ABSTRACT

One category of conducting polymers is characterized by an electrical transport due to ion conduction and therefore they may be effectively considered as polymer electrolytes.
Polymers, which are known as an important group of chemicals can be characterized by a possible periodicity in their conformational structure. Up to several years, polymer chemistry was mainly concerned with the study and understanding of its own chemical synthesis and mechanical properties. Besides, their important role as plastics and in biological processes, polymers now appear to be more and more interesting from electronic point of view. They will presumably exhibit special characteristics and it is hoped that more emphasis will be given to the synthesis of those polymers, which present specific features. Polymers play a very important role as plastics; biopolymers like proteins and nucleic acids (DNA and RNA) and have fundamental importance in life processes. Most recently, highly conducting polymers seem to be the candidates for the discovery of several physical phenomenons.

Conducting polymers find their applications in different fields. Therefore several conducting polymers have been discovered in the past few years. Consequently, it seems at the moment more promising to direct the application of conducting polymers to the development of low rate, thin layer electrochemical devices, possibly designed for the consumer market. One category of conducting polymers is characterized by an electrical transport due to ion conduction and therefore they may be effectively considered as polymer electrolytes. Other types are those polymers which after a reversible electrochemical doping, acquire a high electronic conductivity that to be considered as polymer electrodes. In general,
polymer complexes may be regarded as usual forms of electrolytes with properties, which lie between those of a solid and those of a highly viscous liquid. Another important characteristic of the polymer electrolytes, related to their liquid like property is that both cations and anions can be mobile. In this respect, it would be desirable to replace the liquid electrolyte with a solid polymer electrolyte for higher reliability and versatility to the device. Besides, another class of polymers having a predominante electronic conductivity, has also been characterized.

These are mainly unsaturated polymer with \( \pi \) electrons that can easily be removed or added to the polymeric chains. Typical examples are conjugated polymers, such as polyacetylene and heterocyclic polymers such as polypyrrole and their derivatives. On exposing these polymers to oxidizing agents or reducing agents, oxidation or reduction reactions occurs. Which induce high conductivity in the polymers, and have been termed as p-doping or n-doping processes. To understand the properties of these polymers as electrodes it seems necessary to briefly illustrate their electrical properties, because doping processes greatly modify the properties of polymers.

It would be possible to prepare some polymer electrolytes with increase ionic conductance. Besides, the n-doped and p-doped polymers may also have increased electronic conductance, which may be useful for their possible use in solid-state batteries and other electrical equipments. Some of the new fields of applications of conducting polymers include gas separation membranes, photochemical cell optical devices, non-linear circuits etc. Individual conducting polymer molecules will act as wires, diodes, transistors and other electrical equipments.
Looking at the growing importance of conducting polymers, the author has prepared some conducting polymer electrolytes using polymers viz. polyvinyl pyrrolidone, polyethylene glycol as ligands and rare earths viz. Gadolinium, Neodymium as metals and has also prepared some polymer electrodes by means of doping.

For the study of M: Polymer complexation equilibrium, direct current polarographic method has been used for the determination of metal: ligands stoichiometric ratio between rare earth and polymer. Whereas, the characterization of prepared polymer electrolytes and electrode material has been done using IR spectral studies, XRD analysis and conductance measurements.

The present thesis entitled “Characterization and Electrochemical Properties of Some Conducting Polymer Electrolytes” reports the study of the conducting polymers in a systematic sequence. The work has been presented into five chapters.

CHAPTER–I

INTRODUCTION

The first chapter of the thesis is an introductory part on the topic. It describes a brief introduction to the conducting polymers, their historical profile, their classification and their unique features with advantages. The chapter also describes an introduction to the electro analytical techniques mainly direct current polarography. Besides introductory idea about other techniques viz. infrared spectroscopy, X-ray diffraction has also been mentioned.
CHAPTER II

