Electrochemical Study of the Thermodynamics of Micellization of Hexadecylpyridinium Bromide

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A membrane electrode selective for hexadecylpyridinum bromide was used to study the micellization of the surfactant at various temperatures (25—50 °C). The thermodynamic parameters ΔH°_m and ΔS°_m were calculated from the temperature dependence of the equilibrium constants for micellization of the surfactant. It was clearly shown that the entropy of micellization obtained by the usual approximate method from $\Delta G^\circ_m = (2-\alpha)RT\ln X_{cmc}$ is much more positive than the corresponding exact value calculated from direct activity measurements.

It is known that the critical micelle concentration (cmc) of ionic surfactants is very sensitive to temperature changes.[1—5] The cmc of many ionic surfactants passes through a minimum around 20—30 °C. The decreased cmc with temperature increase at lower temperatures could be related to dehydration of the monomers' head groups, while further temperature increase disrupt the structured water molecules around the hydrophobic tails of surfactants, creating opposition to micellization.

By application of the phase-separation model[6] to ionic surfactants, the free energy change, ΔG°_m, can be derived from the cmc value. The measurement of the variation of cmc with temperature enables ΔG°_m to be split into the ΔH°_m and ΔS°_m, very useful parameters in understanding micelle formation.[7]

In this paper, we report the use of a membrane electrode selective for hexadecylpyridinum bromide to study the micellization of the surfactant at various temperatures (25—55 °C). These electrodes measure the activity of surfactant monomers directly and thus provide information that is difficult to obtain in other ways.

Experimental

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

The hexadecylpyridinum ion-selective electrode was constructed using the procedure described before.[8] The membrane was made of a specially conditioned polyvinyl chloride (PVC) and a commertially available plasticizer. The PVC used in this work contains negatively charged groups that are neutralized by HDP^+ ion before use. All 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 electrode was measured relative to a standard sodium electrode (Orion 4811). The monomer surfactant activities at various temperatures were obtained from emf measurements from cell I:

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

To obtain information about the counter ion binding, simultaneous emf measurements of the sodium electrode relative to a bromide-selective electrode (Orion 94-35) were also done using cell II:

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

During the emf measurements, the temperature was maintained at the desired value ±0.1 °C by circulating thermostatted water through the jacketted glass cell used, while the sample solution was continuously stirred using an air-driven magnetic stirrer. All the emf measurements were done inside a Faraday cage, to minimize instrumental noises.

The emf measurements of the surfactant selective electrode relative to the standard sodium electrode were used to evaluate the monomer surfactant concentration, considering the fact that the HDP^+ and Na^+ ions are both univalent, and also the activity coefficients of the surfactant monomer and its counter anion are expected to be approximately equal. Since the sodium ion concentration is constant, the emf of cell I is given by

$$\mathrm{emf_I} = E^\circ{}_\mathrm{I} + \frac{2.303RT}{F}\log m_\mathrm{I}, \tag{1}$$

where $E^\circ{}_\mathrm{I}$ is a constant and m_I is the monomer surfactant concentration. Figure 1 shows the plots of the resulting $\mathrm{emf_I}$ data vs. $\log C_\mathrm{I}$ (total surfactant concentration) at various temperatures.

The emf of bromide selective electrode relative to the sodium standard electrode from cell II is given by

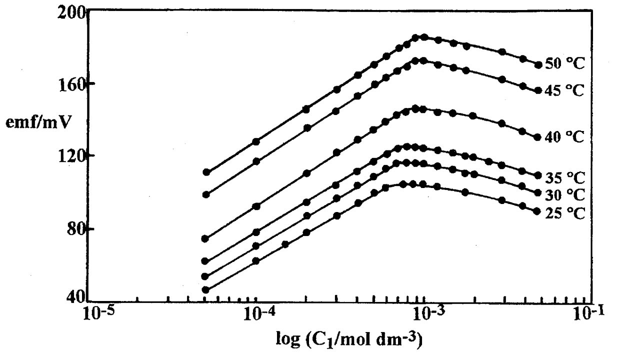

Fig. 1. Plot of emf vs. log C_1 for hexadecylpyridium bromide at various temperatures using Na^+ reference electrode.

