POLYMERIC COMPLEXES - SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS

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Under The Faculty Of Science

BY

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MAY 2004

To my Parents, Husband And Son

Dr. K. Girish Kumar,
Reader in Analytical Chemistry,
Dept. of Applied Chemistry,
Cochin University of Science and Technology,
Kochi-22.

CERTIFICATE

*This is to certify that the thesis entitled "**Polymeric complexes- Synthesis, Characterization and Analytical Applications**" submitted for the award of the Degree of Doctor of Philosophy in Chemistry, of Cochin University of Science and Technology, is a record of bonafide research work carried out by Mrs. Saji John K. under my supervision in the Department of Applied Chemistry.*

K. Girish Kumar

Kochi-22
03.05.2004

DECLARATION

I hereby declare that the thesis entitled ***"Polymeric complexes-Synthesis, Characterization and Analytical Applications"****, submitted for the award of Ph. D. Degree, is based on the original work done by me under the guidance of Dr. K. Girish Kumar, Reader in Analytical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology and further that no part there of has been presented before for any other degree.*

Saji

Kochi-22
03-05-04

Saji John K.

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Thanking Almighty for all his graces,

Saji JohnK.

CONTENTS

CHAPTER I

INTRODUCTION

1.1 POLYMERIC REAGENTS

The idea of using functionalized polymers as carriers for effecting various organic and inorganic synthetic transformations continues to be an active field of investigation ever since the introduction of solid phase synthesis of peptides by R. B. Merrifield in 1963.[1, 2]

The successful use of functional polymers as carriers for attaching synthons by Merrifield, tempted researchers to consider polymers as organic molecules. Since then, polymer chemistry entered into different branches of chemistry so that polymers and polymer bound materials were extensively used as oxidizing agents, reducing agents, catalysts, photosensitizers, ion exchange resins and agriculturally and pharmacologically active agents.[3]

The chemistry and applications of these functionalized polymers depend largely on the characteristics of the specific active functional groups. The architectural characteristics of the macromolecule influence the behaviour of these functional groups. This inter dependence of the polymer microstructure and reactivity of functional groups in functionalized polymers dictate the applications of such systems in a number of areas of functional and technological interest.

The study of the complexation behaviour of polymeric ligands has received increased interest in the various branches of chemistry, chemical technology and biology.[4-7] Polymeric ligands can be obtained by the polymerization of monomers containing coordinating groups or by the introduction of low molecular weight ligands by polymer analogous reactions. In a polymer metal complex, a complex with a specific structure results since the metal ion is surrounds by a structured polymer chain. The suitability of a polymeric ligand in metal ion separation depends on the nature and structure of the chelating group, kind of metal ion to be separated, molecular architecture of the polymer support and the conditions of complexation.

1.2 POLYMER SUPPORTS

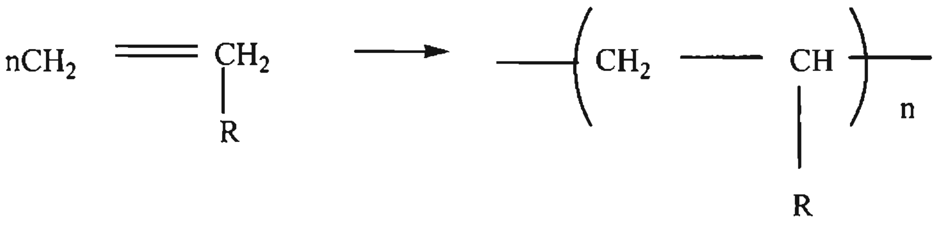
A considerable number of polymeric and inorganic materials have been investigated as support matrices. While many of these are conveniently available from commercial sources, others lend themselves readily to synthesize in the laboratory. Linear and cross linked organic macromolecular species have found wide application in more recent years, the latter in particular being experimentally very attractive because of their ease of filtration and purification. There have also been some attempts to reproduce the elegant synthesis of structurally well defined, polymer supported reagents employing various inorganic supports.[8-9]

1.2.1 Synthesis of Linear Polymers

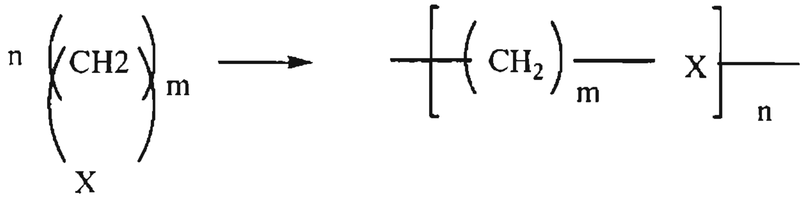
Synthetic linear macromolecules fall into two groups, those formed by polycondensation and those made by addition polymerization.

Polycondensation involves the repetition of a simple condensation process to form a long chain species. Very often these are acid catalyzed processes, although the condensation of acid chlorides or isocyanates with amines or alcohols proceed without the aid of catalyst. The mechanism of each reaction step is usually the same as in simple monomeric systems and chain propagations can occur at both ends of these growing macromolecule.

Addition polymerization takes place, in contrast, by a single chain reaction propagated by a reactive intermediate.



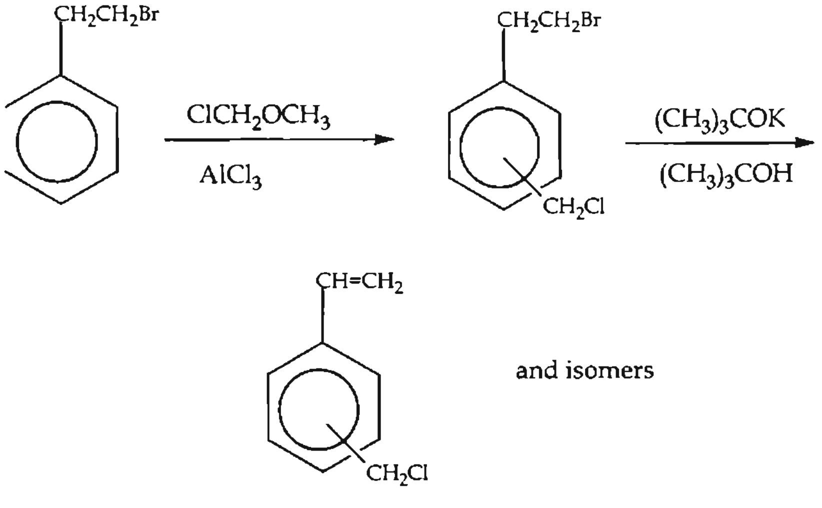
$$nCH_2{=}\underset{\displaystyle R}{\underset{|}{CH_2}} \longrightarrow -\!\left(CH_2-\underset{\displaystyle R}{\underset{|}{CH}}\right)_n\!-$$



$$n\,\underset{\displaystyle X}{\left(CH2\right)_m} \longrightarrow -\!\left[\left(CH_2\right)_m-X\right]_n\!-$$

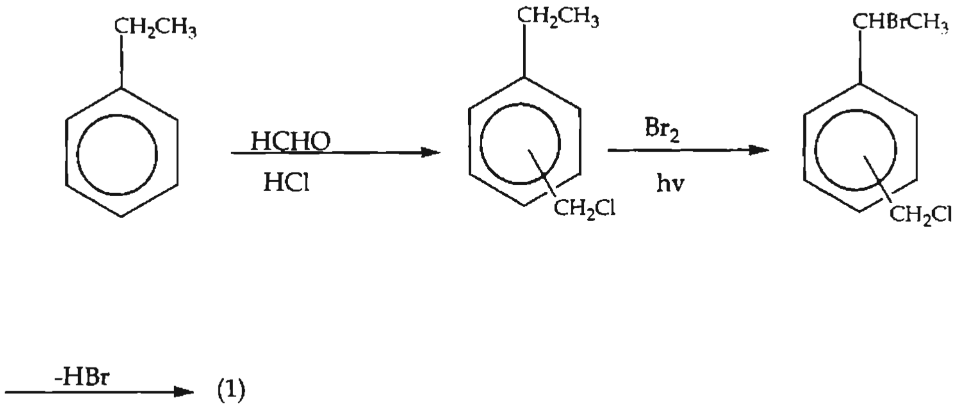
1.2.2 Preparation of Functionalized Supports

A required functional group can be introduced on to a support in two ways. It can either be incorporated during the synthesis of the support itself or by chemical modification of a non functionalized polymer support matrix. The introduction of a functional group during polymerization requires an appropriately substituted monomer. A wide variety of vinyl derivative molecules can be obtained from commercial sources and can be polymerized or copolymerized to produce an appropriately functionalized support. One potentially very useful monomer is 4-chloromethyl styrene, which is reported to be made via, direct chloromethylation of either 2-phenyl ethyl bromide[10] or ethyl benzene[11] as shown in schemes 1 and 2. The product in each case, however, is a mixture of chloromethyl isomers and overall yields are also low. More satisfactory methods have been developed recently[12,13] and yield specially the para isomer (Schemes 3 and 4).

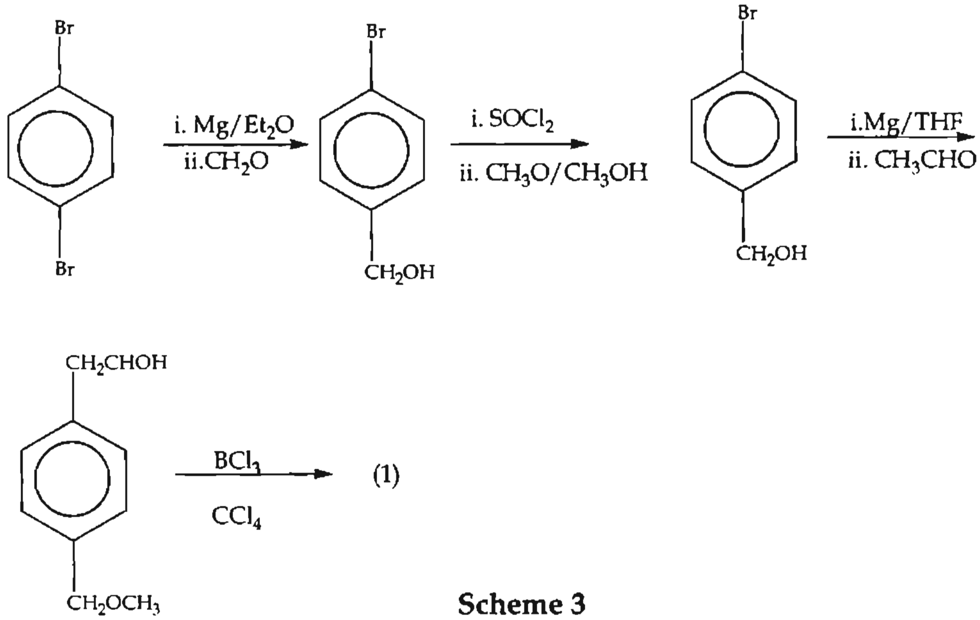


(1)

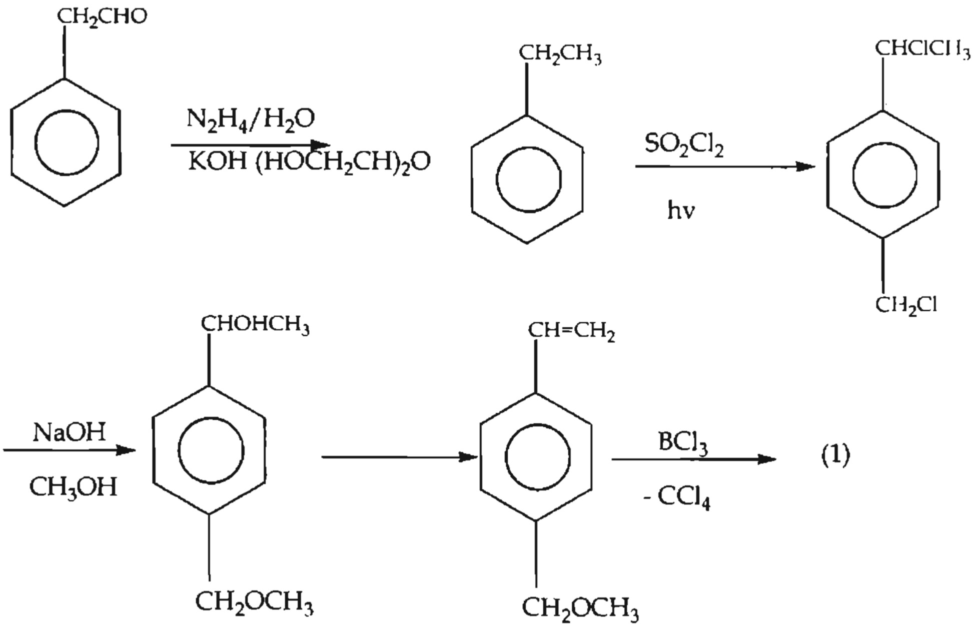
Scheme 1



Scheme 2



Scheme 3



Scheme 4

1.2.3 Characterization of Functionalized Supports

The adequate characterization of chemical changes carried out on supports is a major problem associated with 'supported chemistry' The two most powerful techniques of analysis that are readily applicable are elemental microanalysis and infrared absorption spectroscopy. The former is a much used technique and carbon, hydrogen, halogen, nitrogen, sulphur and phosphorous analysis have been performed widely and routinely.

1.2.4 Interesting Features of Polymer Supported Reagents

Easy separation of the polymer supported species from other species present in the reaction mixture results in the following advantages. The separation is particularly easy when cross linked polymers is used as it then merely involves filtration.

(1) Excess and spent reagent can easily be removed from the final reaction mixture, there by simplifying the work up.

(2) If higher reaction yields can be achieved by using an excess of reagent, then an excess reagent can be used without causing separation problems.

(3) Easy recovery of the polymer may make it possible to regenerate and reuse the reagent. This is very important from an economic point of view because polymer supported reagents will generally be more expensive than the analogous non supported reagents. If the reagent can be recycled many times it becomes very similar to a catalyst and it is then worthwhile to prepare complex reagents, which for example, might be used to achieve asymmetric synthesis.

(4) It may be possible to use and to regenerate the reagent using a column of the polymer, rather like ion exchange resins are used.

(5) In favourable cases, the reaction work up will just involve filtration of the polymer from the products in solution. In such circumstances the work up could be automated.

Other advantage comes from the insolubility and involatility of the polymer. Thus, polymer supported reagents are non toxic and odourless. These are important considerations from an environmental point of view.

Finally, the microenvironment within the vicinity of the polymer chains may differ from that of the corresponding reaction in solution, and that this may lead to interesting rate and specificity effects. One possibility is the microenvironment near the polymer chains is a more favourable medium for the reaction. Another is that the difference in polarity between the polymer and the reaction solvent might cause the substrate to concentrate within the polymer, there by causing an increase in reaction rate.

1.3 POLYMER METAL COMPLEXES

A polymer metal complex is composed of a synthetic polymer and metal ion. Its synthesis represents an attempt to give an organic polymer with inorganic functions. The ability of a polymer supported ligand to form complexes depends on the nature of the main chain. The matrix effect on ion binding is clearly evident when low molecular ligands and their polymeric analogues are compared as in the case of an iminodiacetic acid ligand supported on polystyrene and polyacrylamide.[14] With increasing polarity of the support, the extent of complexation increases. The metal intakes by polymeric ligands are varied by the incorporation of the cross linking agents which differ in their polarity and flexibility. The replacement of the rigid and hydrophobic DVB cross linking by a flexible and hydrophilic cross linking agents results in increased metal ion intake.[15]

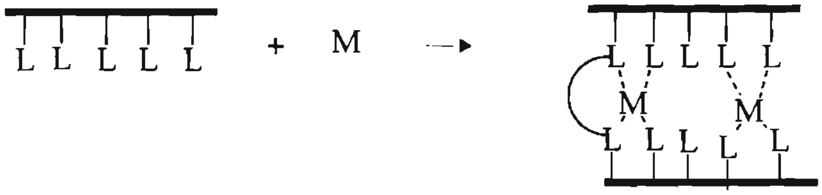
A wide variety of investigations have been carried out on polymeric metal complexes, which include studies of semiconductivity, thermostability, redox reactions, collection of metal ions, bio medical effects and so on. The polymeric metal complexes are classified into the following groups.

Polymer metal complexes, represented by schemes 5 to 9, are defined as complexes composed of a polymer ligand and metal ions in which the metal ions are attached to the polymer ligand by a coordinate bond. Here a polymer ligand is understood to be a polymeric substance that contains coordinating groups or atoms (mainly N, O and S) obtained by polymerization of monomers containing coordinating sites, or by the chemical reaction between a polymer and a low molecular weight compound having coordinating ability. Typical polymer ligands previously reported are listed in Table 1. When a polymer ligand is mixed directly with a metal ion, which generally has four or six coordinating bonding hands, a polymer metal complex is formed. This may be of the intra polymer chelate type (Scheme 5) or of the inter-polymer chelate type (Scheme 6). Complex formation proceeds via scheme 7, where the polymer backbone either contains multi dentate ligands, such as the imino diacetic acid group, or acts as a carrier for low molecular weight multi dentate ligands. Many of the so called chelating resins fit in this scheme. The polymer metal complexes represented by schemes 5 to 7 have chelating structures in their polymer ligands and are therefore called polymer chelates. The pendant type polymer metal complex (Scheme 8) is formed by the reaction of a polymer ligand with a stable metal complex, the central metal ion of which has already been masked with low molecular weight ligands except for one coordinate site that remains vacant as in metalloporphyrins, cobaltic chelates etc. A polymer metal complex is also obtained by polymerizing a monomeric metal complex (Scheme 9).

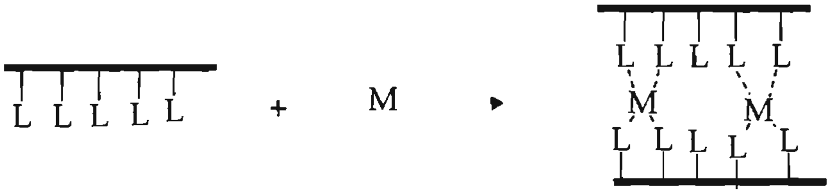
Scheme 10 represents coordinate polymers. A low molecular weight compound with multidentate groups on both ends of the molecule grows into a linear polymer with metal ions, and the polymer chain is composed of coordinate binds. The parquet like polymer complexes, poly (metal-phthalocyanine) and poly (metal-tetracyano ethylene), are classified into scheme 11. They are formed by inserting metal ions into planar-net work polymers or by causing a low molecular weight ligand derivative to react with a metal salt and a condensation reagent.

