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ORIGINAL CONTRIBUTION

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Acid soap formation of oleic acid and catanionic complex formation in the alkyldimethylamine oxide/sodium oleate equimolar mixtures

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Abstract The influence of adding alkyldimethylamine oxide (CnDMAO) with varying alkyl chain lengths (n_c) on the acid soap formation of oleic acid was investigated. The solutions of equimolar mixtures of CnDMAO and sodium oleate (Na^+Ol^-), each 25 mmol kg^{-1}, became turbid at a certain critical pH (pH_c) on decreasing pH. Values of the pH_c depended on n_c and showed the minimum at C10DMAO/NaOl mixture. The presence of the minimum was interpreted in terms of two different kinds of the complex formed in the micelles depending on n_c: the catanionic complex ($CnDMAOH^+/Ol^-$) in the mixed micelles of $n_c = 16$, 14, 12 and 10, and the acid soap of oleic acid for C6DMAO/NaOl and C8DMAO/NaOl mixtures. At pH_c where the amounts of these complexes of double-chain nature reached certain critical values in the mixed micelles, a phase separation (most probably lamella formation) took place. It was expected that the critical amount of the catanionic complex was smaller for the mixtures of higher n_c values and hence pH_c increased with n_c for the mixtures $n_c \geq 10$. For the mixtures of $n_c < 10$, it was expected that the amount of the acid soap in the mixed micelles increased with decreasing n_c at a given pH and the pH_c increased with decreasing n_c. Micelle compositions at cmc were evaluated on the basis of the regular solution theory coupled with the pseudo phase approximation. The micelle compositions at 100 mmol kg^{-1} were examined with ^{13}C-NMR. The results showed the mixed micelle formation for $n_c = 16$–10, while the micelles mostly consisting of oleic acid for the mixtures of $n_c = 8$ and 6. The assumption of two different complexes for the two groups of the mixture was thus supported. The cmc range of mixed micelles was evaluated and it was well correlated with the observed concentration range of pyrene fluorescence change.

Keywords Alkyldimethylamine oxide · Sodium oleate · Catanionic complex · Acid soap · Mixed micelles

Introduction

Soaps are surface-active substance derived from natural oils and fatty acids [1]. They have advantage over synthetic detergents with respect to toxicity and biodegradability. However, soap solutions are unstable at low pH values or in the presence of divalent cations.

Alkyldimethylamine oxide (CnDMAO) has been used mostly as a nonionic surfactant either as single

component or as a member of mixed surfactant systems. Amine oxide exists as either a nonionic or a cationic (protonated form) species depending on the pH of aqueous solutions and also depending on the interaction with other surfactants in the mixed system. From the hydrogen ion titration, 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 [2]. The characteristic property has been interpreted in terms of the hydrogen bond formation between the nonionic and the cationic head groups [2, 3].

Mixed surfactant systems of amine oxides with ionic surfactants, such as sodium dodecylsulfate (SDS) [4, 5, 6], sodium dodecylbenzenesulfonate (SDBS) [7] or alkyltrimethylammonium bromide (CnTAB) [4, 5], have been investigated. Weers et al. reported that from the cmc measurement the interaction parameter β of the regular solution theory (RST) is −1.7 for C12DMAO/SDS mixture [4]. The pH values of the solutions containing C12DMAO and sodium dodecylbenzenesulfonate (DBS) were found to go through a maximum at approximately 1:1 mole ratio below cmc [7]. The increase in pH has been explained by the protonation of amine oxide. Although amine oxides have been used mostly as a nonionic surfactant, the presence of an anionic surfactant in the mixed micelle might promote the protonation of the amine oxides due to the catanionic complex formation between the anionic and the protonated amine oxide. In the mixture of C14DMAO and dihydroperfluorooctanoic acid ($C_6F_{13}CH_2COOH$, DHPFOA), protonation of amine oxide is produced by proton transfer from DHPFOA [8]. As a result of this reaction, the mixed system behaves as a catanionic surfactant system. In a certain range of the mole ratio, the mixture of C14DMAO and DHPFAO is known to form vesicles. For the mixture of C12DMAO and sodium oleate (NaOl), attractive interaction between the head groups is suggested by the interaction parameter $\beta = -3.9$ from cmc measurement [9]. On the other hand, a cationic surfactant C12TAB has little influence on the protonation of the amine oxide [4].

