### Chapter 6

### Influence of Sodium Polystyrenesulfonate on the Aggregation Behaviour of Aqueous Surface Active Ionic Liquid Solutions

### **6.1 Introduction**

Mixed systems of polyelectrolytes and oppositely charged surfactants in solutions manifest a complex and rich aggregation behaviour.<sup>1-8</sup> This behaviour arises due to the strong interactions between the oppositely charged polyelectrolytes and surfactants when present in a solution simultaneously. These interactions have been ascribed to the subtle interplay of electrostatic forces between the surfactant ions and the charged sites on the polyion, and hydrophobic forces between the apolar tails of the surfactant ions. The widespread domestic, industrial, and technological applications of polyelectrolyte-surfactant systems *e.g.*, in detergency, cosmetics, drug delivery, enhanced oil recovery, paints, pharmaceuticals, biomedical application, food and mineral processing, during the past decades,<sup>6-8</sup> necessitates a comprehensive investigation on these systems.

There has been an upsurge of interest in recent years $^{9-17}$  in the self-aggregation aptitude of a novel class of ionic liquids based on organic ions, commonly referred to as surface active ionic liquids, which exhibit surface activity like conventional surfactants. The greater ease of fine-tuning of the hydrophobicity of the surface active ionic liquids in comparison with the conventional surface active agents by modifying the length of the hydrocarbon chains, the kind of the head-group or the nature and size of the counterions permitting the modulation of the structure and the delicate dynamics of their micellar aggregates for specific purposes makes these systems interesting. It may, however, be pointed out that although the systems comprising of polyelectrolytes and the conventional surfactants have been extensively investigated,<sup>1-8</sup> those with polyelectrolytes and surface active ionic liquids have been paid relatively less attention. Recently, we have investigated the interactions prevailing in NaCMC-C<sub>10</sub>MeImCl and NaCMC-C<sub>16</sub>MeImCl systems in aqueous solutions.<sup>18,19</sup> We explored the aggregation behaviour and thermodynamics in these systems at different temperatures. Besides these, till date, there exist only a few reports describing the interactions between polyelectrolytes and oppositely charged surface active ionic liquids by other groups.<sup>20-25</sup> Mixing of surface active ionic liquids with oppositely charged polyelectrolytes in solutions might open up fascinating possibilities of the modulation of material properties of polyelectrolyte-surface active ionic liquid systems on a molecular level in a convenient manner.

In this chapter, we report a comprehensive study on the interaction between an anionic polyelectrolyte NaPSS and two cationic surface active ionic liquids, C<sub>10</sub>MeImCl and C<sub>16</sub>MeImCl in aqueous solutions as probed by tensiometry and conductometry. Here, it should be pointed out that Sharma et al.<sup>26</sup> also investigated the interactional features in one of the systems investigated by us (NaPSS-C<sub>10</sub>MeImCl). The molecular weight of the polyelectrolyte sample employed in that study, however, was not reported. Now, the interactions between polyelectrolyte and surfactant have been found to be dependent on the polyelectrolyte molecular weight.<sup>27</sup> This is quite expected since the extent of counterioncondensation, and hence the charge on the polyion chains have been shown to depend appreciably on the polyelectrolyte molecular weight.<sup>28</sup> Since the charge on the polyion chain governs the electrostatic interaction between the polyion and surfactant ions, there must be a definite dependence of the aggregation behaviour with the polyelectrolyte molecular weight when it is present in a surfactant solution. Moreover, Sharma et al.<sup>26</sup> reported a somewhat low value (around 35 mol.L<sup>-1</sup> at 298.15 K on an average) for the critical micellization concentration of aqueous C<sub>10</sub>MeImCl as compared to the recently reported values which range from 50-60 mol.L<sup>-1</sup> at 298.15 K.<sup>29-34</sup> Moreover, there has, so far, been no report on studies exploring the interactions between NaPSS and  $C_{16}$ MeImCl in aqueous solutions. In view of the above, we have taken up a comprehensive study to address the issues mentioned above.

The counterion-condensation behaviour of aqueous NaPSS relevant to the present study has also been investigated in absence of surface active ionic liquids. NaPSS is an important industrial polymer with a wide spectrum of applications, for example as a super-plastifier in cement, as a dye improving agent for cotton, as proton exchange membranes in fuel cells, as a medication for treating abnormally high potassium levels. It would, therefore, be interesting to study its interacting features with a surface active ionic liquids.