The coordination structure of the derived polymer metal complexes also depends on the molecular character and extent of cross linking in the polymer support[16,17]. The kinetics of metal ion complexation, the adsorption of metal ions and the interaction between the complexed/adsorbed species are also decided by the rigidity of the cross linking agents.[18] The thermal decomposition behaviour of the polymer-metal complexes decreases with increasing rigidity of the cross linking agents.[19,20] This is because of the increased strain at the cross linking points. The thermal stabilities of the same metal complex with varying extent of cross link also depend on the extent of cross linking in the polymer support.

(A) Polymer-metal complexes

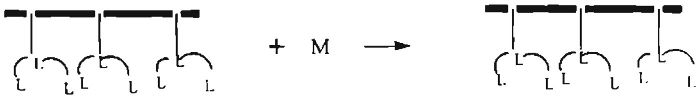


Scheme 5

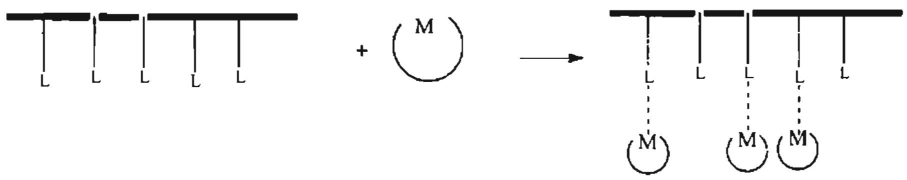


Scheme 6

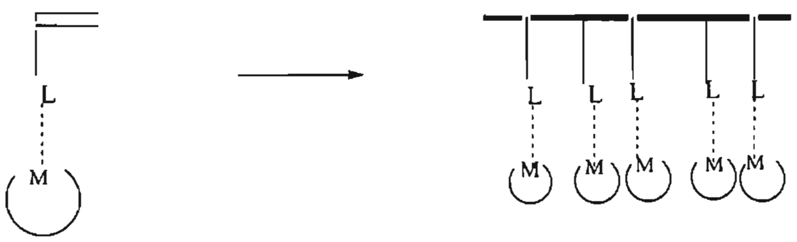
(B) Coordinate polymers



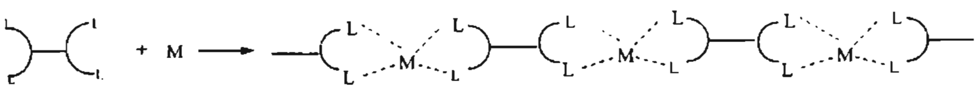
Scheme 7



Scheme 8

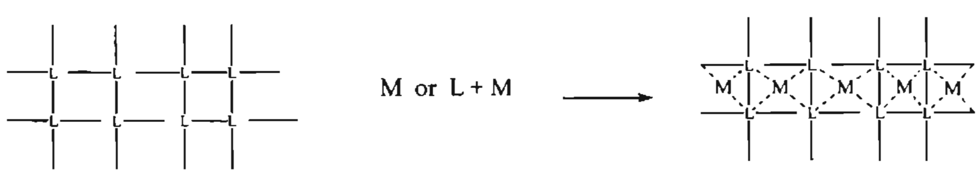


Scheme 9



Scheme 10

(C) Poly(metal-phthalocyanine) type



Scheme 11

L=Coordinating atom or group; M=Metal ion

1.4 POLYMER SUPPORTED LIGANDS AS REAGENTS FOR METAL ION REMOVAL

Polymer supported metal complexes have wide range of applications. Organic synthesis using functional polymers,[21] design of polymeric reagents,[22] polymeric catalysts,[23] complexation and separation of metal ions using polymeric ligands,[24] understanding of the specificity of biological reactions of naturally occurring macromolecules,[25] biomimetic chemistry,[26] enzyme immobilization,[27] conductive polymers,[28] polymeric surfactants,[29] stabilizers,[30] polymeric liquid crystals[31] and ion selective electrodes[32] are some of the important fields where the chemistry of functionalized polymers bear relevance.

Polymer supported metal possess enough flexibility to permit interaction of polymer bound anchoring groups with the metal complex. The practical advantages of attaching insoluble supports are recognized and industrially exploited. High selectivity of chelating sorbents together with advantageous sorption kinetics enable the extraction of trace metals from their complex solutions. They are also used for the separation of metal ions by ion exchange chromatography. The rapid development of functionalized polymers with chelating properties has been due to their inherent advantages over simple ion exchange resins. These advantages include higher metal to polymer bond energies and slower reaction processes between the metal and the polymeric ligand. In addition, the formation of polymeric chelates with vacant coordination sites on the polymeric ligand has led to the concept of selective separation by ligand exchangers based on the relative magnitudes of the stability constants of the ligand metal systems.

Many methods have been used for controlling pollutants in industrial effluents. Polymer complexes are effective for the removal of toxic metals like Hg(II), Cd(II), Pb(II) and As(III) even in microgram level and find promising applications in applied analysis[33,34]. Polymeric ligands prepared by condensing formaldehyde with alicylic or resocyclic acid have been used as selective ion exchange reagent for the extraction of uranyl ion from solution[35]. Attachment of multi dentate ligands to insoluble polymeric supports is a technique commonly utilized for the preparation of selective ion exchange resins, which are capable of separation, and purification of metal ions.[36]

Among the various ligands, amines, dithiocarbamates, iminodiacetic acid, schiff bases and amidoximes are widely used for the collection of heavy metal ions. The specific binding of metal ion by metal ion template cross linked polymers have been reported.[37] If the coordination stereo structure of a polymer metal complex is not destroyed, that polymer will preferentially complex the metal ion which was initially present.[38] In addition to chelating polymers, polymers attached to macrocyclic ethers have been shown to complex metal ions. Recently, three different types of polymeric ethers, crown ethers, cryptands and podands have been introduced as new classes of neutral ligands to replace the conventional ion exchangers. The ion chelating properties of these neutral ligands have led to their selective application in extraction or separation of trace metals, isotopes and organic solutes.[39, 40]

Cross linked polystyrene beads carrying aminomethyl phosphonic acid group[41,42] (ie., Duolite ES 467) and iminodiacetic acid groups[43] (ie., Chelex100) have been demonstrated to be efficient in the removal of trace quantities of metal ions. Due to chelating effects, these are superior to the common ion exchange resins.

Amine ligating polymers react with metal ions and counter anions of the metal cations to form other sphere complexes, and the overall process of complexation is sorption of the metal ions together with their counter anions.[44]

Chlorosulfonated styrene-DVB (10%) resin beads were interacted with excess of ethylene diamine to give the corresponding sulfonamide derivative. Upon treatment with 20% excess of potassium chloroacetate, the amine functional groups on the polymer were carboxymethylated quantitatively. The resulting chelating polymer is an extremely powerful sorbent for Ca(II) and Mg(II) ions.[45] The cross linked polymer has an EDTA like structure and so, is expected to show strong complexation for transition metal ions.

The multi dentate ligand, imino diacetic acid (IDA) and ethylene diamine tetra acetic acid (EDTA) are known to form extremely stable complexes with Ga(III)[46] and In(III).[47] Hence, the chelating resins with these types of functional groups seem promising for the recovery of the metal ions from the leaching solutions.

Phosphates and chromates are selectively removed from contaminated water by a new class of sorbent, referred to as a polymeric ligand exchanger (PLE)[48]. The exchanger bed comprising a styrene-divinyl benzene or poly methacrylate matrix having an electrically neutral chelating functional group with nitrogen or oxygen donor atoms, and a Lewis acid type metal cation, such as Cu, bonded to the chelating functional group in a manner that the positive charges of the metal cation are not neutralized. PLEs are very selective towards phosphates and chromates, chemically stable and amenable to efficient regeneration.

Thus polymeric complexes can be used for the metal ion removal study. Heavy metal ions such as Cu(II), Hg(II), Fe(III), Fe(II), Cr(III), Ni(II), U(IV), etc. can be removed using polymer supported reagents.

1.5 POLYMER SUPPORTED REAGENTS AS ION SELECTIVE ELECTRODE MATERIALS

The need of selective determination of heavy metal ions has increased immensely during last few decades due to growing environmental problems. The ion selective electrodes prepared with suitable polymers are potentially useful to determine the various metal ions in solution. The styrene co-acrylonitrile copolymer (SAN) based electrode has shown an outstanding sensitivity and selectivity for the estimation of copper ions[49] in comparison to the reported ion-selective electrodes. Among the reported electrodes for Cd(II) ions, the cadmium electrode prepared with 3,6-dioxano octane dithiamide has shown a better selectivity over alkali and alkaline earth metal ions but gets poisoned by Cu(II), Pd(II), Pt(II), Ag(I) and Hg(II) ions.[50, 51] The lipophilic 2,2-bipyridine carrier supported PVC based electrode has shown interesting selectivity for Cd(II) over Co(II) and Ni(II) ions.[52] Electrode prepared with styrene acrylonitrile polymer[49] has shown a substantial reduction in anion interference due to highly polar cyano group in the polymer chain, which requires a very small quantity of the anion excluder such as sodium tetraphenyl borate.[53, 54] The cyano copolymer based cadmium ion selective electrodes have better selectivity for Cd(II) ions in the presence of alkali and alkaline earth metal ions.[55]

A novel plastic poly(vinyl chloride) membrane electrode based on pethidine-phosphotungstate ion association as electro active material for the determination of pethidine hydrochloride in injections and tablets has been developed.[56] Also a PVC based capric acid membrane electrode for Pb(II) ion has been developed.[57]

1.6 A BRIEF ACCOUNT OF POLYMER SUPPORTED LIGANDS/COMPLEXES

A close examination of the literature reveals that a number of attempts are reported on the synthesis, characterization and application studies of polymeric ligands/complexes. An account of the selected reports is given as a brief review.

H. A. Goodwin *et. al.*. reported some coordination compounds derived from the polymeric schiff base produced by the condensation of triethylene tetramine with 5,5′-methylene bis(salicylaldehyde) and 5,5'-sulfonyl bis(salicylaldehyde) containing sexadentate units, during 1960s. [58]

The synthesis and thermal stability of bis(8-hydroxy quinoline) schiff base coordination polymers[59] and that of some ferrocene containing polyazines and polymeric schiff bases[60] are also reported. Organolithium reagent has been reported for the synthesis of polyfluoro phenyl Co(II) schiff base complexes.[61]

Polymeric reagents obtained by alkylation of Merrifield resins with diethyl malonate malononitrile or acetyl acetone were reduced by $LiAlH_4$ to the corresponding 1,3-diamine or diol. The diamine serves as a starting material for condensation reactions leading to polymeric schiff bases.[62] These materials are potential ligands for transition metals like Cu(II) and Co(II). There is also a report on the use of polymeric schiff base chromium complexes as stationary phases in adsorption gas chromatography[63] to separate the spin isomers of hydrogen and deuterium (but not of a mixture of both isotopes) at ambient temperature with an extremely short retention time. Only paramagnetic complexes having a pseudo-tetrahedral structure were formed on treating ethylene dimethacrylate-glycidyl methacrylate copolymer with $H_2NCH_2CH_2NH_2$, salicylaldehyde and cobalt or nickel acetate[64]. The effects of the polymer matrix and of the immobility of the bonded schiff bases on the distortion of the coordination sphere of the central ion are discussed. Poly condensation reactions of 5,5′-methylene bis(salicylaldehyde) with alkylene diamines yield polymeric aromatic schiff bases which behave as strong complexing agents towards toxic metals.[65]

Covalently bound polymeric cobalt chelates from divinyl-salenes and their dioxygen binding and catalytic activity was studied by Woehrle D. *et. al.*[66] Polymeric coordination compounds with electronic semiconducting properties and biological activity are prepared by treating metal salts with polydentate ligands obtained by condensation of aromatic dialdehydes with β-hydroxy-α, γ-diamines.[67] Template synthesis of a polymer schiff base Co(II) complex and formation of a specific cavity for chiral amino acid was reported by Fuji Yuki *et. al.*[68] The efficiency of polymeric schiff base complexes as solid phases for the chromatographic separation of low molecular weight gases was tested.[69] Woehrle *et. al*, synthesized some polymeric schiff base chelates which are used as the effective heterogeneous catalyst for the valence isomerization of quadricyclane to norbornadiene.[70]

Three types of the novel polymer ligands in which 6,8,15,17-tetramethyl-dibenzo-5,9,14,18-tetraaza-cyclo-tetradecene was present in an integral part of the polymer back bone were prepared.[71] Among the polymer ligands, one which contained a triethylene glycol bis (p-phenylene) group as a linkage group was an excellent extractant for Cu(II).

Polymer bound 2,2′-dipyridylamine has been prepared. Like naphthyridine and bipyridine, this ligand can be easily bound to the polymer support.[72] Studies on these complexes revealed that polymer bound dipyridylamine ligand has an important application in quantitative and qualitative removal of metal ions like Fe^{3+} in organic media.

A review with seven references on the ESR study of the dissociation and ligation of polymeric Cu(II) and VO(II) complexes was reported by Jezierska Julia *et. al*.[73] Perm selective thin membranes useful for separation of gas mixtures were prepared from polymer bound schiff base complexes.[74] Synthesis, characterization and catalytic properties of mono nuclear and dinuclear complexes of UO_2(II), Cu(II) and Ni(II) with compartmental schiff bases derived from 2,6-diformyl-4-chlorophenol and polyamines was reported by Guerriero *et. al.*[75] Coordination structure and magnetic property of poly(pyridylenemethylidene)nitriloirons was studied by Nishide *et. al.*[76] The counter anion species and spacer length of the polymers affected the coordination structure and magnetism.

Deodrant polymers containing schiff base metal complexes was reported by Osawa Yasuko *et. al.*[77] Osaka Gas Co. Ltd prepared magnetic iron-schiff base polymer chelate compounds.[78] Synthesis and characterization of new polymer supported chelating resins obtained by the condensation of cross linked chloromethylated polystyrene with schiff bases from salicylaldehyde-4-amino-3-hydroxy naphthalene-1-sulfonic acid, salicylaldehyde-anthranilic acid, 3-formyl salicylic acid-o-aminophenol, 3-formyl salicylic acid-o-hydroxy benzylamine were reported.[79] Synthesis and characterization of new redox polymers based on copper containing units and evidence for the participation of copper in the electron transfer mechanism was reported by Audebert *et. al.*[80] Study of metalloorganic schiff base polymers showing anomalous magnetic behaviour was conducted by Garcia Joaquin *et. al.*[81]

A room temperature organic ferro magnet of schiff base polymer synthesized by reacting 2,6-pyridine dicarboxaldehyde-hexamethylene diamine copolymer with Fe(II) sulfate was reported.[82] A partially oxidized copper complex of bis (salicylidine) ethylenediamine which possess conductivity and electro chromic properties is reported.[83] Different hydroxy-functionalized polyazomethines have been modified by complexation using paramagnetic Cu(II) ions.[84] Coordination polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with poly schiff base derived from 5,5′-methylenebis(3-nitrosalicylaldehyde) and 1,3-diaminopropane have been synthesized and characterized.[85] The electronic properties of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) polychelates of 4,4′-dihydroxy-3,3′-diacetyl-biphenyl-butanedione dihydrazone (DDBBD) and 4,4′-dihydroxy-3,3′-diacetyl biphenyl mercapto diaminotriazine (DDBMT) have been studied in their pellet form.[86] There is also another patent on polyazomethine complexes and method for making optical devices and other materials there with.[87]

Synthesis and characterization of polymer supported Cu(II), Ni(II), Fe(III), Zn(II), Cd(II), Zn(IV), Mo(V and VI) and U(VI) complexes of polystyrene supported schiff base derived from 3-formylsalicylic acid and o-aminophenol have been reported.[88] New poly chelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were synthesized from schiff base derived from 4, 4′-dihydroxy-3, 3′-diacetyl-biphenyl and 1,5-diamino naphthalene and were characterized.[89] New compartmental macroacyclic and macrocyclic schiff bases were prepared by reaction of the formyl precursors 2,3-dihydroxybenzaldehyde, 3-methoxy-2- hydroxybenzaldehyde and 2,6-diformyl-4-chlorophenol with 1,2-diaminoethane, 1,3-

diaminopropane and the polyethylene oxydiamines $H_2N(CH_2)_2[O(CH_2)_2]_n NH_2$ (n = 1,2,3) in the presence of a templating ion.[90] In these ligands the shape of one or both compartments has progressively been enlarged and the denticity increased to link up to four metal ions into the coordination moiety. These ligands react with Cu(II), Ni(II) or lanthanide(III) salts to form mono nuclear, homo and hetero trinuclear or homo tetranuclear complexes.

Two types of poly(azomethines) containing repeating pairs of a tri-dentate ligand and an oligo-dimethylsiloxane in the backbone were synthesized and complexed with cobalt ion.[91] The resulting polymer complex membranes showed good oxygen perm selectivity at 1 atm pressure difference. The complexes function as oxygen carrier. Four new schiff base polymers and their Cu(II) and Ni(II) chelates were prepared and characterized.[92] An attempt was done to develop and characterize new air separation membrane materials based upon polymers with tetradentate schiff base.[93] Two new conjugated poly schiff bases (PP_PP and PP_MP) were synthesized by polycondensation of p-phenylene diamine or m-phenylene diamine with 2,6-pyridine dicarboxaldehyde.[94]

Coordination polymers of Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) with poly schiff base derived from 5,5′-methylene bis(3-nitro salicylaldehyde) and 1,4-diamino butane were prepared and characterized.[95] EPR parameters and polarized light micrographs of three polyazomethines bearing OH groups and containing the paramagnetic centres Cu(II), VO(II) or Fe(III) were reported.[96] Mesogenic and thermal properties were studied and discussed with respect to metal complexation.

