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Hexadecylpyridinium Chloride + Trimethyltetradecylammonium Bromide Mixed Micelles in Polyethylene Glycol + Water Mixtures

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The conductances of hexadecylpyridinium chloride (HPyCl) + trimethyltetradecylammonium bromide (TTAB) mixtures over the entire mole fraction range of HPyCl (α_{HPyCl}) were measured in aqueous binary mixtures of polyethylene glycol (PEG) 200, 400, 600, and 4000 containing different amounts of each PEG in their respective binary mixtures at 30 °C. Each conductivity curve showed a single break, except in the presence of PEG 4000 where two breaks were observed. From the conductivity ($\varkappa$) data, the critical micellar concentration (cmc), degree of counter ion association (χ), the equivalent conductivities (Λ) from the slope of $\varkappa$ versus C plots, and the standard Gibb's free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle ($\Delta G^{\circ}_{\mathrm{HP}}$) were computed. It was observed that micelle–PEG interactions in the case of HPyCl and TTAB were quite similar to mixed micelle–PEG interactions especially in the presence of PEG 200, 400, and 600. The results were explained on the basis of medium structure-breaking effects of PEG and adsorption of PEG on the micelle–solution interface. In the presence of PEG 4000, the micelle formation corresponding to the first break was found to be similar to that in the presence of PEG 200, 400, and 600. The second break was designated to the polymer bound micellar aggregates, which became more stable as the amount of PEG 4000 was increased.

The effects of different kinds of additives including various glycols on the micellization of single surfactants have been widely studied.[1—3] Micelle formation has also been reported in pure nonaqueous solvents such as ethylene glycol,[4] glycerol,[5] formamide,[6,7] and hydrazine.[8] All these solvents have high cohesive energies and considerable hydrogen bonding capabilities which favor the aggregation of surfactant monomers to form the micelles. Recently,[9—11] the additive effects of such kind of molecules have also been studied on the mixed micelle formation. Mixed micelles are considered to be more versatile than any single surfactant.[12] They have many applications in surface activity, detergency, wetting, spreading, and foaming. Most of the studies on the mixed micelle formation have been focused in pure water only.[13—17] However, it has been considered to be worthwhile to study the mixed micelle formation with the cationic surfactants in the presence of highly cohesive solvents like polyethylene glycols (PEGs). This is due to the fact that the driving force responsible for surfactant–PEG interactions[18] is still poorly understood. Apart from this, such studies have numerous industrial applications.[19] It has also been observed that cationic surfactants have very weak interactions with low molecular weight PEGs in comparison to high molecular weight ones.[20] Different models have been suggested to explain such kind of interactions; e.g. Nikas and Blankschtein proposed the necklace model.[21] Picullel and co-workers suggested the "spaghetti and meat balls" model.[22] Borisov and Halperin[23] used the concept of polysoap micelles to explain the effect of bridging interactions in polymer–surfactant solutions. In all these theories the micelle size, charge on the surfactant head group, and length of the polymer chain are mainly considered.

In continuation of our earlier work on the micelle–glycol interactions,[2,24] we observed that ethylene and diethylene glycols[9] significantly influence the aqueous medium properties, due to which the mixed micelle formation of HPyCl + TTAB mixtures is delayed. The structure-breaking effects of these glycols have been found to be rather stronger than their adsorption at micelle–solution interface or at the palisade layer. On the other hand, even the increase in the repeating units up to 1000 of additive glycol (i.e. in the presence of PEG 1000) does not show any significant micelle–PEG interactions.[10] However, in the present work, interesting results have been observed when the number of repeating units is systematically increased up to 4000. It has been found that in the presence of PEG 4000, the micelle–polymer interactions have become quite predominant over the structure-breaking properties of glycol. Due to this, the $\varkappa$ profiles for HPyCl+TTAB mixtures show a double break, which is quite contrary to trimethylhexadecylammonium bromide (HTAB)+TTAB+ glycol systems in which only a single break was observed even in the presence of PEG 4000.[11]

The choice of HPyCl and TTAB was due to their unlike hydrophobic tails and polar head groups, in order to discriminate between the unlike micelles–PEG interactions and to compare them with the mixed micelle–PEG interactions. The selection of a series of PEGs from molecular weight 200—

4000 was to investigate such interactions under the effect of increasing hydrophobicity.

Experimental

Hexadecylpyridinium chloride (HPyCl) from Flüka and trimethyltetradecylammonium bromide (TTAB) from Sigma were recrystallized from ethanol+acetone and ethanol+ethyl acetate mixtures, respectively. Both surfactants were dried in vacuo at 60 °C for two days.

