Colloid Polym Sci (2002) 280: 503–508
DOI 10.1007/s00396-001-0635-2

ORIGINAL CONTRIBUTION

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Micellization of decyl- and dodecyldimethylbenzylammonium bromides at various temperatures in aqueous solutions

Received: 13 June 2001
Accepted: 9 November 2001

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Abstract Electrical conductivity and density measurements of aqueous solutions of decyl- and dodecyldimethylbenzylammonium bromides have been determined at various temperatures. From these data the critical micelle concentration (cmc) and the degree of ionization of the micelles were determined. The standard free energy of the micellization process and the minima of the temperature dependent values of the cmc were estimated. From the density data the apparent molal volumes of the monomeric and micellized surfactants as well as the contributions of the methylene and phenylene groups were estimated.

Keywords Alkyldimethylbenzylammonium bromides · Critical micelle concentration · Conductivity · Density · Temperature dependence

Introduction

While the technological and medicinal uses of long-chain alkyldimethylbenzylammonium salts as antiseptics, disinfectants and components in preparations for controlling plant diseases are extensive [1], little is known about their fundamental properties in aqueous solutions. Recently we presented a survey of the literature on micellar properties of decyl-, dodecyl-, tetradecyl- and hexadecyldimethylbenzylammonium chlorides [2], and reported our results on light scattering [3], conductivity, density and ultrasound measurements of these surfactants in the premicellar and postmicellar concentration ranges [3, 4, 5, 6].

Here we present our results on conductivity and density measurements of decyl- and dodecylbenzyldimethylammonium bromides (C10BBr and C12BBr) in aqueous solutions at various temperatures and we confront them with relevant literature data.

Experimental

Materials

C12BBr was obtained from Fluka with a purity of 99% or greater and was used without further purification. C10BBr was synthesized by carrying out the quaternization reaction of stoichiometric amounts of benzyldimethylamine and decyl bromide in a double volume of ethyl alcohol at 80 °C. The mixture was kept at this temperature in a stoppered bottle for 3 days. The solvent was then removed in a vacuum rotatory evaporator and the residue was recrystallized several times from acetone. Karl-Fischer titration indicated that the air-dried salt exists as a monohydrate. Potentiometric determination of the bromide anion content in the monohydrate showed a purity of above 99%.

Methods

All the measurements were performed using distilled water with conductivity below 3 μScm^{-1} at 25 °C. Conductivity measurements were performed using a Kyoto Electronics type CM-117 conductometer and a Kyoto Electronics type K-212 cell. The cell constant was determined in the appropriate concentration range according to the procedure suggested by Monk [7]. The measuring cell and the sample were immersed in a thermostat bath, which maintained the temperature to within ±0.05 °C. The measurements of the conductivity for C10BBr and for C12BBr were carried out by continuous dilution of a concentrated sample.

Density measurements were performed using an Anton Paar DMA 60/602 vibrating tube densimeter with a resolution of 10^{-6} gcm^{-3}. The water and the solutions were properly degassed using an ultrasound unit. The temperature of the fluid was measured with an Anton Paar DT100-20 or DT100-30 thermometer and was kept constant within ±0.005 °C. Solutions of the surfactants were made by weight.

Results and discussion

Specific conductivity against molality plots for C10BBr, in the temperature range from 5 to 35 °C and for C12BBr, in the temperature range from 15 to 35 °C, are shown in Figs. 1 and 2, respectively.

The breaks in the molality against conductivity plots presented in Figs. 1 and 2 are generally attributed to the commencement of micelle formation. The values of the critical micelle molality, m_{cmc}, of the surfactants were estimated from the intersection of two linear fragments, above and below the break, for each temperature. 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 behaviour indicates that micelles of smaller aggregation number and/or higher degree of ionization, β, are formed at higher temperatures. The degree of ionization of the micelles, estimated from the ratio of the slopes of the two intersecting lines [8, 9], increases with temperature as expected. In accordance with the charged pseudo-phase separation model [10], the standard free energy of micellization, $\Delta G_{\mathrm{m}}^{0}$, was calculated from the relation

$$\Delta G_{\mathrm{m}}^{0} = (2-\beta)RT\ln X_{\mathrm{cmc}}, \qquad (1)$$

where X_{cmc} is the cmc value expressed in mole fraction. The temperature- dependent values of m_{cmc}, β and $\Delta G_{\mathrm{m}}^{0}$ for C10BBr and C12BBr are collected in Table 1.

