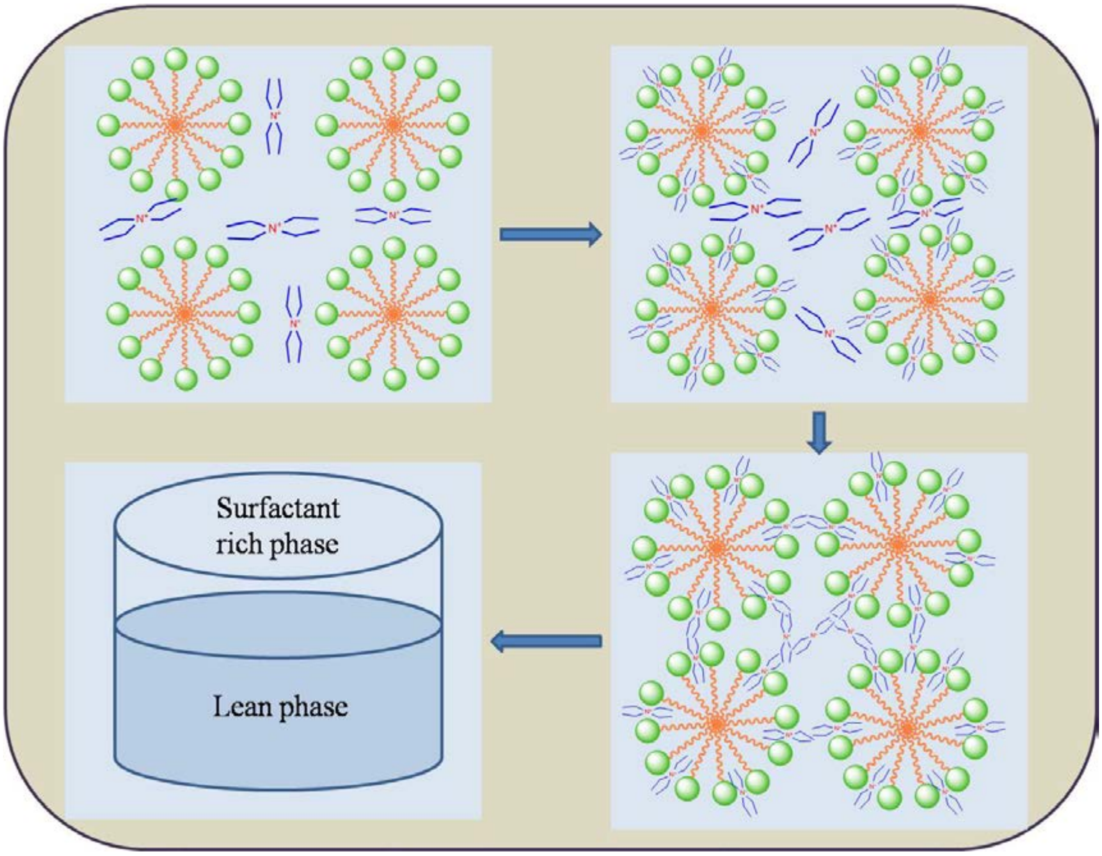
Chapter 4

Clouding Behaviour of Aqueous Anionic Surfactant: Effect of Nature, Structure of head group/ counterion and Additives



4.1. Introduction

It is well known that solution behaviour of ionic and nonionic surfactant solutions, at elevated temperature, are different [1]. Clouding phenomenon is a principle feature in non-ionic surfactant solution while it is less common with aqueous ionic surfactant. Recently, clouding phenomenon has also been reported with ionic surfactant solution under variety of experimental conditions (pH, special counter ion (quaternary) or special head group, molecular architecture, etc) [2-7]. Dehydration of the head group and counterion due to their mutual presence seem important for the occurrence of clouding phenomenon. Many amphiphilic drugs also show clouding phenomenon under specific conditions [8-10].

Surfactant and polymer are frequently investigated systems in the context of Hofmeister series [11-13]. However, progress in that field has been restricted due to lack of systematic work on Hofmeister effects with respect to phenomenon related to surface and colloid science [14]. Collins et al. [15] proposed a “law of matching water affinity” and correlated with the association of oppositely charged ions in aqueous solution. Clouding phenomenon in charged micellar solution is the consequence of the interaction between oppositely charged counterion and headgroup [3-6]. Therefore, the generation of the clouding in ionic surfactant systems mostly requires the presence of a quaternary salt, which screens the charge of the micelles. Another role of such salt is to connect micelles together via short alkyl chains. Compared with single chain single head conventional anionic surfactant (SDSo or SDS), the special molecular structure of anionic gemini surfactant (AG) may bring out some novel properties including the clouding phenomenon. Although, AG exhibits the possibility of producing CP behaviour, only one report is currently available where CP was observed at high quaternary salt concentration [16]. Clouding at lower temperature/concentration may facilitate the cloud point extraction methodology (CPEM) for the extraction of thermally labile moieties [17, 18]. The CP plays a significant role in suggesting the limit of aqueous solubility and hence the use in physicochemical processes. The practical importance of the clouding phenomenon reflects in its application to solute extraction / pre-concentration and detergency (it reaches to maximum just below the CP) [19, 20]. The present surfactant systems can be used to extract/pre-concentration both hazardous metal ions as well as hydrophobic organic material, in a single step, which is not possible with conventional solvent extraction techniques (with hazardous non-polar solvents).

Above facts prompted us to study Hofmeister effect in the context of clouding phenomenon in an anionic surfactant solution. In a previous study, we have established Hofmeister like series of anionic headgroups with respect to a single quaternary ammonium counterion *i.e.* tetra-*n*-butylammonium (TBA^+) [21]. Cloud point (CP) data fitted in the ordering of head groups proposed by Vlachy et al. [22]. Further, sulphate and sulfonate headgroups are more prone to produce clouding with TBA^+ [21]. To generalize the clouding effect, we have chosen few symmetrical/unsymmetrical quaternary counterions and cloud point (CP) measurements have been performed in aqueous solutions of three anionic surfactants namely, sodium dodecylsulphate (SDS), sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfonate (SDSo). The quaternary salts chosen, for driving the corresponding counterions, are: tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylphosphonium bromide (TBPB), tetraphenylphosphonium bromide (TPhPB), tetra-*n*-pentylammonium bromide (TPeAB) and benzyl tributylammonium chloride (BTAC). CP measurements have also been performed with an anionic gemini surfactant (AG) to compare CP behaviour with conventional anionic surfactant.

4.2. Results and Discussion

4.2.1. Clouding Phenomenon in SDS, SDBS and SDSo

Vlachy et.al [23] discussed the role of the head group on the counterion specificity related to micelle-to-vesicle transition. It has been observed that, if the sulphate head group is replaced by carboxylate headgroup, the order of the ions is reversed, i.e. it follows the reversed Hofmeister series, towards micellar structural transition. Hofmeister series is known in many areas, the mechanism is yet to be settled. This may be due to a complex interplay of direct and indirect effects of ions on the solute molecule as well as on the water structure. The situation is even more unclear in the case of clouding phenomenon. With increase of temperature, the hydration of ionic headgroups decreases with a simultaneous increase in interaction with such counterions. The presence of quaternary counterions near the micellar surface may assist in replacing the water from the headgroup region. Thus, the removal of water attributes the lesser degree of hydration of the micelle surface region.

Quaternary counterions have four short alkyl chains in addition to positive charge on the central atom (*e.g.* N or P). Due to this reason, quaternary counterions can interact with anionic micelles via electrostatic as well as hydrophobic interactions. Figure 1 shows the variation of γ with [quaternary salt]. The rate of decrease of γ can be correlated surface area per head group of the surfactant [24]. The same analogy can be drawn with respect to γ variation of hydrophobic quaternary salt. Based on this assumption the surface area per polar head of counterion will be lowest for $TPeA^+$ and highest for TBA^+.

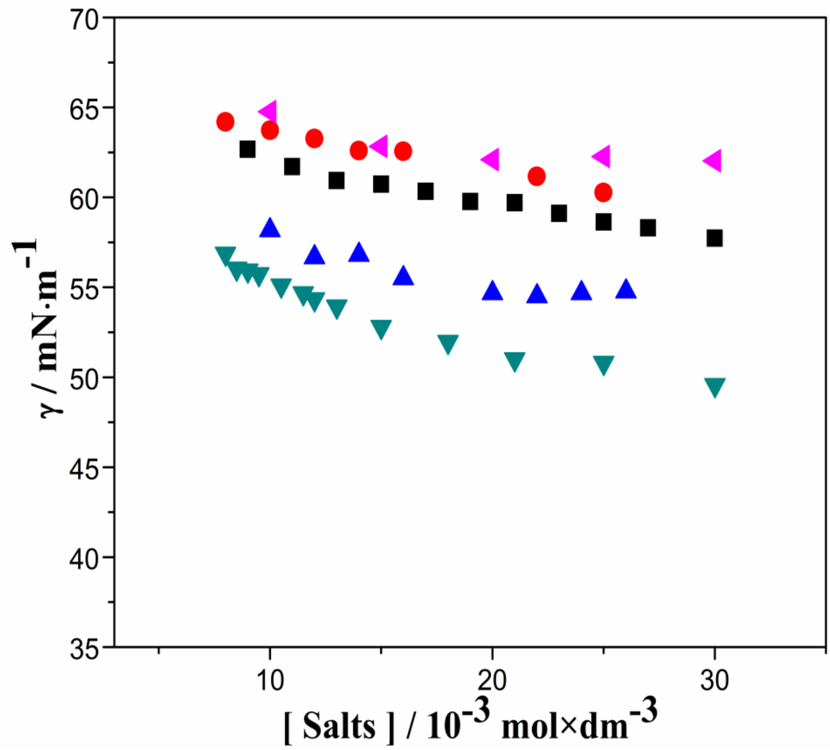


Figure 1. Variation of surface tension (γ) with the concentration of salt in aqueous solution at 303 K: ■, TBPB; ✸, BTAC; ▲, TPhPB; ▼, TPeAB and ◀, TBAB.

