Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

5.1 Introduction

Ionic liquids (ILs), a class of molten electrolytes with melting point below 100°C, are gaining considerable technological, industrial and academic importance in recent years. Most of their utility stems from their unique properties such as high thermal and electrochemical stability, extremely low vapor pressure, large liquid range, nonflammability and strong solvation abilities. Over the years, they have appeared as a novel class of surfactants due to the amphiphilicity which can be imparted to them by attaching a long chain either with cation or anion. These type of ILs are called surface active ionic liquids (SAILs). The surface activity of these SAILs has been found to be dependent upon various factors such as nature of counter-ion, nature of cation and alkyl chain length. The aggregation behavior of SAILs based on imidazolium cation has been extensively explored by many researchers. In addition to imidazolium based ILs, new ILs based on different hydrophilic head groups have also been synthesized and characterized. Zhao and Zheng synthesized and investigated the self assembling behavior of N-alkyl-N-methylpyrrolidinium bromide (CₙMPB n=12, 14 and 16) in aqueous solutions. Owing to their better surfactant like properties, it is important to explore the behavior of ILs in conjunction with other surface active molecules to maximize their potential for various surfactant based applications. Pluronics, the triblock copolymers, consisting of poly (ethylene oxide) and poly (propylene oxide) blocks with general formula EOₙPOₘEOₙ are known to self assemble into micelles having unique core-shell architecture. The low toxicity and interesting solution behavior of these polymers lends them extensive applications in emulsification, detergency, preparation of mesoporous and nanostructure materials, as polymer gel electrolyte and drug delivery systems. Usually, in most of the industrial applications, pluronics are used in the presence of surfactants due to modified rheological properties, higher solubilization capacity and better surface activity of the resulting mixtures. Therefore, a detailed knowledge about the physical properties of mixtures of surfactants and
polymers is of fundamental importance. The interactions between conventional surfactants and triblock polymers have been extensively studied by many research groups including ours.\textsuperscript{22-28} Hecht and Hoffman studied the effect of sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on pluronic F127 (EO\textsubscript{99}PO\textsubscript{69}EO\textsubscript{99}) using multiple techniques.\textsuperscript{29} They reported that SDS leads to complete destruction of F127 micelles and also inhibits the copolymer micelle formation. Schillen and co-workers studied the interactions between triblock copolymers [L121 (EO\textsubscript{5}PO\textsubscript{68}EO\textsubscript{5}), P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}), F127 (EO\textsubscript{99}PO\textsubscript{69}EO\textsubscript{99})] and ionic surfactants, SDS and hexadecyltrimethylammonium chloride (CTAC) using differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC).\textsuperscript{30}

Pluronics in combination with ILs have found applications as templates for designing polymeric materials, as supported catalysts, lithium ion batteries, metal-ion removal and polymer electrolyte membranes.\textsuperscript{31-37} Keeping this in mind, it becomes essential to explore the effect of SAILs on the aggregation behavior of pluronics in order to tune their properties from application viewpoint. However, there are only few reports in literature where the effect of ILs on the aggregation behavior of triblock copolymers has been studied. Most of these reports focus on the effect of short chain ILs (< C\textsubscript{8}) on the aggregation behavior of the polymer.

The aggregation behavior of pluronic triblock copolymers namely L61 (EO\textsubscript{3}PO\textsubscript{30}EO\textsubscript{3}), L64 (EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13}) and F68 (EO\textsubscript{79}PO\textsubscript{30}EO\textsubscript{79}) in the presence of ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF\textsubscript{4}) and 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF\textsubscript{6}) has been examined by Zhang \textit{et al.}\textsuperscript{38} The effect of varying the length of hydrophilic block while keeping the hydrophobic block constant on the aggregation behavior was studied employing tensiometry, isothermal titration calorimetry (ITC) and transmission electron microscopy (TEM) measurements. Tensiometric findings revealed that the investigated pluronics form normal micelles in IL with PPO blocks acting as solvophobic cores and corona made from PEO units extend into continuous IL phase. The micelle formation was found to be driven by solvophobic effect as the $\text{cmc}$ increased in the order L61<
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L64<F68 which is the order of PEO length of the copolymers. The \textit{cmc} of three copolymers in bmimBF\textsubscript{4} was found to be much lower as compared to that in bmimPF\textsubscript{6} suggesting stronger solvatophobic interaction in bmimBF\textsubscript{4} as compared to bmimPF\textsubscript{6}. From the ITC measurements, the micellization of copolymers in ILs was found to be endothermic and entropy driven process.

Zheng \textit{et al.} have explored the aggregation behavior of Pluronic P104 (EO\textsubscript{27}PO\textsubscript{61}EO\textsubscript{27}) in the presence of IL 1-butyl-3-methyl-imidazolium bromide (BmimBr) by using Fourier transform infrared (FTIR) spectroscopy, freeze fracture transmission electron microscopy (FF-TEM), dynamic light scattering (DLS), and NMR spectroscopy.\textsuperscript{39} The FTIR results indicated that when the BmimBr concentration was below 1.232 mol/L, the critical micelle temperature (CMT) of Pluronic P104 remained unchanged whereas an abrupt decrease was observed above this concentration. An increase in size of Pluronic P104 micelles with increasing BmimBr concentration was observed from FF-TEM micrographs and DLS measurements. However, when the concentration of BmimBr was higher than 1.232 mol/L, an abrupt increase in size was observed. The interactions between the Pluronic P104 and BmimBr in aqueous solutions were investigated using selective NOE NMR experiment. The results demonstrated that below 1.232 mol/L, the organic cations of BmimBr interacted with micellar core via hydrophobic interactions between the PPO block and the butyl group of BmimBr forming P104-BmimBr micelle. Increasing the concentration of BmimBr beyond 1.232 mol/L led to the saturation of P104 micelles with BmimBr molecules and formation of BmimBr clusters in aqueous solutions.

The effect of ILs such as 1-alkyl 3-methyl imidazolium tetraflouroborates (C\textsubscript{n}mimBF\textsubscript{4} where \textit{n} = 4, 6, 8) on solution behavior of Pluronic P103 (EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}) was studied by Parmar and co-workers employing small angle neutron scattering (SANS), DLS, cloud point (CP) and NMR measurements.\textsuperscript{40} The addition of C\textsubscript{4}mimBF\textsubscript{4} and C\textsubscript{6}mimBF\textsubscript{4} increased the CP of Pluronic P103 due to the presence of hydrogen bonding interactions between the H of the imidazolium cation and O atom of the PEO/PPO group. However, the addition of C\textsubscript{8}mimBF\textsubscript{4} at first leads to decrease in CP
and then increased it. SANS and DLS results showed that the size of P103 micelles increases with the addition of C₄mimBF₄ and remains unchanged with the addition of C₆mimBF₄. In contrast to this behavior, the size of the P103 micelles first decreased and then increased in the presence of C₈mimBF₄. This kind of behavior was attributed to the partitioning of C₈mimBF₄ into the micelles and formation of mixed micelles between the C₈mimBF₄ and P103. The NOESY measurements revealed strong hydrophobic interactions between the PPO region of the pluronic and butyl chain of the ILs.

