Effects of Protonation on Tetradecyldimethylamine Oxide Micelles

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Solution and surface properties of tetradecyldimethylamine oxide (C14DAO) aqueous solutions were examined and compared with those of dodecyldimethylamine oxide (C12DAO). The following two important behaviors of C12DAO were both observed with C14DAO in the present study. (1) The cmc of the cationic species, cmc_+, was lower than that of the nonionic species cmc_0 in the range of NaCl concentration C_s higher than about 0.2 M. (2) The micelle size was the largest at about 1:1 composition. On the other hand, the following three important aspects different from C12DAO were found for C14DAO. (1) Values of pK_M were greater by 0.4−0.5 than those of C12DAO at three NaCl concentrations C_s examined. This finding is quantitatively explained in terms of different shapes of the two nonionic micelles. (2) The monomer concentration evaluated from the hydrogen ion titration with the Gibbs−Duhem relation differed from the cmc. This difference gave the concentration dependence of the regular solution theory parameter β. (3) At the composition of 1:1 ($\alpha_M = 0.5$), the cooperative diffusion mode was observed in the dynamic light scattering indicative of entanglement of long micelles. The mesh size was about 10 nm. The following quantitative differences were also observed. (1) The salting-out constant, $(-d \log cmc_0/dC_s)$, was 0.40 M^{-1} (0.32 M^{-1} for C12DAO). (2) The slope $d \log cmc_+/d \log$(counterion concentration) in the range $C_s < 1$ M was 0.71 (0.64 for C12DAO). (3) The dependence of the cmc on pH at 0.1 M NaCl was approximately described in terms of the regular solution theory with the parameter $\beta = -1.4 \pm 0.2$, which is less negative than that of C12DAO ($\beta = -2.12$).

Introduction

Alkyldimethylamine oxide has been used mostly as a nonionic surfactant, but it exists as either a nonionic or a cationic (protonated form) species depending on the pH of the aqueous solution and the solution properties vary with pH.[1−21] Among them, dodecyldimethylamine oxide (C12DAO) has been extensively studied. The aggregation number of C12DAO exhibits a maximum around the half-ionized state when the degree of ionization of micelle α_M is varied, as shown previously.[1,15] The interactions giving rise to this characteristic dependence were correlated with the pH dependencies of the critical micelle concentrations (cmc), as shown by Rathman and Christian[11] and us.[16] General correlation of this kind have been extensively discussed by Hoffmann.[22] In the hydrogen ion titrations the intrinsic dissociation constant exponent pK_M of the amine oxide group on the micelle surface has been known to be greater than that of the monomer.[3,6] These characteristic properties have been interpreted in terms of the hydrogen bond formation between the nonionic and the cationic species.[17] Our later study on the effects of ionic strength on the cmc of C12DAO has revealed the interesting result that the cmc of the cationic species is lower than that of the nonionic one at high ionic strengths (higher

than 0.2 M NaCl).[18] A hydrogen bond formation between the two neighboring cationic species is thus suggested.

In the present study, solution properties of tetradecyldimethylamine oxide (C14DAO) are examined by hydrogen ion titration, cmc, surface excesses, and dynamic light scattering (DLS) measurements, with emphasis on the effect of protonation. The hydrogen ion titration of C14DAO was reported though without information on pK_M.[4] The main aim of the present study is to examine whether the above-mentioned extraordinary results found for C12DAO are observed for C14DAO. Another aim is to find possible effects arising from the increased packing ratio of C14DAO on the solution properties.

Experimental Section

Tetradecyldimethylamine oxide (Gerbu Biotechnik Gmbh: 15% aqueous solutions) was freeze-dried and recrystallized from hot acetone. Then, the nonionic amine oxide was dissolved in hot acetone and after the addition of hydrochloric acid the solution was cooled. The precipitated hydrochloride salt was filtered, washed with hexane, dissolved in water, and freeze-dried. In the present study, hydrochloride salt was used to prepare solutions of various compositions unless otherwise stated. Salt solutions were prepared on a weight basis. The salt concentration was expressed in molarity C_s (M) for H_2O

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solutions and in molality c_S (m) for D_2O solutions. Densities of NaCl solutions were used to calculate C_s. At low C_s, the counterion concentration C_g was significantly higher than C_s when pH is below 3, due to the addition of HCl.

Hydrogen ion titrations were carried out at 25 ± 1 °C. Solutions (ca. 20 g) with a surfactant concentration C_D of about 20 mM and a NaCl concentration c_S were titrated with a 0.1 N or 1 N NaOH solution under a nitrogen atmosphere. In the back-titration, 1 N HCl was used. Blank titrations were carried out by the addition of 0.1 N HCl to the solution of the same c_S and the same volume but containing no surfactant. Average degrees of ionization of the total solution $\langle\alpha\rangle$ were calculated according to the neutrality condition and the free hydrogen ion concentration estimated from the blank titration. $\langle\alpha\rangle$ is related to the degrees of ionization of the micelle α_M and the monomer α_1 as follows.

$$C_D\langle\alpha\rangle = (C_D - C_1)\alpha_M + C_1\alpha_1 = (C_D - \text{cmc})\alpha_M + \text{cmc } \alpha_1 \tag{1}$$

The second equality of eq 1 is obtained when the monomer concentration C_1 is approximated with the cmc.

Surface tension was measured at 25 ± 0.05 °C with the drop volume method using a capillary (radius 0.107 cm). The drop was kept for about 10 min to attain the adsorption equilibrium.

Dynamic light scattering (DLS) was carried out with a Malvern System 4000 at the measuring angles of 60°, 90°, and 120°. Sampling times were in the range of $5-10$ μs.

