (17, 18).

Very recently, we performed a thermodynamic study on the micelle formation of a combination of hydrocarbon/fluorocarbon anionic surfactants: sodium n-tetradeceylsulfate (STDS) and sodium perfluoronanate (SPFN) in water, paying special attention to the interaction between the two surfactants and the aggregation number as a function of composition in the binary mixture ($X_2$) by electroconductivity measurement and fluorescence spectroscopy (19). In the previous paper, an azeotrope was found in the relation of critical micellization concentration (CMC) with mole fraction of STDS in the surfactant mixture ($X_{STDS}$) at $X_{STDS} = 0.05$, and almost completely demixing micelles were found to be formed at the ranges on the left hand of the azeotrope and on its right hand side up to $X_{STDS} = 0.2$, while at the range above $X_{STDS} = 0.2$ well mixed micelle formation takes place (19). In addition, another previous study emphasized that the respective degrees of counterion binding ($\beta_1$, and $\beta_2$) should be taken into account when estimating the composition of micelles ($Y_2$) and the interaction parameter ($\omega_0$) between the binary ionic surfactants. The important role played by counterions in micelle formation of surfactants was extensively discussed in the literature (20) as well as in the monographs (2, 4). We have been interested in synergistically enhanced surface activity and the relationship among compositions of monomers in bulk ($X_2$), micelles ($Y_2$) and adsorbed films at air/water interface ($Z_2$) (21). To examine the adsorbed film of mixed surfactants systems, very accurate data of surface tension of the respective surfactant solutions are indispensable. The Wilhelmy type surface tensiometry has been known and used as one of the well established methods; it is convenient, but, this method often suffers from difficulty of temperature control or vaporization of solvents during the measurements (especially at higher temperatures). On the other hand, the manual or automatic drop volume method the temperature of which can be strictly controlled within an accuracy of $0.03^\circ C$, has been known to produce more accurate surface tension data compared with the Wilhelmy method.

In this paper, micelle formation in bulk water and adsorbed film formation at the air/water interface were investigated by surface tension measurement (the drop volume method reported previously (18)) of aqueous solutions of a mixed surfactant system: the combination of top-heavy type anionic surfactants, sodium 1-oxo-1-[4-(tridecafluorohexyl)-phenyl]-2-hexane sulfonate (here, abbreviated as FC6-HC4) vs. Na salt of $\alpha$-sulfonatoyrmyristic acid isopropylester ($\alpha$-SMy·iPr).

2 Experimental

2.1 Materials

Sodium salt of $\alpha$-sulfonatoyrmyristic acid isopropyl ester($\alpha$-SMy·iPr, MW=372.5) which was highly purified was supplied by Lion Co, Tokyo, and used as received. Sodium 1-oxo-1-[4-(tridecafluorohexyl)-phenyl]-2-hexane sulfonate (FC6-HC4, MW=596.3) was synthesized and then purified in a manner similar to that reported previously (22). Sodium chloride (NaCl) as an added salt (from Nakalai Tesque Co, Kyoto) was of analytical grade and roasted at 773 K to remove any surface active impurities before use. Thrice-distilled water was used as the solvent throughout the experiments.

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**2.2 Surface Tension Measurements**

The surface tension (γ) measurements were performed on the basis of essentially the same drop volume method as reported previously (9, 18, 23), but an automated surface tensiometer (Yamashita Giken YDS94) was used in the present study. The measurement temperature was controlled by the use of a system (Yamashita Giken, YCS9211) for the surface tensiometer with an accuracy of ±0.03°C at any temperature ranging from 5 to 50°C. The first drop was permitted to stand for 1.5 h in order to attain the temperature equilibrium, and then, in order to estimate the approximate size of the drop the coarse shift of the micrometer was first determined. To attain the adsorption equilibrium, the drop squeezing process was composed of three steps, using a computer system. First, a pendant drop whose size was given by ca. 80% of the micrometer shift for a drop was permitted to stand for 15 min (or 20 min if necessary, depending on the stability of measured values), and then an additional 5% was exposed taking 10 s as the second step. And finally the pendant drop (of ca. 85% of a falling drop) was squeezed out at a speed of 1 μms⁻¹. One measured point was determined from at least five measured values. Whether the measured values for a sample solution scatter or not depends in most cases on the chemical species (especially on the structure) or its concentration.

