Micellization of dimethylbenzyldodecylammonium bromide and the micelle association with bromide counterions studied by potentiometry and cryoscopy

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Activities of both cations and anions of the antimicrobial surfactant dimethylbenzyldodecylammonium (benzododecinium) bromide were measured in aqueous solutions above critical micelle concentration (CMC) up to 0.1 mol dm^{-3} potentiometrically with ion-selective electrodes at 25°C. The concentrations of the free ions in the micellar region and the degree of association β of the micelles of benzododecinium cations with bromide counterions were calculated from the activities. CMC 0.0024 mol dm^{-3} was found and it decreased upon the addition of KBr, approximately after Shinoda equation. Cryoscopically measured osmotic coefficients of the benzododecinium bromide solutions combined with potentiometric results suggested continuously increasing size of the relatively small micelles above CMC, while the concentrations of the free benzododecinium cations decreased.

The micelles of ionic surfactants in aqueous solutions are always more or less associated with the corresponding counterions [1—3]. Binding of counterions affects markedly properties of ionic micelles and surfactants, namely critical micelle concentrations (CMC), micellar size and shape [1—4], the catalytic [5] and ion-exchange [6] properties of the micelles and, to some extent, also the acid-base equilibria in micellar solutions [5—7]. Formation of cationic micelles and their association with various anions are well documented in the cases of simple surfactant cations, represented by one longer hydrophobic aliphatic chain ended up with the trimethylammonium or similar ionic head group [2, 4, 8—10].

The studied benzododecinium (*i.e.* dimethylbenzyldodecylammonium) cations with two larger hydrophobic groups may analogically form micelles or aggregates associated in this case with bromide anions. If B^+ is the benzododecinium cation, the composition and the charge of the micelles should be $B_nBr_p^{(n-p)+}$, with respect to the mass action model of micellization [11], and

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

In eqn (*1*) β is the degree of association (binding) of the micelles with counterions, whereas α is called the dissociation (ionization) degree of the micelles [3, 8—10, 12].

Our study of the benzododecinium bromide micellization was carried out mostly by potentiometry with ion-selective electrodes at 25 °C and concentrations up to 0.1 mol dm^{-3} In the micellar solution above the found CMC we measured activities of both the benzododecinium cation B^+ and anion Br^-, calculated their respective concentrations and the β value. The dependence of CMC on the total bromide concentration was followed in the solutions with added KBr. Furthermore we measured cryoscopically osmotic coefficients of the aqueous solutions of the benzododecinium bromide and approximated the aggregation number of the micelles.

Experimental and results

Dimethylbenzyldodecylammonium bromide, synonym benzododecinium bromide (Spofa), abbr. BBr, was checked and standardized in aqueous solutions as described previously [13]. Other chemicals were anal. grade and water was redistilled.

Potentiometric measurements

Potentiometry of the benzododecinium bromide solutions was similar to that described in our previous works [13, 14], with some alterations. The precision pH-meter OP 208 (Radelkis, Budapest) was used to measure at 25 °C the electromotive voltage (E) of the cell

$$\text{SCE} \mid \text{measured solution of BBr} \mid \text{ISE}$$

in which SCE was a saturated calomel electrode and ISE an ion-selective electrode measuring the activity of either Br^- or B^+ ions. The activity of Br^- anions, a_{Br^-}, was measured with commercial ISE's Crytur 35-17, the activity of B^+ cations, a_{B^+}, with a home-made ISE.

The bromide ISE's Crytur had to be at first checked by measuring solutions of KBr with known mean activities a_{KBr}, and only those with a stable response and the slope $\Delta E/\Delta \log a_{KBr} = (-59 \pm 1)$ mV were used. The main part of the ISE selective to the B^+ cations was a membrane prepared from PVC plasticized by bis(2-ethylhexyl)phthalate, dissolved in tetrahydrofuran, with the addition of sodium dodecyl sulfate and BBr. The inner solution of the cationic ISE was 0.01 M-(KBr + BBr), the inner reference electrode was another SCE. With the given electrodes the studied benzododecinium bromide solutions were measured in the range of concentrations c_{BBr} from 10^{-5} to 0.1 mol dm^{-3}