### 6.2 Experimental

NaPSS was purchased from Aldrich Chemicals. The average molecular weight of the sample was 70000. NaPSS XRD pattern shows a broad peak at around  $20^{0}$  associated with low crystallinity as has been previously observed.<sup>35</sup> C<sub>10</sub>MeImCl and C<sub>16</sub>MeImCl were purchased from Aldrich Chemicals and Acros Organics respectively, and were used without further

purification. Their purities were checked from tensiometric measurements as a function of concentration, and no minimum<sup>36</sup> was observed within the concentration range used in this work. Triply distilled water with a specific conductance of less than  $10^{-6}$  S.cm<sup>-1</sup> at 298.15 K was used for the preparation of solutions.

A Krüss (Germany) K9 tensiometer was used to measure the surface tension of the solutions  $(\gamma)$  using platinum ring detachment method with an uncertainty of  $\pm 1 \times 10^{-3}$  N.m<sup>-1</sup>. The tensiometer was connected to a water-flow cryostat to control the temperature equilibration. Before each measurement, the platinum ring was heated for a while by holding it above a Bunsen burner till the ring glows. The  $\gamma$  vs. [surface active ionic liquid] profiles for a polyelectrolyte-containing (NaPSS concentration = 0.0001 monomol.L<sup>-1</sup>) solution are shown in Figs 6.1(a) and (b).

The specific conductances ( $\kappa$ ) were measured on a Thermo Scientific conductivity meter with a dip-type cell in a water thermostat maintained within 0.01 K of the desired temperature. Corrections were made for the specific conductance of solvents at all temperatures. The representative plots of  $\kappa$  vs. [surface active ionic liquid] for NaPSScontaining (concentration = 0.0001 monomol.L<sup>-1</sup>) surface active ionic liquid solutions are depicted, respectively, in Figs. 6.2(a) and (b).

Vapour pressure measurements were performed on a vapor pressure osmometer (Osmomat K-7000, Knauer, Germany). Here, the vapour pressure was measured indirectly by using thermistors to record the change of voltage caused by changes in temperature. The measuring chamber contains a reservoir of solvent and paper wicks to provide a saturated solvent atmosphere. At the beginning, a drop of pure solvent was attached to each thermistor with the help of a syringe, and after 5 min of equilibration the reading was adjusted to zero. Then the pure solvent on one of the thermistors was replaced by the solution and condensation of solvent from the vapor phase onto the solution at the thermistor took place. Due to the heat of condensation, the thermistor warmed up and the vapor pressure increased.

Condensation continued until the vapor pressure of the solution became equal to that of the pure solvent. In general, this steady state was reached within 4-8 minutes.

At first, the osmometer was calibrated using aqueous sodium chloride solutions in the concentration range from 0.01 to 1.5 mol.kg<sup>-1</sup> to yield a function correlating the panel

readings to the corresponding concentrations of the sodium chloride solutions. Then the measurements for the different surfactant solutions were carried out. Utmost care was taken to maintain the size and shape of the drop as constant as possible and equal on both thermistors. For each solution, at least five determinations (zero point adjustment and employment of new solution) were made and the average value was reported. Generally, the deviations from the average value were less than 1%.

For the surfactant solution with molality *m*, the osmotic coefficient  $\phi$  was obtained according to

$$\phi = \frac{v_{\text{NaCl}} m_{\text{NaCl}} \phi_{\text{NaCl}}}{v m} \tag{1}$$

where  $m_{\text{NaCl}}$  is the molality of a sodium chloride solution showing the same instrument reading as the surfactant solution, which means the vapor pressure (and therefore the solvent activity) is equal in both solutions. The stoichiometric numbers v and  $v_{\text{NaCl}}$  in Eq. (1) are set equal to 2.  $\phi_{\text{NaCl}}$  is the respective osmotic coefficient of NaCl solution at  $m_{\text{NaCl}}$  and has been calculated as:

The osmotic coefficients of NaCl solutions as a function of molality at the experimental temperatures were obtained from the literature<sup>37</sup> in the concentration range of 0.001 to 1.5 mol.kg<sup>-1</sup>. These were then fitted to the Pitzer ion-interaction equation<sup>38</sup> for the osmotic coefficient of an electrolyte MX:

$$\phi = 1 - \left| z_{\rm M} z_{\rm X} \right| A_{\phi} \frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + m \left( \frac{2\nu_{\rm M} \nu_{\rm X}}{\nu} \right) \left[ \beta_{\rm MX}^{(0)} + \beta_{\rm MX}^{(1)} e^{-2\sqrt{I}} \right] + m \frac{2(\nu_{\rm M} \nu_{\rm X})^{3/2}}{\nu} C_{\rm MX}^{\phi}$$
(2)

where and  $v_{\rm M}$  and  $v_{\rm X}$  are the numbers of ions in the formula and  $z_{\rm M}$  and  $z_{\rm X}$  give their respective charges in electronic units; also  $v = v_{\rm M} + v_{\rm X}$ , also *m* is the molality, *I* the ionic strength and  $A_{\phi}$  the Debye-Hückel coefficient for the osmotic function.<sup>39</sup> The Pitzer parameters,  $\beta_{\rm MX}^{(0)}$ ,  $\beta_{\rm MX}^{(1)}$  and  $C_{\rm MX}^{\phi}$  obtained by the method of least-squares fit of the  $\phi_{\rm NaCl}$  vs.  $m_{\rm NaCl}$  data<sup>37</sup> to Eq. (2) along with the literature  $A_{\phi}$  values at the experimental temperatures are listed in Table 5.1 (chapter 5). These parameters have been used for the calculation of osmotic coefficients of NaCl (aq) solutions. The representative plot (Fig. 6.3) shows the variation of  $m\phi$  vs. m for C<sub>10</sub>MeImCl (aq) solutions in the absence and in presence of NaPSS at 313.15 K.

Steady-state fluorescence measurements were carried out on a Hitachi Model F-7000 spectrofluorimeter equipped with a 150 W xenon lamp at the desired temperatures within 1 K using a stoppered cell of 1 cm path length with pyrene as the fluorescence probe to determine the cmc in NaPSS-C<sub>10</sub>MeImCl and NaPSS-C<sub>16</sub>MeImCl (aq) solutions. The excitation wavelength was selected at 335 nm using a 10 nm band pass, and, while the emission spectra were scanned from 350 to 450 nm with a band pass of 1 nm. Pyrene is a strongly hydrophobic probe and its fluorescence emission spectrum exhibits five characteristic vibronic peaks in region 370-400 nm. The first and the third vibronic peaks of pyrene appear at 375 and 385 nm, respectively. The ratio of the intensity of the first vibronic peak to that of the third  $(I_1/I_3)$  is highly sensitive to the polarity of the environment. A representative plot (Fig. 6.4) displays the variation of the ratio of the intensities of the first to third peaks  $(I_1/I_3)$ as a function of log[C<sub>10</sub>MeImCl] in NaPSS-containing solutions at 308.15 K. The abrupt sigmoidal decrease in  $I_1/I_3$  with increasing surfactant concentration indicates the formation of surfactant aggregates and preferential incorporation of the probe into the hydrophobic microenvironment of the aggregates relative to water. The cmc can be taken as the concentration corresponding to the intersection of the rapidly varying portion of the curve and the relatively steady portion at higher concentration.

#### 6.3 Results and discussion

### 6.3.1 Counterion-condensation Behaviour of Aqueous NaPSS Solution

Using the de Gennes scaling model for the configuration of a polyion chain, Colby<sup>40</sup> derived the following expression for the equivalent conductivity ( $\Lambda$ ) of a polyelectrolyte solution as a function of concentration ( $c_p$ )

$$\Lambda = f \left[ \lambda_{\rm c}^0 + \frac{F |z_{\rm c}| efc_{\rm p} \xi_0^2}{3\pi\eta_0} \ln\left(\frac{\xi_0}{\xi_{\rm e}}\right) \right]$$
(3)

where  $\lambda_c^0$  is the counterion limiting equivalent conductivity, f the fraction of free counterions, F the Faraday number,  $z_c$  the counterion charge, e the electronic charge,  $\eta_0$ thesolvent viscosity coefficient,  $\xi_0$  the correlation blob size and  $\xi_e$  the electrostatic blob size. The values of the relative permittivity and viscosity of water, and the limiting ionic equivalent conductivity of sodium ion required for the calculation have been obtained from our previous work.<sup>41</sup> This equation has been applied to the measured  $\Lambda$  vs.  $c_p$  data for aqueous NaPSS solutions to determine the fraction of free counterions.