Polyethylene glycols with average molecular weights of 200, 400, 600, and 4000 all 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 HPyCl + TTAB mixtures over the entire mole fraction range of HPyCl (α_{HPyCl}) in PEG 200 + water (W), PEG 400 + W, and PEG 600 + W containing 10—40 wt% and in PEG 4000 + W containing 1—10 wt% of each PEG in their respective binary mixtures were measured at 30 (±0.01) °C, as explained earlier.[9] The data in the pure water have been taken from our earlier work.[9] The error in the conductance measurements was ±0.5%.

Results and Discussion

The conductivity ($\varkappa$) is linearly correlated to the concentration of single as well as mixed surfactants in both the pre-micellar and the post-micellar regions,[9] having a slope in the pre-micellar region greater than that in the post-micellar region. The intersection point between the two straight lines gives the critical micelle concentration (cmc) and the ratio of the slope in the post-micellar region to that in the pre-micellar region gives the degree of counter ion dissociation (δ), and subsequently, the degree of counter ion association ($\chi = 1 - \delta$). These values for HPyCl, TTAB, and HPyCl+TTAB mixtures were calculated as explained earlier[9,24] and are listed in Tables 1, 2, and 3. Figure 1 shows such a concentration dependence of $\varkappa$ of HPyCl, TTAB, and their mixtures in aqueous 10 wt% PEG 200 over the entire mole fraction range of HPyCl (α_{HPyCl}). Similar plots were also obtained in other aqueous PEG mixtures except PEG 4000. In aqueous PEG 4000, the $\varkappa$ curves of HPyCl and HPyCl + TTAB mixtures show two breaks, whereas a single break is observed for TTAB (Figs. 2 and 3). These two breaks have been designated as the first (C_1) and the second cmc (C_2). Recently, Garcia-Mateas and co-workers[20] have also observed two breaks for HPyCl in the presence of various water soluble polymers including PEG. Apart from this, Treiner and Makayssi[25] have observed two breaks in some binary cationic combinations and found that, if a pure surfactant exhibits two breaks, then its binary mixtures also demonstrate the same behavior.

Table 1. Values of cmc/10^{-4}mol dm^{-3}, χ, and $\Delta G^{\circ}_{\text{HP}}$/kJ mol^{-1} for TTAB (i) and HPyCl (ii)

	cmc	χ	$\Delta G^{\circ}_{\text{HP}}$
		0 wt% PEG	
(i)	37.92	0.73	−41.82
(ii)	10.69	0.60	−43.78
		10 wt% PEG 200	
(i)	48.90	0.70	−40.01
(ii)	16.30	0.54	−40.51
		20 wt% PEG 200	
(i)	67.00	0.59	−36.16
(ii)	25.60	0.54	−38.75
		40 wt% PEG 200	
(i)	136.8	0.45	−30.36
(ii)	52.90	0.33	−31.04
		10 wt% PEG 400	
(i)	52.70	0.70	−39.69
(ii)	19.80	0.57	−40.53
		20 wt% PEG 400	
(i)	75.20	0.60	−35.92
(ii)	29.50	0.56	−38.70
		40 wt% PEG 400	
(i)	133.9	0.45	−30.44
(ii)	69.90	0.52	−34.40
		10 wt% PEG 600	
(i)	53.70	0.70	−39.61
(ii)	19.50	0.57	−40.59
		20 wt% PEG 600	
(i)	75.10	0.67	−37.50
(ii)	30.50	0.58	−39.06
		40 wt% PEG 600	
(i)	126.7	0.48	−31.28
(ii)	60.00	0.38	−31.76

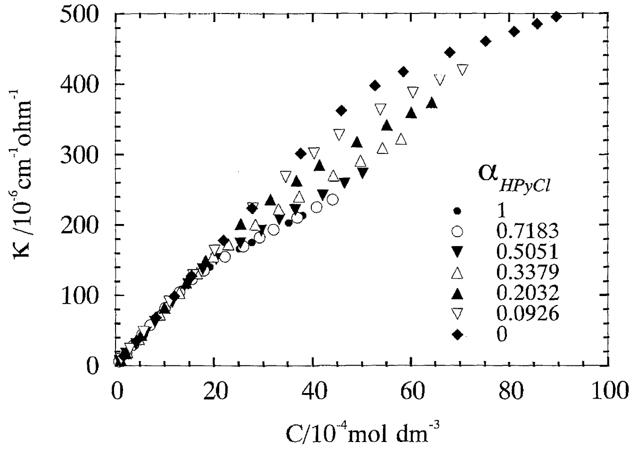

Fig. 1. Plot of conductivity ($\varkappa$) versus concentration (C) of mixed HPyCl + TTAB in 10 wt% PEG 200.

