Chapter 1

Introduction

1.1 Polyelectrolytes

1.1.1 Definition of Polyelectrolytes

Polyelectrolytes consist of polymer chains with attached groups which dissociate in polar media (*e.g.*, water) into a polyion and counterions of opposite charge. The counterions may be dispersed in the solution (free counterions) or these may be condensed onto the polyions (condensed counterions).The driving force for releasing counterions into the solution is a net increase in the entropy of the system, but this is opposed by the electrochemical potential, which attracts the oppositely charged counterions to the polyelectrolyte chain. This gives rise to the equilibrium states of "free" and "condensed" counterions around the polyion chain in dilute solutions, similar to the electrical double layer for dilute colloids. The concept of counterion condensation, which is central to the solution behaviour of polyelectrolytes, was originally introduced by Oosawa's two-phase model.[1,2] This idea was later fully exploited by Manning who derived the well-known limiting laws for salt-free solutions of linear polyelectrolytes.[3-6]

The polyelectrolyte conformation varies self-consistently, together with the variation of the number of condensed counterions. The electrostatic interactions between the charges on the polyion chain and those of the surrounding counterions are strong enough to determine the behaviour of polyelectrolytes in solution, which are quite distinct from those of the uncharged polymers.

The fraction of charged groups on the polymer and the ionic strength of the solution determine the conformations of polyelectrolytes in dilute solutions. In case of weakly charged polyelectrolytes (or macromolecules carrying a small percentage of ionizable groups), non-Coloumbic interactions such as van der Waals interactions, hydrogen bonding and other molecular interactions play an important role and become important in governing the conformation of this kind of macromolecules. The properties of polyelectrolyte solutions are strongly influenced by the solution pH, nature of the ions, chemical structure of the polyion, its size and charge density, the type of charges, the counterion size, its polarizability and valence, the water structure around the counterion, molecular weight, solvent polarity,

temperature etc. Moreover, the presence of multivalent counterions significantly influences the structure and dynamics of the polyelectrolyte solutions.

1.1.2 Classification of Polyelectrolytes

Based on the origin, polyelectrolytes are classified as natural, synthetic and chemically modified species. For example, DNA is a natural polyelectrolyte, NaPSS is a synthetic polyelectrolyte, and NaCMC is an example of a chemically modified natural polyelectrolyte.

Based on molecular architecture, polyelectrolytes may be grouped into two important categories, namely linear and branched. In linear polyelectrolytes, although in a topological sense, the backbone is linear, the shape of the polymer might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.[7] Branched polyelectrolytes do not have linear chains and are less-investigated species compared to their linear analogues.[8-13] The different known branched structures are comb-like, stars (regular and irregular), H-shaped, super H-shaped polymer and dendrimers.[9,14-19]
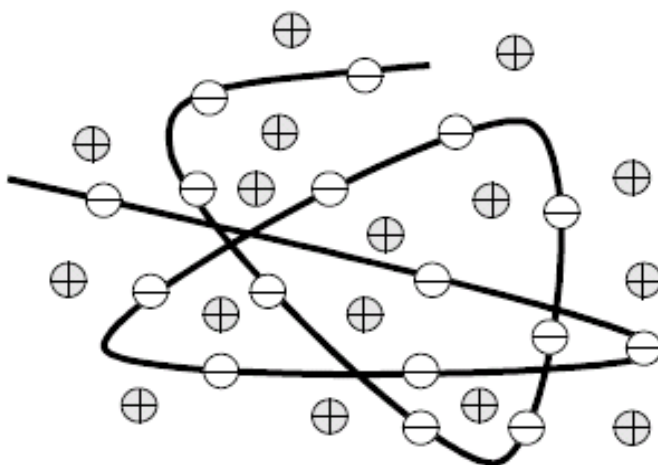

Fig. 1.1. Schematic representation of a flexible polyelectrolyte.

Polyelectrolytes could also be distinguished considering their conformational changes. Flexible polyelectrolytes (Fig. 1.1) consist of a polyion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions. Since both of these interactions occur almost simultaneously, it is rather difficult to study these systems. NaPSS is an example of flexible polyelectrolyte (Fig. 1.2).
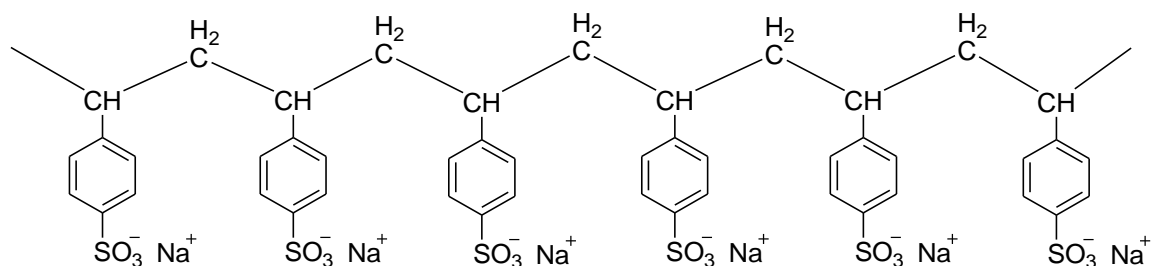
Fig. 1.2. NaPSS with sodium counterions.

Rigid rod-like polyelectrolytes (Fig. 1.3) on the other hand, contain a polyion which does not undergo any conformational change due to steric constraints on such systems. Only the intermolecular coulombic interactions determine the solution properties of these polyelectrolytes.
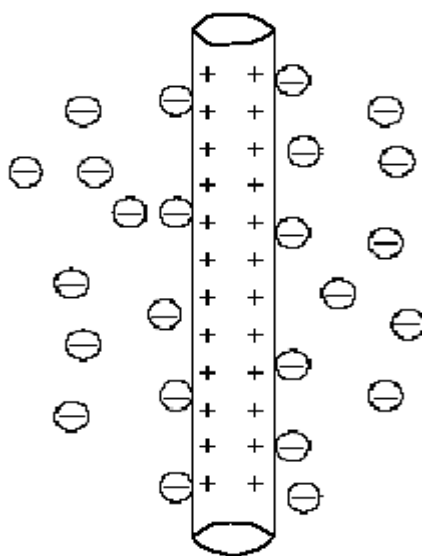

Fig. 1.3. Schematic representation of a rigid rod-like polyelectrolyte.

An example of this type of polyelectrolyte is poly (*p*-phenylene) with iodine counterions (Fig. 1.4). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as DNA, RNA and the tobacco-mosaic virus.
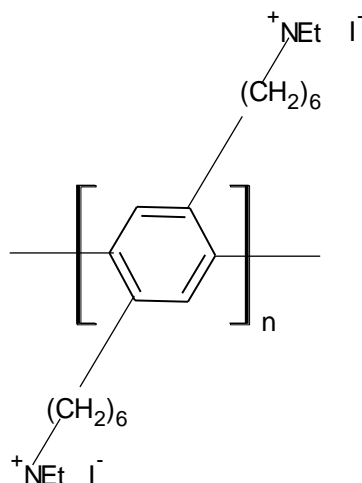
Fig. 1.4. An example of a rigid rod-like polyelectrolyte: poly (*p*-phenylene) with iodine counterions.

Based on their composition, polyelectrolytes may also be classified into homopolymers and copolymers.

Depending upon whether the ionizable groups are all anionic, cationic or a mixture of both, a polyelectrolyte could be classified as polyacids/polyanions, polybases/polycations and polyampholytes.

