Micellization of [1-(Ethoxycarbonyl)pentadecyl]trimethyl-ammonium Bromide Studied by Conductometry and Potentiometry

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Micellization of the title compound, an antimicrobially active surfactant (Septonex), was studied in aqueous solution by conductometry and potentiometry with ion-selective electrodes. The effect of temperature and concentration of bromide anions (addition of KBr) upon critical micelle concentration (CMC) of the surfactant was determined, together with the degree of association of the formed cationic micelles with bromide counterions. The concentrations of the free quaternary ammonium cations and free bromide anions were determined in the micellar solution of the surfactant in the range from CMC (0.0008 mol dm^{-3}) to 0.1 mol dm^{-3}. The results corroborate the formation of relatively small micelles at CMC, which grow continually with the increasing concentration of the surfactant, while the concentration of its free quaternary cations decreases.

Aqueous ionic micellar systems are often theoretically treated from two various standpoints. In the more usual mass action model, the micelles of ionogenic surfactants are considered as unstable chemical species, or flickering clusters, in the chemical equilibrium with both the monomeric amphiphilic surfactant ions and the corresponding counterions [1]. From another point of view, the ionic micelles are regarded rather as a separate charged phase [2, 3]. Since the validity of the various theoretical models is obviously limited to a certain context, further experimental studies of aqueous solutions of micellizing ionogenic surfactants are pertinent. For this purpose, conductometry and potentiometry are simple but useful tools.

Among the cationic surfactants, the most extensively studied and theoretically treated are obviously those with a simple quaternary ammonium cation $R—N^+(CH_3)_3$, where R is a longer unbranched alkyl [4—6]. However, surfactants with more complicated amphiphilic quaternary cations are often practically important, *e.g.* as antimicrobially active compounds. For this reason, in this work, we deal with [1-(ethoxycarbonyl)pentadecyl]trimethylammonium (synonym carbethopendecinium) cation, where R is the group $CH_3(CH_2)_{13}\overset{|}{C}HCOOC_2H_5$. In a recent work, we studied also benzododecinium cation [7], while other authors dealt with micellar solutions of dodecylpyridinium [8] and 1-methyl-4-dodecylpyridinium [9] cations.

The common feature of the ionic micelles is their association with corresponding counterions. After the mass action model, the micelles formed in the solution of a cationic surfactant salt SX can be represented by the formula $S_nX_p^{(n-p)+}$ where n is a number of the monomer amphiphilic cations S$^+$ (aggregation number) and p is a number of counterions X$^-$. In such a case

$$p/n = \beta = 1 - \alpha \qquad (1)$$

where β is a degree of association of the micelles with counterions or $\alpha = (n - p)/n$ is a degree of dissociation (ionization) of the micelles [1, 3—6, 10]. The symbols α and β are sometimes interchanged. The quantities in eqn (1) are important descriptors of ionic micelles. The degree of association β is connected with the concentration of free ions S$^+$ and X$^-$ in the micellar solution and with the effect of eventual addition of a strong electrolyte on the critical micelle concentration (CMC) of the salt SX.

In this work, we measured at first the CMC's of carbethopendecinium bromide (SBr or S$^+$Br$^-$) in aqueous solution at various temperatures by conductometry, at each temperature β was calculated and the aggregation number n approximately estimated. At 25 °C, the dependence of CMC on the total concentration of bromides was followed in the solutions of SBr with the addition of KBr, also by conductometry and in some cases by the surface tension measurements. At the same temperature, concentrations of free ions S$^+$ and Br$^-$ in the micellar solution of SBr, from CMC to 0.1 mol dm^{-3}, were determined by potentiometry with ion-selective electrodes and thus the concentration dependence of β was established.

EXPERIMENTAL

Carbethopendecinium bromide (Septonex, Spofa) was checked by TLC and by the measurement of surface tension of its aqueous solutions. No minimum was observed on the curve demonstrating the surface tension vs. log c_{SBr} in the vicinity of CMC. Other chemicals were anal. grade, redistilled water with conductivity less than 0.1 mS m^{-1}(in equilibrium with atmospheric CO_2) was used.