As mentioned above, the quaternary counterion consist of four alkyl chains (or phenyl group) in addition to positive charge on the central atom (N or P). Therefore, such counterion can interact with anionic micellar surface hydrophobically and coulombically. In the present context, alkyl or phenyl chains/groups may get embedded between anionic monomers of the micelles. However, geometric constraints make it difficult all the four chains/group to penetrate into the micellar interior. Two directions may be chosen for the distribution of alkyl chains (or groups) near micellar surface: one may be towards the aqueous phase and the other towards the micellar interior [25]. The chains towards aqueous phase can connect the anionic micelles together and be responsible for dehydrating the anionic head group region of the micelle on heating. Presently above two concurrent phenomena (connecting and dehydrating the micelles) can be taken as the cause of clouding phenomenon in anionic micellar solutions in presence of quaternary salt [2, 5, 6].

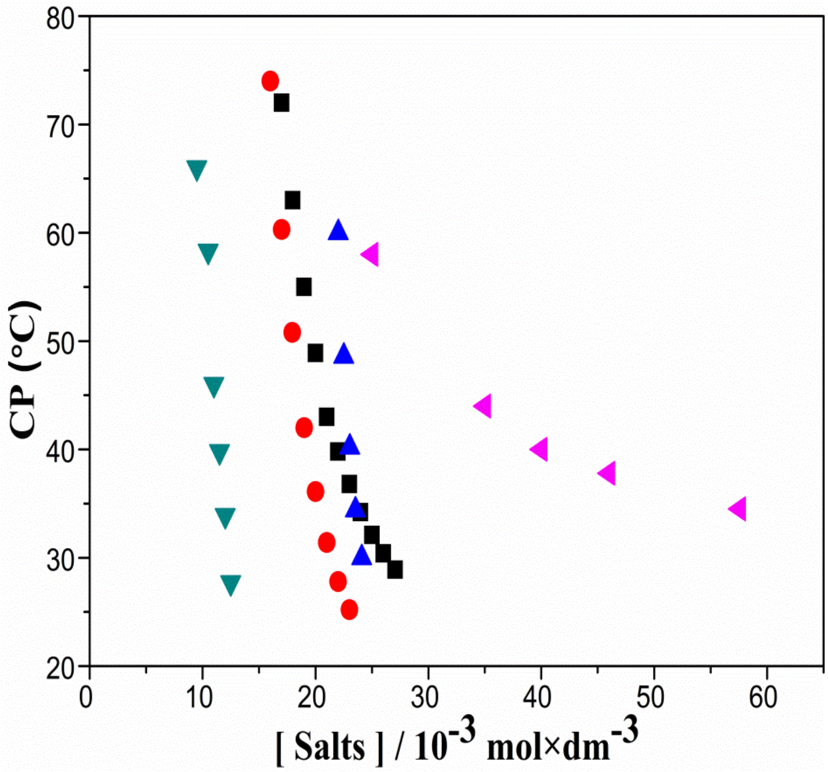


Figure 2. Effect of quaternary salt concentration on the CP of 30 mM SDS aqueous solution: ■, TBPB; ●, BTAC; ▲, TPhPB; ▼, TPeAB and ◀, TBAB.

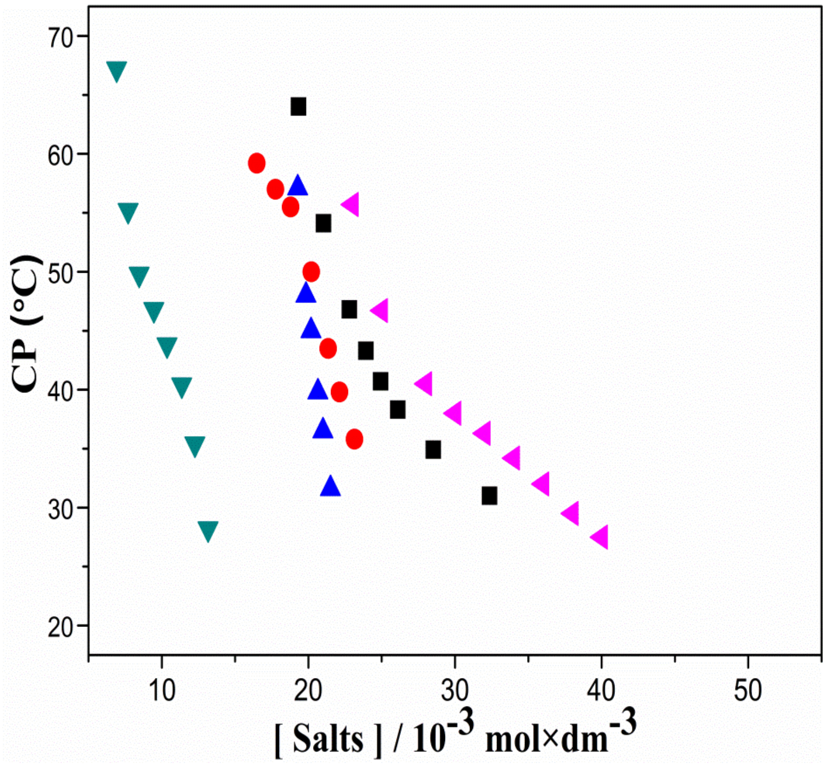


Figure 3. Effect of quaternary salt concentration on the CP of 30 mM SDBS aqueous solution: ■, TBPB; ●, BTAC; ▲, TPhPB; ▼, TPeAB and ◀, TBAB.

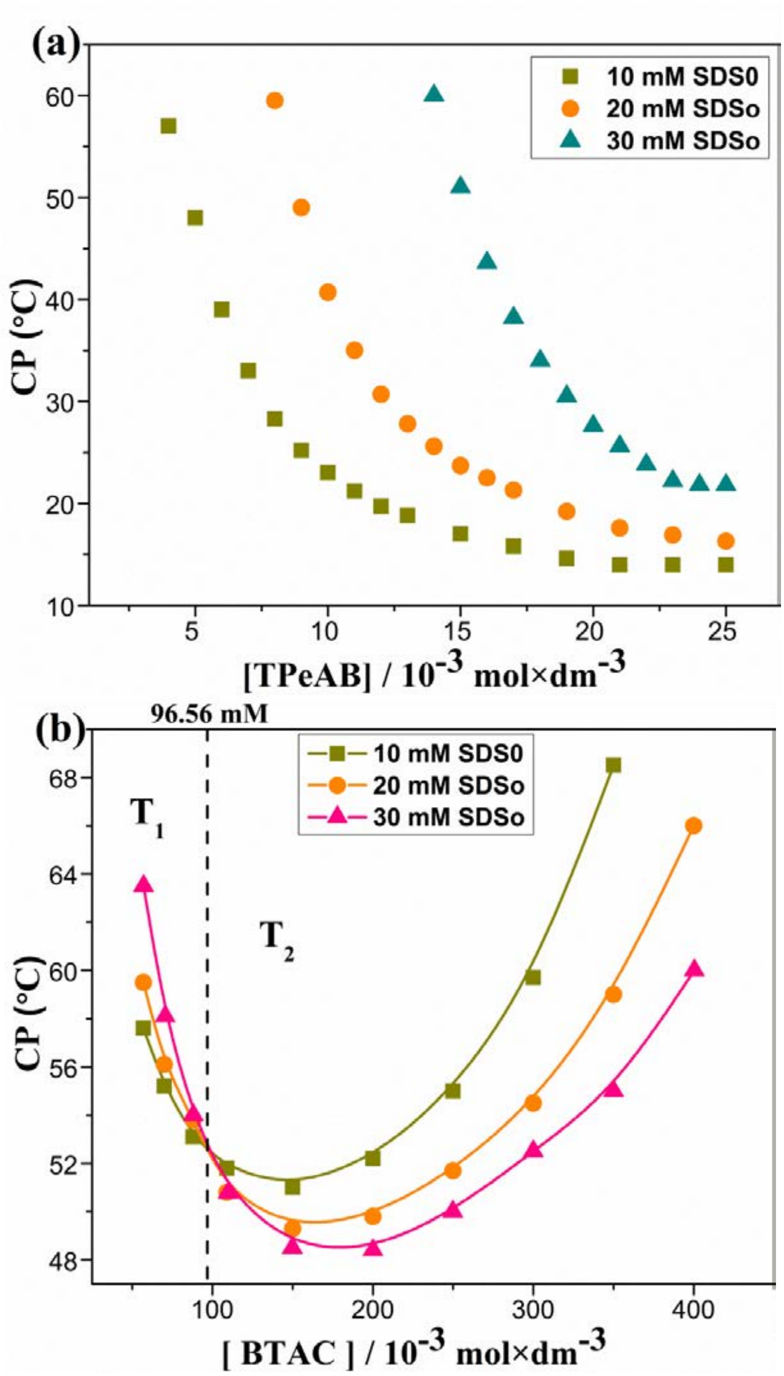


Figure 4. Cloud Point of 30 mM SDSo in presence of quaternary salts: (a) TPeAB; (b) BTAC.