Mahajan and co-workers have examined the interactions of SAILs 1-alkyl-3-methylimidazolium chlorides, \([C_n\text{mim}][\text{Cl}]\), where \(n = 8, 10, \text{and} 12\) with a triblock reverse copolymer, 10R5 (PO₈EO₂₂PO₈) employing tensiometry, conductivity, turbidity, ITC, fluorescence spectroscopy and DLS methods. The results from different techniques revealed the presence of three critical concentrations corresponding to critical aggregation concentration (\(\text{cac}\)), critical saturation concentration (\(c_s\)) and critical micelle concentration (\(\text{cmc}\)) in the SAIL-polymer interactions. At \(\text{cac}\), the SAIL molecules interact with polymer chains leading to formation of polymer-SAIL (monomer complex) which are gradually converted to polymer-SAIL (aggregate complex) on increasing the SAIL concentration. Finally, at much higher concentration, free SAIL micelles are formed. The surface tension results revealed that the adsorption of SAILs at air-water interface decreased in the presence of polymer. ITC and conductivity measurements indicated that the micellization of SAILs in the presence of polymer was enthalpy driven process in the investigated temperature range. The interaction process between the SAILs and the polymer was observed to be controlled via hydrophobic and ion-dipole interactions. From the fluorescence measurements, it was observed that the hydrophobic character of the aggregate complexes increased with increase in alkyl chain length of SAIL. The DLS results showed an initial increase in size upon adding SAIL molecules followed by a rapid decrease in size of complexes as a consequence of electrostatic repulsions supporting the observations made from other techniques.
5.2 Present Work

The present work aims at studying the interactions between surface active ionic liquids (SAILs) 1-dodecyl-3-methylimidazolium bromide \([C_{12}\text{mim}][\text{Br}]\); N-dodecyl-N-methylene piperidinium bromide, \([C_{12}\text{mpip}][\text{Br}]\); N-dodecyl-N-methyl pyrrolidinium bromide, \([C_{12}\text{mpyr}][\text{Br}]\) and pluronic F108 (EO\(_{129}\)PO\(_{50}\)EO\(_{129}\)) in aqueous medium and to draw the comparison between the effect of different SAILs with respect to head group present in them. The basic structures of SAILs and pluronic investigated in the present study are given in Figure 5.1. The investigated SAILs were synthesized in laboratory according to the method mentioned in literature.\(^{16,42,43}\) For synthesis of 1-dodecyl-3-methylimidazolium bromide \([C_{12}\text{mim}][\text{Br}]\), alkylation of 1-methylimidazole with 1-bromododecane was carried out at 80°C for 10 hours without any solvent and the product was recrystallised from ethyl acetate and dried under vacuum for 48 hours. Similarly, the synthesis of N-dodecyl-N-methylene piperidinium bromide, \([C_{12}\text{mpip}][\text{Br}]\) and N-dodecyl-N-methyl pyrrolidinium bromide, \([C_{12}\text{mpyr}][\text{Br}]\) involved alkylation of N-methyl piperidine or N-methylpyrrolidine with 1-bromododecane, respectively at 80°C for 10 hours. The product were purified by recrystallisation in diethyl ether at least four times and dried under vacuum for 48 hours. The purity of the compounds was ascertained by \(^1\text{H} \text{NMR}\) measurements in CDC\(_3\).

The binding of SAILs with pluronic F108 below as well as above the critical micelle temperature (cmt) of the pluronic has been studied by isothermal titration calorimetry (ITC), dynamic light scattering (DLS) and zeta (ζ) potential measurements. Further, using the tensiometric and fluorescence measurements, the characterization of micellar and interfacial behavior of binary mixtures of SAILs with pluronic F108 has been made. The aggregation behavior has been evaluated in terms of micellar parameters like critical micelle concentration (cmc), micellar mole fraction in mixed state \((X_1)\) and interaction parameter \((\beta^m)\) using Clint, Rubingh and Motomura approaches. Surface parameters such as surface tension at cmc \((\gamma_{\text{cmc}})\), surface excess concentration \((\Gamma_{\text{max}})\), minimum area per molecule \((A_{\text{min}})\) have been obtained from surface tension data. Various thermodynamic parameters such as Gibbs free energy of micellization \((\Delta G^\circ_m)\), Gibbs free energy of adsorption \((\Delta G^\circ_{\text{ads}})\) and excess free energy of micellization \((\Delta G^\circ_{\text{ex}})\) for SAIL-F108 mixtures have also been evaluated.
5.3 Results and Discussion

5.3.1 Binding of SAILs with monomeric pluronic F108 at 25°C

5.3.1.1 Isothermal titration calorimetry (ITC) measurements

Isothermal titration calorimetry has been extensively used to study the interaction of surfactants with polymers and it is described as a vital and direct method to monitor the energy changes taking place during the interaction processes. Therefore, ITC measurements were performed to obtain an insight into the interaction mechanism of the SAILs namely 1-dodecyl-3-methylimidazolium bromide \([\text{C}_{12}\text{mim}]\text{[Br]}\); N-dodecyl-N-methylpiperidinium bromide, \([\text{C}_{12}\text{mpip}]\text{[Br]}\); N-dodecyl-N-methylpyrrolidinium bromide, \([\text{C}_{12}\text{mpyr}]\text{[Br]}\) having different cationic head groups
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Figure 5.2: Calorimetric profiles of SAILs as a function of concentration (C) for (a) [C\textsubscript{12}mim][Br] (b) [C\textsubscript{12}mpip][Br] (c) [C\textsubscript{12}mpyr][Br] in the absence and presence of 0.1 wt% pluronic F108 at 25°C. (Inset to Figures shows the calorimetric profile for respective SAILs at concentration of 10 mmol dm\textsuperscript{-3} in the presence of 0.1 wt% Pluronic F108 at 25°C).

with pluronic F108. First of all, the micellization of SAILs in water was studied at 25°C using ITC. The calorimetric titration curves showing the observed enthalpy changes ($\Delta H_{\text{obs}}$) as a function of concentration of respective SAILs are presented in Figure 5.2 (a-c). The $cmc$ values of pure SAILs are obtained from the break point in the calorimetric curve and are summarized in Table 5.1. The values of enthalpy of micellization ($\Delta H^m_m$) are calculated from enthalpy difference between two linear segments of enthalpy curve. Table 5.1 lists the various thermodynamic parameters such
as standard enthalpy of micellization ($\Delta H^\circ_m$), standard entropy of micellization ($\Delta S^\circ_m$) and standard free energy of micellization ($\Delta G^\circ_m$) of pure SAILs obtained from ITC measurements at 25°C. The obtained $cmc$ values are found to be in good agreement with the literature values.$^6,11,16$ The $cmc$ of SAILs depends upon the balance between the various factors such as hydrophobicity of cation, binding strength of cation with the anion and the steric repulsion between the cations.$^{47}$ In [C$_{12}$mpip][Br], the presence of one extra –CH$_2$ group in the saturated six membered piperidine ring as compared to the five membered pyrrolidine ring in [C$_{12}$mpyr][Br] makes the former more hydrophobic than the latter, hence its $cmc$ is comparatively lower. However, the presence of conjugated double bonds in five membered ring leads to an increase in the interactions in case of [C$_{12}$mim][Br], thereby making it highly surface active and hence it has lowest $cmc$.$^{11}$ The negative $\Delta H^\circ_m$ values of SAILs implies that the micelle formation process is exothermic. The negative $\Delta G^\circ_m$ values reveal that the micellization process is spontaneous in nature. The contribution of $T\Delta S^\circ_m$ term to negative $\Delta G^\circ_m$ is much larger than $\Delta H^\circ_m$ term indicating that the micellization process in aqueous solution is entropy driven at this temperature. The micellization process in case of [C$_{12}$mim][Br] has been found to be more spontaneous in comparison to other two SAILs owing to its higher $\Delta G^\circ_m$ values.

**Table 5.1** Critical micellar concentration ($cmc$) and thermodynamic parameters: standard enthalpy of micellization ($\Delta H^\circ_m$), standard entropy of micellization ($\Delta S^\circ_m$) and standard free energy of micellization ($\Delta G^\circ_m$) for pure SAILs at 25±0.1°C using isothermal titration calorimetry (ITC).

