Colloid Polym Sci 278:1155–1163 (2000)

ORIGINAL CONTRIBUTION

M. S. Bakshi

Influence of alkoxyethanols on the mixed micelle formation by hexadecyltrimethylammonium bromide and tetradecyltrimethylammonium bromide surfactant mixtures

Received: 11 January 2000
Accepted: 14 April 2000

M. S. Bakshi
Department of Chemistry
Guru Nanak Dev University
Amritsar 143005, India
e-mail: ms_bakshi@yahoo.com

Abstract The conductances of hexadecyltrimethylammonium bromide (HTAB) and tetradecyltrimethylammonium bromide (TTAB) mixtures over the entire mole fraction range of HTAB were measured in aqueous binary mixtures of ethylene glycol monomethyl ether, monoethyl ether, and monobutyl ether, and of diethylene glycol monomethyl ether and monoethyl ether containing 10–30 wt% additive in their respective binary mixtures at 30 °C. Each conductivity curve showed a single break over the whole mole fraction range of HTAB–TTAB mixtures. From the break in the conductivity curve, various micellar parameters were calculated and the results were discussed with respect to the alkoxyethanol's additive effect on the mixed micelle formation. The micellar parameters of HTAB, TTAB, and of their mixtures showed a strong dependence both on the amount as well as on the number of repeating units in the presence of ethylene glycol derivatives, whereas a significant dependence only on the amount of additive was observed in aqueous diethylene glycol derivatives. The results in the former case were attributed to the hydrophobic hydration of the mixed micelles by the ethylene glycol derivatives, which showed a large dependence on the increase in the alkyl chain length of the additive. The hydrophobic hydration was considerably reduced in the case of diethylene glycol derivatives owing to the presence of an extra ether oxygen. An evaluation of the nonideality in the HTAB–TTAB mixtures revealed that in spite of the strong hydrophobic hydration of the HTAB–TTAB mixtures by the alkoxyethanols, the mixed micelles remain almost free from the additive molecules.

Key words Medium effects · Cationic surfactants · Mixed micelles · Alkoxyethanols · Conductivity measurements

Introduction

Associative organic solvents such as glycol oligomers have achieved considerable importance because of their fascinating solvation behavior, which is quite close to that of water. In the presence of water, glycols act as a water-structure breaker, which leads to the formation of a new structure knitted with the hydrogen bonding between the water and the glycol molecules. Such a combined structured environment also provides a complete hydrophobic environment for amphiphilic molecules as of surfactants to aggregate in a similar way as in pure water. Therefore, it is important to understand the physiochemical process of micelle formation in aqueous glycol solutions, which have wide implications both in fundamental as well as in applied chemistry [1, 2]. From the fundamental point of view, the glycol additive effect on the micelle formation of cationic surfactants is still not so clear in comparison to that on the micelle formation of anionic surfactants [1]. In the case of cationic surfactants, the presence of additive glycols mainly contributes to a change in the aqueous medium properties and the cationic micelles remain more or less unaffected [3–7]. The most accepted explanation for this is based on the fact that the bulky polar head groups of cationic surfactants hinder the approach of additive glycol molecules [8–10] and this is especially true in the presence of polyethylene glycols [6, 7]. From the applied point of view, these additives are widely used in detergents, cosmetics, and in many other industrial applications [2, 11] and, therefore, it is equally important to explore the fundamental nature of glycol–cationic surfactant interactions in order to exploit their properties for appropriate industrial uses.

In order to achieve our goal, in the present work, a cationic surfactant binary combination, i.e. hexadecyl trimethylammonium bromide (HTAB) and tetradecyltrimethylammonium bromide (TTAB) in the presence of aqueous alkoxyethanols was selected. This is due to the fact that the commercial surfactants are generally mixtures of two or more surfactants and are better in many respects than single surfactants; therefore, the evaluation of their physiochemical properties has recently attracted a lot of attention [12, 13]. Most of the work on such properties of binary surfactant systems has been focused only in pure water [12, 13]. In our recent studies [3–7], we have observed that the presence of ethylene glycol oligomers dramatically influences the micellar properties of cationic surfactants, mainly by changing the medium properties. However, the present alkoxyethanols are expected to have quite different behavior from that of ethylene glycol oligomers owing to the presence of an alkyl group. Therefore, such additives apart from influencing the micellar properties by changing the solvent structure are also expected to interact with the surfactant molecules through hydrophobic hydration. The choice of such a surfactant combination and glycol additive system was due to three reasons. First, the driving force responsible for cationic surfactant–glycol interactions is still poorly understood [9, 10]; second, to observe the process of mixed micelle formation under the strong influence of medium effects and hydrophobic hydration by the additive glycols; and third, to compare the medium effects of ethylene glycol with that of diethylene glycol derivatives on the mixing behavior of HTAB–TTAB mixtures. This additive effect can be better visualized by using the conductivity technique, since conductivity is considered to be quite sensitive to the micellar transitions, particularly when ionic surfactants are involved [7, 14].

Experimental

HTAB and TTAB, both from Lancaster, England, were recrystallized from acetone and 2-propanol mixtures. Both surfactants were dried in a vacuum at 60 °C for 2 days.

Ethylene glycol monomethyl ether (EGMME), ethylene glycol monoethyl ether (EGMEE), and ethylene glycol monobutyl ether (EGMBE), all more than 99% pure from Central Drug House, Bombay, were further purified by methods reported elsewhere [15]. Diethylene glycol monomethyl ether (DEGMME) and diethylene glycol monoethyl ether (DEGMEE), both general reagent grade from Merck, Germany, were used as received. Triply distilled conductivity water was used in the preparation of all solutions. All reference and stock solutions were prepared by mass with an accuracy of ± 0.01 mg. The mole fractions were accurate to ± 0.0001 units.

The conductivity measurements were carried out with a digital conductivity meter (Naina Electronics, Chandigarh, India, model NDC-732) at a fixed frequency of 1000 Hz. A dip-type conductivity cell with a double-walled jacket to circulate the thermostated water was used for all the measurements. The capacity of the conductivity cell was about 100 ml. An automatic thermostat bath from Shimadzu, Japan, was used for maintaining the temperature within uncertainties of ± 0.05 °C. All measurements were performed at 30 °C.

