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ORIGINAL CONTRIBUTION

J.L. del Castillo
J. Czapkiewicz
J.R. Rodríguez
B. Tutaj

Micellar properties of alkyldimethylphenylammonium bromides in water

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J.L. del Castillo (✉) · J.R. Rodríguez
Universidad de Santiago de Compostela
Facultad de Física, Departamento de Física
de la Materia Condensada
E-15706 Santiago de Compostela, Spain

J. Czapkiewicz · B. Tutaj
Jagiellonian University
Faculty of Chemistry
Ingardena 3, 30-060 Krakow, Poland

Abstract The synthesis and methods applied for the purification of dodecyl-, tetradecyl-, and hexadecyldimethylphenylammonium bromides are described. The results of surface tension measurements of aqueous solutions of these surfactants show that slight amounts of strongly surface-active nonionic impurities are persistent in the crystalline materials presumably due to their low thermal stability. The Critical micelle concentration (cmc) and the degree of ionization (β) of the micelles of the salts studied in aqueous solutions were determined at 25 °C from specific conductivity versus molality plots. The temperature dependence of the cmc and of β of the tetradecyl homologue was measured in the range 4–34 °C. A minimum cmc amounting to 1.20 mmol/kg was determined at about 14 °C. The values of β were found to grow linearly with temperature. From these results, the standard Gibbs energy, the enthalpy and the entropy of the process of micellization were obtained by application of the pseudo-phase-separation model. Enthalpy and entropy show a compensation effect in their contribution to the Gibbs energy. At low temperatures the process of micellization is driven mainly by the entropic term, whereas with increasing temperature the enthalpic term becomes predominant. At the temperature of the minimum cmc, the value of the enthalpy is far from being zero because of the important contribution of the $(\partial\beta/\partial T)R \ln X_{\mathrm{cmc}}$ term.

Key words Alkyldimethylphenylammonium bromides – Conductivity – Critical micelle concentration – Degree of ionization – Temperature dependence

Introduction

Fundamental research on cationic surfactants is quite intensive due to the fact that they can be easily synthesized [1]. It is generally accepted that they can be easily purified as well. Among the most thoroughly studied surfactants are long-chain alkyltrimethylammonium, dialkyldimethylammonium, alkyldimethylbenzylammonium and alkylpyridinium halides [1–4].

Little attention, however, has been paid to quaternaries with a phenyl group at the nitrogen atom, i.e. to long-chain alkyldimethylphenylammonium halides. An early paper of Cella et al. [5] reports the synthesis and critical micelle concentration (cmc) of dodecyldimethylphenylammonium chloride. Bunton et al. [6] describe the synthesis of hexadecyldimethylphenylammonium bromide and its dimethoxy derivative and report their cmc values and the catalytic efficiency of the micelles. Quite recently a detailed ^{1}H NMR study of the aggregation of the corresponding chloride in D_2O has been reported [7, 8]. On basis of the ^{1}H NMR chemical shifts, the authors calculated the equilibrium constant for micelle formation and the cmc in D_2O. Analysis of the results led them to suggest that the phenyl group in the micelles is oriented perpendicularly to the interface where its freedom of motion is severely restricted, similar to the case of the heterocyclic ring in alkylpyridinium halides. Furthermore, they determined the cmc value of the chloride by surface tension measurements in H_2O.

In this paper we describe the synthesis and purification of dodecyl- (DBr), tetradecyl- (TBr) and hexadecyldimethylphenylammonium (CBr) bromides and present results of surface tension and conductivity studies of their aqueous solutions. The temperature dependence of the conductivity of TBr was studied in detail in the range 4–34 °C.