Two key size parameters, namely the size of the electrostatic blob ( $\xi_e$ ) and that of the correlation blob ( $\xi_0$ ) appearing in Eq. (3) depend upon the quality of the solvent. For poor solvents, these are given by<sup>40</sup>

$$\xi_{\rm e} \cong b \left( \frac{b}{f^2 \lambda_{\rm B}} \right)^{1/3} \tag{4}$$

$$\xi_0 \cong (cb)^{-1/2} \left(\frac{b}{f^2 \lambda_{\rm B}}\right)^{1/3} \tag{5}$$

where c is the number density of monomers. For good solvent cases, on the other hand, these are given by<sup>40</sup>

$$\xi_{\rm e} \cong b \left( \frac{b}{f^2 \lambda_{\rm B}} \right)^{3/7} \tag{6}$$

$$\xi_0 \cong (cb)^{-1/2} \left(\frac{b}{f^2 \lambda_{\rm B}}\right)^{1/7} \tag{7}$$

As pointed out by Colby *et al.*,<sup>40</sup> we used the poor solvent correlations for the analysis of the present experimental data on aqueous NaPSS solutions.

# 6.3.2 $C_{10}MeImCl\ (aq)$ and $C_{16}MeImCl\ (aq)$ in Presence of NaPSS: Aggregation Behaviour

Aqueous NaPSS solutions have been shown to be surface inactive within the polyelectrolyte concentration range investigated here. Such a behaviour of aqueous NaPSS solutions was also reported earlier.<sup>38</sup> Thus, surface activity of NaPSS does not contribute to the observed complexity in the tensiometric profiles of NaPSS-C<sub>10</sub>MeImCl and NaPSS-C<sub>16</sub>MeImCl

systems. Furthermore, at such low NaPSS concentrations, complexity arising out of the polyion-polyion interactions was also considered to be absent.

Addition of NaPSS to C<sub>n</sub>MeImCl solutions modifies the tensiometric behaviour of the investigated surface active ionic liquids differently. Typical surface tension profiles for the NaPSS-C<sub>10</sub>MeImCl and NaPSS-C<sub>16</sub>MeImCl systems as surfactant concentration varies are shown in the representative tensiograms, Figs. 6.2(a) and (b), in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS. For the system NaPSS-C<sub>16</sub>MeImCl, there is a pronounced lowering of surface tension at low surfactant concentrations when the polyelectrolyte is initially administered as compared with the polyelectrolyte-free case. It appears that adsorption of polyelectrolyte-surfactant complexes occurs at surfactant concentrations well below the concentration at which the surfactant molecules on their own are expected to adsorb appreciably. The polyelectrolyte-surfactant complexes are formed by cooperative binding of surfactant monomers onto the polyion backbone caused by strong electrostatic forces among themselves. Because of the monomeric adsorption on the polyionic sites, the hydrophobicity of the complex increases as a whole, and the complexes populate the Langmuirian interface. The initial drop in the surface tension may, therefore, be attributed to the gradual formation of a surface-active complex consisting of surfactant monomers bound to the polyion backbone. The mimima in the profiles indicate the characteristic concentration (critical aggregation concentration, cac) beyond which a non-surface active polyelectrolyte-micellar aggregate where the surfactant molecules cooperatively adsorb on the polyion backbone in the form of micelles to form a necklace-like structure. The formation of these complexes dislodges the surface-active polyelectrolyte-surfactant monomer complex to sink into the bulk from the interface; consequently the interface was stripped off the surface active species which increase the surface tension until the formation of the necklace-like structures was complete. Upon completion of this process, there is monomer build-up at the interface with further increase in the concentration of  $C_{16}$ MeImCl. This is associated with a decline in surface tension until free micelles started to form at a surfactant concentration referred to as the apparent critical micellar concentration (cmc\*) after which surface tension reaches a final constant value. The maximum in a tensiogram represents the concentration at which the polyion chains are saturated with the polyelectrolyte-induced aggregates which will be referred to as the polymer saturation concentration (psc). The values of cac, psc, and cmc\* values obtained from tensiometry are recorded in Table 6.1. Although three critical concentrations, namely cac, psc, and cmc\* could be identified from the tensiometric study

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for the system NaPSS- $C_{16}$ MeImCl, the tensiometric data for the system NaPSS- $C_{10}$ MeImClcould only reveal the *cmc*<sup>\*</sup> values listed in Table 6.2.