Evaluation of CMC, activities and concentrations of Br^- *and* B^+ *ions in the micellar solution, and the* β *value*

It is suitable to process at first the measurements carried out with the bromide ISE. One series of the measured EMV is plotted against $-\log c_{BBr}$ in Fig. 1 and the values of E form a curve Br^- consisting of two practically linear segments (marked *1* and *2*), according to the concentration. The segment *1* in the zone of lower concentrations has a nearly Nernst slope (see below), thus it indicates the range of the unassociated solution. The segment *2* has by about half smaller slope, it indicates the zone of the micellized solution and the intersection of the two lines corresponds to CMC (c_m) of benzododecinium bromide. Both the linear segments were processed by the least-squares method and the mean deviations of the experimental E measured with the selected bromide ISE's did not exceed ±0.7 mV.

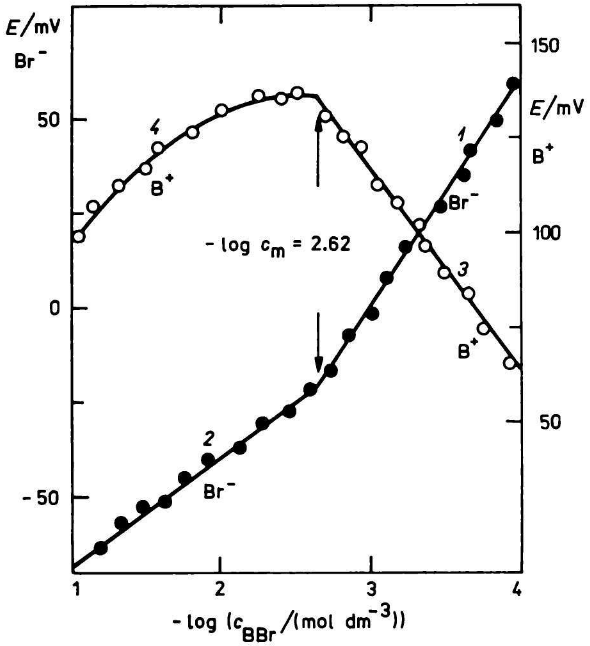

Fig. 1. Measured electromotive voltage as a function of the negative logarithm of the total concentration of benzododecinium bromide. Curve Br^- — bromide ISE, curve B^+ — benzododecinium ISE.

In the range of the unassociated solution below CMC ($c_{BBr} < c_m$), the bromide ion activities can be conventionally calculated as $a_{Br^-} = c_{BBr}\,\gamma_{\pm}$, and, at such small concentrations, the mean activity coefficient $\gamma_{\pm}$ can be approximated after the formula

$$\log \gamma_{\pm} = -0.509\sqrt{I}/(1 + \sqrt{I}) \qquad (2)$$

where the ionic strength $I = c_{\mathrm{BBr}}$. In the unassociated zone, the relationship between the measured EMV and $\log a_{\mathrm{Br}^-}$ was then expressed by the equation

$$E = E^* + b \log a_{\mathrm{Br}^-} \qquad (3)$$

In the series depicted in Fig. 1 (segment *1*) we found $E^* = -181.9$ mV and the slope $b = \Delta E/\Delta \log a_{\mathrm{Br}^-} = -59.7$ mV, near to the Nernst value. Eqn (*3*) was used as a calibration function, to calculate a_{Br^-} in the micellar solutions above CMC, from the EMV values measured there. Since they were also linearly dependent on $\log c_{\mathrm{BBr}}$ (segment *2*), we received the following equation from several series of measurements

$$\log a_{\mathrm{Br}^-} = -1.413 + 0.470 \log c_{\mathrm{BBr}} \qquad (4)$$

Eqn (*4*) is the resulting relationship for the activity of Br^- anions in the equilibrium with micelles of benzododecinium bromide, in the solutions with total concentration c_{BBr} in the range from c_{m} 0.0024 to 0.1 mol dm^{-3}

The described procedure for the determination of a_{Br^-} in equilibrium with micelles, though not without problems, appeared more suitable than the previously [14] used calibration of ISE with another electrolyte (in this case *e.g.* KBr). The transfer of ISE into another solution often brings about disagreeable variations in the term E^* of eqn (*3*). Similar procedure was also used by several authors [15, 16].

