Protonation Behavior and Stability of Micelles of N-Lauroylaminoalkyl-Dimethylamine Oxides-Effects of Added Salt Concentration and Spacer Length

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Abstract: The protonation behavior and the stability of micelles of N-lauroylaminopropyl-N',N'-dimethylamine oxide (C12AmCn; n=3) were studied by the hydrogen ion titration and the equilibrium surface tension measurement. The surface potential of C12AmC3 micelles estimated from the results of hydrogen ion titration was lower than that of dodecyldimethylamine oxide micelles at added NaCl concentration, C_s , of 0.1M. The critical micelle concentration (*cmc*) estimated from surface tension measurements revealed that a reversal of the stability of the cationic and the nonionic micelles of C12AmC3 takes place in the range of C_s higher than about 0.2M, that is, the cationic micelles become more stable than the nonionic ones in the range $C_s \geq 0.2$ M. In addition, the surface tension measurements were carried out for C12AmCn with different spacer length, n , ranging from 2 to 6 methylene units at $C_s = 0.1$ M. The *cmc* values of nonionic species were kept at almost constant for $n \leq 4$, while they decreased with n for $n \geq 4$. The *cmc* values of cationic species also tended to decrease with n for $n \geq 4$. These results were compared with those obtained for alkyl dimethylamine oxides, and the effect of amide group and spacer groups introduced into amine oxide surfactants was discussed.

Key words: N-lauroylaminoalkyl-dimethylamine oxides, protonation behavior, stability of micelles, added salt concentration, spacer length

1 INTRODUCTION

Long alkyl chain amine oxides have been used mostly as nonionic surfactants, but they exist either in the nonionic or the cationic (protonated form) species depending on the pH of the aqueous solutions. The solution properties and the surface properties also vary with pH. The pH (the protonation degree) dependence of the various solution properties, such as the titration behavior¹⁻¹¹⁾, the critical micelle concentration (*cmc*)¹²⁻¹⁷⁾, the micelle aggregation number^{18,19)}, the micelle size^{7,18,20)}, and the aggregate structures²¹⁻²⁶⁾, received much attention. In particular, it is noteworthy that the *cmc* values and the micelle aggregation number for dodecyldimethylamine oxide (C12DMAO) showed minimum and maximum, respectively, when the degree of ionization, α , is around 0.5 (that is, cationic species: nonionic species $\approx 1:1$)¹⁹⁾. The specific dependence of the various solution properties on the protonation degree have been considered to come from the hydrogen

bond between the protonated and unprotonated amine oxide groups^{15,27,28)} and partly from the dipole-dipole interaction among the unprotonated head groups.

In this study, we introduced the amide group into the amine oxide surfactant to increase the number of the hydrogen bonding site on the molecule. We synthesized N-lauroylaminoalkyl-N',N'-dimethylamine oxides (C12AmCn; $n=2-6$). First, the protonation behavior of C12AmC3 micelles was examined by the hydrogen ion titration. Second, the dependence of the stability of micelles on the added salt concentration C_s was studied for both cationic and nonionic species of C12AmC3; it was found that a reversal of the stability of the cationic and the nonionic micelles takes place in the range of C_s higher than about 0.2 M. Next, the dependence of the stability of C12AmC3 micelles on the protonation degree was examined under the condition of $C_s = 0.1$ M, and the *cmc* value at $\alpha \approx 0.5$ was found to be smaller than those at $\alpha = 0$ and 1. Finally,

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the effect of the spacer length between the amine oxide group and the long hydrocarbon chain on the stability of micelles was studied.

Recently Piasecki et al. reported the adsorption behavior of N-alkanoylaminoalkyl-N',N'-dimethylamine-N-oxides (CxAmCy; x = 10, 12, 14, and 16, and y = 2 and 3), only for the nonionic state²⁹⁾. We focused on the protonation behavior of micelles of C12AmCn, and the dependence of stability of both cationic and nonionic C12AmCn micelles on C_s.