The conductometric profiles for NaPSS-C<sub>10</sub>MeImCl system revealed three linear segments (Fig. 6.1(a)) with two clear intersections indicating the *psc* and  $cmc^*$  in order of increasing concentration. The conductometric profiles for  $C_{10}$ MeImCl (aq) in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS as a function of  $C_{10}$ MeImCl concentration are depicted inFig. 6.1(a). The curves show a sharp change in slope at the critical micellization concentration of  $C_{10}$ MeImCl in presence of NaPSS (*cmc*<sup>\*</sup>). The values of *psc* have also been identified although the inflections are not as sharp as those for cmc\*. The conductometric psc and cmc\* values are also listed in Table 6.2. It may be pointed out here that conductivity isotherms manifesting two linear sections with one inflection have also been reported earlier in aqueous NaPSS-alkyltrimethylammonium bromide<sup>42</sup> and in dodecylpyridinium chloride-sodium dextran sulfate systems.<sup>43</sup> Conductometric isotherms with three linear segments and two inflections have been reported in some aqueous NaPSS-surface active ionic liquids solutions although the molecular weight and the degree of substitution of the polyelectrolyte sample used were not mentioined.<sup>26</sup> Isotherms with higher complexity showing up to four linear sections with three inflections (e.g., in aqueous and cetyltrimethylammonium bromide-NaCMC solutions<sup>40</sup> are also available in the literature. It may, however, be noted that for NaCMC-cetyltrimethylammonium bromide<sup>44</sup> solution, where aqueous three-break conductivity isotherm was reported, the slopes of the straight lines before and after the psc differ negligibly from each other. The cac could, however, not be detected by this experimental method. For the NaPSS-C<sub>16</sub>MeImCl solutions, only the cmc\* could be identified from their specific conductance vs. concentration profiles.

Analysis of the conductivity of aqueous NaPSS solutions indicated that *ca*. 62-65% of the counterions would remain free in the concentration range of 0.00005 to 0.0001 monomol.L<sup>-1</sup> NaPSS, whereas in aqueous NaCMC solutions in the concentration range of 0.00001 to 0.0005 monomol.L<sup>-1</sup> NaCMC 71-75% of the counterions were found to remain free. The critical concentrations in aqueous  $C_{10}$ MeImCl (aq) solutions in presence of NaPSS were always found to be higher than the corresponding values in presence of NaCMC. A plausible explanation for the present observation may be sought in the differential counterion-binding by the polystyrenesulfonate and carboxymethylcellulose polyions. There are more polyelectrolyte counterions bound to the polyion chains in case of NaPSS than in NaCMC

solutions.<sup>19</sup> The observation thus indicates that the surfactant ions dislodges the polyelectrolyte counterions and bind to the polyion chains, and that polystyrenesulfonate chains with more bound-counterions could bind more surfactant ions than the carboxymethylcellulose ions. The effect is, however, very marginal for NaPSS-C<sub>16</sub>MeImCl (aq) solutions apparently due to a very low value of the critical micellization concentration of  $C_{16}$ MeImCl (aq).

## 6.3.3 Variation of the Critical Aggregation Concentration (*cac*) of $C_{16}$ MeImCl with Temperature

The effect of temperature on the critical aggregation concentration (*cac*) for C<sub>16</sub>MeImCl can be interpreted on the basis of the temperature dependence of the charge density of the polyelectrolyte. Even though the effect of  $\xi$  of NaPSS at different temperatures on the *cac* values is small, it is clearly discernible from Fig. 6.5 where *cac* values measured at different temperatures have been plotted as a function of  $\xi$  of NaPSS in presence of three different polyelectrolyte concentrations. The profiles demonstrate a slow rise in the *cac* values with the polyelectrolyte charge density for each NaPSS concentration. The observation can be explained in terms of electrostatics: a rise in the temperature causes an increase in the value of  $\xi$ . At elevated temperatures, the "*local cmc*", needed for self-aggregation of the amphiphile on the polyion, is thus reached at a somewhat higher surfactant concentration, leading to an increased *cac*.

# 6.3.4 Thermodynamics of Micellization of $C_{10}MeImCl$ and $C_{16}MeImCl$ (aq) in Presence of NaPSS

The free energy change of the micellization process  $(\Delta G_m^0)$  was calculated using the equation:

$$\Delta G_{\rm m}^0 = (1+\beta)RT \ln x_{\rm cmc} \tag{8}$$

where  $x_{cmc}$  is the *cmc* of C<sub>16</sub>MeImCl in mole fraction scale. The  $\beta$  factor includes the fraction of free energy required to condense the counterions on the aggregate to reduce the repulsion between the adjacent monomer head groups.<sup>45</sup>