**3 Results and Discussion**

**3.1 Surface Tension and Critical Micellization Concentration**

Figure 1 demonstrates the curves of surface tension γ against logarithmic concentration (in mili molality) ln mₙ for the respective single systems of α-SMy·iPr and FC6-HC4 at 30°C (The latter was reproduced from the previous study(18)). The break point corresponding to the critical micellization concentration (CMC) of FC6-HC4 is found at lower concentration, and FC6-HC4 exhibits a higher surface activity which is regarded as surface tension lowering ability when compared with α-SMy·iPr at any fixed surfactant concentration. In particular, it should be noted that the surface tension value at CMC (the minimum value), γCMC is ca 20 mNm⁻¹.

We have a few means to evaluate the surface adsorption or surface activity and micelle formation ability of surfactants. According to Rosen (1), one of them is the adsorption efficiency factor denoted as pC20 (= -log C20), i.e. the minimum bulk concentration of a surfactant required to make an interfacial adsorption maximum. C20 is defined as the concentration which gives a relation of surface pressure, Δπ = πCMC - π = 20 mNm⁻¹. This means that C20 is the concentration which shows a surface tension higher than γCMC by 20 mNm⁻¹. The C20 is nearly equal to the minimum concentration required for attaining saturated adsorption at interface. The pC20’s were determined as 6.7 for FC6-HC4 and 6.5 for α-SMy·iPr, indicating that FC6-HC4 molecules can adsorb a little more effectively, making surface tension lower slightly more effectively, than that of α-SMy·iPr molecules. In comparison with commonly well known surfactants, the pC20 values of both surfactants are very high (for instances, according to Ref. 1, n-C12H25SO4⁻Na⁺: 2.5 at 25°C / n-C12H25C6H4SO3⁻Na⁺: 4.9 at 25°C, 0.1 M NaCl / C12H25(OC2H4)OH: 5.3 at 25°C).

The second means the ratio CMC/C20 is convenient to examine the effect of molecular structure, as well as its environment, on adsorption and micelle formation of surfactants. The increment of the ratio suggests that micelle formation is more interrupted than adsorption, or adsorption is more enhanced than micelle formation (1). The CMC / C20 values were obtained as 3.6 and 4.3 for FC6-HC4 and α-SMy·iPr, respectively; the larger
Fig. 2 (a) The Plots of Surface Tension vs Logarithmic Molality for α-SMy·iPr / FC6-HC4 Mixed Systems at 30°C.

Fig. 2 (b) The Plots of Surface Tension vs Logarithmic Molality for α-SMy·iPr / FC6-HC4 Mixed Systems at 30°C.
value of $\alpha$-SMy·iPr reflects more prominently the relatively higher CMC as compared to the C20, although the C20 of $\alpha$-SMy·iPr is greater than that of FC6-HC4 (C20 values are $1.95 \times 10^{-7}$ mol kg$^{-1}$ for FC6-HC4 and $3.24 \times 10^{-7}$ mol kg$^{-1}$ for $\alpha$-SMy·iPr).

Figure 2 shows the plots of surface tension vs. logarithmic mili molality for selected mixed systems of $\alpha$-SMy·iPr / FC6-HC4 at 30°C. The mole fractions of FC6-HC4 in the surfactant mixture are indicated in the inset. The figure clearly demonstrates that with increase in FC6-HC4 content, CMC lowers. It is noted that the minimum surface tension or $\gamma_{\text{CMC}}$ of each mixed system at the range above $X_{\text{FC6-HC4}} = 0.25$. All the $\gamma_{\text{CMC}}$ values of the systems, the mole fraction of which is higher than 0.25, were very close to that of pure FC6-HC4. As is seen in Fig. 2 (b), a minimum appeared at the CMC in a few cases, suggesting that one surfactant acted as a kind of impurity against the other surfactant, and in addition, the surface activity of the mixed systems seems to be synergistically enhanced by mixing. The lowered surface tension, observed at the range of $X_{\text{FC6-HC4}} > 0.25$, probably indicates that content in the adsorbed film might result from FC6-HC4 having higher pC20 value or greater surface activity than $\alpha$-SMy·iPr. This will be discussed again later.

In order to determine the degree of counterion binding, $\beta$ from the Corrin-Harkins plot (20), we examined the effect of added salt (NaCl) on CMC. In Fig. 3 the $\gamma$ vs $\ln m_i$ plots for $\alpha$-SMy·iPr solutions at different added salt concentrations (indicated in the inset) are shown. As for FC6-HC4, the plots were given in the previous paper (18). Figure 3 shows that CMC decreased with raised NaCl concentration as expected, while the minimum surface tension $\gamma_{\text{CMC}}$ also decreased, in other words, the surface activity is enhanced with the addition of salt. Similar but more marked enhancement of surface activity accompanied by the addition of NaCl (even at the range below 5 m mol kg$^{-1}$) was observed for FC6-HC4(18). Interestingly, the slopes of the curves below CMC are gradually reduced; this seems to correspond to the decrease in the surface excess $\Gamma$, or the increase in the surface area, A, occupied by an adsorbed surfactant molecule. This problem has been discussed previously, in which the increased A with decreased CMC was ascribed to the decrease in bulk concentration itself of surfactants (18).