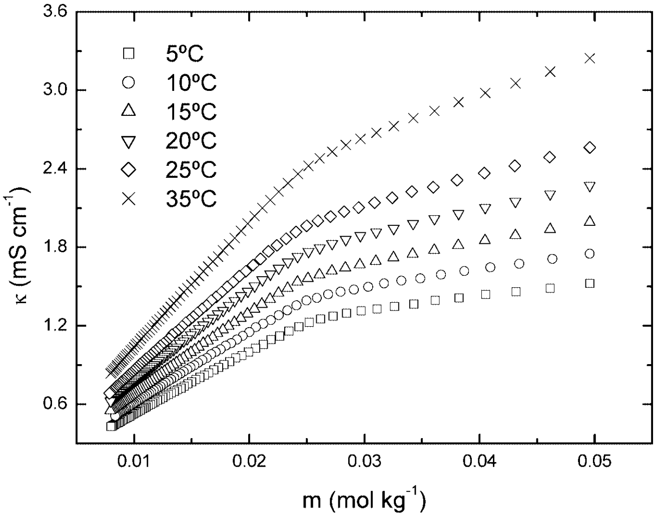

Fig. 1. Temperature dependence of specific conductivity versus molality of decyldimethylbenzylammonium bromide (*C10BBr*)

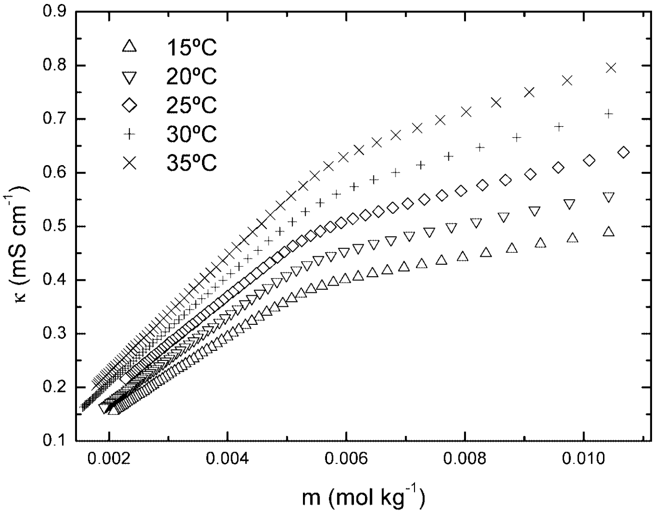

Fig. 2. Temperature dependence of specific conductivity versus molality of dodecyldimethylbenzylammonium bromide (*C12BBr*)

The results show the typical U-shaped temperature dependence of the critical micelle concentration (cmc). Such a phenomenon was observed on several occasions, and was recently reviewed by Muller [11]. A minimum of the cmc, t_{min}, occurs at around 25 and 20 °C for C10BBr and C12BBr, respectively, and support the findings of Zielinski et al. [12] for alkyltrimethylammonium bromides and of González-Pérez et al. [6] for alkyldimethylbenzylammonium chlorides, that the minimum of the cmc is shifted to lower temperature with an increase of

