

## Physicochemical studies of the hexadecylpyridinium bromide micellar system in the presence of various concentrations of sodium bromide using a surfactant-selective electrode

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A membrane electrode selective to hexadecylammonium bromide has been used to study the micellization of the surfactant in the presence of varying amounts of sodium bromide at 27°C. It is found that there is an inverse relationship between the amount of NaBr added and the critical micelle concentration and the degree of counter-ion dissociation of the system studied. The aggregation number of the micelles formed has been determined and found to increase with the concentration of NaBr added. Some evidence for the formation of dimer forms of the surfactant prior to the micelle formation is found at higher concentrations of the electrolyte.

The use of surfactant ion selective electrodes for the study of the micellization equilibria of ionic surfactants has received considerable attention recently<sup>1-11</sup>. Such electrodes provide a direct measure of the surfactant monomer activity alone and, hence, produce information that is difficult to obtain by other techniques. Since these electrodes exhibit a nearly Nernstian response, they may provide values of the surfactant activities above and below critical micelle concentration (CMC). When combined with counter ion selective electrodes, they can be used to characterize the unaggregated ions in micellar region.

Since the solubilizing power of surfactants depends on their state of aggregation<sup>12-14</sup> the knowledge of dependence of the micelle molecular weight (or aggregation number) on the concentration of electrolytes added is of both practical and theoretical importance<sup>15-18</sup>. It is well known that, in aqueous solution, the presence of electrolyte results in the decreased CMC of most surfactants, with the greatest effect being detected for ionic surfactants<sup>14</sup>.

We have recently studied the micellization of hexadecylpyridinium bromide (HDPB) in binary methanol-water mixtures<sup>11</sup> and in aqueous solution<sup>19</sup> using a membrane electrode selective to the surfactant. In this paper we report EMF measurements of aqueous solutions of HDPB in the presence of varying concentration of sodium bromide using electrodes selective to HDP<sup>+</sup>, Br<sup>-</sup> and Na<sup>+</sup> ions, in order

to study the effective degree of micelle dissociation, permicellar aggregation and the modes of surfactant aggregation. It should be noted that, to the best of our knowledge, this is the first report on the determination of micellar aggregation numbers by an electrochemical method.

### Materials and Methods

Doubly distilled deionized water was used throughout. Hexadecylpyridinium bromide (BDH) was recrystallized four times from water and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Reagent grade sodium bromide (Merck) was used without any further purification.

The hexadecylpyridinium (HDP<sup>+</sup>) cation-selective electrode was constructed by the same technique as described elsewhere<sup>20</sup>. The membrane consisted of a specially conditioned polyvinyl chloride (PVC) and a commercially available plasticizer. The PVC used in this study contained negatively charged groups which were neutralized by HDP<sup>+</sup> ion before use. During the experiments, the electromotive force (EMF) measurements were made relative to a stand-

Hexadecylpyridinium bromide electrode	Test solution containing a constant amount of sodium bromide	Electrode reversible to sodium ion
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(1)

Table 1 — The calculated values of CMC,  $\alpha$ , and  $n$  for hexadecylpyridinium bromide in the presence of varying concentrations of sodium bromide

$C_{\text{NaBr}}$ (mol dm <sup>-3</sup> )	$E_{\text{HDPB/Na}}$ (mV decade <sup>-1</sup> )	$E_{\text{HDPB/Br}}$ (mV decade <sup>-1</sup> )	CMC (Mol dm <sup>-3</sup> )	$\alpha$			$n$
				I	II	III	
$1.0 \times 10^{-5}$	57	110	$7.8 \times 10^{-4}$	0.22	-	0.22	-
$1.0 \times 10^{-4}$	59	111	$7.5 \times 10^{-4}$	0.19	0.17	-	-
$1.0 \times 10^{-3}$	55	94	$4.5 \times 10^{-4}$	0.15	0.14	-	-
$1.0 \times 10^{-2}$	46	82	$6.5 \times 10^{-5}$	-	0.05	-	74
$3.0 \times 10^{-2}$	40	88	$4.5 \times 10^{-5}$	-	-	-	86
$5.0 \times 10^{-2}$	41	85	$3.5 \times 10^{-5}$	-	-	-	94
$1.0 \times 10^{-1}$	40	70	$2.0 \times 10^{-5}$	-	-	-	104

