

# Mixed Micelles of Hexadecylpyridinium Bromide + Tetradecyltrimethylammonium Bromide in Aqueous Glycol Oligomers

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**ABSTRACT:** Conductances of hexadecylpyridinium bromide (HPyBr) + tetradecyltrimethylammonium bromide (TTAB) mixtures over the entire mole fraction range of HPyBr ( $\alpha_{\text{HPyBr}}$ ) were measured in pure water as well as in the presence of various aqueous ethylene glycol oligomers containing 10 and 30 wt% of each additive in their respective binary mixtures at 30°C. Each conductivity curve shows two breaks corresponding to two critical micelle concentrations (cmc;  $C_1$  and  $C_2$ ) over the whole mole fraction range of HPyBr + TTAB mixtures except in the presence of pure HPyBr and TTAB, where a single break was observed. From the conductivity data, various micellar parameters in the absence and presence of glycol additives were computed. A variation in the micellar parameters in the presence of additive showed that additive introduction mainly influences the medium properties and therefore the micellar properties. However, no significant micelle-glycol interactions were observed even with an increase in the number of repeating units from ethylene glycol to polyethylene glycol 600. The mixing behavior of HPyBr + TTAB is close to nonideal and is identical in pure water and in the presence of various glycols. This has been attributed to the presence of synergistic interactions between unlike monomers at  $C_1$  that are not influenced even by the presence of additives. The appearance of the second cmc is mainly attributed to structural transitions of the mixed micelles at  $C_1$  with a further increase in surfactant concentration.

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**KEY WORDS:** Cationic surfactants, conductivity measurements, glycol additives, mixed micelle-glycol interactions, mixed micelles.

Aqueous surfactant solutions have recently been widely studied due to their fascinating properties of self-assembly to give organized solution systems (1). Such properties have led to the use of surfactants in a variety of industrial and commercial applications (2). Commercial surfactants are often mixtures of two or more surfactants and are generally more useful than single surfactants. They have been used in surface activity, detergency, wetting, spreading, and foaming (1). Evaluation of their physicochemical prop-

erties has recently attracted much attention. Most of the work on properties of such binary surfactant systems has focused on pure water systems only (3–7); however, in our recent studies, we found that the presence of various kinds of associative and nonassociative organic additives dramatically influences micellar properties (8–11). Associative additives like glycol oligomers not only change the medium properties but also support micelle formation (8–11). Apart from this, they are widely used in detergents, cosmetics, and many other industrial applications. It also was observed that lower glycol homologs significantly affect the process of micelle formation of both single and mixed surfactants owing to their strong water structure-breaking effects (8–11), whereas the higher ones preferentially adsorb at the micelle-solution interface or form polymer-bound micellar aggregates (12).

Many cationic-cationic surfactant mixtures (13), such as tetradecyltrimethylammonium chloride (TTACl) + benzyldimethyltetradecyltrimethylammonium chloride ( $C_{14}\text{BzCl}$ ), TTACl + didodecyldimethylammonium bromide, and hexadecylpyridinium chloride (HPyCl) + benzyldimethylhexadecylammonium chloride ( $C_{16}\text{BzCl}$ ), have shown two breaks in the plots of conductivity vs. total concentration in pure water in the presence of salt, which correspond to the two critical micellar concentrations (cmc) of the mixtures. This behavior can be due to the structural micellar changes in the absence (13) or presence of additive molecules (12). In the former case, it generally happens owing to sphere-to-rod transitions that can be accompanied by a change in the degree of counter-ion binding, whereas in the latter case, micelle-additive interactions can lead to a change in the micelle geometry (12).

Recently, we reported the mixing behavior of binary cationic surfactants with identical surfactant polar head groups in the presence of glycol additives (10,11), but in this work, emphasis is given to an understanding of such behavior with unlike bulky polar head groups such as hexadecylpyridinium bromide + tetradecyltrimethylammonium bromide (HPyBr + TTAB) mixtures with identical counter-ions. The choice of such a surfactant combination and glycol additive system was made for two reasons. First, the driving force responsible for cationic surfac-

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tant–nonionic additive (such as glycols) interactions is still poorly understood (14) in comparison with that of anionic surfactants; and second, the bulky polar head groups of HPyBr + TTAB may have a different packing arrangement from those of the like polar head group cationic mixtures, which generally exhibit ideal mixing behavior (15). Therefore, such a packing arrangement may be affected in the presence of different glycol additives if the additive molecules interact with the mixed micelles. This additive effect can be better visualized by using the conductivity technique, since conductivity is considered to be quite sensitive to micellar transitions, particularly when ionic surfactants are involved (12,13,16).

## EXPERIMENTAL PROCEDURES

HPyBr and TTAB were recrystallized from ethanol + acetone and ethanol + ethyl acetate, respectively. Both surfactants were dried under vacuum at 60°C for 2 d.

Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG), all 99% pure from Central Drug House (Bombay, India) were further purified by methods reported elsewhere (17). Polyethylene glycol 600 (PEG 600) from BDH (Poole, England) was used as received. Conductivity water having a specific conductance of  $4\text{--}8 \times 10^{-7} \text{ S cm}^{-1}$  was used in the preparation of all solutions. All reference and stock solutions were prepared by mass within an accuracy of  $\pm 0.01 \text{ mg}$ . Mole fractions were accurate to  $\pm 0.0001$  units.

