Effects of Added Salts on Surface Tension and Aggregation of Crown Ether Surfactants

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Abstract: Two crown ether surfactants, dodecanoyloxymethyl- (C11Φ6) and octanoyloxymethyl-18-crown-6 (C7Φ6), were synthesized and the surface tension dependence on surfactant concentration of their aqueous solutions was measured both in the absence and presence of alkali chlorides to confirm the critical micelle concentration (CMC) is highest for the added cation that have an ionic diameter comparable to the hole size of the crown ether ring and that several break points on the surface tension vs. concentration curves occur for these crown ether surfactants. For C11Φ6 and C7Φ6, in the absence of salt, the surface tension vs. concentration curves had two break points. Using the solubilization of a water-insoluble dye as an indicator, we found that the break point at the higher concentration (m<sub>h</sub>) for C7Φ6 was due to micelle formation. Two break points were also observed for the aqueous solution of C11Φ6 in the presence of NaCl, KCl, RbCl, and CsCl salts at concentrations of 0.22 mol kg<sup>-1</sup> and for C7Φ6 with 0.22 mol kg<sup>-1</sup> KCl added. The CMC (m<sub>0</sub>) was found to be the highest for solutions containing K<sup>+</sup> salts because K<sup>+</sup> has an ionic diameter comparable to the hole size of 18-crown-6 ring. Furthermore, the CMC decreased as the ionic diameters of the added cations deviated from the hole size. The molecular areas at two break points, estimated by the Gibbs adsorption isotherm, except for that at the break point at m<sub>h</sub> of C7Φ6, were very small for an adsorbed monolayer. Further investigation is required to elucidate the reason for the break point at m<sub>h</sub>.

Key words: Crown ether surfactants, crown ether/alkali cation complex, critical micelle concentration, premicelle formation

1 INTRODUCTION

Crown compounds with a hydrocarbon tail are called crown ether surfactants or amphiphatic crown compounds. They are multifunctional surfactants with the ability to include cation selectively. Many studies on water-soluble crown ether surfactants have been reported, for example, by Le Moigne et al.<sup>1-3</sup>, Moroi et al.<sup>4-7</sup>, Kuwamura et al.<sup>8-10</sup>, Okahara et al.<sup>11-18</sup>, and Ozeki et al.<sup>11-18</sup>. These reports showed that 18-crown-6 compounds with a decyl or longer alkyl tail do not dissolve in water. This lack of solubility is due to their lower hydrophilicities than those of linear polyoxyethylene surfactants. However, long-chain crown ether surfactants dissolve in aqueous solutions of metal salts because of the formation of crown-ether-surfactant/metal-cation complexes, which increase hydrophilicity. Furthermore, in the case of monoaza- and diaza-18-crown-6, even crown ether surfactant with a tetradecyl chain could be dissolved in water.

Ozeki et al.</sup><sup>11, 12</sup> investigated the concentration dependence of the surface tension of aqueous solutions of dodecanoyloxymethyl-18-crown-6 both in the absence and presence of KCl. All surface tension vs. logarithm of surfactant concentration curves were observed to have several break points below the critical micelle concentration (CMC). They suggested that these break points were attributed to the formation of premicellar aggregates with aggregation number from 2 to less than 5. They also proposed possible schematic models of premicelles and micelles.

Previously, we reported the synthesis of two crown-ether surfactants, dodecanoyloxymethyl-(C11Φ5) and octanoyloxymethyl-15-crown-5 (C7Φ5)<sup>19</sup>, and we investigated the effect of adding various salts on the surface tensions of their aqueous solutions in the absence and presence of ammonium and alkali chlorides, in particular, concerning the effect of selective inclusion of the added cations on the adsorbed films and aggregation behavior. In all cases the surface tension vs. logarithm of surfactant concentration curves were observed to have two break points, and we found that the higher-concentration break point corresponded to the CMC. We suggested that the lower-concen-
2 EXPERIMENTAL PROCEDURES

2.1 Materials

Dodecanoyloxymethyl-(C11Φ6) and octanoyloxymethyl-18-crown-6 (C7Φ6) were synthesized according to the method of Dishong et al. as described previously (Scheme 1). Dodecanoyl and octanoyl chlorides (98% and 99% purity) and 2-hydroxymethyl-18-crown-6 (93%) were purchased from Tokyo Chemical Industry Co., Ltd. and used without any purification.

