

Investigation of Mixed Micelles of Dodecyldimethylamine Oxide and Sodium Dodecyl Sulfate by SANS: Shape, Size, Charge, and Interaction

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Mixed solutions of two surfactants, dodecyldimethylamine oxide (C_{12} DAO) and sodium dodecyl sulfate (SDS), were investigated by the small-angle neutron scattering (SANS) method. The SANS intensities were analyzed by using the prolate ellipsoidal model for the intraparticle structure factor and the rescaled mean spherical approximation (RMSA) for the interparticle structure factor. Prolate ellipsoidal micelles with axial ratios of 1.3–4.5 were formed in the mixed solutions. Average numbers of hydrated D_2O per surfactant on micelles were 6–9. At equimolar mixing, micellar sizes became maximum and the D_2O hydration minimum. The formation of ion pairs between protonated C_{12} DAO and SDS is an origin of such nonideal behavior. Electric charge numbers per surfactant in micelles increased with adding SDS, indicating the constant charge number of 0.13–0.15 per SDS. The addition of NaCl shielded the electric charge, resulting in the reduction of the repulsive interaction between micelles.

Introduction

Surfactant molecules are associated into micelles above the critical micelle concentration (cmc). Micelles take various shapes such as globular, rodlike, and disklike, depending on concentration, temperature, and so on. Aqueous micellar solutions were investigated by using various kinds of techniques. Micellar size and shape are obtained with the light scattering method. In contrast to that, the small-angle neutron scattering (SANS) is one of suitable techniques to study fine structures of molecular assemblies and interactions between them. So far, the SANS investigations have been carried out for various kinds of micellar systems^{1–16} in order to determine micellar size and shape. The effect of polydispersity was also discussed.^{17,18} Moreover, the theoretical analysis including the intraparticle and interparticle scattering effects was mainly applied to small micelles with ellipsoidal shape.^{1–3,6–9,19}

Multicomponent surfactant systems are interesting not only from physicochemical aspect but also in practical applications. When ionic surfactants are added into aqueous solutions of alkyldimethylamine oxide (C_n DAO), the mixed solutions display interesting behaviors: Weers et al.²⁰ reported that the pH of mixed solutions linearly changed with adding cationic surfactant, dodecyltrimethylammonium bromide. In contrast, if an anionic surfactant, sodium dodecyl sulfate (SDS), was added, the additivity did not exist but a pH-mixing fraction profile had a maximum. Bakshi et al.²¹ found that the cmc and the partial molar volume as a function of the mixed micelle composition showed negative deviation from the ideal behavior, although the heat capacity behaved ideally. When C_n DAO and ionic surfactants were mixed, the rheological behavior of solutions changed drastically and the viscoelastic character occurred in solutions.^{20,22} These nonideal phenomena result from the specific interaction between heterogeneous surfactants, and such interaction should affect the micellar aggregation and the intermicellar interaction.

SANS investigations associating with the micellar mass

weights and interactions have been reported for aqueous C_{14} DAO solutions mixed with cationic tetradecyltrimethylammonium bromide (C_{14} TAB).²³ The effect of counterion binding was discussed. On the other hand, mixtures of nonionic C_n DAO and anionic surfactants have never been investigated by SANS. Therefore, SANS measurements are carried out for the mixed solutions of C_{12} DAO and SDS. The results are compared between solutions in the absence and presence of 50 mM NaCl.

Experimental Section

A sample of C_{12} DAO (>98% purity) was purchased from Fluka Co. Ltd. and used without further purification. SDS (>99% purity, Nacalai Tesque, Inc.) was purified by recrystallizing three times from ethanol. D_2O (>99.75% purity) was purchased from Wako Pure Chem. Co. Ltd. The commercial NaCl was heated for 1 h in order to remove organic impurity; NaCl (0 and 50 mM) was added in the mixed surfactant solutions of C_{12} DAO and SDS. Total surfactant concentration in the solutions was 80 mM (~1.8 wt %) except in the case of the experiment of total concentration dependence.

SANS was measured by a small-angle neutron scattering instrument SAN at National Laboratory for High Energy Physics (KEK). The measurements were carried out in the momentum transfer Q range between 0.008 and 0.2 \AA^{-1} at room temperature (~25 °C). The sample thickness were 2 mm.