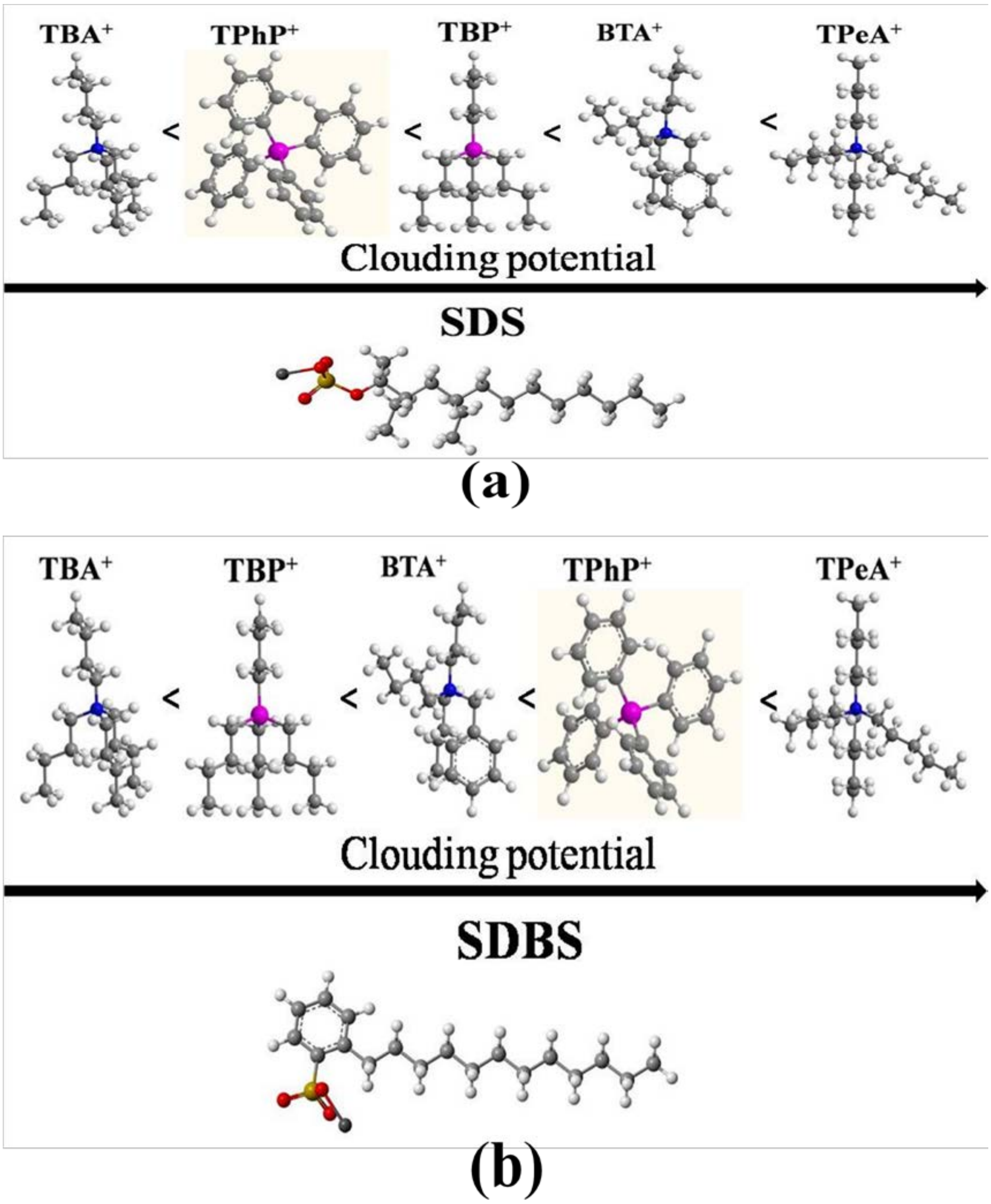
Figures 2-4 shows the variation of CP with the addition of different quaternary salts (TBAB, TBPB, BTAC, TPhPB, TPeAB) in 30 mM anionic surfactant solution (lower concentrations also tried with SDSo). Perusal of the data suggests that CP variations are dependent on the nature and structure of the quaternary counterion. For the same alkyl chain length in a typical counterion (TBAB or TBPB), central atom (N or P) plays an important role to produce clouding. The size of TBP^+ counterion is bigger than TBA^+. Therefore, TBP^+ counterion will occupy more micellar surface than TBA^+. If it is correct, TBP^+ will remove effectively more water from the surface and lower the CP than the TBA^+, at the same surfactant concentration. This indeed observed in Figures 2 and 3. However, $TPeA^+$ counterion has been found most effective in producing clouding in with all the surfactant solutions. This counterion has *n*-pentyl chains which would provide additional hydrophobicity to the counterion (in comparison to TBA^+ or TBP^+) which obviously would provide more hydrophobicity near the micellar surface and can assist in removing the water from the micellar headgroup region. In a separate study, it has been reported that alkyl chains of the counterion can also be used in linking various micelles which are responsible for the phase separation (at CP) [3]. Above factor seems responsible regarding the effectiveness of $TPeA^+$ (Figures 2-4). This explanation found support from the fact that BTA^+ (an unsymmetrical counterion) is more effective in producing clouding than butyl chain salt (TBA^+ or TBP^+). BTA^+ and TBA^+ or TBP^+ contain three similar butyl chains. The fourth butyl chain is substituted by a benzyl group in BTA^+ and is responsible for the increased hydrophobicity of the counterion. The CP data (Figures 2-4) show that BTAC is more effective than TBA^+ or TBP^+. If all the butyl chains of the counterion substituted by phenyl rings (cases of TBP^+ and $TPhP^+$), effectiveness to produce clouding decreases. This could be understood in the light of the fact that the phenyl ring is less hydrophobic than a butyl chain [26]. Therefore, hydrophobicity of the counterion has a definite role in addition to the nature of the central atom (N or P). Further, polarizability of quaternary counterion may increase by increasing the alkyl chain or substituting alkyl chain with benzyl ring [11-13].

Ninham and Yaminsky, based on polarizability, have quantified Hofmeister effect [27]. Polarizable ions have greater surface excess on the micelle compared to less polarizable ions and responsible for greater dispersion forces. The presence of N or P as central atom in a quaternary counterion may also influence the polarizability. Therefore, $TPeA^+$ prefers micellar surface and is responsible for effective dehydration of the headgroup region. Hence, $TPeA^+$ and TBA^+ appear at the two extremes of effectiveness of producing clouding. This indeed observed in from CP data. Based on data shown in Figures 1-3, clouding potential (effectiveness of counterion in producing clouding) can be arranged in the following order: $TPeA^+ > BTA^+ > TBP^+ > TPhP^+ > TBA^+$.

CP data show that SDBS-quaternary counterion combinations give clouding at lower temperature than the SDS or SDSo. This may be due to the presence of benzene ring in the SDBS molecule. Due to this, SDBS behaves as a more hydrophobic surfactant as purposed in the literature [28]. The increased hydrophobicity is responsible for lower CP. Another point worth noting is the ordering of counterion with each anionic surfactant. In case of SDBS, counterion ordering is similar as in SDS (Figure 5a) with a difference that $TPhP^+$ does not follow the trend (Figure 5b) Further, SDSo behaves as SDBS (Figure 5c). This may be due to the presence of phenyl ring in SDBS seems responsible for increased interaction with four phenyl rings present in $TPhP^+$ via aromatic-aromatic interactions [29]. These interactions are known for stabilization of structure of amphiphilic assemblies. The analogy can be drawn in the case of micellar systems which are expected to be stabilized (and hence of bigger size) and responsible for the change in ordering. The ordering is as follows with SDBS: $TPeA^+ > TPhP^+ > BTA^+ > TBP^+ > TBA^+$.

Figure 4 shows the CP variation with [TPeAB or BTAC] at different fixed SDSo concentrations. Figure 4a shows the interplay of [SDSo]-[TPeAB] on the clouding behaviour. At lower [SDSo], the requirement of TPeAB is also lower, which is in consonance with an earlier study [30]. The perusal of data (Figure 4a) indicates that the amount of salt required to produce clouding increases with an increase in [surfactant].

CP measurements have also been performed with BTAC-SDSo aqueous systems (Figure 4b). CP decreases and then increases with the continuous increase in [BTAC] at different fixed [SDSo]. This behaviour is different than what was observed with TPeAB (Figure 4a). The initial decrease and leveling off in CP with [BTAC] is similar to other anionic surfactants-quaternary salt combinations [30, 31]. However, a novel CP increase was observed at higher [BTAC]. This behaviour has not been found in any of the studies on the clouding phenomenon in ionic surfactant solutions. However, it has been reported that CP increases with quaternary salt concentration when added to a nonionic surfactant. Therefore, the BTAC-SDSo system shows the signatures of both ionic (initial part of Figure 4b) and nonionic surfactants (latter part of Figure 4b). This is hard to understand how a surfactant can behave both ways. In a separate small angle neutron scattering (SANS) study, it has been shown that the charge on the anionic micelle decreases on addition of quaternary ammonium salts [32]. In the light of the above fact, at higher [BTAC], micelle can be considered nearly uncharged (pseudo-nonionic micelle [6]). If it is true, the additional BTAC can be used to re-charge the pseudo-nonionic micelle to probably cationic micelle. These cationic micelles may feel electrostatic repulsion which may be the reason of CP increase at higher [BTAC].


