CHAPTER IV

Aggregation Behavior of Benzalkonium Chloride with Triblock Polymers: Surface Tension, Dynamic Light Scattering, Viscosity and Small Angle Neutron Scattering Studies

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4.1 Introduction

Appearance of surfactant-triblock polymer mixtures in numerous commercial formulations has raised interest in their microstructure and mixing behavior. Synergistic mixing of surfactant-triblock polymer mixtures has been extensively exploited for the synthesis of nanostructured materials, micellar catalysis and targeted delivery of therapeutics.\textsuperscript{1-6} In the field of nanotechnology, it is a common practice to incorporate ionic surfactants in the polymeric micellar core to reverse their inherent nonpolar characteristic properties and facilitate their application as nanoreactors for engineering of nanoscale metal colloids. Appealing physicochemical and rheological properties of surfactant-triblock polymer mixtures in aqueous media have also been extensively employed in flow field regulators, emulsification and membrane mimetic media.

In literature, most of the surfactant-polymer mixtures reported are usually composed of surfactant and polyelectrolyte mixtures, however, mixed systems of cationic surfactants with polymeric nonionic surfactants especially triblock polymers have been comparatively less explored.\textsuperscript{7,8} Cationic surfactants play significant role in the biological systems and are employed for commercial applications like corrosion inhibition, road pavement and food industry.\textsuperscript{9,10} Due to inherent diversity in their molecular architecture, triblock polymer colloids offer great potential for creating tailor-made micellar assemblies. Cationic surfactant-triblock polymer mixed systems may associate into different microstructures that will affect their functional properties.\textsuperscript{11-14} Coalescence of nontoxic and biodegradable nature of triblock polymers with antiseptic properties of cationic surfactants in their mixed systems might also pave the way for mitigating the adverse impact of surfactants on the environment and reduce their allergic reactions to the skin. It is well known in literature that polymer bound surfactant micelles restrain higher solubilization power and viscosity that carries immense value in the formulation of medicines, cosmetic products, paints, coatings and related applications.\textsuperscript{15-19} Keeping in view the fascinating properties exhibited by the cationic surfactant-triblock polymer mixed systems, it becomes important to investigate the interactions controlling their structural and functional behavior and a number of research groups are therefore actively engaged in this field of research.
Silva et al\textsuperscript{20} have studied the interaction of triblock polymers: L121 (EO_{5}PO_{68}EO_{5}), P123 (EO_{20}PO_{70}EO_{20}), F127 (EO_{97}PO_{69}EO_{97}) with ionic surfactants: sodium dodecyl sulphate (SDS) and hexadecyltrimethylammonium chloride (HTAC) in the dilute aqueous solution using differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC). It has been reported that the polymers L121, P123 and F127 aggregate in dilute solution to form micelles, while the aggregates of most hydrophobic polymer L121 got eventually separated into liquid crystalline phase. Addition of SDS to P123 and L121 increased the aggregation temperature whereas in F127 system, a reverse effect was observed at initial stages. DSC curve peak too was initially flattened at low concentration of SDS and then disappeared. However, addition of HTAC to triblock polymer solution exhibited no significant effect on the aggregation temperature whereas transition peak decreased and disappeared at 2-3 mM.

Schillen et al\textsuperscript{21} have investigated the mixed micellization of triblock polymer P123 with nonionic surfactant hexaoyxyethylene dodecyl ether (C_{12}EO_{6}) using dynamic and static light scattering techniques. Within temperature range 25 °C - 45 °C, they have reported variation in size and structure of mixed micelles with change in surfactant/polymer ratio. For the investigated temperatures and C_{12}EO_{6}/P123 molar ratios, mixed micelle size decreased with increase in surfactant content up to molar ratio 12. Mixed micelles in the lower molar ratio regime were reported to be spherical that do not grow with concentration. Above molar ratio 48, structural change in the mixed micelles was observed along with concentration induced growth dominated by surfactant characteristics. This behavior was more pronounced at higher temperature.

Brigante and Schulz\textsuperscript{22} have investigated aggregation and adsorption of mixed systems composed of triblock polymer F68 (EO_{77}PO_{29}EO_{77}), F127 (EO_{97}PO_{69}EO_{97}) with cetyltrimethylammonium tosylate (CTAT) using conductivity, surface tension and dye solubilization techniques. They have interpreted non-ideal behavior for F68+CTAT and F127+CTAT mixtures, but in a different manner in both cases. Aggregates of F68+CTAT mixed system were reported to be more close to CTAT micelles having F68 as a solubilizate than the inverse. At low CTAT content, the interaction was repulsive becoming attractive at high F68 content. Aggregates of F127+CTAT mixed system
were different from the structure of both pure component micelles and the interaction was repulsive. In adsorbed monolayers formation both systems how different behavior as in case of F68+CTAT mixed system as shown in their aggregate formation.