Initially, 50 ml of the reference solution consisting of an appropriate amount of each additive in water was put in the conductivity cell. It was then equilibrated at 30 °C for at least 1 h before starting the experiment. Then a known amount of stock solution of HTAB or TTAB or HTAB–TTAB mixtures made with the same reference solution was added from a micropipette (Finnpipette, Labsystems, Finland) and again equilibrated for some time till the conductivity value became constant. In this way, the precise conductances of HTAB + TTAB mixtures over the entire mole fraction range of HTAB (α_{HTAB}) in EGMME and water, EGMEE and water, EGMBE and water, DEGMME and water, and DEGMEE and water containing 10–30 wt% additive in their respective binary mixtures were measured. The error in the conductance measurements was $\pm 0.5\%$. The data in pure water were taken from our earlier work [5].

Results and discussion

Conductivity behavior

Each conductivity (κ) plot in the absence and presence of additive showed a single break. The κ value varied linearly with respect to the increase in the concentration of single as well as of mixed surfactants in both the pre- and the postmicellar regions and the slope in the premicellar region was greater than that in the postmicellar region. The intersection point between the two straight lines gave the critical micelle concentration (cmc). These values for HTAB, TTAB, and HTAB–TTAB mixtures in the presence of various ethylene and diethylene glycol derivatives were calculated as explained earlier [3, 4] and are listed in Tables 1 and 2, respectively. Such a concentration dependence of κ of HTAB, TTAB, and their mixtures in aqueous EGMME and DEGMME over the entire mole fraction range of HTAB is shown in Fig. 1. Similar plots were also obtained for other additives (not shown). The dependence of κ of the present surfactant electrolytes on the nature of alkoxyethanols demonstrates some interesting features.

The additive effect of ethylene glycol derivatives on the variation of the κ of HTAB and TTAB is shown in

Table 1 Values of the critical micelle concentration (*cmc*), the ideal mixed cmc (*cmc**), 100 premicellar slope (S_1), 100 postmicellar slope (S_2), micelle mole fraction of hexadecyltrimethylammonium bromide (*HTAB*) ($\overline{x_2^{\mathrm{m}}}$), and mole fraction of HTAB (x_1) of HTAB–tetradecyltrimethylammonium bromide (*TTAB*) mixtures in the presence of ethylene glycol derivatives at 30 °C

α_{HTAB}	cmc/10^{-4} mol dm^{-3}	cmc*/10^{-4} mol dm^{-3}	$100S_1$/cm^{-1} S mol^{-1} dm^3	$100S_2$/cm^{-1} S mol^{-1} dm^3	$\overline{x_2^{\mathrm{m}}}$	x_1
10 wt% ethylene glycol monomethyl ether						
0.000	47.54	47.54	10.1 ± 0.09	3.08 ± 0.07	0.0	0.0
0.0715	42.55	39.55	10.1 ± 0.04	3.11 ± 0.09	0.17	0.17
0.1614	36.35	32.65	10.1 ± 0.08	3.22 ± 0.10	0.38	0.36
0.2779	29.99	26.63	10.1 ± 0.05	3.35 ± 0.15	0.62	0.55
0.4349	22.91	21.33	10.2 ± 0.08	3.44 ± 0.07	0.86	0.73
0.6580	16.82	16.63	10.3 ± 0.06	3.64 ± 0.03	0.97	0.88
0.7759	14.73	14.90	10.4 ± 0.07	3.55 ± 0.08	0.95	0.93
1.000	12.43	12.43	10.4 ± 0.89	3.65 ± 0.04	1.0	1.0
20 wt% ethylene glycol monomethyl ether						
0.000	70.22		7.90 ± 0.08	3.26 ± 0.08	0.0	
0.0845	67.09		7.54 ± 0.04	3.28 ± 0.06	0.12	
0.1876	64.95		7.00 ± 0.03	3.25 ± 0.14	0.24	
0.3159	63.21		6.22 ± 0.03	3.21 ± 0.15	0.36	
0.4801	61.81		5.20 ± 0.03	3.22 ± 0.12	0.48	
0.6978			3.83 ± 0.02			
0.8061			3.22 ± 0.01			
1.000			2.10 ± 0.01			
10 wt% ethylene glycol monoethyl ether						
0.000	43.08	43.08	10.2 ± 0.03	3.86 ± 0.05	0.0	0.0
0.0844	39.38	36.89	10.2 ± 0.04	4.16 ± 0.09	0.18	0.17
0.1873	34.32	31.39	10.2 ± 0.06	4.03 ± 0.05	0.38	0.36
0.3156	28.93	26.47	10.3 ± 0.04	4.19 ± 0.08	0.60	0.55
0.4797	24.23	22.05	10.3 ± 0.05	4.10 ± 0.07	0.79	0.71
0.6973	17.85	18.06	10.3 ± 0.05	4.22 ± 0.07	0.93	0.87
0.8058	16.05	16.56	10.4 ± 0.06	4.09 ± 0.10	0.95	0.91
1.000	14.42	14.42	10.4 ± 0.03	4.09 ± 0.04	1.0	1.0
20 wt% ethylene glycol monoethyl ether						
0.000	95.75	95.75	5.10 ± 0.03	2.73 ± 0.07	0.0	0.0
0.0877	90.88	87.96	5.09 ± 0.02	2.71 ± 0.06	0.15	
0.1938	84.85	80.08	4.84 ± 0.02	2.71 ± 0.06	0.31	0.29
0.3247	76.16	72.11	4.86 ± 0.02	2.69 ± 0.03	0.49	0.47
0.4903	63.90	64.04	4.82 ± 0.02	2.65 ± 0.05	0.69	
0.7062	58.34	55.89	4.87 ± 0.01	2.63 ± 0.07	0.85	0.83
0.8123	50.14	52.60	4.83 ± 0.03	2.62 ± 0.05	0.92	0.87
1.000	47.64	47.64	4.73 ± 0.02	2.56 ± 0.05	1.0	1.0
10 wt% ethylene glycol monobutyl ether						
0.000	77.75	77.75	9.34 ± 0.04	7.39 ± 0.19	0.0	0.0
0.0876	71.37	70.92	9.37 ± 0.05	7.56 ± 0.03	0.16	
0.1937	63.66	64.10	9.32 ± 0.03	7.69 ± 0.06	0.34	
0.3246	58.01	57.31	9.39 ± 0.03	7.82 ± 0.15	0.52	0.50
0.4899	49.46	50.54	9.45 ± 0.03	8.12 ± 0.09	0.70	0.67
0.7060	43.39	43.78	9.50 ± 0.05	8.30 ± 0.12	0.84	0.83
0.8122	39.91	41.08	9.52 ± 0.04	8.42 ± 0.07	0.89	0.88
1.000	37.04	37.04	9.62 ± 0.05	8.48 ± 0.12	1.0	1.0
20 wt% ethylene glycol monobutyl ether						
0.000			6.13 ± 0.02			
0.0900			6.03 ± 0.02			
0.1982			6.19 ± 0.01			
0.3309			6.10 ± 0.04			
0.4974			6.25 ± 0.03			
0.7121			6.30 ± 0.03			
0.8166			6.33 ± 0.02			
1.000			6.43 ± 0.03			

