The Adsorption of Cetyltrimethylammonium Bromide on Aqueous Surfaces of Sodium Bromide Solutions

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ABSTRACT

Surface tension of aqueous solutions of cetyltrimethylammonium bromide has been measured by the drop weight method, at different NaBr concentrations ranging from 0 to 0.05 M at 25 °C. Surface tension generally decreases with increasing concentrations of surfactant and NaBr, but it reaches a constant value at the critical micelle concentration for a given NaBr concentration. By applying the Gibbs adsorption isotherm for the surface tension at surfactant concentrations lower than the critical micelle concentration, surface excess densities of surfactant cation, Na⁺ and Br⁻ have been derived as functions of surfactant concentration at different NaBr concentrations. Surface excess densities of surfactant cation and Br⁻ increase with increasing surfactant concentration, except for those of surfactant cation at 0.0004 and 0.001 M NaBr, which reach maxima at 3 and 1×10⁻⁴ M, respectively. Furthermore, they do not reach constant values even at the critical micelle concentrations. The adsorption of Na⁺ is negative, and its absolute value is large at high NaBr concentrations. The Corrin-Harkins plot of the critical micelle concentration consists of two straight lines intersecting at 0.01 M NaBr, which could correspond to the regions of spherical and rod-like micelles.

INTRODUCTION

Surface tension of aqueous solutions of surfactant, either ionic or nonionic, even in the presence of added salt or other additive, can provide useful information on the adsorption by surfactant or other species on its aqueous surface. For that purpose, the Gibbs adsorption isotherm is applied to the surface tension of solutions in the region of surfactant concentrations lower than the critical micelle concentration (CMC). However, quantitative treatment of the Gibbs adsorption equation has not yet been adequately carried out on the experimental results, so that only a few adsorption isotherms for the solute species have been derived.
We have established a thermodynamic method for deriving surface excess densities of solute species from the changes in surface tension of aqueous solutions of surfactant [1-3] and applied it to aqueous solutions of cationic surfactant in the presence of a salt having a common anion [4,5].

In the present work we measure surface tension of aqueous NaBr solutions of cetyltrimethylammonium bromide (CTAB) at different NaBr concentrations by means of the drop weight method. The NaBr concentration is restricted to less than 0.05 M, because of the high Krafft point of CTAB, and the CTAB concentration ranges up to $10^{-2}$ M. We can identify the CMC as a break point on the surface tension curve at a given NaBr concentration. Furthermore, by making use of the thermodynamic method we can derive the surface excess densities of surfactant ion (CTA$^+$), co-ion (Na$^+$) and counter-ion (Br$^-$) from the surface tension data. Rijnbout [9] has reported the surface tension of aqueous KBr solutions of CTAB measured by the hanging plate method, but his experimental conditions were very specific, i.e., for a constant concentration of Br$^-$. Grange and Levis [6] and Perea-Carpio et al. [7,8] measured the surface tension of aqueous solutions of alkylammonium chloride and sodium alkyl sulfate and applied the Gibbs adsorption isotherm to derive the surface excess density of surfactant ions.

EXPERIMENTAL

CTAB purchased from Nakarai Chemical Co., Inc., Kyoto, was recrystallized twice from an ethanol-acetone mixture, as previously described [10]. NaBr of special grade from Wako Pure Chemical Industries, Inc., Osaka, was dried on an evaporating dish and stored in a desiccator until use. Water was glass-redistilled from alkaline KMnO$_4$. The surface tension of aqueous solutions was determined at $25 \pm 0.01^\circ$C by the drop weight method [5]. If a drop of a solution is suspended at the top of a capillary tip having outer radius $r$, and the detached drop has a weight $m$, then the surface tension of the solution is given by the equation

$$\gamma = \frac{mg}{r} F$$

(1)

where $F$ is the Harkins–Brown correction factor, determined by the drop volume and the effective radius of capillary tip, $r$, and $g$ is the acceleration due to gravity ($981 \text{ cm s}^{-2}$). The effective radius of the tip was determined by measuring in distilled water, assuming its surface tension to be 71.96 dyne cm$^{-1}$ at $25^\circ$C. Each drop of solution was suspended for 6 min after being formed, and five to ten drops were collected in a weighing bottle placed under the tip. The capillary tip was cleaned by being dipped in chromic acid solution after each filling with solution and measuring.
RESULTS