Another distinction is also possible between strong polyelectrolytes, which acquire spontaneously full charge, and weak polyelectrolytes which are only partially charged upon dissolution.

1.1.3 Importance of Polyelectrolytes

Due to their abundance and a wide range of beneficial physical and chemical properties, polyelectrolytes have become very popular in order to prepare materials for various applications.[8] Many of the applications are based on the functional properties of the polyelectrolytes. Polyelectrolytes play an important role in molecular biology and materials science. For instance, these can be used as membranes, for coating on films and fibers, for isolation and fractionation of proteins, for isolation of nucleic acid, for binding pharmaceutical products, as supports for catalyst and for preparation of microcapsules for drug delivery. Some selected natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building block of life, the nucleic acids and proteins, are polyelectrolytes. These biopolymers play a pivotal role in maintaining and propagating life in

11

the simplest as well as in the complex biological systems. Research in the area of the binding of proteins and nucleic acids, enzymes and other biological components is important to understand the mechanisms of reactions occurring in biological systems.

Synthetic polyelectrolytes have been a very active area of scientific research and commercial growth and these materials have exhibited a number of fascinating properties. Conformations of the polyelectrolytes as well as the interactions in these systems can be controlled by varying some of the parameters thus making such systems not only an interesting and rich area for exploration of novel phenomena but also an area of investigation which could open up novel applications in a variety of fields. Currently polyelectrolytes find widespread applicationsin ion-exchange resins, waste-water treatment, oil-spill treatment, ion and gas selective membranes for fuel cells, polymeric surfactants, personal care products, cosmetics, pharmaceuticals, biosensors, absorbents, stabilizers, flocculants, etc.[8,20-24] Potential applications in medicine and biomedical engineering are also being extensively pursued.

Polyelectrolytes have also found applications in modifying flow and stability properties of aqueous solutions and gels.[8] For instance, they are used to initiate flocculation or to stabilize colloidal suspensions. Polyelectrolytes can also be used to impart a surface charge to neutral particles thus enabling their dispersion in aqueous solution. They are thus often used as thickeners, emulsifiers, conditioners, flocculants, and even as drag reducers. Furthermore they are added to many foods, and some examples of polyelectrolytes which find applications in food products include pectin, carrageenan, alginates, polyvinylpyrrolidone and carboxymethylcellulose. They are also used in a variety of materials, including cement.

1.1.4 Concentration Regimes in Polyelectrolyte Solutions

The properties of polyelectrolytes in solution are very much related to their concentrations (c). There are three different concentration regimes in polyelectrolyte solutions, namely, dilute, semidilute and concentrated. These could be understood from the concept of overlap concentration (c^*) defined as the concentration where the polymer chains start to overlap. A dilute polymer solution refers to the concentration region ($c < c^*$) where the polymer chains are well separated and do not interact with the neighbouring chains. In such solutions, polyelectrolytes have a large overall size and a rather rigid local conformation.[25] The chain is represented by an extended rod-like configuration of N_D electrostatic blobs of size D in the dilute regime. Each of them, with g_e monomers, bears a charge of $q_D = |z_c| e f g_e$, with z_c

being the counterion charge, e the electronic charge, and f the fraction of ionized charged groups on the polyion chain (*i.e.*, the fraction of free counterions). As the polyelectrolyte concentration increases, the chains become more flexible. When $c > c^*$, the chains begin to overlap and the conformations of the single chains are greatly modified. This region is known as the semidilute regime. A polyion chain is modelled as a random walk of N_ξ correlation blobs of size ξ_0, each containing g monomers in semidilute solutions. Each blob bears an electric charge of $q_\xi = |z_c| efg$. Because of strong electrostatic interactions within each correlation blob, the chain is in a fully extended conformation of electrostatic blobs in the semidilute-unentangled regime ($c^* < c < c_e$). At higher concentrations where $c > c_e$, significant overlap of neighbouring chains occurs, and this strongly affects the chain motion (semidilute-entangled regime). The electrostatic blobs begin to overlap in much higher concentrations, and owing to the increase in electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments[26] suggest a polyelectrolyte behaviour similar to that of a neutral polymer solution. Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration c^*, at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length (*i.e.*, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the strand of N/g beads of size ξ_0). To sum up, a polyelectrolyte solution behaves as a concentrated solution for $c > c_D$, as an entangled-semidilute solution for $c_e < c < c_D$, as an unentangled-semidilute solution for $c^* < c < c_e$, and finally as a dilute solution for $c < c^*$. In so far as the experimental evidence is available, it confirms the existence of more concentration regimes for polyelectrolyte solutions in the absence of added low-molar-mass salt than in its presence.[27] This evidence mostly stems from the study of nonequilibrium properties, such as viscosity, conductance, or diffusion. Experiments are difficult to perform below the overlap concentration because of the very low concentrations and subsequently very small effects to be monitored, requiring extreme experimental sensitivity. Measurements above c_D also might be challenging, arising from the high solution viscosity. It is, therefore, not surprising that most of the experimental results described in the literature seem limited to the concentration region between c_D and c^*. The final conclusions as to the existence of these

13

and other possible concentration regimes, if any, require more extensive experimental investigations and further theoretical efforts.

1.1.5 Counterion-condensation in Polyelectrolyte Solutions

1.1.5.1 Polyelectrolyte Conductance

The specific conductance and the equivalent conductivity (Λ) are two experimentally determined parameters which are suitable to describe the electrical transport behaviour of polyelectrolyte solutions because they take into account the movement of any charged species present in the system subjected to an external electric field. Hence, measurement of electrical conductivity of polyelectrolyte solutions should provide information on counterion-condensation in polyelectrolyte solutions.

1.1.5.1.1 Manning Model for the Conductance of Polyelectrolyte Solutions

Different electrical properties of polyelectrolyte solutions are generally described on the basis of the Manning counterion-condensation theory[1-6] for dilute solutions considering counterion-condensation on to an infinitely long and thin line charged chain.

According to this theory, polyelectrolytes can be characterized by the linear charge density parameter defined by[1,3,4]

$$\xi = \frac{e^2}{b \varepsilon k_{\mathrm{B}} T} \tag{1}$$

where e is the protonic charge, ε the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_{B} the Boltzmann constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense onto the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law for the electrical conductivity for a salt-free polyelectrolyte solution is related to ξ by the following equation[4,5]

$$\Lambda = f(\lambda_c^0 + \lambda_{\mathrm{p}}) \tag{2}$$

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and the parameter f is given by[1,3,4]

$$f = \frac{0.866}{\xi} \tag{3}$$

Unlike Huizenga[28] (who considered that the free counterions are not influenced by the polyion), Manning considered that the free counterions are those which are subjected to the Debye-Hückel potential of the polyions. Considering the electrophoretic and relaxation contributions, the polyion equivalent conductivity (λ_p) has been derived theoretically for the cylinder model of polyelectrolytes,[6] and counterions with a charge of z_c it takes the following form

$$\lambda_p = \frac{279A|z_c|^{-1}|\ln(\kappa_D a)|}{1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln(\kappa_D a)|} \tag{4}$$

where the parameter a is the radius of the polymer chain, while

$$A = \frac{\varepsilon k_B T}{3\pi\eta_0 e} \tag{5}$$

with η_0 being the coefficient of viscosity of the solvent. In Eq. (4), κ_D^{-1} is the Debye screening constant defined by

$$\kappa_D^{-1} = \left(\frac{4\pi N_A e^2 \xi^{-1} c_P |z_c|}{\varepsilon k_B T} \right)^{-1/2} \tag{6}$$

where c_p is the stoichiometric equivalent polyion concentration (in moles of monovalent charged groups per unit volume).

