Protonation Behavior and Solution Properties of Amine Oxide Surfactants Containing a Pyridyl Group

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Abstract: Hydrogen bonding between surfactant molecules plays an important role in self-assembly formation. For long alkyl chain amine oxide surfactants, the specific protonation degree dependence of some solution properties has been considered to be due to hydrogen bonding between protonated and deprotonated species. In addition to this type of hydrogen bonding, we introduced a pyridyl group into an amylamine oxide molecule as a new hydrogen-bonding site. The pyridyl group has three different structural isomers based on the position of the substituent. An amine oxide group in pyridylamine oxides was preferentially protonated. In addition, protonation of the pyridyl group revealed a pronounced substituent position effect on the critical micelle concentration, micellar size, and solubilization of oil-soluble dye into micelles. The intermolecular or intramolecular hydrogen bond formation could be controlled by altering the substituent position.

Key words: pyridyl amine oxides, surfactant, hydrogen bond, protonation, solubilization

1 INTRODUCTION

Long alkyl chain amine oxides exist as either nonionic or cationic (protonated form) species in aqueous solutions. The degree of protonation (ionization) depends on the pH of the solution. Various solution and surface properties, such as titration behavior, critical micelle concentration (cmc), micelle aggregation number, micelle size, and aggregation structures are at their minimum and maximum values, respectively. The specific protonation degree dependence of the various solution properties is thought to be due to the hydrogen-bonding between protonated and deprotonated amine oxide groups, and in part to the dipole-dipole interactions among deprotonated head groups. Hydrogen-bonding between protonated and deprotonated species in both the solid state and liquid crystall state has been examined by infrared spectra. Similar protonation behavior is observed for amine oxide surfactants with an amide group. For example, although lauroylamidoalkylmethylamine oxides (C12AmC; 1 = hydrocarbon chain length between the amide group and the amine oxide group) should be less repulsive than C12DMAO in dipole-dipole interactions due to the amino alkyl group introduced, for example, the protonation behavior and cmc values of C12AmC₃ are almost the same as those of C12DMAO. Thus, we think that the hydrogen bonding between protonated and deprotonated species is the most promising attractive interaction in these systems. These findings suggest that hydrogen bonding between polar head groups remarkably affects the aggregate structures and solution properties of amine oxide surfactants.

In the present study, we introduced a pyridyl group into an amylamine oxide molecule as a new hydrogen-bonding site. Pyridyl derivatives of amine oxides have three types of structural isomers based on the substituent position. The substituent position in the surfactant molecule can affect the interaction between neighboring molecules in micelles. For example, 2-pyridylamine oxide surfactants are expected to form intramolecular hydrogen-bonds between amine oxide and the pyridyl group. On the other hand, 3-pyridyl amine oxides might form intermolecular hydrogen bonds, such as those between amine oxide groups, between pyridyl groups, and between amine oxide and pyridyl groups. To examine these pyridylamine oxides, we performed hydrogen ion titration, UV titration, surface tension measurement, estimated the micelle size using the
dynamic light scattering (DLS) method, evaluated the solubilization of a water-insoluble dye Sudan III in micellar solutions, and observed micellar structures by cryogenic transmission electron microscopy (cryo-TEM). The findings revealed that hydrogen bond formation could be controlled based on the isomer structure. In addition, 2-pyridylamine oxides did not form intermolecular hydrogen bonds, but rather intramolecular hydrogen bonds, even in micelles. In general, the protonation of alkylamine oxides in micelles was accompanied by the formation of intermolecular hydrogen bonds between protonated and deprotonated species. Thus, intramolecular hydrogen bond formation in micelles is specific for 2-pyridylamine oxides.

2 MATERIALS AND METHODS

2.1 Materials.

General synthetic routes of pyridymethylalkylmethylamine oxides are shown in Scheme 1. Pyridine carboxaldehydes, alkylamines, solvents, and other reagents were of commercial grade and were not additionally purified before use.