<table>
<thead>
<tr>
<th>SAIL</th>
<th>$cmc$ (mmol dm$^{-3}$)</th>
<th>$\Delta H^\circ_m$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^\circ_m$ (kJ mol$^{-1}$)</th>
<th>$T\Delta S^\circ_m$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_{12}$mim][Br]</td>
<td>9.2</td>
<td>-4.7</td>
<td>-21.6</td>
<td>16.9</td>
</tr>
<tr>
<td>[C$_{12}$mpip][Br]</td>
<td>11.8</td>
<td>-0.8</td>
<td>-20.9</td>
<td>20.1</td>
</tr>
<tr>
<td>[C$_{12}$mpyr][Br]</td>
<td>13.2</td>
<td>-2.9</td>
<td>-20.7</td>
<td>17.8</td>
</tr>
</tbody>
</table>
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To study the interaction of SAILs with polymer, the concentration of pluronic F108 was fixed at 0.1 wt%. Since the reported critical micellization temperature ($cmt$) of 0.1 wt% F108 is 39°C, the calorimetric measurements were performed at two temperatures *i.e.* 25°C and 45°C where the polymer is in the form of monomers and in completely micellized state, respectively. Figure 5.2 (a-c) presents the calorimetric curve of titrating SAILs stock solution into water and 0.1 wt% aqueous F108 solution, respectively, as a function of concentration (C) at 25°C. The calorimetric curves of SAILs in the absence and presence of pluronic F108 have significant differences which indicate the existence of interactions between the polymer and SAILs. It is clearly evident from Figure 5.2 (a-c), for titration of three SAILs into the 0.1 wt% F108 solution at 25°C, the thermograms shows similar varying trends and shape *i.e.* the $\Delta H_{\text{obs}}$ initially shows significant endothermic behavior giving rise to a maximum and then gradually decreases and merges with the dilution enthalpy curve of the SAILs without polymer. The heat changes produced during titration of SAIL into the polymer solution not only involves enthalpy of demicellization but also involves enthalpy of interaction between the surfactant and the polymer as well. As the titration curves for all the three SAILs in polymer display similar trends, therefore, F108-$[\text{C}_{12}\text{mim}][\text{Br}]$ system was chosen as a representative to understand the changes taking place on interaction between the SAILs and F108.

From Figure 5.2 (a), it is observed that the titration of first few injections of $[\text{C}_{12}\text{mim}][\text{Br}]$ into pluronic solution leads to endothermic $\Delta H_{\text{obs}}$ values. This confirms that $[\text{C}_{12}\text{mim}][\text{Br}]$ starts interacting with the F108 monomers forming aggregates at very low concentration. The concentration corresponding to the onset of aggregation of SAIL in the presence of polymer is referred as critical aggregation concentration ($cac$) and is obtained by measuring the heat changes by titration of SAIL at low concentration (10 mmol dm$^{-3}$) (shown as inset to Figure 5.2 (a-c)). The obtained $cac$ values are listed in Table 5.2 and are found to be much lower than the $cmc$ values of SAILs in water reflecting the strong interaction between the SAILs and the polymer. Afterwards, the endothermic curve reaches a maximum at a concentration corresponding to 3.0 mmol dm$^{-3}$. The increase in endothermicity with the addition of $[\text{C}_{12}\text{mim}][\text{Br}]$ to polymer solution is result of various factors such as dissociation of
SAIL micelles, dehydration of polymer micelles, conformational changes in the polymer and interaction between the SAIL and polymer molecules. The binding of [C_{12}mim][Br] with F108 takes place via hydrophobic interaction of alkyl chains of [C_{12}mim][Br] with poly propyleneoxide (PPO) block of polymer. Since during binding, the PPO block has to undergo dehydration to form SAIL-polymer complexes, this factor is main cause of increased endothermicity in the ITC curve. As the concentration of [C_{12}mim][Br] is further increased, more and more number of SAIL molecules will bind hydrophobically to polymer forming SAIL-polymer complexes. These complexes undergo reorganization and the polymer unimers start binding to the SAIL micelles giving rise to SAIL rich polymer complexes and free monomers. This reorganization leads to hydration of polymer and is responsible for the exothermic heat changes (in the region 4.4 < C < 12.7 mmol dm^{-3}) observed during the binding process as this binding of monomers of F108 to the surface of SAIL micelles occurs through ion-dipole interaction. Finally at higher [C_{12}mim][Br] concentration (C >12.7 mmol dm^{-3}), the enthalpy curve of titrating SAIL into the polymer merges with the enthalpy curve in water. This concentration is the critical saturation concentration (C_{2}) defining the saturation of binding of [C_{12}mim][Br] to the polymer. At this concentration the electrostatic repulsion between the head groups at the surface of the mixed micelles increases to such an extent that it ultimately leads to decreased interaction between the [C_{12}mim][Br] and the polymer. At this stage, the F108 monomers are fully saturated with SAIL micelles and added [C_{12}mim][Br] forms only free micelles. A closely similar behavior was observed by Li et al. for titration of TTAB (tetradecyltrimethylammonium bromide) into monomeric F127 solution.\textsuperscript{49} The enthalpy of aggregation (\Delta H_{\text{agg}}) for SAILs in the presence of pluronic F108 can be determined from the difference between the two linear segments of calorimetric curves. The thermodynamic parameters such as Gibbs free energy of aggregation process (\Delta G_{\text{agg}}) for SAILs in the presence of pluronic F108 has been determined using equation \Delta G_{\text{agg}} = RT \ln X_{\text{cac}}, where X_{\text{cac}} is the cac in mole fraction units. The entropy of aggregation (T\Delta S_{\text{agg}}) can be calculated from enthalpy change (\Delta H_{\text{agg}}) and free energy change (\Delta G_{\text{agg}}). The values of cac, C_{2} and various thermodynamic parameters for the SAILs in the presence of pluronic F108 have been listed in Table 5.2.
**Table 5.2** Critical aggregation concentration (cac), critical saturation concentration ($C_2$) and thermodynamic parameters: Gibbs free energy of aggregation ($\Delta G_{agg}$), enthalpy of aggregation ($\Delta H_{agg}$), entropy of aggregation ($T\Delta S_{agg}$), overall enthalpy change ($\Delta H_{max}$) for SAILs in the presence of 0.1 wt% F108 at 25±0.1°C.

<table>
<thead>
<tr>
<th>SAIL</th>
<th>$cac$ (mmol dm$^{-3}$)</th>
<th>$C_2$ (mmol dm$^{-3}$)</th>
<th>$\Delta H_{agg}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_{agg}$ (kJ mol$^{-1}$)</th>
<th>$T\Delta S_{agg}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_{max}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_{12}$mim][Br]</td>
<td>0.60</td>
<td>12.7</td>
<td>-8.5</td>
<td>-28.3</td>
<td>19.8</td>
<td>9.3</td>
</tr>
<tr>
<td>[C$_{12}$mpip][Br]</td>
<td>0.57</td>
<td>19.4</td>
<td>-3.1</td>
<td>-28.4</td>
<td>25.3</td>
<td>4.0</td>
</tr>
<tr>
<td>[C$_{12}$mpyr][Br]</td>
<td>0.37</td>
<td>20.5</td>
<td>-4.5</td>
<td>-29.5</td>
<td>25.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>

**Figure 5.3:** Variation of hydrodynamic diameter ($D_h$) vs. concentration (C) of SAILs for (a) [C$_{12}$mim][Br] (b) [C$_{12}$mpip][Br] (c) [C$_{12}$mpyr][Br] in aqueous solution of 0.1wt% pluronic F108 at 25°C.
5.3.1.2 Dynamic light scattering (DLS) and zeta (ζ) potential measurements