The corresponding standard enthalpy change  $(\Delta H_m^0)$  is given by

$$\Delta H_{\rm m}^{0} = -RT^{2} \left[ (1+\beta) \left( \frac{\partial \ln x_{\rm cmc}}{\partial \Gamma} \right)_{\rm p} - \ln x_{\rm cmc} \left( \frac{\partial \beta}{\partial T} \right)_{\rm p} \right]$$
(9)

Since the temperature derivative of  $\beta$  for aqueous C<sub>16</sub>MeImCl is found to be small over the temperature range investigated here, and Eq. (5) can then be simplified to

$$\Delta H_{\rm m}^0 = -(1+\beta)RT^2 \left(\frac{\partial \ln x_{\rm cmc}}{\partial T}\right)_{\rm p}$$
(10)

The standard entropy of micellization ( $\Delta S_m^0$ ) was calculated from:

$$\Delta G_{\rm m}^0 = \Delta H_{\rm m}^0 - T \Delta S_{\rm m}^0 \tag{11}$$

The  $\Delta G_{\rm m}^0$ ,  $\Delta H_{\rm m}^0$  and  $T\Delta S_{\rm m}^0$  values for aqueous solutions of C<sub>16</sub>MeImCl are listed in Table 6.1.

The  $\Delta G_m^0$  of both the surface active ionic liquids investigated in presence of NaPSS are, in all cases, found to be negative. In Figs. 6.6(a)-(d), the  $\Delta G_m^0$  values of C<sub>10</sub>MeImCl and C16MeImCl have been plotted as a function of temperature in presence of varying concentrations of NaPSS. Also included in these figures are the  $\Delta G_m^0$  values for C<sub>10</sub>MeImCl and C<sub>16</sub>MeImCl in absence of NaPSS was reported earlier.<sup>18,19</sup> It is apparent that micellization becomes somewhat less spontaneous upon addition of NaPSS at any given temperature, and that the spontaneity of micellization decreases as the amount of added NaPSS increases. In presence of NaPSS, however, the micellization becomes more spontaneous upon an elevation of temperature. Some characteristic features of the thermodynamic parameters are manifested in Figs. 6.6(a)-(d), which are common to the polyelectrolyte-free and polyelectrolyte-containing surface active ionic liquid systems studied. The  $\Delta G_m^0$  values for the NaPSS-surface active ionic liquid systems are, however, found to be comparable to the corresponding values for the NaCMC-surface active ionic liquid systems.<sup>18,19</sup> It is directly evident that the micellization processes of both the surface active ionic liquids are always exothermic over the investigated range of temperatures, whether the system contains NaPSS or not, and that these processes become more exothermic at higher temperatures. The value of  $T\Delta S_m^0$ , on the other hand, decreases with the rise of temperature. The results indicate that the entropy terms override the influence of the  $\Delta H_m^0$ 

values in governing the negative  $\Delta G_m^0$  values of the micellization processes of both C<sub>10</sub>MeImCl and C<sub>16</sub>MeImCl in the presence of NaPSS, *i.e.*, the micelle formation processes for the investigated surface active ionic liquids are always entropy-driven. High-entropy changes are generally associated with a phase change. Hence it can be assumed that the micelles form separate phases in these systems. Shaw<sup>46</sup> suggested that the high-entropy change may be due to the freedom of movement of the hydrocarbon chain in the core of the micelle. However, it is not very clear how this movement of hydrocarbon chains in the core of the micellar aggregates can have a dominating effect on  $\Delta H_m^0$ , which is a macroscopic property. According to Rosen,<sup>47</sup> the presence of the hydrated oxyethylene groups of the surfactant introduces structure in the liquid water phase and the removal of the surfactant via micellization results in an increase in the overall randomness<sup>48</sup> and hence an increase in entropy. Similar behaviour has also been observed previously by us for pure alkyltrimethylammonium bromides in the ethylene glycol-water mixed solvent media.<sup>49</sup> In the present system, the entropy term becomes less positive, and the enthalpy term becomes more negative with the increase in temperature, but the former always being the predominant contributor to the free energy of the micellization processes for the system under investigation.