Fig. 2. It can be seen that there is a significant increase in the κ values in the postmicellar region with an increase in the repeating units of additive from EGMME to EGMBE, whereas a large fall in the κ values can be observed with an increase in the amount of each additive from 10 to 20 wt% (not shown). A close inspection of Fig. 2 also demonstrates that the break point in the κ curves of both HTAB and TTAB in pure water is quite

Table 2 Values of cmc, cmc*/ $100S_1$, $100S_2$, $\overline{x_2^m}$, and x_1 of HTAB–TTAB mixtures in the presence of diethylene glycol derivatives at 30 °C

α_{HTAB}	cmc/10^{-4} mol dm^{-3}	cmc*/10^{-4} mol dm^{-3}	$100S_1$/cm^{-1} S mol^{-1} dm^3	$100S_2$/cm^{-1} S mol^{-1} dm^3	$\overline{x_2^m}$	x_1
10 wt% diethylene glycol monomethyl ether						
0.000	51.04	51.04	6.48 ± 0.04	2.09 ± 0.02	0.0	0.0
0.1429	43.27	38.19	6.49 ± 0.03	2.13 ± 0.05	0.30	0.28
0.2943	34.89	30.15	6.41 ± 0.05	2.05 ± 0.00	0.58	0.52
0.4547	29.00	24.66	6.41 ± 0.01	2.00 ± 0.03	0.79	0.70
0.6252	21.59	20.65	6.41 ± 0.04	2.03 ± 0.03	0.95	0.85
0.8066	17.76	17.61	6.48 ± 0.10	2.01 ± 0.02	0.98	0.94
1.000	15.22	15.22	6.46 ± 0.04	1.93 ± 0.02	1.0	1.0
30 wt% diethylene glycol monomethyl ether						
0.000	80.75	80.75	4.19 ± 0.03	2.32 ± 0.06	0.0	0.0
0.1513	74.90	73.18	4.15 ± 0.08	2.13 ± 0.04	0.21	
0.3084	67.86	66.69	4.04 ± 0.04	1.99 ± 0.06	0.42	0.42
0.4714	64.00	61.07	4.01 ± 0.03	1.85 ± 0.06	0.60	0.59
0.6408	59.33	56.15	3.92 ± 0.03	1.67 ± 0.04	0.76	0.74
0.8168	53.73	51.81	3.79 ± 0.03	1.49 ± 0.04	0.90	0.88
1.000	47.96	47.96	3.66 ± 0.02	1.30 ± 0.03	1.0	1.0
10 wt% diethylene glycol monoethyl ether						
0.000	49.28	49.28	6.57 ± 0.03	2.09 ± 0.02	0.0	0.0
0.1096	45.01	40.57	6.49 ± 0.03	2.13 ± 0.05	0.22	0.19
0.2353	37.44	33.73	6.41 ± 0.05	2.05 ± 0.00	0.45	0.42
0.3809	32.21	28.22	6.42 ± 0.09	2.00 ± 0.03	0.66	0.60
0.5516	26.24	23.68	6.41 ± 0.04	2.03 ± 0.03	0.85	0.77
0.7547	20.10	19.88	6.48 ± 0.10	1.99 ± 0.02	0.96	0.90
1.000	16.65	16.65	6.46 ± 0.04	1.93 ± 0.02	1.0	1.0
30 wt% diethylene glycol monoethyl ether						
0.000	111.0	111.0	3.29 ± 0.03	2.24 ± 0.03	0.0	0.0
0.1193	100.7	104.0	3.43 ± 0.01	2.16 ± 0.07	0.19	0.20
0.2529	94.20	97.10	3.38 ± 0.01	2.09 ± 0.03	0.37	0.36
0.4038	85.74	90.34	3.44 ± 0.02	1.97 ± 0.03	0.53	0.52
0.5753	78.25	83.73	3.44 ± 0.02	1.87 ± 0.06	0.68	0.66
0.7719	74.24	77.24	3.47 ± 0.01	1.83 ± 0.07	0.82	0.82
1.000	70.87	70.87	3.35 ± 0.01	1.68 ± 0.04	1.0	1.0

prominent and becomes a broad inflection point as the number of repeating units is increased from EGMME to EGMBE. Similar behavior was also observed for HTAB–TTAB mixtures over the whole mixing range (not shown). These results indicate that the micelle formation process as well as the nature of the micelles are significantly affected by the increase in the alkyl chain length of ethylene glycol derivatives. In contrast, the situation is quite the opposite in the presence of diethylene glycol derivatives (Fig. 3). Unlike previously, the κ decreases both in the pre- as well as in the postmicellar regions and the increase in the number of repeating units from DEGMME to DEGMEE does not show any marked effect on the variation of the κ value. This means that the diethylene glycol derivatives do not have any significant interactions with the micelles and a small decrease in the κ value is most probably due to the change in the medium properties. In order to further evaluate these results, the slopes of the pre- and the postmicellar regions were evaluated as follows.

