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Tetradecyltrimethylammonium Bromide + Dodecyltrimethylammonium Bromide Mixed Micelles in Aqueous Glycol Oligomers

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The conductances of tetradecyltrimethylammonium bromide (TTAB)+dodecyltrimethylammonium bromide (DTAB) mixtures over the entire mole fraction range of TTAB (α_{TTAB}) were measured in pure water as well as in the presence of various aqueous ethylene glycol oligomers containing 5 and 10 wt% of each additive in their respective binary mixtures at 30 °C. From the conductivity data, the critical micellar concentrations (cmc) and degrees of micelle ionization (χ) for TTAB + DTAB mixtures were computed. From the slopes of the conductivity curves, the equivalent conductivities of the monomeric (Λ_{m}), monomeric in the presence of additive ($\Lambda_{\mathrm{m,a}}$) and the micelle (Λ_{mic}) state were calculated, the results are discussed with respect to the glycol-additive effects in the whole mole fraction range of the binary mixture. The micellar parameters of both surfactants and of their mixtures show a significant dependence on the amount in comparison to the number of repeating units of glycol oligomers. These results have been explained on the basis of the medium effects of aqueous additive, which are drastically influenced by the increase in the amount of additive rather than by the increase in the number of repeating units. The non-ideality in TTAB + DTAB mixtures was evaluated by using the regular solution theory and Motomura's formulation based on the excess thermodynamic quantities. It has been found that the regular solution interaction parameter (β) and micellar mole fraction ($\bar{x}_2^m$) remain almost unaffected even in the presence of up to 10 wt% of each additive and molecular weight 4000. These results suggest that there are no significant interactions between the glycol oligomers and the micelles of single and mixed surfactants.

Recently, a lot of work has been done to understand the nature of water soluble polymer-surfactant interactions.[1—7] In the case of ionic surfactants, anionic surfactants have been found to have stronger interactions with such polymers in comparison to cationic ones.[1,5] The latter interactions have yet to be fully understood since most of the studies related to this aspect have demonstrated that very weak interactions or no interactions at all are existing between the cationic surfactants and water soluble polymers.[8,9] However, it has been suggested[1] that such interactions can be better visualized by choosing an appropriate head group of the cationic surfactant and the polymer structure and hydrophobicity. This is due to the fact that, in the course of surfactant–polymer interactions, sometimes a polymer wraps around the micelle and the nature of head group will play a significant role in such kind of association.[1,9] On the other hand, when surfactant adsorbs on the surface of the polymer, the extent of hydrophobicity of the polymer is the main contributing factor.[1,9] Therefore, in view of the above facts, we opted to perform a systematic study on the micellization of binary cationic surfactant mixture viz. TTAB + DTAB in the presence of ethylene glycol oligomers. The choice of TTAB + DTAB mixture was based on the fact that it belongs to a category of structurally similar surfactant mixtures and hence it is expected to behave ideally in the mixed state.[10] Thus, a departure from ideality in the presence of additive will help in determining the surfactant-additive interactions. Consequently, the ethylene glycol oligomers have been selected due to their high cohesive energies[11] and considerable hydrogen bonding capabilities,[12] 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.[13,14] Therefore, it is expected that the additive effect of glycols consisting of different amounts and number of repeating units will also affect the nature of interactions responsible for mixed micelle formation by TTAB and DTAB. This is due to the fact[15] that the additive binding to the surfactant decreases as the solvophobic interactions between water soluble end groups of an additive 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[1,5,16] become stronger with the increase in the number of repeating units.

The measurements have been performed with a 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.

Experimental

Tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB), both from Lancaster, England, were recrystallized from ethanol + acetone and ethanol + ethyl acetate mixtures respectively. Both surfactants were dried in vacuum 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.[17] Polyethylene glycol 600 (PEG 600) and 4000 (PEG 4000) from BDH, England, were used as received. Conductivity water having a specific conductance of 4—8×10^{-7} S cm^{-1} was used in the preparation of all solutions.

The precise conductances of TTAB + DTAB mixtures over the entire mole fraction range of TTAB (α_{TTAB}) in pure water (W), EG + W, DEG + W, TEG + W, PEG 600 + W, and PEG 4000 + W systems containing 5 and 10 wt% of each additive in their respective binary mixtures were measured at 30 (±0.01) °C as explained earlier.[13] The error in the conductance measurements was ±0.5%.