Surface tension was measured by two methods, drops weighing and the air bubbles formation below the solution surface. Electric conductivity of the solutions was measured with the conductometer OK 104 (Radelkis, Budapest) in the thermostatted conductivity cell (15—40 °C), calibrated by the solution of KCl (c = 0.01 mol dm^{-3}). Potentiometric measurements were done at 25 °C, in a similar way as previously [7]. The electromotive voltage of the cells, represented by the pair of electrodes immersed in the investigated solutions, SCE| soln |Br$^-$-ISE, SCE| soln |S$^+$-ISE or Br$^-$-ISE| soln |S$^+$-ISE, was measured with the precision pH-meter OP 208 (Radelkis, Budapest). SCE was a saturated calomel electrode, Br$^-$-ISE was bromide ion-selective electrode (Crytur 35-17) and S$^+$-ISE was home-made PVC membrane electrode responsive to the studied carbethopendecinium cation S$^+$, similar to that in the previous work [7].

RESULTS

Conductometric Determination of CMC and β

CMC and the degree of association β of the micelles of the studied cations S$^+$ and bromide counterions were at first evaluated from the measured conductivities κ of the solutions of SBr (c_{SBr} = 0.0001—0.0015 mol dm^{-3}) at temperatures 15—40 °C. At each temperature, CMC (c^*) was found by the least-squares method as an intersection of two practically linear segments of the plot of κ vs. c_{SBr}. The determined CMC's and the corresponding

slopes of the plot $S_1 = \Delta\kappa/\Delta c_{SBr}$ for $c_{SBr} < c^*$ (below CMC) and $S_2 = \Delta\kappa/\Delta c_{SBr}$ for $c_{SBr} > c^*$ (above CMC) are given in Table 1.

The evaluated plots S_1 and S_2 are used to obtain the degree of association β (or the degree of dissociation α) of the ionic micelles with corresponding counterions. A simple approximation, used by a number of authors [11—13], is $\alpha = S_2/S_1$, or

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

Values of β after eqn (2) are also in Table 1.

If the molar conductivity of the counterion (in this work Br$^-$) is known and an approximate size of the formed micelles (aggregation number n) can be estimated, a more accurate Evans quadratic relation [14] is recommended, in our rearrangement it is

$$(1 - \beta)^2 n^{2/3}(S_1 - \lambda_{Br^-}) + (1 - \beta)\lambda_{Br^-} - S_2 = 0 \qquad (3)$$

The molar conductivity of bromide ions λ_{Br^-} (taken from [15]) must be expressed in the same units as the gradients S_1 and S_2, in this work we use mS m^2 mol^{-1}. Eqn (3) is particularly useful in the studies of simple surfactant ions, with a longer unbranched alkyl, terminated by an ionic head group. Such ions form relatively big spherical micelles at CMC, and for the alkyl length 14—16 carbon atoms, n is known to be about 60 or more. Calculation of β after eqn (3) is then relatively insensitive to the precise value of n [4, 5].

Since the structure of the studied carbethopendecinium ion is more complicated, we calculated β after eqn (3), with the value of n increasing from 3 to 60 (Table 2) and compared the results with those from eqn (2) in Table 1. At all the temperatures, certain agreement of the respective β values from eqns (2) and (3) is observed only for low n = 3, or so. Thus the results may suggest formation of very small micelles of carbethopendecinium ions at CMC. Values of β calculated from the conductivity data refer at any rate only to a region near CMC.

In the solutions of SBr with added KBr, the dependence of CMC on the concentration of bromides was followed mainly by conductometry at

Table 1. Conductometrically Determined CMC (c^*) of the Aqueous Solutions of Carbethopendecinium Bromide, Gradients S_1, S_2, and the Degree of Association β Calculated after Eqn (2)

θ	$c^* \cdot 10^4$	S_1	S_2	β
°C	mol dm^{-3}	mS m^2 mol^{-1}	mS m^2 mol^{-1}	
15	7.86	9.77	4.62	0.53
20	7.93	10.90	5.23	0.52
25	8.07	12.12	5.83	0.52
30	8.20	13.69	7.09	0.48
35	8.36	14.79	8.57	0.42
40	8.50	16.52	9.77	0.41

Table 2. Degree of Association β Calculated after Eqn (3) for Various Aggregation Number n of the Micelles