2-Hydroxymethyl-18-crown-6 (18 mmol) and pyridine (25 mmol) were dissolved in dichloromethane (35 mL) and cooled to less than 5°C in an ice bath. Dichloromethane (3 mL) containing dodecanoyl chloride (17 mmol) was added dropwise into the stirred solution, which was maintained at a temperature below 5°C. Then, the reaction mixture was stirred at room temperature for 86 h, washed three times with 1 mol dm⁻³ HCl, once with 5% aqueous sodium carbonate, and once with water at 30°C. Finally, it was dried using anhydrous sodium sulfate. After removal of dichloromethane and column chromatography using silica gel, the product, C11Φ6, was obtained as a colorless oil in 13% yield (1.03 g).

The second surfactant, C7Φ6, was synthesized from 2-hydroxymethyl-18-crown-6 (15 mmol) and octanoyl chloride (21 mmol) in the same way. However, the reaction time was increased to 169 h, and the product was purified by column chromatography without the last washing step with water. C7Φ6 was obtained as a colorless oil in 63% yield (4.08 g).

Lithium (99%), sodium (99.5%), potassium (99.5%), rubidium (98%), and cesium (99.5%) chlorides purchased from Nacalai Tesque Inc. were dried at 120°C for 10 h before use. Solvent was ultrapure water produced by the Milli-Q Labo.

2.2 Measurements

The surface tensions of the aqueous surfactant solutions were measured at 25 ± 0.02°C using the drop-weight method. A capillary with an outer radius r having a reservoir was kept perpendicular in a glass vessel immersed in a temperature-controlled bath. Its upper end was connected to a micrometer syringe through a rubber tube. A drop of the solution was suspended at the lower end of capillary in a state just before falling for 5 min or more. Then, it was detached from the capillary tip. The surface tension was calculated as follows. If a fallen drop has a weight, w, then the surface tension of the solution is given by \( \gamma = F + g/r \), where g is the gravitational acceleration, and F is the Harkins-Brown correction factor, determined by the drop volume, V, and the outer radius, r, of the tip. The drop volume, V, was obtained by dividing the drop weight, w, by the density of the pure solvent, which was used because of the very low surfactant concentration. The outer radius, r, of the capillary was determined to be 3.340 mm by measuring the drop weight of ultrapure water at 25°C and assuming its surface tension to be 71.96 mN m⁻¹. After each measurement the capillary was cleaned with a chromic acid mixture.

The solubilization measurement was performed using 1-(o-tolylazo)-2-naphthol (Orange OT) as a water-insoluble dye. Orange OT was purchased as Oil Orange SS from Tokyo Chemical Industry Co., Ltd., and was recrystallized three times from ethanol and dried in vacuo. Solid Orange OT was added to an aqueous surfactant solution in a test tube with a plastic screw cap. The suspension was shaken for 96 h and then incubated for 48 h in a water bath incubator at 25 ± 0.2°C. The excess solid dye was filtered off with a 0.22-μm pore size Millipore filter, GSWP01300. The filtrate was diluted with ethanol having 1.5 times weight of the filtrate to destroy micelles and dissolve Orange OT sol-
ubilized in the mixed solution. An absorbance at 492 nm was measured using a Shimadzu double beam spectrophotometer UV-200S with quartz cells of 10-mm path length. The amounts of solubilized dye were determined from the absorbance by using a calibration curve obtained from absorbances of reference solutions prepared by water and an ethanol solution of Orange OT with 2:3 (w:w) ratio.

3 RESULTS AND DISCUSSION

3.1 Dependence of surface tension on surfactant concentration in the absence of added salts

The surface tension dependences on surfactant concentration for aqueous C11Φ6 and C7Φ6 solutions in the absence of added salt are shown in Fig. 1. The plots in both cases had two break points: one at the lower concentration, \( m_1 \), and one at the higher concentration, \( m_0 \), as previously observed for C11Φ5 and C7Φ5\(^{20} \). However, there was a difference in concentration dependence of surface tension between C11Φ6 and C7Φ6.