Conductivity measurements were done with a digital conductivity meter at a fixed frequency of 1000 Hz (model NDC-732; Naina Electronics, Chandigarh, India). A dip-type conductivity cell with a double-walled jacket to circulate thermostated water was used for all measurements. The conductivity cell capacity was about 100 mL. An automatic thermostatted bath from Shimadzu (Kyoto, Japan) was used for maintaining the temperature within uncertainties of  $\pm 0.01^\circ\text{C}$ . The conductivity cell constant was 1.12, which was determined by using different KCl solutions of known conductivities. All measurements were done at 30°C.

Initially, 50 mL of the reference solution consisting of water, or an appropriate amount of each additive in water, was taken in the conductivity cell. It was then equilibrated at 30°C for at least 1 h before starting the experiment. A known amount of stock solution of HPyBr or TTAB or HPyBr + TTAB made with the same reference solution was then added from a micropipette (Finnpipette; Labsystems, Helsinki, Finland) and again equilibrated until the conductivity value became constant. In this way, the precise conductances of HPyBr + TTAB mixtures over the entire mole fraction range of HPyBr ( $\alpha_{\text{HPyBr}}$ ) in EG + water (W), DEG + W, TEG + W, and PEG 600 + W containing 10 and 30 wt% of each glycol in their respective binary mixtures were measured. The error in the conductance measurements was  $\pm 0.5\%$ .

## RESULTS AND DISCUSSION

**Conductivity behavior.** Each conductivity ( $\kappa$ ) plot of pure HPyBr and TTAB shows a single break in all cases, whereas double breaks are observed for HPyBr + TTAB mixtures (Figs. 1–3). The two break points correspond to two cmc; the first one is designated as the first cmc ( $C_1$ ) and the second one as the second cmc ( $C_2$ ). Thus, a single cmc value for pure HPyBr and TTAB, and two cmc values, i.e.,  $C_1$  and  $C_2$ , for HPyBr + TTAB mixtures over the entire mole fraction range in pure water as well as in the presence of various additives were calculated as explained earlier (18). These values are listed in Tables 1–5.

Figures 1–3 show the additive effect of various glycols on the variation of  $\kappa$ . It is seen that  $\kappa$  decreases in the pre- and the postmicellar regions in the presence of additives. However, the decrease is quite significant with respect to an increase in the amount of additive from 10 to 30 wt% in the case of both single and mixed surfactants (Figs. 1 and 2, respectively), whereas the increase in the number of repeating units does not seem to have any marked influence on the variation of  $\kappa$  (Fig. 3). The overall decrease in  $\kappa$  is quite obviously due to changes in the medium properties in view of the structure-breaking effects of additive glycols, and these have also been observed earlier in the case of trimethylhexadecylammonium bromide (HTAB) + TTAB and TTAB + trimethyldodecylammonium bromide (DTAB) mixtures (10,11). Similar results were reported by other authors for single surfactant–glycol systems (19,20). To evaluate  $\kappa$  in a particular region before  $C_1$ , between  $C_1$  and  $C_2$ , and after  $C_2$ , slopes of the respective linear portions of  $\kappa$  plots (Fig. 2;  $S_1$ ,  $S_2$ , and  $S_3$ ) were computed and are also listed in Tables 1–5. Such values in pure water were found comparable with those of similar cationic binary mixtures with comparable hydrophobic tails and head groups such as that of TTACl +  $C_{14}$ BzCl and HPyCl +  $C_{16}$ BzCl mixtures already reported (12). It is interesting to note that  $S_1$  and  $S_3$  values for HPyBr + TTAB mixtures re-