A new hydroxy functionalized liquid crystalline polyazomethine has been synthesized by solution polycondensation of a dialdehyde and a diamine.[97] Studies on the liquid crystal properties reveal its nematic mesomorphic behaviour. Poly schiff bases incorporating dicyano vinyl groups in the main chain were prepared by the solution polymerization of p-bis[1-(4-formylphenoxy)-2, 2-dicyanovinyl] benzene (I) and terephthaldehyde (TA) with 4-aminophenylether (ODA).[98] A magnetically active organometallic iron-schiff base polymer, was synthesized by polymerizing 2,6-diacetyl pyridine with diamino hexane, followed by treatment of the obtained polyazomethine with $FeSO_4$.[99]

Patel *et. al.* synthesized and characterized chelate polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with a schiff base of 5, 5′-methylene-bis(3,3′-dinitrosalicylaldehyde) with 1,6-hexanediamine.[100] There is also a report on the application of polyazomethines in organic electroluminiscence devices.[101] Polychelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with schiff base copolymer derived from 4,4′-dihydroxy-3,3′-diacetylbiphenyl and 2,3-butanedionedihydrazone have been prepared by Aswar *et. al.*[102] Cross linked polymeric materials have been synthesized by Cu(II) complexation of a semiflexible main-chain liquid crystalline polyazomethine.[103]

Coordination polymers of Cu(II), Ni(II) and Zn(II) containing schiff base derived from terephthaldehyde and thiocarbohydrazide were synthesized and characterized by Zabin Sami *et. al.*[104] A number of semiflexible liquid crystalline polyazomethines were synthesized by condensation of dialdehyde monomers (1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane or 1,10-bis[(4-formyl-phenyl)-oxy] decane) with diamines (2-methyl-1,4-phenylenediamine or 3,3′-dimethoxybenzidines.[105] Twelve new poly(etherazomethines) with linear structures were prepared by a conventional procedure by reacting six different diamines with two different bisaldehydes containing ether linkages in the back bone.[106] Polynuclear manganese complexes of 2,5-dihydroxyterephthaldehyde(dhterH$_2$)and its schiff base polymer ligand (PdhterenH$_2$), [MnII(dhter)]n, [MnIIn (Pdhteren)] and [MnIIIn (Pdhteren) (OAC)n] were synthesized and characterized.[107] Catalytic epoxidation of olefins with hydrogen peroxide was studied using the above manganese complexes under heterogenized homogeneous reaction conditions in the presence of a base. A polymer bound schiff base manganese complex prepared from polystyrene bound salicylaldehyde and phenylalanine is found to be a good catalyst for the oxidation of cyclohexene, linear aliphatic olefins and styrene by oxygen.[108] A styrene-divinylbenzene copolymer with (5% and 15% cross linking) containing palladium (II) diaminopropane complexes were found to be active catalyst for hydrogenation.[109] A schiff base activated glycine supported on a soluble polymer(poly(ethylene glycol) was readily alkylated with a wide variety of electrophiles in the presence of a carbonate base in acetonitrile.[110] The presence of the polymer provided a phase transfer catalysis environment which accelerated the reaction.

Electro oxidative polymerization of schiff base of 1,8-diaminonaphthalene and 3-acetylthiophene.[111] The electrodes so obtained were stable chemically and electro chemically both in aqueous solutions and in mixtures containing methanol, making them excellent candidate for sensing and/or electrocatalytic applications. The preparation and electrochemical characteristics of electrodes modified by cobalt complexes of N, N′-bis(salicylidene)-ethane-1,2-diamine were described.[112] A cobalt salen polymer film modified electrode has strong electro catalytic effects for the oxidation of ascorbic acid.

New metal containing epoxy polymers were prepared from diglycidyl ether of bisphenol A and tetradentate schiff base metal complexes.[113] A novel poly schiff base sulphide polymer was synthesized by nucleophilic displacement polymerization of N, N′-bis(p-chlorobenzylidine)4,4′-diaminodiphenyl ether with sodium sulphide in anhydrous condition.[114] There is also a report on the synthesis and properties of polymeric schiff bases of the antibiotic spiramycin.[115]

Polychelates of 4, 4′-bis(N-phenylsalicylaldimine-5) azobiphenyl with some transition metal ions were studied by Aswale *et. al.*[116] Interaction of local anaesthetic drug richlocain with linear polyacrylic acid and cross linked sodium polyacrylate, linear and cross linked acrylic acid schiff base copolymers has been investigated.[117] Similarly manganese bis (salicylidenediaminopropane) thiocyanato dimer polymer has been synthesized and its structure and magnetic properties were studied.[118] Catalytic epoxidation of olefins with molecular oxygen was studied in the presence of a sacrificial aldehyde using polynuclear manganese complexes of ligands, 2,5-dihydroxyterephthalaldehyde and its schiff bases.[119] The Mn(II) schiff base complex with nitrogen coordinating environment is found to be more stable and effective epoxidation catalyst than the oxygen bound complex.

In order to investigate the selective antiproliferative effects shown by 2-(6-hydroxynaphthyl)-b-D-xylopyranoside, the fourteen possible D-xylopyranosidic compounds were synthesized on solid support.[120] An amino methylated polystyrene resin was converted into an acid chloride resin and then esterified using dihydroxynaphthalene. The free hydroxy group was then xylosylated under $BF_3 \times OEt_2$ mediated conditions. The xyloside was deprotected and simultaneously cleaved off the resin using NaOMe/MeOH. Final purification using reverse phase HPLC gave the pure xylosides in 6–42 % yield with virtually no formation of a xyloside. Cross linking of diglycidyl ether of bisphenol A (DGEBA) with tetradentate and hexadentate schiff base metal complexes of transition metals and maleic anhydride (MA) was investigated.[121] The cross linking reaction is proposed to proceed through a complex mechanism.

A schiff base complex of Zn(II) as a neutral carrier for highly selective PVC membrane sensors for the sulfate ion was developed.[122] Novel polymeric membrane (PME) and coated graphite (CGE) sulfate-selective electrodes based on a recently synthesized schiff base complex of Zn(II) were prepared. The electrodes reveal a Nernstian behaviour over wide SO_4^{2-} ion concentration ranges (5.0×10^{-5}-1.0×10^{-1} mol dm^{-3} for PME and 1.0×10^{-7}-1.0×10^{-1} mol dm^{-3} for CGE) and very low detection limits (2.8×10^{-5} mol dm-^{3} for PME and 8.5×10^{-8} mol dm^{-3} for CGE). The electrodes were used as an indicator electrode in the potentiometric titration of sulfate and barium ions and in the determination of iron in ferrous sulfate tablets. The electrochemical formation of films of poly [M (salen)] (M = Ni or Pd, H_2salen = N,N'-ethylenebis (salicylidenimine)) and their halo and methoxy derivatives along with their spectroscopic characteristics in the UV and visible spectrum regions were studied.[123] The spectroscopic characteristics of these polymer complexes in oxidized and reduced forms were recorded at wavelengths of 300-900 nm, after depositing the polymer layer on optically transparent electrode. Cyclic voltammograms are discussed for these polymer complexes on platinum in acetonitrile containing tetrabutylammonium perchlorate.

A novel inorganic-organic hybrid membrane for oxygen/ nitrogen separation containing a Co(II) schiff base complex as oxygen carrier using poly(N-vinylpyrrolidone) as mediator.[124] A series of porous silica supported metal schiff base complexes was prepared and characterized.[125] Thus, treatment of amino functionalized porous silica gave schiff bases, which were further complexed with metal ions. Catalytic properties for oxidation of olefins in the presence of molecular oxygen were investigated. The major products of the aerobic oxidation without reductant were epoxy compounds. The influence of reaction temperature and additives for epoxidation was studied. The selectivity and the conversion of epoxidation varied with reaction time, different additives and different catalysts. Three polymer-Fe(II) complexes were synthesized from Fe(II) and poly(schiff base)s.[126] The poly(schiff base)s were prepared from 2,2'-diamino-4,4'-bithiazole (DABT) with phthalaldehyde, 5,5'-methylene-bis(salicylaldehyde) (MBSA) and terephthalaldehyde, respectively, and characterized by IR, XPS, NMR and ESR spectroscopy. The magnetic behavior of these polymer-Fe(II) complexes was examined as a function of magnetic field strength and temperature (5-300 K), respectively. The hysteresis loops were also studied. Based on these results, several novel ferromagnets were obtained.

A photoacoustic study of the thermal diffusivity of some polymer supported halogenobenzimidazole complexes of Co(II), and Cu(II) was carried out by Raman S. Sankara *et. al.*[127] Synthesis and magnetic properties of a polymeric nitrido-chromium(IV) complex with a tetradentate schiff base ligand has been reported by Tsuchimoto Masanobu *et. al.*[128] New complexes derived from polymeric N-N′-o-phenylene diaminebis(cinnamaldehyde) with Cu(II), Co(II), Ni(II), Zn(II), UO_2(II) and Pd(II) were prepared and characterized.[129] A series of new polystyrene-anchored coordination complexes has been synthesised by the reaction of metal complex/metal salt with the chelating resin containing the schiff base derived from o-hydroxybenzylamine and 3-formylsalicylic acid.[130] Some schiff base Co(II) chelates like ethylenebis [(2-hydroxy-3-methoxy-5-methylphenyl) methylideneiminato]cobalt (II) were coordinatively anchored onto poly(4-vinylpyridine-co-styrene) in diglyme solution and the dioxygen-affinity of the resulting polymeric complexes were measured in situ.[131] A new bidentate oxygen-nitrogen donor schiff base supported on polystyrene matrix has been synthesised by the reaction of amino methylated polystyrene and salicylaldehyde. The chelating resin reacts with Ni(II), Co(II), Cu(II), Fe(III), Zn(II), Mo(VI) and U(VI) and were characterized.[132] There is also a paper which is a review of the metal complex forming coordination polymers[133].

1.7 SCOPE OF THE PRESENT INVESTIGATION

As the application of polymeric complexes is enormous, there exists a continuing interest in the synthesis and characterization of these complexes. The use of polymers as supports for metal complexes has grown tremendously since Merrifield demonstrated the applications of polystyrene resins in peptide synthesis.[134-137]

The development of new methods for purification of water from spent process and effluent streams and recovery of valuable metals from industrial waste is of major concern in research field. Also development of ion-selective electrodes is highly important in that they can give very good results in metal analysis, without much interference. In considering these facts the following objectives were listed and completed as part of the present investigation.

1. Synthesis and characterization of polymer supported Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and U(VI) complexes of schiff bases derived by

    Condensing amino methylated polystyrene with vanillin.

    Condensing amino methylated polystyrene with 2-nitro benzaldehyde.

    Condensing amino methylated polystyrene with veratraldehyde.

2. Metal ion removal studies using

    Schiff base of amino methylated polystyrene with salicyladehyde.

    Schiff base of amino methylated polystyrene with 2-nitro benzaldehyde.

    Schiff base of amino methylated polystyrene with vanillin.

3. Preparation of chloride ion selective electrode using the schiff base cobalt complex of the schiff base of amino methylated polystyrene with salicylaldehyde.

The above mentioned studies have been incorporated in the thesis.

CHAPTER II

MATERIALS AND METHODS

2.1 INTRODUCTION

This chapter deals with the general reagents and procedure adopted for the synthesis and characterization of ligands and metal complexes. Various physico-chemical methods used and procedure for application studies is also included.

2.2 REAGENTS AND INSTRUMENTS

Amino methylated polystyrene was a product of Sigma Aldrich. The aldehydes vanillin, 2-nitro benzaldehyde, veratraldehyde and salicylaldehyde used were products of Merck. The metal salts like anhydrous $FeCl_3$, $CoCl_2.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$ and $UO_2(CH_3COO).2H_2O$ and solvents such as dimethyl formamide (DMF), methanol and diethyl ether were also obtained from Merck. The pH measurements were carried out on a Systronics Digital pH meter 335.

The CHN analysis was performed on PE 2400 model from Perkin Elmer. Magnetic susceptibility measurements were carried out at room temperature using a Guoy balance with $HgCo(NCS)_4$ as standard. The electronic spectra were recorded on a UV 2100 Shimadzu UV-Visible recording spectrophotometer attached with a reflectance arrangement. IR spectra of the free ligand and its polychelates were recorded in KBr on a Perkin Elmer FTIR spectrometer. Thermogravimetric analysis was performed on a Du Pont 915 thermal analyzer. Electrochemical studies were carried out using an UPLAB Digital Multimeter.

2.3 EXPERIMENTAL

2.3.1 Synthesis of Vanillin Schiff Base of Amino Methylated Polystyrene

Amino methylated polystyrene ($1x10^{-3}$ mol dm^{-3}) was suspended in DMF (10 mL) for 1 h, which causes considerable swelling of the polymer. A DMF solution (10 mL) of vanillin ($2x10^{-3}$ mol dm^{-3}) was added to the above suspension. The mixture was heated under reflux for 20 h while stirring and then cooled to room temperature. The flesh coloured polymer bound ligand was filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.3.2 Synthesis of 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

Amino methylated polystyrene ($1x10^{-3}$ mol dm^{-3}) was swelled in DMF (10 mL) for 1 h. 2-Nitro benzaldehyde ($2x10^{-3}$ mol dm^{-3}) in DMF (10 mL) was added to the above suspension. The mixture was refluxed for 20 h with stirring and it was then cooled to room temperature. The flesh coloured polymer bound ligand was filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.3.3 Synthesis of Veratraldehyde Schiff Base of Amino Methylated Polystyrene

To the suspension of amino methylated polystyrene (1 x10^{-3} mol dm^{-3}) in DMF (10 mL), veratraldehyde (2 x10^{-3} mol dm^{-3}) in DMF (10 mL) was added and refluxed for about 20 h. The flesh coloured product so obtained was cooled, filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.4 SYNTHESIS OF COMPLEXES

Using the above mentioned ligands, three series each consisting of six metal complexes [complexes of Co(II), Fe(III), Ni(II), Cu(II), Zn(II) and U(VI)]were synthesized. Procedures adopted are given below.

2.4.1 Metal Complexes of Vanillin Schiff Base of Amino Methylated Polystyrene

A DMF (10 mL) suspension of the appropriate metal salt [$FeCl_3$(anhy), $CoCl_2$. $6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2$. H_2O, $Zn(CH_3COO)_2.2H_2O$ and $UO_2(CH_3COO)_2.2H_2O$] (1 x10^{-3} mol dm^{-3}) was added to the polymeric ligand (1 x10^{-3} mol dm^{-3}) soaked in DMF (10 mL). The ratio of ligand to metal taken was 1:1. The mixture was heated under reflux for 15 h while stirring and then cooled to room temperature. It was then filtered and washed with DMF, methanol, distilled water and diethyl ether and dried in vacuo.

2.4.2 Metal Complexes of 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

The polymer anchored ligand (2 x10^{-3} mol dm^{-3}) was soaked in DMF (10 mL) for 1 h. A DMF (10 mL) solution of the appropriate metal salt [$FeCl_3$ (anhy), $CoCl_2$. $6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2$. H_2O, $Zn(CH_3COO)_2.2H_2O$ and $UO_2(CH_3COO)_2.2H_2O$] (1 x10^{-3} mol dm^{-3}) was added to the above suspension. The ratio of ligand to metal taken was 2:1. The mixture was refluxed for 15 h and then cooled to room temperature. The resin was filtered, washed with DMF, methanol, distilled water and finally with diethyl ether. It was then dried in vacuo.

2.4.3 Metal Complexes of Veratraldehyde Schiff Base of Amino Methylated Polystyrene

These complexes were prepared by soaking the polymeric schiff base (2 x10^{-3} mol dm^{-3}) in DMF (10 mL) for 1 h and refluxing with a DMF solution (10 mL) of the appropriate metal salt [$FeCl_3$(anhy), $CoCl_2$. $6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2$. H_2O, $Zn(CH_3COO)_2.2H_2O$ and $UO_2(CH_3COO)_2.2H_2O$](1 x10^{-3} mol dm^{-3}) for 15 h. The resulting solution was allowed to cool and then filtered. It was then washed with DMF, methanol, distilled water and diethyl ether and dried in vacuo.

2.5 CHARACTERIZATION OF THE COMPLEXES

The complexes synthesized by the above methods were characterized by elemental analysis, IR, UV with diffused reflectance, TG and magnetic susceptibility measurements. The details of the above mentioned techniques are presented below.

2.5.1 Elemental Analysis

The elemental analysis of the complexes was carried out to determine the molecular formulae of complexes. This study was done in order to find out the correlation among the CHN values, observed and calculated. CHN analysis was performed on PE 2400 model instrument from Perkin Elmer. The metal and chloride content were determined by standard methods reported in the literature.[130,138-140] Metal analysis was performed after decomposing the complexes with dilute acids and metal ion concentrations were determined by standard volumetric, gravimetric, complexometric and colorimetric methods. Thus iron and zinc were leached with 50% HCl, nickel with 50% acetic acid, and copper and cobalt with 50% nitric acid. Iron was determined gravimetrically as Fe_2O_3. Cobalt was determined gravimetrically by precipitating it as $[Co(C_5H_5N)_4(SCN)_2]$ using ammonium thiocyanate and pyridine. Copper was analysed iodometrically by titrating with a standard solution of sodium thiosulphate. Nickel was estimated gravimetrically as bis(dimethyl glyoxymato)Nickel(II). Zinc was determined gravimetrically as 8-hydroxyquinaldinate. Uranium was determined as U_3O_8 by igniting the complex in a silica crucible. Chloride was precipitated as AgCl, which was filtered, dissolved in NH_4OH, reprecipitated with dilute HNO_3 and weighed as AgCl.

2.5.2 Infrared Spectral Measurements

Infrared spectroscopy finds widespread application to qualitative and quantitative analyses. The infrared spectrum of a compound provides a unique finger print, which is readily distinguished from the absorption patterns of all other compounds. A comparison of the infrared spectra of the free ligand and that of its complexes is helpful in finding out the atom or atoms through which the ligand is attached to the metal atom. The infrared spectral measurements were taken using KBr pellets on a Perkin-Elmer 1600 series FT-IR spectrometer in 4000-200 cm^{-1} region. It gives an idea of groups coordinated to the metal atom and if coordinated which atom is involved in the coordination.

2.5.3 Magnetic Susceptibility Measurements

A number of methods exist for measurement of magnetic susceptibilities. The method we adopted was the Guoy method. It is based on the determination of the force exerted on a sample by an inhomogeneous magnetic field and measuring the weight of a substance in the presence and the absence of the field. Once an experimental value of χ_m (molar susceptibility of the sample) has been obtained for paramagnetic substance, it can be used to determine how many unpaired electrons are there per molecule. Using the value of χ_m, μ, magnetic moment can be calculated using the equation

$$\mu_{eff} = 2.84(\chi_m^{corr}\ T)^{1/2}\ \text{B. M.}$$

The value of μ for a number of complexes is theoretically known. Thus knowing the value of μ we can find out the geometry of the complexes. The reference used for standardization was $Co[Hg(CNS)_4]$ as recommended by Figgis and Nyholm[141].

2.5.4 Thermogravimetric Studies

In thermogravimetric analysis, the mass of sample is recorded continuously as its temperature is increased linearly from ambient to as high as 1200°C. It provides information about decomposition mechanism of the polymeric complexes and the decomposition pattern is characteristic of the polymer and can be used for identification purposes. Du Pont thermal analyzer was used for taking the thermograms of the complexes.

2.5.5 Diffuse Reflectance UV-Vis Spectroscopy (DR UV-Vis)

Diffuse reflectance UV-Visible spectroscopy allows the study of electronic transitions between orbitals or bands in the case of atoms, ions and molecules in gaseous, liquid or solid state. In the case of polymer supported metal complexes the electronic spectra gives evidence about the coordination environment and hence the structural details of the complexes.