Experimental

Surfactants

The general procedure adopted was as follows. A mixture of 0.2 mol *N*,*N*-dimethylaniline and 0.16 mol of the appropriate alkyl bromide (Koch-Light) in 100 cm^3 of absolute ethanol was heated to boiling and, while hot, the flask was tightly stoppered and kept in a thermostat at 80 °C for 70 h (on some occasions the solution turned blue with time presumably due to partial oxidation of dimethylaniline). Ethyl alcohol was then distilled off in a vacuum rotatory evaporator. To enhance complete removal of the alcohol, the residue was dissolved in 50 cm^3 2-butanone and the solvent was distilled off again. The crude material was then dissolved in warm acetone and traces of the scarcely soluble dimethylanilinium hydrobromide were filtered off and discarded. Copious amounts of the surfactant were obtained upon cooling the filtrate. It was then recrystallized from acetone several times. TBr and CBr were additionally recrystallized from water. TBr crystallized in the form of a monohydrate as determined by the Carl Fischer method and had a melting point (m.p.) of 74–76 °C whereas CBr had a m.p. of 116–118 °C in accordance with previous reports [6, 7]. Electrospray mass spectrometry of DBr revealed some amounts of dimethylaniline and negligible amounts of the tetradecyl and hexadecyl homologues. The well-defined crystals of DBr and TBr appeared to be impure judging by the opalescence which developed with time in the aqueous solutions at room temperature. CBr always yielded optically pure solutions presumably due to the efficient solubilization of the impurities in the micellar system. Prolonged extraction of TBr with ethyl ether in a Soxhlet apparatus did not improve the situation. DBr could not be purified in this manner because it appeared to swell in diethyl ether. We assumed that traces of dimethylaniline and of alkyl bromides and/or alcohols in the crystalline surfactants were responsible for the observed opalescence of the solutions. Substantial amounts of such impurities were removed in three ways.

1. By repeated contact of the aqueous solution of the cationic surfactant with *n*-heptane followed by boiling out the solubilized hydrocarbon.
2. By triturating the gelly material (formed by adding a small amount of water to the crystalline bromide) with *n*-heptane, followed by vacuum evaporation, drying over P_2O_5 and recrystallization from acetone.
3. By steam distillation (or heating to boiling) of the aqueous solution of the quaternary ammonium salts.

The last method appeared to be most simple and effective. CBr and TBr were recovered by cooling the aqueous solutions and were repeatedly recrystallized from acetone and water. DBr was recovered by removing water in a vacuum evaporator while keeping the temperature of the water bath below 50 °C. The residue was then dried over P_2O_5, recrystallized from acetone and finally dried under vacuum at room temperature. Electrospray mass spectroscopy did not reveal the presence of dimethylaniline in the purified materials and their solutions were optically pure.

Measurements

Solutions of the surfactants were made by weighing. Surface tensions of the aqueous solutions were measured at 25 °C using a Krüss model K12 digital tensiometer by the Wilhelmy plate method. Conductivities were measured using a Kyoto Electronics conductometer (model CM-117) and an Elmetron CX-732 conductometer. The cell constants were determined using KCl solutions [9].The temperature was controlled using a thermostated bath with temperature variations of less than 0.1 °C. Two procedures for the measurement of the temperature and the concentration dependence of the conductivity were applied. In one series of experiments weighed amounts of concentrated solutions of the surfactants of known molalities were stirred continuously and the conductivities were measured at constant temperature while the solutions were successively diluted by adding pre-determined amounts of water from a Metrohm 665 Dosimat. In the second series (applied for TBr) solutions of known molalities were cooled in the bath and, while being continuously stirred, their conductivities were measured stepwise in the temperature range 4–34 °C. Appropriate corrections were made for the conductivity of pure water in the temperature range studied.

