Colloid Polym Sci 278:524–531 (2000)

ORIGINAL CONTRIBUTION

M. S. Bakshi

Interactions between cationic mixed micelles and poly(vinyl pyrrolidone)

Received: 26 August 1999
Accepted: 6 November 1999

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

Abstract The conductances of trimethyltetradecylammonium bromide (TTAB) + trimethylhexa decylammonium bromide (HTAB) and TTAB + trimethyldodecylammonium bromide (DTAB) mixtures over the entire mole fraction range were measured in aqueous poly(vinyl pyrrolidone) (PVP) containing 1–10 wt% PVP at 30 °C. Each conductivity (κ) curve for the TTAB + HTAB mixtures showed two breaks corresponding to two aggregation processes over the whole mole fraction range, except in the case of pure TTAB, where a single break corresponding to the conventional critical micelle concentration (cmc) was observed. In the case of TTAB + DTAB mixtures, each κ curve at a particular mole fraction of TTAB showed only one break, which was quite close to a similar one in pure water. In TTAB + HTAB mixtures, the first break is called the critical aggregation concentration. It is close to the conventional cmc and is attributed to the polymer-free micelle formation, whereas the second break is due to the polymer-bound micellar aggregates. However, no polymer-bound micellar aggregation process was observed in the case of TTAB + DTAB mixtures. Therefore, the presence of micelle–PVP interactions in the TTAB + HTAB case have been attributed to the stronger hydrophobicity of HTAB or TTAB + HTAB micelles in comparison to that of single or mixed micelles of TTAB + DTAB mixtures. From the conductivity data, various micelle parameters in the presence of PVP have been computed and discussed in terms of micelle–polymer interactions. The mixing behavior of TTAB + HTAB corresponding to the first break, and that of TTAB + DTAB mixtures in the presence of PVP, is close to ideal and is also identical to that in pure water.

Key words Cationic surfactants · Mixed micelles · Poly(vinyl pyrrolidone) · Conductivity measurements · Mixed micelle–polymer interactions

Introduction

In the field of colloidal chemistry, surfactant–polymer interactions [1–3] have become increasingly important in view of their wide industrial applications. In spite of a lot of work devoted to this field, the complex nature of such interactions is still not fully understood. In the case of charged polymers, it is comparatively easy to understand the electrostatic interactions between the oppositely charged polymer and ionic surfactants as in the case of anionic surfactants–cationic starch [4] and alkyltrimethylammonium bromides–sodium poly(styrene sulfonate) systems [5]. However, in the case of neutral polymers such as poly(ethylene oxide), poly(ethylene glycol), poly(vinyl pyrrolidone) (PVP), etc., the situation is quite intriguing and complex. In these cases, the surfactant–polymer interactions depend upon several factors, such as the nature of the surfactant head group, the nature of the polar groups embedded in the polymer backbone, and polymer hydrophobicity [2]. It has also been observed that anionic surfactants have comparatively stronger interactions with neutral polymers compared to cationic surfactants [2, 3]. Particularly, in the case of cationic surfactants, apart from the electrostatic interactions between the polar head groups of surfactant and neutral polymer as in the case of hexadecylpyridinium chloride–PVP systems [6, 7], the respective hydrophobic interactions also play a significant role in determining the surfactant–polymer interactions as observed in the presence of poly(propylene oxide) [8], poly(vinylmethyl ether) [9], and hydroxypropyl cellulose [10]. Therefore, in conclusion it can be said that the hydrophilic–lipophilic balance between surfactant and polymer moities plays a governing role in such interactions. Recently, we observed that not only pure cationic micelles show strong interactions with neutral polymer, but mixed cationic micelles also have significant interactions with these polymers [11, 12], which are also affected by the variation in the mole fractions of the binary mixture.

Apart from this, mixed micelles are considered to be more versatile than single surfactants [13, 14] in view of their wide industrial applications and hence the evaluation of their physiochemical properties has recently attracted a lot of attention. Most of the work on such properties of binary surfactant systems has been focused on pure water only [13–18]. In our recent studies [11, 19–22], we have found that the presence of various kinds of associative organic additives dramatically influences the micellar properties. Associative additives, such as glycol oligomers, not only change the medium properties but also support micelle formation. However, if the molecular weight of such an additive is increased appreciably, it leads to the formation of polymer-bound micelles with distinct micellar properties from those in the absence of polymer [11]. In view of these results, in the present work, another water-soluble polymer, PVP, has been studied to explore the trimethyltetradecylammonium bromide (TTAB) + trimethylhexadecylammonium bromide (HTAB) and TTAB + trimethyldodecylammonium bromide (DTAB) mixed micelle–PVP interactions. The choice of such surfactant combinations and PVP additive systems was due to two reasons. First, especially the tetraalkylammonium salts–neutral polymer interactions have not been fully understood and, second, to explore the dependence of such interactions on the mixed micelle formation by the surfactants with different hydrophobicity. The micelle–polymer interactions can be better visualized by using the conductivity technique, since conductivity is considered to be quite sensitive to the micellar transitions, particularly when ionic surfactants are involved [5, 6, 23].

Experimental

HTAB, TTAB, and DTAB, all from Lancaster, UK were recrystallized from ethanol–ethyl acetate mixtures. All surfactants were dried in a vacuum at 60 °C for 2 days.

PVP (average molecular weight, M_w = 40,000 g/mol) from BDH, UK was used as received. Conductivity water having a specific conductance of $4\text{–}8 \times 10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$ was used in the preparation of all solutions. All reference and stock solutions were prepared by mass with an accuracy of ± 0.01 mg. The mole fractions were accurate to ± 0.0001 units.