A set of small-angle neutron scattering experiments was performed at the SANS instrument at the DR3 reactor at Risø National Laboratory, Denmark.[23] The range of scattering vectors q was from 0.0037 to 0.45 Å^{-1}. The samples were kept in quartz cells (Hellma) with a path length of 5 mm. The two-dimensional isotropic scattering spectra were azimuthally averaged, converted to an absolute scale, and corrected for backgrounds and for detector efficiency. The scattering intensity was furthermore normalized by dividing by the concentration of C14DAO.

Results

Hydrogen Ion Titration. Hydrogen ion titration was carried out at a surfactant concentration C_D of 20 mM and three different NaCl concentrations C_s (0.01, 0.10, 0.98 M). Since the cmc was about or below 0.1 mM, it turned out that the contribution from the monomer was negligible in eq 1, i.e., $\alpha_M = \langle\alpha\rangle$. Apparent dissociation exponents pK_a, defined as eq 2, are shown in Figure 1 as functions of α_M.

$$pK_a = pH + \log[\alpha_M/(1 - \alpha_M)] \tag{2}$$

Values of pK_M, K_M denoting the intrinsic proton dissociation constant of the micelle, were evaluated by extrapolating pK_a to $\alpha_M = 0$: p$K_M = pK_a$ ($\alpha_M = 0$). Values of pK_M were 6.30 and 6.70 within an error of ± 0.1 at 0.10 ($C_g = 0.13$ M) and 0.98 M. At $C_s = 0.98$ M, an anomalous α_M dependence of pK_a, dpK_a/d$\alpha_M > 0$, was observed in the range $\alpha_M < 0.05$. Although similar behavior was reported on another surfactant,[24] we regard this as originating from our inaccurate evaluations of α_M in this range. This is supported by the SANS measurements described below. Despite this uncertainty to evaluate pK_M values, it is important to note that the pK_M values of C14DAO are significantly greater than those of C12DAO:[5,6] 5.76, 5.89, and 6.33 for NaCl solutions of 0.01, 0.10, and 1.0 M, respectively. Differences of pK_M between the two surfactant micelles, ΔpK_M-(C14−C12), scarcely depended on C_s: 0.41 and 0.37 at 0.10−0.12 and 1.0 M NaCl resulting in a rounded value of about 0.4.
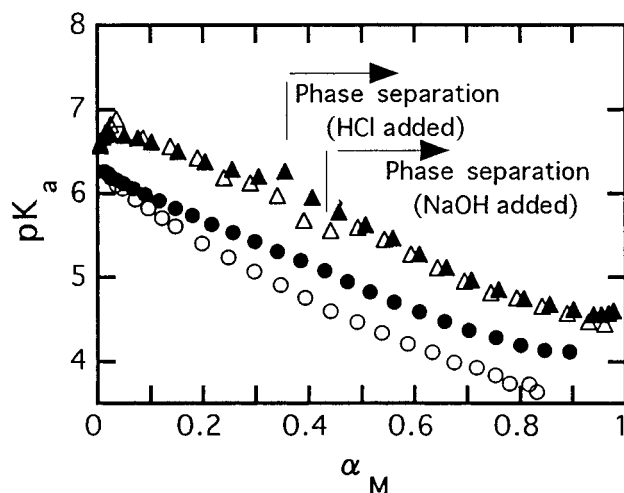

Figure 1. Hydrogen ion titration of C14DAO at 25 °C. pK_a = pH + log[α_M/(1 − α_M)]; surfactant concentrations C_D = 20 mM. NaCl concentrations C_s (M): 0.01 (○), 0.10 (●), and 0.98 (▲, HCl added; △, NaOH added).

The difference ΔpK_M(C14−C12) is undoubtedly related to different shapes of the nonionic micelles: spherical for C12DAO[1,15] and rodlike for C14DAO.[19,21] This further suggests that the α_M values differ for the cylindrical part and the hemispherical part of rodlike micelles, not only to make the surface electric potential uniform but also due to different pK_M values in these two regions.

The electric surface potential ψ_0 of the micelle was calculated according to eq 3 in terms of the protonic charge e_0, the Boltzmann constant k, and the absolute temperature T.

$$pK_M - pK_a = 0.434e_0\psi_0/kT \tag{3}$$

The results showed that the surface potential is larger for C14DAO than C12DAO.

At $C_s = 0.98$ M, a liquid−liquid phase separation took place in the range of α_M greater than about 0.4. A hysteresis was observed about the phase separation: it took place at $\alpha_M = 0.38$ when titrated with HCl (filled triangles) while at $\alpha_M = 0.42$ when titrated with NaOH (open triangles). The hysteresis is just the opposite to what is expected for the nucleation of the concentrated phase. When a water-insoluble dye (Sudan III) was added to the two-phase solutions, only the upper layers became colored while the lower layers remained uncolored. This suggests that the number of micelles in the lower solutions is negligible.