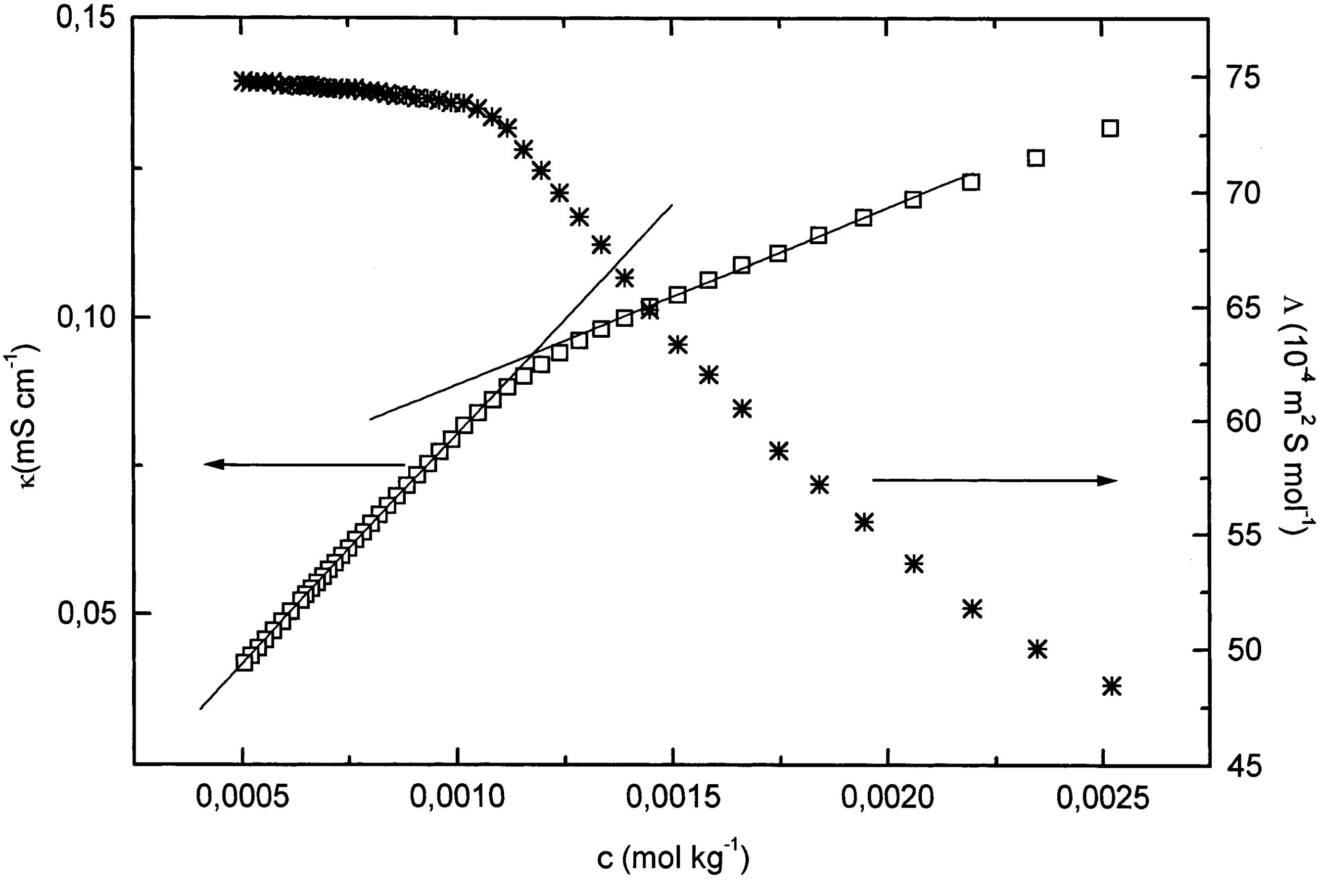
Electrospray mass spectrometry was performed on a Finnigan Mat 95S instrument by the Regional Laboratory of Physico-Chemical Analyses in Krakow.

