CHAPTER V

Effect of Additives on the Phase Separation Behavior of Triblock Polymers and Tritons: A Cloud Point Study

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5.1 Introduction

Phase transition is an important physicochemical property of nonionic surfactants which significantly affects their self assembly behavior and consequently their selection for application in diverse fields like bioprocessing, agricultural and petrochemical industry etc.\textsuperscript{1-8} Phase transition phenomenon is preferable in certain applications especially related to the extraction processes as it is considered to be a convenient and environmentally safe alternative to extraction with organic solvents. Phase transition is a thermorheologically reversible process that is dependent upon balance between hydrophilic and hydrophobic interactions of the system and it can be induced with variation in temperature of the micellar solution. Critical temperature at which phase transition takes place is known as cloud point (CP) temperature.\textsuperscript{9} Cloud point study can prove to be an important tool for the estimation of shelf life and appropriate storage conditions required for nonionic surfactants based commercial and industrial products.

Several factors have been considered to be responsible for CP phenomenon like structure of surfactant molecule, concentration, temperature and the presence of third component known as additive. Additive modifies the clouding behavior of a nonionic surfactant as it effects the surfactant-solvent interactions by modifying solvent structure and the extent of solvation of the clouding species. It consequently affects other physicochemical properties of the micellar solution like critical micellar concentration (cmc), micellar shape and size. Acquiring knowledge of phase transition phenomena under varied thermal conditions therefore carries practical and theoretical interest as it induces dramatic changes in the physical properties and the performance of surfactant.

Study of interaction between nonionic surfactants and biomolecules as additives is the focus of current research as the surfactants are not only being employed as medium but are also being used as important constituents of systems that mimic living systems in vitro. In view of this, a number of research groups are actively engaged in revealing the secrets of surfactant-biomolecular interactions by investigating the additive effect of different biomolecules on physicochemical properties of surfactants.
Rakshit and Sharma\textsuperscript{10} have studied the effect of amino acids: glycine, alanine and valine on the physicochemical properties of decaoxyethylene dodecyl ether (C\textsubscript{12}EO\textsubscript{10}). They have reported depression in \textit{cmc} of the surfactant with increase in the concentration of amino acid. Sharma et al\textsuperscript{11} have studied the effect of amino acids i.e glycine, alanine and valine on the solution and morphological properties of nonaoxyethylene dodecyl ether (C\textsubscript{12}EO\textsubscript{9}) by tensiometric, small angle neutron scattering, dynamic light scattering and viscometric measurements. They have observed that the presence of amino acids lowers the clouding temperature and \textit{cmc} of C\textsubscript{12}EO\textsubscript{9} surfactant. With increase in the concentration of amino acid and temperature, increase in aggregation number of surfactant has been reported. In the concentration region studied, amino acids do not have much effect on the hydrodynamic radius.

Jan et al\textsuperscript{12} have studied the clouding phenomena of nonionic surfactant Triton-X-100 (TX-100) and its mixed systems with anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and cationic surfactant dodecylpyridinium chloride (DPC) in the presence of hydrophobic ions furnished by sodium salts of carboxylic acids viz. sodium ethanoate, sodium propanoate, sodium butanoate, sodium hexanoate and respective carboxylic acids like ethanoic acid, propanoic acid, butanoic acid and hexanoic acid. They have explained the influence of salts on the cloud point (CP) on the basis of salt effect as well as the solubilization of higher alkyl chain hydrophobic ions furnished by these salts. Counterion effect was also taken into account to explain the variation in CP of the mixed systems. Effect of acids on CP has been explained in the light of their aqueous solubility and their partitioning ability between octanol and water.

