

Effect of Urea and Salt on Micelle Formation of Zwitterionic Surfactants

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ABSTRACT: The effect of urea on micelle formation of zwitterionic surfactants was investigated by measuring conductivity, critical micelle concentration (CMC), relative viscosity, and the spectrophotometric shift in wavelength. We examined two zwitterionic surfactants, *N,N*-dimethyl dodecylamine *N*-oxide and *N,N*-dimethyl tetradecylamine *N*-oxide (DMTAO). The CMC values of the surfactants increased with the addition of urea. Also, the relative viscosity of the surfactant solutions decreased at higher concentrations of urea and increased with increasing KCl concentration. The absorbance maxima of the surfactants decreased with increasing urea concentration.

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KEY WORDS: *N*-Dimethyl dodecylamine *N*-oxide, *N,N*-dimethyl tetradecylamine *N*-oxide, urea.

The use of urea as a denaturant of proteins is well known (1,2). The presence of urea and its derivatives modifies the properties of aqueous solutions. Two different mechanisms have been proposed to explain urea action on aqueous solutions (3–5). One is that urea acts as a water structure breaker (indirect mechanism). The other is that urea participates in the solvation of hydrophobic chains in water by replacing some water molecules in the hydration shell of the solute (direct mechanism).

Many investigators have reported that critical micelle concentrations (CMC) of ionic and nonionic surfactants significantly increase with the addition of urea in aqueous solutions (6,10). Hydrophobic interactions play an important role in the formation of micelles. It is generally accepted that urea acts as a breaker of hydrophobic interactions (3). A computer simulation (10) of urea action in aqueous solution showed that urea had a negligible influence on the water structure, whereas urea weakened the water–water interaction by replacing several water molecules from an apolar solvation shell (4,5).

By monitoring the electron spin resonance of nitroxide radicals in sodium dodecyl sulfate and dodecyl-

trimethylammonium bromide aqueous solutions, Baglioni *et al.* (6) showed that urea slightly decreased the micropolarity of the micellar surface and increased the microviscosity of the micellar surface. A systematic study also was made of the effect of addition of salts and organic molecules, singly and jointly, on micellar growth in aqueous ionic surfactant solutions (7,8).

This paper focuses on the effect of urea on zwitterionic micelles as a means to characterize zwitterionic micelles. The CMC values of surfactants in aqueous urea solution were measured by conductivity methods, and the absorbance and shift in wavelength maxima of surfactants in aqueous solution as a function of urea concentration were determined. Viscosity measurements can be used to study how micelles grow and how the combined presence of a salt and organic additive (e.g., urea) influences the viscosity and overall organization of surfactant molecules.

EXPERIMENTAL PROCEDURES

Materials. *N,N*-Dimethyl dodecylamine *N*-oxide (DMDAO) and *N,N*-dimethyl tetradecylamine *N*-oxide (DMTAO) were a gift from Clariant Surfactants Division (Sulzbach, Germany). Urea was obtained from Fluka (Buchs, Switzerland) and was used as received. The other materials used were reagent grade products. Deionized, distilled water was used.

Measurements. Conductivity measurements of aqueous surfactants were carried out using a conductivity meter, WTW 521 IF300 (Frankfurt, Germany). The viscosities of solutions were measured by an Ubbelohde viscometer (9). Absorbance spectra of urea were recorded with a Cecil 1020 ultraviolet-visible spectrophotometer (Cambridge, United Kingdom). All measurements were made at $25 \pm 0.1^\circ\text{C}$ with less than 4% variability between one experiment and the next.

RESULTS AND DISCUSSION

The CMC values of two zwitterionic surfactants, DMDAO and DMTAO, were determined at 25°C by using a conductivity method. The effect of urea on the CMC of DMDAO and DMTAO is summarized in Table 1. The change in conductivity at the CMC became more gradual with increasing

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Abbreviations: CMC, critical micelle concentration; DMDAO, *N,N*-dimethyl dodecylamine *N*-oxide; DMTAO, *N,N*-dimethyl tetradecylamine *N*-oxide.

