Mixed Micelle and Mixed Adsorbed Film Formations of Anionic Fluorocarbon–Nonionic Hydrocarbon Surfactant Mixtures

Sodium Perfluorooctanoate with MEGA-8, 9 and 10

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The formation of mixed micelles and mixed adsorbed films was investigated as a function of the mole fraction of each surfactant mixture for different combinations of an anionic fluorocarbon surfactant, sodium perfluorooctanoate (SPFO) with three nonionic hydrocarbon surfactants, MEGA-8, 9 and 10 (alkyl-N-methylglucamines) in water at 30°C. The results were obtained primarily from surface tension and ESR measurements. The critical micelle concentration (cmc) data for the MEGA-9-MEGA-10 mixed system included those determined from light scattering measurements. Based on the results obtained, the following conclusions were drawn. Mixing of MEGA-n's with SPFO synergetically enhances surface activity, and the cmc vs. composition curves for these show a negative deviation from ideal mixing. Thus possibly, interactions between head groups influence more for the curve than the mutual phobicity between hydrocarbon-fluorocarbon chains. The composition of micelles resembles that of adsorbed films for MEGA-n's-SPFO. ESR data indicate that SPFO and MEGA-n may mix well with each other.

1 Introduction

The investigation on mixed micelles or mixed adsorbed films formed from surfactant mixtures is considered to result in a discovery of some remarkable functions which are unique compared with micelles composed of a single component and give us certain information concerning the intermolecular interaction between hydrophobic and/or hydrophilic groups of surfactant molecules. In fact, the functional molecular aggregates found in nature are composed of two or more kinds of chemical species. Much attention and effort have so far been directed to the interesting behaviors in mixed micelles and mixed adsorbed films formed by various combinations of different surfactants. Consulting the dialog information services by the use of three key words; "mixed micelle", "surfactant mixture" and "mixed adsorbed film", about 190 papers including the proceedings of conferences in relation to the mixed micelle, and 6 papers of mixed adsorbed films were published in the last twelve years. The application of only the three key words, however, does not inform the existence of such leading papers on mixed surfactant systems in water as are cited here1)–5), suggesting that the literature information is easily governed by the key word choice.

A lot of chemists in our country have contributed to various work fields of the mixed micelle and the mixed adsorbed film formations; thermodynamic theories concerning the mixed micelle and/or adsorbed film formation have been developed by several researchers from respectively different points of view and the compositions of micelles and/or adsorbed films were estimated by applying those theories11)–12). Some authors have extensively paid attention to the intermolecular interaction between different surfactant molecules13)–18) or of surfactants with solubilizates19,20). The effects of chain length21)–26) or differ-
ence in type\textsuperscript{29-31} of hydrophobic groups on the solution properties have been widely examined and discussed for the various combinations of different types of surfactants. Several studies on the effects of additives or studies by the use of additives have been made in order to make clear the mixed micelle formation mechanism as well as the structure of micelles\textsuperscript{30,31-35}. The surface potential of mixed micelles has been a matter of concern in research work; some papers were already published concerning this theme\textsuperscript{36-38}.

Application of mixed micelles to medical or pharmaceutical science and technology and to analytical chemistry is now on greater development\textsuperscript{39-45}).

We performed a pressure and temperature study on the mixed systems of sodium perfluorooctanoate (SPFO) with two anionic surfactants, sodium dodecyl sulfate (SDS), and sodium decyl sulfate (SDeS)\textsuperscript{12,46). In these previous works, the aim was to examine the effect of chain length on the pressure and temperature behavior in mixed surfactant solutions\textsuperscript{41) where the temperature data have not been published yet.

