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Electrochemical Study of the Micellization of Hexadecylpyridinium Bromide in Binary Methanol–Water Mixtures

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A membrane electrode selective to hexadecylpyridinum bromide was used to study the micellization of the surfactant in various methanol–water mixtures at 25 °C. There is a linear relationship between log cmc and the weight percent of methanol in solvent mixtures. The degree of counter-ion dissociation at different solvent compositions is reported. The degree of methanol attachment was found to be 2.04. The charged phase-separation model was used to express the mechanism of the mixed micelle formation.

It is well known that the existence of nonelectrolytes in solutions of anionic or cationic surfactants significantly influence their micellization properties.[1,2] In recent years, considerable attention has been focused on studies of surfactant solutions in nonaqueous and mixed solvents in order to reach a better understanding of their relative behavior in different solvents.[3—6] Among a wide variety of methods used in such investigations, the extensive use of surfactant ion selective electrodes to study different equilibria involving ionic surfactants has been reported recently.[5—10]

In this paper we report on the use of an electrode that is selective to the hexadecylpyridinum ion in order to study its micellization in different methanol–water mixtures. Methanol was used as a nonelectrolyte, since it is not only a good solvent for hexadecylpyridinum bromide, but also mixes with water in all proportions. From electromotive force (emf) measurements, the degree of counter-ion dissociation, the degree of nonelectrolyte attachment and the mechanism of micelle formation are discussed.

Experimental

Doubly distilled deionized water was used throughout. Hexadecylpyridinum bromide (HDPB, BDH) was recrystallized four times from water and dried under vacuum over P_2O_5. Reagent-grade sodium bromide and methanol (both from Merck) were used without any further purification.

The hexadecylpyridinum ion-selective electrode was constructed using the same procedure as described before.[5] The membrane comprised a specially conditioned polyvinyl chloride (PVC) and a commercially available plasticizer. The PVC used in this work contained negatively charged groups which were neutralized by hexadecylpyridinum cation before use. All of the surfactant solutions were made up in a constant amount of sodium bromide (i.e. 1.0×10^{-5} mol dm^{-3}), and the emf of the surfactant was measured relative to a standard sodium electrode (Orion 4811). The monomer surfactant activities in various methanol–water mixtures were obtained from emf measurements from the cell I:

hexadecylpyridinum bromide electrode	test solution containing a constant amount of sodium bromide	electrode reversible to sodium ion	(I)

In order to obtain information about the counter-ion binding, simoultaneous emf measurements of the sodium electrode relative to a bromide-selective electrode (Orion 94-35) were also carried out using cell II:

electrode reversible to sodium ion	test solution containing a constant amount of sodium bromide	electrode reversible to bromide ion	(II)

All of the experiments were carried out at 25.0±0.1 °C by circulating thermostated water through a jacketted glass cell, while the sample solution was continuously stirred using an air-driven magnetic stirrer. All of the emf measurements were carried out inside a Farady cage in order to minimize the instrumental noise.

The emf measurements of the surfactant-selective electrode relative to the sodium electrode were used to evaluate the monomer surfactant concentration, considering the fact that the surfactant and sodium cations were both univalent and the activity coefficients of the surfactant monomer and its co-ions were expected to be approximately equal. Since the sodium ion concentration was constant, the emf of cell I is given by

$$\mathrm{emf}_1 = E_1^\circ + \frac{2.303RT}{F}\log m_1, \qquad (1)$$

where E_1° is a constant and m_1 is the monomer surfactant concentration. Figure 1 shows plots of the resulting emf_1 data vs. $\log C_1$ (total surfactant concentration) for different methanol–water mixtures. The emf of a bromide-selective electrode relative to a sodium electrode from cell II is given by

$$\mathrm{emf}_2 = E_2^\circ + 2\frac{2.303RT}{F}\log(\gamma_\pm m_2^{\frac{1}{2}}), \qquad (2)$$

where E_2° is a constant, $\gamma_\pm$ is the mean activity coefficient and m_2 is the concentration of free bromide ion. Figure 2 shows plots of the resulting emf_2 data vs. $\log(C_2^{\frac{1}{2}})$ for different methanol–water mixtures. In the plots, C_1 is the total surfactant concentration and C_2 is the total concentration of the bromide ion ($C_2 = C_1 + s$), where s is the concentration of added sodium bromide.

Results and Discussion

The resulting emf_1 vs. $\log C_1$ plots shown in Fig. 1 clearly indicate that at low concentration of the surfactant the emf_1 is directly proportional to $\log C_1$ with the Nerstian slopes within an acceptable range of 56—60 mV in different methanol–water mixtures. At higher concentrations of the surfactant, however, the plots show a distinct break at the concentration values characteristic of a critical micellar concentration (cmc).

