Colloid Polym Sci (2002) 280: 848–856
DOI 10.1007/s00396-002-0693-0

ORIGINAL CONTRIBUTION

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Thermodynamics of micellization of ionic surfactant/alkoxyethanol mixed micelles as a function of temperature

Received: 23 October 2001
Accepted: 26 February 2002

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Abstract Estimates of the thermodynamic parameters of micellization ($\Delta_{mic}G°$, $\Delta_{mic}H°$, and $\Delta_{mic}S°$) have been determined for a series of mixed micelles consisting of ionic surfactants (sodium dodecylsulfate and dodecyltrimethylamonium bromide) and medium chain length alkoxyethanols as the co surfactant. The enthalpies of micellization have been measured directly for the above systems using isoperibol solution calorimetry; the Gibbs energies and entropies of micellization are obtained by application of the mass-action model to the critical micelle concentration values from the calorimetric titration experiments. The thermodynamic properties of mixed micelle formation with alcohol concentration and temperature are in excellent agreement with our previous results. However, there does appear to be some dependence of the thermodynamic properties of mixed micelle formation on the charge of the ionic surfactant. These dependencies are discussed in terms of the manner in which the ethylene oxide group of the alcohol interacts with the ionic head groups and the location of the solubilizates in the micellar interior.

Introduction

The interaction of organic solubilizates with ionic and nonionic surfactant micelles has been studied widely since the pioneering work of Shinoda [1] and Herzfeld et al. [2]. The presence of solubilizates has a significant impact on micellar properties such as aggregation number, critical micelle concentration values, and the degree of counterion binding) [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Over the past few years, the interactions of ethoxylated alcohols with ionic surfactants have been gaining attention. This interest has stemmed from the unusual difference in the interactions of alkoxyethanols with anionic and cationic micelles, [8, 10, 11] which parallels the manner in which non-ionic polymers, e.g., poly(ethylene) oxide, interact with sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) [14, 15, 16, 17]. In the case of the anionic SDS micelles, Manabe et al. [8] determined that the cmc values of SDS/alkoxyethanol mixed micelles were dependent on the number of ethylene oxide (EO) groups in the alcohol, at a constant alcohol alkyl chain length and at a specific alcohol concentration. Marangoni and Kwak [10] and Rodenhiser et al. [11] determined completely the equilibrium properties (cmc values, aggregation numbers, and distribution coefficients) of SDS/alkoxyethanol and DTAB/alkoxyethanol as a function of alcohol concentration. Their results clearly indicated that the EO groups contributed significantly to the formation of anionic surfactant/alkoxyethanol mixed micelles, but that there was little evidence of any enhancement of the interaction between ethoxylated alcohols and cationic micelles due to the presence of the EO groups. Huang and Verrall [18] determined volumetric and other thermodynamic properties of carboxylate surfactants mixed with ethoxylated alcohols and found that the variation in the properties of the mixed micelles was consistent with the EO groups imparting a contribution to the hydrophobic interactions. However, their work did not examine the differences in the interaction of ethoxylated alcohols with anionic and cationic micelles.

There have been few determinations of the enthalpy and entropy of micellization, especially in the presence of water-soluble additives like n-alcohols [5, 6, 7, 19, 20, 21, 22, 23, 24]. In this paper, we present the results from our calorimetric investigation of the formation of ethoxylated alcohol/ionic surfactant mixed micelles as a function of the concentration of the ethoxylated alcohol in the mixed solvent and the temperature. These results indicate that the addition of EO groups to alcohols has a significant impact on the enthalpy and entropy change of micelle formation, with changing alcohol concentration and temperature. All these results are interpreted in terms of the location of the EO groups in the cationic vs. the anionic surfactant/alkoxyethanol mixed micelle.

Experimental

Sodium dodecylsulfate and dodecyltrimethylammonium bromide were obtained from the Aldrich Chemical Co. and were purified by repeated recrystallizations from ethanol and an acetone/ethanol mixture, respectively. Conductivity grade water (1.0×10^{-6} S cm^{-1}) was obtained by passing previously deionized water through a Millipore 4000 S purification system.

1-Butanol (C_4E_0) and ethylene glycol mono-*n*-butyl ether (C_4E_1) were reagent grade solvents from the Fisher Chemical Company; diethylene glycol mono-*n*-butyl ether (C_4E_2, Spectroscopic Grade) was received from Aldrich. Triethylene glycol mono-*n*-butyl ether (C_4E_3) was obtained from Tokyo Kasei. All ethoxylated alcohols were used without further purification.

The alcohol/water mixed solvent systems were prepared on a molarity basis; the surfactant solutions were made up directly in the mixed solvent. The concentration of the surfactant solutions is reported as the moles of surfactant/l of mixed solvent. Densities of the titrant solutions were obtained using an Anton-Parr DMA 45 density meter. Heat capacity data for the titrant solutions and the micellization enthalpies were obtained as described previously [21].

