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ORIGINAL CONTRIBUTION

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Micellar properties of tetradecyltrimethylammonium nitrate in aqueous solutions at various temperatures and in water-benzyl alcohol mixtures at 25 °C

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Abstract The micellar properties of tetradecyltrimethylammonium nitrate ($C14TANO_3$) in aqueous solutions in the temperature range of 10 to 35 °C and in aqueous solutions of benzyl alcohol (BzOH) at 25 °C were studied conductometrically. The specific conductivity data served for the evaluation of critical micelle concentration, cmc, and the degree of ionization of the micelles, β, of the surfactant. From the temperature dependence of the cmc the thermodynamic parameters for micellization of $C14TANO_3$ were calculated by applying Muller′s modified equation. BzOH was found to affect strongly the cmc and β values of the surfactant. The plot of the cmc/cmc$_o$ ratio (where cmc$_o$ is for pure water) as a function of BzOH molality, exhibits a characteristic break, which was attributed to the commencement of self-association of BzOH in aqueous solution at a molality of ca. 0.05. By applying the theoretical treatment suggested by Motomura for binary surfactant systems, the molar fraction of BzOH in the micelles at cmc, was estimated as a function of molality of the alcohol. $C14TANO_3$ appears to be slightly more hydrophobic compared to the corresponding bromide.

Keywords Tetradecyltrimethylammonium nitrate · Benzyl alcohol · Critical micelle concentration · Mixed micellar system · Conductivity

Introduction

Studies on the influence of type of counter-ion on micellar properties of ionic surfactants were initiated by Samis and Hartley [1] who found that the size of hexadecylpyridinium micelles and the fraction of counter-ions bound, increases in the order: $CH_3COO^- < Cl^- < Br^- < I^-$. This sequence of halide anions was confirmed for dodecylpyridinium micelles by Ford et al. [2]. Emerson and Holtzer carried out light-scattering measurements for n-dodecyltrimethylammonium chloride, bromide and nitrate in aqueous solution containing varying concentrations of NaCl, NaBr and $NaNO_3$ respectively, and found that the micellar weights of the micelles increase in the order $Cl^- < Br^- < NO_3^-$ [3].

A broader series of inorganic counter-ions, based upon decreasing critical micelle concentration, cmc values, was reported by Underwood and Anacker [4]. The authors determined cmc values from light scattering data for decyltrimethylammonium bromide in 0.5000 m NaX aqueous solution, where X represents IO_3^-, F^-, HCO_3^-, $H_2PO_4^-$, CH_3COO^-, $HCOO^-$, Cl^-, BrO_3^-, NO_2^-, N_3^-, Br^-, NO_3^-, ClO_3^-, I^- and SCN^-. These anions are arranged in the order of decreasing cmc values of the surfactant in the presence of the NaX salts. This lyotropic sequence of anions parallels the order found for decreasing energy of transfer of some anions from the aqueous phase to an organic phase of lower polarity, namely 1,2-dichloroethane [5]. In some lyotropic series reported in the literature, the position of the nitrate anion appears to be shifted to the left relative to the bromide anion [6,7,8]. Such differences are of minor importance.

Specific ion effects were found however, to be quite dramatic in the case when simple inorganic anions are replaced by large organic counter-ions (e.g. salicylate or tosilate) [9,10] or in the case of microemulsions as can be exemplified by the phase behaviour of dialkyldimethylammonium/water/alkane mixtures. For the double-long chained surfactant in the form of a bromide, the L_2 phase region is very wide [11], whereas with chloride as counter-ion the L_2 phase is extremely narrow [12]. In both cases the microemulsion region corresponds with oil-in-water structures. When sulfate is used as counter-ion the phase behaviour is reversed [13].

Another example concerns the influence of counter-ion type on the solubility of polyelectrolytes and some surfactants. Chitosan, a highly insoluble hydrophobic polycation material with Cl^- as counter-ion is solubilized in the presence of the CH_3COO^- counter-ion [14]. Didodecyldimethylammonium bromide is soluble in water up to 10^{-4} M, beyond which it forms a lamellar phase. If the bromide counter-ions are replaced with hydroxide, the surfactant is soluble up to 1 M [15].