The DLS and zeta (ζ) potential measurements have been performed to investigate the changes in hydrodynamic diameter ($D_h$) and ζ-potential of microstructures formed by pluronic F108 and SAILs in different concentrations regimes of SAILs at 25°C. The $D_h$ of pure 0.1 wt% F108 at 25°C comes out to be 6 nm. Since, the pluronic is not in self aggregated stage at this concentration, this value corresponds to the size of monomer of F108. The size of pure [C$_{12}$mim][Br] micelle showed two size distributions, one around ~1.2 nm due to the presence of micelles and another one in the range of 100-300 nm which is attributed to micellar agglomerates.\(^5\) Figure 5.3 (a-c) shows the variation of $D_h$ for 0.1 wt% F108 solution as a function of concentration (C) for [C$_{12}$mim][Br], [C$_{12}$mpip][Br] and [C$_{12}$mpyr][Br] at 25°C. In case of F108-[C$_{12}$mim][Br], a look into the Figure 5.3 (a) clearly depicts that initially, at very low concentration of added SAIL, the size of the aggregates begin to increase slowly. In the concentration regime $2.9 \text{ mmol dm}^{-3} < C < 10.2 \text{ mmol dm}^{-3}$, the size of the aggregates increased gradually and reaches to maximum of 78 nm at concentration around 10.2 mmol dm$^{-3}$. The size increases due to the formation of large [C$_{12}$mim][Br]-F108 complexes via adsorption of SAIL onto PPO block of polymer through hydrophobic interactions. Beyond this concentration regime, the disintegration of complexes becomes evident from decrease in $D_h$ value to 4.5 nm at 11.6 mmol dm$^{-3}$. As the amount of SAIL is increased further, the $D_h$ value decreases slowly and becomes stable as a consequence of formation of small SAIL-polymer complexes with size comparable to free [C$_{12}$mim][Br] micelles. Finally, at much higher concentrations, smaller aggregates having $D_h$ approximately ~ 2 nm are observed which corresponds to the size of free SAIL micelle. Beyond this concentration, no interaction between the SAIL and polymer takes place.

In case of F108-[C$_{12}$mpip][Br] system (Figure 5.3 (b)), the size increased slowly with addition of [C$_{12}$mpip][Br] and becomes 20 nm at a concentration corresponding to 4.5 mmol dm$^{-3}$. As [C$_{12}$mpip][Br] is added further, the size of the complexes decreases to some extent and then again increases to a 48 nm at a concentration of 12 mmol dm$^{-3}$. This is followed by a sudden drop in size when the
concentration becomes 15.0 mmol dm\(^{-3}\) after which it decreases a little and remains constant. A look into Figure 5.3 (c) reveals that the size of the aggregates increases gradually on addition of [C\(_{12}\)mpyr][Br] and reaches to a maximum size of approximately 220 nm at a concentration of 17.0 mmol dm\(^{-3}\) followed by a decrease in size at a concentration around 22.2 mmol dm\(^{-3}\). Beyond this concentration, the size remains constant with addition of SAIL. The behavior of DLS changes is quite different from that reported by Sharma et al. in case of [C\(_{12}\)mim][Cl]/10R5 system where the size of polymer was observed to increase with the addition of [C\(_{12}\)mim][Cl] due to formation of complex, followed by a decrease in post saturation stage. However, with the addition of [C\(_{12}\)mim][Cl] beyond cmc, the size of the complexes again increased indicating that the polymer-SAIL(aggregate) complex remains quite stable even in the presence of the micelles.\(^{41}\)

To get further insights on the complexation of pluronic with SAILs, \(\zeta\) potential measurements have been performed. The changes in \(\zeta\) potential with addition of [C\(_{12}\)mim][Br] into the 0.1 wt% F108 solution at 25°C have been shown in Figure 5.4. The \(\zeta\) value for pure polymer is around -11 mV. The negative values of \(\zeta\) may be attributed to the presence of large number of PEO units present in the polymer.\(^{51}\) The \(\zeta\) values for 0.3 mol dm\(^{-3}\) [C\(_{12}\)mim][Br] solution comes out to be +10 mV. As can be seen from Figure 5.4, the \(\zeta\) potential of F108 increases towards the positive side upon adding SAILs and after reaching a maximum, it starts decreasing. The \(\zeta\) potential is a measure of electrophoretic properties of the particle and hence provides information regarding the surface charge of the particle. In this regard, the binding of cationic SAIL to polymer is expected to produce an increase in positive charge on SAIL-F108 complexes. As the concentration of [C\(_{12}\)mim][Br] is increased, the negative charge on the polymer decreases confirming the formation of polymer-SAIL complexes. In the concentration regime 1.5 < C < 13.0 mmol dm\(^{-3}\), the \(\zeta\) value rises to about +14.0 mV. However, beyond this concentration, \(\zeta\) value decreases attaining a plateau which may be attributed to the formation of free [C\(_{12}\)mim][Br] micelles supporting the results obtained from ITC and DLS measurements.
5.3.1.3 Effect of headgroup of SAILs on the F108-SAILs interactions at 25°C

A perusal of Table 5.2 indicates that the values of ΔG_{agg} of SAILs in the presence of pluronic F108 are negative signifying the spontaneity of the aggregation process. Since the values of ΔH_{agg} are smaller than TΔS_{agg} term, this implies that the aggregation process is highly entropy driven. Also, TΔS_{agg} term is more positive than TΔS_m term indicating that during SAIL-F108 interaction process, the entropic contribution leads to more disorder environment. Although, the binding interactions of SAILs with pluronic F108 are identical while comparing the cac values (Table 5.2) for three SAILs, it was observed that they increase in the order [C_{12mpyr}][Br]<[C_{12mpip}][Br]≈[C_{12mim}][Br]. The cac values are quite low when compared with cac values reported for interaction of SAILs with L64 and F68. The lower cac values indicated stronger interaction of the SAILs with pluronic F108 as compared to pluronic F68 and L64. The C_2 values are found to increase in the order [C_{12mim}][Br]<[C_{12mpip}][Br]<[C_{12mpyr}][Br]. Considering the overall enthalpy of interaction (ΔH_{max}) between the SAIL and the polymer, a relatively larger enthalpy change has been observed in case of [C_{12mim}][Br] followed by [C_{12mpyr}][Br] and [C_{12mpip}][Br]. This leads to an estimate of strength of binding interactions between the SAILs and pluronic F108 which follows the sequence [C_{12mim}][Br]>[C_{12mpyr}][Br]>[C_{12mpip}][Br]. This
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order of binding interaction is also justified by the values of critical saturation concentration \( (C_2) \). An increase in \( C_2 \) value indicates that more SAIL is required to achieve saturation of binding with F108. Therefore, \([\text{C}_{12}\text{mim}][\text{Br}]\) was found to interact strongly with F108 monomers as it has the lower \( C_2 \) and also higher \( \Delta H_{\text{max}} \) values in comparison to \([\text{C}_{12}\text{mpip}][\text{Br}]\) and \([\text{C}_{12}\text{mpyr}][\text{Br}]\). The interactions between the pluronic and SAILs are driven mainly via hydrophobic and ion-dipole forces of attraction. Since in the present investigation, the hydrophobic alkyl chain length is same in each SAILs, so the sequence of their interaction with monomeric F108 is attributed to the difference in their head groups. A stronger interaction in case of \([\text{C}_{12}\text{mim}][\text{Br}]\) may therefore, can be accounted for its superior surface activity as it has lesser headgroup-headgroup repulsions as well as to its ability to form H-bond between the imidazolium cation and oxygen atoms of PEO/PPO residues of pluronic in addition to hydrophobic forces, thereby increasing the interactions with the polymer. The presence of such hydrogen bonding interactions between the imidazolium cation and oxygen atoms of pluronics has earlier been exemplified in literature.\(^{53}\)

5.3.2 Binding of SAILs with micellar pluronic F108 at 45°C

5.3.2.1 Isothermal titration calorimetry (ITC) measurements

At 45°C, 0.1 wt% F108 solution exists in the form of micelles. Figure 5.5 (a-c) shows the observed enthalpy changes \( (\Delta H_{\text{obs}}) \) by titration of SAILs in water and 0.1 wt% aqueous F108 solution as a function of concentration \( (C) \) at 45°C. Although the obtained thermograms at this temperature are sigmoidal in nature but the enthalpy changes are relatively more endothermic as compared to thermograms obtained at 25°C. The thermodynamic parameters obtained for pure SAILs at 45°C are listed in Table 5.3. With increase in temperature, the \( \Delta H^\circ_{m} \) values for SAILs become more exothermic. At high temperature, the water molecules around the hydrophobic domain of SAILs become less ordered hence entropic contribution \( (T\Delta S_{m}) \) to micelle formation becomes less significant and the enthalpic contribution overweighs the entropic one. The observed results are consistent with those found in literature.\(^{54}\) The binding of SAILs with F108 at 45°C showed significant differences as compared to the binding of SAILs with F108 at 25°C. This behavior can be understood by considering different states of polymer below as well as above its \( \text{cmt} \). The titration of all the three SAILs into the
polymer solution results in exothermic heat changes as compared to the titration of SAILs into water.