θ/°C	n							
	3	5	10	20	30	40	50	60
15	0.52	0.57	0.62	0.68	0.71	0.73	0.74	0.75
25	0.52	0.56	0.62	0.68	0.71	0.73	0.74	0.75
30	0.49	0.54	0.60	0.66	0.70	0.72	0.73	0.74
40	0.44	0.50	0.57	0.64	0.67	0.70	0.71	0.72

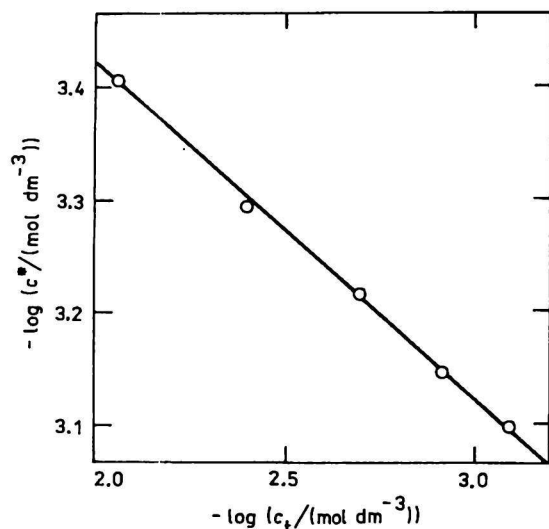**Fig. 1.** Dependence of CMC c^* of carbethopendecinium bromide on the total bromide concentration c_t, in negative logarithms.

Fig. 2. Electromotive voltage E plotted *vs.* negative logarithm of the concentration of carbethopendecinium bromide c_{SBr}. S^+ — cell SCE|soln|S^+-ISE, Br^- — cell SCE|soln|Br^--ISE.

25 °C. Several series of solutions were measured, each series with constant total concentration of bromides, $c_t = c_{SBr} + c_{KBr}$, and varying ratio c_{SBr}/c_{KBr}. The reliable conductometric determination of CMC was however feasible only up to $c_t \leq 0.008$ mol dm^{-3} and the found dependence of log c^* on log c_t is shown in Fig. 1. In the limited measured range, the logarithmic plot is practically linear and expressed by the relation

$$\log c^* = -4.019 - 0.299 \log c_t \qquad (4)$$

Evaluation of the Potentiometric Measurements

Solutions of SBr were potentiometrically measured with the above-mentioned electrodes in the range of concentrations 5×10^{-5}—0.1 mol dm^{-3} at 25 °C. Measured electromotive voltages E of the cells SCE|soln|Br^--ISE and SCE|soln|S^+-ISE are partially seen in Fig. 2, in the form of the plot of E vs. log c_{SBr}. Values of CMC were read off from the curves, as marked by the arrows in Fig. 2. The average values of c^*/(mol dm^{-3}) from several series of measurements are 8.1×10^{-4} (Br$^-$-ISE), 7.8×10^{-4} (S$^+$-ISE), and 7.9×10^{-4} by the combination of Br$^-$-ISE with S$^+$-ISE. The potentiometric CMC's are thus in reasonable agreement with those from conductometry and also with our surface tension measurements. Other authors [16] reported the value of CMC 7.7×10^{-4} mol dm^{-3} at 20 °C.

Conventional activities of the respective free Br$^-$ ions (a_{Br-}) and carbethopendecinium ions (a_{S+}) in the micellar solution, above CMC, were evaluated by a similar procedure as described previously [7]. The procedure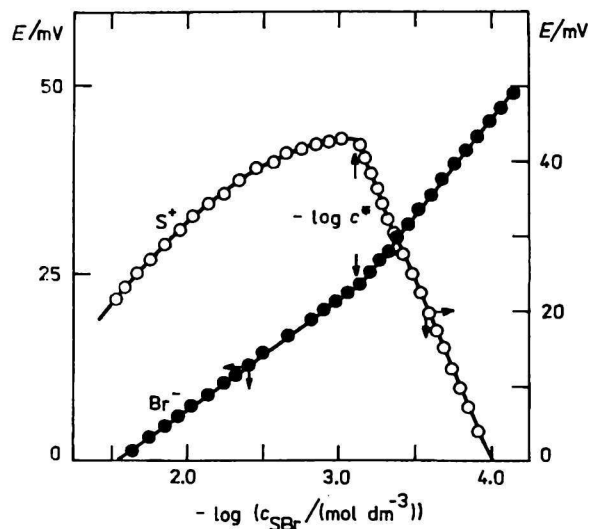 starts with the calculation of the activities in the nonassociated solution, below CMC, where $a_{Br-} = a_{S+} = c_{SBr}\gamma_\pm$. At such low concentrations, the mean activity coefficient $\gamma_\pm$ is given by the formula

