

## CTAB 의 미셀 형성에 미치는 아미드화물의 영향

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## Effects of Amides on the Micelle Formation of Cethyltrimethylammonium Bromide

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In recent years, a great deal of interest has been given to the stability and formation of micelles, because they can be served as a model for biological membranes<sup>1</sup> and as a catalyst in many chemical reactions.<sup>2</sup> The major driving force of micelle formation in an aqueous solution is generally believed to be changes in water structure at interface of hydrophobic part of a surfactant and water, but several other factors including electrostatic force and intermolecular hydrogen bonding are also contributing<sup>3</sup>.

For a better understanding of the phenomena of micelle formation and factors governing the process, the effects of various perturbation, such as temperature, solvent composition, and counter ions on the critical micelle concentration (cmc) are commonly studied. Among these, the effects of organic amides are most widely investigated due to their activity on the denaturation of protein molecules, and similarity between the transfer of surface active materials from the micelle to the monomeric state and denaturation of a protein.<sup>3-8</sup> Most of studies showed that addition of amides in an aqueous solution of a surfactant increases the cmc and the results were explained as weakening of the stability of micelle through decreased hydroph-

obic force by the interaction between water and amide. In this communication, we report different effects of formamide (FA), acetamide (AM) and NN-dimethylformamide (DMF) on the cmc of cethyltrimethylammonium bromide (CTAB) at various temperature, which imply that not only hydrophobic but also electrostatic force influences the formation of a ionic micelle.

CTAB was obtained from Merck and recrystallized twice from 96% ethanol and dried in an oven to a constant weight. Extra pure amides were used as received. The solutions were prepared with deionized distilled water and cmc values were determined from abrupt changes in the specific conductance *vs.* surfactant concentration plots for data taken at constant temperature.

The cmc values of CTAB at various amide mole fraction and temperature are summarized in Table 1. The values in pure water solvent agree well with reported results.<sup>6</sup> Cmc's in H<sub>2</sub>O-DMF media are considerably lower than those determined from surface tension measurement,<sup>5</sup> but the general dependencies of cmc's on solvent composition and temperature are in good accord. Table 1 shows that, at 25 and 35°C, the cmc's of CTAB increases monotonically.

Table 1. Critical micelle concentration of CTAB in H<sub>2</sub>O-amide mixed solvents.

Amide	Mole fraction	CMC(mole/l×10 <sup>3</sup> )			
		25°C	35°C	45°C	55°C
None	0.000	0.92	0.96	1.03	1.08
DMF	0.025	1.33	1.53	1.67	—
	0.050	1.83	2.43	2.90	—
	0.080	2.70	3.53	3.87	—
	0.110	3.88	4.39	5.25	—
	1.00*	9.07	10.90	13.81	14.74
Acetamide	0.025	1.09	1.22	1.47	—
	0.050	1.60	1.96	2.12	—
	0.080	2.00	2.58	2.64	—
	0.110	3.15	3.31	3.75	—
Formamide	0.025	1.10	1.05	1.35	—
	0.050	1.18	1.17	1.13	0.93
	0.080	1.68	1.57	0.75	—
	0.120	2.60	2.06	0.47	—
	0.200	2.80	2.21	0.83	0.62
	0.300	3.25	2.83	1.90	1.28
	1.00*	7.41	10.17	11.22	12.10

\*Taken from ref. 6

cally with increased amide concentrations in the concentration ranges studied. The order of effectiveness in destabilizing micelle structure (increasing cmc) is DMF>AM>FA. This order is in parallel with that of N-substituted ureas on the micelle formation of sodium dodecylsulfate (SDS) and *n*-dodecyl trimethylammonium bromide (DTAB)<sup>3</sup>; the effectiveness increases with increased hydrophobicity of amide. At 45°C, a minimum in cmc for FA-H<sub>2</sub>O medium, but monotonic variations for DMF and AM-H<sub>2</sub>O systems, in the cmc vs amide mole fraction relationships was observed. The different behaviors of cmc vs amide mole fraction relationship with temperature indicate that at least two factors are significantly involved in the perturbation of micelle stability.

Thermodynamic consideration of micelle formation shows that the free energy change of micellization,  $\Delta G_m$ , can be approximated as

$\Delta G_m = RT \ln(\text{cmc})$ , and the slope of  $\Delta G_m/T$  vs.  $1/T$  plot yields  $\Delta H_m$ , heat of micellization.<sup>2</sup> Evaluation of  $\Delta H_m$ 's for pure H<sub>2</sub>O, AM and DMF-H<sub>2</sub>O systems (plots not shown) revealed that  $\Delta H_m$ 's in those media are slightly negative, the same in FA-H<sub>2</sub>O medium is positive and strongly temperature dependent. ( $\Delta H_m$  is rarely temperature independent, and thus the accurate values of  $\Delta H_m$  are difficult to be obtained.<sup>9</sup>) The increases in cmc of CTAB with addition of DMF and AM, and with temperature can be qualitatively explained in terms of water structure near the hydrocarbon part of a micelle: the "iceberg" water structure breaks up with these variations and entropy changes of micellization are less positive, resulting smaller free energy decrease.  $\Delta H_m$  may be also changed and could be smaller compared to the value in pure H<sub>2</sub>O or at lower temperature, but the decreased entropy seems predominating factor in deciding  $\Delta G_m$  and thus stability of micelle for DMF and AM-H<sub>2</sub>O media.

The variation of cmc in FA-H<sub>2</sub>O medium at higher temperature can be attributed the involvement of large effect of dielectric constant on the electrostatic forces between polar head groups in a micelle. Addition of FA ( $\epsilon = 109.5$ ) in H<sub>2</sub>O could increase dielectric constant of solvent medium and result in the reduction of electrostatic repulsion in a charged micelle. The combined enthalpy effects of dielectric constant and negative dependence of  $\Delta H_m$  due to structural factor with addition of amide may overwhelm entropy decrease in determining  $\Delta G_m$ . This enthalpy effects is expected to be more pronounced at higher temperature, at which solvent medium is less structured. The occurrence of a minimum in cmc vs. FA concentration curve indicates that the temperature dependences of the hydrocarbon part (structural effect) and polar head group (electrical effect)

are opposite. These opposite effects may be in parallele with the observed effects of temperature in urea-H<sub>2</sub>O medium,<sup>4</sup> in which ionic surfactants show minimum, but none for non-ionic surfactant in cmc vs. T curve.

Even though, the influence of dielectric constant of solvent medium can qualitatively be attributed to the observation of minimum of cmc vs FA mole fraction curve, we cannot even estimate the magnitude of this effect. Measurement of dielectric constant at various temperature and composition range as well as thermodynamic parameters can give quantitative explanation. Works are in progress on these aspects and for the systems of N-methylformamide ( $\epsilon=182.4$ ) and N-methylacetamide ( $\epsilon=179$ ), which are more hydrophobic, but have higher dielectric constants than FA.

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