Sharma et al\textsuperscript{13} have studied the effect of sugars: (D-ribose, D-glucose and sucrose) on the micellar solution of nonionic surfactant decaoxyethylene dodecyl ether (C\textsubscript{12}EO\textsubscript{10}) at different temperatures 30 °C, 45 °C and 60 °C using small-angle neutron scattering measurements. By determination of various structural parameters like micelle shape and size, aggregation number and micellar density, they have reported that the micellar structure of surfactant significantly depends on the temperature and concentration of sugars. Micelles were found to be prolate ellipsoids at 30 °C and their axial ratio increased with increase in temperature and sugar concentration. Study infers
that the effect of sugar and temperature on C_{12}EO_{10} surfactant was additive, however, the micellar structure remains independent of the nature of sugars used.

Ali et al.\textsuperscript{14} have carried out volumetric, viscometric, refractive index, conductometric and fluorescence probe studies on the interaction of glycine with cationic surfactant hexadecyltrimethylammonium bromide (HTAB), anionic surfactant sodium dodecyl sulphate (SDS) and nonionic surfactant Triton-X-100 (TX-100) at different temperatures. Results indicate that ion-ion and ion-hydrophilic group interactions are dominant over hydrophobic-hydrophobic and hydrophilic-hydrophobic group interactions at temperatures 308.15 K and 313.15 K. At lower temperature, 298.15 K, hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions were reported to be dominating over ion-ion and ion-hydrophilic interactions in aqueous SDS/HTAB solutions. Similar behavior was observed in TX-100 solution and the sequence of strength of ion-ion or ion-hydrophilic interactions of glycine with the surfactant molecules in the solution was found to be SDS > HTAB > TX-100.

Murakani et al.\textsuperscript{15} have examined the effect of different sugars: sucrose, D-glucose, D-maltose on hydrophobic-lipophilic balance and cloud point of polyoxyethylene sorbitan monooleate (MOPS) and D-phase emulsification of triglyceride by MOPS. All these sugars have been reported to decrease the cloud point indicating the enhanced hydrophobicity of MOPS.

Yu et al.\textsuperscript{16} have studied the effect of amino acids on the micellization of HTAB by surface tension measurements. In the study, they have concluded that effect of additives depends on their nature and concentration at a fixed temperature. For glycine, alanine and serine, the steric effect was predominant over hydrophobicity during their interaction between themselves and with HTAB. Hydrophobicity and steric effect of alanine were reported to be stronger than glycine and was similar to serine. The cmc and surface tension at cmc of HTAB in the presence and absence of glycine decreased with increase in temperature. The cmc of HTAB in the presence of amino acids followed the order: alanine \approx serine > glycine. Thermodynamic parameters of micellization like negative free energy, largely positive enthalpy imply that there exists enthalpy-entropy compensation in the micellization of HTAB in the presence and absence of amino acids.
Li et al\textsuperscript{17} have studied the effect of various additives including inorganic salts, nonionic and ionic surfactants, water-soluble polymers and alcohols on the cloud point of nonionic surfactants, Tergitol 15-S-7, Tergitol 15-S-9 and Neodol 25-7. They have observed that ionic surfactants sodium dodecyl sulphate and hexadecyltrimethyl ammonium bromide in the micellar solution of 1 wt\% Tergitol 15-S-7 causes dramatic increase in its cloud point when concentration of ionic surfactants approach their critical micelle concentration. Addition of water-soluble polymers decreased the cloud point, while inorganic salts either increased or decreased the cloud point. Effect of alcohol as an additive on the cloud point was dependent on its chain length or water solubility.

Bharatiya et al\textsuperscript{18} have investigated the micellization of triblock polymer F88 (EO\textsubscript{104}PO\textsubscript{39}PO\textsubscript{104}) in the presence of lipophilic S104 (C\textsubscript{14}diol) using dynamic light scattering and small angle neutron scattering. They have observed that F88 remains molecularly dissolved at ambient temperature even at fairly high concentrations of 5 wt\% or more. Addition of S104 induces the micellization at lower concentration and the micellar growth is accompanied by enhancement in the aggregation number of triblock polymer.