2 EXPERIMENTAL

2.1 Materials

The chemical structure of N-Lauroylaminoalkyl-N',N'-dimethylamine oxides (C12AmC*n*; *n* = 2–6) was shown in **Fig. 1**. C12AmC*n* (*n* = 2–6) and N-capryloylaminopropyl-N',N'-dimethylamine oxide (C8AmC3) were synthesized with the same procedures described in Ref. 30 and purified by column chromatography (silica gel, chloroform:methanol = 1 : 1) followed by recrystallization from acetone/methanol. The purity of the surfactants was confirmed by ¹H NMR.

2.2 Hydrogen ion titration

Hydrogen ion titration of micelles was performed for C12AmC3 aqueous solutions at 25°C. Solutions with a surfactant concentration $C_D = 0.02 \text{ mol kg}^{-1}$ and a NaCl concentration $C_S = 0.1 \text{ mol kg}^{-1}$ were titrated with a 0.1 N NaOH solution under a nitrogen atmosphere at 25°C. In the back-titration, 1N HCl was used. Blank titrations were carried out by the addition of 0.1N HCl or 0.1N NaOH to the solution of the same C_S and the same volume but containing no surfactant. We used C8AmC3 as the monomer analog consisting of the same polar head group as C12AmC3. The value of critical micelle concentration, cmc , of C8AmC3 was much higher than that of C12AmC3; this enables precise determination of the pK_1 due to the high

Fig. 1 Molecular Structures of C12AmCn and CnDMAO, and the Protonation Scheme of an Amine Oxide in the Aqueous Solution.

surfactant concentration for the monomer titration.

2.3 Purification of sample solutions and surface tension measurement

We purified the sample solution again by removing bubbles including the surface-active contaminants, because the recrystallized sample still contained small amount of surface-chemical impurity as Piasecki *et al.* reported²⁹⁾. The procedure is as follows. Nonionic species solid was dissolved in a NaCl aqueous solution, and the solution pH was adjusted to $\text{pH } 2.00 \pm 0.02$ using 1N HCl. After that, the each sample was purified by foam separation method three times. The remained bulk solutions were offered to the surface tension measurement. The surfactant concentrations were determined by liquid chromatography after the purification. The pH values of the solutions were also checked to be 2.00 ± 0.02 after the purification. We performed the equilibrium surface tension measurements of the sample solutions with Kruss K-100 by the Wilhelmy method using a platinum plate at 25°C.

3 RESULTS AND DISCUSSIONS

3.1 Hydrogen ion titration

A protonation scheme of amine oxide surfactants was shown in Fig. 1. We can determine the degree of ionization of C12AmC3 micelles, α_M , by the hydrogen ion titration at concentrations above *cmc*; the parameter α_M corresponds to the fraction of the cationic species in mixed micelles composed of nonionic and cationic species of the surfactant. The total surfactant concentration, C_t , and the average degree of ionization of the overall solution, $\langle\alpha\rangle$, are related to the corresponding quantities for monomeric and micellar surfactants by Eq. (1).

$$C_t \langle \alpha \rangle = C_1 \alpha_1 + (C_t - C_1) \alpha_M \quad (1)$$

We examined the degree of ionization of the monomer, α_1 , using C8AmC3. Values of α_1 and pK_1 were determined at $C_D = 0.02 \text{ mol kg}^{-1}$, which is below the *cmc*, with the aid of Eq. (2) where K_1 denotes the dissociation constant of the monomer.

$$\text{p}K_1 = \text{pH} + \log [\alpha_1/(1-\alpha_1)] \quad (2)$$

C_1 was substituted by cmc since the monomer concentration is rather well approximated by cmc , although they are not exactly the same. With the aid of the cmc values, α_M was determined as a function of pH from the hydrogen ion titration. Then, the apparent dissociation constant of micelles, K_a , was evaluated by Eq. (3).

$$\text{p}K_a = \text{pH} + \log [\alpha_M / (1 - \alpha_M)] \quad (3)$$

The intrinsic dissociation constant of the micelle, K_M , can be obtained from the pK_a value in the limit of $\alpha_M \rightarrow 0$. An extrapolation of the plot of pK_a against α_M gave a pK_M value. Figure 2 shows the pK_a values as a function of α_M for the C12AmC3 solution. In the figure, the pK_1 value is also plotted against α_1 for the C8AmC3 solution. The value of pK_M for C12AmC3 was greater than that of pK_1 for C8AmC3. This means that there is a non-Coulombic interaction favoring the protonation on the surface of micelle compared with that of the monomer in the bulk solution.