HPyCl+TTAB in Aqueous PEG 200, 400, and 600 Conductivity Behavior. Figure 4 shows the additive effect of PEG on the variation of the conductivity of HPyCl. It can be seen that the $\varkappa$ in both the pre and post-micellar regions decreases with the increase in the amount of PEG 200 (Fig. 4a). However, an increase in the number of repeating units does not seem to have a significant influence on the variation of $\varkappa$ (Fig. 4b). Similar behavior for HPyCl + TTAB mixtures has been observed (not shown). Since, the equivalent conductivity of a surfactant electrolyte can be written as $\Lambda = 1000\varkappa/C$, therefore, it is possible to approximately equate a Λ value with $1000S_1$ for a highly dilute electrolyte

Table 2. Values of Mixed cmc/10^{-4} mol dm^{-3}, χ, and β of HPyCl+TTAB in PEG 200+W, PEG 400+W, and PEG 600+W Systems at 30 °C

α_{HPyCl}	cmc	χ	β	α_{HPyCl}	cmc	χ	β	α_{HPyCl}	cmc	χ	β
10 wt% PEG 200				10 wt% PEG 400				10 wt% PEG 600			
0.09260	39.30	0.58	−0.28	0.1253	36.50	0.55	−0.89	0.1275	38.00	0.55	−0.72
0.2032	29.60	0.50	−0.66	0.2637	28.70	0.52	−1.1	0.2677	30.20	0.52	−0.86
0.3379	23.00	0.49	−1.1	0.4174	23.50	0.53	−1.4	0.4217	24.40	0.55	−1.1
0.5051	20.40	0.51	−0.91	0.5890	22.20	0.55	−1.1	0.5935	21.90	0.57	−1.3
0.7183	17.10	0.53	−1.5	0.7819	20.60	0.56	−1.3	0.7852	21.00	0.57	−0.86
	Average $\beta = -0.89 \pm 0.20$				Average $\beta = -1.16 \pm 0.08$				Average $\beta = -0.97 \pm 0.09$		
20 wt% PEG 200				20 wt% PEG 400				20 wt% PEG 600			
0.1028	56.10	0.56		0.1373	52.80	0.51	−0.74	0.1415	53.80	0.55	−0.71
0.2229	42.10	0.50	−0.68	0.2842	39.20	0.46	−1.3	0.2916	43.30	0.53	−0.87
0.3641	35.40	0.53	−0.80	0.4429	34.00	0.49	−1.4	0.4516	36.80	0.56	−1.1
0.5340	29.80	0.54	−1.1	0.6136	30.60	0.52	−1.3	0.6224	33.10	0.57	−1.1
0.7404	26.60	0.55	−1.4	0.7987	30.30	0.55	−1.6	0.8044	31.30	0.57	−1.3
	Average $\beta = -0.92 \pm 0.17$				Average $\beta = -1.27 \pm 0.14$				Average $\beta = -1.12 \pm 0.10$		
40 wt% PEG 200				40 wt% PEG 400				40 wt% PEG 600			
0.1084	103.4	0.35	−0.62	0.1344	118.9	0.39		0.1165	108.7	0.38	−0.22
0.2334	85.90	0.35	−0.66	0.2799	94.00	0.38	−0.59	0.2480	90.30	0.37	−0.43
0.3784	77.50	0.40	−0.49	0.4374	87.70	0.41	−0.43	0.3974	80.60	0.36	−0.35
0.5491	70.30	0.41	−0.44	0.6084	75.20	0.45	−0.75	0.5688	72.20	0.30	−0.43
0.7529	58.70	0.34	−0.77	0.7952	70.50	0.49	−1.2	0.7674	64.50	0.27	−0.70
	Average $\beta = -0.60 \pm 0.06$				Average $\beta = -0.74 \pm 0.16$				Average $\beta = -0.43 \pm 0.08$		

Table 3. Values of C/10^{-4} mol dm^{-3}, χ, and β of HPyCl+TTAB in PEG 4000+W Systems at 30 °C