Similarly, long-chained alkyldimethylbenzylammonium iodides are scarcely soluble in water. However, in the presence of excess of NaCl or KCl they dissolve quite freely and form micelles with a mixed composition of bound counter-ions [16]. An interesting chemical trapping method, that is based on product yields from reaction of an aggregate-bound arenediazonium ion with weakly basic nucleophiles in the interfacial region of the surfactant aggregates, has been developed to estimate the micellar interfacial counter-ion and water concentrations [17].

The counter-ion specificity found for various micellar systems is very intriguing and thus studies in this respect are relevant. In this paper we present results of our conductometric studies of the thermodynamics of micellization of tetradecyltrimethylammonium nitrate ($C14TANO_3$) as a function of temperature and concentration of benzyl alcohol (BzOH) serving as a co-surfactant. We compare the results with literature data for tetradecyltrimethylammonium bromide (C14TABr).

Experimental

Materials

$C14TANO_3$ was prepared by adding dropwise a solution of 0.1 mol of tetradecyltrimethylammonium bromide (Aldrich) in 500 cm^3 of water to a well stirred solution of 0.1 mol $AgNO_3$ dissolved in 400 cm^3 of water. The mixture was left to stand for 2 days in the dark at room temperature and the precipitate of AgBr was then filtered off. The nitrate was recovered from the filtrate by evaporating off the solvent on a water bath. The dry residue was recrystallized three times from acetone. Elemental analysis: calculated for $C_{17}H_{38}N_2O_3$: C, 64,11%; H, 12.03%; and N 8,80%; found: C, 64,12%; H, 12,18% and N 8,89%. BzOH was purchased from Fluka with an assay of >99%. Distilled water with conductivity below 3 μS cm^{-1} at 25 °C was used. The solutions of the surfactant and the alcohol were made by weight.

Methods

The conductivity technique applied for aqueous and water-alcohol solutions was described in [18] and [19] respectively.

Results and discussion

The dependence of specific conductivity of $C14TANO_3$ in aqueous solutions on molality, *m,* was measured at 10, 12, 15, 17, 20, 22, 25, 27, 30 and 35 °C. The Krafft point of $C14TANO_3$ appears to be below 0 °C. Figure 1 shows representative plots of specific conductivity, corrected for that in pure water, as a function of molality of the surfactant. The plots exhibit typical behaviour with two linear fragments whose intersection corresponds to the critical micelle concentration, cmc, of the surfactant. The ratio of the slopes of the linear fragments above and below the break gives an estimate of the degree of ionization, β, of the micelles [20].

According to the charged pseudo-phase separation model of micellization [21], the standard free energy of micellization, ΔG_m^0, can be calculated from the relation:

$$\Delta G_m^0 = (2 - \beta)RT \ln \chi_{\mathrm{cmc}}$$

where χ_{cmc} is expressed in mole fraction units. The relevant values are presented in Table 1.

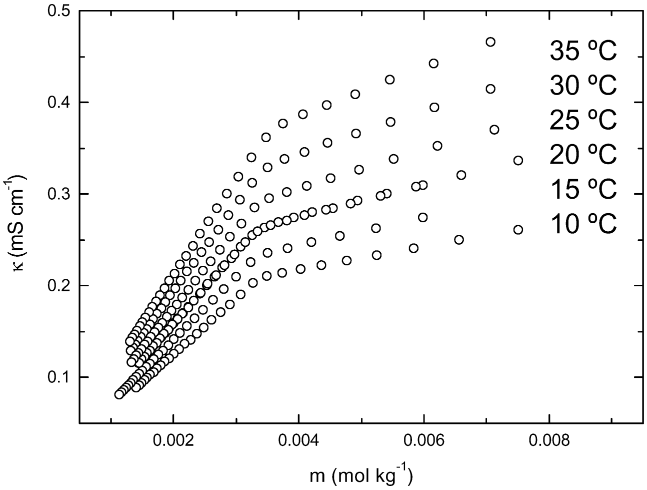

Fig. 1 Plots of the specific conductivity of $C14TANO_3$ in water at various temperatures as a function of molality