Results and discussion

Samples of DBr purified in a standard way and additionally by applying the methods described earlier, yielded isotherms with a surface tension of about 38 mN/m in the micellar concentration range, a shallow minimum at a molality of about 5 mmol/kg and a hump (in the region of 42 mN/m) on the steep course of the isotherm in the premicellar concentration range. Surface tension measurements of aqueous solutions of a sample of TBr, purified in a standard way, i.e. by multiple recrystallizations from acetone and extraction with diethyl ether in a Soxhlet apparatus yielded at 25 °C an isotherm with a value of about 34 mN/m in the micellar range. Upon dilution a minimum in the surface tension occurred at a molality of about 1.3 mmol/kg. Additional purification, as described in the Experimental section, led to micellar solutions whose surface tension amounted to 38 mN/m. A minimum, however, could still be detected at about 1.3 mmol/kg. At lower concentrations, initially, the rate of increase of the surface tension was not as high as that found for surface tension in the region 42–50 mN/m. We ascribe this phenomenon to the existence of minute amounts of a strongly surface-active impurity (tetradecyl bromide and/or alcohol) which had been solubilized in the micelles and which subsequently formed microdroplets of a second phase just below the cmc. Upon dilution, the distinct contribution of this impurity to the lowering of the surface tension is, at first, constant and vanishes only when its concentration drops below its solubility limit in the system. Micellar solutions of CBr exhibited exceedingly low surface tensions amounting to 21 mN/m at the minimum which occurred at a concentration of 0.3 mmol/kg. We presume that the persistent minute amounts of impurities found in the samples of the surfactants studied are formed during the purification procedure, i.e. they are due to slight thermal decomposition of the quaternary ammonium salt when steam distillation and vacuum evaporation procedures are applied. High purity samples of cationics appear to be difficult to attain not only in our case. Rosen et al. [10] reported surface and derived thermodynamic properties of classical surfactants such as *N*-dodecylpyridinium bromide and chloride only after multiple recrystallizations of the salts from organic solvents followed by repeated passage of the aqueous solutions through columns of octadecylsilinized silica gel. No attempt was made by the authors to recover the purified salts in a crystalline form and their concentration in solutions was determined by UV spectroscopy. We have not applied this procedure for purification of our samples and consequently we do not report our detailed surface tension data. We should like, however, to stress that we estimate that the bulk properties of our systems studied through conductivity are not affected by the minute amounts of impurities. We place, however, less reliance on the values determined for DBr because its Krafft point is around 0 °C and thus the surfactant could not be additionally purified by recrystallization from water.

Our conductivity results are illustrated in Fig. 1 where a typical plot of specific conductivity versus molality and a corresponding plot of equivalent conductivity versus molality measured for TBr at 15 °C are presented. The marked breakpoints that occur on the plots are treated as an indication of the onset of micellization. Following the generally accepted procedure, least-squares analysis was carried out for the linear fragments on the plots of conductivity versus molality and the point of their intersection was used for the estimation of the cmc. The ratio of the slopes of the linear plots in the premicellar and postmicellar molality ranges was taken as the degree of ionization, β, of the micelles. Our conductivity data were always checked by examining the equivalent conductivity versus molality

Fig. 1 Specific, κ, and equivalent, Λ, conductivities versus molality of tetradecyldimethylphenylammonium bromide (*TBr*) at 15 °C



plot in the premicellar concentration range and extrapolating it to zero concentration. Humps appeared occasionally on the DBr plots whenever the sample was vacuum dried at elevated (above 40 °C) temperatures: such results were discarded. An estimation of the limiting equivalent conductivity also served as a convenient check of the purity of the surfactant and of the correctness of the concentrations applied. The cmc and β values determined for DBr, TBr and CBr at 25 °C are presented in Table 1 together with available literature data for alkyldimethylphenylammonium halides. The cmc values found for the three homologous bromides, fitted to the relation of Stauff [11] and Klevens [12], $\log \mathrm{cmc} = A - Bn$, where A and B are constants and n is the number of carbon atoms in the hydrocarbon chain, yield values for A and B equal to 1.34 and 0.303, respectively, with a correlation factor of 0.9999. The B value is in conformity with values found for typical quaternary ammonium long-chain electrolytes [3, 4].

We will now discuss the results of our studies on the temperature dependence of the cmc for TBr. The conductivities measured for a set of solutions, of indicted molalities, as a function of temperature are presented in Fig. 2. Included is the curve denoted by S, showing the temperature dependence of conductivities of saturated solutions of TBr . It is seen that only a few conductivity results in the low-temperature region of micellar solutions fall into the range of metastable systems. In the premicellar concentration range the conductivities of aqueous solutions of TBr increase linearly with temperature. The whole set of these results, expressed in the form of equivalent conductivities, Λ, fits very well to the Walden relation ($\Lambda\eta = \text{constant}$) when the temperature dependence of the viscosity of water, η is taken into account. At higher concentrations, above the cmc, the rate of increase of conductivity grows with temperature, mainly due to the increase in the degree of ionization of the micelles shown in Fig. 3. The temperature dependence of β can be expressed by the empirical relation

$$\beta = -0.5141 + 0.00294T(\mathrm{K}). \qquad (1)$$

Table 1 Critical micelle concentration (*cmc*) and degree of ionization of micelles of alkyldimethylphenylammonium halides at 25 °C

