Chapter 7

Summary of the Works Done

Systems containing polyelectrolytes and surfactants in aqueous solutions have been the subject of extensive investigations to obtain a fundamental understanding of their properties and to evaluate their use in various technical applications. Despite decades of research, the mechanisms of polyelectrolyte-surfactant interactions are not completely understood yet. This is due to the interplay of a variety of forces in polyelectrolyte-surfactant solutions.

Such a situation, of course, demands further comprehensive investigation in this area of science with as many different kinds of interacting species, and as many different experimental techniques as possible.

Recently, some surface active ionic liquids - which belong to a class of substances currently being used as greener replacements for traditional volatile organic solvents - have been shown to exhibit surface activity like conventional ionic surfactants. This recent development opens up, in principle, the possibility to use mixtures of polyelectrolytes and surface active ionic liquids in areas where polyelectrolyte-conventional surfactant combinations are used today. Fundamental understanding of the interactions between these species is thus necessary for this purpose.

The interactions between the polyelectrolytes and the surface active ionic liquids were not explored till January 2012 when this study was undertaken. In order to understand the nature of polyelectrolyte - surface active ionic liquid interactions in aqueous solutions, in particular, and that of polyelectrolyte-surfactant systems, in general, a comprehensive multi-method approach would be suitable. With this objective, we performed a study using conductometric, tensiometric, osmometric and spectrofluorimetric techniques to probe various interactions prevailing in these solutions.

The aim of this thesis is to provide a better understanding about interactions between polyelectrolytes and oppositely charged surface active ionic liquids: What are the parameters affecting these interactions and how the subtle interplay of various forces determine their physico-chemical properties. Another important part of this study was to clarify the nature of interactions in pure polyelectrolyte and pure surface active ionic liquid solutions and how these interactions might be modified in each others presence. For the study, we selected two negatively charged polyelectrolytes – sodium carboxymethylcelulose and sodium polystyrenesulfonate, and two surface active ionic liquids – 1-decyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride. Four different experimental techniques, namely, conductometric, tensiometric, osmometric and spectrofluorimetric techniques were employed to explore and elucidate the nature of interactions in the investigated polyelectrolyte-surface active ionic liquid solutions.

Specifically, the wok embodied in this thesis includes:

- 1. Investigation on the counterion-condensation behaviour of the polyelectrolytes sodium carboxymethylcelulose and sodium polystyrenesulfonate in aqueous solutions.
- Investigation on the ion-association behaviour of the surface active ionic liquids1decyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride in aqueous solutions in the premicellar regime.
- Investigation on the aggregation behaviour of the surface active ionic liquids 1-decyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride in aqueous solutions.
- 4. Investigation on the aggregation behaviour of the aqueous surface active ionic liquids (1-decyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride) induced by the polyelectrolytes (sodium carboxymethylcelulose and sodium polystyrenesulfonate).

Both sodium carboxymethylcelulose and sodium polystyrenesulfonate are important industrial polymers with a wide spectrum of applications. Besides exploring the interactional features in the investigated polyelectrolyte-surface active ionic liquid systems, the present study is, therefore, expected to help extend the fruitful use of these polyelectrolytes.

The present dissertation has been summarized in seven chapters.

Dissertation begins with a preface which describes the aim and scope of work.

Chapter 1 provides a general introduction to polyelectrolytes and their counterioncondensation behaviour in solutions, surface active ionic liquids and their interfacial and micellization properties, and polyelectrolyte-surface active ionic liquid interactions. A brief review of the notable works in the fields of polyelectrolyte solution chemistry with particular reference to the condensation of counterions onto the polyions and those in the fields of surface active ionic liquids and polyelectrolyte-surface active ionic liquid mixed systems have been given. This is followed by an account of conductometry, tensiometry, osmometry, and spectrofluorimetry to investigate the interactions between polyelectrolytes and surfactants with special reference to the surface active ionic liquids has been given since these techniques have been employed to study the behaviour of polyelectrolyte-surface active ionic liquid interactions in this dissertation.