The values of pK_M for C12AmC3 and the other amine oxides⁸⁾ are summarized in Table 1. Some pK_1 values are listed as well. Let's compare both the pK_M value for C12AmC3 and the pK_1 value for C8AmC3 with those for other amine oxides without amide group. First, the pK_1

Fig. 2 Hydrogen Ion Titration Curves of C12AmC3 (filled circles) and C8AmC3 (open circles) at 25°C ($C_S = 0.1 \text{ mol kg}^{-1}$ and $C_D = 0.02 \text{ mol kg}^{-1}$).

value for C8AmC3 was almost the same as those for the other amine oxides. Second, the pK_M value for C12AmC3 was close to those for decyldimethylamine oxide (C10DMAO), *N,N*-bis (2-hydroxyethyl) dodecylamine oxide (C12DHEAO), and *N,N*-bis (2-hydroxyethyl) tetradecylamine oxide (C14DHEAO). In contrast, the pK_M value for C12AmC3 was smaller than those for alkyl dimethylamine oxides ($C_n\text{DMAO}$; $n = 12, 14$, and 16) whose hydrocarbon chain is relatively long. It is noted that C10DMAO, C12DHEAO, and C14DHEAO are predicted to form micelles with larger curvature than those of $C_n\text{DMAO}$ ($n = 12, 14$, and 16). A greater pK_M value indicates a smaller distance between the adjacent head groups on the micelle surface, that is, a smaller curvature of the micelle. Thus, the agreement of pK_M values of C12AmC3 with those of C10DMAO, C12DHEAO, and C14DHEAO implies that C12AmC3 also forms micelles with a larger curvature because of the bulky polar head group having an amide and a bridging propyl group.

We also listed the difference between pK_1 and pK_M values in Table 1. The $pK_M - pK_1$ value for C12AmC3 agreed with those for C10DMAO, C12DHEAO, and C14DHEAO. The positive $pK_M - pK_1$ value indicates that there is a non-Coulombic interaction favoring the protonation on the surface of micelles compared with that of the monomer in the bulk solution as we described above. That is, $pK_M - pK_1$ is expected to be a net result of the short-range interaction and the image force contribution. We assume the hydrogen bond between the nonionic and the cationic head groups on the micellar surface as the most probable candidate of the short-range interaction^{15,27,28)}. The short-range attractive interaction must be related to the distance between the polar head groups on the micellar surface. The amine oxides without amide group, C10DMAO, C12DHEAO, and C14DHEAO, could form the micelles with larger curvatures than $C_n\text{DMAO}$ ($n = 12, 14$, and 16)⁸⁻¹¹⁾. The fact that

Table 1 The Values of pK_M , pK_1 , and $pK_M - pK_1$ for C12AmC3, $C_n\text{DMAO}$ ($n=10, 12, 14$, and 16), and $C_n\text{DHEAO}$ ($n=12$ and 14) at $C_S=0.1 \text{ M}$ and $C_D=0.02 \text{ M}$.

	pK_M	pK_1	$pK_M - pK_1$	Temperature/°C
C12AmC3	5.6 ± 0.1	4.8 ± 0.1	0.8 ± 0.2	25
C10DMAO ^a	5.6 ± 0.1	4.9 ± 0.1	0.7 ± 0.2	25
C12DMAO ^a	5.9 ± 0.1		1.0 ± 0.2	25
C14DMAO ^a	6.3 ± 0.1		1.4 ± 0.2	25
C16DMAO ^a	6.2 ± 0.1		1.3 ± 0.2	45
C12DHEAO ^a	5.6 ± 0.1	4.8 ± 0.1	0.8 ± 0.2	25
C14DHEAO ^a	5.5 ± 0.1		0.7 ± 0.2	25

^aRef. 8.

the $pK_M - pK_1$ values obtained for C12AmC3 and C10DMAO etc are similar to each other supports again that C12AmC3 can form nonionic micelles with a larger curvature. As to the contribution from the dipole-dipole interactions operating in the nonionic micelles, its quantitative estimation is not reliably achieved, though in some cases it could explain about 1/3 of the $pK_M - pK_1$ values¹⁰.