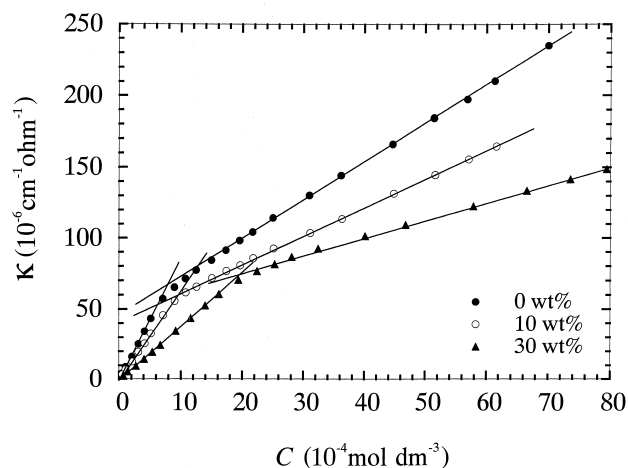
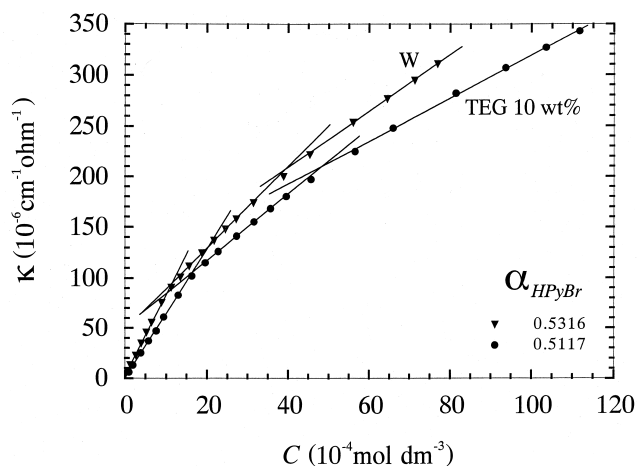
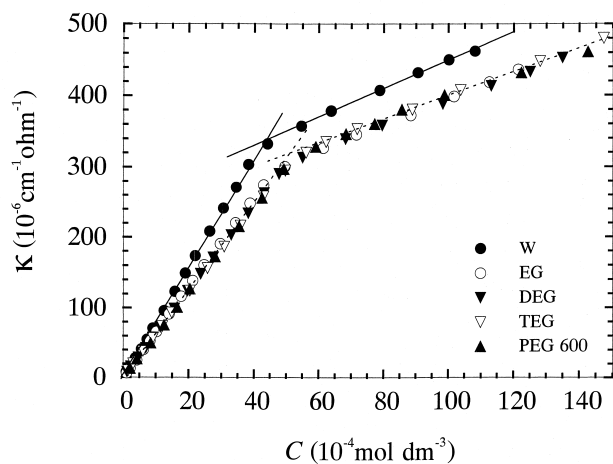


FIG. 1. Plot of conductivity ( $\kappa$ ) vs. concentration ( $C$ ) of hexadecylpyridinium bromide (HPyBr) in ethylene glycol (EG) + water (W).

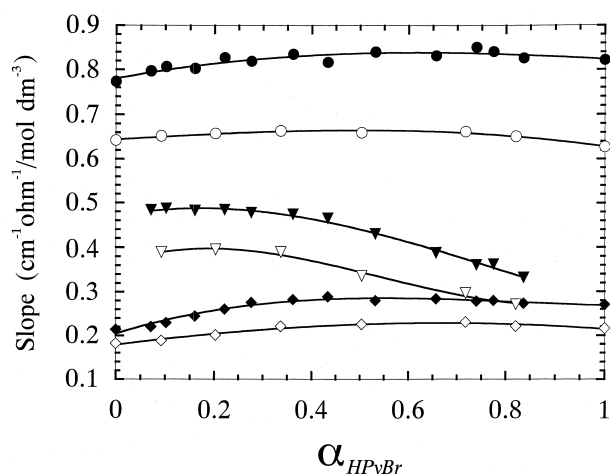


**FIG. 2.** Plot of conductivity ( $\kappa$ ) vs. concentration ( $C$ ) of HPyBr + TTAB mixtures in pure water and triethylene glycol (TEG) + W. TTAB, tetradecyltrimethylammonium bromide; for other abbreviations see Figure 1.

main almost constant over the whole mole fraction range both in the absence and in the presence of additives (Fig. 4 and Tables 1–5). This may suggest that the equivalent monomer and micellar states, respectively, are present over the whole mole fraction range. On the other hand, a regular decrease in  $S_2$  values with the increase in  $\alpha_{\text{HPyBr}}$  may indicate that the mixed micelles corresponding to the transition state between  $C_1$  and  $C_2$  become more compact upon further addition of HPyBr monomers and hence their contribution to  $\kappa$  decreases. Apart from this, on comparing a single-break HPyBr system with double-break HPyBr + TTAB systems, we see that  $S_3$  values for HPyBr + TTAB mixtures particularly in the HPyBr-rich region are quite close to the one of postmicellar value of HPyBr (i.e.,  $\alpha_{\text{HPyBr}} = 1$ ). This may be due to equivalent micellar states existing over these mole fractions in both cases, which indicates micelles at  $C_2$  are predominantly rich in HPyBr monomers. In the presence of additives,  $S_1$ ,  $S_2$ , and  $S_3$  are significantly



**FIG. 3.** Plot of conductivity ( $\kappa$ ) vs. concentration ( $C$ ) of TTAB in aqueous 10 wt% additive. DEG, diethylene glycol; PEG 600, polyethylene glycol 600; for other abbreviations see Figures 1 and 2.



**FIG. 4.** Plot of slopes ( $\times 10^{-2}$ ),  $S_1$  ( $\bullet, \circ$ ),  $S_2$  ( $\blacktriangledown, \triangledown$ ), and  $S_3$  ( $\blacklozenge, \lozenge$ ) vs. mole fraction of HPyBr ( $\alpha_{\text{HPyBr}}$ ) in HPyBr + TTAB: in pure water ( $\bullet, \blacktriangledown, \blacklozenge$ ) and in aqueous 10 wt% EG ( $\circ, \triangledown, \lozenge$ ). For abbreviations see Figures 1 and 2.

lower than corresponding values in pure water, and decrease further with an increase in the amount of each additive (Fig. 4 and Tables 1–5), demonstrating the medium effect. However, the difference between these values among all the additives at a particular amount is not so significant and it appears that they slightly decrease with an increase in the number of repeating units from EG to PEG 600.