Mahajan et al\(^{23}\) have investigated aggregation behavior of cationic surfactants hexadecyltrimethylammonium bromide: HTAB, tetradecyltrimethylammonium bromide: TTAB, Brij-35 with triblock polymers L64 (EO\(_{13}\)PO\(_{30}\)EO\(_{13}\))/F127 (EO\(_{97}\)PO\(_{69}\)EO\(_{97}\)) using cyclic voltammetric technique. They have observed that the mixed micelles were rich in triblock polymer component in the ionic surfactant rich region of the mixture. Formation of mixed micelles in these systems was reported to be due to the synergistic interactions which were more intense in F127 system than L64. Interactions observed in L64/F127+HTAB/TTAB mixed systems were reported to be stronger than the interactions in Brij-35+HTAB/TTAB mixed systems. In another study, they have investigated mixed micellization of monomeric cationic surfactants: HTAB and TTAB, dimeric cationic gemini surfactants: dimethylene bis(tetradecyldimethyl ammonium bromide) (14-2-14) and dimethylene bis(hexadecyldimethylammonium bromide) (16-2-16) with Triton-X-100 (TX-100) and F68 (EO\(_{77}\)PO\(_{29}\)EO\(_{77}\)) in the presence of 0.1 M KCl using cyclic voltammetric measurements.\(^{24}\) They have reported synergistic mixing of both the monomeric cationic surfactants and dimeric gemini surfactants with TX-100/ F68. These interactions were found to be stronger in mixed systems containing triblock polymer F68 in comparison to TX-100. Better synergism was exhibited by the system containing triblock polymer F68 and the cationic gemini surfactants 14-2-14/16-2-16.

Vieira et al\(^{25}\) have reported the micellization and adsorption behavior at air-solution interface for the binary mixtures of triblock polymer EO\(_{23}\)PO\(_{52}\)EO\(_{23}\) with sodium dodecyl sulphate (SDS), dodecyltrimethylammonium bromide (DTAB) and tetraethyleneglycol mono-octyl ether (C\(_8\)EO\(_4\)) using neutron reflectivity and surface tension techniques. They have reported synergistic interactions in the binary mixture of EO\(_{23}\)PO\(_{52}\)EO\(_{23}\)+SDS/DTAB while EO\(_{21}\)PO\(_{52}\)EO\(_{23}\)+C\(_8\)EO\(_4\) mixture exhibited strong repulsive interactions.
Zhang et al.\textsuperscript{26} have carried out surface tension studies on the binary mixtures of nonionic surfactant, hexaoxyethylene dodecyl ether (C\textsubscript{12}EO\textsubscript{6}) and cationic surfactant, tetradecyltrimethylammonium bromide (TTAB) with triblock polymer F127 and its poly(vinyl pyrrolidone) grafted (g-PVP) derivatives: F127(PO)-g-PVP and F127(EO)-g-PVP. In all cases, mixed micellar aggregates were formed and interaction parameter from regular solution theory was reported to be indicating the synergistic behavior. Results also indicated that grafting of more hydrophobic PVP component increases synergistic interactions between polymer and cationic/nonionic surfactant.

Singh et al.\textsuperscript{27} investigated interaction of cationic surfactant hexadecyltrimethyl ammonium bromide (HTAB) with triblock polymers F88 (EO\textsubscript{104}PO\textsubscript{39}EO\textsubscript{104}) and P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}). Using time-resolved fluorescence and small angle neutron scattering studies, authors investigated the impact of these interactions on the location of anionic solute in the mixed micelles. It has been reported that the addition of HTAB to the micellar solution of triblock polymers results in the formation of supramolecular assemblies wherein the hydrocarbon chain of HTAB resides in the core of triblock polymer micelle and head group of HTAB resides at core-corona interface. Thus formed positively charged layer in the mixed micelles pulls anionic probe from the micellar surface to the interior. Concentration of surfactant required for dragging the probe molecule from micellar surface to the core-corona interface was reported to be varying linearly with the thickness of corona region of the micelle.

Kumar et al.\textsuperscript{28} have investigated the influence of triblock polymer P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) on the aggregation behavior of anionic surfactant sodium dodecyl sulphate (SDS) in aqueous solution using NMR, self-diffusion and nuclear spin-relaxation techniques. They have observed triblock polymer-surfactant interactions in distinct regimes of SDS. At lower and intermediate concentration of SDS, polymeric micelles interact strongly with SDS monomers, while, at higher concentrations these interactions were weakened. It has been reported that micelle formation of SDS was facilitated by the presence of triblock polymer P123, as manifested from notable
decrease in the *cmc* of SDS, whereas, ionic surfactant at higher concentrations disrupted the polymer network.

Li et al.\textsuperscript{29} have studied the aggregation behavior of triblock polymer EO\textsubscript{77}PO\textsubscript{29}EO\textsubscript{77} (F68) with sodium dodecyl sulphate (SDS) and sodium bis(2-ethylhexyl)sulfo succinate (AOT) by surface tension, fluorescence and dynamic light scattering (DLS) measurements. They have observed that addition of SDS to solutions of F68 generates two transition points in surface tension isotherms, corresponding to the beginning and the end of surfactant binding on F68. However these two transition points were observed in AOT/F68 system, at higher concentration of F68. It has been reported that presence of F68 induced more pronounced effect on the micropolarity of AOT micelle than SDS. DLS study of these systems inferred that micellar size get enhanced on addition of surfactants in triblock polymer solution. They found that SDS interacts with F68 mainly through hydrophobic forces and form pearl-necklace complex structure, however F68/AOT complex at lower F68 concentration, interacts mainly through ion-dipole interactions and form complexes with a wrapping structure.

Mata et al.\textsuperscript{30} have reported cloud point, surface tension, viscosity and dynamic light scattering studies on the solution of triblock polymer P105 (EO\textsubscript{36}PO\textsubscript{57}EO\textsubscript{36}) with anionic surfactant, sodium dodecyl sulphate (SDS) and cationic surfactant, dodecyl trimethylammonium bromide (DTAB) in the presence and absence of sodium bromide. They observed that addition of sodium bromide to the polymer decreases cloud point, increases surface activity and shifts micellization to lower concentration. DLS results revealed that the presence of ionic surfactant at concentration below its *cmc* value leads to demicellization of polymer P105. Furthermore, in the presence of sodium bromide, more surfactant is needed for demicellization of P105 micelles. Surface tension study on P105-ionic surfactant indicated stronger interaction with SDS as compared to DTAB and these interactions were diminished in the presence of sodium bromide.