Results and Analysis

Small-Angle Neutron Scattering. Figure 1 shows SANS results for mixed solutions of C_{12} DAO and SDS with a total surfactant concentration of 80 mM at different mixing molar fractions $X = [SDS]/([SDS] + [C_{12}DAO])$. There was a peak around $Q \sim 0.03 \text{ \AA}^{-1}$ for aqueous C_{12} DAO solutions without SDS ($X = 0$). In the absence of NaCl, the peak shifted to a larger Q value with the addition of SDS, while the maximum scattering intensity was highest at $X = 0.4$. For systems with 50 mM NaCl, SANS showed a peak for solutions at $X > 0.5$

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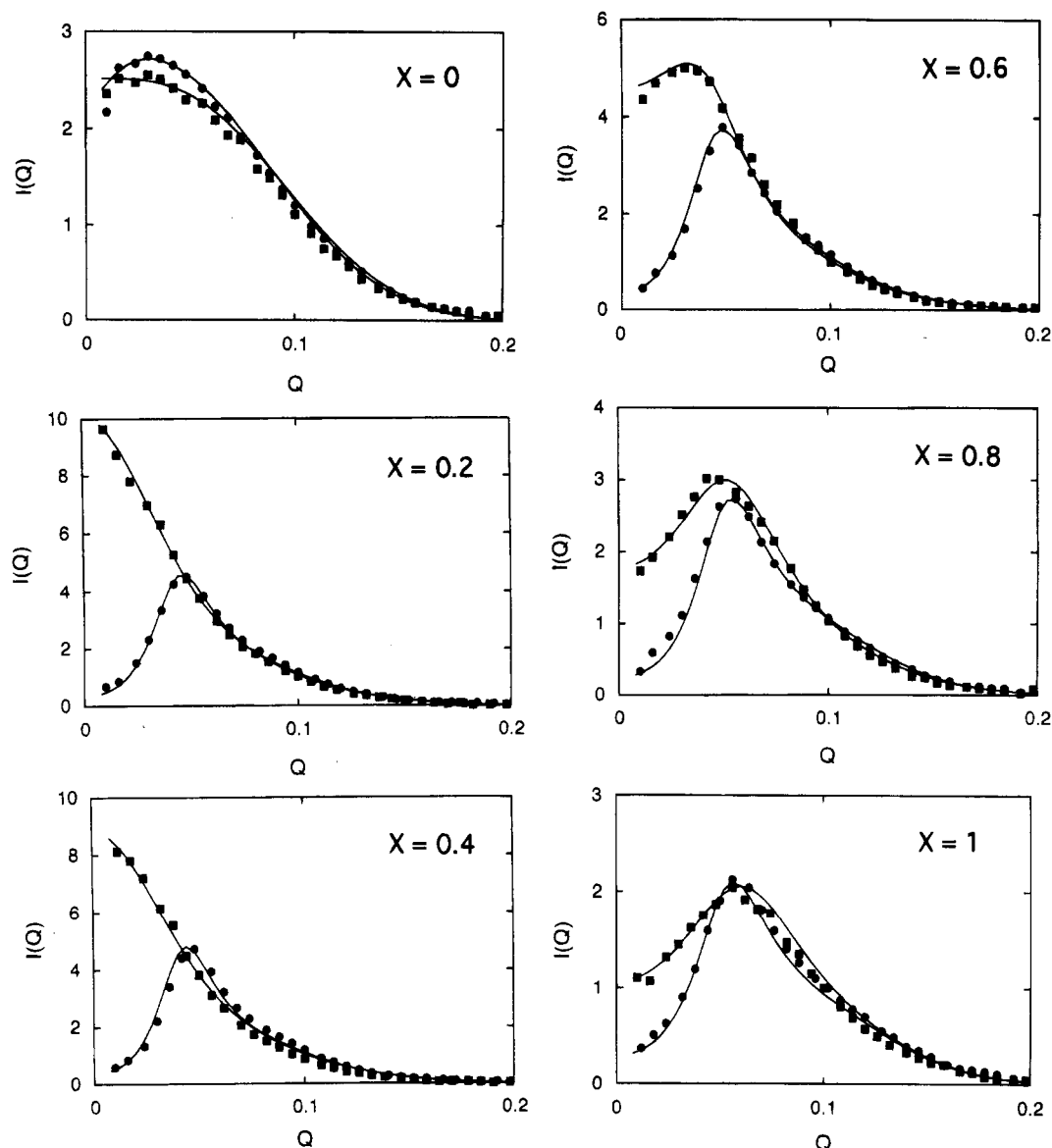


