Salt Effects on the Critical Micelle Concentration and Counterion Binding of Cetylpyridinium Bromide Micelles

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The effects of electrolyte on the critical micelle concentration (cmc) and bromide counterion binding in the micelles of cetylpyridinium bromide (CPB) have been investigated by UV spectroscopy and conductance measurements. Salts used in this study decreased cmc in the order $Cl^- < Br^- < NO_3^-$ (which parallels the lyotropic series for the inorganic anions) and the effects on cmc followed the equation proposed by Shinoda: $\log cmc = A - B \log (cmc + [NaX])$. In the equation, constant B represents the counterion binding to the micelles at cmc and for the micelle of CPB at 25°C, $B = 80.76\%$. The association constant for the binding of counterions to long chain cations within micelles was also derived from the cmc values and counterion binding constant to the micelles.

Introduction

A large variety of reactions catalyzed by micelle-forming surfactants have served as valuable model processes for the study of microenvironmental factors which affect the high efficiency of chemical transformations in the biological realm.[1] Interactions of foreign ions with the chromophoric groups of amphiphilic compounds are of interest in several areas of chemistry and biochemistry, where it has been established that neutral salts can influence the conformation of proteins and other macromolecules by affecting the prevalent hydrophobic or ionic interactions. Such processes can usually be explained by invoking the breaking up of the water structure around the amphiphilic compounds due to lyophilic electrolytes.[2] The amphiphilic compounds become insufficiently solvated and inclined to aggregate or form micelles, possibly due to the reduction of electrostatic repulsion forces by the counterions. For a proper understanding of micellar catalysis, knowledge of fundamental micellar properties such as size, shape, stability, counterion binding.[3] and micropolarity in the Stern layer and micellar core is indispensable. In this paper, we report a study of the aggregation process of cetylpyridinium bromide at 25°C in water and in several salt solutions (NaCl, NaBr, and NaNO₃) to investigate the effects of added salts on the critical micelle concentration (cmc) and counterion binding to the micelles.

Experimental Section

Materials. Cetylpyridinium bromide (CPB) and all the salts were used as received from Merk A. G. without further purification. The surfactant-salt solutions were made by diluting the stock solutions. The water used in all experiments was Millipore "reagent grade" water. The specific conductivity of this water was 1.8×10^{-7} ohm⁻¹ cm⁻¹.

Method. The absorption spectra were recorded manually with a double-beam Shimatzu Model 265 spectrophotometer. Optical densities were read from the digital display at 270 nm and 275 nm. The solutions in the cell compartment were thermostated at 25°C at least 15 min, before the measurements were started. The method of least square was used for the spectrophotometric data treatment. In fact, the
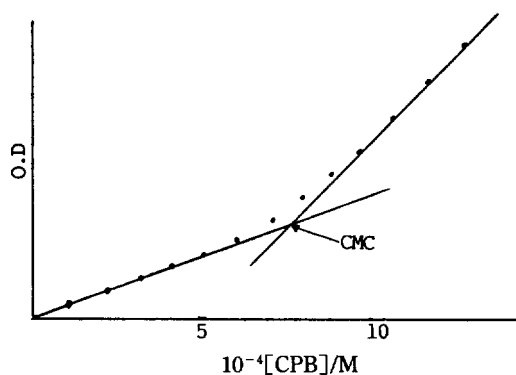

**Figure 1.** CMC determination of CPB in water at 25°C as determined by UV-Vis spectrophotometer.

Table 1. The CMC of CPB in the Presence of Sodium Salt (NaX) at 25°C

[NaX](M)	10⁴ CMC/M		
	X=Cl	X=Br	X=NO₃
0	7.09	7.09	7.09
0.002	4.45	2.69	2.40
0.004	3.35	1.62	1.48
0.006	2.70	1.27	1.20
0.008	2.43	0.88	—
0.010	1.93	0.81	—

cmc values obtained by the conductivity mether agreed well with those measured by the UV spectrophotometer. So the cmc values obtained by the UV spectroscopy method were used in this paper.

