Adsorption and Micelle Formation of Mixed Surfactant Systems in Water. IV. Three Combinations of SDS with MEGA-8, -9 and -10

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Abstract: By means of surface tension measurement (Wilhelmy method), micellization and adsorbed film formation were investigated for three combinations of mixed surfactant systems: a typical anionic surfactant, sodium dodecyl sulfate (SDS) was combined with three nonionic surfactants used as membrane-protein solubilizers, n-alkyl (octyl, nonyl and decyl)-N-methylglucamides (MEGA-8, MEGA-9 and MEGA-10, respectively) in water at 30 °C. The data of surface tension (γ) versus logarithmic total molality of both single and mixed surfactant systems (m_t) plots as a function of mole fraction of surfactant 2 (2 corresponds to MEGA-n’s), X₂, enabled us to determine critical micellization concentration (CMC), minimum surface tension at CMC (γ_{CMC}), surface excess (Γ_0), mean surface area occupied by a molecule (A_m) and parameters related to synergism in surface activity such as pC_{20} and CMC/C_{20}. Based on the regular solution theory, the relation of compositions of the singly dispersed phase (X₂) and the composition of the adsorbed film phase (Z₂) were estimated, and then the interaction parameters in micelles (ω_b) and in adsorbed film (ω_A) were also calculated. Both the CMC-X₂ and CMC-Y₂ curves were found for all combinations to show a negative deviation from ideal mixing, and even the curve of m_t (bulk phase concentration) versus Z₂ produced a prominent negative ω_A. A marked synergism in surface tension reduction was observed for these MEGA-n’s mixtures with SDS; the extent of the synergism increased in the order of MEGA-8, -9 and -10. A positive synergism was observed, even from the partial molecular area (PMA) and the minimum free energy at surface $G_{min}^{(S)} = (γ_{CMC} \cdot A_m \cdot L)$ where, L is the Avogadro’s number.

Key words: mixed surfactant system, mixed micelle, mixed adsorbed film, sodium dodecyl sulfate, MEGA-8, -9 and -10, synergism, surface tension, partial molecular area, interaction parameter

1 Introduction

The mixing of surfactants as well as synergism upon mixing has long been the subject of intense interest in academic and commercial circles, and this interest has accelerated the accumulation of knowledge regarding the performance of surfactants in the theoretical as well as applied aspects. We can consult an overview of the theoretical aspect of mixed micelle formation (Chap.10 in ref.1, or Chap.3 in ref.2), a convenient monograph

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dealing with the molecular interaction and synergism in mixtures of two surfactants (Chap.11 in ref.2, or Chap.3 and Chap.4 in ref.3). Among these monographs, for example, how the Krafft points can be changed, which is desired to be lowered for application, is known from the text (3) on the basis of the previous work performed in 1980 (4).

A few monographs collecting systematically the most recent studies are also available for mixed surfactant systems (5-7). On the other hand, a new field in the research of such binary mixed systems involving different fatty acids is being opened up (8,9); this will probably result in crucial hints for improving surfactant performance.

Previously, we have reported some studies performed by means of surface tension measurements in the series work of this paper, i.e., adsorption and micelle formation of mixed surfactant systems in water: a combination of top-heavy type anionic surfactants (10), II: a combination of cationic gemini-type surfactant with MEGA-10 (11), and III: a combination between cationic gemini/cationic and cationic gemini/nonionic combinations (12). This series work has followed the previous surface tension study on binary mixed systems of anionic/nonionic surfactants, in which synergistically enhanced surface activity and the relationship among compositions of monomers in bulk ($X_2$), micelles ($Y_2$), and adsorbed film at air/water interface ($Z_2$) were discussed in detail (13).

The present paper reports that marked synergistic phenomena in surface activity as well as in micellization were found for three combinations of a typical anionic surfactant, sodium dodecylsulfate (SDS) with $n$-alkyl (octyl, nonyl and decyl)-$N$-glucamides (MEGA-$n[n=8,9,10]$) by means of surface tension measurements (Wilhelmy method), suggesting that these combinations have a strong intermolecular interaction, particularly between head groups.

2 Experimental

2.1 Materials

$n$-Octanol-$N$-methylglucamide (MEGA-8; Lot. FD 046), $n$-nonaoyl-$N$-methylglucamide (MEGA-9; Lot. GM 105), and $n$-decanoyl-$N$-methylglucamide (MEGA-10; Lot. GK 017) of high purity grade were obtained from Dojindo Laboratories (Japan), and purified by recrystallization from absolute methanol. Sodium dodecylsulfate (SDS) was obtained from Fluka, and purified by successive recrystallizing from distilled water (vide infra), drying, and then washing with absolute diethylether. These pure surfactants did not show any shallow minimum in their surface tension ($\gamma$) vs concentration curves. Triple distilled and deionized water ($\gamma = 71.2$ mN m$^{-1}$ at 30°C $\pm 0.03°C$) was used for the preparation of all aqueous solutions. A series of binary mixed solutions were prepared by diluting the respective stock solutions ($0.124 \sim 0.245$ mol kg$^{-1}$ for MEGA-8, $0.101 \sim 0.120$ mol kg$^{-1}$ for MEGA-9, $0.023$ mol kg$^{-1}$ for MEGA-10, and $0.038 \sim 0.083$ mol kg$^{-1}$ for SDS)

