

## EFFECT OF ADDITION OF KX TYPE ELECTROLYTES AND TEMPERATURE ON THE CRITICAL MICELLAR CONCENTRATIONS OF 1-CETYLPYRIDINIUM AND CARBETHOPENDECINIUM BROMIDES

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The critical micellar concentrations (*cmc*) of the title cationic surfactants were measured in aqueous solutions at 25 °C in the presence of KBr, KF, KCl, KI, KSCN, KNO<sub>3</sub>, KAc and HCOOK. The conductometric and, in part, potentiometric methods employing ion selective electrodes were used. For 1-cetylpyridinium bromide in the absence of any of the electrolytes, the decreasing temperature dependence of *cmc* was measured conductometrically over the region of 12 – 40 °C and the association degree of the micelles with Br<sup>–</sup> anions was calculated. The decrease in *cmc* of the two surfactants due to the presence of electrolytes (in concentrations up to tenfold *cmc*) was expressed by means of a semiempirical equation. There are indications that I<sup>–</sup> and SCN<sup>–</sup> anions enter into specific interactions with micelles.

Strong electrolytes tend to promote micellization and to lower the critical micellar concentration (*cmc*) of ionogenic surfactants in aqueous solutions, which is apparently related with the bonding of the oppositely charged ions to the ionic micelles<sup>1–5</sup> and with the effect on their structure<sup>6</sup>. The observed dependences of *cmc* on the electrolyte concentration, however, only partly obey the logarithmic equation<sup>3–5</sup> according to Corrin<sup>7</sup> and Shinoda<sup>8</sup> which has some theoretical background. The dependences therefore continue to be studied systematically, and are also expressed by empirical relations<sup>9</sup>.

In fact, changes in *cmc* caused by additions of electrolytes have some practical impacts as well. Cationic surfactants in aqueous solutions induce shifts of acid–base equilibria and changes in the absorption spectra of colour indicators, and such changes are affected markedly by the presence of strong electrolytes<sup>10</sup>. There are some antimicrobially acting quaternary ammonium salts among cationic surfactants, and the concentration of free amphiphilic quaternary anions has been found to be roughly limited

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by the *cmc* value of the corresponding salt<sup>11,12</sup>. If a substance causing a decrease in the *cmc* is present, the maximum attainable concentration of free surfactant cations in the solution is also decreased in this manner.

In the present work we used the conductometric and potentiometric techniques to examine the effect of presence of some univalent potassium salts of the KX type on the *cmc* of two cationic surfactants which are quaternary ammonium salts, viz. 1-cetylpyridinium bromide (*I*) and carbethopendecinium bromide ([1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide, Septonex) (*II*). For the former, the temperature dependence of *cmc* and the degree of association of the 1-cetylpyridinium cations with bromide anions in the absence of any other electrolyte were also determined.

## EXPERIMENTAL

### Chemicals

1-Cetylpyridinium bromide monohydrate, purum (Lachema, Brno, The Czech Republic) and carbethopendecinium bromide of purity conforming to PhBS 4 (supplied by Slovafarma, Hlohovec, The Slovak Republic) were checked as described previously<sup>12</sup>. The other chemicals were of reagent grade purity and solutions were prepared using redistilled water whose conductivity was below 0.2 mS m<sup>-1</sup> (in equilibrium with atmospheric CO<sub>2</sub>).

### *cmc* Measurement

The conductometric and potentiometric apparatus was as described elsewhere<sup>11,12</sup>. The electrode pair for the potentiometric measurement was adequately chosen from among the following three electrodes: S<sup>+</sup> and Br<sup>-</sup> ion selective electrodes (ISE) and a saturated calomel electrode (S<sup>+</sup> stands for cations of the surfactants SBr).