However, it may be considered that the strong added salt effect on adsorption as well as micelle formation is a matter of course, because, the activity of counterions coming from surfactant molecules does decrease with
raised concentration of added salt so that the negative slope of surface tension vs surfactant concentration becomes smaller in the absolute value (2).

The CMC values of both single surfactants, with and without the addition of NaCl, are tabulated in Table 1. The Corrin-Harkins plots are shown in Fig. 4. From the slopes, the degrees of counterion binding were determined as $\beta = 0.57$ for FC6-HC4 and $\beta = 0.61$ for $\alpha$-SMy:iPr. As compared with common surfactants, which have a straight hydrocarbon chain and a head group of simple structure, these $\beta$ values are small. This results from the molecular structure of top-heavy hydrophilic (big head) groups leading to the lower charge density of the micellar surface due to hardness of packing in the palisade layers.

### 3.2 Correlation between Compositions in Bulk Solution ($X_2$) and in Micelles ($Y_2$)

Figure 5 (a) shows the measured CMC values (closed circles) as a function of $X_{FC6-HC4}$. In the figure, the broken line indicates the relation when the two surfactants were projected to form micelles of thermodynamically ideal mixing; this curve was obtained by the equations described below (Eqs. 1 and 2). Interestingly, the measured points on the left hand side (below $X_{FC6-HC4} = 0.3$) positively deviate from the curve of ideal mixing, while those on the right hand side ($0.6 < X_{FC6-HC4} < 1$) show a slightly negative deviation. Let us consider these results.

Rubingh has given theoretical equations for relating the composition of micelles formed at CMC with that of bulk solution; his useful equations have been widely applied to analyze the relations of CMC-compositions (of singly dispersed phase) with micellar phase (24). His equations were derived without taking into account the effect of counterions on mixed micelle formation in the case of ionic surfactant mixtures. It may be said that in his equations a mixed CMC value itself involves the effect of counterion binding on micelle formation. The authors, however, have considered that since a surfactant in the binary mixed system does act as an added salt against the other, the respective degrees of counterion binding should be more explicitly taken into consideration.

We have applied the following equations for micelle formation of ideal mixing to binary ionic surfactant systems (25-28).

\[
Y_i = X_i(C_m / C_i^0)^{1+\beta_i} \\
X_i = \frac{1-(C_m / C_i^0)^{1+\beta_i}}{(C_m / C_i^0)^{1+\beta_i} - (C_m / C_j^0)^{1+\beta_j}}
\]

where $\beta_1$ and $\beta_2$ denote the degrees of counterion binding for surfactants 1 and 2, respectively. These equations allow us to calculate $C_m$ as a function of $X_1$, if $C_i^0$, $C_j^0$, $\beta_1$, and $\beta_2$ are known. The broken line curve in Fig. 5 (a), was obtained using Eqs. 1 and 2. Micellar

### Table 1 The Effect of Added NaCl on the CMC Determined by Surface Tension Measurements at 30°C.

<table>
<thead>
<tr>
<th>Concentration of added NaCl / mmol·kg⁻¹</th>
<th>CMC / mmol·kg⁻¹</th>
<th>ln mₑ</th>
<th>ln CMC</th>
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<tbody>
<tr>
<td>0</td>
<td>1.40</td>
<td>-6.57</td>
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<td>1.00</td>
<td>1.10</td>
<td>-6.17</td>
<td>-6.81</td>
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<tr>
<td>2.00</td>
<td>0.96</td>
<td>-5.82</td>
<td>-6.95</td>
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<td>4.00</td>
<td>0.70</td>
<td>-5.36</td>
<td>-7.26</td>
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<tr>
<td>8.00</td>
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<table>
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<tr>
<th>$\alpha$-SMy·iPr</th>
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<th>-7.39</th>
<th>-7.39</th>
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</tr>
<tr>
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<td>1.00</td>
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<td></td>
<td>3.00</td>
<td>0.24</td>
<td>-5.73</td>
<td>-8.34</td>
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<tr>
<td></td>
<td>5.00</td>
<td>0.17</td>
<td>-5.26</td>
<td>-8.66</td>
</tr>
</tbody>
</table>