\(N\)-Alkanoyl-\(N\)-methylglucamines (MEGA-n, \(n=8, 9\) and \(10\)) which belong to a new group of nonionic surfactants have been known to show some interesting and useful behaviors in water. Recently, we reported the temperature effect on micelle formation of MEGA-n\textsuperscript{47), and the mixed micelle formation in aqueous solution of MAGA with SPFO at different pressures\textsuperscript{41} and of MEGA\(n=9\) with MEGA\(n=10\) at 30°C at 1 atm\textsuperscript{41). The structural formula for MEGA-n is as follows.

\[
\text{CH}_3^+ (\text{CH}_2)_n \cdot \text{C} \cdot \text{N} \quad \text{OH} \quad \text{OH} \\
\text{OH} \quad \text{OH} \\
(n=6: N\text{-methyl-}N\text{-octanoyl glucamine, MEGA-8}) \quad (n=7: N\text{-methyl-}N\text{-nonanoyl glucamine, MEGA-9}) \quad (n=8: N\text{-decanoyl-}N\text{-methylglucamine, MEGA-10})
\]

In this paper, we study the properties of the mixed micelle together with the mixed adsorbed film formed by a combination of MEGA\(n=8\) with SPFO. The two surfactants, MEGA8 and SPFO are similar to each other only regarding the chain length of hydrophobic group, but quite different from each other, especially in physicochemical properties of hydrophobic and hydrophilic groups.

The similarity and difference between the surfactants studied here must be reflected on various aspects such as surface tension of solution, cmc, the aggregated states (number, size and shape) etc. The studies will give us some important and interesting information in comparison with previous works on mixed surfactant systems.

### Experimental

#### Materials

Surfactants used here and their purifications were described elsewhere\textsuperscript{11,24,45). Spin label 5-stearic acid methyl ester (abbreviated as 5-MeSL) was used without further purification. All solvents used were purified by two or three distillations. Inorganic salts were analytical grades and used as received.

#### Method

The cmc's were determined from surface tension data measured by the use of a Kyowa Surface Tensiometer (Whyhelmy method) for SPFO-MEGA-\(n\) mixed systems and by the use of the same apparatus for drop volume measurement as used by Uryu \textit{et al.}\textsuperscript{41) at 30°C.

ESR measurements were carried out with the JEOL PE-IX at 25°C. The usual spectrometer setting 100 kHz modulation amplitude, 1.0 G; microwave power, 8 mW; scan range, 100 G; scan speed, 8 min.

#### Results and Discussion

In order to determine precisely the cmc and to estimate the composition of adsorbed films as a function of mole fraction in the surfactant mixture, a lot of surface tension data were obtained over a wide range below and above cmc. In the plot of the surface tension \(\gamma\) against \(\ln m_t\), where \(m_t\) is the total molality of surfactant (\(m_1 + m_2\)), all mixed systems were found to show a surface activity much stronger than the pure systems and a minimum (corresponding to cmc) which is located at a concentration much lower than cmc's of the pure systems. As has been observed for the mixed system of MEGA9 with SPFO\textsuperscript{11,41) in the SPFO-MEGA8 system too, the synergistical enhancement of surface activity leads to a lowering of the cmc.

Plotting the cmc values thus obtained against the mole fraction of MEGA8 (or MEGA9), \(X_2\),
defined by $X_i = m_i / m_0$, $i = 1, 2$ where the surfactant 1 ($S_1$) corresponds to SPFO and 2 ($S_2$) to MEGA8 (or MEGA9), the SPFO-MEGA8 system as well as the SPFO-MEGA9 system shows a negative deviation from ideal mixing, and behaves in striking contrast to SPFO-SDS and SPFO-SDeS systems. The negative deviation found in the present system implies that SPFO is miscible with MEGA- $n$ and indicates a reduction in the repulsive force between the ionic head groups of SPFO probably resulting from penetration of nonionic surfactant molecules between ionic head groups and also from a kind of coulombic interaction of slightly positive charge at the nitrogen atom (strictly speaking, the carbon atom of carboxyl group) of MEGA- $n$ with negative charge of carboxyl group of SPFO.

Comparing the SPFO-MEGA8 system with the SPFO-MEGA9 system, the contribution degree of attractive factor between head groups for the former mixed system is likely to be larger than for the latter, in other words, the mutual phobicity between hydrophobic chains of the SPFO-MEGA8 is smaller due to the shorter chain length of MEGA8 than the mutual phobicity of the SPFO-MEGA9. This may result in the larger negative deviation from ideal mixing compared with that of the SPFO-MEGA9 system.