**Figure 5.5**: Calorimetric profiles of SAILs as a function of concentration (C) for (a) [C\(_{12}\text{mim}\)][Br] (b) [C\(_{12}\text{mpip}\)][Br] (c) [C\(_{12}\text{mpyr}\)][Br] in the absence and presence of 0.1 wt% pluronic F108 at 45°C.

It can be observed from **Figure 5.5 (a)**, the addition of very first injection of [C\(_{12}\text{mim}\)][Br] into the polymer solution results into endothermic changes in \(\Delta H_{\text{obs}}\) clearly indicating the start of interaction process between the SAIL and micellar F108. The endothermicity increases in next few injections (1.6 mmol dm\(^{-3}\) < C < 8.8 mmol dm\(^{-3}\)) because of the penetration of alkyl chains of added [C\(_{12}\text{mim}\)][Br] into the core of F108 micelles leading to the formation of F108 rich mixed micelles induced by hydrophobic interactions. As the titration proceeds, in the region 8.8 mmol dm\(^{-3}\) < C <
22.9 mmol dm$^{-3}$, more number of [C$_{12}$mim][Br] molecules get adsorbed on the F108 micelles and the process becomes less endothermic indicating that the mixed micelles are broken into smaller mixed micelles. With further addition of [C$_{12}$mim][Br], the head group-head group repulsions exceeds the hydrophobic interactions leading to breakdown of mixed micelles into smaller mixed micelles. This break down of micelles continues until all [C$_{12}$mim][Br]-F108 mixed micelles are completely broken and free F108 monomers are liberated. The added [C$_{12}$mim][Br] will start binding to F108 monomers. When concentration reaches 22.9 mmol dm$^{-3}$, F108 monomers get saturated with [C$_{12}$mim][Br] micelles and further addition of IL leads to formation of free [C$_{12}$mim][Br] micelles. This concentration is called the critical saturation concentration ($C_2$). Similar variations in $\Delta H_{obs}$ have been obtained for F108-[C$_{12}$mpip][Br]/[C$_{12}$mpyr][Br] systems. Li et al. have studied the binding of 12-EO$_x$-12 Gemini surfactants with Pluronic F108 and P103 at varying concentrations both below and above the micellization temperature. The binding of these surfactants to unassociated polymer resulted in endothermic enthalpy changes similar to our observations at 25°C. However, the interaction of surfactants with pluronic micelles resulted in endothermic peak followed by exothermic enthalpy changes with a broad minimum in the ITC curve which has not been observed in our system. The discrepancy in such behavior can be rationalized in terms of delicate balance between the nature of ionic surfactant and the polymer which in turn governs how the surfactant influences the aggregation phenomenon.

Table 5.3: Critical micellar concentration ($cmc$) and thermodynamic parameters: standard enthalpy of micellization ($\Delta H_m^o$), standard entropy of micellization ($\Delta S_m^o$) and standard free energy of micellization ($\Delta G_m^o$) for pure SAILs at 45±0.1°C using isothermal titration calorimetry (ITC).

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<th>$\Delta G_m^o$ (kJ mol$^{-1}$)</th>
<th>$T\Delta S_m^o$ (kJ mol$^{-1}$)</th>
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<td>10.3</td>
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<td>-11.1</td>
<td>-21.7</td>
<td>10.6</td>
</tr>
</tbody>
</table>
5.3.2.2 Dynamic light scattering (DLS) and zeta (ζ) potential measurements

To aid the interpretations of ITC results, DLS and zeta (ζ) potential measurements have been performed. **Figure 5.6 (a-c)** shows the variation of $D_h$ of 0.1 wt% F108 solution as a function of concentration (C) of [C$_{12}$mim][Br], [C$_{12}$mpip][Br] and [C$_{12}$mpyr][Br], respectively at 45°C. The variation of $D_h$ of F108 with the addition of SAILs at 45°C differs remarkably as compared to its variation at 25°C. At 45°C, the polymer exists in the form of micelles with $D_h$ ~28 nm. A perusal of **Figure 5.6 (a)** clearly depicts that in F108-[C$_{12}$mim][Br] system, upon addition of [C$_{12}$mim][Br], the $D_h$ of aggregates decreases continuously and becomes stable after a certain concentration.

![Figure 5.6](image)

**Figure 5.6** Variation of hydrodynamic diameter ($D_h$) vs. concentration (C) of SAILs for (a) [C$_{12}$mim][Br] (b) [C$_{12}$mpip][Br] (c) [C$_{12}$mpyr][Br] in aqueous solution of 0.1wt% pluronic F108 at 45°C.
In the concentration regime $0.75 \text{ mmol dm}^{-3} < C < 20.9 \text{ mmol dm}^{-3}$, addition of $[\text{C}_{12}\text{mim}][\text{Br}]$ into the F108 solution leads to rapid decrease in $D_h$ of aggregates to 3.5 nm indicating the breakdown of F108 rich mixed micelles into smaller micelles. As $[\text{C}_{12}\text{mim}][\text{Br}]$ concentration is increased further, more and more number of cationic head groups will be adsorbed on the polymer micelles to avoid the unfavorable contact with the water. The inclusion of SAIL molecules in the core of F108 micelles will ultimately lead to expansion of core due to water penetration as the repulsive interactions dominate between the headgroups. This, in turn, decreases the aggregation number of the mixed micelle and hence the size also decreases. In this process, some of the monomers of the polymer micelles will also be released into the solution. At higher concentrations ($>22.0 \text{ mmol dm}^{-3}$), almost all the mixed micelles break down giving rise to the small SAIL-polymer complexes having $D_h \approx 2.2 \text{ nm}$. These complexes further break down to give smaller aggregates having $D_h \approx 1.5 \text{ nm}$ which correspond to the presence of $[\text{C}_{12}\text{mim}][\text{Br}]$ micelles. Thus, the addition of $[\text{C}_{12}\text{mim}][\text{Br}]$ leads to complete destruction of the F108 micelles. The reason for this behavior has been ascribed to larger number of PEO units of F108 which efficiently shield the hydrophobic region of polymer from solvent leading to complete dissolution of F108-SAIL mixed micelles. From the light scattering measurements, Li et al. reported the complete dissociation of F127 micelles with the addition of TTAB. In a similar manner the complete demicellization of F108 micelles by $[\text{C}_{12}\text{mpip}][\text{Br}]$ and $[\text{C}_{12}\text{mpyr}][\text{Br}]$ has also been observed.