2.2 Surface Tension Measurements

Surface tension was measured using Wilhelmy plate method (≈ 4 cm perimeter) with a Dataphysics DCAT 11 tensiometer connected to a water circulator (HAAKE B3). Measurement was conducted at 30°C $\pm 0.03°C$ and at atmospheric pressure. The sample chamber of the surface tensiometer was also kept at the same temperature as the circulating thermostated water. All aqueous surfactant solutions were immersed in a constant temperature water bath of 30°C $\pm 0.1°C$ for 3 hours before placing them on the surface tensiometer. Critical micellization concentrations (CMCs) were determined from the break points of the respective surface tension curves. The standard deviation for the experimental surface tension was less than 0.02 mN m$^{-1}$.

3 Results and Discussion

3.1 Surface Tension Measurements Determining CMC, pC20, CMC/C20, the Surface Excess Concentration, $\Gamma_1$, and the Minimum Free Energy of Adsorbed Film, $G_{\min}^{\infty}$

Figure 1 shows three sets of the plot of surface tension ($\gamma$) against logarithmic total concentration in molality ($m_t$) for the respective pure systems together with two mixed systems, the mole fractions of which are indicated in the respective frames (a), (b) and (c). The $\gamma$-$\ln m_t$ curves for other mixtures at different mole fractions are not shown in order to avoid overcrowding. The concentration giving a clear break in the curve of each single system is, needless to say, critical micellization concentration (CMC), while the CMC for the mixtures is assumed to be the concentration giving the minimum as has previously been reported (13,14). In some
cases surfactant mixtures show such minima because one surfactant acts as an impurity against the others, especially in the case of mixed systems of monovalent ionic surfactants with MEGA-n’s (13-17). Figure 1 tells us the following. (i) The CMC value of MEGA-n single systems decreases with increased hydrocarbon chain length (MEGA-8 > -9 > -10) as was reported previously (18). (ii) The slope of the \( \gamma - \ln m_t \) curve below the CMC of SDS is steeper than those of MEGA-n’s. (iii) Examining the measure of efficiency of adsorption, \( pC_{20} \), as proposed by Rosen (2), the obtained values are 2.2, 2.7 and 3.2 for MEGA-8, -9 and -10, respectively. (iv) Compared with SDS, MEGA-n’s have a stronger ability of surface tension reduction which is presented in terms of surface tension at CMC, \( \gamma_{CMC} \); \( \gamma_{CMC} \) values are 35.5, 34.0 and 32.0 mNm\(^{-1}\) for MEGA-8, -9 and -10 respectively.

\[ \text{Fig. 1} \quad \text{The Plots of Surface Tension } \gamma \text{ versus Logarithmic Concentration in Molality, } \ln m_t. \text{ The curves shown in each frame are for the respective pure systems and two representative mixed systems whose mole fractions are shown in each inset. M8, M9 and M10 indicate MEGA-8, -9 and -10 respectively. Frame (a) shows how to determine } pC_{20}, m_1^0, m_2^0 \text{ and } m_t^0 \text{ for mixtures as example.} \]
-10, respectively, while the $\gamma_{\text{CMC}}$ of SDS is 38.7 mNm$^{-1}$. Comparing the $\gamma_{\text{CMC}}$ values among MEGA-10's the reducing order is in line with that of CMC; this order reflects the extent of hydrophobicity of molecules and accordingly the strength of surface activity. (v) The most important feature is that all the mixed systems show a great synergism in terms of CMC as well as $\gamma_{\text{CMC}}$; the curves of mixed systems are located on the lower concentration side of those of the pure systems. In the previous studies on combinations of MEGA-10 with $\alpha$ sulfonato-myristic acid methyl ester ($\alpha$-SMy·Me) and the propyl ester ($\alpha$-SMy·Pr) (13) in addition to the studies on the mixed systems of sodium perfluorooctanoate (SPFO) with MEGA-9 (14,15), the $\gamma$-ln $m_t$ curves were found to appear on the lower concentration side of those of the respective single systems. These mixed systems are typical examples showing a marked synergism. 

