Experimental and Theoretical Studies of Cationic Gemini Surfactant and Anionic Sodium Lauryl Ether Sulfate

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Abstract: The mixed micellization of dimeric 1,2-bis(dodecyl[dimethyl ammonium]ethane dibromide (CGS1) and sodium lauryl ether sulfate (SLES) has been investigated. The surface tension was measured as a function of the concentration of the surfactants in aqueous solutions at 25 and 35°C using a surface tensiometry and electrical conductometry apparatus. From these measurements, the critical micelle concentration (CMC), the thermodynamic parameters (X, γ, α, ΔH_mic), and the interfacial parameters (γ_{CMC}, pC_{20}, Θ_{max}, dγ/dlogC, A_{min}, CMC/C_{50}) were calculated and analyzed by means of equations derived from the nonideal mixed micelle model. Structural effects on the adsorption and micellization and the effectiveness of surface tension reduction are discussed in terms of these parameters. The kinds and degrees of interactions between the different surfactant molecules are explained on the basis of a regular solution model. The interaction parameter, β, was calculated to be -4.38 for the SLES/CGS1 system at 25°C and -4.72 at 35°C. These negative values indicate a reduction in the free energy of micellization over that predicted by the ideal solution theory, and reflect the synergistic behavior of the components (SLES and CGS1) in the mixed micelle. The behavior of this mixed surfactant system at interfaces and in dilute solution (viscosity, solubilization, and foaming power) is also reviewed.

Keywords: mixed micellization, dimeric 1,2-bis(dodecyl[dimethyl ammonium]ethane dibromide (CGS1), sodium lauryl ether sulfate (SLES), synergistic behavior, thermodynamic

Introduction

Surfactants are used in many industrial fields, such as paints [1], cosmetics [2], pharmaceuticals [3], pesticides [4], foods [5], and enhanced oil recovery [6]. In technological and domestic applications, surfactant mixtures are frequently used, either because the commercial surfactants contain mixtures of different alkyl chain lengths and isomeric forms or because the surfactants are deliberately mixed to optimize some aspect of their performance [7]. The superior properties of mixed surfactants, as compared to single surfactants, and their relatively lower production costs, have been highlighted in several cases. Because mixtures of different surfactant types often provide synergistic effects, such as lowering the surface tension, CMC, and the growth of micelles, mixed surfactant systems, including all combinations of typical nonionic, anionic, and cationic surfactant types, have been studied from economical and practical standpoints.

Studies on the synergism of mixed surfactant systems have been conducted on mixed ionic-ionic and ionic-nonionic surfactants. In particular, cationic-anionic surfactant mixtures have much higher surface activities than do their individual components, owing to the strong interactions between the two oppositely charged surface-active ions [8]. Most mixed cationic-anionic surfactant systems precipitate at equimolar concentrations in aqueous solutions, but at nonequimolar concentration, the mixtures form micelles of various sizes and shapes, liquid crystalline phases, small bilayer vesicles, and dilute lamellar phases. The formation of aggregates and their transformations are decided in terms of interaction forces and the geometric structures of the surfactants. Cationic-anionic surfactant mixtures are used widely in household goods, such as cosmetics, hair care, and body care, products, because their manufacturers require the washing effect of an anionic surfactant and the conditioning effect (anti-static effect and softness) of a cationic surfactant. We selected a cationic gemini surfactant and a conventional

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anionic surfactant for this present study. Very few studies of synergistic effects and measurements involving mixtures of conventional and Gemini surfactants have been reported to date.

Surfactants having two identical hydrophilic head groups and two hydrophobic tail groups in same molecule are called gemini surfactants [9], and they are an attractive subject for advanced international research. A gemini surfactant is covalently connected by a spacer. The spacer can vary in length and chemical structure, be rigid or flexible, and be hydrophobic or hydrophilic. The presence of two charge-sites in an ionic gemini surfactant suggests that both neutral and charged forms can exist, unlike conventional surfactants. The current interest in such surfactants arises from two essential properties:

1. Gemini surfactants have a lower value of CMC, and can produce lower surface tensions for an equivalent molar or mass concentration, and have better wetting properties than do the corresponding conventional (monomeric) surfactants [10-19].

