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ORIGINAL CONTRIBUTION

Clouding behavior of nonionic–cationic and nonionic–anionic mixed surfactant systems in presence of carboxylic acids and their sodium salts

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Abstract The study is focused on evaluation of clouding phenomena of the aqueous single nonionic surfactant system Triton X-100 (TX-100) and its mixed systems with anionic aerosol-OT (AOT) and cationic dodecylpyridinium chloride (DPC) in presence of hydrophobic ions furnished by sodium salts of carboxylic acids, viz., sodium ethanoate, sodium propanoate, sodium butanoate, and sodium hexanoate and the respective carboxylic acids [ethanoic acid, propanoic acid, butanoic acid, and hexanoic acid]. The influence of salts on the cloud point (CP) has been explained on the basis of salt effect as well as the solubilization of higher alkyl chain hydrophobic ions furnished by these salts. Moreover, the co- and counterion effect has been taken into account to explain the variation of the CP in the mixed systems. However, the effect of acids on CP has been explained in the light of their aqueous solubility and their partitioning ability between octanol and water as reflected by their K_{OW} values.

Keywords Cloud point · Hydrophobic co-ions · Counterions · Salt effect · Solubilization

Introduction

One of the characteristic features of the nonionic surfactant solutions is their instant separation upon heating into two coexisting isotropic phases [1–4]. The temperature at which this phase separation occurs is known as the cloud point (CP) which is an important property of nonionic surfactants. Clouding is attributed to the efficient dehydration of hydrophilic portion of the micelles at higher temperature. In some situations, the solution phase separates into a surfactant-rich phase and a surfactant-poor phase. The value of CP depends on the structure and concentration of the surfactant and the presence of additives [5–7]. Several trends in CP with surfactant molecular structure are known. CP increases with increase in relative polyoxyethylene chain content and decreases with increasing alkyl chain length. Additives modify the surfactant–solvent interactions and in consequence change the CMC, the size of the micelle, and the phase behavior of the surfactant solution. CP is increased by polar organic compounds infinitely miscible with water and water structure maker anions $\left(F^-,\ OH^-,\ SO_4^{2-}Cl^-\right)$ and decreased by addition of polar organic compounds partially miscible in water and water structure-breaking anions (SCN^-, I^-) [8–10].

The CP of a dilute nonionic surfactant solution increases upon addition of ionic surfactants [11–13]. Various mechanisms such as the formation of mixed micelles, solubilization, or complex formation [12] have been suggested to explain this phenomenon. The incorporation of ionic surfactant molecules into the nonionic micelles introduces electrostatic repulsions between the micelles [14], thus raising the CP [13, 14] by delaying their coalescence. Valaulikar and Manohar [15] have demonstrated that the increase in CP can be related to the surface charge per micelle that keeps the micelles apart. This supports the viewpoint that micelle coalescence, rather than linear micellar growth, is responsible for the clouding process [16, 17]. Clouding in surfactant and polymer solutions has also been interpreted in thermodynamic terms [18, 19]. The balance between hydrophilic/hydrophobic interactions seems to determine the temperature at which phase separation occurs [20].

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Most of the reports deal with either the effect of varied chain length of alcohols on CP of nonionic surfactants [9, 20] or sodium salts of aromatic hydrotropes [22] on CP of mixed nonionic–anionic and nonionic–cationic surfactant systems. Marszall [22] has shown that in addition to electrostatic shielding effect, the specific interactions of these hydrophobic salts must be taken into account for explaining the CP behavior of mixed nonionic–ionic systems. The systematic study involving the effect of hydrophobic chain length of hydrophobic salts on CP of nonionic and mixed nonionic–ionic surfactants has received little attention. The effect of carboxylic acids and their respective sodium salts on clouding behavior of such systems has not been reported. The prime foci of this work are: (a) to evaluate the influence of various concentrations of sodium carboxylates, viz., sodium ethanoate (EtNa), sodium propanoate (PrNa), sodium butanoate (BuNa), and sodium hexanoate (HxNa) on the CP of the nonionic surfactant Triton X-100 (TX-100) and its mixed systems with anionic surfactant, aerosol-OT (AOT), and cationic surfactant dodecylpyridinium chloride (DPC) and then to correlate their effect with that of sodium chloride; and (b) to compare and contrast the effect of sodium carboxylates on CP of above systems with their respective carboxylic acids, viz., ethanoic acid (EtH), propanoic acid (PrH), butanoic acid (BuH), and hexanoic acid (HxH). The studies would be helpful in: (a) gaining the insight into the effect of hydrophobic co- and counterions on CP of mixed anionic–nonionic and cationic–nonionic surfactant systems, respectively, through addition of sodium carboxylates as a function of their number of carbons in their hydrophobic part; (b) evaluating the influence of carboxylic acids, being neutral counterparts of sodium carboxylates, on the said systems; and (c) understanding the solvent-modifying and solubilization effects of these additives on clouding phenomena.

Experimental section

Reagents

TX-100—a polydisperse preparation of 1,1,3,3-tetramethylbutylphenylpoly (oxyethylene) with an average of 9.5 oxyethylene units per molecule—from Sigma Chemical with a minimum assay of 99% was used as such. 1-Dodecylpyridinium chloride monohydrate (Merck, 99%) was used after two recrystallizations from methanol followed by drying for 24 h under vacuum. Sodium octylsulfosuccinate (AOT, Sigma) was used as received. EtH, PrH, BuH, and HxH from Merck (99%) were used without further purification. EtNa and sodium chloride (NaCl) were procured from Qualigens. PrNa, BuNa, and HxNa were synthesized by neutralizing the corresponding acids with concentrated sodium hydroxide solution. The salts were precipitated by acetone and purified by recrystallization from water with acetone followed by drying under vacuum.