Values of EMV obtained with the ISE selective to benzododecinium cations B^+ were processed analogously. Representative series is also seen in Fig. 1, curve B^+ The segment *3* of the curve, below CMC, was linear again, while the down-curved segment *4* in the micellar zone was fitted to a quadratic expression. Activities of B^+ cations in the unassociated zone below CMC were again calculated from a conventional assumption $a_{\mathrm{B}^+} = c_{\mathrm{BBr}} \gamma_{\pm}$ using eqn (*2*) and the determined parameters of eqn (*3*) were in this case $E^* = 278.5$ mV and $b = 54.0$ mV Corresponding to the cationic electrode, the slope b was positive but deviated from the Nernst value more than that of the Br^- ISE. EMV values of the curved segment *4* of the micellar zone then yielded a quadratic expression for $\log a_{\mathrm{B}^+}$; from several series of measurements it was

$$\log a_{\mathrm{B}^+} = -4.641 - 1.609 \log c_{\mathrm{BBr}} - 0.322 \log^2 c_{\mathrm{BBr}} \qquad (5)$$

Eqn (*5*) thus gives the activity of benzododecinium cations in equilibrium with micelles in the range of total concentrations of benzododecinium bromide c_{BBr} from c_{m} to the value of 0.1 mol dm^{-3} A comparison of eqns (*4*) and (*5*) shows a steady increase in the activity of Br^- anion, while the activity of micellizing cation B^+ actually decreases at higher total concentrations above CMC.

CMC was more readily evaluated from the measurements with Br^- ISE as an intersection of the linear segments *1* and *2* seen in Fig. 1, than from measurements with B^+ ISE, where it is an intersection of the linear segment *3* with the curve *4*. The differences were, however, not significant and the average CMC value from several series was $c_m = 0.0024 \pm 0.0003$ mol dm^{-3} For analogous benzododecinium chloride, the reported CMC (conductivity) is 0.0084 mol dm^{-3} [17], this higher value may indicate the micelles are less associated with chlorides than with the studied bromides.

The respective concentrations of free monomeric ions B^+ and Br^- in the equilibrium with micelles were computed from the corresponding activities (eqns (*5*) and (*4*)) as $c_{B^+} = a_{B^+}/\gamma_\pm$ and $c_{Br^-} = a_{Br^-}/\gamma_\pm$, using an iteration procedure. It started with the estimate of the ionic strength $I = (a_{B^+} + a_{Br^-})/2$, this was inserted into eqn (*2*), to obtain $\gamma_\pm$ and the first estimates of c_{B^+} and c_{Br^-}, respectively. The second estimate of the ionic strength was then $I = (c_{B^+} + c_{Br^-})/2$, *etc.* The difference between the second and third iteration was always less than 0.1 %.

The found concentrations of the free benzododecinium and bromide ions, respectively, are seen in Fig. 2 as a function of the total concentration c_{BBr}. A striking feature is the decrease of c_{B^+} in the micellar region above CMC, at $c_{BBr} = 0.1$ mol dm^{-3} it is $c_{B^+} = 0.000\,49$ mol dm^{-3} while $c_{Br^-} = 0.014$ mol dm^{-3} Similar trend was however reported with some other surfactant ions [12, 16, 18].

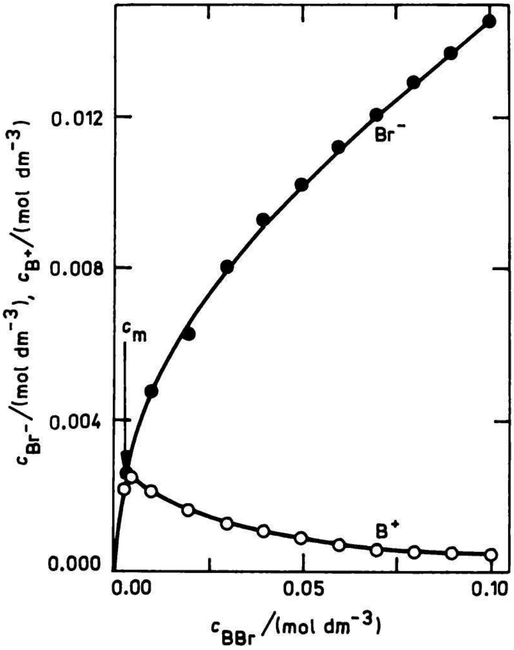

Fig. 2. Concentrations of the free bromide and benzododecinium ions in the micellar solution of benzododecinium bromide.