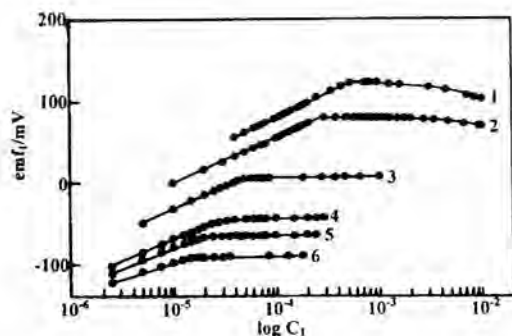


Fig. 1 — Plot of  $EMF_1$  vs  $\log C_1$  at various NaBr concentrations for the  $HDP^+/Na^+$  electrode system. Concentration of NaBr (mol dm<sup>-3</sup>) is: (1)  $1.0 \times 10^{-4}$ , (2)  $1.0 \times 10^{-3}$ , (3)  $1.0 \times 10^{-2}$ , (4)  $3.0 \times 10^{-2}$ , (5)  $5.0 \times 10^{-2}$ , (6)  $1.0 \times 10^{-1}$ .

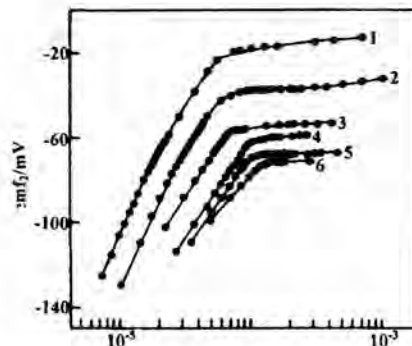


Fig. 2 — Plot of  $EMF_2$  vs.  $\log (C_1 C_2)^{1/2}$  at various NaBr concentrations for the  $HDP^+/Br^-$  electrode system. Concentration of NaBr (mol dm<sup>-3</sup>) is: (1)  $1.0 \times 10^{-4}$ , (2)  $1.0 \times 10^{-3}$ , (3)  $1.0 \times 10^{-2}$ , (4)  $3.0 \times 10^{-2}$ , (5)  $5.0 \times 10^{-2}$ , (6)  $1.0 \times 10^{-1}$ .

and sodium ion electrode (Orion 4811). The monomer surfactant activities in various solutions were obtained from EMF measurements from the cell.

All the solutions studied were prepared in constant amounts of sodium bromide so that the  $Na^+$  ion concentration in a given experiment was constant.

In order to obtain information about counter ion binding, simultaneous measurements using a bromide-selective electrode (Orion 94-35) were also carried out using cell (II)

Hexadecylpyridinium bromide electrode	Test solution containing a constant amount of sodium bromide	Electrode reversible to bromide ion.
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(II)

All the experiments were carried out at  $27.0 \pm 0.1^\circ C$  by circulating thermostated water through a jacketted glass cell, while the sample solu-

tion was continuously stirred using an air-driven magnetic stirrer. All the EMF measurements were carried out inside a Faraday 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 are both univalent and the activity coefficients of the surfactant monomer and its co-ions are expected to be approximately equal. Thus, in favourable cases, the ratio (surfactant monomer concentration)/(sodium ion concentration) is measured. Since during each series of experiments, the sodium ion concentration was kept constant, the EMF of cell (I) is given by

$$EMF_1 = E^\circ + \frac{2.303 RT}{F} \log m_1 \quad \dots(1)$$

where  $E^\circ$  is a constant and  $m_1$  is the monomer surfactant concentration. Fig. 1 shows plots of the

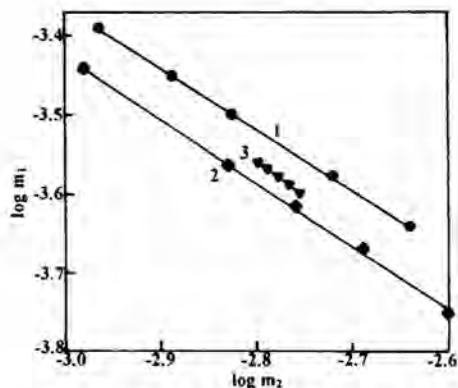


Fig.3 — Plot of  $\log m_1$  vs  $\log m_2$  at various NaBr concentrations: (1)  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , (2)  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , (3)  $1.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ .

resulting EMF data vs.  $\log$  total surfactant concentration,  $C_1$ , for a series of solutions containing different but constant amounts of sodium bromide.