Figure 1. SANS data from mixed solutions of $C_{12}DAO$ and SDS at different mixing molar fractions. Total surfactant concentration is 80 mM. NaCl concentration: \bullet , 0 mM; \blacksquare , 50 mM. The solid lines are the calculated curves.

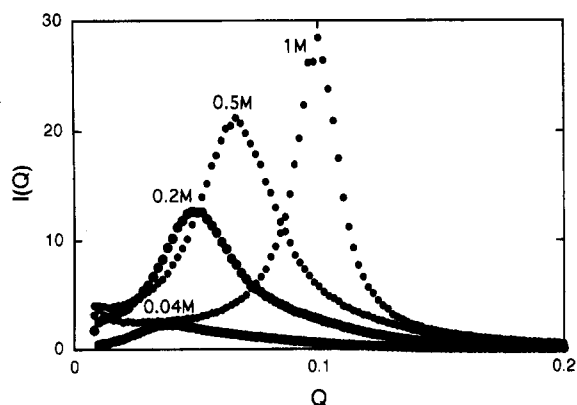


Figure 2. Total surfactant concentration dependence of SANS for mixed solutions of $C_{12}DAO$ and SDS at $X = 0.2$ without NaCl. Numerical values in figure represent total surfactant concentrations.

but not at $X = 0.1-0.5$. The total surfactant concentration dependence of SANS in the absence of NaCl at $X = 0.2$ is given in Figure 2. With increasing total surfactant concentration, the peak shifted to a higher Q value and the peak intensity increased.

Micelles of pure $C_{12}DAO$ or SDS are known to be small.^{2,24} Therefore, it is estimated that micelles formed in mixed solutions

of $C_{12}DAO$ and SDS are also small. With the assumption that micelles are monodisperse and their shape is spherical or nearly so, SANS intensity $I(Q)$ is written by^{25,26}

$$I(Q) = n_p P(Q) S(Q) \quad (1)$$

where $P(Q)$ and $S(Q)$ are the intraparticle and interparticle structure factors, respectively. n_p is a number density of micelles and have a relation of

$$n_p = (C_t - C_{cmc}) N_A / 1000m \quad (2)$$

in cm^{-3} units, where C_t and C_{cmc} are total surfactant and critical micelle concentrations in M unit, respectively. N_A is Avogadro's number, and m is a micellar aggregation number. The intraparticle structure factor, which is governed by the micelle geometry, changes monotonously with Q value. On the other hand, the interparticle structure factor, which is related to the interparticle interaction potential on the basis of the theory of simple liquid,²⁷ oscillates and is damped around unity as a function of Q .

There was the apparent contribution of the interparticle interaction in the mixed solutions examined here, except the

solutions of $X = 0.1-0.5$ in the presence of 50 mM NaCl. The stronger interaction was observed at higher surfactant concentration. In very few cases, the contribution of the intermicellar interaction has been elucidated from light scattering for dilute solutions of C_{12} DAO and ODAO.^{28,29}

Intraparticle Structure Factor. The intraparticle structure factor for ellipsoidal particles^{25,26} is applied for small mixed micelles of C_{12} DAO and SDS. The ellipsoid structure is based on a two-layer model which is composed of a hydrophobic inner core and a surrounding hydrophilic shell.² The core consists of surfactant hydrocarbon chains, and the shell includes surfactant polar heads and hydrated D_2O molecules under the assumption that aqueous solvent molecules can permeate in the shell but not in the core.

If v_{sf} , v_{hc} , and v_{hg} represent volumes of surfactant, hydrocarbon chain, and polar head, respectively, the following relation is described.

$$v_{sf} = v_{hc} + v_{hg} \quad (3)$$

Supposing that the head group takes the spherical shape with a diameter d , the volume v_{hg} is calculated by

$$v_{hg} = 4\pi(d/2)^3/3 \quad (4)$$

Then the thickness of ellipsoidal shell is equal to the diameter d . The volume v_{hc} in unit of \AA^3 is calculated by an equation presented by Tanford.³⁰

$$v_{hc} = 27.4 + 26.9(n_c - 1) \quad (5)$$

where n_c is the number of carbon atoms in an alkyl chain.