The degree of association β of the micelles of benzododecinium cations with bromide counterions is defined by eqn (*1*) and, with respect to the mass action law [11, 12] it can be calculated as follows

$$\beta = (c_{\mathrm{BBr}} - c_{\mathrm{Br^-}})/(c_{\mathrm{BBr}} - c_{\mathrm{B^+}}) \qquad (6)$$

Here again $c_{\mathrm{B^+}}$ and $c_{\mathrm{Br^-}}$ stand for the respective concentrations of the free (monomeric) benzododecinium and bromide ions in the equilibrium with micelles, *i.e.* at $c_{\mathrm{BBr}} > c_{\mathrm{m}}$. The found β as a function of the total benzododecinium bromide concentration c_{BBr} is seen in Fig. 3. Eqn (*6*) is unsuitable to calculate β when c_{BBr} is too near to c_{m}, but the extrapolated estimate at c_{m} is $\beta \approx 0.62$. At higher concentrations it markedly increases and at $c_{\mathrm{BBr}} = 0.1\ \mathrm{mol\,dm^{-3}}$ it is $\beta = 0.86$.

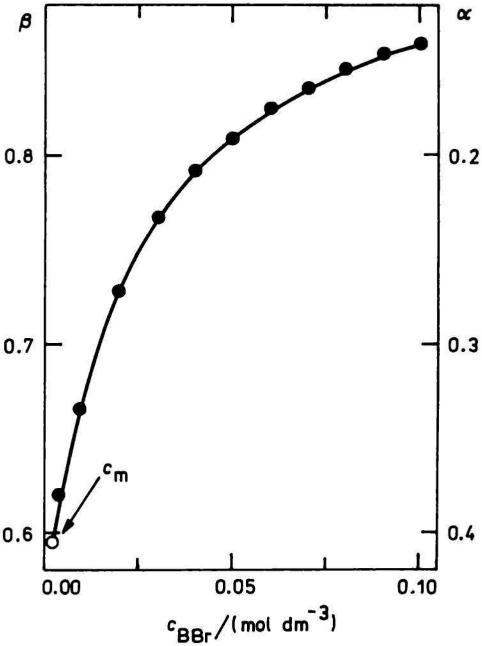

Fig. 3. Degree of association of the benzododecinium micelles with bromide counterions (degree of dissociation $\alpha = 1 - \beta$) as a function of the total concentration.

Dependence of CMC on the concentration of bromide ions

The CMC was followed potentiometrically in the series of the solutions of benzododecinium bromide with the added KBr, using bromide ISE. In each solution, the total bromide concentration $c_{\mathrm{TBr}} = c_{\mathrm{BBr}} + c_{\mathrm{KBr}}$ was kept constant while the ratio $c_{\mathrm{BBr}}/c_{\mathrm{KBr}}$ was varied and the EMV was measured. The CMC (c_{m}) was always found as a break on the measured curve $E = f(\log c_{\mathrm{BBr}})$, with the constant c_{TBr}. Since CMC diminishes with increasing c_{TBr}, the measurements were feasible only to $c_{\mathrm{TBr}} = 0.05\ \mathrm{mol\,dm^{-3}}$ ($c_{\mathrm{m}} = 0.000\,35\ \mathrm{mol\,dm^{-3}}$), at the greater excess of KBr the evaluation of yet smaller c_{m} becomes unreliable.

The obtained plot of $-\log c_{\mathrm{m}}$ against $-\log c_{\mathrm{TBr}}$ in Fig. 4 is a curve with somewhat increasingly negative slope towards higher c_{TBr}. In the range of c_{TBr} 0.01—0.05 $\mathrm{mol\,dm^{-3}}$ its slope is $\Delta\log c_{\mathrm{m}}/\Delta\log c_{\mathrm{TBr}} = -0.7$, approximately.

