Study on Colloid Vibration Current in Aqueous Solution of Binary Surfactant Mixtures: Effects of Counterions and Hydrophobic Chains

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Abstract: In order to elucidate an electroacoustic phenomenon of mixed micelles in an aqueous solution, we measured the colloid vibration current (CVI) in aqueous solutions of binary surfactant mixtures. Based on the thermodynamic treatment of critical micelle concentration (cmc) values determined by conductivity measurements, it was expected that dodecyltrimethylammonium bromide (DTAB) and dodecyltrimethylammonium chloride (DTAC) molecules would mix ideally in the micelle. However, the micelle composition as evaluated from the CVI measurement, based on the linear dependence of the CVI value on the micelle composition, differed from the aforementioned ideality. Considering these observations, we concluded that the CVI measurement was more sensitive to the counterion distribution near the micelle surface, whereas the thermodynamically determined micelle composition included the counterions more loosely bound in the diffuse double layer due to the electroneutrality condition included in its assumption. On the other hand, the phase diagram illustrating micelle formation in the lithium dodecyl sulfate (LiDS) – lithium perfluorooctane sulfonate (LiFOS) mixture system showed a heteroazeotropic point arising from the stronger interactions between homologous surfactants than between heterologous ones. Although the concentration dependence of CVI values was expected to drastically change at a heteroazeotropic point due to the enormous variation in the density of the micelle core, the results showed a monotonous change, which suggests that the density of the micelle core varies continuously. By taking the partial molar volume of fluorocarbon compounds in the hydrocarbon compounds into account, the density of the micelle core was affected by the size of the micelle as well as its constituents.

Key words: colloid vibration current, mixed micelle, counterion, hydrocarbon surfactant, fluorocarbon surfactant

1 INTRODUCTION

Electroacoustic phenomena are a type of electrokinetic phenomenon\textsuperscript{1}, and in previous studies\textsuperscript{2, 3} we have investigated electroacoustic phenomena in aqueous solutions of ionic surfactants. By vibrating the micelle particles in aqueous solution using ultrasonic irradiation, a distorted electrical double-layer is formed around the micelle particles, which results from the combination of the heavier micelle core and the lighter counterions in the electrical double-layer, and the cations and anions are periodically collected in the solution. The induced potential difference is referred to as the colloid vibration potential (CVP)\textsuperscript{4–6} and the corresponding current is known as the colloid vibration current (CVI)\textsuperscript{4–6}. In this respect, the principle of CVP resembles that of the sedimentation potential, which is attributable to gravity instead of ultrasonic waves. Since this method is useful for various particle concentrations and radii, we believe that the elucidation of electroacoustic phenomena of surfactant micelles may play an important role in nanotechnology.

Up to this point we have focused on the electroacoustic properties of single surfactant systems and obtained the following results by applying the theory of Ohshima\textsuperscript{7, 8} to the experimental data\textsuperscript{2, 3}: 1) The dependence of CVI values on the concentration of an aqueous solution of the surfactant varied with micelle formation. 2) The CVI values were affected by the type of counterion due to the difference in \( \zeta \)-potential between different micelle particles. 3) The alkyl
chain length of the surfactant molecules hardly affected the concentration dependence of CVI values. 4) Variation of the hydrophobic chain from a hydrocarbon chain to a fluorocarbon chain resulted in a significantly increased concentration dependence of CVI values arising from the larger density difference between water and a micelle core composed of fluorocarbon compared to that between water and a micelle core composed of hydrocarbon. Thus, by measuring the CVI of aqueous solutions of various kinds of surfactants, we have determined the important factors affecting the CVI such as the type of counterion and hydrophobic chain.