Table 1 Cmc, ionization degree of the micelles, β, and free energy of micellization, ΔG^o_m, for C14TANO$_3$ as a function of temperature

t (°C)	cmc (mmol kg^{-1})	β	ΔG^o_m(kJ mol^{-1})
10	3.41	0.206	-40.9_5
12	3.37	0.210	−41.2
15	3.35	0.216	−41.5
17	3.35	0.220	−41.7
20	3.35	0.226	−42.0
22	3.36	0.230	−42.2
25	3.38	0.236	−42.4
27	3.41	0.240	−42.6
30	3.45	0.246	−42.8
35	3.57	0.255	-43.1_5

The cmc value of 3.38 mmol/kg for C14TANO$_3$ at 25 °C is lower, which is in accord with previous observations for other systems [3,4]; a few selected literature values of cmc are reported for the bromide analogue: 3.79–3.82 mmol/kg [22], 3.75 mM [23], 3.70 mM [24] and 3.72 mM [25]. It is worth noting that the present cmc value for the nitrate is distinctly higher compared to the values of 2.0 mM and 3.1 mM reported by Gaillon et al. [26] derived from their e.m.f and conductivity measurements respectively as well as compared to the value of 2.7 mM derived by Sepúlveda and Cortés [8] from surface tension data. The difference resulting from the use of either molality or molarity is of minor importance. Similarly, the present value of β equal to 0.24 is higher than the literature values of 0.19 [26] and 0.18 [8]. On the other hand, it is close to the values of 0.23 [23] and 0.25 [22] reported for C14TABr on the basis of conductometric measurements.

The β values for C14TANO$_3$ collected in Table 1 increase linearly with temperature showing that the process of ionization of the micelles is endothermic. The β_o and β_1 parameters in the relation $\beta = \beta_o + \beta_1$T amount to −0.3329 and 0.0019 respectively. The latter coefficient is distinctly lower compared to those of 0.0030 [22] and 0.0033 [27] reported for C14TABr. A corresponding value of 0.0026 can be estimated from the conductometric data of Aguiar et al. [23].

The temperature dependence of the cmc for C14TANO$_3$ is illustrated in Fig. 2. The solid line on the plot represents a fit of the experimental points to a truncated form of Eq. 1 as explained below.

We have shown recently [28] that interesting thermodynamic data on micellization of surfactants in aqueous solutions can be obtained upon analysis of the course of the U-shaped plot by applying Muller's equation [29], modified by taking into account the fact that β changes linearly with temperature, and by assuming that the change in heat capacity upon micellization, $\Delta C^o_{P,m}$ varies also linearly with temperature. The resulting equation reads:

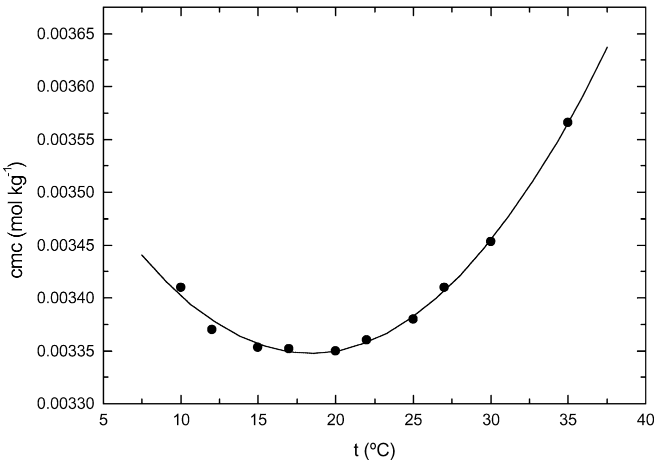

Fig. 2 Temperature dependence of cmc for C14TANO$_3$

$$\ln \chi_{\text{cmc}} = \ln\ \chi^*_{\text{cmc}}\left\{1+\beta_1 T^*\left[\frac{1}{2-\beta}\left(\frac{T^*}{T}-2-\frac{\beta_0-2}{B_1 T^*}\right)\right.\right.$$
$$\left.\left.+\frac{1}{2-\beta^*}\left(1+\frac{\beta_0-2}{\beta_1 T^*}\right)\right]\right\}$$
$$+\frac{\Delta C^{0*}_{P,m}}{(2-\beta)R}\left(1-\frac{T^*}{T}-\ln\frac{T}{T^*}\right)$$
$$+\frac{\alpha}{(2-\beta)R}\left(\frac{T^{*2}-T^2}{2T}+T^*\ln\frac{T}{T^*}\right) \qquad (1)$$

where $\ln\chi^*_{\text{cmc}}$, T* and $\Delta C^{o*}_{P,m}$are the values of In χ_{cmc}, T and $C^o_{P,m}$ at the minimum, whereas α is the thermal coefficient in the linear equation:

$$\Delta C^o_{P,m} = \Delta C^{o*}_{P,m} + \alpha(T - T^*).$$

It was also shown that at the minimum:

$$\Delta H^{0*}_m = RT^{*2}\beta_1 \ln\chi^*_{\text{cmc}}$$

and

$$\Delta S^{0*}_m = \frac{\Delta H^{0*}_m}{T^*}\left(2+\frac{\beta_0-2}{\beta_1 T^*}\right).$$

Equation 1 relates thus in a formal way the entropy, enthalpy, and heat capacity of micellization with the Gibbs free energy as a function of temperature. Since the thermal coefficient, α, appears to be close to zero we have neglected the last term in Eq. 1upon fitting the set of our experimental cmc and temperature values to the thus truncated form. The following parameters were thus derived: T* = 291.4 K, $\ln\chi^*_{\text{cmc}} = -9.7165$, $\Delta C^{o*}_{p,m} = -692 \pm 10$ J mol^{-1}K^{-1}, $\Delta H^*_m = -13.5$ kJ mol^{-1} and $\Delta S^{o*}_m = 97.1$ J mol^{-1}. Note that the change in heat capacity upon micellization of C14TABr, determined by Kresheck calorimetrically at 25 °C, amounts to −502 J mol^{-1}K^{-1} [30]. His ΔH_mvalue for this surfactant, −5 kJ mol^{-1}, is however, distinctly higher compared to our values for C14TANO$_3$.

The values of ΔH_m^o, ΔS_m^o and $\Delta G_m^o$for the whole set of temperatures were calculated from the following relations:

$$\Delta H_m^0 = \Delta H_m^{0*} + \Delta C_{p,m}^{0*}(T - T*)$$

$$\Delta S_m^0 = \Delta S_m^{0*} + \Delta C_{p,m}^{0*} \ln (T/T*)$$

and

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0$$

Thus calculated values are illustrated in Fig. 3 where ΔS_m^o is multiplied by T.

Typically for ionic surfactants ΔG_m^o decreases only slightly with temperature and the enthalpic contribution of micelle formation becomes more important with increase in temperature. The thermodynamic data exhibit also the so-called enthalpy-entropy compensation phenomenon reflected by a linear relation between enthalpy and entropy as can be seen in Fig. 4.

The relationship, expressed by:

$$\Delta H_m^o = \Delta H_m^* + T_c\Delta S_m^o$$

exhibits a high correlation coefficient of 0.9999. The slope of the plot, Tc, known as the compensation temperature, amounts to 302 K. This value falls within the range characteristic for ionic surfactants [31,32]. The intercept, ΔH_m^*, amounts to -42.9 ± 0.1kJ mol^{-1} and corresponds to the enthalpy change at a specific temperature giving at which the driving force of the micelle formation comes only from the enthalpy term.