These previous studies of mixed surfactant system containing amine oxides suggest an attractive interaction between the head group of amine oxide and that of anionic surfactant. In the present study, we investigate the influence of adding amine oxides of varying alkyl chain lengths on the acid soap formation of oleic acid. It is known that sodium oleate (NaOl) solutions become turbid due to the acid soap formation by decreasing pH. It is expected that the acid soap formation of oleic acid can be prevented by the attractive interaction between the head groups of amine oxide and oleate anion. Equimolar mixtures of CnDMAO/NaOl were examined in the present study. We found that the lowest pH was attained without a phase separation in the case of C10DMAO/NaOl mixture.

Experimental

Materials Tetradecyldimethylamine oxide (C14DMAO) and hexadecyldimethylamine oxide (C16DMAO) were prepared as reported previously [10]. Dodecyldimethylamine oxide (C12DMAO), decyldimethylamine oxide (C10DMAO) and hexyldimethylamine oxide (C6DMAO) were obtained from Fluka (all were of 99% purity). Octyldimethylamine oxide (C8DMAO, 99% purity) and trimethylamine oxide (C1DMAO, 98% purity) were obtained from Aldrich. Sodium oleate samples were prepared by neutralization (in ethanol) of highly pure oleic acid (purity: 99.999%), a gift from Research Institute of Biological Materials Japan, Ltd. The surfactant concentration C_d was in mol kg^{-1}.

Turbidity Turbidity measurements were performed at 25 °C with a Jasco Ubest-50 UV/vis spectrophotometer, equipped with a thermostated cell holder and a magnetic stirring device, using a quartz cell of 1 cm path length. Turbidity was measured at 400 nm. The pH of the sample solutions (about 4 ml) was decreased by a stepwise addition of about 2 μl of 1 mol l^{-1} HCl solution (Nacalai tesque).

Fluorescence measurement Fluorescence measurements were carried out with a Fluorescence Spectrophotometer F-2500 (HITACHI) to determine the cmc by means of the solubilization of pyrene in the micelle [11]. The concentration of pyrene was about 3 μmol kg^{-1}. The solutions were incubated for one day before the measurements.

Light microscopy Interference contrast microscopy measurement (OPTIPHOT-2, Nikon) was used to identify emulsions, vesicles and solid crystals.

1H-NMR measurement Proton magnetic resonance (^{1}H-NMR) technique was employed to determine the composition of the turbid upper solution phase near the critical pH. The cloudy materials were separated from the turbid solution by centrifugation. The collected samples were dissolved in D_2O by adding NaOH. ^{1}H-NMR measurements were carried out with a JNM GX-400 (Japan Electron Optics Laboratory Co., Ltd.) at 400 MHz using sodium 3-(trimethylsilyl)-1-propan-sulfonate as an internal reference. Mole ratios of CnDMAO and NaOl were determined from the following ^{1}H-NMR signals: protons of the methylene next to nitrogen of the head group of CnDMAO (3.3 ppm from the internal reference), *N*-methyl protons of the head group of CnDMAO (3.2 ppm) and methine protons of NaOl (5.4 ppm), and methylene protons next to the head group of NaOl (2.1 ppm).

13C-NMR measurement ^{13}C-NMR measurement was employed to determine the micelle composition at $C_d = 100$ mmol kg^{-1}. ^{13}C-NMR spectra were obtained on a JMN GX-400 (Japan Electron Optics Laboratory Co., Ltd.) at 100 MHz, using sodium 3-(trimethylsilyl)-1-propan-sulfonate as an external reference. Complete proton decoupling was used and the deuterium signal from D_2O was employed as the internal lock signal. The assignments of the carbon atoms of C12DMAO in deuterium oxide have previously been determined by Chang et al. [12].

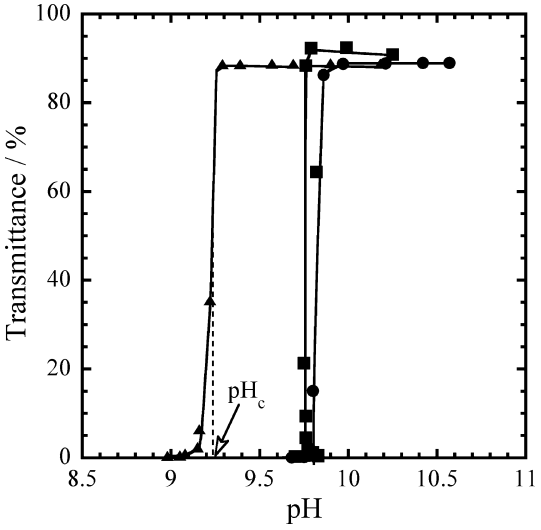

Fig. 1 The transmittance of CnDMAO/NaOl equimolar mixtures at 25 °C as a function of the pH. *Circles*, C16DMAO/NaOl; *triangle*, C10DMAO/NaOl; *square*, C6DMAO/NaOl. The total surfactant concentration is 50 mmol kg^{-1}

