# Chapter 5

# Sodium Carboxymethylcellulose-induced Aggregation of 1-Decyl-3-methylimidazolium Chloride ( $C_{10}$ MeImCl ) in Aqueous Solutions

## **5.1 Introduction**

Solutions of ionic surfactants coupled with oppositely charged polyelectrolytes exhibit a complex aggregation behaviour<sup>1-8</sup> originating from the strong interactions between these species. These interactions have been attributed to an interplay of Coulombic forces between the surfactant ions and the polyion, and hydrophobic forces between the hydrocarbon tails of amphiphile ions. Recently, researchers found that like ionic surfactants, some amphiphilic cationic drugs also form micelles.<sup>9-14</sup>

Considerable attention has been paid to polyelectrolyte-surfactant mixtures during the past decades<sup>2,5,6</sup> because of their widespread applications in such areas as detergency, cosmetics, drug delivery, enhanced oil recovery, paints, pharmaceuticals, biomedical application, food and mineral processing.

In recent years, ionic liquids capable of self-aggregation (known as the surface active ionic liquids) have received much attention.<sup>15-20</sup> The interest in these species stems from the greater ease of fine-tuning of the hydrophobicity of surface active ionic liquids and hence their surface properties compared to the conventional surfactants by varying the alkyl chain lengths, the type of the head-group or the nature and size of the counterions which might permit the modulation of the structure and the delicate dynamics of their micellar aggregates for specific purposes.

It is, however, worth noting that even though the polyelectrolyte-conventional surfactant systems have been extensively studied,<sup>1-8</sup> the situation is far from satisfactory for polyelectrolyte-surface active ionic liquid systems. The presence of oppositely charged polyelectrolytes in surface active ionic liquid solutions is expected to open up fascinating possibilities for the exploitation of material properties of polyelectrolyte-surface active ionic liquid systems on a molecular scale. This might particularly be useful in assessing the possible role of polyelectrolytes in modulating the known antimicrobial activity of surface active ionic liquids.<sup>21</sup>

In this chapter, we investigated the aggregation phenomena and their thermodynamics of a cationic surface active ionic liquid 1-decyl-3-methylimidazolium chloride ( $C_{10}$ MeImCl) in aqueous solutions in absence as well as in presence of an anionic polyelectrolyte sodium carboxymethylcellulose (NaCMC) as a function of temperature as probed by tensiometry, conductometry, vapor pressure osmometry, and spectrofluorimetry.

NaCMC is a chemically modified cellulose derivative with high water solubility, broadly used in food industry, cosmetics, pharmaceuticals, suspension agents, formulation agents in controlled release of drugs and pesticides, papers and paper products, adhesives, ceramics etc. due to its low cost, lack of toxicity, and biodegradability.<sup>22</sup> It would, therefore, be interesting to study its interacting features with a surface active ionic liquid.

#### 5.2 Experimental

NaCMC with an average molecular weight (MW) of 90000 a degree of substitution (DS) of 0.7 was obtained from Acros Organics. The average molecular weight of the sample was estimated from the intrinsic viscosity value (198 mL.g<sup>-1</sup> in 0.2 M NaCl aqueous solution at  $25^{0}$ C) using the Mark-Houwink equation with the constants obtained from the literature.<sup>23</sup> DS was determined by a conductometric procedure as described by Eyler *et al.*<sup>24</sup> These values (MW = 89,200 and DS = 0.71) agree well with those declared by the producer. C<sub>10</sub>MeImCl (Aldrich Chemicals), was used as received. The diffractogram of C<sub>10</sub>MeImCl is similar to that of C<sub>16</sub>MeImCl shown earlier (chapter 4) showing broad and small diffraction peaks.

Triply distilled water with a specific conductance of less than 10<sup>-6</sup> S.cm<sup>-1</sup> at 298.15 K was used for the preparation of solutions.

The surface tension ( $\gamma$ ) measurements were performed on a Krüss (Germany) K9 tensiometer by the platinum ring detachment method (uncertainty = ± 0.01 mN.m<sup>-1</sup>). The tensiometer was connected to a water-flow cryostat in order to maintain the temperature equilibration. Before each measurement, the ring was briefly heated above a Bunsen burner until glowing. For relatively viscous solutions in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC particularly at low surface active ionic liquid concentrations, care was taken to ensure equilibration. The  $\gamma$  vs. log[C<sub>10</sub>MeImCl] profiles for NaCMC-free solution and those for a NaCMC-containing solution are shown, respectively, in Figs. 5.1(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  $\kappa$  vs. [C<sub>10</sub>MeImCl] profile for NaCMC-free solution and that for a representative NaCMC-containing solution with a concentration of 0.0005 monomol.L<sup>-1</sup> are depicted, respectively, in Figs. 5.1(c) and (d).

The vapor pressure osmometery was performed on an Osmomat K-7000 (Knauer Inc., Germany) vapor pressure osmometer. Here, the vapor pressure is measured indirectly by using two thermistors to measure voltage change caused by changes in temperature. The measuring chamber contains a reservoir of solvent and paper wicks to provide a saturated solvent atmosphere. At first, a drop of pure solvent is attached to each thermistor with the help of a syringe and after 5 minutes of equilibration, the reading is adjusted to zero. Then the pure solvent on one thermistor is replaced by the experimental solution and condensation of solvent from the vapor phase onto the solution at the thermistor takes place. Due to the heat of condensation, the thermistor will be warmed up and the vapor pressure rises. Condensation continues until the vapor pressure of the solution becomes equal that of the pure solvent. Generally, a time of 5-10 minutes was found to be sufficient to reach this steady state.