It is noted here that, as has been reported (11,12), for the mixed system of a cationic gemini type surfactant: bis-trimethyl ammonium gemini derived from tartaric acid bromide (BAGTB) with MEGA-10, synergism in surface tension reduction was found to be negligible or rather weak from the examination of partial molecular area (PMA) and the minimum free energy at air/water interface ($G_{\text{CMC}}^{(S)}$) In the case of BAGTB/MEGA-10, the $\gamma$-ln $m_t$ curves of mixed systems showed neither a minimum around CMC nor notable synergism when compared with those of the respective single systems: the curves of different mixtures fit between those of the two single systems and they appeared in the order of mole fraction (11). It is of interest to note that the combination of MEGA-10 with a bile salt, sodium deoxycholate (NaDC) also showed neither a minimum around CMC nor positive synergism in regards to CMC (19).

As for the synergism in terms of surface tension reduction efficiency and its effectiveness, both of which were defined by Rosen (2), these combinations mentioned above will be discussed later in comparison with the present three mixed systems. 

Other than the measure of ‘Efficiency’ of adsorption, pC20, the CMC/C20 ratio itself is also a kind of measure for evaluating micellization and adsorption behavior (eq.5.1 in p.217 of Ref.2), so this value was also determined for each as is listed in Table 1.

In regard to effectiveness of adsorption, i.e. the total surface excess $\Gamma_t = \Gamma_1 + \Gamma_2$, the following relation can be derived for such a mixed system as composed of a 1-electrolyte type ionic surfactant 1 and a nonionic surfactant 2 (11,12).

$$\Gamma_t = -\frac{1}{(2-X_2)RT} \frac{d\gamma}{d\ln m_t}$$  \[1\]

where $X_2$ denotes mole fraction of the surfactant 2 (non-ionic) in bulk solution. It is noted here that $X_2$ can be related to composition in adsorbed film $Z_2$, as will be shown later, so $\Gamma_t$ is also expressed as a function of $Z_2$ (11,12). The total surface excess, $\Gamma_t$ was thus evaluated using the slopes of the straight line just below the CMC of $\gamma$ vs. $ln m_t$ curves (Fig. 1), and together with the slope over $RT (\sigma=-(d\gamma/d\ln m_t)/RT)$, $\Gamma_t$ values are tabulated in Table 1. In parallel with this, the value of mean molecular area, $A_m$ was calculated from the next equation:

$$A_m = \frac{1}{L \cdot \Gamma_t}$$  \[2\]

where, $L$ is the Avogadro’s number. Calculated $A_m$ values in Å$^2$ unit are also included in Table 1. Note that when $A_m$ in Å$^2$ is calculated, eq.2 should be multiplied by 10$^{30}$. The $A_m$ values as a function of mole fractions of $X_2$ or $Z_2$ can offer us important information concerning the interaction between molecules in the adsorbed film, as will be discussed later.

We have proposed a thermodynamic quantity for the evaluation of synergism in mixing, that is, the free energy of the given air/water interface $G_{\text{CMC}}^{(S)}$ which is defined as follows (11,12).

$$G_{\text{CMC}}^{(S)} = A_m \cdot \gamma_{\text{CMC}} \cdot L$$  \[3\]

It is possible to regard $G_{\text{CMC}}^{(S)}$ as the work needed to make an interface per mole or the free energy change accompanied by the transition from the bulk phase to the surface phase of the solution components. In other words, the lower the value of the free energy, the more thermodynamically stable a surface is formed, or the greater surface activity is attained (12). $G_{\text{CMC}}^{(S)}$ values are listed in Table 1.

3·2 Estimate of Compositions of Mixed Micelles ($Y_2$) and Mixed Adsorbed Films ($Z_2$) at Equilibria as well as Interaction Parameters ($\omega_b$ and $\omega_s$)

We are interested in the relation of net mole fraction or bulk solution composition ($X_2$) with micellar composition ($Y_2$) as well as the interaction extent between different molecules in micellar and adsorbed monolayer states. To analyze the CMC as a function of $X_i$ ($i=1,2$)
in terms of the composition of micelles formed at CMC ($Y$) and the interaction parameter ($\omega_R$), Rubingh’s equations (20) have been so far commonly and conveniently used (not shown here. See, for example, refs.1, 2 and 10-17). The interaction parameter, $\omega_R$ has been known to be related with activity coefficients ($f_i$) based on the regular solution theory (RST). Rubingh himself used the symbol $\beta$ for denoting the interaction parameter, however, we have used $\beta$ for denoting the degree of counterion binding since before Rubingh’s use. So we have given the interaction parameter as $\omega_R$. Applying these equations to the CMC data given in Table 1, $\omega_R$, $Y$, and $f_i$ were calculated for the present three mixed systems. The results are included in Table 2, where the ideal CMC values (assumed to be ideal mixing) and the difference of real CMC less ideal one ($\Delta$CMC) are also included; negative values were obtained for all the mixtures. The obtained phase diagrams are shown in Fig. 2.

In Fig. 2, the CMC-$X_2$ curve corresponding to the singly dispersed phase curve of each real mixed system

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Table 2 Values of ideal CMC, $\Delta$CMC, $Y_i$, $\omega_k$, and $f_i$ ($i=1,2$) for mixed systems of SDS with MEGA-n’s. Numerical figures 1 and 2 correspond to SDS and each MEGA-n.