Table 1. Values of the critical micelle concentration (*cmc*), the degree of ionization of the micelles, β, and the standard free energy of micellization ΔG_{m}^{0}, of decyldimethylbenzylammonium bromide (*C10BBr*) and dodecyldimethylbenzylammonium bromide (*C12BBr*) at different temperatures

t (°C)	m_{cmc} (mmolkg^{-1})	β	ΔG_{m}^{0} (kJmol^{-1})
C10BBr			
5	25.6	0.22	–31.6
10	25.1	0.24	–32.0
15	24.4	0.26	–32.2
20	24.2	0.27	–32.6
25	24.1	0.31	–32.3
35	25.3	0.32	–33.0
C12BBr			
15	5.5	0.28	–38.1
20	5.4	0.29	–38.6
25	5.5	0.30	–39.0
30	5.6	0.31	–39.3
35	5.8	0.32	–39.6

the length of the alkyl chain. The minima for the corresponding C10BCl and C12BCl salts were reported to occur at 30 and 25 °C, respectively [4], thus reinforcing the view that the minimum of the cmc for ionic surfactants passes to lower temperatures upon increasing the hydrophobicity of the cation and anion as well [4]. The recent finding of Yamabe et al. [13] that the cmc values of perfluorodecyl-*N*,*N*,*N*-trimethylammonium chloride surfactant have a shallow minimum around 15 °C, whereas the cmc values of the dodecyl homologue increase monotonically with temperature over the temperature range from 15 to 55 °C fits well to the previously described view and indicates that the latter surfactant should have a minimum cmc value just below 15 °C.

The m_{cmc} values for the bromides studied are self-consistent in the sense that the factor by which they decrease upon adding one methylene group to the alkyl chain amounts, at 25 °C, to 2.095 and compares well with the factor of 2.105 found for the corresponding chlorides [6], thus conforming to the empirical rule of Stauff [14] and Klevens [15].

The standard free energies of micellization for the homologous salts reported in Table 1 show that at 25 °C the difference per mole of methylene groups in the alkyl chain amounts to 3.31_5 kJ. It is worth mentioning that the surfactants with the more hydrophobic bromide counterion have m_{cmc} values which are lower by a factor of 1.62 and 1.60 when compared with those found for C10BCl and C12BCl, respectively [4]. The difference in hydration of the two counterions is also reflected by higher degrees of ionization (by a factor of around 1.5 at 25 °C) of the micelles in the chloride form. It is worth noting that at low temperatures the degree of ionization of the micelles of C10BBr appears to be slightly lower compared with the values found for C12BBr (Table 1). This effect presumably may be due to the neglect of activity coefficients for the ionic species in the premicellar concentration range, which for C10BBr amounts to 25 mmolkg^{-1}. Some premicellar association processes at the nonelevated temperatures cannot be excluded as well. The m_{cmc} value reported here for C12BBr agrees satisfactorily with the value of 5.52 mmolkg^{-1} estimated conductometrically by Adderson and Taylor [16] and the cmc value of 5.6 mmoldm^{-3} estimated by Trompette et al. [17] from surface tension data.

Knowledge of the temperature dependence of the cmc and β of the salts enables calculation of the enthalpy of micellization from the Gibbs–Helmholtz relation [18]. The $(\partial \ln X_{\text{cmc}}/\partial \text{T})_{\text{P}}$ term was calculated for C12BBr by fitting the $\ln X_{\text{cmc}}$ versus T data to a second-order polynomial and differentiation. The $(\partial\beta/\partial T)_P$ term was assumed to be constant in the temperature range studied. TheΔH_{m}^0 value calculated in this way amounts for C12BBr, at 25 °C, to –17.2 kJmol^{-1} This value is distinctly lower compared to the calorimetrically determined value of –5.3 kJmol^{-1} reported by Zajac et al. [19]. It should be noted that the estimated values of ΔH_{m}^0 appear to be strongly dependent on the magnitude of the $(\partial\beta/\partial T)_P$ term. Neglecting this term and assuming that β is constant in the temperature range studied and amounts to 0.30 leads to a $DeltaH_{\text{m}}^0$ value of –3.6 kJmol^{-1}. The corresponding value for C10BBr (at $\beta = 0.275$) amounts to –2.18 kJmol^{-1}.

The results of the density measurements are presented in the form of ρ–ρ_0 against molality plots, where ρ_0 is the density of pure water at the appropriate temperature of 15, 25 and 35 °C for C10DBABr (Fig. 3) and at 15, 20 and 25 °C for C12DBABr (Fig. 4).