*Degree of micelle ionization.* To further evaluate these results, the degree of micelle ionization ( $\chi$ ) was evaluated. In this work, the choice of the HPyBr + TTAB mixture was made due to the common  $\text{Br}^-$  counter-ion of both the surfactants in the mixed state, and hence the mixture can be treated as a single surfactant solution. The degree of micelle ionization was calculated by the method suggested by Evans (21) based upon Stokes' law for micelle mobility, with the micelles considered to be spherical in shape. It is given by

$$\chi = (n - m)/n \quad [1]$$

where  $n$  is the micelle aggregation number and  $m$  the number of micelle-bound counter-ions. The numbers  $n$  and  $m$  are related as follows:

$$1000S_2 = \frac{(n - m)^2}{n^{4/3}} (1000S_1 - \Lambda_{\text{Br}^-}) + \left(\frac{n - m}{n}\right) \Lambda_{\text{Br}^-} \quad [2]$$

where  $\Lambda_{\text{Br}^-}$  is the ionic equivalent conductivity, which can be set equal to the value at infinite dilution at low concentration. The two  $\chi$  values, i.e.,  $\chi_1$  and  $\chi_2$  corresponding to  $C_1$  and  $C_2$ , can be computed from  $S_1$  and  $S_2$  in the former case and from  $S_2$  and  $S_3$  in the latter case, for the present mixtures in pure water as well as in the presence of each additive. To calculate  $\chi$ , an arbitrary value must be given to  $n$ . The value of  $\chi$  is quite insensitive to  $n$ . For example, by choosing 40, 60, and 80 as the values of  $n$  for TTAB, 0.24, 0.25, and 0.26 values, respectively, were computed for  $\chi$ . Therefore, a value of  $n$  equal to 60 was selected for this

**TABLE 1**  
**Values of  $C_1$ ,  $C_2$ ,  $1000S_1$ ,  $1000S_2$ ,  $1000S_3$ ,  $\chi_1$ ,  $\chi_2$ , and  $\beta$  for HPyBr + TTAB Mixtures in Pure Water at 30°C**

$\alpha_{\text{HPyBr}}$	$C_1^a$	$C_2^a$	$1000S_1^b$	$1000S_2^b$	$1000S_3^b$	$\chi_1^c$	$\chi_2^c$	$\beta^d$
0.000	37.92		77.36		21.39		0.25	
							0.26 <sup>e</sup>	
0.0710	28.24	48.12	79.72	48.36	22.07	0.57	0.26	-0.35
0.1019	25.54	46.96	80.65	48.73	22.96	0.57	0.28	-0.40
0.1604	21.21	43.72	80.26	48.21	24.46	0.57	0.29	-0.57
0.2210	17.41	40.96	82.75	48.43	26.08	0.57	0.31	-0.81
0.2765	16.22	39.31	81.90	47.77	27.67	0.56	0.33	-0.75
0.3620	13.79	38.20	83.51	47.44	28.28	0.55	0.34	-0.92
0.4333	12.37	37.74	81.70	46.52	28.96	0.55	0.35	-1.0
0.5316	11.00	35.77	84.04	43.06	28.02	0.50	0.34	-1.2
0.6566	10.22	31.35	83.15	38.80	28.42	0.45	0.35	-1.2
0.7394	9.500	26.95	85.08	36.05	27.92	0.42	0.34	-1.2
0.7748	8.820	25.21	84.10	36.22	28.04	0.42	0.34	-1.9
0.8363	8.450	23.24	82.65	33.20	27.37	0.39	0.34	-1.8
1.000	8.240		82.17		27.04		0.32	

<sup>a</sup> $C_1$  and  $C_2$ , critical micelle concentrations ( $10^{-4}$  mol dm<sup>-3</sup>).

<sup>b</sup> $S_1$ ,  $S_2$ , and  $S_3$ , slopes, explained in text: units are cm<sup>-1</sup> ohm<sup>-1</sup>/mol dm<sup>-3</sup>.

<sup>c</sup>Degree of micellization, corresponding to  $C_1$  and  $C_2$ .

<sup>d</sup>Interaction parameter.

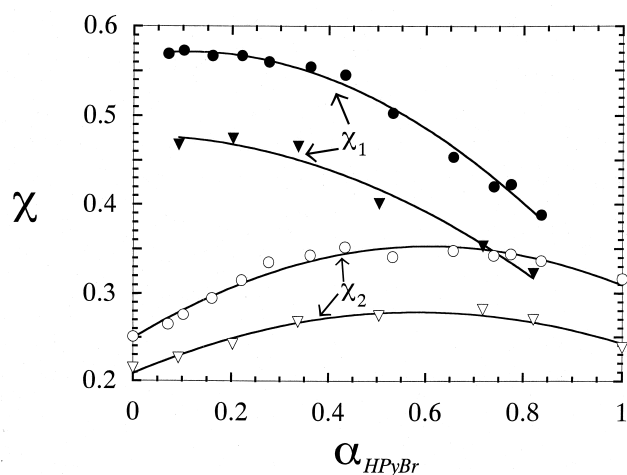
<sup>e</sup>From Reference 13. HPyBr, hexadecylpyridinium bromide; TTAB, tetradecyltrimethylammonium bromide.