The conductivity measurements were carried out with a digital conductivity meter (Naina Electronics, Chandigarh, India, model NDC-732) at a fixed frequency of 1000 Hz. A dip-type conductivity cell with a double-walled jacket to circulate the thermostated water was used for all the measurements. The capacity of the conductivity cell was about 100 ml. An automatic thermostat bath from Shimadzu, Japan, was used for maintaining the temperature within uncertainties of ± 0.01 °C. The cell constant of the conductivity cell was 1.12, which was determined using the known conductivities of different KCl solutions. All measurements were performed at 30 °C.

Initially, 50 ml of the reference solution consisting of an appropriate amount of PVP in water was put in the conductivity cell. It was then equilibrated at 30 °C for at least 1 h before starting the experiment. Then a known amount of stock solution of single or mixed surfactants made with the same reference solution was added from a micropipette (Finnpipette, Labsystems, Finland) and was again equilibrated for sometime till the conductivity value became constant. In this way, the precise conductances of TTAB + HTAB and TTAB + DTAB mixtures over the entire mole fraction range in aqueous PVP containing 1–10 wt% PVP were measured. The error in the conductance measurements was $\pm 0.5\%$. The data for pure water were taken from our earlier work [20, 21].

Results and discussion

Conductivity behavior

The conductivity (κ) plots of pure HTAB (Fig. 1a) and TTAB + HTAB (Fig. 1b) mixtures show double breaks in all cases, whereas a single break is observed for pure TTAB and DTAB (Fig. 2) and TTAB + DTAB mixtures (Fig. 3) in the presence of PVP. The two break points in the former case (Figs. 1) can be attributed to the occurrence of two kinds of aggregation processes, whereas a single break in the latter case (Figs. 2, 3) indicates only one kind of aggregation process even in the presence of PVP. It is interesting to compare the κ plot of pure HTAB (Fig. 1a) in pure water with that in the presence of PVP. The single break in pure water is the critical micelle concentration (cmc) of HTAB (10.30×10^{-4} mol dm^{-3}) [20]. In the presence of PVP, the first break is close to that in pure water and can be regarded as the critical aggregation concentration (c_{cac}) of HTAB in the presence of PVP, whereas the second one is at least 2–3 times higher than the first one and can be attributed to the polymer-bound micelles [6, 11] (c_{p}). Similarly, in the case of mixed TTAB + HTAB mixtures (Fig. 1b), the former is the mixed c_{cac} of TTAB + HTAB mixtures whereas the latter can be ascribed to the polymer-bound mixed

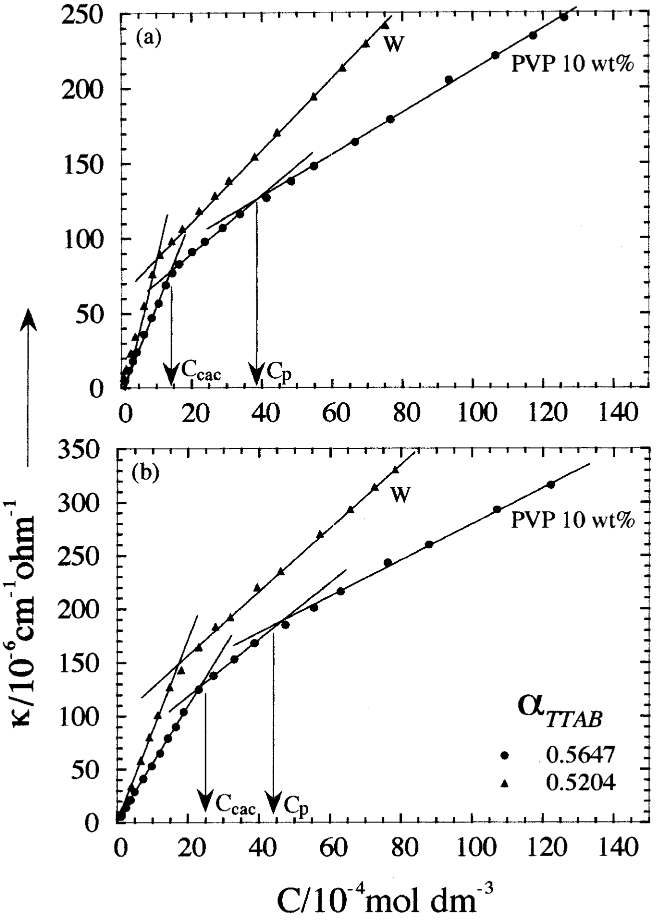

Fig. 1 Plot of conductivity (κ) versus concentration (c) of **a** trimethylhexadecylammonium bromide (*HTAB*) and **b** trimethyltetradecylammonium bromide (*TTAB*) + HTAB mixtures in water (w) and in aqueous poly(vinyl pyrrolidone) (*PVP*)

micelles (c_p). In the case of TTAB + DTAB mixtures (Fig. 3), the single break represents the mixed c_{cac} in the presence of PVP. The two values of the two aggregation processes for HTAB and TTAB + HTAB mixtures and the single value for DTAB, TTAB, and TTAB + DTAB mixtures were calculated as explained earlier [24] and are listed in Tables 1 and 2. The c_{cac} values increase with an increase in the amount of PVP. In the literature a decrease in the c_{cac} values with an increase in the amount of polymer has also been reported [25]. These two opposite variations of c_{cac} mainly depend upon the nature of the polymer. A decrease in the c_{cac} value is mainly related to the strong interactions between the oppositely charged polar sites on the surfactant and the polymer and to a large degree of flexibility in the polymer backbone as in the case of polyelectrolytes [5]. Such opposite electrostatic interactions are not expected to be so prominant in the case of the present PVP and alkyltrimethylammonium bromides in view of the presence of bulky tetraalkylammonium head groups.