In contrast to what has been observed for C10BCl and C12BCl [4, 6], the ρ–ρ_0 values for the corresponding bromides are positive over the whole molality and temperature ranges studied as in the case of other quaternary ammonium bromides [20, 21, 22, 23]. The insert in Fig. 3 serves as a guide for the eye to demonstrate more clearly the change of slopes on the ρ–ρ_0 against molality plots. The breaks are exemplified for the data at 25 °C. Analysis of the linear plots obtained at 25 °C in the premicellar and postmicellar ranges reveals breaks which occur at 26 and 5.4 mM for C10BBr and C12BBr, respectively. These values are close to the m_{cmc} values determined from the breaks in the conductivity against molality plots.

We estimated the apparent molal volumes, V_ϕ, of the bromides studied using the relation

$$V_\phi = \frac{M}{\rho} + 10^3 \frac{(\rho_0 - \rho)}{\rho\rho_0 m} \quad , \tag{2}$$

where M is the molecular mass of the solute and m is the molality of the surfactant. In the premicellar region the system may be described by the relation of Redlich and Rosenfeld [24]:

$$V_\phi = V_\phi^0 + A_v m^{\frac{1}{2}} + B_v m \quad , \tag{3}$$

where V_ϕ^0 is the apparent molar volume at infinite dilution, A_v is the Debye–Hückel limiting law coefficient and B_v is an adjustable parameter. For electrolytes of type 1:1, A_v is 1.696, 1.781, 1.865 and 2.04 $\text{cm}^3\text{kg}^{1/2}\text{mol}^{-3/2}$ at 15, 20, 25 and 35 °C respectively [25]. The temperature-dependent values of $V_\phi^0$for C10BBr and C12BBr are shown in Table 2 together with the results found earlier for the chloride analogues [2, 4].

Comparison of the data for the bromides and chlorides at 25 °C shows a difference of 6.7 and 7.9 $\text{cm}^3\text{mol}^{-1}$ for the decyl and the dodecyl salts, respectively. The former value is in good agreement with that of 6.9 $\text{cm}^3\text{mol}^{-1}$ resulting from comparison of the conventional partial molal volumes of the bromide and chloride ions in water reported by Millero [25]. The higher value found for the dodecyl analogues is due presumably to the lower accuracy of the data collected below the cmc.