The EMF of the surfactant selective electrode relative to a bromide-selective electrode from cell (II) is given by:

$$\text{EMF}_2 = E^\circ_2 + \frac{2 \times 2.303 RT}{F} \log (m_1 m_2)^{1/2} \gamma_{\pm} \quad \dots(2)$$

where  $E^\circ_2$  is constant,  $\gamma_{\pm}$  is the mean activity coefficient and  $m_2$  is the concentration of free bromide ion. Fig.2 shows plots of the resulting EMF data vs.  $\log (C_1 C_2)^{1/2}$  at various but constant concentrations of sodium bromide. In the plots  $C_2$  is the total concentration of bromide ion ( $=C_1+C_s$  where  $C_s$  is the concentration of sodium bromide added).

In order to evaluate the concentration of free surfactant,  $m_1$ , and free bromide ion,  $m_2$ , and their mean activity coefficient,  $\gamma_{\pm}$ , in the micellar region, the following iterative method was used<sup>6-9,11,19</sup>. The starting point is to estimate  $m_1$  close to the CMC in the intermicellar region. 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,

$$\log \gamma_{\pm} = \frac{-A I^{1/2}}{1 + I^{1/2}} \quad \dots(3)$$

where  $A$  is a constant. The ionic strength  $I$  is defined as

$$I = 1/2(m_1 + m_2 + C_s) \quad \dots(4)$$

In this calculation the concentration of the micelle is neglected. Substitution of the new  $\gamma_{\pm}$  in Eq.(2) leads to a new estimate of  $m_2$  which, in turn, results

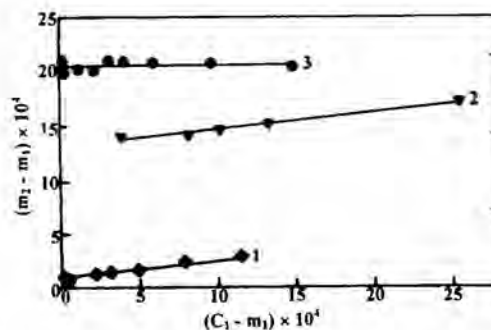


Fig.4 — Plot of  $(m_2 - m_1)$  vs.  $(C_1 - m_1)$  at various NaBr concentrations: (1)  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , (2)  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , (3)  $1.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ .

in a new estimate of  $\gamma_{\pm}$  via Eq.(3). This cycle is then repeated until  $\gamma_{\pm}$  and  $m_2$  converge.

## Results

The experimental data taken from cell(I) are shown in Fig.1, where the EMF of the surfactant electrode relative to the sodium reference electrode is plotted as a function of the logarithm of total surfactant concentration,  $C_1$ , for a series of solutions containing different but constant amounts of sodium bromide. As seen, at concentrations below the CMC, the surfactant is in monomeric form (i.e.,  $m_1$  and  $C_1$  are superimposed in this region) and the plots show a good linear response. While, the plots show a distinct break at the concentration values characteristic of a critical micelle concentration (CMC). Once micelles are formed, the monomer surfactant concentration,  $m_1$ , decreases with total surfactant concentration,  $C_1$  a characteristic behaviour of ionic surfactants<sup>6-11</sup>. All the determined CMC values are listed in Table 1.

The purpose of the EMF measurements in cell(II) to evaluate the free concentration of  $\text{Br}^-$  counter ion in the micellar region,  $m_2$  and the mean activity coefficient,  $\gamma_{\pm}$ , as pointed out before. The plots of  $\text{EMF}_2$  against the logarithm of mean concentration which is the product  $(C_1 C_2)^{1/2}$  are shown in Fig.2 for all solutions containing different but constant amounts of sodium bromide.