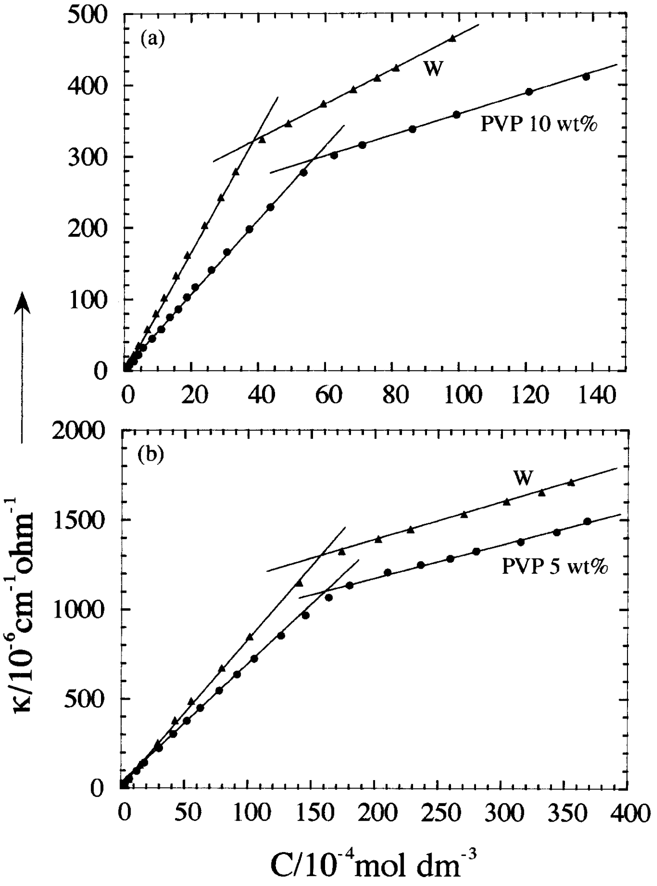

Fig. 2 Plot of conductivity versus concentration of **a** TTAB and **b** trimethyldodecylammonium bromide (*DTAB*) in water and in aqueous PVP

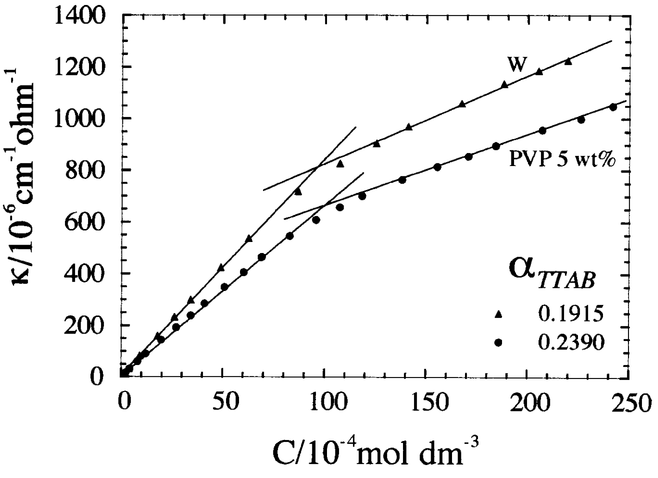

Fig. 3 Plot of conductivity versus concentration of TTAB + DTAB mixtures in water and in aqueous PVP

Let us first discuss the variation in κ of single and mixed surfactants in the presence PVP. Figures 1–3 show that the κ value decreases both in the premicellar as well

Table 1 Values of $c_{cac}/10^{-4}$ mol dm^{-3}, $c_p/10^{-4}$ mol dm^{-3}, χ_1 and χ_2 for trimethyltetradecylammonium bromide (*TTAB*) + trimethylhexadecylammonium bromide (HTAB) mixtures in aqueous poly(vinyl pyrrolidone) (*PVP*) at 30 °C

α_{TTAB}	c_{cac}	c_p	χ_1	χ_2
0 wt% PVP[a]				
1.000	37.90		0.27	
0.8444	29.00		0.30	
0.6846	23.05		0.32	
0.5204	18.00		0.32	
0.3517	14.80		0.31	
0.1783	12.12		0.30	
0.000	10.30		0.27	
1 wt% PVP				
1.000	39.64			0.23
0.8579	30.33	61.49	0.30	0.23
0.7073	23.50	60.13	0.30	0.23
0.5471	18.66	59.61	0.31	0.23
0.3765	14.87	58.18	0.30	0.22
0.1946	12.16	58.41	0.28	0.21
0.000	10.82	58.11	0.26	0.20
5 wt% PVP				
1.000	47.45			0.20
0.8787	36.37	53.54	0.28	0.21
0.7434	28.70	52.74	0.29	0.21
0.5916	22.13	51.60	0.31	0.22
0.4200	17.93	50.28	0.30	0.21
0.2246	15.17	47.84	0.27	0.20
0.000	13.02	45.23	0.23	0.18
10 wt% PVP				
1.000	55.64			0.17
0.8664	40.06	48.02	0.27	0.18
0.7217	30.96	47.50	0.28	0.18
0.5647	25.48	43.39	0.27	0.18
0.3934	20.96	40.56	0.24	0.18
0.2059	17.50	39.57	0.22	0.17
0.000	15.36	39.34	0.20	0.16