Next, we attempt an analysis of the curve of cmc vs. $X_2$. To estimate the micellar composition, equations for the regular mixing were applied, but agreement with the measured values was not obtained. Thus, the equations given by Motomura$^6$ were applied.

$$
\hat{Y}_2 = \hat{X}_2 - (\hat{X}\hat{X}_2/m_{cmc}) (\partial m_{cmc}/\partial \hat{X}_2)_{X_2} \\
\hat{X}_2 = m_2 / (2m_1 + m_2) = X_2 / (2X_1 + X_2) \\
\hat{Y}_2 = Y_2 / (2Y_1 + Y_2) \\
m_{cmc} = (2X_1 + X_2) m_{cmc}
$$

Here, $Y_2$ is the mole fraction of $S_2$ in the mixed micelle and $m_{cmc}$ is the molality of the cmc for the mixed system. Computed curves for $\hat{Y}_2$ (here $\hat{Y}_{MEGA8}$ or $\hat{Y}_{MEGA9}$) are given by the broken line in Fig.-1 (a) and (b). Both of the mixed systems show that the micelles formed are mixed better than singly dispersed species, i.e., the ratio $S_i/S_2$ for micelles is always closer to $S_i/S_2$ at minimum of $m_1$ vs. $\hat{X}$ curve compared with that for the singly dispersed species equilibrated with micelles in bulk. Figure-1 shows that the mixing degree of SPFO with MEGA8 is higher than that of SPFO with MEGA9.

We are interested in the composition of the adsorbed film formed at the air/liquid interface and in comparing it with the composition in micelles. Motomura has proposed the following equations to estimate the composition, $\hat{Z}$, in adsorbed film under constant surface tension, temperature and pressure$^7$.

![Fig.-1 Phase diagrams of the MEGA-$n$-SPFO mixed system at 30°C and 1 atm.](image)

Singly dispersed (monomeric) phase curve = cmc curve (solid line) and micellar phase curve (broken line) calculated from the Motomura equation.

![Fig.-2 Phase diagrams of adsorbed films at respective constant surface tension for MEGA8-SPFO system.](image)
The reason why a variable with circumflex, \( \hat{Z} \), is introduced is the same as in the case of \( \hat{Y} \)11). Figure-2 demonstrates the phase diagrams of adsorbed films at respective constant surface tension for the SPFO-MEGA8 system at 30°C. The solid curve 2 indicates the composition of adsorbed film, and the curve 1 with circles, the composition of bulk phase. Comparing these diagrams with that in Fig.-1 (a), we can see that they are similar to each other, i.e., the composition of adsorbed film at the interface basically resembles that of micelles, although their curvatures are infinitely great for the former and finite for the latter. A similar result was obtained for the SPFO-MEGA9 system, too.

Next we try to perform an ESR study to obtain some information on the interaction between hydrocarbon and fluorocarbon chains and between anionic and nonionic head groups. The rotational correlation time \( \tau_c \) of a spin label is a measure of the mobility of the spin probe which is directly influenced by the surroundings, i.e., \( \tau_c \) can be related to the intermolecular interaction acting around a spin probe. The rotational correlation time \( \tau_c \) is calculated from the following equation5°)

\[
\tau_c = 6.5 \times 10^{-14} W_0 \left[ \sqrt{\left( h_o / h_{-1} \right)} + \sqrt{\left( h_o / h_{+1} \right)} - 2 \right]
\]

where \( W_0 \) is the peak line width of the ESR midfield line (in gauss); and \( h_o, h_{-1} \) and \( h_{+1} \) are peak to peak heights of the mid-, high-, and low-field lines, respectively. Figure-3 demonstrates a typical ESR spectrum for 5-MeSL in 100 mM mixed surfactant solution of SPFO-MEGA8 system. In this study 5-MeSL was chosen as the spin probe to obtain the information concerning the interaction between hydrophobic groups since the spin label has to be solubilized in the interior of surfactant micelle.