First the instrument was calibrated using NaCl (aq) solutions in the concentration range 0.001 to 1.5 mol.kg<sup>-1</sup>, yielding a calibration curve which correlates the osmometer readings to the corresponding concentrations of the NaCl solution. Then the measurements for the different solutions were carried out. Special care was taken to keep the drop size and shape as constant as possible and equal on both thermistors. For each solution, at least five determinations (zero point adjustment and new solution) were performed and the mean value is reported. Generally, the deviations from the mean 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 NaCl solution showing the same osmometer reading as the C<sub>10</sub>MeImCl or NaCMC-C<sub>10</sub>MeImCl solution, which means an equality of the vapor pressures in both solutions. The stoichiometric numbers  $\nu$  and  $\nu_{\text{NaCl}}$  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>25</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>26</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>27</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>25</sup> to Eq. (2) along with the literature  $A_{\phi}$  values at the experimental temperatures are listed in Table 5.1. These parameter have been used for the calculation of osmotic coefficients of NaCl (aq) solutions. The  $m\phi$  vs. *m* profiles for C<sub>10</sub>MeImCl (aq) solutions in the absence and in presence of NaCMC at 313.15 K are shown in the representative Fig. 5.2.

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. 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.

#### 5.3 Results and Discussion

# 5.3.1 Ion-association Behaviour of Pure Aqueous C<sub>10</sub>MeImCl in the Pre-micellar Regime

Conductometric study provided important information as to the ion-association behaviour of  $C_{10}$ MeImCl below its critical micellar concentration (*cmc*) where it behaves as a 1-1 electrolyte. Such a knowledge would help understand its aggregation behaviour past *cmc*.

The molar conductance ( $\Lambda$ ) vs. concentration data below *cmc* have been analyzed by the Fuoss conductance equation.<sup>28,29</sup> For any given set of  $\Lambda$  values ( $c_j$ ,  $\Lambda_j$ ; j = 1, ..., n), three adjustable parameters, namely the limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), and the association diameter (R) are derived from a solution of the following set of equations :

$$\Lambda = [1 - \alpha(1 - \gamma)][\Lambda^0(1 + RX) + EL]$$
(3)

$$K_{\rm A} = K_{\rm R} (1 + K_{\rm S}) = (1 - \gamma) / c \gamma^2 f^2$$
(4)

$$-\ln f = \frac{e^2 \kappa_{\rm D}}{2\varepsilon k_{\rm B} T (1+kR)}$$
(5)

where *RX* and *EL* are the relaxation and hydrodynamic terms respectively, and the other symbols have their usual significance. The initial  $\Lambda^0$  values for the iteration procedure were obtained from Fuoss-Shedlovsky extrapolation<sup>30</sup> of the data.

Calculations were made to find out  $\Lambda^0$  and  $\alpha$  values minimizing the standard deviation,  $\sigma$ ,

$$\sigma = \left[ \Sigma [\Lambda_j (\text{calcd}) - \Lambda_j (\text{obsd})]^2 / (n-2) \right]^{1/2}$$
(6)

for a sequence of R values and then plotting  $\sigma$  vs. R; the best-fit R corresponds to the minimum of the curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the  $\sigma$  vs. R curves, the R values were preset at the Bjerrum length.

Table 5.2 lists the  $\Lambda^0$ ,  $K_A$ , and R values along with the limiting equivalent conductances of Cl<sup>-</sup> ( $\lambda_{C\Gamma}^0$ ) and Na<sup>+</sup> ions ( $\lambda_{Na^+}^0$ ) at the experimental temperatures. The  $\lambda_{C\Gamma}^0$  and  $\lambda_{Na^+}^0$  values at 298.15, 308.15, and 318.15 K have been taken from the literature.<sup>31</sup> Since the values at 303.15 and 313.15 K are not available, these were obtained by regressing the available literature.<sup>32</sup>  $\lambda_{C\Gamma}^0$  or  $\lambda_{Na^+}^0$  values as a function of temperature. The very low  $K_A$  values of C<sub>10</sub>MeImCl (aq) indicate the existence of C<sub>10</sub>MeImCl essentially as free ions over the temperature range investigated. A comparison of the  $\lambda_{C_{10}MeIm^+}^0$  and  $\lambda_{Na^+}^0$  values reveals that the Na<sup>+</sup> ions are approximately 2.2-2.6 times more mobile that the C<sub>10</sub>MeIm<sup>+</sup> ions within the investigated temperature range. The  $\lambda_{C_{10}MeIm^+}^0$  values are found to be greater than the  $\lambda_{C_{10}MeIm^+}^0$ 

values reported earlier,<sup>32</sup> indicating that the Stokes' radius of the former is smaller than that of the later. This demonstrated that these cations remain unsolvated in aqueous solutions.

#### 5.3.2 Aggregation Processes in Pure C<sub>10</sub>MeImCl and Their Thermodynamics

Aggregation behaviour of pure  $C_{10}$ MeImCl (aq) was investigated by four experimental techniques, *viz.*, tensiometry, conductometry, vapor pressure osmometry, and spectrofluorimetry.