Commercial detergents predominantly contain multiple surfactants that offer higher performance than single surfactant systems, and several studies on binary surfactant systems have consequently been performed using various techniques. It is particularly well known in thermodynamics that the composition of mixed micelles is highly dependent on the combination of surfactants. Principal factors affecting the mixing behavior of micelles include counterions and hydrophobic groups, the details of which are shown below; according to our previous studies, we can detect both factors sensitively using CVI measurements. Considering these facts, we tried to investigate the ultrasonic vibration behavior of mixed surfactant systems. It is interesting to observe how the CVI is affected by the mixture of surfactants, which show different behaviors in terms of electroacoustic response in the single system.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Dodecyltrimethylammonium bromide (DTAB, Wako Pure Chemical Industries, Ltd.)\(^2\), dodecyltrimethylammonium chloride (DTAC, Tokyo Chemical Industry Co., Ltd.)\(^2\), lithium dodecyl sulfate (Lids, Sigma-Aldrich Co.)\(^3\), and lithium perfluorooctane sulfonate (LiFOS, Wako Pure Chemical Industries, Ltd.)\(^3\) were repeatedly purified by recrystallization and extraction from a mixture of organic solvents according to the procedures described in each reference. The purity of surfactants was monitored by observing no minimum value of the surface tension versus molarly of aqueous solution of surfactants curves around the cmc. Milli-Q water from Millipore was used for sample preparation.

2.2 Conductivity measurements

In order to determine the cmc of surfactant mixtures in the aqueous solution, we performed conductivity measurements as a function of total molarity \(C\) and bulk composition \(X_2\), of surfactant mixtures, respectively, are defined as follows:

\[ C = C_1 + C_2 \]  
\[ X_2 = \frac{C_2}{C_1 + C_2} \]

where \(C_i\) is the molarity of component \(i\).

2.3 Ultrasonic vibration current measurement

The ultrasonic vibration current measurement in the aqueous solution of surfactant mixtures was measured using a DT-1200 Acoustic and Electroacoustic Spectrometer (Dispersion Technology, Inc.). The details of this spectrometer have been described elsewhere\(^4\). The frequency of ultrasonic waves generated from a piezoelectric device in the probe was held at 3 MHz in this study, and the probe was calibrated by measuring the \(ζ\)-potential of standard colloidal silica (Ludox TM-50, Nihon Rufuto Co., Ltd.), which yields \(-38\) mV. Thus, the ultrasonic vibration current was measured as a function of \(C\) and \(X_2\) at 298.15 K under atmospheric pressure.

3 RESULTS AND DISCUSSION

3.1 Thermodynamic consideration of mixed micelles

It is well known that the dependence of cmc on the bulk composition gives the micelle composition \(X_2^M\) from a thermodynamic perspective. In the case of ionic surfactant mixtures with common ions, the \(X_2^M\) values can be estimated using the following equation\(^5\):

\[ X_2^M = X_2 - \frac{2X_2 \alpha_{\text{cmc}}}{\frac{d\text{cmc}}{dX_2}} \frac{\partial \kappa}{\partial \rho} \]

Here, the micelle composition \(X_2^M\) is defined with respect to the excess thermodynamic quantities as follows:

\[ X_2^M = \frac{N_2^M}{N_1^M + N_2^M} \]

where \(N_i^M\) refers to the excess number of molecules of component \(i\) in one mixed micelle particle defined with reference to a spherical dividing plane that makes the excess number of molecules of water zero. Furthermore, the electroneutrality conditions of ionic surfactants must be satisfied in this system.

The cmc vs \(X_2^M\) curve (curve 2) in the DTAB – DTAC system was constructed by applying Eq. 3 to the cmc vs \(X_2\) curve (curve 1) in Fig. 1, which is called the phase diagram of micelle formation since it displays the relationship between the compositions of the bulk phase and micelle particles. It was found from Fig. 1 that the \(X_2^M\) values are smaller than the \(X_2\) values at the same cmc, which suggests that the micelle particle contains more DTAB molecules, i.e. bromide ions, compared to the bulk phase, an observation which is consistent with the theory that bromide ions...
are preferable to chloride ones for adsorption to the charged plane\(^1\). Curve 4 shows the micelle composition estimated from the CVI measurement using Eq. 9, and the difference between curve 2 and curve 4, in which both curves yield the micelle composition, is discussed in Section 3.2.

