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MICELLIZATION OF DODECYLDIMETHYLETHYLAMMONIUM BROMIDE IN AQUEOUS SOLUTION
Thermal parameters

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Abstract

Specific conductivity of aqueous solutions of dodecyldimethylethylammonium bromide has been determined in the temperature range of 15–40°C. The critical micelle concentration (*cmc*) and ionization degree of the micelles, β, were determined from the data. Thermodynamic functions, such as standard Gibbs free energy, ΔG°_m, enthalpy, ΔH°_m, and entropy, ΔS°_m, of micellization, were estimated by assuming that the system conforms to the mass action model. The change in heat capacity upon micellization, $\Delta C^\circ_{p,m}$, was estimated from the temperature dependence of ΔH°_m. An enthalpy-entropy compensation phenomenom for the studied system has been found.

Keywords: conductivity, critical micelle concentration, dodecyldimethylethylammonium bromide, enthalpy, entropy and standard Gibbs free energy, heat capacity, temperature dependence

Introduction

Cationic surfactants became important because of their bacteriostatic properties. They have been introduced into several commercial products as antiseptic agents in cosmetics and as germicides [1]. Cationic surfactants have found also wide application in phase transfer catalysis [2] and, more recently, in the production of silica-based mesoporous catalysts [3]. Their performance in these fields is related to their self-association properties. Interactions of cationic surfactants with polymers and vesicles were evaluated by applying the DSC technique [4, 5]. Knowledge of thermodynamic parameters of micellization of cationics in aqueous solution is thus essential. In a previous paper we used an aproximative method to estimate the thermal parameters related with the self-association process of dodecylpyridinium salts [6]. In this paper we report our results of conductivity measurements of dodecyldimethylethylammonium bromide (C12DEABr) in aqueous solution at 15, 20, 25, 30, 35 and 40°C. Although the micellar and thermodynamic properties of homologous alkyltrimethylammonium halides have been studied extensively, little attention was devoted to the homologous group of alkyldimethylethyl-

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ammonium halides even though one of the representatives of this series, the title compound, is available commercially. As far as we are aware, only three contributions to the knowledge of micellar properties of this salt have been reported as yet. One is due to Zana *et al*. [7], who studied conductometrically and potentiometrically the micellar behaviour of C12BEABr, and the other two are due to Peña *et al*. [8, 9] who studied the molecular encapsulation and micellization process of this surfactant in aqueous solution in the presence of β-cyclodextrin and its derivatives.

Our conductometry results enabled us to determine the temperature dependence of *cmc* and β and hence to estimate the relevant thermodynamic parameters associated with the process of micellization of the studied surfactant.

Experimental

C12DEABr was provided by Fluka with a purity of 99% and it was used without further purification. This salt is monohydrated according to potentiometric and thermogravimetric analysis. All solutions were prepared by mass using distilled water with a conductivity below 3 μS cm^{-1} at 25°C. The concentrations are expressed in molalities.

The conductivity measurements were made with a Wheatstone bridge conductometer (CM-177 Kyoto Electronics and cell type K-212 Kyoto electronics). The cell constant was determined by calibration with several different concentrations of KCl solutions using the procedure suggested by Monk [10]. All measurements were carried out in a thermostat bath (Polyscience 9010) maintaining the temperature constant to within ±0.05°C.

Results and discussion

Conductance results were used to estimate the values of the *cmc* and β, at several temperatures. In Fig. 1 the conductivity *vs.* molality plots are presented for C12DEABr in water in the range of 15 to 40°C at 5°C intervals.

In this figure breaks in the specific conductivity *vs.* molality plots can be observed. These breaks are generally attributed to the beginning of formation of micelles, i.e., to critical micelle concentration (*cmc*). In order to estimate the values of critical micelle molality, we fit the linear fragments, above and below the breaks and we treat the molality at which intersection of these lines occurs as the *cmc*. Ionization degree of the micelles, β, has been calculated as the ratio of the slopes of the two intersecting lines.

The values obtained for *cmc* and β for C12DBABr at 25°C amount to 0.0137 mol kg^{-1} and 0.26, respectively. These values are close to previous results of 0.0144 mol kg^{-1} and 0.28, respectively reported by Junquera *et al*. [9] and 0.014 mol kg^{-1} and 0.28, respectively reported by Zana [7]. Taking into account the values of *cmc* and β reported for dodecyltrimethylammonium bromide [7, 11, 12] it appears that the introduction of a methylene group into the headgroup has an almost negligible effect on the hydrophobicity of the cation. It is well known that increase in the length of the main hydrocarbon chain by one methylene group leads to about a two-fold decrease in *cmc* [7].