Bhadane and Patil\textsuperscript{19} have studied clouding in non-ionic surfactant Brij-58 by measuring the cloud point of pure surfactant and its mixed system with alanine (Ala) and phenylalanine (PA). They have observed that CP of pure surfactant decrease with increase in Brij-58, Ala and PA concentration due to increase in micelle concentration. Phase separation results from micelle-micelle interaction support the macromolecule-surfactant interactions in aqueous medium.

Prasad et al\textsuperscript{20} have studied the effect of hydrotropes and glycols on the clouding behavior of nonionic surfactants TX-100, Brij-56, polyvinylmethyl ether and P85 (EO\textsubscript{26}PO\textsubscript{40}EO\textsubscript{26}). By evaluating thermodynamic parameters, they found that the enthalpy behavior of TX-100 is different from polyvinylmethyl ether and P85. Hydrotropes were found to decrease the cloud point of TX-100, Brij-56, polyvinylmethyl ether and P85, however, sodium cholate and salicylate increased the cloud point.
5.2 Present Work

In view of the importance of surfactant-biomolecular interactions, present study is focused on the investigation of additive effect of different biomolecules like amino acids, amino alcohols, sugars, hydroxy acids and dicarboxylic acids on the clouding behavior of Triblock polymers: L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13}), P84 (EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}) and Tritons: Triton-X-100 (TX-100) and Triton-X-114 (TX-114). Different systems studied are:

- L64/P84 + Amino Acids (Glycine, Proline, Valine, Serine, Threonine)
- L64/P84 + Dipeptides (Glycylglycine, Glycyl-DL-Valine)
- L64/P84 + Amino Alcohols (Leucinol, Isoleucinol, 2-Amino-1-butanol)
- L64/P84 + Sugars (Fructose, Sucrose, Maltose)
- L64/P84 + Hydroxy Acids (Citric acid, Lactic acid)
- L64/P84 + Dicarboxylic Acids (Succinic acid, Oxalic acid)
- TX-100/TX-114 + Amino Acids (Glycine, Proline, Valine, Serine, Threonine)
- TX-100/TX-114 + Dipeptides (Glycylglycine, Glycyl-DL-Valine)
- TX-100/TX-114 + Amino Alcohols (Leucinol, Isoleucinol, 2-Amino-1-butanol)
- TX-100/TX-114 + Sugars (Fructose, Sucrose, Maltose)
- TX-100/TX-114 + Hydroxy Acids (Citric acid, Lactic acid)
- TX-100/TX-114 + Dicarboxylic Acids (Succinic acid, Oxalic acid)

Triblock polymers (TBPs) and Tritons represent an important class of nonionic surfactant that possesses unique features like mild nature, structural polymorphism and self assembly behavior.\textsuperscript{21-29} In case of triblock polymers, systems have been chosen in such a way that the hydrophobicity of both the triblock polymers remains almost constant while their EO (polyethylene oxide) and PO (polypropylene oxide) units vary. Due to variation in EO and PO units, size of core and corona of the micelle vary. In case of Tritons (TX-100 and TX-114), system selection has been carried out on the basis of hydrophobicity variation.
5.3 Results and Discussion

Cloud point (CP) values of pure triblock polymers: L64, P84 and Tritons: TX-100, TX-114 at fixed concentration level of 1 wt% are in good agreement with their literature values\textsuperscript{30-32}. Effect of biologically important additives: amino acids, dipeptides, amino alcohols, sugars, hydroxy acids and dicarboxylic acids on the cloud point behavior has been investigated at the constant concentration of TBP and Tritons (1 wt%) by varying the additive concentration. Cloud point values for triblock polymers (TBPs) and Tritons in the pure state at fixed concentration of 1 wt% as well as in the presence of 0.5 mol dm\textsuperscript{-3} concentration of different biomolecules are given in Table 5.1.

