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ORIGINAL CONTRIBUTION

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Effects of Cs and Na ions on the interfacial properties of dodecyl sulfate solutions

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Abstract The competitive binding of counterions to anionic dodecyl sulfate ions in aqueous solutions of cesium dodecyl sulfate (CsDS) and sodium dodecyl sulfate (SDS) mixtures, which significantly influences the critical micelle concentration (cmc) and surface (or interfacial) tension of surfactant solutions, was investigated. The cmc and degree of counterion binding were obtained through electrical conductivity measurements. The curve of cmc versus the mole fraction of CsDS in the surfactant mixture was simulated by Rubingh's equations, which enabled us to estimate the interaction parameter in micelles (W_R) based on the regular solution approximation. The curve-fitting exhibited a slightly negative value ($W_R = -0.1$), indicating that the mixing (SDS + CsDS) enhances micelle formation owing to a greater interaction between surfactant molecules and counterions than in pure systems (SDS). On going from SDS, SDS:CsDS(75:25), SDS:CsDS(50:50), SDS:CsDS(25:75) to CsDS, interfacial tension at the hexadecane/surfactant-solution interface showed a negative deviation from the mixing rule (interaction parameter in adsorbed film $W_A = -0.38$), indicating the replacement of Na^+ bound to anionic dodecyl sulfate by Cs^+ ions owing to the stronger interaction between the Cs^+ and the dodecyl sulfate ions. Droplet sizes of emulsion formed with hexadecane and aqueous dodecyl sulfate solutions were investigated using the light scattering spectrophotometer. The higher binding capacity of Cs^+, having a smaller hydrated ionic size than Na^+, also resulted in a negative deviation in emulsion droplet size in mixed systems.

Key words Cesium dodecyl sulfate · Sodium dodecyl sulfate · Counterion binding · Critical micelle concentration · Interfacial tension

Introduction

The surface chemical properties of ionic surfactants are affected by their counterions because the substitution of one kind of counterion by another alters the interaction between counterion and surface-active molecules, changing the extent of counterion binding or ionization of surfactants in water. The degree of binding of counterions into micellar surfaces or surface-active parts in surfactant molecules significantly influences the surface chemical properties of surfactants, such as critical micelle concentration (cmc), micellar size, reduction of interfacial (or surface) tension, etc [1, 2]. The degree of counterion binding to micelles was measured by different experimental techniques, including ultrafiltration[3], specific ion electrode[4], conductometry [5, 6], NMR chemical shift [7], Corrin–Harkins plot [8, 9], etc.

One of the most obvious consequences of the degree of counterion binding is a change in the cmc. Increased binding of the counterion in aqueous solutions generally causes a decrease in the cmc. The extent of binding of counterions increases with an increase in the polarizability and the valence of the counterions and decreases with an increase in their hydrated ionic radius. Thus, in aqueous solution, for anionic dodecyl sulfate (DS^-), the cmc decreases in the order $Li^+ > Na^+ > K^+ > Cs^+$ [10]. The cmc of lithium dodecyl sulfate (LDS), sodium dodecyl sulfate (SDS) and cesium dodecyl sulfate (CsDS) were reported to be 8.92, 8.32 and 6.09 mM at 25 °C [11] by the measurement of the specific conductance of solutions. Missel et al. [12] have reported that the micellar size decreases in the following order: $R_h(\mathrm{CsDS}) > R_h(\mathrm{SDS}) > R_h(\mathrm{LDS})$ at a given surfactant concentration and temperature. These facts are consistent with a higher Cs^+ ion binding to the micellar surface compared with that of Na^+ or Li^+, as also seen in the higher aggregation number of CsDS.

As shown in Table 1, the nonhydrated ionic size follows the order $Li^+ < Na^+ < K^+ < Cs^+$, but the hydrated ionic size is in the reverse order owing to the greater hydration of Li^+ than Na^+ or Cs^+ [10, 13]. The smallest hydrated ionic size of Cs^+ results in the highest extent of counterion binding among Li^+, Na^+, K^+ and Cs^+, followed by the lowest cmc and largest micellar size.