1.1.5.1.2 Limitation of the Manning Model

Since the Manning theory applies, as stated above, to highly diluted systems where polyion-polyion interactions are assumed to be absent and to polyions modeled as a linear array of

point charges, its validity is limited to very low concentration regimes of polyelectrolyte solutions.

A review of the literature revealed that although within a narrow concentration range, the change of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not, in general, agree with the predictions. This aspect has been amply described in the reviews by Bordi *et al.*[29] and Wandrey and Hunkeler[30] and no attempt is, therefore, made here to provide a comprehensive review of the vast literature which exists on this subject.

1.1.5.1.3 Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions

Another model for the electrical conductivity of semidilute salt-free polyelectrolyte solutions has been later put forwarded by Colby *et al.*[31] which relies on the scaling description proposed by Dobrynin *et al.*[32] for the configuration of a polyelectrolyte chain.
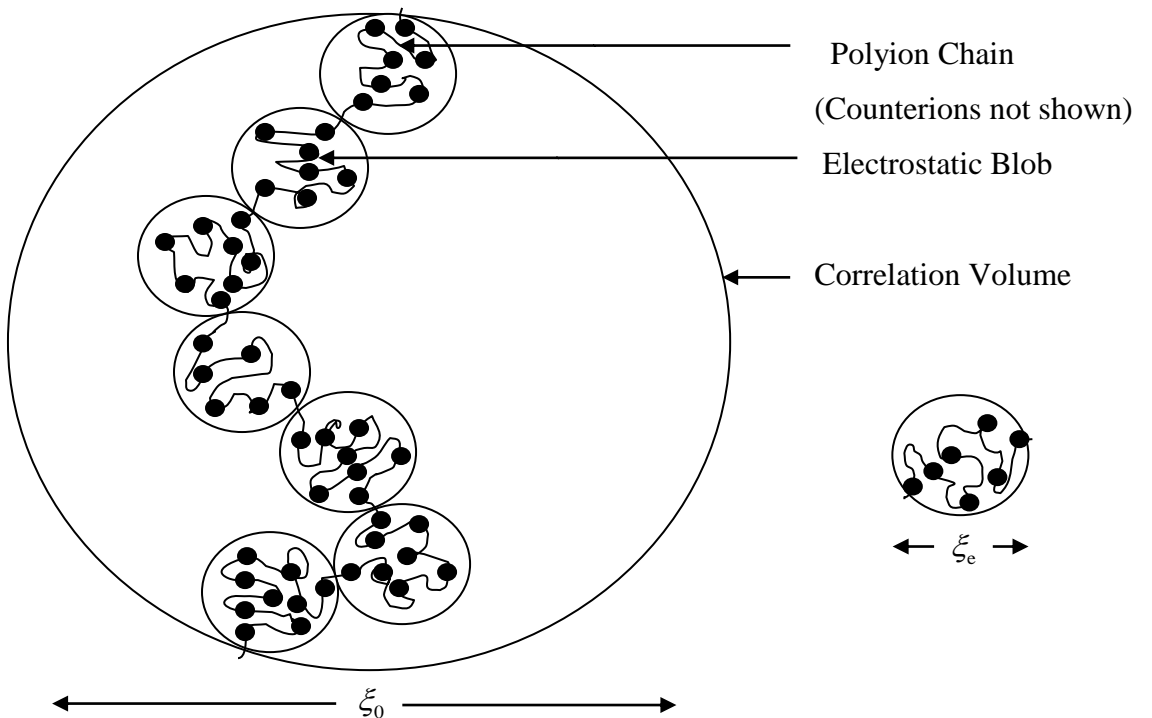

Fig. 1.5. Schematic representation of correlation volume in a semidilute polyelectrolyte solution.

In semidilute solutions, a polyion chain is modelled (*c.f.* Fig. 1.5) as a random walk of N_ξ correlation blobs of size ξ_0, each of them containing g monomers. Each blob bears an

16

electric charge of $q_\xi = |z_c| efg$ (z_c being the charge on the counterion, e the electronic charge and f the fraction of free counterions) and the complete chain, of contour length $L = N_\xi \xi_e$, bears a charge of $Q_P = N_\xi q_\xi = |z_c| efg N_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e. This means that for length scales less than ξ_0, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0.

In accordance with this model, in absence of an added salt, the equivalent conductivity of a polyion in a semidilute solution is given by

$$\lambda_p = \frac{F|z_c|efg \ln(g/g_e)}{3\pi \eta_0 \xi_0} \tag{7}$$

where F is the Faraday number.

Under the condition of $g/g_e = \xi_0/\xi_e$ and making use of the fact that the electrostatic blobs are space filling ($g = c\xi_0^3$, c being the number density of monomers) Eq. (7) reduces to

$$\lambda_p = \frac{F|z_c|efc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi \eta_0} \tag{8}$$

The equivalent conductivity of the polyelectrolyte solution is then given by

$$\Lambda = f\left[\lambda_c^0 + \frac{F|z_c|efc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi \eta_0}\right] \tag{9}$$

Colby et al.[31] derived the above expression taking into account the scaling arguments proposed by Dobrynin et al.[32] neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units i.e., the correlation blobs and neglecting the asymmetry field effect. This model has a single free parameter f, the fraction of free counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion-condensation theory. While the Manning theory applies to highly dilute

polyelectrolyte solutions and predicts a fraction of free counterions independent of the polymer concentration given by the charge density parameter, Eq. (9) can be applied to more concentrated systems, up to the concentration c_D, where the electrostaticblobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This later model has been applied, so far, to a limited number of polyelectrolyte solutions[28,31,33,34] and good agreement with the experiment was observed. This model is capable of providing a reliable estimate of countertion-condensation in polyelectrolyte solutions. Moreover, this model has been successfully employed to identify the concentration regimes differing in the fractions of free counterions.[35]

1.1.5.1.4 Effect of Salts on the Conductance of Polyelectrolyte Solutions

Although the polyelectrolyte conductivities have been well understood in salt-free semidilute solutions[31,34] in the light of the scaling description for the configuration of a polyion chain in accordance with Dobrynin et al.,[32] the situation was quite unsatisfactory for salt-containing polyelectrolyte solutions. Devore and Manning[36] were the first to make an attempt to describe the electric transport properties of polyelectrolyte solutions in presence of a simple salt using the Manning counterion-condensation theory[37] without much success.

In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.[38-42]

Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_p + \kappa_S \tag{10}$$

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_S is the specific conductance of the simple salt in the absence of polyelectrolyte.

However, earlier investigations[38-42] suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, Eq.(10).

Later Ander *et al.*[43,44] modified Eq. (10) by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa = \kappa_p + \kappa_S (D_2 / D_2^0) \tag{11}$$

where D_2 and D_2^0 are the coion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients (D_2 / D_2^0) has been used as a quantitative measure[2] of the effective interaction of free small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s (D_2 / D_2^0)$.

Although the Eq. (11) has been shown to be somewhat better than Eq. (10), the departures from the experimental results are still prominent.[38-42] Later, Bordi *et al.*[45] evaluated equivalent conductivities for a hydrophilic polyion with a salt in the light of scaling theory approach[32] and compared them with their experimental results. The agreement was rather good, although a quantitative description was still awaiting.

