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SHORT COMMUNICATION

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Thermodynamics of micellization of tetradecyltrimethylammonium bromide in ethylene glycol–water binary mixtures

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Abstract The aggregation behaviour of tetradecyltrimethylammonium bromide in ethylene glycol–water mixtures across a range of temperatures has been investigated by electrical conductivity measurements. The critical micelle concentration (cmc) and the degree of counterion dissociation of micelles were obtained at each temperature from plots of differential conductivity, $(\partial\kappa/\partial c)_{T,P}$, versus the square root of the total concentration of the surfactant. This procedure not only enables us to determine the cmc values more precisely than the conventional method, based on plots of conductivity against total concentration of surfactant, but also allows straightforward determination of the limiting molar conductance and the molar conductance of micellar species. The equilibrium model of micelle formation was applied to obtain the thermodynamics parameters of micellization. Only small differences have been observed in the standard molar Gibbs free energies of micellization over the temperature range investigated. The enthalpy of micellization was found to be negative in all cases, and it showed a strong dependence on temperature in the ethylene glycol poor solvent system. An enthalpy–entropy compensation effect was observed for all the systems, but whereas the micellization of the surfactant in the solvent system with 20 wt% ethylene glycol seems to occur under the same structural conditions as in pure water, in ethylene glycol rich mixtures the results suggest that the lower aggregation of the surfactant is due to the minor cohesive energy of the solvent system in relation to water.

Key words Critical micelle concentration – Thermodynamics properties – Tetradecyltrimethylammonium bromide – Ethylene glycol–water mixtures

Introduction

There are many reasons why most studies related to the self-assembly of surfactant systems have been conducted in aqueous media. From these investigations a number of properties of great interest for their technical applications are now fairly well known. However, the appearance of certain applications of surfactants in areas such as lubrication or cleaning operations, which require water-free or water-poor media, has stimulated interest in the surfactant aggregation phenomenon in nonaqueous media. Among these media, strongly polar solvents with properties resembling those of water, such as ethylene glycol (EG), glycerol and formamide, have been used [1, 2]. In recent years, investigations of surfactant aggregation in nonaqueous polar solvents have focused mainly on two aspects: what is required from a solvent for amphiphilic assembly, and what structural properties the aggregates formed in these media have. In order to obtain answers to these questions, a usual and obvious approach is the gradual replacement of water with other polar solvents, as this allows one to explore a wide range of polarities (so that the surfactant tails could experience a range of solvophobicities). In this way, several studies of surfactant aggregation have been carried out using solvents such as glycerol [3-5], formamide [6–11] and EG [5, 12–22], to name only a few. In relation to the physical properties of the solvent needed for amphiphilic aggregation to occur, previous studies indicate that these solvents must have three characteristics in common: a high cohesive energy, a high dielectric constant and a high hydrogen-bonding ability [15]. In particular, it must be pointed out that some authors [23] have proposed that the last point, namely, the ability for hydrogen-bond formation is a necessary condition for surfactant aggregation.

As already mentioned a large number of studies have been performed where water is gradually substituted with another polar solvent. This methodology has a double objective: it allows a simple characterization of the system, and it is possible to investigate the possibility of a chosen experimental technique to provide significant and easily interpretable data [2]. In addition, since the micellization process is most often revealed by the surfactant concentration value at which the aggregation takes place, i.e. the so-called critical micelle concentration (cmc), it is important to have appropriate procedures to obtain reliable cmc values in these media. On the other hand, a lot of information on the strength and nature of solvent–surfactant and solvent–solvent interactions can be obtained from the thermodynamic properties of micellization. These properties can be derived from a study of surfactant aggregation as a function of temperature. This kind of information provides a further understanding of the so-called solvophobic effect as opposed to the hydrophobic effect [23].