### 4.2 Present Work

In continuation of our search for new surfactant mixtures with desired properties,\textsuperscript{23,24,31} present work reports the micellization behavior of cationic surfactant
benzalkonium chloride (BC) with triblock polymers (TBPs). Selection of surfactants in the present study was made on the basis of their indispensable usage in commercial and daily-life products.\textsuperscript{32-41} Benzalkonium chloride used in the present study, is an integral component of a wide range of commercial products ranging from household disinfectant formulations to the industrially useful microbial and corrosion inhibition formulations.\textsuperscript{42} Second component of the study i.e. triblock polymers are nonionic polymeric surfactants which are biocompatible in nature as well as efficient solubilizers of the active agents. Triblock polymers find significant use in scientific, biomedical and industrial applications.\textsuperscript{43-46} Triblock polymers used for the study were F127 (EO\textsubscript{97}PO\textsubscript{69}EO\textsubscript{97}), P105 (EO\textsubscript{36}PO\textsubscript{57}EO\textsubscript{36}), L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13}) and P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}). Selection of different TBPs has been made on the basis of their polypropylene oxide (PO) and polyethylene oxide (EO) units. Surface tension, dynamic light scattering (DLS), viscometric and small angle neutron scattering (SANS) techniques have been employed to study the mixing behavior of these cationic surfactant-triblock polymer mixtures. Cationic surfactant-triblock polymer combinations studied in this study are as follows:

\begin{align*}
\text{Benzalkonium chloride+P123} & \quad \text{Benzalkonium chloride+P105} \\
\text{Benzalkonium chloride +L64} & \quad \text{Benzalkonium chloride+F127}
\end{align*}

Interaction of benzalkonium chloride (BC) with different triblock polymers (P123, P105, L64, F127) has been investigated in the presence of 0.1 mol dm\textsuperscript{-3} KCl at 303.15 K. Surface tension measurements have been carried out to evaluate the critical micelle concentration (cmc) and associated interaction parameters for the proposed binary mixtures. Dynamic light scattering (DLS) and small angle neutron scattering (SANS) techniques have been employed to elucidate the microstructure of these binary mixtures. DLS study yields information about average dimensions of the micelles by measuring mutual diffusion coefficient (D) and calculating the effective hydrodynamic diameter ($D_h$). SANS has been used to determine the micellar shape and size from scattering intensity measurements. Viscometric investigations were carried out for these systems so as to get an insight of micellar size variation.
4.3 Results and Discussion

4.3.1 Critical Micelle Concentration

Critical micelle concentration (cmc) values in present study have been computed from the breakpoint in the plots of surface tension (γ) versus Log of surfactant concentration. Figure 4.1 shows representative plots of surface tension versus Log of surfactant concentration for pure components BC and P123 and their binary mixture BC+P123 at two mole fractions of BC (a_{BC} = 0.4, 0.8) in the presence of 0.1 mol dm\(^{-3}\) KCl. Similar plots have been obtained for other mixed systems: BC+P105/L64/F127 (plots not shown). Analysis of cmc data obtained for pure components indicates reduction in cmc value of BC in the presence of 0.1 mol dm\(^{-3}\) KCl, whereas, cmc values for TBPs are comparatively less affected and match closely with literature values.\(^{42,47,48}\)

![Figure 4.1 Representative plots of surface tension vs Log [Surfactant] / mol dm\(^{-3}\) for pure components (BC/P123) and BC+P123 binary mixture at two mole fractions of BC (a_{BC} = 0.4, 0.8)](image-url)
The decrease in cmc of cationic surfactant (BC) in presence of salt is attributable to screening effect of salt on the electrostatic repulsions between surfactant head groups in the micelle.\textsuperscript{40} However, in nonionic polymeric surfactants (TBPs), reduction in cmc value is comparatively smaller due to weak salting out effect.\textsuperscript{47} Figure 4.2 shows that observed cmc values for the mixed micelles of BC with TBPs (P123/P105/L64/F127) lie within cmc range for pure ones. Experimental cmc values were correlated to the corresponding ideal state mixed cmc values simulated on the basis of Clint equation\textsuperscript{49} Eq. 4.1

\[
\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \left(1 - \frac{\alpha_1}{cmc_2}\right) \\
\text{………… (4.1)}
\]

where cmc\(^*\) is the ideal state mixed cmc, \(\alpha_1\) is mole fraction of the first component BC, cmc\(_1\) and cmc\(_2\) are the cmc values for first component BC and second component TBPs (P123/P105/L64/F127) respectively. Experimental cmc and ideal cmc\(^*\) values for various mole fractions of BC (\(\alpha_\text{BC}\)) have been represented in Figure 4.2. From the plots in Figure 4.2a-4.2b, it is clear that cmc values lie lower than ideal cmc\(^*\) values for the investigated binary mixtures BC+P105/L64 and BC+P123/F127. Negative deviation in cmc from ideal cmc\(^*\) values indicates favorable mixing of surfactants in these binary mixtures. Occurrence of mixed micellization at lower concentration can be attributed to the weakening of head group repulsions in BC as triblock polymer intercalates between charged head groups of the surfactant molecules. The cmc values for different binary compositions of these mixtures show an increase with increase in mole fraction of BC although it remains lower than ideal cmc\(^*\) values. This can be related to the steric factor that comes into force on account of the bigger head group of BC. At higher mole fraction of BC, this steric factor leads to comparatively inefficient packing of the constituent surfactant molecules in the mixed state than in the pure micelles.
Figure 4.2 Plots of $cmc$ (experimental) and $cmc^*$ (predicted from Clint equation) vs $\alpha_{BC}$ for (a) BC+P105/L64 and (b) BC+P123/F127 systems
4.3.2 Interaction Parameter and Mixed Micellar Composition