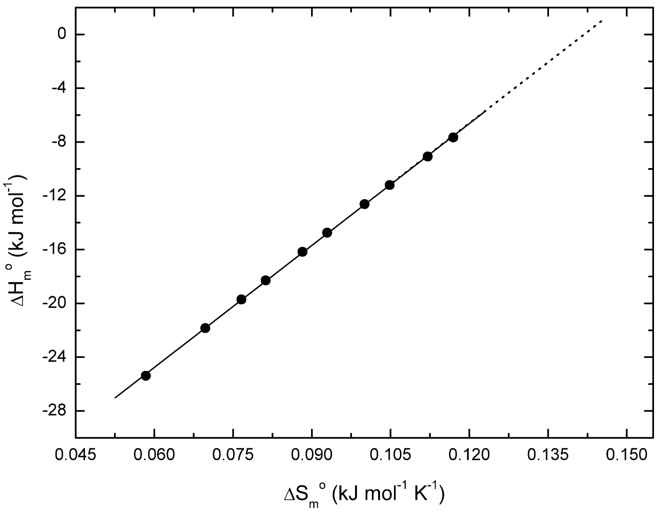

Fig. 4 Enthalpy-entropy compensation plot for C14TANO$_3$

We will now discuss the influence of BzOH on the value of cmc and ionization degree, β, of micelles of C14TANO$_3$ as determined from conductivity data at 25 °C. The change in the course of the plots of conductivity against molality of the surfactant, due to the presence of the additive, is illustrated in Fig. 5 where the two plots are for the system without BzOH and for the system which is 0.14 m with respect to the alcohol.

It is seen that BzOH slightly lowers the slope of the plot in the premicellar concentration range whereas a reverse but more distinct phenomenon occurs in the post-micellar range, the latter effect being due to the increased ionization of the micelles. Note that the break on the plot for the 0.14 m BzOH solution is markedly shifted to lower molality of the surfactant. The dependence of β as a function of molality of BzOH is shown in Fig. 6 where, for comparison, the corresponding plot for C14TABr is included [19]. The degree of ionization of

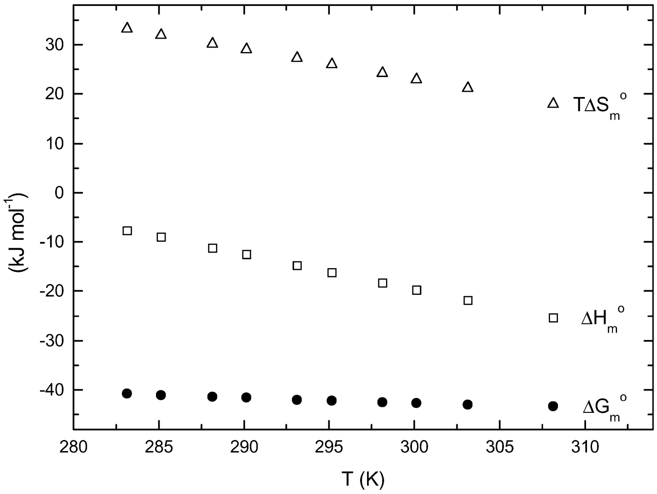

Fig. 3 ΔG_m^o, ΔH_m^o and $T\Delta S_m^o$ values for C14TANO$_3$ as a function of temperature

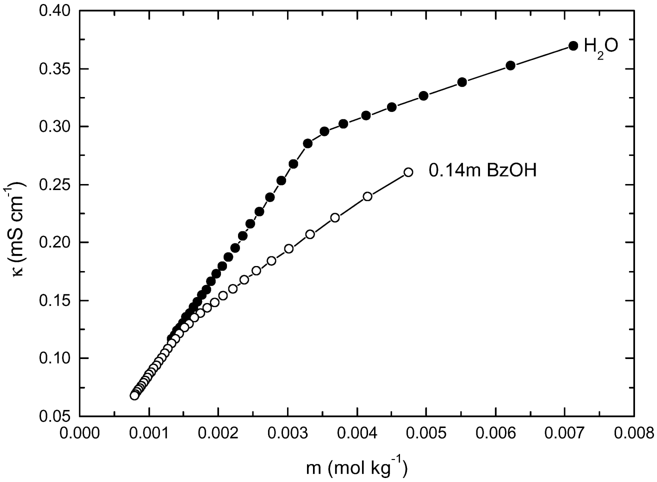

Fig. 5 Specific conductivity against molality of C14TANO$_3$ in water and in 0.14 m BzOH at 25 °C

the micelles of both surfactants increases with increase in concentration of the additive at a comparable rate.