Tensiometry records the threshold surfactant concentration required to saturate the air/solution interface as the *cmc*, which is obtained from a sharp break in the  $\gamma$  versus log[surfactant] profiles as shown in Fig. 5.1(a). This type of tensiometric behaviour is also reported earlier for other aqueous surface active ionic liquid solutions.<sup>33, 34</sup>

An inflection in the specific conductance ( $\kappa$ ) vs. [C<sub>10</sub>MeImCl] isotherm corresponds to the onset of micellization in the bulk solution as shown in Fig. 5.1(c), the corresponding concentration being the *cmc* of the surfactant.

Using the measured osmotic coefficients of  $C_{10}$ MeImCl solutions ( $\phi$ ) as a function of molal concentration (*m*), we plotted the product  $m\phi$  vs. *m* (*cf.* Fig. 5.2). The intersection of the linear segments below and above *cmc* provides a measure of the *cmc* of  $C_{10}$ MeImCl solutions.

Steady-state fluorescence measurements using pyrene as a probe were performed to determine the *cmc* of C<sub>10</sub>MeImCl (aq) solution. Pyrene is a strongly hydrophobic probe and its fluorescence emission spectrum exhibits five characteristic vibronic peaks in region 370-400 nm (Fig. 5.3(a)). 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. 5.3(b)) displays the variation of the ratio of the intensities of the first to third peaks ( $I_1/I_3$ ) as a function of  $\log[C_{10}MeImCl]$  in NaCMC-free and in NaCMC-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.

The *cmc* values of  $C_{10}$ MeImCl in aqueous solutions at different temperatures obtained using these four different experimental methods are listed in Table 5.3 and there is a very good agreement among these values. It is observed that the *cmc* of pure  $C_{10}$ MeImCl increases with increasing temperature within the investigated temperature interval.

The  $\gamma_{cmc}$  values upon complete air/solution interfacial saturation ( $\gamma_{cmc}$ ) of pure C<sub>10</sub>MeImCl are also listed in Table 5.3;  $\gamma_{cmc}$  values are found to decrease slightly with temperature elevation.

The values of Gibbs surface excess ( $\Gamma_{max}$ ), which provide a measure of the efficacy of adsorption of C<sub>10</sub>MeImCl molecules at the interface as compared to the bulk phase, were calculated using the following equation:<sup>35</sup>

$$\Gamma_{\max} = -\frac{1}{nRT} \lim_{[C_{10} \text{MeImCl}] \approx cmc} \left( \frac{\partial \gamma}{\partial \ln[C_{10} \text{MeImCl}]} \right)_{\text{T,p}}$$
(7)

where *n* is the number of species per surfactant monomer in solution, *R* the gas constant, and *T* the absolute temperature. The  $\Gamma_{max}$  values thus obtained are reported in Table 5.3. A decrease in the  $\Gamma_{max}$  values with the rise in the temperature manifests an enhancement of the efficacy of the surfactant monomers to populate the interface at lower temperatures. A comparison of the  $\Gamma_{max}$  values of C<sub>10</sub>MeImCl solutions with those of C<sub>16</sub>MeImCl solutions reported earlier,<sup>32</sup> demonstrates a greater efficiency of accumulation of the interface for the later case.

The area of exclusion per surfactant monomer was calculated assuming complete monolayer formation at *cmc* using the following equation:

$$A_{\min} = \frac{10^{18}}{N_{\rm A} \Gamma_{\max}} \tag{8}$$

in m<sup>2</sup>.molecule<sup>-1</sup>, where  $N_A$  is the Avogadro's number. The values of  $A_{min}$  are also listed in Table 5.3. The increase in the  $A_{min}$  values with temperature may be ascribed to the greater kinetic motion of the monomers populating the air/water interface. The  $A_{min}$  values for aqueous C<sub>10</sub>MeImCl are always found to be greater than the corresponding literature values,<sup>32</sup> for aqueous C<sub>16</sub>MeImCl. This observation supports our earlier conclusion concerning the

unsolvation of the surface active ionic liquid cations reached from conductivity study. From Table 5.3 it may be noticed that the values of  $\Gamma_{\text{max}}$  decrease and those of  $A_{\text{min}}$  increase, when the temperature of the system increases. It shows that the higher the temperature is, the weaker is the tendency of those molecules to escape from the solvent to the air/solvent, resulting in a less packed surface at elevated temperatures.

The degree of counterion binding ( $\beta$ ) onto the self-aggregated assemblies was obtained from the slopes of the  $\kappa$  versus [C<sub>10</sub>MeImCl] isotherm in the premicellar region ( $S_1$ ) and the postmicellar region ( $S_2$ ) using the following relationship:

$$\beta = 1 - S_2 / S_1 \tag{9}$$

The  $\beta$  values, recorded in Table 5.3, decreased slightly with temperature.