Results and discussion

Micellization enthalpies from calorimetric titrations

For an alcohol/surfactant mixed micelle, the $\Delta_{mic}H^\circ$ values refer to the enthalpy change that occurs when N_s moles of surfactant S (charge a), N_c moles of counterion C (charge b), and N_a moles of additive A aggregate in aqueous solution to form a mixed micelle, M, of charge $\pm z$

$$N_sS^a + N_cC^b + N_aA \Leftrightarrow M^{\pm Z} \qquad (1)$$

It has been stated that the direct measurement of the $\Delta_{mic}H^\circ$ by calorimetry is the preferred method of obtaining thermodynamic properties of micelle formation [6]. A typical plot of q vs. V for the dilution of a 0.200 M SDS into water is given in Fig. 1; the break in the curve (corresponding to the cmc value) is clearly visible in Fig. 1. The $\Delta_{mic}H^\circ$ values are determined from the q vs. volume of added titrant curves (q vs. V plots) from the following equation

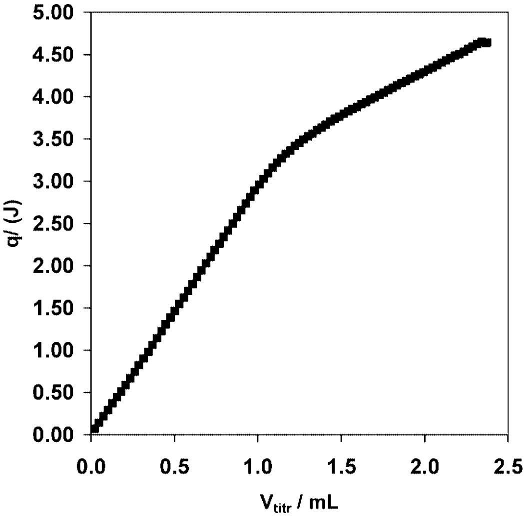

Fig. 1. Plot of q vs. V for the dilution of 0.200 M SDS into water at 318.2 K

$$\Delta_{mic}H^\circ = \frac{1000}{M}\left(\frac{dq}{dV}(\text{post cmc}) - \frac{dq}{dV}(\text{pre cmc})\right) \qquad (2)$$

where dq/dV (post cmc) and dq/dV (pre cmc) are the observed q vs. V slopes from the calorimetric titration curves (Fig. 1), and M is the molarity of the titrant solution. The Gibbs energy change upon micelle formation, $\Delta_{mic}G^\circ$, is obtained from the simple mass-action model and the calorimetric cmc values as follows

$$\Delta_{mic}G^\circ = (2-\alpha)RT\ \mathrm{In}X_{cmc} \qquad (3)$$

where $X_{cmc} \approx \mathrm{cmc}\ (M)/55.5$, and α is the degree of counterion dissociation (obtained in separate experiments). From the calorimetric $\Delta_{mic}H^\circ$ and the $\Delta_{mic}G^\circ$ values, the $\Delta_{mic}S^\circ$ may be found from the equation

$$\Delta_{mic}S^\circ = \frac{(\Delta_{mic}H^\circ - \Delta_{mic}G^\circ)}{T} \qquad (4)$$

Micelle formation enthalpies of surfactant/C_4E_n mixed micelles

The enthalpy changes upon micelle formation ($\Delta_{mic}H^\circ$ values) are presented in Table 1 for the SDS/C_4E_n systems and in Table 2 for the DTAB/C_4E_n mixed micellar systems. The micelle formation enthalpies are plotted in Figs. 2, 3, 4, and 5 for the SDS/alkoxyethanol systems. The corresponding values for the DTAB/alkoxyethanol mixed micelles are plotted in Figs. 6, 7, 8, and 9. The

Table 1. Cmc values and micelle formation enthalpies for SDS/C_4E_n systems as a function of temperature and alcohol concentration