POLAROGRAPHIC STUDY OF RARE EARTH (S): POLYMER COMPLEXES

The second chapter deals with the preparation of polymer electrolytes and electrode materials understudy. In polymer electrolytes, preparation of the complexes of each of Polyvinyl pyrrolidone, Polyethylene glycol, Polyvinyl alcohol with rare earths (Gadolinium, Neodymium, praseodymium and dysprosium) has been reported. The polagrographic study of each of Gadolinium, Neodymium, Praseodymium and Dysprosium and their complexes with PVP, PVA, and PEG polymers have also been reported. On gradual increase of each of the polymer concentration the half wave potential of each of the metals i.e. Gdsup III, sup Nd, sup III Prsup III and Dy sup III shifted towards more negative value and the diffusion current also decreased. Plots of shift in half wave potential against logarithm of the concentration of the polymer were drawn. All the plots were linear showing single complex species formation in the solution. The results of polagrographic studies on the interaction of polymers (PVP, PVA, and PEG) with Gdsup III, sup Nd, sup III Prsup III and Dy sup III metals reveal complex formation between metal and ligands and the Lingane's treatment of the observed polarographic data provides 1:1, M : L stoichiometric ratio. The values of formation constants log βsup 1 for all the complexes have also been calculated. The values of log βsup 1 for Gdsup III–PVP, Ndsup III–PVP, Prsup III–PVP and Dy sup III–PVP complexes are 4.43, 4.13, 3.65 and 3.83 respectively, for Gdsup III–PVA, Ndsup III–PVA, Prsup III–PVA and Dy sup III–PVA complexes these values are 3.38, 3.63, 4.13 and 3.83 respectively, whereas, for the complexes of PEG and rare earths, log βsup 1 values are 2.35, 2.28, 2.35 and 2.36 for Gd sup III–PEG, Ndsup III–PEG, Prsup III–PEG and Dy sup III–PEG complexes respectively. The polarographic analysis of complex formation was done in
0.1M KCl (used as a supporting electrolyte) with 0.01% gelatin at the pH 3.5 ± 0.1.

CHAPTER-III

INFRARED SPECTRAL STUDIES

The third chapter of the thesis describes the infrared spectroscopic studies on pure polymers, PVP, PVA, PEG and their complexes with Gd$^{III}$, Nd$^{III}$, Pr$^{III}$ and Dy$^{III}$ metals and doped forms of PEG. An IR spectral absorption bands have been used for assigning the metal : polymer sites in complexes. A critical comparison of the IR spectra of pure polymers and their complexes under study have been reported which show significant shifts in the important IR absorption bands and therefore confirming the complex formation between metal and polymer through the particular atom of polymer.

CHAPTER-IV

X-RAY DIFFRACTION ANALYSIS

Chapter fourth deals with the X-ray diffraction studies on the pure polymers and their complexes. The XRD pattern shows the structural changes in the polymer samples. Since many of the properties of solids are structure sensitive therefore XRD analysis has been used for studying the internal structure. It has been observed that under suitable treatment a polymer in a crystalline state could be changed to the amorphous state and vice-versa. XRD studies provide information about the orderedness and disorderedness of crystal lattice of the polymers (PVP, PVA and PEG) and their complexes with Gd$^{III}$, Nd$^{III}$, Pr$^{III}$ and Dy$^{III}$. 
ABSTRACT

A comparative study of pure polymers and their complexes with rare earths in each case has also been presented in this chapter in which number of peaks and their intensities clearly indicate that the prepared complexes are more semi crystalline as compared to their corresponding pure polymer. The 20 values of the peaks with their corresponding d values also reveal the fact that the complexes are semi crystalline.

CHAPTER-V

CONDUCTANCE MEASUREMENTS

The last chapter (chapter-5th) deals with the conductance measurement of pure polymers (PVP, PVA and PEG) and their complexes with Gd^{III}, Nd^{III}, Pr^{III} and Dy^{III} and doped polymers. Conductance of pure PVP is 4.7 X 10^{-8} Scm^{-1}, whereas, the values of conductance for Pr^{III}-PVP, Nd^{III}-PVP, Gd^{III}-PVP and Dy^{III}-PVP complexes are 5.2 X 10^{-7}, 2.0 X 10^{-7}, 3.0 X 10^{-7} and 9.2 X 10^{-6} Scm^{-1} respectively, which are greater than that of pure polymer. For Pure PVA the value of conductance is 5.8 X 10^{-9} Scm^{-1}, whereas, for Pr^{III}-PVA, Nd^{III}-PVA, Gd^{III}-PVA and Dy^{III}-PVA complexes these values are 5.5 X 10^{-7}, 2.8 X 10^{-7}, 3.7 X 10^{-7} and 5.6 X 10^{-6} Scm^{-1} respectively, these values are also higher than that of pure PVA. The conductance of pure PEG is 1.8 X 10^{-8} Scm^{-1}, whereas, the conductance of Pr^{III}-PEG, Nd^{III}-PEG, Gd^{III}-PEG and Dy^{III}-PEG complexes are 3.1 X 10^{-5}, 4.9 X 10^{-6}, 5.8 X 10^{-6} and 1.6 X 10^{-5} Scm^{-1} which are far greater than that of pure PEG. Result of the conductance measurements clearly shows that on complex formation the conductance increases, similarly on doping also the value of conductance attains the higher value. The conductance of pure
polymers under study are between of $10^{-8}$ to $10^{-9} \text{ Scm}^{-1}$ which is found to be increased for prepared polymeric samples. Therefore the conductances of polymer complexes and doped polymers are far greater than that of pure polymers. The increase in conductance of the polymer complexes under study has been explained on the bases of XRD data in the fourth chapter.