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Solubilization of Alcohols in Aqueous Solution of Cetylpyridinium Chloride

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The critical micelle concentration (CMC) values of cetylpyridinium chloride (CPC) in some alcohol-aqueous solutions were determined by UV-Vis spectroscopy at 25°C. The CMC of CPC was increased with the addition of methanol and ethanol, while with the addition of propanol it was decreased because of the solubilization of propanol into the micelle of CPC. The ratio (β) of the number of counterions to that of surfactant ions associated into micelles in alcohol (methanol, ethanol and propanol) aqueous solutions was measured by using the Shinoda equation[17]. The ratio of counterion binding to the CPC micelles in methanol- and ethanol-water mixtures was larger than in pure water, while the ratio in propanol-water mixture might be much decreased.

Introduction

A large number of studies have been reported on the effect of various electrolytes and alcohols on the micellization of nonionic and anionic surfactants[1-7].

The association of ionic surfactant in aqueous solution is governed by two opposing forces[8]: The hydrophobic force between the hydrophobic tails attracts the surfactant molecules or surfactant ions to the micelle core from the aqueous bulk solution. The ionic head groups, on the other hand, favor the aqueous bulk phase, because the electrostatic repulsive force between the head groups prevents the surfactant molecules from associating. In this connection, the effects of inorganic salts and alcohols on the aggregation (micellization) of ionic surfactant may be discussed. The effect of inorganic electrolytes is explained in terms of the shielding of the electrostatic repulsion by the counterions[9,10], while the effect of alcohols which have a long hydrophobic part is explained from the reduction of the free energy of mixing and the reduction of the surface charge density by the alcohols entering in the palisade layer of the micelle[11,12]. Therefore, the effect of short chain alcohols on the micellization of a cationic surfactant may be interesting.

From these points of view, we have studied the effect of short chain alcohols (methanol, ethanol, and propanol) on the micelle formation of cationic surfactant, cetylpyridinium chloride (CPC) in aqueous KCl-solutions. The CMC values of CPC in alcohol-salt (KCl)-water mixtures were determined by the UV-Vis. spectroscopy method previously reported[10]. The ratio (β) of the number of counterion to that of surfactant ion in micelles was measured in order to understand the solubilization of propanol more clearly.

Experimental

Materials. Cetylpyridinium chloride (CPC) and KCl were used as received from Merk A. G. without further purification. The organic additives (methanol, ethanol, and propanol) were received from Merk A. G. and distilled before use. 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 critical micelle concentration (CMC) values of CPC in alcohol-slat-water mixtures were determined by the UV spectroscopy method. Optical densities of about 12 sample concentrations of CPC were read from the digital display at 271 nm with a double-beam Shimadzu Model 265 spectrophotometer. The solutions in the cell compartment were thermostated at 25°C for about 15 minutes before the measurements were started.

Results and Discussion

The Effect on CMC. The CMC values of CPC in seve-

Table 1. CMC×10⁴ Values of CPC in Methanol-Water Mixtures with Adding KCl at 25℃

[KCl]×10³/M	[CH₃OH]/M				
	0.0	0.1	0.3	0.5	0.7
0.00	9.845	10.393	10.944	11.558	12.491
2.00	4.828	5.125	5.434	5.712	6.084
4.00	3.154	3.412	3.930	4.267	4.429
6.00	1.957	2.161	2.381	2.644	3.015
8.00	1.722	1.848	1.994	2.201	2.427

Table 2. CMC×10⁴ Values of CPC in Ethanol-Water Mixtures with Adding KCl at 25℃

[KCl]×10³/M	[CH₃CH₂OH]/M				
	0.0	0.1	0.3	0.5	0.7
0.00	9.845	10.024	10.239	10.499	10.648
2.00	4.828	4.893	44.976	5.049	5.124
4.00	3.154	3.193	3.267	3.356	3.451
6.00	1.957	1.966	2.199	2.174	2.204
8.00	1.722	1.734	1.741	1.751	1.768