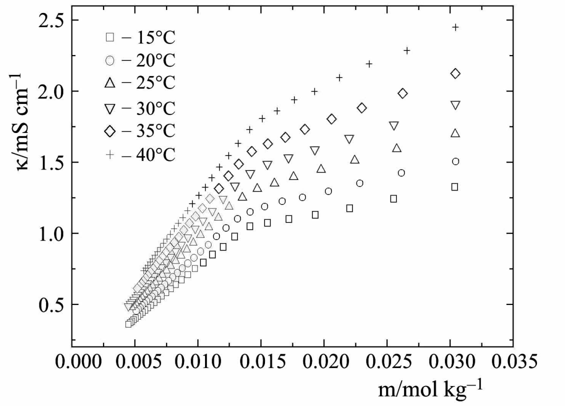

Fig. 1 Specific conductivity *vs*. molality of C12DBABr at 15, 20, 25, 30, 25, 35 and 40°C

Figure 2 represents the temperature dependence of *cmc* (a) and the ionization degree of the micelles (b) for C12DEABr.

Figure 2a shows the typical U-shaped dependence of *cmc* on temperature. The minimum of this curve is close to 25°C. This result appears to conform to a general finding that the minimum, for ionic surfactants with a dodecyl alkyl chain is close to room tem-

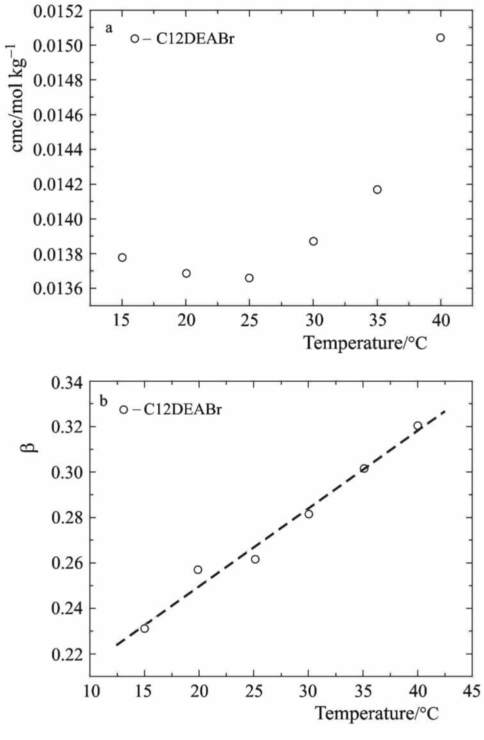

Fig. 2 Temperature dependence of *cmc* of a – C12DEABr and ionization degree of the micelles of b – C12DEABr

perature. Thus e.g. T_{mim} at 25°C was reported for sodium dodecylsulfate by Goddard *et al.* [13] whereas the results of Zielinski *et al.* [14] for dodecyltrimethylammonium bromide show a T_{mim} around 20°C. According to Chen *et al.* [15] the minimum which appears on the *cmc vs.* temperature plots is a consequence of two opposing effects: 1) the decrease in the hydration of the ionic head group (and presumably of the counterion) with temperature which leads to growth of hydrophobicity of the surfactant and hence to lowering of *cmc* 2) the breakdown of the structure of water which leads to decrease of hydrophobic interactions and hence to growth of the *cmc* value.

The rate of change of the specific conductivity with molality in the region of the breaks appears to be lower the higher the temperature. Such behavior indicates that β grows with temperature. Figure 2b shows a linear dependence of β on the temperature.