The influence of BzOH alcohol on the value of the cmc of C14TANO$_3$ and of C14TABr [19] at 25 °C is shown in Fig. 7 in the form of a plot of cmc/cmc$_o$ ratio versus molality of the alcohol. In both cases a distinct break on the plots occurs when the molality of BzOH falls in the range of 0.05–0.06 m. The present result supports the suggestion that the break may be accounted for by assuming that BzOH at this concentration range may start to aggregate to such an extent that its activity becomes distinctly lower than that expected on the basis of molality [19]. Such a phenomenon has not been observed for other systems as yet. One may expect that homologous ω-phenylalkyl alcohols should exhibit aggregational properties at even lower concentrations in the aqueous phase.

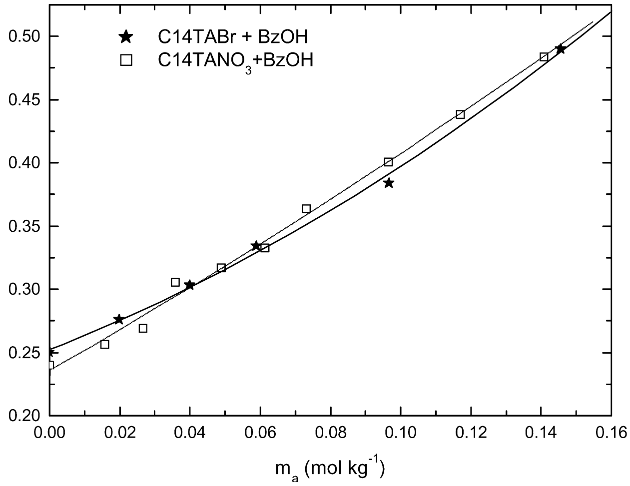

Fig. 6 Degree of ionization of micelles, β, of C14TANO$_3$ and C14TABr at 25 °C as a function of molality of BzOH

It should be born in mind however, that it might be suggested as well that the observed break in the curve of Fig. 7 is due to some changes in the micelle structure, or due to onset of solubilization of BzOH not only in the palisade layer, but also inside the micellar core.

The increase in the degree of ionization of the micelles observed in the presence of BzOH occurs most probably due to the incorporation of the additive in the region of the ionic head-groups of the micelles. The thermodynamic treatment of binary micellar systems proposed by Motomura et al. [33] enables the estimation of the distribution of the alcohol between aqueous and micellar phases. The molar fraction of alcohol in the micellar phase, X_2^Mcan be calculated from Eq. 2 which describes the dependence of mole fraction of the alcohol in the micelle on the molality of the alcohol in the aqueous phase:

$$X_2^M = \frac{\left\{\alpha_1\left[\frac{1}{m_1} - \frac{\alpha_1}{\mu}\right]\left(\frac{\partial m_1}{\partial m_2}\right)_{T,P} - \frac{\alpha_1\alpha_2}{\mu}\right\}}{\left\{\frac{\alpha_2-\alpha_1}{\mu}\left[\alpha_2 + \alpha_1\left(\frac{\partial m_1}{\partial m_2}\right)_{T,P}\right] + \frac{\alpha_1}{m_1}\left(\frac{\partial m_1}{\partial m_2}\right)_{T,P} - \frac{\alpha_2}{m_2}\right\}} \qquad (2)$$

where $\alpha_1 = 2$ and $\alpha_2 = 1$ for the ionic surfactant and alcohol, respectively, m_1 and m_2(m$_a$) are the molalities of the surfactant and alcohol correspondingly, and $\mu = \alpha_1 m_1 + \alpha_2 m_2 + (1000/M_w)$, where M_w equals the molecular mass of water.

The X_2^M vs. m_a plots for C14TANO$_3$ and for C14TABr [19] are shown in Fig. 8.