Electronic transitions of transition elements are of two types, metal-centered Transitions [d-d or (n-1)d-ns] and charge-transfer (CT) transitions. d-d Transitions give information about the oxidation state and coordination environment of transition metal ion. (n-1)d-ns transitions are often too high in energy to be observed in the spectrum. The CT transitions are intense since they are Laporte-allowed and are sensitive to the nature of donor and acceptor atoms[142]. In DR measurements the light emitted by the sample and the reference material is collected by an integration sphere and the detector of double beam spectrometer gives the apparent absorbance.

Diffuse reflectance UV-Vis spectra of the samples were recorded using a conventional spectrophotometer (Ocean Optics-2000) with CCD detector. Magnesium oxide (MgO) was used as the reference material.

2.6 APPLICATION STUDIES

2.6.1 Ion Removal Studies

Salicylaldehyde schiff base of amino methylated polystyrene, vanillin schiff base of amino methylated polystyrene and 2-nitrobenzaldehyde schiff base of amino methylated polystyrene were developed as suitable metal ion removing reagents for Fe(III), Cu(II) and Ni(II) respectively. Systematic analytical studies have been carried out to develop ion removing agents and optimum conditions for the removal of the above metal ions using these ligands were developed.

A known amount of the polymer ligand (salicylaldehyde schiff base of amino methylated polystyrene, 2-nitro benzaldehyde schiff base of amino methylated polystyrene and vanillin schiff base of amino methylated polystyrene respectively) was soaked in DMF for 1 h. Metal salt solution (copper chloride, ferric ammonium sulphate and nickel acetate respectively) of known concentration was added to this suspension and the mixture was refluxed for a fixed time. It was then filtered through a Whatmann No.41 filter paper. The filtrate was quantitatively transferred to a standard flask and the solution was diluted to known volume (50 mL). From this, a definite quantity was taken and the amount of metal ion present [Fe(III), Cu(II) and Ni(II)]was determined by the standard spectrophotometric procedures[143]. The above experiment was repeated to study the effect of time, pH, metal ion concentration, ligand concentration and finally the interference due to other ions like Co(II), Zn(II), U(VI), Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, NO_2^- and CH_3COO^-

For studying the interference due to other ions, the metal salt solutions [Fe(III), Cu(II) and Ni(II)] of fixed concentration was mixed with a definite concentration of solution containing foreign ions and to this mixture corresponding DMF suspension of the ligand was added and the removal experiment was repeated.

2.6.2 Fabrication of the Chloride Ion Selective Electrode

Co(II) complex of amino methylated polystyrene-salicylaldehyde schiff base was developed as the electro active material (ionophore) for the fabrication of the chloride ion selective electrode. The ionophore was prepared as reported in the literature[132], by soaking the salicylaldehyde schiff base of amino-methylated polystyrene (1x10^{-3} mol dm^{-3}) in DMF (10 mL) for 1 h and refluxing with a DMF solution (10 mL) of $CoCl_2$. $6H_2O$ (1x10^{-3} mol dm^{-3}) for 15 h. The resulting solution was allowed to cool and then filtered. It was then washed with DMF, methanol, distilled water and diethyl ether and finally dried in vacuo.

About 100 mg of dried electro active material (Co(II) complex of amino methylated polystyrene-salicylaldehyde schiff base) was mixed with 400 mg of Araldite and the paste was spread over a Whatmann No.41 filter paper to 0.1 mm thickness and air dried for 48 h. It was then separated from the filter paper by dipping it in a solution of chloride ion. It was then cut to size and attached to one end of a pyrex glass tube with Araldite. The tube was filled with chloride solution (0.1 mol dm^{-3}) and kept immersed in chloride solution of same strength for one week. Potentials were determined by direct potentiometry at room temperature. A saturated calomel electrode was used as the reference electrode. The cell set-up was as follows.

Chloride solution (0.1 mol dm^{-3}) / ion selective membrane/ test solution// SCE

The emf of the cell so set up was measured using an UPLAB digital multimeter at room temperature. Response behaviour of the electrode was studied by measuring the potential of the electrode at different concentrations of chloride ion. The pH dependence of the electrode potential was studied by varying the pH of the chloride solution of fixed concentration with buffer solutions. Interference studies were also carried out by mixing the chloride solution of fixed concentration (0.05 mol dm^{-3}) with solutions of different concentrations of foreign ions like Na^+, Ca(II), Mn(II), Co(II), Fe(III), Ni(II), Cu(II), Zn(II), CH_3COO^- NO_3^- SO_4^{2-} Br^- and NO_2^- and measuring the potentials one after another.

CHAPTER III

SYNTHESIS AND CHARACTERIZATION

3.1 INTRODUCTION

Chemical modification is used extensively to modify the properties of polymers of various applications.[144] A functional polymer can be considered as a macromolecule on which reactive functions are attached. These macromolecules are often tailored to perform specific functions and are sought for these properties.

A polymer metal complex is composed of synthetic polymer and metal ions, where in the metal ions are bound to the polymer ligand by a coordinate bond. A polymer ligand contains anchoring sites like nitrogen, oxygen or sulphur obtained either by polymerization of the monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability. The synthesis results in an organic polymer with inorganic functions. Polymer metal complexes have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields.

As part of the present investigations, three series of metal complexes of polymeric ligands such as vanillin schiff base of amino methylated polystyrene (VASAP), 2-nitro benzaldehyde schiff base of amino methylated polystyrene (NBSAP) and veratraldehyde schiff base of amino methylated polystyrene (VESAP) were synthesized and characterized. The metal ions taken for the studies include

Co(II), Fe(III), Ni(II), Cu(II), Zn(II) and U(VI). The details of the characterization studies of these newly synthesized eighteen complexes are presented in this chapter.

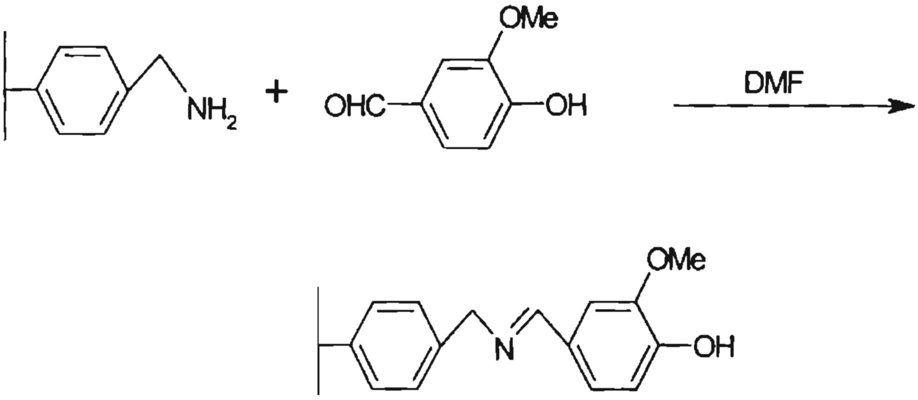
3.2 EXPERIMENTAL

Experimental part is discussed in chapter II.

3.3 RESULTS AND DISCUSSION

3.3.1 Metal Complexes of Vanillin Schiff Base of Amino Methylated Polystyrene

The ligand (VASAP) (Scheme 12) and its metal complexes were synthesized as discussed in chapter II. Analytical data of the complexes show 1:1 geometry (Table 2). On complexation, the flesh colour of the ligand changes to brick red, ash, brown, chocolate, light flesh colour and brown colour depending on the metal ion. The ligand and complexes were insoluble in most of the common organic solvents and are stable at room temperature.



SCHEME 12

3.3.1.1 Infrared spectra

The binding sites of the ligand have been inferred by comparing its infrared spectrum with that of the complexes (Table 3 and Figure 1). The strong IR band at 1640 cm^{-1} (C=N) in the ligand underwent a negative shift by about 30 cm^{-1} in the complexes indicating coordination of the nitrogen of the azomethine group.[145] The intense band at 1511 cm^{-1} (phenolic C-O) in the ligand shifted to lower frequency by (1490 ± 10 cm^{-1}) in the complexes.[146] This shift suggest the coordination of phenolic oxygen to the metal ion. The coordination of metal ions through nitrogen of azomethine group and oxygen of hydroxy group of the ligand is further confirmed by the appearance of new bands at 520-460 cm^{-1} (M-O) and 450-380 cm^{-1} (M-N)[147] in all the complexes. The ν_{asy}(OCO) and ν_{sym}(OCO) appear at 1630 ± 10 cm^{-1}, 1390 ± 10 cm^{-1} respectively with ΔOCO = 240 ± 10 cm^{-1} suggesting the unidentate nature of the acetate ion.[132] The oxygen coordination of the solvent DMF is indicated by the shift of ν(C=O) band at 1680 cm^{-1} to lower energy by 20-55 cm^{-1}.[132] In the uranyl complex, new bands were observed at 915 and 845 cm^{-1} and were attributable to the asymmetric and symmetric stretching vibrations of the UO_2 moiety respectively, indicating the linear nature of the UO_2 group.[148]

3.3.1.2 Electronic spectra

The electronic spectral data and the observed bands are presented as Table 4 and Figure 2. The Fe(III) complex [Fe(VASAP).Cl_2.2DMF] exhibits bands at 11745 cm^{-1}, 15675 cm^{-1} (shoulder) and 18720 cm^{-1} attributed to $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4A_{1g}(G)$ respectively indicating an octahedral structure for the Fe(VASAP).Cl_2.2DMF.[149] The reflectance spectrum of the Co(II) complex [Co(VASAP).Cl.DMF] exhibited bands at 10120 cm^{-1} and 15200 cm^{-1}. The second band was assigned to $^2A_{1g}\rightarrow{}^2Eg$ and the first to d_{xy}-d_{yz} spin allowed transition in a square planar field.[153] The Ni(II) complex [Ni(VASAP).OAc.3DMF] gives two bands at 15210 cm^{-1} and 25715 cm^{-1} due to the $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ suggesting an octahedral structure.[150] Actually it should have one more band at 8500 cm^{-1} due to $^3A_{2g}\rightarrow{}^3T_{2g}(F)$ transition. As the scan range was limited up to 10000 cm^{-1}, this band was not observed. The electronic spectrum of the Cu(II) complex [Cu(VASAP).OAc.DMF] shows two bands at 15640 cm^{-1} and 24770 cm^{-1} assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$ and charge transfer transitions. This is in favour of square planar geometry.[151] The electronic spectrum of the uranyl complex [UO_2(VASAP).OAc.DMF] show three bands at 19380 cm^{-1}, 23400 cm^{-1} and 38985 cm^{-1}. The position of these bands indicates that this complex has an octahedral structure.[152]

3.3.1.3 Magnetic susceptibility

The magnetic data are presented as Table 5. The magnetic moment value of 5.95 BM in the case of Fe(VASAP).Cl_2.2DMF indicates the spin free octahedral nature.[154] The Co(VASAP).Cl.DMF shows a magnetic moment value of 2.42 BM suggesting its low spin square planar geometry.[154] The magnetic moment of the Ni(VASAP).OAc.3DMF was found to be 3.27 BM, which is indicative of the octahedral structure of the complex.[154] While the Cu(VASAP).OAc.DMF display a magnetic moment value of 1.83 BM corresponding to the square planar geometry of the magnetically dilute Cu(II) complex.[155] The Zn(VASAP).OAc.DMF and UO_2 (VASAP).OAc.DMF are diamagnetic as expected for a d^{10} and f^0 configuration.

3.3.1.4 Thermogravimetric analysis

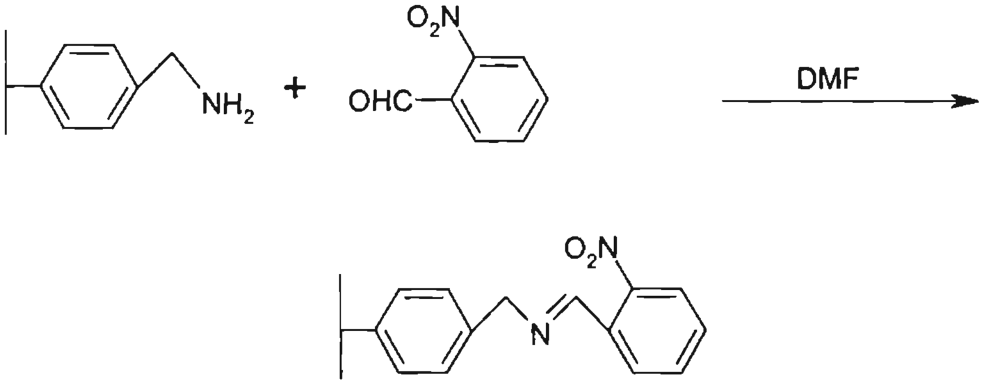
The thermal data and TG curves of selected complexes are presented as Table 6 and Figure 3. The weight loss (27 to 37%) observed in thermogravimetric analysis at 110 to 200°C corresponds to the elimination of two and three molecules of coordinated DMF in Fe(III) and Ni(II) complexes. A loss of weight (11 to 16%) in the temperature range 180 to 300°C in the case of Co(II), Cu(II), Zn(II) and U(VI) complexes suggests the loss of one molecule of coordinated DMF. Thus thermal analysis is also in agreement with the assigned structural formula of the complexes.

3.3.1.5 Conclusion

A series of six metal complexes of vanillin schiff base of amino methylated polystyrene have been synthesized. From the analytical, IR, UV, magnetic susceptibility and thermal data it is confirmed that the Fe(III) complex [Fe(VASAP).Cl_2.2DMF], Ni(II) complex [Ni (VASAP). OAc.3DMF] and U(VI) complex UO_2(VASAP).OAc.DMF have an octahedral structure (Figure 4, 6 and 9). While the Co(II) complex [Co(VASAP).Cl.DMF] and Cu(II) complex [Cu(VASAP).OAc.DMF] have square planar geometries (Figures 5 and 7) the Zn(II) complex [Zn(VASAP).OAc.DMF] has a tetrahedral structure (Figure 8).

3.3.2 Metal Complexes of 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

2-Nitro benzaldehyde schiff base of amino methylated polystyrene (NBSAP) (Scheme 13) and its metal complexes were synthesized as already explained in Chapter II. The ligand was flesh coloured and displayed characteristic IR spectra. Analytical data of the ligand and its complexes are shown in Table 7 They showed a change of colour from flesh to brick red, ash, sandalwood, chocolate, dark flesh and brown depending on the metal ion and are stable under atmospheric conditions. They were found insoluble in water and all the common organic solvents including DMF. Due to their insolubility it is not possible to characterize them by X-ray studies.



SCHEME 13

3.3.2.1 Infrared spectra

The IR spectral data and spectra are shown in Table 8 and Figure 10 respectively. The polymer anchored ligand displayed the characteristic stretching frequencies of the schiff base at 1655 cm^{-1} (C=N). In the spectra of the complexes this band was shifted to lower frequency by 15-20 cm^{-1}, suggesting nitrogen coordination of the ligand to the metal.[145] The monodentate nature of the acetate ion is revealed from the energy difference between ν_{sym}(COO) and ν_{asy} (COO) which occur at 1392-1397 cm^{-1} and 1600-1608 cm^{-1} respectively.[132] The coordination of the solvent DMF through oxygen is indicated by the shift of band at 1680 cm^{-1} to lower energy by 30-60 cm^{-1}.[132]

The coordination of nitrogen of the ligand to the metal in the complexes is also confirmed by the presence of new bands at 450-435 cm^{-1}.[147] The ν_{asy}(OUO) band of the uranyl complex occur at 923 cm^{-1} which fall normally in the range 870-960 cm^{-1} as was found to be observed for the majority of uranyl complexes.[148]

3.3.2.2 Electronic spectra

The structure of the complexes was also confirmed by reflectance electronic spectra (Table 9 and Figure 11). Three peaks observed at 11780 cm^{-1}, 15300 cm^{-1} and 18750 cm^{-1} in the spectra of Fe(III) complex [Fe(NBSAP)$_2$.Cl$_2$.2DMF] were due to ${}^6A_{1g}\rightarrow{}^4T_{1g}(G)$, ${}^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and ${}^6A_{1g}\rightarrow{}^4A_{1g}(G)$ transitions respectively suggesting its octahedral nature.[149] The electronic spectra of Co(II) complex [Co(NBSAP)$_2$.Cl.DMF] exhibited bands at 15200 cm^{-1} and 10120 cm^{-1}. The bands were assigned due to d_{xy}-d_{yz} spin allowed transition and ${}^2A_{1g} \rightarrow {}^2E_g$ transition in a square planar field.[153] The appearance of three bands in the regions 10526 cm^{-1} [${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$], 15670 cm^{-1} [${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$] and 24490 cm^{-1} [${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$] in the electronic spectra of Ni(II) complex [Ni(NBSAP)$_2$.OAc.3DMF] suggested its octahedral geometry.[150] The Cu(II) complex (CuNBSAP) register two broad bands at 14708 cm^{-1} and 24857 cm^{-1}. These may be respectively due to ${}^2B_{1g}\rightarrow{}^2A_{1g}$ and ${}^2B_{1g}\rightarrow{}^2E_g$ transitions of square planar Cu(II) complex.[151] Reflectance spectra of the uranyl polychelates [UO$_2$(NBSAP)$_2$.OAc.DMF] exhibit bands at 18181 cm^{-1}, 23125 cm^{-1} and 39020 cm^{-1} consistent with the vibronic structure of the triatomic entity UO_2.[152]

3.3.2.3 Magnetic susceptibility

The magnetic moment value of all the complexes is summarized in Table 10. The magnetic moment of the Fe(III) complex is 5.92 BM which is closer to the spin only value indicating an octahedral structure for the complex.[154] The Co(II) complex displayed a magnetic moment of 2.75 BM which corresponds to the low spin square planar geometry of the complex[154]. The effective magnetic moment value of 3.34 BM of the Ni(II) complex indicates the octahedral structure of the complex.[154] The magnetic moment of the Cu(II) complex is 1.83 BM which fall in the normal range (1.75-2.20 BM) expected for magnetically dilute Cu(II) complexes.[155] The Zn(II) and U(VI) complexes are diamagnetic.