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

where $E^\circ{}_2$ is a constant, $\gamma_\pm$ is the mean activity coefficient, and m_2 is the concentration of free bromide ion in the micellar region. Figure 2 shows the plots of the resulting emf_2 data vs. $\log C_2^{1/2}$ at various temperatures. In these plots C_2 is the total concentration of bromide ion($=C_1+s$) where s is the concentration of added sodium bromide.

To evaluate m_2 and $\gamma_\pm$ in the micellar region, the following iterative procedure was done. First, by assuming $\gamma_\pm=1$ in Eq. 2, an initial estimate of m_2 is obtained. Using the estimated value of m_2, the $\gamma_\pm$ can be evaluated from Eq. 3

$$\log\gamma_\pm = \frac{-A\sqrt{I}}{1+\sqrt{I}}, \qquad (3)$$

where the ionic strength I is defined as

$$I = 1/2(m_1+m_2+s), \qquad (4)$$

and A is the Debye–Hückel constant at the corresponding temperature. Once $\gamma_\pm$ is obtained, it is used in Eq. 2 and a new value of m_2 is evaluated, which in turn results in a new estimate of $\gamma_\pm$ via Eq. 3. This procedure is then repeated until $\gamma_\pm$ and m_2 converge.

Results and Discussion

The emf_1 vs. $\log C_1$ plots shown in Fig. 1 clearly indicate that, at low concentration of HDPB, emf_1 is directly proportional to $\log C_1$ with the Nerstian slopes within the acceptable range 57—60 mV at the different temperatures studied. However, at higher concentrations of the surfactant, the resulting plots show a distinct break at the concentration value characteristic of a critical micelle concentration (cmc).

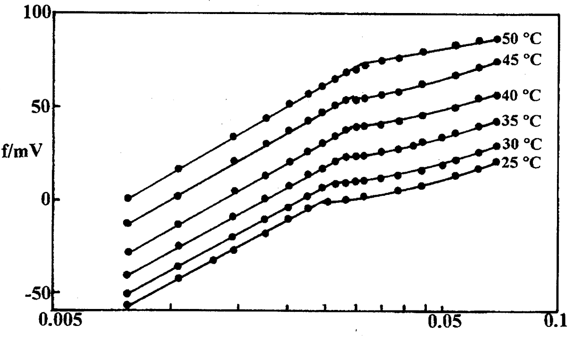

Fig. 2. Plot of emf vs. log C_2 for hexadecylpyridinium bromide at various temperatures using Br^- reference electrode.

From the emf plots shown in Fig. 2 it is seen that, with an increase in logarithmic concentration of the surfactant, emf_2 increased linearly with a Nernstian slope to the cmc, and through a plateau region increased at all temperatures studied. All of the cmc values calculated are listed in Table 1.

As can be seen, in the temperature range studied, the cmc of HDPB increases almost linearly with temperature. An increase in temperature may have two opposite effects on the tendency of ionic surfactants toward micelle formation. On one hand, the head group hydration is reduced with increasing temperature, which favors micelle formation. On the other hand, because of the diminished interactions among isolated water molecules at higher temperatures, there will be an increase in the solubility of the surfactant tail in water, resulting in an opposition to micelle formation. The observed trend in the cmc of HDPB shows the predominance of the second parameter in the temperature range studied.

To evaluate the thermodynamic parameters for the micellization of the surfactant, it is necessary to define the standard states. For the free surfactant, the hypothetical standard state is taken as unit activity. For the micelled surfactant, the micellar state itself is considered as the standard state. Since the free surfactants in solution and surfactants in the micellar phase, with respective chemical potentials of μ_s, and μ_m, are in equilibrium, then

$$\mu_s = \mu_m, \qquad (5)$$

with

$$\mu_s = \mu^\circ{}_s + RT\ln a_s, \qquad (6)$$

and

$$\mu_m = \mu^\circ{}_m, \qquad (7)$$

Thus, at equilibrium

$$\mu^\circ{}_s + RT\ln a_s = \mu^\circ{}_m, \qquad (8)$$

and

$$\Delta G^\circ{}_m = \mu^\circ{}_m - \mu^\circ{}_s = RT\ln a_s. \qquad (9)$$

Based on the phase separation model,[6] in the case of ionic surfactants, for the calculation of $\Delta G^\circ{}_m$ it is necessary to consider not only the transfer of surfactant molecules but also the transfer of $(1-\alpha)$ moles of counter ion, where α is the degree of counter ion dissociation. Thus