As the C11Φ6 concentration increased, the surface tension decreased, and at concentrations greater than 27.7 \( \mu \text{mol kg}^{-1}(m_1) \), it decreased slightly more slowly. Finally, when the concentration reached 131 \( \mu \text{mol kg}^{-1}(m_0) \), the surface tension ceased to change. The almost constant surface tension above \( m_0 \) would indicate that \( m_0 \) is the CMC of C11Φ6. Using the Gibbs adsorption isotherm\(^{24} \), the surface excess of C11Φ6 at \( m_1 \) was calculated to be 12.4 \( \mu \text{mol m}^{-2} \) from the slope of the data plotted in Fig. 1. From this value the molecular area at the aqueous surface was evaluated to be 0.13 nm\(^2 \), which is very small for an adsorbed monolayer.

For C7Φ6 the surface tension decreased more rapidly above 22.1 \( \mu \text{mol kg}^{-1}(m_1) \) than below it, and it continued to decrease a little at concentrations greater than 388 \( \mu \text{mol kg}^{-1}(m_0) \). The solubilization measurements indicate that \( m_0 \) is the CMC of C7Φ6, as discussed in the next section. The surface excess and molecular area of C7Φ6 at \( m_1 \) were calculated to be 4.8 \( \mu \text{mol m}^{-2} \) and 0.35 nm\(^2 \), respectively, suggesting that C7Φ6 molecules exist at an aqueous surface with their crown ether ring perpendicular to the surface because the diameter and the thickness of 18-crown-6 ring are about 1.1 and 0.4 nm, respectively. A similar orientation of the crown ether ring at the water surface has been reported for octyl\(^{25} \) and dodecyloxy-methyl-18-crown-6\(^{22} \). But, at \( m_0 \), the surface excess and molecular area were found to be 15.6 \( \mu \text{mol m}^{-2} \) and 0.11 nm\(^2 \), respectively, and this molecular area was too small for a monolayer as observed for C11Φ6.

Ozeki \textit{et al}.\(^{20} \) reported several break points on surface tension vs. concentration curves of other crown ether surfactants. They proposed that this was attributed to the formation of premicellar aggregates. In addition, Imae \textit{et al}.\(^{25} \) observed two break points on surface tension vs. concentration curve for a nonionic surface-active dye, and Sakai \textit{et al}.\(^{27} \) observed the same behavior for some fatty acid N-methylethanolamides; in both cases the premicelle formation was suggested. In our previous work\(^{19} \), we also observed two break points for C11Φ5 and C7Φ5 and concluded that a break point at the lower concentration, \( m_1 \), would be caused by the formation of premicellar aggregates. In the cases of C11Φ6 and C7Φ6, however, very small molecular areas were observed, so the break point at \( m_1 \) may be due to reasons other than premicelle formation.

3.2 Solubilization of water-insoluble dye by C7Φ6 in the absence of added salt

To confirm that \( m_0 \) is the CMC for C7Φ6, solubilization measurements were performed. In Fig. 2 the solubility of dye \( (m_0) \) is plotted against the C7Φ6 concentration. The solubility of the dye was zero below 319 \( \mu \text{mol kg}^{-1} \). Above this concentration, the solubility increased linearly with increasing surfactant concentration. This C7Φ6 concentration at the onset of solubilization was consistent with \( m_0 \), although slightly lower. This indicates that sufficiently large aggregates such as micelles have not formed yet just above \( m_1 \). Consequently, in the absence of salt, we believe that \( m_0 \) is the CMC of C7Φ6.

The solubilization power\(^{20} \) of C7Φ6, which was evaluated from the slope of the data plotted in Fig. 2 at concentrations above the CMC, was 1.5 \( \times 10^{-2} \), lower than that of C11Φ5, 1.9 \( \times 10^{-2} \). This could be because C7Φ6 micelles...
have less space to accommodate a solubilizate in their palisade layers because of their shorter C7\(\Phi_6\) alkyl chains than those of the C11\(\Phi_6\) micelle.