Micellar composition and interaction parameter ($\beta^m$) values were evaluated in the light of Regular Solution Approximation using Eq. 4.2 and Eq. 4.3.

\[
\frac{X_{1}^m \ln(\text{cmc}_{1}/X_{1}^m)}{(1-X_{1}^m)^2 \ln(\text{cmc}(1-\alpha_1)/\text{cmc}_2(1-X_{1}^m))} = I \quad \text{......... (4.2)}
\]

\[
\beta^m = \frac{\ln(\text{cmc}_{12}/\text{cmc}_1X_{1}^m)}{(1-X_{1}^m)^2} \quad \text{......... (4.3)}
\]

where, $X_{1}^m$ is the mole fraction of component 1 (BC) in the total mixed micellar system, $\alpha_1$ is the mole fraction of component 1 (BC) in the total mixed micellar solution and all other terms carry their usual meanings. Mole fraction in the ideal state ($X_{\text{ideal}}$) has been calculated using Eq. 4.4.51

\[
X_{\text{ideal}} = \left[ \frac{\alpha_1 \text{cmc}_2}{\alpha_1 \text{cmc}_2 + (1-\alpha_1) \text{cmc}_1} \right] \quad \text{......... (4.4)}
\]

Extent of interaction between two components in the mixed micelles at a particular mixing ratio can be determined from the appearance of azeotropic phenomena in phase diagram. Plots in Figure 4.3a-4.3d reveal that azeotropic point for the proposed binary mixtures of BC with TBPs (P123/P105/F127) lies at lower mole fraction of BC with the exception of BC+L64 system. Appearance of azeotropic point at lower mole fraction of BC in BC+P123/P105/F127 can be explained on the basis of incorporation of TBP into BC micelle that not only reduces the head group repulsions of BC but also increases its hydrophobicity in comparison to the micelles of pure component. For cationic-nonionic mixed surfactant systems, electrostatic self repulsion of cationic and steric self repulsion of nonionic surfactant undergo significant reduction on mixing by dilution effects.52 After dilution, the electrostatic self-repulsions in the cationic surfactants are probably replaced by attractive ion-dipole interaction between hydrophilic groups of the cationic surfactant (BC) and TBPs. Figure 4.4 represents variation in $X_{i}^m$ and $X_{\text{ideal}}$ with respect to mole fraction of BC and throws light on the micellar composition in the mixed state.
Figure 4.3  Plots of $cmc$ vs $\alpha_{BC}$, $cmc$ vs $X_1^m$ and $cmc^*$ vs $\alpha_{BC}$ for various mixed systems (a) BC+P123 (b) BC+L64 (c) BC+P105 and (d) BC+F127
Figure 4.4 Plots of $X_1^m$ and $X_{ideal}$ vs $\alpha_{BC}$ for BC+P123, BC+P105, BC+L64 and BC+F127 mixed systems

Keen observation of the plots in Figure 4.4 makes it clear that $X_1^m$ values for BC+F127 system display positive deviation upto 0.40 mole fraction of BC and negative deviation at higher mole fraction of BC. For binary mixtures BC+P105/P123, $X_1^m$ remains higher than ideal micellar mole fraction values ($X_{ideal}$) over the complete mixing range. Higher value of $X_1^m$ indicates predominance of the first component (BC) in the mixed micelles and lower value means mixed micelle is richer in the second component (TBP). For BC+L64 system, $X_1^m$ remains lower than $X_{ideal}$ over complete mixing range indicating predominance of L64 in the mixed micelle. This exceptional behavior of BC+L64 system can be accountable to the smaller EO and PO units in L64 (EO=13;
PO=30) that allows L64 monomers to penetrate into mixed micelle more efficiently in comparison to other TBPs with comparatively larger EO and PO units. These results have been correlated to variation in $\beta^m$ parameter for the proposed binary mixtures and presented in Figure 4.5.

![Figure 4.5 Plots of $\beta^m$ vs $\alpha_{BC}$ for binary mixtures: BC+P123, BC+L64, BC+P105 and BC+F127](image)

Values of activity coefficients $f_{1m}$ and $f_{2m}$ for both components are given in Table 4.1. These are related to interaction parameters $X_{i}^{m}$ and $\beta^m$ through Eq. 4.5 and Eq. 4.6.

$$f_{1m} = \exp\left\{\beta^m\left(1 - X_{1}^{m}\right)^2\right\}$$  \hspace{1cm} \text{(4.5)}

$$f_{2m} = \exp\left\{\beta^m\left(X_{2}^{m}\right)^2\right\}$$  \hspace{1cm} \text{(4.6)}
Activity coefficient values the mixed micelles are less than unity that supports the existence of synergistic interactions between BC and TBP in the mixed state. Value of interaction parameter $\beta^m$ comes out to be negative for all the binary mixtures of BC with TBPs (P123/L64/P105/F127) studied in the present work. The negative value of $\beta^m$ indicates synergistic mixing of the two components in the mixed state. It can be attributed to the curtailing of self-repulsive forces and emergence of ion dipole interactions after mixing.\textsuperscript{52} With an increase in mole fraction of BC, interaction parameter $\beta^m$ becomes less negative which indicates enhancement of repulsive and steric factors due to bulky head group of BC.