α_{HPyCl}	C_1	C_2	χ_1	χ_2	β
			1 wt% PEG 4000		
0.000	39.74				
0.1434	21.07	44.85	0.40	0.43	-1.6
0.2950	16.16	37.87	0.43	0.31	-1.8
0.4557	13.22	35.54	0.48	0.24	-2.0
0.6260	12.65	33.40	0.52	0.20	-1.9
0.8071	13.25	33.06	0.56	0.15	-1.3
1.000	13.03	32.91	0.52	0.25	Average $\beta = -1.72 \pm 0.13$
			2 wt% PEG 4000		
0.000	40.74				
0.1408	22.61	43.10	0.38	0.39	-1.5
0.2907	15.40	36.33	0.40	0.31	-2.0
0.4504	14.55	33.75	0.46	0.27	-1.8
0.6211	13.51	31.77	0.47	0.24	-1.6
0.8038	12.55	30.79	0.47	0.26	-2.3
1.000	13.25	29.98	0.44	0.30	Average $\beta = -1.54 \pm 0.33$
			5 wt% PEG 4000		
0.000	45.47				
0.1455	23.07	41.36	0.33	0.34	-1.7
0.2986	17.77	35.30	0.37	0.30	-1.8
0.4599	14.80	32.52	0.41	0.29	-1.8
0.6301	13.65	31.36	0.43	0.28	-1.7
0.8098	12.46	30.03	0.42	0.30	-2.0
1.000	13.38	29.03	0.40	0.32	Average $\beta = -1.79 \pm 0.05$
			10 wt% PEG 4000		
0.000	53.00				
0.1425	34.15		0.32		-1.1
0.2935	25.26		0.36		-1.2
0.4538	18.67	31.39	0.39	0.31	-1.6
0.6243	16.90	29.15	0.41	0.30	-1.8
0.8060	16.47	28.18	0.38	0.32	-2.3
1.000	16.03	27.21	0.37	0.33	Average $\beta = -1.59 \pm 0.21$

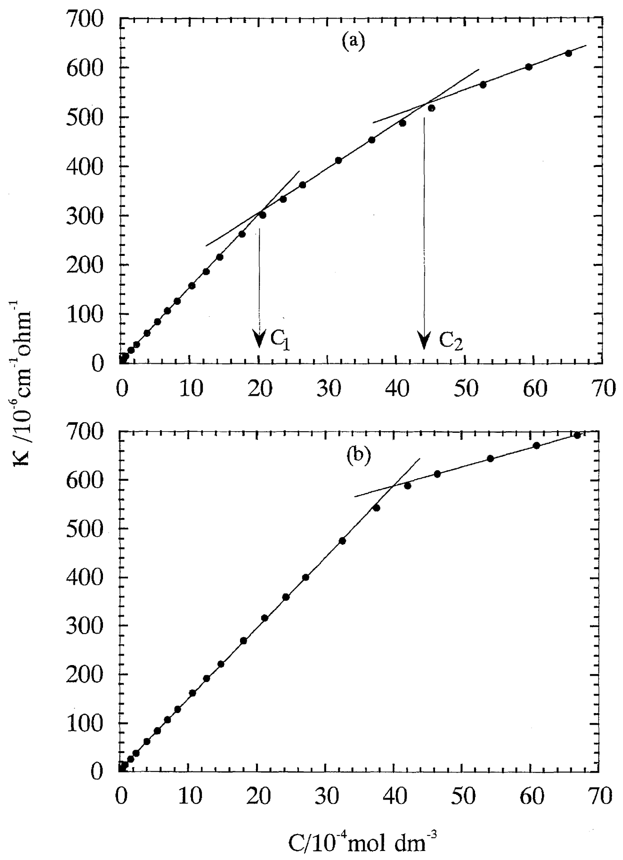

Fig. 2. Plot of conductivity ($\varkappa$) versus concentration (C) of HPyCl+TTAB in 1 wt% PEG 4000. (a) $\alpha_{\text{HPyCl}} = 0.1434$ and (b) $\alpha_{\text{HPyCl}} = 0$.

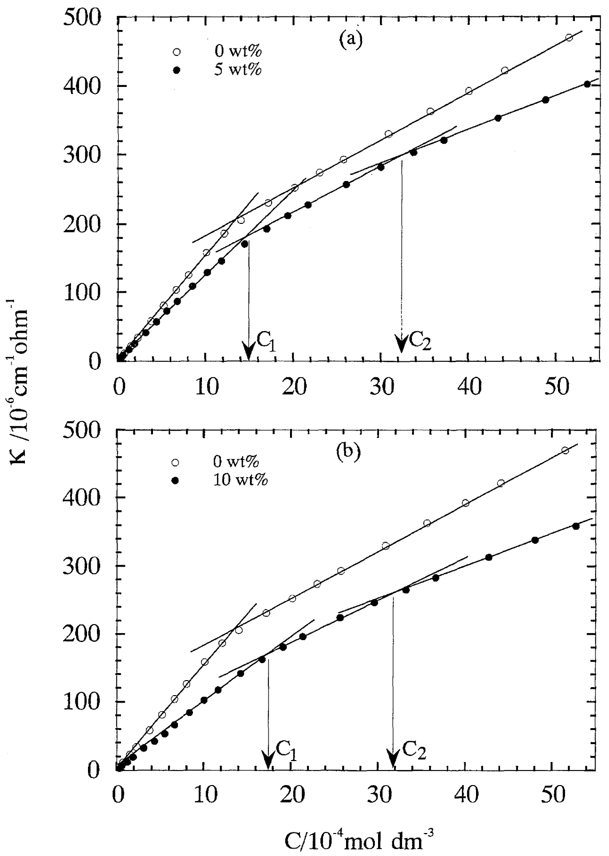

Fig. 3. Plot of conductivity ($\varkappa$) versus concentration (C) of HPyCl in pure water and in the presence of 5 wt% PEG 4000 (a) and 10 wt% PEG 4000 (b).