**Figure 5.7** Plot showing variation of zeta potential ($\zeta$) vs. concentration (C) of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solution of 0.1 wt% pluronic F108 at 45°C.
The changes in the zeta (ζ) potential of mixed aggregates formed by 0.1 wt% F108 and [C_{12}mim][Br] as a function of concentration (C) of SAIL at 45°C is shown in Figure 5.7. With the progressive addition of [C_{12}mim][Br], the ζ value increases rapidly, reaches to a maximum and then starts to decrease. The ζ value of pure F108 solution changes from negative to positive with increasing addition of SAIL which has been ascribed to the formation of mixed micelles between the pluronic F108 and SAIL. Nambam et al. have also reported that the ζ-potential of 1 wt% F108 at 40°C changes from -5 mV to +4 mV up to CTAB concentration of 10 mM. As more SAIL molecules participate in the formation of mixed aggregates, the F108 molecules will be replaced by charged SAIL molecules, thereby increasing the ζ-potential towards positive side. It has been well documented in literature that larger micelles have lesser charge density and hence lower ζ potential values and vice-versa. Since from DLS measurements, a decrease in size of mixed micelles has been observed with gradual increase in concentration of [C_{12}mim][Br], hence, ζ values also increase up to a concentration of 21.0 mmol dm^{-3}. Beyond this concentration, ζ potential decreases and becomes constant. The results obtained from zeta potential measurements give the same picture obtained from DLS and ITC measurements.

Figure 5.8: Schematic diagram showing the binding interactions of SAILs with pluronic F108.
5.3.2.3 Effect of headgroup of SAILs on the F108-SAIL interactions at 45°C

The value of critical saturation concentration ($C_2$) obtained for [C$_{12}$mim][Br] (22.9 mmol dm$^{-3}$) is lower as compared to [C$_{12}$mpyr][Br] (25.4 mmol dm$^{-3}$) whereas its value could not be determined for [C$_{12}$mpip][Br]. The $C_2$ values obtained at 45°C are higher as compared to the values obtained at 25°C signifying that higher amount of SAIL is required to achieve the saturation of binding at higher temperatures. The $\Delta H_{agg}$ values in case of [C$_{12}$mim][Br] (-11.0 kJ/mol) and [C$_{12}$mpip][Br] (-11.3 kJ/mol) are almost similar whereas its value is -9.7 kJ/mol for [C$_{12}$mpyr][Br]. The micellization of SAILs is less favored in the presence of polymer at 45°C as the process becomes less exothermic or relatively more endothermic. Considering the overall enthalpy of interaction, a larger enthalpy change has been displayed by [C$_{12}$mim][Br] followed by [C$_{12}$mpyr][Br] and then [C$_{12}$mpip][Br]. It can be therefore concluded that the binding of SAILs to micellar F108 at 45°C follows the order: [C$_{12}$mim][Br] > [C$_{12}$mpyr][Br] > [C$_{12}$mpip][Br]. Based on the evidences made from ITC, DLS and zeta potential measurements, a proposed molecular mechanism describing the binding interaction as well as changes in the microstructure of pluronic F108 with the addition of cationic SAILs is shown in Figure 5.8.

**Figure 5.9:** (a) Plots showing variation of surface tension ($\gamma$) vs. log of concentration for pure SAILs (Inset to Figure 5.9(a) shows the variation of $\gamma$ vs. log of concentration for pluronic F108) (b) Plots showing variation of pyrene intensity ratio ($I_1/I_3$) vs. concentration for pure SAILs (Inset to Figure 5.9(b) shows the variation of ($I_1/I_3$) vs. concentration for pluronic F108)
5.3.3 Aggregation behavior of F108-SAILs mixtures

The mixed surfactants systems exhibit interesting solution properties and are important from physiochemical and industrial point of view. Hence, the effect of SAILs on the self-aggregation behavior of pluronic F108 has been studied. Since the investigated SAILs differ in their head groups only, a comparative evaluation of their bulk and solution behavior has been made using surface tension and fluorescence measurements. The results have been assessed by using Clint, Motomura and Regular solution theory.57-59

5.3.3.1 cmc and molecular interactions in F108-SAIL mixed aggregates

Surface tension and fluorescence measurements have been employed to determine the cmc of the pure amphiphiles i.e. SAILs and pluronic F108 as well as their binary mixtures. The variations of surface tension and $I_1/I_3$ values as function of concentration for pure amphiphiles have been presented in Figure 5.9. However, the related plots for determining cmc of mixtures of F108 and SAILs at various mole fractions of F108 ($\alpha_{F108}$) are presented in Figure 5.10 (surface tension measurements) and Figure 5.11 (fluorescence measurements). The critical micelle concentration (cmc) of pure SAILs, F108 and their binary mixtures i.e. F108+[C$_{12}$mim] [Br]/[C$_{12}$mpip][Br]/[C$_{12}$mpyr][Br] evaluated using the above techniques have been tabulated in Table 5.4. The cmc values obtained from surface tension measurements are in line with those obtained from the fluorescence measurements. Hence, the cmc values obtained from the two techniques have been averaged to obtain the cmc$_{av}$ which was used for further calculations (listed in Table 5.4). The cmc values obtained for the pure pluronic F108 and SAILs are found to be in accordance with the literature values.6,11,16,60 The cmc value of pluronic F108 is lower as compared to the SAILs because of the higher surface activity of the non-ionic pluronic in comparison to the cationic SAILs. The cmc values for the binary mixtures of SAIL-F108 system have been found to be much lower as compared to the pure components in the whole mole fraction range. Also, as the concentration of F108 is increased, the cmc values of the mixtures were observed to decrease. The decrease in cmc values of the mixtures has been assigned to the facilitation of mixed micelle formation by reducing the
Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

electrostatic repulsions between the charged head groups. This kind of behavior has also earlier been reported for cationic/non-ionic surfactant mixtures.61,62

![Graphs showing variation of surface tension (γ) vs. log of total mixture concentration](image)

**Figure 5.10:** Plots showing variation of surface tension (γ) vs. log of total mixture concentration for (a) F108+[C12mim][Br] (b) F108+[C12mpip][Br] (c) F108+[C12mpyr][Br] mixed systems at different mole fractions of pluronic F108 (α_{F108}) at 25°C.

The Clint’s equation based on pseudo phase separation model was used to evaluate the ideality in the mixed micelles of SAILs and pluronic F108. The ideal values of \(cmc\) i.e. \(cmc^*\) have been calculated using the Clint’s equation\(^57\)

\[
\frac{1}{cmc^*} = \frac{α_t}{cmc_t} + \frac{(1-α_t)}{cmc_2}
\]  

(5.1)
Figure 5.11: Plots showing variation of pyrene intensity ratio ($I_1/I_3$) with total mixture concentration for (a) F108+[C$_{12}$mim][Br] (b) F108+[C$_{12}$mpip][Br] (c) F108+[C$_{12}$mpyr][Br] mixed systems at different mole fractions of pluronic F108 ($\alpha_{F108}$) at 25°C.

where $\alpha_1$ is the mole fraction of pluronic F108 and $cmc_1$ and $cmc_2$ are the $cmc$ values for component 1 (F108) and component 2 (SAILs), respectively. The values of $cmc^*$ have been listed in Table 5.4. The lower values of $cmc_{av}$ as compared to $cmc^*$ indicates that the micelles are formed at a concentration lower than that expected from the ideal mixing. Also, the lowering of $cmc_{av}$ as compared to $cmc^*$ reflects non-ideality in the system and suggests that the mixtures are formed by attractive interactions.
Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

The non-ideality in mixed systems is estimated in light of Rubingh’s Regular Solution Approximation. Equations 5.2 and 5.3 have been employed to determine the micellar mole fraction, $X_1$, of pluronic as well as the interaction parameter ($\beta^m$) which determines the nature and strength of interactions between pluronics and the SAILs.

\[
\frac{X_1^2 \ln(\alpha_{cmc}/X_{cmc})}{(1 - X_1)^2 \ln[(1 - \alpha_c)/mc/(1 - X_1)]} = 1
\]  
(5.2)

\[
\beta^m = \frac{\ln(a_{cmc}/X_c)}{(1 - X_1)^2}
\]  
(5.3)

The micellar mole fraction of mixed systems in ideal state $X_1^{id}$ has been computed using Motomura’s approximation using eq (5.4):

\[
X_1^{id} = \frac{\alpha_{cmc}X_c}{\alpha_{cmc}X_c + (1 - \alpha_c)mc}
\]  
(5.4)