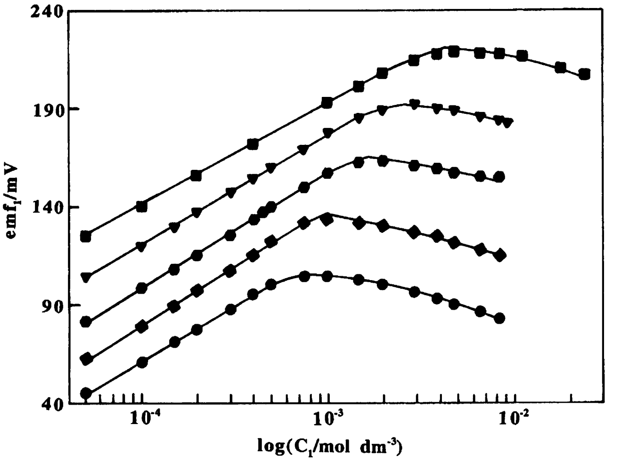

Fig. 1. Plot of emf_1 vs. $\log C_1$ for hexadecylpyridinium bromide in different methanol–water mixtures at 25 °C using Na^+ reference electrode. vol% MeOH: (●) 0, (◆) 10, (●) 20, (▼) 30, (■) 40.

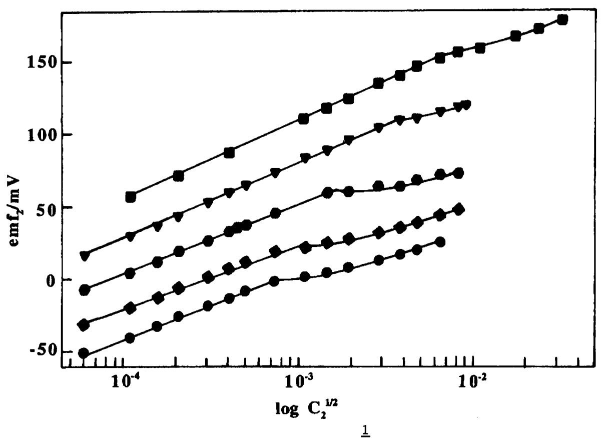

Fig. 2. Plot of emf_2 vs. $\log C_2^{\frac{1}{2}}$ for hexadecylpyridinium bromide and sodium bromide in different methanol–water mixtures at 25 °C using Br^- reference electrode. vol% MeOH: (●) 0, (◆) 10, (●) 20, (▼) 30, (■) 40.

From the emf plots shown in Fig. 2, it can be seen that along with an increase in the logarithmic concentration of hexadecylpyridinum bromide emf_2 increased linearly with a Nerstian slope to the cmc, and through a plateau region increased in all methanol–water mixtures. All of the determined cmc values are listed in Table 1.

The degree of counter ion dissociation (α) was evaluated from an approximation method introduced by Hall.[11] Based on a theoretical consideration of the thermodynamics of the micelle formation in ionic surfactants, he has suggested that when the micelles are present in solution in sufficiently large aggregation numbers, it would be acceptable to use Eq. 3 as a good approximation to evaluate the values,

$$\log m_1\gamma_\pm = \log K_i - (1-\alpha)\log m_2\gamma_\pm, \qquad (3)$$

where K_i is a constant. Thus, the first step in the calculation of the α values is to evaluate the m_2 and $\gamma_\pm$ values, which was done by an iterative method, as follows. The starting point is to estimate m_1 close to the cmc in the intermicellar region.[12] At the same surfactant concentration m_2 is then estimated from Eq. 2 by assuming $\gamma_\pm = 1$. Once an estimate of m_2 is obtained, $\gamma_\pm$ can be evaluated from the Debye–Hückel equation in the form

$$\log\gamma_\pm = \frac{-AI^{\frac{1}{2}}}{1+I^{\frac{1}{2}}}, \qquad (4)$$

where A is a constant. The A value for each methanol–water mixture was determined from the corresponding dielectric constant shown in Table 1.[13] The ionic strength is defined as

$$I = 1/2(m_1 + m_2 + s). \qquad (5)$$

In this calculation the concentration of the micelle is neglected. Substitution of the new $\gamma_\pm$ in Eq. 2 leads to a

Table 1. The Calculated Values of cmc, α, and K_i or Hexadecylpyridinium Bromide in Different Methanol–Water Solution at 25 °C