#### **6.4 Conclusions**

Aggregation behaviour of  $C_{10}$ MeImCl and  $C_{16}$ MeImCl was studied in aqueous solution in absence as well as in presence of NaPSS using tensiometry, conductometry, vapor pressure osmometry and spectrofluorometry with particular reference to the influence of NaPSS concentration and temperature. The results demonstrated gradual formation of *surface-active* complexes consisting of surfactant monomers bound to the polyion backbone, and *nonsurface active* necklace-like polyion-micellar aggregates, and free surfactant micelles in NaPSS-C<sub>16</sub>MeImCl solutions upon addition of C<sub>16</sub>MeImCl. Three characteristic concentrations, *viz.*, critical aggregation concentration (where polyelectrolyte-surfactant monomer complexes begins to form), polymer saturation concentration (at which the polyion chains are saturated with the polyelectrolyte-induced aggregates), and critical micellization concentration (at which free surface active ionic liquid micelles start to form) have been identified in NaPSS-C<sub>16</sub>MeImCl solutions. For NaPSS-C<sub>10</sub>MeImCl solutions, however, polymer saturation concentration, and critical micellization concentration could only be identified. The thermodynamic parameters for micelle formation in aqueous solutions of NaPSS- $C_{10}$ MeImCl and NaPSS- $C_{16}$ MeImCl were estimated and the micellization processes were always found to be spontaneous. The contribution of the entropy terms to the free energy of micellization always predominates over that of the enthalpy terms.

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**TABLE 6.1.** Critical Micellar Aggregation Concentrations  $(cmc^*)$  of C<sub>16</sub>MeImCl in Presence of Varying Concentration of Added NaPSS Along With Critical Aggregation Concentrations (cac), Polymer Saturation Concentrations (psc) in Aqueous Solutions at 298.15, 303.15, 308.15, 313.15, and 318.15 K

<i>T</i> (K)	$c_{\rm p}$ (mono	Method	cac	psc	cmc <sup>*</sup> /	av. cmc*
	$mol.L^{-1}$ )		(mM)	mM	(mM)	(mM)
298.15	0.00005	Conductometry	-	-	0.909	0.968
		Tensiometry	0.178	0.404	1.026	
		Fluorimetry			0.985	
	0.00010	Conductometry	-	-	0.953	1.048
		Tensiometry	0.287	0.410	1.143	
		Fluorimetry			1.059	
303.15	0.00005	Conductometry	-	-	0.988	1.052
		Tensiometry	0.203	0.411	1.116	
	0.00010	Conductometry	-	-	1.014	1.101
		Tensiometry	0.343	0.432	1.189	
308.15	0.00005	Conductometry	-	-	1.064	1.125
		Tensiometry	0.218	0.419	1.185	
	0.00010	Conductometry	-	-	1.068	1.156
		Tensiometry	0.347	0.486	1.243	
313.15	0.00005	Conductometry	-	-	1.098	1.171
		Tensiometry	0.235	0.420	1.243	
	0.00010	Conductometry	-	-	1.177	1.220
		Tensiometry	0.365	0.545	1.262	
318.15	0.00005	Conductometry	-	-	1.163	1.230
		Tensiometry	0.248	0.439	1.297	
	0.00010	Conductometry	-	-	1.212	1.272
		Tensiometry	0.387	0.565	1.331	

*T* (K)  $c_{\rm p}$  (mono Method cmc<sup>\*</sup>/ psc av. psc av. (mM)cmc (mM)(mM) $mol.L^{-1}$ ) (mM)298.15 0.00005 Conductometry 23.87 24.92 60.78 57.72 Tensiometry 25.96 50.77 61.70 Fluorimetry Osmometry 57.64 0.00010 Conductometry 25.93 26.66 62.45 59.22 Tensiometry 27.39 51.78 Fluorimetry 63.57 59.08 Osmometry 303.15 Conductometry 25.60 61.81 57.89 0.00005 24.93 Tensiometry 26.26 51.97 59.88 Osmometry 0.00010 Conductometry 26.93 27.79 63.18 59.31 52.78 Tensiometry 28.65 Osmometry 61.97 308.15 0.00005 Conductometry 25.90 26.22 62.22 58.51 52.23 Tensiometry 26.54 Osmometry 61.08 \_ 0.00010 Conductometry 27.92 28.91 63.96 60.22 Tensiometry 29.90 53.33 Osmometry 63.38 \_ 313.15 26.18 0.00005 Conductometry 27.28 63.09 59.52 Tensiometry 28.37 53.29 Osmometry 62.19 0.00010 Conductometry 61.02 29.27 29.67 65.19 54.29 Tensiometry 30.07 Osmometry 63.58 318.15 0.00005 Conductometry 27.45 29.06 64.89 60.63 Tensiometry 30.67 53.57 Osmometry 63.43 Conductometry 31.44 66.73 62.59 0.00010 30.29 55.97 Tensiometry 32.58 Osmometry 65.07 \_