In this paper, we present the results obtained in an experimental study of the aggregation behaviour of tetradecyltrimethylammonium bromide (TTAB) in EG–water mixtures at different temperatures. Previously, two studies on the same system have been reported. Backlund et al. [13] investigated the aggregation and the phase behaviour of TTAB in water, EG and their respective mixtures at 30 °C. Gharibi et al. [16] have also carried out electrochemical studies associated with micellization of TTAB, among other cationic surfactants, in the same solvent mixtures at 25 °C. Unlike these investigations the aim of this work is the study of the influence of temperature in the micellization process of TTAB in different EG–water mixtures. In this investigation we have carried out conductivity measurements up to 60 wt% EG in the binary mixtures and in the temperature range 25–45 °C. The cmc values, degree of counterion dissociation (β), limiting molar conductance (Λ^0) and molar conductance of micelles (Λ^M) corresponding to each temperature were obtained by using a new approach recently proposed by Sugihara and coworkers [24–26]. From the cmc values as a function of temperature, and considering the equilibrium model for micelle formation, we have obtained the corresponding thermodynamic parameters of micellization.

Experimental

The surfactant TTAB was obtained from Sigma Chemical Co. and was used without any pretreatment. EG (spectrophotometric grade, >99%) was from Aldrich and was used as received. Water was doubly distilled (Millipore).

Conductometric measurements were made with a Crison model microCM 2202 digital conductivity meter using a dip-type cell of cell constant 1.03 cm^{-1}. All measurements were done in a jacketed vessel, which was maintained at the appropriate temperature (±0.1 °C) with a Mendingen E1 temperature bath. Specific conductivity values of each set containing 15–20 different concentrations at a fixed solvent composition (expressed as EG/water ratio in weight percent) were measured at different temperatures. The surfactant molar concentrations were converted to the molar fraction scale by using density values of solvents and solutions. These densities were measured with an Anton-Paar DMA 58 density meter. This apparatus determines the density value by placing the sample in a U-shaped tube and measuring the period of oscillation of this tube. The instrument was calibrated with air and water over the temperature range investigated. The temperature was maintained within ±0.01 °C.

The cmc values at each solvent composition were determined by using two different procedures. First, we used the conventional method based on the plot of conductivity (κ) against surfactant total concentration (c). In this plot we have fitted by least-squares analysis the conductivity–concentration data above and below the break point with a correlation coefficient greater than 0.9995. Second, in accordance with Sugihara and coworkers [24–26], we have plotted the derivative $(\partial\kappa/\partial c)_{T,P}$ versus $\sqrt{c}$. From these plots, which show a reverse sigmoidal curve, the cmc values are taken as the inflection point, i.e. as the centre of the reverse sigmoid.

Results and discussions

Degree of counterion dissociation and cmc

The determination of the cmc for each solvent composition at different temperatures was first carried out by plotting specific conductivity (κ) against total concentration of surfactant (c). Figure 1 shows a number of these plots at different temperatures and at fixed solvent composition. From these plots the degree of counterion dissociation (β) was also obtained as the ratio between the slope of the postmicellar region (S^M) to that of the premicellar region (S^1). However, as the temperature and concentration of EG increased, we found that a smaller curvature appeared around the cmc; consequently the cmc and β values obtained are affected to a greater uncertainty. Therefore we decided to use a new approach that has recently been applied successfully in a study of the micellization of mixed surfactant systems [24] and some α-sulfonate fatty acid methyl esters as a function of temperature [25, 26]. This approach is based on the analysis of the plots of differential conductivity, $(\partial\kappa/\partial c)_{T,P}$, which will henceforth be written as $\mathrm{d}\kappa/\mathrm{d}c$, versus the square root of concentration expressed in millimoles litre. Some examples of these plots are shown in Fig. 2. In all cases it can be seen that the curves show an abrupt fall, showing a reverse sigmoid. The cmc value is given by the centre of the sigmoid and can be obtained from fitting the data to a sigmoid. It is important to point out that this treatment is different from the usual procedure in which differential conductivity is plotted against concentration. Several authors have used this last approach [27], in which the cmc is determined as the shoulder point of the $\mathrm{d}\kappa/\mathrm{d}c$ versus c plot. In particular, the procedure that we have applied here has the advantage that one can evaluate to what extent the experimental data obey Kohlrausch's law of the square root of concentration. Furthermore, it is possible to determine the limiting molar conductance Λ^0, given by $\mathrm{d}\kappa/\mathrm{d}c$ at infinite dilution, in addition to the micellar conductance, Λ^M, determined from the tangential line drawn from the minimum of the sigmoidal curve of $\mathrm{d}\kappa/\mathrm{d}c$ versus $\sqrt{c}$ (see Fig. 2). In fact, the values of Λ^0 and Λ^M are directly given by the fitting parameters of the sigmoid. The ratio between these parameters (Λ^M/Λ^0) provides the degree of counterion dissociation, from which the degree of counterion binding $\alpha(\alpha = 1 - \beta)$ can be obtained. An interesting and detailed study of these aspects, including the physical meaning of the respective parameters, can be found in Refs. [24–26].