The relevant thermal parameters, such as $\Delta G^{\circ}_{\mathrm{m}}$, $\Delta H^{\circ}_{\mathrm{m}}$ and $\Delta S^{\circ}_{\mathrm{m}}$, can be obtained assuming the mass action model [16]. According to this model the relations among thermal functions are as follows

$$\Delta G^{\circ}_{\mathrm{m}} = (2-\beta)RT\ln cmc \tag{1}$$

$$\Delta H^{\circ}_{\mathrm{m}} = \left[\frac{\partial(\Delta G^{\circ}_{\mathrm{m}}/T)}{\partial(1/T)}\right] \tag{2}$$

$$\Delta S^{\circ}_{\mathrm{m}} = \frac{\Delta H^{\circ}_{\mathrm{m}} - \Delta G^{\circ}_{\mathrm{m}}}{T} \tag{3}$$

where the *cmc* is the molality of the surfactant solution at *cmc*. The temperature dependence of the thermal parameters $\Delta G^{\circ}_{\mathrm{m}}$, $\Delta H^{\circ}_{\mathrm{m}}$ and $\Delta S^{\circ}_{\mathrm{m}}$ is shown in Fig. 3.

The temperature dependence of ln*cmc* was fitted to a second order polynomial curve to derive relevant values from Eqs (1)–(3). The micellization process is exothermic and $\Delta G^{\circ}_{\mathrm{m}}$ is negative in the whole temperature range studied as seen in Fig. 3. On the other hand, the entropy of micellization is positive in the low temperature range, but decreases with temperature.

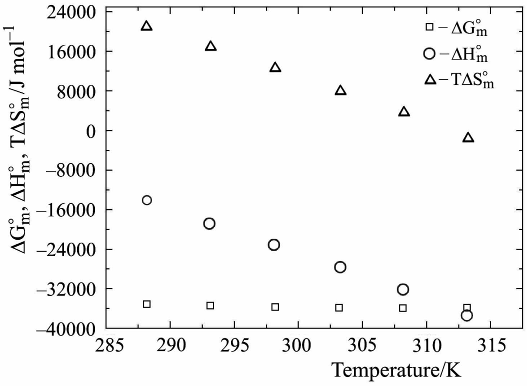

Fig. 3 Temperature dependence of $\Delta G^{\circ}_{\mathrm{m}}$, $\Delta H^{\circ}_{\mathrm{m}}$ and $T\Delta S^{\circ}_{\mathrm{m}}$ for C12DEABr

The apparent change in heat capacity of the surfactant upon micellization can be estimated from data of $\Delta H^\circ_\mathrm{m}$ using the following relation

$$\Delta C^\circ_\mathrm{p,m} = \left(\frac{\partial \Delta H^\circ_\mathrm{m}}{\partial T}\right)_\mathrm{p} \tag{4}$$

the results yield a value of –867 J mol^{-1} K^{-1}. According to some authors [17–19] the values of $\Delta C^\circ_\mathrm{p,m}$ estimated from Eqs (2) and (4) show better agreement with calorimetric data when the ionization degree of the micelles is neglected. In our case such an approach leads to a $\Delta C^\circ_\mathrm{p,m}$ value of –471 J mol^{-1} K^{-1}.

Several chemical processes exhibit a linear relation between $\Delta H^\circ_\mathrm{m}$ and $\Delta S^\circ_\mathrm{m}$. This phenomenona is known as enthalpy-entropy compensation [15, 19]. The enthalpy-entropy compensation are shown for the present compound in Fig. 4.

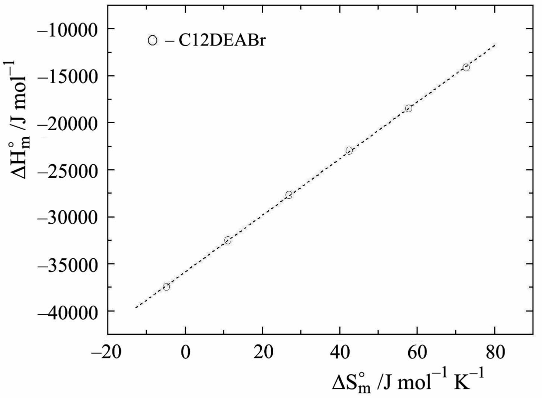

Fig. 4 Enthalpy-entropy compensation plots for C12DEABr

In general the compensation effect can be described by the relation

$$\Delta H^\circ_\mathrm{m} = \Delta H^*_\mathrm{m} + T_\mathrm{c}\Delta S^\circ_\mathrm{m} \tag{5}$$

where T_c is the so-called compensation temperature and $\Delta H^\circ_\mathrm{m}$ is the intercept. T_c for the present system amounts to 301±3 K in satisfactory agreement with the value of 308±4 K reported by Chen *et al.* [15] for homologous alkyltrimethylammonium bromides.

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