The surface (or interfacial) tension of surfactant solutions depends on the number of surfactant molecules at the interface. The surface tension of DS surfactants with monovalent counterions has been determined for different counterions. Oh and Shah [14] reported that the surface tension of LDS in aqueous solution was higher than that of SDS or CsDS owing to the largest hydrated ionic size of Li^+. The same results were obtained for the interfacial tension at the hexadecane/surfactant solution interface. The emulsion droplet size increased as the interfacial tension increased. These results were explained on the basis of the difference in the ionic size of the hydrated counterions.

The binding of Li^+, Na^+, K^+ and Cs^+ to anionic DS^- or micellar surfaces in water has been well characterized by many researchers, but studies on the competitive binding of alkali metal ions onto DS micelles in mixed systems have not been reported. We report here the competitive binding of Cs^+ and Na^+ counterions to DS^- and micellar surfaces in SDS and CsDS mixtures. Electrical conductivities were obtained to measure the degree of binding of counterions to micelles or DS molecules. From the ratio of the slopes in the plots of conductivity versus concentration below and above the cmc, the degree of counterion binding (β) was calculated. Absolute values may not be fully reliable, but trends within a series of structurally related surfactants can be compared with confidence, particularly since only the counterion is varied [15]. The interfacial tensions and the emulsion droplet sizes of hexadecane and aqueous surfactant solutions of SDS, CsDS and their mixtures were measured to investigate the effect of the size of counterions and the competitive binding of counterions to surface-active molecules at the interface.

Experimental

Materials

Reagent grade SDS (Sigma, 99%) and hexadecane (Sigma, purity greater than 99%) were used as received. CsDS was synthesized as follows. Chlorosulfonic acid (Aldrich, 553.5 mmol) was added to dodecanol (KAO, Japan, 536.65 mmol) drop by drop with vigorous mixing at 25 °C under a nitrogen environment. The sulfation reaction was performed very slowly since the sulfation process generates a large amount of heat. The addition of chlorosulfonic acid to dodecanol took 40 min even with cooling, in order to keep a constant temperature. After the sulfation process, nitrogen gas was used to purge the reaction mixture to remove the HCl produced during the reaction. Aqueous CsOH solution (Aldrich, 50.0 wt%) was added to the reaction mixture to neutralize the acid at a 1:1 molar ratio. The neutralization with CsOH was also accompanied by the generation of heat. The CsDS was recrystallized three times with distilled water, keeping the solution at 5 °C. The interfacial tension and cmc of CsDS were measured and compared with the reported values to confirm the purity. These values coincided with the reported values [16]. All solutions were made with twice-distilled deionized water

Methods

Conductivity measurement

The cmcs and the fraction of counterion binding (β), were determined using a conductivity meter (Delta Ohm, model HD8706, Italy) at various surfactant concentrations at 25 °C. The cmc was taken from the intersection of the lines fitted through an array of points before and after the inflection in the conductivity versus concentration plot.

Interfacial tension measurement

The interfacial tensions at the hexadecane/surfactant solution interface were measured using a surface tensiometer (Krüss

Table 1 Values for the nonhydrated ionic radius, hydrated ionic radius, solvated layer thickness and solvated volume of sodium and cesium

	Nonhydrated ion radius (nm)	Hydrated ion radius (nm)	Solvation layer thickness (nm)	Solvation volume (nm^3)
Li^+	0.068	0.38	0.312	0.230
Na^+	0.095	0.36	0.265	0.195
K^+	0.133	0.33	0.197	0.150
Cs^+	0.169	0.33	0.161	0.150

K10ST, Germany) using a platinum–iridium ring at 25 °C. The mixed surfactants were composed of SDS and CsDS at 100:0, 75:25, 50:50, 25:75 and 0:100 molar mixing ratios.

Emulsion droplet size measurement

Hexadecane (about 0.008 g) was added to 20 ml surfactant solutions at 13 mM concentration and the mixtures were stirred using a homogenizer (Ika, Germany) for 3 min, resulting in the formation of an oil-in-water emulsion. The emulsion droplet size was measured using a light scattering spectrophotometer (ELS-800, Otsuka Electronics, Japan) just after the formation of emulsions to avoid the coalescence or flocculation of droplets. The same experiments were performed with systems of SDS and CsDS mixtures at the molar mixing ratios 0:100, 25:75, 50:50, 75:25 and 100:0.