Result

The cmc values of CPB in water and in several aqueous salt solutions (NaCl, NaBr, and NaNO₃) were obtained from plots of the absorbance data at 270 nm[4,5] vs the concentration of CPB (Figure 1). In the sufactant concentration range near the cmc, the slopes of these plots underwent an abrupt cha-
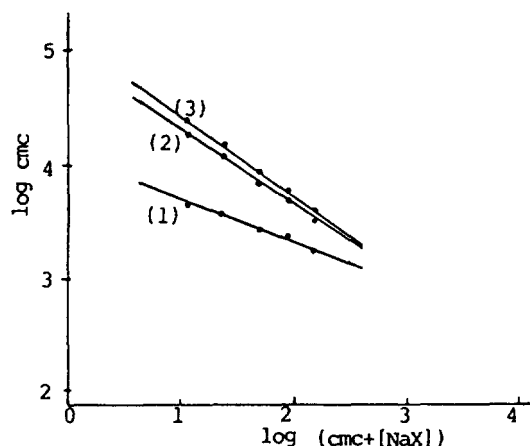
Figure 2. log cmc (of CPB) as a function of log (total counterion conc. at the cmc) for added NaCl (1), NaBr (2), and NaNO$_3$ (3) at 25℃.

Table 2. Linear Regression Analysis of the CMC Decrease with Increasing Salt Concentration [NaX] at 25℃

X	A	B	r^2
Cl	−4.6157	0.4734	0.9794
Br	−5.6983	0.8076	0.8187
NO$_3$	−5.7517	0.8187	0.9869

r^2: coefficient of determination

nge. The cmc was determined by the intersection of the two lines. The results are listed in Table 1.

From the data of Table 1, the cmc of the surfactant CPB decreases with increasing salt concentration. And the decrease of the cmc with increasing salt concentration follows the Shinoda equation[6] which represents the total counterion binding to the micelles at the cmc, *i.e.*,

$$\log \text{cmc} = A - B \log (\text{cmc} + [\text{NaX}]) \quad (1)$$

where A and B are constants. Plots of log cmc against log (cmc+[NaX]) are shown in Figure 2. The results of plots of log cmc *vs.* log (cmc+[NaX]) are listed in Table 2. Clearly, the salt effect on the cmc and counterion binding to the micelles becomes more pronounced in the order Cl⁻ < Br⁻ <NO$_3$⁻. The constant B in the Shinoda equation represents the counterion binding to the micelles at the cmc. For micelles of CPB at 25℃, B=80.76%. This value is somewhat greater than 74.40% of Dodecyltrimethyl ammonium bromide [7] reported previously.

The cmc values and conuterion binding to the micelles allow the calculation of the association constant for binding of bromide ions to the long-chain pyridinium cations within the micelles formed from CPB. If only bromide ions are present as counterions in the micella solution, the following 1:1 association equilibrium can be assumed:

$$P_{yr}{}^+ + Br^- \xrightarrow{K} P_{yr}{}^+ \cdot Br^- \quad (2)$$
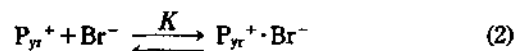
$$K = \frac{[P_{yr}{}^+ \cdot Br^-]}{[P_{yr}{}^+][Br^-]} \quad (3)$$
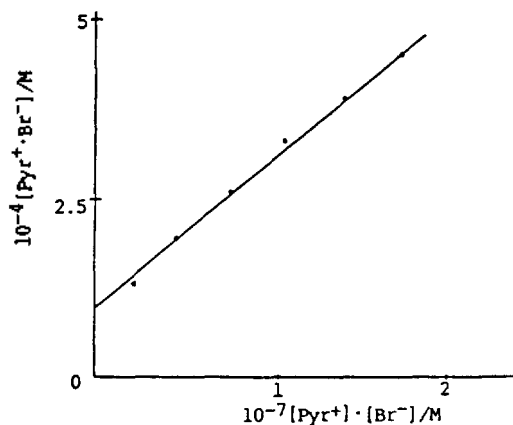
Figure 3. Plot of $[P_{yr}{}^+ \cdot Br^-]$ *vs* $[P_{yr}{}^+][Br^-]$ in water at 25℃.

Table 3. The Association Constants for Binding of Bromide Ions to the Long-chain Pyridinium Cations Within the Micelles in Aqueous NaBr Solution at 25℃

[NaBr](M)	10⁴ CMC/M	10³ K/M⁻¹
0	7.09	3.484
0.002	2.69	0.503
0.004	1.62	0.982
0.006	1.27	1.454
0.008	0.88	1.929
0.010	0.81	2.396

where $P_{yr}{}^+$ represents the long chain pyridinium cation and $P_{yr}{}^+ \cdot Br^-$ represents a pyridinium bromide charge transfer (CT) complex, both within the micelle. K is the equilibrium constant. Neglecting the effect of sodium cation, we may write

$$[P_{yr}{}^+ \cdot Br^-] = B \ (C\text{-cmc}) \quad (4)$$

$$[P_{yr}{}^+] = (1-B)(C\text{-cmc}) \quad (5)$$

$$[Br^-] = (1-B)(C\text{-cmc}) + [\text{NaBr}] \quad (6)$$

in which B is the counterion binding, C is the stoichiometric concentration of CPB, and [NaBr] is the added stoichiometric concentration of sodium bromide.