	Cmc Values (±20 mmol/l)				$\Delta_{mic}H^\circ$ values ±0.50 kJ/mol			
C_4E_0								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	7.9	8.1	8.3	8.6	–0.2	–5.1	–9.6	–13.2
0.025	7.2	7.6	7.7	8.1	0.7	–4.4	–11.2	–13.7
0.050	6.6	6.9	7.0	7.6	1.2	–4.5	–11.9	–14.3
0.075	5.9	6.6	6.8	7.3	1.4	–4.8	–12.5	–14.7
0.100	5.2	6.2	6.4	6.9	1.9	–4.7	–13.2	–15.4
C_4E_1								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	7.9	8.1	8.3	8.6	–0.2	–5.1	–9.6	–13.2
0.025	6.8	7.0	7.2	7.5	1.2	–4.7	–9.3	–13.7
0.050	5.6	6.0	6.1	6.4	2.3	–4.6	–9.6	–13.8
0.075	4.5	4.8	5.0	5.3	3.2	–3.6	–9.2	–14.3
0.100	3.6	3.7	3.9	4.2	3.6	–3.7	–9.8	–14.5
C_4E_2								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	7.9	8.1	8.3	8.6	–0.2	–5.1	–9.6	–13.2
0.010	7.2	7.5	7.6	8.0	0.7	–6.3	–9.8	–12.6
0.025	6.5	6.6	6.8	7.1	2.0	–4.7	–10.4	–12.0
0.040	5.9	5.9	6.1	6.4	2.8	–4.2	–10.1	–13.4
0.050	5.1	5.6	5.8	6.1	3.7	–2.6	–10.5	–14.0
0.075	4.9	5.0	5.1	5.5	4.8	–3.7	–8.8	–14.9
0.100	4.5	4.8	5.0	5.3	5.1	–1.6	–6.0	–15.4
C_4E_3								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	7.9	8.1	8.3	8.6	–0.2	–5.1	–9.6	–13.2
0.010	6.9	7.2	7.3	7.7	0.6	–7.1	–10.3	–13.6
0.025	5.6	6.0	6.2	6.5	2.7	–5.5	–9.9	–14.0
0.040	4.9	5.1	5.3	5.6	3.8	–5.1	–10.4	–14.3
0.050	4.4	4.7	4.8	5.2	3.7	–4.7	–10.1	–15.1
0.075	4.1	4.2	4.4	4.7	5.3	–4.6	–10.0	–15.6
0.100	4.2	4.2	4.6	4.8	6.4	–3.4	–8.0	–16.2

enthalpies in Tables 1 and Table 2 were obtained from the calorimetric slopes above and below the cmc region (the break in the curve) via Eq. 2. The error in the $\Delta_{mic}H^\circ$ values is estimated to be ±0.5 kJ/mol from repeated measurements on the SDS/H_2O and DTAB/H_2O systems. The cmcs, obtained from the breaks in the enthalpic titration curves, were used in the calculations of the $\Delta_{mic}G^\circ$ values (Eq. 3).

From the $\Delta_{mic}H^\circ$ values in Tables 1 and Table 2, we observe a general trend towards more negative enthalpies of mixed micelle formation with increasing temperature, in excellent agreement with the literature [4, 5, 6, 7]. We note however, that there is a distinct difference in the magnitude of the enthalpy changes for the SDS/$C_4E_{1\text{–}3}$ systems versus the DTAB/$C_4E_{1\text{–}3}$ systems with increasing temperature. For the SDS systems, the measured micellization enthalpies become substantially more exothermic at higher temperatures as the amount of ethoxylated alcohol in the mixed solvent is increased. For the DTAB/$C_4E_{1\text{–}3}$ mixed micelles, the dependence of the enthalpies of mixed micelle formation on temperature is weak. This indicates a difference in the manner in which the ethoxylated alcohol interacts with the anionic and cationic surfactant micelles. For the DTAB/C_4E_0 mixed systems, we note that the trends in the enthalpy values as a function of both alcohol concentration and temperature are similar to those of SDS/C_4E_0 systems. However, the micelle formation enthalpies for the DTAB/$C_4E_{1\text{–}3}$ systems are only slightly more exothermic with increasing temperature, especially at the higher alcohol concentrations. This is an indication that the heat capacity change upon micelle formation is quite small for these systems, which is significantly different from most other surfactant systems investigated in the literature [4, 5, 6, 7, 19, 20, 21, 22, 23]. This is a further indication that there are substantial differences in the manner in which these alcohols interact with ionic surfactants according to the headgroup charge.

Under isothermal conditions, for the SDS/C_4E_n systems, the mixed micelle formation enthalpies increase steadily in value in the direction of increasing alcohol concentrations at temperatures of 298 and 308 K, in excellent agreement with our previous paper [21]. At higher temperatures, the enthalpy values for the SDS/C_4E_n systems stay relatively constant or decrease slightly, i.e., become more exothermic. For the DTAB $C_4E_{1\text{–}3}$ systems, however, this small trend towards more exothermic values of the mixed micelle formation enthalpies is absent, and is in fact towards more endothermic values over similar alcohol concentration ranges.

Table 2. Cmc values and micelle formation enthalpies for DTAB/C_4E_n systems as a function of temperature and alcohol concentration