Table 1. The Calculated Values of cmc, α, K/n, and $(2-\alpha)\log \mathrm{cmc}/w$ for Hexadecylpyridinium Bromide at Various Temperatures

Temperature °C	cmc mol dm^{-3}	α	$-\log K/n$	$(2-\alpha)\log\mathrm{cmc}/w$
25.0	7.8×10^{-4}	0.22	−5.70	−8.63
30.0	8.4×10^{-4}	0.22	−5.62	−8.55
35.0	8.9×10^{-4}	0.23	−5.52	−8.48
40.0	9.2×10^{-4}	0.24	−5.43	−8.41
45.0	9.6×10^{-4}	0.25	−5.39	−8.33
50.0	1.0×10^{-3}	0.27	−5.26	−8.18

$$\Delta G^\circ{}_\mathrm{m} = RT\ln a_\mathrm{s} + (1-\alpha)RT\ln a_\mathrm{Br}, \qquad (10)$$

or

$$\log a_\mathrm{s} = \frac{\Delta G^\circ{}_\mathrm{m}}{2.303RT} - (1-\alpha)\log a_\mathrm{Br}. \qquad (11)$$

In Eq. 11, $\Delta G^\circ{}_\mathrm{m}/2.303RT$ can be replaced by $-\log(K/n)$,[9,10] where K is the equilibrium constant for the process of micelle formation and n is the aggregation number of micelles, i.e.

$$\log a_\mathrm{s} = -\log(K/n) - (1-\alpha)\log a_\mathrm{Br}. \qquad (12)$$

According to Eq. 12, a plot of $\log a_\mathrm{s}$ vs. $\log a_\mathrm{Br}$ is expected to result in a straight line from the slope and intercept of which $(1-\alpha)$ and $\log K/n$ can be evaluated, respectively. The resulting linear plots at various temperatures are shown in Fig. 3 and the corresponding α and $\log K/n$ values are given in Table 1. As can be seen, the K/n value decreases with increasing temperature, indicating the occurrence of an exothermic micellization process. On the other hand, the α value increases slightly with temperature, emphasizing the increased tendency of bromide counter ion dissociation at elevated temperature.[11]

The changes in enthalpy and entropy of the micellization reaction were obtained by plotting $\log K/n$ vs. $1/T$ (Fig. 4A) according to Eq. 13

$$-\log K/n = -\frac{\Delta S^\circ{}_\mathrm{m}}{2.303R} + \frac{\Delta H^\circ{}_\mathrm{m}}{2.303RT}. \qquad (13)$$

The thermodynamic parameters obtained from the slope and intercept of the resulting van't Hoff plot are $\Delta H^\circ{}_\mathrm{m} = -31.4\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ{}_\mathrm{m} = 3.9\ \mathrm{J\,mol^{-1}\,K^{-1}}$. The magnitude and sign of the $\Delta H^\circ{}_\mathrm{m}$ and $\Delta S^\circ{}_\mathrm{m}$ values are identifiable with destruction of hydrophobic hydration in the process of micelle formation.[5,7,11—16]

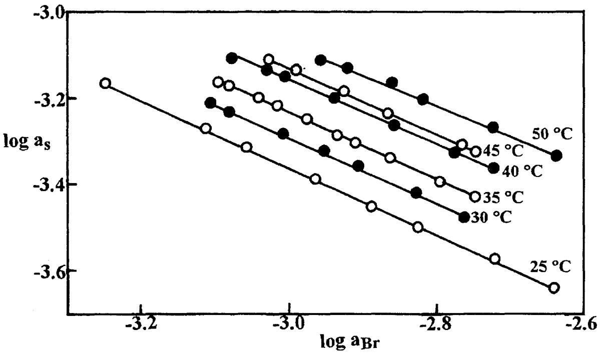

Fig. 3. Plot of $\log a_1$ vs. $\log a_2$ at various temperatures.