Stock solutions of TX-100, AOT, DPC, and sodium salts of carboxylic acids of higher concentrations than used in the experiments were prepared by dissolving accurately weighed quantities (±0.1 mg) in requisite volumes of double-distilled water. Carboxylic acids were titrated with standard NaOH solution to determine their molarities and then diluted to the requisite concentration. Experimental solutions with required concentrations of TX-100, AOT, DPC, and additives were then prepared by mixing calculated volumes of the respective stock solutions. The concentration of TX-100 in all the solutions was maintained at 10 mM, and those of AOT and DPC in the nonionic–anionic and nonionic–cationic mixtures were 0.05 and 0.5 mM, respectively. In all experiments, freshly prepared solutions were used.

Cloud point determination

To determine the CP, a thermostatic water bath having an accuracy of ±0.1 °C was used. A 30-ml test tube containing 10 ml of experimental solution was immersed in the water bath, which was then slowly heated while continuously stirring the solution in the test tube. The temperature at which the solution became cloudy was recorded. The solution was then allowed to cool slowly, and the temperature at which it became clear again was also recorded. A magnifying glass was used for observation. Heating and cooling rates of ~1 °C min^{-1} were regulated around the CP. For each solution, measurements were made at least three times, and the mean of the temperatures recorded was taken as the CP. The measurements were reproducible to within ±0.2 °C.

Results and discussions

Clouding behavior of Triton X-100 in presence of additives

Figures 1a and 2a show the CP measurements of TX-100 as a function of electrolyte (NaCl, EtNa, PrNa, BuNa, and HxNa) and carboxylic acid (EtH, PrH, BuH, and HxH) concentrations in the relatively low range of 0–10 mM. CP of pure 10 mM TX-100 (67.5 °C) is in good agreement with the literature value [15, 20–24]. A significant depression in the CP of TX-100 is observed on the addition of the sodium salts except for HxNa where CP decreases initially up to 1 mM and thereafter rises very slightly. In the case of EtNa, PrNa, and BuNa, initially the depression in

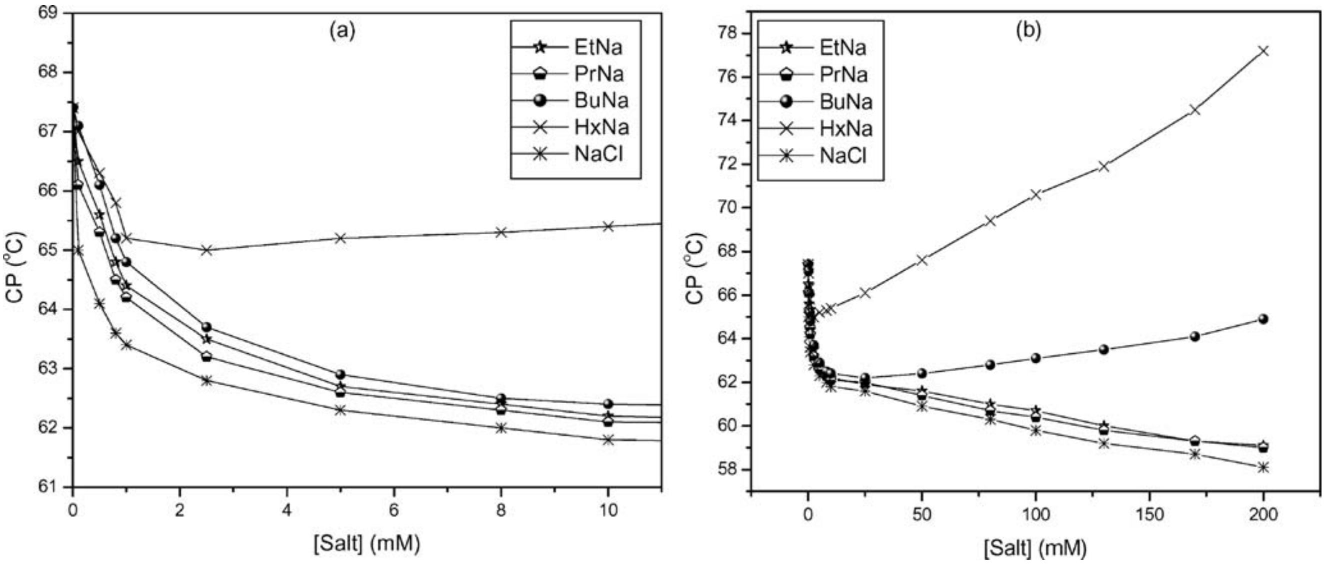

Fig. 1 Cloud point (CP) variation of 10 mM TX-100 aqueous system as a function of salt concentrations: **a** in low salt concentration range, **b** in whole salt concentration range

CP is greater (~4 °C up to 2.5 mM) and then becomes quite meager as the concentration of salt increases (~1 °C beyond 2.5 up to 10 mM). The initial depression with NaCl is steeper. The effectiveness of depression of the CP is in the order NaCl > EtNa > PrNa > BuNa. As evident from Fig. 2a, there is a similar initial lowering of the CP of TX-100 in presence of the acids EtH, PrH, and BuH. However, the behavior of HxH is quite distinct from the rest of its homologous members in that there is a sharp continuous lowering in the CP with increase in the concentration of the acid.