$$\log \gamma_\pm = -0.509 \sqrt{I}/(1 + \sqrt{I}) \qquad (5)$$

and the ionic strength $I = c_{SBr}$.

Below CMC, the measured electromotive voltage E can be expressed in the form of the respective linear functions, $E = f(\log a_{Br-})$, for electrodes SCE with Br$^-$-ISE, and $E = f(\log a_{S+})$, for SCE with S$^+$-ISE. These calibration functions are then used to calculate a_{Br-} and a_{S+} in the micellar solution, from the values of E measured at $c_{SBr} > c^*$. The resulting free ion activities in the micellar solution of SBr are given as follows

$$\log a_{Br-} = -1.497 + 0.527 \log c_{SBr} \qquad (6)$$

$$\log a_{S+} = -4.601 - 0.896 \log c_{SBr} - 0.131 \log^2 c_{SBr} \qquad (7)$$

Eqns (6) and (7) are valid in the measured range of the micellar solution, *i.e.* from CMC to $c_{SBr} = 0.1$ mol dm^{-3}, and they reflect the shape of the respective curves in Fig. 2.

Concentrations of the free bromide c_{Br-} and carbethopendecinium c_{S+} ions in the equilibrium with micelles were from the respective activities (eqns (6) and (7)) calculated by an approximate iteration procedure. Here, $c_{Br-} = a_{Br-}/\gamma_\pm$, $c_{S+} = a_{S+}/\gamma_\pm$, and $\gamma_\pm$ is again calculated after eqn (5), where in the first approximation $I = (a_{Br-} + a_{S+})/2$ and in the second or further approximations $I = (c_{Br-} + c_{S+})/2$ from the previous round [7]. The resulting free ion concentrations c_{Br-} and c_{S+}, in the micellar solution, are plotted against the total concentration c_{SBr} in Fig. 3. While c_{Br-} increases steadily, though slowly, the
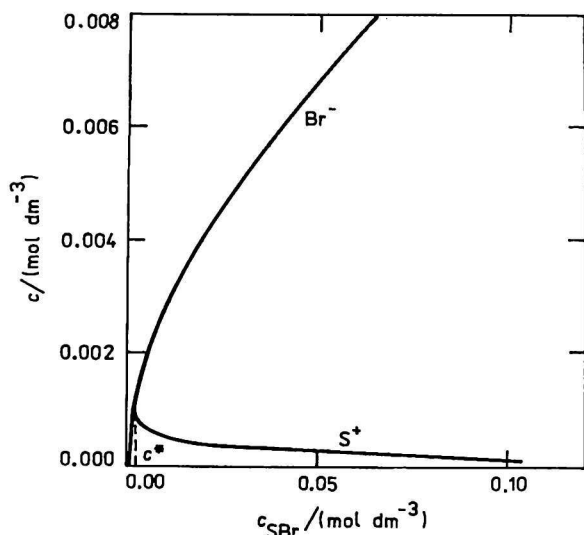
Fig. 3. Concentrations of the free bromide anion c_{Br^-} resp. free carbethopendecinium cation c_{S^+} in the micellar solution of SBr.

Fig. 4. Degree of association β (or degree of dissociation α) of carbethopendecinium micelles with bromide counterions *vs.* concentration of SBr.

c_{S^+} actually decreases above CMC, with increasing c_{SBr}. At c_{SBr} 0.01 mol dm^{-3}, the respective c_{Br^-} and c_{S^+} are 0.0029 and 0.000 49 mol dm^{-3}, at c_{SBr} 0.1 mol dm^{-3}, they are 0.010 and 0.000 16 mol dm^{-3}.

