NOTE

Determining the Degree of Counterion Binding to Aqueous Alkylammonium Chloride Micelles by an Electrode Method

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Abstract: The degree of counterion binding ($\beta$) to micelles of aqueous $n$-alkylammonium chlorides ($C_n$AC; $\text{H(CH}_2\text{)}_n\text{NH}_3\text{Cl}$, $n = 8-12$) was evaluated from the ionic activity coefficient ($\gamma_{\text{AC}}$), which was determined by use of a conventional chloride ion selective electrode at 25°C. In the $\gamma_{\text{AC}}$ plot of $C_{12}$AC, a bend indicating the critical micelle concentration (cmc) was found, at concentrations above which the Botré plot was examined, and a value of 0.80 was determined for $\beta$. Very similar $\beta$ values were obtained for the other alkylammonium chloride surfactants. The standard free energy of the micellization ($\Delta G_m$) of $C_n$AC was estimated from the $\beta$ and micellar aggregation numbers.

Key words: alkylammonium chloride, ionic activity coefficient, degree of binding, chloride ion selective electrode, standard free energy of micellization

1 INTRODUCTION

When ionic surfactants form micelles, the association between hydrophobic tails is disturbed by the electrostatic repulsion between ionic heads; however, counterion binding to micelles reduces the repulsion, and thus ionic micelles are stabilized. The interaction between counterions and ionic heads is affected by different ions, geometric factors of the ionic heads, hydrophobicity, and a combination of counterions and polar groups. Counterion binding is also influenced by temperature, the nature and concentration of additives, and solvent properties. Several reviews have considered counterion binding to surfactant micelles.

The degree of counterion binding ($\beta$) to micelles has been investigated by means of various measurements. Among them, electromotive force measurement with ion selective electrodes is advantageous for the direct determination of the standard free energy of micellization. The values of $\beta$ and micellar aggregation numbers ($N$) are necessary to estimate the standard free energy of micellization ($\Delta G_m$). However, there seems to be only a few values of $\beta$ reported for homologs of $n$-alkylammonium chlorides ($C_n$AC; $\text{H(CH}_2\text{)}_n\text{NH}_3\text{Cl}$, $n = 8-12$), although the dependence of $\beta$ on chain length has been investigated for some other surfactants. The $N$ data were not found in the literature except for $N$ at concentrations 6-7 times higher than the cmc of $C_{12}$AC.

The purpose of this note is therefore to examine the dependence of the $\beta$ of $C_n$AC on chain length ($n$) and to evaluate $N$ and $\Delta G_m$.

2 EXPERIMENTAL

2.1 Samples

$n$-Octylamine (purity > 99%) was obtained from Acros Organics (Fair Lawn, NJ, USA), $n$-Nonylamine (purity > 98.0%), $n$-decylamine (purity > 98.0%), and $n$-undecylamine (purity > 98.0%) were obtained from Tokyo Chemical Industry Corporation (Tokyo, Japan). The $C_n$AC surfactants were obtained by dissolution of the corresponding $n$-alkylamines in EtOH, neutralization of the solutions with aqueous HCl, and finally recrystallization of the products from acetone-EtOH mixtures. $C_{12}$AC was prepared as described in the literature. Sodium chloride was a commercial product provided as a standard reagent.

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2.2 Measurement of Electromotive Force

The electromotive force \( E \) of the cell containing a \( C_n\text{AC} \) solution was measured at 25.0 ± 0.02°C on a DELTA350-type pH/mV meter (METTLER-TOLEDO LTD, England) equipped with a 941700-type chloride ion selective electrode (ORION RESEARCH INC, USA) and a 900200-type reference electrode with double junctions (do.). The solution examined was connected by an agar gel bridge containing 1 M NH₄NO₃ to a 0.1 M NaCl solution in which the reference electrode was dipped.

3 RESULTS and DISCUSSION

The chloride ion activity of \( C_n\text{AC} \) was evaluated as follows according to a procedure similar to that described in the literature.

The single ion activity coefficient of chloride ion \( \gamma_{\text{Cl}} \) in water at 25°C was calculated from the extended Debye-Hückel equation (1),

\[
\log \gamma_{\text{Cl}} = -0.358 \Gamma^{1/2}(1 + 0.6975\Gamma^{1/2}) - \log(1 + 0.036 m)
\]

where \( \Gamma \) and \( m \) refer to the total ionic concentration and the molality of the solution, respectively. A simple 1:1 electrolyte such as NaCl that obeys the Debye-Hückel equation without ionic association or hydrophobic aggregation should be used to get the relation between the single ion activity \( a_{\text{Cl}} \) and the \( E \) of the solution. Values of \( E \) for NaCl solutions were experimentally determined against \( m \) (see Fig. 1) and then evaluated as a function of \( a_{\text{Cl}} \).

\[
E = -58.4(\log m + \log a_{\text{Cl}}) - 13.4 = -58.4 \log a_{\text{Cl}} - 13.4
\]

\( E \) showed an almost Nernstian response between 1 log \( a_{\text{Cl}} \) values of -3.5 to -0.8.

For \( C_{12}\text{AC} \), \( E \) changed linearly with a slope of -55.3 mV decade⁻¹ until the cmc was reached, after which it showed increasing deviation from linearity with increasing \( m \) above the cmc (1.4 × 10⁻² mol kg⁻¹). As shown in Fig. 1, \( E \) showed similar behavior for the other surfactant systems.