2. Aqueous solutions of dimeric surfactants having short spacers can have very high viscosities at relatively low concentrations, whereas solutions of the corresponding monomeric surfactants have low viscosities.

Gemini surfactants are widely used as effective emulsifiers, corrosion inhibitors, dispersants, anti-foaming agents, and detergents. Recently, these compounds have also found application in the solubilization of dyes and pigments in the textile industry [20], in the synthesis of highly mesoporous materials [21], and in gene therapy [22].

The cationic Gemini surfactant that we studied was dimeric 1,2-bis(dodecyldimethyl ammonium)ethane dibromide (CGS1). For the anionic surfactant, sodium lauryl ether sulfate (SLES) was used. This surfactant does not wash the lipids completely from the surface of skin, and so it keeps skin smooth after washing. It is also highly biodegraded in water and is less skin-irritative than alkaline soap. SLES is widely used in cosmetics, such as cleansers, cream soaps, shampoos, and rinsers.

Studies involving these cationic gemini (CGS1) and anionic surfactants (SLES) have focused on the search for synergism in micellization. In this paper, we have studied the thermodynamic parameters [23-28], interfacial parameters [29-37], the mixed CMC, the interaction parameter, the solubilization, the viscosity, and the foaming power of aqueous solutions of these mixtures when their mixing ratio was changed. For the sake of comparison, we have also measured the interaction parameter (β) for a mixture of the conventional nonionic surfactant and the cationic Gemini surfactant (CGS1).

**Materials**

The cationic Gemini surfactant of the type \(N\)-alkanediy1 1,2-ethanebis(dimethylammonium bromide) was prepared from \(N,N,N,N\)-tetramethylethylenediamine (Aldrich Chemical Co.) and the corresponding alkyl bromide (n = 12) in acetonitrile under reflux for 24 h using an excess of the bromide (20%). After evaporation of the solvent, the crude product was recrystallized from acetone ethanol. The anionic surfactant SLES (Sunjin Chemical Co.) was used after recrystallization (three times) from ethanol. Figure 1 shows the chemical structures of CGS1 and SLES.

**Surface Tension Measurements**

Surface tensions were measured using a CBVP-A3 tensiometer equipped with a Pt-Ir du Nouy ring. All measurements were performed using freshly made solutions at 25 ± 0.1 and 35 ± 0.1°C. Measurements were taken until constant surface tension values indicated that equilibrium had been reached. The surfactant solution was added through a micropipet to water in a thermostatted glass beaker. The water was deionized and ultrapure and was provided by a Milli-Q Ultrapure Water System (Millipore Ltd., Canada). This water had an electrical conductivity of 11 nS m⁻¹ and a pH of 5.5 when it was saturated with CO₂ from air.

**Electrical Conductivity Measurements**

For determining the CMC of the mixed surfactant solution, specific conductivity data were measured using a conductometer (type WTW LF90) and a WTW KLE1 cell. The water was doubly distilled after passing it through a reverse osmosis membrane and ion exchange resin. The temperature was controlled within 0.1°C using a thermostat bath (Water BATH C-WBE, Chang Shin Science, Korea). Critical micellar concentrations (CMCs) were derived from the break points in the plots of specific conductivity versus concentration.

**Relative Viscosity Measurements**

The relative viscosities of aqueous solutions of the binary surfactant systems were measured using an Ostwald-type viscometer.
Solubilization Measurements
The solubilization of azobenzene in SLES/CGS1 surfactant mixtures was measured as follows. Aqueous solutions of a given surfactant mixture, covering a suitable range of concentrations below and above its critical micelle concentration (CMC), were prepared using distilled water. After an excess of azobenzene was added to these solutions, they were sonicated for 30 min and then shaken to reach saturation for 3 days at 298 ± 0.2 K in a water bath incubator. These mixtures were then centrifuged and the supernatants obtained were diluted with 70% aqueous ethanol solution. The concentration of azobenzene in 70% aqueous ethanol solution was determined spectrophotometrically from the absorbance of the solution at λmax. The optical density of the solution at the maximum absorption was measured using a Shimadzu UV 3100 spectrophotometer at 25°C. It is important to be aware that the solubility method is a very empirical parameter; slight variations in the centrifugation or hydration conditions could cause a change in the apparent solubility. The concentration of solubilized azobenzene was determined from the calibration curve.