Very recently, De and Das[46] put forwarded a simple approach to analyze the conductivity of semidilute polyelectrolyte solutions in presence of a salt based on the scaling theory for the conductivity of semidilute polyelectrolyte solutions neglecting the asymmetry field effect.[31] This new model has been extensively tested with data on NaPSS in the presence of NaCl in 2-ethoxyethanol-water mixed solvent media at different temperatures considering a number of parameters *e.g.*, temperature, relative permittivity of the medium, and concentration of the added salt. Very good quantitative agreement with only one adjustable parameter has been achieved. A brief description of this model is given below.

According to Colby *et al.*,[31] the specific conductance of a salt-free polyelectrolyte solution (κ_p) neglecting the asymmetry field effect is given by

$$\kappa_{\text{p}} = f c_{\text{p}} \left[\lambda_{\text{c}}^0 + \frac{F|z_{\text{c}}| efg \ln(\xi_0 / \xi_{\text{e}})}{3\pi\eta_0\xi_0} \right] \tag{12}$$

where the symbols have their usual significance. Here, the term f, the fraction of free counterions, also provides a measure of polyion-counterion interaction in the absence of an electrolyte.

The interactions between the polyion and the counterions would, obviously, be modified in the presence of a salt resulting in a different level of counterion-condensation, *i.e.*, in a different value of f and will be designated as f'. The effective specific conductance due to the polyelectrolyte in the presence of a simple salt $\kappa_{\text{P(eff)}}$ can then be expressed as

$$\kappa_{\text{P(eff)}} = f' c_{\text{P}} \left[\lambda_{\text{c}}^0 + \frac{F|z_{\text{c}}| ef' g \ln(\xi_0 / \xi_{\text{e}})}{3\pi\eta\xi_0} \right] \tag{13}$$

The total specific conductance of a polyelectrolyte solution with added salt should, thus, be equal to the sum of the specific conductance of the simple salt in the absence of a polyelectrolyte and the effective specific conductance due to the polyelectrolyte in the presence of the simple salt

$$\kappa = \kappa_{\text{s}} + f' c_{\text{P}} \left[\lambda_{\text{c}}^0 + \frac{F|z_{\text{c}}| ef' g \ln(\xi_0 / \xi_{\text{e}})}{3\pi\eta\xi_0} \right] \tag{14}$$

In the above equation, f' has been treated as an adjustable parameter and this can be conveniently obtained by the method of a least-squares fit of the experimental specific conductance of the polyelectrolyte solution (κ) in presence of a salt to Eq. (14) provided κ_{s} is known. This value of f' takes care of the changed polyion-counterion interactions under the influence of the added salt. The second term in Eq. (14) is the actual contribution of the polyelectrolyte species towards the total specific conductance in the presence of an added salt.

1.2 Ionic Liquids

1.2.1 Brief Introduction to Ionic Liquids

Ionic liquids have been described as molten salts that are entirely ionic in nature, composed of a bulky hydrophobic cationic partner and a smaller but generally multi-atomic and more hydrophilic anionic partner having a melting point below 100 ^{0}C.[47-52] The official definition of ionic liquid uses the boiling point of water as a point of reference: "ionic liquids are ionic compounds which are liquid below 100 °C". This temperature does not have any significance but have been adopted to distinguish it from molten salts, which are typically inorganic salt with high melting points.

Historically, the following four main stages must be mentioned. The field of ionic liquids began in 1914 with the observation by Paul Walden,[53] who reported the physical properties of ethylammonium nitrate $[C_2H_5NH_3][NO_3]$ (m.p. 12-14 ^{0}C) formed by the neutralization of ethylamine with concentrated nitric acid.

The second major studies of room temperature molten salts were made in the 1940s by a group led by Frank Hurley and Tom Weir at Rice University.[54] When they mixed and gently warmed powdered pyridinium halides with aluminium chloride, a clear, colorless liquid was obtained.

The third stage was the introduction of alkylimidazolium salts in the early 1980s by Wilkes and Hussey.[55] It was the discovery of 1-ethyl-3-methylimidazoluim-based chloroaluminate ionic liquids in 1982 that accelerated the activities in the area of room temperature ionic liquids. The exciting property of halogenoaluminate ionic liquids is their ability for acid-base chemistry, which can be varied by controlling the molar ratio of the two components.[56] A major drawback of all chloroaluminate(III) ionic liquids was their moisture sensitivity.

More recently, "Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids" was reported by Wilkes and Zaworotkoin 1992.[57] These ionic liquids have received extensive attention not only because of their water stability, but also because of their water immiscibility.

There are different categories of ionic liquids according to their constitution. Majority of the studied ionic liquids comprises of bulky, asymmetric nitrogen-containing organic cations. Common ionic liquids contain imidazolium, pyridinium, pyrrolidinium cations in

combination with a wide variety of anions, ranging from simple inorganic ions to more complex organic species (*e.g.*, triflate or trifluoromethylsulfonate, bis[(trifluoromethyl)sulfonyl]imide or bistriflate (i.e.,[NTf2]$^-$), trifluoroacetate etc.). The most widely studied ionic liquids are imidazolium-based, followed by ammonium-based in the field of colloid and interface science, accounting for most of the work having been done on ionic liquid aggregation behaviour.

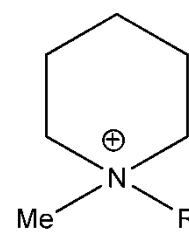## 1.2.2 Physical and Chemical Properties of Ionic Liquids

Properties of ionic liquids mainly depend on the nature of substituents and can be largely modified by varying the structure of the later. The choice of cations and anions has a large influence on their properties. Usually, ionic liquids consist of a large organic cation and an organic or inorganic anion. The structural modification of ionic liquids can be made either to the anion, cation, or to the substituents on the cation or anion, so that an almost limitless number of ionic liquids are possible. Hence, by changing the cation or anion of the ionic liquids, their solvation properties, physical properties including melting point, density, viscosity, solubility, hydrophobicity etc. can be tailored according to the requirements of a process. Ionic liquids have a special place in the current scientific literature owing to their special properties, which distinguish them from conventional organic solvents; these have negligible vapour pressure, high thermal stability, high ion-conductivity, wide liquid range, large electrochemical window, non-flammability and unique catalytic properties. Some commonly used ionic liquid cations are presented in Fig. 1.6.
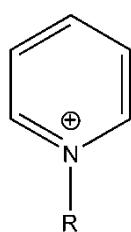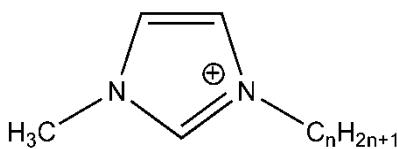
N-alkylpyridinium   1-alkyl-3-methylimidazolium   N-methylpiperidinium

Fig. 1.6. Some commonly used ionic liquid cations.

1.2.3 Brief Introduction to Surface Active Ionic Liquids

Many of the ionic liquids, especially those comprising of a combination of organic and inorganic ions, are emerging as novel surfactants due to their amphiphilic nature and have

been explored for self-association behaviour by a number of researchers. Ionic liquids with amphiphilicity are commonly referred to as surface active ionic liquids.

Although ionic liquids have been known for a long time, the term "surface active ionic liquids" in the general sense was used as early as in 1943.

Surface active ionic liquids which are liquid at room temperature, are known as room temperature surface active ionic liquids.