The degree of association β of the carbethopendecinium micelles with bromide counterions can be calculated also from the free ion concentrations in the micellar solution

$$\beta = (c_{SBr} - c_{Br^-})/(c_{SBr} - c_{S^+}) \qquad (8)$$

Eqn (8) follows from the mass action model of micellization [1, 10]. Contrary to eqns (2) and (3), it facilitates calculation of β in a broad concentration range of the micellar solution, if the concentrations of free monomer ions can be determined there by potentiometry or by another method. However, eqn (8) is not suitable too close to CMC. The dependence of β on c_{SBr}, calculated from eqn (8) is depicted in Fig. 4. Values of β increase continuously with increasing concentration of carbethopendecinium bromide, at CMC ($c_{SBr} = c^* = 0.0008$ mol dm^{-3}) the extrapolated β is 0.59, at $c_{SBr} = 0.01$ and 0.1 mol dm^{-3}, the corresponding β is 0.74 and 0.90, respectively.

DISCUSSION

Conductometric measurements and the determination of free monomer ions concentration in the micellar solutions yield usually only a rough estimate of the aggregation number n of the formed ionic micelles [10]. The conductometric values of the degree of association of the studied carbethopendecinium cationic micelles with bromide counterions, calculated after the respective eqns (2) and
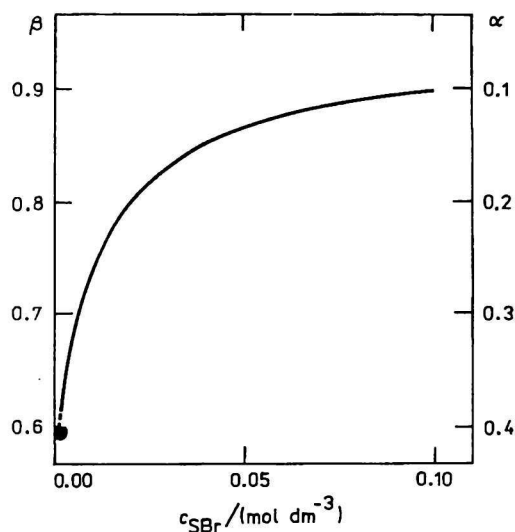
(3), are in a mutual agreement for $n = 3$. The potentiometric value of β, calculated from eqn (8) and extrapolated to CMC, agrees satisfactorily with the conductometric β from eqn (3) for $n < 10$. Our results therefore suggest the formation of rather small cationic micellar aggregates of SBr in its aqueous solution at CMC.

However, the potentiometrically determined β exhibits a continuous increase with concentration, the parameters of the formed cationic micelles apparently depend on the concentration. The higher association degree β probably characterizes bigger micelles [3], thus the observed trend indicates that the small micelles, formed at CMC, grow continuously larger with increasing total concentration of carbethopendecinium bromide. Similar trend was also observed in our recent study of micellization of benzododecinium ions [7]. On the other hand, simple ionogenic surfactants, like alkyltrimethylammonium cations with a comparable alkyl (14—16 carbon atoms), form relatively big spherical micelles ($n \approx 60$), which usually do not change much from CMC to an eventual sudden transition into rod-like micelles [4, 6]. The formation of continuously varying micelles in dependence on concentration seems to characterize our studied surfactant cations with more complicated structure.

The observed slight increase of CMC of SBr with temperature (Table 1) is similar to that of the above-mentioned simple chain surfactant cations [17]. As expected, the increasing total bromide concentration c_t lowers CMC (see Fig. 1 and eqn (4)). The linear relationship log $c^* = f(\log c_t)$, found in the limited measured range, is in agreement both with the mass action model of micellization [1] and the Shinoda equation [18], but the gradient $\Delta\log c^*/$

$\Delta \log c_t$ in eqn (4) differs markedly from the value $-\beta$, expected by the models [1, 18].

With respect to the antimicrobial activity of carbethopendecinium bromide, it is proper to point out the observed decrease of its free cation concentration in the micellar solution above CMC (Fig. 3). Actually, it follows from the counterion binding to the micelles [1]. It is therefore quite counterproductive to increase the concentration of SBr above CMC, if higher concentration of the free S^+ cation is required. It appears that c_{S+} cannot be appreciably higher than CMC and, consequently, it is also diminished by larger addition of bromides or any solute which decreases CMC.

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