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HEXADECYLTRIMETHYLAMMONIUM BROMIDE TETRADECYLTRIMETHYL-AMMONIUM BROMIDE MIXED MICELLES IN AQUEOUS GLYCOL OLIGOMERS

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HEXADECYLTRIMETHYLAMMONIUM BROMIDE + TETRADECYLTRIMETHYL-AMMONIUM BROMIDE MIXED MICELLES IN AQUEOUS GLYCOL OLIGOMERS

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Key Words: Cationic Surfactants, Mixed Micelles, Ethylene Glycol Oligomers, Conductivity Measurements, Surfactant-Polymer Interactions

ABSTRACT

The conductances of hexadecyltrimethylammonium bromide (HTAB) + tetradecyltrimethylammonium bromide (TTAB) mixtures over the entire mole fraction range of HTAB (α_{HTAB}) were measured in pure water as well as in the presence of various aqueous ethylene glycol oligomers containing 5, 10 and 20 wt% of each additive in their respective binary mixtures at 30°C. From the conductivity data, the critical micellar concentration (cmc), degree of counter ion association (χ) and the standard free energy of transfer of the surfactant hydrocarbon chain from the

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medium to the micelle (ΔG^{O}_{HP}) for HTAB and TTAB were computed. From the conductivity data of mixed surfactants systems, apart from cmc and χ, the regular solution theory parameters were also computed in order to explore the non-ideality in the mixed micelle formation in the presence of additives. The micellar parameters of both kind of surfactants and their mixtures show a significant dependence on the amount as well as on the number of repeating units of glycol oligomers. However, the non-ideality of mixed micelle formation remains unaffected in the presence of additives. These results have been explained on the basis of the medium effects of aqueous additive and it has been concluded that there are no significant interactions of glycol oligomers with the micelles of single and mixed surfactants.

INTRODUCTION

Recently, polymer-surfactant systems are under extensive investigation due to their wide industrial applications. For example, in the adhesion processses of polymers on metals [1], silica [2, 3] and other surfaces [4, 5], the presence of a suitable surfactant makes such a process more favorable. This is due to the fact that both amphiphilic and polymer form the supramolecular assemblies in solution. They have special structures like liquid crystalline mesophases [6, 7], which are formed due to the conformational changes in the polymer structure [8, 9]. Such structural aspects of polymer-surfactant systems are the objective of many recent studies [10-16]. In our ongoing investigation to study the mixed micelle formation between two cationic surfactants in the presence of additives, ethylene glycol oligomers have been selected as additives for the present study. These additives have high cohesive energies [17] and considerable hydrogen bonding capabilities [18] which favor the aggregation of surfactant monomers to form the micelles. It has been observed that the presence of such additives not only supports the micelle formation of single surfactants but also that of mixed surfactants [19].

Mixed micelle formation is considered to be more versatile than single surfactant [20, 21]. It has many applications in surface activity, detergency, wetting, spreading, foaming, etc. Most of the work on the mixed micelle formation has been focused in pure water only [22-26]. In our recent studies [19, 27], we have reported the additive effect of ethylene (EG) and diethylene glycols (DEG) on the micelle formation by single as well as by mixed surfactant systems. It was observed that EG and DEG destabilize both kind of micelles (i.e., single and mixed) due to their hydrophobic hydration. In the present work, the binary mixture of cationic surfactants viz. HTAB+TTAB has been selected for two reasons. First, the driving force responsible [25] for cationic surfactant-polyethylene glycol interactions is still poorly understood [28] in comparison to that of anionic surfactants; and second, the binary cationic combinations with identical polar head groups generally exhibit ideal behavior in the mixed state [29] which may be affected by the presence of additives. Therefore, it is expected that the additive effect of glycols consising of different number of repeating units will affect the nature of interactions responsible for the single and mixed micelle formation by HTAB and TTAB. This is due to the fact [30] that the additive binding to the surfactant decreases as the solvophobic interactions between water soluble end groups and solvent molecules predominate the hydrophobic interactions between the additive and surfactant micelles. On the contrary, the binding with surfactant increases as the hydrophobic interactions [13, 14, 31] become stronger with the increase in the number of repeating units.

The measurements have been performed with the conductivity technique which seemed to be the most useful tool in order to detect the micellar transitions accurately due to its high sensitivity and reproducibility. We have limited our conductivity measurements in the region of critical micellar concentration so as to compare the additive effect on the micelle formation by single and mixed surfactants.

EXPERIMENTAL

Hexadecyltrimethylammonium bromide (HTAB) and tetradecyltrimethylammonium bromide (TTAB), both from Lancaster, England, were recrystallized from ethanol+acetone and ethanol+ethyl acetate mixtures respectively. Both surfactants were dried *in vacuo* at 60°C for two days.

Ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG), all 99% pure from Central Drug House, Bombay, were further purified by the methods reported elsewhere [32]. Polyethylene glycol 600 (PEG 600) and 4000 (PEG 4000) from BDH, England, were used as received. Conductivity water having a specific conductance of 4-8 x 10^{-7} S cm^{-1} was used in the preparation of all solutions.