### 4.3.3 Interfacial and Thermodynamic Properties

The values of surface excess ($\Gamma_{\text{max}}$) and minimum surface area ($A_{\text{min}}$) were calculated using Eq. 4.7 and Eq. 4.8\textsuperscript{53} respectively and are summarized in Table 4.1.

\[
\frac{d\gamma}{d \ln c} = -nRT\Gamma_{\text{max}} \tag{4.7}
\]

\[
A_{\text{min}} = \frac{1}{\Gamma_{\text{max}}N_A} \tag{4.8}
\]

where, $\gamma$ is the surface tension (mNm\textsuperscript{-1}), $R$ is gas constant, $T$ is the temperature (Kelvin), $c$ is the surfactant concentration, $N_A$ is the Avogadro number and $n$ are the number of species at the air/solution interface. Here value of $n$ was taken unity for pure as well as mixed systems due to the presence of electrolyte (0.1 mol dm\textsuperscript{-3} KCl). It has been observed that $\Gamma_{\text{max}}$ values for mixed micelles are greater than the corresponding $\Gamma_{\text{max}}$ values for pure BC (except in BC+L64 system) indicates that the said mixed systems possess more adsorbing tendency at the interface which in turn favors micellization in the bulk solution. The minimum surface area per molecule ($A_{\text{min}}$) of the mixed micelle remains lower than $A_{\text{min}}$ for the pure BC. It is accountable to an increase in the hydrophobicity of mixed micelles due to progressive charge shielding and closer packing of BC and TBP mixed systems.
Table 4.1 Micellar activity coefficients \((f_1^m, f_2^m)\), interfacial parameters \((\Gamma_{\text{max}}, A_{\text{min}}, \pi_{\text{cmc}})\) and thermodynamic properties \((\Delta G_m, \Delta G_{\text{ex}}, \Delta G_{\text{ads}})\) for mixed surfactant systems: BC+TBPs at 303.15 K

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<th>System</th>
<th>(\alpha_{BC})</th>
<th>(f_1^m)</th>
<th>(f_2^m)</th>
<th>(\Gamma_{\text{max}}/10^6) (mol m(^{-2}))</th>
<th>(A_{\text{min}}) (Å(^2))</th>
<th>(\pi_{\text{cmc}}) (mN m(^{-1}))</th>
<th>-(\Delta G_m) (kJ mol(^{-1}))</th>
<th>-(\Delta G_{\text{ex}}) (kJ mol(^{-1}))</th>
<th>-(\Delta G_{\text{ads}}) (kJ mol(^{-1}))</th>
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<td>0.87</td>
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<td>36.2</td>
<td>30.1</td>
<td>-</td>
<td>42.4</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Among all the systems studied, lowest $A_{\text{min}}$ value has been calculated to be $33.3\text{Å}^2$ for BC+P123 system suggesting the closest possible packing of BC+P123 monomers at air/water interface. The low values of $\Gamma_{\text{max}}$ and high values of $A_{\text{min}}$ exhibited by BC+L64 mixed system indicate loose packing in the mixed micelles with relatively high charge density. Values of surface pressure ($\pi_{\text{cmc}}$) for different mixed systems of BC with different TBPs at their $cmc$ points have been calculated from Eq. 4.9\textsuperscript{53} and are given in Table 4.1.

$$\pi_{\text{cmc}} = \gamma_o - \gamma_{\text{cmc}} \quad \text{.............(4.9)}$$

where, $\gamma_o$ is the surface tension of the solvent and $\gamma_{\text{cmc}}$ is the surface tension at $cmc$. BC+TBP mixed systems (Table 4.1) exhibit higher values of surface pressure ($\pi_{\text{cmc}}$) than pure BC, which reflect their effectiveness in surfactant based applications. Free energy of micellization, $\Delta G_m$ and free energy of adsorption, $\Delta G_{\text{ads}}$ were calculated using standard Eq 4.10 and Eq 4.11:\textsuperscript{53}

$$\Delta G_m = RT \ln X_{\text{cmc}} \quad \text{.............(4.10)}$$

$$\Delta G_{\text{ads}} = \Delta G_m - \pi_{\text{cmc}} / \Gamma_{\text{max}} \quad \text{.............(4.11)}$$

where, $X_{\text{cmc}}$ is the critical micelle concentration in terms of mole fraction unit and $\pi_{\text{cmc}}$ is the surface pressure of surfactant systems at their $cmc$. Data presented in Table 4.1 shows that $\Delta G_m$ values for the mixed micelles carry more negative values in comparison to pure components. Table 4.1 also makes it clear that $\Delta G_{\text{ads}}$ values are more negative than $\Delta G_m$ for all the binary mixtures. It indicates that adsorption of mixed surfactant system at air/water interface is more spontaneous and work has to be done to transfer surfactant molecules from saturated interface to the mixed micelles. Intercalation of triblock polymer into BC micelles favors mixed micellization and reduces difference between free energy of micellization and adsorption i.e. $(\Delta G_m - \Delta G_{\text{ads}})$ as shown in Table 4.1. Excess free energy of micellization ($\Delta G_{\text{ex}}$) can be calculated using Eq. 4.12:\textsuperscript{53}

$$\Delta G_{\text{ex}} = RT \left[ X_1^m \ln f_1^m + X_2^m \ln f_2^m \right] \quad \text{.............(4.12)}$$
The negative value of $\Delta G_{ex}$ (Table 4.1) over complete mixing range for all the mixed micellar systems indicates the thermodynamic stability of BC+TBPs mixed micelles.