Results and discussion

Figure 1 shows the pH dependence of the transmittance for the equimolar mixtures of CnDMAO and NaOl at 25 °C with different alkyl chain lengths of amine oxide, n_c. The total surfactant concentration, C_d was fixed to be 50 mmol kg^{-1}. Above pH˜10, all solutions were optically clear and oleate micelles or mixed micelles were expected to be dispersed. At a certain pH, transmittance of the solutions decreased sharply for all mixtures, where a phase separation occurred. The upper solutions were turbid and the lower solutions appeared less turbid. We defined the pH value of the mid-point of the transmittance change (see Fig. 1) as the critical pH (pH_c). Under an interference contrast microscope, large spherical aggregates were observed in the upper turbid solution around pH_c for both C12DMAO/NaOl and C6DMAO/NaOl mixtures (Fig. 2).

The dependence of pH_c on the alkyl chain length of amine oxide (n_c) is shown in Fig. 3. We could divide the mixtures into two groups. In one group (Group 1:16≥n_c≥10), the pH_c monotonously decreases as the alkyl chain length of amine oxide decreases from $n_c = 16$ to $n_c = 10$. In the other group (Group 2: $n_c = 6$ and 8), pH_c monotonously increases as the alkyl chain length decreases. Thus, pH_c shows a minimum at $n_c = 10$ (C10DMAO/NaOl mixture). To examine the composition of the upper turbid solution, we carried out ^{1}H-NMR measurements on the material recovered from the turbid solutions of CnDMAO/NaOl mixtures at pH values lower than pH_c. We obtained the mole ratio, (NaOl + HOl)/(CnDMAO + CnDMAOH), in the turbid upper solution. For the C12DMAO/NaOl mixture at pH 9.4, the mole ratio was 1.1 that is nearly equal to one, suggesting that the 1:1 complex between cationic amine oxide and anionic oleate (catanionic complex formation). For C6DMAO/NaOl mixture at pH 9.8, on the other hand, the mole ratio was 3.5. The result indicates that the turbid solution contains the acid-soap of oleic acid as well as the catanionic complex in case of C6DMAO/NaOl. From the results, we see that the phase separation at pH_c is due to the lamella formation, since the catanionic complex and the acid soap are both of double-chain nature and they favor the structures of less curvature like lamella. The result furthermore suggests that the catanionic complex is formed for all the mixtures examined, while the acid soap is formed only for Group 2.

Different complex formations between the two groups are likely to be correlated with the composition

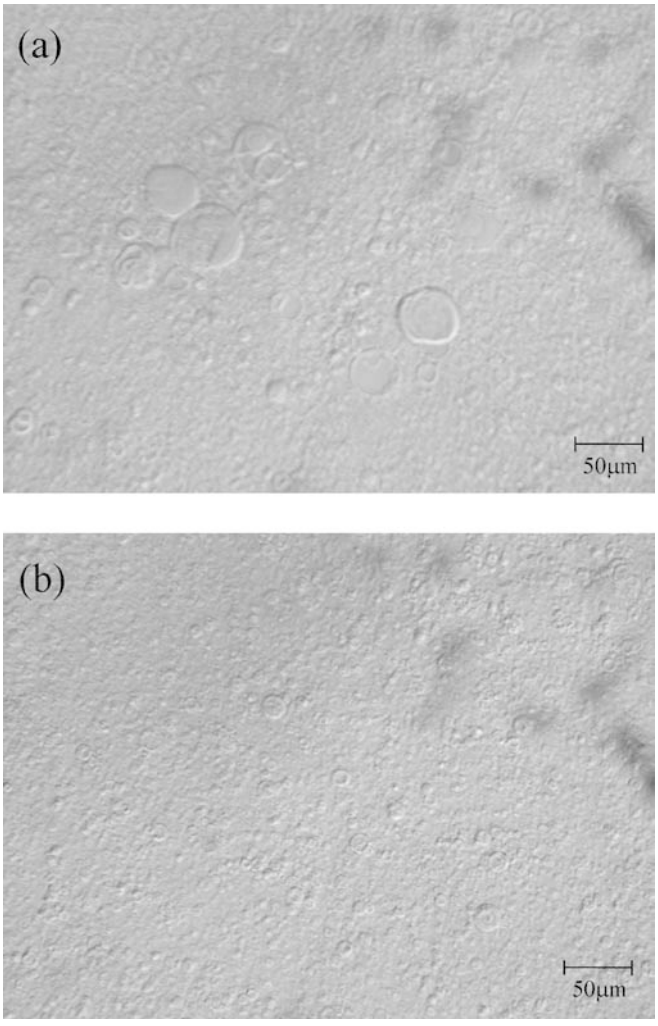

Fig. 2a,b The interference contrast microscope micrograph of spherical lamellar like aggregates in the turbid solution around pH_c at 25 °C: **a** C12DMAO/NaOl; **b** C6DMAO/NaOl. The total surfactant concentration is 50 mmol kg^{-1}