Results and Discussion

The conductivity of TTAB + DTAB mixtures in aqueous TEG over the entire mole fraction range of TTAB (α_{TTAB}) is plotted against the total concentration in Fig. 1. Similar plots were also obtained in the presence of other 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[13,14] of mixed surfactant systems when they are not associated with each other in the pre-micellar region and have different degrees of association in the post-micellar region. A single break has been observed in each $\varkappa$ curve of surfactant + glycol + water system in the concentration range studied herein. However, it is to be noted that in most of the surfactant-polyethylene glycol (PEG) studies[18,19] with substantially high molecular weight of PEG, two breaks were observed in the $\varkappa$ 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 where the polymer is quite hydrophobic in nature and the molecular weight of PEG is at least higher than the present oligomers.[1] Since the aim of the present work is to explore the surfactant–glycol interactions by studying the mixed micellar behavior of TTAB + DTAB in the presence of various glycols, therefore, the $\varkappa$ measurements have been restricted to the cmc region of the whole TTAB + DTAB mixture. Although the difference between the cmc of TTAB and DTAB is approximately four times, the concentration range covered in the case of pure TTAB (Fig. 2) and DTAB (Fig. 3) is more than three and two times their cmc values respectively. Therefore, in spite of this large concentration range, only a single break in the $\varkappa$ plots of TTAB and DTAB has been observed (Figs. 2 and 3, respectively).

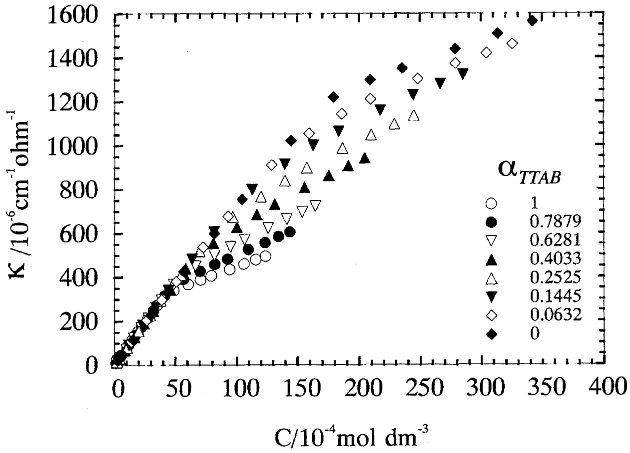

Fig. 1. Plot of $\varkappa$ versus C for TTAB + DTAB in 5 wt% aqueous TEG.

From the single break in the $\varkappa$ curve, the critical micelle concentration (cmc) has been calculated as explained earlier.[13,20,21] Such values in pure water and in the presence of various glycols are reported in Tables 1 and 2 respectively.

Conductivity Behavior. Figures 2 and 3 show the $\varkappa$ behavior of TTAB and DTAB in the presence of glycol additives respectively. It is interesting to note that there is a significant decrease in the $\varkappa$ value in both the pre and the post-micellar regions with the increase in the amount of glycol oligomers

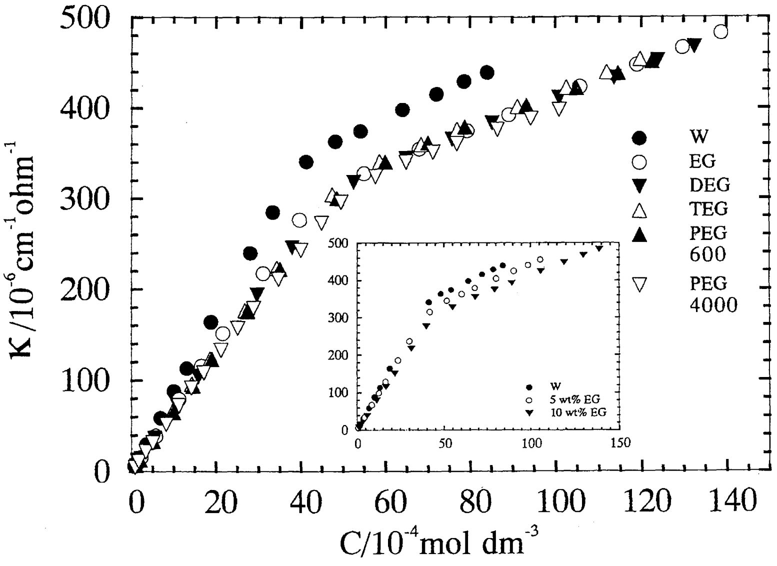

Fig. 2. Plot of $\varkappa$ versus C for TTAB in 10 wt% aqueous EG oligomers and in aqueous EG of different amounts (inset).