Foaming Power Measurements
Foamability measurements were performed by vigorous shaking of a 100-mL graduated cylinder, which was placed in a water bath at 30°C. The measurements were undertaken by shaking 15 mL of the sample solution for 20 s. The foamability was recorded as the volume of foam produced immediately after shaking. The measurement was repeated at least five times for each sample.

Results and Discussion
Critical Micelle Concentration of CGS1/SLES/Water Systems
Figure 2 show the surface tension curves of SLES/CGS1 mixed surfactant systems as a function of the logarithm of the total surfactant concentration. The surface tensions decreased upon increasing the total surfactant concentration, and each surface tension curve had a break point, which was taken as the mixed critical micelle concentration (CMC).

Typical conductance total concentration plots of SLES/CGS1 surfactant mixtures at 25 and 35°C are shown in Figures 3 and 4, respectively. The CMC was determined as the concentration at the intersection of the lines from the plots of conductance vs. total molar concentration. Figures 2-(a) and 3-(a) show that the values of CMC of CGS1 at these temperatures are low, 41.7 and 38.7 mM, respectively. These concentration correspond closely to the values of 50.2 and 41.7 mM obtained by the surface tension method at 25 and 35°C. For SLES, the plots in Figures 2-(d) and 3-(c) yield CMC values of 59.5 and 17.9 mM. For the SLES/CGS1 mixture having SLES molar fraction of 0.2, the conductivity plots shown in Figures 2-(b) and 3-(b) yield mixed CMC values of 64.5 and 48 mM at 25 and 35°C, respectively. Meanwhile, for SLES/CGS1 mixtures having SLES molar fractions of 0.4, 0.6,
and 0.8, the CMC could not be determined from the conductivity data. For these values, the conductivities appeared to have constant slopes, as shown in Figure 2-(c). In contrast to the mixed surfactant systems, those of pure SLES and CGS1 exhibited sharp changes in slopes in their electrical conductivity data. The values of mixed CMC for SLES/CGS1 surfactant mixtures are listed in Table 1 in relation to their mixture compositions.

Thermodynamic Properties for SLES/CGS1 Surfactant Mixtures with Respect to their Mixture Compositions

According to Rubingh [38], if two surfactants are mixed together, their mixed CMC ($C^*$) values are given by the equation

$$\frac{1}{C^*} = \frac{\alpha}{f_1C_{1*}} + \frac{(1-\alpha)}{f_2C_{2*}}$$

(1)

Table 1. Values of Mixed CMC for SLES/CGS1 Surfactant Mixtures with Respect to their Mixture Compositions at 25°C and 35°C

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Method</th>
<th>Mixed CMC ($\times 10^4$ mol/kg) at 25°C</th>
<th>Mixed CMC ($\times 10^4$ mol/kg) at 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface Tension</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td>5.02</td>
<td>4.17</td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>7.85</td>
<td>6.45</td>
</tr>
<tr>
<td>0.4</td>
<td></td>
<td>4.14</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>5.64</td>
<td>5.95</td>
</tr>
</tbody>
</table>
where $\alpha$ is the mole fraction of surfactant 1 in the total mixed solute, $f_1$ and $f_2$ are the activity coefficients of surfactants 1 and 2, respectively, and $C_1$ and $C_2$ are the values of CMC of surfactants 1 and 2, respectively. In the case of ideal behavior, $f_1 = f_2 = 1$; hence, Equation (1) may be written as

$$\frac{1}{C^*} = \frac{\alpha}{C_1} + \frac{(1-\alpha)}{C_2} \quad (2)$$

The mixed CMC ($C^*$) value calculated using the equation above for ideal behavior is also plotted against the mole fraction of SLES in Figures 5 and 6. We observe that the mixed CMC values obtained experimentally are lower than those obtained by assuming ideal behavior.