Since the variation in the κ of a surfactant electrolyte is quite linear before and after the break or inflection point, a comparison among the monomeric and the micellar species under the additive effect of a series of alkoxyethanols can be made by computing the premicellar (S_1) and the postmicellar (S_2) slopes over the whole mole fraction range of mixtures. Both the S_1 and S_2 values were determined from the linear regression analysis of the κ data in the premicellar as well as in the postmicellar regions with a correlation factor always much better than 0.999 and are listed in Tables 1 and 2 along with their uncertainties. Since, the equivalent conductivity of a surfactant electrolyte can be written as $\Lambda = 1000\ \kappa/c$, it is possible to approximately equate a Λ value with $1000S_1$ for a highly dilute electrolyte solution [16]. On the other hand, since the conductivity of the monomers can be assumed to be constant after the cmc and it would be permissible particularly for the micelles of large aggregation numbers, the micellar state conductivity with reference to the monomer can be equated with the slope of the κ versus c profile in the postmicellar region. However, it is to be noted that the real ionic equivalent conductivity of the aggregated micelles can be computed if the aggregation number of the micelle is

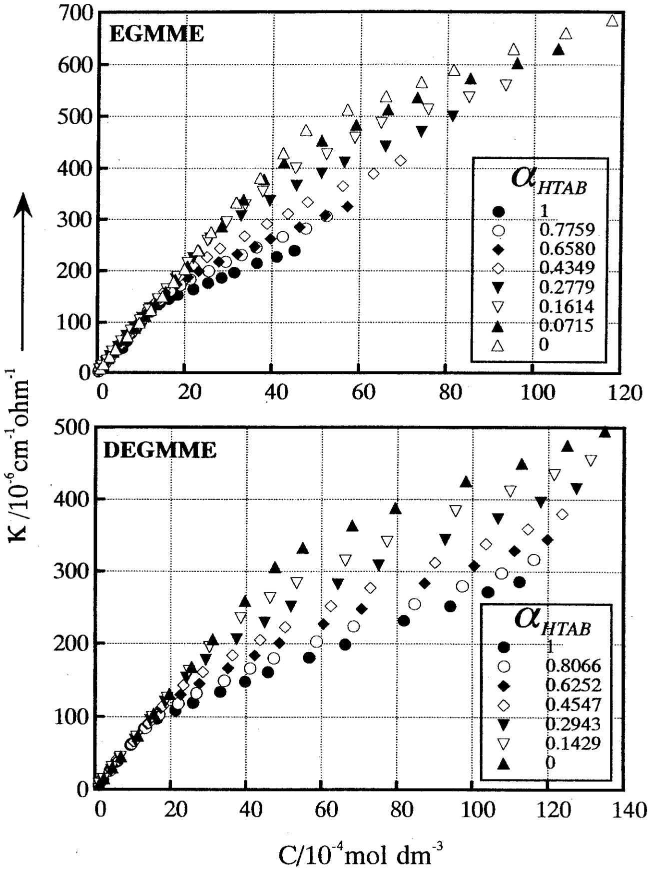

Fig. 1 Plot of conductivity (*κ*) versus concentration (*c*) of mixed hexadecyltrimethylammonium bromide (*HTAB*)–tetradecyltrimethylammonium bromide (*TTAB*) mixtures in aqueous 10 wt% additive: ethylene glycol monomethyl ether (*EGMME*); diethylene glycol monomethyl ether (*DEGMME*)

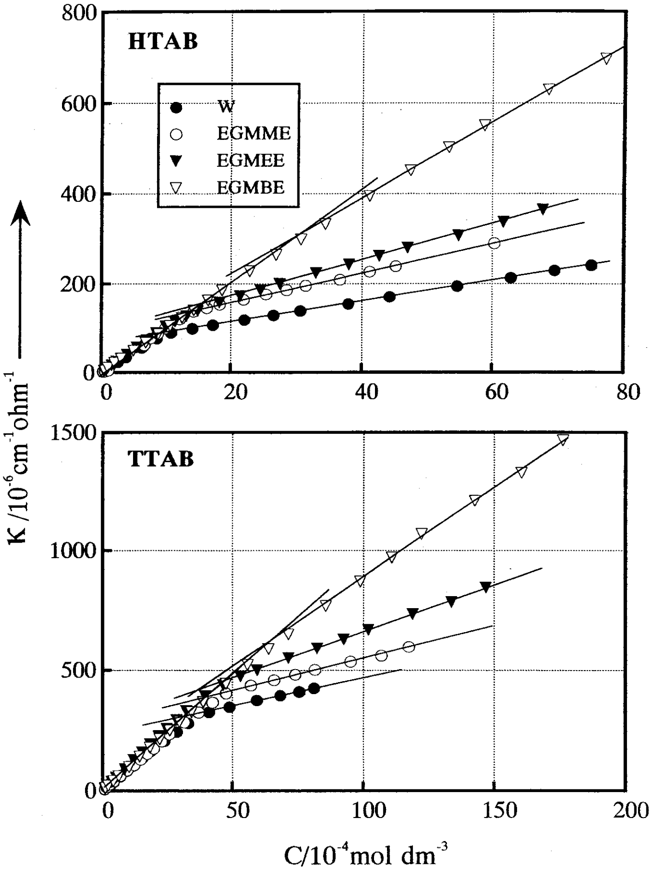

Fig. 2 Plot of *κ* versus *c* of HTAB and TTAB in pure water (*w*) and in aqueous 10 wt% ethylene glycol derivatives: ethylene glycol monomethyl ether (*EGMME*); ethylene glycol monoethyl ether (*EGMEE*); ethylene glycol monobutyl ether (*EGMBE*)

known. Similar quantities for single and mixed surfactant systems in the absence and presence of additives have already been discussed by some authors [14, 16–18].