Synthesis of pyridyl methylenealkylamines (1a-c, 2a-c, 3a-c): general procedure

n-Hexane (25 ml) solution containing 2-pyridinemethylenedodecylamine (16.0 g, 58.3 mmol) and dodecylamine (11.3 g, 60.8 mmol) was heated to reflux for 2 h. The solution was evaporated and 2-pyridinemethylenedodecylamine (2a) was afforded in 100% yield (16.6 g, 60.8 mmol) as a yellow solid.

Synthesis of N-alkyl-pyridymethylamine (4a-c, 5a-c, 6a-c): general procedure

Methanol (20 ml) solution containing 2-pyridinemethylene-dodecylamine (2a) (16.0 g, 58.3 mmol) was stirred at room temperature, and NaBH₄ (2.21 g, 58.4 mmol) was added to the solution slowly over 10 min and stirred at room temperature for 17 h. The reaction mixture was poured into water (50 ml), extracted with ethyl acetate (100 ml × 2), and purified by column chromatography (silica gel, chloroform: methanol = 1:1). N-Dodecyl-2-pyridylmethylamine (5a) was afforded in 59% yield (9.57 g, 34.6 mmol) as a yellow liquid.

Synthesis of N-alkyl-N-methyl-pyridylmethylamines (7a-c, 8a-c, 9a-c): general procedure

N-dodecyl-2-pyridylmethylamine (5a) (10.0 g, 37 mmol), 37% formaldehyde (5.36 ml) and formic acid (6.82 g, 130 mmol) were added to 2-propanol (10 ml) and stirred at 100°C for 1.5 h. The reaction mixture was poured into 2N Na₂CO₃ (100 ml) and extracted with ethyl acetate (200 ml × 2). After evaporation of solvents and purification by column chromatography (silica gel, chloroform: methanol = 1:2), N-dodecyl-N-methyl-2-pyridylmethylamine (8a) was afforded in 97% yield (9.14 g, 31.4 mmol) as a yellow liquid.

Synthesis of N-alkyl-N-methyl-pyridylmethylamine oxides (10a-c, 11a-c, 12a-c): general procedure

2-Propanol (20 ml) solution containing N-dodecyl-N-methyl-2-pyridylmethylamine (8a) (8.64 g, 29.7 mmol) and 34.5% H₂O₂ (8.87 g, 90 mmol) was stirred at room temperature for 48 h and Pd/C (20 mg) was added to the solution and stirred for 3 h. The solution was filtered and the solvents removed by evaporation. The residue was purified by column chromatography (silica gel, chloroform: methanol = 1:1) and recrystallized from acetone/hexane. N-Dodecyl-N-methyl-2-pyridylmethylamine oxide (11a) was afforded in 65% yield (5.89 g, 19.2 mmol) as a white crystalline powder.

We abbreviate N-alkyl-N-methyl-x-pyridylmethylamine oxide as Cn-x (n = the number of carbons in the alkyl chain, n = 8, 12, and 14; x = substituent position, x = 2, 3, and 4).

Figure 1 shows the chemical structures of C12-x.

10a (C8-2): 'H NMR (δ ppm) 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 10H), 1.88-2.02 (m, 2H), 3.09 (s, 3H), 3.22 (t, 2H, J = 8.25), 4.44 (d, 1H, J = 12.3), 4.50 (d, 1H, J = 12.3), 7.28-7.38 (m, 1H), 7.74-7.81 (m, 2H), 8.61 (d, 1H, J = 4.8); 13C NMR (δ ppm) 151.2, 149.2, 136.7, 127.8, 123.9, 74.2, 69.7, 55.9, 52.6, 29.0, 29.0, 26.7, 23.4, 22.5, 14.0; ESIMS m/z 273 (M + Na)⁺

10b (C8-3): 'H NMR (δ ppm) 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 10H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.00 (s, 3H), 3.10-3.25 (m, 2H), 4.34 (s, 2H), 7.38 (dd, 1H, J = 4.8, 7.8), 8.12 (d, 1H, J = 7.8), 8.62-8.69 (m, 2H); 13C NMR (δ ppm) 115.2, 150.8, 140.3, 126.3, 123.5, 70.4, 69.6, 55.0, 52.6, 29.2, 29.0, 26.7, 23.5, 22.5, 13.9; ESIMS m/z 273 (M + Na)⁺