**Fig. 4** Corrin-Harkins Plots for Determination of Degree of Counterion Binding at 30°C. ($mₑ = m_{CMC} + m_{NaCl}$)
Adsorption and Micelle Formation of Mixed Systems of Top-heavy Type Anionic Surfactants

composition $Y_1$ can be also calculated. Further, for any mixed system of either ideal or non-ideal mixing, we have derived equations including an interaction parameter, $\omega_0$, from the idea introduced in Eqs. [1] and [2] so as to be more generally applicable to given systems, as follows (25-28).

\begin{equation}
ln \frac{Y_1}{X_i} + \kappa_1 \ln C_i^0 + (1 - Y_i)^2 \omega_0 = \kappa_1 \ln C_m,
\end{equation}

\begin{equation}
ln \frac{Y_1^u}{1 - Y_1^u} + \left[ U(1 - Y_1)^2 - Y_1^2 \right] \omega_0 - \ln \frac{X_i^u}{1 - X_i} = U\kappa_1 \ln \frac{C_i^0}{C_m^0},
\end{equation}

where $U = \kappa_2 / \kappa_1 = (1 + \beta_2) / (1 + \beta_1)$.

Here, the interaction parameter is related to the activity coefficients $f_1$ and $f_2$ and the micellar composition $Y_1$, as follows.

\begin{equation}
f_1 = \exp \left\{ \omega_0 (1 - Y_1)^2 \right\}
\end{equation}

\begin{equation}
f_2 = \exp \left\{ \omega_0 Y_1^2 \right\}
\end{equation}

Applying Eqs. [3] and [4] in addition to Eq.[5], the values of $Y_{FC6-HC4}$, $\omega_0$ and activity coefficients $f_1$ and $f_2$ were determined, as listed in Table 2.

In Fig. 5 (b) are given calculated values of micellar composition ($Y_{FC6-HC4}$, open circle) and simulated curve of singly dispersed phase (CMC-$X_{FC6-HC4}$ curve) along with the measured points of CMC (closed circles). In addition, the micellar phase curve (dotted line) and singly dispersed phase curve (broken line) of ideal mixing are included for comparison. Looking at the micellar composition curve (CMC-$Y_{FC6-HC4}$), it is known that even if the bulk composition ($X_{FC6-HC4}$) is low in FC6-HC4 content, the $Y_{FC6-HC4}$ values are markedly high, especially at the range below $X_{FC6-HC4} = 0.4$. This is considered to result from the stronger

\begin{figure}
(a) CMC as a Function of Mole Fraction of FC6-HC4 in the Surfactant Mixture.
The solid line with closed circles indicates singly dispersed phase curve.
The broken line indicates the CMC-$X$ curve of ideal mixing based on our own theory.

(b) Phase Diagram of $\alpha$-SMy·iPr / FC6-HC4 Mixed System at 30°C and 1 atm.
Solid line with closed circles: Singly dispersed phase curve for the mixture.
Solid line with open circles: Micellar phase curve simulated for the mixture based on our theory.
Broken line: CMC-$X$ curve of ideal mixing based on our own theory.
Dotted line: Micellar phase curve of ideal mixing.
Interaction Parameter / $\omega_0 : X_{FC6-HC4} < 0.5 \text{ \cdots } \omega_0 = 0.70$
$X_{FC6-HC4} > 0.5 \text{ \cdots } \omega_0 = -0.70$

Table 2  Values of CMS, Micellar Composition \( Y_2 \), Interaction Parameter \( \omega_0 \), and Activity Coefficients \( f_1 \) and \( f_2 \) at 30°C. FC6-HC4 Corresponds to 2.

<table>
<thead>
<tr>
<th>( X_{\text{FC6-HC4}} )</th>
<th>CMC (mmol·kg(^{-1}))</th>
<th>( Y_2 )</th>
<th>( \omega_0 )</th>
<th>( f_1 )</th>
<th>( f_2 )</th>
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</tr>
<tr>
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<td>0.60</td>
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<td>1.01</td>
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<td>0.99</td>
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<td>0.90</td>
<td>-0.7</td>
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<td>0.91</td>
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<td>1.00</td>
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\( \omega_0 \) ave. = 0.2

hydrophobicity of FC6-HC4 and its excluding tendency against hydrocarbon molecules.