In Figure 3, the calculated values for $[P_{yr}{}^+ \cdot Br^-]$ are plotted against $[P_{yr}{}^+][Br^-]$. The slope of the straight line represents the association constant (K) per long-chain pyridinium cation (Table 3). As may be seen from Table 3, the association constant decreases with the addition of a little salt, while it becomes progressively greater as the salt concentration increases. Where, it is thought that the decrease in the association constant by the addition of a little salt is due to the salting-in effect, which is the phenomenon increasing the solubility strongly by the interaction between the strong dipole moment of the solute and the anions of salts, while the increase in the association constant by the addition of excessive salt is due to the salting-out effect, the phenomenon decreasing the solubility by the activity decrease of solvent, and the activity decrease of solvent is because many ions produced by adding the excessive salt are hydrated.

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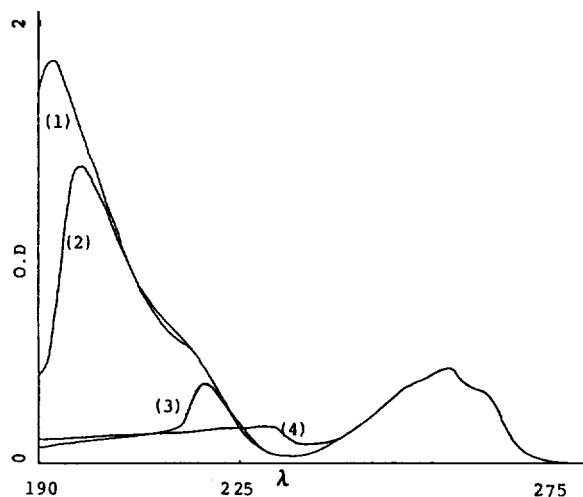
Figure 4. The appearance of the charge-transfer band of CPB in water (1), 0.006 M NaCl (2), 0.006 M NaBr (3), and 0.006 M NaNO₃ (4).

Discussion

As the added salt concentration is increased, the intramicella electrostatic repulsion is reduced by the shielding of micelle charge, so that spherical micelles are more closely packed by surfactant ions.[8] On the other hand, an increase in the added salt concentration would cause charged micelles to dehydrate by the salting-out effect.[9] The optical absorption measurements clearly showed the decrease of cmc with increasing concentration of the salts NaX (X=Cl⁻, Br⁻, and NO₃)(Table 1). The order of effectiveness of the anion studied in this work was Cl⁻<Br⁻<NO₃. The same order applies for the ability of these anions to displace Br⁻ from the Stern layer of the micelles. These results closely parallel the lyotropic series.[10-13] which represent relative salt effects on precipitation and denaturation process of proteins.

In fact the order of effectiveness of anions in reducing the cmc of CPB, as given above, is in accord with the relative order of the effects of the anions on water structure.[14] The λ_{max} of $\pi \to \pi^*$ transition is shifted to the long wavelength in the order Cl⁻→ Br⁻→ NO₃ (Figure 4). Therefore, it may be suggested that the position of an anion within the series corresponds to the effect of the anion on the magnitude of

the hydrophobic term in the free energy of micellization. It is highly likely that the decrease in the cmc with increasing salt concentration is mainly the result of a reduction in charge density per surface area of the micelle which leads to a lowering of coloumbic repulsions between the head groups. That is, the cmc is decreased in the presence of added electrolytes owing to screening of the electrostatic repulsion between the head groups. For the above anions, the effect on the cmc parallels the anion radii. In fact the greater the anion radius, the greater the polarizability and the lower the heat of dehydration. Both factors will enhance the attraction between the polarizable pyridinium cation and the added anion and will determine the lowering of the cmc and the tendency of the noncommon anion to repel bromide anions from the electrical double layer. Therefore, we concluded that the salt effect on the cmc and counterion binding to the micelles becomes more pronounced in the order Cl⁻<Br⁻<NO₃⁻ (the lyotropic series).

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