10c (C8-4): 'H NMR (δ ppm) 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 10H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.02 (s, 3H), 3.17 (t, 2H, J = 8.4), 4.35 (s, 2H), 7.53 (d, 2H, J = 5.7), 8.68
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\[\text{N-dodecyl-N-methyl-x-pyridylmethylamine oides C12-x (x = 2, 3, and 4).}\]

\[(d, 2H, J = 5.7); ^{13}C\text{ NMR (δ ppm)} 150.1, 138.7, 126.7, 72.0, 69.9, 55.4, 31.6, 29.2, 29.0, 26.6, 23.5, 22.5, 14.0; \text{ESIMS m/z 329 (M+Na)} ^+\]

11a (C12-2): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 18H), 1.88-2.02 (m, 2H), 3.13 (s, 3H), 3.26 (t, 2H, J = 8.25), 4.53 (s, 2H), 7.26-7.36 (m, 1H), 7.66-7.83 (m, 2H), 8.60 (d, 1H, J = 4.8); \(^{13}C\text{ NMR (δ ppm)} 151.1, 149.2, 136.7, 127.9, 124.0, 74.0, 69.6, 55.7, 31.8, 29.5, 29.4, 29.3, 29.2, 26.6, 23.4, 22.6, 14.0; \text{ESIMS m/z 329 (M+Na)} ^+\]

11b (C12-3): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 18H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.01 (s, 3H), 3.16-3.25 (m, 2H), 4.34 (s, 2H), 7.38 (dd, 1H, J = 5.0, 7.6), 8.13 (d, 1H, J = 8.1), 8.63-8.69 (m, 2H); \(^{13}C\text{ NMR (δ ppm)} 150.1, 138.6, 126.8, 71.8, 69.8, 55.3, 31.8, 29.5, 29.4, 29.3, 29.2, 26.7, 23.5, 22.6, 14.0; \text{ESIMS m/z 329 (M+Na)} ^+\]

11c (C12-4): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 18H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.04 (s, 3H), 3.18 (t, 2H, J = 8.25), 4.33 (s, 2H), 7.52 (d, 2H, J = 8.7), 8.68 (d, 2H, J = 5.7); \(^{13}C\text{ NMR (δ ppm)} 150.9, 149.2, 136.8, 128.0, 124.0, 73.6, 69.4, 55.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 26.6, 23.3, 22.6, 14.0; \text{ESIMS m/z 357 (M+Na)} ^+\]

12a (C14-2) (Fig. 2): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 22H), 1.88-2.02 (m, 2H), 3.17 (s, 3H), 3.24-3.37 (t, 2H, J = 8.25), 4.55 (d, 1H, J = 12.6), 4.60 (d, 1H, J = 12.6), 7.28-7.38 (m, 1H), 7.72-7.83 (m, 2H), 8.61 (d, 1H, J = 4.5); \(^{13}C\text{ NMR (δ ppm)} 150.9, 149.2, 136.8, 128.0, 124.0, 73.6, 69.4, 55.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.6, 23.3, 22.6, 14.0; \text{ESIMS m/z 357 (M+Na)} ^+\]

12b (C14-3): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 22H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.01 (s, 3H), 3.10-3.25 (m, 2H), 4.34 (s, 2H), 7.37 (dd, 1H, J = 4.8, 7.8), 8.14 (d, 1H, J = 7.8), 8.64 (d, 1H, J = 1.5), 8.66 (dd, 1H, J = 1.5, 4.8); \(^{13}C\text{ NMR (δ ppm)} 152.2, 150.8, 140.3, 126.3, 123.5, 70.4, 69.7, 55.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.7, 23.5, 22.6, 124.0; \text{ESIMS m/z 357 (M+Na)} ^+\]