Hayter and Zulauf [1] have suggested that the phase separation or clouding in nonionic micellar solutions is due to the van der Waals attractive forces between micelles, but there exists an obstacle between the micelles produced by the presence of at least a monolayer of highly structured water at each micellar surface. The extent of this enhanced structure is decreased at high temperature because of entropic reasons and hence the system phase separates [25–27]. Lowering of CP of TX-100 in presence of NaCl, EtNa, PrNa, and BuNa can be attributed to the salting-out effect of these electrolytes resulting in remarkable alteration in the hydration shell of the POE chains in the micelles. The effect seems to be greater in presence of NaCl than EtNa, PrNa, and BuNa. It is known [28] that salting-out capacity of electrolytes is due to the enhanced degree of

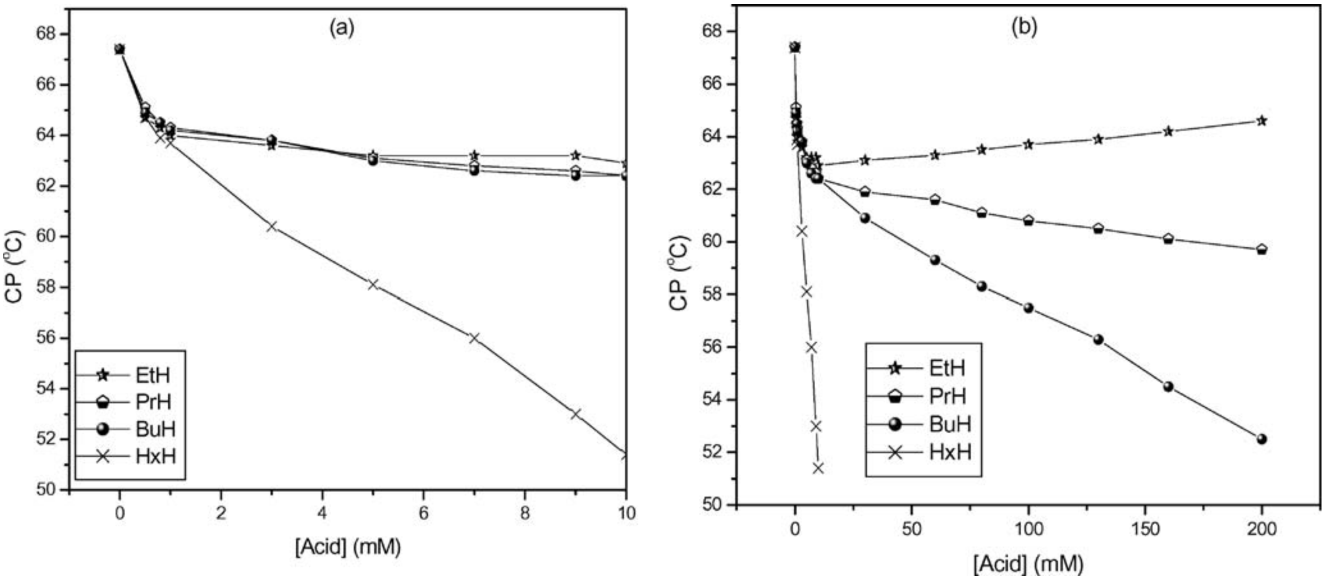

Fig. 2 Cloud point (CP) variation of 10 mM TX-100 aqueous system as a function of carboxylic acid concentrations: **a** in low acid concentration range, **b** in whole acid concentration range

hydration of the respective cations. Decrease in CP may thus be correlated to the alteration of localized water structure on the micelle surface. Cations, being heavily hydrated, decrease the concentrations of water molecules in hydration layer, thereby allowing increased micelle–micelle interactions and hence appearance of clouding at lower temperatures. The different CP depressions of TX-100 produced by NaCl, EtNa, PrNa, and BuNa may be attributed to the different nature of anions furnished by these electrolytes. The extent of hydration of the anions decreases in the order $Cl^{-} > CH_3COO^{-} > C_2H_5COO^{-} > C_3H_7COO^{-}$. Hence, NaCl is expected to produce maximum depression in CP as is borne out by the results. The decrease in the degree of hydration of organic anions with the increase in alkyl chain length and hence an increase in their hydrophobic character is obvious. Moreover, these organic anions have a tendency to solubilize into the micelles, which would result in charging up of the micelles, thereby increasing the micelle–micelle repulsions. This would have the effect of elevating the CP of the surfactant solution. It has been reported [29] that the acetate and propionate ions penetrate into SDS micelles only at high concentrations even though being coions to SDS. Recently, the penetration of propionate ions into the nonionic-rich mixed cationic–nonionic micelles has been reported [30] at a lower concentration than in SDS. This means that in the case of TX-100, the incorporation of these ions is expected to occur above a certain concentration. Therefore, the observed shift in the CP of TX-100 solution could be attributed to combined effect of:

(i) a large lowering of CP with the increase in concentration of more hydrated Na^{+} ions,
(ii) a slight lowering of CP with the increase in concentration of less hydrated organic anions, and
(iii) an elevation of CP with the increase in organic anion concentration due to their penetration into micelles.

However, the effect of last term would become significant only above a certain concentration after which penetration occurs.

Figure 1b depicts the variation of CP at a much higher concentration range of the sodium alkanoates. It is clear that BuNa and HxNa elevations of the CP of TX-100 are above 25 and 10 mM, respectively, indicating that solubilization of these organic anions into TX-100 micelles effectively contributes by charging the micelles and thus introducing intermicellar repulsions. This rise is observed to be substantial in the case of HxNa than in the presence of BuNa, showing greater propensity of hexanoate ions to incorporate into micelles. This is quite expected because hydrophobic character of hexanoate ion is large compared to that of butanoate ion, and therefore, it finds hydrocarbon micellar interior more suitable for its free-energy reduction. EtNa and PrNa exhibit a lowering effect on CP in the whole salt concentration range in tune with NaCl, indicating thereby that only the salt effect prevails that leads to the reduction in CP of surfactant solution. The order of depression in CP by NaCl, EtNa, PrNa, and BuNa in the low concentration range and by NaCl, EtNa, and PrNa in higher concentration range may be due to contribution (ii) as discussed above. The leveling-off of the CP of TX-100 by HxNa at ~10 mM and by BuNa at ~25 mM (Fig. 1b) may be an indication of initiation of solubilization even below these concentrations. However, at lower concentrations, the extent of solubilization is very small so that compensation of contribution (iii) with combined effect of (i) and (ii) takes place. However, above these concentrations, the predominant role of solubilization raises the CP. It may be that similar effects would be prevalent in the case of EtNa and PrNa, but to exhibit the effect of solubilization to elevate the CP by these electrolytes would require larger concentration than 200 mM.