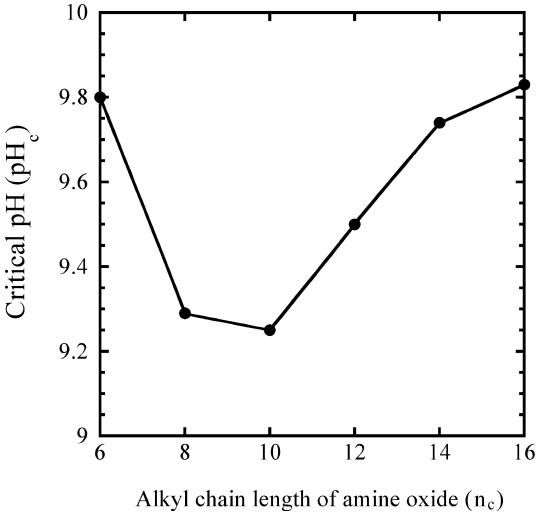

Fig. 3 The critical pH (pH_c) at 25 °C as a function of the alkyl chain length (n_c) of amine oxide. The total surfactant concentration is 50 mmol kg^{-1}

of the mixed micelles. We determined the cmc of CnDMAO/NaOl mixtures by fluorescence intensity ratio of pyrene (I_3/I_1) [11]. Figure 4 shows the dependence of pyrene fluorescence intensity ratio (I_3/I_1) on the total surfactant concentration for the various equimolar mixtures. Three concentrations can be assigned to the cmc from the data: the onset concentration / the mid-point, and the leveling off concentration. They are indicated in Fig. 4 as cmc_1, cmc_2 and cmc_3. Figure 5 shows the logarithm of cmc_1 and cmc_2 values of CnDMAO/NaOl equimolar mixtures at 25 °C as a function of the chain length of amine oxide, n_c. Dashed and solid lines represent the cmc_1 and cmc_2 of pure NaOl, respectively. Values of three kinds of cmc in water were reported as 0.22, 0.70 and 2.3 mmol l^{-1}[13]. For $n_c = 1$, 6 and 8 (Group 2), the cmc values of CnDMAO/NaOl mixtures are about 2 mmol kg^{-1}. This value corresponds to 1 mmol kg^{-1} of oleate. The cmc_2 value of pure NaOl was 1.1 mmol kg^{-1} (Fig. 5). This strongly suggests that the amine oxides in Group 2 do not form mixed micelles with oleate anions or the content of CnDMAO in the mixed micelles is very low as far as the composition at the cmc is considered. For Group 1 ($n_c \geq 10$), on the other hand, the cmc decreases with increasing the chain length, suggesting the mixed micelle formation between the amine oxide and oleate anion.

To evaluate the compositions of the mixed micelles (X_{AO} or X_{Ol}) and the monomers ($X_{AO,1}$ or $X_{Ol,1}$), the equilibria between them are considered assuming the pseudo-phase model for micelles and the ideal behavior for both monomers. The standard state for the chemical potential of each component in the mixed micelles is taken as the pure one-component micelle placed in the same solvent condition as the mixed micelle, i.e., 1–1