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

$$\Delta G_{\rm m}^0 = (1+\beta)RT\ln x_{\rm cmc} \tag{10}$$

where  $x_{cmc}$  is the *cmc* of C<sub>10</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>36</sup>

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

$$\Delta H_{\rm m}^{0} = -RT^{2} \left[ (1+\beta) \left( \frac{\partial \ln x_{\rm cmc}}{\partial \Gamma} \right)_{\rm p} - \ln x_{\rm cmc} \left( \frac{\partial \beta}{\partial T} \right)_{\rm p} \right]$$
(11)

Since the temperature derivative of  $\beta$  for aqueous C<sub>10</sub>MeImCl is found to be small over the temperature range investigated here, and Eq. (11) can then be simplified to

$$\Delta H_{\rm m}^0 = -(1+\beta)RT^2 \left(\frac{\partial \ln x_{\rm cmc}}{\partial T}\right)_{\rm p}$$
(12)

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

$$\Delta G_{\rm m}^0 = \Delta H_{\rm m}^0 - T \Delta S_{\rm m}^0 \tag{13}$$

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>10</sub>MeImCl are listed in Table 5.3.

A reduction in the  $\Delta H_m^0$  values on increasing temperature implies the less enthalpycontrolled system at elevated temperatures.

The  $\Delta G_m^0$  values are found to be negative over the entire range of the temperatures studied for aqueous C<sub>10</sub>MeImCl. This observation indicates that the process of micellization of C<sub>10</sub>MeImCl in aqueous solution is spontaneous. A comparison of the  $\Delta G_m^0$  values of aqueous C<sub>10</sub>MeImCl with those of aqueous C<sub>16</sub>MeImCl reveals that the process of micellization is more spontaneous in the later case.<sup>32</sup> The  $\Delta H_m^0$  and  $T\Delta S_m^0$  values contribute oppositely to  $\Delta G_m^0$ , so the value of  $\Delta G_m^0$  is dependent on relative changes of enthalpy and entropy in the system. It is seen that the variations of enthalpy and entropy of micellization nearly compensate each other, and hence  $\Delta G_m^0$  is found to be only slightly dependent on temperature.

The  $\Delta S_m^0$  values are positive over the whole temperature range of measurement and decrease with the rise of temperature. The positive entropy values indicate that the process of micellization of pure aqueous surface active ionic liquid is entropically driven. Entropy of micellization - the principal driving force towards micelle formation - is initiated by the highly ordered arrangement of the water molecules around the hydrophobic domain of the surface active ionic liquids. The contributing factors to  $T\Delta S_m^0$ , are: (*a*) release of a substantial fraction of the water molecules "frozen" around the hydrophobic surfactant chains, (*b*) readjustment of the head-group in response to the charge density on the micellar surface caused by monomer association and counterion binding, (*c*) increase in the degrees of freedom of the surfactant molecules in the micelle, and (*d*) decrease in the degrees of freedom of the head-groups at the interface. The present results indicate an increase in the degrees of freedom of the system. With the increase in temperature, there is an attenuation in the contribution of entropy of micellization, because at higher temperatures water molecules around the hydrophobic core of the molecules become less organized.

Chiefly, three factors contribute to the value of  $\Delta H_m^0$ . These include: (a) a positive contribution associated with the release of structural water molecules from the hydration

layer around the hydrophilic domain, (*b*) an additional positive contribution arising from the release of water molecules from the water cage around the hydrophobic moiety of the surface active ionic liquids, and (*c*) a negative contribution associated with the transfer of the hydrocarbon chains into the micelle and restoration of the H-bonding structure of the water around the micelle. With increasing temperature the degree of H-bonding around the surface active ionic liquids molecules decreases, and therefore the energy required to break it also diminishes. The experimental values indicate that the negative contribution predominates in aqueous solutions of  $C_{10}$ MeImCl over the investigated range of temperature, *i.e.*, micellization of  $C_{10}$ MeImCl in the aqueous solution is exothermic.

Table 5.3 reveals that while the  $\Delta H_m^0$  value is negative and becomes more negative as temperature increases, the  $T\Delta S_m^0$  values are, in general, positive and becomes less positive with increasing temperature. It is, thus, obvious, that the micellization of C<sub>10</sub>MeImCl in aqueous solution is governed by the entropy-enthalpy compensation effect, and that it is driven by the positive entropy. Similar behaviour has also been observed previously by us for pure alkyltrimethylammonium bromides in the ethylene glycol-water mixed solvent media.<sup>38</sup>

### 5.3.3 Influence of NaCMC on the Aggregation Behaviour of C<sub>10</sub>MeImCl (aq)

NaCMC(aq) has been shown to be surface inactive below 7 g.L<sup>-1.32</sup> The maximum concentration of NaCMC employed in this study (*ca.* 0.16 g.L<sup>-1</sup>) was much lower than the critical concentration above which NaCMC becomes surface active. Hence, surface activity of NaCMC has nothing to do with the observed complexity in the tensiograms of NaCMC- $C_{10}$ MeImCl systems. Moreover, at such low NaCMC concentrations, complexity arising out of the polyion-polyion interactions was also considered to be absent.