Comparison of Figs. 1a and 2a indicates a quite distinct clouding behavior of TX-100 in presence of the acids as compared to that in presence of the corresponding salts in the low additive concentration range. Figures 1b and 2b depict a similar contrasting behavior in the high additive concentration range. While the CP lowers slowly with PrH concentration and rapidly with BuH concentration, it actually shows a slight elevation in presence of EtH. In presence of salts, particularly BuNa and HxNa, the trend is exactly the reverse. While the CP rapidly rises with HxNa, it goes down very fast with the corresponding acid concentration. In fact, in this high additive concentration range, detection of CP was not possible in presence of HxH because the turbidity appeared as soon as the acid concentration in the solution exceeded 10 mM. This points out to the lowering of CP well below the room temperature. Very slight decrease of the CP in presence of acids at their very low concentrations may be due to furnishing of salt effect by these acids as a result of their ionization. However, the presence of carboxylic acids in water may simultaneously make the medium less polar, thereby rendering phase separation more difficult. Probably, compensation between the two opposing effects in the case of EtH, PrH, and BuH makes the clouding independent of additive concentration.

It has been indicated that the reason behind clouding and micellar growth are likely the same because both of the phenomena are determined by the counterbalance of hydrophilic/hydrophobic interactions [26, 31]. Therefore, additives which are infinitely miscible with water and disfavor micellization should also elevate CP. In this case, additive molecules decrease the polar character of solution [32–36] and hence retard the micellization and phase separation process. Formic and acetic acids have been found [8] to elevate the CP of TX-100 in high concentration range (0.3–1.0 M) in tune with their efficiency in decreasing polar character of solution. Because the efficiency of acids to lower the polar character of solvent is in the order of their hydrophobic character, viz., EtH < PrH < BuH < HxH, we expect the CP of TX-100 to rise in presence of all the additives in the higher concentration region. However, our observation shows only EtH to be effective in elevating the CP at higher acid concentration (Fig. 2b), while the others only lower it.

To explain the results, the charge produced in micelles themselves due to partitioning of these additives between micelles and bulk solution must be taken into account. Many studies [37–40] indicate that hydrophobic chains of polar compounds penetrate the micelle interior while the polar groups remain on the micelle surface, thereby reducing the amount of water near the head-group region. This results in appreciable lowering of CP due to dehydration of surfactant head groups, thus facilitating micellar growth [41]. We expect this effect to be roughly dictated by the amount of carboxylic acid which enters the micelle in this manner. The partition coefficients, K_{ow}, for the carboxylic acids between octanol and water have been measured and are found to be EtH ~0.08, PrH ~2.13, BuH ~6.16, and HxH ~83.18 [42]. This shows that hardly any EtH but a considerable amount of HxH may be present inside the micellar phase. Also, as the total concentration of acid increases in the solution, more and more acid would get partitioned into the micellar phase, thereby depressing the CP. While the solubilization of HxH will be effective even at low concentrations, as dictated by the large partition coefficient, the partitioning of BuH becomes apparent only at relatively high concentration owing to its smaller K_{ow} value. Hence, lowering of CP by BuH begins at elevated concentration, though relatively slowly. Elevation of CP in presence of higher concentration of some additives indicates predominance of hydrophobic and dielectric changes produced in the solvent medium over its partitioning characteristic. The role of lowering of the CP by carboxylic acids containing more than two carbon atoms is obviously related to the hydrophobic chain length of the molecules. In general, the larger the alkyl chain length, the lower the acid concentration needed for obtaining phase separation at a certain temperature. This observation is in agreement with the results obtained for other nonionic surfactants [33, 43, 44] in presence of a variety of organic compounds.

It must be emphasized at this point that the effect of carboxylic acids and their corresponding salts is quite distinct. The carboxylate ions furnished by higher members of salts after penetration charge the nonionic TX-100 micelles and, therefore, have a tendency to increase the CP above certain concentrations. With regard to the corresponding acids, being neutral with a very small degree of ionization, their inclusion does not change the electrical (repulsive) properties of micelles too much; however, the hydrophobic (attractive) interactions between hydrocarbon chains near the micellar surface are enhanced, thus inducing micellar growth and hence phase separation at a lower temperature.

Clouding behavior of mixed anionic–nonionic (TX-100 + AOT) and cationic–nonionic (TX-100 + DPC) systems in presence of additives

In experiments involving mixed micelles of TX-100 with anionic and cationic surfactants, the concentration of TX-100 being again 10 mM, the same as in the single surfactant system, the concentrations of anionic and cationic surfactants were 0.05 and 0.5 mM, respectively, corresponding to approximately one (AOT) and eight (DPC) surfactant molecules per micelle of TX-100. For calculation of this ratio, the approach of Valaulikar and Manohar [15] was used. The use of different concentrations of ionic surfactants was to enable a comparison of the effect on CP over similar temperature ranges. This difference is clear because AOT shows more dramatic effect than DPC on CP of TX-100 perhaps due to greater propensity of AOT to micellize (lower CMC) than DPC, which has CMC approximately two orders of magnitude higher.

The increase in CP of TX-100 in presence of AOT or DPC is easily understood. The incorporation of an anionic or cationic surfactant into nonionic micelles introduces charge onto the micelle surface, and in consequence the repulsion between the micelles is increased. This leads to an increase in CP of the mixed system. Carboxylic acids and their sodium salts are, however, expected to affect the CP of the systems differently owing to different nature of charge on micellar surface and different head groups of the ionic surfactants.