3.3 Effect of kind of added salt on \(m_I\) and \(m_0\)

Figure 3 shows surface tension vs. surfactant concentration plots of aqueous C11\(\Phi_6\) solutions in the presence of 0.22 mol kg\(^{-1}\) NaCl, KCl, RbCl, and CsCl. At this salt concentration, the mole fractions of C11\(\Phi_6\) complexes with Na\(^+\), K\(^+\), Rb\(^+\), and Cs\(^+\) were predicted to be larger than 0.55, based on the stability constants of 18-crown-6 complexes with these cations in water\(^{29}\). In all cases, two break points were observed, at which C11\(\Phi_6\) concentrations and surface tensions are given in Table 1. In the presence of 0.22 mol kg\(^{-1}\) LiCl the aqueous C11\(\Phi_6\) solution was clouded, so its surface tension was not measured.

Figure 4 shows the concentration dependence of surface tension of the aqueous C7\(\Phi_6\) solution with 0.22 mol kg\(^{-1}\) KCl. The other salts clouded the C7\(\Phi_6\) solution. In this case, the two break points were also observed, at which the C7\(\Phi_6\) concentrations and surface tensions are given in Table 2.

Plots of \(m_i\) and \(m_0\) against the crystal ionic diameter of the cation of the added salt are shown in Fig. 5. The highest CMC was found for the salt of K\(^+\), which has an ionic diameter comparable to the hole size of 18-crown-6 ring (0.26-0.32 nm\(^{30}\)), and the CMCs decreased as the ionic diameters of the added cations deviate from the hole size. However, we did not determine the dependence of \(m_i\) values on ionic diameter of added cations. The order of stability constant of the 18-crown-6 complex with various cations had been reported to be Na\(^+\) < K\(^+\) > Rb\(^+\) > Cs\(^+\) in water\(^{20}\), and the trend in the CMCs of C11\(\Phi_6\) is similar to the trend in stability constants of 18-crown-6/cation complexes.

### Table 1

C11\(\Phi_6\) concentrations and surface tensions at two break points of the surface tension vs. surfactant concentration curves shown in Figs. 1 and 3 in the absence and presence of various salts of 0.22 mol kg\(^{-1}\).

<table>
<thead>
<tr>
<th>salt</th>
<th>(m_I) / (\mu)mol kg(^{-1})</th>
<th>(\gamma_I) / mN m(^{-1})</th>
<th>(m_0) / (\mu)mol kg(^{-1})</th>
<th>(\gamma_0) / mN m(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>27.7</td>
<td>43.7</td>
<td>131</td>
<td>29.2</td>
</tr>
<tr>
<td>NaCl</td>
<td>21.1</td>
<td>48.8</td>
<td>121</td>
<td>30.1</td>
</tr>
<tr>
<td>KCl</td>
<td>23.9</td>
<td>46.9</td>
<td>189</td>
<td>28.4</td>
</tr>
<tr>
<td>RbCl</td>
<td>8.6</td>
<td>54.8</td>
<td>139</td>
<td>28.8</td>
</tr>
<tr>
<td>CsCl</td>
<td>10.6</td>
<td>52.8</td>
<td>55</td>
<td>33.8</td>
</tr>
</tbody>
</table>
3.4 Cause of the break point at \( m_1 \)

Imae et al.\(^{26}\) estimated the premicelle aggregation number \( (n) \) from the apparent surface excess values of the surfactants \( (\Gamma_1 \text{ and } \Gamma_0) \) at \( m_1 \) and \( m_0 \), which can be calculated from the slopes of surface tension vs. concentration plots at these break points, assuming two-step micellization. That is, the aggregation of premicelles into a micelle. The equations, \( \Gamma_1 = \Gamma_1' \Gamma_0 / n \) and \( \Gamma_0 = \Gamma_0' \Gamma_1 / n \), where \( \Gamma_1 \) is the surface excess of surfactant monomer, are derived from the Gibbs adsorption isotherm, assuming that premicelles do not adsorb at the solution surface. Therefore, the aggregation number of the premicelles can be estimated to be \( \Gamma_1 / \Gamma_0 \) by assuming that the values of \( \Gamma_1 \) at \( m_1 \) and \( m_0 \) are nearly equal.