For the prolate ellipsoid structure with hemimajor and hemiminor axes a and b , respectively, volumes of core and ellipsoid are described by

$$V_i = 4\pi ab^2/3 = mv_{hc} \quad (6)$$

$$\begin{aligned} V_M &= 4\pi(a+d)(b+d)^2/3 \\ &= mv_{hc} + mv_{hg} + ymv_s \end{aligned} \quad (7)$$

respectively, where y is a number of hydrated D_2O per surfactant, and v_s is a volume of D_2O , being equal to 30.2\AA^3 .

The intraparticle structure factor for the monodisperse system of prolate ellipsoid is written by

$$\begin{aligned} P(Q) &= \int_0^1 d\mu [(q_a - q_s)V_M J_1(U_m)/U_m + \\ &\quad (q_i - q_a)V_i J_1(U_c)/U_c]^2 \\ U_m &= Q[(a+d)^2\mu^2 + (b+d)^2(1-\mu^2)]^{1/2} \\ U_c &= Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2} \\ J_1(x) &= 3(\sin x - x \cos x)/x^2 \\ \mu &= \cos \theta' \end{aligned} \quad (8)$$

where q_i , q_a , q_s are scattering length densities of core, shell, and solvent, respectively. $J_1(X)$ is the first-order spherical Bessel function. θ' is an angle between the major axis and the Bragg wave vector. The corresponding equations for oblate ellipsoid are also derived.^{25,26}

Interparticle Structure Factor. The electrophoretic light scattering investigation for aqueous C_{12} DAO solutions in the

presence of NaCl displayed negative electrophoretic mobility, indicating the partial ionization of C_{12} DAO micelles.³¹ The negative mobility was observed even if SDS was added to aqueous C_{12} DAO solutions at fractions $X = 0-1$.³² These results suggest that the intermicellar interaction in mixed solutions of C_{12} DAO and SDS is the Coulomb force.

The electrostatic repulsive potential between two identical spherical macroions of finite diameter σ ($=2(ab^2)^{1/3}$ for a prolate ellipsoid) with hard core is described by³³

$$\begin{aligned} V(r) &= \pi\epsilon_0\epsilon\sigma^2\psi_0^2 \exp[-\kappa(r-\sigma)]/r \quad r > \sigma \\ V(r) &= \infty \quad r < \sigma \end{aligned} \quad (9)$$

if $\kappa\sigma < 6$, where ϵ_0 is the permittivity of free space, ϵ the dielectric constant of solvent medium, κ the Debye-Hückel inverse screening length, and r the interionic center-to-center distance. ψ_0 is the surface potential and related to the electric charge of macroion z_m to a good approximation by

$$\psi_0 = z_m/\pi\epsilon_0\epsilon\sigma(2 + \kappa\sigma) \quad (10)$$

According to the theory of simple liquid,²⁷ an Ornstein-Zernike equation is described by

$$h(r) = c(r) + n_p\sigma^3 \int h(|r-r'|)c(r') dr'$$

where

$$\begin{aligned} c(r) &= -V(r)/k_B T \quad r > \sigma \\ h(r) &= g(r) - 1 = -1 \quad r \leq \sigma \end{aligned} \quad (11)$$

where k_B is the Boltzmann constant, and T is the absolute temperature. $h(r)$ is the total correlation function and $c(r)$ is the direct correlation function. $g(r)$ is the radial distribution function, which is expressed as follows:

$$g(r) = 1 + (1/12\pi\eta r) \int_0^\infty [S(Q) - 1] Q\sigma \sin Q\sigma r dQ \quad (12)$$

where η ($=\pi n_p\sigma^3/6$) is the volume fraction.