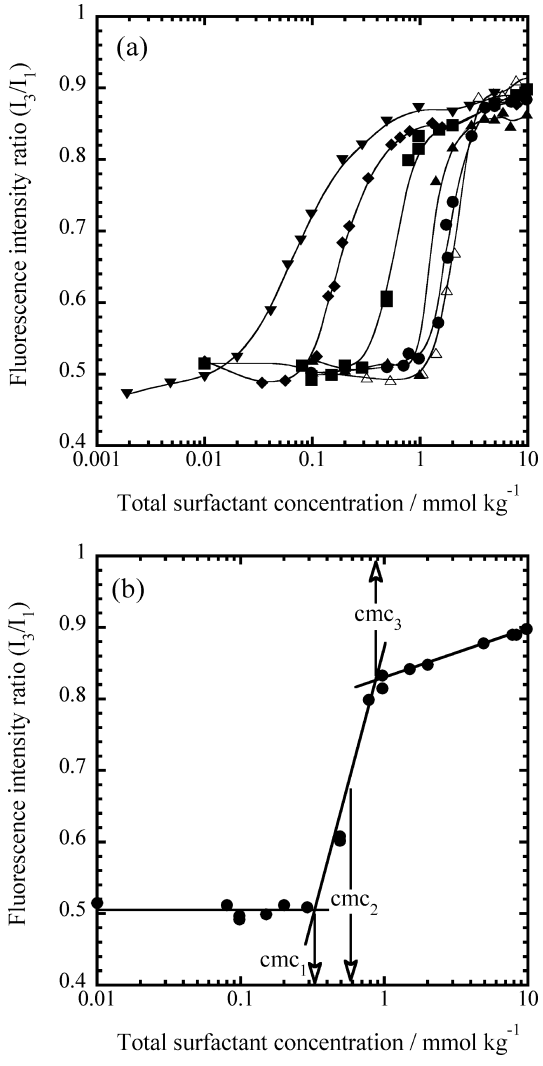

Fig. 4 **a** The total surfactant concentration dependence of pyrene fluorescence intensity ratio (I_3/I_1) for different chain length amine oxide. Symbols are: *open triangles*, C6DMAO/NaOl; *filled circles*, C8DMAO/NaOl; *filled triangles*, C10DMAO/NaOl; *filled squares*, C12DMAO/NaOl; *filled diamonds*, C14DMAO/NaOl; *inverted filled triangles*, C16DMAO/NaOl. **b** C12DMAO/NaOl mixture. The onset, the mid-point and the leveling off concentrations are represented as cmc_1, cmc_2 and cmc_3, respectively

type salt (Na oleate) solution of the concentration of (1/2×cmc). The activity coefficient in the mixed micelle is denoted as γ_{AO} for amine oxide and γ_{Ol} for oleate anion. The cmc values of respective pure one-component micelle are denoted as cmc_{AO} or cmc_{Ol}. From the equilibrium conditions we obtain the following relations:

$$\frac{\text{cmc}}{\text{cmc}_{AO}} = \frac{\gamma_{AO} X_{AO}}{X_{AO,1}} \tag{1a}$$

$$\frac{\text{cmc}}{\text{cmc}_{Ol}} = \frac{\gamma_{Ol} X_{Ol}}{X_{Ol,1}} \tag{1b}$$

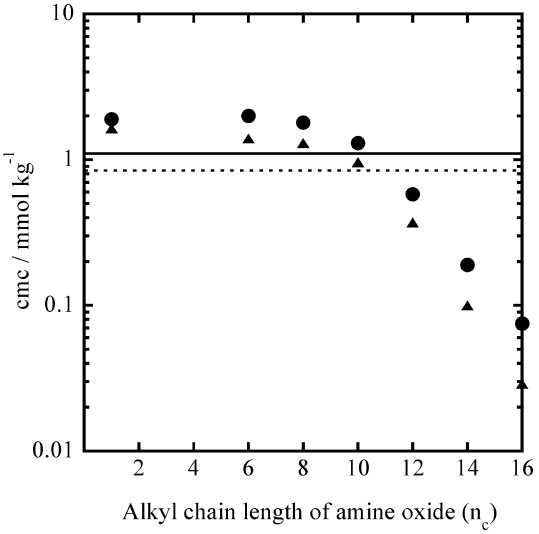

Fig. 5 The cmc of CnDMAO/NaOl equimolar mixtures at 25 °C as a function of alkyl chain length (n_c) of amine oxide. cmc_1 (*filled triangles*) and cmc_2 (*filled circles*). *Dashed and solid lines* are cmc_1 and cmc_2 of pure NaOl, respectively

The mole-fraction of oleate anion in the mixed micelle and the interaction parameter β are evaluated by using the regular solution theory (RST) [14, 15], although the RST cannot be applied in a strict sense to the ionic/nonionic mixed micelle in the media of low ionic strength [16], as encountered in the present study. According to the RST, the activity coefficients of both species are given as follows in terms of the interaction parameter β:

$$\gamma_{AO} = \exp\left[\beta X_{Ol}^2\right] : \gamma_{Ol} = \exp\left[\beta(1 - X_{Ol})^2\right] \tag{2}$$

Introducing Eq. (2) into Eqs. (1a) and (1b), we have

$$\frac{\text{cmc}}{\text{cmc}_{\text{AO}}} = \frac{(1 - X_{Ol})}{(1 - X_{Ol,1})} \exp\left(\beta X_{Ol}^2\right) \tag{3a}$$

$$\frac{\text{cmc}}{\text{cmc}_{\text{Ol}}} = \frac{X_{Ol}}{X_{Ol,1}} \exp\left[\beta(1 - X_{Ol})^2\right] \tag{3b}$$