Solvent composition		Dielectric[a]	cmc	α	$-\log K_i$
vol% MeOH	wt% MeOH	constant	mol dm^{-3}		
0	0	78.9	7.8×10^{-4}	0.22	—
10	8.0	75.3	1.1×10^{-3}	0.37	−4.97
20	16.5	71.4	1.8×10^{-3}	0.42	−4.52
30	25.5	67.4	2.8×10^{-3}	0.43	−4.24
40	34.5	63.2	4.5×10^{-3}	0.44	−3.85

a) Data from Ref. 13.

new estimate of m_2, which, in turn, results in a new estimate of $\gamma_\pm$ via Eq. 4. This cycle is then repeated until $\gamma_\pm$ and m_2 converge. Using the final values obtained for m_2 and $\gamma_\pm$, linear plots of $\log m_1\gamma_\pm$ vs. $\log m_2\gamma_\pm$ were constructed (Fig. 3) and the values for different solvent mixtures were estimated from the slopes of the linear graphs. The resulting α and K_i values obtained from the slopes and intercepts of the graphs, respectively, are also included in Table 1.

The relationships between log cmc and the weight percent of methanol (W_MeOH) in the mixed solvents is shown in Fig. 4. The variation of the dielectric constant (ε) of the solvent mixtures with W_MeOH are also included in Fig. 4 for a comparison. As can be seen, log cmc increases linearly with increasing weight percent of methanol in the solvent mixture. The same kind of linear variation has been reported before.[4,6] It is interesting to note that, at the same time, the dielectric constant of the solvent mixture also decreases linearly with increasing weight percent of methanol.

It is well known, however, that addition of organic additives, such as methanol, at relatively high concentrations to aqueous surfactant solutions may affect the cmc of the resulting micelle in two opposite ways. On one hand, the energy requirements of bringing the hydrophobic tail into solution could decrease, which would result in an increase in cmc. On the other hand, the added organic solvent would result in a significant decrease in the dielectric constant of the solvent mixture, leading to a decrease in the cmc of ionic surfactants due to their lower solubility and reduced repulsion between adjacent head groups at the micellar surface. From the results obtained in this study, it can then be concluded that the change in the dielectric constant of water upon the addition of methanol is the predominant factor contributing to the observed solvent effect on the cmc of hexadecylpyridinum bromide.

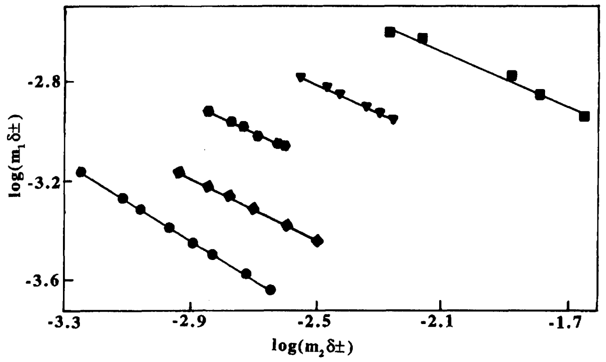

Fig. 3. Plot of $\log m_1\gamma_\pm$ vs. $\log m_2\gamma_\pm$ in different methanol–water mixtures at 25 °C. vol% MeOH: (●) 0, (◆) 10, (●) 20, (▼) 30, (■) 40.

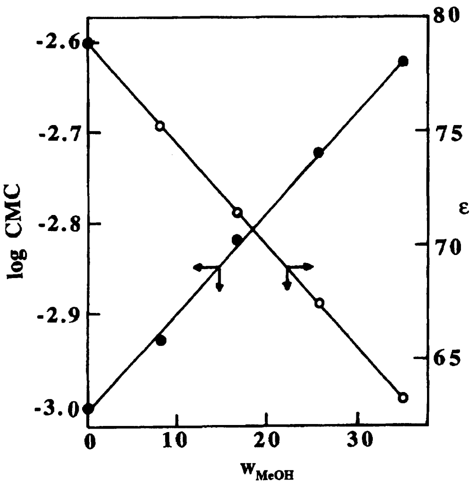

Fig. 4. Plots of log cmc (●) and ε (O) vs. weight percent methanol in the solvent mixtures.