### 4.3.4 Hydrodynamic Diameter

Variation in microstructure of mixed micelles of all the binary mixtures of BC with TBPs has been probed by dynamic light scattering (DLS) and viscosity measurements. For both these studies, micellar solutions containing different molar ratio of BC to TBP ($\alpha' = n_{BC}/n_{TBP}$) were prepared by mixing 2 wt% solutions of both the components in different fractions. DLS is widely employed to determine the hydrodynamic diameter ($D_h$) of the micelles. Hydrodynamic diameter of the micelles in the binary mixtures of BC+P123/P105/L64/F127 containing 0.1 mol dm$^{-3}$ KCl was monitored by DLS at 303.15 K. Value of hydrodynamic diameter $D_h$ was obtained from Eq. 4.13

$$D = \frac{k_BT}{3\pi \eta_r D_h} \quad \text{.........(4.13)}$$

where, $D$ is the diffusion coefficient, $k_B$ is Boltzmann constant, $T$ is the sample temperature in absolute scale, $\eta_r$ is relative viscosity of the solvent and $D_h$ is the hydrodynamic diameter of the aggregate. It was observed from Figure 4.6a that with decrease in molar ratio of BC, diameter of mixed micelles goes on increasing. This increase in $D_h$ is more pronounced in TBP rich region. For different BC+TBP mixed systems, value of $D_h$ varies between corresponding values for the pure components i.e. BC and TBP. As we move from higher to lower molar ratio of BC, $D_h$ values for the mixed systems show a gradual shift from $D_h$ value of BC micelle (3.9 nm) to $D_h$ value of TBP ($D_h$ of F127 = 23.4 nm; P123 = 19.5 nm; P105 = 17.5 nm; L64 = 14.4 nm). At higher molar ratio of BC, micellar size remains almost constant as the micelles are predominated by cationic surfactant BC. Micellar growth observed is accountable to two converse factors, one being the electrostatic repulsion term originating from coulombic interactions between charged head groups and other is hydrophobic interactions between hydrocarbon parts of the micelles. The observed micellar growth for the mixed micelles at low molar ratio of BC can be attributed to an increase in the hydrophobic interactions and decrease in head group repulsions on account of the
Figure 4.6 Plots showing variation of (a) Hydrodynamic diameter, $D_h$ (b) Polydispersity index, PDI with molar ratio $\alpha' = n_{BC} / n_{TBP}$ for various binary mixtures: BC+P123, BC+P105, BC+F127 and BC+L64.
incorporation of nonionic component TBP into the BC micelles. At higher molar ratio of BC, nearly constant $D_h$ value is observed due to an increase in surface charge density on the incorporation of ionic monomers into the micelles that causes greater repulsion between ionic surfactants. Polydispersity index (PDI) which is a measure of the width of size distribution, decreases with an increase in the molar ratio of BC in these binary mixtures\textsuperscript{56} as shown in Figure 4.6b.

Plots in Figure 4.7 represent collective variation of relative viscosity ($\eta_r$) for different binary mixtures of BC+TBP with respect to molar ratio of BC. It is clear from plots that increase in BC concentration decreases the relative viscosity of mixture. This trend is in line with the trend obtained from DLS study. It is well known that large micelles possess higher viscosity than the smaller micelles, therefore, increasing viscosity trend exhibited by all the binary mixtures at lower mole fraction of BC can be ascribed to the micellar growth due to hydrophobicity effect produced by hydrophobic tail of BC and PO part of TBP.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure47.png}
\caption{Plots of relative viscosity, $\eta_r$ vs molar ratio $\alpha' = n_{BC}/n_{TBP}$ for various binary mixtures: BC+P123, BC+P105, BC+F127 and BC+L64}
\end{figure}
4.3.5 **Micellar Structure and Aggregation Number**

Micellar structure and aggregation number of pure and mixed surfactant systems in the present study were examined by small angle neutron scattering studies (SANS). Analysis of SANS data was made by measuring the scattering cross-section per unit volume $d\Sigma/d\Omega$ as a function of scattering wave vector $Q$. For monodispersed systems, scattering cross-section per unit volume can be expressed as per relation in Eq. 4.14.

$$\frac{d\Sigma}{d\Omega}(Q) = nV^2(\rho_p - \rho_s)^2 P(Q)S(Q) \quad \text{...............(4.14)}$$

where, $n$ is number density of the particle, $V$ is volume of the particle, $(\rho_p - \rho_s)^2$ is the square of difference between average scattering length density of the particle $(\rho_p)$ and solvent $(\rho_s)$ and is referred to as contrast factor, $P(Q)$ is intraparticle structure factor which provides information regarding the shape of micelle. Parameters in the analysis were optimized by means of nonlinear least-square fitting program. For pure cationic surfactant BC and mixed BC+TBPs systems, prolate ellipsoidal model was found to be best suited for data evaluation and therefore intraparticle structure factor $P(Q)$ was calculated by treating the proposed system as prolate ellipsoidal. Micellar dimensions: semimajor axis and semiminor axis have been determined as fitting parameters from the analysis. Prolate ellipsoidal shape $(a \neq b = c)$ of the micelles is widely used in analysis of small-angle neutron scattering data as it also represents other different possible shapes of micelles such as spherical $(a = b)$ and rod-like $(a \gg b)$. For ellipsoidal micelles, Eqs. 4.15, 4.16 and 4.17 have been used