[a] Ref. [20]

Table 2 Values of $c_{cac}/10^{-4}$ mol dm^{-3} and χ for TTAB + trimethyldodecylammonium bromide (DTAB) mixtures in aqueous PVP at 30 °C

α_{TTAB}	c_{cac}	χ	α_{TTAB}	c_{cac}	χ
0 wt% PVP[a]			2 wt% PVP		
0.000	151.9	0.29	0.000	157.9	0.22
0.0452	138.1	0.31	0.0623	140.0	0.25
0.1059	119.9	0.35	0.1426	117.9	0.28
0.1915	92.23	0.35	0.2496	92.06	0.32
0.3091	69.20	0.38	0.3995	71.26	0.35
0.5422	51.90	0.38	0.6245	54.75	0.32
0.8120	40.00	0.33	0.7853	47.10	0.28
1.000	37.90	0.25	1.000	41.79	0.22
1 wt% PVP			5 wt% PVP		
0.000	156.8	0.23	0.000	168.1	0.19
0.0521	143.1	0.26	0.0591	149.2	0.23
0.1267	123.9	0.29	0.1357	120.0	0.26
0.2157	98.82	0.32	0.2390	98.63	0.30
0.3548	74.53	0.35	0.3858	73.85	0.34
0.5789	53.86	0.35	0.6110	59.43	0.31
0.7515	47.97	0.31	0.7755	51.02	0.27
1.000	40.34	0.24	1.000	44.32	0.21

[a] Ref [21]

as in the postmicellar regions in the presence of PVP. In order to evaluate κ in a particular region before c_{cac}, between c_{cac} and c_p, and after c_p, the slopes, i.e. S_1, S_2, and S_3 of the respective linear portions of the κ plots (Fig. 1) of TTAB + HTAB mixtures were computed and represent the monomeric, micellar, and polymer-bound micellar states, respectively. These values are plotted in Fig. 4. Similar values for single-break TTAB + DTAB mixtures were also computed and are plotted in Fig. 5. It is interesting to note that all the S_1, S_2, and S_3 curves for TTAB + HTAB mixtures (Fig. 4) remain predominantly constant over the whole mole fraction range and this may indicate that the equivalent respective states are present mainly over the whole more fraction range. The constancy in the S_2 and S_3 values with respect to the increase in the amount of TTAB can be attributed to the ideal mixing of unlike monomers in the polymer-free and polymer-bound mixed micelles, respectively. A comparison among all the S_1, S_2, and S_3 values indicates that κ of the corresponding species decreases with an increase in the bulkiness of the aggregated species from the monomeric state at S_1 to the polymer-bound bulkier state at S_3. On the other hand, in the case of TTAB + DTAB mixtures, the overall behavior of the monomeric and micellar species (Fig. 5a, b, respectively) in the presence of PVP is almost the same as that in pure water, thus suggesting insignificant interactions between the monomeric or micellar species and PVP. However, a significant decrease with an increase in the amount of PVP in both cases (Figs. 4b, 5) can be attributed to the medium effects of PVP, due to which the relative permittivity (ε) of an aqueous medium is decreased [6] and the viscosity is increased in comparison to that in the absence of PVP. The increase in the nonpolar character (i.e. the decrease in ε) and the viscous drag of the medium will result in the hydrophobic hydration of the surfactant monomers by the solvent molecules in the former case and in a reduction in the mobility of the ionic species [24, 26] in the latter case. Both factors will, therefore, reduce κ and this will be further reduced with an increase in the amount of PVP.

Degree of micelle ionization

In order to further evaluate these results, the degree of micelle ionization (χ) is evaluated. In the present work, the choice of TTAB + HTAB and TTAB + DTAB mixtures was also due to the common Br^- counterion of both mixtures in the mixed state and hence the mixtures can be treated as single surfactant solutions. The degree of micelle ionization was calculated by the method