The well known charged phase-separation model[3,14] has been used as a successful model in describing the micelle formation mechanism and counter-ion attachment in solution. According to this model, in aqueous solution,

$$n\mathrm{HDP}^+ + m\mathrm{Br}^- = \mathrm{HDP}_n\mathrm{Br}_m{}^{(n-m)+}, \qquad (6)$$

where a micelle consists of n hexadecylpyridinium and m bromide ions. Thus,

$$n\log a_\mathrm{HDP} + m\log a_\mathrm{Br} = \text{constant}. \qquad (7)$$

On the other hand, in methanol–water mixtures, because of the involvement of penetrated methanol molecules in the micelle structure, the formation of a mixed micelle according to the charged phase-separation model can be expressed as

$$n\mathrm{HDP}^+ + m\mathrm{Br}^- + p\mathrm{MeOH} = \mathrm{HDP}_n\mathrm{Br}_m\mathrm{MeOH}_p{}^{(n-m)+}. \qquad (8)$$

with

$$n\log a_\mathrm{HDP} + m\log a_\mathrm{Br} + p\log a_\mathrm{MeOH} = \text{constant}. \qquad (9)$$

Equation 9 can be written in the form

$$\log a_\mathrm{HDP} = \frac{\text{constant}}{n} - \frac{p}{n}\log a_\mathrm{MeOH} - \frac{m}{n}\log a_\mathrm{Br}. \qquad (10)$$

Since in each series of the experiments the activity of methanol (a_MeOH) is kept constant, Eq. 10 is equivalent to Eq. 3 with

$$\log K_i = \frac{\text{constant}}{n} - \frac{p}{n}\log a_\mathrm{MeOH} \qquad (11)$$

and

$$m/n = (1-\alpha). \qquad (12)$$

It should be noted that the decrease in the methanol activity due to the mixed micelle formation can be neglected, because the concentration of methanol is much larger than that of HDPB (at least 4×10^2 times).

According to Eq. 11, the variation of $\log K_i$ with $\log a_\mathrm{MeOH}$ (or $\log C_\mathrm{MeOH}$) should give a stright line, from the slope of which the degree of methanol attachment (p/n) can be obtained. Figure 5 shows that the $\log K_i$ vs. $\log C_\mathrm{MeOH}$ plot is collinear in the methanol

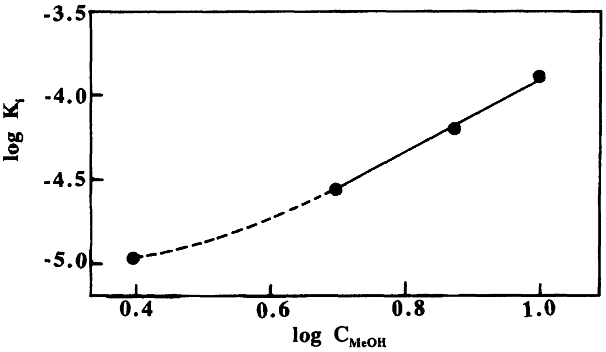

Fig. 5. Plot of log K_i vs. log C_{MeOH} in the solvent mixtures.

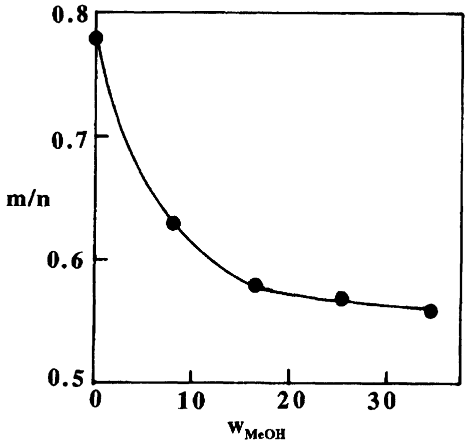

Fig. 6. Plot of the degree of counter ion attachment vs. weight percent methanol in the solvent mixtures.

vol% range of 20—40 with a slope of 2.04, indicating that for each surfactant cation (HDP^+) two methanol molecules participate in the structure of the resulting micelle. However, it should be noted that, at methanol concentrations lower than 20% (vol%), the resulting plot (Fig. 5) is no longer collinear, emphasizing that the equilibrium 8 might not hold at such methanol contents of the solvent mixture.

The degree of counter-ion attachment (m/n) obtained from Eq. 12 is then equal to 0.78 for an aqueous solution, 0.63 for 10 vol%, 0.57 for 30 vol%, and 0.56 for 40 vol% methanol. The variation in the degree of counter-ion attachment with the weight percent of methanol in the solvent mixture is shown in Fig. 6. As can be seen, the m/n value decreases sharply with W_{MeOH} up to about 15 vol%, and then tends to level off gradually. This behavior could be explained by the penetration of methanol into the HDPB micelle, which results in decrease in the charge density on the micelle surface and in the micelle size.[3] It is interesting to note that the observed constancy in the degree of methanol attachment at a methanol composition range of 20—40 vol% is in agreement with the nearly constant values calculated for the degree of counter-ion attachment at these methanol compositions.

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