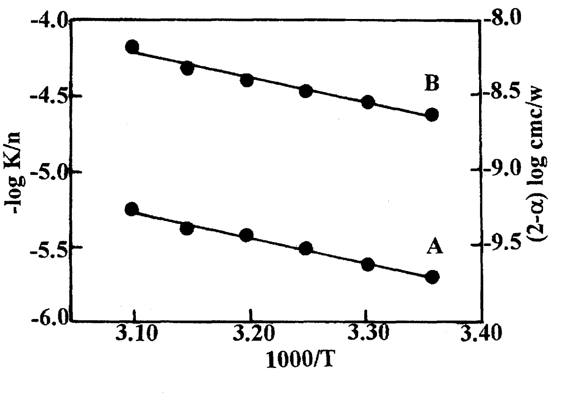

Fig. 4. Van't Hoff plots of $-\log K/n$ vs. $1/T$ (A) and $(2-\alpha)$ log cmc/w vs. $1/T$ (B).

It should be noted that, in most of the thermodynamic studies of the micellization of ionic surfactants,[5,11—16] the Gibbs free energy of micellization has been calculated using the equation

$$\Delta G^\circ{}_\mathrm{m} = (2-\alpha)RT\ln X_\mathrm{cmc}, \qquad (14)$$

and hence

$$(2-\alpha)\log X_\mathrm{cmc} = -\frac{\Delta S^\circ{}_\mathrm{m}}{2.303R} + \frac{\Delta H^\circ{}_\mathrm{m}}{2.303RT}. \qquad (15)$$

According to Eq. 15, a plot of $(2-\alpha)\log X_\mathrm{cmc}$ vs. $1/T$ will result in a straight line (Fig. 4B) from the slope and intercept of which $\Delta H^\circ{}_\mathrm{m}$ and $\Delta S^\circ{}_\mathrm{m}$ can be obtained, respectively. The thermodynamic parameters obtained by this method are $\Delta H^\circ{}_\mathrm{m} = -31.3\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ{}_\mathrm{m} = 60.6\ \mathrm{J\,mol^{-1}\,K^{-1}}$. It is obvious that while the enthalpies of micellization obtained by the two methods are very close to each other, the $\Delta S^\circ{}_\mathrm{m}$ value obtained by the latter method is much more positive than that obtained from direct activity measurements. However, in obtaining Eq. 14, two questionable assumptions have been made, first, that the concentration of counter ion in the presence of micelle is constant and equal to that of the free surfactant ion and, second, that the activity of the free surfactant ion, a_s, can be replaced by its mole fraction, X_cmc.

To account for such a large difference between the $\Delta S^\circ{}_\mathrm{m}$ values obtained by the two methods, the following corrections can be made: Eq. 11 is rearranged as

$$\frac{\Delta G^\circ{}_\mathrm{m}}{2.303RT} = \log a_\mathrm{s} + (1-\alpha)\log a_\mathrm{Br} = \log a_\mathrm{s} a_\mathrm{Br}^{(1-\alpha)}. \qquad (16)$$

If we assume

$$a = \beta X, \qquad (17)$$

where β and X are the activity coefficient and the mole fraction of the species involved, respectively, then

$$a_\mathrm{s} a_\mathrm{Br}^{(1-\alpha)} = \beta_\mathrm{s} X_\mathrm{s} \cdot \beta_\mathrm{Br}^{(1-\alpha)} X_\mathrm{Br}^{(1-\alpha)} = K' X_\mathrm{s} X_\mathrm{Br}^{(1-\alpha)}. \qquad (18)$$