work. The  $\chi$  values thus obtained for the present mixture in pure water also are listed in Tables 1–5. Such a value for TTAB in pure water has also been compared with that available in the literature (13). Good agreement is observed between the present and the reported value. Figure 5 shows a plot of  $\chi$  values in pure water as well as in the presence of 10 wt% EG. Both  $\chi_1$  and  $\chi_2$  can be seen to decrease significantly in the presence of 10 wt% EG over the whole mole fraction range, and the overall variation in the presence and absence of EG is almost identical. Similar results were obtained in the presence of other additives (Tables 1–5). This suggests that the decrease in degree of counter-ion dissociation in the presence of additives for both kind of micelles, i.e., corresponding to  $C_1$  as well as to

$C_2$ , is mainly due to the predominance of solvophobic interactions over hydrophobic ones. Apart from this, it is also expected that additive introduction in such a large amount may increase the viscous drag of the medium. This will decrease the ionic mobility and will subsequently reduce  $\chi$ . However, the overall micellar transitions from  $C_1$  to  $C_2$  remain predominantly identical even in the presence of different additive glycols.

In a particular system,  $\chi_1$  decreases nonlinearly with an increase in  $\alpha_{\text{HPyBr}}$ , suggesting a somewhat nonideal mixing behavior, whereas  $\chi_2$  remains constant over a broad but weak maximum in the whole mole fraction range. A contrasting difference in the variation of  $\chi_1$  and  $\chi_2$  may be explained on the basis that the former can also be linked to the transition from  $C_1$  to  $C_2$  whereas the latter may indicate the formation of stable mixed micellar aggregates at higher surfactant molarities. Therefore, a decrease in  $\chi_1$  with an increase in  $\alpha_{\text{HPyBr}}$  suggests that the transitions from  $C_1$  to  $C_2$  are accompanied by an increase in the number of HPyBr monomers in the mixed micelles, and the mixed micelles are approaching that of pure HPyBr micelles. On the other hand, a weak maximum in the variation of  $\chi_2$  over a broad range of  $\alpha_{\text{HPyBr}}$  may suggest the presence of almost equivalent micellar states at  $C_2$ , which are expected to be influenced by the repulsions of unlike bulky polar head groups, particularly around equimolar proportions.

**Micelle formation.** All HPyBr + TTAB mixtures show two cmc values over the whole mole fraction range, which is quite contrary to the presence of single cmc values of pure HPyBr and TTAB (Tables 1–5). This indicates that mixed micelles at  $C_1$  undergo strong structural changes with an increase in total surfactant concentration, which may be responsible for the appearance of  $C_2$ . A nonlinear variation



**FIG. 5.** Plot of the degree of micelle ionization ( $\chi$ ) vs. mole fraction of HPyBr ( $\alpha_{\text{HPyBr}}$ ) of HPyBr + TTAB in pure water ( $\bullet$ ,  $\circ$ ) and in aqueous 10 wt% EG ( $\blacktriangledown$ ,  $\triangledown$ ). For abbreviations see Figures 1 and 2.

**TABLE 2**  
**Values of  $C_1$ ,  $C_2$ ,  $1000S_1$ ,  $1000S_2$ ,  $1000S_3$ ,  $\chi_1$ ,  $\chi_2$ , and  $\beta$  for HPyBr + TTAB Mixtures in Ethylene Glycol + Water at 30°C**

$\alpha_{\text{HPyBr}}$	$C_1^a$	$C_2^a$	$1000S_1^b$	$1000S_2^b$	$1000S_3^b$	$\chi_1^c$	$\chi_2^c$	$\beta^d$
Ethylene glycol (10 wt%)								
0.000	46.43		64.23		18.18		0.21	
0.0922	32.94	54.10	64.18	38.91	18.83	0.47	0.23	-0.26
0.2025	22.78	49.34	65.72	39.55	20.08	0.47	0.24	-0.59
0.3367	16.46	42.08	68.36	38.99	22.10	0.47	0.27	-1.0
0.5038	13.64	39.48	65.93	33.60	22.54	0.40	0.27	-1.2
0.7174	11.61	30.40	66.12	29.70	23.07	0.35	0.28	-1.6
0.8204	10.00	25.04	65.06	27.13	22.09	0.32	0.27	-1.6
1.000	9.690		62.72		21.58		0.24	
Ethylene glycol (30 wt%)								
0.000	81.85		36.55		12.74		0.15	
0.0894	56.01	94.05	37.28	21.27	13.47	0.26	0.16	-0.70
0.1970	42.40	85.28	38.12	20.90	14.55	0.25	0.18	-0.87
0.3292	33.99	80.93	39.17	20.16	14.50	0.24	0.17	-0.98
0.4953	25.98	63.05	38.76	20.25	14.43	0.24	0.17	-1.4
0.7104	24.29		38.35		15.04	0.39		-1.1
0.8154	22.79		37.55		14.22	0.36		-2.2
1.000	20.79		37.82		12.02		0.14	