TBA⁺
TPhP⁺
TBP⁺
BTA⁺
TPeA⁺
Clouding potential
SDS
(a)
TBA⁺
TBP⁺
BTA⁺
TPhP⁺
TPeA⁺
Clouding potential
SDBS
(b)

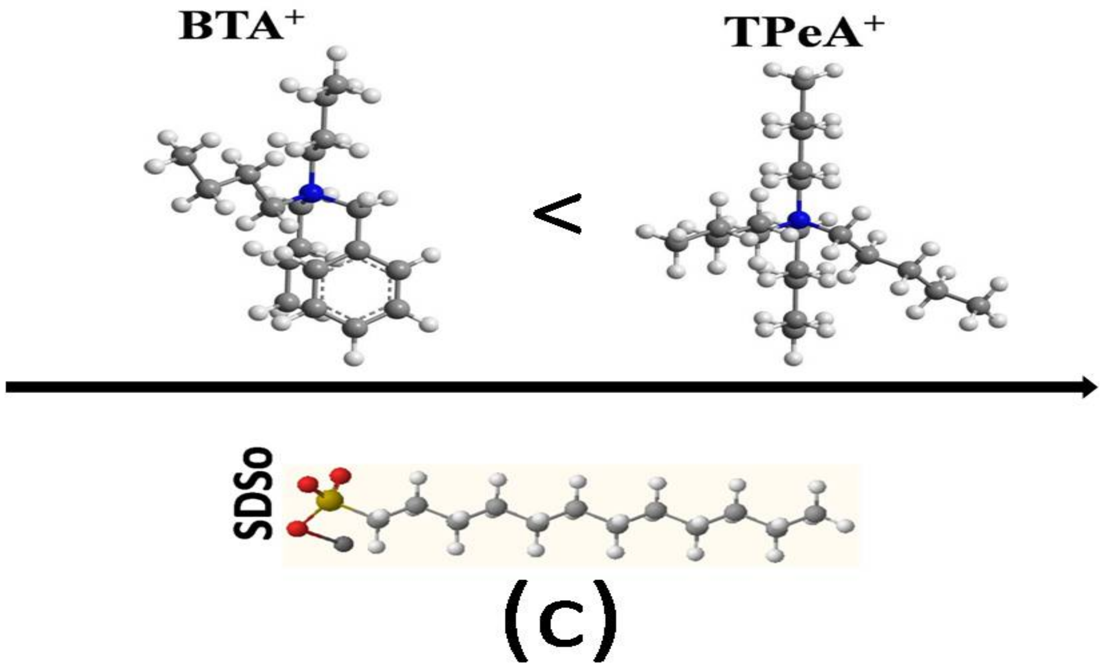
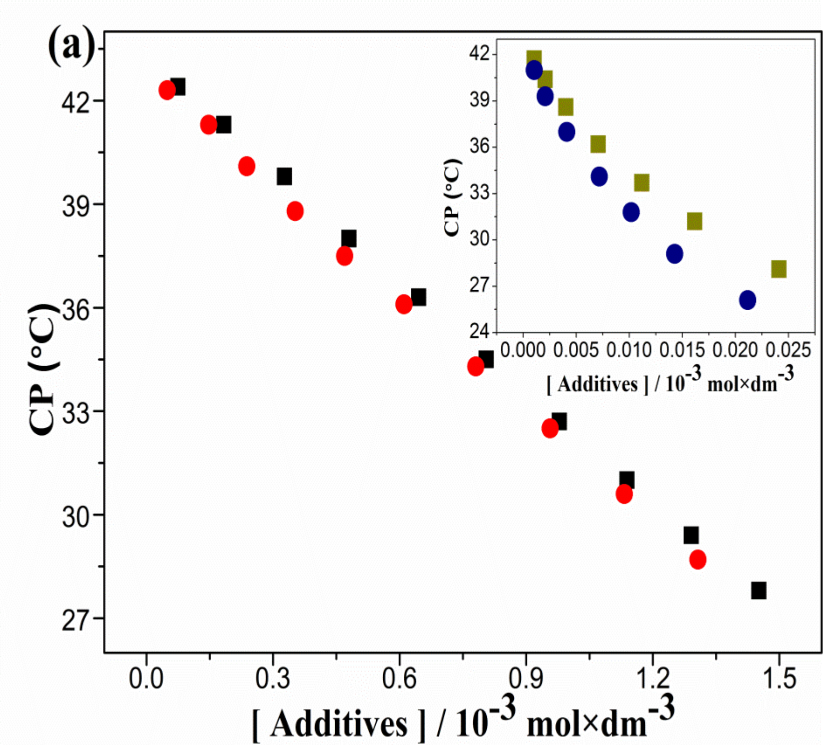


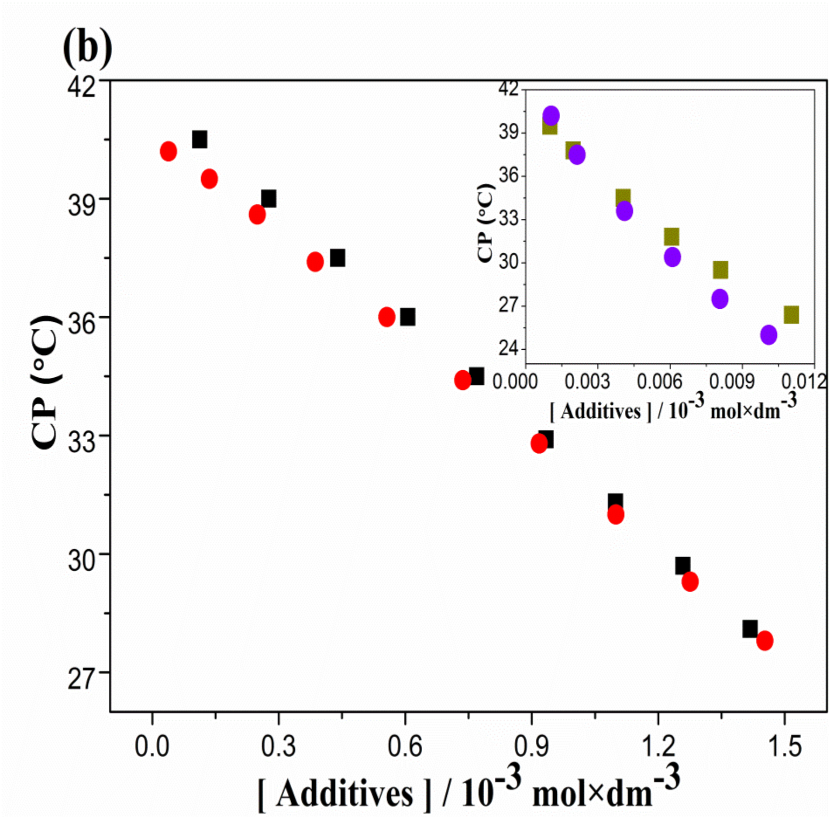
Figure 5. The order of effectiveness of counterion in producing clouding: (a) SDS; (b) SDBS and (c) SDSo.

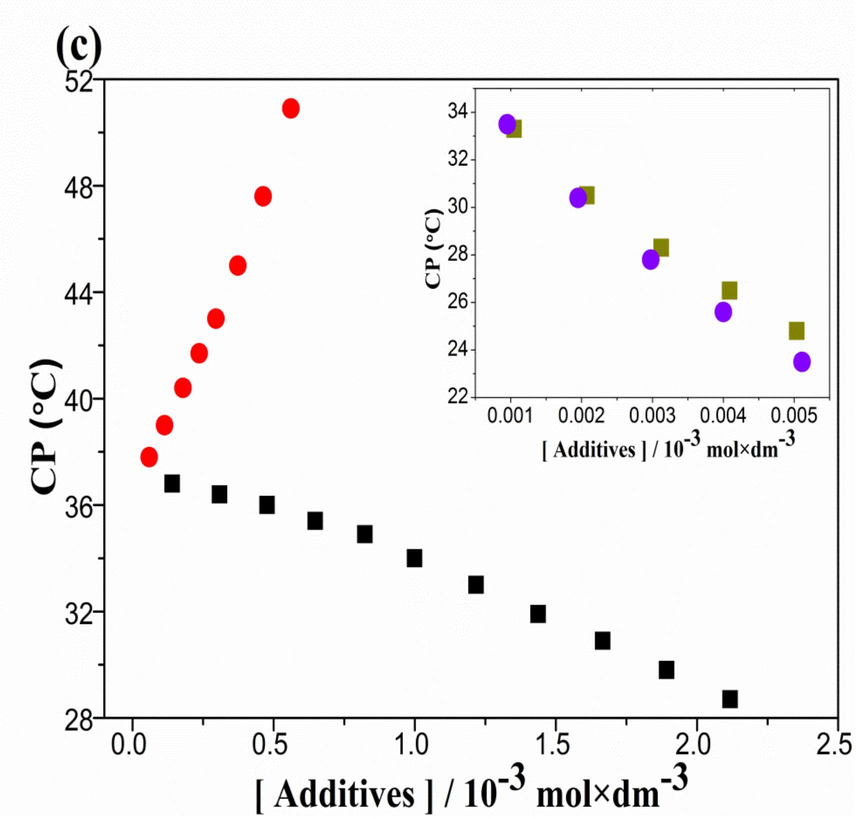
4.2.2. Clouding in Presence of Additives

4.2.2.1. Effect of Sugars

Figures 6-8 show the variation of CP with carbohydrate addition (sugar or cyclodextrin). Generally, CP decreases with all the sugars. However, sucrose addition in presence of TPhPB show (Figures 6c and 7c) an increase in CP with both SDS and SDBS (TPhPB does not give clouding with SDSo). Sugars decrease the cmc of surfactant due to their water structure forming property [33]. The temperature range in which single-phase appears reduces indicate a salting out effect of a typical sugar.