SANS Measurements on the Solutions of Low Degrees of Ionization α_M. Since the observed unusual titration behavior in 1 m NaCl solutions at a low ionization range ($\alpha_M < 0.05$) (Figure 1) might be related to possible changes of size and/or shape of the micelles, SANS measurements on D_2O solutions of the similar surfactant concentration and the corresponding range of α_M were carried out. However, the measured intensities of neutron scattering $I(q)/c$ (concentration c in g/mL, the scattering vector $q = 4\pi \sin \theta/\lambda$, 2θ is the scattering angle, and λ is the wavelength) of C14DAO in 1 m NaCl/D_2O with varying degrees of ionization were similar in the statistical errors. An example of the scattering data is shown in Figure 2 with filled circles for the solution ($\alpha = 0.1$). Therefore, we cannot ascribe the anomalous titration behavior observed in the narrow range of $\alpha < 0.05$ to any shape and/or size change of micelles. Since we deal with micelles of low charge densities in a high ionic strength (1 m NaCl), we can safely ignore the intermicelle
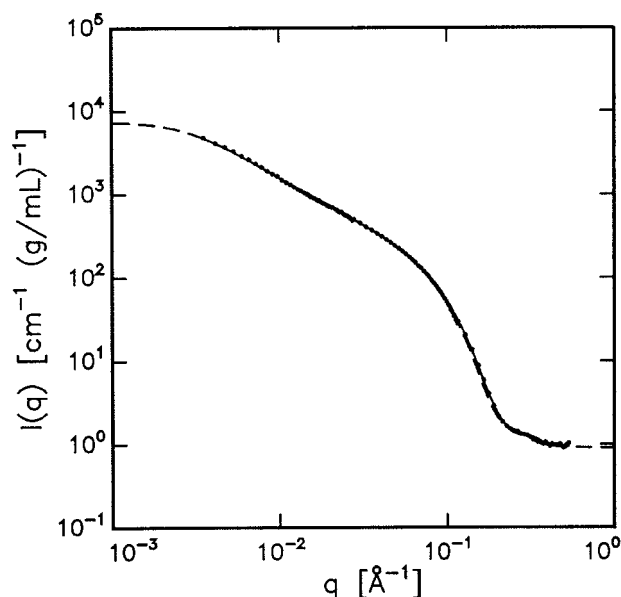
Figure 2. Neutron scattering curves in 1 *m* NaCl/D$_2$O solution. α_M = 0.1; surfactant concentrations C_D = 20 mM. A dashed line represents the fitted curve calculated according to eq 4 with parameters given in Table 1.

electric repulsion in the analyses of the SANS data. The experimental scattering data shown in Figure 2 were fitted with an expression based on the modified random-phase approximation:[25]

$$I(q)/c = \frac{M_W \Delta \rho_m^2 S_{WC}(q) \, S_{CS}(q)}{1 + \dfrac{1 - S(0)}{S(0)} f_{excl}(q^2 \bar{R}_g^2)} \quad (4)$$

where M_W is the molecular weight and $\Delta \rho_m = -7.37 \times 10^{10}$ cm/g[26] is the average excess scattering length per unit mass of the micelle. $S_{WC}(q)$ denotes the scattering function of self-avoiding wormlike chains with contour length L and Kuhn length b, $S_{CS}(q)$ is the cross section scattering function, which was taken to be that of an elliptical cross section with semiaxes A and B, and $f_{excl}(q^2 R_g^2)$ is the scattering function of self-(avoiding flexible chains with radius of gyration R_g equal to that of wormlike chains with L and b. The reduction of the forward scattering $S(0)$ due to interaction effects was calculated from an expression based on renormalization group theory and the growth law. For the growth law in the present study, we used the result determined for micelles with $\alpha = 0.5$ in 0.1 M NaCl.[27] The concentration for the sample in Figure 2 is only 5.26 mg/mL, which is expected to be only slightly above the overlap concentration of the micelles (cf. Figure 7). We estimated the value for $S(0)$ to be 0.20 and the contour length L to be 7600 Å. The results of the fit is given in Table 1. Note that the flexibility of the micelles as given by the value of the Kuhn length is similar to that found in other micellar systems.[28] Note also that the cross section has a relatively large eccentricity (B/A = 1.7) which is similar to that found in SDS−DTAB micelles.[29]

Critical Micelle Concentration. Critical micelle concentrations (cmc) were determined from the break point of the surface tension vs log C_D plots shown in Figure 3. The surface tension at cmc, γ_{cmc}, did not change much with pH at C_s = 0.1 M. They were (±0.1) 31.3, 28.8 (minimum), and 29.8 mN/m for α_1 of 0, 0.5, and 1, respectively. At C_s = 0.01 M, they were (±0.1) 31.9, 30.5, and 30.4 mN/m for α_1 of 0, 0.7, and 1,

respectively. Values of cmc were also obtained from the pH-break method previously used.[14,16] Open and filled circles in Figure 4 show the respective results for the cationic (cmc$_+$) and the nonionic (cmc$_0$) species. Values of cmc$_0$ are smaller than cmc$_+$ at C_s lower than about 0.2 M, as expected from the electric repulsion among cationic headgroups. It is remarkable, however, that in the range of C_s greater than 0.2 M, cmc$_+$ are smaller than cmc$_0$. The same crossing of the stability of the micelle has been observed for C12DAO.[18]

The following relation generally found for nonionic micelles[30] also holds in the present case, as shown in Figure 4A.

$$\log[\text{cmc}_0] = -K_s C_s + \text{constant} \quad (5)$$

The parameter K_s is closely related to the salting-out effect and it was 0.40 ± 0.1 M^{-1} in the present case. The constant was 0.76 ± 0.01. The K_s value of C12DAO is 0.32 ± 0.01 M^{-1}.[18] The difference in K_s of about 0.08 per two methylene groups is in good agreement with the corresponding value observed for alkylbetaine:[31] 0.134, 0.215, and 0.291 for C8, C10, and C12, respectively.

Cmc values of ionic surfactants have been known to obey the following Corrin−Harkins relation,[30,32] in terms of the counterion concentration C_g and a constant k_{CH}.

$$\log \text{cmc} = -k_{CH} \log C_g + \text{constant} \quad (6)$$

In the present study, log cmc$_+$ linearly decreased with log C_g in the range C_g < 1 M, as shown in Figure 4B, and the data were expressed as

$$\log(\text{cmc}_+/\text{mM}) = -(0.71 \pm 0.01) \log(C_g/\text{M}) - (1.37 \pm 0.01) \quad (C_g < 1 \text{ M}) \quad (7)$$

The k_{CH} value 0.71 is slightly greater than 0.64 for C12DAO.[18] From the consideration of micelle size, the k_{CH} value are expected to increase with increasing hydrocarbon chain length in a homologous series.

