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ORIGINAL CONTRIBUTION

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Electrokinetic properties of mixed solutions of dodecyldimethylamine oxide and sodium dodecyl sulfate: specific adsorption effects of small ions

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Abstract Electrophoretic light-scattering measurements and potentiometric titrations were carried out on aqueous mixtures of dodecyldimethylamine oxide and sodium dodecyl sulfate. The electrophoretic mobility and the surface charge density of the micelles were always negative, ranging from -2.5 to -3.1×10^{-4} cm^{2}V^{-1}s^{-1}, and -0.033 to -0.045 cm^{-2}, respectively, for all surfactant mixing ratios, indicating the specific adsorption of Cl^-, in addition to Na^+, on micelles. The solution pH, as well as the aggregation number previously reported, displayed maxima at intermediate surfactant mole fractions, that is, the non-ideal behavior. The fractional adsorption of Na^+ per surfactant molecule in the micelles increased gradually with mixing fraction up to 0.82 at $X = [\mathrm{SDS}]/([\mathrm{SDS}] + [\mathrm{C_{12}DAO}]) = 1$, while that of Cl^- decreased from 0.25 at $X = 0$ to zero at $X > 0.4$.

Key words Electrophoretic light scattering – potentiometric titration – surface charge density – fractional binding – dodecyldimethylamine oxide – sodium dodecyl sulfate

Introduction

Surfactant mixtures may display ideal miscibility, non-ideal miscibility, or immiscibility on the microscopic scale. There are many reports of ideal and non-ideal miscibility, while experimental reports of immiscibility refer to surfactant mixtures of hydrocarbon and fluorocarbon surfactants [1–6]. Both experiment and theory indicate that such miscibility behaviors should be interpreted on the basis of the interaction between molecules [7–9].

Micellar properties have been investigated for aqueous solutions of the weak-base surfactant, alkyldimethylamine oxide (C_nDAO), at degrees of protonation between 0 and 1, where nonionic amine oxide molecules coexisted with N-hydroxyammonium ions [10, 11]. Micellar size and rheological properties were largest at medium degree of protonation [12, 13], indicating non-ideal behavior due to hydrogen bonding between nonionic molecules and protonated ions. Non-ideal miscibility also resulted in liquid–liquid phase separation [14].

The surface charge density of nonionic C_nDAO micelles can be altered by the addition of ionic surfactants such as alkyltrimethylammonium bromide (C_nTAB) and sodium dodecyl sulfate (SDS) to an aqueous C_nDAO solution. C_nDAO–C_nTAB and C_nDAO–SDS mixtures displayed ideal and non-ideal behavior, respectively [15,16]. The solution pH and micellar aggregation numbers of C_nDAO–C_nTAB mixtures changed linearly with the mixing fraction. On the other hand, the dependence of critical micelle concentration (CMC), partial molar volume, solution pH, and micellar aggregation number on mixing fraction for SDS in aqueous C_nDAO solutions deviated from ideal behavior, although the deviation was not observed for heat capacity [15,17,18]. Both C_nDAO–C_nTAB and C_nDAO–SDS mixtures in water displayed non-ideal viscosity and viscoelasticity behavior [15,19].

The solution phenomena mentioned above are related to electrostatic interactions, which are controlled by the mixing fraction of ionic surfactant in C_nDAO micelles and the existence of small ions on micelles and in solution bulk. However, such effects have never been reported for mixed systems of C_nDAO and SDS. Therefore, in this work mixed solutions of $C_{12}DAO$ and SDS were investigated by electrokinetic measurement and potentiometric titration. The specific adsorption of small ions on micelles is discussed in relation to the ideal and non-ideal behavior of mixed solutions.

Experimental section

Sample of $C_{12}DAO$ was a commercial product from Fluka Co. Ltd. SDS (Nacalai Tesque, Inc.) was purified by recrystallizing from ethanol and ethanol–acetone mixture, respectively. Commercial NaCl and NaBr were heated for 1 h. Water was redistilled from alkaline KM_nO_4. Mixed solutions of $C_{12}DAO$ and SDS with a total concentration C_T of 80 mM were prepared with different mixing fractions $X = [SDS]/([SDS] + [C_{12}DAO])$ at NaCl concentrations C_s of 0 and 50 mM.