Next, we estimated the electric surface potentials of the micelles, ψ_0 , from the hydrogen ion titration curves, adopting the same analytical procedure applied to linear polyelectrolytes. In terms of the protonic charge e_0 , the Boltzmann constant k , and the absolute temperature T , ψ_0 is evaluated according to Eq. (4).

$$pK_M - pK_a = 0.434e_0\psi_0/kT \quad (4)$$

Figure 3 shows ψ_0 values against α_M for C12AmC3 and some alkylamine oxides. While the ψ_0 values for C12AmC3 were a little greater than those for C12DMAO in the range $\alpha_M < 0.4$, they were clearly smaller than those for C12DMAO in the range $\alpha_M > 0.4$. The ψ_0 values were significantly smaller than those for C12DHEAO and C14DHEAO⁸) at any α_M , although the pK_M values for C12AmC3 agreed with them. Compared with C10DMAO, the ψ_0 values for C12AmC3 were greater in the range $\alpha_M < 0.7$, whereas they were smaller in the range $\alpha_M > 0.7$. The ψ_0 values for C10DMAO increased almost linearly with α_M , on the other hand, the ψ_0 values for C12AmC3 increased

Fig. 3 The Surface Potential of Amine Oxides against α_M ($C_s = 0.1 \text{ mol kg}^{-1}$ and $C_D = 0.02 \text{ mol kg}^{-1}$): C10DMAO at 25°C (open circles), C12DMAO at 25°C (open diamonds), C14DMAO at 25°C (open triangles), C16DMAO at 45°C (open squares), C12AmC3 at 25°C (filled circles), C12DHEAO (filled diamonds), C14DHEAO (filled triangles).

only slightly in a high α_M region. All these results suggest that the electric repulsion among charged head groups of C12AmC3 is relaxed effectively due to the presence of a long flexible bridging region. As a result of the relaxation, the ψ_0 values for C12AmC3 are quite smaller than those for C12DMAO, and a little smaller than even C10DMAO in the high α_M region.

3.2 Surface tension behavior of C12AmC3 solutions

The surface tension (γ) for C12AmC3 solutions was measured as a function of the surfactant concentrations ($\log C_D$) at several C_s (10 mM to 1 M). Figures 4 and 5 showed the results for nonionic and cationic species, respectively. At pH 10 (nonionic species), the γ vs. $\log C_D$ curves were close to one another regardless of the C_s as shown in Fig. 4. In contrast, Fig. 5 showed significant C_s dependence of the curves at pH 2 (cationic species) due to the electrostatic interaction. We estimated the *cmc* values from the curves of γ against $\log C_D$, which are summarized in Table 2 and Fig. 6. The *cmc* values of nonionic species slightly decreased with C_s . We obtained the relation for nonionic species as follows, $\log [cmc/cmc(C_s = 0)] = -KC_s$; $K = 0.27$. For example, $K = 0.32$ for C12DMAO¹⁶). In case of pH 2 (cationic species), in contrast, the *cmc* values significantly reduced with C_s . The *cmc* values of C12DMAO¹⁴) were 2.0 mM for the cationic species and 1.6 mM for the nonionic species at $C_s = 0.1 \text{ M}$. Both values of C12DMAO are higher than those of C12AmC3. The propyl group of C12AmC3 might partially contribute to the hydrophobicity;

Fig. 4 The C_s Dependence of Surface Tension Curves of Nonionic Species of C12AmC3 at pH10 at 25°C: $C_s = 0.01 \text{ M}$ (circles), $C_s = 0.1 \text{ M}$ (triangles), $C_s = 0.2 \text{ M}$ (diamonds), $C_s = 0.5 \text{ M}$ (squares), and $C_s = 1 \text{ M}$ (inverted triangles).

Table 2 The Added Salt Concentration, C_s , the Counterion Concentration, $C_g (=C_s + cmc)$ and Critical Micelle Concentrations, cmc , for C12AmC3 at 25°C.