3.3.2.4 Thermogravimetric analysis

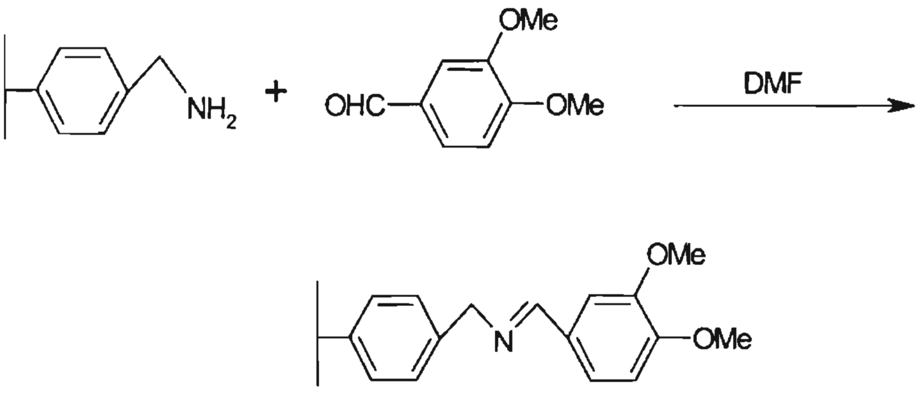
The thermal data and TG curves of the complexes (selected) are given in Table 11 and Figure 12. A weight loss of 10 to 7% in the temperature range 140 to 300°C was observed in the case of Co(II), Cu(II), Zn(II) and U(VI) complexes suggesting the loss of one molecule of coordinated DMF. For Fe(III) and Ni(II) complexes, a loss of weight of 18 to 25% was observed in the temperature range 150 to 280°C, which shows the coordination of two and three molecules of DMF respectively.

3.3.2.5 Conclusion

A series of six metal complexes of 2-nitro benzaldehyde schiff base of amino methylated polystyrene was prepared and characterized by analytical, IR, UV, thermal analysis, and magnetic susceptibility studies. While an octahedral structure is proposed for $Fe(NBSAP)_2.Cl_2.2DMF$, $Ni(NBSAP)_2.OAc.3DMF$ and $UO_2(NBSAP)_2$. OAC.DMF (Figures 13, 15 and 18) a square planar structure is assigned for $Co(NBSAP)_2.Cl.DMF$ and $Cu(NBSAP)_2.OAc.DMF$ (Figures 14 and 16). The Zn(II) complex $[Zn(NBSAP)_2.OAc.DMF$ is assigned a tetrahedral structure (Figure 17).

3.3.3 Metal Complexes of Veratraldehyde Schiff Base of Amino Methylated Polystyrene

The veratraldehyde schiff base of amino methylated polystyrene (VESAP) (Scheme 14) and its metal complexes were prepared as discussed in Chapter II. The analytical data was presented in Table 12. VESAP was flesh coloured, stable at room temperature and found insoluble in water and common organic solvents. The structure of the ligand was confirmed by IR spectra. On complexation the ligand showed a change of colour from flesh to brick red, dark ash, sandalwood, chocolate, dark flesh and brown depending on the metal ion and are stable at room temperature. They were insoluble in water and all common organic solvents.



SCHEME 14

3.3.3.1 Infrared spectra

The IR spectra of ligand and polychelates are given in Table 13 and Figure 19. The band at 1643 cm^{-1} shows the presence of azomethine group. This band was shifted to 5-20 cm^{-1} lower frequency in polychelates suggesting the coordination of nitrogen of azomethine group to the metal ion.[145] The coordination of nitrogen to the metal was also confirmed by the appearance of new bands at 465-430 cm^{-1}.[147] The linear nature of the UO_2 moiety was ascertained from the bands observed at 920 cm^{-1} and 840 cm^{-1}.[148] The oxygen coordination of solvent DMF was indicated by the shift of (C=O) band at 1686 cm^{-1} to lower energy by 20-55 cm^{-1} in the complexes.[132] The energy difference of 240 cm^{-1} between ν_{sym}(COO) and ν_{asy}(COO) of the acetate ion showed its monodenate nature.[132]

3.3.3.2 Electronic spectra

The electronic spectral data and spectra of the complexes are shown in Table 14 and Figure 20. The Fe(III) complex [Fe(VESAP)$_2$.Cl$_2$.2DMF] shows three bands at 11780 cm^{-1}, 15432 cm^{-1} and 18518 cm^{-1} due to $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4A_{1g}(G)$ respectively indicating the octahedral geometry around the iron.[149] The Co(II) complex [Co(VESAP)$_2$.Cl.2DMF]shows two bands at 10416 cm^{-1} and 15151 cm^{-1} due to d_{xy}-d_{yz} spin allowed transition and $^2A_{1g}\rightarrow{}^2E_g$ transition respectively which are characteristic of the square planar arrangement.[153] The electronic spectrum of the Ni(II) complex [Ni(VESAP)$_2$.OAc.3DMF] exhibits bands at 10548 cm^{-1}, 15432 cm^{-1} and 25125 cm^{-1} due to $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ respectively suggesting an octahedral structure.[150] The reflectance spectrum of the Cu(II) complex [Cu(VESAP)$_2$.OAc.DMF] exhibits bands at 25000 cm^{-1} and 14306 cm^{-1} due to charge transfer transition and $^2B_{1g}\rightarrow{}^2A_{1g}$ transition respectively in a square planar field.[151] The reflectance spectrum of the uranyl complex [UO$_2$(VESAP)$_2$.OAc.DMF] shows bands at 18867 cm^{-1}, 23255 cm^{-1} and 40000 cm^{-1} which were in the usual range as reported for majority of dioxouranium(VI) complexes.[152] Thus the reflectance UV spectral data is in well agreement with the proposed structure.

3.3.3.3 Magnetic susceptibility

The magnetic susceptibility data of the complexes are given in Table 15. The magnetic moment value of the Fe(III) complex is 5.72

BM which is almost near to the spin only value of an octahedral structure.[154] The square planar geometry of the Co(II) complex was confirmed from its magnetic moment value of 2.64 BM.[154] The Ni(II) complex has got a magnetic moment value of 3.35 BM indicating the octahedral structure of the complex.[154] The Cu(II) complex has 1.81 BM as the magnetic moment value which corresponds to the square planar geometry of the magnetically dilute Cu(II) complex.[155] As expected Zn and U complexes are diamagnetic which is in agreement with the d^{10} and f^0 configuration.

3.3.3.4 Thermogravimetric analysis

Thermal data and TG curves of the complexes (selected) are presented in Table 16 and Figure 21. The Fe(III) and Ni(II) complexes show a weight loss of 15 to 24% in the temperature range 120 to 260°C, which suggest the loss of two and three molecules of coordinated DMF. A weight loss of 7 to 10% occur in the temperature range 110-230°C for Co(II) , Cu(II), Zn(II) and U(VI) complexes which shows the loss of one molecule of coordinated DMF.

3.3.3.5 Conclusion

Six metal complexes were prepared using the veratraldehyde schiff base of amino methylated polystyrene (VESAP) and were characterized by analytical studies, IR and UV spectra, magnetic susceptibility measurements and thermal analysis. For the Fe(III), Ni(II) and U(VI) complexes [$Fe(VESAP)_2.Cl.2DMF$, $Ni(VESAP)_2.$

OAc.3DMF and $UO_2(VESAP)_2$.OAc.DMF] an octahedral structure (Figures 22, 24 and 27) is proposed. The Co(II) and Cu(II) complexes [Co$(VESAP)_2$.Cl.DMF and Cu$(VESAP)_2$.OAc.DMF] have been assigned a square planar structure (Figures 23 and 25) and Zn(II) complex [Zn$(VESAP)_2$.OAc.DMF] has been given a tetrahedral structure (Figure 26).

CHAPTER IV

ION REMOVAL STUDIES USING POLYMERIC LIGANDS

4.1 INTRODUCTION

The separation of metal ions present as contaminants in water is complicated by the number of variables that must be considered including the solution composition, the pH and the presence of organic substances. Although several technologies exist for the removal of metal ions from water, the most common ones are solvent extraction and ion exchange techniques. Solvent extraction[156,157] involves contacting the contaminated water with an organic liquid extractant, which is insoluble in water. The extractant is capable of ion exchanging or forming chelates with the metal ion. Upon mixing, the metal ions are transported to the organic phase. The phases are allowed to separate, and the metal ions are stripped from the loaded organic phase with an appropriate solution. The concentrated metal ion solution can then be purified or disposed.

Solvent extraction offers the advantages of fast kinetics, high capacities and selectivity for target metal ions.[158] The finite aqueous solubility of the extractants, solvents and modifiers is, however, a significant disadvantage.[156] This not only adds to the cost of the procedure through loss of reagents, but contaminates the water with potentially toxic organics. There is also loss of the organics through evaporation and entrainment.[156] In addition, solvent extraction is not recommended for dilute metal ion solutions due to the large volumes of extractants needed.[159]

Ion exchange resins operate on the same principles as solvent extraction. These resins contain functional groups capable of complexing or ion exchanging with metal ions. The resins are subjected to contact with the contaminated solution, loaded with metal ions, and then stripped with an appropriate eluent.[160] Because the functional group interacting with the metal ion is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The resins can be regenerated and reused for continuous processes.[161] A disadvantage of ion exchange resins is the slower kinetics compared to solvent extraction.[158] However, increasing the porosity of the resin or decreasing the bead size or cross linking can help to improve the kinetics by increasing the accessibility of the polymer supported ligands to the metal ions.

Chelating polymers have many potential applications for the selective removal and recovery of metal ions from industrial waste solutions.[36] The selective removal of mercury, using resins[162] with thiol groups, is one such application. The main applications for the chelating polymers are based on the high selectivity of the materials for particular ions. They have been used in the preconcentration of trace elements from solutions so dilute that no analytical determinations are possible.[163] Another promising new application for chelating resins is in nuclear medicine, where very short lived isotopes must be removed quickly and selectively from mother and daughter ions. A recent example is the use of a pyrogallol-formaldehyde polymer made for the separation of ^{68}Ga and ^{68}Ga ions.[164] However, in general, the commercially available resins are not quite selective enough and the few extremely selective chelating polymers discovered have not yet been made into the physical forms beads, fibers, membranes, etc., that will give the required kinetic, physical and most importantly, the economic properties required for large scale commercial isolation of individual ions. Many chelating polymers have been fabricated on a small scale into forms, membranes and hollow fibers, other than ion exchange resins in attempts to get more convenient materials for the selective separation of ions in special applications.[165]

A series of new copper selective amino pyridine Dowex resins[166] were designed for large scale hydrometallurgical separation of copper from its ores. Another possible large scale application of chelating resins is in the selective removal of precious metals from sea water. Selective removal of gold from sea water, although the subject of a number of patents is equally far from reality. However, the use of chelating resins from precious metal manufacturing is important. Activated carbon or various commercial anion exchange resins[167] are now used to recover gold from such solutions, but they are very unselective and recover a mixture of metals. Very selective chelating resins such as srafion,[168] monivex[169] etc., with isothiouronium structures are available and can be used to separate the anionic gold complex ions from other non precious metal ions.

There has been growing emphasis on the studies involving polymer bound ligands.[170, 171] Due to the macro environment created at the coordination centre, the polymer bound ligands have considerable difference from the simple ligands. In literature, only a relatively small number of reports are available on polymers carrying multidentate ligands that completely surround the metal ions. Polyethylene imines,[172] their dithio carbamates,[173] carboxy methyl[174] or phosphomethyl[175] derivatives are the most common examples of polydentate ligands forming four chelate rings around the metal ions. The practical advantages of attaching insoluble supports are recognized and industrially exploited. Of these, catalysis and metal ion removal capacity are the most important ones. Cross linked polystyrene beads carrying amino methyl phosphoric acid groups[176, 177] and imino diacetic acid groups[178] have been demonstrated to be efficient in the removal of trace quantities of metal ions. Due to chelating effects, these are superior to common ion exchange resins. Poly(styrene-sulphonamides) with EDTA like chelating groups are used for the removal of transition metal ions. Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals.[179-183] A large number of these complexes containing both transition and non transition metal ions and a variety of oxime ligand systems have been reported.[184-188] There is also a report on the selective removal of Pb(II), Hg(II) and Cd(II) using the schiff base ligands supported on chelating polymer resins.[189]

As the concern on industrial pollution is increasing, the demand for newer method for its control is also increasing. In the present study three types of schiff base ligands supported on amino methylated polystyrene namely, salicylaldehyde schiff base, 2-nitro benzaldehyde schiff base and vanillin schiff base have been developed as promising reagents for removal of Fe(III), Cu(II) and Ni(II) respectively from solutions. The suitability of a polymeric ligand in metal ion separation depends on the nature and structure of the chelating group, kind of metal ion to be separated, molecular architecture of the polymer support and the conditions of complexation.

This chapter explains the complete analytical studies carried out to establish the above three ligands for the effective removal of the three metal ions. For each ligand studied, optimum conditions have been developed for the removal of the corresponding metal ion.

4.2 EXPERIMENTAL

The metal ion removal studies were conducted according to the procedure described under Chapter II.

4.3 RESULTS AND DISCUSSION

4.3.1 Removal of Fe(III) Using Salicylaldehyde Schiff Base Supported on Amino Methylated Polystyrene

The following studies were conducted and optimum conditions were developed for the removal of Fe(III) using the ligand.

4.3.1.1. Effect of time

Standard Fe(III) solution (30 ppm) was refluxed with a DMF (5 mL) suspension of the polymeric ligand (0.01 g) at different time intervals. The results are presented in Table 17 The concentration of Fe(III) was determined spectrophotometrically.[143] As expected, the metal ion removal capacity of the ligand increases as the time of reflux increases. Almost 100% removal was obtained within a time span of 20 min.

4.3.1.2. Effect of pH

The original mixture has got a pH of 2.18. The pH of the mixture was changed using buffer solutions and then determinations were carried out. The results are summarized in Table 18 and Figure 28. A close examination of this table and figure reveals that the most effective removal happened at the mixing pH itself. This is an advantage of the method, as in most of the metal ion removal studies adjustment of pH of the reaction mixture has to be carried out.

4.3.1.3. Effect of metal ion concentration

The effect of metal ion concentration on the removal capacity of the reagent was studied. For a fixed amount of the ligand (0.01 g), the removal was monitored for a set of the metal ion solutions of varying concentrations. The results are shown in Table 19. A close examination of this table reveals that, at lower concentrations of the metal ion (10-30 ppm), the removal was almost complete and it was about 85% when the concentration of the metal ion solution taken was 50 ppm. Thereafter the percentage removal was decreased, due to the insufficient amount of the ligand, as expected. It can be concluded from the above discussions that an amount of only 0.01 g of the ligand is needed to achieve 100% removal of the metal ion, if the concentration of the original solution is 30 ppm.

4.3.1.4 Effect of ligand concentration

The effect of ligand concentration was studied in the range 0.0005 to 0.05 g for a solution of metal ion concentration of 30 ppm. The result presented in Table 20 explains that for a 30 ppm Fe(III) solution, the minimum amount of ligand required for about 100% removal was 0.0075 g. But on safer side 0.01 g was used uniformly.

4.3.1.5 Interference due to other ions

A complete interference study has been carried out taking different concentration of ions. The results are presented in Table 21. It is seen that the interference due to ions such as Co(II), Ni(II), Cu(II), Zn(II), U(VI), Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, NO_2^-, and CH_3COO^- are highly negligible. This is one of the achievements of the method because in most of the metal ion removal procedures reported in the literature, interference due to other ions is the most practical difficulty.

4.3.2 Removal of Cu(II) Using 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

Optimum conditions were developed for the removal of Cu(II) using the ligand by conducting the following experiments.

4.3.2.1 Effect of time

A known volume of standard Cu(II) solution was refluxed with 2-nitro benzaldehyde schiff base of amino methylated polystyrene suspended in DMF (5 mL) at different intervals of time. Concentration of the metal ion left was determined spectrophotometrically.[143] From Table 22, it is clear that about 90% removal was achieved within 20 min. Hence the time of reflux was fixed as 20 min.

4.3.2.2 Effect of pH

Effect of pH on the removal of Cu(II) was studied by varying the pH of the mixture and the results are shown in Table 23 and Figure 29. Interestingly, maximum metal ion removal was obtained with the original mixture itself at the mixing pH of 4.4.

4.3.2.3 Effect of metal ion concentration

The effect of metal ion concentration was studied in the range 5 to 70 ppm with a fixed amount of ligand (0.01 g) and the results are presented in Table 24. It is found that at lower concentrations (5 to 20 ppm) less than 90% removal was achieved. With 30 ppm solution 90% removal was achieved and as the concentration of the metal ion increases, the percentage of metal ion removed decreases due to insufficient amount of the ligand. Thus for the studied amount of the ligand, the most effective removal was achieved with a metal ion solution of 30 ppm.

4.3.2.4 Effect of ligand concentration

The effect of ligand concentration was studied in the range 0.005 g to 0.1 g for a 30 ppm Cu(II) solution. From the results shown in Table 25 it is clear that the percentage of metal ion removed remains the same in the range 0.01 to 0.1 g. Hence it can be concluded that 0.01 g is the optimum mass of the ligand for achieving a 90% removal from a 30 ppm Cu(II) solution.

4.3.2.5 Interference due to other ions

A systematic interference study was carried out with foreign ions of different concentrations and the results are presented in Table 26 and 26 A. It was found that most of the ions studied, have no interfering action in the removal of Cu(II). However, Fe(III) and

Co(II) interfered severely and in fact, Fe(III) interfered even in the presence of ascorbic acid which was used as a masking agent.

4.3.3 Removal of Ni(II) Using Vanillin Schiff Base of Amino Methylated Polystyrene

The following studies were carried out for the removal of Ni(II) using vanillin schiff base of amino methylated polystyrene.

4.3.3.1 Effect of time

A known volume of standard Ni(II) solution was taken and refluxed with the ligand soaked in DMF (5 mL) under different intervals of time. The metal ion left in the solution was determined spectrophotometrically[143] and the results are presented in Table 27 As expected, as the time increases the percentage of metal ion removed was also increased. Within a period of 15 min. about 100% removal was achieved. Hence the refluxing time was fixed as 15 min.

4.3.3.2 Effect of pH

Similar to the above two cases here also a change in the pH has got no effect in the metal removing capacity. The maximum removal was obtained with the original mixture itself. The graphical representation of the effect of pH on metal ion removal is shown in Figure 30 and the results are presented in Table 28.

4.3.3.3 Effect of metal ion concentration

The effect of metal ion concentration on the removal was studied with solutions of Ni(II) in the range 10 to 70 ppm using 0.01g of the ligand. The results presented in Table 29, reveal that at lower concentrations (10 to 20 ppm) almost complete removal of the metal ion was achieved and as the concentration increased metal ion uptake capacity decreased due to insufficient amount of the ligand. The most efficient removal occured in the 10-30 ppm range for the studied amount of the ligand.