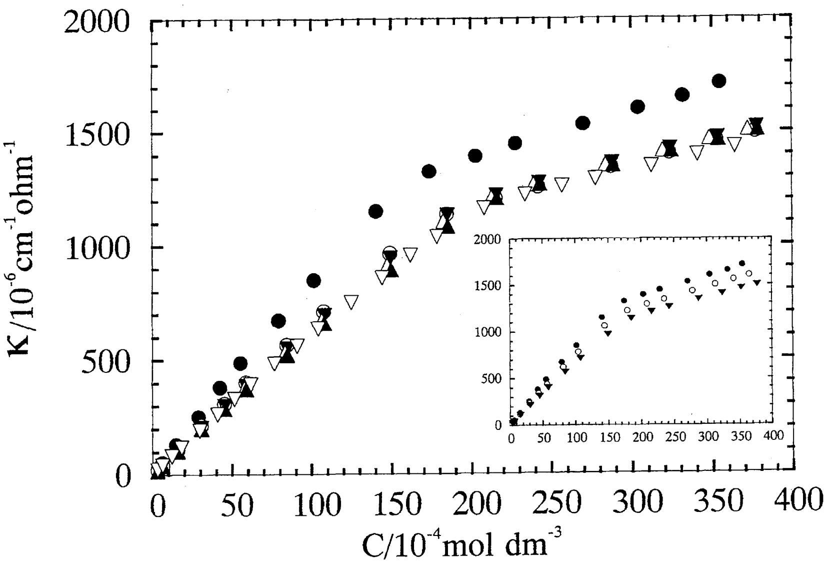

Fig. 3. Plot of $\varkappa$ versus C for DTAB in 10 wt% aqueous EG oligomers and in aqueous EG of different amounts (inset). Symbols as for Fig. 2.

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

α_{TTAB}	cmc	χ
0.000	151.9	0.292
0.0452	138.1	0.307
0.1059	119.9	0.353
0.1915	92.23	0.350
0.3091	69.20	0.379
0.5422	51.90	0.377
0.8120	40.00	0.326
1.000	37.90	0.251 (0.270)[a]

a) Ref. 26.

(Figs. 2 and 3, inset, only plots in aqueous EG are shown) in comparison to the increase in the number of repeating units. However, it is possible to compute the equivalent conductivities of the monomeric (Λ_{m}), monomeric in the presence of glycols ($\Lambda_{\mathrm{m,a}}$) and the micelle (Λ_{mic}) state of surfactant electrolytes from the slope of the $\varkappa$ plots in the pre as well as in the post-micellar regions, as suggested by Okubo et al.[22] In the presence of the respective glycol, the conductivity of monomeric species, $\Lambda_{\mathrm{m,a}}$, can be determined from the slope of the $\varkappa$ line in the pre-micellar region. Similarly, Λ_{m} can be obtained in the absence of glycols. On the other hand, since the conductivity of the monomers remains almost constant after the cmc, therefore, Λ_{mic} can be calculated from slope of the $\varkappa$ line in the post-micellar region with reference to the

Table 2. Values of cmc/10^{-4}mol dm^{-3} for TTAB+DTAB in Water+Additive Systems at 30 °C

EG+W		DEG+W		TEG+W		PEG600+W		PEG4000+W	
α_{TTAB}	cmc	α_{TTAB}	cmc	α_{TTAB}	cmc	α_{TTAB}	cmc	α_{TTAB}	cmc
				5 wt% additive					
0.000	157.5	0.000	169.5	0.000	167.1	0.000	162.4	0.000	166.7
0.0546	142.5	0.0534	148.3	0.0632	152.4	0.0639	154.3	0.0529	148.8
0.1261	117.6	0.1237	129.8	0.1445	115.2	0.1457	125.7	0.1225	130.9
0.2239	96.00	0.2202	97.70	0.2525	94.00	0.2543	97.20	0.2183	100.3
0.3659	73.30	0.3609	76.20	0.4033	73.30	0.4055	76.00	0.3583	80.70
0.5906	55.20	0.5853	56.30	0.6281	56.30	0.6303	58.30	0.5827	63.02
0.8140	43.00	0.8150	45.40	0.7879	48.00	0.7895	52.90	0.7544	53.44
1.000	41.20	1.000	43.80	1.000	42.20	1.000	44.60	1.000	44.04
				10 wt% additive					
0.000	171.4	0.000	182.2	0.000	181.0	0.000	190.5	0.000	188.5
0.0685	144.5	0.0655	158.1	0.0603	158.6	0.0607	171.4	0.0537	161.3
0.1554	115.3	0.1491	133.0	0.1383	143.6	0.1392	144.4	0.1244	138.7
0.2690	94.60	0.2595	112.2	0.2431	105.0	0.2444	108.8	0.2213	113.8
0.4239	74.30	0.4121	80.50	0.3911	83.80	0.3928	92.00	0.3624	90.86
0.6479	55.40	0.6333	64.60	0.6163	64.30	0.6179	69.00	0.5869	67.84
0.8804	47.60	0.8700	50.20	0.7794	57.00	0.7806	61.80	0.7576	60.52
1.000	44.30	1.000	47.90	1.000	49.50	1.000	52.10	1.000	52.35