	C_s/M	$\log (C_s/M)$	$\log (C_g/M)$	cmc/mM	$\log (cmc/M)$
pH2	0	–	–2.37	4.3	–2.37
	0.01	–2	–1.852	4.1	–2.39
	0.1	–1	–0.994	1.3	–2.88
	0.2	–0.699	–0.697	1.0	–3
	0.5	–0.301	–0.300	0.63	–3.2
	1.0	0	0.000154	0.36	–3.45
pH10	0.01	–2		1.2	–2.92
	0.1	–1		1.1	–2.94
	0.2	–0.699		1.1	–2.95
	0.5	–0.301		0.93	–3.03
	1.0	0		0.66	–3.18

Fig. 5 The C_s Dependence of Surface Tension Curves of Cationic Species of C12AmC3 at pH2 at 25°C: $C_s=0.01$ M (circles), $C_s=0.1$ M (triangles), $C_s=0.2$ M (diamonds), $C_s=0.5$ M (squares), and $C_s=1$ M (inverted triangles). **Fig. 6** The Dependence of the cmc Values of C12AmC3 on the Added Salt Concentration at 25°C: pH2 (open circles) and pH10 (filled circles).

indeed, the bulky polar head group of C12AmC3 can make dipole-dipole interaction between neighboring amine oxide groups less repulsive than for CnDMAO micelles. As to the cationic species of C12AmC3, the installation of an amide group is likely to lead to intermolecular hydrogen bond,

and result in the stable micelle formation.

In addition, surface tension values of C12AmC3 at pH = 10, 4.6, and 2 (corresponding to $\alpha_M = 0, 0.5$, and 1, respectively) were compared at $C_s = 0.1$ M. The obtained cmc values were in the following order: $\alpha_M = 0.5$ (0.87 mM) < $\alpha_M =$

0 (1.1 mM) < $\alpha_M = 1$ (1.3 mM). The α_M dependence of cmc values is similar with those for the amine oxides without amide group¹⁹, and implies the attractive interaction between protonated and unprotonated species.

Figure 6 shows a plot of $\log cmc$ against $\log C_s$. The cmc values for cationic species (pH 2) are greater than those for nonionic species (pH 10) at C_s lower than about 0.18–0.20 M, as expected from the electric repulsion among the cationic head groups. However, it is noted that the cmc value for the cationic species is smaller than that for the nonionic species in the range of C_s greater than about 0.18–0.20 M. The result indicates that the ionic micelles are more stable than the nonionic ones obviously at $C_s = 0.5$ M. We have thus observed a reversal of the stability of the cationic and the nonionic aggregates of C12AmC3 at $C_s = 0.5$ M, that is, the cmc value of the cationic species was less than that of the nonionic species. The unusual behavior was observed previously for C12DMAO¹⁶) and C14DMAO²³) as well. In the case of CnDMAO, we suggested two possible mechanisms^{15,27,28}). The first one is the dipole-dipole repulsive interaction for the nonionic micelles which cannot be shielded well by small ions and becomes greater than the electric repulsion of the cationic micelles in the media of high ionic strengths. The second one is the stabilization by the hydrogen bond between neighboring cationic head groups. However, the two mechanisms become ineffective in the case of C12AmC3 due to the bulky head group. As a substitute for the second mechanism, we suggest the hydrogen bond between the oxygen atom of the amide carbonyl group and the hydrogen atom of the protonated NOH of the amine oxide group, as proposed above. Both the Γ value and the cmc value for cationic species of C12AmC3 support a kind of attractive interaction between the cationic head groups. The observation of the stability reversal for C12AmC3 in the present study strongly suggests the first mechanism to be unlikely not only for C12AmC3 but also for CnDMAO. This result suggests, in turn, that the stability reversal for CnDMAO micelles probably originates from some attractive interaction between the cationic headgroups, such as the hydrogen bond. Thus, the short-range attractive interaction arisen from the protonation of amine oxide groups seems to be important for the stability of the cationic micelles of C12AmC3.

The cmc values of many ionic surfactants have been known to obey the following Corrin-Harkins relation regarding the effect of the counter ion concentration C_g .

$$\log cmc = -k_{CH} \log C_g + \text{constant} \quad (5)$$

The Corrin-Harkins constant, k_{CH} , has been interpreted as representing the degree of the counterion binding^{31–33}). For the cationic species, $\log cmc$ approximately shows a linear dependence on $\log C_g$ ($k_{CH} = 0.55 \pm 0.01$ for $0.01 \text{ M} \leq C_g \leq$

0.50 M). In the previous study, we obtained $k_{CH} = 0.64 \pm 0.01$ for C12DMAO¹⁶). The smaller k_{CH} value of C12AmC3 corresponds to the smaller degree of counterion binding. This is consistent with the result that the surface potential of C12AmC3 micelles was lower than that of C12DMAO ones.