The other useful point to note in this phase diagram is the behavior of ideal mixing in the micelle particle. Once the cmc values, \(c_{mic}c\), of each surfactant are determined, we can obtain the cmc vs \(X_2^M\) curve of ideal mixing (curve 3 in Fig. 1) on the phase diagram using the following relationship:

\[
(cmc)^2 = \langle cmc_1 \rangle^2 + \left[ \langle cmc_2 \rangle^2 - \langle cmc_1 \rangle^2 \right]X_2^M
\]  

(5)

It should be emphasized that this equation is valid for the monovalent ionic surfactant mixture system with common ions\(^1\). As shown in Fig. 1, the cmc vs \(X_2^M\) curve coincides with that of ideal mixing within experimental error. Therefore, it is concluded that the DTAB and DTAC molecules mix almost ideally in the micelle particle.

On the other hand, the phase diagram of micelle formation in the LiDS – LiFOS system shown in Fig. 2 is significantly different from that observed in the DTAB – DTAC system. A heteroazeotropic point exists on the cmc vs \(X_2^M\) curve (curve 1) at \(X_2 = 0.46\), and as a result the cmc vs \(X_2^M\) curve (curve 2) exhibits a fairly large positive deviation from that of ideal mixing (curve 3), which suggests that the LiDS and LiFOS molecules mix non-ideally in the micelle particle. It is particularly important to note that the DTAB and DTAC molecules mix in the micelle at any composition, while the LiDS and LiFOS molecules mix only at limited compositions \((0 \leq X_2^M < 0.12 \text{ and } 0.86 < X_2^M \leq 1)\). Thus, the micelle particle formed at \(X_2 < 0.46\) is mainly composed of the hydrocarbon surfactant, LiDS. Conversely, the micelle particle formed at \(X_2 > 0.46\) is predominantly composed of the fluorocarbon surfactant, LiFOS. Such a strong tendency to gather the same kinds of surfactant molecules is attributable to the weaker interaction between hydrocarbon and fluorocarbon chains than the mutual interactions between hydrocarbon chains and those between fluorocarbon chains.

It has so far been described from a thermodynamic perspective that the miscibility of micelle particles in the DTAB – DTAC system is significantly different from that in the LiDS – LiFOS system. We subsequently examined the difference in the electroacoustic behavior of these mixed micelles in the aqueous solution.

### 3.2 Colloid vibration current in the DTAB – DTAC system

Figure 3 shows the results of ultrasonic vibration current (TVI)/measurement as a function of molarity and composition in the DTAB – DTAC system. At all compositions, the TVI values increased linearly with increasing molarity, and a break point appeared on each curve. In our previous studies\(^2\), we proved that the concentration at the break point corresponds to the cmc (see the dotted line in Fig. 3), and the TVI values at the concentration regime below the cmc provide information regarding the surfactant monomer whilst the TVI values at concentrations above the cmc give information concerning the surfactant micelle. In this paper, we focus on the electroacoustic behavior of surfactant micelles and therefore consider the ultrasonic vibration current in the concentration regime above the cmc.
which is referred to as the CVI below.

Theoretically, the CVI values are calculated using the following equation:  
\[
\text{CVI} = \frac{\phi (\rho_s - \rho_0)}{\rho_0} \mu(\omega) \Delta P
\]  
\[
\phi = \frac{(4\alpha)^2 \pi N_s}{V}
\]  
where \(\alpha\) and \(N_s\) represent the radius and the number of micelle particles, respectively, and \(V\) refers to the volume of aqueous solution. Assuming that the volume fraction of micelle particles corresponds to the surfactant concentration in aqueous solution, the concentration dependence of CVI is described by the following equation:
\[
\frac{\text{CVI}}{\phi} = \frac{\rho_s - \rho_0}{\rho_0} \mu(\omega) \Delta P = \text{(slope)}
\]  
Considering the density of liquid hydrocarbon corresponding to the alkyl chain, which forms the core of micelle, as the mass density of micelle, the \(\rho_s\) values of DTAB and DTAC micelles are equal to each other since these surfactants have the same alkyl chain in their hydrophobic group. Therefore, the difference in the dependence of CVI on the concentration, namely the difference in the slope of CVI in Fig. 3, may be caused by only \(\mu(\omega)\) values according to Eq. 8 in the DTAB – DTAC mixture system. Although the equation of \(\mu(\omega)\) is very complicated, it is certain that \(\mu(\omega)\) is proportional to the \(\zeta\)-potential of charged particles in the solution.\(^\text{7,8}\)