(a) SDS / MEGA-8

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$\omega_k$ ave. = -2.7

(b) SDS / MEGA-9

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$\omega_k$ ave. = -3.1

(c) SDS / MEGA-10

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$\omega_k$ ave. = -3.6

(solid curve with open circles) together with those of ideal mixing calculated using the equation derived from Raoult’s law (shown as indicated by a broken line), are shown in each frame. The CMC-$Y_2$ curve simulated from the resultant CMC-$X_2$ relation is also included (shown as thicker solid line with closed circles) in each
frame. When the two surfactants can form micelles of ideal mixing, needless to say, the CMC-$Y_2$ relation should be linear. As can be seen in Fig. 2 (a), (b) and (c), all of the mixed systems show a conspicuously negative deviation from ideal mixing, producing the averaged $\omega_k$ values of -2.7 for SDS/MEGA-8, -3.1 for SDS/MEGA-9 and -3.6 for SDS/MEGA-10. The obtained values show us that the order in the absolute

---

**Fig. 2** Phase Diagrams of SDS/MEGA-n’s Mixed Systems in Water at 30°C and 1 Atm. (○) Singly dispersed phase curve (CMC-$X_2$ relation) of real mixing; (●) Micellar phase curve simulated for the mixture based on Rubingh’s equations, or CMC-micellar composition ($Y_2$) relation. The broken line in each diagram indicates the CMC-$X_2$ relation of ideal mixing calculated according to Raoult’s law. (The numeral 2 denotes each MEGA-n)
value is strictly in accordance with the order of hydrocarbon chain length and the greatness of the values seems to reflect the extent of synergistic enhancement of micelle formation.

Attention should be paid to azeotropic phenomena caused by a strong attractive interaction and to the fact that the azeotropic point shifts toward the higher X2 as the chain length increases and the interaction extent becomes greater; the azeotropic point is observed at X₂ = 0.25 for SDS/MEGA-8, at X₂ = 0.33 for SDS/MEGA-9 and at X₂ = 0.50 for SDS/MEGA-10. Azeotropic phenomenon as seen here has been observed even for mixtures of MEGA-8, -9 and -10 with perfluorooctanoates (SPFO) (14,15,17), although a kind of mutual phobicity acts between hydrocarbon and fluorocarbon chains (15,21), indicating that the interaction between head groups plays a great role for mixed micelle formation.

Next, let us examine the composition of adsorbed film. In order to estimate compositions of surfactants 1 and 2 in adsorbed film formed at air/water interface (Z₂ and Zᵢ, Zᵢ + Z₂ = 1), we have derived the following equations based on the regular solution theory (RST) (11-13). When the composition of species i (i = 1 or 2) in the adsorbed film phase and the activity coefficient are denoted as Zᵢ and fᵢ, respectively, the concentration is related as:

\[ mᵢ = fᵢZᵢ mᵢ^0 \]  \[4\]

where mᵢ^0 is the bulk concentration of the pure system of i at the constant surface tension, and corresponds to either molarity or molality depending on the concentration chosen. The mass balance leads to eq. 5,

\[ mᵢ + m₂ = (1 - X₂)mᵢ + X₂m₂ = mᵡ \]  \[5\]

where, mᵡ 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.

\[ X₂ = \frac{m₂}{mᵡ + m₂} = \frac{f₂Z₂m₂^0}{f₁(1 - Z₂)m₁^0 + f₂Z₂m₂^0} \]  \[6\]

Based on the RST model, the activity coefficients f₁ and f₂ can be related to Z₂ and the interaction parameter ωᵢ, as follows.

\[ f₁ = \exp[ωᵢZ₂^2] \quad f₂ = \exp[ωᵢ(1 - Z₂)^2] \]  \[7\]

From analogy with the derivation of Rubingh’s equations (20), we obtained the following equations.

\[ (1 - Z₂)^2 \ln \left( \frac{(1 - X₂)mᵡ / (1 - Z₂)m₁^0}{Z₂ \ln(X₁m₁ / Z₂m₂^0)} \right) = 1 \]  \[8\]

\[ ωᵢ = \frac{\ln(X₂mᵡ / Z₂m₂^0)}{(1 - Z₂)^2} \]  \[9\]

Eqs.8 and 9 simultaneously tell us that if the m₁^0, m₂^0 and mᵡ at the given γ are determined against net mole fraction X₂, then the adsorbed film composition Zᵡ is given by eq.8, and ωᵢ can be evaluated from eq.9 by using the Z₂ values (11-13, 22 p.394 in Ref.2). Taking m₁^0 as the CMC of the first component SDS, and m₂^0, for pure MEGA-n’s, the mᵡ for each mixed system was determined by reading the curves of the γ vs ln mᵡ plot (See Fig. 1(a)). The mᵡ values are listed in Table 3. Substituting the data of mᵡ’s, m₁^0 and m₂^0, the composition of surfactant 2 (corresponding to MEGA-n’s), Z₂ was calculated as functions of the net mole fraction, X₂ and mᵡ. The results are shown in Fig. 3 (and the Z₂ values are included in Table 3). Figure 3 is a phase diagram indicating the composition (Z₂) of the adsorbed film phase related with that of the bulk phase (X₂), in other words, the curves of the phase equilibrium by open circles). The calculated Z₂ values are indicated by closed circles. The X₂ values along with the interaction parameter, ωᵢ, and activity coefficients f₁ and f₂ (1 corresponds to SDS and 2 to MEGA-n’s) are listed in Table 3 as a function of X₂.