12c (C14-4): \(^1\text{H NMR (δ ppm)} 0.88 (t, 3H, J = 6.6), 1.20-1.40 (m, 22H), 1.78-1.93 (m, 1H), 1.93-2.10 (m, 1H), 3.03 (s, 3H), 3.18 (t, 2H, J = 8.4), 4.32 (s, 2H), 7.53 (d, 2H, J = 6.0), 8.68 (d, 2H, J = 6.0); \(^{13}C\text{ NMR (δ ppm)} 152.2, 150.8, 140.3, 126.3, 123.5, 70.4, 69.7, 55.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.7, 23.5, 22.6, 124.0; \text{ESIMS m/z 357 (M+Na)} ^+\]

As an example, \(^1\text{H NMR spectrum of C14-2 is shown in Fig. 2. No impurity peaks were observed in the spectrum, indicating the high purity of C14-2. Similarly, the other compounds we synthesized in this study were shown to be of high purity by the NMR spectra.}

2.2 Methods
\(^1\text{H NMR (300 MHz) and }^{13}C\text{ NMR (75 MHz) spectra were obtained in CDCl}_3 with a JEOL JNM-AL300 spectrometer at 25°C. Mass spectrometry measurements were performed by electron spray ionization in methanol with a Finnigan LCQDeca instrument.}

All sample solutions were prepared with a NaCl concentration, \(C_n\), of 0.10 mol kg\(^{-1}\). All experiments except for the cryo-TEM observations were performed at 25°C.

Hydrogen ion titrations of micelles and monomers were performed as follows: Solutions with a surfactant concentration (\(C_m\)) of 0.02 mol kg\(^{-1}\) were titrated with a 0.1N NaOH solution under a nitrogen atmosphere. 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 \(C_n\) and the same volume, but containing no surfactant. We used C8-x as the monomer analog comprising the same polar head group as both C12-x and C14-x.
The surfactant concentration of 0.02 mol kg\(^{-1}\) was above the cmc for C12-x and C14-x, and below the cmc for C8-x.

The UV absorption spectra for \(C_0 = 1.5 \text{ mmol kg}^{-1}\) aqueous solutions of C8-x and C14-x were measured using a Shimazu UV-3100 spectrophotometer at various pH values. The \(C_0\) of 1.5 mmol kg\(^{-1}\) was below the cmc of C8-x, and above the cmc of C14-x. Accordingly, the pH dependence of the spectra of C8-x and C14-x corresponded above the \(C_0\) for C12-x, and below the \(C_0\) for C14-x. The pH values were adjusted by adding 1N HCl solution.

Equilibrium surface tension measurements of the sample solutions were obtained using a Kruss K-100 tensiometer operating in zero-loss bright field mode at 80 kV. Specimens were prepared in a chamber with controlled temperature and humidity. A drop of the sample solution was added to an aqueous surfactant solution (0.025 M aqueous acetic acid solution: methanol). The composition of the mobile phase was 15:85 for micelles, and 1:9 for monomers for the first and second protonation sites, respectively. The dissociation constant \(K_m\) for monomers is proposed as follows;

\[
0 < \alpha < 1, \quad K_m = \frac{[\text{PyAO H}^+][\text{PyAO}^{-}]}{[\text{PyAO}^{2-}]} = K_1 + K_2 [\text{PyAO} H^+] = pH + \log (\alpha / (1 - \alpha))
\]

\[
1 \leq \alpha < 2, \quad K_m = \frac{[\text{PyAO H}^+][\text{PyAO} H^+]^2}{[\text{PyAO}^{2-}][\text{PyAO} H^+]} = pH + \log (\alpha / (1 - \alpha))
\]
the pH titration curves. The intrinsic dissociation coefficients of the micelles $K_{M1}$ and $K_{M2}$ can be obtained as the $pK_i$ values extrapolated to $\alpha = 0$ and to $\alpha = 1$ for the first and second protonation sites on the micelles, respectively.