From Table 2 it is seen that at \( X_{\text{FC6-HC4}} = 0.2 \), a maximum value of the interaction parameter was obtained and at the range below \( X_{\text{FC6-HC4}} = 0.2 \) the activity coefficient of FC6-HC4 is much greater than that of \( \alpha \)-SMy·iPr, while at the range above \( X_{\text{FC6-HC4}} = 0.2 \) up to ca. 0.4, the coefficient of the latter is greater than the former. Even though the hybrid surfactants having a fluorocarbon chain is a minor component, its stronger ability of micelle formation than \( \alpha \)-SMy·iPr’s leads to forming micelles richer in FC6-HC4. This may be interpreted in terms of CMC/C\(_{20}\), that is, the lower CMC/C\(_{20}\) value of FC6-HC4 [CMC/C\(_{20} \) = 3.6] corresponds to the higher micelle forming trend at the range below \( X_{\text{FC6-HC4}} = 0.25 \), while \( \alpha \)-SMy·iPr [CMC/C\(_{20} \) = 4.3] has a relatively weaker micelles forming ability in this mole fraction region, as already described.

In contrast to the above, after the CMC-\( X_{\text{FC6-HC4}} \) at \( X_{\text{FC6-HC4}} = 0.5 \) (mixing ratio = 1:1) showed apparently ideal mixing, the behavior is converted into slightly negative deviation as is indicated by negative value of \( \omega_0 \) and activity coefficients being less than one. This seems to suggest that when FC6-HC4 molecules are surrounded by about two or more \( \alpha \)-SMy·iPr molecules, structurally favorable conditions for the formation of mixed micelles are attained. The types of micelle structure may be roughly divided into three, i.e., (I) \( X_{\text{FC6-HC4}} = 0 \sim \) ca. 0.3, (II) 0.4~0.6 and (III) 0.7~1 or into two; either \( X_{\text{FC6-HC4}} \) is higher or lower than ca. 0.4. A similar but clearer distinction depending on the mixing ratio, has been observed for a binary mixed system consisting of fluorocarbon and hydrocarbon surfactants: sodium perfluorononate (SPFN) and sodium tetradecylsulfate (STDS). In this combination an azeotrope was found at \( X_{\text{STDS}} = 0.05 \), and in the region up to \( X_{\text{STDS}} = 0.2 \) almost completely demixing micelles were formed, while in the region above \( X_{\text{STDS}} = 0.2 \) up to 1.0, the mixing seems to be almost ideal. This was confirmed not only by composition analysis using Eqs. 3, 4 and 5 but also by fluorescence spectrometry (19).

3.3 The Composition of Adsorbed Film (\( Z_2 \))

In order to estimate compositions of surfactants 1 and 2 in adsorbed film formed at air / water interface (\( Z_1 \) and \( Z_2 \), \( Z_1 + Z_2 = 1 \)), we have derived the following equations based on the regular solution theory (RST) (21).

When the composition of species \( i (i = 1 \) or 2) in the adsorbed film phase and the activity coefficient are denoted as \( Z_i \) and \( f_i \), respectively, the chemical potentials at temperature, \( T \); pressure, \( P \); and a constant surface tension (\( \gamma \)) are given for adsorbed film (a) and bulk (b) phases, respectively as (9):

\[
\mu_{i(a)} = \mu_{i(b)}(T, P, \gamma) + RT \ln f_i Z_i \\
\mu_{i(b)} = \mu_{i(b)}(T, P) + RT \ln (m_i / m_i^0)
\]  

Also the following Eqs. 7, 8 and 9 have been given in the literature (21). The concentration is related as:

\[
m_i = f_i Z_i m_i^0
\]

where \( m_i^0 \) is the bulk concentration of pure system of \( i \) at the constant surface tension, and corresponds to either molarity or molality as a concentration chosen. The mass balance leads to Eq. 8,

\[
m_1 + m_2 = (1 - X_2) m_1 + X_2 m_1 = m_t
\]

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 following relations are given:

\[
m_t = f_1 Z_1 m_1^0 + f_1 (1 - Z_2) m_2^0 = (1 - X_2) m_t \\
m_2 = f_2 Z_2 m_2^0 = X_2 m_t
\]

It is noted that in this study, \( m_i^0 \) is the CMC of \( \alpha \)-
SMy·iPr and the surface tension fixed was taken at the CMC of α-SMy·iPr, so that \( m_2^0 \) and each \( m_1 \) were read from the \( \gamma \) vs ln \( m_1 \) curves as schematically shown in Fig. 6.