Table 3. CMC×10⁴ Values of CPC in Propanol-Water Mixtures with Adding KCl at 25℃

[KCl]×10³/M	[CH₃CH₂CH₂OH]/M				
	0.0	0.1	0.3	0.5	0.7
0.00	9.845	8.821	7.902	7.043	6.142
2.00	4.828	4.411	4.023	3.631	3.268
4.00	3.154	2.660	2.109	1.802	1.526
6.00	1.957	1.618	1.309	0.933	0.447
8.00	1.722	1.312	0.824	0.409	0.132

Figure 1. The relation between ln CMC of cetylpyridinium chloride and concentration of added alcohols in pure water at 25℃.

ral alcohol-salt (KCl)-water mixtures were determined from sharp breaks in the plots of the absorbance data at 271 nm *vs.* the concentration of CPC. The results are shown in Table 1, 2 and 3. As shown in these tables, the CMC of CPC in aqueous alcohol solutions is decreased with increasing salt (KCl) concentration. And the CMC of CPC in aqueous KCl solutins is increased with increasing methanol and ethanol concentration, while it is decreased with increasing propanol concentration.

As the added salt concentration is increased, the electrostatic repulsive force between ionic head groups of he surfactant molecules is reduced by the shielding of micelle charge, so that spherical micelles are more closely packed by surfactant ions[13]. And the increase of the added salt concentration would cause charged micelles to dehydrate by the salting-out effect[14]. It is, therefore, expected that the CMC of CPC should be decreased with the increase in the concentration of KCl added.

In Fugure 1, the CMC of CPC in pure water is shown as a function of added alcohol concentrations. Methanol and ethanol show a CMC-increasing effect, and n-propanol shows a CMC-decreasing effect.

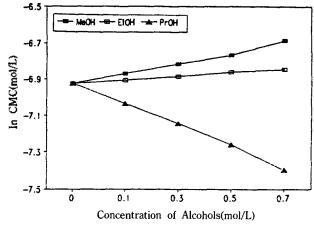It is well known that all substances containing hydrophobic

moieties decrease the CMC of surfactants[15]. This decrease can be explained only by the incorporation of the added substances into the micelle. In fact, from the detailed literature survey on the effect of organic additives, particularly alcohols and other related substances, which markedly influence the hydrophobic effect and the micelle formation, it seems that there exist two different views regarding the effect of additives on micelle formation. The first view deals with the solubilization of organic additives in micelle, and the second is that they have direct effect on the water structure. Therefore, the CMC-decreasing effect of n-propanol as shown in Figure 1 is attributable to the solubilization of n-propanol into the palisade layer of the micelle (which contains water, ionic head groups, and some counterions in addition to the first two or three methylene groups of the surfactant alkyl chain). On the other hand, the CMC-increasing effect of methanol and ethanol may be due to the increasing solvent power of these alcohol-water mixtures, if we neglect the solubilization of alcohols into the palisade layer of the micelle. Hence it is reasonable to expect that methanol and ethanol would be a kind of denaturating agents, *viz.*, hydrophobic bond breakers as is shown in the effect of urea on the micellization of surfactant[16].

The Effect on β. In order to elucidate more clearly the effect of methanol, ethanol and propanol on the micellization of CPC, the ratio (β) of the number of counterion to that of surfactant ion in micelles in methanol-, ethanol-, and propanol-water mixtures are compared. As shown in Table 1, 2 and 3, the CMC of the surfactant CPC in alcohol-water mixtures is decreased with increasing KCl concentration. Therefore, it is thought that the CMC-decrease with increasing salt concentration follows the Shinoda equation[17] which can represent the total counterion binding to the micelles at the CMC, *i.e.*,

$$\log \text{CMC} = A - \beta \log (\text{CMC} + [\text{KCl}]) \qquad (1)$$

where β represents the ratio of the number of counterion to that of surfactant ion (cetylpyridinium cation) in micelles, and is determined from the slope of plots of log CMC against log (CMC+[KCl]). The results of plots of log CMC *vs.* log (CMC+[KCl]) are listed in Table 4.