In order to obtain the expression of the interparticle structure factor $S(Q)$ by solving the Ornstein-Zernike equation, the treatment by Hansen and Hayter¹⁹ is applied here. The treatment, called the rescaled mean spherical approximation (RMSA), is based on the mean spherical approximation (MSA) which was introduced by Hayter and Penfold.² The MSA method is applicable for solutions at high concentrations. When the treatment is expanded to solutions at low concentrations, the radial distribution function becomes negative at the distance σ . This is not physically reasonable. Therefore, in the RMSA method, σ is replaced by a diameter σ' of spherical macroions determined by a Gillan criterion as follows:

$$g^{\text{RMSA}}(r = \sigma') = 0$$

with

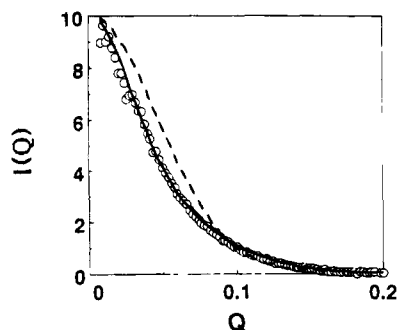
$$s = \sigma/\sigma' \quad (13)$$

where s is a rescaled factor.

Calculation. C_{cmc} values for mixed solutions of C_{12} DAO and SDS without NaCl were evaluated by the interpolation of data reported by Bakshi et al.²¹ C_{cmc} in 50 mM NaCl was regarded to be negligible. By using v_{sf} values calculated from data by Bakshi et al.,²¹ the volume v_{hg} and the thickness d were evaluated from eqs 3-5. The scattering length b_s of D_2O and its density q_s were $19.15 \times 10^{-13} \text{ cm}$ and $6.38 \times 10^{-14} \text{ cm}$

TABLE 1: Parameters Used in SANS Analysis for Mixed Solutions of C₁₂DAO and SDS

<i>X</i>	<i>C</i> _{cmc} in water, ^a mM	<i>v</i> _{sf} , ^a Å ³	<i>v</i> _{hg} , Å ³	<i>d</i> , Å	<i>b</i> _a , 10 ⁻¹³ cm	<i>q</i> _a , 10 ⁻¹⁴ cm Å ⁻³
0	2.00	410.2	60.0	4.86	6.60	1.01
0.1	0.79	408.7	58.5	4.82	8.43	1.44
0.2	0.56	407.2	57.0	4.77	10.8	1.89
0.3	0.62	405.7	55.5	4.73	13.2	2.37
0.4	0.71	404.1	53.9	4.69	15.5	2.88
0.5	0.85	402.7	52.5	4.65	17.9	3.41
0.6	1.12	401.1	50.9	4.60	20.2	3.98
0.7	1.71	399.6	49.4	4.55	22.6	4.58
0.8	2.53	398.0	47.8	4.50	25.0	5.22
0.9	4.23	396.5	46.3	4.46	27.3	5.90
1.0	8.00	395.0	44.8	4.41	29.7	6.63

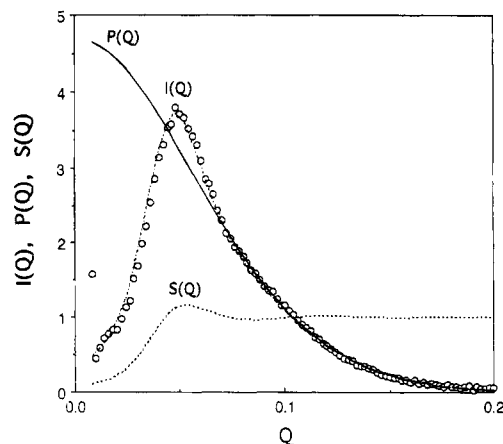
^a Intrapolated the data from ref 21.**Figure 3.** SANS data (○) from a mixed solution of C₁₂DAO and SDS at *X* = 0.2 with 50 mM NaCl. Total surfactant concentration is 80 mM. The solid line is the calculated curve for a prolate ellipsoidal model with parameters *b* = 18.5 Å and *a/b* = 4. The broken line is the calculated curve for an oblate ellipsoidal model with parameters *b* = 18.5 Å and *a/b* = 2.

Å⁻³, respectively. The corresponding *b*_i and *q*_i values of hydrocarbon core were -13.59×10^{-13} cm and -0.39×10^{-14} cm Å⁻³, respectively. The *b*_a and *q*_a values of polar shell are listed in Table 1, where the other parameters used here are included. The *b*_a and *q*_a values for mixtures at $0 < X < 1$ were calculated as the arithmetic average at each *X* value by using *b*_a and *q*_a values at *X* = 0 and 1 for dimethylamine oxide and sulfate, respectively.

