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SHORT COMMUNICATION

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Temperature dependence of second critical micelle concentration of dodecyldimethylbenzylammonium bromide in aqueous solution

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Abstract The specific conductivity of dodecyldimethylbenzylammonium bromide (C12BBr) in aqueous solutions, in the temperature range of 15 to 40 °C, has been measured as a function of molality. The two breaks which were found on the conductivity against molality plots were attributed to the critical micelle concentration, cmc, and second critical micelle concentration, 2nd cmc, respectively. The ratio of the slopes, S, of the three linear fragments on the plots, S2/S1 and S3/S1, was attributed to the degree of ionization of the micelles at cmc and 2nd cmc respectively. It was shown that the values of the 2nd cmc estimated above 27 °C are only apparent due to thermal disintegration of the micelles. In the temperature range of 15 to 27 °C, the values of the 2nd cmc increase gradually and the plot of the 2nd cmc against temperature is concave. The ratio of 2nd cmc/cmc for C12BBr at 25 °C amounts to 15 and appears to be high compared to the literature values for other surfactants. For comparative purposes the cmc and 2nd cmc values were also estimated conductometrically for decyldimethylbenzylammonium bromide (C10BBr) at 25 °C. The 2nd cmc value for this surfactant is higher compared to the value for the C12 homologue by a factor of 2.6. The standard Gibbs free energies of micellization at cmc and at the 2nd cmc were estimated from the experimental data for both surfactants at 25 °C.

Keywords Decyl- and dodecyldimethylbenzylammonium bromide · Second critical micelle concentration · Conductivity · Temperature dependence

Introduction

The idea that amphiphilic molecules self-assemble in aqueous solutions was introduced ninety years ago by McBain [1]. He observed unusual changes in electrical conductivity upon changing soap concentration and coined the name micelle for the aggregates. It was soon generally accepted that the aggregation process becomes detectable above a narrow concentration range over which an abrupt change occurs in many physicochemical properties of the aqueous solution of the amphiphile. This narrow concentration range has been called the critical micelle concentration (cmc). The value of the cmc depends mainly on the structure of the amphiphile, temperature and presence of additives [2,3,4,5].

Some less distinct changes in the properties of solutions of the amphiphiles occur at concentrations exceeding the cmc and it was McBain and co-workers who had already found that potassium and sodium salts of saturated fatty acids in aqueous solutions exhibit variation of the equivalent conductance and osmotic activity at concentrations higher than the first breakpoint and assigned these changes to some transformation in structure of the micelles [6]. Later X-ray diffraction measurements on association colloid solutions carried out by Hess et al [7] and Stauff [8] seemed to suggest that there exists a more or less well defined concentration range above which a change in properties reflects a change in the structure of the aggregates. The latter author suggested for this concentration range the term: second critical micelle concentration,"2^{nd} cmc".

Strong evidence for the existence of a 2^{nd} cmc for two-component aqueous systems was provided by results of detailed studies carried out by Ekwall et al on the variation of the density and partial specific volume [9], viscosity [10], and vapor pressure and osmotic coefficient [11] of aqueous sodium caprylate solutions. According to these authors the cmc value for this salt amounts to 0.38 m at 20 °C whereas the 2^{nd} cmc was estimated to be within the range of 1.15 to 1.4 m. At still higher concentrations (2.5–2.7 m for viscosity and density measurements), (2.6–2.9 m for osmotic coefficient measurements) a "third critical micelle concentration" was attributed to growth of spherical micelles into cylindrical ones. Further evidence for the existence of a 2^{nd} cmc was supplied by the results of extensive studies done by Miura and Kodama on conductivity [12], viscosity and density [13] and light scattering [14] of solutions of sodium dodecyl sulphate (SDS) for which, in addition to the cmc value at 8.3 mM, a 2^{nd} cmc was established at 65 mM. Their viscosity results confirmed previous findings of Tyuzyo et al [15,16].