monomer conductivity. 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 known. Apart from this, it has been assumed that the changes in the above equivalent conductivities of various states with respect to the concentration of the surfactant are negligibly small; and the concentration of the monomer species above the critical micellar concentration remains constant, which would be permissible for the micelles of large aggregation numbers. The Λ values thus obtained for TTAB+DTAB in different states have been plotted in Figs. 4 and 5. The Λ_{mic} values for various colloidal electrolytes have been mostly reported in the range of 15—35 Ω^{-1} cm^2 even in the presence of different kinds of additives.[22] Thus Λ_{mic} values demonstrated in Fig. 5 for single and mixed surfactants seem to be reasonable.

A comparison between Λ_{m} and $\Lambda_{\text{m,a}}$ shows (Fig. 4) that $\Lambda_{\text{m,a}}$ is always less than Λ_{m} over the whole mole fraction range in the pre-micellar region and Λ_{mic} is the lowest among all, which is obviously due to the bulkiness of the micelles. Furthermore, $\Lambda_{\text{m,a}}$ and Λ_{mic} again significantly and systematically decrease with the increase in the amount and in the molecular weight of the glycol. It is to be noted here that the latter additive effect was not so clear in the $\varkappa$ plots (Figs. 2 and 3). Such a decrease can be attributed mainly to a large change in the medium properties[20] like the relative permittivity (ε) and viscosity (η) due to the structure breaking nature[23] of the additive glycol oligomers. This will reduce the ε and enhance the η of the medium[24] since the respective properties of additive glycols[17] are lower and higher than those of water, thus the additive effect will become stronger with the increase in the amount and the molecular weight of glycol. This will result in a decrease in the Λ value due to the increase in the nonpolar character and viscous drag of the medium which will subsequently reduce the mobility of the ionic species.[20,21]

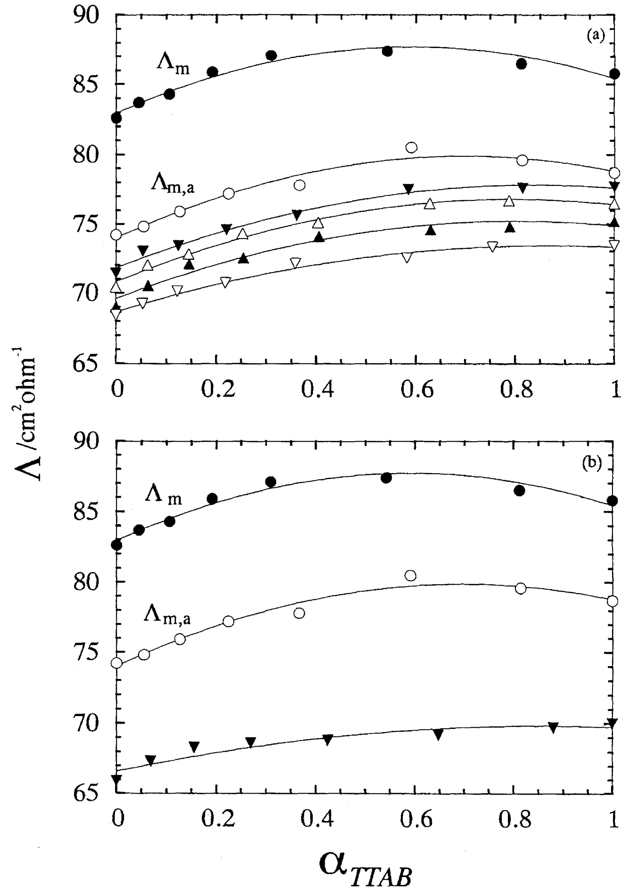

Fig. 4. Plot of Λ versus α_{TTAB} for TTAB+DTAB in pure water and in 10 wt% aqueous EG oligomers (a) and in aqueous EG of different amounts (b). Symbols as for Fig. 2.