Potentiometric titrations of H^+ and Na^+ were carried out with an Iwaki Glass pH/ion meter M-225 and a Horiba ion meter N-8F, respectively, by using ion selective electrodes. The solution pH was measured, and free Na^+ concentrations in solutions were calculated from electromotive force. Both measurements were carried out at 25 °C.

Electrophoretic drift velocity was measured on an Otsuka Electronics ELS-800 electrophoretic light-scattering spectrophotometer. Solutions were purified through 0.22 μm millipore membrane filter which was washed by circulating distilled water for 1–2 hours before used. The cell, which was cleaned by circulating water filtered beforehand, was set in a jacket circulating water at 25 °C. A He-Ne laser at 633 nm wavelength was used as a light source. Measurement was carried out at 7.5–12.5° scattering angles under the applied electric field strength of 50–100 Vcm^{-1}.

Under the external electric field E applied perpendicularly to the incident radiation, the first-order autocorrelation power spectrum, $F_1(\mu, \omega)$, of the light scattered from particles moving in solutions is written as follows;

$$F_1(\mu, \omega) = \frac{\langle N \rangle}{\pi} \frac{\mu^2 D}{(\omega + \boldsymbol{\mu} \cdot \mathbf{v})^2 + (\mu^2 D)^2} \,. \tag{1}$$

Then the Doppler-shift frequency is

$$\Delta\omega_{\text{shift}} = \boldsymbol{\mu} \cdot \mathbf{v} = \mu v \cos(\theta/2) \tag{2}$$

where $\boldsymbol{\mu}$ and μ are the scattering vector and its magnitude, respectively. $\mathbf{v}$ and v are the velocity vector and its magnitude, respectively. ω is the angular frequency, and $\langle N \rangle$ is the average number of scatterers. D is the mutual diffusion coefficient, and θ the scattering angle.

The electrophoretic mobility U was calculated as the velocity per unit electric field, that is,

$$U = v/E \,. \tag{3}$$

After the electroosmosis effect was corrected by using the theoretical equation by Mori and Okamoto [20], the true mobility at the stationary level was obtained. Details of the experimental procedure are given elsewhere [21, 22].

Results and discussion

Solution pH

Figure 1 shows the pH of mixed solutions of $C_{12}DAO$ and SDS in 0 and 50 mM NaCl at a total surfactant concentration of 80 mM and at different X values. Numerical values are listed in Table 1. While homogeneous solutions of $C_{12}DAO$ and SDS were neutral (pH = 7 – 9), mixed solutions displayed higher pH up to 11.5 in maximum. The change was more pronounced in the absence of NaCl than in 50 mM NaCl.

The pH behavior in mixed solution suggests that small fraction (approximately less than few %) of $C_{12}DAO$ molecules is self-protonated to form dodecyldimethylammonium hydroxyion ($C_{12}DA^+OH$) under the addition of

Fig. 1 pH of $C_{12}DAO$–SDS mixed solutions at 25 °C as a function of X. A total surfactant concentration is 80 mM. NaCl concentration: ■, 0 mM; □, 50 mM

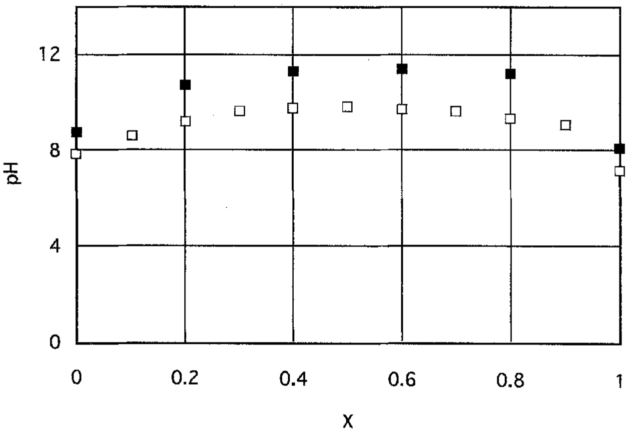


Table 1 Potentiometric titration data of C_{12}DAO–SDS mixed solutions at 25 °C. Total surfactant concentration is 80 mM