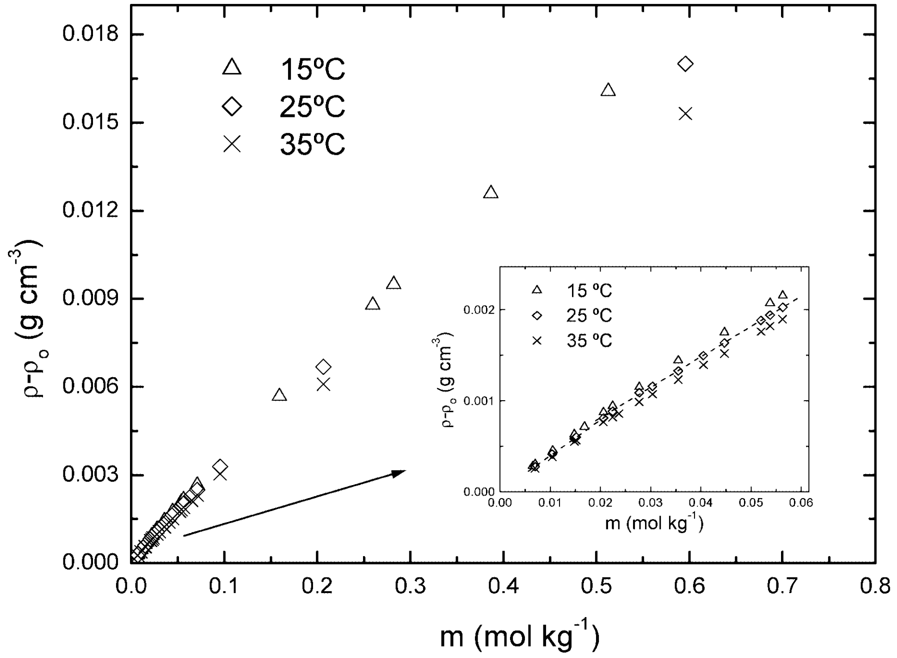

Fig. 3. Density against molality plot for C10BBr at 15, 25 and 35 °C

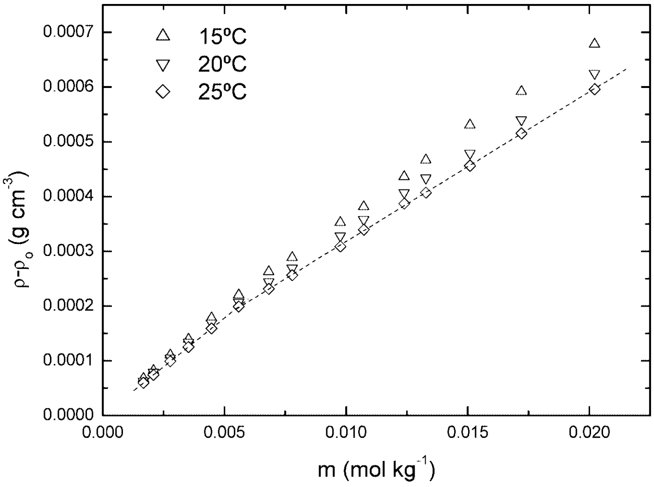

Fig. 4. Density against molality plot for C12BBr at 15, 20 and 25 °C

Table 2. Temperature dependence of the apparent molal volumes at infinite dilution, $V_\phi^0$of C10BBr, C12BBr, decyldimethylbenzylammonium chloride (*C10BCl*) [2] and decyldimethylbenzylammonium chloride (*C12BCl*) [4]

T (°C)	V_ϕ^0 (cm^{3}mol^{-1})			
	C10B$^+$		C12B$^+$	
	Cl$^-$	Br$^-$	Cl$^-$	Br$^-$
15	307.2	312.6	335.6	344.6
20	–	–	338.9	347.2
25	310.7	317.4	341.6	349.5
35	314.3	321.1	–	–

The contribution to the apparent molal volume at infinite dilution of 1 mol of methylene groups calculated from the data for C12BBr and C10BBr amounts to 16.05 cm^3 and compares well with the generally accepted value of 16.0 cm^{3}mol^{-1} found for various homologous compounds [26]. In view of the expected additive character of the apparent molal volumes of the surfactants with respect to the chain length of homologous salts and to the type of counterion, it appears that the set of data in Table 2 may attain self-consistency when the correct value of V_ϕ^0 for C12BCl is assumed to amount to 342.6 cm^{3}mol^{-1}. In such a case, the contribution of the methylene group to the apparent molal volumes of the two chlorides would amount to 16.05 cm^{3}mol^{-1}, whereas the difference in the volumes of the dodecyl surfactants with bromide and chloride counterions would be 6.9 cm^{3}mol^{-1} as expected. Assuming again the additivity rule for the apparent molal volumes and taking into account the charged pseudo-phase separation model, we can estimate the apparent molal volumes of the micelles by applying equations derived earlier [4].

$$V_\phi = (V_\mathrm{f} + V_\mathrm{c}) \qquad m \le m_\mathrm{cmc}, \tag{4}$$

$$V_\phi = \left(\frac{V_\mathrm{m}}{N_\mathrm{agg}} + \beta V_\mathrm{c}\right) - \left(\frac{V_\mathrm{m}}{N_\mathrm{agg}} + (\beta - 1)V_\mathrm{c} - V_\mathrm{f}\right)\frac{m_\mathrm{cmc}}{m} \qquad m \ge m_\mathrm{cmc}, \tag{5}$$

where N_agg is the aggregation number, and V_m' V_f and V_c denote the apparent molal volume of the micelles, the