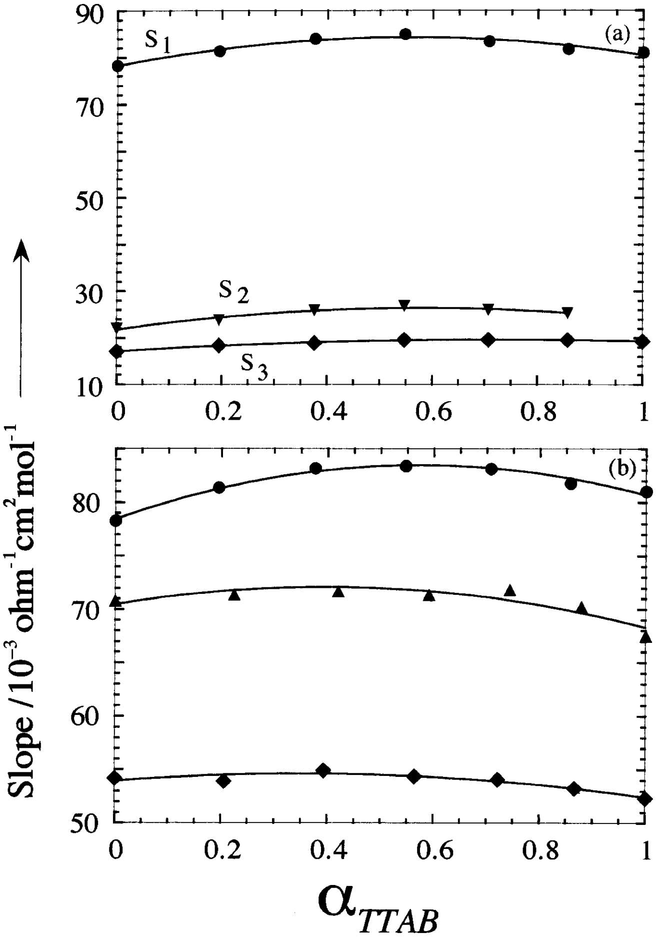

Fig. 4 **a** Plot of slopes (S_1, S_2, S_3) of the linear portions of the κ plots versus mole fraction of TTAB (α_{TTAB}) of TTAB + HTAB mixtures in the presence of 1 wt% PVP. **b** Plot of S_1 versus mole fraction of TTAB (α_{TTAB}) of TTAB + HTAB mixtures in the presence of 1 wt% PVP (*circles*), 5 wt% PVP (*triangles*), and 10 wt% PVP (*diamonds*)

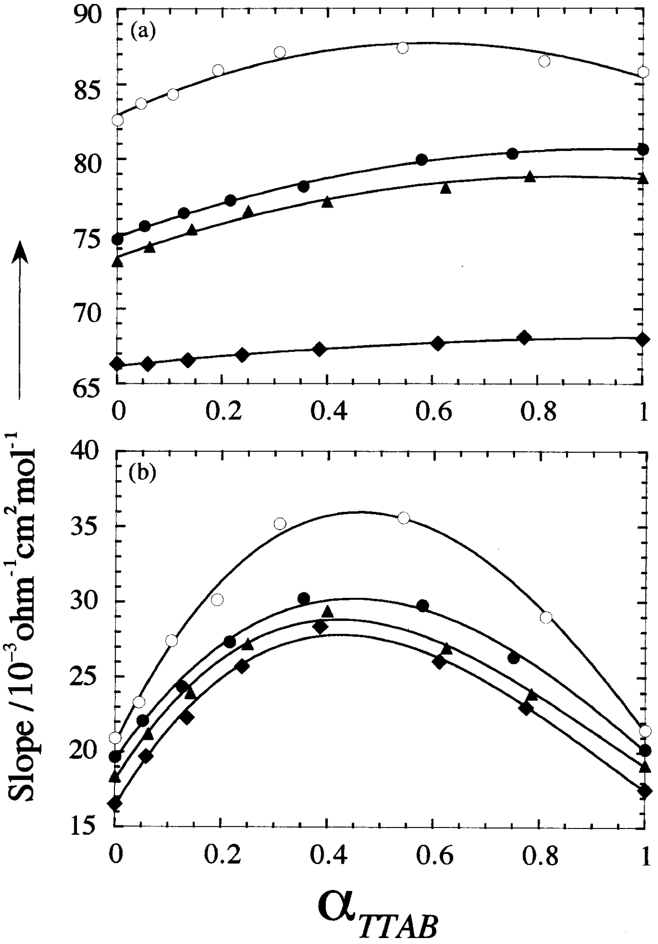

Fig. 5 Plot of **a** S_1 and **b** S_2 versus mole fraction of TTAB (α_{TTAB}) of TTAB + DTAB mixtures in water (*open circles*) and in the presence of 1 wt% PVP (*filled circles*), 2 wt% PVP (*triangles*), and 5 wt% PVP (*diamonds*)

suggested by Evans [27] based upon Stokes law for the mobility of micelles and the micelles are 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 counterions. n and m are related through the following relation

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

where Λ_{Br^-} is the ionic equivalent conductivity, which can be set equal to the value at infinite dilution at low concentration. Obviously, two χ values i.e. χ_1 and χ_2 corresponding to c_{cac} and c_p can be computed from S_1 and S_2 in the former case and from S_1 and S_3 in the latter case for the present mixtures in the presence of PVP. In order to calculate χ, an arbitrary value must be given to n. The value of χ is quite insensitive to n. For example, by choosing 40, 60, and 80 as the values of n for TTAB, values of 0.24, 0.25, and 0.26, respectively, were obtained for χ. Therefore, a value of n of 60 was selected for the present work. A χ value of 0.25 obtained by using $n = 60$ is in good agreement with that available in the literature [28]. The χ values thus obtained for TTAB + HTAB and TTAB + DTAB mixtures in the presence of different amounts of PVP are listed in Tables 1 and 2, respectively. It is interesting to observe that the χ values in pure water for TTAB + HTAB are quite close to χ_1 in the presence of 1 wt% PVP and the overall variation in the presence and absence of PVP is almost identical. Similar behavior can be observed for TTAB + DTAB mixtures. This suggests that the basic morphology of the mixed micelle of TTAB + HTAB mixtures at c_{cac} and that for TTAB + DTAB mixtures remain almost the same in the absence and presence of

PVP, since the presence of PVP does not significantly alter the χ value. On the other hand, the χ_2 values for TTAB + HTAB mixtures in the presence of PVP are significantly lower from those of χ_1. This can be explained on the basis of the reduced interfacial polarity due to the accomodation of polymer macromolecules at the micelle solution interface in the course of polymer-bound micellar aggregatation. However, an increase in the amount of PVP from 1 to 10 wt% leads to a decrease in both the χ_1 and χ_2 values and results in the respective χ values being shifted towards lower values (Tables 1, 2). This can again be attributed to the medium effects of PVP and, thus, the decrease in relative permittivity of an aqueous medium will suppress the ionization of the micelles.