4.3.3.4 Effect of ligand concentration

After a certain limit there is no change in the metal ion concentration left in the mixture indicating that the ion removing capacity of the ligand is not dependent on the amount present after a fixed limit. In the present case the optimum quantity of the ligand needed for efficient removal of 20 ppm metal ion solution was 0.01 g as is clear from Table 30.

4.3.3.5 Interference due to other ions

The ions Co(II), Fe(III), Cu(II), Zn(II), U(VI), Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, NO_2^- and CH_3COO^- were not interfering in the removal of Ni(II) using vanillin schiff base of amino methylated polystyrene. The results are presented in Table 31.

4.4 CONCLUSION

Out of the three ligands presently developed for the removal of different metals, polystyrene based schiff base ligand of salicylaldehyde gave a 100 percentage removal of Fe(III) from 30 ppm metal solution. While 2-nitro benzaldehyde schiff base is able to remove 90 percentage of Cu(II), vanillin schiff base gave a result of 100 percentage removal of Ni(II) from 20 ppm solution. The consolidated results presented in Table 32, reveal that for the removal of Fe(III), only 0.0075g of the ligand is required, while for the other two systems, 0.01g of the respective ligands are needed. The only limitation to these methods of metal ion removal is that Fe(III) and Co(II) interfere with the removal action of 2-nitro benzaldehyde for Cu(II).

It is also to be noted that all these three methods can be successfully utilized for metal ion removal, without any control of the pH.

CHAPTER V

DEVELOPMENT OF A CHLORIDE ION SELECTIVE ELECTRODE BASED ON A POLYMERIC COMPLEX

5.1 INTRODUCTION

Ion selective electrodes (ISEs) are the chemical sensors with the longest history and probably with the most frequent routine application. The ISE era began with the development of calcium and fluoride ISEs by James Ross and Martin Frant of the Orion Research in the mid 1960's. Because of their simplicity, low cost, improved applicability to unusual or extreme conditions and timeliness, ISEs are considered as novel analytical tools. [190, 191]

Glass electrodes for pH have been used widely for more than 60 years. With their high selectivity and applicability for a wide variety of samples, it appears unlikely that they will be replaced at large any time soon by ISEs based on H^+ ionophore.[192] However, as many users of glass electrodes learned the hard way during their first experience with this type of electrode, pH sensitive glass membranes break quite easily. Therefore, solvent polymeric membranes offer a distinct advantage. Among the different materials reported to be used as ionophore include crown ethers,[193,194] polyamines,[195] calixarenes,[196] metalloporphyrins,[197] metallocenes[198] and Lewis acids.[199] The ionophores based liquid membrane sensors are the most successful class among the ISEs.[192] Further, most of the polymer based ionophores are reported to be supported on PVC based polymer.[200-204] PVC is regarded as the best candidate as it can be plasticized with both polar and non polar water immiscible solvents. But, because of its intrinsic negatively charged impurities PVC is not an inert support. In 1970, G. J. Moody and Ron Thomas developed the procedure for compounding, casting, drying and mounting PVC sensor membranes.[205] These membranes provide a nearly liquid membrane interior, yet a dry and robust membrane exterior. PVC, whilst being a very successful matrix material poses certain difficulties in the manufacture of the membrane, which arise from the need for a solvent (normally tetrahydrofuran) to dissolve the polymer, which is then evaporated to cast the membrane.[206]

To improve the performance of the PVC based electrodes, compatible polymers[207] have also been added in PVC matrix in place of the lipophilic salts.[208]In addition to PVC, other polymers such as methacrylated polysiloxanes[209], polyurethanes,[210,211] epoxyacrylates,[212,213] methacrylates,[214] polyvinylidene chloride[215] polystyrene[216] and copolymers of butylacrylates[217,218] and acrylonitrile[55] have been tried. There is also a report on the use of a photocured polymer for making ion selective electrodes.[219]

Based on the recent advance of host-guest chemistry, polymeric membrane ISEs for inorganic metal cations have been extensively developed by the use of crown ethers and related macrocyclic hosts as well as acyclic ligands[220-224]. A number of reports are there in the literature on ion selective electrodes for Ni(II), Ca(II), Cr(III), Sr(II), Ag(I), Hg(II), Co(II), Pb(II) etc.[192,193,225-228] Many of these ISEs exhibit excellent selectivity for metal cations as guests and are now commercially available. The Li^+ion is the only major analyte among the alkali metal ions for which no appreciable calixarene ionophore has been reported. Reports are also available on semi conducting polymers which act as ion selective electrodes when doped with anions.[229] Naader Alizadeh *et. al.* prepared dodecylbenzenesulfonate - doped polypyrrole (Ppy-DBS) electrochemically by anodic polymerization of pyrrole in the presence of dodecylbenzene sulfonate (DBS^-) ions in aqueous solution and used as the ionophore for construction of sensor.[230] Ion selective electrodes of fluoride,[231] phosphate,[232] sulfate,[233] nitrate,[204] iodide[234] etc. were also developed. Reports are available on ISEs for organic cations and anions.[235]The concepts from medicine and physiology also spurred the development of ISEs. Guilbault's group were the first to immobilize purified enzymes, stabilizing trace elements and buffer into the outer layer of potentiometric electrodes[236] and Rechnitz's group extended this idea to whole live cells.[237] Cosofret and Richard P. Buck have also made significant contributions in the pharmaceutical field.[238]

Ionophore based ISEs have been developed for halide ions, oxoanions and thiocyanate.[235,239] Whereas most ionophores for anions are organometallic compounds that interact with the analyte by formation of a coordination bond, a number of other approaches to analyte recognition have been used.[240] The by far practically most relevant halide ion is Cl^-, first of all because of the interest to measure this analyte in clinical chemistry. Use of microelectrodes based on chloro(5,10, 15, 20-tetraphenylporphyrinato)manganese(III) has been demonstrated for intracellular measurements.[241] A number of attempts have been made to develop chloride ion selective electrodes which are based on conducting polymers[242, 243], polyvinyl chloride[244] etc. Measurements of Cl^- have been demonstrated with ISEs based on (octaethylporphyrinato)indium(III)[245] or a bis-thiourea ionophore.[246] In searching for new monomer candidates for preparation of modified electrodes, schiff bases containing free aromatic amine moiety for polymerization seems to be promising for the electrodeposition of electroactive polymer films.[247]

As part of the present investigations, a sensitive ion selective electrode, selective to chloride ion has been developed. The presently fabricated electrode has a stable shelf life of about three months and is inert towards most of the transition metal ions and a variety of anions. Co(II) complex of amino methylated polystyrene-salicylaldehyde schiff base has been developed as the ion selective material in the fabrication of the electrode.

5.2 EXPERIMENTAL

Procedure for the fabrication of the electrode is presented in Chapter II. The developed chloride ion selective electrode was used to study the response behaviour, effect of pH and interference due to foreign ions. Response behaviour of the electrode was studied by measuring the potential of the electrode at different concentrations of chloride solutions (2.5×10^{-5} to 5×10^{-2} mol dm^{-3}). The effect of pH was studied by taking the potential of the electrode at different pHs (1 to 6.8). Interference was studied by measuring the potential of the electrode after mixing the chloride solution of fixed concentration (5×10^{-2} mol dm^{-3}) with solutions of varying concentrations of different foreign ions such as Ni(II), Co(II), Fe(III), Mn(II), Cu(II), Zn(II), Na^+, Ca^{2+}, CH_3COO^-, NO_3^-, SO_4^{2-}, Br^- and NO_2^-

5.3 RESULTS AND DISCUSSION

5.3.1 Response Behaviour of the Electrode

The cell set up may be represented as follows:

0.05 mol dm^{-3} chloride solution/ion selective membrane/test solution//SCE

Stable potentials are developed within a time span of 30 s, when the chloride ion-selective electrode is placed in a solution of chloride ion. The electrode potentials show a linear response in the range 2.5×10^{-5} to 0.5×10^{-1} mol dm^{-3} of chloride concentration. The slope of E vs. -log Cl^- is 57.7mV (Figure 31) indicating the Nerstian nature of the performance of the electrode. The mechanism may be a smooth exchange of Cl^-ions between the complex and the solution. The slope remained constant for about four weeks even after continuous use and the linear response was maintained for about three months, although absolute potential values changed as is commonly observed with ISEs.[248] The response time of the membrane was measured at various concentrations of test solutions. Stable potential was obtained within 30 s which remained unaltered up to 7 min.

Potentials were determined for five different concentrations of chloride ion and the percentage error and precision parameters were calculated (Table 33). The results presented in Table 33 reveal that the method is accurate and precise.

5.3.2 Effect of pH

The pH dependence of the electrode potential was also studied (Figure 32). The potential remains constant in the pH range of 2.8 to 6.8. This may be taken as the working range of pH of the electrode. The concentration of chloride ion taken was 0.5 x 10^{-2} mol dm^{-3} for these studies.

5.3.3 Interference Studies

The influence of interfering ions on the response behaviour of ion selective electrode is usually described in terms of selectivity coefficient. The potential response of the chloride ion sensor to different ions have been investigated by determining the selectivity coefficient of the electrode ($K_{i,j}^{Pot}$) using the equation

$$K_{i,j}^{Pot} = \frac{a_i}{(a_j)^{z_i/z_j}} \times \left(10^{\frac{\Delta EMF \times F \times z_i}{2.303\ RT}} - 1 \right) \quad \longrightarrow \quad 1$$

where a_i and a_j are the activities of the chloride ion and the interfering ions respectively, Z_i, Z_j are the valencies of the chloride and interfering ions, ΔEMF is the difference between the EMFs of the cell containing 'i' and 'j' ions and only 'i' ions and a_i is the same in both solutions. Equation 1, a transformation of the Nikolski-Eizenman (N-E) equation[249] derived on the basis of thermodynamic consideration of Nernst, predicts a constant value of the selectivity coefficient. Its value is determined by the ability of the disturbing ion to affect the electrode potential relative to that of the main ion. The resulting $K_{i,j}^{Pot}$ values are summarized in Table 34. The results show that Na^+, Ca^{2+}, Mn(II), Co(II), Fe(III), Ni(II), Cu(II), Zn(II), CH_3COO^-, NO_3^-, SO_4^{2-}, Br^- and NO_2^- will not affect the selectivity of the chloride ion electrode significantly over the concentration range studied. The results of the interference studies reveal that, the $K_{i,j}^{Pot}$ value is very small even when the concentration of the foreign ion is four fold molar excess of the analyte. This is a highly interesting result, as it implies the fact that the electrode can be selectively used for the determination of Cl^- ions, in presence of the above cations and anions which are at a very high concentration. Hence the electrode may be highly recommendable for the determination of Cl^- ions present in industrial effluents, where the presence of other ions is maximum.

5.4 CONCLUSION

A chloride ion selective electrode, based on the polymeric schiff base complex of amino methylated polystyrene and salicylaldehyde is developed, which is highly sensitive to chloride ions. The electrode works at a convenient pH range of 2.8 to 6.8 without interference from other ions. Determination can be carried out at a concentration range of 2.5×10^{-5} to 0.5×10^{-1} mol dm^{-3}. A quick response time of less than 30 s and a comparatively long shelf life period of 3 months are the striking advantages of the presently developed electrode.

CHAPTER VI

SUMMARY

As the application of polymeric complexes is enormous, there exists a continuing interest in the synthesis and characterization of these complexes. The synthetic and characterization parts are very important in an academic point of view. Further in an application point of view also polymeric ligands/complexes are gaining attention.

In this context, the present studies are highly important with respect to academic as well as the application parts are concerned. An attempt is made in the synthetic and characterization part and also the application part.

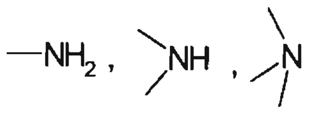
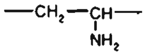
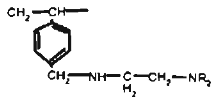
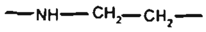
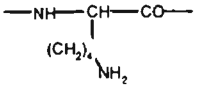
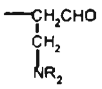
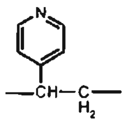
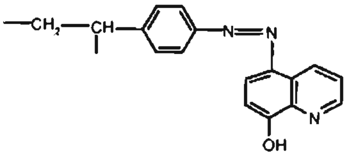
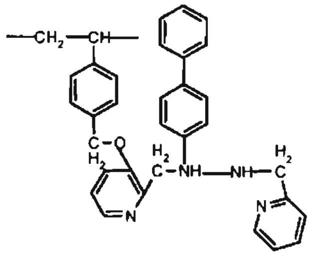
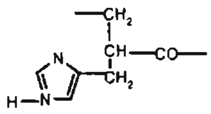
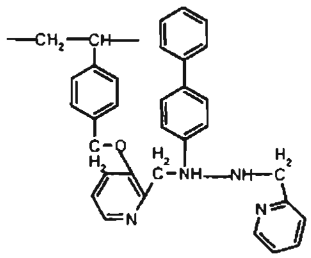
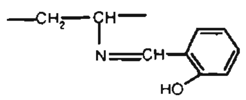
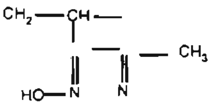
As part of the present studies, three series of polymeric complexes (each series containing six complexes) have been synthesized. All the synthesized complexes have been characterized using physical, analytical, spectroscopical and thermal methods.

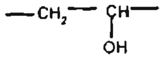
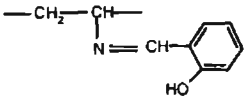
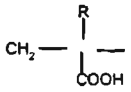
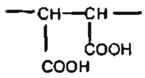
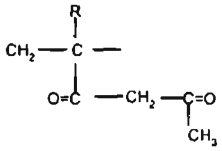
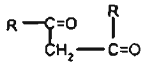
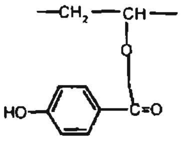
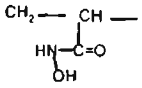
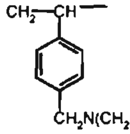
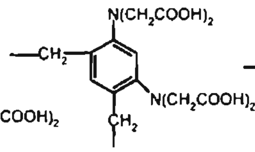
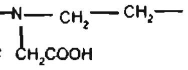
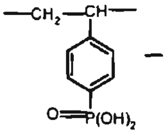
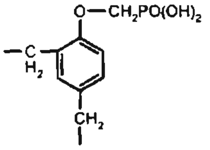
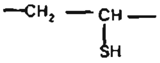
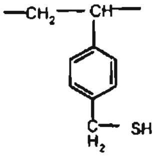
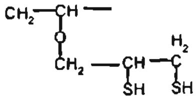
Three polymeric ligands were developed as promising metal ion removing agents, for the removal of Fe(III), Cu(II) and Ni(II). The results of the complete analytical studies are included in this thesis. Further, the Co(II) complex of the salicylaldehyde schiff base of amino methylated polystyrene has been developed as an excellent ionophore in the fabrication of Cl^- selective electrode.

The thesis is divided in to six chapters, in which the first chapter gives an introduction along with a brief review on polymeric ligands/complexes. The second chapter explains the different procedure adopted for the whole work along with the details of the reagents/instruments used. The third chapter gives a report of the detailed study regarding the synthesis and characterization of eighteen complexes. While the fourth chapter is a report of the ion removal studies using three polymeric ligands, the fifth chapter explains the development of a polymeric complex as ion selective electrode material for the fabrication of a Cl^- ion selective electrode. The sixth chapter presents the summary and tables, figures and references are given separately at the end.

TABLES & FIGURES

Table 1: Typical polymer ligands

Coordinating groups	Repeating units of polymer ligands
Amines 	    
Nitrogen of heterocyclic compounds	   
Schiff base >C=N-	  

Alcohols -OH	 
Carboxylic acids -COOH	 
Ketones >C=O Esters, amides	   
Amino polycarboxylic acids	  
Phosphonic acids -PO(OH)2	 
Thiols -SH	  

CHARACTERIZATION OF COMPLEXES

Table 2: Analytical data of vanillin schiff base of amino methylated polystyrene and its complexes

Compound	Found (calculated)				
	C	H	N	Cl	M
VASAP	76.63 (76.40)	6.44 (6.36)	5.01 (5.24)	---	
Fe(VASAP).Cl$_2$.2DMF	51.36 (51.12)	5.56 (5.74)	8.12 (7.78)	13.29 (13.15)	10.45 (10.34)
Co(VASAP).Cl.DMF	55.65 (55.24)	5.32 (5.29)	6.52 (6.44)	8.43 (8.17)	13.17 (13.56)
Ni(VASAP).OAc.3DMF	55.81 (55.65)	6.74 (6.62)	9.37 (9.27)		9.94 (9.72)
Cu(VASAP).OAc.DMF	57.26 (57.07)	5.63 (5.62)	6.21 (6.05)		13.52 (13.73)
Zn(VASAP).OAc.DMF	56.97 (56.84)	5.61 (5.59)	6.27 (6.02)		14.35 (14.08)
UO$_2$(VASAP).OAc.DMF	39.41 (39.46)	3.69 (3.88)	4.16 (4.18)		35.54 (35.57)

Table 3: IR spectral data of vanillin schiff base of amino methylated polystyrene and its complexes

Compound	C=N cm^{-1}	Phenolic (C-O) cm^{-1}	C=O (DMF) cm^{-1}	(COO)$_{sym}$ cm^{-1}	(COO)$_{asy}$ cm^{-1}	M-O cm^{-1}	M-N cm^{-1}
VASAP	1640	1511					
Fe(VASAP).Cl$_2$.2DMF	1616	1492	1668			535	450
Co(VASAP).Cl.DMF	1628	1486	1656			530	453
Ni(VASAP).OAc.3DMF	1624	1480	1668	1391	1623	482	450
Cu(VASAP).OAc.DMF	1620	1481	1651	1386	1628	480	390
Zn(VASAP).OAc.DMF	1615	1484	1666	1400	1634	530	420
UO$_2$(VASAP).OAc.DMF	1616	1482	1654	1384	1633	525	430

Table 4: Diffuse reflectance spectral data of metal complexes of vanillin schiff base of amino methylated polystyrene

Complex	Absorption (cm^{-1})	Tentative assignments
Fe(VASAP).Cl_2.2DMF	11745 15675 (shoulder) 18720	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
Co(VASAP).Cl.DMF	10120 15200	d_{xy}- d_{yz} $^2A_{1g} \rightarrow {}^2E_g$
Ni(VASAP).OAc.3DMF	8500 (not found) 15210 25715	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Cu(VASAP).OAc.DMF	15640 24770	$^2B_{1g} \rightarrow {}^2A_{1g}$ Charge transfer
UO_2(VASAP).OAc.DMF	19380 23400 38985	

Table 5: Magnetic moment data of metal complexes of vanillin schiff base of amino methylated polystyrene