Like surfactant molecules, surface active ionic liquids consist of two different kinds of moieties namely, a polar part (known as the hydrophilic part in aqueous solution) and a nonpolar (hydrophobic) part shown in Fig. 1.7.
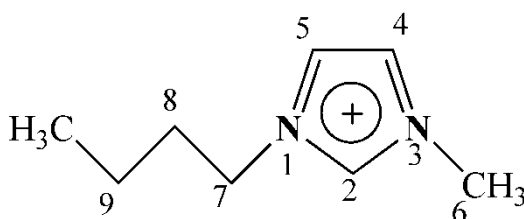

Fig. 1.7. General structure of a surface active ionic liquid molecule.

Classical imidazolium-based surface active ionic liquids are 1,3-disubstituted although there are examples of 1-monosubstituted variety.

Fig. 1.8 displays the structure of the surface active ionic liquids used in the present study.

      (a)   (b)
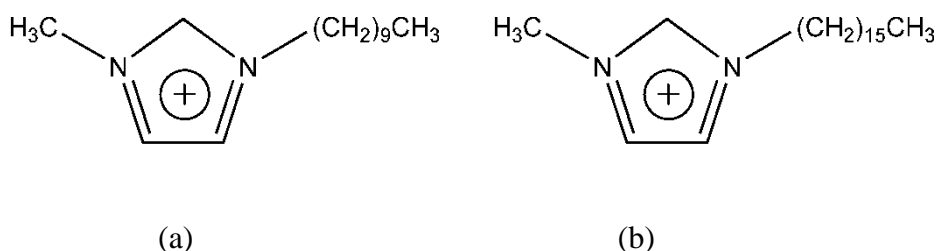
Fig. 1.8. Molecular structures of a) 1-decyl-3-methylimidazolium chloride (C_{10}MeImCl), and b) 1-hexadecyl-3-methylimidazolium chloride (C_{16}MeImCl).

In general, the substituents can be rather long alkyl chains, giving hydrophobicity to the corresponding cation, or contain some polar functional groups, providing the cation with a hydrophilic character.[58-61]

1.2.4 Behaviour of Surface Active Ionic Liquids in Solutions: Significance of Ionic Liquid Aggregation

Surfactant-like ionic liquids show a self-aggregation behaviour in aqueous solutions beyond a characteristic critical concentration and have been a focus of recent investigations.[62-71] It is known that the formation of ionic liquid aggregates in aqueous solutions results from a balance of two opposing interactions: (1) electrostatic repulsion between the cationic groups which disfavours aggregation and (2) attractive hydrophobic interaction involving the alkyl chains which favours aggregation. The former interaction can be reduced by adsorption of the ionic liquid anions onto the surface of the aggregates thereby enhancing the aggregation of the ionic liquid. The later interaction can also be reduced by increasing the attractive interactions of the alkyl chains with solvents. From a physical point of view, ionic liquids are more complex than typical aqueous surfactant solutions because of the coupling of the properties of two vastly different types of materials: molten salts and organic liquids.

Micelles consist of hydrophobic interior regions, where hydrophobic tails interact with one another. These hydrophobic regions are surrounded by the hydrophilic regions where the heads of the surface active ionic liquid molecules interact with water. At very low concentration in water, surface active ionic liquid molecules are unassociated. Above a certain concentration, the so-called critical micellar concentration (*cmc*), almost all of the added surface active ionic liquid molecules are consumed in micelle formation, and the monomer concentration does not increase as the concentration is increased. The *cmc* indicates usually a narrow range of concentration separating the limits below which most of the surface active ionic liquid molecules is in the monomeric state and above which virtually all additional surface active ionic liquid molecules enter the micellar state. The *cmc* is a very important solution property of the surface active ionic liquids.

The aggregation behaviour of surface active ionic liquids have been thoroughly studied. Bowers *et al*.[62] were the first to suggest that ionic liquid forms aggregate in aqueous solutions. These authors investigated the aggregation behaviour in aqueous solutions of three ionic liquids based on the 1-alkyl-3-methylimidazolium cation by means of surface tension, conductivity, and small-angle neutron scattering measurements. It was observed that for a given ionic liquid, there should be a required minimum length of the hydrocarbon chains to form well-defined aggregates. Blesic *et al*.[63] reported the effect of alkyl chain length on the self-aggregation behaviour of a series of imidazolium-based ionic liquids through

fluorescence spectroscopy and proton nuclear magnetic resonance measurements and interfacial tension measurements (using a drop-shape analysis technique) and concluded that the short alkyl chain ionic liquids behave as simple salts. Dong *et al.*[64] demonstrated that the surface activity of long-chain imidazolium ionic liquids to be somewhat superior to that of conventional ionic surfactants with identical chain lengths. El Seoud *et al.*[65] demonstrated that the micellization of benzyl (3-acylamionioethyl)dimethylammonium chlorides is more favourable than that of 1-alkyl-3-methylimidazolium chlorides due to the formation of hydrogen bonds by the –CONH- groups of the former surfactant series both to the counterions and the neighbouring molecules in the micelle. The surface active ionic liquid 1-hexyl-3-methylimidazolium chloride was shown[3] to behave in an interesting manner – it was found to develop a monolayer at the aqueous solution-air interface but showed no noticeable self-aggregation in the bulk fluid. In general, no evident aggregates were found to form in systems with $n = 2$ and 4 (n is the alkyl chain length) whereas systems with n greater than or equal to 8 unambiguously form aggregates in solution.[66,67] However, inspection of the data on surface active ionic liquids with short alkyl chains ($n = 4$) for example 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium methylsulfate solutions indicated the appearance of micellar aggregation onset. The dependency of the critical micellar concentrations of imidazolium ionic liquids in aqueous solutions on the alkyl chain lengths was thoroughly investigated by Jungnickel *et al.*[68] and the critical micellar concentrations were found to be reduced as the chain length was increased. The self-aggregation and thermodynamic properties of a number of surface active ionic liquids have been investigated by El Seoud's group[69,70] and by Naderi and Sadeghi[71] and micelle formation was found to be entropy driven for the investigated systems.

The aggregation behaviour of surface active ionic liquids in solution plays an important role in the emerging fields of nanostructured inorganic material synthesis, biochemical separation, analytical chemistry, microextraction, waste water-treatment and are used as classical surfactant micellization modifier.[72-81]

1.3 Interaction of Polyelectrolytes with Surface Active Ionic Liquids

The properties of polyelectrolyte solutions are extremely sensitive to their environment. The effect is ascribed to the coiling of the initially highly extended polyion chain due to the shielding of polyelectrolyte charges in presence of simple electrolytes. Another interesting

problem is related to the changes of chain conformation arising from the binding of surface active ionic liquid ions.

Attractive electrostatic forces dominate in the case of polyelectrolytes and oppositely charged surface active ionic liquids. In the presence of an oppositely charged polyelectrolyte, micelle-like aggregates start to form along the polymer chain as the surface active ionic liquid concentration exceeds a critical value referred to as the critical aggregation concentration (*cac*). A characteristic feature of this parameter is that it is always lower than the *cmc* of the corresponding surface active ionic liquid. The lower *cac* is particularly pronounced in solutions of polyelectrolytes in presence of an oppositely charged surface active ionic liquid. With the increase in the surface active ionic liquid concentration, a second transition known as the polymer-saturation concentration (*psc*) is obtained. Afterwords, the concentration of surface active ionic liquid monomer builds up until free surface active ionic liquid micelles start to form at a concentration commonly known as the apparent critical micellar concentration (*cmc**).