Figure 1 shows the relationship of surface tension of solutions, $\gamma$, and the logarithm of molar concentration of surfactant, $\log C$, at different NaBr concentration, $C_s$. Surface tension decreases sharply with increasing surfactant concentration up to the CMC, $C_0$, but at concentrations higher than the CMC it always remains constant, $\gamma_0$. Surface tension also decreases with increasing NaBr concentration.

In accordance with the Gibbs adsorption isotherms, the lowering of surface tension can be represented by

$$-d\gamma = RT(\Gamma \, d\ln C + \Gamma_s \, d\ln C_s)$$

where $R$ is the gas constant, $T$ is the temperature, and $\Gamma$ and $\Gamma_s$ are defined by

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_c$$

and

$$\Gamma_s = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_s}\right)_c$$

As can be seen in Fig. 1, it is clear that $\Gamma = 0$ for $C \geq C_0$. 

Fig. 1. Surface tension of aqueous solutions of cetyltrimethylammonium bromide at different NaBr concentrations. $C_s (M)$: (●) 0; (○) 0.0001; (▲) 0.0004; (△) 0.001; (■) 0.002; (▼) 0.005; (○) 0.01; (▲) 0.02; (□) 0.05.
Fig. 2. Surface tension of aqueous solutions of cetyltrimethylammonium bromide at different surfactant concentrations. - log C (M): (A) 3.1; (B) 3.2; (C) 3.3; (D) 3.4; (E) 3.5; (F) 3.6; (G) 3.7; (H) 3.8; (I) 3.9; (J) 4.0; (K) 4.1; (L) 4.2; (M) 4.3; (N) 4.4; (O) 4.5; (P) 4.6; (Q) 4.7; (R) 4.8; (S) 4.9; (T) 5.0; (U) 5.2. (O): The critical micelle concentration observed on the γ-C curves.

In Fig. 2 surface tension is replotted against log C_s at different surfactant concentrations. The lowest curve shows dependence of the constant surface tension on NaBr concentration, the constancy being observed at surfactant concentrations higher than the CMC.

Values of I and I_s can be obtained from the slopes of the surface tension curves in Figs 1 and 2. Table 1 summarizes related numerical data at the CMC. With increasing NaBr concentration, the value of I at the CMC decreases for

TABLE 1

Adsorption properties of cetyltrimethylammonium bromide on aqueous surfaces at the critical micelle concentration

<table>
<thead>
<tr>
<th>C_s (M)</th>
<th>C_m (10^{-4} M)</th>
<th>Γ (10^{-10} mol cm^{-2})</th>
<th>Γ_s (10^{-10} mol cm^{-2})</th>
<th>γ_0 (dyn cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.82</td>
<td>6.17</td>
<td>—</td>
<td>36.8</td>
</tr>
<tr>
<td>0.0001</td>
<td>9.82</td>
<td>6.17</td>
<td>0.28</td>
<td>36.8</td>
</tr>
<tr>
<td>0.0004</td>
<td>7.94</td>
<td>5.69</td>
<td>1.72</td>
<td>36.7</td>
</tr>
<tr>
<td>0.001</td>
<td>6.11</td>
<td>5.19</td>
<td>2.60</td>
<td>36.4</td>
</tr>
<tr>
<td>0.002</td>
<td>4.29</td>
<td>5.27</td>
<td>3.30</td>
<td>35.6</td>
</tr>
<tr>
<td>0.005</td>
<td>2.33</td>
<td>5.41</td>
<td>3.59</td>
<td>34.8</td>
</tr>
<tr>
<td>0.01</td>
<td>1.36</td>
<td>6.60</td>
<td>3.72</td>
<td>33.8</td>
</tr>
<tr>
<td>0.02</td>
<td>0.968</td>
<td>7.72</td>
<td>3.76</td>
<td>32.8</td>
</tr>
<tr>
<td>0.05</td>
<td>0.715</td>
<td>8.54</td>
<td>3.16</td>
<td>32.0</td>
</tr>
</tbody>
</table>
NaBr concentrations up to 0.001 M, but increases at higher NaBr concentrations. On the other hand, the value of $I_s$ at the CMC increases progressively with increasing NaBr concentration up to 0.02 M, then decreases slightly at 0.05 M NaBr. In addition, the constant term, $\gamma_0$, of surface tension is lowered with increasing NaBr concentration. The value of the CMC decreases with increasing NaBr concentration.