5.3.1 Effect of Amino Acids on the Cloud Point of Triblock Polymers/Tritons

Amino acids (AA) are one of the simplest biomolecules that act as prototypes of complex biomolecules\textsuperscript{33,34}. In the present study, different amino acids (AA): glycine (Gly), proline (Pro), valine (Val), serine (Ser) and threonine (Thre) have been employed to study the additive effect on the cloud point of triblock polymers (L64/P84) and Tritons (TX-100/TX-114). Variation in cloud point of L64/P84 in the presence of amino acids has been given in Figure 5.1a-5.1b whereas variation in the cloud point of TX-100/TX-114 in the presence of amino acids has been given in Figure 5.2a-5.2b. In case of systems containing TBPs: L64/P84 and different amino acids: Gly/Pro/Val/Ser/Thre, amino acids cause CP of TBPs to appear at relatively lower temperature. The observed order for decrease in CP at the highest used concentration of 0.5 mol dm\textsuperscript{-3} of AA for L64 has been found to be: Gly > Pro > Thre > Ser > Val, whereas the corresponding order for P84 is Ser > Thre > Gly > Pro > Val as given in Table 5.1. In case of TX-100, except proline and serine all other amino acids initially increased the CP at lower concentrations used while at their higher concentration, a decrease in CP was observed. Proline and serine decreased the CP of TX-100 at all the concentrations used as shown in Figure 5.2a. For TX-100+AAAs system, trend observed for the CP decrease at higher concentration of AA was: Thre > Gly > Pro > Ser > Val. In case of TX-114+AA system, all the amino acids except serine initially caused an increase followed by a decrease in the CP with an increase in the concentration of amino acids. In TX-114+Ser system, CP has been found to be showing a decrease at all the concentrations of serine.
Figure 5.1 Plots of CP variations of (a) L64 (b) P84 in the presence of amino acids
Figure 5.2 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of amino acids
Table 5.1 CP values of triblock polymers (L64 and P84) and Tritons (TX-100 and TX-114) at highest concentration of additives (0.5 mol dm$^{-3}$)

<table>
<thead>
<tr>
<th>Additive</th>
<th>CP (K) of Nonionic surfactants</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L64 (331.2 K)$^*$</td>
<td>P84 (346.7 K)$^*$</td>
<td>TX-100 (339.7 K)$^*$</td>
<td>TX-114 (297.9 K)$^*$</td>
</tr>
<tr>
<td>Glycine (Gly)</td>
<td>320.6</td>
<td>330.4</td>
<td>334.1</td>
<td>295.1</td>
</tr>
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<td>Proline (Pro)</td>
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<td>334.1</td>
<td>336.6</td>
<td>292.2</td>
</tr>
<tr>
<td>Valine (Val)</td>
<td>325.1</td>
<td>336.9</td>
<td>337.6</td>
<td>299.3</td>
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<tr>
<td>Serine (Ser)</td>
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<td>328.9</td>
<td>337.3</td>
<td>290.7</td>
</tr>
<tr>
<td>Threonine (Thre)</td>
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<td>330.3</td>
<td>330.1</td>
<td>297.2</td>
</tr>
<tr>
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<td>328.5</td>
<td>330.9</td>
<td>296.2</td>
</tr>
<tr>
<td>Glycyl-DL-Valine</td>
<td>323.7</td>
<td>330.1</td>
<td>332.4</td>
<td>298.3</td>
</tr>
<tr>
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<td>358.3</td>
<td>305.4</td>
</tr>
<tr>
<td>Isoleucinol</td>
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<td>334.5</td>
<td>334.6</td>
<td>302.8</td>
</tr>
<tr>
<td>2-Amino-1-butanol</td>
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<td>343.1</td>
<td>353.1</td>
<td>309.5</td>
</tr>
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<td>333.9</td>
<td>341.7</td>
<td>297.8</td>
</tr>
<tr>
<td>Sucrose</td>
<td>326.2</td>
<td>330.2</td>
<td>343.4</td>
<td>293.1</td>
</tr>
<tr>
<td>Maltose</td>
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<td>331.9</td>
<td>344.9</td>
<td>298.6</td>
</tr>
<tr>
<td>Citric acid</td>
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<td>348.5</td>
<td>342.9</td>
<td>298.8</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>331.4</td>
<td>343.5</td>
<td>344.4</td>
<td>297.7</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>317.1</td>
<td>342.9</td>
<td>336.9</td>
<td>292.9</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>312.9</td>
<td>346.3</td>
<td>336.4</td>
<td>293.3</td>
</tr>
</tbody>
</table>