The effect of various carboxylic acids and their corresponding sodium salts on the CP of TX-100+AOT mixed system is depicted in Figs. 3a and 4a, respectively, in the low concentration range up to 10 mM. Figures 3b and 4b depict the same in the whole additive concentration range studied, viz., 0–200 mM. The figures show that CP of TX-100+AOT mixed system is lowered sharply with the addition of carboxylic acids and their corresponding sodium salts in the low concentration range of 0–10 mM. Figure 3a indicates that the effectiveness of various salts to depress the CP of TX-100+AOT system is in the order of NaCl > EtNa > PrNa > BuNa. HxNa initially leads to relatively smaller lowering of CP followed by almost constant behavior up to 10 mM. Figure 3b shows that EtNa and PrNa depress the CP in the whole concentration range in tune with the behavior of NaCl, but there is a gradual rise above 75 mM in presence of BuNa and a sharp rise above 25 mM in presence of HxNa.

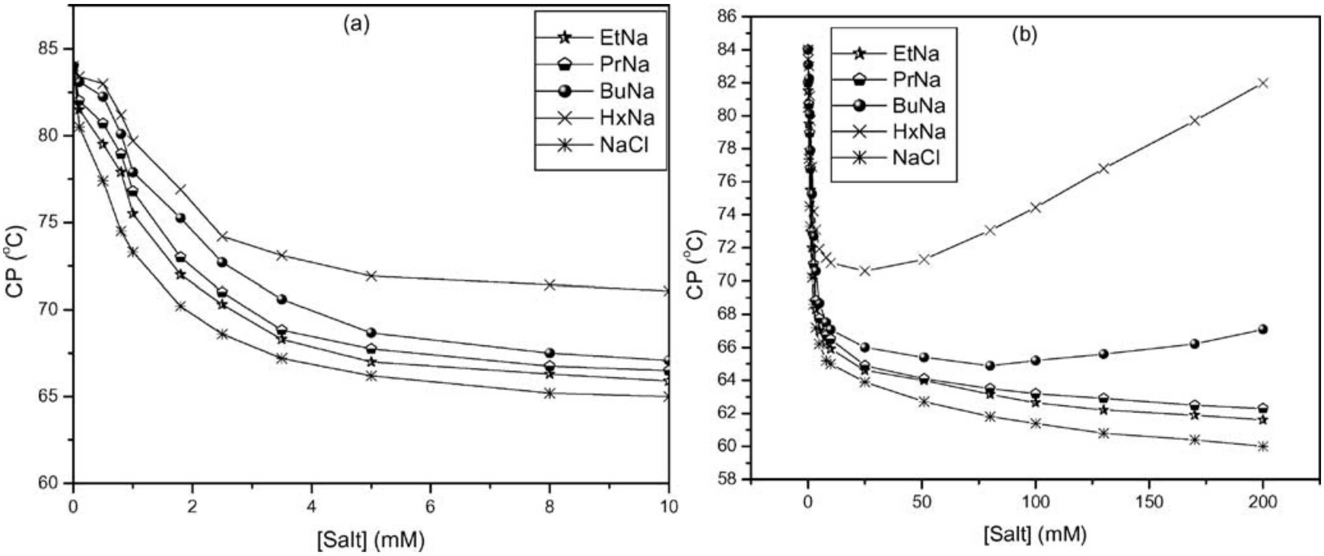

Fig. 3 Cloud point (CP) variation of 10 mM TX-100+0.05 mM AOT mixed surfactant system as a function of salt concentration: **a** in low salt concentration range, **b** in whole salt concentration range

The behavior of TX-100+AOT mixed system in presence of carboxylic acid salts is quite similar to that observed for the TX-100 single system and can be explained in the same manner. However, certain major differences are observed. Firstly, there is quite a sharp depression in the CP (about 18 °C) of the mixed system in the low salt (NaCl, EtNa, PrNa, and BuNa) concentration range of 0–10 mM (Fig. 3a), in contrast to just about 6 °C fall in the single system. This shows greater salt effect on the CP of charged mixed micelles compared to that on the neutral TX-100 micelles. Rathman and Scamehorn [45], on the basis of their electrostatic model, have observed that at low ionic–surfactant mole fractions in the mixed micelles, the counterion binding decreases sharply and can be treated to be negligible. The resulting uncompensated charge on mixed micellar surface gives rise to repulsion between the micelles. The extent or magnitude of repulsion varies as per composition of solution. On addition of electrolyte to the solution, the original charge distribution is swamped, leading to screening of repulsions. This results in a dramatic CP lowering in contrast to the simple nonionic micelles of TX-100 where depression of CP occurs due to