TABLE 1
Effect of Urea Concentration on CMC Values of DMDAO and DMTAO^a at 25°C

Urea concentration (M)	DMDAO		DMTAO	
	10 ³ CMC (M)	S ₂ /S ₁	10 ³ CMC (M)	S ₂ /S ₁
0.00	1.90	0.40	6.50	0.46
0.10	2.39	0.46	9.75	0.55
0.20	2.90	0.51	12.6	0.63
0.30	3.40	0.57	14.5	0.71
0.40	3.90	0.66	17.4	0.80
0.50	4.50	0.73	20.4	0.87
0.60	5.00	0.82	23.0	0.95

^aCMC, critical micelle concentration; DMDAO, *N,N*-dimethyl dodecylamine *N*-oxide; DMTAO, *N,N*-dimethyl tetradecylamine *N*-oxide.

urea concentration. Figure 1 illustrates how the CMC value is determined as the point of discontinuity in plots of measured conductivity vs. surfactant concentration profile. In this paper S_1 and S_2 are used to denote the slope of conductivity tangents vs. surfactant concentration curves below and above the CMC, respectively. The value of S_1 in Figure 1 is 0.66, and the value of S_2 is 0.36. The S_2/S_1 ratio may be used as an index of the degree of dissociation of the micelle (10) (Table 1). The difference in S_2/S_1 ratios for DMDAO (0.40) and DMTAO (0.46) is related to the greater hydrophobic character of DMTAO compared with DMDAO, which may enhance the dipole moment ($N \rightarrow O$) of the zwitterionic head group (11). The S_2/S_1 ratios always increased with the addition of urea, which may encourage the polarity of the surfactant head group.

The CMC values of DMDAO and DMTAO increased with added urea. Traditionally, the behavior of micelles in the presence of urea could be explained in terms of the weakening of hydrophobic interactions by urea, which

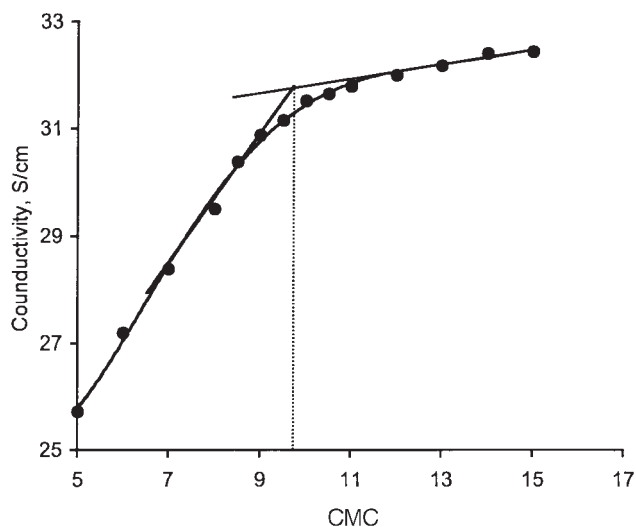


FIG. 1. Critical micelle concentration (CMC) of *N,N*-dimethyl tetradecylamine *N*-oxide (DMTAO) in the presence of 0.1 M urea at 25°C, using the conductivity method. The dotted line represents the CMC.

acts as a water structure breaker (10,12). Urea tends to stabilize the surfactant monomer since urea enhances the solubility of hydrocarbons in water. This trend is more evident with DMTAO than DMDAO because DMTAO has more hydrocarbon character and a greater solubilization capability in the presence of urea. Figure 2 displays the dependence of experimental CMC/CMC₀ ratios for DMDAO and DMTAO as a function of urea concentration, where CMC₀ denotes the CMC of surfactant in the absence of urea. The significant difference between two surfactants is attributed to the difference in their hydrophobicity. DMTAO chains have a higher hydrophobicity than DMDAO chains as judged from their lower water solubility and greater CMC values (13,14). The change in