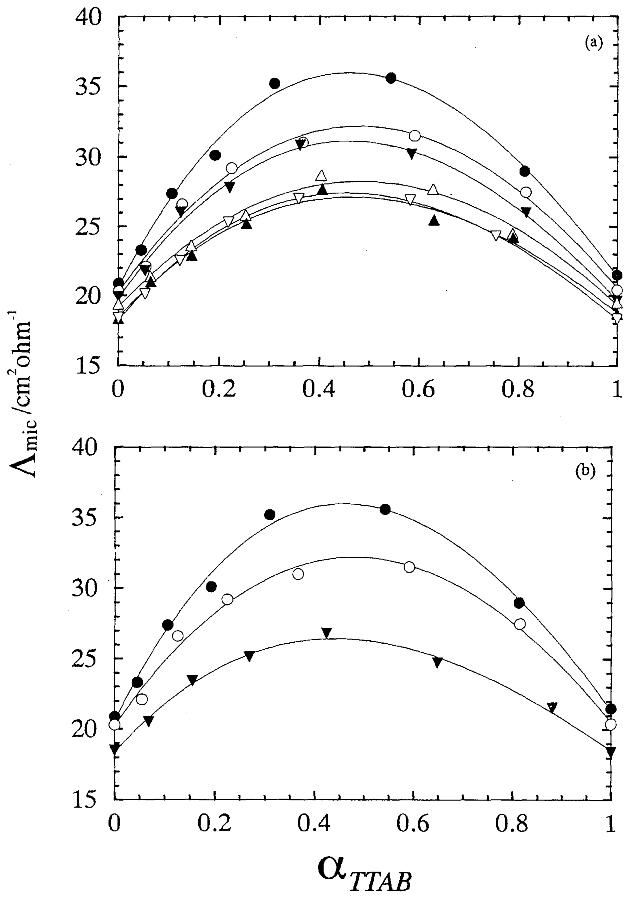

Fig. 5. Plot of Λ_{mic} versus α_{TTAB} for TTAB+DTAB in pure water and in 10 wt% aqueous EG oligomers (a) and in aqueous EG of different amounts (b). Symbols as for Fig. 2.

Apart from this, a nonlinear variation in Λ_{mic} (Fig. 5) is quite significant in comparison to Λ_{m} and $\Lambda_{\text{m,a}}$ (Fig. 4) and is identical in the absence and presence of additive. A clear broad maximum in each curve of Λ_{mic} demonstrates that the mixed micelles undergo strong structural changes around α_{TTAB} = 0.5 and the presence of a series of glycols seems to slightly suppress such micellar transitions.

Degree of Micelle Ionization. The degree of micelle ionization (χ) is closely related to the micellar transitions, therefore, a χ value computed by a suitable method can give significant information about the non-ideality in the mixed state. In the present work, the choice of TTAB+DTAB mixture was also due to the common counter ion of both the surfactants in the mixed state, so that the mixture can be treated as a single surfactant solution. The degree of micelle ionization has been calculated by the method suggested by Evans[25] based upon Stoke's law for the mobility of the micelles and the micelles are considered to be spherical in shape. It is given by

$$\chi = (n - m)/n, \tag{1}$$

where n is the micelle aggregation number and m the number of micelle-bound counter ions. The n and m are related through the following relations

$$1000S_2 = \frac{(n-m)^2}{n^{4/3}}(1000S_1 - \Lambda_{\text{br}^-}) + \left(\frac{n-m}{n}\right)\Lambda_{\text{br}^-}, \tag{2}$$

where S_1 and S_2 are the slopes of the specific conductivity versus concentration plot in the pre- and the post-micellar regions respectively and Λ_{br^-} is the ionic equivalent conductivity which can be set equal to the value at infinite dilution at low concentration. In order to calculate χ, an arbitrary value must be given to n. The value of χ is quite insensitive to n. For example, choosing 40, 60, and 80 as the values of n for TTAB, 0.25, 0.26, and 0.27 values, respectively, were computed for χ. Therefore, a value of n equal to 60 was selected for the present work. The χ values thus obtained for present mixture in pure water are also listed in Table 1. Such a value for TTAB has also been compared with that available in the literature from free electrophoretic method.[26] A good agreement can be observed between the present and the reported value. Figure 6 shows a graphical representation of χ values in the presence of various glycol additives. It is interesting to note that χ values significantly decrease in the presence of additive. They seem to decrease further with the increase in the molecular weight. This suggests that, upon addition of additive, the hydrophobic hydration of the surfactant increases which subsequently suppresses the ionization of the micelles, as a result of which the micellization is delayed.[1] However, over the whole mole fraction range, χ values go through a maximum in pure water, which becomes less significant with the increase in the molecular weight of additive glycols, as observed previously in the case of Λ_{mic}.