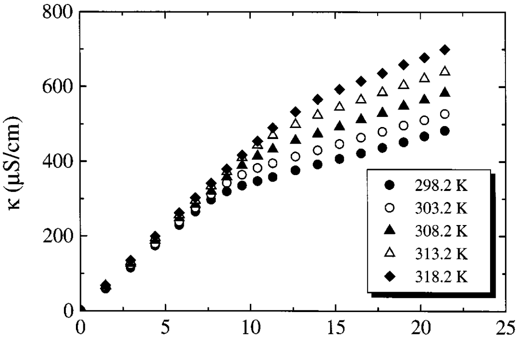

Fig. 1 Conductivity (κ) versus total concentration of tetradecyltrimethylammonium bromide (*TTAB*) c in a 40 wt% ethylene glycol (*EG*)–water mixture at different temperatures

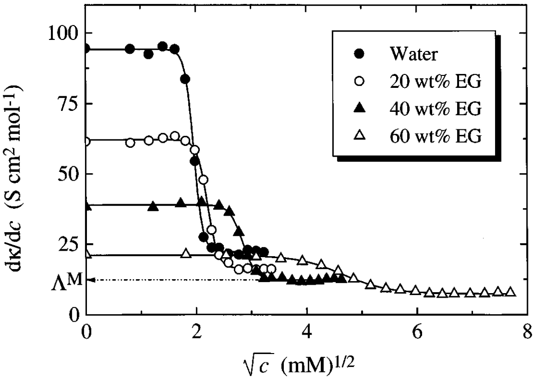

Fig. 2 Plots of differential conductivity versus square root of total concentration of TTAB in different EG–water mixtures at 298.2 K (The *arrow* indicates how the molar conductance of micelles, Λ^M, is determined)

The cmc and β values obtained from both conventional and differential conductivity methods are listed in Table 1. The cmc values in water were found to be in good agreement with those previously reported in the same temperature range [28]. It can be seen from the data in Table 1 that while in the absence of EG, or at low concentrations of EG in the solvent mixture, the cmc and β values are in reasonable agreement, but as the concentration level of EG increases the differences between the values obtained by both methods become pronounced, especially for the solvent composition of 60 wt% EG. On the other hand, it is important to point out that the cmc values obtained by the differential

Table 1 Critical micellar concentration (*cmc*) and degree of counterion dissociation (β) for tetradecyltrimethylammonium bromide (*TTAB*) in ethylene glycol (*EG*)–water mixtures at different temperatures