	Cmc Values (±0.20 mmol/l)				$\Delta_{mic}H°$ values ±0.50 kJ/mol			
C_4E_0								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.00	15.8	16.4	17.3	18.4	–1.2	–5.7	–9.3	–12.2
0.10	13.8	14.6	15.4	15.9	2.1	–2.0	–5.2	–12.3
0.20	11.9	11.7	14.6	14.6	3.2	–3.7	–8.3	–11.6
0.30	9.9	12.0	14.3	14.9	4.7	–4.8	–10.1	–13.0
0.40	10.1	13.3	14.0	15.2	7.2	–4.9	–10.7	–13.5
C_4E_1								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.00	15.8	16.4	17.3	18.0	–1.2	–5.7	–9.3	–12.2
0.10	12.1	14.1	14.9	15.3	–0.5	–1.6	–2.6	–6.4
0.20	10.9	12.8	13.0	13.6	0.7	1.2	–1.5	–1.8
0.30	8.1	9.6	11.0	13.5	1.5	0.5	0.7	0.4
0.40	9.7	10.0	11.7	13.0	2.1	1.6	1.4	0.9
C_4E_2								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.00	15.8	16.4	17.3	18.0	–1.2	–5.7	–9.3	–12.2
0.10	12.7	14.3	14.6	14.9	1.4	–1.2	–4.9	–8.1
0.20	10.1	12.7	13.4	13.9	2.6	0.5	–2.7	–6.5
0.30	7.6	9.0	11.2	13.5	2.5	1.7	0.7	–4.1
0.40	10.1	10.3	11.7	13.8	1.9	1.4	1.4	0.9
C_4E_3								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.00	15.8	16.4	17.3	18.0	–1.2	–5.7	–9.3	–12.2
0.10	13.0	14.0	15.0	15.6	2.1	–1.2	–1.6	–7.1
0.20	10.8	12.4	13.5	14.0	1.8	0.4	0.6	–2.4
0.30	8.5	11.4	11.8	13.2	3.7	1.7	1.8	–1.4
0.40	7.8	10.0	11.7	13.8	2.1	1.4	2.0	1.3

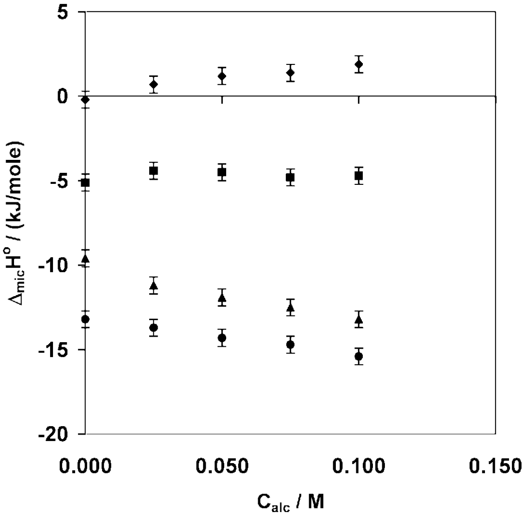

Fig. 2. Micellization enthalpies ($\Delta_{mic}H°$ values) for SDS in C_4E_0 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

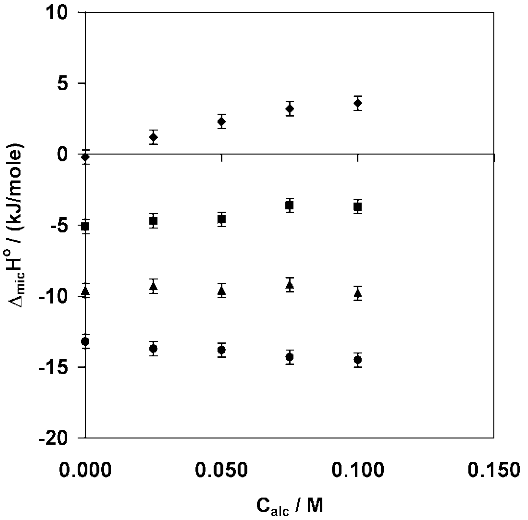

Fig. 3. Micellization enthalpies ($\Delta_{mic}H°$ values) for SDS in C_4E_1 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

To interpret the micelle formation enthalpies from the isoperibol solution calorimeter, one must examine the enthalpic contributions from the hydrophobic effects, alkyl chain interactions, and electrostatic contributions to the mixed micelle formation process. In the case of the SDS/C_4E_n mixed micelles in Table 1, we note that the positive $\Delta_{mic}H°$ values indicate the dominance of the hydrophobic effects at 298 K. Wang and Olofsson [6, 23] examined the enthalpy changes for poly(ethylene oxide)/surfactant systems at 298 K using isothermal titration calorimetry. Their results suggested that the transfer of the ethylene oxide group from the aqueous

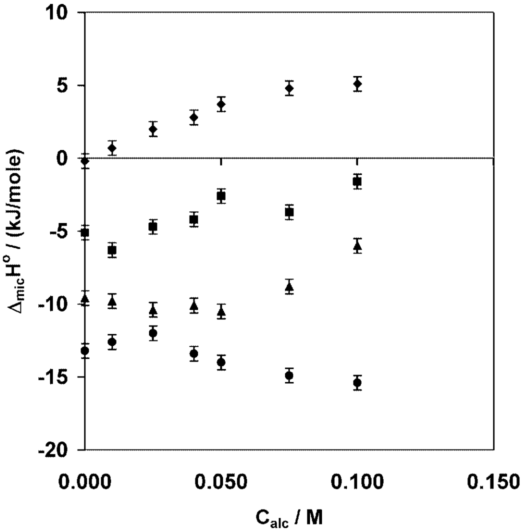

Fig. 4. Micellization enthalpies ($\Delta_{mic}H^\circ$ values) for SDS in C_4E_2 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