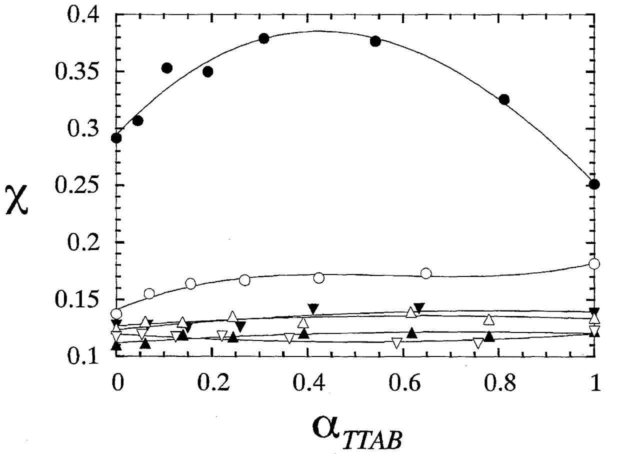

Fig. 6. Plot of χ versus α_{TTAB} for TTAB+DTAB in pure water and in 10 wt% aqueous EG oligomers. Symbols as for Fig. 2.

Critical Micellar Concentration in Pure Water and Water+Glycol Systems. The mixed cmc values for TTAB+DTAB mixtures in pure water are plotted in Fig. 7. For comparison, these values for the same binary mixture already reported[10] in the literature have also been plotted in Fig. 7. A good agreement can be observed between the two sets of data. In the presence of glycol additives, such values increase with the increase in the amount of each additive as well as with the increase in the molecular weight (Fig. 8). However, at higher molecular weight, the increase is not so significant as observed previously in Figs. 2, 3, and 6. Similar results for other cationic combinations have already been observed.[13,14,27] This additive effect can be attributed firstly to the medium effect which is mainly influenced by increase in the amount of each additive and secondly to the inability of mixed micelles to form polymer-bound micelles even with the additive of higher molecular weight. The former may be arising because of the structure breaking nature of the additive glycols, as has been discussed in the previous section. As far as the latter is concerned, some studies have demonstrated[1,5,18,19] that an association between ionic micelles and polymeric additives usually leads to a stabilization of the micelles, as indicated by the lowering in the cmc value. This is true particularly in those cases where the additive is appreciably hydrophobic[18,19,28] in nature and helps in the polymer-bound micelles for example in the case of PEG 20000, PEG 35000, poly(vinylpyrrolidone), poly(propylene oxide). Apart from this, it has been observed[29] that, in order to stabilize the micelles, a minimum hydrophobicity of a polymer is required which is around molecular weight 4000 for poly(ethylene oxide), for the present glycol additives, this number seems to be even higher than 4000. On the other hand, in the case of alkyltrimethylammonium surfactants as for the present mixture, the bulky head groups shield most of the core from the water[30,31] and hence the steric repulsions between the head groups and polymer may produce an unfavorable contribution to the free energy of formation of polymer-bound micelles[29,32]. This happens particularly in those cases where the polymer is not so appreciably hydro-

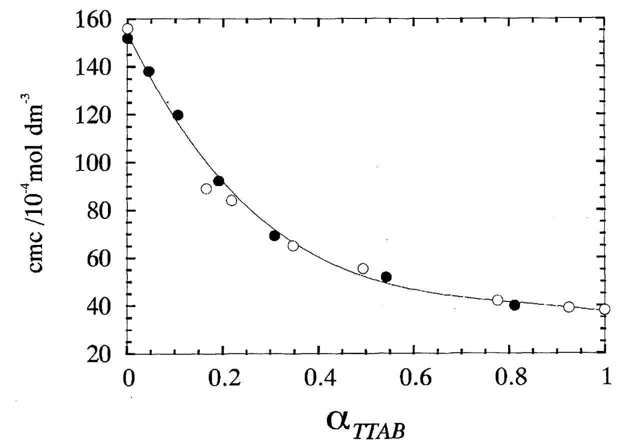

Fig. 7. Plot of cmc versus α_{TTAB} in pure water. This work (Filled circles); Ref. 10 (Empty circles).