1.4 Experimental Efforts for Studying the Polyelectrolyte-Surface Active Ionic Liquid Interactions

To understand the self-organization behaviour, a significant amount of research has been devoted to study the aggregation behaviour of ionic liquids in aqueous solution.[82--90] It can be seen that the results from different laboratories are not always consistent. This may be attributed to a large variety of experimental techniques, including conductometry, tensiometry, viscometry, calorimetry, turbidimetry, volumetry, nuclear magnetic resonance (NMR) measurements, fluorescence, gel permeation chromatography (GPC), pulsed gradient stimulated echo (PGSE)–NMR, isothermal titration microcalorimetry (ITC), fourier transform infrared (FTIR) spectroscopy, electromotive force (EMF) measurements, mass spectrometry, potentiometry, near-infrared spectroscopy, polarized optical spectroscopy, apparent molar volumes, light scattering and small-angle X-ray and neutron scattering techniques (SAXS and SANS) that has been employed to study the aggregation behaviour of surface active ionic liquids.[82-90] However, not all methodologies have been carried out with the same care and rigor, and therefore some uncertainties exist in the results of a number of surface active ionic liquids.

Besides two publications on aqueous NaCMC-C$_{10}$MeImCl and NaCMC-C$_{16}$MeImCl systems derived from this study,[91,92] a few papers have, so far, been published on different polyelectrolyte-surface active ionic liquid systems by other groups.[93-98]

Here, we will give a brief account of the conductometry, tensiometry, osmometry, and spectrofluorimetry to investigate the interactions between polyelectrolytes and surfactants with special reference to surface active ionic liquids since these techniques have been employed to study the behaviour of polyelectrolyte-surface active ionic liquid interactions in this dissertation. The experimental efforts in this thesis were devoted to the quantification of counterion-condensation in polyelectrolyte solutions and to the determination of various critical concentrations in surface active ionic liquid solutions and polyelectrolyte-surface active ionic liquid solutions, and different thermodynamic parameters pertaining to polyelectrolyte-surface active ionic liquid solutions.

1.4.1 Conductometry

Conductometry has been extensively used to study the aggregation behaviour of surfactants in absence as well as in the presence of a polyelectrolyte, and to study the interactions between polyelectrolytes and surfactants/surface active ionic liquids. Conductometry provides the *cmc* of a pure surfactant solution as the intersection of two straight lines in the pre- and postmicellar regimes of the specific conductance (κ) *vs.* surfactant concentration profile. It may be pointed out here that conductivity isotherms manifesting two linear sections with one inflection have been reported earlier in aqueous alkyltrimethylammonium bromide-NaPSS[99,100] and in dodecylpyridinium chloride-sodium dextran sulfate systems[101] and those with higher-complexity showing three or four linear sections with two or three inflections, respectively are also available in the literature.[93,94,96-98,102] Thus, conductometric study on polyelectrolyte-surfactant/surface active ionic liquid solutions is capable of identifying various characteristic critical concentrations in these solutions and hence is suitable for proving information on different kinds of species formed as a result polyelectrolyte-surfactant/surface active ionic liquid interactions.

1.4.2 Tensiometry

The tensiometry has been an elegant method for the understanding of polyelectrolyte-surfactant/surface active ionic liquid interactions. In tensiometric determination of the *cmc* of pure surfactant/surface active ionic liquid, the surface tensions (γ) are plotted as a function

27

of logarithm of the surfactant/surface active ionic liquid concentration and the *cmc* is realized as the surfactant/surface active ionic liquid concentration where the profile reaches a plateau. The tensiograms for polyelectrolyte-surfactant/surface active ionic liquid solutions, on the other hand, are not so simple. Like conductivity, tensiometric profiles also helped identify various characteristic critical concentrations in these solutions.[93,94,96-98,102]

1.4.3 Osmometry

A colligative property is one that depends primarily on the number of species concerned and not on their nature. Measurement of the osmotic coefficient of surfactant solutions as a function of molality can conveniently provide information on their critical micellar concentrations (*cmc*). If the products of molality and osmotic coefficient are plotted as a function of the molal concentration of a surfactant solution, the resulting osmograms can be fitted to two straight lines one below the *cmc* and the other above it, the intersection being the *cmc* of the surfactant solution. Osmotic coefficient measurements have been successfully applied to estimate the *cmc*s of a number of amphiphilic drugs *e.g.*, chlorpromazine hydrochloride, promethazine hydrochloride, clomipramine hydrochloride and imipramine hydrochloride in aqueous solutions.[103,104] Inspite of the potential of osmometry towards evaluation of the *cmc* of surface active agents, it has very limited application as far as surfactant solution is concerned.[103,104] Unfortunately, there has been no attempt to study the aggregation behaviour in polyelectrolyte-surfactant or polyelectrolyte-surface active ionic liquid solutions. Here, we have employed this method for the investigated polyelectrolyte-surface active ionic liquid systems and have been successful in obtaining information on the critical micellar concentrations.

1.4.4 Fluorimetry

Since Kalyanasundaram and Thomas[105] established that the characteristic dependence of the fluorescence vibrational fine structure of pyrene could be used to determine the *cmc* of surfactant solutions, the so-called pyrene 1:3 ratio method has become one of the most popular and useful procedures for the determination of this important surface parameter.[106] 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 peak (I_1/I_3) is highly sensitive to the polarity of the environment. The abrupt sigmoidal decrease in the I_1/I_3 value with increasing surfactant or surface active ionic

liquid concentration in the plot of (I_1/I_3) *vs*. log[surfactant or surface active ionic liquid] indicates the formation of surfactant/surface active ionic liquid 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. This method has been widely used not only in pure micellar solutions, but also in mixed-surfactant systems,[107-109] to investigate polymer-surfactant interactions,[110-113] and in studies on the effect of additives on the micellar properties of ionic and nonionic surfactants.[114-116] In the present study, we have used this method to study the polyelectrolyte-surface active ionic liquid interactions.

1.5 Present Investigation

In view of the above discussion, it is apparent that the subtle interplay of both hydrophobic and electrostatic forces between polyelectrolytes and surface active ionic liquids when present together in a solution, makes the interaction between them not only complicated but also challenging. 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 experimental techniques as possible. Moreover, thorough understanding of the behaviour of the individual mixing components prior to their mixing is also essential in order to elucidate the interactions prevailing in polyelectrolyte-surface active ionic liquid solutions. This prompted us to undertake a study exploring the interactions and related phenomena in some selected polyelectrolyte-surface active ionic liquid solutions. In particular, we have investigated the interactions in NaCMC-C_{10}MeImCl, NaCMC-C_{16}MeImCl, NaPSS-C_{10}MeImCl, and NaPSS-C_{16}MeImCl systems in aqueous solutions using conductometry, tensiometry, osmometry, and spectrofluorimetry. We have also investigated the counterion-condensation behaviour of aqueous NaCMC and NaPSS solutions, electrolyte and micellar behaviour of C_{10}MeImCl and C_{16}MeImCl in aqueous solutions. This study helped us gain more insight into polyelectrolyte-surface active ionic liquid interactions.