DISCUSSION

Surface tension

As we already pointed out [5], the Wilhelmy plate method failed to give reproducible results for the surface tension measurement of aqueous solutions of a cationic surfactant, because wetting of the hanging plate by the solutions varied with the dipping conditions. This was also the case for aqueous NaBr solutions of CTAB. Consequently, we employed the drop weight method for the measurement of surface tension in the current investigation of the solution, $H_2O + CTAB + NaBr$.

The relationships between surface tension and surfactant concentration and between surface tension and salt concentration in the system, $H_2O + CTAB + NaBr$, are similar to those for the systems, $H_2O + DDAC + NaCl$ [4,11] and $H_2O + DDAB + NaBr$ [5], except that the ranges of concentrations of CTAB and NaBr are both lower than those for DDAC and NaCl or those for DDAB and NaBr. At surfactant concentrations higher than the CMC, the surface tension remains constant in the system $H_2O + CTAB + NaBr$ as is the case for the systems $H_2O + DDAC + NaCl$ and $H_2O + DDAB + NaBr$. This is a general occurrence in the common ion ternary systems. However, in the indifferent ternary systems such as $H_2O + DDAC + NaBr$ [12] and $H_2O + DDAB + NaCl$ [13], the surface tension at surfactant concentrations higher than the CMC increases or decreases with increasing surfactant concentration, depending on whether the anion of the simple salt has greater or lower surface activity than that of the surfactant.

As shown in Fig. 1, the decrease in surface tension with increasing logarithm of surfactant concentration provides a family of graphs with curved and linear parts, related to the NaBr concentration. This suggests that there is no aggregation of surfactant such as formation of dimer or pre-micelle at surfactant concentrations lower than the CMC [14], in agreement with Rijnbout's conclusion.

The Gibbs adsorption isotherm

At surfactant concentrations up to the CMC, we can apply the equation for the Gibbs adsorption isotherm perviously developed [1–3]. If the surface excess
density, based on the Gibbs convention, and the chemical or electrochemical potential of ion, \( i \), are expressed by \( \Gamma_i \) and \( \mu_i \), respectively, then the Gibbs adsorption isotherm for aqueous NaBr solutions of a cationic surfactant, DBr, at surfactant concentrations lower than the CMC, is given by

\[
-d\gamma = \Gamma_{D^+} d\mu_{D^+} + \Gamma_{Na^+} d\mu_{Na^+} + \Gamma_{Br^-} d\mu_{Br^-} \tag{5}
\]

where \( D^+ \) indicates the surfactant cation, and the surface excess densities are subject to the condition of electroneutrality of the surface:

\[
\Gamma_{D^+} + \Gamma_{Na^+} = \Gamma_{Br^-} \tag{6}
\]