It is interesting to note that, although in Figs 1 and 2 the resulting breaks indicate the same point, there is some difference in evaluation of CMC from the two series of plots (i.e.  $\text{EMF}_1$  vs.  $\log C_1$  and  $\text{EMF}_2$  vs.  $\log (C_1 C_2)^{1/2}$ ). While the observed breaks in the plots of Fig.1 directly correspond to  $\log \text{CMC}$  values, the breaks of the plots of Fig.2 are observed at  $\log [(CMC)(CMC + C_s)]^{1/2}$ . Obviously, in the latter case,

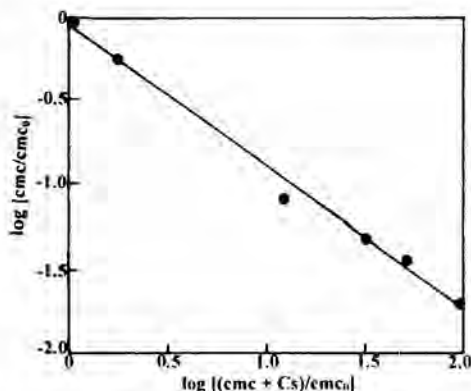


Fig. 5 — Plot of  $\log [(CMC)/(CMC_0)]$  vs.  $\log [(CMC + C_s)/CMC_0]$

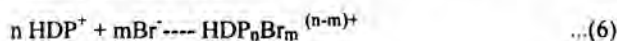
the concentration of added sodium bromide should be considered in the calculation of CMC values.

The degree of effective dissociation of the micelle,  $\alpha$ , was determined by three different methods as a function of added sodium bromide. First, the  $\alpha$  values were evaluated from the Hall's approximate method<sup>21</sup>. 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 (5) as a good approximation to evaluate the  $\alpha$  values,

$$\log m_1 \gamma_{\pm} = \log K_i - (1 - \alpha) \log m_2 \gamma_{\pm} \quad \dots(5)$$

where  $K_i$  is a constant. The  $\alpha$  values were obtained from the slopes of linear plots of  $\log m_1 \gamma_{\pm}$  vs  $\log m_2 \gamma_{\pm}$  (Fig.3).

In method two, the well known charged phase-separation model<sup>22,23</sup> was used to evaluate the  $\alpha$  values, as follows



where,

$$C_1 = m_1 + n [\text{micelle}] \quad \dots(7)$$

$$C_2 = m_2 + m [\text{micelle}] \quad \dots(8)$$

Combination of Eqs.(7) and (8) and rearrangement then results in,

$$\frac{m}{n} = 1 - \alpha = \frac{C_2 - m_2}{C_1 - m_1} \quad \dots(9)$$

or,

$$m_2 - m_1 = C_s + \alpha(C_1 - m_1) \quad \dots(10)$$

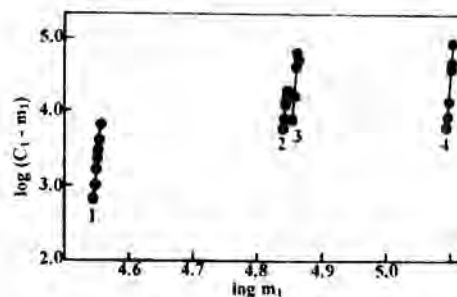


Fig. 6 — Plot of  $\log (C_1 - m_1)$  vs.  $\log m_1$  at various NaBr concentrations: (1)  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , (2)  $3.0 \times 10^{-2} \text{ Mol dm}^{-2}$ , (3)  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , (4)  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$

The  $\alpha$  values then were evaluated from the slopes of the linear plots of  $m_2 - m_1$  against  $C_1 - m_1$  (Fig.4).

In the third method, the  $\alpha$  values were evaluated using equation<sup>9,21</sup>,

$$\log \frac{CMC}{CMC_0} = -(1 - \alpha) \log \frac{CMC + C_s}{CMC_0} \quad \dots(11)$$

where  $CMC_0$  is the critical micelle concentration in the absence of NaBr and  $C_s$  is the salt concentration (Fig.5). All the calculated values of  $\alpha$  are also included in Table 1.