*Experimental value of pure TBP/Tritons
Decrease in CP for TX-114+AA system follows the order: Ser > Pro > Gly > Thre > Val. Results obtained for the above systems can be explained by considering the two factors which are effective in controlling the cloud point variation namely solvation capacity and hydrophobicity of micelles in the aqueous environment. The observed decrease in CP of TBPs/Tritons can be related to decreased solvation capacity of micelles in the presence of amino acids. Amino acids being zwitterionic possess high affinity for water molecules and are soluble in aqueous medium. In their mixed system, a competitive interaction exists between TBPs/Tritons and amino acids for the water molecules present around them. As a result, interaction between polyethylene oxide group (EO) of TBPs/Tritons and water molecules decreases. It leads to the dehydration of micelles of TBPs/Tritons that consequently reduces the CP of TBPs/Tritons+AA system. It clarifies the fact that additives which lower the solvation of micelles cause a decrease in CP. Results indicate that valine causes a minimum decrease in CP for all the systems investigated due to its least solubility in water. An initial increase in CP observed for Tritons at lower concentration of amino acids can be attributed to the presence of the insufficient amount of amino acids to attract water molecules from the micellar system and thereby water molecules remain primarily associated with EO groups of Tritons. It facilitates the solvation of Triton micelles and consequently increases its CP.

Results obtained for TBPs/Tritons+AA systems can also be explained in terms of hydrophobicity. Being hydrophobic in nature, amino acids tend to get incorporated into the interfacial layer that results into increase in hydrophobic interaction of TBP/Tritons to varying extents. However, observed cloud point variation is not in accordance with the order of hydrophobicity for different amino acids: Val > Gly > Thre > Ser > Pro. It is to be noted hereby that although TBPs: L64 and P84 have similar hydrophobicity, yet, order of CP variation on addition of amino acids is not same. Similarly, a relevant order is not obtained for Tritons with varying hydrophobicity. These observations reveal that hydrophobicity is not the only decisive criteria for cloud point variation but structural and orientation aspects of different constituents in the solution also account for this variation.
5.3.2 Effect of Dipeptides on the Cloud Point of Triblock Polymers/Tritons

Dipeptides act as building blocks for proteins and complex biological compounds with enzymatic activities.\textsuperscript{37-40} Effect of dipeptides glycylglycine (Gly-GLy) and glycyl-DL-valine (Gly-DL-Val) on the CP behavior of triblock polymer has been given in Figure 5.3a-5.3b while effect of dipeptides on the CP behavior of Tritons has been given in Figure 5.4a-5.4b. It is clear from Figure 5.3a-5.3b that decrease in CP caused by dipeptides is relatively more pronounced in case of P84 than L64. Relatively higher decrease obtained for P84 as compared to L64 can be accounted to the difference in micellar structure of these TBPs. Both the TBPs: L64 and P84 have similar hydrophobicity and percentage amount of EO content (EO\% = 40), but, PO core of P84 is relatively larger in comparison to L64. Larger PO core in P84 facilitates the solubilization of dipeptides in comparison to L64.

