## Preface

# Scope and Object of the Work

Polyelectrolytes have been the subject of extensive investigation since the early days of polymer science. They still continue to be a very active area of research in a variety of fields *e.g.*, chemistry, physics, biology, medicine, materials science and nanotechnology. The extensive interest in the area of polyelectrolytes shoots from the scientific curiosity in understanding their behaviour and also from their enormous potential in commercial applications. Polyelectrolytes have been utilized to accumulate nanostructured materials with desired properties. Potential applications in biomedical engineering and medicine are also being vigorously pursued. Complexes of polyelectrolytes with conjugated polymers such as polythiophenes and polyanilines are being used commercially as conducting coatings. These are widely used in industry as surface-active agents for water treatment and oil-spill treatment. These also find applications in the industrial production of personal care products, cosmetics, pharmaceuticals, biosensors, surfactants, absorbents, ion exchange resins, stabilizers, adhesives, paints, papers etc. A very promising and emerging area of application of polyelectrolytes is the assembly of thin films of novel materials. When polyelectrolytes and surfactants are present together in solution either inherently or by design, there can be significant interaction between them that can be important in such long-established areas as mineral and material processing, enhanced oil recovery, detergency and paint and cosmetic formulation. More interest also stems from the potential for utilizing the microstructural environment of polyelectrolyte-surfactant complexes in applications such as control of chemical reactivity, drug delivery, solar energy conversion and isotope separation. Accounts of some of the important applications of polyelectrolytes are available in various books and reviews.[1-17]

Physicochemical properties of polyelectrolyte solutions have been studied for several decades, but several of them have not yet found a satisfactory theoretical explanation. In many cases a qualitative understanding is available, but a quantitative understanding is still awaited. For others, the origin of the phenomena observed remains partly obscure, indicating that the present treatment of the polyelectrolyte behaviour is incomplete and that some fundamental new views are required to gain a full understanding. Keeping in view of widening fields of applications based on the specific properties of the polyelectrolytes, it, thus, appears that the situation is far from satisfactory.

In recent years, the study of polyelectrolytes has witnessed a revival stimulated by the use of newly available experimental techniques and the introduction of new theoretical approaches. Although new insight has been gained, no real breakthrough has been realized so far and much remains to be done.

The study of polyelectrolyte solutions has been conducted very extensively in aqueous solutions.[13-22] This is partly because many polyelectrolytes, usually with high charge densities, are difficult to dissolve in solvents besides water. Moreover, because of the great interest in the naturally occurring polyelectrolytes such as proteins, nucleic acids, and polysaccharides in aqueous medium, the behaviour of these species in aqueous solutions has become a main subject of study.[13-26]

The main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between ionic sites in the polymer chain and secondly, the interactions between the polyions and counterions surrounding the polyion chains. The first factor is concerned with expansibility of the polymer chains, whereas the second is not only reflected in counterion binding but also in the amount of solvation and the solvent structure in the vicinity of polyelectrolytes. On the other hand, the main factors operative in the case of oppositely charged polyelectrolyte and surfactants in solutions are strong interactions due to the contributions of electrostatic forces and cooperative hydrophobic effects, if any, between bound surfactant ions. This is accompanied by a release of considerable amount of counterions of the polyelectrolytes and surfactants into the solution. Electrostatic interactions, thus, play an important role in controlling the solution behaviour of polyelectrolytes in absence as well as in presence of an oppositely charged surfactant, which, in turn, is intimately related to the relative permittivity of the solvent media. Now, use of a series of mixed solvents corresponds to the systematic change in the relative permittivity of the media and thus provides an opportunity to study these interactions from a more general point of view.

The present dissertation, therefore, aims at elucidating the behaviour of a selected polyelectrolyte (sodium polstyrenesulfonate, NaPSS) in absence and in presence of an oppositely charged surfactant cetyltrimethylammonium bromide (CTAB) in methanol-water mixed solvent media using different experimental techniques with a view to unravel the nature of interactions of polyelectrolyte-surfactant interactions.

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