The presence of NaCMC in  $C_{10}$ MeImCl solutions greatly modifies the tensiometric behaviour of the surfactant in solution. Typical surface tension profiles for the present NaCMC- $C_{10}$ MeImCl system as surfactant concentration varies are complex in nature, as shown in the representative tensiogram, Fig. 5.1(b), in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC, and clearly show the existence of a hump in the profile. In all cases, there is a marked lowering of surface tension at lower surfactant concentrations when NaCMC is initially introduced compared to the NaCMC-free case. It appears that adsorption of NaCMC-surfactant complexes occurs at surfactant concentrations well below the concentration at which the surfactant molecules on their own are expected to adsorb appreciably. The NaCMC- surfactant complexes are formed by cooperative binding of surfactant monomers onto the NaCMC backbone due to strong electrostatic forces of attraction among themselves. Because of the adsorption of the monomers on the polyions, the hydrophobicity of the complexes increases, and the complexes occupy the Langmuirian interface. The initial decrease 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 tensiograms indicate the characteristic concentration (critical aggregation concentration, cac) beyond which are formed the non-surface active polyelectrolyte-micellar aggregates where the surfactant molecules cooperatively adsorb on the polyion strand 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 with an increase in 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  $C_{10}$ 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 increases again. The maximum in a tensiogram represents the concentration at which the polyion chains are saturated with the polyelectrolyte-induced aggregates and is referred to as the polymer saturation concentration (psc). Similar tensiometric behaviour of surfactants in presence surfactants was also observed by other groups.<sup>39-41</sup> The values of *cac*, *psc*, and *cmc*\* values obtained from tensiometry are recorded in Table 5.4. The polymer shrinkage as observed from the drop in the viscosity value is very extensive above *cac*, and the viscosity of the solution reaches a plateau close to psc (reduced viscosity is found to plunge by a factor of ca. 0.33 from its value at cac) indicating a saturation of chain coiling. Appreciable coiling of the macromolecular chains in presence of conventional surfactants beyond cac probed by viscosity have also been reported earlier.<sup>42-43</sup>

The conductometric profiles for  $C_{10}$ MeImCl (aq) in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC as a function of  $C_{10}$ MeImCl concentration are depicted in Fig. 5.1(d). The curves show a sharp change in slope at the critical micellization concentration of  $C_{10}$ MeImCl in presence of NaCMC (*cmc*\*). 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 listed in Table 5.4. It may pointed out here that conductivity isotherms manifesting two linear sections with one inflection have also been reported earlier in aqueous alkyltrimethylammonium bromide-NaPSS<sup>42-43</sup> and in dodecylpyridinium chloride-sodium dextran sulfate systems<sup>44</sup> and those with higher-complexity showing up four linear sections with three inflections (*e.g.*, in aqueous NaCMC-cetyltrimethylammonium bromide solution<sup>45</sup> are also available in the literature. It may, however, be noted that for aqueous cetyltrimethylammonium bromide-NaCMC solution, where 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. The lower complexity in the conductivity profiles of the NaCMC-C<sub>10</sub>MeImCl(aq) system observed here may be attributed to the predominance of the electrostatic interactions over the hydrophobic effect in presence of the highly charged polyions.

Although osmotic coefficient data on pure surfactants are available,<sup>46-50</sup> those on polyelectrolyte-surface active ionic liquid solutions have, to the best of our knowledge, not been reported so far. Here, we have employed vapor pressure osmometry to understand the interactions prevailing in NaCMC-C<sub>10</sub>MeImCl solutions. The product of the C<sub>10</sub>MeImCl molality (*m*) and the measured osmotic coefficient of NaCMC-C<sub>10</sub>MeImCl solutions ( $\phi$ ) for a given NaCMC concentration when plotted against *m* manifest three linear segments with two intersections. The first intersection has been identified as the *psc* and the second as the *cmc*\*. The representative profile (Fig.5.2) displays the variation of  $m\phi$  vs. *m* for a selected system. Like conductivity study, here also the *cac* could not be detected.

The variation of  $I_1/I_3$  was measured for aqueous solutions containing fixed concentrations of the polyelectrolyte and variable concentrations of C<sub>10</sub>MeImCl. The results of NaCMC-C<sub>10</sub>MeImCl system are shown in Fig. 5.3(b). It is interesting to note that the medium polarity decreases with increasing amount of the added NaCMC to C<sub>10</sub>MeImCl solutions. This may be ascribed to greater condensation of counter and surfactant ions onto the polyion backbone.

Ideally the  $I_1/I_3$  vs. [surfactant] profiles of polyelectrolyte-surfactant systems should give rise to three regions where  $I_1/I_3$  values are almost independent of the surfactant concentration with two breaks.<sup>51</sup> The first inflection corresponds to the formation of minimicelles bound to the polymer chains and hence gives a measure of the *cac*, whereas the second to the formation free surfactant micelles and provides a measure of the *cmc*\*. These three regions are not always detectable through fluorescence study.<sup>45</sup> Sodium dodecylsulfate-poly(*N*vinylprrrolidone) system reveals three regions very nicely although the later break is not sharp at higher polymer concentrations<sup>51</sup> Sodium dodecylsulfate-poly(ethylene oxide), on the other hand, shows only one sharp break when the concentration of the polymer employed was very small.<sup>51</sup> In the present study, only one very sharp break has been identified, and hence only the *cmc*\* values could be determined. The *cac* and *psc* could, however, not be detected by fluorescence studies.

# 5.3.4 Variation of *cmc*, *cac*, *psc*, and *cmc*\* Values with Temperature and NaCMC Concentration

The values of *cac* and *psc* along with the average of the *cmc*<sup>\*</sup> values obtained from the four experimental techniques are listed in Table 5.4. The *cac* values could not, however, be detected in presence of 0.0001 monomol.L<sup>-1</sup> of NaCMC even with tensiometric method.