Increase in solubilization of dipeptides increases the hydrophobicity of the system and decrease in CP is observed for TBPs+Dipeptide systems. In case of L64+Dipeptide systems, order of decrease in CP at higher concentration of dipeptide is Gly-Gly > Gly-DL-Val. However, order gets reversed in P84+Dipeptide system. This reversal in order of CP decrease can be attributed to the increase in hydrophobicity of the system with increase in dipeptide concentration. In TX-100/TX-114+Gly-Gly systems, an initial increase in CP at lower concentrations is followed by decrease at higher concentration of dipeptides as shown in Figure 5.4a-5.4b. TX-100+Gly-DL-Val system exhibits a decrease in CP for all the concentrations investigated. However, CP decrease is not so prominent in TX-114+Gly-DL-Val system and an overall increase in CP is observed over complete concentration range of Gly-DL-Val. Anomalous behavior of TX-114+Gly-DL-Val system can be attributed to the inefficient packing of TX-114 and Gly-DL-Val in the mixed micelles. Although Gly-DL-Val has high hydrophobicity, yet, steric factors play dominant role and raise the CP of TX-114+Gly-DL-Val system. Variation in interaction of TX-100 and TX-114 with Gly-DL-Val is due to difference in values of their hydrophilic-lipophilic balance (HLB of TX-100=13.5, TX-114=12.4). It influences the surfactant-water interaction and promotes the hydrophobic interactions in the aqueous medium. Reduction in CP at higher concentration of dipeptides can be
Figure 5.3 Plots of CP variations of (a) L64 (b) P84 in the presence of dipeptides
Figure 5.4 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of dipeptides
explained in terms of an increase in hydrophobicity of the mixed system. Mutually different trend for CP variation followed by systems of TBPs and Tritons with dipeptides can be related to the structural differences between Tritons (polar head and nonpolar tail micellar structure) and TBPs (core and shell micellar structure).

5.3.3 Effect of Amino Alcohols on the Cloud Point of Triblock Polymers/Tritons

Amino alcohols are important constituents of cancer and HIV drugs. Figure 5.5a-5.5b and Figure 5.6a-5.6b represents the plots for additive effect of Leucinol, Isoleucinol and 2-Amino-1-butanol on the CP of triblock polymers: L64/P84 and Tritons: TX-100/TX-114 respectively. Decrease in CP of L64 on addition of amino alcohols has been observed over the complete concentration range with an order: Isoleucinol > Leucinol > 2-Amino-1-butanol as revealed from Figure 5.5a. In case of P84, isoleucinol has been found to be decreasing the CP over all the concentrations while, leucinol and 2-amino-1-butanol cause decrease in CP at low concentration as given in Figure 5.5b. However, at higher concentrations of leucinol and 2-amino-1-butanol, an abrupt rise in CP of P84 is observed. On an average, decrease in CP is observed for P84+2-Amino-1-butanol system. Addition of amino alcohol to TX-100/TX-114 causes CP to appear at higher temperature over complete concentration range with an exception of TX-100+Isoleucinol system where a decrease in CP is obtained as shown in Figure 5.6a-5.6b. Observed CP variation can be explained on the basis of polar nature of amino alcohols and their tendency to form hydrogen bond with water molecules. Due to this property of amino alcohols, availability of non-associated water molecules for the hydration of EO groups decreases that result in lowering of CP. In L64, this lowering occurs over the complete concentration range, however, in P84, similar behavior is observed only at lower concentrations of amino alcohols. At higher concentrations of amino alcohols in P84 system, steric hindrance produced by excess amino alcohol molecules raises the CP of system. A continuous increase in the CP for Tritons can be attributed to the tendency of amino alcohols to provide the sufficient polar medium which increases the solubility of Tritons in aqueous medium and consequently rise in CP is observed. Leucinol and isoleucinol form hydrogen bond with water molecules that causes dehydration of EO groups and lowers the CP.

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Figure 5.5 Plots of CP variations of (a) L64 (b) P84 in the presence of amino alcohols
Figure 5.6 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of amino alcohols
However, due to structural differences, this interaction is developed to varying extents in TX-100 and TX-114. This differential behavior ultimately results in decrease in CP of TX-100+Isoleucinol and increase in CP of TX-114+Isoleucinol system. Besides this, lower solubility of TX-114 in comparison to TX-100 also affects the CP behavior of Tritons+Isoleucinol system. Due to differential solubility, similar results are not obtained for variation in CP of TX-100 and TX-114.