	$C_s = 0$ mM	$C_s = 50$ mM			
X	pH	pH	β_{Na^+}	β'_{Na^+}	$\beta_{Na^+} - X$
0	8.74	7.80	0.04		0.04
0.1		8.61	0.07	0.71	−0.03
0.2	10.73	9.26	0.14	0.68	−0.06
0.3		9.68	0.23	0.76	−0.07
0.4	11.35	9.82	0.30	0.76	−0.10
0.5		9.89	0.38	0.77	−0.12
0.6	11.45	9.82	0.47	0.78	−0.13
0.7		9.70	0.56	0.79	−0.14
0.8	11.29	9.40	0.63	0.79	−0.17
0.9		9.18	0.72	0.80	−0.18
1	8.21	7.28	0.82	0.82	−0.18

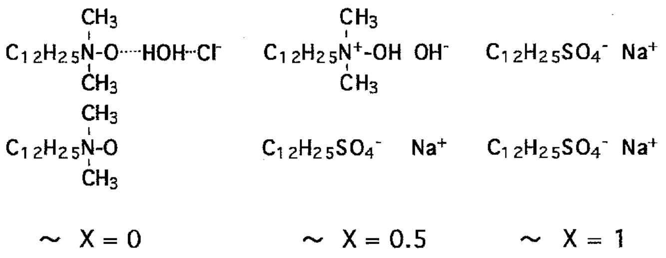


Fig. 2 Schematic representation of molecular species in micelles at different mixing molar fractions

SDS and to bind electrostatically with dodecyl sulfate ion, as illustrated in Fig. 2 (middle). Then free OH ions increase in bulk, that is, alkalinity of solutions increases. The tendency of higher pH increase in mixed solutions without NaCl than with 50 mM NaCl is related to the protonation of C_{12}DAO: pK of C_{12}DAO is higher in water than in 50 mM NaCl [14]. The difference of protonation between C_{12}DAO and C_{14}DAO also affects the pH of mixed solutions of C_nDAO and SDS.

The solution pH of similar mixed systems was previously reported by Weers et al. [15]. They found that the addition of SDS to aqueous C_{12}DAO and C_{14}DAO solutions induced the non-ideal behavior in solution pH. The increase of pH was higher for C_{12}DAO–SDS solutions than for C_{14}DAO–SDS solutions. This is consistent with the fact that the pK of C_{12}DAO is higher than that of C_{14}DAO [14]. Weers et al. [15] also explained the non-ideal and ideal pH behaviors of C_nDAO–SDS and C_nDAO–C_nTAB solutions, respectively, by the difference in the orientation of amine oxide dipole bound to SDS and C_nTAB.

Na ion adsorption

The concentration of Na^+ adsorbed on micelles in mixed solutions of C_{12}DAO and SDS, $C_{Na^+,b}$, in 50 mM NaCl at a total surfactant concentration of 80 mM was calculated by subtracting the measured free Na^+ concentration from the total Na^+ concentration. Numerical values of the fractional binding of Na^+ per surfactant and per dodecyl sulfate in micelles, β_{Na^+} and β'_{Na^+}, respectively, were evaluated.

$$\beta_{Na^+} = C_{Na^+,b}/(C_T - C_1)$$

$$\beta'_{Na^+} = C_{Na^+,b}/C_{SDS} \tag{4}$$

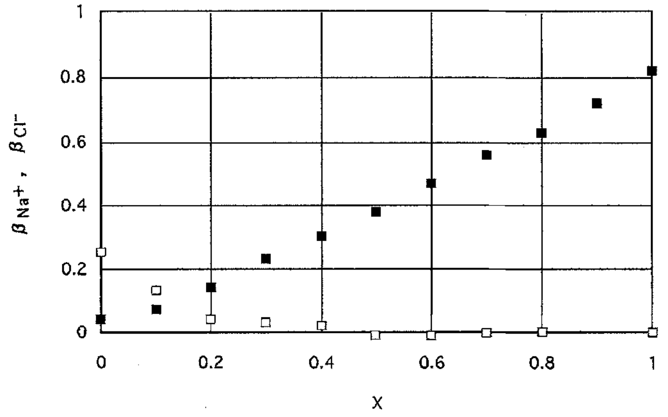
where C_T, C_1, and C_{SDS} are total surfactant concentration, critical micelle concentration, and SDS concentration, respectively. C_1 was taken as zero, since $C_1 \ll C_T = 80$ mM.