Cationic surfactants also exhibit breaks on the plots representing various physicochemical properties of aqueous solutions as a function of concentration, which were attributed to the 2^{nd} cmc. Such breaks were found, among others, on the conductivity against concentration plots for dodecyltrimethylammonium bromide [17] and the tetradecyl- [18] and hexadecyl-homologous [19] as well as for homologous (C12, C14 and C16) alkylbenzyldimethylammonium chlorides [18, 19,20]

As noted earlier [18], the second breaks detected on the conductivity against molality plots may not be simply due to structural changes of the micelles but rather due to ion/ion and micelle/micelle interactions leading thus to some curvature on the plot above the cmc. There is thus a need of additional evidence for the existence of structural changes in the micelles at the suggested 2^{nd} cmc. To support our conductivity results for dodecyldimethylbenzylammonium chloride (C12 BCl), we have applied in our previous paper [18] refractive index, density and sound velocity measurements and we found that the less distinct break detected by the four methods occurs in the molality range of 0.082 to 0.104 m. This range is narrow if one takes into account the different approaches applied. A very convincing support for the existence of the 2^{nd} cmc in solutions of SDS, as suggested earlier by Tyuzyo et al. [15,16] and Miura and Kodama [12,13,14], was supplied by results of NMR studies of Zhao and Fung [21] who reported a value of 70 mM on the basis of the proton chemical shift of the α-CH2 group. Again this value is quite close to the conductivity value of 65 mM.

Analysis of the available data on the 2^{nd} cmc estimated on the basis of conductivity data has shown that the ratio of the 2^{nd} cmc/ cmc values varies in the range of about 2 to 10 [18]. A distinctly more narrow range and lower value of this ratio, amounting to almost exactly 2 for homologous (C12, C14 and C16) alkyltrimethylammonium bromides and 2.5 for homologous alkylpyridinium chlorides has been advocated by Lee and Woo [22] who deduced such values from the measurements of chemical shifts and spin-lattice relaxation rates of protons in the alkyl chain of the surfactants in D_2O. According to these authors two types of micelles (spheroidal and larger ellipsoidal), having different physical properties coexist at the concentration range up to the 2^{nd} cmc which they call the micellar structure transition concentration, mstc. Interestingly, the authors claim that they were able to confirm their NMR results by electrical conductivity and viscosity measurements. Notice that all these experiments were carried out at 35 °C, whereas most of literature data on the 2^{nd} cmc are for 25 °C.

It has been well established that the cmc values of a variety of ionic and nonionic surfactants exhibit a U-shaped temperature dependence [23,24,25,26]. The temperature at which the minimum T_{min} appears, depends upon the hydrophobicity of the alkyl chain and, in the case of cationic surfactants, on the hydrophobicity of the counter-ion. The more hydrophobic the surfactant, the lower the temperature at which T_{min} occurs [20,25,26,27].

One may thus expect that the value of the 2^{nd} cmc may also exhibit some peculiar temperature dependence on temperature. Such studies do not seem to have been carried out as yet and it is the aim of this paper to investigate the problem. Dodecyldimethylbenzylammonium bromide was chosen for this purpose.

Experimental

Materials

Decyldimethylbenzylammonium bromide monohydrate (C10BBr) was synthesized and purified as described previously [28]. The dodecyl homologue, (C12BBr) was supplied by Fluka with an assay of 99% and was used without further purification.

Methods

Conductivity measurements were performed using a Kyoto Electronics conductometer, model CM-117, and a Kyoto Electronics cell type K-121. The cell constant was determined in the appropriate concentration range according to the procedure suggested by Monk [29]. The measurements of the conductivity of C10BBr and C12BBr were carried out by continuous dilution of a concentrated sample at the temperature maintained to within ±0.05 °C. All measurements were performed using distilled water with a conductivity below 3 μS cm^{-1} at 25 °C. Appropriate corrections were made for the conductivity of pure water in the whole range of temperatures applied.

Results and discussion

The specific conductivity against molality plot for aqueous solutions of C12BBr at 25 °C is shown in Fig. 1. The insert illustrates more clearly the course of the plot for the low concentration range. The first break corresponding to the cmc appears at 0.0056 mol kg^{-1} and is in satisfactory agreement with our previous result of 0.0055 mol kg^{-1} [28]. The second, less distinct break, which we attribute to the 2nd cmc, appears at the molality of 0.085. The 2nd cmc/cmc ratio amounts thus to 15.2 and appears to be the highest among the ratios found for various other surfactants [18].

The slopes of the three apparently linear fragments of the plot in Fig. 1 amount to S1 = 87.81, S2 = 23.02 and S3 = 14.93 mS cm^{-1}mol^{-1}kg respectively. The degree of ionization of the micelles at cmc, β, is assumed to be equal to the S2/S1 ratio [30] and amounts to 0.26 ± 0.01. It is lower by some 10% than that reported previously [28]. We take the S3/S1 ratio, equal to 0.17 ± 0.02, as the corresponding degree of ionization of the micelles at 2nd cmc, β_t. The β and β_t results for the chloride analogue are higher due to the stronger hydration of the counterion and amount to 0.44 ± 0.01 and 0.37 ± 0.01 respectively [18].