<sup>a-d</sup>For footnotes and abbreviations see Table 1.

in  $C_1$  with respect to  $\alpha_{\text{HPyBr}}$  (Fig. 6) indicates that the bulk mole fraction is different from the mixed micellar mole fraction. On the other hand, the almost linear dependence of  $C_2$  on  $\alpha_{\text{HPyBr}}$  (Fig. 6) may suggest that, at higher surfactant concentration, micellar mole fraction approaches that of bulk mole fraction. To explore why mixed micelles undergo structure transitions, it is possible to simulate the dependence of  $C_1$  on the micellar mole fraction of HPyBr + TTAB mixtures in pure water. This can be done quantitatively by taking in consideration the regular solution ap-

proximation (22), which relates the mixed cmc to the individual cmc, i.e.,  $\text{cmc}_1$  and  $\text{cmc}_2$  by

$$\alpha_1 \text{cmc} = x_1 f_1 \text{cmc}_1 \quad [3]$$

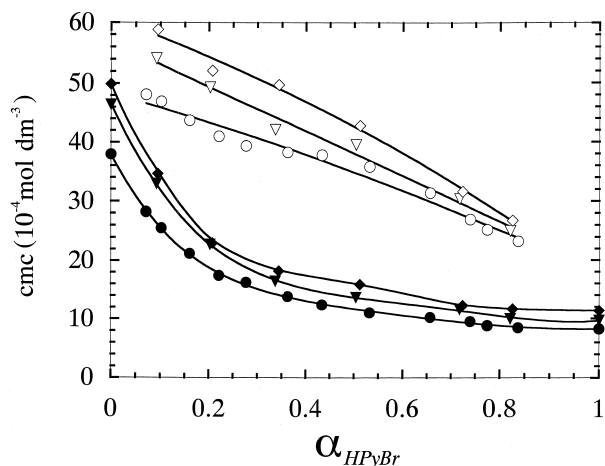
$$\alpha_2 \text{cmc} = x_2 f_2 \text{cmc}_2 \quad [4]$$

where  $x_1$ ,  $x_2$  and  $f_1$ ,  $f_2$  are the mole fractions in the mixed micelle and the activity coefficients of surfactant 1 (HPyBr)

**TABLE 3**  
**Values of  $C_1$ ,  $C_2$ ,  $1000S_1$ ,  $1000S_2$ ,  $1000S_3$ ,  $\chi_1$ ,  $\chi_2$ , and  $\beta$  for HPyBr + TTAB Mixtures in Diethylene Glycol + Water at 30°C**

$\alpha_{\text{HPyBr}}$	$C_1^a$	$C_2^a$	$1000S_1^b$	$1000S_2^b$	$1000S_3^b$	$\chi_1^c$	$\chi_2^c$	$\beta^d$
Diethylene glycol (10 wt%)								
0.000	49.91		60.83		17.13		0.20	
0.0948	34.63	58.88	64.77	37.62	19.00	0.45	0.23	-0.45
0.2076	22.98	52.11	65.55	38.41	20.32	0.46	0.25	-1.0
0.3438	18.17	49.74	64.08	34.44	21.27	0.41	0.26	-1.2
0.5117	15.89	42.76	64.86	30.97	21.86	0.37	0.27	-1.0
0.7237	12.27	31.58	68.28	31.52	22.10	0.37	0.27	-1.5
0.8250	11.64	26.75	67.98	26.75	21.72	0.32	0.27	-1.7
1.000	11.36		68.76		19.92		0.23	
Diethylene glycol (30 wt%)								
0.000	90.78		34.85		12.57		0.15	
0.0802	70.40		35.85		13.63	0.33		-0.28
0.1791	48.64	94.00	36.36	23.53	12.51	0.29	0.15	-0.93
0.3037	39.99	85.30	36.47	21.43	13.43	0.26	0.16	-0.89
0.4660	33.67	74.52	36.77	19.16	13.77	0.23	0.17	-0.87
0.6856	27.74	56.44	37.41	18.31	14.34	0.22	0.17	-1.2
0.7970	25.66		37.17		13.74	0.36		-1.3
1.000	23.34		36.97		13.33		0.16	

<sup>a-d</sup>For footnotes and abbreviations see Table 1.



**FIG. 6.** Plot of mixed critical micelle concentration (cmc) vs. mole fraction of HPyBr ( $\alpha_{\text{HPyBr}}$ ) for HPyBr + TTAB mixtures in pure water ( $\bullet, \circ$ ) and in 10 wt% aqueous EG ( $\blacktriangledown, \triangledown$ ) and DEG ( $\blacklozenge, \lozenge$ ). First cmc ( $C_1$ ) ( $\bullet, \blacktriangledown, \blacklozenge$ ) and second cmc ( $C_2$ ) ( $\circ, \triangledown, \lozenge$ ). For abbreviations see Figures 1–3.