The β_{Na^+} and β'_{Na^+} values are listed in Table 1 and plotted in Figs. 3 and 4 as a function of X. Fractional binding of Na^+ per surfactant in micelles increased almost linearly with X, meaning that Na^+ adsorption increased with increasing SDS content in micelles. The fractional binding per dodecyl sulfate in micelles increased only slightly from 0.76 at $X = 0.3$ to 0.82 at $X = 1$. The value at $X = 1$ was consistent with that previously reported [23, 24].

Electrophoretic mobility

The electrophoretic mobility U was measured for mixed solutions of C_{12}DAO and SDS in 50 mM NaCl at a total surfactant concentration of 80 mM. Numerical values are listed in Table 2. Mobilities of -2.5 to -3.1×10^{-4} cm^2 V^{-1}s^{-1} were found almost independent of mixing fraction.

Fig. 3 Fractional binding of Na^+ and Cl^- per surfactant in micelles in C_{12}DAO–SDS mixed solutions at 25 °C as a function of mixing molar fraction. A total surfactant concentration is 80 mM. ■, β_{Na^+}; □, β_{Cl^-}



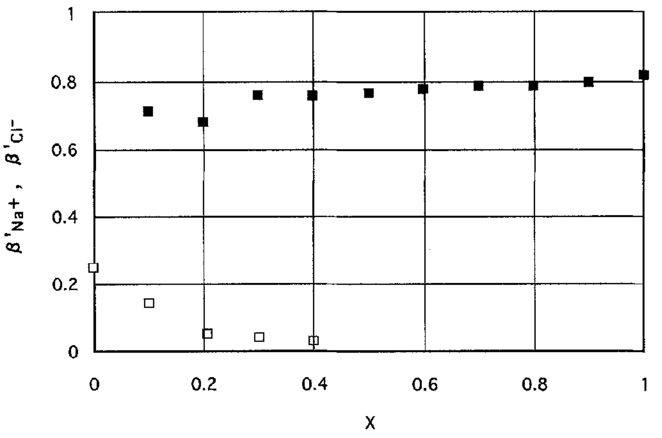


Fig. 4 Fractional binding of Na^+ and Cl^- per dodecyl sulfate and dodecyldimethylamine oxide, respectively, in micelles in $C_{12}DAO$–SDS mixed solutions at 25 °C as a function of mixing molar fraction. A total surfactant concentration is 80 mM. ■, β'_{Na^+}; □, β'_{Cl^-}

The result of electrophoretic mobility is rather inconsistent with those of solution pH and Na^+ adsorption. The negative mobility for aqueous $C_{12}DAO$ solutions without SDS indicates a negative surface (zeta) potential, although $C_{12}DAO$ micelles at pH 7.8 should be nearly neutral. The negative surface potential is possible only if Cl^- molecules are adsorbed on nonionic $C_{12}DAO$ micelles.

Surface charge density

Small-angle neutron scattering showed that mixed micelles of $C_{12}DAO$ and SDS in 50 mM NaCl are small prolate ellipsoid with axial ratios less than 4 [18]. If micelles are modeled as spheres having a volume equivalent to the ellipsoids, Henry's equation [25] for the electrophoretic mobility of rigid spherical macroions may be applied to the systems examined here. In this model, the micellar surface is surrounded by small ions, which form immobile and mobile parts of electric double layer, that is, Stern layer and diffuse double layer. The charge density per unit area at the Stern layer surface, σ, is then related to the electrophoretic mobility by Henry's equation:

$$U = (\sigma Am/f)\,(1 + \kappa R_i)\,X_1(\kappa R)/(1 + \kappa(R + R_i)) \qquad (5)$$

where $A(= 4\pi R^2/m)$ is the surface area per surfactant, m is the micellar aggregation number, $f(= 6\pi\eta_0(R + R_i))$ is the frictional coefficient, and $X_1(\kappa R)$ is a Henry's function. κ is the Debye–Huckel shielding parameter, R is the radius of the rigid spherical particle, and R_i is an effective radius of bound ion, that is, the Stern layer thickness. η_0 is the viscosity of solvent. Equation (5) suggests that the electrophoretic mobility depends on the surface charge density, the size and aggregation number of micelles and the ionic strength. The mobility should then be a function of X. Nevertheless, the observed mobility did not depend on X.

Numerical values of R and m were calculated by theoretical analysis of small-angle neutron scattering data [18]. The radii of Na^+ and Cl^-, R_{Na^+} and R_{Cl^-}, were 2.5 A and 1.8 A, respectively [26]. Numerical values of the Henry's function were 1.05 for $X \leq 0.5$ and 1.04 for $X > 0.5$. Numerical values of surface charge density evaluated from Eq. (5) are listed in Table 2, where the utilized parameters are included. The surface charge density of micelles at -0.033 to $-0.045\ cm^{-1}$ was almost independent of the change in X as well as the electrophoretic mobility, as expected.

Fractional binding of small ions

The surface charge density for mixed solutions of $C_{12}DAO$ and SDS is related to fractional binding of small ions β as follows

$$\sigma = e(\beta - X)/A \qquad (6)$$

Table 2 Electrophoretic light scattering data of $C_{12}DAO$–SDS mixed solutions with 50 mM NaCl at 25 °C. Total surfactant concentration is 80 mM

X	U $10^{-4} cm^2 V^{-1} s^{-1}$	m[a]	R[a] A	σ cm^{-2}	$\beta - X$	β	β_{Cl^-}	β'_{Cl^-}
0	-2.87 ± 0.15	98	25.05	-0.041	-0.21	-0.21	0.25	0.25
0.1	-2.69 ± 0.04	144	27.75	-0.037	-0.16	-0.06	0.13	0.14
0.2	-2.68 ± 0.27	302	34.15	-0.035	-0.11	0.09	0.04	0.05
0.3	-2.54 ± 0.11	328	34.85	-0.033	-0.10	0.20	0.03	0.04
0.4	-2.79 ± 0.30	279	33.25	-0.037	-0.12	0.28	0.02	0.03
0.5	-2.62 ± 0.15	328	34.80	-0.035	-0.10	0.40	-0.02	
0.6	-2.93 ± 0.06	341	34.80	-0.039	-0.11	0.49	-0.02	
0.7	-2.94 ± 0.08	208	30.45	-0.042	-0.14	0.56	-0.00	
0.8	-3.08 ± 0.43	159	28.15	-0.045	-0.17	0.63	0.00	
0.9	-3.05 ± 0.34							
1.0	-2.70 ± 0.24	106	25.10	-0.040	-0.19	0.81	0.00	

[a] The values were cited from ref. [17].

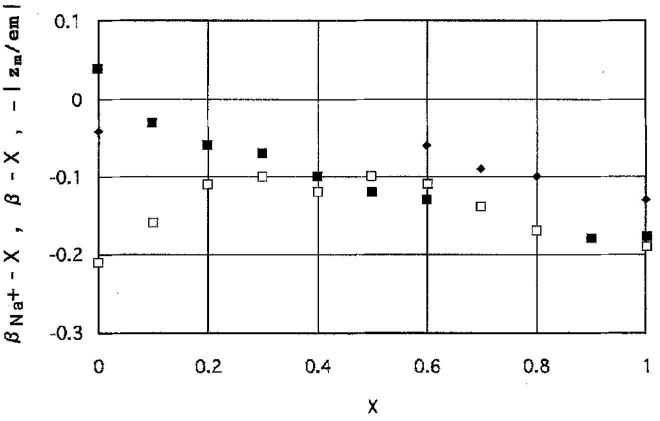


Fig. 5 β_{Na^+}–X, β–X, and $-|z_m/em|$ of micelles in C_{12}DAO–SDS mixed solutions at 25 °C as a function of mixing molar fraction. A total surfactant concentration is 80 mM. ■, β_{Na^+}–X; □, β–X; ◆, $-|z_m/em|$

where e is an elementary electric charge. The calculated $\beta - X$ and β values were listed in Table 2. The β–X values are plotted as a function of X in Fig. 5, where the β_{Na^+}–X values (listed in Table 1) from the potentiometric titration are included.