Tables 1 and 2 show that the variation in the S_1 values over the whole mole fraction range is predominantly constant and linear except in 20 wt% EGMME, thus suggesting that there are practically no interactions between the unlike surfactant monomers in the premicellar region and that equal monomeric states are present over the whole mole fraction range of the mixture. No appropriate explanation can be given regarding a steep fall in the S_1 values in the presence of 20 wt% EGMME at the moment. Interestingly, the S_2 values (Fig. 4) in the presence of ethylene glycol derivatives are higher and those in the presence of diethylene glycol derivatives are lower than that in pure water. Such opposite behavior indicates that the micelles are more conducting in the presence of EGMME, EGMEE, and EGMBE, whereas the reverse is true in the presence of diethylene glycol derivatives. This indicates that the reverse additive effect of the latter has been caused by the presence of an extra ether oxygen and may have caused stronger structure-breaking effects in comparison to the former [19–21]. Thus, a stronger structure-breaking additive, like a diethylene glycol derivative, will prefer to remain in the medium and thereby reduce the relative permittivity and increase the viscous drag of the medium with the result being that the *κ* value decreases both in the pre- and in the postmicellar regions. Similar results have already been observed by Marangoni et al. [22] for dodecyltrimethylammonium bromide and tetraethylene glycol (TeEG) and water systems and they concluded that TeEG remains in the aqueous phase and only acts as a structure breaker. On the other hand, at least similar structure-breaking effects are also expected to be demonstrated by the ethylene glycol derivatives, but an increase in the *κ* value, particularly in the postmicellar region, can only be explained on the basis of the hydrophobic hydration of the micelles by the additive molecules (Figs. 2, 4). The

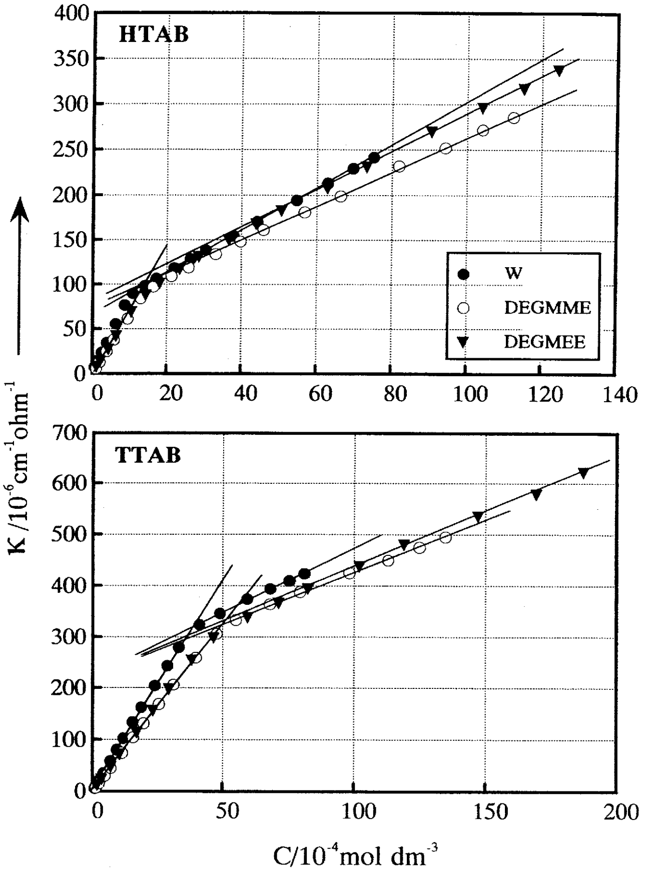

Fig. 3 Plot of κ versus c of HTAB and TTAB in pure water and in aqueous 10 wt% diethylene glycol derivatives: diethylene glycol monomethyl ether (*DEGMME*); diethylene glycol monoethyl ether (*DEGMEE*)

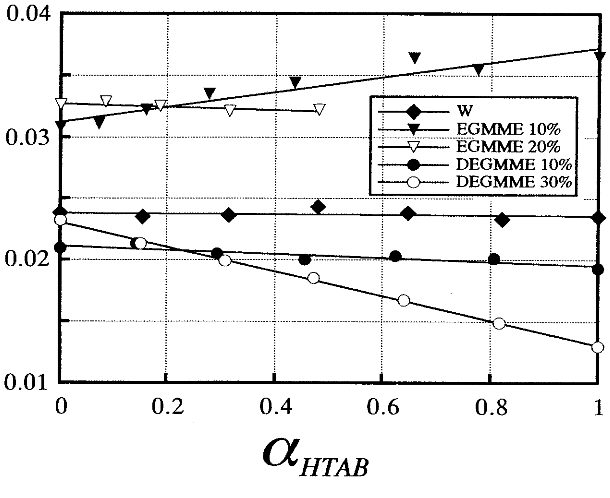

Fig. 4 Plot of postmicellar slope (S_2) ($\mathrm{cm^{-1}\ S\ mol^{-1}\ dm^3}$) versus mole fraction of HTAB (α_{HTAB}) for HTAB–TTAB mixtures in pure water and in aqueous additive

origin of such interactions can be attributed to the preferential solubilization of the surfactant hydrophobic tails by aqueous ethylene glycol derivatives through nonpolar–nonpolar interactions, which are also expected to be facilitated by the reduced polarity and enhanced viscosity of the medium. They will increase with an increase in the alkyl chain length of the substituted alkyl group and are also expected to result in the formation of loose micelles with comparatively high mobilities. This effect will certainly not be so prominent in aqueous diethylene glycol derivatives owing to the presence of an extra ether oxygen, which is expected to reduce nonpolar–nonpolar cohesive interactions between the surfactant tail and the substituted alkyl group of the additives.

Micelle formation

The mixed cmc values for HTAB–TTAB mixtures in some of the systems are shown graphically in Fig. 5. It is evident from Fig. 5 and Tables 1 and 2 that the mixed cmc values are regularly shifted towards higher values with an increase in the number of repeating units as well as with an increase in the amount of the respective alkoxyethanol. The overall variation in the cmc is identical both in the absence and in the presence of glycol oligomers. Similar results have been obtained previously [4–7]. Figure 5 shows that there is a regular, nonlinear decrease in the cmc value with an increase in the amount of HTAB in the HTAB–TTAB mixtures; therefore, it is expected that the course of initial decrease in the mixed cmc value with the induction of HTAB monomers should be affected by the preferential solvation of surfactant monomers by aqueous alkoxyethanol molecules. This effect can be determined by fitting the cmc data using the following equation:

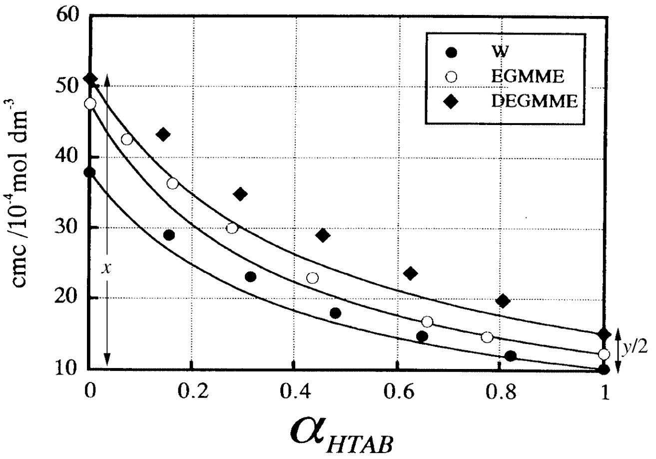

Fig. 5 Plot of the critical micelle concentration (*cmc*) versus α_{HTAB} for HTAB–TTAB mixtures in pure water and in aqueous 10 wt% additive. Experimental cmc: *points*; predicted cmc*: *solid line*

$$\mathrm{cmc} = a\exp(-\tau x_{\mathrm{TTAB}}) + b \ , \qquad (1)$$

where τ can be defined as a parameter which depends upon the rate of change of the mixed cmc value with the increase in the amount of HTAB in the HTAB–TTAB mixtures in the presence of additives. Thus, a change in the τ value in the presence of alkoxyethanols can be directly related to the influence of the additive molecules on the mixed micelle formation in comparison to a reference situation of pure water. Therefore, a τ value less than that for water will demonstrate the slowing down of the mixed micelle formation process in comparison to that in pure water. In order to compute the value of τ, one has to put the values of the a and b parameters in Eq. (1), where $a \approx x - y/2$ and $b \approx y/2$ (Fig. 5). The τ values thus obtained from Eq. (1), with a correlation factor in most of the cases close to 0.999, are plotted in Fig. 6 against the molecular weight of the alkoxyethanols. It is interesting to observe that the τ value decreases regularly with an increase in the molecular weight of the additive. This indicates that the process of mixed micelle formation is slowed down owing to the medium effects of the additive glycols from ethylene glycol to diethylene glycol derivatives. The stability in the mixed micelle formation can be evaluated by computing the standard Gibbs free-energy change of micelle formation (ΔG^0_{M}) [23, 24] in the absence and in the presence of additives. This is given by the following equation:

$$\Delta G^0_{\mathrm{M}} = (2 - \chi)RT\ln \mathrm{cmc} \ , \qquad (2)$$

where χ is the degree of micelle ionization and is calculated from the ratio of S_2/S_1. Of course, the evaluation of χ by such a simple method has some shortcomings [18, 23], but the χ value calculated by this method was found to be quite close to that calculated by other methods [6, 7]. The ΔG^0_{M} values thus calculated are plotted in Fig. 7. It can be seen that there is not much difference between the values in aqueous EGMME and EGMEE and in aqueous DEGMME and DEGMEE. However, in aqueous EGMBE, the values are significantly less negative and may also be responsible for the absence of any micelle formation process in aqueous 20 wt% EGMBE owing to the strong hydrophobic hydration of the micelles. As a consequence, the lesser stability of the micelles in the presence of ethylene glycol derivatives is also evident from the nonappearance of any break in the κ plot for HTAB–TTAB mixtures in the HTAB-rich region in aqueous 20 wt% EGMEE, whereas this is not so in aqueous 20 wt% DEGMEE.

In order to explore the morphology of the mixed micelles, i.e. whether the mixed micelles show ideal or nonideal behavior in the presence of additives, it is possible to obtain quantitative information about the micellar aggregate formation by using the pseudophase thermodynamic model [25, 26]. The model relates the ideal mixed cmc (cmc*) with the experimental cmc of the pure components by using the following equations in the case of ideal mixing,

$$c_1 = x_1\mathrm{cmc}_1 = \alpha_1\mathrm{cmc}^* \ , \qquad (3)$$

and

$$c_2 = (1 - x_1)\mathrm{cmc}_2 = (1 - \alpha_1)\mathrm{cmc}^* \ . \qquad (4)$$

Equation (5) can be obtained after combining Eqs. (3) and (4)

$$\frac{1}{\mathrm{cmc}^*} = \frac{\alpha_1}{\mathrm{cmc}_1} + \frac{(1 - \alpha_1)}{\mathrm{cmc}_2} \ , \qquad (5)$$

where α_1 and x_1 are the mole fractions of surfactant 1 (HTAB) in total mixed solute and in the mixed micelle; cmc_1, cmc_2 and c_1, c_2 are the critical micellar concentrations and the overall concentrations involved in the

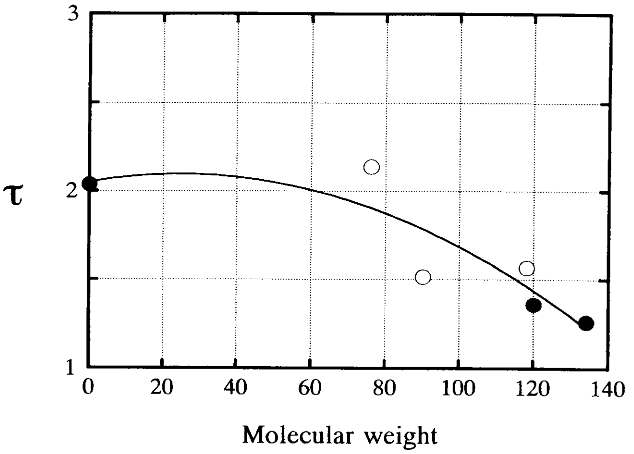

Fig. 6 Plot of τ versus molecular weight of ethylene glycol derivatives (*open circles*) and of diethylene glycol derivatives (*filled circles*). Pure water is represented by a molecular weight of the additive of 0