**TABLE 6.2.** Critical Micellar Aggregation Concentrations  $(cmc^*)$  of C<sub>10</sub>MeImCl in Presence of varying Concentration of Added NaPSS Along With Critical Aggregation Concentrations (cac), Polymer Saturation Concentrations (psc) in Aqueous Solutions at 298.15, 303.15, 308.15, 313.15, and 318.15 K



**Fig. 6.1(a).** Surface tension ( $\gamma$ ) *vs.* log[C<sub>10</sub>MeImCl] profiles in water at 298.15 K ( $\circ$ ), 303.15 K ( $\Box$ ), 308.15 K ( $\Delta$ ), 313.15 K ( $\bullet$ ), and 318.15 ( $\blacksquare$ ). The tensiograms have been shifted vertically by 20 mN.m<sup>-1</sup> from each other for clarity.



**Fig. 6.1(b).** Surface tension ( $\gamma$ ) *vs.* log[C<sub>16</sub>MeImCl] profiles in water at 298.15 K ( $\circ$ ), 303.15 K ( $\Box$ ), 308.15 K ( $\Delta$ ), 313.15 K ( $\bullet$ ), and 318.15 ( $\blacksquare$ ). The tensiograms have been shifted vertically by 20 mN.m<sup>-1</sup> from each other for clarity.



**Fig. 6.2(a).** Specific conductance ( $\kappa$ ) *vs.* [C<sub>10</sub>MeImCl] profiles in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS (aq) at 298.15 K ( $\circ$ ), 303.15 K ( $\Box$ ), 308.15 K ( $\Delta$ ), 313.15 K ( $\bullet$ ), and 318.15 ( $\blacksquare$ ).



**Fig. 6.2(b).** Specific conductance ( $\kappa$ ) *vs.* [C<sub>16</sub>MeImCl] profiles in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS (aq) at 298.15 K ( $\circ$ ), 303.15 K ( $\Box$ ), 308.15 K ( $\Delta$ ), 313.15 K ( $\bullet$ ), and 318.15 ( $\blacksquare$ ).



**Fig. 6.3.** Osmotic coefficient ( $\phi$ ) multiplied by molality (*m*) *vs. m* of C<sub>10</sub>MeImCl (aq) at 313.15 K in water ( $\circ$ ), and in presence of 0.0001 ( $\Box$ ), and 0.00005 ( $\Delta$ ) of NaPSS (aq).



**Fig. 6.4.**  $I_1/I_3$  Ratio of pyrene *vs.* log[C<sub>10</sub>MeImCl] in aqueous solution ( $\circ$ ) and in 0.00005 ( $\Box$ ) and 0.0001 monomol.L<sup>-1</sup> ( $\Delta$ ) NaPSS (aq).



**Fig. 6.5.** Effect of the charge density of NaPSS on the *cac* in aqueous  $C_{16}$ MeImCl solution in the presence of varying concentrations of NaPSS: 0.00005 monomol.L<sup>-1</sup> ( $\circ$ ), 0.0001 monomol.L<sup>-1</sup> ( $\Box$ ).



**Fig. 6.6(a).** Thermodynamic parameters of micellization of  $C_{10}$ MeImCl in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS at different temperatures:  $\Delta G_m^0(\circ)$ ,  $\Delta H_m^0(\Box)$ ,  $\Delta S_m^0(\Delta)$ 



**Fig. 6.6(b).** Thermodynamic parameters of micellization of  $C_{10}$ MeImCl in presence of 0.00005 monomol.L<sup>-1</sup> NaPSS at different temperatures:  $\Delta G_m^0(\circ)$ ,  $\Delta H_m^0(\Box)$ ,  $\Delta S_m^0(\Delta)$ .



**Fig. 6.6(c).** Thermodynamic parameters of micellization of C<sub>16</sub>MeImCl in presence of 0.0001 monomol.L<sup>-1</sup> NaPSS at different temperatures:  $\Delta G_m^0(\circ)$ ,  $\Delta H_m^0(\Box)$ ,  $\Delta S_m^0(\Delta)$ .



**Fig. 6.6(d).** Thermodynamic parameters of micellization of C<sub>16</sub>MeImCl in presence of 0.00005 monomol.L<sup>-1</sup> NaPSS at different temperatures:  $\Delta G_m^0(\circ)$ ,  $\Delta H_m^0(\Box)$ ,  $\Delta S_m^0(\Delta)$ .