The values of $X_1$, $X_1^{id}$ and $\beta^m$ obtained using these equations are listed in Table 5.4. The $X_1$ values were found to be lower as compared to $X_1^{id}$ indicating that the mixed micelles are richer in SAIL component than its expected value except for $\alpha_{F108} = 0.1$ where $X_1$ values are higher as compared to $X_1^{id}$ signifying that the pluronic is major component at this mole fraction. The $X_1$ values are found to increase with $\alpha_{F108}$ suggesting that as the mole fraction of F108 increases, more number of F108 molecules contribute to the mixed micelles. As per Table 5.4, the values of $\beta^m$ are negative over whole mole fraction range for each of the three systems indicating that the interactions between pluronic F108 and SAILs are more attractive in the mixed micelle than the self interaction of the surface active molecules, individually. The negative $\beta^m$ values have earlier been reported for other cationic-nonionic mixtures. However, our results were different from those of reported F108/10-2-10 [dimethylen bis(decyldimethylammonium bromide)] mixtures where increasing the concentration of F108 leads to an increase in antagonism. The antagonism arises due to intercalation of 10-2-10 monomers having two headgroups in the F108 micelles thus increasing the intermicellar repulsive interactions. The synergistic interactions between F108-SAIL binary mixtures can be ascribed to the presence of ion-dipole interactions between the positively charged head groups of SAILs and PEO groups of pluronic F108.
Table 5.4 Micellar parameters: Critical micellar concentration; \(\text{cmc} \) (experimental) and \(\text{cmc}^*\) (ideal), micellar mole fraction: \(X_1\) (experimental) and \(X_1^{\text{id}}\) (ideal), interaction parameter (\(\beta_m\)) and activity coefficients (\(f_1\) and \(f_2\)) for various F108-SAIL mixtures at different mole fractions of F108 (\(\alpha_{\text{F108}}\)) at 25±0.1°C.

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<th>(\text{cmc}^*)</th>
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<tr>
<td>0.7</td>
<td>5.34</td>
<td>1.77</td>
<td>3.55</td>
<td>35.01</td>
<td>0.60/0.93</td>
<td>-11.33</td>
</tr>
<tr>
<td>0.9</td>
<td>0.94</td>
<td>0.95</td>
<td>0.94</td>
<td>27.70</td>
<td>0.60/0.98</td>
<td>-18.00</td>
</tr>
</tbody>
</table>

\(^a\) \text{cmc} \text{ obtained from surface tension measurements} \quad \(^b\) \text{cmc} \text{ obtained from fluorescence measurements} \quad \(^c\) \text{Average cmc obtained from both techniques}
Another factor responsible for this may be the reduction of electrostatic repulsions between the headgroups of SAILs due to the addition of pluronic F108. The average calculated values of $\beta_m$ are -11.22, -10.23 and -10.86 for F108-[C$_{12}$mim][Br], F108-[C$_{12}$mpip][Br] and F108-[C$_{12}$mpyr][Br] systems, respectively. The average $\beta_m$ values were found to be most negative for F108-[C$_{12}$mim][Br] system. Thus the [C$_{12}$mim][Br] system has higher synergistic interactions in comparison to F108-[C$_{12}$mpip][Br] and F108-[C$_{12}$mpyr][Br] systems. The values of activity coefficients for F108 ($f_1$) and SAILs ($f_2$) in mixed micelles, according to Regular solution theory are evaluated using following equations:

$$f_1 = \exp \left[ \beta_m \cdot (1 - X_1)^2 \right]$$  \hspace{1cm} (5.5)

$$f_2 = \exp \left[ \beta_m \cdot (X_1) \right]$$  \hspace{1cm} (5.6)

The values of $f_1$ and $f_2$ (Table 5.4) are less than unity for all the F108-SAILs mixed system signifying non-ideality and attractive interactions between the cationic SAILs and non-ionic pluronic F108.

### 5.3.3.2 Interfacial properties of F108-SAIL mixtures

Applying the Gibb’s adsorption isotherm to tensiometric data, the maximum surface excess concentration ($\Gamma_{\text{max}}$) for SAILs as well as their mixtures with F108 can be evaluated using equation (5.7)$^{65}$

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left( \frac{\partial \gamma}{\partial \log C} \right)$$  \hspace{1cm} (5.7)

where $\partial \gamma / \partial \log C$ is the slope below the $cmc$ in surface tension plots, $R$ is the universal gas constant (8.314 JK$^{-1}$mol$^{-1}$), $T$ is the absolute temperature and $n$ is the pre-factor denoting the number of species formed in solution by the dissociation of amphiphile (for non-ionic surfactants, $n=1$; for univalent totally dissociated ionic surfactant, $n=2$) as long as all sources of contamination should be eliminated while using surface tension measurements.$^{66}$ The minimum area per molecule ($A_{\text{min}}$) at air-water interface is calculated using equation 5.8
where \( N_A \) is the Avogadro number. The values of \( \Gamma_{\text{max}} \) and \( A_{\text{min}} \) are summarized in Table 5.5. The \( \Gamma_{\text{max}} \) and \( A_{\text{min}} \) values for pure amphiphiles are found to be in good agreement with the literature values.\(^6,11,16,28\) The \( \Gamma_{\text{max}} \) values of SAILs were found to be greater as compared to F108. This signifies that the pluronic molecules are less surface active in comparison to the SAIL molecules. However, in case of binary mixtures of F108-SAILs, an overall decrease in the \( \Gamma_{\text{max}} \) with increase in mole fraction of pluronic F108 was observed and consequently a reverse trend in variation of \( A_{\text{min}} \) values was observed. Table 5.5 shows that the calculated \( A_{\text{min}} \) values for the mixed systems were found to be greater as compared to the ideal ones. This suggests that there is an expansion of monolayer in the mixed F108-SAILs systems. Due to the penetration of SAIL molecules into the PPO region, the intermixing of PEO and PPO chain takes place resulting in thickening of the monolayer in SAIL-F108 mixed systems.\(^67\) Also this binding of SAIL molecules with the hydrophobic PPO block is evident from the ITC experiments described in Section 5.3.1.1.

The values of surface tension at \( \text{cmc} \) (\( \gamma_{\text{cmc}} \)) for pure SAILs and pluronic F108 as well as for their mixtures have been listed in Table 5.5. The \( \gamma_{\text{cmc}} \) values are found to be higher for F108 as compared to SAILs indicating that the SAILs are more effective in reducing the surface tension of water at \( \text{cmc} \). In case of binary mixtures of F108-SAILs, the \( \gamma_{\text{cmc}} \) values are found to increase with increasing concentration of pluronic F108 indicating the reduced surface activity of the mixtures at higher pluronic concentrations.

Another parameter called surface pressure (\( \Pi_{\text{cmc}} \)), indicates the efficiency of the investigated system to reduce the surface tension and is defined as \( \Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \) where \( \gamma_0 \) is the surface tension of pure solvent and \( \gamma_{\text{cmc}} \) is the surface tension of solution at \( \text{cmc} \). Table 5.5 lists the \( \Pi_{\text{cmc}} \) values for the pure SAILs following the order [\( \text{[C}_{12}\text{mim}][\text{Br}] \) < [\( \text{[C}_{12}\text{mpip}][\text{Br}] \) < [\( \text{[C}_{12}\text{mpyr}][\text{Br}] \) which is the order of their \( \text{cmc} \). However, for the binary mixtures of F108 with the SAILs, \( \Pi_{\text{cmc}} \) values were observed to decrease as the mole fraction of F108 increase in the mixtures.
Table 5.5: Interfacial and thermodynamic parameters: Surface tension at cmc ($\gamma_{\text{cmc}}$), surface pressure at cmc ($\Pi_{\text{cmc}}$), surface excess concentration ($I_{\text{max}}$), minimum area per molecule ($A_{\text{min}}$), Gibbs free energy of micellization ($\Delta G^\circ_m$), Gibbs free energy of adsorption ($\Delta G^\circ_{\text{ads}}$) and excess free energy ($\Delta G_{\text{ex}}$) for F108- SAIL mixtures at various mole fractions of pluronic F108 ($\alpha_{\text{F108}}$) at 25±0.1°C.