Surfactant	cmc (mmol/kg)	β
DBr	5.0[a]	0.45
DCl	7.65[b]	
TBr	1.28[a]	0.36
CBr	0.306[a]	0.3
	0.27[c]	
CCl	0.8[d]	

[a] Present results
[b] Ref. [5]
[c] Ref. [6]
[d] Ref. [7]

The cmc values derived from the collection of data, exhibit the typical temperature dependence found for ionic and nonionic surfactants [13–19] as shown in Fig. 4 where the minimum for TBr is at around 14 °C. Quite recently Muller [20] has derived an equation relating the temperature dependence of the cmc to the value of the cmc* at the temperature of the minimum T^*:

$$\ln(\mathrm{cmc}/\mathrm{cmc}^*) = \frac{\Delta C_p}{(2-\beta)R}[1 - T^*/T + \ln(T^*/T)], \qquad (2)$$

where ΔC_p is the change in heat capacity for the micellization process. The fit of our set of cmc data to this equation is represented by the solid line in Fig. 4.

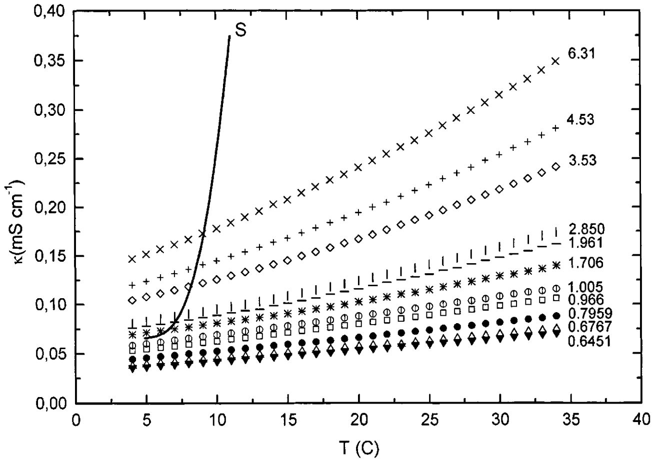


Fig. 2 Temperature and concentration dependence of the specific conductivity of TBr in aqueous solutions. *S* represents the temperature dependence of the conductivity of saturated solutions

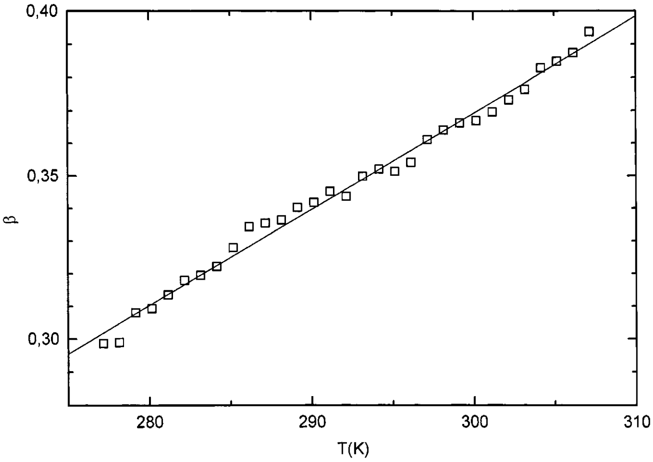


Fig. 3 Temperature dependence of the degree of ionization of TBr micelles

The derived values of cmc*, T^* and $\Delta C_p/(2-\beta)R$ amount to 1.21 mmol/kg, 286 K and −34, respectively. For β equal to 0.35 the latter value yields an estimate of ΔC_p amounting to −466 J/mol K. This value is close to those collected for long-chain quaternary ammonium bromides [20].