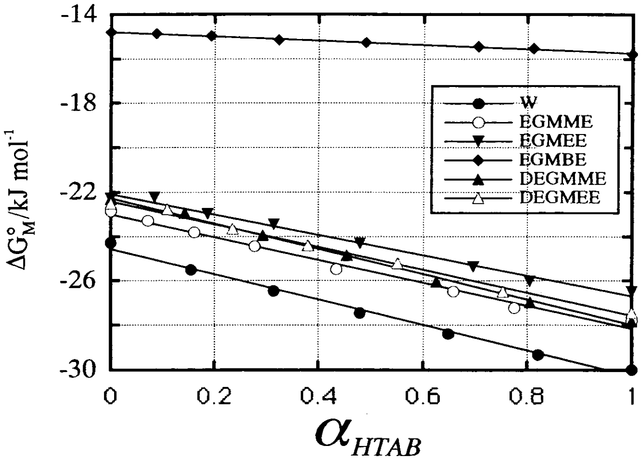

Fig. 7 Plot of ΔG^0_{M} versus α_{HTAB} for HTAB–TTAB mixtures in pure water and in aqueous 10 wt% additive

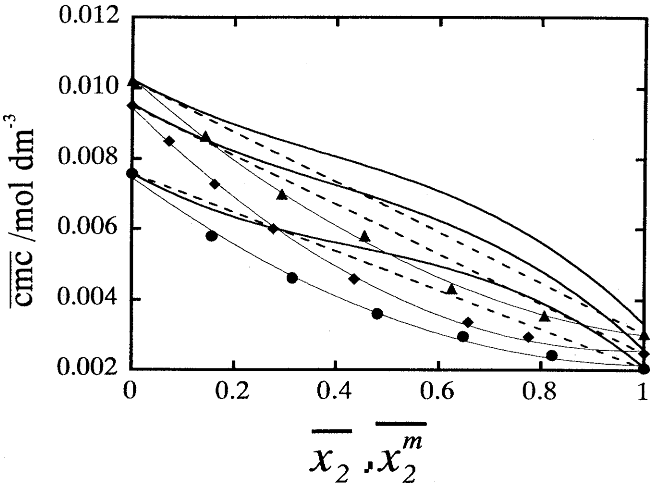

Fig. 8 Plot of $\overline{\mathrm{cmc}}$ versus $\overline{x_2}$ (experimental points-*thin line*), $\overline{x_2^m}$ (predicted behavior-*solid line*), and $\overline{x_2^m}$ (predicted ideal behavior-*broken line*) of HTAB–TTAB mixtures in pure water (*circles*), in 10 wt% aqueous EGMME (*rectangles*), and in 10 wt% aqueous DEGMME (*triangles*)

micelle formation of components 1 and 2, respectively. The cmc* values thus calculated using Eq. (5) are also listed in Tables 1 and 2. The values for some systems are also plotted in Fig. 5 along with the experimental mixed cmc. It is evident from Fig. 5 and Tables 1 and 2 that the experimental cmc values lie slightly higher than those of the cmc* over the whole mixing range, which demonstrates that a small degree of nonideality exists in the mixed micelle formation between HTAB and TTAB monomers. Shinoda and Nomura [27, 28] have also demonstrated from a similar theoretical equation that the deviation from the theoretically calculated mixed cmc values increases as the difference between the number of carbon atoms in the hydrophobic tails of the unlike surfactant monomers increases. These results have been further evaluated by using the regular solution formulation [26], which relates the mixed cmc to the individual cmc, i.e. cmc_1 and cmc_2, by

$$c_1 = x_1 \mathrm{cmc}_1 f_1 = \alpha_1 \mathrm{cmc} \ , \tag{6}$$

and

$$c_2 = (1 - x_1)\mathrm{cmc}_2 f_2 = (1 - \alpha_1)\mathrm{cmc} \ , \tag{7}$$

where f_1 and f_2 are the activity coefficients of surfactant 1 (HTAB) and surfactant 2 (TTAB) respectively. x_1 can be computed from the following equation:

$$\frac{x_1^2 \ln(\mathrm{cmc}\alpha_1/\mathrm{cmc}_1 x_1)}{(1 - x_1)^2 \ln[\mathrm{cmc}(1 - \alpha_1)/\mathrm{cmc}_2(1 - x_1)]} = 1 \ . \tag{8}$$

Equation (8) can be solved iteratively to obtain the value of x_1. The x_1 values thus obtained are listed in Tables 1 and 2. From x_1, the interaction parameter, β, can be computed by using the following equation:

$$\beta = \frac{\ln\left(\frac{\mathrm{cmc}\alpha_1}{\mathrm{cmc}_1 x_1}\right)}{(1 - x_1)^2} \tag{9}$$

The β value demonstrates the extent of the interactions between the two surfactants which lead to the deviations from the ideal behavior. A β value of zero indicates no interactions, whereas a negative and a positive value suggest attractive and repulsive interactions, respectively. Also, the higher the negative or positive value, the stronger the respective interactions. For the present surfactant binary mixtures, weak nonideal behavior was observed in pure water, since the average β value reported earlier [5] for pure water is 2.9. On the other hand, such values computed in the presence of 10 wt% additives are 0.33, 0.15, −0.16, 1.3, and 1.3 for EGMME, EGMEE, EGMBE, DEGMME, and DEGMEE, respectively. All these values are not so significant and they represent close-to-ideal behavior. However, it is quite strange to find ideal mixing behavior between the unlike monomers of HTAB–TTAB mixtures in aqueous additive systems in view of their strong hydrophobic hydration by the additive molecules. Therefore, it seems that the regular solution theory does not fully predict the mixing behavior owing to the complex nature of the present systems. In order to further evaluate the present results, the formulation proposed by Motomura and Aratono [13] based on the excess thermodynamic quantities was applied; this also takes into consideration the dissociation of the surfactant electrolyte. The details of this formation have been given elsewhere [29]. The composition of the mixed micelle can be determined by using the following equations:

$$\overline{x_2^m} = \overline{x_2} - (\overline{x_1}\alpha_2/\overline{\mathrm{cmc}})(\partial\overline{\mathrm{cmc}}/\partial\overline{x_1})_{T,P} \ , \tag{10}$$

and

$$\overline{\mathrm{cmc}} = (v_1 x_1 + v_2 x_2)\mathrm{cmc} \ , \tag{11}$$

where $\overline{x_2^m}$ is the micelle mole fraction and $\overline{x_2}$ is the bulk mole fraction of HTAB in the HTAB–TTAB mixtures. $\overline{x_2}$ is given by

$$\overline{x_2} = v_2\alpha_2/(v_1\alpha_1 + v_2\alpha_2) \ , \tag{12}$$

where v_1 and v_2 are the number of ions produced by the surfactant upon dissociation. Since, each surfactant is a 1:1 electrolyte, two ions, i.e. anion and cation, are produced upon dissociation. Thus, v_1 and v_2 are given by $v_1 = v_{1,\mathrm{a}} + v_{1,\mathrm{c}}$ and $v_2 = v_{2,\mathrm{a}} + v_{2,\mathrm{c}}$, and, hence, $\overline{\mathrm{cmc}} = 2\ \mathrm{cmc}$.