3.3 Surface excesses and surface tension values at cmc

A synergism between the nonionic and the cationic species also showed up in the surface excesses Γ in 0.1 M NaCl as shown in Table 3: Γ (pH 4.6) > Γ (pH 2) > Γ (pH 10). The Γ values were estimated under the condition of the high ionic strengths compared with the surfactant concentrations and a constant pH, according to the previous paper¹⁶). Both nonionic and cationic species showed quite slight C_s dependence of surface excesses Γ . The Γ values were close to those for C12DMAO. Although the Γ values of cationic species looked a little greater than those of nonionic species, the differences were too small to be discussed. On the other hand, values of γ_{cmc} for cationic species approximately decreased with $\log C_s$, while those for nonionic species showed no significant change. The tendencies were similar to those for C12DMAO. The values of $d\gamma_{cmc}/d\log(C_s/\text{M})$ of cationic species in the range $C_s > 0.1 \text{ M}$ were -1.6 mN m^{-1} and $-3.1 \pm 0.1 \text{ mN m}^{-1}$ for C12AmC3 and C12DMAO, respectively. As to the values of γ_{cmc} for C12AmC3, both cationic and nonionic species were greater than those for C12DMAO by about 3 mN m^{-1} . Table 3 indicates that $\gamma_{cmc}(\text{cationic}) < \gamma_{cmc}(\text{nonionic})$ for $C_s \geq 0.1 \text{ M}$, while $\gamma_{cmc}(\text{cationic}) > \gamma_{cmc}(\text{nonionic})$ for $C_s \leq 0.1 \text{ M}$. The reversal of γ_{cmc} values of cationic and nonionic species at high C_s will be related to the reversal of cmc values in the similar C_s region. In other words, the species which form more stable micelles can be more surface active.

3.4 Effect of the spacer length on the stability of micelles

We performed the surface tension measurements for solutions of C12AmCn, in which the spacer length is varied from $n = 2$ to $n = 6$. Figure 7 shows the cmc values against the spacer length n at $C_s = 0.1 \text{ M}$. The cmc values for the cationic species were greater than those for the nonionic ones at $C_s = 0.1 \text{ M}$ in the all samples examined because of the electrostatic interaction for the cationic ones. For both the nonionic and the cationic micelles, the cmc decreased with n in the range 4–6, suggesting the spacer moiety to work as a hydrophobic part for C12AmC5 and C12AmC6. It is not clear at present, however, whether or not amide groups are incorporated in the hydrophobic part as in the case of native globular proteins. For the nonionic species, the cmc values of C12AmCn ($n = 4$ –6) plotted against the spacer length n gave the following relation, $\log cmc = -2.29 - 0.18n$. On the other hand, the cmc values of C12AmCn ($n = 2$ –4) were kept almost constant. For the cationic species, the dependence of the cmc values on the spacer length cannot be concluded from the present data.

Table 3 Surface Excess, Γ , Surface Occupied Area, A , and Surface Tension Value at cmc , γ_{cmc} , of C12AmC3 at 25°C.

	NaCl/M	$\Gamma/\mu\text{mol m}^{-2}$	A/nm^2	$\gamma_{cmc}/\text{mN m}^{-1}$
pH2	0.01	3.1 ± 0.1	0.54 ± 0.02	38.0 ± 0.2
	0.1	3.7 ± 0.1	0.45 ± 0.01	36.3 ± 0.2
	0.2	3.9 ± 0.1	0.43 ± 0.01	36.2 ± 0.2
	0.5	3.9 ± 0.2	0.43 ± 0.02	35.1 ± 0.2
	1	3.7 ± 0.2	0.45 ± 0.02	33.6 ± 0.2
pH10	0.01	3.4 ± 0.1	0.49 ± 0.02	37.5 ± 0.2
	0.1	3.4 ± 0.1	0.49 ± 0.01	37.2 ± 0.2
	0.2	3.4 ± 0.1	0.49 ± 0.01	37.5 ± 0.2
	0.5	3.4 ± 0.2	0.49 ± 0.03	37.5 ± 0.2
	1	4.4 ± 0.2	0.37 ± 0.02	37.2 ± 0.2
pH4.6	0.1	4.3 ± 0.1	0.39 ± 0.01	34.9 ± 0.2