At the cmc of mixtures where we can assume $X_{\text{Ol},1} = X_{\text{Ol,t}}$, the total composition and the values of X_{Ol} and β were obtained. In the analysis, we use the values of cmc_2 rather than cmc_1 or cmc_3 [17]. The results are shown in Table 1 together with the cmc values of amine oxides, taken from [18]. The data in [18] were extrapolated to yield the cmc vales of C6DMAO and C16DMAO at 25 °C. For the mixtures between $n_c = 10$ and 14, we obtained negative values of β, suggesting an attractive interaction between amine oxide and oleate anion in the mixed micelles. Values of β vary significantly with the cmc values employed in the analysis. They become less negative as the cmc value increases from cmc_1 to cmc_3. Values of X_{Ol} were 0.39, 0.55 and 0.73 for $n_c = 14$, 12 and 10, respectively, and these values did not change much even when cmc_1 or cmc_3 was used in place of cmc_2. From these results, it is clear that the amine oxide and oleate anion form mixed micelles in Group 1 ($n_c = 10$ or greater).

Values of the cmc of C6DMAO/NaOl and C8DMAO/NaOl mixtures are almost identical to the cmc of pure Na oleate. Also, for C16DMAO/NaOl mixture, the cmc was closer to the hypothetical cmc of pure C16DMAO micelle than that of Na oleate. For these three mixtures, the micelle formed at the cmc was expected to be close to pure one-component micelle, either Na oleate or amine oxide. The analysis in terms of RST therefore seemed not adequate for these mixtures and we estimated the micelle compositions assuming the ideal behavior from the following relation:

$$\text{cmc} = \text{cmc}_{\text{AO}}(1 - X_{\text{Ol}}) + \text{cmc}_{\text{Ol}} X_{\text{Ol}} \tag{4}$$

Value of X_{Ol} was 1.0 for both C6DMAO/NaOl and C8DMAO/NaOl. The value indicates that the micelles mainly consist of oleate anions. For C16DMAO/NaOl mixture, X_{Ol} was about 0.04 and the micelle mainly consists of amine oxides.

It is to be noted, however, that the above analysis gives the micelle composition at the cmc. At $C_d = 100$ mmol kg^{-1}, the micelle compositions were evaluated from the chemical shift of ^{13}C-NMR of amine oxide. It has been

Table 1 The cmc, compositions of the micelle and the interaction parameter β of the regular solution theory

	C6	C8	C10	C12	C14	C16	NaOl
cmc[a], mmol kg^{-1}	1040 ± 40[e]	150	15	2.0	0.28	0.035 ± 0.005[e]	
cmc_1[b], mmol kg^{-1}	1.4 ± 0.1	1.3 ± 0.1	0.96 ± 0.03	0.37 ± 0.02	0.10 ± 0.01	0.029 ± 0.005	0.86 ± 0.06
cmc_2[c], mmol kg^{-1}	2.13 ± 0.02	1.91 ± 0.05	1.25 ± 0.03	0.577 ± 0.007	0.190 ± 0.005	0.076 ± 0.004	1.10 ± 0.01
XOl[1]			0.73	0.55	0.39		
β			−3.5 ± 0.1	−3.7 ± 0.1	−4.0 ± 0.1		
$X_{\text{Ol}}(\beta = 0)$	1.0	1.0				0.039 ± 0.008	
cmc_3[d], mmol kg^{-1}	3.2 ± 0.2	2.8 ± 0.3	1.7 ± 0.1	0.87 ± 0.03	0.38 ± 0.01	0.21 ± 0.04	1.34 ± 0.09

[a]The cmc values of pure amine oxides are taken from [18]
[b]The onset concentration for the change of I_3/I_1 ratio
[c]The mid-point concentration for the change of I_3/I_1 ratio
[d]The leveling off concentration for the change of I_3/I_1 ratio
[e]These cmc values are obtained by extrapolation of the data in [18]

Table 2 ^{13}C-NMR chemical shifts (ppm) of amine oxides

	Monomer[a]	Micelle[b]	CnDMAO/NaOl mixed micelles		
			C6	C12	C16
C-1	73.25	73.30	73.40	73.58	73.56
C-2	28.03	29.28	28.26		
C-3	25.52	26.16	25.78	26.49	26.60