Rubingh used the phase separation model of micellization and regular solution [39,40] approximation to explain

\[
\begin{align*}
\text{(a) SLES/CGS1 = 0/1} & \quad y = 11.127x + 37.051 \quad r = 0.999 \\
\text{(b) SELS/CGS1 = 1/4} & \quad y = 30.157x + 48.115 \quad r = 0.999 \\
\text{(c) SLES/CGS1 = 1/0} & \quad y = 44.860x + 34.694 \quad r = 0.999 \\
\end{align*}
\]

Figure 4. Typical plots of conductance vs. total concentration for SLES/CGS1 surfactant mixtures at 35°C.

Figure 5. Mixed CMC of SLES/CGS1 surfactant mixtures at 25°C. The solid line represents nonideal mixing ($\beta = -4.38$) and the dashed line represents ideal mixing.
Table 2. Thermodynamic Parameters for SLES/CGS1 Surfactant Mixtures with Respect to their Mixture Compositions at 25°C

<table>
<thead>
<tr>
<th>α</th>
<th>X₁</th>
<th>β</th>
<th>ΔHmic</th>
<th>f₁(SLES)</th>
<th>f₂(CGS1)</th>
<th>α₁&lt;sup&gt;M&lt;/sup&gt;</th>
<th>α₂&lt;sup&gt;M&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.4134</td>
<td>-0.9940</td>
<td>-2.5000</td>
<td>0.7103</td>
<td>0.8438</td>
<td>0.2936</td>
<td>0.4950</td>
</tr>
<tr>
<td>0.4</td>
<td>0.5128</td>
<td>-9.2575</td>
<td>-23.987</td>
<td>0.1111</td>
<td>0.0877</td>
<td>0.0570</td>
<td>0.0427</td>
</tr>
<tr>
<td>0.6</td>
<td>0.5685</td>
<td>-7.2532</td>
<td>-18.4534</td>
<td>0.2591</td>
<td>0.0959</td>
<td>0.0959</td>
<td>0.0414</td>
</tr>
<tr>
<td>0.8</td>
<td>0.3657</td>
<td>-5.4435</td>
<td>-13.1401</td>
<td>0.5281</td>
<td>0.0951</td>
<td>0.3472</td>
<td>0.0326</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Thermodynamic Parameters for SLES/CGS1 Surfactant Mixtures with Respect to their Mixture Compositions at 35°C

<table>
<thead>
<tr>
<th>α</th>
<th>X₁</th>
<th>β</th>
<th>ΔHmic</th>
<th>f₁(SLES)</th>
<th>f₂(CGS1)</th>
<th>α₁&lt;sup&gt;M&lt;/sup&gt;</th>
<th>α₂&lt;sup&gt;M&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3465</td>
<td>0.7472</td>
<td>1.8136</td>
<td>1.3759</td>
<td>1.0939</td>
<td>0.4767</td>
<td>0.7149</td>
</tr>
<tr>
<td>0.4</td>
<td>0.5411</td>
<td>-5.0070</td>
<td>-13.3271</td>
<td>0.3484</td>
<td>0.2308</td>
<td>0.1885</td>
<td>0.1059</td>
</tr>
<tr>
<td>0.6</td>
<td>0.5621</td>
<td>-9.1569</td>
<td>-24.1602</td>
<td>0.1728</td>
<td>0.0554</td>
<td>0.0971</td>
<td>0.0243</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6575</td>
<td>-5.4435</td>
<td>-13.1401</td>
<td>0.5281</td>
<td>0.0951</td>
<td>0.3472</td>
<td>0.0326</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6. Mixed CMC of SLES/CGS1 surfactant mixtures at 35°C. The solid line represents nonideal mixing (β = -4.72) and the dashed line represents ideal mixing.

This nonideal behavior [41,42] to derive the equation. For the present mixed solutions, we have used the following equation at constant temperature and pressure:

\[ \frac{X_1^2 \ln(C^*_{a_1}/C_1 X_1)}{(1-X_1)^2 \ln [C^*(1-\alpha)/C_x(1-X_1)]} = 1 \]  

(3)

where \( X_1 \) is the mole fraction of surfactant 1 in the mixed micelle. Equation (3) can be solved iteratively to obtain the value of \( X_1 \), from which the interaction parameter, \( \beta \), can be evaluated using the equation

\[ \beta = -\ln \left[ \frac{C^*_{a_1}}{(1-X_1)^2 \ln [C^*(1-\alpha)/C_x(1-X_1)]} \right] \]