The pH dependence of the cmc obtained from the surface tension measurements and the pH-break points are shown in Figure 5 for C_s = 0.010 and 0.10 M. The dependence of the cmc on α_M shown in Figure 6 was analyzed in terms of the regular solution model[33,34] with the parameter β = −1.6 to −1.2 for C_s = 0.10 M. At C_s = 0.010 M, cmc$_+$ was estimated to be 1.2 mM.[35] With this cmc$_+$ value, the dependence of the cmc on α_M was reproduced (not shown) with the regular solution model with β = −2.2 to −2.6. More negative β values at lower ionic strengths are well-known for other mixed micelles.[33,34]

It has been known that eq 9 holds in the hydrogen ion titration if the Gibbs−Duhem relation is assumed to be valid for the chemical potentials μ of the nonionic (T) and the cationic (TH) species in the micelle of C14DAO.[16]

$$\alpha_M \, d\mu_{TH} + (1 - \alpha_M) \, d\mu_T = 0 \quad (8)$$

$$\log[C_1/C_1(\alpha_M=0)] = pK_a \alpha_M - \int_0^{\alpha_M} pK_a \, d\alpha_M + \log[(1 - \alpha_M)/(1 - \alpha_1)] \quad (9)$$

Cmc values relative to cmc$_0$ can be evaluated from eq 9 when they are approximated with the monomer concentrations C_1 and $C_1(\alpha_M=0)$. This is in marked contrast to the case of C12DAO, where these two results coincide well.[16] Values of $C_1/C_1(\alpha_M=0)$ at C_D = 20 mM were calculated from eq 9 and are compared with cmc/cmc(0) values in Figure 6. As clearly shown in Figure 6, C_1 differs from the cmc. Under this situation, cmc values

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TABLE 1: Results of SANS Analysis of C14DAO Micelles in 1 *m* NaCl/Heavy Water Mixture[a]

α	L, Å	b, Å	A, Å	B, Å	R_g, Å	$10^{14}M_L$, g/cm	R_{CS}, Å
0.1	7600	370 ± 10	15.1 ± 0.1	25.9 ± 0.2	740 ± 20	6.72 ± 0.05	14.2 ± 0.1

[a] L: contour length of micelle. A: minor axis of elliptical cross section of micelle. B: major axis of elliptical cross section of micelle. b: Kuhn length. R_g: radius of gyration of micelle. M_L: weight of micelle per unit length. R_{CS}: radius of gyration of cross section of micelle.

Figure 4. Logarithm of cmc against (A) NaCl concentration C_s (M) and (B) the logarithm of the Cl ion concentration C_g (M) at 25 °C. Open and filled circles refer to the cationic and the nonionic micelles. Solid lines in A and B are drawn, respectively, according to eq 5 and according to the Corrin−Harkins relation eq 7.
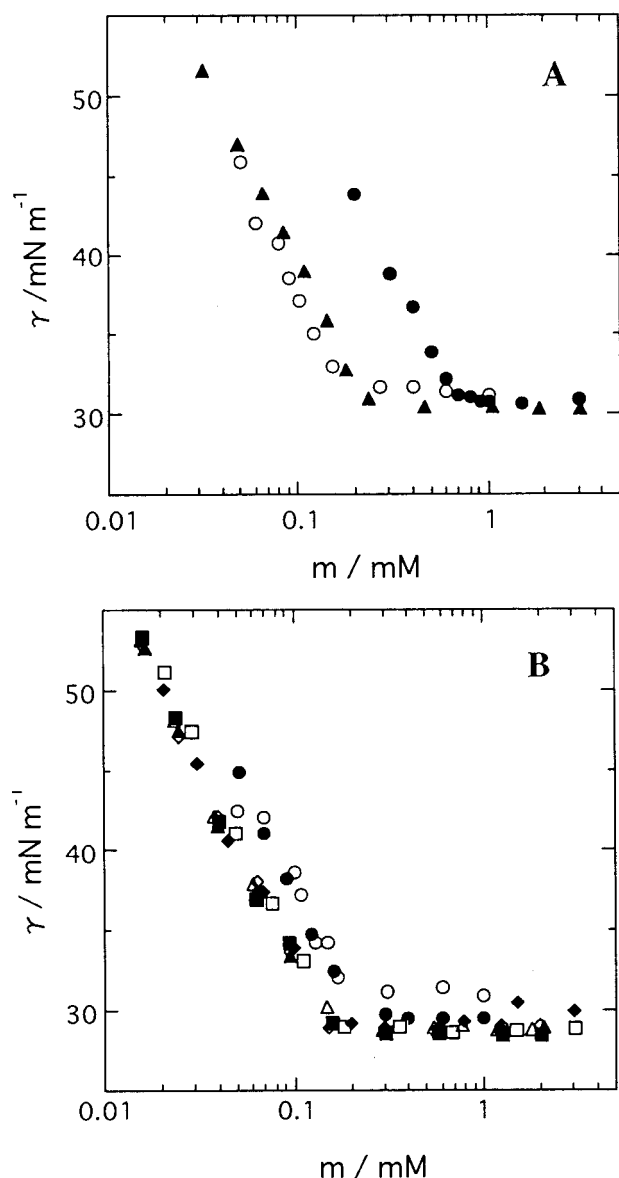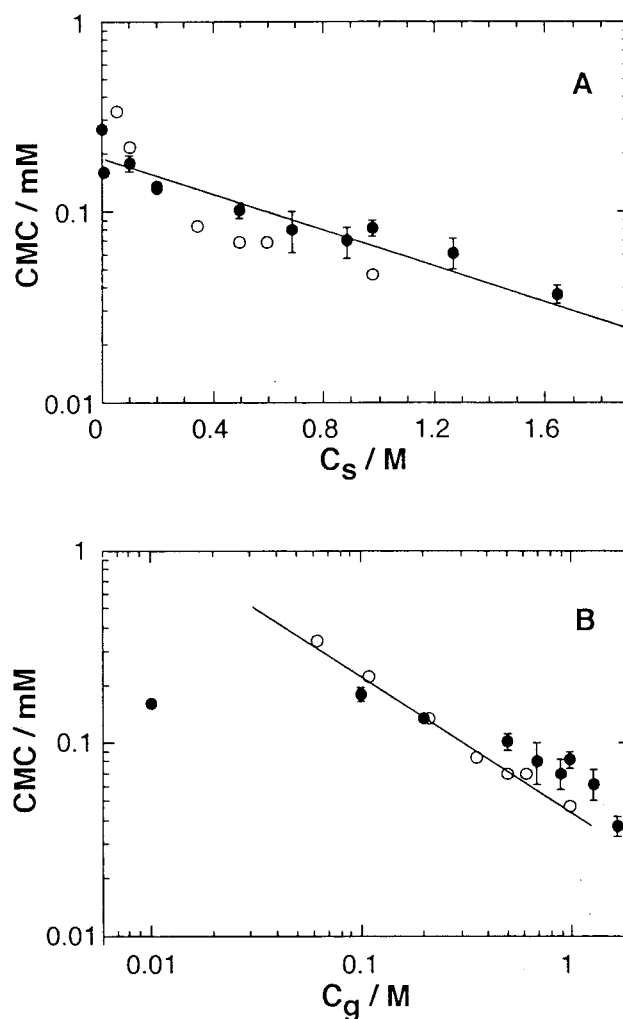
Figure 3. Surface tension as functions of the surfactant concentration at various pH values at 25 °C. (A) 0.010 M NaCl. pH (±0.02): (●) 3.00, (▲) 4.46, and (○) 9.00. (B) 0.10 M NaCl. pH (±0.02): (●) 3.00, (□) 4.10, (■) 4.37, (△) 4.88, (▲) 5.00, (◇) 5.23, (◆) 6.47, and (○) 9.00.