and surfactant 2 (TTAB), respectively. The value of  $x_1$  is computed from the following equation:

$$\frac{x_1^2 \ln(\text{cmc } \alpha_1 / \text{cmc}_1 x_1)}{(1-x_1)^2 \ln[\text{cmc}(1-\alpha_1) / \text{cmc}_2(1-x_1)]} = 1 \quad [5]$$

Equation 5 can be solved iteratively to obtain  $x_1$ , from which the interaction parameter  $\beta$  can be computed using Equation 6:

$$\beta = \frac{\ln[(\text{cmc } \alpha_1) / (\text{cmc}_1 x_1)]}{(1-x_1)^2} \quad [6]$$

The  $\beta$  value demonstrates the extent of interaction between

the two surfactants that lead to the deviations from ideal behavior. A  $\beta$  value equal to zero indicates no interactions, whereas a negative or positive value indicates attractive or repulsive interactions, respectively. Also the higher the negative or positive values, the stronger will be the respective interactions. Within the regular solution approximation (22),  $\beta$  values are expected to be invariant with respect to the change in composition for a given binary surfactant mixture. For our structurally similar binary mixtures, ideal behavior is expected, since interactions between monomers in the mixed micelles are considered to be similar, as in the case of homomicelles (23). However, perusal of Table 1 shows that  $\beta$  values vary with respect to the change in composition and are negative in pure water over the whole mole fraction range. There are many examples (24–26) of binary surfactant combinations including cationic + cationic ones in which  $\beta$  values vary with respect to the bulk composition. These negative  $\beta$  values demonstrate attractive interactions between unlike monomers of HPyBr + TTAB in the mixed state which may be originating from electrostatic interactions of the  $\pi$ -electron cloud of the aromatic ring of HPyBr with the ammonium head group of TTAB, as was reported in the case of HPyCl + cetyltrimethylammonium chloride (27). Since the behavior of HPyBr + TTAB mixtures in pure water is quite similar to that in the presence of various glycols, it may therefore also be possible to extend the same thermodynamic treatment to such systems. The  $\beta$  values thus obtained in the presence of additives are also listed in Tables 2–5. Note that the difference between the  $\beta$  values in pure water and in the presence of various additives is insignificant, and they mainly vary between  $-0.2$  to  $-2$ . This may indicate that the overall micelle formation at  $C_1$  in the absence and presence

**TABLE 4**  
Values of  $C_1$ ,  $C_2$ ,  $1000S_1$ ,  $1000S_2$ ,  $1000S_3$ ,  $\chi_1$ ,  $\chi_2$ , and  $\beta$  for HPyBr + TTAB Mixtures in Triethylene Glycol + Water at 30°C

$\alpha_{\text{HPyBr}}$	$C_1^a$	$C_2^a$	$1000S_1^b$	$1000S_2^b$	$1000S_3^b$	$\chi_1^c$	$\chi_2^c$	$\beta^d$
Triethylene glycol (10 wt%)								
0.000	53.34		59.81		16.85		0.20	
0.0832	42.31		60.85		17.60			
0.1848	28.56	63.84	63.51	32.73	18.06	0.39	0.22	-0.61
0.3120	22.96	58.38	60.74	33.07	19.03	0.40	0.23	-0.52
0.4756	17.18	53.21	62.92	31.66	20.70	0.38	0.25	-0.93
0.6940	14.17	44.56	62.75	27.99	21.80	0.33	0.27	-1.5
0.8032	12.83	33.87	64.17	27.10	21.63	0.32	0.26	-1.6
1.000	11.98		67.30		21.70		0.26	
Triethylene glycol (30 wt%)								
0.000	94.41		39.19		10.89		0.13	
0.0801	75.15		39.04		12.75	0.31		
0.1787	56.00	91.41	39.42	20.14	14.27	0.24	0.17	-0.40
0.3033	40.70	70.54	41.63	25.71	13.04	0.31	0.16	-0.91
0.4654	33.48	61.34	41.95	21.99	15.17	0.27	0.18	-0.97
0.6852	28.44	54.28	41.11	20.65	15.67	0.25	0.19	-1.0
0.7966	24.54	50.35	42.17	19.54	14.32	0.23	0.17	-1.6
1.000	23.82		41.85		13.28		0.16	

<sup>a-d</sup>For footnotes and abbreviations see Table 1.

**TABLE 5**  
**Values of  $C_1$ ,  $C_2$ ,  $1000S_1$ ,  $1000S_2$ ,  $1000S_3$ ,  $\chi_1$ ,  $\chi_2$ , and  $\beta$  for HPyBr + TTAB Mixtures in Polyethylene Glycol + Water at 30°C**