By using known parameters, on the basis of eqs 1, 2, and 6–10, the SANS intensity for a given system was calculated by assuming the ellipsoid structure for the intraparticle structure factor and the RMSA for the interparticle structure factor. An optimum set of unknown fitting parameters, *a*, *b*, and $|z_m/em|$ (*e*, the elementary electric charge), was determined from the fitting of the calculated values to the observed ones by using the rescaled parameter *s* which satisfies the boundary condition (eq 13).

The prolate and oblate ellipsoidal models were compared, as illustrated in Figure 3 for a mixed solution of C₁₂DAO and SDS at *X* = 0.2 in the presence of 50 mM NaCl. The solid and broken lines are the calculated curves for prolate (at *a/b* = 4) and oblate (at *a/b* = 2) ellipsoidal models, respectively, with *b* = 18.5 Å. The fitting was very good for the prolate ellipsoid structure but not for the oblate one. Therefore, all other fittings presented here are based on the prolate ellipsoidal model.

Figure 4 is the decomposition of *I(Q)* to *P(Q)* and *S(Q)* for a mixed solution of C₁₂DAO and SDS at *X* = 0.6 in the absence of NaCl. The fitting was carried out for a prolate ellipsoidal model with parameters *b* = 18.5 Å and *a/b* = 4. It is obvious that there is the meaningful contribution of the interparticle structure factor. Similar results were also obtained for the other solutions examined here.

**Figure 4.** SANS data (○) from a mixed solution of C₁₂DAO and SDS at *X* = 0.6 without NaCl. Total surfactant concentration is 80 mM. The lines are the calculated SANS intensity and its decomposition to intraparticle and interparticle structure factors, which were evaluated on the basis of the prolate ellipsoidal model with parameters *b* = 18.5 Å and *a/b* = 4.**TABLE 2: Parameters Obtained from SANS Analysis for Mixed Solutions of C₁₂DAO and SDS in the Absence of NaCl**

<i>X</i>	<i>s</i>	<i>b</i> , Å	<i>a/b</i>	<i>σ</i> , Å	<i>m</i>	<i>η</i>	<i>y</i>	$ z_m/em $
0	1	18.5	1.45	51.6	110	0.0307	8.2	0.015
0.1	0.718	18.5	1.95	55.9	148	0.0295	7.3	0.06
0.2	0.602	18.5	2.30	58.4	174	0.0287	6.9	0.08
0.3	0.595	18.5	2.37	58.7	179	0.0283	6.9	0.079
0.4	0.592	18.5	2.58	60.0	195	0.0277	6.7	0.075
0.6	0.618	18.5	2.10	56.6	159	0.0284	6.9	0.080
0.7	0.607	18.5	1.75	53.7	133	0.0287	7.2	0.10
0.8	0.600	18.5	1.50	51.4	113	0.0294	7.8	0.12
1.0	0.593	18.5	1.30	49.2	98	0.0276	8.1	0.14

TABLE 3: Parameters Obtained from SANS Analysis for Mixed Solutions of C₁₂DAO and SDS in the Presence of 50 mM NaCl

<i>X</i>	<i>s</i>	<i>b</i> , Å	<i>a/b</i>	<i>σ</i> , Å	<i>m</i>	<i>η</i>	<i>y</i>	$ z_m/em $
0	1	18.5	1.3	50.1	98	0.0324	8.7	0.04
0.1		18.0	1.9	55.5	144	0.0299	6.0	
0.2		18.5	4.0	68.3	302	0.0265	6.1	
0.3		19.0	4.0	69.7	328	0.0260	5.8	
0.4		18.0	4.0	66.5	279	0.0266	6.2	
0.5		19.0	4.0	69.6	328	0.0259	5.7	
0.6	0.732	18.5	4.5	69.6	341	0.0249	5.8	0.06
0.7	0.697	18.5	2.75	60.9	208	0.0274	6.4	0.09
0.8	0.727	18.5	2.1	56.3	159	0.0283	6.8	0.10
1.0	0.735	18.5	1.4	50.2	106	0.0301	7.7	0.13

The solid lines in Figure 1 show results of the fitting. The determined fitting parameters, the hemiminor axis *b* of an ellipsoidal core, the axial ratio *a/b*, the average electric charge number $|z_m/me|$ per surfactant, and the rescaled factor *s*, are listed in Tables 2 and 3 for solutions with 0 and 50 mM NaCl, respectively. Tables include the calculated parameters, the diameter *σ*, the aggregation number *m* of a micelle, the volume fraction *η*, and the number *y* of hydrated D₂O per surfactant.