(a)
CP (°C)
[Additives] / 10^-3 mol×dm^-3
CP (°C)
[Additives] / 10^-3 mol×dm^-3


(b)
CP (°C)
[Additives] / 10^-3 mol×dm^-3
CP (°C)
[Additives] / 10^-3 mol×dm^-3



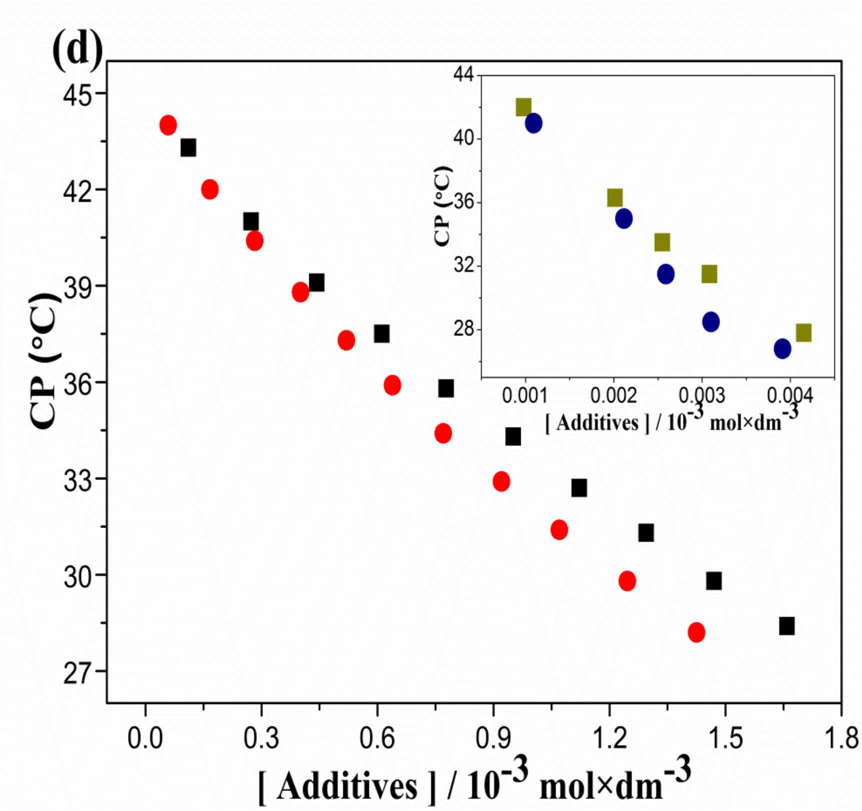
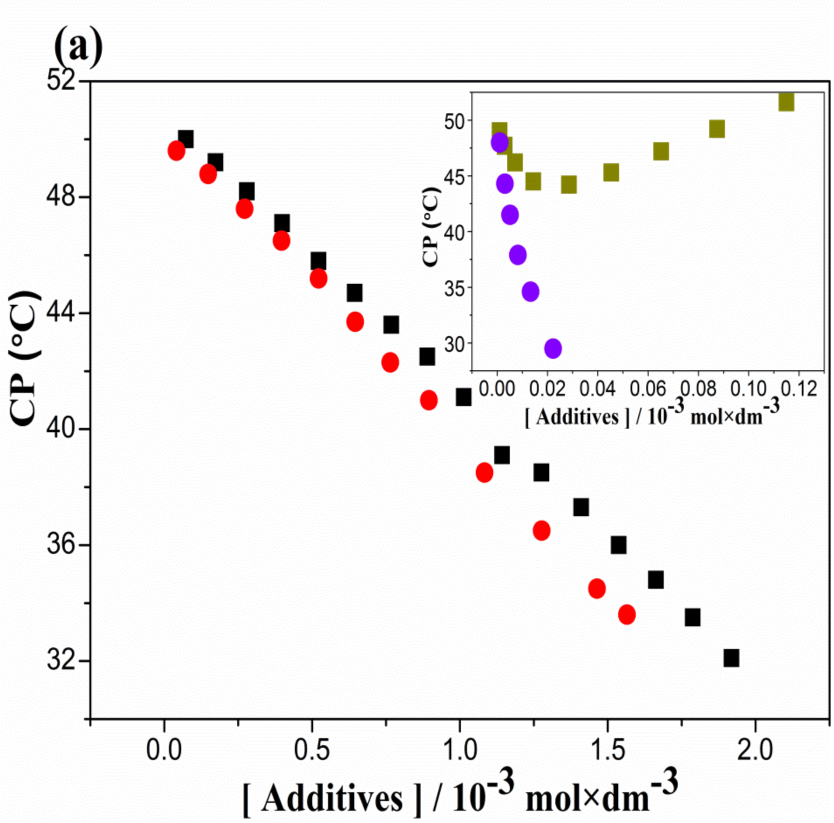
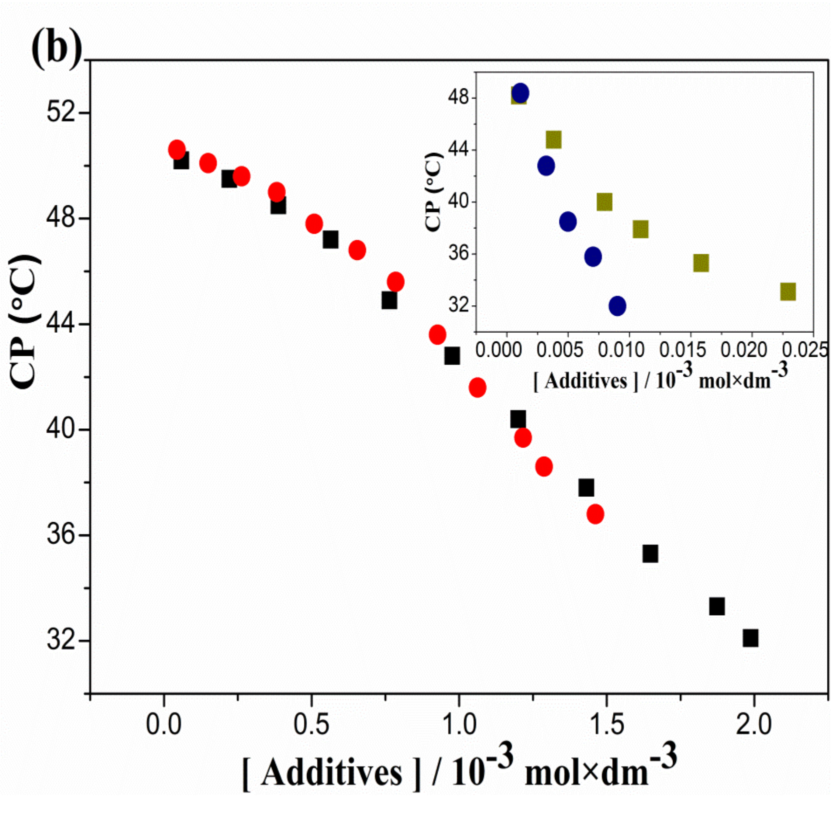


Figure 6. Effect of Carbohydrates on the CP of 30 mM SDS with: (a) 22mM TBPB, (b) 19 mM BTAC, (c) 20 mM TPhPB and (d) 11mM TPeAB : ■, D-glucose and ✸, sucrose (insets are for : ■, α-cyclodextrin and ✸, β -cyclodextrin).


(a)
CP (°C)
[Additives] / 10-3 mol×dm-3
CP (°C)
[Additives] / 10-3 mol×dm-3


(b)
CP (°C)
[Additives] / 10-3 mol×dm-3
CP (°C)
[Additives] / 10-3 mol×dm-3

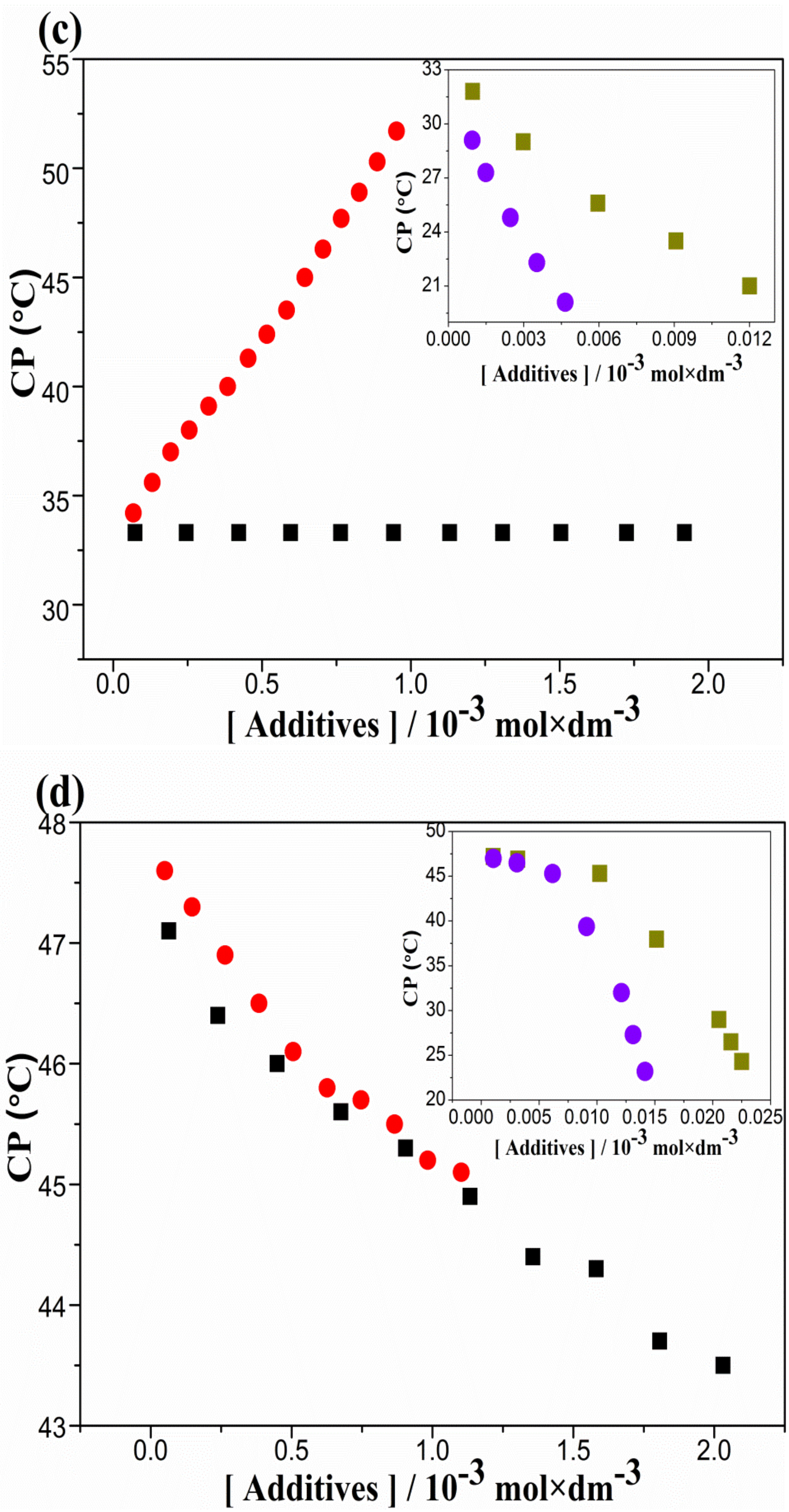


Figure 7. Effect of Carbohydrates on the CP of 30 mM SDBS with: (a) 22 mM TBPB, (b) 20 mM BTAC, (c) 21.5 mM TPhPB and (d) 9.03 mM TPeAB system: , D-glucose and , sucrose (insets are for : , α-cyclodextrin and , β-cyclodextrin).