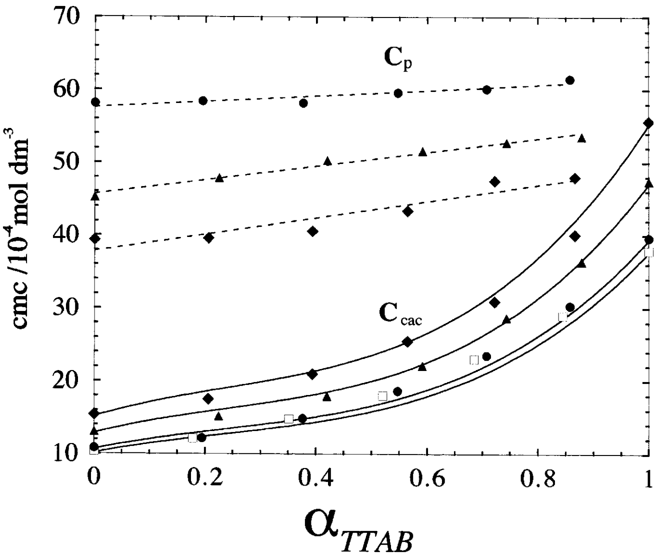

Fig. 6 Plot of c_{cac} and c_p versus mole fraction of TTAB (α_{TTAB}) of TTAB + HTAB mixtures in water (*open squares*) and in aqueous PVP. *Symbols* as for Fig. 4b. *Solid lines* represent the respective cmc* values

Micelle formation

All TTAB + HTAB mixtures show two aggregation processes over the whole mole fraction range except in the case of pure TTAB (Table 1), whereas a single aggregation process is observed in TTAB + DTAB mixtures. If we compare the aggregation of pure HTAB, TTAB, and DTAB in aqueous PVP, it can be said that HTAB undergoes two aggregation processes in contrast to TTAB and DTAB. The first aggregation process of HTAB in the presence of PVP is similar to that in pure water since the cmc and the χ values in the presence of 1 wt% PVP are almost the same as those in pure water. Similar behavior is also shown by TTAB and DTAB; however, the appearance of a second aggregation process, which is absent in TTAB and DTAB, indicates that the HTAB–PVP interactions are much stronger in comparison to TTAB micelle–PVP and DTAB micelle–PVP interactions. Perhaps this could be the reason why TTAB + HTAB mixtures also show two breaks, since the same stronger interactions are also expected to be experienced by HTAB in the mixed state with TTAB. The variation in the c_{cac} and c_p values of TTAB + H-TAB mixtures in the presence of PVP is shown in Fig. 6. For comparison the mixed cmc values in pure water [20] are also plotted in Fig. 6. It is interesting to observe that there is quite an insignificant difference between the mixed cmc values in pure water and the c_{cac} values in 1 wt% PVP. Similar results have also been obtained in the case of TTAB + DTAB mixtures (not shown). This may be taken as additional evidence that the first break for TTAB + HTAB mixtures in the presence of PVP almost corresponds to that in pure water and thus indicates very weak or insignificant polymer–micelle interactions. However, the curves for the c_{cac} values for both the binary mixtures are further shifted towards higher values with an increase in the amount of PVP, again demonstrating the medium effects [20–22] (Fig. 6, Table 2), whereas those for the c_p values for TTAB + HTAB are shifted towards lower values (Fig. 6), indicating the stabilization of the polymer-bound micelles with an increase in the amount of polymer in accordance with earlier studies [11].

In order to further strengthen the previous evidence from the quantitative point of view, a pseudophase thermodynamic model [28, 29] can be applied to evaluate the nonideality at c_{cac} in the presence of PVP, since the variation in c_{cac} is expected to be similar to that in the case of pure water. The model relates the mixed cmc at c_{cac} (cmc*) with the cmc of the pure components by the following equation:

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

where α_1 is the mole fraction of surfactant 1 (TTAB) in the total mixed solute and cmc_1 and cmc_2 are the c_{cac} values of pure components 1 and 2, respectively. For the present structurally similar binary mixtures, 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 [28], and the activity coefficients should be taken as unity. The cmc* values thus calculated using Eq. (3) are also shown in Fig. 6. A comparison between the cmc* and c_{cac} values shows that ideal mixing behavior is predicted in both the binary mixtures at c_{cac} in the presence of PVP (cmc* values for TTAB + DTAB are not shown).

In order to support these results further and owing to the similarities in the c_{cac} values in the absence as well as in the presence of PVP, the compositions of the monomeric and the micellar phases corresponding to

c_{cac} were evaluated using the formulation proposed by Motomura and Aratono [30] based on the excess thermodynamic quantities. The details of this formulation have been given elsewhere [30]. The composition of the mixed micelle is determined by using the following equation:

$$\bar{x}_2^{\mathrm{m}} = \bar{x}_2 - (\bar{x}_1 \alpha_2\, \overline{\mathrm{cmc}})(\partial \overline{\mathrm{cmc}}/\partial \bar{x}_2)_{T,P} \ , \tag{4}$$

$$\text{and } \overline{\mathrm{cmc}} = (v_1 x_1 + v_2 x_2) c_{\mathrm{cac}} \ , \tag{5}$$

where $\bar{x}_2^{\mathrm{m}}$ is the micelle mole fraction and $\bar{x}_2$ is the bulk mole fraction of HTAB in TTAB + HTAB mixtures and that of TTAB in TTAB + DTAB mixtures. $\bar{x}_2$ is given by

$$\bar{x}_2 = v_2 \alpha_2 / (v_1 \alpha_1 + v_2 \alpha_2) \ , \tag{6}$$

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

The $\bar{x}_2$ and $\bar{x}_2^{\mathrm{m}}$ values thus computed for TTAB + HTAB and TTAB + DTAB mixtures are plotted against cmc in Fig. 7. This figure can be regarded as the phase diagram that represents the equilibrium of micelles with aqueous solution. The $\overline{\mathrm{cmc}}$ versus $\bar{x}_2^{\mathrm{m}}$ curves in pure water as well as in the presence of PVP predict almost ideal behavior since they vary more or less similarly and are quite close to the curves computed for ideal mixing behavior [31] (Fig. 7) over the whole mole fraction range. This suggests that the composition of the mixed micelles at c_{cac} for both mixtures remains almost constant even in the present of PVP.