Introducing the chemical potentials of the two solute components as

\[
\mu_{DBr} = \mu_{D^+} + \mu_{Br^-} \tag{7a}
\]

\[
\mu_{NaBr} = \mu_{Na^+} + \mu_{Br^-} \tag{7b}
\]

the Gibbs adsorption isotherm can then be expressed in terms of the solute components for surfactant concentrations lower than the CMC as

\[
-d\gamma = \Gamma_{D^+} d\mu_{DBr} + \Gamma_{Na^+} d\mu_{NaBr} \tag{8}
\]

The chemical potentials of solute components are expressed by their molar concentrations, \( C \) and \( C_s \), for the surfactant and NaBr, respectively, assuming the solution is ideal. The molar concentrations of ions are expressed by

\[
C_{D^+} = C \tag{9a}
\]

\[
C_{Na^+} = C_s \tag{9b}
\]

\[
C_{Br^-} = C + C_s \tag{9c}
\]

We can express the Gibbs adsorption isotherm in the form of Eqn (2), in which \( \Gamma \) and \( \Gamma_s \) are defined by

\[
\Gamma = \left(1 + \frac{C}{C + C_s}\right) \Gamma_{D^+} + \frac{C}{C + C_s} \Gamma_{Na^+} \tag{10a}
\]

\[
\Gamma_s = \frac{C_s}{C + C_s} \Gamma_{D^+} + \left(1 + \frac{C_s}{C + C_s}\right) \Gamma_{Na^+} \tag{10b}
\]

Solving Eqns (10) we can obtain the surface excess densities or adsorption densities of the surfactant ions, \( Na^+ \) and \( Br^- \), i.e., \( \Gamma_{D^+} \), \( \Gamma_{Na^+} \) and \( \Gamma_{Br^-} \), as functions of \( \Gamma \), \( \Gamma_s \), \( C \) and \( C_s \) as follows

\[
\Gamma_{D^+} = \frac{1}{2(C + C_s)} \{(C + 2C_s)\Gamma - C\Gamma_s\} \tag{11a}\]
\begin{equation}
\Gamma_{Na^+} = \frac{1}{2(C+C_s)}\left\{ -C_s \Gamma + (2C+C_s) \Gamma_s \right\}
\tag{11b}
\end{equation}

\begin{equation}
\Gamma_{Br^-} = \frac{1}{2}(\Gamma + \Gamma_s)
\tag{11c}
\end{equation}

For high NaBr concentrations, Eqn (11a) reduces to
\begin{equation}
\Gamma_{D^+} = \Gamma
\tag{12}
\end{equation}

We can show that Eqn (8) still remains valid above the CMC, if \( \Gamma_{D^+} \) includes the contribution from the adsorbed micelles as well as the monomers, since the monomeric and micellar forms are in equilibrium. If the chemical potential of NaBr is considered to be approximately constant at constant NaBr concentrations, we have
\begin{equation}
-d\gamma = 0
\tag{13}
\end{equation}
since the chemical potential of surfactant remains constant above the CMC.

Surface excess densities of ions

We can now derive the surface excess densities of species in aqueous NaBr solutions of CTAB, i.e., surface excess densities of surfactant cation D\(^+\), co-ion Na\(^+\) and counter-ion Br\(^-\), by estimating the values of \( \Gamma \) and \( \Gamma_s \) using Eqns (3) and (4) with the observed data, and by applying Eqns (11). Figure 3 shows the surface excess densities of D\(^+\), Na\(^+\) and Br\(^-\) for the aqueous NaBr solutions of CTAB plotted against the surfactant concentration:

It is seen in Fig. 3 (a) that the value of surface excess density of surfactant cation, \( \Gamma_{D^+} \), increases very sharply even at low surfactant concentrations. The increase in \( \Gamma_{D^+} \) with concentration is more pronounced for CTAB than for DDAB and DDAC, all at low salt concentrations. The value of \( \Gamma_{D^+} \) does not necessarily reach its saturated value even at the CMC except for NaBr concentrations 0.004 \( M \) and 0.001 \( M \). Such behavior was also observed for aqueous NaCl solutions of DDAC [4,11] and for aqueous NaBr solutions of DDAB [5]. This is likely to be due to an incomplete electrostatic shielding effect of NaBr on the charged layer of adsorbed surfactant. On the other hand, at NaBr concentrations of 0.0004 \( M \) and 0.001 \( M \) the value of \( \Gamma_{D^+} \) passes through a maximum then decreases slowly with increasing surfactant concentration. Such a phenomenon of change in \( \Gamma_{D^+} \) with surfactant concentration was not observed in the system H\(_2\)O + DDAC + NaCl or in the system H\(_2\)O + DDAB + NaBr.