It is observed that the values of *cac*, *psc*, and *cmc*\* values increase monotonically with increasing amount of added NaCMC at any given temperature. They are also found to increase with increasing temperature in presence of a given amount of NaCMC. A slight increase in *cac* and *psc* with NaCMC concentration was observed (*cf*. Table 5.4).

An increase in the *cmc* and *cmc*<sup>\*</sup> values with increasing amount of the added NaCMC at any given temperature may be ascribed to the lowering in the amount of free  $C_{10}$ MeImCl molecules since more  $C_{10}$ MeImCl molecules are required to saturate an increased amount of NaCMC.

This behavior is similar to that observed in NaCMC-C<sub>16</sub>MeImCl solutions (*cf.* Chapter 4), the critical concentrations being, however, 50-60 times higher in NaCMC-C<sub>10</sub>MeImCl solutions. Pure aqueous  $C_{10}$ MeImCl solutions are also found to form micellar aggregates at a much higher surfactant concentration than the pure aqueous  $C_{16}$ MeImCl solutions (*cf.* Tables 4.2 and 5.3). Thus alkyl chain length of the surface active ionic liquid molecules investigated has a profound influence on their aggregation behaviour in absence as well as in presence of NaCMC. Both temperature and polyelectrolyte concentration have similar influence on the surface active ionic liquid systems investigated.

### 5.3.5 Thermodynamics of Micellization of C<sub>10</sub>MeImCl (aq) in Presence of NaCMC

The  $\Delta G_m^0$  of C<sub>10</sub>MeImCl in presence of NaCMC are, in all cases, found to be negative. In Fig. 5.4 (a), and (b), the  $\Delta G_m^0$  values of C<sub>10</sub>MeImCl have been plotted as a function of temperature in presence of 0.0005 monomol.L<sup>-1</sup> of NaCMC. Also included in this figure are

the  $\Delta G_m^0$  values for C<sub>10</sub>MeImCl in absence of NaCMC. From this figure, it is apparent that micellization becomes less spontaneous upon addition of NaCMC at any given temperature, and that the spontaneity of micellization decreases as the amount of added NaCMC increases. In presence of NaCMC, however, the micellization becomes more spontaneous upon an elevation of temperature. Some characteristic features of the thermodynamic parameters are manifested in Fig. 5.4 (a) and (b), which are common to the polyelectrolyte-free and polyelectrolyte-containing C<sub>10</sub>MeImCl systems studied. It is directly evident that the micellization processes of C<sub>10</sub>MeImCl are always exothermic over the investigated range of temperatures, whether the system contains NaCMC or not, and that these processes become more exothermic at higher temperatures. The value of  $-T\Delta S_m^0$ , on the other hand, increases 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 C<sub>10</sub>MeImCl micellization processes both in absence as well as in the presence of NaCMC, *i.e.*, the micelle formation process for the investigated surface active ionic liquids is always entropy-driven. Highentropy changes are generally associated with a phase change. Hence it can be assumed that the micelles form separate phases in these systems. Shaw<sup>52</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>35</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>53</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>38</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.

In accordance with Lumry and Rajender <sup>54</sup> an important information on the bulk structural property of aqueous solutions can be obtained from a linear correlation between  $\Delta H_m^0$  and  $\Delta S_m^0$  (enthalpy-entropy compensation). Such a correlation can be generally described by the relation

$$\Delta H_{\rm m}^0 = \Delta H_{\rm m}^* + T_{\rm c} \Delta S_m^0 \tag{14}$$

where  $T_c$  is the compensation temperature, and  $\Delta H_m^*$  is the corresponding intercept.  $T_c$  has been proposed as a measure of the "hydration part" of the micellization process (dehydration of the hydrophobic chains).<sup>55,56</sup>  $\Delta H_m^*$  provides information on the solute-solute interactions and is considered as an index of the "chemical part" of micelle formation (association of the non-polar chains to form a micellar unit).  $T_c$  for the micellization process of C<sub>10</sub>MeImCl (aq) is found to be 245 K, while for NaCMC-C<sub>10</sub>MeImCl solutions the  $T_c$  values are 211, 208 and 130 K respectively in presence of 0.00001, 0.00010 and 0.00050 monomol.L<sup>-1</sup> NaCMC.  $T_c$ values in aqueous solutions are expected to lie in the range 270-294 K for processes dominated by hydration.<sup>55-57</sup> However, the deviations observed here might be due to the appreciable departure of the bulk structural property of the solution from that of the water, particularly in NaCMC-C<sub>10</sub>MeImCl solutions containing 0.0005 monomol.L<sup>-1</sup> of NaCMC. It may, however, be pointed out that the linear relationship of the  $\Delta H_m^0$  vs.  $\Delta S_m^0$  plots should not be overinterpreted, even though this linearity is quite often seen.

#### **5.4 Conclusions**

Micellization behaviour of C<sub>10</sub>MeImCl was studied in aqueous solution in absence as well as in presence of NaCMC using tensiometry, conductometry, vapor pressure osmometry and spectrofluorometry with particular reference to the influence of NaCMC concentration and temperature. It is observed that in the premicellar regime  $C_{10}$ MeImCl can exist essentially as free ions which remain unsolvated. The results demonstrated gradual formation of surfaceactive complexes consisting of surfactant monomers bound to the polyion backbone, and non-surface active necklace-like polyion-micellar aggregates, and free surfactant micelles in NaCMC-C<sub>10</sub>MeImCl solutions upon addition of C<sub>10</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 crititical micellization concentration (at which free surface active ionic liquids micelles start to form) have been identified in NaCMC-C<sub>10</sub>MeImCl solutions. The thermodynamic parameters for micelle formation of aqueous C<sub>10</sub>MeImCl were estimated both in absence and in the presence of NaCMC 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. The bulk structural property of aqueous NaCMC- $C_{10}$ MeImCl solution was found to be deviated appreciably from that of the pure water, particularly in solutions containing 0.0005 monomol.L<sup>-1</sup> of NaCMC.