The precise conductances of HTAB+TTAB mixtures over the entire mole fraction range of HTAB (α_{HTAB}) in pure water (W), EG+W, DEG+W, TEG+W, PEG 600+W and PEG 4000+W systems containing 5, 10, and 20 wt% of each additive in their respective binary mixtures were measured at 30 (±0.01) ˚C as explained earlier [19]. The error in the conductance measurements was ±0.5%.

RESULTS AND DISCUSSION

The conductivity of HTAB+TTAB mixtures in pure water over the entire mole fraction range of HTAB (α_{HTAB}) is plotted against the total concentration in Figure 1. Similar plots were also obtained in the presence of various glycols. Figure 1 shows that all curves are tracing the same path in the pre-micellar region whereas distinct lines can be observed in the post micellar region. This is a general behavior [19] of mixed surfactant systems when they are not associated with each other in the pre-micellar region and a different degree of association in post-micellar region. Single break has been observed in each κ curve in each system in the concentration range studied herein. But, it is to be noted that in most of the surfactant-polyethylene glycol (PEG) studies [33, 34] two breaks were observed in the κ curve. The second break is generally observed at a comparatively higher concentration of the surfactant or polymer. The two breaks have been designated as the first and the second critical micellar concentrations (cmc). Such a phenomenon may be occurring particularly in those surfactant-PEG systems

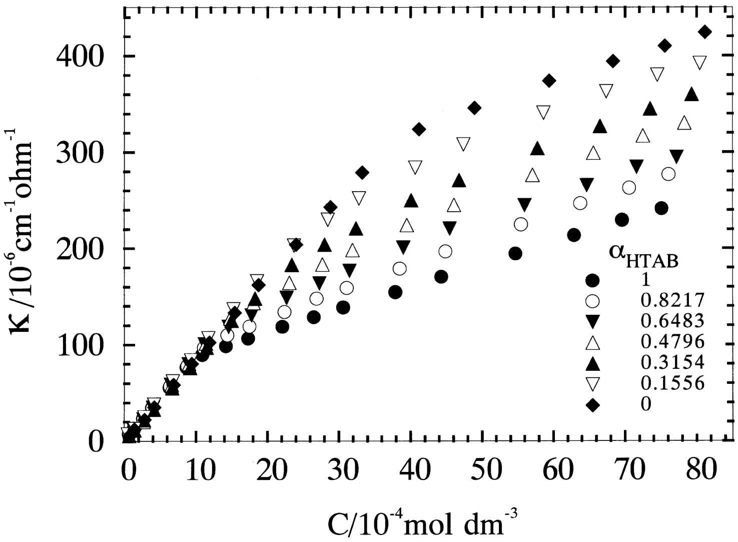

Figure 1. Plot of conductivity (κ) versus concentration (C) of mixed HTAB+TTAB in water.

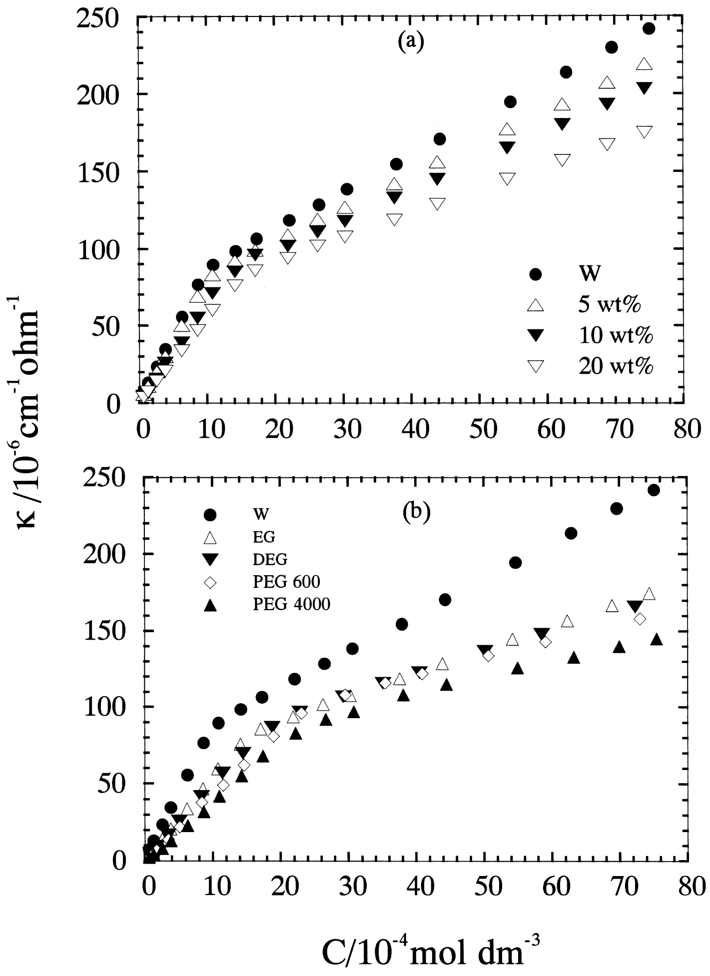

Figure 2. Plot of conductivity (κ) versus concentration (C) of HTAB in (a) aqueous EG;(b) aqueous 20 wt% additive.

where the molecular weight of PEG is substantially high and at least higher than the present oligomers. Since, the aim of the present work is to compare the additive effect of glycol oligomers on the micelle formation by single and mixed surfactants, therefore, the κ measurements have been restricted to the cmc region of the whole HTAB+TTAB mixture. Although the difference between the cmc of HTAB and TTAB is approximately four times but the concentration range covered in the case of pure HTAB goes upto eight times than its cmc. Therefore, inspite of this large concentration range only single break in the κ plots of HTAB has been observed (Figure 2).