The value of \( \Gamma_{Na^+} \) shown in Fig. 3 (b) is negative except at high surfactant concentrations for 0.004 \( M \) and 0.001 \( M \) NaBr solutions. The positive adsorption of Na\(^+\) must be related to the occurrence of maximum adsorption of D\(^+\).

As shown in Fig. 3 (c) \( \Gamma_{Br^-} \) also increases even at the CMC with increasing
surfactant concentration at all NaBr concentrations, as was observed in the system H₂O + DDAB + NaBr.

Table 2 gives values of \( \Gamma_D^+, \Gamma_{Na^+} \) and \( \Gamma_{Br^-} \) at the CMC for different NaBr concentrations, and in Fig. 4 they are plotted against the square root of NaBr concentration. With increasing NaBr concentration, the saturated adsorption of surfactant cation increases continuously. This behavior of CTA ion is similar to that of dodecyl sulfate ion in aqueous NaCl solutions of sodium dodecyl
TABLE 2

Surface excess densities of surfactant cation, Na⁺ and Br⁻ at the critical micelle concentration

<table>
<thead>
<tr>
<th>Cₛ (M)</th>
<th>Γₐ (10⁻¹⁰ mol cm⁻²)</th>
<th>Γₖa (10⁻¹⁰ mol cm⁻²)</th>
<th>Γₖb (10⁻¹⁰ mol cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.09</td>
<td>-</td>
<td>3.09</td>
</tr>
<tr>
<td>0.0001</td>
<td>3.25</td>
<td>-0.02</td>
<td>3.22</td>
</tr>
<tr>
<td>0.0004</td>
<td>3.23</td>
<td>0.47</td>
<td>3.70</td>
</tr>
<tr>
<td>0.001</td>
<td>3.71</td>
<td>0.18</td>
<td>3.89</td>
</tr>
<tr>
<td>0.002</td>
<td>4.51</td>
<td>-0.23</td>
<td>4.28</td>
</tr>
<tr>
<td>0.005</td>
<td>5.21</td>
<td>-0.71</td>
<td>4.50</td>
</tr>
<tr>
<td>0.01</td>
<td>6.53</td>
<td>-1.37</td>
<td>5.16</td>
</tr>
<tr>
<td>0.02</td>
<td>7.69</td>
<td>-1.95</td>
<td>5.74</td>
</tr>
<tr>
<td>0.05</td>
<td>8.54</td>
<td>-2.69</td>
<td>5.85</td>
</tr>
</tbody>
</table>

sulfate, i.e., the adsorption of the dodecyl sulfate ion is strongly promoted by
the addition of NaCl [15–17]. However, this is different from that of the dodecyl-
dimethylammonium ion in the systems H₂O+DDAC+NaCl and
H₂O+DDAB+NaBr, i.e., the adsorption of dodecylammonium ion
slightly decreases at first then increases at higher concentrations of sodium.

Fig. 3. Adsorption isotherms of ions on aqueous surfaces at different NaBr concentrations. (a) Γₐ versus C, (b) Γₖa versus C, (c) Γₖb versus C. Arrows indicate the location of the critical micelle concentrations. Cₛ (M): (A) 0; (B) 0.0001; (C) 0.0004; (D) 0.001; (E) 0.002; (F) 0.005; (G) 0.01; (H) 0.02; (I) 0.05.
salts, by increasing their concentrations [4,5,10]. The adsorption of co-ion, Na⁺, at the CMC has a small positive value for low NaBr concentrations then decreases considerably as NaBr concentration increases.