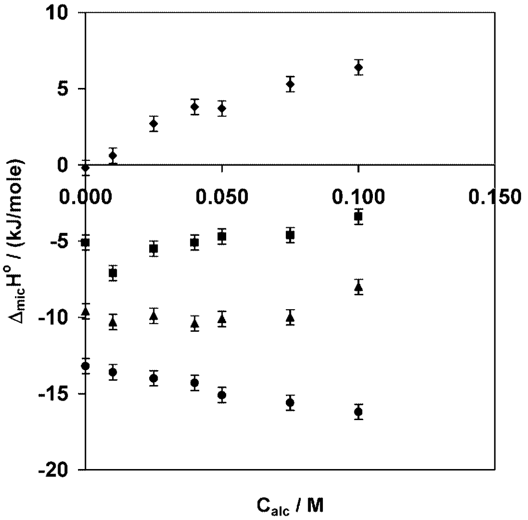

Fig. 5. Micellization enthalpies ($\Delta_{mic}H^\circ$ values) for SDS in C_4E_3 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

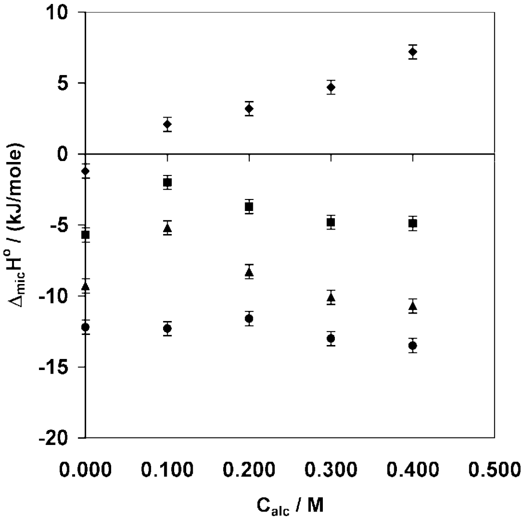

Fig. 6. Micellization enthalpies ($\Delta_{mic}H^\circ$ values) for DTAB in C_4E_0 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

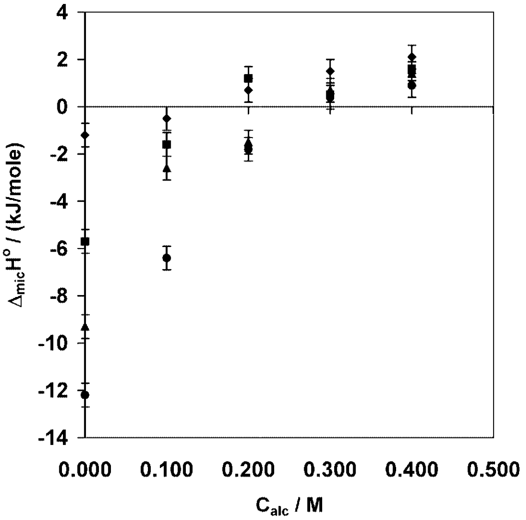

Fig. 7. Micellization enthalpies ($\Delta_{mic}H^\circ$ values) for DTAB in C_4E_1 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

phase to the micelles leads to more positive enthalpy changes in the systems and that this increase is dependent on the polymer chain length and concentration. For the SDS/C_4E_n systems, the micelle formation enthalpies are indeed more endothermic with increasing alcohol concentration at constant temperature. However, the trend towards more negative values above 308 K indicates that the micelle formation process is shifting from an entropy-dominated process at lower temperatures, to an enthalpy driven process at higher temperatures. These trends in the $\Delta_{mic}H^\circ$ values with T are in agreement with the literature [5, 6, 19, 20, 21, 22. 23].

From Table 1, we observe that at 298 K, at a constant alcohol concentration, the micelle formation enthalpies are more endothermic with increasing number of ethylene oxide groups. At higher temperatures, the tendency for the increasing alcohol concentration to increase the $\Delta_{mic}H^\circ$ values becomes less apparent, due to a breakdown in the water structure at higher temperatures and a smaller contribution from the hydrophobic effects. The enthalpy data for the SDS/C_4E_n systems are plotted in Fig. 10 at 298 K as a function of the alcohol concentration. From the slope of the enthalpy change with added alcohol concentration, the increase in the

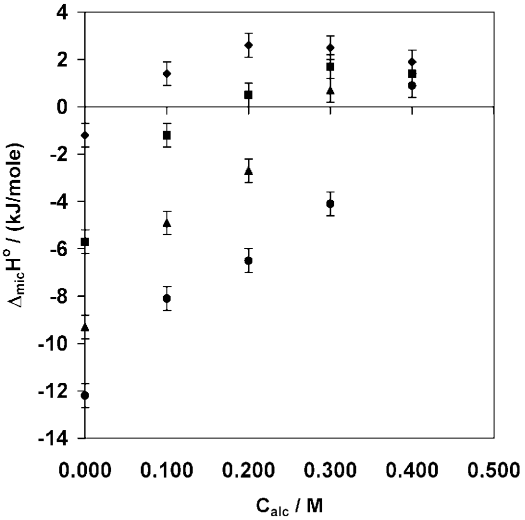

Fig. 8. Micellization enthalpies ($\Delta_{mic}H°$ values) for DTAB in C_4E_2 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