A similar interpretation of the conductivity data for C10BBr yields the following values: cmc = 0.025 mol kg^{-1}, 2nd cmc = 0.22 mol kg^{-1}, $\beta = 0.29 \pm 0.01$ and $\beta_t = 0.14 \pm 0.02$ respectively.

The dependence of β and β_t on temperature found for C12BBr is shown in Fig. 2. The values of β grow linearly with temperature as found previously for a variety of cationic surfactants [26,31]. The temperature dependence of β can be described by the relation: $\beta = 0.197 \pm 0.005 + (0.0026 \pm 0.0002)t$, t(°C). The β_t values grow linearly only in the low temperature range at a rate distinctly lower when compared to the variation of β. A break on the plot of β_t against temperature appears just above 25 °C and the apparent degree of ionization of the micelles starts to grow with temperature.

In order to gain more information on this unexpected phenomenon we have studied the variation of conductivity with temperature of a solution of C12BBr at constant molality exceeding twice the 2nd cmc (0.1743m) and, for comparative purposes, of a micellar solution of the surfactant at a molality below the 2nd cmc (m = 0.027). The results are shown in Fig. 3 where we can see a linear increase of conductivity for the solution below 2nd cmc throughout the whole temperature range studied and a departure from linearity at the temperature of about 27 °C for the solution at high molality.

Figure 4 illustrates the temperature dependence of the 2nd cmc as estimated from the breaks on conductivity against molality plots. For comparison are included the data for the cmc [31]. The course of the plot for the 2nd cmc is convex and a maximum appears at about 27 °C. Above this critical temperature, the break

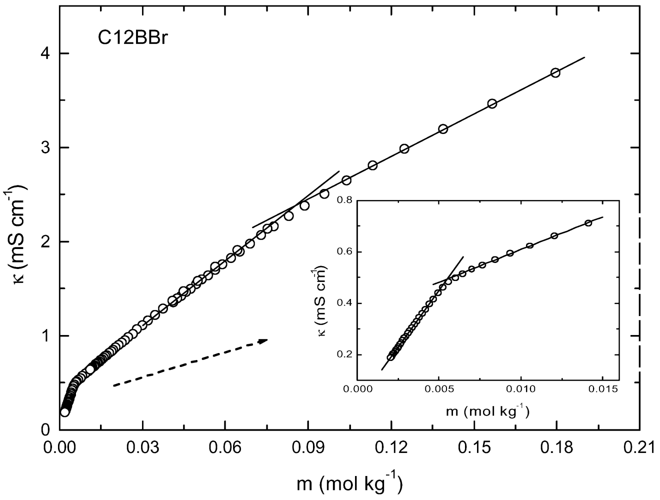

Fig. 1 The specific conductivity against molality plot for aqueous solutions of C12BBr at 25 °C