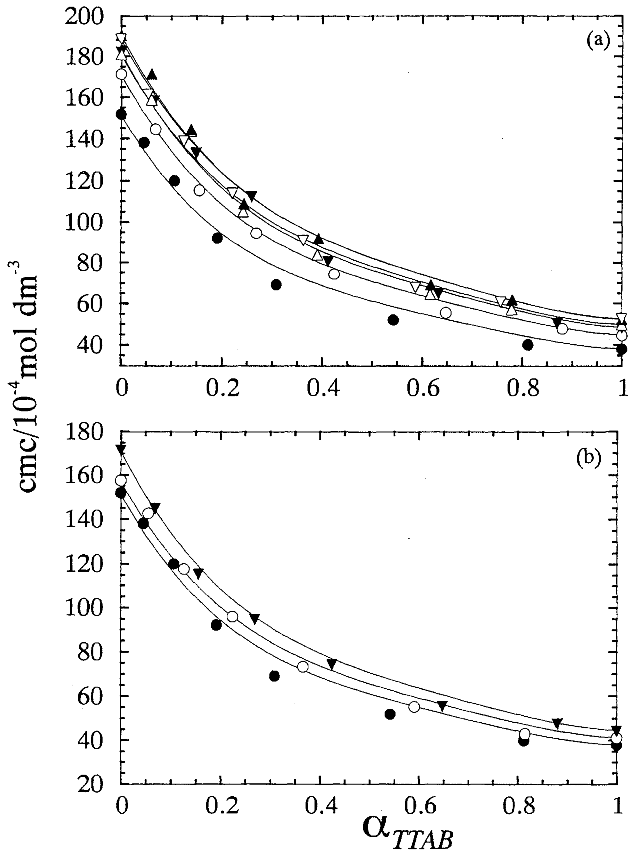

Fig. 8. Plot of cmc (points) and cmc* (solid line) in pure water and in 10 wt% aqueous EG oligomers (a) and in aqueous EG of different amounts (b). Symbols as for Fig. 2.

phobic and is unable to penetrate into the micelle. This may result in the increase in the polar head group repulsions and decrease in the χ value, subsequently will consequently lead to the increase in the cmc.

From the mixed cmc values it is possible to obtain some quantitative information about the micelle aggregates formed by using the pseudo phase thermodynamic model.[33,34] The model relates the mixed cmc (cmc*) with the cmc of the pure components by the following equation:

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

where α_1 is the mole fraction of surfactant 1 (TTAB) in total mixed solute, and cmc$_1$ and cmc$_2$ are the critical micellar concentrations of component 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[34] and hence the activity coefficients should be taken as unity. The cmc* values thus calculated using Eq. 3 have also been plotted in Fig. 8. A comparison between the cmc* and the experimental cmc values shows that it does not predict fully the ideal behavior in pure water as well as in the presence of additives. However, this is not so surprising since cmc* does not account for the variation in the solution ionic strength with changing composition, and cmc$_1$ and cmc$_2$ are independent of composition only if the ionic strength is constant; therefore, any change in the ionic strength of the mixture with the change in the composition will influence the ideality of the mixture. These results can further be evaluated by considering the regular solution formation[34] based on the phase separation model of micellization which relates the mixed cmc to the individual cmc i.e. cmc$_1$ and cmc$_2$ by

$$\alpha_1\mathrm{cmc} = x_1 f_1 \mathrm{cmc}_1, \tag{4}$$

and

$$\alpha_2\mathrm{cmc} = x_2 f_2 \mathrm{cmc}_2, \tag{5}$$

where α_1, α_2; x_1, x_2; and f_1, f_2 are the mole fraction in the bulk, in the mixed micelle and the activity coefficients of surfactant 1 (TTAB) and surfactant 2 (DTAB) respectively. x_1 can be computed from the following equation:

$$\frac{x_1^2 \ln\,(\mathrm{cmc}\alpha_1/\mathrm{cmc}_1 x_1)}{(1-x_1)^2 \ln\,(\mathrm{cmc}(1-\alpha_1)/\mathrm{cmc}_2(1-x_1))} = 1. \tag{6}$$

Equation 6 can be solved iteratively to obtain the value of x_1, from which the interaction parameter, β, can be computed using Eq. 7:

$$\beta = \frac{\ln\left(\frac{\mathrm{cmc}\alpha_1}{\mathrm{cmc}_1 x_1}\right)}{(1-x_1)^2}. \tag{7}$$

This β value demonstrates the extent of interactions between the two surfactants which lead to the deviations from the ideal behavior. Within the regular solution approximation,[34] β value should be constant with respect to the change in composition for a given binary surfactant mixture.