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<i>T</i> (K)	$A_{\phi}(\text{kg.mol}^{-l/2})$	$\beta_{\text{MX}}^{(0)}$ (kg.mol <sup>-1</sup> )	$\beta_{\text{MX}}^{(1)}$ (kg.mol <sup>-1</sup> )	$10^{-4} C_{\rm MX}^{\phi}$ (kg.mol <sup>-1</sup> )
298.15	0.39148	0.0764	0.274	16.70
303.15	0.39492	0.0804	0.277	9.04
308.15	0.39852	0.0838	0.280	2.36
313.15	0.40228	0.0869	0.283	-3.21
318.15	0.40620	0.0895	0.286	-8.31

**TABLE 5.1.** Pitzer Ion-interaction Parameters and Debye-Hückel Coefficient for the Osmotic Function for NaCl (aq) Solutions at 298.15, 303.15, 308.15, 313.15, and 318.15 K.

**TABLE 5.2.** Conductance Parameters of C<sub>10</sub>MeImCl in the Premicellar Regime Along With the  $\lambda_{C\Gamma}^0$ ,  $\lambda_{C_{10}MeIm^+}^0$ , and  $\lambda_{Na^+}^0$  Values in Water at 298.15, 303.15, 308.15, 313.15, and 318.15 K.

<i>T</i> (K)	$ \begin{array}{c} \Lambda^0 \\ (\text{S.cm}^2. \\ \text{eqv}^{-1}) \end{array} $	$K_{\rm A} \\ (\rm dm^3. \\ \rm mol^{-1})$	10 <sup>8</sup> <i>R</i> (cm)	$\sigma$ %	$\lambda_{\rm CF}^0$ (S.cm <sup>2</sup> . eqv <sup>-1</sup> )	$\lambda^0_{\mathrm{C}_{10}\mathrm{MeIm}^+} \ (\mathrm{S.cm}^2. \ \mathrm{eqv}^{-1})$	$\lambda_{{ m Na}^{+}}^{0} \ ({ m S.cm}^{2}. \ { m eqv}^{-1})$
298.15	98.47	6.97	7.16	0.14	76.35	22.12	50.10
303.15	109.58	3.66	7.20	0.02	84.38	25.20	55.80
308.15	119.56	3.49	7.25	0.02	92.21	27.35	61.54
313.15	128.20	3.46	7.30	0.07	100.42	27.78	67.61
318.15	137.08	3.11	7.35	0.04	108.92	28.16	73.73

<i>T</i> (K)		298.15	303.15	308.15	313.15	318.15
	Tensiometry	49.19	49.89	50.02	51.20	52.73
	Conductometry	58.03	58.87	59.03	60.85	61.25
cmc	Fluorimetry	57.09	-	58.05	-	-
(IIIIVI)	Osmometry	54.27	55.69	56.06	57.87	58.89
	Average	54.65	54.82	55.79	56.64	57.62
	$\gamma_{ m cmc}$	34.81	34.28	33.96	33.68	33.22
	$(mN.m^{-1})$					
	$\Gamma_{\rm max} \ge 10^6$	2.01	1.78	1.72	1.48	1.42
	$(\text{mol.m}^{-2})$					
	$A_{\min} \ge 10^{18}$	0.826	0.933	0.965	1.122	1.169
	(m <sup>2</sup> )					
	β	0.52	0.51	0.50	0.48	0.47
	$\Delta G_{ m m}^0$	-26.12	-26.27	-26.41	-26.39	-26.59
	(kJ.mol <sup>-1</sup> )					
	$\Delta {H}_{ m m}^0$	-1.70	-2.64	-3.62	-4.61	-5.69
	(kJ.mol <sup>-1</sup> )					
	$T\Delta S_{\mathrm{m}}^{0}$	24.41	23.64	22.80	21.78	20.91
	(kJ.mol <sup>-1</sup> )					

**TABLE 5.3.** Critical Micellar Concentrations (*cmc*) and Related Thermodynamic Parameters for Pure  $C_{10}$ MeImCl in Aqueous Solutions at 298.15, 303.15, 308.15, 313.15, and 318.15 K.