The obtained mᵡ-Z₂ curve as well as the mᵡ-X₂ curve shows a markedly negative deviation and correspondingly, the curve results in a large negative value of ωᵢ for all the mixed systems. In addition, the absolute values of the negative ωᵢ are greater than those of micelles (|ω₁|>|ω₂|); this situation is similar to that of various mixed systems of MEGA-n’s (10,11,13,15-17). The increasing order of the absolute values (ωᵢ) is in parallel with the order of hydrophobicity or hydrocarbon chain length: -4.2 for SDS/MEGA-8, -4.4 for SDS/MEGA-9 and -4.5 for SDS/MEGA-10 (See Table 3). All the frames in Fig. 3 clearly demonstrate the existence of azeotropic point, found at (a) X₂ = 0.38 for MEGA-8, (b) X₂ = 0.48 and (c) X₂ = 0.55. Similar to these three combinations, azeotropic points have been found at around X₂ = 0.5 for different mixed systems with MEGA-n’s, such as α-SMMy Me/MEGA-10 and α-SMMy Pr/MEGA-10 (13) and SPFO/MEGA-8, -9 and -10 (17).
4 Discussion

4.1 Examination of Adsorbed Film Properties in Terms of Surface Excess $\Gamma$, Partial Molecular Area and Minimum Gibbs Energy at Surface $G^{(S)}$ as Functions of $X_2$ and/or $Z_2$

Plotting the $\Gamma$ data against $X_2$ and $Z_2$ leads to Fig. 4 (a), (b) and (c) for the mixed systems with MEGA-8, -9 and -10, respectively. The left and right hand sides of the azeotropic mixture gave completely independent curves. The curves from both sides seem to coincide at a point; this is the very point of azeotrope. The $\Gamma$ value at the azeotropic point (AzP) itself is determinable, if intrapolated value of $\sigma$ (see Table 1) at the determined azeotropic point in $X_2$ is applied to eq.1. Anyway, at the

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$X_2$ & $m$, at $\gamma = 38.7$ mN m$^{-1}$ & $Z_1$ & $Z_2$ & $\omega_\lambda$ & $f_1$ & $f_2$ \\
\hline
0.000 & 7.64 & & & & & 50.0 \\
0.216 & 5.79 & 0.748 & 0.252 & -3.6 & 0.79 & 0.13 \\
0.399 & 5.00 & 0.657 & 0.343 & -4.3 & 0.60 & 0.15 \\
0.601 & 5.83 & 0.597 & 0.403 & -1.41 & 0.51 & 0.23 \\
0.799 & 6.85 & 0.517 & 0.483 & -4.5 & 0.35 & 0.30 \\
1.000 & 37.85 & & & & & 45.0 \\
\hline
\end{tabular}
\caption{Values of $m$, at $\gamma = 38.7$ mN m$^{-1}$, $Z_i$, $\omega_\lambda$, and $f_i$ ($i = 1, 2$) and PMA for mixed systems of SDS(1) with MEGA-n's(2).
(a) SDS / MEGA-8}
\end{table}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$X_2$ & $m$, at $\gamma = 38.7$ mN m$^{-1}$ & $Z_1$ & $Z_2$ & $\omega_\lambda$ & $f_1$ & $f_2$ \\
\hline
0.000 & 7.640 & & & & & 98.5 \\
0.200 & 3.010 & 0.627 & 0.373 & -4.9 & 0.50 & 0.14 \\
0.402 & 2.970 & 0.559 & 0.441 & -4.5 & 0.41 & 0.24 \\
0.600 & 2.780 & 0.498 & 0.502 & -4.9 & 0.29 & 0.30 \\
0.799 & 4.710 & 0.408 & 0.592 & -3.4 & 0.31 & 0.57 \\
1.000 & 11.160 & & & & & 46.4 \\
\hline
\end{tabular}
\caption{Values of $m$, at $\gamma = 38.7$ mN m$^{-1}$, $Z_i$, $\omega_\lambda$, and $f_i$ ($i = 1, 2$) and PMA for mixed systems of SDS(1) with MEGA-n's(2).
(b) SDS / MEGA-9}
\end{table}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$X_2$ & $m$, at $\gamma = 38.7$ mN m$^{-1}$ & $Z_1$ & $Z_2$ & $\omega_\lambda$ & $f_1$ & $f_2$ \\
\hline
0.000 & 7.640 & & & & & 48.0 \\
0.200 & 2.160 & 0.357 & 0.463 & -4.0 & 0.42 & 0.31 \\
0.399 & 1.330 & 0.463 & 0.537 & -5.3 & 0.22 & 0.32 \\
0.600 & 1.310 & 0.404 & 0.596 & -5.0 & 0.17 & 0.44 \\
0.799 & 1.920 & 0.296 & 0.704 & -3.6 & 0.17 & 0.73 \\
1.000 & 2.980 & & & & & 45.2 \\
\hline
\end{tabular}
\caption{Values of $m$, at $\gamma = 38.7$ mN m$^{-1}$, $Z_i$, $\omega_\lambda$, and $f_i$ ($i = 1, 2$) and PMA for mixed systems of SDS(1) with MEGA-n's(2).
(c) SDS / MEGA-10}
\end{table}
AzP the two curves drawn from the lower mole fraction side and the higher side should coincide to give a $\Gamma_i$ value. (Concerning the extrapolation in Fig. 4(b) and (c), see the figure caption.) If extrapolation of each curve is made so as to coincide at a point, that must be the $\Gamma_i$ value of azeotrope. Extrapolation was used to estimate it as shown with dotted lines in the figures from which it is estimated for azeotrope to form high density film compared to the others, suggesting that a kind of complex of SDS and MEGA-n molecules may be formed to take a thermodynamically favorable state. As for interpretation of the azeotrope the following treat-