Solvent system	Temperature (K)	cmc[a] (mM)	$\beta = \frac{S^M}{S^1}$[a]	cmc[b] (mM)	$\beta = \frac{\Lambda^M}{\Lambda^0}$[b]
H_2O	298.2	3.86	0.238	3.84	0.235
	303.2	3.93	0.250	3.91	0.248
	308.2	4.08	0.265	4.02	0.257
	313.2	4.22	0.285	4.22	0.280
	318.2	4.39	0.296	4.33	0.287
20 wt% EG	298.2	4.97	0.263	4.86	0.268
	303.2	5.18	0.278	5.13	0.278
	308.2	5.45	0.290	5.37	0.289
	313.2	6.09	0.319	6.10	0.315
	318.2	6.70	0.353	6.72	0.344
40 wt% EG	298.2	8.15	0.315	8.08	0.316
	303.2	9.00	0.329	8.90	0.323
	308.2	10.00	0.353	9.94	0.348
	313.2	11.13	0.362	11.01	0.357
	318.2	12.41	0.395	12.41	0.392
60 wt% EG	298.2	22.21	0.354	21.70	0.353
	303.2	24.25	0.385	23.65	0.364
	308.2	26.47	0.411	25.73	0.368
	313.2	29.06	0.461	28.84	0.384
	318.2	31.36	0.498	29.90	0.438

[a] Data obtained from the plot of conductivity (κ) against total surfactant concentration (c)

[b] Data obtained from the $\mathrm{d}\kappa/\mathrm{d}c$ versus $\sqrt{c}$ plot curves

conductivity method are affected by a maximum error smaller than ± 3%, while when we applied the conventional method the error was ± 10%. From the data in Table 1 it can be seen that at a fixed temperature the cmc increases with EG concentration. Two factors must be considered to explain this behaviour:

1. The presence of EG decreases the cohesive energy density, or the solubility parameter, of water, thus increasing the solubility of the monomeric form of the surfactant and hence the cmc.

2. The cosolvent causes a reduction in the dielectric constant of the aqueous phase, favouring the mutual repulsion of the ionic heads in the micelle, thus opposing micellization and increasing the cmc.

On the other hand, at a fixed solvent composition it can be seen that the cmc increases with temperature in the range investigated. The effect of temperature on the cmc of surfactants in aqueous solution is usually analysed in terms of two opposing factors. First, as the temperature increases the degree of hydration of the hydrophilic group decreases, which favours micellization; however, an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group, and this is unfavourable to micellization. From the data in Table 1 it seems that this second effect is predominant in the temperature range studied. An additional aspect that is implied from plots of $d\kappa/dc$ versus $\sqrt{c}$ is that for a micellization process in aqueous medium $d\kappa/dc$ decreases abruptly over a narrow range of concentrations (Fig. 2); however, when increasing the EG–water it is observed that $d\kappa/dc$ shows a less marked decrease. This suggests that the micellization process in the presence of EG takes place in a more gradual way, i.e. premicellar aggregation occurs before the micelles are formed.

On the other hand, the degree of counterion dissociation in TTAB micelles, β, also increases regularly with both EG addition and temperature increase (Table 1). This observed increase in β is probably due to a decrease in the charge density at the micellar surface caused by the decrease in the aggregation number of the micelle. Figure 3 shows the behaviour of the limiting conductivity of singly dispersed species, Λ^0, and the molar conductivity of micellar species, Λ^M, as determined from the $d\kappa/dc$ versus $\sqrt{c}$ plots, as functions of temperature. For all systems a linear increase for both Λ^0 and Λ^M with increasing temperature is observed. Moreover, from Fig. 3 it can be seen that Λ^0 values in pure water are greater than those of EG–water systems. This behaviour is the result of the enhancement of viscosity and the reduction of the dielectric constant of the medium with EG addition, as suggested from the Stokes–Einstein and the Debye–Hückel relations, respectively. To explain the trend of Λ^M values we must take into account two opposing effects: the increase in the viscosity of the medium and the reduction in the micellar size with EG addition. The lower Λ^M values for systems with EG added suggest that the enhanced viscosity of the medium is, in this case, the main factor controlling the molar conductivity of micelles.