cannot be obtained from the hydrogen ion titration but should be determined with other proper methods, as done in the present study.

Since the regular solution approach essentially deals with C_1 rather than cmc, the dependence of $C_1/C_1(\alpha_M=0)$ on α_M can be analyzed by this approach. At $C_s = 0.1$ M the results shown in Figure 6 gave $\beta = -3.3 \pm 0.1$ for $C_D = 20$ mM. We have thus found that the β value at a concentrations higher than cmc is more negative than that at the cmc ($\beta = -1.4 \pm 0.2$). We expect that this might be the first observation on the effect of the surfactant concentration on the parameter β with the reservation that the regular solution approach is valid for the present mixed micelles.

Dynamic Light Scattering from Dilute and Semidilute Micelle Solutions. Radii of the equivalent hydrodynamic sphere R_H of the micelles were determined with dynamic light scattering on the solutions mostly for the nearly cationic ($\alpha_M = 0.9$) and 1:1 composition ($\alpha_M = 0.5$). The dependence of R_H on C_D is shown in Figure 7. For 1:1 composition in 0.1 M NaCl, R_H scarcely changes with C_D in the range below 30 mM but decreased with increasing C_D in the range $C_D > 30$ mM. In this C_D range, a network formed by entangled long threadlike micelles is expected in the solution. The concentration fluctuation in this range is governed by the cooperative diffusion and we can evaluate the mesh size ξ instead of R_H. The mesh size decreased from about 20 nm to 6 nm as C_D increased from 0.05 to 0.2 M. The straight line drawn in Figure 7 has a slope of -0.75. This is consistent with the value predicted for entangled polymers in a good solvent.[36] A single Maxwell-type viscoelasitic behavior was observed on the solutions of 1:1 composition ($\alpha_M = 0.5$).[37] The micelle growth at $\alpha_M = 0.5$ was found more
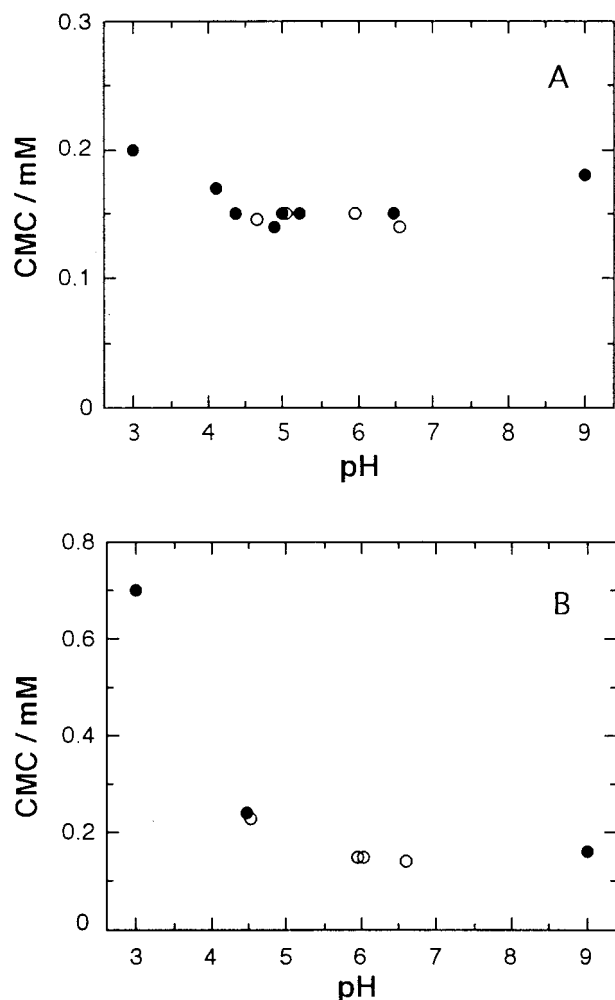
Figure 5. Dependence of the cmc on pH at 25 °C. NaCl concentration (M): (A) 0.1 and (B) 0.01. Open (filled) circles refer to the results obtained from the pH-break method (the surface tension).
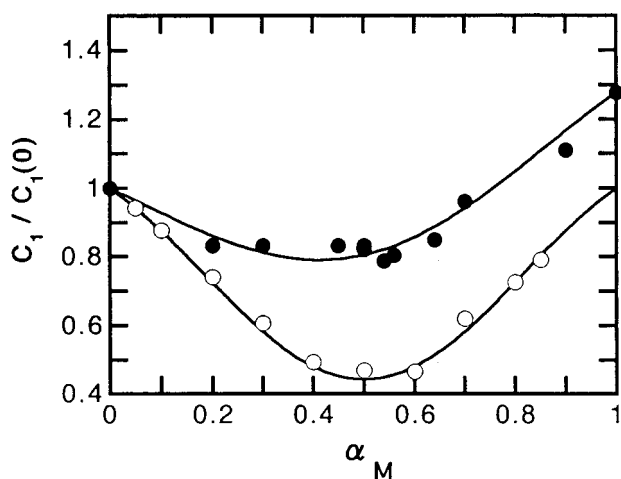