The average β values computed for TTAB+DTAB in pure water and in the presence of 10 wt% of EG, DEG, TEG, PEG 600, and PEG 4000 are −0.63, −0.65, −0.19, −0.52, −0.06, and −0.53 respectively. These values are not so significant as to denote a clear non-ideal behavior, but they are somewhat close to each other within the experimental uncertainties suggesting that the mixed micelle formation is very similar in the absence and presence of various glycols.

In order to support these results further, the compositions of the monomeric and the micellar phases for TTAB in the mixture in the absence as well as in the presence of glycol additives were evaluated by using the formulation proposed by Motomura and Aratono[35] based on the excess thermodynamic quantities. The details of this formulation have been given elsewhere.[35] The composition of the mixed micelle is determined by using the following equation:

$$\bar{x}_2^m = \bar{x}_2 - (\bar{x}_1\alpha_2/\overline{\mathrm{cmc}})(\partial\overline{\mathrm{cmc}}/\partial\bar{x}_2)_{T,P}, \tag{8}$$

where $\bar{x}_2^m$ is the micelle mole fraction and $\bar{x}_2$is the bulk mole fraction of TTAB. The latter is given by

$$\bar{x}_2 = \nu_2\alpha_2/(\nu_1\alpha_1 + \nu_2\alpha_2), \tag{9}$$

where ν_1 and ν_2 are the number of ions produced by the surfactant upon dissociation and $\overline{\mathrm{cmc}} = (\nu_1\alpha_1 + \nu_2\alpha_2)\mathrm{cmc}$.

The $\bar{x}_2$ and $\bar{x}_2^m$values thus computed are plotted against $\overline{\mathrm{cmc}}$ in Fig. 9. This figure can be regarded as the phase diagram

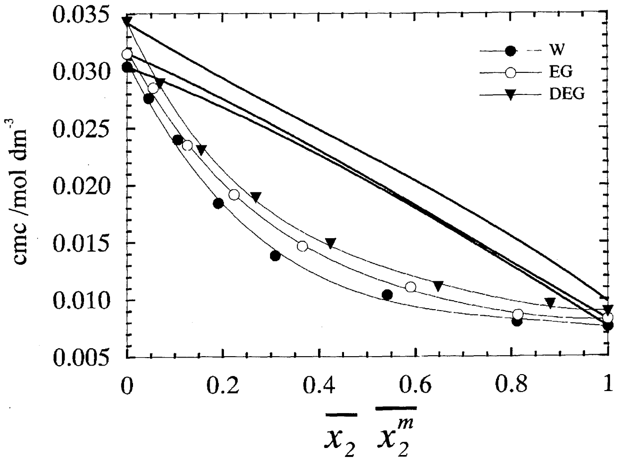

Fig. 9. Plot of $\overline{\text{cmc}}$ versus $\bar{x}_2$ (points), $\bar{x}_2^m$ (solid line) for TTAB+DTAB in pure water and 10 wt% EG and DEG.

that represents the equilibrium of micelles with aqueous solution. The $\overline{\text{cmc}}$ versus $\bar{x}_2^m$ curves in pure water as well as in the presence of various additives predict almost an ideal behavior, since they vary more or less linearly over the whole mole fraction range. It suggests that the composition of the mixed micelles remains almost constant even in the present of different glycols.

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. However, it is a strange behavior in view of the fact that, in spite of the increase in the molecular weight of glycol additives up to 4000, there are no significant changes in the mixed micelle composition of TTAB+DTAB mixtures except from those observed due to the change in the medium properties. This can be attributed to the fact that the additive may remain only in the aqueous phase and perhaps will change the environment surrounding the micelles. Since the main force resisting the aggregation is the crowded arrangement of the ionic head groups at the periphery of the micelles, therefore, a sufficiently hydrophobic additive stabilizes the micelles by incorporating nonpolar groups in the palisade layer and polar groups in-between the repelling head groups of surfactant monomers. This will always be accompanied by a decrease in the cmc and the increase in the ionic dissociation of the micelles.[1] However, in the present work, both the factors vary in the reverse order which indicates that the additive may not be penetrating into the micelles since both the value of β and the $\bar{x}_2^m$ remains almost unaltered in the presence of a series of glycol additives. Therefore, it can reasonably be believed that the present glycol oligomers remain in the bulk and influence the micellar behavior by changing the medium properties.

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