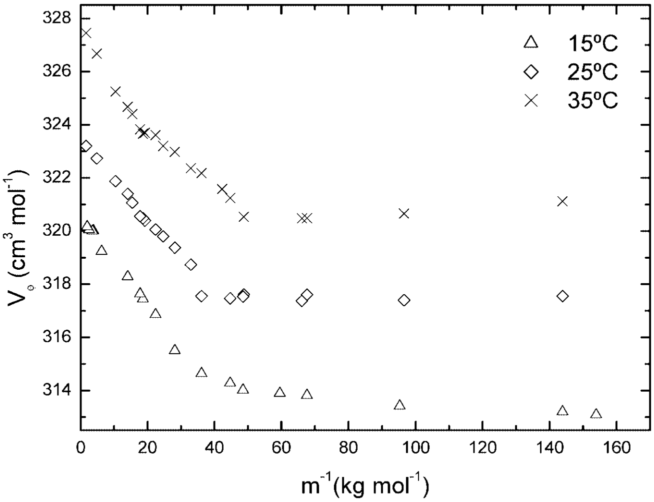

Fig. 5. Apparent molal volumes as a function of the inverse of the molality for C10BBr at 15, 25 and 35 °C

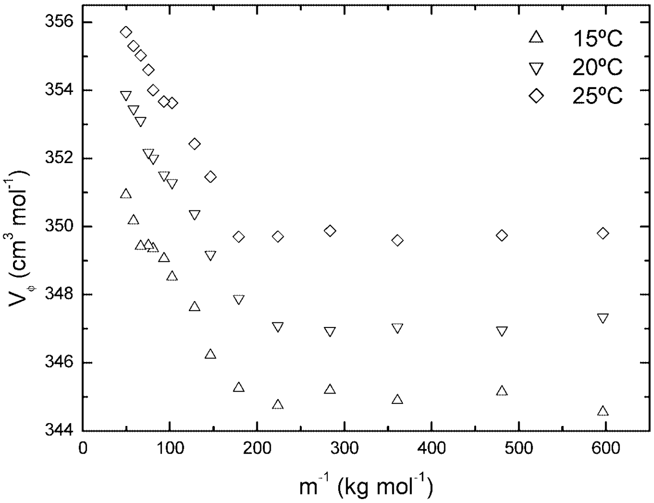

Fig. 6. Apparent molal volumes as a function of the reverse of the molality for C12BBr at 15, 20 and 25 °C

Table 3. Temperature dependence of the apparent molal volumes at the cmc, V_ϕ^{cmc}, and the difference between the limiting value and the apparent molal volume at the cmc, $\Delta V_\phi^{\mathrm{m}}$, for C10BBr and C12BBr

T (°C)	C10BBr		C12BBr	
	V_ϕ^{cmc} (cm^{3}mol^{-1})	$\Delta V_\phi^{\mathrm{m}}$ (cm^{3}mol^{-1})	V_ϕ^{cmc} (cm^{3}mol^{-1})	$\Delta V_\phi^{\mathrm{m}}$ (cm^{3}mol^{-1})
15	313.7	6.8	344.9	7.7
20	–	–	347.7	8.2
25	317.1	6.3	349.8	8.1
35	321.1	5.9	–	–

cations and the counterions, respectively. The temperature-dependent apparent molal volumes, V_ϕ, are plotted against the inverse of molality for C10BBr and C12BBr in Figs. 5 and 6. According to Eq. (4), V_ϕ should be constant below the cmc as can be seen in the figures. The apparent molal volume of the surfactant salt at the cmc, V_ϕ^{cmc}, as well as the change in the apparent molal volume upon micellization, $\Delta V_\phi^{\mathrm{m}}$, may be estimated by applying Eq. (5). The relevant results for C10BBr and C12BBr are collected in Table 3.

As usual, the change in the apparent molal volumes of the surfactants upon micellization is positive. Compared with the chlorides, the bromides do not exhibit marked temperature dependence of $\Delta V_\phi^{\mathrm{m}}$.

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