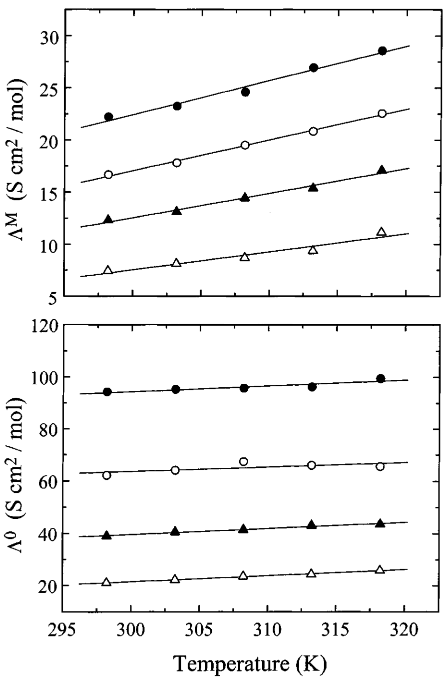

Fig. 3 The molar conductance of micellar species, Λ^M, and the limiting molar conductance of singly dispersed species, Λ^0, as a function of temperature. Symbols as in Fig. 2

Thermodynamics of micellization

In order to analyse the change in the cmc with temperature we have considered the equilibrium model for micelle formation. According to this model, the process of micellization of cationic surfactants may be described by

$$nS^+ + (n-p)C^- \rightleftharpoons M^{p^+} \ , \qquad (1)$$

where S^+ represents the surfactant ions, C^- the corresponding counterions, and M^{p+} the aggregate of n monomers with an effective charge of p. The standard free energy change of micelle formation per mole of surfactant, ΔG^0_{mic}, is given by

$$\Delta G^0_{\text{mic}} = RT\left(-\frac{1}{n}\ln a_{M^{p+}} + \ln a_{S^+} + \left(1-\frac{p}{n}\right)\ln a_{C^-}\right) \ , \qquad (2)$$

in which a represents the activity of the species indicated. If the aggregation number, n, is large ($n \geq 50$), the first term in the parantheses is negligibly small and both a_{S^+} and a_{C^-} can be replaced by the activity at the cmc. In addition, taking into account that cmcs occur in dilute solutions, the activity can be replaced by the concentration of the surfactant (expressed in mole fractions) at the cmc. Introducing these approximations in Eq. (2) yields [29]

$$\Delta G^0_{\mathrm{mic}} = (2 - \beta)RT \ln X_{\mathrm{cmc}} \ , \tag{3}$$

where $\beta = p/n$ is the degree of dissociation of counterions. The corresponding enthalpy change, $\Delta H^0_{\mathrm{mic}}$, is given by

$$\Delta H^0_{\mathrm{mic}} = -RT^2 \left[(2 - \beta) \left(\frac{\partial \ln X_{\mathrm{cmc}}}{\partial T} \right)_P - \ln X_{\mathrm{cmc}} \left(\frac{\partial \beta}{\partial T} \right)_P \right] \ . \tag{4}$$

If the change in β with temperature is small over the temperature range investigated, this equation can be expressed as

$$\Delta H^0_{\mathrm{mic}} = -(2 - \beta)RT^2 \left(\frac{\partial \ln X_{\mathrm{cmc}}}{\partial T} \right)_P \ . \tag{5}$$

Therefore, the enthalpy of micellization may be obtained if the dependence of the cmc on temperature is known. In the present study the contribution of the third term of Eq. (4), due to the variation of β with temperature, is negligible, so we have used Eq. (5) to estimate $\Delta H^0_{\mathrm{mic}}$ values. With this purpose $\ln X_{\mathrm{cmc}}$ was plotted against T and the slope at each temperature was taken as $[\partial \ln X_{\mathrm{cmc}}/\partial T]_P$. These plots are shown in Fig. 4. A linear plot was observed for systems where the EG content was 40 wt% or above, while for the other two systems the best fit was found to be a second-order polynomial. Finally, once $\Delta G^0_{\mathrm{mic}}$ and $\Delta H^0_{\mathrm{mic}}$ have been calculated, the entropic contribution, $T\Delta S^0_{\mathrm{mic}}$, may be determined from

$$T\Delta S^0_{\mathrm{mic}} = \Delta H^0_{\mathrm{mic}} - \Delta G^0_{\mathrm{mic}} \ . \tag{6}$$

