CHAPTER I

INTRODUCTION

In recent years there has been a growing awareness in the field of the coordination chemistry of polymer metal complexes, since they constitute an important part of the contemporary chemistry of high molecular weight, bioinorganic and coordination compounds. This development was delayed due to the absence of powerful analytical tools. The lack of vigorous theoretical understanding and the instrumentation for studying the physicochemical aspects of metal complexes also affected the development adversely. The complete understanding of the complexation reaction, the coordination structure, the conformation state in solution and the effects of the macromolecular system in polymer metal complexes are areas which still remain unsolved completely.

The correlation between the trends of complexation and the structural factors characteristic of the macromolecular matrix is important in the design and the development of new and selective complexons for metal ions. The macromolecular structural features of the polymer support material have been proved to contribute
significantly to the reactivity of the functional groups. The diversity possible in the macromolecular structural parameters can provide modified and unique complexation behaviour for the attached ligands. The specificity of the functional polymeric species is achieved by the unique interaction of the macromolecular support with the functional groups. The nature of the interaction is either physical or chemical and therefore the support itself creates a specific microenvironment for the functional group and controls the reactivity. The support material can also interact with the surrounding medium depending on its thermodynamic affinity with the medium. A systematic investigation of the variables of macromolecular structure on complexation would contribute to the study of polymeric complexing agents which find varied applications in metal ion separation, preconcentration and recovery of trace metal ions, catalysis, organic synthesis, waste water treatment, nuclear chemistry, pollution control, hydrometallurgy and in the modelling of mechanochemical and bioinorganic systems.

Coordinated macromolecules can participate in practically any reaction which low molecular weight complexes are known to undergo. In many cases the complexes with macromolecular ligands possess higher activity as catalysts compared to their low molecular
weight analogues. The polymer supported analogues of transition metal catalysts are currently being vigorously investigated. It is believed that the resin binding will provide typical homogeneous catalytic chemistry plus the convenience and economy of heterogeneous catalysts. Resin binding can change the steric environment and consequently the substrate specificity found in homogeneous systems. The catalytic activity of a polymer metal complex is decided by the ligand molecule surrounding the metal ion. The one-, two- or multi-dimensional structure of the polymeric ligand and its rigid conformation decide not only the coordination site but also the oxidation state and redox behaviour. The technique for the easy preparation of polymer-metal complexes having a predetermined structure could lead to the development of biomimetic catalyst systems where a geared reaction cycle is realizable by carrying out many steps in one assembly.

Specific correlation between the variables of polymeric ligand and its complexing ability forms the overall thrust of the present study. The systems selected for these investigations are the amino and amino acid ligands supported on crosslinked polyacrylamide matrix. The preparation of crosslinked polyacrylamides with varying molecular character and extent of crosslinking, their functionalisation with ligand groups by polymer
analogous reactions, study of their complexation parameters like metal ion intake, time course, pH dependence, equilibrium water content, recyclability, physicochemical investigation of the polymeric ligands and complexes, selective separation of metal ions and catalytic action of various Cu(II) complexes on the decomposition of $\text{H}_2\text{O}_2$ are investigated here.

A brief survey of the existing literature on the macromolecular effects on complexation, polymer supported amino and amino acid ligands, physicochemical characterisations of polymeric ligands and complexes and important applications of polymer metal complexes is given in section II.

Section III deals with the complexes of crosslinked polyacrylamide supported amino ligands with Cu(II), Cr(III), Fe(III), Mn(II), Cd(II) and Pb(II) ions. Macromolecular effects on complexation with these metal ions were studied by preparing copolymers of acrylamide with different kinds and extents of crosslinking agents. The DVB crosslinking imparts rigidity and hydrophobicity to the polymer. TEGDMA makes the polymer more polar, hydrophilic and flexible. NNMBMA-crosslinked polyacrylamide is semi-rigid and of medium hydrophobicity. EGDMA, BDDMA and HDDA differ in the number of methylene groups in
between the difunctional vinyl groups and thus the steric strain and microenvironment of the ligand function in the polymer matrix can be varied. By changing the crosslinking agents and the monomer ratio one can prepare polymer supported amino ligands with optimum complexing ability towards metal ions in aqueous solution. The coordination sites and structures were followed by spectral and magnetic studies. The thermal stability and kinetics of complexation of polyacrylamide amino ligand systems were studied in the case of Cr(III) complexes. The equilibrium water content which is a measure of the compatibility of the polymer with aqueous metal ions and the recyclability of the polymeric ligands were also discussed in this section.

Section IV comprises the incorporation of glycine, arginine and aspartic acid into the crosslinked polyacrylamides and the investigation of the complexation characteristics of Co(II), Ni(II), Cu(II), Cr(III), Fe(III), Mn(II), Cd(II) and Pb(II) ions. Amino acid incorporated DVB-crosslinked polystyrene systems are also subjected to complexation with metal ions. Encapsulation of amino acid ligand in crosslinked polyacrylamide matrix and its selective complexation of the desorbed metal ion are also described here. The polymer supported amino acids and complexes are subjected to spectral studies, thermal
analysis, and morphological investigations. Two important applications of polymeric ligands and polymer metal complexes in the separation of metal ions and in the catalytic decomposition of $\text{H}_2\text{O}_2$ are also presented in this section.

Section V is the experimental part of the thesis and section VI gives the summary and conclusions of the investigations.