[a]C6DMAO
[b]C12DMAO

explained that the downfield shifts originate from an increase in the population of *trans* conformer on micellization [12, 19]. Table 2 shows the ^{13}C-NMR chemical shifts of the first (C-1), the second (C-2) and the third (C-3) carbons from nitrogen atom of the amine oxides for the C6DMAO/NaOl, C12DMAO/NaOl and C16DMAO/NaOl mixtures. The chemical shifts of C-2 and C-3 carbon of amine oxide were 29.28 ppm and 26.16 ppm for C12DMAO micelle, while they were 28.03 ppm and 25.52 ppm for the monomers of C6DMAO, respectively. The reported values of C-2 and C-3 of C12DMAO were 26.60 ppm and 23.48 ppm for micelles, while they were 25.66 ppm and 22.91 ppm for monomers [12]. Assuming negligible dependence of the chemical shift value in the mixed micelles on the micelle composition, we can evaluate the fraction of amine oxide in the monomer state f_1 or the micelle state f_m from the observed chemical shifts, δ_{obs}, using the following equation:

$$\delta_{obs} = f_1\delta_1 + f_m\delta_m, (f_1 + f_m = 1) \tag{5}$$

Here, δ_m and δ_1 represent the chemical shifts for the micelle and for the monomer, respectively. For C6DMAO/NaOl mixture, the chemical shifts of C-2 and C-3 carbon of amine oxide were 28.26 ppm and 25.78 ppm, respectively. The values of f_m were 0.18 and 0.41 from the chemical shifts of C-2 and C-3 carbon for C6DMAO/NaOl mixture. The mole-fractions of amine oxide in the mixed micelles, X_{AO}, were estimated to be 0.15 (C-2) and 0.29 (C-3) from the f_m values. This suggests that the micelles for Group 2 mainly consisted of oleate anions even at $C_d = 100$ mmol kg^{-1}.

In the case of C16DMAO/NaOl mixture, the chemical shifts of C-1 and C-3 of the amine oxide were more downfield than that of the pure amine oxide micelle (Table 2). The chemical shift of C-1 of the oleate anion for the C16DMAO/NaOl mixture (40.67 ppm) was roughly equal to that of the pure micelles of the oleate anion (40.52 ppm). These two results suggest that the amine oxide and oleate anion form mixed micelles for the C16DMAO/NaOl mixture, which may be approximately identical to the over-all composition at $C_d =$ 100 mmol kg^{-1}, although the micelles mainly consist of the amine oxides at the cmc (Table 1).

It should be noted that there was almost no change in the chemical shift of C-1 accompanying the micellization of pure amine oxide (less than 0.1 ppm), while more downfield chemical shifts (0.2–0.3 ppm) were observed for the micellization of the C12DMAO/NaOl and C16DMAO/NaOl mixtures (Table 2). The ^{13}C-NMR chemical shift of C-1 carbon of amine oxides is a useful measure to examine the mixed micelle formation with oleate and hopefully other ionic surfactants.

At this point, it is pertinent to examine the mechanisms responsible for the width of a concentration range where the I_3/I_1 ratio of pyrene fluorescence varies with the total concentration C_t, as shown in Fig. 4. In the case of mixed micelles, we can generally define two characteristic concentrations, C^* and C^{**}. The concentration C^* corresponds to the cmc where the monomer composition X_1 is well approximated with the total composition X_t. At a high concentration where the micelle composition can be well approximated with X_t, the monomer concentration C_1 reaches the maximum level, $C_1(\max) = \mathrm{cmc}_{AO}(1-X_{Ol,t}) + \mathrm{cmc}_{Ol} X_{Ol,t}$. Another characteristic concentration C^{**} could be introduced by defining $C^{**} = C_1(\max)$. Then, we can take the ratio C^{**}/C^* as a measure of the width of a concentration rage where both C_1 and the micelle composition vary significantly. In the case of RST, we have Eq. (6) for a binary mixed micelle consisting of species A and B, in terms of X_t, the total mole fraction of species A, and the cmc ratio y defined as $y = \mathrm{cmc}_A/\mathrm{cmc}_B$:

$$\frac{C^{**}}{C^*} = X_t^2\left(\frac{\gamma_A^{**}}{\gamma_A^*}\right) + (1-X_t)^2\left(\frac{\gamma_B^{**}}{\gamma_B^*}\right) + X_t(1-X_t)\cdot\left[y\left(\frac{\gamma_A^{**}}{\gamma_B^*}\right) + \frac{1}{y}\left(\frac{\gamma_B^{**}}{\gamma_A^*}\right)\right] \tag{6}$$

Here, γ^{**}_i and γ^{*}_i represent the activity coefficients of i-th component at C^{**} and C^*, respectively. For the ideal mixture, Eq. (6) reduces to Eq.(7):

$$\frac{C^{**}}{C^*} = X_t^2 + (1-X_t)^2 + X_t(1-X_t)\left(y + \frac{1}{y}\right) \tag{7}$$

In the present study $X_t = 1/2$ and values of $y = \mathrm{cmc}_{AO}/\mathrm{cmc}_{Ol}$ are 1.8, 0.25 and 0.032, for C12, C14 and C16, respectively. The corresponding C^{**}/C^* values are 1.1 and 1.4 for C12 and C14, respectively. In the case of the ideal mixed micelles, Eq. (7), the values of C^{**}/C^* are 1.1, 1.6 and 8.3, for C12, C14 and C16, respectively. On the other hand, observed $\mathrm{cmc}_3/\mathrm{cmc}_1$ ratios were 2.4, 3.8 and 7.2 for C12, C14 and C16, respectively. Thus, we can see that the C^{**}/C^* significantly contributes to the observed width of the range where I_3/I_1 ratio changes.