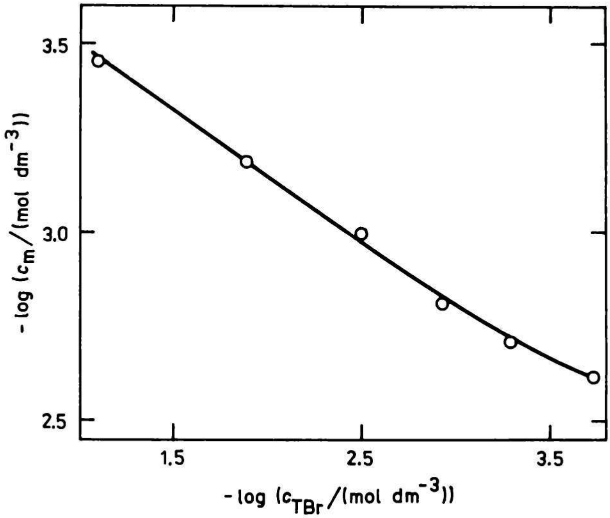

Fig. 4. Dependence of CMC of benzododecinium bromide on the total bromide concentration in negative logarithms.

Cryoscopic measurements of the osmotic coefficients and the estimate of the micelle size

The depression of the freezing point of the aqueous benzododecinium bromide solutions was measured with a cryoscopic instrument Knauer 2400 with a recorder. Solutions had the concentration range c_{BBr} 0.01—0.2 $\mathrm{mol\,dm^{-3}}$ and the measured freezing point depressions were found in the temperature range *ca.* 0.018—0.09 K. Measurements of more diluted solutions, particularly in the neighbourhood of CMC, were useless since the instrument measured temperature differences with the precision about ±0.001 K. The instrument was calibrated with NaCl solutions, like in another work [19].

Osmotic coefficients φ of the benzododecinium bromide solutions (Fig. 5) were calculated from the measured freezing point depressions θ after the formula

$$\varphi = \theta/(2c_{\mathrm{BBr}}E_{\mathrm{c}}) \qquad (7)$$

where $E_{\mathrm{c}} = 1.86\ \mathrm{K\,mol^{-1}\,dm^{-3}}$ was the molar depression. As the solutions were rather diluted, the concentration $c/(\mathrm{mol\,dm^{-3}})$ (molarity) was used also in these measurements (instead of molality). The obtained osmotic coefficients were fitted by the nonlinear least-squares procedure to a suitable empirical function

$$\varphi = 1 - 135.4\,c_{\mathrm{BBr}}/(1 + 149.2\,c_{\mathrm{BBr}}) \qquad (8)$$

Eqn (*8*) holds in the range of the benzododecinium bromide concentrations c_{BBr} 0.01—0.2 $\mathrm{mol\,dm^{-3}}$, at freezing temperature, and the mean deviation of the experimental values from this function is ±0.015.

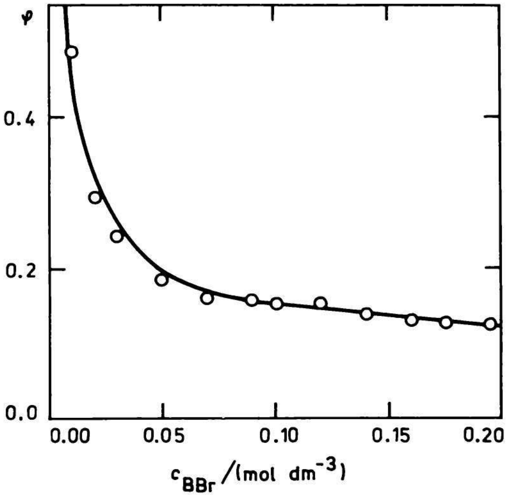

Fig. 5. Osmotic coefficient of the aqueous solutions of benzododecinium bromide at freezing point.