$$P(Q) = \int_0^1 \{F(Q, \mu)^2 \} d\mu \quad \text{...............(4.15)}$$

$$F(Q, \mu) = \frac{3(sinx - xcosx)}{x^2} \quad \text{...............(4.16)}$$

$$x = Q[a^2\mu^2 + b^2(1 - \mu^2)]^{1/2} \quad \text{...............(4.17)}$$

where, $a$ and $b$ are semi-major and semi-minor axis of ellipsoidal macromolecules, respectively and $\mu$ is cosine of angle between directions of $a$ and wave vector transfer $Q$. Interparticle structure factor $S(Q)$ gives information about spatial arrangement of the particles and thereby interparticle interaction $S(Q)$ for
charged micelles can be calculated as per the method of Hayter and Penfold\textsuperscript{57} based on Ornstein Zernike equation using the rescaled mean spherical approximation.\textsuperscript{58} Interparticle structure factor $S(Q)$ has been calculated from Eq. 4.18 given below

$$S(Q) = 1 + \frac{1}{n} \left\{ \sum_k \sum_{k'} \exp[iQ \cdot (R_k - R_{k'})] \right\} \quad \text{..........(4.18)}$$

The micelles are assumed to be a rigid equivalent sphere of diameter, $\sigma = 2(ab^2)^{1/3}$ interacting through a screened coulomb potential, which is given by Eq. 4.19,

$$u(r) = u_0 \sigma \frac{\exp[-\kappa (r - \sigma)]}{r}, \quad r > \sigma \quad \text{..........(4.19)}$$

where, $\kappa$ is the Debye-Huckel inverse screening length and is calculated by Eq. 4.20

$$\kappa = \left[ \frac{8\pi N_A e^2 I}{10^3 \varepsilon k_B T} \right]^{1/2} \quad \text{..........(4.20)}$$

The ionic strength $I$ of the solution is defined by Eq. 4.21

$$I = \text{cmc} + \frac{1}{2} \alpha C \quad \text{..........(4.21)}$$

In pure micellar solution, $I$ is determined by the concentration of the surfactant monomers which is equal to $\text{cmc}$ and dissociated counterions from the micelles. $\alpha'$ (= $Z/N$, where $Z$ is the micellar charge) is the charge fraction on the micelle and $C$ is the concentration of the surfactant. The contact potential $u_0$ is given by Eq. 4.22

$$u_0 = \frac{Z^2 e^2}{\varepsilon \varepsilon_0 \sigma (2 + \kappa \sigma)^2} \quad \text{..........(4.22)}$$

where, $\varepsilon$ is the dielectric constant of the solvent medium, $\varepsilon_0$ is the permittivity of free space and $e$ is the electronic charge.

Figure 4.8a depicts SANS distribution curves for 2 wt% of pure BC and mixture of BC with 2 wt% and 4 wt% of F127. SANS analysis from Figure 4.8a shows that value of scattering cross-section for BC i.e. peak height increases with increase in F127 concentration which indicates micellar growth in the mixed state with an increase in the
Figure 4.8 SANS distribution for pure BC (2 wt%) and binary mixtures: (a) BC (2 wt%) + F127 (2 wt%, 4 wt%) (b) BC (2 wt%) + (2 wt%) TBPs: P123, P105, F127, L64
F127 concentration from 2 wt% to 4 wt%. Figure 4.8b represents SANS profile for 2 wt% BC in the presence of 2 wt% of TBPs (L64/F127/P105/P123). The parameters in the analysis were optimized by means of nonlinear least-square fitting program. For the pure cationic surfactant (BC) and mixed BC+TBPs systems, prolate ellipsoidal model was found to be best suited for data evaluation. Micellar dimensions i.e. semi-major axis and semi-minor axes have been determined as the fitting parameters from the analysis. It was found that micelles of pure BC and mixed micelles of BC with TBPs have prolate ellipsoidal shape. On the basis of SANS measurements, pure triblock polymers have been reported to be spherical in shape.30

It was observed that extent of micellar growth in these mixtures varies with hydrophobicity of triblock polymers and follows the order: BC+P123 > BC+P105 > BC+L64 > BC+F127 shown in Table 4.2. Mixed micelles of P123 are bigger in size in comparison to the mixed micelles of F127 as P123 has higher value of hydrophobicity (PO/EO = 2.00) than F127 (PO/EO = 0.47) as shown in Table 4.2. It makes clear the fact that shape of mixed micelle is predominantly controlled by BC, whereas, triblock polymer only controls the growth of mixed micelles. Although having higher hydrophobicity, comparatively lower scattering cross-section value for L64 in comparison to P105 in their mixed micelles can be attributed to the smaller PO and EO units in L64. Aggregation number of micelles, $N_{agg}$, is calculated by using Eq. 4.23:

$$N_{agg} = \frac{V_m}{V_h} \quad \text{.........(4.23)}$$

where, $V_m$ is the micellar volume and $V_h$ is the volume of hydrophobic part of the surfactant monomer/mixture. Fact that neutron scattering mostly occurs from hydrophobic core of the micelles, contribution from hydrophilic part because of its poor scattering is neglected. Table 4.2 shows that aggregation number of mixed micelles increases on the addition of fixed concentration of 2 wt% of TBPs to the binary mixtures. Keeping BC concentration fixed at 2 wt% and varying F127 concentration from 2 wt% to 4 wt% in BC+F127 system, aggregation number for both BC and F127 components increases which indicates micellar growth. Furthermore, decrease in charge fraction also supports micellar growth in BC+F127 system. Aggregation number in the mixed micelles of BC+P123 mixture has been found to be maximum, which can be
Table 4.2 Values of semi-major axis \((a)\), semi-minor axis \((b)\), axial ratio \((a/b)\), charge fraction \((\alpha'')\) and aggregation number \((N_{agg})\) of BC, aggregation number \((N'_{agg})\) of TBPs in BC+F127/L64/P105/P123 mixed systems