Complex	Colour	Magnetic moment (BM)	Geometry
Fe(VASAP).Cl_2.2DMF	Brick-red	5.95	Octahedral
Co(VASAP).Cl.DMF	Ash	2.42	Square planar
Ni(VASAP).OAc.3DMF	Brown	3.27	Octahedral
Cu(VASAP).OAc.DMF	Chocolate	1.83	Square planar
Zn(VASAP).OAc.DMF	Flesh colour	Diamagnetic	Tetrahedral
UO_2(VASAP).OAc.DMF	Brown	Diamagnetic	Octahedral

Table 6: TG data of metal complexes of vanillin schiff base of amino methylated polystyrene

Complex	Weight loss %	Temperature range °C	Conclusion
Fe(VASAP).Cl_2.2DMF	27	200-300	2 DMF loss
Co(VASAP).Cl.DMF	17	150-200	1 DMF loss
Ni(VASAP).OAc.3DMF	36	150-300	3 DMF loss
Cu(VASAP).OAc.DMF	16	150-220	1 DMF loss
Zn(VASAP).OAc.DMF	16	110-200	1 DMF loss
UO_2(VASAP).OAc.DMF	11	160-280	1 DMF loss

Table 7: Analytical data of 2-nitro benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	Found (calculated)				
	C	H	N	Cl	M
NBSAP	72.36 (72.18)	5.28 (5.26)	10.44 (10.52)		
Fe$(NBSAP)_2$.Cl_2.2DMF	56.83 (56.65)	4.98 (5.21)	10.37 (10.43)	8.62 (8.82)	6.63 (6.93)
Co$(NBSAP)_2$.Cl.DMF	60.47 (60.04)	5.14 (5.00)	10.12 (10.01)	5.33 (5.07)	8.28 (8.42)
Ni$(NBSAP)_2$.OAc.3DMF	59.35 (59.39)	5.67 (5.98)	11.02 (11.28)		6.89 (6.75)
Cu$(NBSAP)_2$.OAc.DMF	60.97 (61.02)	4.96 (5.22)	9.42 (9.62)		8.58 (8.73)
Zn$(NBSAP)_2$.OAc.DMF	61.50 (60.87)	4.94 (5.20)	9.75 (9.59)		8.63 (8.96)
$UO_2(NBSAP)_2$.OAc.DMF	47.45 (47.53)	3.82 (4.06)	7.46 (7.49)		25.27 (25.48)

Table 8: IR spectral data of 2-nitro benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	C=N cm^{-1}	C=O (DMF) cm^{-1}	$(COO)_{sym}$ cm^{-1}	$(COO)_{asy}$ cm^{-1}	M-N cm^{-1}
NBSAP	1655				
Fe(NBSAP)$_2$.Cl$_2$.2DMF	1639	1629			450
Co(NBSAP)$_2$.Cl.DMF	1637	1617			445
Ni(NBSAP)$_2$.OAc.3DMF	1640	1617	1392	1606	442
Cu(NBSAP)$_2$.OAc.DMF	1640	1650	1397	1600	440
Zn(NBSAP)$_2$.OAc.DMF	1630	1625	1394	1608	447
UO$_2$(NBSAP)$_2$.OAc.DMF	1641	1651	1398	1606	436

Table 9: Diffuse reflectance spectral data of metal complexes of 2-nitro benzaldehyde schiff base of amino methylated polystyrene

Complex	Absorption (cm^{-1})	Tentative assignments
Fe(NBSAP)$_2$.Cl$_2$.2DMF	11780 15300 (shoulder) 18750	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
Co(NBSAP)$_2$.Cl.DMF	15200 10120	d_{xy}- d_{yz} $^2A_{1g} \rightarrow {}^2E_g$
Ni(NBSAP)$_2$.OAc.3DMF	10526 15670 24490	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Cu(NBSAP)$_2$.OAc.DMF	14708 24857	$^2B_{1g} \rightarrow {}^2A_{1g}$ Charge transfer
UO$_2$(NBSAP)$_2$.OAc.DMF	18181 23125 39020	

Table 10: Magnetic moment data of metal complexes of 2-nitro benzaldehyde schiff base of amino methylated polystyrene

Complex	Colour	Magnetic moment (BM)	Geometry
$Fe(NBSAP)_2.Cl_2.2DMF$	Brick-red	5.92	Octahedral
$Co(NBSAP)_2.Cl.DMF$	Ash	2.75	Square planar
$Ni(NBSAP)_2.OAc.3DMF$	Sandalwood	3.34	Octahedral
$Cu(NBSAP)_2.OAc.DMF$	Chocolate	1.83	Square planar
$Zn(NBSAP)_2.OAc.DMF$	Flesh colour	Diamagnetic	Tetrahedral
$UO_2(NBSAP)_2.OAc.DMF$	Brown	Diamagnetic	Octahedral

Table 11: TG data of metal complexes of 2-nitro benzaldehyde schiff base of amino methylated polystyrene

Complex	Weight loss %	Temperature range °C	Conclusion
$Fe(NBSAP)_2.Cl_2.2DMF$	18	150-240	2 DMF loss
$Co(NBSAP)_2.Cl.DMF$	10	150-220	1 DMF loss
$Ni(NBSAP)_2.OAc.3DMF$	25	180-280	3 DMF loss
$Cu(NBSAP)_2.OAc.DMF$	10	140-240	1 DMF loss
$Zn(NBSAP)_2.OAc.DMF$	10	200-300	1 DMF loss
$UO_2(NBSAP)_2.OAc.DMF$	8	170-275	1 DMF loss

Table 12: Analytical data of veratraldehyde schiff base of amino methylated polystyrene and its complexes

Compound	Found (calc)				
	C	H	N	Cl	M
VESAP	76.54 (76.86)	6.82 (6.76)	4.73 (4.98)		
Fe(VESAP)$_2$.Cl$_2$.2DMF	60.36 (60.37)	6.13 (6.22)	6.54 (6.70)	8.67 (8.50)	6.92 (6.68)
Co(VESAP)$_2$.Cl.DMF	64.57 (64.15)	6.28 (6.16)	5.81 (5.75)	4.95 (4.86)	8.06 (8.07)
Ni(VESAP)$_2$.OAc.3DMF	62.43 (62.75)	6.74 (6.89)	7.80 (7.78)		6.45 (6.53)
Cu(VESAP)$_2$.OAc.DMF	65.27 (64.94)	6.04 (6.33)	5.32 (5.54)		8.26 (8.38)
Zn(VESAP)$_2$.OAc.DMF	64.72 (64.78)	6.22 (6.32)	5.86 (5.53)		8.76 (8.61)
UO$_2$(VESAP)$_2$.OAc.DMF	51.19 (51.03)	4.47 (4.97)	4.23 (4.35)		24.97 (24.68)

Table 13: IR spectral data of veratraldehyde schiff base of amino methylated polystyrene and its complexes

Compound	C=N cm^{-1}	C=O (DMF) cm^{-1}	(COO)$_{sym}$ cm^{-1}	(COO)$_{asy}$ cm^{-1}	M-N cm^{-1}
VESAP	1643				
Fe(VESAP)$_2$.Cl$_2$.2DMF	1633	1644			452
Co(VESAP)$_2$.Cl.DMF	1634	1642			450
Ni(VESAP)$_2$.OAc.3DMF	1630	1651	1380	1626	465
Cu(VESAP)$_2$.OAc.DMF	1634	1648	1397	1629	430
Zn(VESAP)$_2$.OAc.DMF	1636	1651	1400	1622	436
UO$_2$(VESAP)$_2$.OAc.DMF	1633	1644	1380	1618	460

Table 14: Diffuse reflectance spectral data of metal complexes of veratraldehyde schiff base of amino methylated polystyrene

Complex	Absorption (cm^{-1})	Tentative assignments
$Fe(VESAP)_2.Cl_2.2DMF$	11780 15432 (shoulder) 18518	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
$Co(VESAP)_2.Cl.DMF$	10516 15151	d_{xy}- d_{yz} $^2A_{1g} \rightarrow {}^2E_g$
$Ni(VESAP)_2.OAc.3DMF$	10548 15432 25125	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$Cu(VESAP)_2.OAc.DMF$	25000 14306	$^2B_{1g} \rightarrow {}^2A_{1g}$ Charge transfer
$UO_2(VESAP)_2.OAc.DMF$	18867 23255 40000	

Table 15: Magnetic moment data of metal complexes of veratraldehyde schiff base of amino methylated polystyrene

Complex	colour	Magnetic moment (BM)	geometry
$Fe(VESAP)_2.Cl_2.2DMF$	Brick-red	5.72	Octahedral
$Co(VESAP)_2.Cl.DMF$	Ash	2.64	Square planar
$Ni(VESAP)_2.OAc.3DMF$	Sandalwood	3.35	Octahedral
$Cu(VESAP)_2.OAc.DMF$	Chocolate	1.81	Square planar
$Zn(VESAP)_2.OAc.DMF$	Flesh colour	Diamagnetic	Tetrahedral
$UO_2(VESAP)_2.OAc.DMF$	Brown	Diamagnetic	Octahedral

Table 16: TG data of metal complexes of veratraldehyde schiff base of amino methylated polystyrene

Complex	Weight loss %	Temperature range °C	Conclusion
$Fe(VESAP)_2.Cl_2.2DMF$	17	120-240	2 DMF loss
$Co(VESAP)_2.Cl.DMF$	10	110-190	1 DMF loss
$Ni(VESAP)_2.OAc.3DMF$	24	140-260	3 DMF loss
$Cu(VESAP)_2.OAc.DMF$	9	140-200	1 DMF loss
$Zn(VESAP)_2.OAc.DMF$	9	120-220	1 DMF loss
$UO_2(VESAP)_2.OAc.DMF$	8	140-230	1 DMF loss

METAL ION REMOVAL STUDIES

(i) Removal of Fe(III) Using Salicylaldehyde Schiff Base of Amino Methylated Polystyrene

Table 17: Effect of time

Fe (III) taken = 30 ppm; mass of ligand = 0.01 g

Time (min.)	5	10	15	20	30
Fe(II) concentration after complexation (ppm)	8	5	1.5	Negligible	Negligible
Percentage removal	73	83	95	100	100

Table 18: Effect of pH

Fe (III) taken = 30 ppm; mass of ligand = 0.01 g
time = 20 min.

PH	1.1	1.36	1.7	1.84	2	2.18	2.3	2.5
Fe(III) concentration after complexation (ppm)	9.2	8.4	6.4	5.5	3.2	Negligible	4	13
Percentage removal	69	72	79	82	89	100	86	57

Table 19: Effect of metal ion concentration

Mass of ligand taken = 0.01 g; time = 20 min.

Fe(III) taken (ppm)	10	20	30	40	50	60	70
Fe(III) concentration after complexation (ppm)	Negligible	Negligible	Negligible	3.1	6.8	15	20.5
Percentage removal	100	100	100	92	86	75	71

Table 20: Effect of ligand concentration

Ferric ion concentration = 30 ppm; time = 20 min.

Mass of ligand (g)	0.0005	0.001	0.0025	0.005	0.0075	0.01	0.05
Fe (III) concentration after complexation (ppm)	9.4	6.7	5.9	3.6	Negligible	Negligible	Negligible
Percentage removal	68	78	80	88	100	100	100

Table 21: Interference due to ions

Fe(III) taken = 30 ppm; mass of ligand = 0.01 g;

range of foreign ion = 10-50 ppm; time = 20 min.

Ion taken	Fe(III) concentration after complexation (ppm)	Percentage removal
Fe(III)	Negligible	100
Fe(III)+Ni(II)	Negligible	100
Fe(III)+Cu(II)	Negligible	100
Fe(III)+Zn(II)	Negligible	100
Fe(III)+Co(II)	Negligible	100
Fe(III)+U(VI)	Negligible	100
Fe(III)+Na^+	Negligible	100
Fe(III)+K^+	Negligible	100
Fe(III)+Ca^{2+}	Negligible	100
Fe(III)+NH_4^+	Negligible	100
Fe(III)+F^-	Negligible	100
Fe(III)+Cl^-	Negligible	100
Fe(III)+Br	Negligible	100
Fe(III)+NO_3	Negligible	100
Fe(III)+NO_2^-	Negligible	100
Fe(III)+CH_3COO^-	Negligible	100

(ii) Removal of Cu(II) Using 2-Nitro Benzaldehyde Schiff Base of Amino Methylated Polystyrene

Table 22: Effect of time

Cu(II) taken = 30 ppm; mass of ligand = 0.01 gm

Time (min.)	5	10	15	20	30
Concentrationn after complexation (ppm)	21	10	5.5	2.92	2.92
Percentage removal	30	67	81.6	90	90

Table 23: Effect of pH

Cu(II) taken = 30 ppm; mass of ligand =0.01 gm;

time= 20 min.

PH	1.48	2.05	2.86	4.4	5.09	6
Cu(II) concentration after complexation (ppm)	25	20	12	2.92	17	28
Percentage removal	17	33	60	90	43	7

Table 24: Effect of metal ion concentration

Mass of ligand = 0.01 g; time = 20min.

Cu(II) concentration (ppm)	5	10	20	30	40	50	60	70
Cu(II) concentration after complexation (ppm)	0.75	1.3	2.27	2.92	13.68	20.9	27	33.75
Percentage removal	85	87	89	90	66	58	55	52

Table 25: Effect of ligand concentration

Cu (II) taken = 30 ppm; time = 20 min.

Mass of ligand (g)	0.005	0.0075	0.01	0.02	0.03	0.05	0.07	0.1
Cu(II) concentration after complexation (ppm)	5.2	3.4	2.92	2.92	2.92	2.92	2.92	2.92
Percentage removal	83	88	90	90	90	90	90	90

Table 26: Interference studies

Cu (II) taken = 30 ppm; mass of ligand = 0.01 g;

range of foreign ion = 10-50 ppm; time = 20 min.

Ion taken	Cu(II) concentration after complexation (ppm)	Percentage removal
Cu(II)	2.92	90
Cu(II)+Ni(II)	2.92	90
Cu(II)+Zn(II)	2.92	90
Cu(II)+U(VI)	2.92	90
Cu(II)+Na^+	2.92	90
Cu(II)+K^+	2.92	90
Cu(II)+Ca^{2+}	2.92	90
Cu(II)+NH_4^+	2.92	90
Cu(II)+F^-	2.92	90
Cu(II)+Cl^-	2.92	90
Cu(II)+Br^-	2.92	90
Cu(II)+NO_3^-	2.92	90
Cu(II)+NO_2^-	2.92	90
Cu(II)+CH_3COO^-	2.92	90

Table 26 A: Interference studies of Fe(III) and Co(II)

Cu(II) taken = 30 ppm; mass of ligand = 0.01 g; time = 20 min.

Ion taken	Concentration of foreign ion (ppm)	Cu (II) concentration after complexation (ppm)	Percentage removal
Cu(II)+Fe(III)*	10	8	73
	20	8.5	72
	30	11	63
	40	15	50
	50	17	43
Cu(II)+Co(II)	10	12	60
	20	12.4	59
	30	14	53
	40	17	43
	50	20	33

* Ascorbic acid is used as the masking agent

(iii) Removal of Ni(II) Using Vanillin Schiff Base of Amino Methylated Polystyrene

Table 27: Effect of time

Ni(II) taken = 20 ppm; mass of ligand = 0.01 g

Time (min.)	5	10	15	20
Ni(II)concentration after complexation(ppm)	3.4	1.6	Negligible	Negligible
Percentage removal	83	92	100	100

Table 28: Effect of pH

Ni(II) taken = 20 ppm; mass of ligand = 0.01 g; time = 15 min.

PH	1	1.5	2.2	3	4.2	4.9	5.7	6.1
Ni(II)concentration after complexation (ppm)	16	12	9.5	7.2	5.6	negligible	10	18.2
Percentage removal	20	40	53	64	72	100	50	9

Table 29: Effect of metal ion concentration

Mass of ligand = 0.01 g; time = 15 min.

Ni(II) taken (ppm)	10	20	30	40	50	60	70
Ni(II)concentration after complexation (ppm)	Complete removal	Complete removal	2	5.5	10.6	30	35
Percentage removal	100	100	93	86	79	50	50

Table 30: Effect of ligand concentration

Ni(II) taken =20 ppm; time =15 min.

Mass of ligand (gm)	0.005	0.0075	0.01	0.02	0.03	0.05	0.07	0.1
Ni(II)concentration after complexation (ppm)	2.2	2.2	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible
Percentage removal	89	89	100	100	100	100	100	100

Table 31: Interference due to ions

Ni(II) taken = 20 ppm; mass of ligand = 0.01 g;

range of foreign ion = 10-50 ppm; time = 15 min.