3.2 Hydrogen ion titration

Hydrogen ion titration was performed to evaluate the protonation degree, $\alpha$, of the monomers and micelles at a given pH. As described above, $\alpha$ represents the number of protons bound to a pyridylamine oxide molecule. We estimated the dissociation constant for the monomer based on eqs. (1) and (2) from the relation between $\alpha$ and pH.

Three isomers of pyridylamine oxides with an alkyl chain length of 8, C8-x (x = 2-4), were used for the monomer titration. The titration curves of $pK_1$ against $\alpha$ are shown in Fig. 3. All of the curves of C8-x in the range of $\alpha < 1$ were almost the same, whereas that of C8-2 was different, in the range of $\alpha > 1$. The $pK_1$ values estimated from the titration curves were also the same (ca. 4.7) for the first protonation of the monomers, as listed in Table 1. On the other hand, the $pK_2$ value of C8-2 (ca. 1.2) was clearly different from that of C8-3 and C8-4 (ca. 2.9) for the second protonation.

![Fig. 3] Hydrogen ion titration curves for monomers (C8-x).

Table 1 | Dissociation coefficients for pyridylamine oxides at 25°C. C_S = 0.1 mol dm^{-3}, C_D = 0.02 mol dm^{-3}.
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Monomer (C8-x)</td>
<td>$pK_1$ (± 0.1)</td>
<td>$pK_2$ (± 0.1)</td>
</tr>
<tr>
<td>C8-2</td>
<td>4.7</td>
<td>1.2</td>
</tr>
<tr>
<td>C8-3</td>
<td>4.7</td>
<td>2.9</td>
</tr>
<tr>
<td>C8-4</td>
<td>4.6</td>
<td>2.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Micelle (C12-x and C14-x)</th>
<th>$pK_{M1}$ (± 0.1)</th>
<th>$pK_{M2}$ (± 0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12-2</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>C12-3</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>C12-4</td>
<td>5.6</td>
<td>2.3</td>
</tr>
<tr>
<td>C14-2</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>C14-3</td>
<td>5.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

![Fig. 4] Hydrogen ion titration curves for micelles (C12-x).

The $pK_1$ values of C8-x were similar to those of simple amine oxide surfactants, such as decyldimethylamine oxides ($pK_1 = 4.9$). Therefore, the first protonation was expected to occur in the amine oxide group. The pH dependence of UV spectra of the pyridyl group also indicated that the first protonation occurred in the amine oxide group, as explained later. Here, we concluded that the first protonation occurred in the amine oxide group and the second protonation occurred in the pyridyl group in the pyridylamine oxide molecule. The much smaller value of $pK_2$ for C8-2 than for C8-3 and C8-4 indicates that the second protonation was less likely to occur on the C8-2 molecule than on C8-3 and C8-4, because of the electrostatic repulsion between charges within the molecule.

Although all three titration curves of the C12-x micelles agreed with each other in the range of $\alpha < 0.5$, they provided obvious differences in the range of $\alpha > 0.5$, as shown in Fig. 4. The protonation behavior of C14-x micelles other than C14-4 was similar to that of the C12-x micelles (Fig. 5). The solubility of C14-4 was poor at pH values higher than 4 due to both the symmetrical chemical structure and the hydrophobicity of the long alkyl chain of C14. The C12-2 molecule was bound to at most one proton, same as in the monomer titration of C8-2. That is, binding of two protons to a 2-pyridyl substituent was quite difficult because of the electrostatic repulsion between charges on the molecule. Based on the small $pK_{M2}$ value (ca. 1), the C14-2 molecule does not easily bind the two protons (Fig. 5).

Comparing the titration curves of monomers with those of micelles, the first protonation was more favorable in micelles than in monomers because of the hydrogen bonding between deprotonated and protonated species. As the protonation continued, however, the protonation degree of the micelles decreased compared with that of monomers at the same pH value. The second protonation in micelles was less favorable than that in monomers because of the elec-
trostatic repulsion between charges on the micellar surface.