<table>
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<tr>
<th>Systems</th>
<th>Molar ratio (\alpha' = n_{BC}/n_{TBP})</th>
<th>Semi-major (\text{axis} \text{ Å} (a))</th>
<th>Semi-minor (\text{axis} \text{ Å} (b))</th>
<th>Axial ratio ((a/b))</th>
<th>Charge fraction ((\alpha''))</th>
<th>(N_{agg}) (Surf.)</th>
<th>(N'_{agg}) (TBPs)</th>
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<tr>
<td>BC (2 wt%) pure</td>
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<td>0</td>
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<td>2</td>
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<td>5</td>
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<tr>
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<tr>
<td>BC (2 wt%)+P123 (2 wt%)</td>
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<td>45.96</td>
<td>19.51</td>
<td>2.356</td>
<td>0.15</td>
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Table 4.3 Values of core radius ($R_c$), hard sphere radius ($R_{hs}$), and volume fraction ($\phi$) and aggregation number ($N'_{agg}$) of pure TBPs: L64, P105, P123, F127

<table>
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<tr>
<th>TBP</th>
<th>$\text{EO}_x\text{PO}_y\text{EO}_z$</th>
<th>Molecular weight</th>
<th>Hydrophobicity PO/EO ratio</th>
<th>Core radius ($R_c$) Å</th>
<th>Hard sphere radius ($R_{hs}$) Å</th>
<th>Volume fraction ($\phi$)</th>
<th>Aggregation number ($N'_{agg}$)</th>
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<tbody>
<tr>
<td>F127</td>
<td>$\text{EO}<em>{97}\text{PO}</em>{69}\text{EO}_{97}$</td>
<td>12600</td>
<td>0.47</td>
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<td>98.3</td>
<td>0.07</td>
<td>11</td>
</tr>
<tr>
<td>P105</td>
<td>$\text{EO}<em>{36}\text{PO}</em>{57}\text{EO}_{36}$</td>
<td>6500</td>
<td>1.00</td>
<td>30.7</td>
<td>88.0</td>
<td>0.05</td>
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<tr>
<td>L64</td>
<td>$\text{EO}<em>{13}\text{PO}</em>{30}\text{EO}_{13}$</td>
<td>1900</td>
<td>1.32</td>
<td>20.9</td>
<td>57.2</td>
<td>0.03</td>
<td>13</td>
</tr>
<tr>
<td>P123</td>
<td>$\text{EO}<em>{20}\text{PO}</em>{70}\text{EO}_{20}$</td>
<td>5800</td>
<td>2.00</td>
<td>49.8</td>
<td>92.5</td>
<td>0.04</td>
<td>77</td>
</tr>
</tbody>
</table>
attributed to the highest hydrophobicity of P123 in comparison to other TBPs. The observed decrease in charge fraction and increase in axial ratio for the proposed mixed systems in comparison to pure BC proves micellar growth and supports the observed synergistic mixing of the two components in line with the aforesaid studies. Mixed system of BC+L64 exhibits exceptional behavior in terms of aggregation number, charge fraction ($\alpha'$) and axial ratio ($a/b$) due to its structural variance. SANS data for pure TBPs in Table 4.3 reveals that core radius ($R_c$) and aggregation number ($N_{agg}$) increase while hard sphere radius ($R_{hs}$) and volume fraction ($\phi$) decrease with an increase in the hydrophobicity of TBPs except L64. These results are in agreement with DLS and surface tension measurements.

4.5 Conclusions

Microstructure and mixing behavior of benzalkonium chloride with different triblock polymers (P123/P105/L64/F127) has been analyzed using surface tension, dynamic light scattering, viscosity and small angle neutron scattering measurements. Results from the study indicate that penetration of TBP into the micelle of pure cationic surfactant BC results into micellar growth that is accompanied by improvement in characteristic micellar properties like lower $cmc$ values, synergistic interactions and spontaneous micellization. Due to improved micellar characteristics, these mixtures are required in smaller quantities for a particular application and are more economical and eco-friendly in nature. Reduced head group repulsions and increased hydrophobicity of mixed micelles upon incorporation of nonionic triblock polymer in the mixed micelle are conducive for the observed micellar growth in these binary mixtures. Among different systems investigated, anomalous behavior was exhibited by BC+L64 system that is accountable to the structural variance of L64 in terms of its smaller PO and EO units. Appearance of azeotropic point and maximum synergism at lower mole fractions of BC suggests that improvement in characteristic features is more pronounced if the concentration of BC is kept low in BC+TBP mixed systems. As synergistic behavior is being affected by the method of surfactant mixing so it suggests that proposed mixtures
should be prepared in terms of lower mole fraction of BC. It indicates that surfactant mixtures formulated following right method of mixing perform better than pure surfactants and are more suitable for commercial applications. Results obtained from this study thereby provide valuable information that can be helpful for the appropriate selection and formulation of surfactant mixtures for use in different surfactant based applications.
References