solution,[25] where S_1 is the slope of $\varkappa$ versus C plot in the pre-micellar region. Thus, Λ_m and $\Lambda_{m,a}$ values, which represent the equivalent conductivities of the monomeric state of surfactant electrolytes in the absence and presence of additive, respectively, can be determined from the slope of the $\varkappa$ versus C plots in the respective pre-micellar regions. On the other hand, since the conductivity of the monomers remains constant after the cmc and it would be permissible for the micelles of large aggregation numbers, therefore, Λ_{mic}, which represents the conductivity of the micellar state with reference to the monomer, can be computed from the slope of the $\varkappa$ versus C profile in the post-micellar 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 known. Similar quantities for single and mixed surfactant systems in the absence and presence of additives have already been discussed by some authors.[25—27] The Λ values thus obtained for the present systems in different states have been plotted in Fig. 5. The Λ_{mic} values for various colloidal electrolytes have been mostly reported in the range of 15—40 Ω^{-1} cm^2 mol^{-1} even in the presence of different kind of additives.[26] Thus the Λ_{mic} values demonstrated in Fig. 5b for single and mixed surfactants seem to be reasonable.

A comparison between Λ_m and $\Lambda_{m,a}$ shows (Fig. 5a) that $\Lambda_{m,a}$ is always less than Λ_m over the whole mole fraction range in the pre-micellar region and Λ_{mic} (Fig. 5b) is the lowest among all. The lowest value can easily be understood from the bulkiness of the micelle state in comparison to the monomeric state. Such value further decreases with the increase in the number of repeating units of PEG additive. This may be attributed to the adsorption of PEG at the micelle–solution interface. Thus, it will make the micelle–PEG aggregate more bulky in comparison to that in the absence of PEG. It will have comparatively less mobility and subsequently less contribution towards the conductivity. The $\Lambda_{m,a}$ systematically decreases more significantly with the increase in the amount rather than with the increase in the molecular weight of PEG. This can be attributed mainly to a large change in the medium properties[2] due to the structure-breaking nature[28] of the additive glycol oligomers, which consequently reduce the relative permittivity (ε) and enhance the viscosity (η) of the medium.[29] It will result in a decrease in the Λ value, due to the increase in the non-polar character and viscous drag of the medium, which will subsequently reduce the mobility of the ionic species.[2,24] Similar results have also been observed in the presence of ethylene and diethylene glycols.[9] On the other hand, the Λ_{mic} shows a pronounced decrease (Fig. 5b) even with the increase in molecular weight, contrary to what is observed in Fig. 5a. Such a decrease can be attributed to the adsorption of PEG macromolecules at the micelle–solution interface and the adsorption increases with

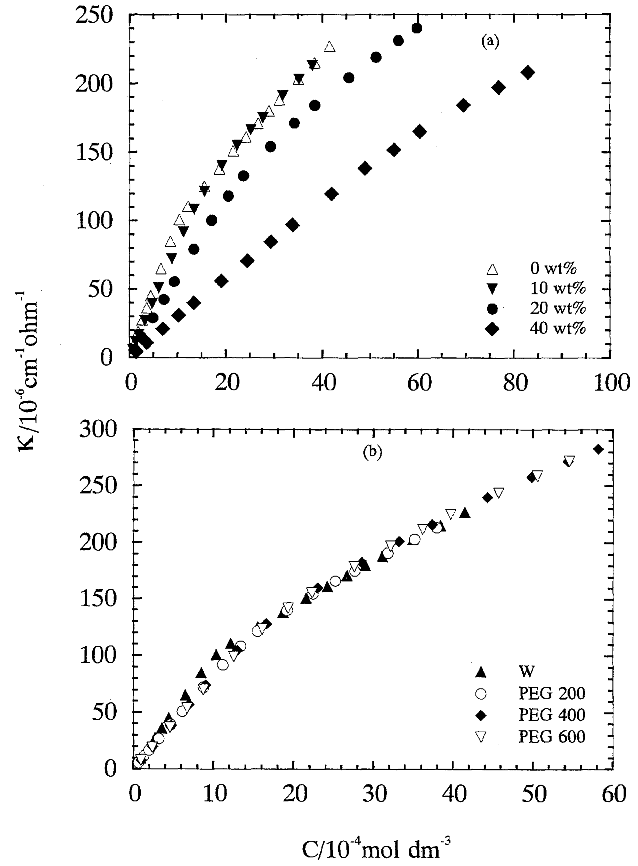

Fig. 4. Plot of conductivity (κ) versus concentration (C) of HPyCl in aqueous PEG 200 (a) and in aqueous 10 wt% additive (b).