Results and discussion

The values of the cmc, i.e., the surfactant concentration when micelles start to be formed in the SDS or CsDS systems and their mixtures, were determined through the conductivity measurement. When micelles are formed, counterions are adsorbed into the micellar surface, thus reducing the charge density and facilitating the micellization. Increased binding of the counterion in aqueous systems causes a decrease in the cmc of the surfactant [17–19]. Sometimes, counterions are bound by specific interactions that depend on the nature of the headgroups and counterions at the micellar surface [20–23]. The electrical conductivities of SDS and CsDS mixtures at 100:0, 75:25, 50:50, 25:75 and 0:100 mixing ratios with respect to surfactant concentration at 25 °C are presented in Fig. 1. The values of the cmc obtained from the inflections in these plots are given in Table 2. The cmc of SDS and CsDS coincided with the reported values [11]. It is clear that there is a strong effect of counterion on the cmc. It has been suggested that the differences in the cmc with respect to the nature of the counterions are caused by the degree of binding of the counterions to the micelle. Robb and Smith [24] have reported that binding of the counterion to the micelle in aqueous solution appeared to decrease with an increase in the radius of the hydrated ion.

Therefore, the hydrated Cs^+, having a smaller hydrated ion size than Na^+, will interact more strong with the oppositely charged heads. Consequently, Cs^+ association is higher and the headgroup interactions are more screened, which favors micelle formation. With mixtures of counterions there is competition between Na^+ and Cs^+ association to the micellar surface. The cmcs determined are shown by filled circles in Fig. 2 as a function of the mole fraction of CsDS in the surfactant mixture (X_{CsDS}) .The cmc of the ideal mixed system, c_m, is related to X_1, the mole fraction of surfactant 1 in the total mixed solute, by Eq. (1) [25, 26].

Table 2 Critical micelle concentration (*cmc*) and degree of counterion binding (β) of mixed surfactant solutions of sodium dodecyl sulfate (*SDS*) and cesium dodecyl sulfate (*CsDS*) at various mixing ratios as a function of surfactant concentration

	cmc (mM)	β(%)
SDS	8.3	59
SDS:CsDS(75:25)	7.5	61
SDS:CsDS(50:50)	7.0	64
SDS:CsDS(25:75)	6.5	64
CsDS	6.2	65

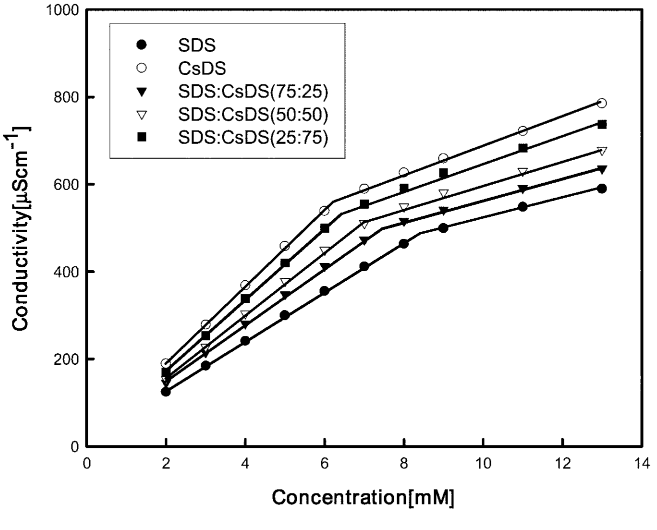

Fig. 1 Electrical conductivity of mixed surfactant solutions of sodium dodecy sulfate (*SDS*) and cesium dodecyl sulfate (*CsDS*) at various mixing ratios as a function of surfactant concentration

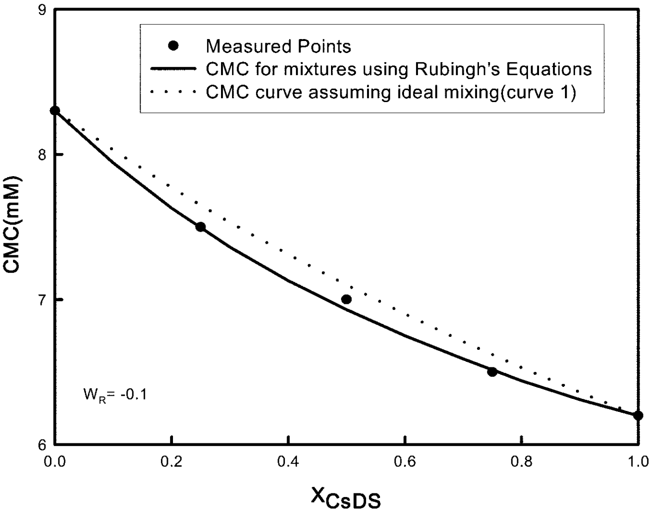

Fig. 2 Critical micelle concentration (*cmc*) data as a function of the mole fraction of CsDS in surfactant mixtures. cmc curve (singly dispersed phase curve) simulated by Rubingh's equation (nonideal theory) (*solid line*), singly dispersed phase curve of ideal mixing (calculated from Raoult's law) (*curve 1*)