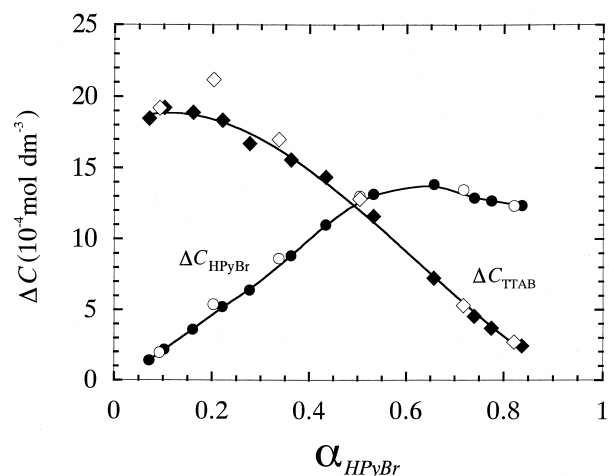
$\alpha_{\text{HPyBr}}$	$C_1^a$	$C_2^a$	$1000S_1^b$	$1000S_2^b$	$1000S_3^b$	$\chi_1^c$	$\chi_2^c$	$\beta^d$
Polyethylene glycol 600 (10 wt%)								
0.000	55.63		60.34		15.73		0.19	
0.0984	41.83	82.87	59.27	24.94	14.57	0.30	0.18	
0.2144	29.46	76.93	65.19	27.19	15.27	0.32	0.18	-0.44
0.3531	20.85	71.50	56.51	24.21	15.50	0.29	0.19	-1.0
0.5219	17.06	67.21	62.68	26.98	16.90	0.32	0.20	-1.2
0.7319	14.57	60.13	61.66	24.28	17.71	0.29	0.21	-1.4
0.8309	13.24	55.31	60.07	22.97	17.44	0.27	0.21	-1.3
1.000	12.56		59.80		16.97		0.20	
Polyethylene glycol 600 (30 wt%)								
0.000	112.8		26.44		7.990		0.095	
0.0946	88.24		26.51		8.970	0.30		-0.20
0.2071	64.67	125.8	27.08	14.05	7.940	0.17	0.094	-0.58
0.3432	53.15	116.7	26.18	13.44	8.250	0.16	0.098	-0.54
0.5110	44.39	100.5	27.00	13.11	8.530	0.16	0.10	-0.80
0.7232	39.87	90.30	26.47	10.60	6.980	0.13	0.083	
0.8246	36.04	79.13	25.76	10.84	7.130	0.13	0.085	-1.6
1.000	31.80		27.11		6.780		0.080	

<sup>a-d</sup>For footnotes and abbreviations see Table 1.

of additives is identical, or in other words, there are no significant mixed micelle-glycol interactions at  $C_1$ . Thus, the presence of glycol is the only factor responsible for the delay in  $C_1$  and  $C_2$  values (Fig. 6), which is due to the additive-water molecule interactions that leave less room for surfactant monomers to maneuver in solution and hence lead to surfactant micellization.

From these results, one thing seems to be quite clear. Mixed micelle formation at  $C_1$  mainly results from synergistic interactions between unlike monomers of HPyBr + TTAB mixtures, and it cannot be assigned to ideal mixing of unlike monomers. This suggests that the appearance of  $C_2$  is definitely related to synergistic interactions at  $C_1$ . This is because there are few examples of cationic surfactants and their combinations in which the second cmc appears at low surfactant concentration (i.e., 2–3 times the first cmc). Therefore, it appears from these results that head group modification may be responsible for bringing about the second cmc, as was observed for TTACl +  $C_{14}$ BzCl and CPyCl +  $C_{16}$ BzCl mixtures (13). However, to elaborate this point, it is possible to determine the amount of HPyBr and TTAB separately that is needed to induce structure transitions in mixed micelles at  $C_1$ . The difference ( $\Delta C$ ) between  $C_1$  and  $C_2$  can be assigned to a collective amount of HPyBr and TTAB required to induce the structure transition at  $C_1$  in view of almost linear variation of  $C_2$  against  $\alpha_{\text{HPyBr}}$ . Since  $C_2$  appears at a higher concentration than  $C_1$ , it is also possible to assume that the micellar mole fraction at such a high concentration is equal to that of the bulk mole fraction, which is perhaps also evident from the almost linear dependence of  $C_2$  on  $\alpha_{\text{HPyBr}}$  (Fig. 6). Therefore, the product of  $\Delta C \cdot \alpha_{\text{HPyBr}}$  should give the amount of HPyBr ( $\Delta C_{\text{HPyBr}}$ ) used to induce the structure transition, and such a value

can be obtained similarly for the case of TTAB ( $\Delta C_{\text{TTAB}}$ ). Both values are plotted in Figure 7. There, the variation of  $\Delta C_{\text{HPyBr}}$  and  $\Delta C_{\text{TTAB}}$  in the TTAB-rich region of the mixture is predominantly linear and thus structure transitions introduced at  $C_1$  are likely due mainly to the additive contribution of both unlike monomers until mixed micelles attain an ideal mixing in this region. In contrast, in the HPyBr-rich region,  $\Delta C_{\text{HPyBr}}$  remains almost constant, which can be attributed to the fact that the micelles are expected to be rich in HPyBr monomers already, as observed in the case of  $\chi_2$  in the same region. Hence the contribution of HPyBr is constant, but the structure transition is brought about by the removal of TTAB monomers from the mixed micelles.



**FIG. 7.** Plot of  $\Delta C$  vs. mole fraction of HPyBr ( $\alpha_{\text{HPyBr}}$ ) for HPyBr and TTAB in pure water (●,◆) and in aqueous 10 wt% EG (○,◇). For abbreviations see Figures 1–3.

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