**Fig. 3** Phase Diagrams Indicating the Relation of Bulk Concentration ($m_i$) with Compositions in Bulk Solution ($X_2$) and in Adsorbed Film ($Z_2$) at $\gamma=38.7$ mN m$^{-1}$, 30°C and 1 Atm. (The numeral 2 corresponds to each MEGA-n)
Applying eq.2, the mean molecular area, $A_m$, was calculated for each mixed system and the results are shown in Fig. 5. In each frame of Fig. 5 too, similar to the $\Gamma_1$ vs $X_2$ plots, two discrete curves seem infallibly to intersect at a point, and the plot rather easily enables us to find the azeotropic point, $Azp$. (2 = MEGA-n)
to extrapolate the respective curves, as indicated with dotted lines. From both Fig. 4 and 5 the parameters corresponding to each azeotrope, the $I^{(1)}_{(a)}$, $A_m^{(a)}$ and the mole fraction, $X_{2(az)}$ can be estimated for the respective mixed systems as follows: SDS/MEGA-8 (3.4 x 10^{-6} mol m^{-2}, 49 A^2 molecule^{-1}, $X_{2(az)}$=0.38), SDS/MEGA-9 (4.2 x 10^{-6} mol m^{-2}, 40 A^2 molecule^{-1}, $X_{2(az)}$=0.48) and SDS/MEGA-10 (4.8 x 10^{-6} mol m^{-2}, 35 A^2 molecule^{-1}, $X_{2(az)}$=0.55). Increases in $A_m$ and $X_{2(az)}$ with hydrocarbon chain length may be connected not only with the extent of interaction acting between hydrophobic groups but also with the probability of formation of thermodynamically stabilized complexes, or in other words, the population of dimeric complexes formed with one SDS molecule and one MEGA-n molecule. It has been known that from the real mixed systems with MEGA-n’s (13).

Fig. 6 (a), (b) and (c) were obtained in the same manner as done in the previous studies (11-13, 23). The plot of PMA vs $X_2$ is not shown, but basically a similar figure is obtainable.

Before describing the results shown in Fig. 6, one should know that if binary components are ideally mixed, the PMAs of both components are not varied with composition change but keep the same area as those of the respective pure systems (as indicated by dotted straight lines). Frames (a) and (b) in Fig. 6 indicate that the absolute values themselves are different but such common trends as the following are seen. Namely, looking at PMA in the range value $Z_2=0.2 \sim 0.3$ (on l. h. s. of azeotrope), where the minor component is MEGA-n and the major one is SDS, the PMA of the major (SDS) hardly changes, but approaching AzP it increases very rapidly toward positive infinity. On the other hand, the PMA of the minor (MEGA-n) is wider than that of pure MEGA-n but it decreases rapidly toward negative region as the composition closes to AzP. In contrast, in the range above $Z_2=0.8 \sim 0.9$, although the PMA of the major (MEGA-n) remains approximately constant and that of the minor component (SDS) shows a wider area than that of pure SDS (the relation of the major with the minor is similar to the r. h. s of AzP), as the composition or $Z_2$ moves closer to AzP, very rapid increases and decreases are seen. In other words, the relation of the positive or negative sign of each infinity goes into reverse at AzP, or the majority has a positive approach to AzP while the minority has a negative approach to AzP.