From these equations it is known that the mole fraction of 2 in bulk solution is expressed by using Eq. 10.

\[
X_2 = \frac{m_2}{m_1 + m_2} = \frac{f_2 Z_2 m_2^0}{f_1 (1 - Z_2) m_1^0 + f_2 Z_2 m_2^0} \tag{10}
\]

Based on the RST model, the activity coefficients \( f_1 \) and \( f_2 \) can be related to \( Z_2 \) and the interaction parameter \( \omega_A \), as follows.

\[
f_1 = \exp \left[ \omega_A Z_2^2 \right] \\
f_2 = \exp \left[ \omega_A (1 - Z_2)^2 \right] \tag{11}
\]

From analogy with the derivation of Rubingh’s equations (24), we obtained the following equations.

\[
\left(1 - Z_2\right)^2 \ln \left[\frac{1 - X_2 m_1}{1 - Z_2 m_2^0}\right] = l 
= \frac{Z_2^2 \ln \left( X_2 m_1 / Z_2 m_2^0 \right)}{Z_2^2 \ln \left( X_2 m_1 / Z_2 m_2^0 \right)} \tag{12}
\]

\[
\omega_A = \frac{\ln \left( X_2 m_1 / Z_2 m_2^0 \right)}{\left(1 - Z_2\right)^2} \tag{13}
\]

Eqs. 12 and 13 simultaneously tell us that if the \( m_1^0 \), \( m_2^0 \) and \( m_t \) at the given \( \gamma \) are determined against net mole fraction \( X_2 \), then the adsorbed film composition \( Z_1 \) is given by Eq. 12, and \( \omega_A \) can be evaluated from Eq. 13 by using the \( Z_2 \) values (19). [Similar equations had been derived by Rosen and Hua as early as in 1982 (1, 29)].

Taking \( m_1^0 \) as the CMC of the first component α-SMy·iPr, and \( m_2^0 \), for pure FC6-HC4, the \( m_t \) for each mixed system was determined by reading the curves of \( \gamma \) vs \( m_t \) plot (See Fig. 6). The \( m_t \) values are listed in Table 3. Substituting the data of \( m_t \)'s, \( m_1^0 \) and \( m_2^0 \), the composition of surfactant 2 (corresponding to FC6-HC4), \( Z_2 \) was calculated as a function of the net mole fraction, \( X_2 \). The results are shown in Fig. 7 (and the \( Z_2 \) values are included in Table 3). Figure 7 is a phase diagram indicating the composition \( Z_2 \) of the adsorbed film phase related with that of the bulk phase \( X_2 \), in other words, the curves of the phase equilibrium between the adsorbed film and monomeric species. To
obtain the \( m_t \) vs \( Z \) curve along with simultaneous satisfaction of the relation of \( m_t \) vs \( X \), the \( \omega_A \) value was given as -2.0 on average; this negative value suggests that a considerably strong interaction does act between surfactant molecules in the adsorbed film as compared with that inside micelles (on average \( \omega_0 = 0.2 \) (See Table. 2)). Here, it is noted that the curve along the estimated \( Z \) values is smoothed one (not simulated one using the averaged \( \omega_A \) value).

The great difference between \( \omega_0 \) and \( \omega_A \) may come from the difference in the curvature of formed aggregates: the radius of the adsorbed film is infinitely great, while that of a micelle is extremely small (the order of molecular length), and the micellar surface must have greater surface tension so as to withstand the Laplace pressure acting inside micelles. Probably, molecular packing of the former differs from that of micelles and accordingly the extent or the mode of interaction between different molecules must be changed depending on packing.

Looking in detail at the phase diagram in Fig. 7, since all the measured points have a certain error margin, we cannot strongly assert that an azeotrope-like but very shallow minimum seems to exist at \( X = Y = Z = \text{ca} 0.83 \). However, again examining Fig. 5 (b), we see a very slight minimum is likely to appear at \( X = Y = \text{ca} 0.9 \). Although it is hard to conclude that there exists an azeotropic point around \( X = Y = Z = 0.8 \sim 0.9 \), it can at least be said that around this range the most energetically stable micelles or adsorbed film are formed; that is attained when the mixing ratio is \( \alpha\text{-SMy} \cdot \text{iPr}: \text{FC6-HC4} = 1:4 \sim 1:9 \). It has been concluded that 10 to 20% addition of \( \alpha\text{-SMy} \cdot \text{iPr} \) to FC6-HC4 leads to synergistically enhanced surface activity or micelle formation. On the other hand, in the case where FC6-HC4 is a minor component, FC6-HC4 molecules encounter difficulty to fit in three-dimensionally with \( \alpha\text{-SMy} \cdot \text{iPr} \) dominant micelles, resulting in the positive \( \omega_0 \) value in micelle formation. However, this is not the case for adsorbed film formation. When the adsorbed film is formed, more hydrophobic FC6-HC4 molecules rise to the surface more quickly to occupy the surface than \( \alpha\text{-SMy} \cdot \text{iPr} \) molecules. Similar behavior has been observed for mixed systems of SPFO (sodium perfluorooctanoate) with MEGA-8 and MEGA-9 (n-alky-N-methylglucamides) (30). This trend is reflected in the \( \gamma \) vs \( \ln m_t \) curves (Fig. 2) and in the \( m_t \) vs \( Z_{\text{FC6-HC4}} \) curve (Fig. 7).