<table>
<thead>
<tr>
<th>$\alpha_{\text{F108}}$</th>
<th>$\gamma_{\text{cmc}}$ (mN/m)</th>
<th>$\Pi_{\text{cmc}}$ (mN/m)</th>
<th>$I_{\text{max}} \times 10^6$ (mol m$^{-2}$)</th>
<th>$A_{\text{min}}/A_{\text{min}}^{\text{id}}$ (Å$^2$)</th>
<th>$\Delta G^\circ_m$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^\circ_{\text{ads}}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_{\text{ex}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F108-</td>
<td>C$_{12}$mim</td>
<td></td>
<td>Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>33.4</td>
<td>37.6</td>
<td>2.61</td>
<td>63.5</td>
<td>-21.4</td>
<td>-35.8</td>
<td>-</td>
</tr>
<tr>
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<td>36.4</td>
<td>0.86</td>
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<td>-69.4</td>
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</tr>
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<td>35.7</td>
<td>0.46</td>
<td>360.9/122.2</td>
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<td>-105.2</td>
<td>-4.8</td>
</tr>
<tr>
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<td>36.3</td>
<td>34.7</td>
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<td>251.5/161.4</td>
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<td>-84.5</td>
<td>-6.4</td>
</tr>
<tr>
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<td>34.8</td>
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<td>281.4/200.6</td>
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<td>-89.6</td>
<td>-7.5</td>
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<tr>
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<td>0.69</td>
<td>240.6/239.8</td>
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<td>-81.1</td>
<td>-9.9</td>
</tr>
<tr>
<td>1</td>
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<td>-</td>
</tr>
<tr>
<td>F108-</td>
<td>C$_{12}$mpip</td>
<td></td>
<td>Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>41.0</td>
<td>2.67</td>
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</tr>
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<tr>
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<td>291.2/121.2</td>
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<td>34.6</td>
<td>0.54</td>
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<td>395.3/239.6</td>
<td>-30.1</td>
<td>-111.0</td>
<td>-7.6</td>
</tr>
<tr>
<td>F108-</td>
<td>C$_{12}$mpyr</td>
<td></td>
<td>Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>29.2</td>
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<td>52.64</td>
<td>-20.3</td>
<td>-33.6</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>32.6</td>
<td>38.4</td>
<td>0.76</td>
<td>217.6/73.3</td>
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<td>-76.4</td>
<td>-4.6</td>
</tr>
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<td>33.9</td>
<td>37.1</td>
<td>0.55</td>
<td>301.8/114.6</td>
<td>-26.7</td>
<td>-94.2</td>
<td>-1.8</td>
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<td>35.3</td>
<td>0.43</td>
<td>386.1/156.0</td>
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<td>-110.9</td>
<td>-6.1</td>
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<td>34.9</td>
<td>0.36</td>
<td>461.1/197.4</td>
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<td>-126.6</td>
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<td>1.22</td>
<td>136.0/238.7</td>
<td>-33.0</td>
<td>-61.6</td>
<td>-10.7</td>
</tr>
</tbody>
</table>
5.3.3.3 Energetics of micellization and interfacial adsorption

The thermodynamics of micellization and interfacial adsorption of SAIL-F108 mixtures has been quantified in terms of the standard Gibbs free energy of micellization, $\Delta G_m^{\circ}$, and standard Gibbs free energy of adsorption $\Delta G_{ads}^{\circ}$, given by the following equations:

$$\Delta G_m^{\circ} = RT \ln X_{cmc}$$  \hspace{1cm} (5.9)

$$\Delta G_{ads}^{\circ} = \Delta G_m^{\circ} - \frac{\Pi_{cmc}}{\Gamma_{max}}$$  \hspace{1cm} (5.10)

where $cmc$ is the critical micelle concentration of pure components or their mixture in mole fraction units. Table 5.5 shows that the $\Delta G_m^{\circ}$ values are more negative for mixed systems in comparison to pure counterparts because of presence of synergism between them. The values are found to be negative for all the mixed systems at whole mole fraction range indicating that the thermodynamically stable micelles form spontaneously. At a given mole fraction, more negative values have been obtained for F108-[C$_{12}$mim][Br] system confirming a more favorable micellization process in the system as compared to the other systems. Also, the magnitude of $\Delta G_m^{\circ}$ values is found to increase as the F108 content increases. The values of $\Delta G_{ads}^{\circ}$ have been found to be more negative as compared to $\Delta G_m^{\circ}$ indicating that the adsorption process is more favorable as compared to micellization process. The values of excess free energy of micellization, $\Delta G_{ex}$, were calculated by using the following equation:

$$\Delta G_{ex} = [X_1 \ln f_1 + (1-X_1) \ln f_2]RT$$  \hspace{1cm} (5.11)

The values obtained have been listed in Table 5.5 and it is clear that the values evaluated for the mixed systems are negative indicating the formation of stable mixed micelles in these systems. With an increase in mole fraction of pluronic F108, the $\Delta G_{ex}$ values increase indicating the increased stability of mixed aggregates as compared to the aggregates of the individual components. This is also in accordance with their interaction parameter values.

5.4 Conclusions

In summary, the interactional and aggregation behavior of SAILs having different cationic head groups viz. 1-dodecyl-3-methylimidazolium bromide
Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

[C$_{12}$mim][Br]; N-dodecyl-N-methylpiperidinium bromide, [C$_{12}$mpip][Br]; N-dodecyl-N-methylpyrrolidinium bromide, [C$_{12}$mpyr][Br] with pluronic F108 has been investigated using various techniques. The binding of SAILs to the pluronic F108 has been studied using ITC, DLS and zeta potential measurements at two different temperatures. An increase in temperature leads to the changes in the enthalpy curves indicating that the interaction leads to changes in thermal effects. Addition of SAILs to pluronic F108 monomers leads to endothermic enthalpy changes whereas comparatively, exothermic changes have been observed when SAILs have been added to pluronic F108 micellar solution. DLS results clearly depicts that at 25°C, the increasing concentration of SAILs induces structural changes in F108 by interplay of hydrophobic forces leading to formation of larger aggregates which reorganize to give IL rich mixed micelle. However, at 45°C when polymer micelles are present, at low concentration of added SAILs, micellar aggregates are formed which are progressively disintegrated to give IL micelles. The interactions between the polymer and SAILs have also been confirmed by the changes in zeta potential of pluronic F108 with addition of SAILs. Among the investigated SAILs, the interaction of [C$_{12}$mim][Br] with monomeric F108 is observed with relatively higher $\Delta H_{\text{max}}$ values, indicating its higher binding interaction that has been ascribed to its superior surface activity and the presence of H-bonding interactions between the imidazolium cation and oxygen atoms of pluronic F108 in addition to the hydrophobic forces. On the other hand, the interaction with micellar F108 followed the order [C$_{12}$mim][Br]>[C$_{12}$mpyr][Br]>[C$_{12}$mpip][Br]. Using tensiometry and fluorescence measurements, the interactions between the binary F108-SAIL mixtures have been found to be non-ideal and strongly synergistic in mixed micelles due to increased hydrophobicity of the mixed micelles as the pluronic molecules incorporate into the IL micelles. The mixed SAIL-F108 systems exhibit improved micellar and interfacial properties as compared to the pure components individually such as lower cmc and spontaneous micellization. To sum up, the results suggest that the micellar properties and microstructure of pluronics can be tuned with the addition of surface active ILs that may prove beneficial in designing materials with improved physicochemical properties or functional attributes.
5.5 References


Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium