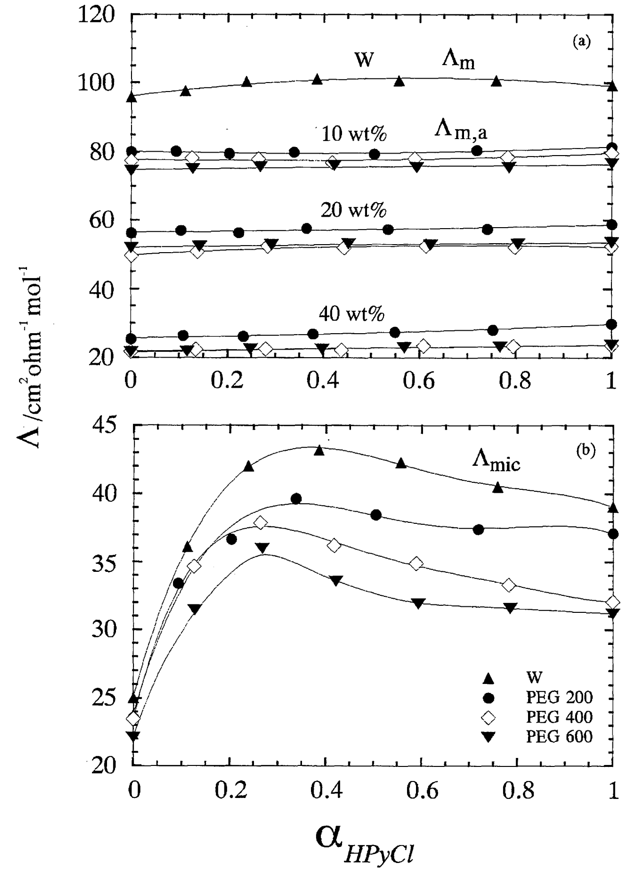

Fig. 5. Plot of Λ versus α_{HPyCl} for HPyCl+TTAB mixtures. (a) in pure water (W) and in aqueous PEG 200, PEG 400, and PEG 600. Symbols as for Fig. 5(b). (b) in aqueous 10 wt% of different PEG additives.

the increase in the hydrophobicity of the PEG, thus providing the micelle with more non-polar environment. However, comparing the Λ_{mic} values of HPyCl with TTAB (Fig. 5b), one can observe that the micelles of HPyCl are more strongly affected with the increase in the molecular weight of PEG than with that of TTAB.

Micelle Formation by Single Surfactant. In the case of a single surfactant, the free energy of micelle formation in the presence of additives consists of surfactant–surfactant, additive–surfactant, and additive–additive interactions. These interactions can be divided into hydrophobic and hydrophilic contributions. In order to estimate hydrophobic contributions, the thermodynamics of micelle formation proposed by Evans and Ninham,[30] has been taken into account, which gives

$$\Delta G^{\circ}_{\mathrm{M}} = \Delta G^{\circ}_{\mathrm{HP}} + \Delta G^{\circ}_{\mathrm{s}}, \qquad (1)$$

where $\Delta G^{\circ}_{\mathrm{HP}}$ is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle, and $\Delta G^{\circ}_{\mathrm{s}}$ 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 energy per surfactant molecule ($\Delta G^{\circ}_{\mathrm{M}} = RT\ln X_{\mathrm{cmc}}$) associated with forming micelles. The $\Delta G^{\circ}_{\mathrm{HP}}$ values for HPyCl and TTAB were computed by a method reported elsewhere[24,31] and are reported in Table 1.