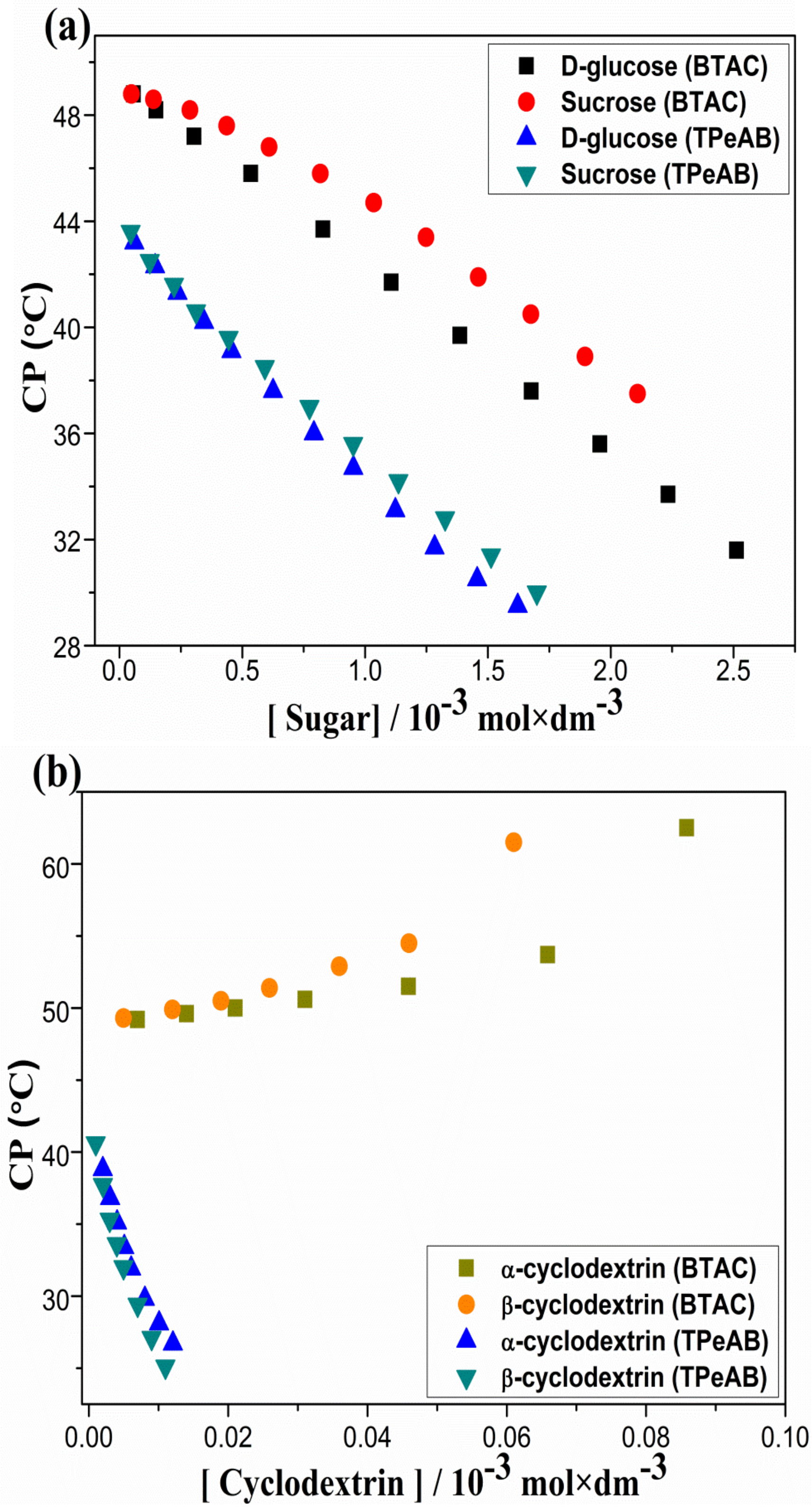


Figure 8. Effect of Carbohydrates on the CP of 30 mM SDSo + 150 mM BTAC / 16 mM TPeAB system of: (a) sugar; (b) cyclodextrin.

Sucrose-TPhPB combination does not fit in above generalization. Probably, four phenyl rings in $TPhP^+$ brings sucrose molecule in the micellar palisade layer which draws water from the background solution and minimize the salting out effect of sugar due to change in its site of localization. This additional water in the headgroup region is responsible for the CP increase. Among the carbohydrates, cyclodextrins are having better effect for decreasing the CP. Since cyclodextrin is having certain hydrophobic cavity in the molecular structure, it can interact hydrophobically with the surfactant micelles [34]. Further, hydroxyl groups of cyclodextrin may assist to draw headgroup region water. Above interrelated factors may be responsible for CP decrease. Recently, CP decrease is observed in an ionic drug solution and explained in the light of above factors [35]. CP decrease in the presence of hydrophobic alkanols has also been interpreted in terms of hydrophobic interaction [36].

4.2.2.2. Effect of Amino Acids

Figures 9-11 show the variation of CP with addition of amino acid in presence of various quaternary counterions. CP variation depends on the nature of both amino acid and quaternary salt. However, TPhPB (increase in CP and TPeAB (decrease in CP) fall at two different extreme. Other salts behave, accordingly, between of the above two extremes. The behaviour of TPhPB is similar as found with carbohydrate (*supravide*) and can be interpreted in the similar fashion as mentioned with sugars. Similarly, TPeAB, being a more hydrophobic salt, induces hydrophobic interaction both with the amino acids and with the hydrophobic chain of the surfactant. Probably, this is responsible for continuous decrease in CP as depicted in Figures 9-11.

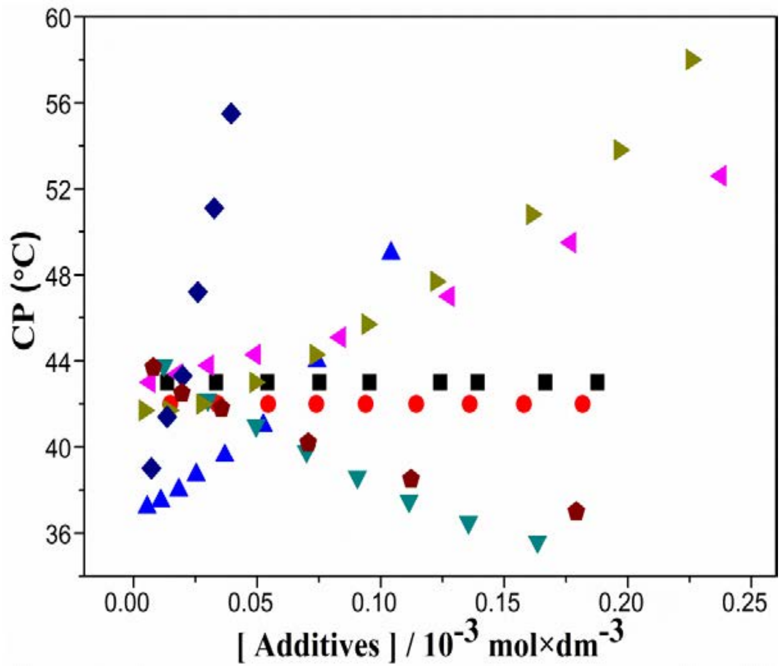


Figure 9. Effect of amino acid on the CP of 30 mM SDS + quaternary salt system (TBPB (22mM); BTAC (19 mM); TPhPB (20 mM) and TPeAB (11 mM)): ■, L-leucine (TBPB); ✸, L-leucine (BTAC); ▲, L-leucine (TPhPB); ▼, L-leucine (TPeAB); ◀, L-phenylalanine (TBPB); ▶, L-phenylalanine (BTAC); ◆, L-phenylalanine (TPhPB) and ⬟, L-phenylalanine (TPeAB).

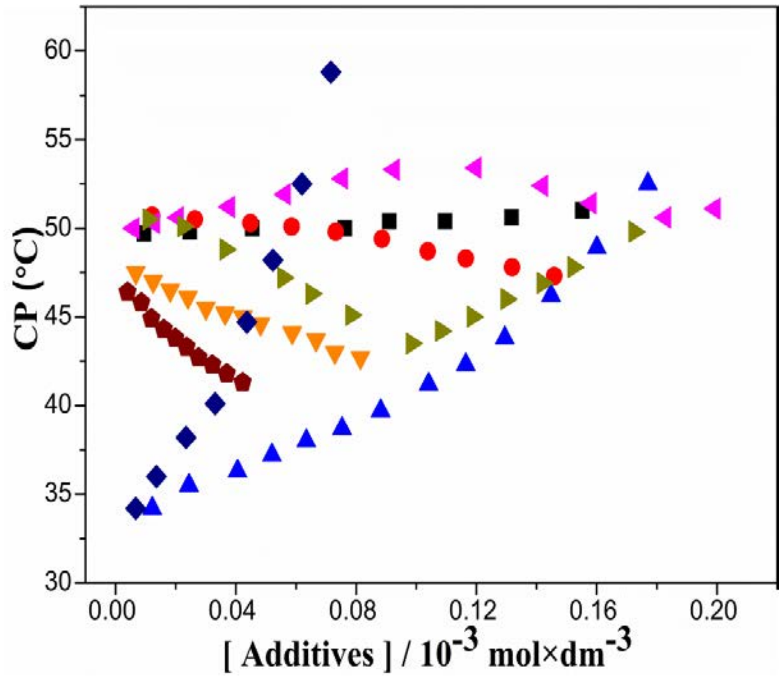


Figure 10. Effect of L-leucine and L-phenylalanine on the CP of 30 mM SDBS + quaternary salt systems (TBPB (22 mM); BTAC (20 mM); TPhPB (21.5 mM) and TPeAB (9.03 mM)):)): ■, L-leucine (TBPB); ✸, L-leucine (BTAC); ▲, L-leucine (TPhPB); ▼, L-leucine (TPeAB); ◀, L-phenylalanine (TBPB); ▶, L-phenylalanine (BTAC); ◆, L-phenylalanine (TPhPB) and ⬟, L-phenylalanine (TPeAB).