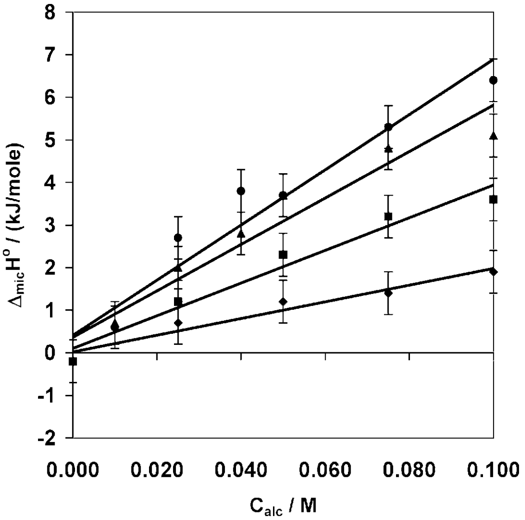

Fig. 10. Micellization enthalpies ($\Delta_{mic}H°$ values) for SDS in C_4E_n mixed micelles as a function of alcohol concentration at 298.2 K (◆ – C_4E_0; ■ – C_4E_1; ▲ – C_4E_2; ● – C_4E_3)

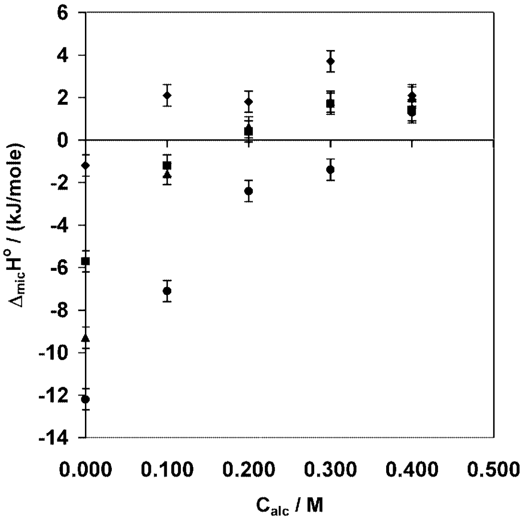

Fig. 9. Micellization enthalpies ($\Delta_{mic}H°$ values) for DTAB in C_4E_3 mixed micelles as a function of temperature (◆ – 298 K; ■ – 308 K; ▲ – 318 K; ● – 328 K)

$\Delta_{mic}H°$ value per EO group at constant alcohol concentration is ≈2 kJ/mol. This is significantly different from the value for the dehydration enthalpy per EO group of about 7 kJ/mol [25, 26]. This difference may be in part due to the release of extra counterions from the micellar surface (due to the decrease in the β values with higher ethoxylated alcohols) or it may be that for the transfer of the EO group to the micellar phase, some contact with water is maintained, consistent with the location of the solubilizates in the micellar interior from nmr NOESY experiments [27, 28]. We note that this trend towards more positive micellization enthalpy values with increasing number of EO groups becomes diminished at higher temperatures, due to the decrease in the enthalpic contribution to the hydrophobic effects.

In the case of the DTAB/C_4E_n mixed systems, it is clear from the enthalpy data in Table 2 and Fig. 5, the DTAB/C_4E_0 systems behave very much like all the SDS/C_4E_n systems. Hence, we can interpret the substantial increase in the $\Delta_{mic}H°$ values at 298 K as being due to the increased hydrophobic effects as the alcohol and surfactant co-micellize in solution. As the temperature is increased, the breakdown in the water structure leads to a diminished contribution from the hydrophobic effects, and the increase in $\Delta_{mic}H°$ is not as significant. For the DTAB C_4E_{1-3} systems, the smaller and somewhat irregular changes in the micellization enthalpy as a function of alcohol concentration and temperature must be due to lack of interaction between the hydrophobic part of the EO moiety and the DTAB micellar interior, whereas for the SDS/C_4E_n systems, the penetration of the EO group into the micellar interior [10, 11] is accompanied by an increase in the mixed micellization enthalpy at lower temperatures. The bulky nature of the trimethylammonium headgroup effectively shields the micellar core from water contact [26, 29]; this would mean that the EO group would undergo dehydration if it penetrated the micelle patisade layer, which reduces the driving force for the transfer of the ethylene oxide group from the aqueous phase to the micellar interior.