The $\Delta G^{\circ}_{\mathrm{HP}}$ values have been found to decrease in magnitude predominantly with the increase in the amount of each PEG additive in comparison to the increase in the molecular weight especially in the case of TTAB. This decrease indicates that the transfer of the hydrophobic tail from the medium to the micelles becomes unfavorable with the increase in both factors. This may be attributed mainly to the decrease in ε of the medium, as a result of which the hydrophobic hydration of the surfactant monomer increases with the increase in solvophobic interactions with the solvent.[2,24] In the case of HPyCl, contrary to that of TTAB, $\Delta G^{\circ}_{\mathrm{HP}}$ value slightly increases with the increase in the molecular weight of the PEG, suggesting that the PEG bound micelles become energetically favorable. This behavior of HPyCl is in line with that of Λ_{mic} (Fig. 5b) and demonstrates that the HPyCl micelles have stronger interactions with PEG rather than with TTAB. Saito and co-workers[32,33] have suggested that an appropriate head group of cationic surfactant is a requirement for fruitful surfactant–polymer interactions. Therefore, it is expected that pyridinium head group of HPyCl is more effective in comparison to that bulky tetraaklylammonium to undergo specific interactions with –OH group of PEG which will help in reducing polar head group repulsions more effectively in HPyCl than in TTAB.

Micelle Formation by Binary Surfactant Mixtures. From the mixed cmc values, it is possible to obtain some quantitative information of the micellar aggregates formed in the presence of PEG and subsequently mixed micelle–PEG interactions by using the pseudo phase thermodynamic model.[34,35] The model relates the mixed cmc (cmc*) with the cmc of the pure components by the following equation:

$$\frac{1}{\text{cmc}^*}=\frac{\alpha_1}{\text{cmc}_1}+\frac{(1-\alpha_1)}{\text{cmc}_2}, \qquad (2)$$

where α_1 is the mole fraction of surfactant 1 (HPyCl) in total mixed solute, 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,[35] and hence the activity coefficients should be taken as unity. The cmc* values thus calculated using Eq. 2 have been plotted along with the mixed cmc in Fig. 6. A comparison between the cmc* and the experimental cmc values shows that it does not predict fully the ideal behavior both 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. These results can further be evaluated by considering the regular solution formulation[35] 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

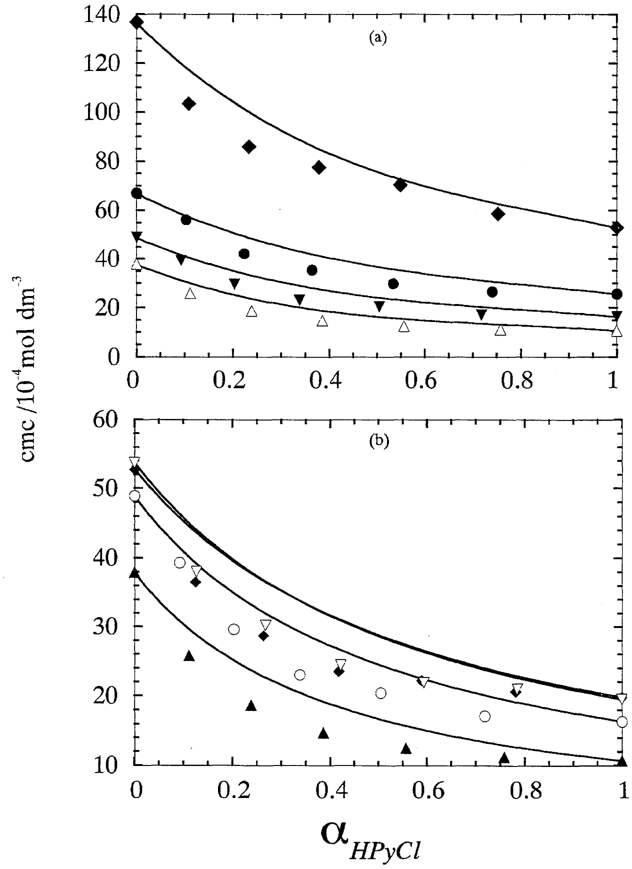

Fig. 6. Plot of cmc versus α_{HPyCl} for HPyCl+TTAB mixtures. Experimental data (points) and predicted curve (solid curve). (a) in aqueous PEG 200. Symbols as for Fig. 4a. (b) in aqueous 10 wt% additive. Symbols as for Fig. 4b.

$$\alpha_1\text{cmc}^* = x_1 f_1 \text{cmc}_1, \qquad (3)$$

and

$$\alpha_2\text{cmc}^* = x_2 f_2 \text{cmc}_2, \qquad (4)$$

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 (HPyCl) and surfactant 2 (TTAB), respectively. The value of x_1 can be computed from the following equation:

$$\frac{x_1^2 \ln\,(\text{cmc}^*\alpha_1/\text{cmc}_1 x_1)}{(1-x_1)^2 \ln\,(\text{cmc}^*(1-\alpha_1)/\text{cmc}_2(1-x_1))}=1. \qquad (5)$$

Equation 5 can be solved iteratively to obtain the value of x_1, from which the interaction parameter, β, can be computed using Eq. 6.