(4)

Values of \( \beta \) not only indicate the interaction between the two surfactants but also the deviation from the ideal behavior. We found for the SLES/CGS1 surfactant system that the \( \beta \) values obtained at various mole fractions of SLES no longer remained constant. The interaction parameter, \( \beta \), was calculated to be -4.38 for the SLES/CGS1 surfactant system at 25°C and -4.72 at 35°C. These negative values indicate a reduction in the free energy of micellization over that predicted by the ideal solution theory, i.e., for synergistic behavior of SLES and CGS1 surfactants in the mixed micelle, and is quite comparable to the value \( \beta = -2.2 \) for the mixed CMC of CGS1/hexaoxyethylene dodecylether (C₁₂E₆).

The mole fraction \( X_1 \) of SLES in the mixed micelles increased with increasing \( \alpha \), as expected [Tables 2 and 3]. The value of \( \Delta H_{mic} \) was negative, except at \( \alpha = 0.2 \) at 35°C. These negative values signify that the mixed micellization of SLES/CGS1 surfactant mixtures are characterized by exothermic desolvation.

The thermodynamic parameter of micellization, expressed by standard enthalpies, \( \Delta H_{mic} \), are calculated from the equation

\[ \Delta H_{mic} = X_1(1-X_1) \beta RT \]  

(5)

The values of the activity coefficients (\( f_1 \) and \( f_2 \)) are calculated as follows [43]:

\[ f_1 = \exp[\beta(1-X_1)^2] \]

(6)

\[ f_2 = \exp[\beta X_1^2] \]

(7)

In addition, the activity coefficients (\( \alpha_1^M \) and \( \alpha_2^M \)) in the mixed micelle are calculated using the following expressions [44,45]:

\[ \alpha_1^M = f_1 X_1 \]

(8)

\[ \alpha_2^M = f_2(1-X_1) \]

(9)
Table 4. Interfacial Parameters for SLES/GCS1 Surfactant Mixtures with Respect to their Mixture Compositions at 25°C

<table>
<thead>
<tr>
<th>α</th>
<th>γ_{CMC}</th>
<th>pC_{20}</th>
<th>10^{14} \Gamma_{\text{max}}</th>
<th>-dγ/d\log C</th>
<th>A_{\text{min}}</th>
<th>CMC/C_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>39.57</td>
<td>4.40</td>
<td>1.78</td>
<td>20.32</td>
<td>93.32</td>
<td>12.61</td>
</tr>
<tr>
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<td>47.35</td>
<td>4.27</td>
<td>2.96</td>
<td>16.88</td>
<td>56.17</td>
<td>14.77</td>
</tr>
<tr>
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<td>45.86</td>
<td>4.83</td>
<td>3.51</td>
<td>20.06</td>
<td>47.29</td>
<td>27.79</td>
</tr>
<tr>
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<td>3.91</td>
<td>22.34</td>
<td>42.44</td>
<td>6.19</td>
</tr>
<tr>
<td>0.8</td>
<td>11.45</td>
<td>-</td>
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<td>0.70</td>
<td>73.30</td>
<td>-</td>
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<td>40.27</td>
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<td>1.78</td>
<td>10.17</td>
<td>93.25</td>
<td>13.31</td>
</tr>
</tbody>
</table>

Table 5. Interfacial Parameters for SLES/GCS1 Surfactant Mixtures with Respect to their Mixture Compositions at 35°C

<table>
<thead>
<tr>
<th>α</th>
<th>γ_{CMC}</th>
<th>pC_{20}</th>
<th>10^{14} \Gamma_{\text{max}}</th>
<th>-dγ/d\log C</th>
<th>A_{\text{min}}</th>
<th>CMC/C_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>38.97</td>
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<td>1.63</td>
<td>19.15</td>
<td>102.37</td>
<td>9.74</td>
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<td>13.68</td>
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</tr>
<tr>
<td>0.4</td>
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<td>5.71</td>
<td>3.53</td>
<td>20.84</td>
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<td>38.29</td>
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<tr>
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<td>58.98</td>
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<td>67.05</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>40.29</td>
<td>5.44</td>
<td>1.96</td>
<td>11.55</td>
<td>84.84</td>
<td>42.76</td>
</tr>
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</table>