Chapter 2 describes the electrical conductivities of aqueous solutions of the anionic polyelectrolyte sodium carboxymethylcelulose with different degrees of substitution as a function of concentration and temperature. It gives a description of an investigation on the thermodynamic, transport and frictional properties of sodium carboxymethylcelulose in aqueous solution. The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter following the model for the electrical conductivity of solutions of semidilute polyelectrolytes without added salt proposed by Colby et al. [R. H. Colby, D. C. Boris, W. E. Krause, and J. S. Tan, J. Polym. Sci. Part B: Polym. Phys., 35, 2951 (1997)] using a scaling description for the configuration of a polyion chain according to Dobrynin et al. [A. V. Dobrynin, R. H. Colby, and M. Rubinstein, Macromolecules, 28, 1859 (1995)]. Excellent agreement with the experimental results were obtained. 36-55% of the counterions were found to remain condensed and the condensation process was shown to be spontaneous. Although the level of counterion-condensation depends appreciably on the degree of substitution of the polyelectrolyte, it was found to remain invariant with the polyelectrolyte concentration and the temperature. The free energies of counterioncondensation, the ratios of the mobility of the polyion to that of the counterion, the polyion transference numbers, and the coefficients of monomer-solvent friction have been evaluated. The effects of the polyion charge, its size, and the bulk viscosity of the media on the polyioncounterion interactions have also been discussed.

Chapter 3 reports a study on the interactions between a polyion and its counterions in aqueous solutions of another anionic polyelectrolyte sodium polystyrenesulfonate in the presence of NaCl using electrical conductivity as the probe. The specific conductance *vs.* polyelectrolyte concentration data have been analyzed with an equation put forwarded recently [R. De, and B. Das, *J. Chem. Eng. Data*, **55**, 2108 (2010)] considering the scaling description for the conformation of apolyion chain. The influences of (a) the molecular weight and the concentration of the polyelectrolyte, (b) the added electrolyte concentration, and (c) the temperature on polyion–counterion interactions were investigated. The extent of

counterion-condensation was found to be greatly affected by the concentration and molecular weight of the polyelectrolyte, the concentration of the added electrolyte, and the temperature. The polyion equivalent conductivity in conjunction with the derived coefficient of friction between the monomer units and the solvent provided important information concerning the relative importance of the size and charge of the polyions. The overall results have been elucidated taking the relative permittivity of the medium, the hydration behaviour of the counterions, and the coiling behaviour of the polyion chains into account. The present study provides new insight as to how the polyelectrolyte molecular weight influences the counterion-condensation behaviour in a polyelectrolyte solution in the presence of an added electrolyte.

Chapter 4 pertains to a study exploring the influence of sodium carboxymethylcelulose on the aggregation phenomena of a surface active ionic liquid 1-hexadecyl-3-methylimidazolium chloride in aqueous solutions using electrical conductivity and surface tension measurements. The counterion-condensation behaviour of sodium carboxymethylcelulose (aq) and the premicellar ion-association behaviour of 1-hexadecyl-3-methylimidazolium chloride (aq) were also investigated. Two characteristic concentrations, namely the critical aggregation and polymer saturation concentration, before free 1-hexadecyl-3concentration methylimidazolium chloride micelles appear in sodium carboxymethylcelulose + 1hexadecyl-3-methylimidazolium chloride solutions, have been identified. Effects of temperature, sodium carboxymethylcellulose concentration, and the charge density parameter of sodium carboxymethylcelulose on the self-aggregation of the 1-hexadecyl-3methylimidazolium chloride have been discussed to elucidate sodium carboxymethylcelulose + 1-hexadecyl-3-methylimidazolium chloride interactions. The thermodynamic parameters for micellization of 1-hexadecyl-3-methylimidazolium chloride were estimated both in absence and in the presence of sodium carboxymethylcelulose. The observed enthalpyentropy compensation effect in 1-hexadecyl-3-methylimidazolium chloride and sodium carboxymethylcelulose + 1-hexadecyl-3-methylimidazolium chloride systems provided important insight as to how micellization processes are governed by the bulk structural property of the solution with respect to that of the water.