The solutions of the surfactants with the electrolyte (KX salt) were measured conductometrically and partly also potentiometrically at 25 °C. The measurements in the presence of a salt KX were invariably made on series of solutions with increasing concentration  $c_{\text{SBr}}$  of the ionogenic surfactant in question (*I* or *II*), while the total electrolyte concentration was held at a constant value  $c_t$ :

$$c_{\text{SBr}} + c_{\text{KX}} = c_t = \text{const.} \quad (I)$$

The *cmc* value at a given  $c_t$  was evaluated from the knee on the curve of experimental conductivity versus  $c_{\text{SBr}}$ . In the potentiometric measurements, the *cmc* value was found from the knee or, in the case of the S<sup>+</sup>-ISE/Br<sup>-</sup>-ISE pair, from the maximum in the EMV vs  $c_{\text{SBr}}$  plot. Each individual *cmc* value was obtained from measurement of 10 to 15 solutions at a given  $c_t$ . Although the values obtained potentiometrically were usually more dispersed than those from the conductometric measurements, no systematic differences were observed between the two methods and the results were therefore combined. For solutions of *I* in the absence of any other electrolyte, conductometric measurements of the temperature dependence of *cmc* were also performed over the region of 12 – 40 °C.

Unless the surfactant *I* or *II* precipitated on the addition of the salt, the measurements were performed at  $c_t$  values as high as 0.008 mol l<sup>-1</sup>, which corresponds to more than a tenfold excess of KX over the surfactant at *cmc*. The evaluation of the *cmc* value by the two methods at still higher concentrations of KX was difficult. For the rather low soluble *I* the measurements with additions of KBr,

KAc ( $\text{CH}_3\text{COOK}$ ), or HCOOK were only possible up to  $c_t = 0.007 \text{ mol l}^{-1}$  and with KI only up to  $0.001 \text{ mol l}^{-1}$ ; small additions of KSCN caused precipitation of *I*. For *II*, the maximum  $c_t$  was  $0.007 \text{ mol l}^{-1}$  with KAc and HCOOK,  $0.006 \text{ mol l}^{-1}$  with KSCN, and  $0.003 \text{ mol l}^{-1}$  with KI.

## RESULTS AND DISCUSSION

In aqueous solution at  $25^\circ\text{C}$  in the absence of any other electrolyte, the resultant *cmc* of compound *I*, determined conductometrically and potentiometrically, is  $6.0 \cdot 10^{-4}$  (Table I) and  $5.8 \cdot 10^{-4} \text{ mol l}^{-1}$ , respectively. For *II*, the conductometrically determined *cmc* at  $25^\circ\text{C}$  is  $8.1 \cdot 10^{-4} \text{ mol l}^{-1}$ , the potentiometric value is<sup>12</sup>  $7.9 \cdot 10^{-4} \text{ mol l}^{-1}$ , and the value reported in ref.<sup>13</sup> at  $20^\circ\text{C}$  is  $7.7 \cdot 10^{-4} \text{ mol l}^{-1}$ . The conductometrically determined micellization parameters of *I* at various temperatures are given in Table I, including the *cmc* value ( $c^*$ ) and association degree  $\beta$  of the ionic micelles with the counterions<sup>14</sup>. In this case,  $\beta$  is the ratio of the number of the quaternary cations  $\text{S}^+$  to that of the  $\text{Br}^-$  anions in a micelle. The values were calculated by means of the simplified relation<sup>14,15</sup>

$$\beta = 1 - S_2/S_1, \quad (2)$$

where  $S_1 = \Delta\kappa/\Delta c_{\text{SBr}}$  is the slope of the concentration dependence of conductivity ( $\kappa$ ) at  $c_{\text{SBr}} < c^*$  (below *cmc*) and  $S_2$  is the analogous slope at  $c_{\text{SBr}} > c^*$  (above *cmc*) at not too high concentrations of *I*, where the  $\kappa = f(c_{\text{SBr}})$  dependence is roughly linear. The slopes  $S_1$  and  $S_2$  are also given in Table I. The temperature dependence of *cmc* of *I* is compared to that of *II* (ref.<sup>12</sup>) in Fig. 1. The observed *cmc* values of *I* and *II* at  $25^\circ\text{C}$  in aqueous

TABLE I  
Conductometrically determined *cmc* ( $c^*$ ) and association degree ( $\beta$ ) of micelles of 1-cetylpyridinium bromide with  $\text{Br}^-$  anions