Micelle–polymer interactions

A close inspection of Fig. 6 shows that the c_{p} values vary linearly with a very weak slope over the whole mole fraction range in the presence of different amounts of PVP. This further strengthens the earlier conclusion that the equivalent states are present predominantly over the whole mixing range of TTAB + HTAB mixtures. However, it is interesting to observe that the c_{p} values are regularly shifted towards the lower values with an increase in the amount of PVP from 1 to 10 wt%. This can be better explained by computing the Gibbs free-energy change (ΔG_{t}^0) upon transfer of surfactant monomers from the medium consisting of polymer-free mixed micelles to the polymer-bound mixed micelles [25, 32]. This is given by

$$\Delta G_{\mathrm{t}}^0 = RT\left[(2 - \chi_2)\ln c_{\mathrm{p}} - (2 - \chi_1)\ln c_{\mathrm{cac}}\right] \ . \tag{7}$$

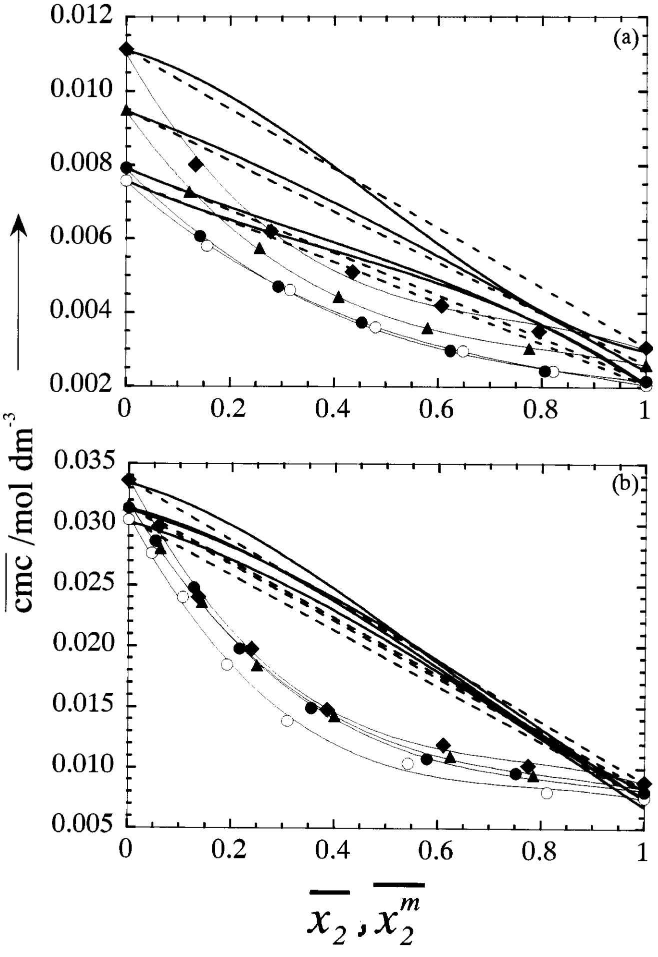

Fig. 7 Plot of $\overline{\mathrm{cmc}}$ versus $\bar{x}_2$ (experimental points: *thin line*), $\bar{x}_2^{\mathrm{m}}$ (predicted behavior: *solid line*) and $\bar{x}_2^{\mathrm{m}}$ (predicted ideal behavior: *broken line*) of **a** TTAB + HTAB and **b** TTAB + DTAB mixtures in pure water (*open circles*) and in aqueous PVP (*symbols* as for Figs. 4b and 5 for **a** and **b**, respectively)

The ΔG_{t}^0 values thus computed are shown in Fig. 8. It can be seen that ΔG_{t}^0 decreases with an increase in the amount of PVP, suggesting that the transfer of the surfactant monomers becomes more favorable from the medium to the polymer-bound micelles with an increase in the amount of PVP. Therefore, in view of these results, it can reasonably be believed that the micelle–polymer interactions mainly start after the formation of mixed micelles at c_{cac} and that the ideal nature of the mixed micelles remains basically the same even in the course of the micelle–polymer aggregation process. Similar results have also been reported for (sodium dodecyl sulfate + sodium dodecanoate) + poly(ethylene oxide) [33] and for (dodecylpyridinium chloride + tetradecylpyridinium chloride) + polyelectrolyte [34] systems. Therefore, it can be said that the micelle–polymer interactions, particularly in the case of ionic micelles, originate due to the delicate balance between