From the single break in the κ curve, the critical micelle concentration (cmc) and from the ratio between the slopes of the post micellar region to that in the pre-micellar region, the degree of counter ion dissociation (δ) which can subsequently give a degree of counter ion association (χ=1-δ), have been calculated [19, 27, 35-37] and are reported in Table 1.

TABLE 1. Values of cmc/10^{-4} mol dm^{-3} and χ, for HTAB and TTAB in Water+Additive Systems at 30°C

		HTAB		TTAB	
wt% additive		cmc	χ	cmc	χ
	0	10.30	0.73	37.90	0.73
EG	5	10.80	0.73	39.90	0.73
	10	13.15	0.72	43.70	0.73
	20	15.60	0.72	53.50	0.72
DEG	5	12.61	0.72	43.27	0.72
	10	13.37	0.72	48.29	0.72
	30	19.11	0.71	62.83	0.71
TEG	5	12.55	0.72	45.59	0.72
	10	14.27	0.72	48.63	0.70
	20	24.15	0.70	68.94	0.69
PEG 600	5	13.18	0.72	45.28	0.71
	10	16.15	0;71	52.80	0.71
	20	24.28	0.70	73.39	0.70
PEG 4000	5	13.31	0.70	46.92	0.70
	10	16.54	0.70	55.68	0.70
	20	24.37	0.69	74.48	0.69

Micelle Formation by Single Surfactant

Figures 2 and 3 show the κ behavior of HTAB and TTAB in the presence of additives. There is a significant decrease in the κ in both the pre and the post-micellar regions with the increase in the amount as well as in the number of repeating units of glycol oligomers. Apart from this, a persual of the Table 1 shows that there is a significant and systematic additive effect on the micelle formation of HTAB and TTAB. It can be seen that the cmc of HTAB and TTAB increases with the increase in both the above mentioned factors of glycol oligomers. The decrease in the κ and increase in the cmc in the presence of additives can be attributed to a large change in the medium properties [27] such as relative permittivity (ε) and the viscosity (η) due to the structure breaking nature

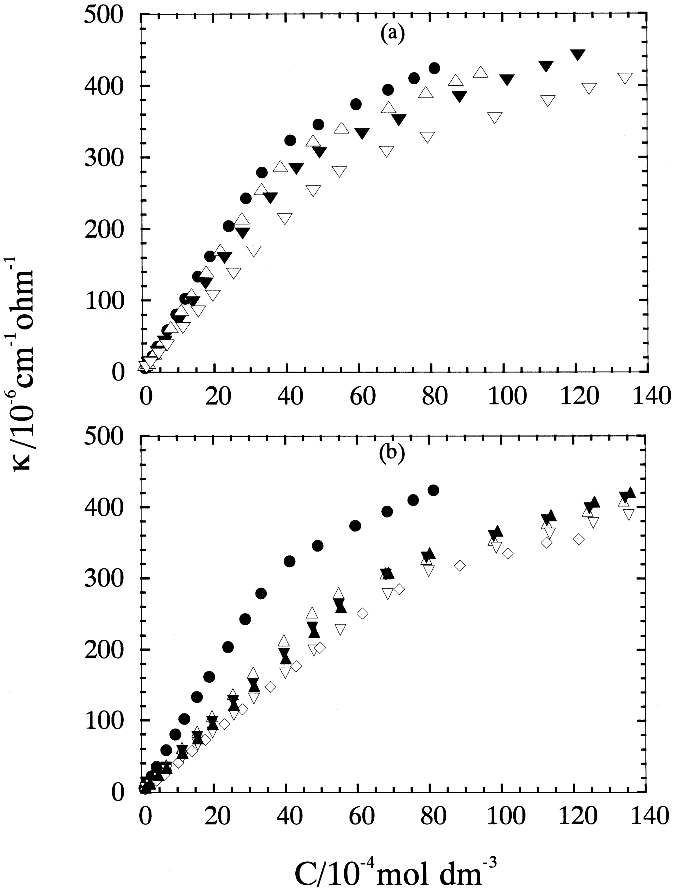

Figure 3. Plot of conductivity (κ) versus concentration (C) of TTAB in (a) aqueous EG; (b) aqueous 20 wt% additive. Symbols as for Figure 2.

[38] of the additive glycol oligomers. This will reduce the ε and enhance the η of the medium [39] since the respective properties of additive glycols [32] are lower and higher than that of water. This will result in the decrease in the κ due the increase in the non-polar character and viscous drag of the medium which will subsequently reduce the mobility of the ionic species [27, 35]. On the other hand, the structure breakage may also be responsible for the decrease in the hydrophobic effects of the medium which is the main driving force for micellization of surfactants [40-42]. This will reduce the minimum number of free surfactant monomers required for the aggregation and hence the cmc is increased.Therefore, an increase in the amount or the number of repeating units of a structure breaking solute in water will shift the cmc to further higher surfactant concentration. Similar results have already been observed by Marangoni *et al.* [30] for dodecyltrimethylammonium bromide (DTAB) + tetraethylene glycol (TeEG) + water systems. They have found an increase in the cmc of DTAB with the increase in the amount of TeEG and concluded that TeEG remains in the aqueous phase and only acts as a structure breaker. Such a behavior of additive oligomers in the present study can be better understood in terms of the stability of the micelles in the presence of additives.