Table 6. Degree of Micellar Ionization (M) for SLES/GCS1 Surfactant Mixtures with Respect to their Mixture Compositions at 25 and 35°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Above CMC (S1)</td>
<td>Below CMC (S2)</td>
</tr>
<tr>
<td>0.0</td>
<td>9.6098</td>
<td>17.6600</td>
</tr>
<tr>
<td>0.2</td>
<td>72.5409</td>
<td>30.4026</td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>65.3606</td>
<td>31.6585</td>
</tr>
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</table>

Interfacial Properties for SLES/GCS1 Surfactant Mixtures with Mixture Composition

The term γ_{CMC} is the surface tension value at the CMC and pC_{20} is the negative log of the surfactant molar concentration, C_{20}, required to reduce the surface tension of the solvent by 20 mN/m. The CMC/C_{20} ratio is the tendency to form micelles relative to the tendency to adsorb at the air/water interface. This parameter measures the efficiency of adsorption. The term Γ_{max} denotes the surface excess, which is a measure of how much of the interface that has been changed by the surfactant depends on the structural groupings in the surfactant molecule and its orientation at the interfaces; it is expressed by the equation [46]

\[ Γ_{\text{max}} = -\frac{(dγ/d\log C)}{2.333nRT} \]  

where dγ/d\log C is the slope of the plot of γ versus log C at a constant absolute temperature T; R = 8.314 J/molK. The n value is a constant number that depends on the number of species constituting the surfactant and that are adsorbed at the interface. For the gemini surfactant under study, n was taken as 2 and Γ_{max} is measured in mol/m². The effectiveness of adsorption is related to the interfacial area occupied by the surfactant molecules (A); the smaller the effective cross-sectional area of the surfactant at interface, the greater is its effectiveness of adsorption. The Γ_{max} values were used to calculate the minimum area (A_{min} in Å²/molecule⁻¹) at the aqueous-air interface using the relationship

\[ A_{\text{min}} = \frac{10^{15}}{N\Gamma_{\text{max}}} \]  

where N is Avogadro’s number and the unit of A is measured in Å².

The values of γ_{CMC}, pC_{20}, Γ_{max}, -dγ/d\log C, A_{min}, and CMC/C_{20} are listed in Tables 4 and 5.

The degree of micellar ionization (M) calculated from the slope below and above the CMC obtained from the conductance data in Figures 3 and 4 is shown in Table 6. The degree of micelle ionization (M) decreases as the surface charge density increases or as the surface area per ionic head group decreases. The degree of micelle ionization of the SLES/GCS1 surfactant mixture was smaller than those of the corresponding pure surfactants.

Cationic-anionic surfactant mixtures have much higher surface activities than do their individual components.
Relative Viscosity, Solubilization, and Foaming Power of SLES/CGS1 Surfactant Mixtures with Respect to Their Mixture Composition

The relationship between the relative viscosity and the mole fraction of SLES for SLES/CGS1 surfactant mixtures is shown in Figure 7. The relative viscosities of SLES/CGS1 mixtures were almost identical in the mole fraction range 0.0~0.8 of SLES and then they decreased suddenly. Assuming that no interaction takes place between the two surfactants, the ideal line can be drawn between the relative viscosities of two single surfactants, as shown by the dashed line in Figure 7. Thus, the experimental values are higher than the ideal values at all mole fractions of SLES. This deviation from ideal behavior is obviously due to the formation of mixed micelles in the two surfactants systems.

Figure 8 shows the solubilization behavior of azobenzene for the SLES/CGS1 surfactant mixture. The solubilized amounts were almost identical in the mole fraction range 0.2~0.8 of SLES and were considerably larger than those of the respective surfactants. It has been reported [47] that azobenzene is soluble in the hydrocarbon core for ionic surfactant micelles. Accordingly, increased solubilization [48-52] in the mixed micelles may indicate that the hydrocarbon core of the mixed micelles is mixed tightly. The difference in the solubilization is probably due to the different solubilization sites of the two compounds in the micelle. The polar materials are solubilized in the outer shell of the micelle having its polar groups at the micelle-water interface, while the nonpolar materials are solubilized in the inner core of the micelle. We conclude, therefore, that the location of the azobenzene is one of the most important factors that determines the solubilization behavior, which reflects both the azobenzene and micelle structures.