5.3.4 Effect of Sugars on the Cloud Point of Triblock Polymers/Tritons

Sugars constitute an important part of complex biological systems. Additive effect of sugars: fructose, sucrose and maltose on the cloud point of triblock polymers (L64/P84) has been given in Figure 5.7a-5.7b while effect of sugars on the cloud point of tritons (TX-100/TX-114) has been given in Figure 5.8a-5.8b. Variation in CP of triblock polymer systems reflects water structure influencing tendency of these sugars. Continuous decrease in CP of TBP, with an increase in concentration of sugar has been observed as shown in Figure 5.7a-5.7b. It can be accounted to the introduction of sugar molecules into the micellar core that strengthens hydrophobic interactions and cause micellar growth. As micellar size increases, water solubility of surfactant decreases and phase separation takes place comparatively at lower temperature. In other words, dehydration of EO groups of triblock polymers take place at comparatively lower temperature thus lowering their CP. In case of TX-100/TX-114+Sugar system, there is an initial increase in CP at low concentration of sugar, however, further increase in the concentration of sugar decreases the CP. In case of TX-100/TX-114+Sugar system, an overall increase in the CP is observed except for TX-114+Sucrose system. In TX-100/TX-114+Sucrose systems, comparatively larger decrease in CP with increase in concentration of sucrose is observed for TX-114 than TX-100. Results for TX-100/TX-114+Sugar systems indicate that sugar molecules are contributing to the solvation of micelles at lower concentrations and promoting the desolvation at higher concentrations. At low concentration, orientation of constituents in the micelle might be the reason behind inefficient packing that causes an increase in the CP of the system.
Figure 5.7 Plots of CP variations of (a) L64 (b) P84 in the presence of sugars
Figure 5.8 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of sugars
5.3.5 Effect of Hydroxy Acids on the Cloud Point of Triblock Polymers/Tritons

Presence of hydroxy acids in shampoos, cosmetics, soaps and detergents improve their physicochemical properties. Citric acid and lactic acid are frequently used for the preparation of these products. Additive effect of these hydroxy acids on the CP of triblock polymers: L64/P84 has been shown in Figure 5.9a-5.9b while effect of hydroxy acids on Tritons: TX-100/TX-114 has been given in Figure 5.10a-5.10b. Plots for triblock polymers reveal that CP of L64+Hydroxy acid systems initially decreases and then increases as concentration of hydroxy acids increases in the bulk. At higher concentration, these hydroxy acids behave as water structure breakers and lead to increase in CP. Observed order of increase in cloud point is: Lactic acid > Citric acid as shown in Table 5.1. Addition of hydroxy acids provide sufficient polar medium for the hydration of EO group in TBPs which increases their CP. Similar behavior has been observed for P84+Hydroxy acids systems, but, order gets reversed. These observations may be attributed to the different PO and EO units present in L64 and P84. It was observed that hydroxy acids increase the CP of TX-100 over complete concentration range. However, CP of TX-114 initially decreases and then increases with an increase in concentration of hydroxy acids. CP variation observed in Tritons clearly reflects the influence of hydrophobicity of surfactants on the surfactant-hydroxy acid interactions as TX-114 is more hydrophobic than TX-100.
**Figure 5.9** Plots of CP variations of (a) L64 (b) P84 in the presence of hydroxy acids
Figure 5.10 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of hydroxy acids
5.3.6 Effect of Dicarboxylic Acids on the Cloud Point of Triblock Polymers/Tritons