| Table 3 | Values of \( m_t \), \( Z_2 \), \( \Gamma \), \( A_m \), \( \bar{A}_1 \) and \( \bar{A}_2 \) of \( \alpha\text{-SMy} \cdot \text{iPr} / \text{FC6-HC4} \) Mixed Systems at 30 °C. |
|---------|-----------------|-----------------|-----------------|-----------------|----------------|
| \( X_{\text{FC6-HC4}} \) (mmol·kg\(^{-1}\) ) | \( m_t \) at \( y = 34.45 \) mNm\(^{-1}\) | \( Z_2 \) | \( \Gamma \) | \( A_m \) | \( \bar{A}_1 \) | \( \bar{A}_2 \) |
| 0.00 | 1.40 | 2.66 | 65 | 62 | 0.42 | 0.53 |
| 0.10 | 0.66 | 0.42 | 2.56 | 65 | 67 | 62 | 0.50 | 0.53 | 2.64 | 63 | 89 | 40 |
| 0.20 | 0.48 | 0.57 | 2.74 | 61 | 104 | 27 |
| 0.30 | 0.40 | 0.60 | 2.96 | 56 | 83 | 40 |
| 0.40 | 0.34 | 0.64 | 2.98 | 56 | 56 | 56 |
| 0.50 | 0.34 | 0.70 | 2.98 | 56 | 56 | 56 |
| 0.60 | 0.27 | 0.73 | 2.78 | 56 | 56 | 56 |
| 0.70 | 0.27 | 0.77 | 2.98 | 56 | 56 | 56 |
| 0.80 | 0.27 | 0.81 | 2.98 | 56 | 56 | 56 |
| 0.90 | 0.25 | 0.85 | 2.98 | 56 | 56 | 56 |
| 1.00 | 0.28 | 2.98 | 56 | 56 | 56 |

Fig. 7 Phase Diagram Curves of Monomers in Bulk Solution (\( X_2 - m_t \)) and Adsorbed Film at Air / Water Interface (\( Z_2 - m_t \)) for \( \alpha\text{-SMy} \cdot \text{iPr} / \text{FC6-HC4} \) Mixed Surfactant System at 30 °C and 1 atm.
3.4 Surface Excess and Partial Molecular Area

The surface excess (the surface concentration), $\Gamma$, was determined for the respective single and mixed systems by applying the Gibbs adsorption isotherm (1-4) to the $\gamma - \ln m_t$ relations. In Fig. 8 the resultant surface excess, $\Gamma$, is demonstrated as a function not only of $X_{\text{FC6-HC4}}$ but also of $Z_{\text{FC6-HC4}}$ estimated at each $X_{\text{FC6-HC4}}$. It should be noted that (1) the surface excess changes greatly in the region below $X_{\text{FC6-HC4}} = 0.3 \sim 0.4$ in parallel with the CMC-$X_{\text{FC6-HC4}}$ relation, and correspondingly, in this region composition of the adsorbed film $Z_{\text{FC6-HC4}}$ is greater than 0.5 (See open circles in Fig. 8) and, (2) irrespective of changes in mole fraction at the range $X_{\text{FC6-HC4}} > 0.3$ or $Z_{\text{FC6-HC4}} > 0.6$, the surface excess is kept at the same as the value of FC6-HC4. The mean surface (occupation) area per molecule, $A_m$, can be calculated from the relation $A_m = 1 / L \gamma$, where $L$ denotes the Avogadro’s number. By the use of surface excess data, Fig. 9 was constructed.

Figure 9 indicates the change in $A_m$ with estimated mole fraction in the adsorbed film. Corresponding to the positive and negative deviations from ideal mixing as were shown in Figs. 4, 5 and 7, the $A_m$ also deviates positively from ideal mixing in the lower region of mole fraction and negatively from ideal mixing in the higher region (indicated by a linear broken line).