1.6 References

1. G. S. Manning, *Ann. Rev. Phys. Chem.*, **23**, 1179 (1972).

2. G. S. Manning, *J. Chem. Phys.*, **51**, 924 (1969).

3. G. S. Manning, *Biopolymers*, **9**, 1543 (1970).

4. G. S. Manning, *J. Phys. Chem.*, **79**, 262 (1975).

5. G. S. Manning, *J. Chem. Phys.*, **51**, 934 (1969).

6. G. S. Manning, *J. Phys. Chem.*, **85**, 1506 (1981).

7. G. Ströbl, *The Physics of Polymers*, Springer, Berlin (1997).

8. H. Dautzenberg, W. Jager, J. Kötz, B. Philipp, C. Seidel, and D. Stcherbina, *Polyelectrolytes: Formation, Characterization and Application*, Hanser Publishers, Munich (1994).

9. A. D. Schlüter, *Synthesis of Polymers*, Wiley VCH (1999).

10. B. L. Rivas, and K. E. Geckeler, *Adv. Polym. Sci.*, **102**, 171 (1992).

11. M. A. Winnik, S. M. Bystryak, Z. Liu, and J. Siddiqui, *Macromolecules*, **31**, 6855 (1998).

12. V. O. Borisov, and M. Daoud, *Macromolecules*, **34**, 8286 (2001).

13. W. Burchard, *Adv. Polym. Sci.*, **143**, 113 (1999).

14. F. Vögtle, J. F. Stoddart, and M. Shibasaki, *Stimulating Concepts in Chemistry*, Wiley VCH (2000).

15. G. Rewcome, C. N. Moorefiled, and F. Vögtle, *Dendritic Molecules: Concepts, Synthesis, Perspectives*, Wiley VCH (1996).

16. C. N. Likos, M. Schmidt, H. Löwen, M. Ballauff, D. Potschke, and P. Linder, *Macromolecules*, **34**, 2914 (2001).

17. M. Ballauff, *Topics in Current Chem.,* **212**, 177 (2001).

18. D. Muscat, and R. A. T. M. van Benthem, *Topics in Current Chem.*, **212**, 42 (2001).

19. K. Inoue, *Prog. Polym. Sci.*, **25**, 453 (2000).

20. G. Petzold, and K. Lunkwitz, *Colloids Surf. A*, **98**, 225 (1995).

21. L. Whipple, and C. Maltesh, *Langmuir*, **16**, 3124 (2000).

22. L. Krasemann, and B.Tieke, *J. Membr. Sci.*, **150**, 23 (1998).

23. T. Lupascu, I. Dranca, M. Sandu, S. Dragan, and L. Ghimici, *Angew Makromol. Chem.*, **220**, 11 (1994).

24. D. Li, S. Zhu, R. H. Pelton, and M. Spafford, *Colloid Polym. Sci.*, **277**, 108 (1999).

25. F. Bordi, C. Cametti, and T. Gili, *Phys. Rev. E*, **66**, 021803 (2002).

26. M. Muthukumar, *J. Chem. Phys.*, **107**, 2619 (1997).

27. M. Mandel, In *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges (Eds.), Vol. 11, p. 739, NY (1988).

28. J. R. Huizenga, P. Grieger, and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 4228 (1950).

29. F. Bordi, C. Cametti, and R. H. Colby, *J. Phys.: Condens. Matter*, **16**, R1423 (2004).

30. C. Wandrey, and D. Hunkeler, In *Handbook of Polyelectrolytes and Their Applications*, S. K. Tripathy, J. Kumar, and H. Nalwa (Eds.), Vol. 2, p. 147, American Scientific Publishers, Stevenson Ranch, CA (2002).

31. R. H. Colby, D. C. Boris, W. E. Krause, and J. S. Tan, *J. Polym. Sci. Part* B: *Polym. Phys.*, **35**, 2951 (1997).

32. A. V. Dobrynin, R. H. Colby, and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).

33. F. Bordi, C. Cametti, M. Motta, and G. Paradossi, *J. Phys. Chem. B*, **103**, 5092 (1999).

34. D. Truzzolillo, F. Bordi, C. Cametti, and S. Sennato, *Phys. Rev. E.*, **79**, 011804 (2009).

35. F. Bordi, R. H. Colby, C. Cametti, L. D. Lorenzo, and T. Gili, *J. Phys. Chem. B*, **106**, 6887 (2002).

36. D. I. Devore, and G.S. Manning, *J. Phys. Chem.*, **78**, 1242 (1974).

37. G. S. Manning, *J. Chem. Phys.*, **51**, 934 (1969).

38. M. Kowblansky, and P. Ander, *J. Phys. Chem.*, **81**, 2024 (1977).

39. D. E. Wingrove, and P. Ander, *Macromolecules*, **12**, 135 (1979).

40. J. Nagaya, A. Minakata, and A. Tanioka, *Langmuir*, **15**, 4129 (1999).

41. A. Minakata, H. Takahashi, T. Nishio, J. Nagaya, and A. Tanioka, *Colloids Surf. A*, **209**, 213 (2002).

42. J. Nagaya, A. Minakata, and A. Tanioka, *Colloids Surf. A*, **148**, 163 (1999).

43. M. Kowblansky, and P. Ander, *J. Chem. Phys.*, **81**, 2024 (1977).

44. D. E. Wingrove, and P. Ander, *Macromolecules*, **12**, 135 (1979).

45. F. Bordi, C. Cametti, and T. Gili, *Phys. Rev.* E, **68**, 011805 (2003).

46. R. De, and B. Das, *J. Chem. Eng. Data*, **55**, 2108 (2010).

47. J. Dupont, *Acc. Chem. Res.*, **44**, 1223 (2011).

48. S. Chowdhury, R. S. Mohan, and J. L. Scott, *Tetrahedron*, **63**, 2363 (2007).

49. P. Wasserscheid, and W. Keim, *Angew. Chem., Int. Ed.*, **39**, 3772 (2000).

50. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).

51. N. V. Plechkova, and K. R. Seddon, *Chem. Soc. Rev.*, **37**, 123 (2008).

52. M. G. Freire, P. J. Carvalho, A. M. Fernandes, I. M. Marrucho, A. J. Queimada, and J. A. P. Coutinho, *J. Colloid Interface Sci.,* **314***, 621 (2007).

53. P. Walden, *Bull. Acad. Imp. Sci.* (*St.-Petersbourg*), **8**, 405 (1914).

54. F. H. Hurley, and T. P. W. Jr., *J. Electrochem. Soc.*, **98**, 207 (1951).

55. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982).

56. R. J. Gale, and R. A. Osteryoung, *Inorg. Chem.*, **18**, 1603 (1979).

57. J. S. Wilkes, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, **13**, 965 (1992).

58. J. Luczak, M. Markiewicz, J. Thoming, J. Hupka, and C. Jungnickel, *J. Colloid Interface Sci.*, **362**, 415 (2011).

59. N. M. Vaghela, N. V. Sastry, and V. K. Aswal, *Colloid Polym Sci.*, **289**, 309 (2011).

60. S. Suresh, and J. Sandhu, *Green Chem. Lett. Rev.*, **4**, 311 (2011).

61. S. Suresh, and J. Sandhu, *Green Chem. Lett. Rev.*, **4**, 289 (2011).

62. J. Bowers, C. P. Butts, P. J. Martin, M. C. Vergara-Gutierrez, and R. K. Heenan, *Langmuir*, **20**, 2191 (2004).

63. M. Blesic, A. Lopes, E. Melo, Z. Petrovski, N. V. Plechkova, J. N. Canongia Lopes, K. R. Seddon, and L. P. N. Rebelo, *J. Phys. Chem. B*, **112**, 8645 (2008).