The intrinsic dissociation coefficients of micelles, \( K_{M1} \)
were evaluated from the extrapolation to \( \alpha = 0 \) of plots of \( pK \) against \( \alpha \). As listed in Table 1, we found little effect of isomers on the values of \( pK_{M1} \). The longer alkyl chain resulted in a substantial increase in the protonation behavior, except for in 4-pyridylamine oxides. For 2- and 3-pyridyl amine oxides, longer alkyl chains increased the \( pK_{M1} \) value and decreased the \( pK_{M2} \) value. The \( pK_{M1} \) values for pyridylamine oxides (ca. 5.6 for C12-x and ca. 5.9 for C14-x) were slightly smaller than those for C12DMAO (5.9) and tetradecyldimethylamine oxide (C14DMAO; 6.3). On the other hand, the \( pK \) values for C8-x (ca. 4.7) were almost the same as those for the simple amine oxide monomers (ca. 4.9), as described above. The protonation behavior differed based on the substituent position when the pyridylamine oxide surfactant molecules assembled.

3.3 The pH dependence of UV absorption spectra of the pyridyl group in pyridylamine oxides

Pyridylamine oxide surfactant has two protonation sites comprising a pyridyl group and an amine oxide group. Because the pyridyl group absorbs UV light, protonation of the pyridyl group causes a change in the absorption curve. Thus, the protonation behavior of the pyridylamine oxide surfactant molecule is revealed by both the pH dependence of the UV spectra and the hydrogen titration curves.

First, we examined the pH dependence of the UV spectra of C8-x solutions to study the protonation behavior of the monomer. The spectra of C8-2 for a pH of 10 to 3 were nearly identical, and changed for a pH of 2 (Fig. 6 (a)). The results suggested that the protonation occurred at the amine oxide group for a pH of 10 to 3. After that, the pyridyl group was protonated at ca. pH 2. For C8-3 and C8-4, the spectra began to change at pH 5, as shown in Fig. 6(b) and (c). That is, the second protonation of both C8-3 and C8-4 occurred at a higher pH value than that of C8-2.

![Fig. 5 Hydrogen ion titration curves for micelles (C14-x).](image)

![Fig. 6 The pH dependence of UV absorption curves of pyridyl group for C8-x monomers and C14-x micelles. (a) C8-2, (b) C8-3, (c) C8-4, (d) C14-2, (e) C14-3, (f) C14-4.](image)
The results indicate that the pyridyl group of both C8-3 and C8-4 is more easily protonated than that of C8-2.

We then measured the UV spectra of C14-x solutions. The pH dependence of UV spectra for C14-x at $C_0=1.5$ mmol dm$^{-3}$ corresponds to the protonation behavior of micelles. The spectra of C14-2 from pH10 to 3 were consistent, whereas the spectra changed slightly with a pH of 2 (Fig. 6(d)). The results for C14-2 agreed with those for C8-2. Protonation of the amine oxide group predominantly occurred in the pH range from 10 to 3 for both the monomer and the micelle solutions. Protonation of the pyridyl group then occurred at a pH less than 3. The spectra for C14-3 started changing at ca. pH 3 (Fig. 6(e)). The solubility of C14-4 was poor in the high pH region, as described above, and thus spectra of C14-4 were not obtained in the pH range of 10 to 5 (Fig. 6(f)).

The $pK$ value of the ionizing group depends on whether the substituent group is electron-donating or electron-withdrawing. Moreover, the $pK$ value depends on the substituent position. For example, both the amine oxide group and pyridyl group are electron-withdrawing. The $pK$ values of the pyridyl group in the pyridylamine oxide surfactants were smaller to those of pyridine because the substituent was an amine oxide group, although the pyridyl group did not affect the $pK$ value of the amine oxide group.