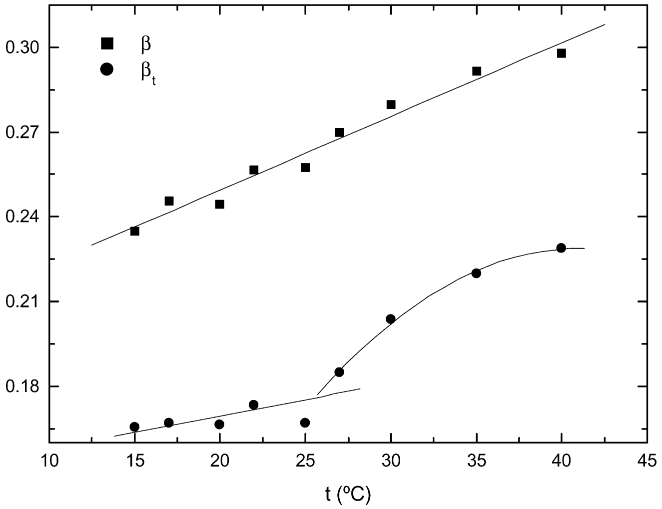

Fig. 2 Temperature dependence of β and β_t for micelles of C12BBr

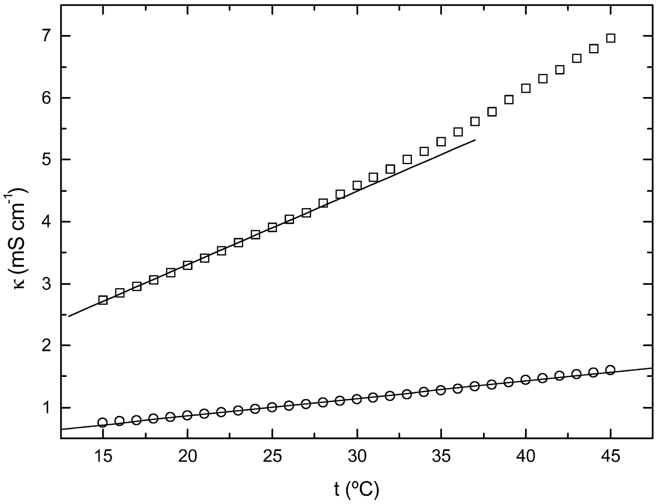

Fig. 3 The variation of specific conductivity with temperature for aqueous solutions of C12BBr at $m = 0.0270$ and $m = 0.1743$ mol kg^{-1}

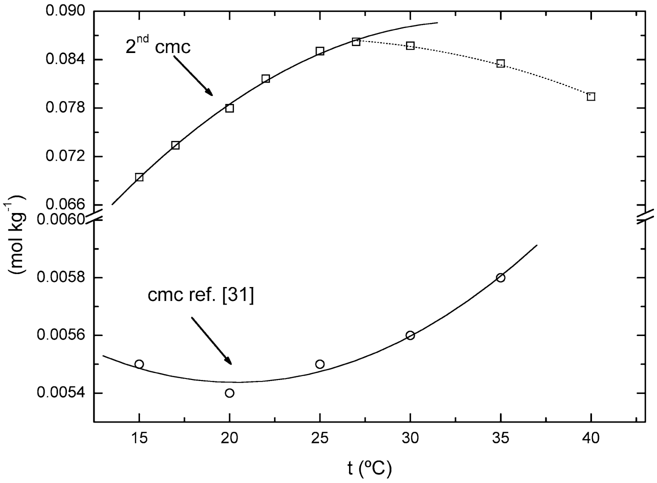

Fig. 4 Variation of 2nd cmc with temperature for micelles of C12BBr

appearing on the conductivity against molality plots, is shifted towards lower concentrations of the surfactant with an increase in temperature. This effect is accompanied by an increase in the S3/S1 ratio. It thus seems plausible to assume that the departure from linearity observed in Fig. 3 and the apparent decrease of the 2nd cmc values observed in Fig. 4 account for a gradual thermal disintegration and/or to retransformation of the micelles to a spherical form of higher degree of ionization. For this reason we will consider only the 2nd cmc values estimated for the low temperature range.

We have recently suggested [18] that the 2nd cmc values seem to conform to a relation of the form: log 2nd cmc = A – Bn where A and B are some empirical parameters both depending upon the type of surfactant considered and n is the number of carbon atoms in the alkyl chain. Taking into account the 2nd cmc values of 0.22 and 0.078 mol kg^{-1} determined at 25 °C for C10BBr and C12BBr respectively and assuming that these values conform to the above relation, one can estimate that the literature value of 0.01 mol kg^{-1} (at 30 °C) [19] is about 3 times too low. Our present results cannot thus confirm the validity of the relation suggested earlier [18].

Knowing the values of the cmc and 2nd cmc as well as the values of β and β_t one may estimate the free energies of micellization at the cmc and 2nd cmc from the relations:

$$\Delta G^o_m = (2 - \beta)RT \ln \chi_{cmc} \tag{1}$$

$$\Delta G^o_t = (2 - \beta_t)RT \ln \chi_{\mathrm{cmt}} \tag{2}$$

respectively, where χ_{cmc} and χ_{cmt} are the molar fractions at the cmc and 2nd cmc respectively. Thus the estimated free energy values at 25 °C amount to: $\Delta G^o_m = -32.65$ kJ mol^{-1} and $\Delta G^o_t = -25.5$ kJ mol^{-1} for C10BBr and $\Delta G^o_m = -39.6$ kJ mol^{-1} and $\Delta G^o_t = -29.3$ kJ mol^{-1} for C12BBr respectively. The difference between ΔG^o_m and ΔG^o_t accounts for the decrease in stability of the micelles in the region above the 2nd cmc.

The conductivity results here presented support the view that ionic surfactants in aqueous solutions are characterized by two critical concentrations, one called the critical micelle concentration (cmc) which indicates the onset of formation of spherical micelles and a second critical concentration (called 2nd cmc) which corresponds to the concentration above which structural transformations of the micelles become detectable by a variety of techniques which measure the dependence of physical properties of solutions of the surfactants on their concentration.

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