By making the assumption of $X_\mathrm{s} = X_\mathrm{Br} = X_\mathrm{cmc}$, Eq. 18 is written as

$$a_\mathrm{s} a_\mathrm{Br}^{(1-\alpha)} = K' X_\mathrm{cmc}^{(2-\alpha)}, \qquad (19)$$

or

$$K' = \frac{a_\mathrm{s} a_\mathrm{Br}^{(1-\alpha)}}{X_\mathrm{cmc}^{(2-\alpha)}}, \qquad (20)$$

By using the values of a_s, a_Br, α, and X_cmc (=cmc/w, where w is the number of moles of water per liter at the corresponding temperature) obtained in different sets of experiments, the average value for $\log K'$ was evaluated as 2.91. Then, from Eqs. 16, 19, and 20

$$\begin{aligned}\Delta G^\circ{}_\mathrm{m} &= \Delta H^\circ{}_\mathrm{m} - T\Delta S^\circ{}_\mathrm{m} = 2.303RT\log a_\mathrm{s} a_\mathrm{Br}^{(1-\alpha)} \\ &= 2.303RT(2.91 + \log X_\mathrm{cmc}^{(2-\alpha)}) \end{aligned} \qquad (21)$$

By rearrangement

$$(2-\alpha)\log X_{\mathrm{cmc}} = -2.91 - \frac{\Delta S^{\circ}{}_{\mathrm{m}}}{2.303R} + \frac{\Delta H^{\circ}{}_{\mathrm{m}}}{2.303RT}. \qquad (22)$$

According to Eq. 22, the $\Delta H^{\circ}{}_{\mathrm{m}}$ and $\Delta S^{\circ}{}_{\mathrm{m}}$ values can be evaluated from the slope and intercept of the linear plot of $(2-\alpha)\log X_{\mathrm{cmc}}$ vs. $1/T$, respectively. The results showed that $\Delta H^{\circ}{}_{\mathrm{m}}$ remained unchanged (and equal to $-31.3\ \mathrm{kJ\,mol^{-1}}$), but the corrected $\Delta S^{\circ}{}_{\mathrm{m}}$ obtained is equal to $4.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$, which is very close to the value of $3.9\ \mathrm{J\,mol^{-1}\,K^{-1}}$ obtained from the direct activity measurements.

References

1) E. D. Goddard and G. C. Benson, *Can. J. Chem.*, **35**, 986 (1957).

2) D. Patterson and Barbe, *J. Phys. Chem.*, **80**, 2435 (1976).

3) K. Shinoda, *J. Phys. Chem.*, **81**, 130 (1977).

4) D. F. Evans and P. J. Wightman, *J. Colloid Interface Sci.*, **86**, 515 (1982).

5) K. Shinoda, M. Kobayashi, and N. Yamaguchi, *J. Phys. Chem.*, **91**, 5292 (1987).

6) M. Koshinuma and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **48**, 2755 (1975).

7) D. Myers, "Surfactant Science and Technology," VCH Publishers, Weinheim (1988).

8) D. M. Painter, D. M. Bloor, N. Takisawa, D. G. Hall, and E. Wyn-Jones, *J. Chem. Soc., Farady Trans. 1*, **84**, 2087 (1988).

9) D. G. Hall, *J. Chem. Soc., Faraday Trans. 1*, **77**, 1121 (1981).

10) N. Alizadeh, H. Gharibi, and M. Shamsipur, *Bull. Chem. Soc. Jpn.*, **68**, 730 (1995).

11) D. F. Evans, M. Allen, B. W. Ninham, and A. Fouda, *J. Solution Chem.*, **13**, 87 (1984).

12) P. Molyneux, C. T. Rhodes, and J. Swarbrick, *Trans. Faraday Soc.*, **61**, 1043 (1965).

13) J. H. Clint and T. Walker, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1946 (1975).

14) Z. Guoxi and Z. Buyao, *Acta Phys. Chim. Sin.*, **6**, 513 (1990).

15) A. Callaghan, R. Doyle, E. Alexander, and R. Palepu, *Langmuir*, **9**, 3422 (1993).

16) M. J. Rosen, "Surfactants and Interfacial Phenomena," Wiley, New York (1978).