Since the above calculation is based on the assumption of an ideal solution, it is relevant to examine the effect of nonideality on the adsorption densities of ions, by introducing mean activity coefficients of DBr and NaBr. In previous work on the system H₂O + DDAB + NaBr [5], we gave appropriate expressions to the activity coefficients and their approximations. By applying these numerical values, e.g. the partial specific volume of CTAB of 0.96 cm³ g⁻¹, we obtain the values of Γ⁺ only 2~3% higher, and those of Γ⁻ by, at most, 5% higher. Correspondingly, the corrected values of Γ⁺ are also slightly higher. However, qualitative features of adsorption isotherms of the three ions are not influenced by this more elaborate procedure.

Fig. 4. Surface excess densities of ions at the critical micelle concentration. (a) Γ⁺ (— O —), (b) Γ⁻ (— O —), (c) Γ⁻ (— O —).
Figure 5 shows the Langmuir plots of adsorption density of the surfactant ion. The isotherm is expressed by

$$\Gamma_{D^+} = \Gamma_{D^+}^\infty \frac{KC}{1 + KC} \quad (14)$$

where $\Gamma_{D^+}^\infty$ is the saturation and $K$ is the adsorption coefficient.

In water and $10^{-4}$ M NaBr, only the part of the graph at high surfactant concentrations follows the Langmuir adsorption isotherm. At very low surfactant concentrations there is a delay in the adsorption of surfactant ion and also of $\text{Br}^-$ as shown in Fig. 3. At higher NaBr concentrations, the adsorption isotherms follow the Langmuir type. Table 3 lists the numerical values of the adsorption coefficient, $K$, and the molecular area, $A^\infty = 10^{16}/N_A \Gamma_{D^+}^\infty$. It is clear that the adsorption coefficient of CTAB is nearly constant above 0.1 M NaBr and has a value more than ten times higher than that of DDAB. However, the molecular area of saturation decreases with increasing NaBr concentration. The strong electrostatic repulsion in the adsorbed layer of surfactant ion will induce a decrease in molecular area. This is the opposite effect to that shown by the system $\text{H}_2\text{O} + \text{DDAC} + \text{NaCl}$ [11].

**Critical micelle concentration and surface tension**

As is known generally, CTAB is a cationic surfactant with high surface activity and can form micelles at rather low surfactant concentrations. It is seen in Table 1 that values of the CMC at different NaBr concentrations are lower
TABLE 3

The saturation of $\Gamma_D^*$, molecular areas and adsorption constant of cetyltrimethylammonium bromide

<table>
<thead>
<tr>
<th>$C_s$ ($M$)</th>
<th>$\Gamma_D^*$ ($10^{-10}$ mol cm$^{-2}$)</th>
<th>$A^\infty$ (A$^2$/molecule)</th>
<th>$K$ ($M^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.47</td>
<td>47.9</td>
<td>$6.8 \times 10^3$</td>
</tr>
<tr>
<td>0.0001</td>
<td>3.55</td>
<td>46.8</td>
<td>$1.3 \times 10^4$</td>
</tr>
<tr>
<td>0.0004</td>
<td>3.59</td>
<td>46.3</td>
<td>$3.3 \times 10^4$</td>
</tr>
<tr>
<td>0.001</td>
<td>3.91</td>
<td>42.5</td>
<td>$1.4 \times 10^5$</td>
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<td>0.002</td>
<td>4.57</td>
<td>36.3</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>0.005</td>
<td>5.38</td>
<td>30.9</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>0.01</td>
<td>6.90</td>
<td>24.1</td>
<td>$9.7 \times 10^4$</td>
</tr>
<tr>
<td>0.02</td>
<td>8.77</td>
<td>18.9</td>
<td>$7.9 \times 10^4$</td>
</tr>
<tr>
<td>0.05</td>
<td>9.71</td>
<td>17.1</td>
<td>$1.0 \times 10^5$</td>
</tr>
</tbody>
</table>