**TABLE 5.4.** Critical Micellar Aggregation Concentrations  $(cmc^*)$  of C<sub>10</sub>MeImCl in Presence of Varying Concentration of Added NaCMC alongwith 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)	$c$ (monomol. $L^{-1}$ )	Method	cac (mM)	<i>psc</i> mM	<i>cmc</i> */ (mM)	<i>av. cmc</i> <sup>*</sup> (mM)
298.15	0.00001	Conductometry	-	22.72	58.86	
		Tensiometry	-	-	49.67	56.38
		Fluorimetry	-	-	59.25	
		Osmometry	-	17.95	57.72	
	0.00010	Conductometry	-	24.19	60.39	
		Tensiometry	6.24	15.82	50.09	57.44
		Fluorimetry	-	-	61.06	
		Osmometry	-	18.17	58.23	
	0.00050	Conductometry	-	24.87	62.67	
		Tensiometry	7.69	19.05	58.06	60.25
		Fluorimetry	-	-	-	
		Osmometry	-	20.88	60.02	
303.15	0.00001	Conductometry	-	23.11	60.22	
		Tensiometry	-	-	52.69	57.19
		Fluorimetry	-	-	-	
		Osmometry	-	18.45	58.67	
	0.00010	Conductometry	-	25.13	62.13	
		Tensiometry	7.38	16.11	52.89	57.96
		Fluorimetry	-	-	-	
		Osmometry	-	19.42	58.87	

	0.00050	Conductometry	-	25.20	63.22	
		Tensiometry	7.93	20.02	59.39	61.28
		Fluorimetry	-	-	-	
		Osmometry	-	21.16	61.23	
308.15	0.00001	Conductometry	-	24.15	60.25	
		Tensiometry	-	-	52.82	58.26
		Fluorimetry	-	-	61.09	
		Osmometry	-	18.86	58.89	
	0.00010	Conductometry	-	25.63	62.21	59.49
		Tensiometry	7.58	17.02	53.11	
		Fluorimetry	-	-	62.86	
		Osmometry	-	20.64	59.79	
	0.00050	Conductometry	-	25.83	63.29	62.18
		Tensiometry	8.01	20.85	60.74	
		Fluorimetry	-	-	-	
		Osmometry	-	22.73	62.51	
313.15	0.00001	Conductometry	-	25.23	61.98	
		Tensiometry	-	-	54.93	58.91
		Fluorimetry	-	-	-	
		Osmometry	-	19.89	59.83	
	0.00010	Conductometry	-	26.32	63.17	
		Tensiometry	7.65	17.42	55.71	60.23
		Fluorimetry	-	-	-	
		Osmometry	-	21.36	61.82	
	0.00050	Conductometry	-	26.85	63.77	
		Tensiometry	8.15	21.42	61.84	63.08

		Fluorimetry	-	-	-	
		Osmometry	-	23.77	63.63	
318.15	0.00001	Conductometry	-	26.21	62.83	
		Tensiometry	-	-	56.23	60.31
		Fluorimetry	-	-	-	
		Osmometry	-	20.87	61.81	
	0.00010	Conductometry	-	26.95	64.97	
		Tensiometry	7.68	17.49	55.95	61.29
		Fluorimetry	-	-	-	
		Osmometry	-	22.09	62.95	
	0.00050	Conductometry	-	27.07	65.07	
		Tensiometry	8.26	22.10	63.11	64.21
		Fluorimetry	-	-	-	
		Osmometry	-	24.44	64.45	



**Fig. 5.1(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 10 mN.m<sup>-1</sup> from each other for clarity.



**Fig. 5.1(b).** Surface tension  $(\gamma)$  *vs.* log[C<sub>10</sub>MeImCl] profiles in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC (aq) 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 10 mN.m<sup>-1</sup> from each other for clarity.



**Fig. 5.1(c).** Specific conductance ( $\kappa$ ) *vs.* [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 ( $\blacksquare$ ).



**Fig. 5.1(d).** Specific conductance ( $\kappa$ ) *vs.* [C<sub>10</sub>MeImCl] profiles in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC (aq) at 298.15 K ( $\circ$ ), 303.15 K ( $\Box$ ), 308.15 K ( $\Delta$ ), 313.15 K ( $\bullet$ ), and 318.15 ( $\blacksquare$ ).



**Fig. 5.2.** 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 0.00001 ( $\Box$ ), 0.0001 ( $\Delta$ ), and 0.0005 monomol.L<sup>-1</sup> ( $\bullet$ ) of NaCMC (aq).



**Fig. 5.3(a).** Pyrene fluorescence emission spectra in  $C_{10}$ MeImCl (aq) solution at concentrations 0.0050, 0.0120, 0.0520, 0.0540, 0.0592, 0.0620, 0.0690 and 0.0750 mol.L<sup>-1</sup> (bottom to top) in presence of 0.00001 monomol.L<sup>-1</sup> NaCMC at 298.15 K. Excitation wavelength: 335 nm.



**Fig. 5.3(b).**  $I_1/I_3$  ratio of pyrene *vs.* log[C<sub>10</sub>MeImCl] in aqueous solution ( $\circ$ ) and in 0.00001 ( $\Box$ ) and 0.0001 monomol.L<sup>-1</sup> ( $\Delta$ ) NaCMC (aq) at 308.15 K.



**Fig. 5.4(a).** Thermodynamic parameters of micellization of C<sub>10</sub>MeImCl in water at different temperatures:  $\Delta G_m^0(\Delta)$ ,  $\Delta H_m^0(\circ)$ ,  $-T\Delta S_m^0(\Box)$ .



**Fig. 5.4(b).** Thermodynamic parameters of micellization of  $C_{10}$ MeImCl in presence of 0.0005 monomol.L<sup>-1</sup> NaCMC at different temperatures:  $\Delta G_m^0(\Delta)$ ,  $\Delta H_m^0(\circ)$ ,  $-T\Delta S_m^0(\Box)$ .