$t, {}^\circ\text{C}$	$c^* \cdot 10^3, \text{ mol l}^{-1}$	$S_1, \text{ mS m}^2 \text{ mol}^{-1}$	$S_2, \text{ mS m}^2 \text{ mol}^{-1}$	$\beta$
12	0.75	8.93	2.91	0.67
15	0.73	9.82	3.73	0.62
20	0.685	12.0	4.29	0.64
25	0.60	13.4	5.75	0.57
30	0.57	16.1	6.59	0.59
35	0.49	18.3	8.90	0.51
40	0.45	19.7	10.1	0.49

$S_1, S_2$  are the  $\Delta\kappa/\Delta c_{\text{SBr}}$  slopes below and above *cmc*, respectively.

solutions containing electrolytes KX were expressed, applying the least squares method, in the form of the extended logarithmic function

$$\log c^* = p_0 + p_1 \log c_t + p_2 \log^2 c_t, \quad (3)$$

where  $c_t$  is the total concentration according to Eq. (1).

The empirical coefficients  $p_0$ ,  $p_1$  and  $p_2$ , which are negative, are given, along with the statistical parameters, in Table II. For additions of KBr, KF, KCl, KNO<sub>3</sub> and KSCN (for compound II only), the coefficients of Eq. (3) were calculated from 18 to 20 conductometric and potentiometric *cmc* values, for the remaining electrolytes, from 8 to 10 conductometric values. The validity of the coefficients is, naturally, limited by the span of the total concentrations  $c_t$  as given in the Experimental.

The effect of the concentration of the electrolyte,  $c_{\text{KX}}$ , on the *cmc* value at 25 °C is shown in Figs 2 and 3. The curves also demonstrate the maximum attainable concentrations of the free S<sup>+</sup> cations of the surfactants I and II at a given concentration of the salt KX, the concentration of the free surfactant ions being limited by the *cmc* value in the given solution. A similar decrease in the *cmc* value of II has been observed by other authors<sup>13</sup> in the presence of NaCl and NaNO<sub>3</sub> at 20 °C.

The *cmc* of I decreases appreciably if the temperature is increased to 40 °C, in which respect I differs from II (Fig. 1) as well as from a number of other cationic surfactants whose temperature dependence of *cmc* is known<sup>16,17</sup>. In contrast to II, micellization of

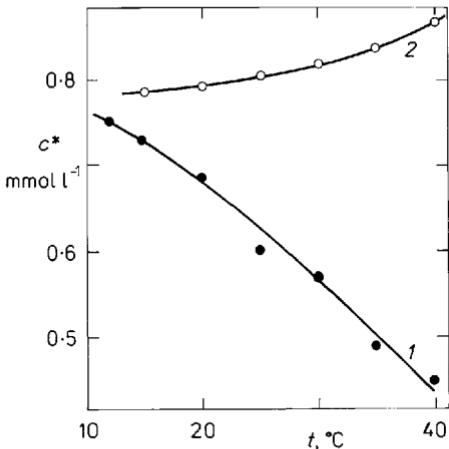


FIG. 1  
Temperature dependences of *cmc* ( $c^*$ ) of 1-cetylpyridinium bromide (1) and carbethopendecinium bromide<sup>12</sup> (2)

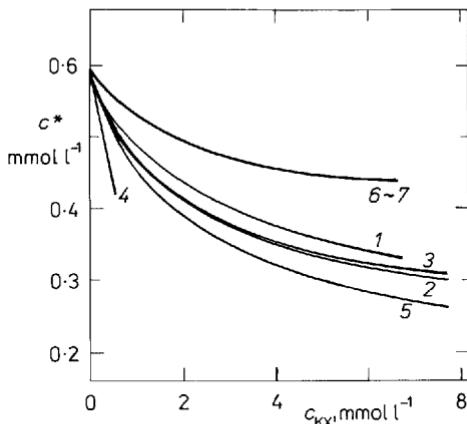


FIG. 2  
Effect of concentration of electrolyte KX on the *cmc* value ( $c^*$ ) of 1-cetylpyridinium bromide; KX: 1 KBr, 2 KF, 3 KCl, 4 KI, 5 KNO<sub>3</sub>, 6 KAc, 7 HCOOK

TABLE II

Coefficients in Eq. (3) expressing the dependence of  $cmc$  on the total concentration  $c_i$ ;  $\delta$  is the standard deviation of the observed  $\log c^*$  values from Eq. (3),  $r$  is the correlation coefficient