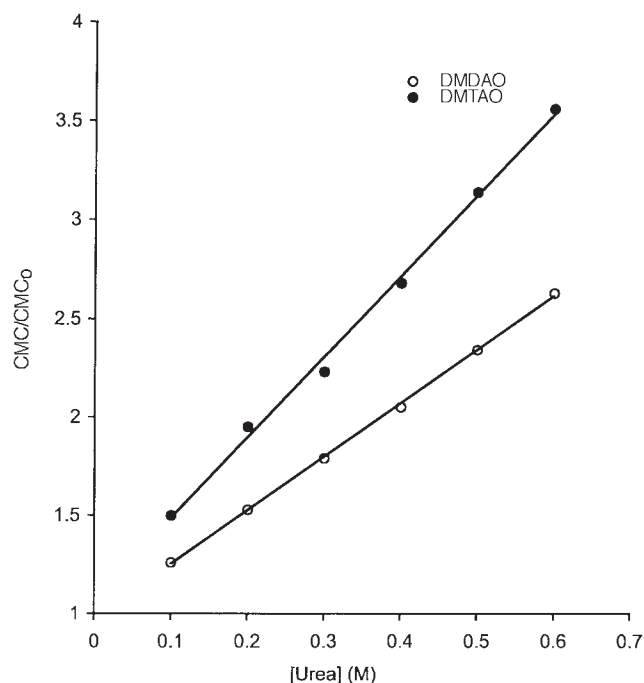


FIG. 2. Dependence of CMC/CMC₀ on urea concentration for *N,N*-dimethyl dodecylamine *N*-oxide (DMDAO) and DMTAO using the conductivity method. For other abbreviation see Figure 1.

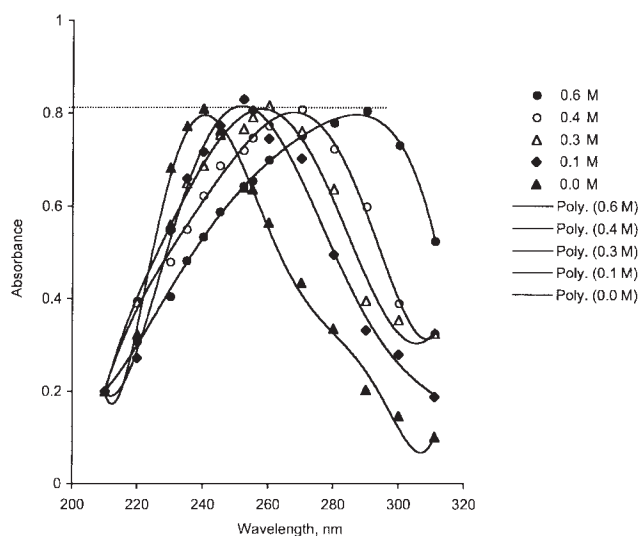


FIG. 3. Absorbance at different wavelengths of 0.03 M DMTAO in the presence of different concentrations of urea at $T = 25^\circ\text{C}$. The dotted line is added as a baseline to make a comparison between the maxima and to show the shift in wavelength. For abbreviation see Figure 1.

TABLE 2
Effect of Urea Concentration on Wavelength of DMDAO and DMTAO^a at 25°C

Urea concentration (M)	Wavelength (nm)	
	DMDAO	DMTAO
0.0	240	230
0.1	245	250
0.2	250	260
0.3	255	270
0.4	260	280
0.5	260	280
0.6	270	290

^aFor abbreviations see Table 1.

the contact area of the DMTAO chain to water would be larger than that of DMDAO with micelle formation (15). Therefore, the extent of structural reorganization of water around DMTAO chains would be larger, with a resultant gain in entropy as to the micelle formation (15). Also, urea may enhance the repulsive force between the polar zwitterionic monomer head group of either surfactant at the micellar surface, judged from the increase of S_2/S_1 ratios.

The binding of urea with DMDAO and DMTAO micelles also is reflected by the slight shift in wavelength (λ_{max}) in the plot of absorbance of a surfactant solution in the presence of different concentrations of urea (16,17) as shown in Figure 3. The shift is more dramatic for DMTAO micelles than for DMDAO micelles as shown in Table 2, because it has more hydrocarbon content, thus improving solubilization when combined with urea. Also, an increased concentration of urea may decrease the aggregation number and provide slightly more surfactant absorbance. Surfactant addition to the urea–water interface will occur primarily near the hydrocarbon region and will facilitate the presence of the surfactant monomer (18).

Figure 4 illustrates the interplay between the effect of surfactant and urea concentrations on the variation in relative viscosity η_r ($= \eta/\eta_0$, where η and η_0 are the viscosities of the sample solution and the solvent, water, respectively). Surfactant concentration has an effect on the position of the relative viscosity peak. The peak shift shows that increasing the urea concentration decreases the viscosity because urea molecules are embedded between monomers of the micelle through hydrophobic interaction. This shift is greater for DMTAO than for DMDAO, owing to its large hydrophobicity.

For a constant surfactant concentration and varying salt content, the viscosity shows a rather complicated behavior when plotted against urea concentration (Fig. 5). The

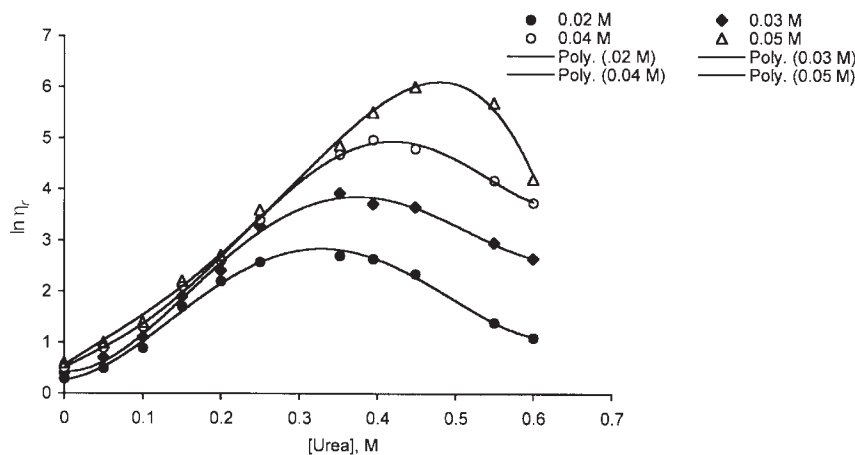


FIG. 4. Relative viscosity (η_r) as a function of urea concentration for different concentrations of DMDAO at 25°C . For abbreviation see Figure 2.

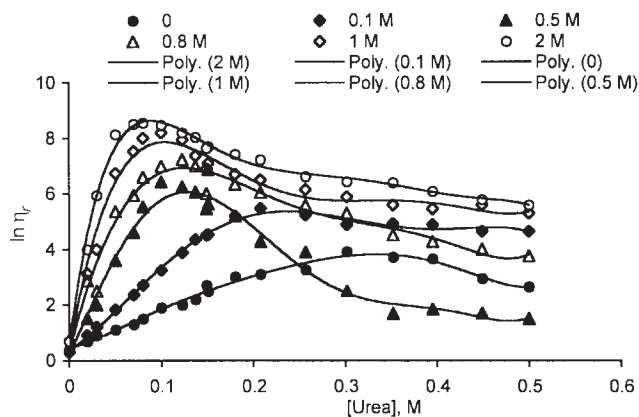


FIG. 5. Relative viscosity (η_r) of a 0.3 M DMTAO micellar solution as a function of urea concentration for different concentrations of KCl at 25°C.

presence of KCl imparts higher surfactant micellar solution viscosity than when no salt is present in the system. Furthermore, the presence of salt causes the viscosity to increase and reach a maximum (η_r^{\max}), then decrease as the concentration of urea is increased. The most plausible explanation for this synergistic effect is the decrease in electrostatic repulsion between monomers, which is like other cationic surfactants. It is conceivable that the positive charge on the surfactant will remain in the inner sphere relative to the negative charge (19). The charge dipole interaction between the dipole (N \rightarrow O) and KCl reduces the water solubility of urea. The reduction of water solubility causes partitioning of the additive toward the micellar interface, where it may act as a charge-shielding agent (9). Furthermore, at a higher concentration of urea the grown micelles become more flexible as they contain more urea. This is especially true when the KCl content is high enough to shield the repulsive interaction (9,18). Mukerjee (18) showed that an additive (KCl) that is surface active to a hydrocarbon–water interface will primarily become solubilized near the head group region and will facilitate micellar growth (9,18). The decrease in viscosity observed at a higher urea concentration may result from solubilization in both the palisade layer and the core. This core solubilization of urea provides swelling to the grown micelle (9,18).

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