As for the PMA behavior around AzP, the conspicuously negative/positive PMAs may be cancelled out between the binary components to give an averaged value of PMA. This also suggests that adsorption (and micellization, too) accompanies a dimeric complex formation of SDS with MEGA-n molecules as has been considered for mixed systems with MEGA-n’s (13).

Turning our attention to the minimum surface free energy $G_{\min}^{(S)}$ defined as eq.3, the extent of lowering the free energy may be a measure for evaluation of synergism in mixed surfactant systems. In previous studies, $G_{\min}^{(S)}$ was plotted against $X_2$ and the $G_{\min}^{(S)}$ value of the BAGTB pure system was connected with that of HTAB or MEGA-10 pure system by a straight line by which it was shown how the real mixed systems deviated from it (12). Here note that the linear relation between $X_2$ and $G_{\min}^{(S)}$ was based on the assumption that $G_{\min}^{(S)}$ might satisfy the additivity rule, when an ideally mixed film is formed. However, reconsidering this, it is known that area $A_m$ itself satisfies the additivity rule in the case of ideal mixing, $G_{\min}^{(S)}$ which is the product of $\gamma_{\CMC}$ and $A_m$(See eq.3) cannot simultaneously satisfy this rule. Then, the following assumption may be necessary. Supposing that not only the mean molecular area $A_m$ but also the minimum surface tension $\gamma_{\CMC}$ is linear with mole fraction $X_2$ in the mixture of surfactants 1 and 2, $G_{\min}^{(S)}$ as a function of $X_2$, $G_{\min}^{(S)}(X_2)_{\text{ideal}}$, may be given as:

$$G_{\min}^{(S)}(X_2)_{\text{ideal}} = A_m^{(X_2)} \gamma_{\CMC}(X_2) \cdot L$$

$$= G_{\min}^{(S)}(1) + \left[ \left( \frac{\Delta A_{m}}{\Delta X_2} \gamma_{\CMC}^{(1)} X_2^2 \right) \right] \cdot L$$

where, $\Delta A_{m}^{(1)}$ denotes the difference of $\gamma_{\CMC}^{(1)}$ minus $\gamma_{\CMC}^{(2)}$ and $\Delta A_{m}^{(1)}=A_m^{(1)} - A_m^{(1)}$. In Fig. 7, the dotted curve indicates the relationship calculated according to eq.10.

One of the present authors (together with other coworkers) has reported two papers on thermodynamic studies of solution properties of nonionic surfactants and their mixtures: one is regarding the combination of MEGA-9 with MEGA-10 (24) and the other is regarding the two combinations of polyoxyethylene (10) alkyl ethers $[C_{E_{10}, n=12 \sim 16 (Brij 56)]$ with MEGA-10 (25). In the former mixed system, as can be expected from the combination of like molecules, MEGA-9 and MEGA-10 were found to form micelles of ideal mixing. In contrast, the latter two combinations demonstrated...
note-worthy positive synergism in terms of different thermodynamic parameters such as Gibbs energy, enthalpy and adsorption in addition to aggregation number.

It is noted that for the respective 1:1 mixtures of C12E10/MEGA-10 and Brij 56/MEGA-10 for example, the \( \omega_R \) value was -6.1 and -7.7 and throughout the mixtures at different mole fractions the \( \omega_R \) was in average -6.5 and -6.7, respectively, at 30 °C. This indicates that the interaction between polyoxyetylene and -N methyl glucamide is markedly strong and it can interpret the remarkable synergism. In connection with the head group interaction, the cloud points (C.P.) of both C12E10 and Brij 56 mixed with MEGA-10 at varied mole ratios in the presence of 1M and 2M NaCl were found to be prominently raised, e.g., the C.P. of Brij in 2M NaCl was 50 °C but it was raised up to 90 °C with addition of MEGA-10 (\( X_2 = 0.8 \)). Although the C.P. decreased in the presence of NaCl for pure C12E10 and Brij 56, MEGA-10 caused an increase in C.P. for both mixed systems.

*Fig. 5* Mean Surface Area, \( A_m \), Occupied by a Molecule in Mixed Adsorbed Film. The intersection of two dotted curves extrapolated from lower and higher mole fraction ranges appears at the azeotropic point. (2 = MEGA-n)
Synergism of Surface Activity

According to Hua and Rosen (p. 404 in Ref. 2), the efficiency of surface tension reduction by a surfactant has been defined as the solution phase surfactant concentration required to produce a given surface tension. Synergism in this respect is present in an aqueous system containing two surfactants when a given surface tension can be attained at a total mixed surfactant concentration lower than that required of either surfactant singularly. From the relation upon which equations 8 and 9 are based and the definition of synergism, it has been shown mathematically, that i) \( \omega_\lambda \) must be negative, and ii) \( |\omega_\lambda| \) must be greater than \( |\ln m_{t1(1)}/m_{t2(2)}| \).