Discussion

SANS investigation was carried out for aqueous solutions of neutral C₁₄DAO at a concentration of 60 mM¹⁶ and oligooxyethylene alkyl ethers (C_{*n*}E_{*m*}) at a dilute concentration.^{3,4} The SANS intensities for such nonionic surfactant solutions did not display a peak. On the other hand, the SANS intensities for aqueous C_{*n*}E_{*m*} solutions at high concentrations had a peak.^{3,9,12,13} The same behavior was observed for an aqueous C₁₂DAO solution (*X* = 0) of 80 mM examined here. The scattering angle

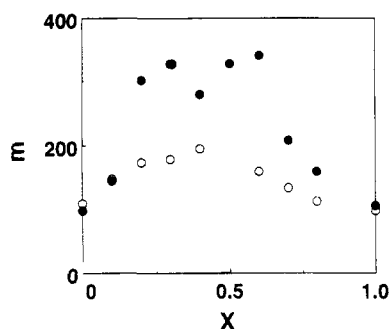


Figure 5. Aggregation numbers of micelles in mixed solutions of C_{12} DAO and SDS as a function of the mixing molar fraction. Total surfactant concentration is 80 mM. NaCl concentration: \circ , 0 mM; \bullet , 50 mM.

dependence of light scattering intensity for aqueous solutions of C_n DAO and oleyldimethylamine oxide^{28,29} was consistent with the latter SANS behavior: the light scattering intensities increased with scattering angle or had a maximum.

The SANS profile with a remarkable peak for aqueous SDS solutions ($X = 1$) observed here coincided with that reported previously¹ and is a common behavior for ionic surfactant solutions at finite micellar concentrations.^{5-7,10,11,17,18} The SANS investigation was performed for aqueous 0.1 M C_{16} TAB solutions.¹⁵ The intermicellar interaction disappeared when 0.2 M KCl was added. This is comparable with the fact that the intermicellar interaction was shielded by the addition of 50 mM NaCl in mixed solutions of C_{12} DAO and SDS at $X = 0.1-0.5$. Since micelles composed of ionic and nonionic surfactants have charges less than those of pure ionic surfactant micelles, the charge of micelles is shielded by a less amount of added salt.

As seen in Tables 2 and 3, the evaluated volume fraction was ~ 0.03 . This means that solutions were dilute enough to satisfy the condition of $\eta < 0.2$ for the application of RMSA.¹⁹ The calculated $k\sigma$ values were lower than 6, satisfying the condition for the application of eq 9. The hemimajor axis b of prolate ellipsoids was always 18–19 Å for all systems and consistent with the calculated alkyl chain length. For a homogeneous solution of C_{12} DAO or SDS, axial ratio was as small as 1.3–1.4, whereas it increased with mixing surfactants. The increase was dominant in the presence of 50 mM NaCl owing to the salting-out effect. This behavior was related to that of micellar aggregation number. While aggregation numbers obtained were ~ 100 for systems at $X = 0$ and 1, they were maximum at equimolar mixing, as seen in Figure 5. The maximum value was 1.6 times larger in the presence of 50 mM NaCl than in the absence of NaCl. These results suggest that micelles in the mixed solutions are ellipsoid or very short rod.

It should be noticed that the micellar size did not display additivity but was maximum at equimolar mixing. This coincides with the nonideal behavior in pH of solutions.³² The solution pH at equimolar mixing was very high (pH = 10–11.5) in comparison with that (pH = 7–9) of SDS or C_{12} DAO.