Dicarboxylic acids find use in a variety of industrial applications in perfumery, biodegradable solvents, lubricants, adhesives, powder coatings, pharmaceuticals and corrosion inhibitors.\textsuperscript{45,46} Additive effect of dicarboxylic acids: succinic acid, oxalic acid on CP of triblock polymers: L64/P84 has been shown in Figure 5.11a-5.11b while effect of dicarboxylic acids on Tritons: TX-100/TX-114 has been shown in Figure 5.12a-5.12b. For TBP/Tritons+Dicarboxylic acid systems, decrease in CP was observed over the complete concentration range except for P84+Oxalic acid system. In P84+Oxalic acid system, CP initially increases and then decreases with an increase in concentration of oxalic acid. On the other hand, P84+Succinic acid system displays initial decrease and then increase in CP with an overall decrease as shown in Figure 5.11b. In L64+Dicarboxylic acid system, CP decreases but variation remains more or less constant with increase in concentration of dicarboxylic acid as shown in Figure 5.11a. CP of TX-100 decreases at all the concentrations of dicarboxylic acid and decrease was more for oxalic acid than succinic acid as given in Table 5.1. Reversal in the order of CP decrease is observed for TX-114+Dicarboxylic acid system. Decrease in CP of TBP/Tritons+Dicarboxylic acid systems is due to tendency of dicarboxylic acids to form hydrogen bond with water molecules that decreases the availability of water molecules to hydrate the micelles and lowers the CP. Reversal in the order of CP decrease on shifting from TX-100 to TX-114 in Tritons+Dicarboxylic acid systems can probably be due to variation in hydrophobicity of Tritons. Observed anomalous behavior of L64/P84+Oxalic acid systems can be accounted to the less hydrophobic environment provided by oxalic acid in comparison to succinic acid.
Figure 5.11 Plots of CP variations of (a) L64 (b) P84 in the presence of dicarboxylic acids
Figure 5.12 Plots of CP variations of (a) TX-100 (b) TX-114 in the presence of dicarboxylic acids
5.4 Conclusions

In the present work, we have investigated the cloud point behavior of triblock polymers (TBP): L64/P84 and Tritons: TX-100/TX-114 in the presence of biomolecules as additives. Among various biomolecules employed as additives, amino acids were found to be promoting desolvation of micelles of triblock polymers over the complete concentration range and cause a decrease in CP. However, Tritons exhibited decrease in CP at higher concentrations of amino acids except for proline and serine, where a continuous decrease in CP has been observed. Dipeptides have been found to be causing an increase in micellar core of the triblock polymers that disturbs hydrophilic-lipophilic balance of the system and ultimately lead to decrease in CP of the system. Despite similar hydrophobicity of L64 and P84, decrease in CP caused by dipeptides is relatively more in P84 than L64 system due to larger PO core of P84. TX-100/TX-114+Gly-Gly systems, exhibit increase in CP at lower concentrations and decrease at higher concentration of dipeptides. TX-100+Gly-DL-Val system exhibits a decrease in CP for all the concentrations investigated while in TX-114+Gly-DL-Val system an overall increase in CP is observed over complete concentration range. Presence of amino alcohols lowers the CP of triblock polymers L64 over the complete concentration range of amino alcohols while in P84 decrease is observed at low concentration of amino alcohols. A continuous increase in the CP for Tritons in the presence of amino alcohols can be attributed to the tendency of amino alcohols to provide the sufficient polar medium which increases the solubility of Tritons in aqueous medium and consequently rise in CP is observed. Sugar brings variation in hydrophobicity and solvation/desolvation properties of the micellar systems and decreases the CP of TBP/Tritons. Higher concentration of hydroxy acids increases the CP of TBP/Tritons due to an increase in polarity of the medium. Dicarboxylic acids have tendency to form hydrogen bond with water molecules and were found to decrease the CP of TBP/Tritons+Dicarboxylic acid systems over the complete concentration range with exception of P84+Oxalic acid system. It can possibly be due to variation in the hydrophobicity of system. Results discussed above reveal that molecular associations (micellar structure), orientation aspects and hydrophobicity of the system collectively augment the process of clouding.
References


7. N.A. Smirnova, Russian Chemical Review 74, 2005, 129-144.