Figure 6. Dependence of the monomer concentration C_1 and cmc on the micelle composition α_M. Ratios of C_1 to that at $\alpha_M = 0$ are calculated by eq 9 for $C_D = 20$ mM (O). Filled circles represent the ratios cmc/cmc ($\alpha_M = 0$). Solid curves are drawn according to the regular solution approach with $\beta = -1.4$ (●) and -3.3 (O).

accentuated for C14DAO than C12DAO. The cationic micelles grow with C_D as shown in Figure 7. A similar growth has been reported for the nonionic C14DAO micelles.[19,21] However, neither the nonionic nor the cationic micelles grow enough to develop a highly entangled network exhibiting significant viscoelasticity.[37]
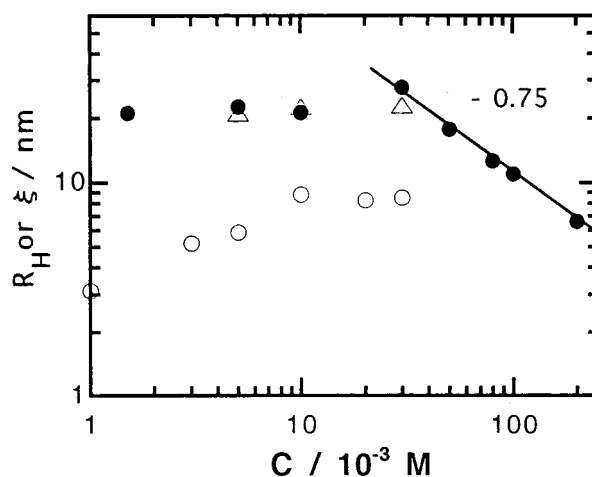

Figure 7. Micelle size or mesh size from the dynamic light scattering as functions of the surfactant concentration C. Open symbols refer to the cationic micelles (pH = 3) at NaCl concentration $C_s = 0.1$ M (circles) and 0.5 M (triangles). Filled circles refer to the micelles of the composition $\alpha_M = 0.5$ in 0.1 M NaCl.

At $C_s = 0.1$ M and $C_D = 10$ mM, the R_H value showed the maximum at $\alpha_M = 0.5$: $R_H/\text{nm} = 4.7 \pm 0.5$, 21.3 ± 2.1, and 8.8 ± 0.5 for $\alpha_M = 0$, 0.5, and 0.9, respectively. The maximum micelle size at $\alpha_M = 0.5$ should not be taken as trivial, since the mixed micelle size is shown to decrease with the charged species fraction when the headgroup sizes of the two components are similar, as in the present case.[38]

Surface Excesses. The surface excesses of the surfactant Γ_D are given by the following equation under the conditions of excess salt and others as shown previously.[18]

$$\Gamma_D = -(0.434/RT)(\partial\gamma/\partial \log C_D)_{\text{pH},C_s,T} \tag{10}$$

Values of Γ_D were evaluated in the range $C_s > 0.05$ M to ensure the condition of excess salt. Surface excesses of both the nonionic and the cationic species were very similar to each other over the whole range of C_s examined, as in the case of C12DAO. In contrast to the case of C12DAO where Γ_D remained at a nearly constant value (4×10^{-6} mol m^{-2}), however, it significantly increased with C_s from about 4.5×10^{-6} mol m^{-2} ($C_s = 0.1$ M) to 6×10^{-6} mol m^{-2} ($C_s = 1$ M) in the case of C14DAO. Values of Γ_D in 0.1 M NaCl were 4.5×10^{-6}, 4.4×10^{-6}, and 4.4×10^{-6} mol m^{-2} at pH values corresponding to α_M of 0, 0.50, and 0.90, respectively, with an error range of $\pm 0.2 \times 10^{-6}$ mol m^{-2}.