The nonideal behavior of micellar aggregation number as a function of mixing fraction can be compared with that as a function of degree of ionization.²⁴ The aggregation numbers for aqueous C_{12} DAO solutions increased in addition of NaCl and had a maximum value at the degree of ionization of ~ 0.5 . This suggests the possible ion pairing between C_{12} DAO and SDS in the mixed solutions and between nonprotonated and protonated C_{12} DAO in the moderately titrated C_{12} DAO solutions.

The behavior of micellar size in the mixed solutions of C_{12} DAO and SDS is in contrast to that in the mixtures of C_{14} DAO and C_{14} TAB.²³ In the latter system, micellar sizes

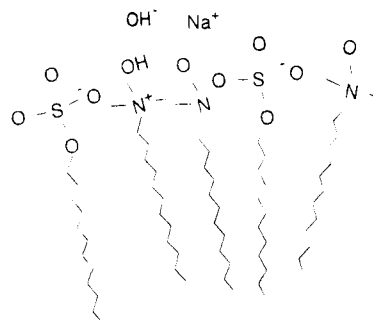


Figure 6. Schematic representation of ion pair formation in mixed solutions of C_{12} DAO and SDS.

decreased with increasing C_{14} TAB content. Similar difference was observed for solution pH: the pH of mixed solutions of C_{12} DAO and C_{12} TAB almost linearly changed.³² The different behavior between C_n DAO–anionic surfactant and C_n DAO–cationic surfactant complexes is due to the formation of different orientation of amine oxide dipole with anionic and cationic surfactants.³²

Hydrated D_2O for pure C_{12} DAO or SDS micelles was 8–9 per surfactant, as listed in Tables 2 and 3. These are close to values reported for SDS micelles and higher than values for alkyltrimethylammonium halide micelles.² In the mixed solutions of C_{12} DAO and SDS, hydrated D_2O decreased to 6–7. This variation can be compared with that of micellar aggregation number. Hydrated D_2O decreased with increasing the aggregation number, although Hayter and Penford² reported the inverse dependence.

The average electric charge number $|Z_m/em|$ per surfactant in micelles increased with an increase in molar fraction of SDS as expected. If the charge numbers result from the desorption of Na ion from SDS, the average charge numbers per SDS in micelles are 0.145 for solutions without NaCl and 0.13 for solutions with 50 mM NaCl. This means that the counter ion binding per SDS is 0.85–0.87, in agreement with the result estimated from Na ion potentiometric titration.³² In this connection, Hayter and Penford² and Bendedouch and Chen^{7,8} evaluated the degree of ionization of 0.12–0.35 for aqueous solutions of SDS and lithium dodecyl sulfate, depending on the surfactant and salt concentrations. Hayter³⁴ calculated the degree of ionization of SDS on the basis of the dressed micelle model. Their values agreed well with the average electric charge numbers per surfactant obtained in this work.

In the mixed solutions of C_{12} DAO and SDS, a self-protonated C_{12} DAO molecule interacts electrostatically with a SDS molecule to form an ion pair, as illustrated in Figure 6, inducing the nonideal behavior in the micellar aggregation number and the solution pH. The formation of ion pair allows surfactants to behave like double-tailed surfactant, that is, a hydrophobic one, which promotes the formation of micelles with larger aggregation number. Since a self-protonated C_{12} DAO releases hydroxyl ion, the solution pH increases.

Conclusions

C_{12} DAO molecules which are weak-base surfactants self-protonate and make an ion pair with SDS by electrostatic interaction, following the rise in solution pH. The ion pairs behave like double-tailed surfactants and induce larger micelles.

While the shape of pure C_{12} DAO or SDS micelles is a prolate ellipsoid with axial ratio of 1.3–1.4, micelles at equimolar mixing of C_{12} DAO and SDS have a maximum size: these grow to larger ellipsoids like short rod. Hydrated D_2O is 6–9, depending on the mixing fraction and salt concentration.

The electric charge number per surfactant in micelles increases with mixing fraction of SDS, indicating the constant charge number per SDS in micelles. This corresponds to the counterion binding of 0.85–0.87 to SDS.

The electrostatic repulsion force acts mainly between micelles in the mixed solutions of C₁₂DAO and SDS. The addition of NaCl to the surfactant solutions shields the micellar electric charge and the electrostatic interaction, disturbing the ion pairing and the intermicellar interaction.

References and Notes

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