On the basis of a charged pseudo-phase-separation model [21], an analysis of the cmc and β values enables the standard Gibbs energy of micellization $\Delta G^\circ_\mathrm{m}$ to be calculated.

$$\Delta G^\circ_\mathrm{m} = (2-\beta)RT\ln X_\mathrm{cmc}, \tag{3}$$

where X_cmc is the cmc expressed in mole fraction. The points in Fig. 5 represent the values of $\Delta G^\circ_\mathrm{m}$ calculated from experimental cmc and β data: the solid line was calculated using Muller's equation (Eq. 2) and the empirical relation (Eq. 1), whereas the dashed line was obtained using a third-order polynomial fit of the cmc versus temperature dependence and Eq. (1) for β. The set of three results shows a smooth decrease of the Gibbs energy with increasing temperature from a value of −42 to −44 kJ/mol. Assuming a charged pseudo-phase-separation model for which the micellar aggregation number does not change with temperature, one can estimate the enthalpic contribution to $\Delta G^\circ_\mathrm{m}$ from the Gibbs–Helmholtz relation

$$\left[\frac{\partial(\Delta G^\circ_\mathrm{m}/T)}{\partial(1/T)}\right]_P = \Delta H^\circ_\mathrm{m} \tag{4}$$

and taking $\Delta G^\circ_\mathrm{m}$ from Eq. (3)

$$RT^2\left[(2-\beta)\left(\frac{\partial\ln X_\mathrm{cmc}}{\partial T}\right)_P - \ln X_\mathrm{cmc}\left(\frac{\partial\beta}{\partial T}\right)_P\right] = -\Delta H^\circ_\mathrm{m}. \tag{5}$$

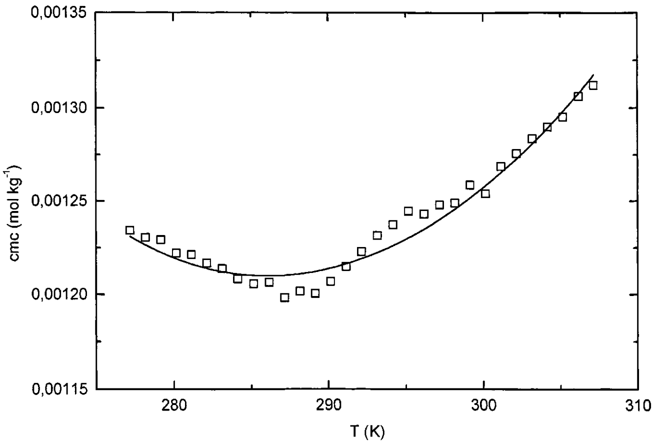


Fig. 4 Temperature dependence of the critical micelle concentration (*cmc*) for TBr

The entropy of the process of micellization of TBr can be calculated from the relation

$$\Delta S^\circ_\mathrm{m} = \frac{\Delta H^\circ_\mathrm{m} - \Delta G^\circ_\mathrm{m}}{T}. \tag{6}$$

The Gibbs energy of micellization and the contributions of the enthalpic and entropic terms are shown in Fig. 6. The compensation of the two terms is clearly seen and such effects have been observed on several occasions [19]. In the low-temperature range entropy dominates the micellization process, whereas when the temperature rises the influence of the enthalpic contribution becomes more important. Our results clearly indicate that at the temperature of the minimum cmc the enthalpy of the process of micellization is far from attaining a zero value. It has frequently been postulated

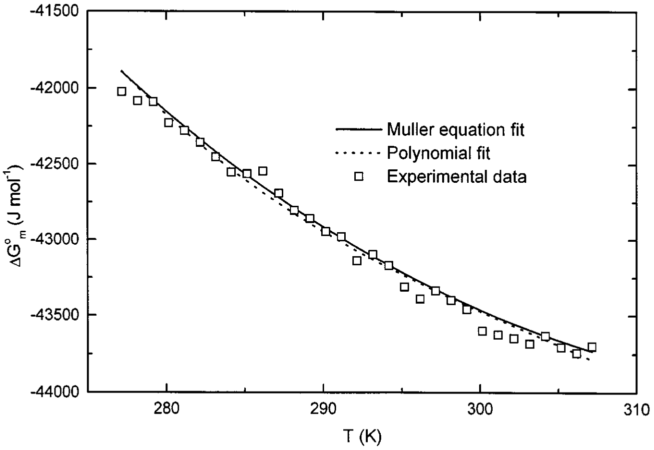


Fig. 5 Standard Gibbs energy of micellization of TBr as a function of temperature