$$\frac{1}{c_{\mathrm{m}}} = \frac{X_1}{c_0^1} + \frac{1 - X_1}{c_2^0} \quad , \tag{1}$$

where c_1^0 and c_2^0 denote cmc values of pure surfactants 1 and 2.

In Fig. 2, the c_{m} curve was calculated from Eq. (1) and the figure shows that the measured cmc values deviate negatively from curve 1. This deviation leads us to the conclusion that the present mixed micelle formation is slightly nonideal.

In order to examine the apparent nonideality, we applied equations from Rubingh [25, 26],

$$\frac{Y_1^2 \ln\left(c_{\mathrm{m}} X_1 / c_1^0 Y_1\right)}{(1 - Y_1)^2 \ln\left[c_{\mathrm{m}}(1 - X_1)/c_2^0(1 - Y_1)\right]} = 1 \quad , \tag{2}$$

where Y_1 is the mole fraction of surfactant 1 in a mixed micelle. Rubingh has introduced an interaction parameter in the mixed micelle on the basis of the regular solution approximation.

$$W_{\mathrm{R}} = \ln\left(c_{\mathrm{m}} X_1 / c_1^0 Y_1\right) / (1 - Y_2)^2 \quad . \tag{3}$$

The substitution of Y_1 values calculated from Eq. (2) into Eq. (3) produces a W_{R} value at each X_1. In the present case, the calculated W_{R} value showed a small difference depending on X_1, and so the values obtained were averaged as $W_{\mathrm{R}} = -0.1$. By using the averaged W_{R} value, the cmc versus X_1 curve and the micelle composition curve were simulated. As shown in Fig. 2, the computed cmc versus X_1 curve is in excellent agreement with the experimental values. The negative value of W_{R} is responsible for a "nonideal mixing" of counterions Cs^+ and Na^+. This is caused by the difference in the interaction between the counterions and the micellar surface. Since the value of W_{R} is related to the free energy of mixing of two surfactants, a negative value indicates an attractive interaction between two surfactants and a positive value indicates a repulsive interaction [1]. The larger the absolute value of W_{R}, the stronger the interaction between two surfactants. Thus, the value of $W_{\mathrm{R}} = -0.1$ implies that the interaction between SDS and CsDS is weakly attractive, probably owing to the increased binding of Cs^+ to micelles.

However, Eq. (2) was originally derived for nonionic–nonionic mixed surfactant systems and is different from the present ionic–ionic mixed system. Since the interaction parameter obtained in mixed micelles must be merely an apparent one, Eq. (2) is still applicable to ionic–ionic mixed systems [27]. Sugihara et al. [28] have derived the equations taking account of the mutual counterion effect on the mixed cmc formed by binary ionic surfactants: their equations are needed to know the degrees of counterion binding for the respective pure systems. They compared the interaction parameter, W_{R}, of Rubingh's equation with their interaction parameter, $\mathrm{W_O}$, in a study on the micelle formation of dodecylamine (DA) surfactant with mixed counterions: perfluorocarboxylate ions [trifluoroacetate (PA) and pentafluoropropionate (PP)] and alkane sulfonate ions [methane sulfonate (MS) and ethane sulfonate (ES)], i.e., DAPA/DAMS, DAPA/DAES, DAPP/DAMS and DAPP/DAES. The W_{R} obtained values are −0.247 and −0.674 for the respective DAPA/DAMS and DAPP/DAMS mixtures and −0.140 and −0.569 for the respective DAPA/DAES and DAPP/DAES mixtures. On the other hand, the latter W_{O} values were −0.227 and −0.409 for DAPA/DAMS and DAPP/DAMS mixed systems, respectively, while compared with the mixtures with MS, those for mixed systems with ES are found to have smaller absolute values: −0.134 for DAPA/DAES and −0.224 for DAPP/DAES. The comparison of W_{R} and W_{O} values, the absolute values of the respective combinations, indicates that, in general, the former are larger in absolute value. This suggests that if the equations of Sugihara et al. were employed to estimate the interaction parameter as well as the micellar composition curve for the present mixed system, the results would show almost ideal mixing for the formation of micelles.