In the case of single surfactant, the free energy of micelle formation in the presence of additives, consists of surfactant-surfactant interactions, additive-surfactant interactions and addtitive-additive interactions. These interactions can be divided into hydrophobic and hydrophilic contributions. In order to estimate both kind of contributions, the thermodynamics of micelle formation, proposed by Evans and Ninham [43], has been taken into account, which gives

$$\Delta G_M^O = \Delta G_{HP}^O + \Delta G_S^O \tag{1}$$

where ΔG_{HP}^O is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle, and ΔG_S^O corresponds to the energy associated with the surface contributions consisting of electrostatic interactions between the head groups and counter ions and all other contributions due to specific interactions. The sum of these two terms is equivalent to the total Gibbs free energy per surfactant molecule ($\Delta G_M^O = RT \ln X_{cmc}$) associated with forming micelles. The ΔG_{HP}^O was computed by the method reported elsewhere[35].

By using the values of ΔG_{HP}^{O} for HTAB and TTAB in each case, respective term $\Delta G_{HP}^{o(II)}$, which represents [35] the effect of an additive on micellisation can be calculated by means of the following equation:

$$\Delta G_{HP}^{o(II)} = \Delta G_{HP}^{O}(\textit{in aqueous additive}) + \Delta G_{HP}^{o}(\textit{in water}) \quad (2)$$

Figure 4 shows the variation in $\Delta G_{HP}^{o(II)}$ with the increase in the amount as well as in the number of repeating units in a series of glycol oligomers for HTAB and TTAB. It can be seen that with an increase in both the factors of additive,

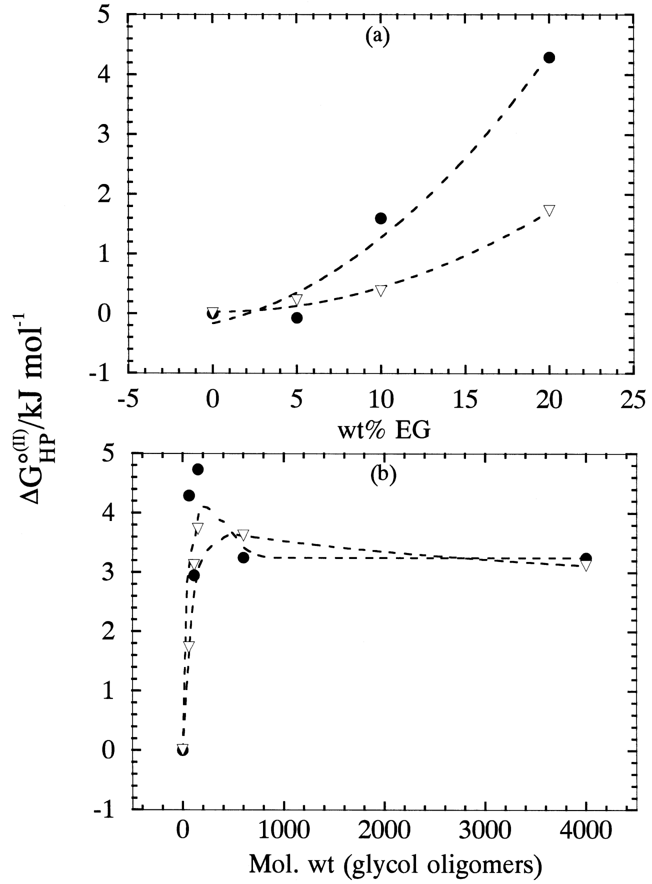

Figure 4. (a) Plot of versus $\Delta G_{HP}^{o(II)}$ wt% EG in aqueous EG: HTAB (circles); TTAB (triangles). (b) Plot of $\Delta G_{HP}^{o(II)}$ versus Mol. wt of additive in 20 wt% additive: Symbols as for (a).

$\Delta G_{HP}^{o(II)}$ tends to increase. This can be due to the fact that the transfer of the hydrophobic tail from the medium to the micelles becomes energetically unfavorable [35]. The origin of such kind of behavior can be attributed firstly to the medium effects and secondly to increase in the hydrophobicity of the glycol oligomers with the increase in the number of repeating units. The medium effects may arise due to the structure breaking nature of the additive glycols as has been discussed in the previous section. However, as far as the hydrophobicity is concerned, some studies have demonstrated [14, 15, 33, 34] that an association between ionic micelles and polymeric additives usually leads to a stabilization of the micelles indicated by the lowering in the cmc value. This is true particularly in those cases where the additive is appreciably hydrophobic [15, 33, 34] in nature such as PEG 20,000, PEG 35,000, poly(vinylpyrrolidone), poly(propylene oxide) and poly(ethylene oxide). But in the case of alkyltrimethylammonium surfactants, the bulky head groups shield most of the core from the water [44, 45] and hence, the steric repulsions between the head groups and polymer may produce the unfavorable contribution to the free energy of formation of polymer-bound micelles [46, 47]. This may also result in the increase in the polar head group repulsions which should lead to the decrease in χ values. Our results indeed show (Table 1) that the binding of common Br^- counter ion somewhat decreases with the increase in the amount as well as in the number of repeating units.

From the above variation in the micellar parameters of HTAB and TTAB, it can be said that though the micelle formation of these two surfactants is dramatically affected as the amount or the number of repeating units of glycol oligomers are increased, but such an additive effect is predominantly attributed to the change in the medium properties on addition of an additive. Therefore, it can be reasonably believed that practically there are no significant interactions between the ethylene glycol oligomers and HTAB or TTAB micelles as observed by other authors[13] in such kind of systems.

Micelle Formation by Binary Surfactant Mixtures

In the mixed state, the κ plots for HTAB+TTAB mixtures show only a single break (Figure 1) which is assigned to the mixed micelle formation by the unlike monomers. The critical micellar concentration (cmc) and the degree of counter ion association (χ) in the mixed state are also calculated in a similar way [19] as explained for pure surfactants and are listed in Table 2.

TABLE 2. Values of cmc/10^{-4} mol dm^{-3}, χ and Average β for HTAB+TTAB Mixtures in Water+Additive Systems at 30°C

α_{HTAB}	cmc	χ	α_{HTAB}	cmc	χ
	W		**10 wt.% TEG**		
	Average β=-0.43±0.14*		Average β=-0.29±0.18*		
0.1556	25.00	0.70	0.1367	35.01	0.68
0.3154	19.05	0.68	0.2837	28.05	0.67
0.4796	16.00	0.68	0.4420	23.30	0.65
0.6483	13.20	0.69	0.6130	19.21	0.66
0.8217	11.62	0.70	0.7984	16.28	0.68
	5 wt.% EG		**20 wt.% TEG**		
	Average β=-0.41±0.15*		Average β=-0.51±0.37*		
0.1366	27.70	0.72	0.1270	55.40	0.66
0.2634	22.20	0.70	0.2667	45.89	0.63
0.4417	17.40	0.69	0.4211	35.89	0.64
0.6127	14.80	0.70	0.5926	29.77	0.66
0.7982	12.40	0.72	0.7843	25.66	0.68
	10 wt.% EG		**5 wt.% PEG 600**		
	Average β=-0.34±0.08*		Average β=-0.01±0.18*		
0.1096	32.20	0.72	0.1380	33.29	0.70
0.2353	27.10	0.70	0.2955	26.31	0.68
0.3809	21.90	0.69	0.4446	21.53	0.68
0.5517	18.30	0.69	0.6155	17.99	0.70
0.7547	15.80	0.70	0.8001	15.50	0.71

TABLE 2. (cont.)

	20 wt.% EG		**10 wt.% PEG 600**		
	Average β=-0.31±0.16*		Average β=0.12±0.22*		
0.0997	41.10	0.69	0.1068	42.01	0.69
0.2168	34.00	0.67	0.2350	33.80	0.67
0.3564	27.40	0.66	0.3743	29.06	0.66
0.5255	22.90	0.67	0.5513	23.80	0.67
0.7347	19.00	0.69	0.7544	19.50	0.69
	5 wt.% DEG		**20 wt.% PEG 600**		
	Average β=-0.36±0.20*		Average β=-0.17±0.10*		
0.1368	31.34	0.71	0.1289	57.21	0.68
0.2837	25.00	0.68	0.2700	47.01	0.66
0.4421	20.42	0.67	0.4252	38.50	0.65
0.6131	17.00	0.68	0.5967	32.80	0.66
0.7984	14.40	0.71	0.7872	28.00	0.70
	10 wt.% DEG		**5 wt.% PEG 4000**		
	Average β=-0.25±0.18*		Average β=-0.01±0.32*		
0.1396	35.27	0.69	0.1363	34.64	0.69
0.2887	27.00	0.66	0.2829	27.86	0.68
0.4480	21.96	0.64	0.4411	22.12	0.68
0.6188	18.27	0.66	0.6122	18.04	0.69
0.8023	15.46	0.70	0.7978	15.70	0.70
	20 wt.% DEG		**10 wt.% PEG 4000**		
	Average β=-0.24±0.11*		Average β=0.25±0.32*		
0.1282	47.14	0.68	0.1227	47.46	0.69
0.2688	38.17	0.66	0.2591	37.52	0.68
0.4238	31.47	0.65	0.4115	28.71	0.67
0.5953	26.36	0.65	0.5831	23.63	0.69
0.7862	22.31	0.68	0.7776	19.34	0.70

TABLE 2. (cont.)

	5 wt.% TEG		**20 wt.% PEG 4000**		
	Average β=-0.21±0.09*		Average β=-0.19±0.09*		
0.1373	32.00	0.70	0.1105	59.42	0.68
0.2847	25.26	0.68	0.2369	49.19	0.66
0.4432	20.83	0.64	0.3831	41.00	0.64
0.6142	17.03	0.67	0.5540	34.49	0.66
0.7992	14.42	0.70	0.7564	28.90	0.68

*Standard deviation

In HTAB+TTAB mixtures, the deviation in the mixed micelle formation from the ideal behavior can be evaluated by using the following Equation (3) [48, 49]:

$$\frac{1}{\mathrm{cmc}^*} = \frac{\alpha_1}{f_1 \mathrm{cmc}_1} + \frac{(1-\alpha_1)}{f_2 \mathrm{cmc}_2} \tag{3}$$

where α_1 is the mole fraction of surfactant 1 in total mixed solute, f_1 and f_2 are the activity coefficients and cmc_1 and cmc_2 are the critical micellar concentrations of components 1 and 2, respectively. For the present structurally similar binary mixtures, the ideal behavior is expected since the interactions between the monomers in the mixed micelles are considered to be similar as in the case of homomicelles and hence the activity coefficients should be taken as unity in Equation 3.

Therefore, in case of the ideal behavior, Equation 4, can be written as

$$\frac{1}{\mathrm{cmc}^*} = \frac{\alpha_1}{\mathrm{cmc}_1} + \frac{(1-\alpha_1)}{\mathrm{cmc}_2} \tag{4}$$

By using Equation 4, the values for mixed critical micellar concentration (cmc*) in ideal state were calculated in water and in various glycol+W systems. The extent of non-ideality in the mixed micelle formation between HTAB+TTAB can be estimated from regular solution theory [49] by evaluating the interaction parameter, β. The value of β can be computed by using the following Equations 5 and 6.

$$\frac{x_1^2 \ln(\mathrm{cmc}^*\alpha_1/\mathrm{cmc}_1 x_1)}{(1-x_1)^2 \ln\left(\mathrm{cmc}^*(1-\alpha_1)/\mathrm{cmc}_2(1-x_1)\right)} = 1 \tag{5}$$

where x^1 is the mole fraction of surfactant 1 in the mixed micelle. Equation (5) can be solved iteratively to obtain the value of x^1, from which β, can be computed using the following Equation 6.

$$\beta = \frac{\ln\left(\dfrac{\mathrm{cmc}^*\alpha_1}{\mathrm{cmc}_1 x_1}\right)}{(1\text{-}x_1)^2} \tag{6}$$

The average values of β, thus computed in pure water and in the presence of each additive are also listed in Table 2.

When β=0, the two surfactants form an ideal mixture. The negative β values have generally been ascribed to the synergistic interactions responsible for the mixed micelle formation. The positive β values indicate the incompatibility of surfactant species and thus represent a measure of the antagonistic behavior of the concerned surfactants.

The activity coefficients, f_1 and f_2 of components 1 and 2, respectively, in the mixed micelle formation can be computed from the following relations:

$$f_1 = \exp\left[\beta\,(1-x_1)^2\right] \tag{7}$$

and

$$f_2 = \exp\left[\beta\, x_1^{\ 2}\right] \tag{8}$$

From the regular solution theory, it is also possible to calculate the excess free energy of mixing (G^E) by using the following Equation (9):

$$G^E = RT\left[x_1 \ln f_1 + (1-x_1) \ln f_2\right] \tag{9}$$

HTAB+TTAB Mixtures in Water

The mixed cmc values in pure water along with the cmc* are plotted in Figure 5. For comparison, these values for the same cationic mixture already reported [50] in the literature at 25°C have also been plotted in Figure 5. A small difference between the present and the reported data can be due to the difference

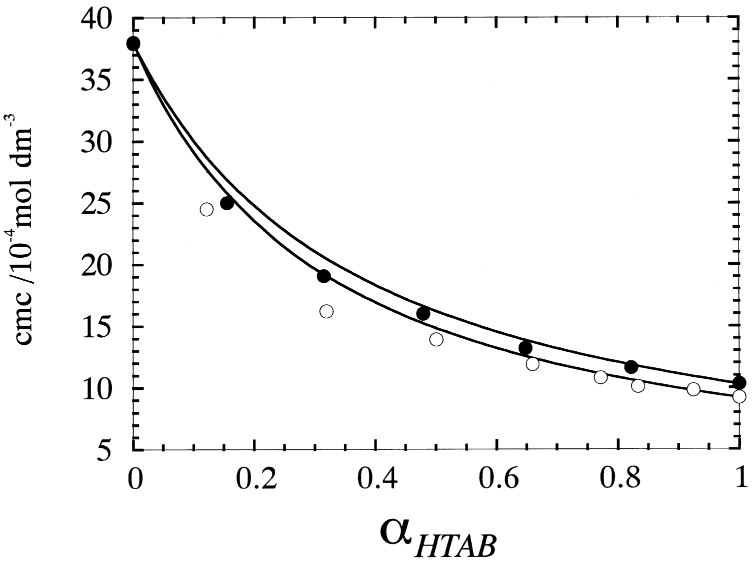

Figure 5. Plot of cmc (points) and cmc* (solid line) versus α_{HTAB} for HTAB+TTAB in water. This work (filled circles); Reference 50 (empty circles).

in the experimental temperatures. In the present work, the experimental cmc and predicted cmc* values are lying quite close to each other. Quantitative information in the mixed micelle formation can be obtained from the variation in interaction parameter, β, and the activity coefficients, f. The average β values calculated for the present and the reported data [50] (–0.43 and -0.64, respectively) are quite small and negative. The f values are also less than one (Figure 6). This suggests that weak synergistic interactions may exist between the unlike monomers in the mixed micelles. However, some studies [50, 29] have reported the ideal mixing behavior for such kind of binary cationic mixtures, but on the contrary, there are some examples which demonstrate a small degree of non-ideality for similar systems in the mixed state [19, 36, 51-53]. Generally, the ideal mixing behavior in the unlike monomers of tetraalkylammonium surfactants has been attributed to the non-compatability between the bulky head groups due to the steric repulsions in the mixed state, [54]. But, it is to be mentioned here that there are some other factors like the unequal hydrophobic tails and the variation in the ionic strength upon mixing the two cationic surfactants can impart a non-ideality in the mixed state [54]. Although HTAB and TTAB have bulky head groups they also have quite longer unequal hydrophobic tails i.e., C_{16} and C_{14}, respectively. Hence, it can reasonably be expected that a small degree of non-ideality

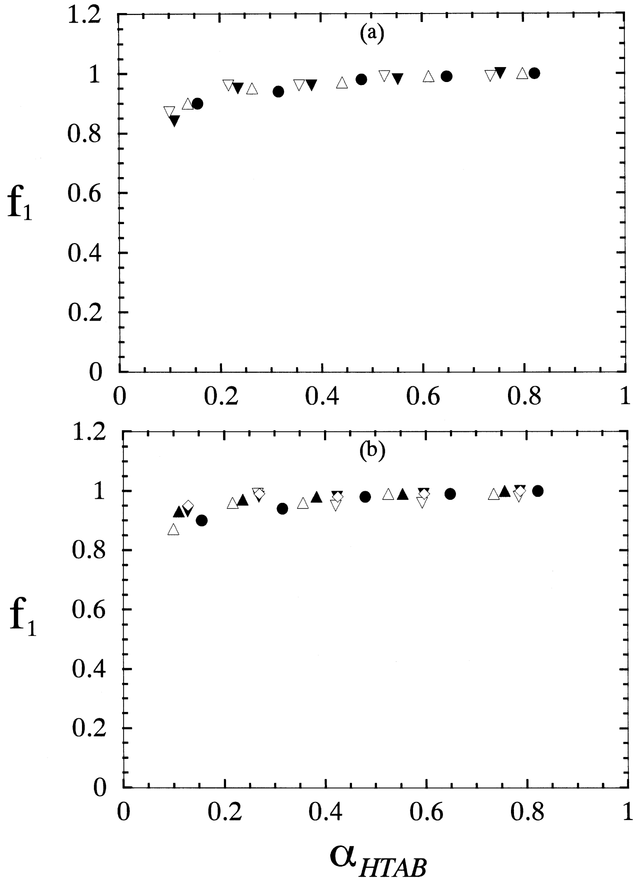

Figure 6. Plot of f_1 versus α_{HTAB} for HTAB+TTAB in (a) aqueous EG; (b) aqueous 20 wt% additive. Symbols as for Figure 2 and (∇) TEG.

may be due to the differences in the surface activities of these surfactants as observed previously in the case of dodecylammonium chloride + teteradecylammonium chloride [51] and cetylpyridinium chloride + TTAB [53] mixtures.

HTAB+TTAB Mixtures in Aqueous Glycol Systems

Figure 7 and Table 2 show the additive effect on the mixed micelle formation of HTAB+TTAB mixtures. It can be seen that the mixed cmc and χ values increase and decrease with increase in the amount as well as in the number of repeating units of glycol additives in comparison to that in pure water. This behavior is quite similar to the one observed in the case of pure surfactants and can be attributed mainly to the reasons discussed in the previous section. In order

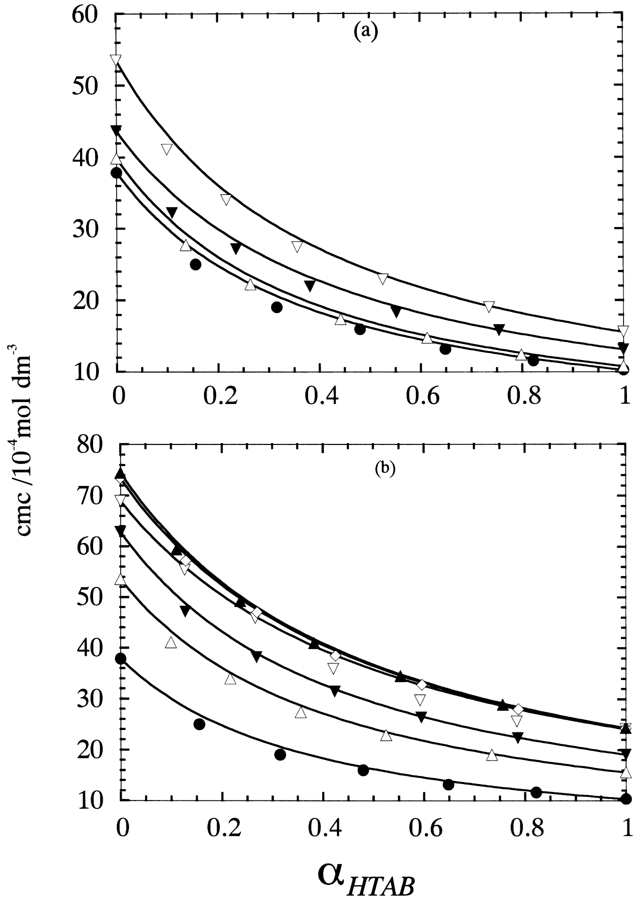

Figure 7. Plot of cmc (points) and cmc* (solid line) versus α_{HTAB} for HTAB+TTAB in (a) aqueous EG; (b) aqueous 20 wt% additive. Symbols as for Figure 2 and (∇) TEG.

to explore the non-ideality in the mixed micelle formation in the presence of additive, cmc* values have also been plotted along with the cmc values in Figure 7. It is interesting to note that practically there is an insignificant difference between the mixed cmc and cmc* values in the presence of each glycol additive as observed in pure water. Therefore, it would be worthwhile to discuss the stability in the mixed micelle formation in water as well as in the presence of each additive. Figure 8 shows the variation in the G^E values. These values for the mixed micelle formation of HTAB +TTAB mixtures in pure water as well as in the presence of additives are lying quite close to each other and are showing a negative deviation from the ideality. This suggests that the mixed micelle for-

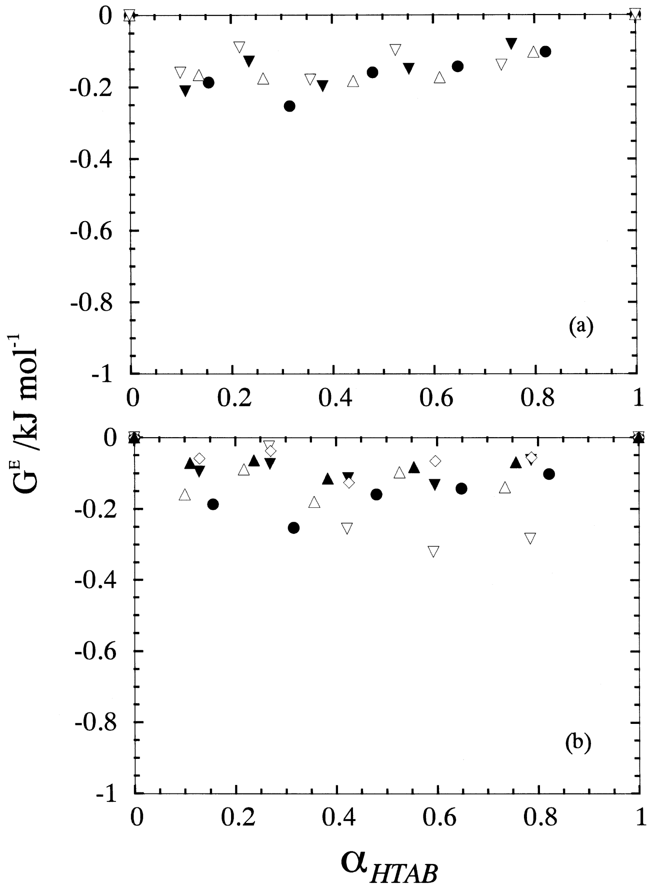

Figure 8. Plot of GE versus α_{HTAB} for HTAB+TTAB in (a) aqueous EG; (b) aqueous 20 wt% additive Symbols as for Figure 2 and (∇) TEG.

mation between HTAB and TTAB monomers is energetically favored both in pure water, as well as in the presence of additives though there is no significant influence of the additive on the variation of G^E. However, a quantitative information can be obtained from the variation in the β and f values. In most of the cases, the average β value is quite small and negative (Table 2) suggesting a small degree of non-ideality in the mixed micelle formation of HTAB+TTAB mixtures in the presence of additives as observed in pure water. Apart from this, the f values are always less than one and quite close to each other in the absence and presence of additive (Figure 6). These results can be attributed to the fact that glycol oligomers are expected to influence only the medium properties but they do not have any significant interactions with the mixed micelles. Thus, the additive is thought to remain only in the aqueous phase which may influence the environment surrounding the micelles due to which the cmc of single and mixed surfactants increases. On the other hand, as far as the hydrophobicity is concerned, the additive becomes more hydrophobic with the increase in the number of repeating units from EG to PEG 4000, therefore, it is expected to interact with both kind of micelles though the mixed micelles are considered to be more hydrophobic than micelles of single surfactants. But the regular solution theory parameters such as β and f do not show any significant dependence on the increase in the number of repeating units of additive glycol demonstrating that the mixed micelles composition in the presence and absence of additives remains almost constant. Therefore, it can be said that the present glycol oligomers remain in the aqueous phase and do not interact significantly even with the mixed micelles. However, it is to be explored whether such additives with appreciably high hydrophobicity can interact with the mixed micelles or not.

CONCLUSION

It has been concluded that the micellar properties of the HTAB, TTAB and HTAB+TTAB are equally affected due to the presence of a series of ethylene glycol oligomers. This has been mainly attributed to a change in the medium properties due to the water structure breaking effects of additive glycols. The increase in the number of repeating units also does not have any significant influence on the composition of the mixed micelles suggesting that the mixed micelles are more or less free from even higher glycol oligomers.

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