Here, we note that with expectation to obtain some information on the interaction between head groups, TEMPO was tentatively used to determine \( \tau_c \) in the palisade layer, but TEMPO was not applicable due to its high solubility in water. Looking at Fig.-3, the high-field peak (\( h_{-1} \)) is much lower than the others. This is ascribed to the solubilization of the spin label in mixed micelles, since the ESR spectrum for a spin label having a nitrooxide free radical in water, in general shows three sharp peaks.

The concentration dependence of \( \tau_c \) for 5-MeSL was examined at different mole fractions in the SPFO-MEGA8 mixture. As shown in Fig.-4, each curve shows a concentration dependence of \( \tau_c \) in the lower concentration range. This may correspond to the changes in aggregation number and/or composition (in the case of mixed system). The higher value of \( \tau_c \) for MEGA8 suggests that the mobility of 5-MeSL is more
restricted in MEGA8 micelles than in SPFO micelles, the difference of which comes from the difference in cohesion.

Figure-5 shows a plot of \( \tau_0 \) vs. \( X_{\text{MEGA8}} \). \( \tau_0 \) at each \( X_{\text{MEGA8}} \) was read at 100 mM in Fig.-5. Judging from the phase diagram (Fig.-1), the composition of micelles formed at this concentration is considered to be the same as the mole fraction of the surfactant mixture, i.e., \( X_2 = Y_2 \).

From Fig.-5, it is seen that \( \tau_0 \) continuously changes with \( X_2 \) and shows a slightly positive deviation from the linear relation (broken line). These findings seem to imply that two surfactants are well miscible and the interaction between the two surfactants is stronger than that of ideal mixing however, the word 'interaction' used here includes an interaction between head groups, in other words, the mobility of 5-MeSL is influenced not only by hydrophobic groups but also by head groups.

From the present study the following conclusion will be derived: (1) Mixing of MEGA-\( n \) with SPFO synergistically enhances surface activity. (2) The cmc-composition curve shows a negative deviation from ideal mixing, suggesting that the interaction between head groups compensates more than the mutual phobicity between hydrocarbon-fluorocarbon chains. The possible interactions between head groups are schematically shown in Fig.-6. (3) The composition of micelles resembles that of adsorbed films. (4) ESR data suggest that SPFO and MEGA-\( n \) may mix well with each other.

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アミオン性炭化フッ素系-非イオン性炭化水素系界面活性剤混合系の混 合ミセル及び混合吸着膜の形成
ペルフルオロオクタン酸ナトリウムと MEGA-8, 9, 10 との混合系について
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次のアミオン性炭化フッ素界面活性剤と非イオン性炭化水素界面活性剤の組み合わせに対して混合ミセルの形
成と混合吸着膜の研究を行った：①アミオン性炭化フッ素界面活性剤（ペルフルオロオクタン酸ナトリウム、SPFO）と非アミオン性炭化フッ素界面活性剤（N-アルカノイル-N-メチルグルルタミン、それぞれMEGA-8、MEGA9及びMEGA10）との混合物（SPFO-MEGA8、①-I、SPFO-MEGA9、①-II、SPFO-MEGA10、①-III）、②非イオン性のMEGA-n同士（MEGA8-MEGA9、②-I、MEGA9-MEGA10、②-II）以上30℃純水溶液中で検討を進めた。

研究には主に表面張力法とESR測定法を用いて行った。MEGA9-MEGA10では吸着剤によって決定したcmcを含めている。

それらの結果から、MEGA-nとSPFOを混合すると界面活性性は相乗的に高められ、またそれらのcmc相互作用が組成曲線に影響を及ぼすと示唆した。その結果、炭化フッ素鎖-炭化フッ素鎖の間の相互反発（mutual phobicity）をヘッドグループ間の相互作用が抑制するかという点を示唆している。MEGA-n-SPFO混合系に対して、ミセルの組成は吸着膜の組成に似ていることがわかった。ESRのデータをみると、SPFOとMEGA-nがおろらくお互いによく混合することを示唆している。