The degree of counterion binding is shown in Table 2. The ratio of the slopes below the cmc and above the cmc in the conductivity versus molarity curve gives an estimation of the degree of ionization, $\alpha = p/n$, of the micelles, where p and n are the effective charge and the aggregation number of the micelle, respectively. The degree of counterion binding, β, can be calculated from $\beta = 1.0 - \alpha$ [29]. The degree of counterion bindings of SDS and CsDS were 59 and 65% at 25 °C. These differences are understandable because they agree with the fact that the Cs^+ counterion, whose hydrated radius is smaller than that of Na^+, favors greater interaction with the headgroup in the micellar surface.

On going from SDS to SDS:CsDS(75:25) to SDS:CsDS(50:50) to SDS:CsDS(25:75) to CsDS, the cmc values decrease and the degrees of counterion binding increase, indicating stronger interactions between the counterions and the micellar surface.

The interfacial tension in the mixed surfactant systems of SDS and CsDS are shown in Fig. 3 at various mixing ratios as a function of surfactant concentration. In connection with miscibility in terms of mole fraction in bulk solution, X_2, and in the adsorbed film phase, Z_2, of binary surfactant mixtures, Aratono et al. [30] have derived m_{t} versus X_2 and m_{t} versus Z_2 relations at a given surface tension, γ. The chemical potential of surfactant i ($i = 1, 2$) is denoted as

$$\mu_{\mathrm{i(a)}} = \mu_{\mathrm{i(a)}}^0 + RT \ln f_{\mathrm{i(a)}} Z_{\mathrm{i}} \quad , \tag{4}$$

where $\mu_{\mathrm{i(a)}}^0$ is the chemical potential of the adsorbed film of the pure surfactant i at the given T, P, γ and $\mathrm{f_{i(a)}}$ is defined symmetrically as $\mathrm{f_{i(a)}} \rightarrow 1$ when $Z_{\mathrm{i}} \rightarrow 1$ for both components.

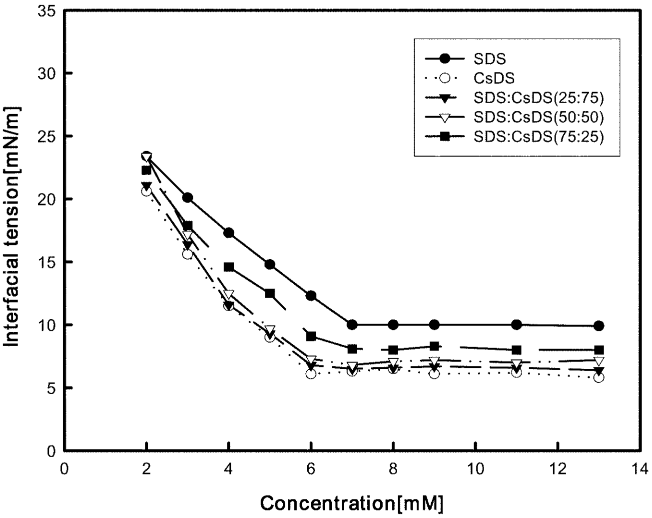

Fig. 3 Interfacial tension at the hexadecane/mixed surfactant solution interface for various mixing ratios as a function of surfactant concentration

At equilibrium between the bulk solution and the adsorbed film with regard to the pure and mixed adsorbed films, Aratono et al. have obtained

$$\frac{m_t X_i}{m_i^0} = f_{i(a)} Z_i \qquad (5)$$

and

$$m_t = m_1 + m_2 = m_1^0 f_{1(a)} Z_1 + m_2^0 f_{2(a)} Z_2\ , \qquad (6)$$

where m_i^0 is the molality of the surfactant at the same T, P, γ.