Surface excesses of small ions at surfactant concentrations above cmc were evaluated according to the procedure given previously[18] from the variation of γ_{cmc} with C_s (shown in Figure 8) for both the nonionic and the cationic species. For the nonionic species, the following relation was derived previously.[18]

$$\Gamma_{\text{Cl}} = \Gamma_{\text{Na}} = \Gamma_S = (-d\gamma_{\text{cmc}}/d \ln a_\pm)/(2RT) \tag{11}$$

As shown in Figure 8A, the slope ($-d\gamma_{\text{cmc}}/d \log C_s$) increases with C_s and reaches a constant value [$-d\gamma_{\text{cmc}}/d \log a_\pm = 4.91 \pm 0.13$ mN m^{-1}]. Hence, $\Gamma_s/10^{-7}$mol m$^{-2} = 4.25 \pm 0.1$. This value is about 5 times greater than that of C12DAO (0.86×10^{-7}mol m^{-2}).[18]

For the cationic species, $d\gamma_{\text{cmc}}/d \log C_s = -1.88 \pm 0.11$ mN m^{-1} in the range $C_s > 0.1$ M. Values of ($\Gamma_{\text{Cl}} + \Gamma_{\text{Na}}$) were calculated from Γ_D and this value. With the electroneutrality condition, $\Gamma_{\text{Cl}} = \Gamma_{\text{Na}} + \Gamma_D$, Γ_{Cl} and Γ_{Na} were separately

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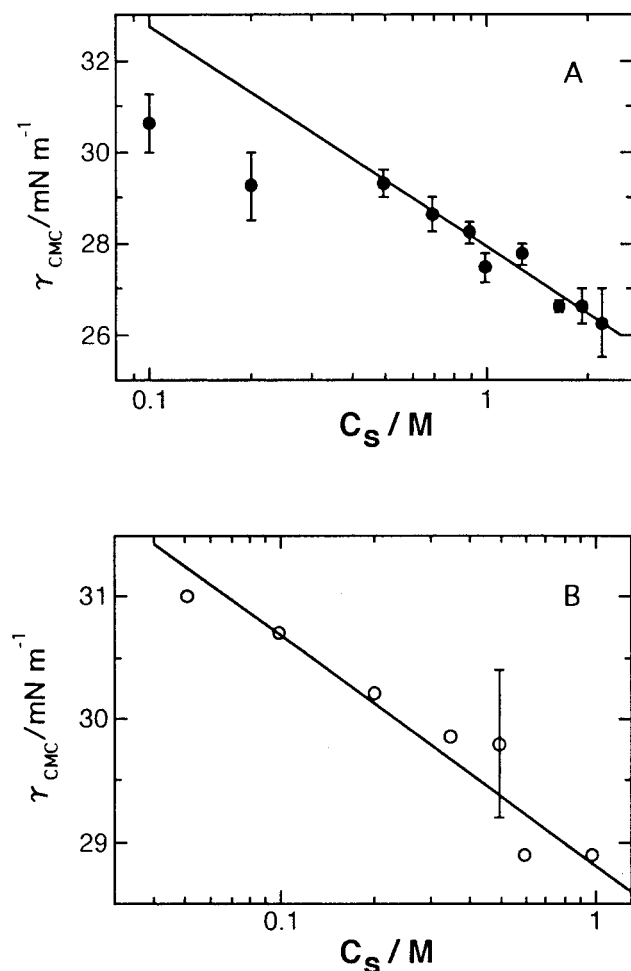

Figure 8. Surface tensions at cmc as functions of NaCl concentration C_s (M): (A) the nonionic micelles and (B) the cationic micelles.

TABLE 2: Surface Excesses of the Cationic Surfactant G_D and Small Ions in the Concentration Range above the cmc[a]

	experimetally found			calculated			
C_s/M	Γ_D	$\Gamma_{Na} + \Gamma_{Cl}$	Γ_{Na}	Γ_{Cl}	$\Gamma_{Na} + \Gamma_{Cl}$	Γ_{Na}	Γ_{Cl}
0.050	3.97	1.80	−1.08	2.89	3.71	−0.07	3.84
0.099	4.13	1.86	−1.13	3.00	3.76	−0.09	3.95
0.200	4.53	2.01	−1.26	3.27	4.02	−0.13	4.27
0.344	5.28	2.29	−1.50	3.79	4.61	−0.17	4.95
0.496	5.40	2.33	−1.53	3.87	4.61	−0.20	5.01
0.592	5.44	2.35	−1.55	3.89	4.58	−0.21	5.01
0.785	6.22	2.64	−1.79	4.43	5.24	−0.25	5.73
0.979	6.02	2.56	−1.73	4.29	4.94	−0.27	5.48

[a] Surface excesses G are given in mmol m^{-2}.

evaluated. The results shown in Table 2 indicate the presence of the salt exclusion effect; i.e., Γ_{Na} is negative, and its magnitude increases with Γ_D.

The calculated results from the Gouy−Chapman electrical double layer theory by the use of the Poisson−Boltzmann (PB) equation are also shown in Table 2. The PB results indicate nearly complete counterion binding of the macroscopic charged surface. However, the agreement with experimental surface excesses was not good.