Cmc values, Gibbs energies, and micelle formation entropies

The cmc values were obtained from the breaks in the enthalpic titration curves and are presented in Tables 1 and Table 2 along with the micelle formation enthalpies. The $\Delta_{mic}G^{\circ}$ values were calculated from the calorimetrically determined cmc values and the counterion binding data, obtained from conductometric titrations over the temperature range of interest. We note that the calorimetric cmcs for the mixed micelles are slightly different than those determined conductometrically; however, the trends in the present cmc values as a function of both alcohol concentration and temperature are in excellent agreement with previous papers.[11, 12] The calorimetric cmc values for the mixed micelles are presented in Tables 1 and Table 2. The Gibbs energies and entropies are given in Tables 3 and Table 4. We now set about discussing the trends in the entropies and the Gibbs energies, beginning with the anionic surfactant mixed micelles.

From the tabulated values of the Gibbs energy changes (Tables 3 and Table 4), it appears that the addition of the alcohols to the mixed systems has a similar effect on micellization process at all temperatures, in that a steady increase in ΔG^{o}_{mic} is observed over the entire concentration range of the surfactant/C_4E_n mixed micelles. As more alcohol is added, it appears that the driving force of micellization is diminished and micelle formation becomes less spontaneous. The origin of this increase is likely electrostatic in nature, as the reduction in the degree of counterion binding would lead to increased interactions between neighboring charged surfactant head groups. In the case of the anionic surfactant, however, if we look at the SDS/C_4E_0 → SDS/C_4E_1 systems, there appears to be an initial decrease in the $\Delta_{mic}G^{\circ}$ values consistent with the EO groups imparting a hydrophobic contribution to the mixed micelle formation process. In the DTAB/C_4E_0 → DTAB/C_4E_3 case, the Gibbs energy changes increase as the first EO group is added (i.e., C_4E_0 – C_4E_1) at constant alcohol concentration and stays the same thereafter (C_4E_2 – C_4E_3). If we examine Eq. 3, it is clear that this initial increase must be electrostatic in origin, consistent with the lack of penetration of the EO groups into the micellar interior in the cationic surfactant case. For the anionic surfactants, the effect on the Gibbs energy of micellization for each of the ethoxylated alcohols is the same at the lowest concentration range investigated (up to about 0.10 M), due to the compensatory relationship between $\Delta_{mic}H^{\circ}$ and $\Delta_{mic}S^{\circ}$.

For the SDS/C_4E_n mixed micelles, the $\Delta_{mic}S^{\circ}$ values decrease with increasing temperature at constant alcohol

Table 3. Derived thermodynamic quantities of micelle formation for SDS/C_4E_n systems as a function of temperature and alcohol concentration

	$\Delta_{mic}G^{o}$ (±0.50 kJ/mol)				$\Delta_{mic}S^{o}$ values (±3 J/(K mol))			
C_4E_0								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	–34.9	–36.7	–37.8	–38.8	116	102	89	78
0.025	–34.6	–35.0	–35.5	–36.2	118	99	76	69
0.050	–34.1	–34.6	–35.6	–35.8	118	98	74	66
0.075	–34.1	–34.2	–35.0	–35.5	119	96	71	63
0.100	–34.0	–33.9	–34.7	–35.2	120	95	68	60
C_4E_1								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	–34.9	–36.7	–37.8	–38.8	116	102	89	78
0.025	–34.8	–35.9	–36.9	–37.9	121	101	87	74
0.050	–33.6	–34.4	–35.5	–36.4	120	97	81	69
0.075	–32.5	–33.4	–34.3	–35.1	120	96	79	63
0.100	–31.4	–32.3	–33.2	–33.9	117	93	73	59
C_4E_2								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	–34.9	–36.7	–37.8	–38.8	116	102	89	78
0.010	–35.1	–36.1	–37.2	–38.2	120	97	86	78
0.025	–33.7	–34.7	–35.7	–36.7	119	97	80	75
0.040	–33.1	–34.2	–35.2	–36.1	121	97	79	69
0.050	–33.2	–34.0	–34.9	–35.8	124	102	77	67
0.075	–32.9	–33.9	–34.9	–35.8	126	98	82	64
0.100	–31.3	–32.1	–33.1	–33.9	122	99	85	56
C_4E_3								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	–34.9	–36.7	–37.8	–38.8	116	102	89	78
0.010	–34.6	–35.6	–36.6	–37.6	118	92	83	73
0.025	–34.7	–35.6	–36.6	–37.6	125	98	84	72
0.040	–33.8	–34.8	–35.7	–36.6	126	96	80	68
0.050	–33.0	–33.9	–34.9	–35.7	123	95	78	63
0.075	–31.6	–32.6	–33.5	–34.3	124	91	74	57
0.100	–31.1	–31.8	–32.6	–33.4	126	92	77	52

Table 4. Derived thermodynamic quantities of micelle formation ($\Delta_{mic}G^o$ values ± 0.50 kJ/mol and $\Delta_{mic}S^o$ values ± 3 J/(K mol) for DTAB/C_4E_n systems as a function of temperature and alcohol concentration