Therefore, the ideal mixing of the surfactants in the adsorbed film is described by putting $f_{i(a)} = 1.0$ in Eqs. (5) and (6), and the straight line connecting m_i^0 values is the criterion of the ideal mixing in the phase diagram of adsorption. That is, if the mixed system could form an adsorbed film, the relation should be as follows.

$$m_t = m_1^0 + \left(m_2^0 - m_1^0\right) Z_2 \qquad (7)$$

Aratono et al. have derived the relation between X_2 and Z_2 as

$$Z_2 = X_2 - \left(\frac{X_1 X_2}{m_1}\right)\left(\frac{\partial m_1}{\partial X_2}\right)_{T,P,\gamma}\ . \qquad (8)$$

An analysis has been done with the interfacial tension of 10.5 dyn/cm in Fig. 3 using Eq. (6) and the results are shown in Table 3 and Fig. 4. Thus, it can be shown that DS^- bound by Cs^+ are preferably located at the interface compared to those bound with Na^+.

Apart from Aratono's theory, Okano et al. [31] have derived the following equations to describe the interactions in ionic mixed systems.

Table 3 $Z_{2(=\mathrm{CsDS})}$ versus $X_{2(=\mathrm{CsDS})}$ calculated using Eq. (8) when the interfacial tension is 10.5 dyn/cm in Fig. 3. The molality was considered to be the same as the molarity

X_2	m_t (mM)	$\frac{\partial m_1}{\partial X_2}$ (mM)	Z_2
1.0	4.3		1.0
0.75	4.6	−0.5	0.84
0.5	4.9	−2.5	0.63
0.25	5.6	−4.0	0.38
0.0	7.0		0.0

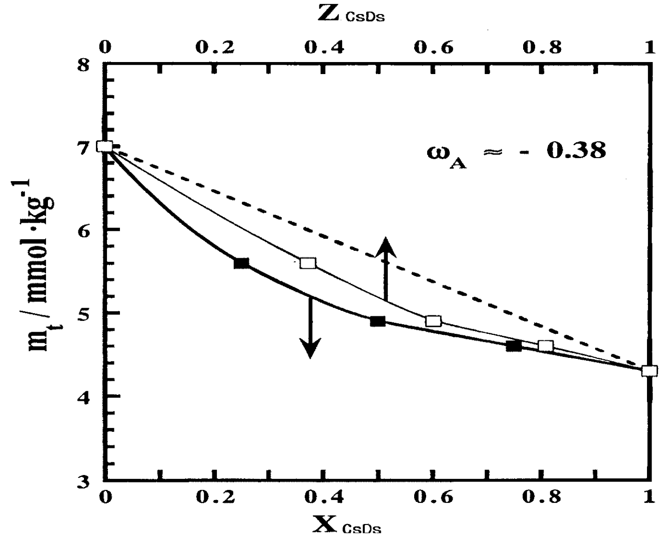

Fig. 4 The diagram for the relationship between the composition of CsDS in bulk and that at interface when the interfacial tension is 10.5 dyn/cm

$$\frac{(1-Z_2)^2 \ln\left[\frac{(1-X_2)m_t}{(1-Z_2)m_1^0}\right]}{Z_2^2 \ln\left(\frac{X_2 m_t}{Z_2 m_2^0}\right)} = 1\ , \qquad (9)$$

$$W_A = \frac{\left[\ln\left(\frac{X_2 m_t}{Z_2 m_2^0}\right)\right]}{(1-Z_2)^2}\ . \qquad (10)$$

By using the values in Table 3 and Eqs. (9) and (10), the interaction parameter at the adsorbed film (W_A) was found to be −0.38. This means that the interaction at the oil/water interface is stronger than that for the micelle formation in CsDS/SDS mixed system.

The interfacial tensions at 11 mM surfactant concentration in mixed systems are shown in Fig. 5. The negative deviation in the interfacial tension from the additivity rule at 11 mM surfactant concentration represents the replacement of hydrated Na^+ by the smaller hydrated Cs^+. This substitution by smaller hydrated counterions resulted in the smaller area/molecule of DS^- at the interface, followed by the lower interfacial tension as discussed in a previous report [14].