The estimated \( n \) values, with the apparent surface excesses and molecular areas at \( m_1 \) and \( m_0 \), are given in Table 3. The \( n \) values enclosed in brackets are less than unity and, thus, do not meet the criteria for a two-step micellization. Only C11Φ6 solutions without salt and with KCl and RbCl yielded values of \( n \) greater than unity. However, because these values are close to unity, they are not conclusive indications of premicelle formation.

In addition, the \( a_0 \) values of C7Φ6 and the \( a_1 \) and \( a_0 \) values of C11Φ6 were smaller than the molecular cross-sectional area of fatty acid, 0.2 nm\(^2\), as shown in Table 3. Therefore, unlike the cases of C11Φ5 and C7Φ5, the break point at \( m_1 \) may be due to a phenomenon other than premicelle formation. Further investigation is required to find the cause of the break point at \( m_1 \).

4 CONCLUSION

As previously observed for dodecanoyloxymethyl- and octanoyloxymethyl-15-crown-5, we found that the surface tension vs. concentration curves had two break points: one at a lower concentration, \( m_1 \), and one at a higher concentration, \( m_0 \), for dodecanoyloxymethyl-\( (\text{C11Φ6}) \) and octanoyloxymethyl-18-crown-6\( (\text{C7Φ6}) \) both in the absence and presence of alkali chlorides. The CMC\( (m_0) \) was con-

### Table 2

<table>
<thead>
<tr>
<th>salt</th>
<th>( m_1 ) / ( \mu \text{mol kg}^{-1} )</th>
<th>( \gamma_1 ) / mN m(^{-1} )</th>
<th>( m_0 ) / ( \mu \text{mol kg}^{-1} )</th>
<th>( \gamma_0 ) / mN m(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>22.1</td>
<td>65.8</td>
<td>388</td>
<td>41.6</td>
</tr>
<tr>
<td>KCl</td>
<td>40.2</td>
<td>65.1</td>
<td>341</td>
<td>51.7</td>
</tr>
</tbody>
</table>

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firmed to be the greatest when potassium cations (K⁺) were added because they have an ionic diameter comparable to the hole size of 18-crown-6 ring. Furthermore, the CMC was found to decrease as the ionic diameter of the added cation deviates from the hole size. The cause of the break point at m₁ still remains unknown.

References


Table 3  Surface excesses, $\Gamma_1$ and $\Gamma_0$, and molecular areas, $a_1$ and $a_0$, at two break points of the surface tension vs. surfactant concentration curves and aggregation number of premicelle $n = \Gamma_1/\Gamma_0$ in the absence and presence of various salts.

<table>
<thead>
<tr>
<th>salt</th>
<th>$\Gamma_1 / \mu$mol m$^{-2}$</th>
<th>$a_1 / \text{nm}^2$</th>
<th>$\Gamma_0 / \mu$mol m$^{-2}$</th>
<th>$a_0 / \text{nm}^2$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11Φ6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>12.4</td>
<td>0.13</td>
<td>9.9</td>
<td>0.17</td>
<td>1.25</td>
</tr>
<tr>
<td>NaCl</td>
<td>9.7</td>
<td>0.17</td>
<td>16.6</td>
<td>0.10</td>
<td>(0.59)</td>
</tr>
<tr>
<td>KCl</td>
<td>9.9</td>
<td>0.17</td>
<td>9.3</td>
<td>0.18</td>
<td>1.07</td>
</tr>
<tr>
<td>RbCl</td>
<td>14.9</td>
<td>0.11</td>
<td>10.7</td>
<td>0.16</td>
<td>1.40</td>
</tr>
<tr>
<td>CsCl</td>
<td>11.0</td>
<td>0.15</td>
<td>12.8</td>
<td>0.13</td>
<td>(0.86)</td>
</tr>
<tr>
<td>C7Φ6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>4.8</td>
<td>0.35</td>
<td>15.6</td>
<td>0.11</td>
<td>(0.31)</td>
</tr>
<tr>
<td>KCl</td>
<td>5.8</td>
<td>0.29</td>
<td>18.5</td>
<td>0.09</td>
<td>(0.30)</td>
</tr>
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