Here, from analogy of the partial molar volume of a solution, the partial molecular area (PMA) for each component is evaluated using the following equation (21, 31, 32).

\[ A_m = \overline{A}_i + Z_2 \left( \frac{\partial A_m}{\partial Z_2} \right)_{T, V, \gamma, m} \]  

[14]

Here $\overline{A}_i$ is the PMA of component 1 and defined as:

\[ \overline{A}_i = \left( \frac{\partial A_m}{\partial n_i} \right)_{T, V, \gamma, m} \]  

[15]

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

---

**Fig. 8** The Surface Excess ($\Gamma$) Curves as Function of $X_{\text{FC6-HC4}}$ and $Z_{\text{FC6-HC4}}$ Obtained for $\alpha$-SMy·iPr / FC6-HC4 Mixed Systems. $\Gamma$ was calculated according to Gibbs’ Adsorption Isotherm:

\[ \Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln m_t} \]

**Fig. 9** The Change in Mean Molecular Area with Mole Fraction in the Surfactant Mixture, and Determination of Partial Molecular Area.
Equation 14 means that $\bar{A}_1$ and $\bar{A}_2$ are determinable from the respective intercepts on $A_m$-axis at $Z_2 = 0$ and $Z_2 = 1$ under conditions of constant temperature and volume or pressure, and fixed surface tension. The $A_m$ curve obtained from the $\Gamma$ data satisfies the required conditions and allows us to evaluate PMA of the respective components as a function of $Z_2$. A tangential line drawn at any given point, P on the $A_m$ vs $Z_2$ curve gives two intercepts on the $A_m$-axis. An example for determining $\bar{A}_1$ and $\bar{A}_2$ is shown in Fig. 9. At point P we have an equation of the tangential line: $A_m = \bar{A}_1 + (\bar{A}_2 - \bar{A}_1)Z_2$.

Figure 10 shows the changes in PMA of $\alpha$-SmMy·iPr and FC6-HC4 as a function of $Z_{FC6-HC4}$, the respective data points of which were obtained from the curve given in Fig. 9. The values are included in Table 3. The numerical values given at point’s side indicate the mole fraction in bulk solution ($X_{FC6-HC4}$). In the characteristic region of CMC’s positive deviation (0 < $X_{FC6-HC4}$ < ca. 0.3) it is seen that the PMA of $\alpha$-SmMy·iPr expands while FC6-HC4’s contracts. Viewing Fig. 10 in terms of film composition, the expansion and contraction phenomenon appears at around $Z_{FC6-HC4} = 0.5$ (1:1 mixture), and in contrast the PMA in the region of $X_{FC6-HC4} > 0.4$ or $Z_{FC6-HC4} > 0.6$ shows constancy. This constancy, not satisfying the additive rule: $A_m = \bar{A}_1 + (\bar{A}_2 - \bar{A}_1)Z_2$, indicates an enhancement of interaction between both surfactants at the interface that brings about a negative deviation from ideal mixing even in the adsorbed film, as the $\omega_A$ value (-2.0) has already shown, while in the lower mole fraction region (0 < $X_{FC6-HC4}$ < 0.4 or 0 < $Z_{FC6-HC4}$ < 0.6) the reverse is the case.

Summarizing the behavior on adsorption and micellization of the present binary mixed surfactant systems, a remarkable dependence on mixing ratio was observed: At the lower mole fraction range of FC6-HC4 (below $X_{FC6-HC4} = ca. 0.4$), where FC6-HC4 is a minor component, the mixed system behaves non-ideally in regard to micelle formation (CMC) and adsorption ($\Gamma$, $A_m$, PAM) showing positive deviation from ideal mixing. On the other hand, at the higher mole fraction range (above $X_{FC6-HC4} = ca. 0.4$) the mixture was observed to form micelles and adsorbed film with aid of little enforced interaction between two surfactants. In particular, the mixed micelles as well as the mixed film seem to benefit from the presence of FC6-HC4, that is, micelles and adsorbed film are better thermodynamically stabilized by higher FC6-HC4 content. It is noted, however, that the extent of interaction between two surfactants is stronger in the adsorbed film than in micelles. Addition of 10 to 20% $\alpha$-SmMy·iPr to FC6-HC4 results in a marked enhancement of surface activity and micelle formation ability accompanying a favorable packing in two-dimensional and three-dimensional structuring by the two top-heavy type surfactants.

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