Equation (2) was used as the calibration line to evaluate the \( \gamma_{\text{Cl}} \) and \( a_{\text{Cl}} \) values of \( C_n\text{AC} \) in water. Since equation (2) gives \( \log(\text{single ion activity of chloride} a_{\text{Cl}}) \) and \( \log(\text{molality of chloride ion} m \text{ of } C_n\text{AC}) \) at the same \( E \) value, the difference between these logarithms (1 log \( a_{\text{Cl}} \) - log \( m \)) gives \( \gamma_{\text{Cl}}(C_n\text{AC}) \). Figure 2 shows the plot of \( \gamma_{\text{Cl}} \) vs. \( m \), \( \gamma_{\text{Cl}}(C_n\text{AC}) \) decreased with \( m \) in the concentration range below the cmc and then decreased greatly with increasing \( m \) at concentrations above the cmc.

\[ \gamma_{\text{Cl}}(C_n\text{AC}) \]

abbreviated below as \( \gamma_{\text{exp}} \), in micellar solution is expressed by equation (3),

\[
\gamma_{\text{exp}} = \gamma [(1 - \alpha) m_t / m + \alpha]
\]

where \( \alpha \) is the degree of counterion dissociation from the micelles, \( m_t \) is the molarity of the surfactant in single dispersion state, and \( \gamma \) is the ionic activity coefficient of chloride ions in micellar solution. \( m_t \) was assumed as the cmc value given in Table 1. The Botré plot in Fig. 3 shows that the \( \gamma_{\text{exp}} \) of \( C_{12}\text{AC} \) vs. \( m_t / m \) has fairly good linearity, and thus \( \gamma \) and \( \alpha \) could be determined from the slope and intercept (\( \gamma = 0.87 \) and \( \alpha = 0.20 \); namely, \( \beta = 0.80 \)). These values are comparable to those already reported (6-9). The same procedure was applied to solutions of other alkylammonium chloride surfactants, and the results obtained are listed in Table 1.

Although the \( \alpha \) or \( \beta \) values of the homologs were expected to show some kind of dependence on the chain length for all the systems examined, the counterions were attracted at the same level to the micellar surface, \( \alpha = 0.20 \pm 0.02 \) for all the systems examined, the counterions were attracted at the same level to the micellar surface, \( \alpha = 0.20 \pm 0.02 \) and \( \beta = 0.80 \pm 0.02 \). This finding suggests that the micellar surfaces have the same charge density irrespective of the alkyl chain length. The \( \gamma \) value had a tendency to increase with increasing \( n \).

It is well known that equation (4) holds between the cmc and carbon number \( n \) in nonpolar chains of surfactants,

\[
\log X_{\text{cmc}} = b - c n
\]

(4)

where \( X_{\text{cmc}} \) is the cmc value expressed in terms of the mole fraction, and \( b \) and \( c \) are empirical constants. For ionic surfactants, the value of \( c \) was reported to be approximately 0.3 (20), which means that the cmc increases by about one-half with the addition of a CH₄ group to the surfactant chain. Good linearity (correlation coefficient 0.996) was found between \( n \) and \( \log X_{\text{cmc}} \) in this experiment. The values of \( b \) and \( c \) were determined to be 0.07 and 0.31, re-
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When equation (4) is rearranged into the form of
\[
\log \text{cmc/mol kg}^{-1} = b' - c' \cdot n
\]

it is found that \(b' = 1.82\) and \(c' = 0.31\). These values are comparable to those already reported. \(^{(20)}\)

Equation (4) was predicted theoretically by Shinoda\(^{(21)}\) and Rosen and Kunjappu\(^{(22)}\) for ionic surfactant solutions. The latter theory was based on assumptions that 1) the contribution of the hydrophilic head group to \(\Delta G_m\) and 2) the fraction of counterions bound to the micelles do not change with an increase in the length of the hydrophobic group. The independence of \(\beta\) values from \(n\) in \(C_n\)AC supports the validity of these assumptions.

\(\Delta G_m\) could be evaluated when the aggregation numbers \((N)\) of micelles are known. On the basis of 72 molecules determined newly as \(N\) of the \(C_{12}\)AC micelle (Murata, M. unpublished data), values of \(N\) for the other \(C_n\)AC were estimated. \(^{(23)}\) The shape of the micelle was assumed to be spherical, and the length of a \(C_{12}\)AC molecule was taken to be 1.6 nm. The micelle surface area was then calculated, and \(N\) was determined by dividing the micellar surface area by the cross-sectional area of the hydrophilic group (0.43 nm\(^2\)). The values of \(N\) are listed in Table 1. \(\Delta G_m\) is calculated from equation (5)\(^{(15)}\).

\[\Delta G_m = \frac{\text{cmc}}{N} \]
where

\[
\gamma_{\text{exp}} = \frac{m_f}{m} \chi_{\text{mic}} + \ln[2N^2(1 + \beta)]
\]  

(5)

where \( R \) is the gas constant and \( T \) is the absolute temperature. \( \Delta G_m \) was plotted against \( n \) in Fig. 4. Good linearity was found and the regression line was expressed as equation (6),

\[
\Delta G_m / \text{kJ mol}^{-1} = 1.5 - 3.2 n
\]  

(6)

Figure 4 also contains \( \Delta G_m \) previously reported for sodium \( n \)-alkyl sulfates (SC\(_n\)S; H(CH\(_2\))\(_{n}\)SO\(_4\)Na, \( n = 8-12 \))\(^{24}\). The plot of \( \Delta G_m \) vs. \( n \) for SC\(_n\)S is closely located to that for C\(_{12}\)AC, and the slope of equation (6) indicates that \( \Delta G_m \) changes by \(-3.2\) kJ mol\(^{-1}\) upon micellization for every methylene group added. Detailed discussions concerning the enthalpy and entropy of micellization will be presented in a forthcoming paper.

### 4 ACKNOWLEDGMENT

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### References

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