As shown in Table 4, for micelles of CPC in pure water

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Table 4. Linear Regression Analysis of CMC Decrease of CPC with Increasing KCl Concentration in Aqueous Alcohol Solutions at 25℃

Alcohols	A	β	r²
0.0	−5.3205	0.7694	0.9999
0.1 M MeOH	−5.4791	0.8385	0.9995
0.1 M EtOH	−5.5058	0.8383	0.9991
0.1 M PrOH		much decrease	

A : intercept. β : the ratio of the number of counterion to that of surfactant ion in micelles. r² : determination coefficient.

at 25℃, the ratio β is *ca.* 0.77. And β of CPC in methanol- and ethanol-water mixtures is a little higher than β in pure water. In the case of propanol-water mixture, on the other hand, it may be expected to be much decreased. This result on propanol may be explained by saying that the β-decrease effect as well as CMC-decrease effect of propanol is due to the partial solubilization of propanol into micelles and corporation with hydrophobic chain of micelles.

If we assume that the alcohol solubilization site is essentially the palisade layer, we may expect the two effects of propanol on miceller properties. The first effect is a steric effect: the propanol molecules solubilized between surfactant ions (cetylpyridinium cations) increase the average distance between surfactant ionic head groups for steric reasons. This effect results in the decrease of micelle charge density and the increase of micelle ionization degree, that is, in the decrease of counterion binding to micelles. The second effect is the decrease of the dielectric constant of the palisade layer of micelle. Upon the addition of propanol, some water in the palisade layer is probably replaced by propanol added, which should result in the decrease of dielectric constant. R. Zana *et al.*[18] have already checked this prediction by studying the fluorescence emission of monomeric pyrene solubilized in micelles. The decrease of dielectric constant of the palisade layer increases electrostatic repulsive force between ionic head groups which prevents surfactants molecules from associating. The increase of this repulsive force results in a destabilization of the micelle and the dissociation of a certain number of surfactant ions so that the repulsive forces may be reduced and propanol molecules replace some surfactant ions of the micelles, forming the mixed micelles. And then the charge density of micelle surface is thought to be decreased. In fact, it is well known that the decrease of surface charge density is reflected in an increased micelle ionization[19], where the increased micelle ionization means that the degree (β) of counterion binding to micelles is decreased. Therefore, β of CPC in propanol-water mixture is thought to be much decreased. In fact, the Shinoda equation could not be applied in determining the β value of CPC in propanol-water mixture because propanol is anticipated to be solubilized into micelles. But from the above discussion, β of CPC in propanol-water mixture is expected to be much decreased.

On the contrary, the β-increase effect as well as CMC-in-

crease effect of methanol and ethanol may be explained by saying that methanol and ethanol behave as cosolvent with water. Methanol and ethanol may reduce the hydration of micelle surface through the hydrogen bonding with water hydrated to micelle surface, and increase the repulsive force between ionic head groups because of the increase of the charge density of micelle surfaces. Therefore, it is expected that the ratio of counterion binding to micelles in methanol- and ethanol-water mixtures should be higher than in pure water.

Conclusion

In this paper, we studied the effects of short chain alcohols (methanol, ethanol and propanol) on the critical micelle concentration (CMC) and the degree (β) of counterion binding to the micelles of CPC. And then, we concluded that the β-increase effect as well as the CMC-increase effect of methanol and ethanol may be due to the increase of cosolvent power of these alcohol-water mixtures through the hydrogen bonding with water, while the β-decrease effect as well as the CMC-decrease effect of propanol is probably due to the partial solubilization of propanol molecules in micelles.

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