As expected, the courses of the plots are similar, BzOH being only slightly less solubilized by the micelles in the nitrate form. In both cases a maximum in solu-

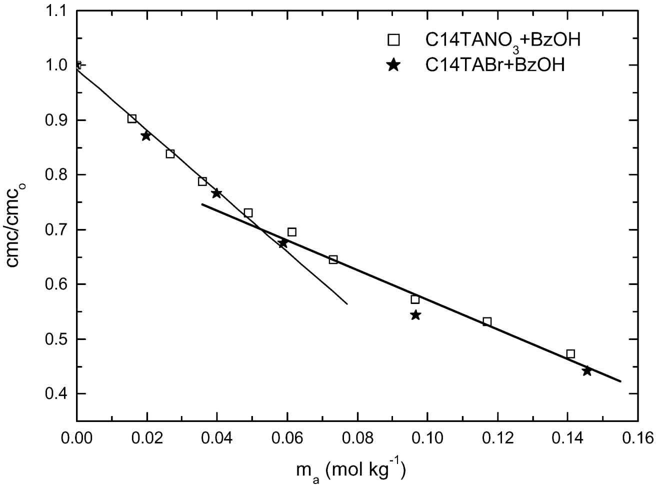

Fig. 7 Plots of cmc/cmc$_o$ against molality, m$_a$, of BzOH for C14TANO$_3$ and C14TABr

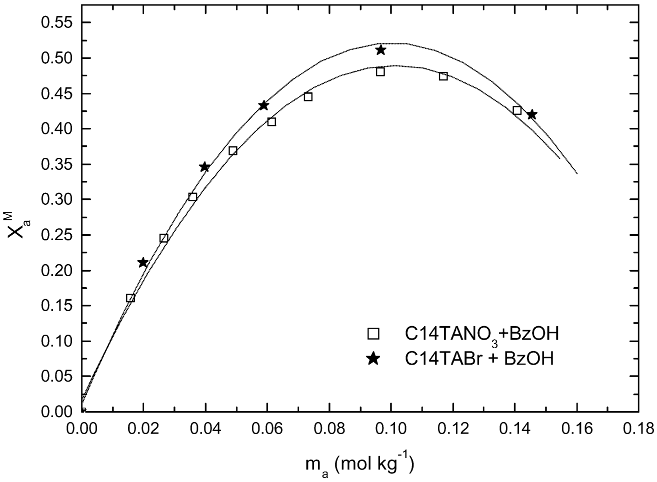

Fig. 8 Mole fraction, $X_2^M$of BzOH in micelles as a function of molality

bilization is observed when the total molality of the alcohol amounts to ca. 0.10 m. The apparent abrupt decrease in solubilization at higher concentrations of alcohol may again be accounted for by the onset of its aggregation in the aqueous phase as discussed earlier [19]. It should be pointed out that Pons et al. [34] revealed the specificity of BzOH in aqueous solutions of C14TABr on the basis of their calorimetric results of enthalpy of the solutions. The authors found a very large enthalpy change of the solution upon increasing alcohol concentration and suggested that solubilization of BzOH alcohol in C14TABr solutions is specifically favoured by intramolecular, BzOH/BzOH, interactions between molecules within the cationic micelles, at the micellar surface. In fact both phenomena i.e. aggregation of BzOH in the bulk aqueous solution and at the interface may operate simultaneously, the latter phenomenon being responsible for the observed increase in dissociation of the micelles.

Conclusions

The micellar properties of tetradecyltrimethylammonium nitrate appear to be quite comparable to those reported earlier for the bromide analogue. The cmc value for the nitrate surfactant places this anion immediately after the bromide anion in the lyotropic series. Plots of cmc/cmc$_o$ against molality of added benzyl alcohol and the mole fractions, X_2^M, of the alcohol solubilized by the micelles, are also comparable for the surfactants in the nitrate and bromide form. The breaks on the cmc/cmc$_o$ vs. m_a plots and on the X_2^M vs. m_a plots suggest that the observed phenomena are due to aggregation of benzyl alcohol in the aqueous phase.

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