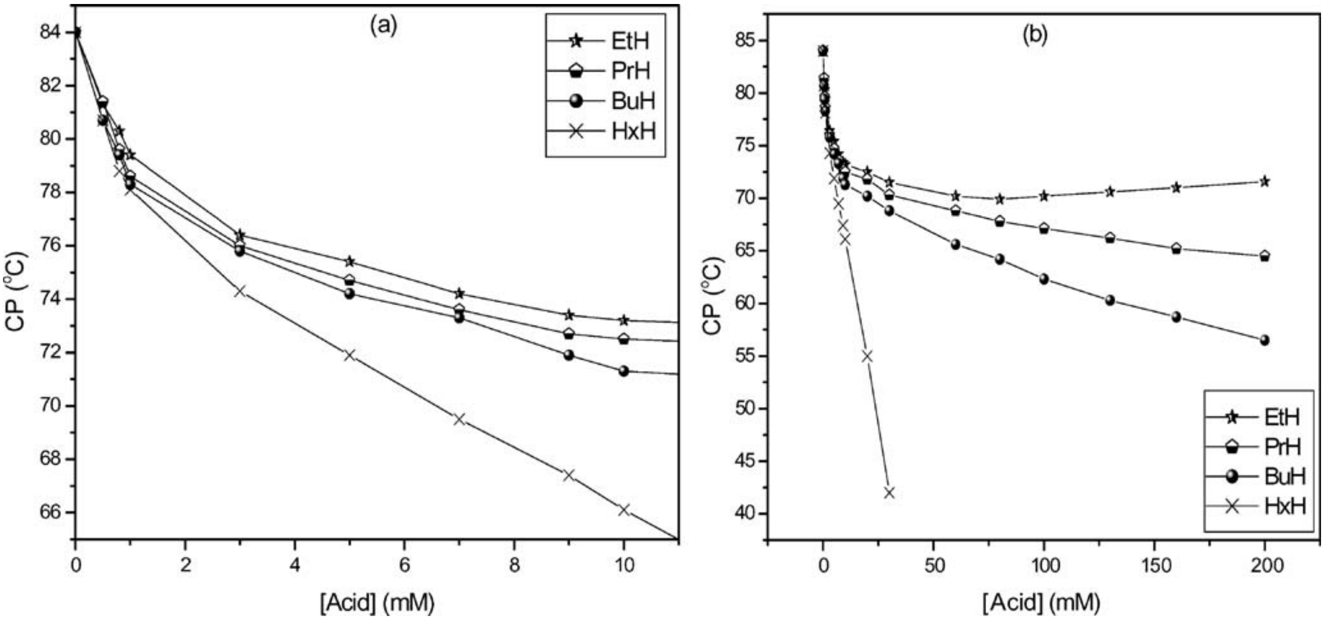

Fig. 4 Cloud point (CP) variation of 10 mM TX-100+0.05 mM AOT mixed surfactant system as a function of carboxylic acid concentration: **a** in low acid concentration range, **b** in whole acid concentration range

dehydration of head groups by heavily hydrated Na^+ ions furnished by the salts. The observed lowering of CP is in the order of NaCl > EtNa > PrNa > BuNa > HxNa and is attributable to the difference in anions furnished by the salts (Fig. 3a). The fall in the CP due to salting-out effect of HxNa at low concentrations is partly compensated by the tendency of hexanoate ion to get solubilized into the mixed micelles, thereby increasing the charge on the micellar surface and thus raising the CP. At high salt concentrations, the salting-out effect of BuNa and HxNa is overwhelmed by their solubilization effect, leading to a net rise in the CP with concentration of salt. However, this elevation of CP of the mixed TX-100+AOT system commences at a somewhat higher salt concentration of 25 and 75 mM, respectively, in contrast to 10 and 25 mM for the simple TX-100 system. Possibly, the negative charge on the mixed TX-100+AOT micelles delays the solubilization of similarly charged carboxylate coions.

In the case of TX-100+AOT mixed system in presence of carboxylic acids in the low concentration range of 0–10 mM (Fig. 4a), there occurs a gradual lowering of almost 12 °C in the CP for EtH, PrH, and BuH compared to a fall of only about 4 °C in the TX-100 system. However, in both the TX-100 and TX-100–AOT systems, there is a similar but sharper lowering (of approximately 16 °C) in presence of HxH (Figs. 2a and 4a). Larger depression in CP for TX-100+AOT system may be attributed to the presence of uncompensated micellar surface charge. Ionization of the acids, at least in the low concentration range, will furnish H^+ ions which may get adsorbed on the micellar surface, thereby decreasing the magnitude of uncompensated negative charge. Consequent reduction of intermicellar repulsions will reduce the CP of the system. However, due to its large K_{ow} value (~83.18) and low dissociation in contrast to other acids, HxH has a strong tendency to get into the micellar phase even at low concentrations, so that as the concentration of acid increases, more of it may get partitioned into the palisade layer of micelles, thereby reducing the amount of water near the head-group region and hence appreciably lowering the CP. In the higher concentration region (Fig. 4b), EtH shows a slight rise in CP, while PrH and BuH depress it in the order BuH > PrH. As pointed out earlier, K_{ow} values would indicate that hardly any EtH but increasing amounts of PrH and BuH more so HxH will be present in the micellar phase, partitioning becoming apparent only in high concentration region, thereby increasing the hydrophobic interaction between hydrocarbon chains near micellar surface and hence inducing phase separation at lower temperatures. EtH will be predominantly present in the bulk phase producing only dielectric charges in the solvent medium and hence delaying phase separation to higher temperature. HxH, on the contrary, will predominate the micelle interior throughout the concentration range, with a consequent continuous lowering of CP.

The effect of sodium salts of carboxylic acids on TX-100+DPC mixed system is depicted in Fig. 5a,b in the low and high salt concentration regions, respectively. Figure 5a shows that in the low concentration range of 0–10 mM, CP of this system continuously falls on the addition of electrolytes in the order HxNa > BuNa > PrNa > EtNa, which is in opposite order to that observed for TX-100 or TX-100+AOT systems. The micelles of TX-100+DPC system are positively charged due to the incorporation of DPC surfactant ions into the TX-100 micelles. The ions furnished by the salts may exhibit both a salt effect as well