64. B. Dong, N. Li, L. -Q. Zheng, L. Yu, and T. Inoue, *Langmuir*, **23**, 4178 (2007).

65. O. A. El Seoud, P. A. R. Pires, T. Abdel-Moghny, and E. L. Bastos, *J. Colloid Interface Sci*., **313**, 296 (2007).

66. M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo, and A. Lopes, *Green Chem*., **9**, 481 (2007).

67. I. Goodchild, L. Collier, S. L. Millar, I. Prokes, J. C. D. Lord, C. P. Butts, J. Bowers, J. R. P. Webster, and R. K. Heenan, *J. Colloid Interface Sci*., **307**, 455 (2007).

68. C. Jungknickel, J. Luckzak, C. Ranke, J. F. Fernandez, A Mueller, and J. Thoeming, *Colloids Surf. A*, **316**, 278 (2008).

69. P. D. Galgano, and O. A. El Seoud, *J. Colloid Interface Sci*., **345**, 1 (2010).

70. O. P. D. Galgano, and A. El Seoud, *J. Colloid Interface Sci*., **361**, 186(2011).

71. O. Naderi, and R. Sadegi, *J. Chem. Thermodyn*., **102**, 68 (2016).

72. J. Bowers, C. P. Butts, P. J. Martin, M. C. Vergara-Gutierrez, and R. K. Heenan, *Langmuir*, **20**, 2191 (2004).

73. F .Rantwijk, R. M. Lau, and R. A. Sheldon, *Trends Biotechnol*, **21**, 131(2003).

74. N. Jain, A. Kumar, S. Chauhan, and S. M. S. Chauhan, *Tetrahedron*, **61**, 1015 (2005).

75. F. Endres, and S. Z. E. Abedin, *Phys. Chem. Chem. Phys.*, **8**, 2101 (2006).

76. J. Liu, J. A. Jonsson, and G. Jing, *Trends. Anal. Chem.*, **24**, 20 (2005).

77. X. Fan, X. Zhang, and J. Wang, *Curr. Org. Synth.*, **8**, 721 (2011).

78. J. Cybulski, A. Wisniewska, A.K. Adamiak, Z. Dabrowski, T. Praczyk, Michalczyk, F. Walkiewicz, K. Materna, and J. Pernak, *Tetrahedron Lett.*, **52**, 1325 (2011).

79. K. Kawai, K. Kaneko, and T. Yonezawa, *Langmuir*, **27**, 7353 (2011).

80. Z. Ma, J. Yu, and S. Dai, *Adv. Mater*, **22**, 261 (2010).

81. S. Werner, M. Haumann, and P. Wasserscheid, *Annu. Rev. Chem. Biomol. Eng.*, **1**, 203 (2010).

82. T. Singh, K. Srinivasa Rao, and A. Kumar, *J. Phys. Chem. B*, **116**, 1612 (2012).

83. M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo, and A. Lopes, *Green Chem*., **9**, 481 (2007).

84. A. Cornellas, L. Perez, F. Comelles, I. Ribosa, A. Manresa, and M. T. Garcia, *J. Colloid Interface Sci*., **355**, 164 (2011).

85. O. A. El Seoud, P. A. R. Pires, T. Abdel-Moghny, and E. L. Bastos, *J. Colloid Interface Sci.*, **313**, 296 (2007).

86. J. Sirieix-Plenet, *Talanta*, **63**, 979 (2004).

87. J. Bowers, C. P. Butts, P. J. Martin, M. C. Vergara-Gutierrez, and R. K. Heenan, *Langmuir*, **20**, 2191 (2004).

88. I. Goodchild, L. Collier, S. L. Millar, I. Prokes, J. C. D. Lord, C. P. Butts, J. Bowers, J. R. P. Webster, and R. K. Heenan, *J. Colloid Interface Sci*., **307**, 455 (2007).

89. Z. Miskolczy, K. Sebok Nagy, L. Biczok, and S. Gokturk, *Chem. Phys. Lett.*, **400**, 296 (2004).

90. M. Tariq, M. G. Freire, B. Saramago, J. A. P. Coutinho, J. N. C. Lopes, and P. N. Rebelo, *Chem. Soc. Rev.*, **41**, 829 (2012).

91. B. Das, D. Ray, and R. De, *Carbohydr. Polym.*, **113**, 208 (2014).

92. D. Ray, S. Das, R. De, and B. Das, *Carbohydr. Polym.*, **125**, 255 (2015).

93. J. Liu, Q. Zhang, Y. Huo, M. Zhao, D. Sun, X. Wei, S. Liu, and L. Zheng, *Colloid Polym Sci*., **290**, 1721 (2012).

94. R. Sharma, A. Kamal, T. S. Kang, and R. K. Mahajan, *Phys. Chem. Chem. Phys.*, **17**, 23582 (2015).

95. J. Liu, L. Zheng, D. Sunb, and X. Wei, *Colloids Surf. A*, **358**, 93 (2010).

96. Z. Barhoumi, M. Saini, N. Amdouni, and A. Pal, *Mor. J. Chem.*, **4**, 911 (2016).

97. A. Pal, and S. Yadav, *Fluid Phase Equilib*., **412**, 71 (2016).

98. Z. Barhoumi, M. Saini, N. Amdouni, and A. Pal, *Chem. Phys. Lett*., **661**, 173 (2016).

99. K. Kogez, and J. Skerjanc, *Acta Chim. Slov.*, **46**, 481 (1999).

100. K. Kogez, and J. Skerjanc, *Langmuir*, **15**, 4251 (1999).

101. D. F. Anghel, D. M. Mihai, G. Stinga, A. Iovescu, A. Baran, and R. V. Klitzing, *Rev. Roum. de Chem.*, **52**, 781 (2007).

102. T. Chakraborty, I. Chakraborty, and S. Ghosh, *Langmuir*, **22**, 9905 (2006).

103. D. Attwood, N. A. Dickinson, V. Mosquera, and V. P. Villar, *J. Phys. Chem*., **91**, 4203 (1987).

104. J. M. Ruso, D. Attwood, P. Taboada, M. J. Suarez, F. Sarmiento, and V. Mosquera, *J. Chem. Eng. Data*, **44**, 941 (1999).

105. K. Kalyanasundaram, and J. K. Thomas, *J. Am. Chem. Soc*., **99**, 2039 (1977).

106. K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, NY (1987).

107. C. C. Ruiz, and A. Aguiar, *Langmuir*, **16**, 7946 (2000).

108. R. Zana, H. Levy, and K. Kwetkat, *Langmuir*, **13**, 402 (1997).

109. X. G. Lei, X. D. Tang, Y. C Liu, and N. J. Turro, *Langmuir*, **7**, 2872 (1991).

110. U. Kästner, and R. Zana, *J. Colloid Interface Sci*., **218**, 469 (1999).

111. E. Feitosa, W. Brown, M. Vasilescu, and M. Swanson-Vethamuthu, *Macromolecules*, **29**, 6837 (1996).

112. H. Evertsson, S. Nilsson, C. Holmberg, and L. O. Sundelöf, *Langmuir*, **12**, 5781 (1996).

113. N. J. Turro, B. H. Baretz, and P. L. Kuo, *Macromolecules*, **17**, 1321 (1984).

114. J. A. Molina-Bolivar, J. Aguiar, and C. C. Ruiz, *Mol. Phys*., **99**, 1729 (2001).

115. C. Ruiz, *Colloid Polym. Sci*., **273**, 1033 (1995).

116. C. C. Ruiz, and F. G. Sánchez, *J. Colloid Interface Sci*., **165**, 110 (1994).