Figure 5 includes data of $-|z_m/em|$, which is the average electric charge number per surfactant monomer calculated from small-angle neutron scattering intensity on the basis of prolate ellipsoidal model for micelles and a rescaled mean spherical approximation [27] for the intermicellar interaction [18]. In the analysis, the electrostatic repulsive interaction potential was taken into account. Therefore, the $-|z_m/em|$ values are compared with the β–X values. It is apparent that the former is systematically lower than the latter. This can be interpreted as the difference of definition of Stern layer thickness detected by the electrophoretic method and the small-angle scattering method.

The β–X and β_{Na^+}–X values were in agreement with each other at $X > 0.4$, while there were meaningful differences between them at $0 \le X \le 0.4$. This suggests the adsorption of Cl^- besides Na^+ in the Stern layer, as estimated above. According to the relation of

$$\beta = \beta_{Na^+} - \beta_{Cl^-}, \tag{7}$$

numerical values of β_{Cl^-} and β'_{Cl^-} were calculated, as listed in Table 2 and plotted in Figs. 3 and 4. β_{Cl^-} and β'_{Cl^-} are the fractional binding of Cl^- per surfactant and per C_{12}DAO in micelles, respectively, that is,

$$\beta_{Cl^-} = C_{Cl^-,b}/(C_T - C_1)$$
$$\beta'_{Cl^-} = C_{Cl^-,b}/C_{C12DAO} \tag{8}$$

where $C_{Cl^-,b}$ and C_{C12DAO} are adsorption concentration of Cl^- and C_{12}DAO concentration, respectively.

Both β_{Cl^-} and β'_{Cl^-} values decreased with increasing X, and are negligibly small at $X > 0.4$. As expected, this suggests that the adsorption of Cl^- is meaningful only for C_{12}DAO micelles without or with few ionic surfactants. The interaction between C_{12}DAO and Cl^- may involve hydrated water, different from the electrostatic binding between dodecyl sulfate ion (DS^-) and Na^+, as illustrated in Fig. 2. The adsorption of Cl^- was clarified in the investigation of electrophoretic mobility change of aqueous C_{12}DAO solutions as a function of degree of protonation, although it disappeared by protonating C_{12}DAO [22]. Similarly, the addition of ionic surfactant in aqueous C_{12}DAO solutions diminished the Cl^- adsorption on nonionic C_{12}DAO in micelles. The interaction between C_{12}DAO and Cl^- is overcome by the electrostatic interaction in the presence of ionized surfactants. Then the binding equilibrium of Na^+ and Cl^- on micelles can be described as

$$DS^- + Na^+ = SDS \quad \text{for } 0 < X \le 1$$
$$C_{12}DAO + Cl^- = C_{12}DAOCl^- \quad \text{for } X \le 0.4\,. \tag{9}$$

The β_{Cl^-} values were slightly negative at $X = 0.5 - 0.6$. This may be interpreted as the numerical errors but can also be interpreted as the contribution of protonated C_{12}DAO molecules, as estimated above (see Fig. 2).

Surface potential was evaluated from electrophoretic mobility for nonionic–anionic surfactant mixture [28]: the surface potential decreased with downward deviation with increasing mixing ratio of nonionic surfactant. Counterion binding on mixed micelles was investigated by Rathman and Scamehorn [29]. Fractional counterion binding changed linearly for cationic–cationic and anionic–anionic surfactant mixtures. On the other hand, the binding for ionic–nonionic surfactant mixtures varied with upward deviation from ideal variation. This variation was different with the variation for C_{12}DAO–SDS mixture examined here.

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