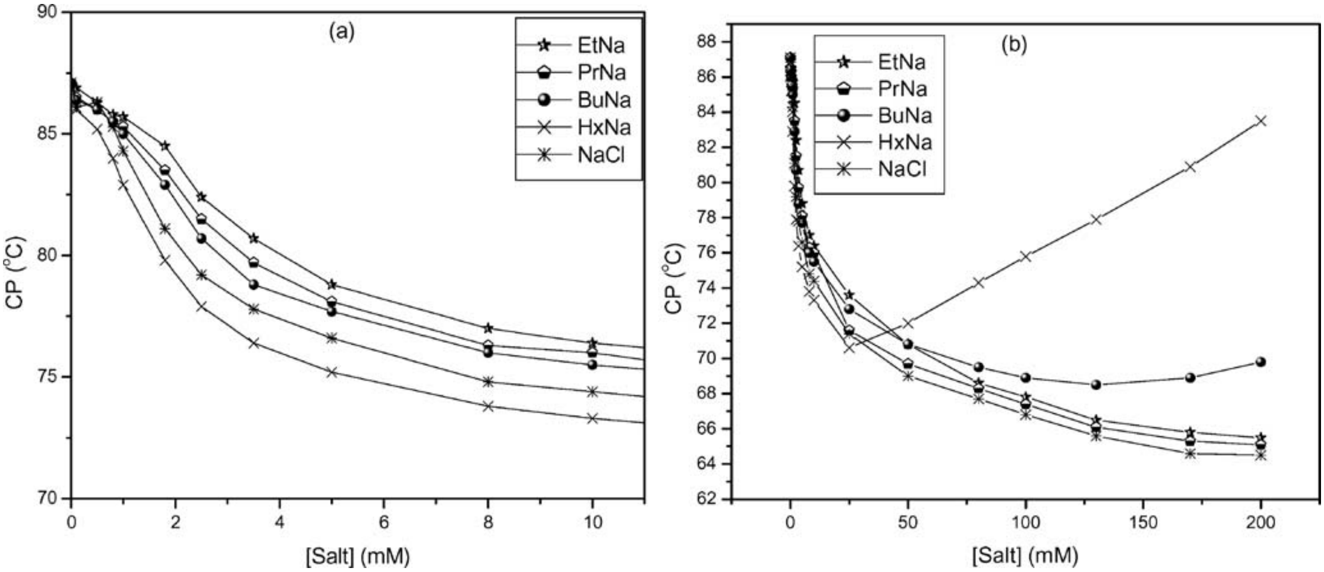

Fig. 5 Cloud point (CP) variation of 10 mM TX-100+0.5 mM DPC mixed surfactant system as a function of salt concentration: **a** in low salt concentration range, **b** in whole salt concentration range

as the solubilization effect even at low concentrations due to their opposite charge to that of mixed micelles. Both of these effects would facilitate phase separation and hence lower the CP. Because the penetrating tendency of these alkanoate counterions into the mixed micelles would be a function of their hydrophobic chain length, therefore, the tendency to lower the CP of the nonionic–cationic system follows the order HxNa > BuNa > PrNa > EtNa. It can be seen that HxNa produces even greater lowering than NaCl in CP of TX-100+DPC system, which may be ascribed to much higher tendency of Hx^- ion to get incorporated into mixed micelles, thereby neutralizing the micellar surface charge which results in decreasing the electrostatic repulsion between micelles and hence easy phase separation.

Figure 5b shows that in the high salt concentration range, CP of the TX-100+DPC system is actually elevated appreciably with the addition of HxNa beyond 25 mM concentration, while NaCl, PrNa, and EtNa gradually lowers the CP in that order. In the case of BuNa, the initial slow lowering is followed by a similar rise above 130 mM. From these results, we can infer that Hx^- ions are excessively solubilized into the positively charged mixed micelles to the extent that after compensation of the positive charge, a resultant negative charge is produced in the micelle. Hence, with the increase in concentration of HxNa, the repulsive interactions between micelles will decrease initially, go through a minimum, and then begin to increase. This effect is reflected in the variation of the CP with salt concentration in a similar manner, thus displaying a minimum. However, the effect is less pronounced in BuNa because of the smaller hydrophobic chain length of the butyrate ion. Different behavior of HxNa and BuNa in the two systems in low concentration range but similar behavior at high concentrations emphasizes the different mode of action of carboxylate ions in respect of the two systems. Butyrate and hexanoate ions readily solubilize into TX-100+DPC micelles because they act as counterions and hence lower the CP more effectively at low concentrations. The excess solubilization at high concentration ultimately leads to induction of negative charge on micelles, forcing an elevation of CP. On the other hand, these ions depress the CP at a lower pace in TX-100+AOT system in low concentrations due to their salt effect but raise the CP at higher concentrations by introducing more negative charge on micellar surface due to solubilization.

In presence of acids (EtH, PrH, and BuH), the TX-100+DPC mixed system displays an initial elevation of CP with acid concentration (Fig. 6a). At higher concentrations, all the acids, viz., EtH, PrH, BuH, and HxH, produce a depression (Fig. 6b). Therefore, maxima in the CP–[acid] curves are observed for EtH, PrH, and BuH, which get shifted toward lower concentration as the hydrophobic chain length of acid increases. No maximum is observed in case of HxH. As already pointed out, organic additive molecules with hydrophobic groups decrease the polar character of solution in the order of their solubility in the solution. This retards the phase separation process and thus raises the CP of system like TX-100+DPC. However, in the TX-100+AOT system, H^+ ion adsorption at low acid concentrations would be facilitated in presence of negatively charged head groups than in presence of positive micellar surface charge in TX-100+DPC system. Had the