It appears that the slope of the CVI versus molarity curves is almost constant at the low composition regime (curves 1-4 in Fig. 3), and then becomes large in the vicinity of \(X_2 = 1\) (curves 6 and 7 in Fig. 3). This is clearly shown in Fig. 4, which illustrates the slope of CVI against the bulk composition. It is worth noting in Fig. 4 that the slope of CVI at \(X_2 < 0.5\) is almost constant within experimental error, whereas that at \(X_2 > 0.5\) increases rapidly with increasing the bulk composition. Considering that the slope of CVI is theoretically related to the \(\zeta\)-potential of micelle particles,\(^\text{7,8}\) it is expected that although the distribution of bromide and chloride ions around the micelle particles remains unaltered in the composition regime of \(X_2 < 0.5\), that distribution is highly changed in the composition regime of \(X_2 > 0.5\).

We subsequently estimated the composition of mixed micelles from the results of CVI measurements. The difference in the concentration dependence of CVI, i.e. the difference in the slope of CVI in the DTAB – DTAC mixture system, is only affected by \(\mu(\omega)\) values since the \(\rho_s\) values of the DTAB and DTAC molecules are the same. The \(\mu(\omega)\) value is dependent on the \(\zeta\)-potential and the variation of \(\zeta\)-potential arises from the distribution of counterions. We therefore assumed that the slope of CVI is simply proportional to the mixing ratio of bromide and chloride ions, and then estimated the micelle composition \(X_2^{\text{MCVI}}\) from the CVI measurement by applying the following linear-relationship to Fig. 4:
\[
\text{(slope)}_{\text{mixture}} = \text{(slope)}_{\text{DTAC}}X_2^{\text{MCVI}} + \text{(slope)}_{\text{DTAB}}(1 - X_2^{\text{MCVI}})
\]  
The cmc vs \(X_2^{\text{MCVI}}\) curve is drawn in Fig. 1 (curve 4). On studying Fig. 1 we discovered that the \(X_2^{\text{MCVI}}\) values estimated from the CVI measurement are not in agreement with the thermodynamic micelle composition \(X_2\) (curve 2). The former is less than the latter at the same bulk composition, and this difference is explained as follows: As mentioned above, the thermodynamic micelle composition is defined by using the excess thermodynamic quantity and
considers the distribution of counterions from the micelle surface to the region in which the electroneutrality condition holds. On the other hand, the ultrasonic vibration method provides information regarding the distribution of counterions in close proximity to the micelle surface because the CVI values reflect the ζ-potential of colloidal particles. Therefore, the results in Fig. 1 suggest that the micelle surface strongly attracts the bromide ions due to stronger counterion binding compared to the chloride ions. Imai et al. investigated the counterion distribution near the air/water surface of the DTAB/DTAC mixture system by using the total reflection X-ray absorption fine structure (TR-XAFS) technique and showed that the ratio of bound Br, which refers to the bromide ions adsorbed preferentially to the hydrophilic group of surfactant in the adsorbed film, was hardly affected by the composition of adsorbed film, i.e. the variation of the quantity of chloride ions. The conclusions from this study conform with the observations of Imai et al.