At the initial state prior to the addition of HCl to lower pH, it is now concluded that mixed micelles of near the equimolar compositions are present for Group 1 but for Group 2 micelles are rich in oleate. This

difference in the micelle composition between the two groups must be related to the formation of different complexes in the micelles. We briefly examine this point as follows. We compare the free energies ΔG^{prot} of the following two protonation reactions on the surface of the mixed micelles:

$$R_{AO}NO + H^+ \rightarrow R_{AO}N^+OH \quad \text{(Reaction 1)},$$
$$R_{Ol}COO^- + H^+ \rightarrow R_{Ol}COOH \quad \text{(Reaction 2)}.$$

The intrinsic part of the ΔG^{prot} is expected to be rather similar for the two reactions, since the proton dissociation constants K_1 are similar: $pK_1 = 4.9$ for amine oxide [2] and 5.0 for fatty acid [1]. As to the short range interactions, hydrogen bonds are also equally expected: $R_{AO}N^+OH...^-OOCR_{Ol}$, $R_{AO}N^+OH...ONR_{AO}$ and $R_{Ol}COOH...^-OOCR_{Ol}$. An important remaining contribution to be examined is the electrostatic free energy G_{el}. In Reaction 2, G_{el} decreases by the annihilation of one negative charge. In Reaction 1, the same decrease of G_{el} is expected and in addition to this, there is another contribution arising from the attractive interactions between positive-negative charge pairs created by the protonation reaction. Consequently, protonation is expected to proceed via Reaction 1 for Group 1. This explains why only the catanionic complex is formed in Group 1. For Group 2, the catanionic complex is also formed but its amount is relatively small due to the poor populations of amine oxides in the micelle. Then, protonation is expected to be take place mainly via Reaction 2 leading to the acid soap formation.

It is reasonable to assume that the amount of the catanionic complex formed at a given pH is larger but the critical amount of the catanionic complex allowed (or solubilization limit) in the mixed micelle is smaller for the mixture of larger n_c values, because of increased double-chain nature of the complex with increasing n_c. Because of these two factors, pH_c is expected to decrease with the decreasing n_c. The critical amount of the acid soap in the micelle should be much smaller than that of the catanionic complex in the case of Group 2, since the former consists of two C_{18} chains while the latter consists of C_{18}-C_8 or C_{18}-C_6 pair. At a given pH, the amount of the acid soap is larger for the mixture of smaller n_c, since the population of amine oxide in the micelle is poorer. This explains why pH_c decreases with increasing n_c for Group 2.

Values of pH of the equimolar mixtures of NaOl and CnDMAO before the addition of HCl solutions depended on the chain length of alkylamine oxides: 10.2–10.3 for NaOl and its mixtures with C6, C8, and C10DMAO but 10.5 and 10.6 for the mixtures with C14 and C16 DMAO, respectively. It is expected that the more catanionic complex is formed, the higher the pH. Hence, these initial pH values also support the different tendencies of the catanionic complex formation suggested above.

In this way, we can understand the results shown in Fig. 3, in terms of different complexes formed which is, in turn, a consequence of the different micelle compositions.

Conclusions

We found that the pH_c of the CnDMAO/NaOl mixtures depended on the alkyl chain length of amine oxide (n_c). At C10DMAO/NaOl mixture, the pH_c showed the minimum value. This phenomenon was considered to be caused by different complex formations between $n_c \geq 10$ and short chain length such as $n_c = 6$ and 8. For $n_c \geq 10$, protonated amine oxide (cationic) and anionic oleate form a catanionic complex. This catanionic complex formation increases the surfactant packing parameter and tends to form a lamellar like phase. With decreasing chain length n_c, the increase of the packing parameter caused by the complex formation becomes small. For C6DMAO/NaOl and C8DMAO/NaOl, on the other hand, the content of amine oxide is expected to be much smaller than the total composition. Thus, both oleate anion and amine oxide were protonated with adding HCl. As a consequence, both the acid soap of oleic acid and the catanionic complex are expected to be formed for these mixtures.

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