Added KX	$-p_0$	$-p_1$	$-p_2$	$\pm\delta$	$r$
1-Cetylpyridinium bromide (I)					
KBr	4.009	0.242		0.012	0.992
KF	4.050	0.252		0.016	0.989
KCl	4.047	0.253		0.016	0.990
KNO <sub>3</sub>	4.253	0.319		0.016	0.993
KAc	3.638	0.127		0.013	0.974
HCOOK	3.617	0.120		0.008	0.989
Carbethopendecinium bromide (II)					
KBr	4.293	0.524	0.0445	0.013	0.993
KF	3.742	0.208		0.009	0.995
KCl	4.546	0.760	0.0945	0.025	0.968
KI	5.845	0.887		0.015	0.997
KSCN	6.120	1.615	0.2056	0.019	0.992
KNO <sub>3</sub>	3.946	0.277		0.015	0.992
KAc	3.869	0.250		0.008	0.997
HCOOK	4.033	0.303		0.008	0.998

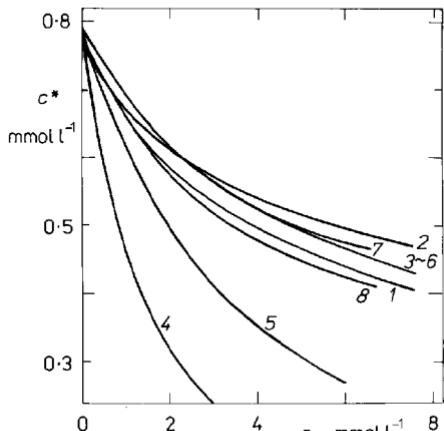


FIG. 3

Effect of concentration of electrolyte KX on the  $cmc$  value ( $c^*$ ) of carbethopendecinium bromide; KX: 1 KBr, 2 KF, 3 KCl, 4 KI, 5 KSCN, 6 KNO<sub>3</sub>, 7 KAc, 8 HCOOK

*I* is promoted by temperature increase. Although the temperature dependence of *cmc* on its own is insufficient to determine the thermodynamic functions of micellization<sup>16,18</sup>, the appreciable decrease in *cmc* of *I* indicates that the heat of micellization is positive and hence, hydrophobic interaction has a major effect on the micellization<sup>16</sup>.

The logarithmic equation (3) is based on a relation derived for a model of equilibrium bonding of a one kind of univalent counterions to the ionic micelles<sup>4,7,8,18,19</sup>; however, we augmented this relation with the quadratic term. The surfactants *I* and *II* are bromides, and if addition of KBr affected their *cmc* by the model concept solely, we would have  $p_2 = 0$  and  $p_1 = -\beta$ . Actually, however, the coefficient  $p_2$  is significantly nonzero for one surfactant even over the relatively narrow KBr concentration region examined (Table II). Moreover, the  $\beta$  value for *I* is 0.05 – 0.12 higher than for *II* (ref.<sup>12</sup>) over the temperature region measured and applying the same procedure of determination, whereas the effect of KBr and of the majority of the remaining electrolytes on the *cmc* value is lower for *I* than for *II*. Presumably, some counteracting effects are involved: addition of electrolyte promotes the formation of micelles with a larger bonding of oppositely charged ions, but the increased concentration of ions weakens simultaneously the hydrophobic interaction, whereupon the micelles of *I* are destabilized to a greater extent.

The substantial decrease in *cmc* for the two surfactants on the addition of KI (Figs 2 and 3) and, for *II*, on the addition of KSCN (*I* precipitates) indicates a specific interaction of anions of the two salts with the micelles. For iodide, a charge transfer interaction is conceivable, as has also been evidenced spectrally for some surfactants containing pyridine rings<sup>2,5</sup>. The quaternary ammonium cations of *II* do not possess any aromatic system but they possess an ester group. The different effect of the remaining halides on the *cmc* of *I* and *II*, as well as the relatively low effect of KAc and HCOOK on *cmc* of *I*, is more difficult to account for. The order of the ionic conductivities of the anions and their order in the lyotropic series<sup>1</sup> do not play unequivocal role.

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