In principle, the size of the micelles can be calculated from osmotic coefficients combined with the concentrations of free (monomeric) ions in the micellar region. With some simplifications, a relationship for the aggregation number n of the considered micelles $\mathrm{B}_n\mathrm{Br}_p^{(n-p)+}$ can be derived

$$n = (c_{\mathrm{BBr}} - c_{\mathrm{B^+}})/(2\varphi c_{\mathrm{BBr}} - c_{\mathrm{B^+}} - c_{\mathrm{Br^-}}) \qquad (9)$$

Practically it is, in fact, difficult to determine in the diluted solution both the osmotic coefficient and the respective ionic concentrations $c_{\mathrm{B^+}}$, $c_{\mathrm{Br^-}}$ at the same temperature. In this case, osmotic coefficients were determined at about 0 °C whereas the concentrations at 25 °C. If, in spite of it, the corresponding values are inserted in eqn (*9*), the outcomes suggest the benzododecinium bromide micelles are rather small but they grow larger continuously with the total concentration. At $c_{\mathrm{BBr}} = 0.01\ \mathrm{mol\,dm^{-3}}$ ($\beta = p/n = 0.67$) the outcome is $n = 3.5$

and at $c_{\mathrm{BBr}} = 0.1\ \mathrm{mol\,dm^{-3}}$ ($\beta = 0.86$) $n = 6.6$, however, it must be taken with some reservations.

Discussion

Concentrations of free monomeric species in equilibrium with their micelles in the aqueous solution are a subject of interest, particularly when a biologically active compound is considered, like the studied antimicrobial benzododecinium bromide. Fig. 2 shows that the concentration of the free benzododecinium ions B^+ does not substantially exceed the value of the observed CMC ($c_m = 0.0024\ \mathrm{mol\,dm^{-3}}$) and, furthermore, it decreases markedly at higher total concentration of benzododecinium bromide. At higher concentrations above CMC, an increasing fraction of the B^+ ions is bound into micelles so that the free B^+ concentration actually decreases.

The degree of association β of the benzododecinium micelles with bromide counterions is also a useful parameter, especially if determined in a broader concentration range, as with our potentiometric method. CMC's of ionic surfactants are known to be lowered upon the addition of an electrolyte [20, 21], apparently due to the counterions binding to the micelles [22—24]. After Shinoda equation [23, 24], the slope of the logarithmic relationship between CMC of benzododecinium bromide and the total bromide concentration (c_{TBr}) should be $-\beta$

$$\Delta \log c_m / \Delta \log c_{\mathrm{TBr}} = -\beta \qquad (10)$$

The concentrational variation of the found β (Fig. 3) is, therefore, in accordance with the observed nonlinearity and the slope of the plot of $\log c_m$ against $\log c_{\mathrm{TBr}}$ (Fig. 4), within the limitations of the measurements of CMC in the presence of the excess of KBr. It is noteworthy that the eventual addition of an electrolyte diminishes not only CMC but also the concentration of the free benzododecinium ions in the region above CMC, after the β value of corresponding counterions. Concentrational variations of β may also explain some other reported nonlinear relationships between $\log c_m$ and the logarithm of the counterion concentration [21].

The theoretical models of the association of ionic micelles with counterions are rather conflicting as yet [1, 3]. Still the more recent model [1] points out a connection between the degree of association β and the micellar size and shape, for smaller and spherical micelles, a smaller β is expected than that for greater and cylindrical micelles. There are plenty of experimental β (or α) values reported in literature, but their concentration dependences are less known to test the theory properly. Only a few simple surfactants with one aliphatic chain were measured at various concentrations and β was mostly constant, at least within a certain concentration range [10, 11].

In contrast, our measured β of benzododecinium bromide (Fig. 3) is relatively small at CMC but increases so markedly that at higher concentrations it reaches or outgrows values reported for quaternary ammonium bromides with one aliphatic chain [2, 8—10]. With respect to the mentioned theoretical model [1] it suggests that the benzododecinium cations form small micelles at CMC but they grow continuously larger with increasing concentration. Such conclusion is also supported by our cryoscopic results. The aggregates of the studied benzododecinium cations characterized by two large hydrophobic groups thus behave like the micelles of ill-defined packing, the properties of which change continuously with the concentration [25], contrary to the bigger and well-defined micelles of simple ionic surfactants with one long aliphatic chain.

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