The results of the foaming experiments for SLES, CGS1, and the SLES/CGS1 mixtures are shown in Figure 9. Gemini surfactants are generally used as antifoaming agents. Figure 9 shows that the foam volume of the SLES/CGS1 mixtures is consistently lower than that of pure SLES solutions, irrespective of the SLES concentration. Antifoaming agents (AFA) are surface-active substances that decrease the surface elasticity of liquids and prevent the formation of a metastable foam. The foam breaks as a result of the tendency to attain an equilibrium between the surface elasticity of the liquid and the surface active substances.
Conclusions

We studied a mixed system of a cationic gemini surfactant and sodium lauryl ether sulfate by measuring its mixed CMC, surface tension, specific conductivity, solubilization, viscosity, and foaming power. The results obtained in the present study clearly show the presence of an interaction between the cationic and anionic surfactants in the various binary systems. The conclusions obtained are as follows:
(1) The surface tensions decreased upon increasing the total surfactant concentration, and each surface tension curve had a break point, which was taken as the value of the mixed CMC.
(2) The variation of the CMC of mixtures of the SLES/CGS1 surfactants in the mixed micelle shows nonideal behavior and synergism in micelle formation.
(3) It is seen that the mixed CMCs are considerably lower than those of the respective surfactants for the SLES/CGS1 system. Thus, these changes in the mixed CMC deviate from an ideal solution. This negative value indicates a reduction in the free energy of micellization over that predicted by the ideal solution theory. The excess enthalpy of micellization was negative (except at \( \alpha = 0.2 \) at 35°C). These negative values signify that the mixed micellization of SLES/CGS1 surfactant mixtures are characterized by exothermic desolvation. The minimum areas (\( A_{\text{min}} \)) were considerably smaller than those of the respective surfactants.
(4) The degree of micelle ionization decreases as the surface charge density increases or as the surface area per ionic head group decreases. For SLES/CGS1 surfactant mixtures, the degree of micelle ionization was larger than those of the corresponding pure surfactants.
(5) The relative viscosities of the SLES/CGS1 surfactant mixtures were higher than ideal values at all mole fractions of SLES. This deviation from ideal behavior is obviously due to the formation of mixed micelles in the two-surfactant systems.
(6) The solubilized amounts of azobenzene were almost identical in the mole fraction range 0.2~0.8 of SLES and were considerably larger than those of the respective surfactants. Effectively, azobenzene is soluble in the hydrocarbon core of the ionic surfactant micelles.
(7) The foam volumes of the SLES/CGS1 mixtures were consistently lower than that of pure SLES solutions, irrespective of the SLES concentration.

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Nomenclature

- \( C^* \) : Mixed CMC (mol/kg)
- \( f \) : Activity coefficient of surfactant
- \( C \) : CMC of surfactant (mol/kg)
- \( X \) : Mole fraction of surfactant in the mixed micelle
- \( \Delta H_{\text{mic}} \) : Standard enthalpies of micellization (J/mol)
- \( a_i^M \) : Activity coefficients in the mixed micelle
- \( \gamma_{\text{CMC}} \) : Surface tension value at the CMC (mN/m)
- \( pC_{20} \) : Negative log of the surfactant molar concentration (mol/kg)
- \( C_{20} \) : Concentration required to reduce the surface tension of the solvent by 20 mN/m (mol/kg)
- \( \text{CMC}/C_{20} \) : Tendency to form micelles relative to the tendency to adsorb at the air/water interface
- \( I_{\text{max}} \) : Gibbs surface excess (mol/m²)
- \( d\gamma/dnC \) : Slope of plots of \( \gamma \) versus \( \ln C \)
- \( R \) : Gas constant
- \( n \) : Constant that depends on the number of species constituting the surfactant
- \( A_{\text{min}} \) : Minimum area per surfactant molecule (m²)
- \( N \) : Avogadro’s number

Greek Symbols

- \( \alpha \) : Mole fraction of SLES
- \( \beta \) : Interaction parameter

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