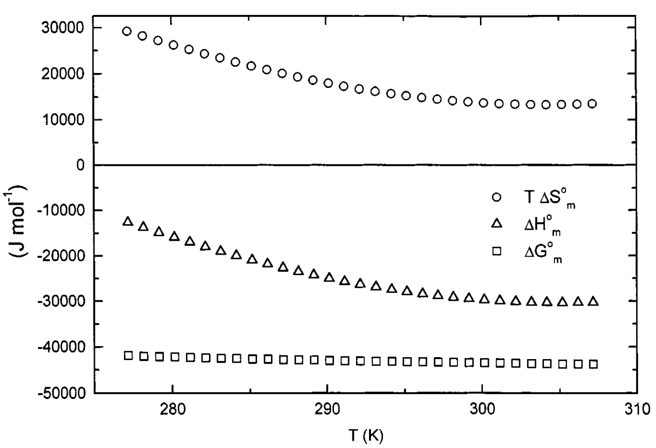


Fig. 6 Enthalpic and entropic contributions to the Gibbs energy of micellization of TBr as a function of temperature

that at T^* the enthalpy is zero. Such an assumption is not correct for ionic surfactants because it neglects the temperature dependence of β as has already been indicated by Matsuoka et al. [22]. The present results show that for TBr, β is strongly temperature dependent, which explains the highly negative value of ΔH°_m found at T^*.

The contributions of the two terms on the left-hand side of Eq. (5) to the total value of ΔH°_m are shown in Fig. 7. It appears that highly negative values of ΔH°_m found for TBr are due to the second term for which the $\partial\beta/\partial T$ value amounts to 2.94×10^{-3}. This value compares well with the corresponding value of 3×10^{-3} reported by Evans et al. [23] for tetradecyltrimethylammonium bromide in the broad concentration range of 25 to 160 °C. These authors assumed an equilibrium between monomers, counterions and monodisperse micelles of the latter salt and derived a value of −28.5 kJ/mol for the enthalpy of micellization in aqueous solution at 25 °C. Note that the value we have found for TBr is −29.2 kJ/mol. Assumption that $\partial\beta/\partial T$ is zero leads to a value of ΔH°_m of only −5.9 kJ/mol which, in turn, is comparable with −4.1 kJ/mol found by Adderson and Taylor [24] for a related salt, namely for dodecylbenzyltrimethylammonium bromide. The literature is abundant with enthalpy of micellization data, estimated under the assumption that the second term in Eq. (5) is negligible. Such an approach leads to positive values of ΔH°_m at sufficiently low temperatures as exemplified in Fig. 7.

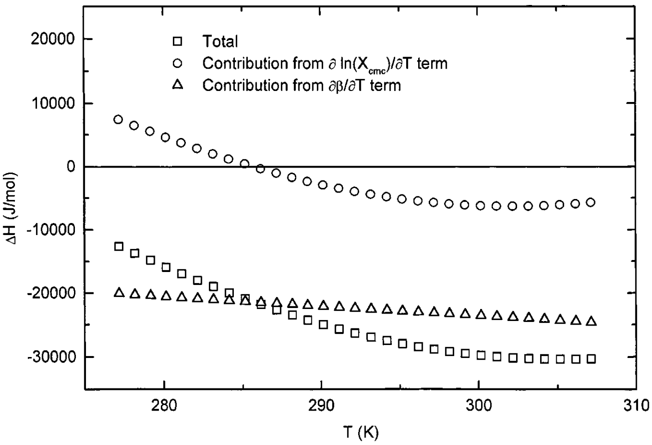


Fig. 7 Enthalpy of micellization as a function of temperature and contributions of the two terms in Eq. (5)

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