In addition, the effect of a cosolvent or additive on the micellization process can be studied by means of the so-called free energy of transfer, $\Delta G^0_{\mathrm{trans}}$, which is defined by [30]

$$\Delta G^0_{\mathrm{trans}} = \left(\Delta G^0_{\mathrm{mic}}\right)_{\mathrm{EG+H_2O}} - \left(\Delta G^0_{\mathrm{mic}}\right)_{\mathrm{H_2O}} \ . \tag{7}$$

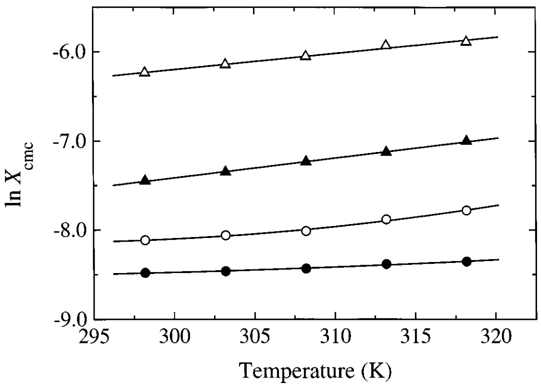

Fig. 4 Plots of in X_{cmc} versus temperature for different solvent system compositions: (●) water, (○) 20 wt% EG, (▲) 40 wt% EG, and (△) 60% EG

Following the above procedure we have obtained the thermodynamic parameters of micellization listed in Table 2. Our results show that the free energy of micellization is in all cases negative and becomes less negative as the EG content in the mixed solvent system increases, which it remains almost constant across the whole temperature range. This behaviour suggests that aggregation becomes less favorable at higher EG contents, but it is roughly independent of temperature. The enthalpy of micellization is negative and strongly dependent on temperature in EG-poor mixtures (water and 20 wt% EG), and becomes more negative and roughly independent of temperature in EG-rich mixtures. On the other hand, the entropic contribution shows the opposite behaviour; namely the $T\Delta S^0_{\mathrm{mic}}$ values are, in general, positive and become less positive as both the EG content and temperature increase. These results could suggest, at first sight, that the micellization of TTAB in EG–water mixtures is entropy-driven in EG-poor solvent mixtures and at lower temperatures, while it is enthalpy-driven in EG-poor solvent mixtures and at higher temperatures; however, in relation with the dependence on temperature these appearances can be misleading. Evans and Miller [23] have pointed out that water provides a highly structured medium, in particular near room temperature, which leads to entropy–enthalpy compensation. This fact could impede us from extracting any useful conclusion from the observed trend

Table 2 Thermodynamic parameters of micellization of TTAB in EG–water mixtures at different temperatures

Solvent system	298.2 K	303.2 K	308.2 K	313.2 K	318.2 K
	$\Delta G^0_{\mathrm{mic}}$ (kJ/mol)				
Water	−37.12	−37.38	−37.67	−37.55	−37.87
20 wt% EG	−34.86	−34.99	−35.13	−34.58	−34.09
40 wt% EG	−31.10	−31.07	−30.62	−30.49	−29.79
60 wt% EG	−25.47	−25.35	−25.32	−24.96	−24.34
	$\Delta H^0_{\mathrm{mic}}$ (kJ/mol)				
Water	−5.94	−7.51	−9.18	−10.86	−12.69
20 wt% EG	−8.96	−15.53	−22.57	−29.68	−36.80
40 wt% EG	−27.73	−28.55	−29.06	−29.84	−30.15
60 wt% EG	−22.13	−22.72	−23.42	−23.95	−23.89
	$T\Delta S^0_{\mathrm{mic}}$ (kJ/mol)				
Water	31.18	29.87	28.49	26.69	25.18
20 wt% EG	25.90	19.46	12.56	4.90	−2.71
40 wt% EG	3.37	2.52	1.56	0.65	−0.36
60 wt% EG	3.34	2.63	1.90	1.01	0.45
	$\Delta G^0_{\mathrm{trans}}$ (kJ/mol)				
20 wt% EG	2.26	2.39	2.54	2.97	3.78
40 wt% EG	6.02	6.31	7.05	7.06	8.08
60 wt% EG	11.65	12.03	12.35	12.59	13.53