Chapter 5 gives an account of a study on the aggregation behaviour of the surface active ionic liquids1-decyl-3-methylimidazolium chloride in aqueous solutions in absence and in presence of sodium carboxymethylcelulose using electrical conductivity, surface tension,

vapor pressure, and fluorescence measurements. Ion-association behaviour of 1-decyl-3methylimidazolium chloride (aq) in the premicellar regime has also been investigated. Two characteristic concentrations, namely the critical aggregation concentration and polymer saturation concentration, before free 1-decyl-3-methylimidazolium chloride micelles appear in sodium carboxymethylcelulose + 1-decyl-3-methylimidazolium chloride solutions were identified. Effects of temperature, sodium carboxymethylcelulose concentration, and the bulk solution structural property on the self-aggregation of 1-decyl-3-methylimidazolium chloride elucidate sodium carboxymethylcelulose been discussed to + 1-decyl-3have methylimidazolium chloride interactions. Thermodynamics of the micellization processes provided important insight regarding the (a) release of water molecules from the hydration layer around the hydrophilic domain, and from the water cage around the hydrophobic moiety of the surface active ionic liquids, and (b) transfer of the hydrocarbon chains into the micelle and restoration of the H-bonding structure of the water around the micelle.

In Chapter 6, the influence of sodium polystyrenesulfonate on the aggregation phenomena of 1-decyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride was studied in aqueous solutions using electrical conductivity, surface tension, fluorescence and vapour pressure osmometric measurements. Several characteristic concentrations signifying different kinds of interactions, namely the critical aggregation concentration and polymer saturation concentration, prior to the formation of free surface active ionic liquid micelles in sodium polystyrenesulfonate + surface active ionic liquid solutions have been identified. Effects of alkyl chain length, temperature, sodium polystyrenesulfonate concentration, and the charge density parameter of sodium polystyrenesulfonate on the self-aggregation of the surface active ionic liquids have been discussed to elucidate sodium polystyrenesulfonate + surface active ionic liquid interactions. The thermodynamic parameters for micellization of liquids were estimated in the presence of sodium the surface active ionic polystyrenesulfonate.

The dissertation ends with a summary of the works done in this chapter (Chapter 7).

Publication

List of Publications derived from this Study:

- 1. **D. Ray**, R. De, and B. Das, Thermodynamic, transport and frictional properties in semidilute aqueous sodium carboxymethylcellulose solution, *J. Chem. Thermodyn.*, **101**, 227 (2016).
- 2. R. De, **D. Ray**, and B. Das, Influence of temperature, added electrolyte, and polymer molecular weight on the counterion-condensation phenomenon in aqueous solution of sodium polystyrenesulfonate: a scaling theory approach, *RSC Advances*, **5**, 54890 (2015).
- 3. **D. Ray**, S. Das, R. De, and B. Das, Sodium carboxymethylcellulose-induced aggregation of 1-decyl-3-methylimidazolium chloride in aqueous solutions, *Carbohydr. Polym.*, **125**, 255 (2015).
- 4. B. Das, **D. Ray**, and R. De, Influence of sodium carboxymethylcellulose on the aggregation behaviour of aqueous 1-hexadecyl-3-methylimidazolium chloride solutions, *Carbohydr. Polym.*, **113**, 208 (2014).
- 5. **D. Ray**, and B. Das, Influence of sodium polystyrenesulfonate on the aggregation behaviour of aqueous surface active ionic liquid solutions, *communicated*.

List of other Publications:

- 6. S. Mondal, **D. Ray**, and B. Das, Thermodynamics of aggregation of imidazoliumbased surface activesurface active ionic liquids in aqueous poly(ethylene oxide) media, *J. Chem. Thermodyn.*, **116**, 61 (2018).
- 7. P. Sar, A. Ghosh, S. Malik, **D. Ray**, B. Das and B. Saha, Selective heteroaromatic nitrogen base promoted chromium(VI) oxidation of isomeric pentanols in aqueous micellar media at room temperature *J. Ind. Eng. Chem.*, **42**, 53 (2016).