than those of surfactants such as sodium dodecyl sulfate, DDAC and DDAB. On the other hand, the surface tension at the CMC with different NaBr concentrations is not as low as expected from the lower value of the CMC. For example, the surface tension of an aqueous solution of CTAB alone is higher than that of DDAB alone, but at 0.05 M NaBr it has almost the same value for both CTAB and DDAB [5].

The Corrin–Harkins relation of the CMC is closely related to the electrostatic shielding effect of the simple salt. Figure 6 shows the Corrin–Harkins plot for the $H_2O +$ CTAB + NaBr system. Linear relations hold at both low and high NaBr concentrations, respectively:

$$\log C_0 = -0.409 \log (C_0 + C_s) - 4.69, \quad C_s \leq 0.01 \ M$$

Fig. 6. The Corrin–Harkins plot of aqueous NaBr solutions of cetyltrimethylammonium bromide.
TABLE 4

Standard free energy of micellisation of cetyltrimethylammonium bromide in aqueous NaBr solutions at 25 °C

<table>
<thead>
<tr>
<th>Cs (M)</th>
<th>$-\Delta G^0_m$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.1</td>
</tr>
<tr>
<td>0.0001</td>
<td>27.1</td>
</tr>
<tr>
<td>0.0004</td>
<td>27.6</td>
</tr>
<tr>
<td>0.001</td>
<td>28.3</td>
</tr>
<tr>
<td>0.002</td>
<td>29.2</td>
</tr>
<tr>
<td>0.005</td>
<td>30.7</td>
</tr>
<tr>
<td>0.01</td>
<td>32.0</td>
</tr>
<tr>
<td>0.02</td>
<td>32.9</td>
</tr>
<tr>
<td>0.05</td>
<td>33.6</td>
</tr>
</tbody>
</table>

$\log C_0 = -0.853 \log (C_0 + C_s) - 5.58, \quad C_s \geq 0.01 \ M \quad (15b)$

According to the results of light scattering measurements on aqueous NaCl solutions of DDAC [18] and aqueous NaBr solutions of DDAB [19], the Corrin–Harkins plot is linear as long as spherical micelles are formed but it deviates from a linear relation when rod-like micelles become more stable. It is inferred that the sphere-rod transition of ionic micelles is due to the difference in electrostatic effect of added salt, i.e. the degree of counter-ion binding [4].

The results of light scattering measurements for aqueous NaBr solutions at CTAB at 35 °C show that at NaBr concentrations higher than 0.06 M rod-like micelles are formed [10]. This is not necessarily clear in the results obtained here from the measurements of surface tension at 25 °C, but it would indicate that the break point of the Corrin–Harkins relation is associated with the salt-induced sphere–rod transition.

**Standard free energy of micellisation**

If it is considered that the solution of a surfactant monomer is ideal and the micelle is a separated pseudo-phase [20], then the standard free energy of micellisation per mole of surfactant is given by

$$\Delta G^0_m = RT \ln X_0$$

where $X_0$ is the mole fraction of surfactant at the CMC. It can be rewritten in terms of the molar concentration of surfactant at the CMC, $C_0$, as

$$\Delta G^0_m = RT \ln \frac{M_w C_0}{1000 \rho_0 - (M_s - M_w) C_s}$$

(17)
where $M_w$ and $M_s$ are the molecular weights of water and salt, respectively, and $\rho_0$ is the density of solution at the CMC.

Table 4 gives values of $-\Delta G_m^0$ for the CTAB–NaBr system. It can be seen that the micelle is considerably stabilised and $-\Delta G_m^0$ becomes much larger, with increasing NaBr concentration.

REFERENCES

13 H. Okuda and S. Ikeda, to be published.