Discussion

Different pK_M values for C14DAO and C12DAO. In the present study we have found that the pK_M values of C14DAO are greater than the corresponding values of C12DAO by about

0.4 at the two ionic strengths examined. This difference per se supports the presence of some short-range interaction between the neighboring headgroups in couple with the protonation. Otherwise, we should expect little or no dependence of pK_M on the hydrocarbon chain length in a homologous series. This difference is associated with the different nonionic micelle shapes: spherical for C12DAO and rodlike for C14DAO. According to our hydrogen bond model, the protonation leads to the pairing or dimer formation between a nonionic and a cationic species, leaving some increased contact area Δa between water and the hydrocarbon core. The difference $\Delta(\Delta a)$ between the two micelles of C12DAO and C14DAO can be related to the observed ΔpK_M in terms of the interfacial tension $\gamma_{w/HC}$ as follows.

$$-2.3RT\Delta pK_M = \gamma_{w/HC}\Delta(\Delta a) \qquad (12)$$

The area for the cationic−nonionic pair is assumed to be the same for both micelles. An estimate of this quantity is 2×0.35 nm^2 = 0.70 nm^2 if based on the data of C12DAO at the air/water interface.[16] According to this assumption, $\Delta(\Delta a)$ is the difference of the area occupied by these two molecules before protonation between C12DAO and C14DAO. This area is 2×0.60 nm^2 = 1.20 nm^2 for C14DAO[19] and 2×0.72 nm^2 = 1.44 nm^2 for C12DAO. The value of 0.72 nm^2 for C12DAO was evaluated from the hydrodynamic radius (2.0 nm) and the aggregation number (70) of the nonionic C12DAO micelles.[15] This is in good agreement with 0.74 nm^2 given in ref 22. It might be argued that the area per headgroup in the cylindrical part should be used for C14DAO instead of 0.60 nm^2, which is an average value over the whole rodlike micelle including spherical end caps. The validity of this claim is not obvious since some rearrangements as a result of the protonation are likely to occur including a slight change of the aggregation number. This point needs to be examined in the future. Hence, $\Delta(\Delta a) = 1.20 − 1.44 = −0.24$ nm^2. From eq 12, we have $\gamma_{w/HC}$ = 16 mJ/m^2, which is consistent with 20 mJ/m^2 found in the literature.[39]

Regular Solution Parameter β. In the present study, the effect of the surfactant concentration C_D on the monomer concentration C_1 was first detected from the hydrogen ion titration data as shown in Figure 6. It is to be noted that the results originate from the assumed Gibbs−Duhem relation (eq 8).

What is represented in β is the relative stability of mixed micelles referred to respective pure component micelles, the nonionic and the cationic in the present case. The electrostatic repulsion contributes to give more negative β values. Since the micelles grow with C_D, the charge density will increase with C_D due to the increased fraction of rodlike region; hence, more negative β values are expected at higher C_D. This is the trend found in the present study.

In the present study, it is shown that the regular solution theory parameter β is less negative for C14DAO (−1.4) than that of C12DAO (−2.1) in 0.1 M NaCl at the respective cmc. Effects of hydrocarbon chain length n_C on β have been described in the literature.[33] For mixed micelles of alkyltrimethylammonium chloride (CnTMAC)/heptaethylene glycol n-alkyl ether (Cn'E5) in water, $\beta = −1.5$ for ($n = 14$, $n' = 10$) and $\beta = −2.4$ for ($n = 16$, $n' = 12$). It is shown that β is influenced by the electrostatic contribution in such a way that it becomes more negative as the electric repulsion between ionic heads is larger.[40] Because of this, it has been observed frequently that β becomes more negative at low ionic strengths, especially in no added salt solutions. Since the above two examples were measured in water, we expect stronger electric repulsion for larger mixed

micelles formed by the surfactant pair with larger n_C. It is reasonable, therefore, to observe a more negative value for the surfactant pair of larger n_C ($n = 16$, $n' = 12$). In the present study, on the other hand, the parameter β was evaluated in the presence of 0.1 M NaCl and hence the electrostatic contribution is expected to be much smaller than for the CnTMAC/Cn'E5 pair. Under the condition of a sufficient supporting electrolyte, we have found less negative β values for the pair of larger n_C. Although considerations based on the general and elaborate theory recently developed[38,41] will be required, we will discuss below on the basis of the hydrogen bond hypothesis. In the case of C12DAO, the micelles at $\alpha_M = 0$ and $\alpha_M = 1$ are both spherical in 0.1 M NaCl but rodlike at $\alpha_M = 0.5$.[15] For C14DAO, on the other hand, micelles are rodlike irrespective of α_M and the rod grows extremely at $\alpha_M = 0.5$, as shown in Figure 7. Therefore, the average stabilization effect coupled with pairing of the nonionic and the cationic species would be smaller for C14DAO than for C12DAO. This may be reflected in their β values. The same mechanism causes the difference in pK_M as discussed above.

Stability of the Mixed Micelle at the Crossing Composition. It has been shown[16] that the maximum stability of the amine oxide micelles is found at the pH where the compositions of the micelle and the monomer become identical, $\alpha_M = \alpha_1 = \alpha^*$. This is a direct consequence of the Gibbs−Duhem relation. This maximum is a result of a compromise between the electric repulsion and the attractive interaction between the headgroups associated with protonation. The latter contribution is given as $RT\alpha_M$ (pK_M − pK_1) in the simplest case. As shown in Figure 1, values of α^* increases with C_s: 0.36 (pH = 5.07), 0.54 (pH = 4.79), and 0.69 (pH = 4.60) for $C_s = 0.01$, 0.10, and 0.98 M, respectively. On the other hand, the minimum of the cmc at $C_s = 0.1$ M was observed around $\alpha_M = 0.55$, as shown in Figure 8. The coincidence between the minimum of the cmc with α^* suggests the assumption of the Gibbs−Duhem relation is valid for the present mixed micelles. The maximum stability of the mixed micelle at this particular composition is given simply as RT ln cmc as if it were single component micelles, since $\alpha_M = \alpha_1$ and the micelle is an azeotropic mixture. The values in RT units were −0.76, −0.94, and −1.61 for $C_s = 0.01$, 0.10, and 0.98 M, respectively. Since the maximum stability of ionic micelles increases with ionic strength, the attractive interaction contribution increases with α_M.

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