3.4 The $\alpha$ dependence of critical micelle concentrations

The $cmc$ were estimated from the break points of the plots of surface tension against the surfactant concentration. Figure 7 shows the relation between $cmc$ values and $\alpha$ in the C14-2 and C14-3 systems. The $cmc$ values of C14-3 showed a clear minimum at $\alpha=0.5$. The $\alpha$ dependence of $cmc$ values of C14-3 coincided with that of simple amine oxides, such as C12DMAO and C14DMAO. Therefore, we concluded that intermolecular hydrogen bonds are formed between protonated and deprotonated species for C14-3, as well as simple amine oxides. On the other hand, the $cmc$ values of C14-2 showed a slight minimum in the range $\alpha=0.2-0.3$. The $\alpha$ dependence of $cmc$ of C14-2 was different from that of simple amine oxides and C14-3. Goldsipe et al. predicted the $\alpha$ dependence of $cmc$, the micelle aggregation number, and the micelle deprotonation equilibrium constant for a pH-sensitive surfactant like C12DMAO and C14DMAO, and compared the predicted values with the experimental values. The predicted minimum in the plot of the $cmc$ versus $\alpha$ occurs at $\alpha=0.2$, while the experimental minimum is located at $\alpha=0.5$. Their theory includes hydrophobic, interfacial, packing, steric, electrostatic, and entropic contributions as the free energy of micellization, but not hydrogen-bonding. They described that the predicted location of the $cmc$ minimum might better coincide with the experimental location by incorporating hydrogen-bonding into the theory for simple amine oxide surfactants. Note that their prediction of the $cmc$ minimum at $\alpha=0.2$ coincided with the results of C14-2. We concluded that the C14-2 system is different from other simple amine oxides and might not include intermolecular hydrogen bonding.

3.5 The $\alpha$ dependence of micelle size

We estimated the hydrodynamic diameters of micelles, $d_H$, as a function of $\alpha$ by DLS measurements. For both C14-2 and C14-3, there were first increases followed by decreases with an increase in $\alpha$, as shown in Fig. 8. Both C14-2 and C14-3 micelles formed not only spherical but also thread-like micelles, as described later. Thus, the Einstein-Stokes Equation cannot be applied in some cases. We used the $d_H$ values obtained for the relative comparison among some $\alpha$ values. The largest size of C14-3 micelles was observed at $\alpha=0.5$. The result for the C14-3 micelles is consistent with that of the simple amine oxide surfac-
3.6 The $\alpha$ dependence of the maximum amount of solubilization of Sudan III in micellar solutions

The solubilized amount of Sudan III in the micellar solution against $\alpha$ is shown in Fig. 9. In the C14-2 system, the maximum amount of solubilization of Sudan III, $S_{\text{max}}$, increased with an increase in $\alpha$ in the range $0 \leq \alpha \leq 0.2$, and was kept constant at approximately 50 mg dm$^{-3}$ for $0.2 \leq \alpha \leq 0.6$. The $S_{\text{max}}$ decreased with an increase in $\alpha$. That is, by introducing charges to the micelle, $S_{\text{max}}$ increased for $0 \leq \alpha \leq 0.2$ and decreased for $\alpha \geq 0.6$. The $\alpha$ dependence of $S_{\text{max}}$ was somewhat similar to that of the micelle size, and related to that of the $\text{cmc}$. The $S_{\text{max}}$ in the C14-3 system also increased with an increase in $\alpha$ in the range of $0 \leq \alpha \leq 0.2$. Unlike in the C14-2 system, however, the $S_{\text{max}}$ in the C14-3 system markedly decreased with an increase in $\alpha$ for $0.2 \leq \alpha \leq 0.5$, and showed a pronounced minimum at $\alpha = 0.5$. After that, $S_{\text{max}}$ again increased with an increase in $\alpha$ for $0.5 \leq \alpha \leq 0.8$, and then decreased with an increase in $\alpha$ for $0.8 \leq \alpha$. $S_{\text{max}}$ in the C14-3 system showed a clear minimum at $\alpha$ where the micelle size was largest. The relation between $\alpha$ and $S_{\text{max}}$ in the C14-3 system was the same as that in the C12DMAO system reported by Uchiyama et al. previously$^{30}$. Based on their report, the solubilization equilibrium constants of 2-phenylethanol decreased with an increase in $\alpha$ for $0 \leq \alpha \leq 0.75$, although the micelle diameter reached a maximum at $\alpha \approx 0.5$. The Sudan III we applied, which is partially hydrophilic, might be located near the hydrophilic region in the C14-3 micelle. The $S_{\text{max}}$ value in the C14-3 systems at $\alpha = 0.5$ was lower because of the hydrogen bonding between the protonated and deprotonated head groups. Similar results were observed by Abe et al. for some hydrophilic perfumes in the mixed micelles of sodium dodecyl sulfate/hexadecyl poly(oxyethylene) ethers$^{31-33}$. They reported that the maximum additive concentrations of hydrophilic perfume in the mixed micelles were smaller than that predicted by the additive mixing rule because of hydrophilic-hydrophilic interactions between the head groups of anionic and nonionic surfactants in the mixed micelles$^{31-33}$. On the other hand, C14-2 showed good dye solubilization for a wide $\alpha$ range, $0.2 \leq \alpha \leq 0.6$. Unlike C14-3, C14-2 might not form intermolecular hydrogen bonds. As a result, dye solubilization on C14-2 micelles was better than that on C14-3 micelles.