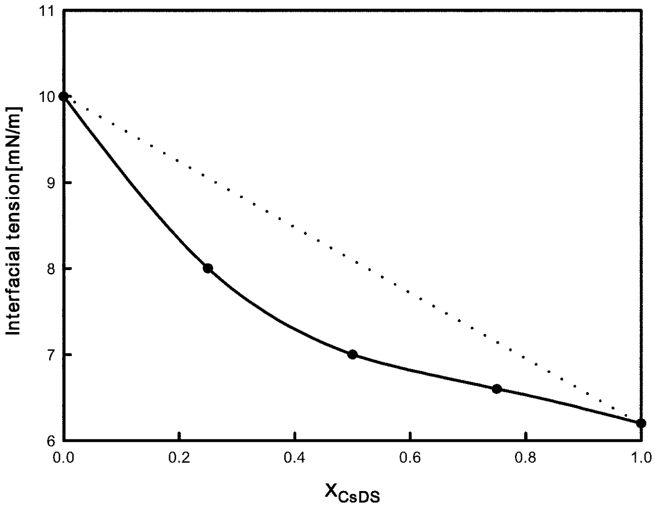

Fig. 5 Interfacial tension at 11 mM surfactant concentration of the mixed system

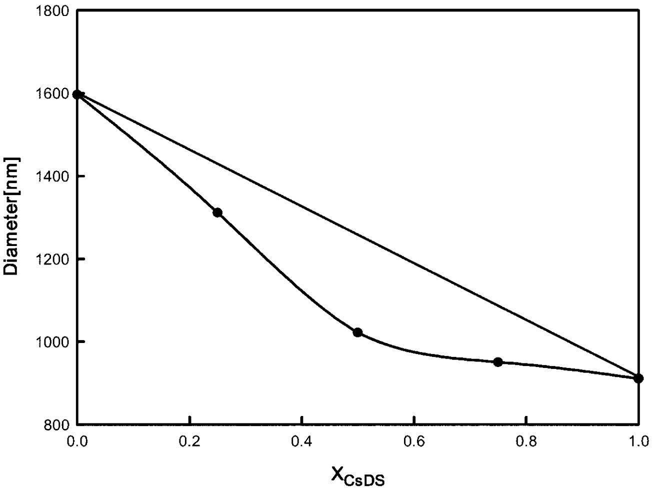

Fig. 6 Average emulsion droplet size for the mixture of hexadecane/mixed surfactant solution (SDS + CsDS)

The droplet sizes of emulsions of SDS/hexadecane, SDS:CsDS(75:25)/hexadecane, SDS:CsDS(50:50)/hexadecane, SDS:CsDS(25:75)/hexadecane and CsDS/hexadecane systems at 13 mM surfactant concentration are shown in Fig. 6. An emulsification process needs energy to disperse one liquid into another liquid as fine droplets. The interfacial area dramatically increases during the emulsification process. The work required, W, to expand the interfacial area is given by [32]

$$W = \gamma \Delta A \ , \tag{11}$$

where γ is the interfacial tension and ΔA is the increase in the interfacial area. For constant W, a higher value of γ yields a smaller ΔA; thus, the emulsion droplet size increases as the interfacial tension increases.

The emulsion droplet size for the SDS/hexadecane system was larger than that of the CsDS/hexadecane or the SDS + CsDS/hexadecane systems owing to a larger value of interfacial tension as explained by Eq. (11). The droplet size of the emulsion formed with hexadecane/aqueous SDS + CsDS mixed solutions showed a negative deviation, which was induced from the negative deviation in the interfacial tension as shown in Fig. 5. Indirectly, this shows that the emulsion droplet size was affected by the binding of counterion to the anionic surfactant headgroup.

Conclusions

Hydrated Na^+ has the larger radius and its center of charge is further from the surface of the negatively charged surfactant heads. It must therefore interact less strongly with the DS^- and screen the headgroups less effectively. The hydrated Cs^+ has a smaller hydrated ionic size than Na^+ and interacts more strongly with the oppositely charged heads. Consequently, Cs^+ association is higher and the headgroup interactions are more screened, which favors micelle formation and binding to the DS^- at the surface. It has been shown that the cmc increases when the size of the hydrated counterion increases, whereas the degree of counterion binding decreases. The binding interaction between DS^- and Cs^+ was stronger than that between DS^- and Na^+, resulting in the replacement of bound Na^+ by Cs^+. This replacement (competitive binding) induced the slight negative deviation ($W_R = -0.1$) from ideal mixing in the cmcs of the surfactant mixtures and ($W_A = -0.38$) at the adsorbed film. Moreover, the interfacial tension and the emulsion droplet sizes displayed a negative deviation from the ideal solution rule. Even at low concentrations, the Cs^+ determine the behavior in SDS/CsDS mixed surfactant systems.

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