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

The 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,[35] the β value should be constant with respect to the change in composition for a given binary surfactant mixture.

The average β values thus obtained in the presence of PEG 200, 400, and 600 are predominantly around -1 (Table 2) and are somewhat close to that in pure water[9] ($\beta = -1.17$). However, in the presence of PEG 4000, the average β values corresponding to C_1 are slightly higher and are around -1.6 (Table 3). This suggests that the mixed micelle formation is almost identical in the absence and presence of PEG and can be attributed to the fact that the PEG macromolecules do not penetrate into the micelle but adsorb at the micelle-solution interface, as observed previously.

HPyCl+TTAB in Aqueous PEG 4000. The variation in C_1 and C_2 shows some interesting features (Fig. 7a). The C_1 curve over the whole mole fraction range is shifted towards the higher values, whereas that of C_2 is shifted towards the lower values with the increase in the amount of PEG 4000. The overall variations in C_1 and corresponding micellar properties are just like those in the presence of lower PEGs as observed in the previous section and can be mainly attributed to the reasons discussed earlier. On the other hand, decrease in the C_2 with the increase in the amount of PEG may indicate the stabilization of polymer bound micelles. This can be further explained by computing the Gibbs free energy change (ΔG_t°) upon transfer of surfactant monomers from aqueous phase to the micelles in the presence as well as in the absence of PEG.[20] This is given by

$$\Delta G_t^\circ = RT\left[(2-\delta_2)\ln \text{cmc}_2-(2-\delta_1)\ln \text{cmc}_1\right], \qquad (7)$$

where $\delta_1 = S_2/S_1$ and $\delta_2 = S_3/S_2$ are the degree of dissociation corresponding to C_1 and C_2, and S_1, S_2, and S_3 are the

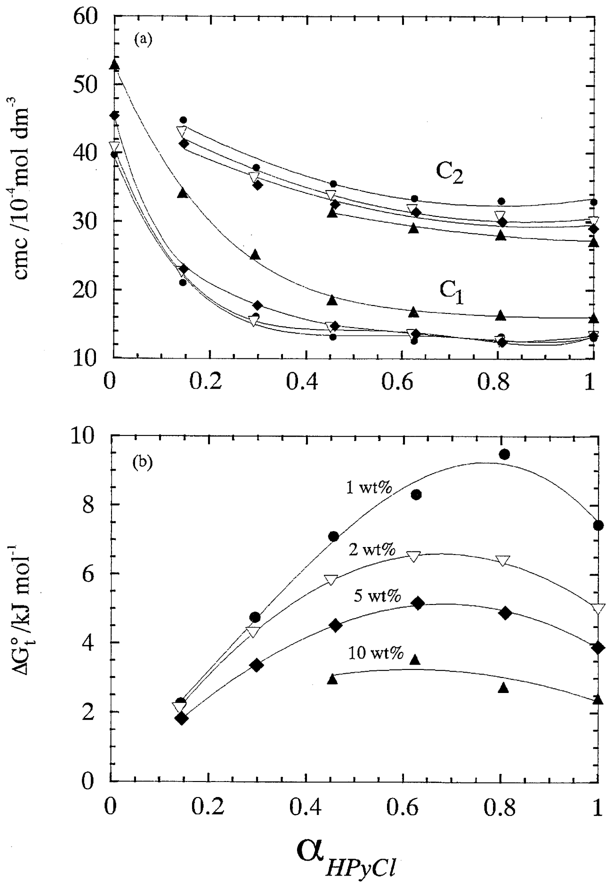

Fig. 7. (a) Plot of C_1 and C_2 versus α_{HPyCl} for HPyCl+TTAB mixtures in aqueous PEG 4000. Symbols as for Fig. 7(b). (b) Plot of ΔG_t° versus α_{HPyCl} for HPyCl+TTAB in aqueous PEG 4000.

slopes of the $\varkappa$ plot (Figs. 2a and 3), before C_1, between C_1 and C_2, and after C_2, respectively. The ΔG_t° values thus computed are shown in Fig. 7b. It can be seen that ΔG_t° decreases with the increase in the amount of PEG 4000, suggesting that the transfer of the surfactant monomers becomes more favorable.

Conclusion. We conclude that the micelle formations of single and of mixed surfactants are equally affected by the presence of PEG. This has been attributed to the medium structure-breaking effects of additive PEGs as well as their adsorption at micelle–solution interface. The micelle–PEG interactions become stronger as the molecular weight of PEG is increased, due to which the presence of PEG 4000 leads to the appearance of two breaks in $\varkappa$ curve. The first break is similar to the cmc in the presence of PEG 200, 400, and 600, whereas the second one is due to the PEG bound micelles.

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