3.3 Colloid vibration current in the LiDS – LiFOS system

In the previous study, we showed that the CVI values of fluorocarbon surfactant, LiFOS, are significantly larger than those of hydrocarbon surfactant, LiDS, and it was concluded that this difference is due to the significant difference in density between the micelle and the surrounding medium, i.e. ρp - ρ0 in Eq. 6. As shown in Fig. 2, the LiDS and LiFOS mixture system exhibits peculiar behavior upon micelle formation in water. According to curve 2 in Fig. 2, the mixed micelle at X2<0.46 is almost totally composed of hydrocarbon surfactant (LiDS), while the mixed micelle at X2>0.46 is almost completely composed of fluorocarbon surfactant (LiFOS). We therefore expected the slope of CVI to be small in the region of LiDS-rich micelles at X2<0.46, and large in the region of LiFOS-rich micelles at X2>0.46. As a result, the abrupt change in the slope of CVI appears at around X2=0.46 in this system.

Figure 5 shows the results from TVI measurements as a function of molarity and composition in the LiDS – LiFOS system. In addition, curve 1 in Fig. 6 yields the slope of CVI in the LiDS – LiFOS system read from Fig. 5. It was discovered that the slope of CVI in the LiDS – LiFOS system is much larger than that in the DTAB – DTAC system (curve 2 in Fig. 6). On the basis of a previous study, this result is attributable to the difference in density between the micelle and water rather than the ζ-potential of the micelle surface. As shown in Section 3.2, the micelle composition (curve 4 in Fig. 1) in the DTAB – DTAC system was estimated from the slope of CVI and Eq. 9. However, it is impossible to estimate the micelle composition in the LiDS – LiFOS system since the linear-approximation of Eq. 9 does not apply in this system since the difference in the micelle core formed at the bulk composition is less and larger than 0.46, which explains why curve 4 is missing in Fig. 2.

Fig. 5 TVI signal magnitude vs molarity of aqueous solution of LiDS-LiFOS mixture. Curves: (1) X2 = 0 (LiDS); (2) 0.1; (3) 0.2; (4) 0.3; (5) 0.4; (6) 0.5; (7) 0.6; (8) 0.7; (9) 0.9; (10) LiFOS.

Fig. 6 slope of CVI vs composition curves in the aqueous solution of (1) LiDS-LiFOS and (2) DTAB-DTAC mixtures.

The slope of CVI in the LiDS – LiFOS system gradually increases with increasing the bulk composition at X2<0.46. On the other hand, the slope at X2>0.46 steeply increases as the bulk composition approaches 1. Considering that the micelle formed at X2>0.46 is almost entirely composed of LiFOS molecules as shown in Fig. 2, this result differs from the above expectation. The difference between the CVI values of LiDS and LiFOS systems is due to the mass densities of micelle and water, i.e. ρp - ρ0 in Eq. 6. At X2<0.46, the mixed micelles are almost regarded as pure LiDS micelles, and it was thereby expected that the ρp - ρ0 values are almost constant and the slope of CVI is hardly influenced by the mixing. A similar discussion applies at X2>0.46. However, the experimental results showed the continuous increase in the slope of CVI with increasing compo-
which causes the decrease of addition of small amounts of hydrocarbon surfactant, surfactant therefore becomes largely associated with the increase of bulk composition.

4 CONCLUSION

We have measured the CVI values in the mixture systems of DTAB – DTAC and LiDS – LiFOS. In the DTAB – DTAC mixture system, the composition dependence of CVI increased significantly above the composition \( X_2 > 0.5 \). Furthermore, the composition of mixed micelle estimated using the data from CVI measurements was smaller than that of ideal mixing. These results suggest that the micelle surface is preferentially adsorbed by the bromide ions.

The LiDS – LiFOS mixture system exhibited peculiar thermodynamic behavior due to the very weak mutual interactions between hydrocarbons and fluorocarbons. However, the composition dependence of CVI did not show similar peculiar behavior although the change was not so monotonous. This is attributable to the partial molar volume of fluorocarbon compounds in hydrocarbon solvents.

Although the CVI measurement technique has been widely applied to concentrated colloidal dispersions, we have found in this study that information including the ion distribution near the micelle surface and the effect of partial molar volume on CVI can be obtained when this technique is applied to dilute colloidal dispersions. In future studies, we may generate more quantitative discussions by measuring the CVI values of various surfactants and their mixtures.

References