Based on the charged phase-separation model introduced for the micelle formation of ionic surfactants (Eq.(6))<sup>22,23</sup>, the equilibrium constant for the micellization of HDPB can be written as,

$$K = \frac{[\text{HDP}_n \text{Br}_m^{(n-m)+}] \gamma_m}{[\text{HDP}^+]^n [\text{Br}^-]^m \gamma_{\text{HDP}} \gamma_{\text{Br}}} \quad \dots(12)$$

or,

$$K K_{\gamma} = \frac{[C_1 - m_1]}{[m_1]^n [m_2]^m} \quad \dots(13)$$

In solutions in which  $C_s \geq 10^{-2} \text{ mol-dm}^{-3}$ , since the change in the counter ion concentration ( $\text{Br}^-$ ) compared with  $C_s$  of added NaBr is negligible,  $m_2 = C_s$ . Then Eq. (13) can be written as,

$$K' = \frac{[C_1 - m_1]}{[m_1]^n} \quad \dots(14)$$

or,

$$\log [C_1 - m_1] = \log K' + n \log [m_1] \quad \dots(15)$$

According to Eq.(15), under the conditions where  $C_s \geq 10^{-2} \text{ mol-dm}^{-3}$ , a plot of  $\log [C_1 - m_1]$  vs  $\log [m_1]$  will be linear with a slope equal to the micellar aggregation number,  $n$ . The resulting plots at various concentrations of NaBr are shown in Fig.6 and the obtained  $n$  values are included in Table 1.

### Discussion

The results given in Table 1 clearly indicate that the presence of electrolyte causes a decrease in the CMC and  $\alpha$  value of HDPB<sup>24,25</sup>. The observed depression of the CMC could be mainly due to a reduction in the electrostatic repulsion between head groups of the resulting micelle and, consequently, a smaller contribution of these groups to the free energy term opposing micellization.

It is interesting to note that there is an excellent agreement between the  $\alpha$  values obtained by the three different methods used. First of all, this is indicative of the high ability of the cells constructed with HDPB surfactant-selective membrane electrodes to extract valuable information about the intermicellar properties. Furthermore, such a good consistency in the  $\alpha$  values provides good support for a recent theoretical treatment<sup>26</sup>.

From the data given in Table 1, it is seen that the aggregation number increases from 74 to 104 upon increasing the NaBr concentration from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-1} \text{ mol-dm}^{-3}$ <sup>27</sup>. This observation can be mostly related to the diminished effective charge of the micelles with increasing the NaBr content. The observed behaviour may be interpreted in terms of a counterbalance of hydrophobic and electrostatic interactions<sup>28</sup>. The size-limiting parameters in ionic micelles would be the length of the hydrocarbon chains of the surfactants and the Coulomb interaction between the head groups. The coulomb interaction between the head groups, however, can be reduced by increasing the counter ions in the Stern-layer, which encloses the hydrocarbon core, facilitating an increase in the aggregation number of the resulting micelle. Since the aggregation number of the spherical micelles is limited by the length of the fully extended hydrocarbon chain, the larger aggregation numbers can be obtained only by changes of the micelle shape, presumably to an oblate spherical shape in the present case<sup>29</sup>. In a previously published model of micellar aggregation<sup>30</sup>, it was proposed that the following general relationship is expected between  $n$  and CMC for all kinds of ionic micelles:

$$\ln \text{CMC} = K_1/(n)^{1/2} - K_2 \quad \dots(16)$$

where the constant  $K_1$  corresponds to the micelle-water interfacial tension and  $K_2$  corresponds to the

hydrophobic interaction arising from the free energy of transfer of the alkyl chain from water phase to micellar phase. The data obtained here (Table 1) are nicely fitted to Eq.(16) (with a correlation coefficient of 0.99) which emphasizes the practical applicability and proper theoretical basis of this model.

It is interesting to note that, although the resulting EMF vs.  $\log C$  plots (Fig.1 and 2) are linear below the CMC values, the corresponding slopes deviate from Nernstian behaviour in the presence of NaBr concentration  $\geq 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  (see Table 1). This is most probably due to the increased tendency of the surfactant molecule to form dimer (and even tetramer) aggregates prior to micelle formation, in the presence of increasing amount of the electrolyte used. A similar conclusion has been arrived at earlier<sup>1,3</sup>.

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