Fig. 6  Partial Molecular Surface Area, PMA, as a Function of Mole Fraction in the Adsorbed Film of the Respective Mixed Systems. (2 = MEGA-n)
Further, one of the conditions for synergism in surface tension reduction effectiveness to occur is: iii) $\omega_A - \omega_B$ must be negative (another condition is given (p.409 in Ref.2), but is not introduced here). Based on these synergism conditions, the data of surface tension measurements were examined in terms of “efficiency” and “effectiveness”. Table 4 lists the results for various combinations not only of SDS with MEGA-n’s but also other surfactant mixtures for comparison. All the values in the table are based on our previous surface tension studies of binary surfactant mixed systems: $\alpha$-Sulfonylmyristic acid methyl ester ($\alpha$-SMy·Me)/MEGA-
the same acid’s isopropyl ester (α-SMy·iPr)/MEGA-10 (13), sodium perfluorooctanoate (SPFO)/MEGA-9) (15,17), sodium deoxycholate (NaDC)/MEGA-10 at pH=10 in borate buffer solution at 30°C (19)), bis-ammonium Gemini derived from tartaric acid dibromide salt (BAGTB)/MEGA-10 (11) and in addition, α-SMy·iPr/a hybrid surfactant FC6-HC4 (10) and BAGTB/hexadecyl trimethyl ammonium bromide (HTAB) (10). In the table, “yes” or “no” denotes whether the conditions for synergism are satisfied or not, respectively. From the table it can be seen that the mixed systems of MEGA-9 or MEGA-10 with surfactants having a single alkyl chain, such as SDS, α-SMy·Me and α-SMy·iPr and even SPFO which has a phobicity against hydrocarbon, show a marked synergism.

Even the hybrid surfactant FC-6HC-4 having a fluoro-carbon chain revealed to some appreciable extent a positive synergism; this also suggests that the interaction between head groups or steric fitness of different groups also contributes to the display of synergism.

It should be noted, here, that a bile salt whose hydrophobicity comes from β-side surface of its steroid skeleton, NaDC and MEGA-9 do form micelles of positive Ωb although they form an adsorbed film of negative Ωa, but this combination, in total, shows little effectiveness as well as efficiency in regard to surface tension reduction. Similar to this combination, neither combination of BAGTB, which has a bulky hydrophobic moiety, with MEGA-10 or with HTAB displayed appreciable synergism: the former is poor in effectiveness and

<table>
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<th>Efficiency</th>
<th>Effectiveness</th>
<th>References</th>
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<td>(19) J. Colloid Interface Sci., 208 (1998)</td>
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<td>(12) J. Oleo Sci., 52, 509 (2003)</td>
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the latter is weak in efficiency. Interestingly, these combinations being poor in synergism did not show characteristic minima around CMC in the plot of $\gamma$ vs $\ln m_t$.

Considering the results shown in Table 4, it may be concluded that mixed systems of BAGTB with conventional single-chain surfactants can exert little or no synergism. Similar to the case of BAGTB, combinations of a cationic Gemini with HTAB and with dodecyl trimethylammonium bromide (DTAB) have shown no synergism (26). However, a different Gemini mixed with conventional surfactants could have positive synergism (27). These contrasting results suggest that synergism in micelle formation as well as surface activity depends on the combination of both interactions between hydrophobic groups and between hydrophilic groups, resulting from a favorable packing of different molecules with each other.

In studies on a mixed system of an anionic Gemini surfactant with a sodium soap with twelve carbon atoms in terms of mixed CMC, foam volume and degree of micellization (28) and solubilization of orange OT by the same surfactant mixture (29), positive and negative deviations from ideal mixing in regard to micelle formation were found below and above $X_2=0.6$ (2 corresponds to the soap), respectively. Further, maximum foam volume and minimum surface tension were attained at $X_2=0.6$. Even in solubilization behavior, a break at $X_2=0.6$ was found. From the results 2:1 complex formation over a broad region of composition during micellization was suggested (29). Similar behavior, i.e., dimeric units formation of SDS with MEGA-n’s can be speculated and dimers or complexes formation may be related to the exertion of synergism.

In conclusion, the three mixed systems of SDS with MEGA-8, -9 and -10 were found to show remarkable synergism in micelle formation as well as adsorbed film formation. Analyses of CMC-$X_2$ curve and $m_t$-$X_2$ curve on the basis of RST show us that between bulk composition ($X_2$) and micellar composition ($Y_2$) and between $X_2$ and adsorbed film composition ($Z_2$), an azeotropic point exists in both relations for the three mixed systems. Including the surface tension data of mixed surfactant systems reported previously, it was found that MEGA-n series surfactants can, in general, synergistically enhance surface activity and micelle forming ability by mixing with conventional surfactants, suggesting that their head group-N-methyl glucamide can interact with any type of head groups; i.e. nonionic, anionic and cationic ones.

Acknowledgments

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