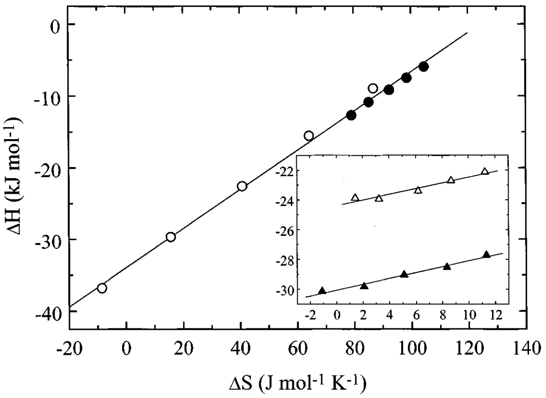

Fig. 5 Enthalpy–entropy compensation plots for the different solvent systems studied: (●) water, (○) 20 wt% EG, (▲) 40 wt% and (△) 60 wt% EG

for ΔH^0_{mic} and $T\Delta S^0_{\text{mic}}$, with temperature. In order to analyse this possibility we have considered the plots of ΔH^0_{mic} versus ΔS^0_{mic} i.e. the so-called compensation plot. These plots are shown in Fig. 5, where a linear correlation between the enthalpy and the entropy of micellization is observed for all systems. Nevertheless, while the compensation plots of water and 20 wt% EG exhibit a similar slope (273 K), for solvent systems with high EG content the slope in smaller (∼197 K for 40 wt% EG and 192 K 60 wt% EG). The slope value of 273 K falls in the suggested range of 270–294 K for the water system [31]. This means that the micellization process in the system with 20 wt% EG is still governed by the same structural property of pure water, and the presence of EG only has a minor effect on the solute–solvent interactions. Similar behaviour has been observed previously [20] for sodium dodecyl sulfate in different solvent–water binary mixtures, including EG and glycerol. In contrast, in EG-rich solvent mixtures the presence of the cosolvent molecules results in a less-structured medium, where the solvophobic interactions are much weaker as revealed by the smaller $T\Delta S^0_{\text{mic}}$ values in these cases. In this way, the dependence of ΔH^0_{mic} on temperature is probably due to the destruction of the ordered aqueous regions surrounding the hydrocarbon chain of the surfactant with increasing temperature. This could explain the fact that ΔH^0_{mic} is less dependent on temperature as the EG content in the solvent system increases.

Finally, the $\Delta G^0_{\text{trans}}$ values that we have found are positive in all cases, and are similar in order of magnitude to those previously reported for different ionic surfactants in EG–water mixtures [18, 19]. The positive values of $\Delta G^0_{\text{trans}}$ can be understood on the basis of a reduction in the solvophobic interactions caused by improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of EG, and consequently to an increase in the cmc. In summary, the results obtained in this study indicate that the presence of EG in the solvent system induces a decrease in the solvent cohesiveness, thereby increasing the solubility of the hydrocarbon tails and decreasing the solvophobic effect.

Conclusions

In this investigation we have shown that the procedure based on plots of differential conductivity against the square root of the total surfactant concentration provides an appropriate method for the determination of cmc values in the systems studied, where the breakpoint in plots of conductivity versus concentration is ambiguous or hard to determine. Furthermore, this procedure allows one to determine parameters such as the limiting molar conductance of singly dispersed species and the molar conductance of micelles, and hence the degree of counterion dissociation. The most important conclusion that we can extract from the thermodynamic parameters obtained in this study is that the driving force for the solvophobic effect seems to have the same source as the hydrophobic effect, i.e. the large cohesive energy of the solvent. The minor cohesive energy of EG in relation to water justifies the lower aggregation of TTAB when the presence of EG in the solvent system increases.

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