The cmc values of C12AmC n against the spacer length n provided the following relations, $\log cmc = -2.57 - 0.10n$ ($n = 2-6$) and $\log cmc = -2.27 - 0.16n$ ($n = 4-6$). When we focus on the range of $n = 4-6$, the dependence of cmc values on the spacer length for cationic species is quite similar to that for nonionic species.

According to the literature³⁴, the relation between cmc values at 25°C and the alkyl chain length of surfactants is given by $\log cmc = 1.89 - 0.50x$ for alkyloctaoxyethylene glycol ethers (CxE8), $\log cmc = 1.82 - 0.49x$ for alkylhexaoxyethylene glycol ethers (CxE6), and $\log cmc = 1.23 - 0.33n$ for n -alkyltrimethylammonium chlorides in 0.1M NaCl. Compared with these results³⁴, the spacer length dependence of cmc values for C12AmC n is evidently weaker, that is, the effect of the spacer length on cmc values is less than that of the hydrocarbon chain length of hydrophobic part. In other words, the spacer moiety of C12AmC n might not fully contribute to the hydrophobicity as described before. The exhibited results suggest, for the nonionic species and probably for the cationic species too, that the spacer moiety and the amide group remain in the aqueous solution for C12AmC n ($n = 2-4$). If the dipole-dipole repulsion between amine oxide groups plays a significant role, the repulsion can be reduced as the spacer length n increases, and the decrease of the cmc with increasing n should be observed for the nonionic micelles. However, the cmc values of non-ionic species did not decrease with the spacer length as shown in Fig. 7. For the cationic species, the dependence of cmc values on n is not clear. The reduction of the electrostatic repulsion between charged head groups with increasing n might be approximately shown by the corresponding decrease of the cmc with increasing n , however,

Fig. 7 The Dependence of the cmc Values for C12AmC n on the Spacer Length in 0.1M NaCl Solutions at 25°C: pH2 (open circles) and pH10 (filled circles).

we cannot conclude that so far.

4 SUMMARY

Both the intrinsic dissociation constant and the surface potential behavior evaluated from the hydrogen ion titration suggest that C12AmC3 form larger curvature micelles than other amine oxides without amide group because of the bulky polar head group including an amide group. We

found that the ionic micelles are more stable than the non-ionic ones under the condition of high salt concentrations, $C_s \geq 0.2$ M. The C_s dependence of the stability of C12AmC3 micelles was similar to that of C12DMAO. In addition, the ionization degree (α) dependence of the *cmc* values is as follows, *cmc* ($\alpha = 0.5$) < *cmc* ($\alpha = 0$) $\sim$ *cmc* ($\alpha = 1$) at $C_s = 0.1$ M. This result indicates that the micelles for $\alpha = 0.5$ is more stable than both nonionic and cationic micelles. That is, a short range attraction such as the hydrogen bond between protonated and unprotonated amine oxide groups plays an important role in the stability of micelles. The maximum stability should be observed around $\alpha = 0.2$, if the dipole-dipole contribution is significant¹⁰.

The Corrin-Harkins coefficients for the cationic species, k_{CH} , was 0.55 ± 0.01 for C12AmC3, which is smaller than 0.64 ± 0.01 for C12DMAO¹⁶. A smaller k_{CH} value corresponds to a smaller degree of counterion binding degree. This is consistent with the result that the surface potential of C12AmC3 micelles was lower than that of C12DMAO ones.

The spacer length (n) dependence of *cmc* values for C12AmC n implies that the whole amidepropyl group is exposed to water and works as a bulky polar head group for C12AmC n ($n = 2-4$). In contrast, the amide group might be incorporated in the hydrophobic part for C12AmC n ($n = 5$ and 6). For the cationic species, the distance of the charged amine oxide group from the micellar core surface is likely to be more effective on the *cmc* values.

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