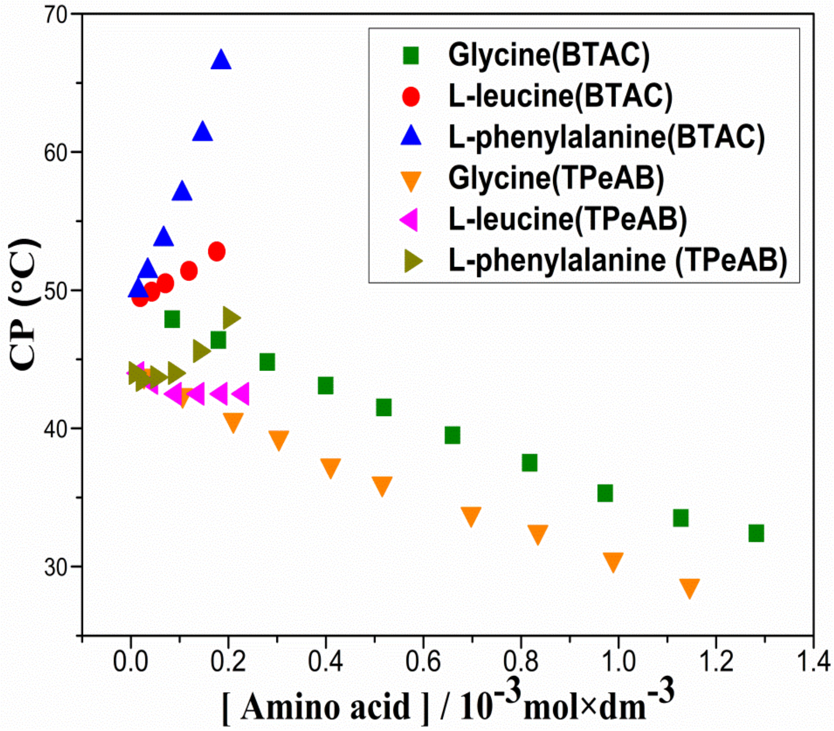


Figure 11. Effect of Glycine, L-leucine and L-phenylalanine on the CP of 30 mM SDSo + 150 mM BTAC / 16 mM TPeAB.

4.2.2.3. Effect of Ascorbic Acid

Variation of CP with L-ascorbic acid for 30mM surfactant + quaternary salt system has been shown in Figures 12 and 13 without controlling the pH of the solution. With all the salts, a decrease in CPhas been observed. L-Ascorbic acid (or vitamin C) molecule contains four hydroxyl groups which help in removing water from the head group region (due to water structure forming nature). With TPhPB, CP decreasing effect has been found more pronounced than with other salts (which may be due to the presence of four phenyl rings). These phenyl rings can interact with allyl ring of ascorbic acid [37] and responsible for significant decrease in CP. However, TPhPB dose not give clouding with SDSo and can not be compare with SDS or SDBS behaviour. But SDS/SDSo-TPeAB combination show better CP decrease than SDBS in presence of L-ascorbic acid. Probably, bezene ring in SDBS monomer plays a role in interaction with allyl ring of ascorbic acid.

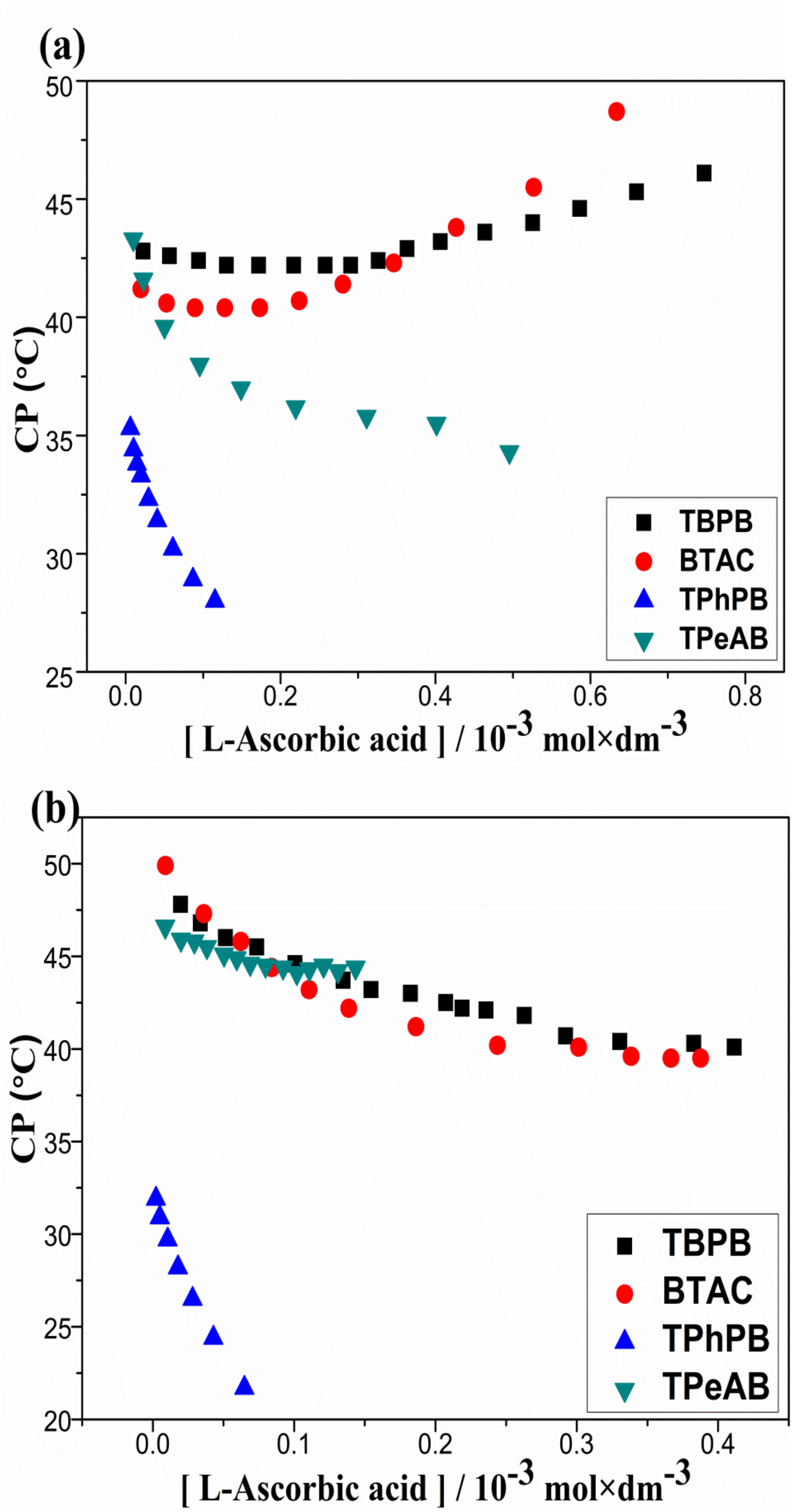


Figure 12. Effect of L-Ascorbic acid on the CP: (a) 30 mM SDS + quaternary salt systems (TBPB (22 mM); BTAC (19 mM); TPhPB (20 mM) and TPeAB (11 mM)) and (b) 30 mM SDBS + quaternary salt systems (TBPB (22 mM); BTAC (20 mM); TPhPB (21.5 mM) and TPeAB (9.0 mM)): ■, TBPB; ✸, BTAC; ▲, TPhPB and ▼, TPeAB.

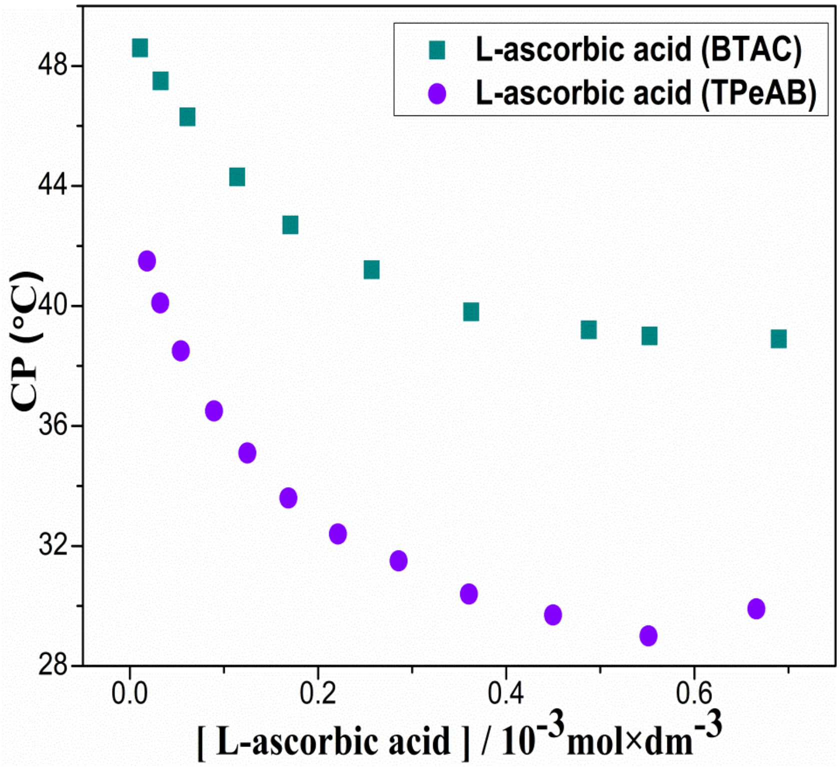


Figure 13. Effect of L-ascorbic acid on the CP of 30 mM SDSo + 150 mM BTAC / 16 mM TPeAB system.