	$\Delta_{mic}G^o$ (± 0.50 kJ/mol)				$\Delta_{mic}S^o$ values (± 3 J/(K mol))			
C_4E_0								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	−35.4	−36.0	−37.4	−36.9	115	98	88	76
0.100	−34.6	−35.1	−37.0	−36.3	123	107	100	73
0.200	−34.3	−34.7	−35.1	−35.3	126	101	84	72
0.300	−34.0	−33.7	−34.3	−34.6	130	94	76	66
0.400	−32.2	−31.6	−32.2	−33.4	132	87	68	60
C_4E_1								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	−35.4	−36.0	−36.5	−37.0	115	98	85	76
0.100	−34.5	−33.9	−33.9	−34.0	114	105	98	84
0.200	−33.0	−32.4	−31.8	−32.2	113	109	95	93
0.300	−32.6	−31.5	−31.1	−30.0	114	104	100	93
0.400	−30.9	−31.8	−30.0	−29.7	111	108	99	93
C_4E_2								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	−35.4	−36.0	−36.5	−37.0	115	98	85	76
0.100	−34.3	−33.9	−34.0	−34.1	120	106	92	79
0.200	−33.3	−32.4	−31.7	−32.1	120	107	91	78
0.300	−32.9	−31.8	−31.7	−30.0	119	109	102	79
0.400	−30.1	−31.7	−30.0	−29.4	107	107	99	92
C_4E_3								
C_{alc}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.000	−35.4	−36.0	−36.5	−37.0	115	98	85	76
0.100	−33.8	−34.0	−33.7	−33.5	120	106	104	80
0.200	−32.6	−31.7	−31.5	−32.1	115	104	104	91
0.300	−31.6	−30.7	−30.4	−30.3	118	105	105	88
0.400	−30.1	−29.8	−29.8	−29.2	108	101	103	93

concentration in the mixed solvent. At 298 K, the entropies of micelle formation become larger in magnitude with increasing alcohol concentration, and this increase appears to be more substantial for the alcohols with larger numbers of EO groups. At higher temperatures, the entropies decrease with increasing alcohol concentration. The contributions to the micelle formation entropy include a) the hydrophobic effects; b) the partial molar entropy decrease for the surfactant and alcohol as the mixed micelles form; c) an entropy of mixing contribution. The DTAB/C_4E_0 system is similar to the SDS/C_4E_0 system for the observed trends of the $\Delta_{mic}S°$ as a function of temperature and alcohol concentration. For the DTAB/C_4E_n systems, we observe, in general, an entropy increase after the first addition of alcohol to the mixed micelles, with the micellization entropy remaining essentially constant thereafter. If the EO groups do not penetrate the micelle palisade layer, we can assume that the contribution of the EO groups to the hydrophobic effects is diminished to ≈ 0 in these systems, and that essentially only the four carbon chain of the alcohol is mixing with the micellar interior. The first initial increase may be due to the release of water molecules from an EO group as it interacts with the hydrophobic and bulky trimethylammonium headgroup. The fact that the entropy changes are essentially constant after this initial increase indicates the decrease in the partial molar entropy of both the surfactant and alcohol is compensated by the entropy increase due to the mixing of the surfactant and the four-carbon alcohol chain in the micellar phase. We note that this entropy increase is consistent over the temperature range investigated, which is not what we would expect from the breakdown of the hydrophobic effects at higher temperatures [16]. This indicates that even at higher temperatures where the more open micellar structure should enable the penetration of the EO groups into the micellar interior, exclusion of the EO groups from the micellar phase of DTAB appears likely.

Conclusions

From the results of calorimetric titrations, the thermodynamic properties of micelle formation for the SDS/alkoxyethanol and DTAB/alkoxyethanol mixed micelles have been determined over a wide range of temperature and alcohol concentrations. We note that in agreement with previous work in these systems, the contribution of the EO group to the hydrophobic effects results in an increase in the enthalpy change upon micelle formation as the number of EO groups in the alcohol is increased. The entropy values, determined via the application of the mass action models to the calorimetric cmc values, are consistent with the hydrophobic effects dominating the changes in the thermodynamics properties of micelle formation over the majority of the temperature range investigated. For the mixed micelles composed of the cationic surfactant (DTAB) and alkoxyethanols, the enthalpy and entropy changes upon micelle formation show little temperature variation upon the addition of successive EO groups to the four-carbon backbone. These results are consistent with previous work indicating the penetration of the EO group into the micellar interior of an anionic micelle, whereas the EO group would have a negligible contribution to the interactions between cationic surfactants and ethoxylated alcohols.

Acknowledgments The financial support of NSERC (research grant, D.G.M) and the St. F.X. University Council for Research is greatly appreciated. C.A.K., D.J.F., and J.A.H. wish to acknowledge the grant of NSERC Undergraduate Summer Research Awards. S.M.K, B.E.H. and S.M.K. are grateful to St. F.X. University for financial support.

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