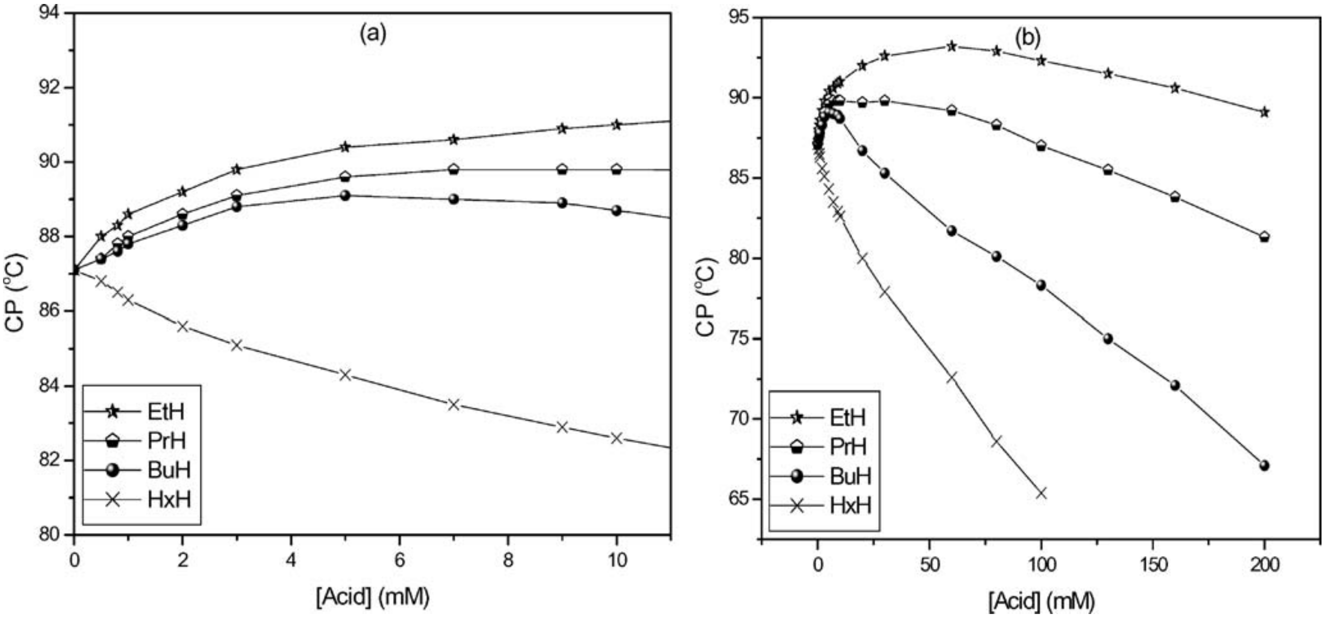

Fig. 6 Cloud point (CP) variation of 10 mM TX-100+0.5 mM DPC mixed surfactant system as a function of carboxylic acid concentration: **a** in low acid concentration range, **b** in whole acid concentration range

H^+ ion adsorption been occurring on oxyethylene groups, the CP elevation would have also been observed in the case of TX-100 system. The rise in CP of TX-100+DPC system is related to the solubility of these acids in water, which decreases in the order EtH > PrH > BuH; therefore, the initial rise in CP observed is in the same order. The continuous lowering of CP by HxH may be attributed to its early solubilization into the mixed micelles. However, at higher concentrations, the increasing solubilization of EtH, PrH, and BuH into the micelles reduces the CP of the system in that order. Solubilization of EtH in TX-100+DPC may also be expected to occur due to the complex formation between positively charged pyridinium group and –COOH group of acids. Such a complexation would be opposed by negatively charged $-COO^-$ group of AOT in TX-100+AOT system. Therefore, the slight rise of CP in presence of EtH at higher concentrations in TX-100+AOT system as opposite to a fall in TX-100+DPC system is obvious. The acids PrH and BuH, due to their increasing K_{ow} values, tend to get solubilized and hence reduce the CP as observed for both TX-100 and TX-100+AOT systems.

Conclusion

The following conclusions have been drawn from the present studies:

1. The CPs of the mixed systems TX-100+AOT and TX-100+DPC are significantly higher than that of the single TX-100 system due to the presence of charge in the micelles of the mixed system.
2. At low concentrations, both the sodium salts and the corresponding acids exert their salt effect that leads to dehydration of micelles and hence a lowering of the CP. However, in the nonionic–cationic TX-100+DPC mixed system, the acids initially raise the CP in the order EtH > PrH > BuH, which can be related to the solubility of the acids in the same order, thus decreasing the polar character of the solution.
3. At high additive concentrations, the salts in addition to their salt effect have a solubilization effect in the order of increasing alkyl chain length of the anions. The acids, in addition to decreasing the polar character of the solution in the order EtH > PrH > BuH > HxH, get increasingly solubilized in the reverse order, thus showing predominant solubilization effect in the case of the HxH and the Hx^- anion.
4. In the TX-100 system, EtH above 25 mM slightly elevates the CP by decreasing the polar character of the solution, while PrH, BuH, and HxH depress it by increased solubilization and hence growth of micelles. The effect of HxH in this respect is extraordinarily large. The solubilization of Bu^- and more so of Hx^- ions produces negative charge in the micelles, leading to repulsions and hence rise in CP.
5. In the TX-100+AOT system with negatively charged micelles, at low additive concentration, the salt effect predominates, but at high concentrations, the solubilization of additive becomes important. Incorporation of Hx^- ions introduces additional negative charge in the micelles, thereby increasing the intermicellar repulsions and hence the CP. On the other hand, decrease of polar character of solution by HxH and its penetration into the micelles leading to growth of micelles result in lowering the CP.
6. At high acid concentrations, in the TX-100+DPC system containing positively charged mixed micelles, the initial elevation in CP is followed by lowering, thus displaying maxima. However, HxH leads to a continuous decrease from the very beginning, being practically insoluble in water and highly solubilized in the micelles.
7. The initial decrease of CP by the salts in the TX-100+DPC system is in the opposite order to that in TX-100 and TX-100+AOT system. This is because the charge reducing tendency on micelles by negative alkanoate ions will follow their solubilization extent which is in the order $Hx^- > Bu^- > Pr^- > Ac^-$. The raising of CP by HxNa at high concentration may be attributed to extra solubilization of Hx^- ions, which after neutralization of the positive charge on the micelles introduces a net negative charge. This is supported by the fact that the change over from CP lowering to CP elevating influence of HxNa occurs above 25 mM compared to 10 mM for TX-100 system.

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