4.2.3. Clouding Phenomenon in Presence of Anionic Gemini Surfactant

All the salts were added in anion gemini (AG) surfactant solutions followed by heating. Only, TPeAB produces clouding in the anionic gemini surfactant solutions. Figure 14 shows an interplay of [AG]-[TPeAB] towards CP. Here again, more salt is needed to produce clouding as the [AG] was increased. This behaviour was found similar as observed with SDSo (Figure 4a) as well as in a recent study [38]. However, [TPeAB] required to produce CP is more with AG than with SDSo at the same surfactant concentration (10 mM). This may be due to the fact that AG contains two negatively charged head groups with increased amount of hydrated water with each monomer. To remove this hydrated water, additional amount of TPeAB required in the case of AG. This indeed observed in Figure 14.

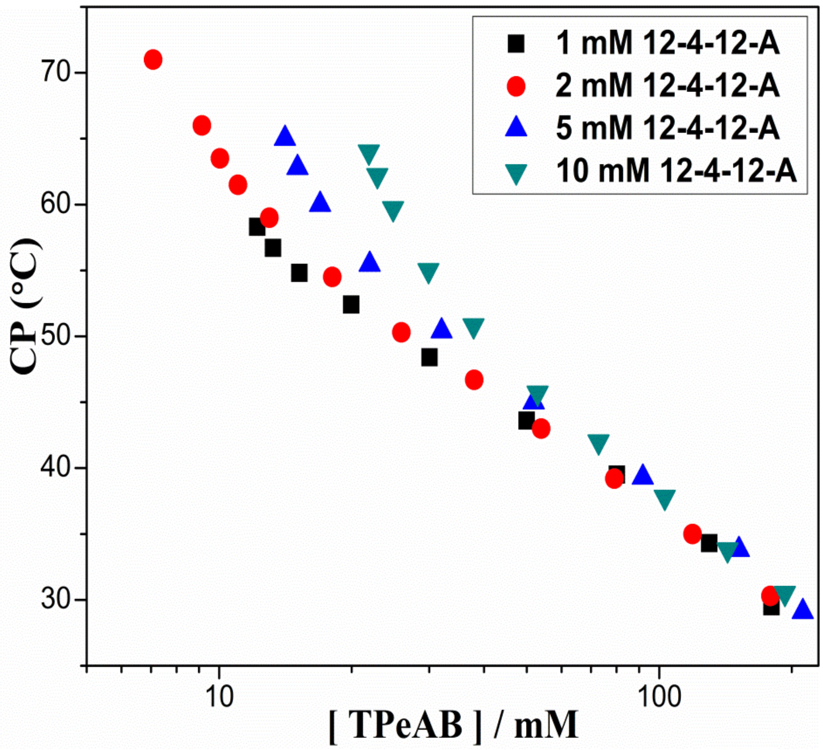


Figure 14. Cloud Point of anionic gemini surfactant (12-4-12-A) in presence of quaternary ammonium bromide (TPeAB).

4.2.3.1. Effect of cyclodextrins

From the CP studies with aqueous AG + TPeAB (Figure 14), 2mM AG + 38mM TPeAB system has been selected to see the effect of additives. Figure 15 shows the variation of CP with the addition of cyclodextrin. The behaviour has been found similar as discussed in the previous section with other anionic surfactants. However, addition of α-cyclodextrin shows an increasing CP behaviour with AG. Probably presence of spacer group in AG create water mediated interaction with α-cyclodextrin which bring additional water near head group and required more heating to remove water of hydration and responsible for increasing trend of CP value.

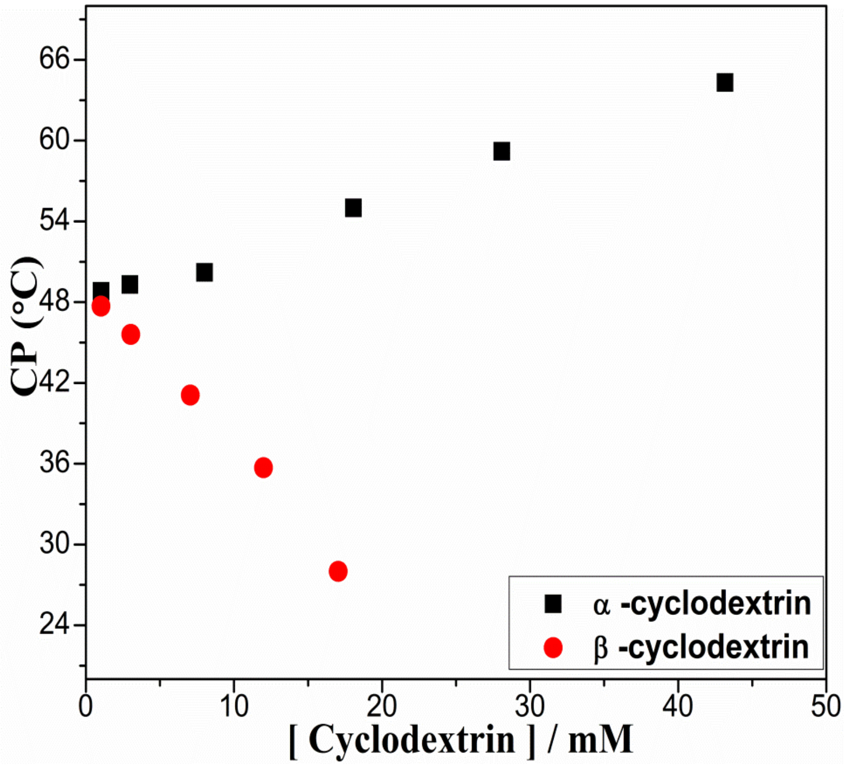


Figure 15. Effect of [cyclodextrin] on the CP of 2mM AG + 38mM TPeAB system.

4.2.3.2. Effect of Amino Acid

Figure 16 shows the variation CP with addition of amino acid to 2mM AG + 38mM TPeAB system. Similar variation of CP with [amino acid] has been observed as was seen with other anionic surfactants discussed above. Therefore, AG behaves in a similar fashion like conventional anionic surfactants and the data can be understood in the light of the facts mentioned for other anionic surfactants.

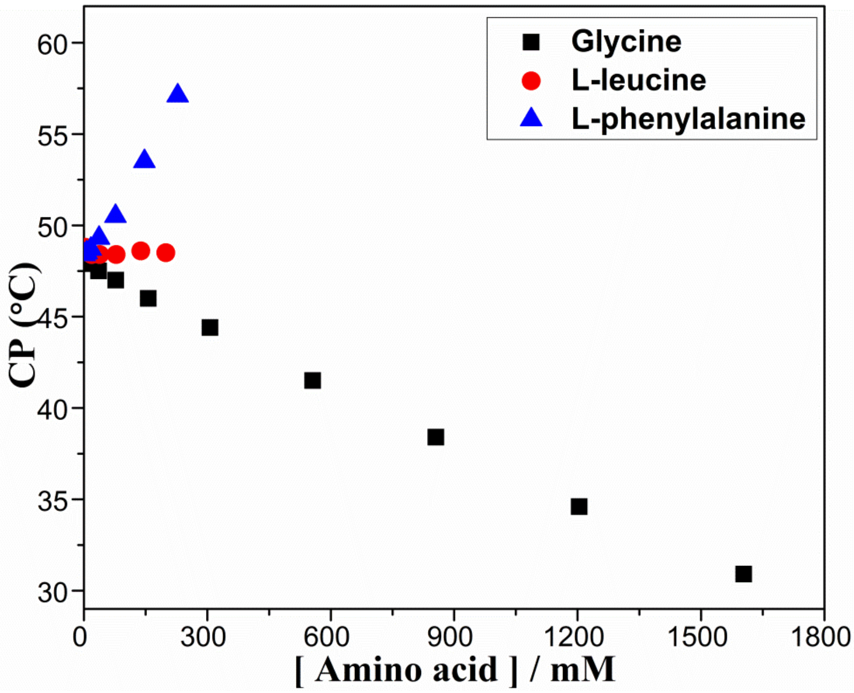


Figure 16. Effect of [amino acid] on the CP of 2mM AG + 38mM TPeAB system.

4.3. Conclusion

In this chapter, influence of nature of counterion and head group of the quaternary salt and anionic surfactant, respectively, has been investigated on the clouding behaviour. The data are interpreted in the light of head group-counterion interaction and their mutual dehydration. It has been noticed that most CP studies in anionic micellar solution were conducted by adding TBA^+. However, present study shows that other quaternary counterions can produce similar effect with even better performance (Figure 5). Hydrophobicity of the counterion plays a pivotal role in interacting with anionic micellar surface and dehydrating it. This dehydration is responsible for the clouding phenomenon observed. Similar dehydration occurs with non-ionic micelle on heating and responsible for the phenomenon. However, there is a difference in the mechanism of dehydration in the two cases (ionic and non-ionic). In former case (ionic), water is bound to the micellar surface via stronger ion-dipole interaction then the case of latter where water is bound via weaker dipole-dipole interactions. With ionic surfactants, heating may cause dehydration of the counterion and head group both, which enhances electrostatic attraction between the two, in addition to the increased hydrophobic interaction between hydrophobic parts of counterion and micellar interior. A counterion ordering is reported, with respect to clouding phenomenon. The effect of different classes of additives on CP (carbohydrate, amino acid or vitamin), has been found to be dependent on the nature and hydrophobicity of a typical salt and nature of head group. The work may find use in various applications such as metal extraction, solvent extraction, pollution control among others [39, 40].

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