The present results suggest that intermolecular hydrogen bonds between protonated and deprotonated species affect $\text{cmc}$ values, micellar size, and solubilization of Sudan III in the micelles. Although intermolecular hydrogen bonding makes the $\text{cmc}$ lower and the micellar size larger, it decreases the solubilization of Sudan III.

3.7 Observation of micelles by cryo-TEM

Figure 10 (a)-(d) shows the cryo-TEM images of C14-2 and C14-3 aqueous solutions ($\alpha = 0.2$ and 0.5). All images obtained at $C_{\text{H}} = 0.02$ mol kg$^{-1}$ and $C_{\text{N}} = 0.1$ mol kg$^{-1}$ exhibited similar thread-like micelles. There were nonsignificant differences between the two $\alpha$ values in the $\text{cmc}$, the micelle size, and the $S_{\text{max}}$ for C14-2. On the other hand, there were pronounced differences in the $S_{\text{max}}$ for C14-3 systems. Interestingly, although the C14-3 micelles at $\alpha = 0.2$ and 0.5 looked similar with thread-like micelles on the cryo-TEM images, they had distinct solubilization behavior. The results implied that the interaction between surfactant molecules might differ in strength, even if similar thread-like micelles are formed. The fact that the dye was poorly solubilized in the C14-3 solution at $\alpha = 0.5$ might be due to the strong attractive interaction between the protonated and deprotonated species. That is, the interaction between molecules seems to have more of an effect than micelle shape and size on solubilization.

4 SUMMARY

In the present study, we synthesized octyl-, dodecyl-, and tetradecylpyridylamine oxides, and examined the protonation behavior by hydrogen ion titration and UV absorp-

![Figure 9](image-url)
tion. The amine oxide group was preferentially protonated in the pyridylamine oxide surfactants we examined in the study. The first protonation, which is the protonation of the amine oxide group, showed nonsignificant effects of the substituent position of the pyridyl group. On the other hand, the second protonation, which is the protonation of the pyridyl group, showed a pronounced effect of the substituent position due to steric interaction.

From the α dependence of the cmc values, we found that C14-3 formed the most stable micelles at α = 0.5. For C14-2, a subtle α dependence of the stability of micelles was observed. The difference in the α dependence of the cmc values between C14-2 and C14-3 might be due to differences in the strength of the interaction between molecules in the micelles. That is, the interaction for the C14-2 system comes from the introduction of charge into the nonionic micelles, but not from hydrogen bonding between protonated and deprotonated species. The interaction for the C14-3 system, however, is mainly thought to be due the hydrogen bonding between protonated and deprotonated head groups in the micelles. Therefore, we concluded that the number of solubilization sites for Sudan III adjacent to the more compact hydrophilic region of the mixed micelles decreases as a result of hydrogen bonding between protonated and deprotonated head groups at α = 0.5 in the C14-3 systems.

References