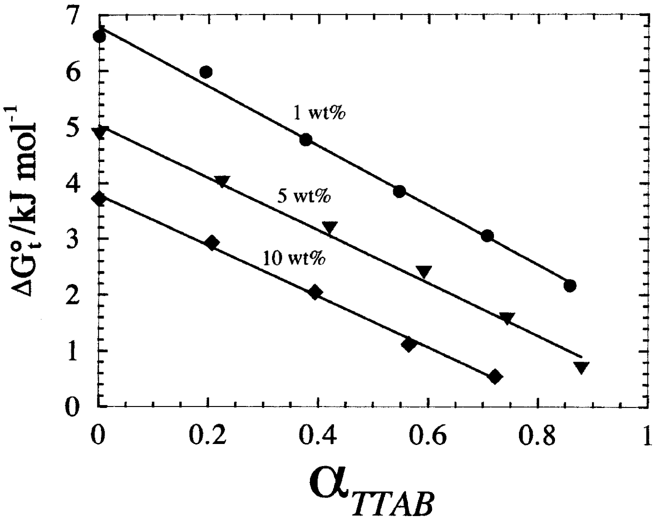

Fig. 8 Plot of ΔG^0_t versus α_{TTAB} for TTAB + HTAB mixtures in aqueous PVP

the hydrophobic–lipophilic forces of unlike moieties operating at the micelle–solution interface. In the present case, the stronger (TTAB + HTAB) + PVP interactions over the (TTAB + DTAB) + PVP ones may be attributed to the stronger hydrophobicity of the former over the latter. Since PVP, though a nonionic polymer, is hydrophilic in nature, lipophilic interactions between PVP and the partially positively charged tetraalkylammonium head groups should be identical in TTAB + HTAB and in TTAB + DTAB mixtures. Hence, the stronger hydrophobicity of HTAB in comparison to TTAB and DTAB is expected to be the predominant factor in governing the mixed micelle–PVP interactions [7].

Conclusion

A conductometric study of TTAB + HTAB and TTAB + DTAB mixtures in water + PVP systems was carried out. Both pure HTAB and TTAB + HTAB mixtures showed two aggregation processes, whereas pure TTAB, DTAB, and TTAB + DTAB mixtures showed only one. In the former case, the first aggregation process is identical to conventional micelle formation, whereas the second aggregation process is due to polymer-bound micellar aggregates. In (TTAB + DTAB) + PVP systems no polymer-bound micellar aggregates were observed. The mixing behavior corresponding to the first break in TTAB + HTAB and TTAB + DTAB mixtures was close to ideal. The appearance of polymer-bound micellar aggregates in HTAB and TTAB + HTAB mixtures were mainly attributed to the stronger hydrophobicity of HTAB in comparison to TTAB and DTAB.

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

References

1. Breuer MM, Robb ID (1972) Chem Ind 530
2. Goddard ED (1986) Colloids Surf 19:255
3. Hayakawa K, Kwak JCT (1991) In: Holland P, Rubingh D (eds) Cationic surfactants, vol 37. Dekker, New York, Chap. 5
4. Merta J, Stenius P (1995) Colloid Polym Sci 273:974
5. Kogej K, Skerjanc J (1999) Langmuir 15:4251
6. Garcia-Mateas I, Perez S, Valazquez MM (1997) J Colloid Interface Sci 194:356
7. Brackman JC, Engberts JBFN (1993) Chem Soc Rev 22:85
8. Witte FM, Buwaldn PL, Engberts JBFN (1987) Colloid Polym Sci 265:42
9. Brackman JC, Engberts JBFN (1991) Langmuir 7:2097
10. Winnik FM, Winnik MA, Tazuke SJ (1987) Phys Chem 91:594
11. Bakshi MS, Doe H (1999) Bull Chem Soc Jpn 72:2041
12. Bakshi MS, Mahajan S (2000) J Jpn Oil Chem Soc 49:17
13. Pinazo A, Wen X, Perez L, Infante M-R, Franses EI (1999) Langmuir 15:3134
14. Scamehorn JF, Schechter RS, Wade WHJ (1982) Colloid Interface Sci 85:494
15. Bhat M, Gaikar VG (1999) Langmuir 15:4740
16. Vora S, George A, Desai H, Bahadur P (1999) J Surfactant Deterg 2:213
17. Mysels K (1978) J Colloid Interface Sci 66:331
18. Griffiths PC, Whatton ML, Abbott RJ, Kwan W, Pitt AR, Howe AM, King SM, Heenan RK (1999) J Colloid Interface Sci 215:114
19. Bakshi MS (1997) J Chem Soc Faraday Trans 93:4005
20. Bakshi MS, Kaur G, Kaur G (1999) J Macromolecular Sci A36:697
21. Bakshi MS, Kaur U (1999) Bull Chem Soc Jpn 72, 1483
22. Bakshi MS (1999) J Macromol Sci A 36:879
23. Minatti E, Zanette D (1996) Colloids Surf 113:237
24. Bakshi MS (1993) J Chem Soc Faraday Trans I 89:4323
25. Kamenka N, Burgaud I, Treiner C, Zana R (1994) Langmuir 10:3455
26. Bakshi MS (1996) Bull Chem Soc Jpn 69:2723
27. Evans HC (1956) J Chem Soc 579
28. Treiner C, Makayssi A (1992) Langmuir 8:794
28. Clint JH (1975) J Chem Soc Faraday Trans 1 71:1327
29. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, p 337
30. Motomura K, Aratono M (1993) In: Ogino K, Abe M (eds) Mixed surfactant systems. Dekker, New York, pp 99
31. Aratono M, Villeneuve M, Takiue T, Ikeda N, Iyota H (1998) J Colloid Interface Sci 200:161
32. Hunter RJ (1987) Foundations of colloid science, Clarendon Press, vol 1. Oxford, p 596
33. Zanette D, Frescura VLA (1999) J Colloid Interface Sci 213:379
34. Liu J, Takisawa N, Shirahama K (1999) Colloid Polym Sci 277:247