The $\overline{x_2}$ and $\overline{x_2^m}$ values thus computed are plotted against $\overline{\mathrm{cmc}}$ in Fig. 8. This figure can be regarded as the phase diagram that represents the equilibrium of the micelles with aqueous solution. The $\overline{\mathrm{cmc}}$ versus $\overline{x_2^m}$ curves in pure water as well as in the presence of 10 wt% EGMME and DEGMME predict a somewhat nonideal behavior especially in the HTAB-rich region of the mixture. This is due to the fact that the curve for $\overline{x_2^m}$ lies slightly higher than the corresponding curve for ideal mixing [29], indicating that the micelles are rich in the more-surface-active surfactant, i.e. HTAB. Practically, there is no difference between the magnitude of the $\overline{x_2^m}$ values in aqueous EGMME and DEGMME from the corresponding curves for ideal mixing. From these results, it can be said that the mixed micelle formation by HTAB and TTAB monomers in the presence of alkoxyethanols remains more or less free from the additive molecules. Similar results have also been obtained by Liu and coworkers [30, 31] for surfactant–polyelectrolyte systems. In spite of the present results, the adsorption of ethylene glycol derivatives on the micelle–solution interface cannot be completely ruled out in view of the drastic change in the micellar conductivities (Figs. 2, 4). A systematic increase in the mixed cmc values in the presence of both kinds of alkoxyethanols can mainly by attributed to the non-availability of the unsolubilized surfactant monomers to undergo the process of micelle formation.

Conclusion

A conductometric study of HTAB, TTAB, and their mixtures in aqueous alkoxyethanols was carried out. The presence of ethylene glycol derivatives has significant effects on the micellar properties, which have been attributed to the change in the medium properties as well as the adsorption of the additive molecules at the micelle–solution interface. On the other hand, diethylene glycol is more effective in changing the medium properties owing to the presence of an extra ether oxygen, with the result that mixed micelle formation is much delayed. An evaluation of the mixing behavior suggests that the mixed micelles are more or less close to ideal in the presence of alkoxyethanols.

Acknowledgements The author is grateful to the referees for their helpful suggestions. Thanks are due to Gurinder Kaur, Department of Applied Physics, for computational assistance. A research grant from the CSIR, New Delhi, [no. 01(1468)/97/EMR-II] is thankfully acknowledged.

References

1. Kwak JCT (1988) Polymer–surfactant systems. Surfactant Science Series, vol 77. Dekker, New York
2. Jonsson B, Lindman B, Holmberg K, Kronberg B (eds) (1988) Surfactants and polymers in aqueous solutions Wiley, New York
3. Bakshi MS (1993) J Chem Soc Faraday Trans 89:4323
4. Bakshi MS (1997) J Chem Soc Faraday Trans 93:4005
5. Bakshi MS, Kaur G, Kaur G (1999) J Macromol Sci A 36:697
6. Bakshi MS, Kaur U (1999) Bull Chem Soc Jpn 72:1483
7. Bakshi MS, Doe H (1999) Bull Chem Soc Jpn 72:2041
8. Brackman JC, Engberts JBFN (1993) Chem Soc Rev 22:85
9. Goddard ED (1986) Colloids Surf 19:255:301
10. Nagarajan R, Kalpakci B (1985) In: Dubin P (ed) Microdomains in polymer solutions. Plenum, New York, p 369
11. Glass JE (ed) (1989) Polymers in aqueous media: performance through association. Advances in Chemistry Series 223. American Chemical Society, Washington, DC
12. Holland P, Rubingh D (1991) In: Holland P, Rubingh D (eds) Cationic Surfactants, vol 37. Dekker, New York, chapter 4
13. Motomura K, Aratono M (1993) In: Ogino K, Abe M (eds) Mixed surfactant systems. Dekker, New York, pp 100
14. Manabe M, Kawamura H, Yamashita Y, Tokunaga S (1990) In: Bloor BM, Wyn-Jones E (eds) The structure dynamics and equilibrium properties of colloidal systems. Kluwer, The Netherlands, pp 63–69
15. Riddick JA, Bunger WB (1970) Organic solvents. Wiley Interscience, New York
16. Treiner C, Makayssi A (1992) Langmuir 8:794
17. Okubo T, Kitano H, Ise N (1976) J Phys Chem 80:2661
18. Sugihara G, Hisatomi M (1998) J Jpn Oil Chem Soc 47:661
19. Sailaja D, Raju KN, Devi GSS, Subbarangaiah (1998) Eur Polym J 34:887
20. Shinyashiki N, Sudo S, Abe W, Yagihara S (1998) J Chem Phys 109:9843
21. Benigno AJ, Ahmed E, Berg M (1996) J Chem Phys 104:7382
22. Marangoni DG, Rodenhiser AP, Thomas JM, Kwak JCT (1993) Langmuir 9:438
23. Moroi Y (1992) Micelles. Theoretical and applied aspects. Plenum, New York
24. Sugihara G, Era Y, Funatsu M, Kunitake T, Lee S, Sasaki Y (1997) J Colloid Interface Sci 187:345
25. Clint JH (1975) J Chem Soc Faraday Trans 1 71:1327
26. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants vol 1. Plenum, New York, p 337
27. Shinoda K (1954) J Phys Chem 58:541
28. Shinoda K, Nomura T (1980) J Phys Chem 84:365
29. Aratono M, Villeneuve M, Takiue T, Ikeda N, Iyota H (1998) J Colloid Interface Sci 200:161
30. Liu J, Takisawa W, Shirahama K (1999) Colloid Polym Sci 277:247
31. Liu J, Kobayashi K, Yang L, Takisawa N, Shirahama K (1999) J Colloid Interface Sci 213:412