Ion taken	Ni(II) concentration after complexation (ppm)	Percentage removal
Ni(II)	Negligible	100
Ni(II)+Fe(III)	Negligible	100
Ni(II)+Cu(II)	Negligible	100
Ni(II)+Zn(II)	Negligible	100
Ni(II)+Co(II)	Negligible	100
Ni(II)+U(VI)	Negligible	100
Ni(II)+Na^+	Negligible	100
Ni(II)+K^+	Negligible	100
Ni(II)+Ca^{2+}	Negligible	100
Ni(II)+NH_4^+	Negligible	100
Ni(II)+F^-	Negligible	100
Ni(II)+Cl^-	Negligible	100
Ni(II)+Br^-	Negligible	100
Ni(II)+NO_3^-	Negligible	100
Ni(II)+NO_2^-	Negligible	100
Ni(II)+CH_3COO^-	Negligible	100

Table 32: Comparison of the results of the removal studies of Fe(III), Cu(II) and Ni(II)

Metal taken	Ligand	Optimum amount of ligand(g)	Optimum time of reflux(min.)	Optimum pH	Interference	Percentage removal
Fe(III) (30 ppm)	Salicylaldehyde schiff base	0.0075	20	Original pH(2.18)	Nil	100
Cu(II) (30 ppm)	2-Nitro benzaldehyde schiff base	0.01	20	Original pH(4.4)	Fe(III) & Co(II)	90
Ni(II) (20 ppm)	Vanillin schiff base	0.01	15	Original pH(4.9)	Nil	100

DEVELOPMENT OF Cl^- ION SELECTIVE ELECTRODE

Table 33: Determination of chloride

Chloride taken		E (mV)	Chloride found		Error (%)	S.D
$[Cl^-]$	$-\log[Cl^-]$		$-\log[Cl^-]$	$[Cl^-]$		
$1.5X10^{-1}$	0.823	54	0.822	$1.505X10^{-1}$	0.33	0.57
$1.5X10^{-2}$	1.823	116	1.831	$1.475X10^{-2}$	1.6	
$1.5X10^{-3}$	2.823	172	2.819	$1.515X10^{-3}$	1.0	
$1.5X10^{-4}$	3.823	232	3.818	$1.52X10^{-4}$	1.3	
$1.5X10^{-5}$	4.823	293	4.825	$1.495X10^{-5}$	0.33	

Table 34: Selectivity coefficient of various interfering ions for the chloride ion selective electrode

Concentration of the chloride ion = 0.05 mol dm^{-3}

Interfering ion (j)	Molar concentration of the interfering ion (mol dm^{-3})	$K_{i,j}^{Pot}$	Interfering ion (j)	Molar concentration of the interfering ion (mol dm^{-3})	$K_{i,j}^{Pot}$
Zn^{2+}	0.01	6.1X10^{-2}	Ca^{2+}	0.1	3.3X10^{-2}
	0.1	1.2X10^{-2}		0.2	4.3X10^{-3}
	0.2	5.0X10^{-3}			
Fe^{3+}	0.01	1.8X10^{-3}	SO_4^{2-}	0.1	2.6X10^{-2}
	0.1	4.2X10^{-3}		0.2	4.4X10^{-3}
	0.2	3.3X10^{-3}			
Cu^{2+}	0.01	3.9X10^{-2}	NO_3	0.1	4.0X10^{-2}
	0.1	2.6X10^{-2}		0.2	2.0X10^{-2}
	0.2	8.9X10^{-3}			
Mn^{2+}	0.1	6.1X10^{-3}	Br	0.1	6.1X10^{-3}
	0.2	1.8X10^{-2}		0.2	5.3X10^{-2}
Co^{2+}	0.1	4.1X10^{-2}	CH_3COO^-	0.1	1.9X10^{-2}
	0.2	5.6X10^{-3}		0.2	2.0X10^{-2}
Na^+	0.1	1.9X10^{-2}	NO_2	0.1	1.9X10^{-2}
	0.2	9.7X10^{-3}		0.2	9.7X10^{-3}
K^+	0.1	8.3X10^{-2}			
	0.2	9.7X10^{-3}			

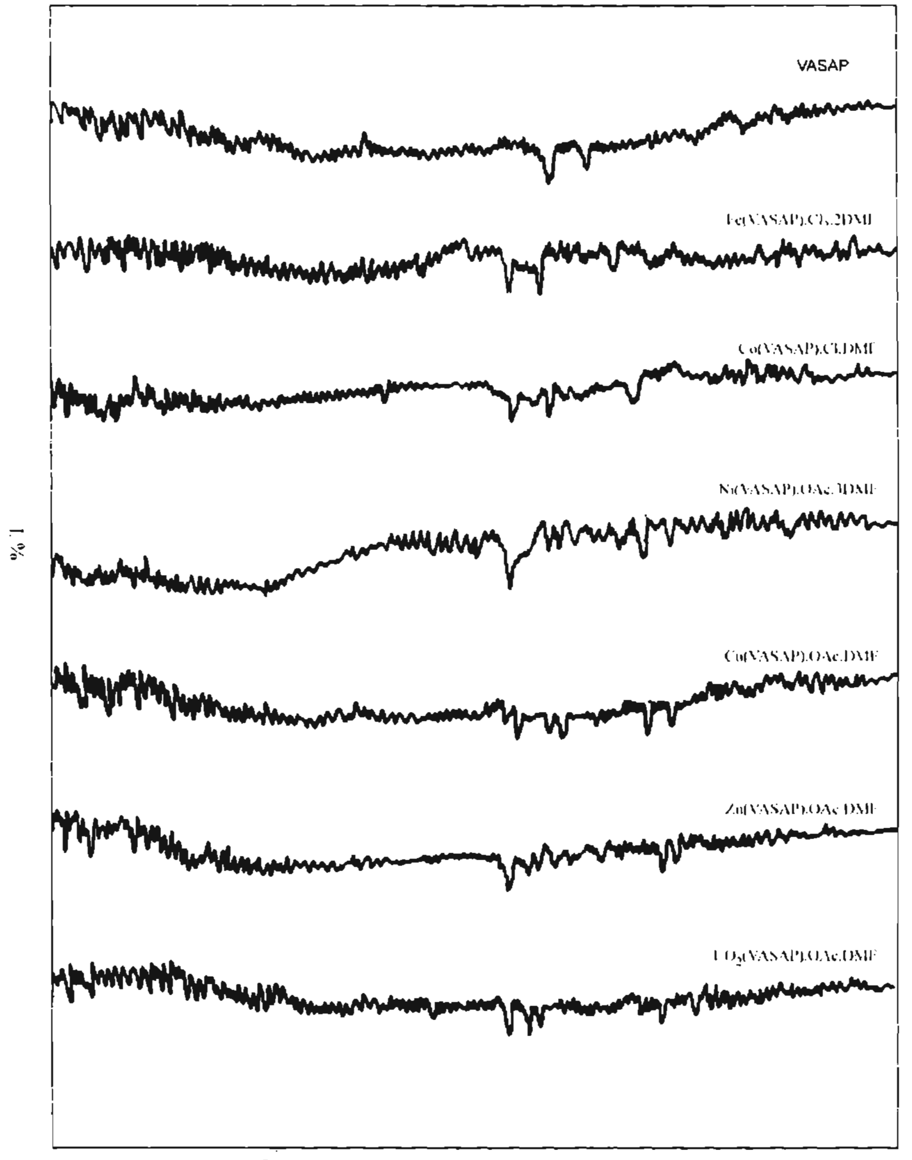


Figure 1: IR Spectra of VASAP and its Complexes

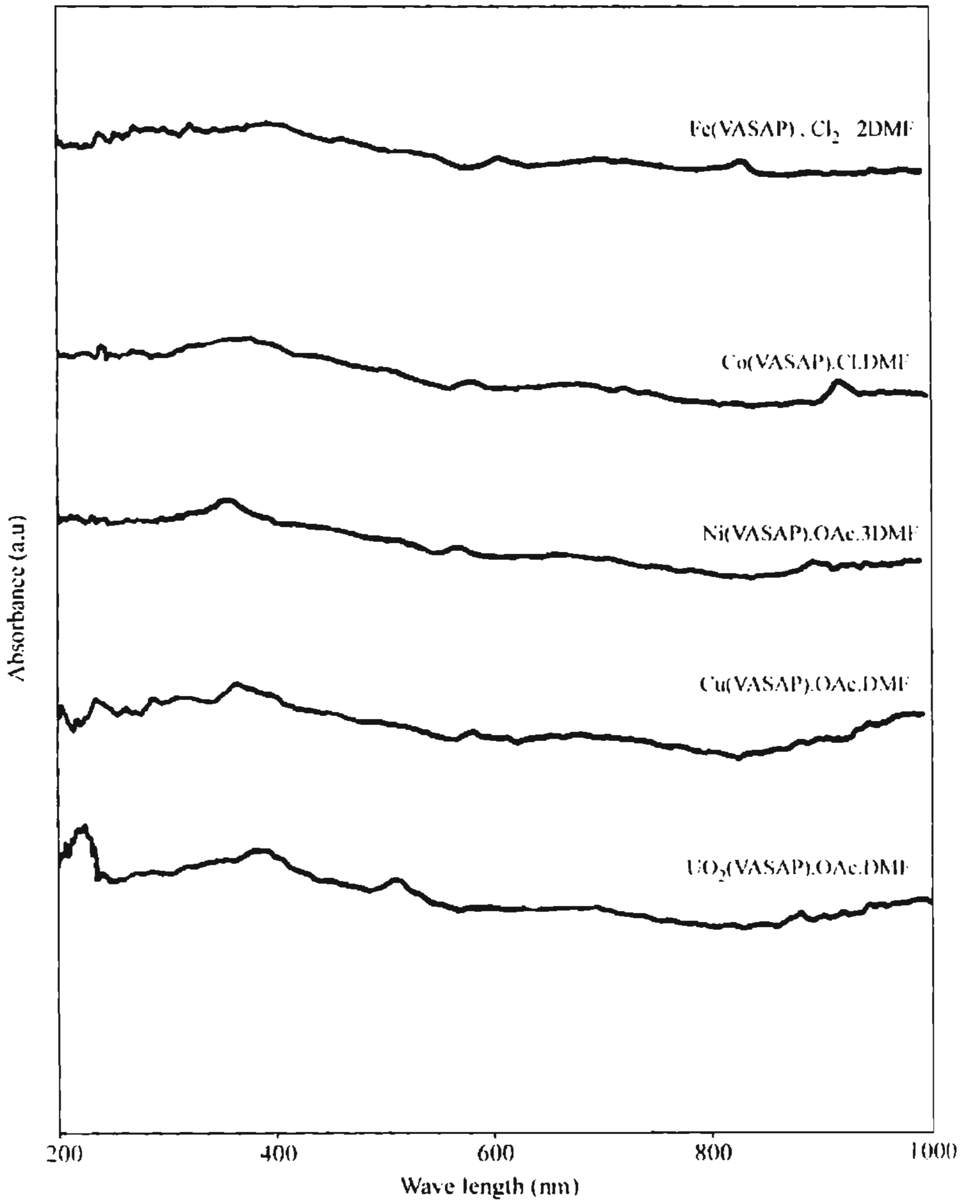


Figure 2: Electronic Spectra of VASAP Complexes

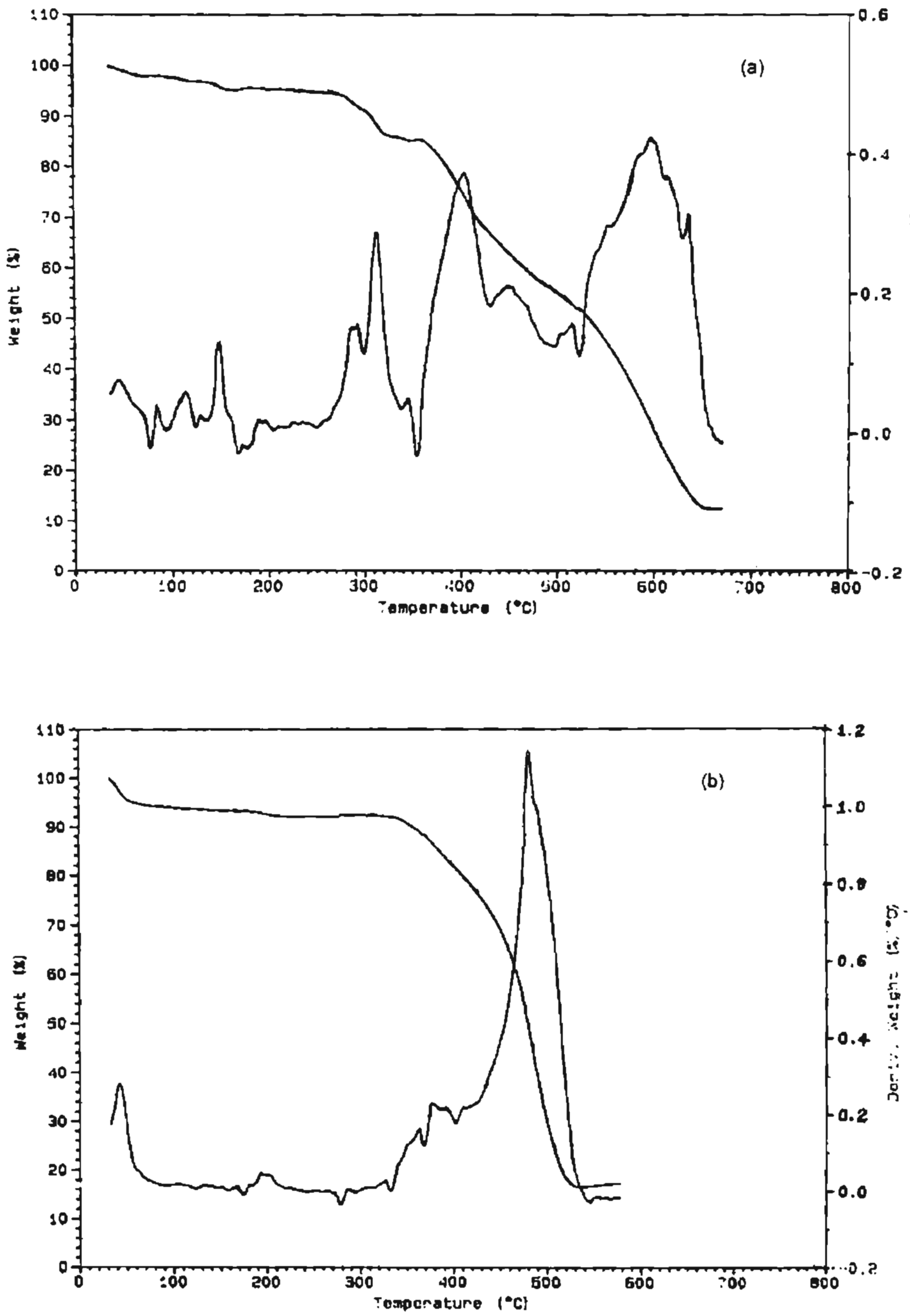


Figure 3: TG-DTG Curves of VASAP Complexes (a) Ni, (b) U.

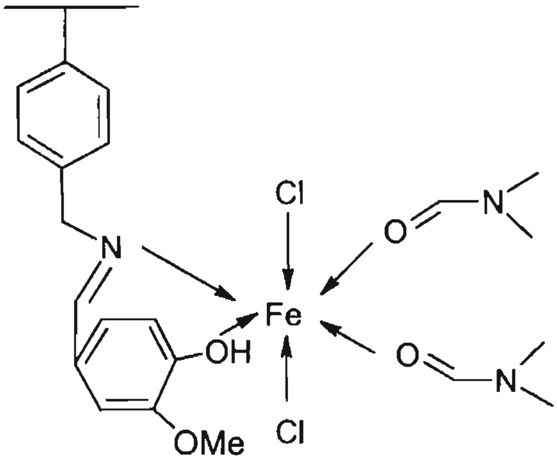


Figure 4: Structure of Fe(VASAP).Cl_2.2DMF

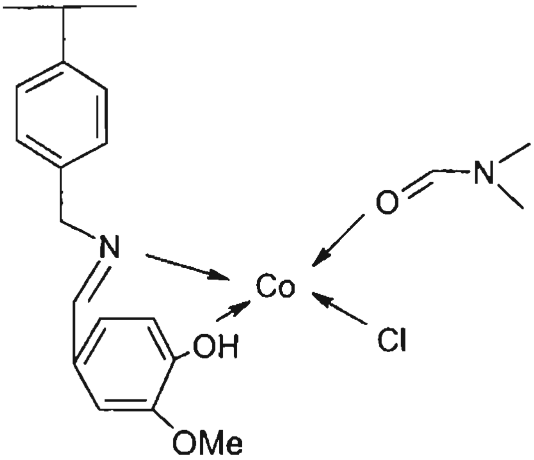


Figure 5: Structure of Co(VASAP).Cl.DMF

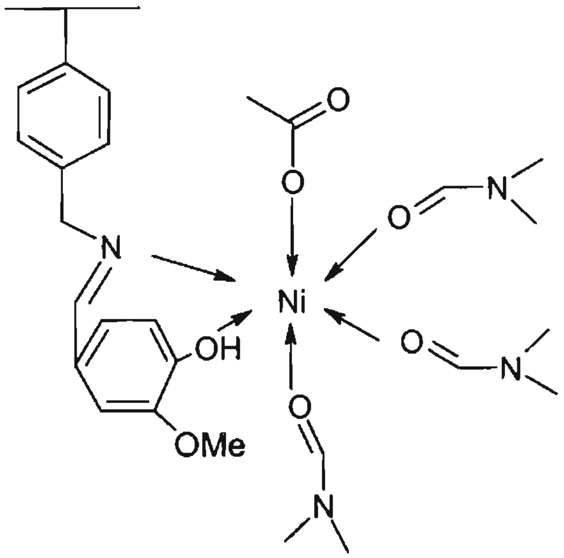


Figure 6: Structure of Ni(VASAP).OAc.3DMF

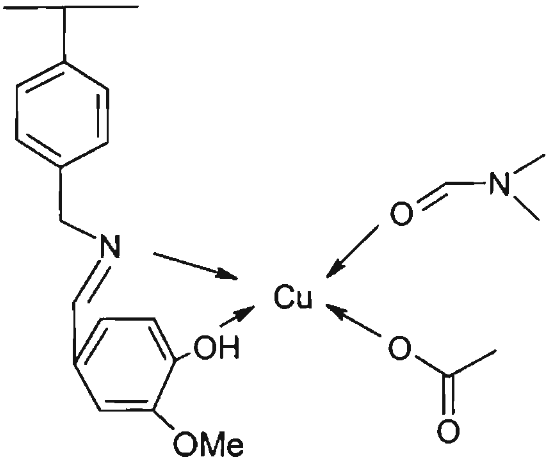


Figure 7: Structure of Cu(VASAP).OAc.DMF

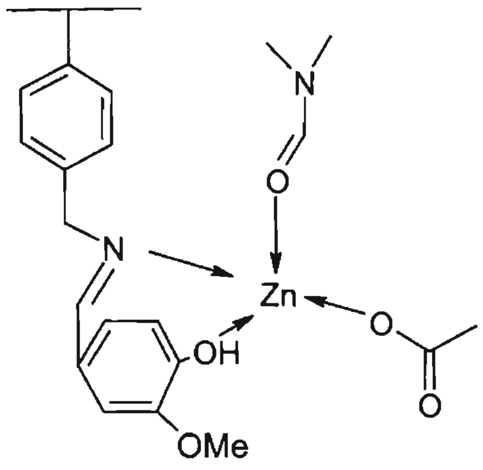


Figure 8: Structure of Zn(VASAP).OAc.DMF

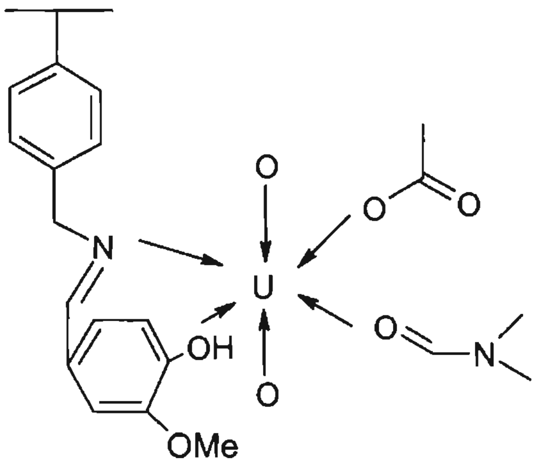


Figure 9: Structure of UO_2(VASAP).OAc.DMF

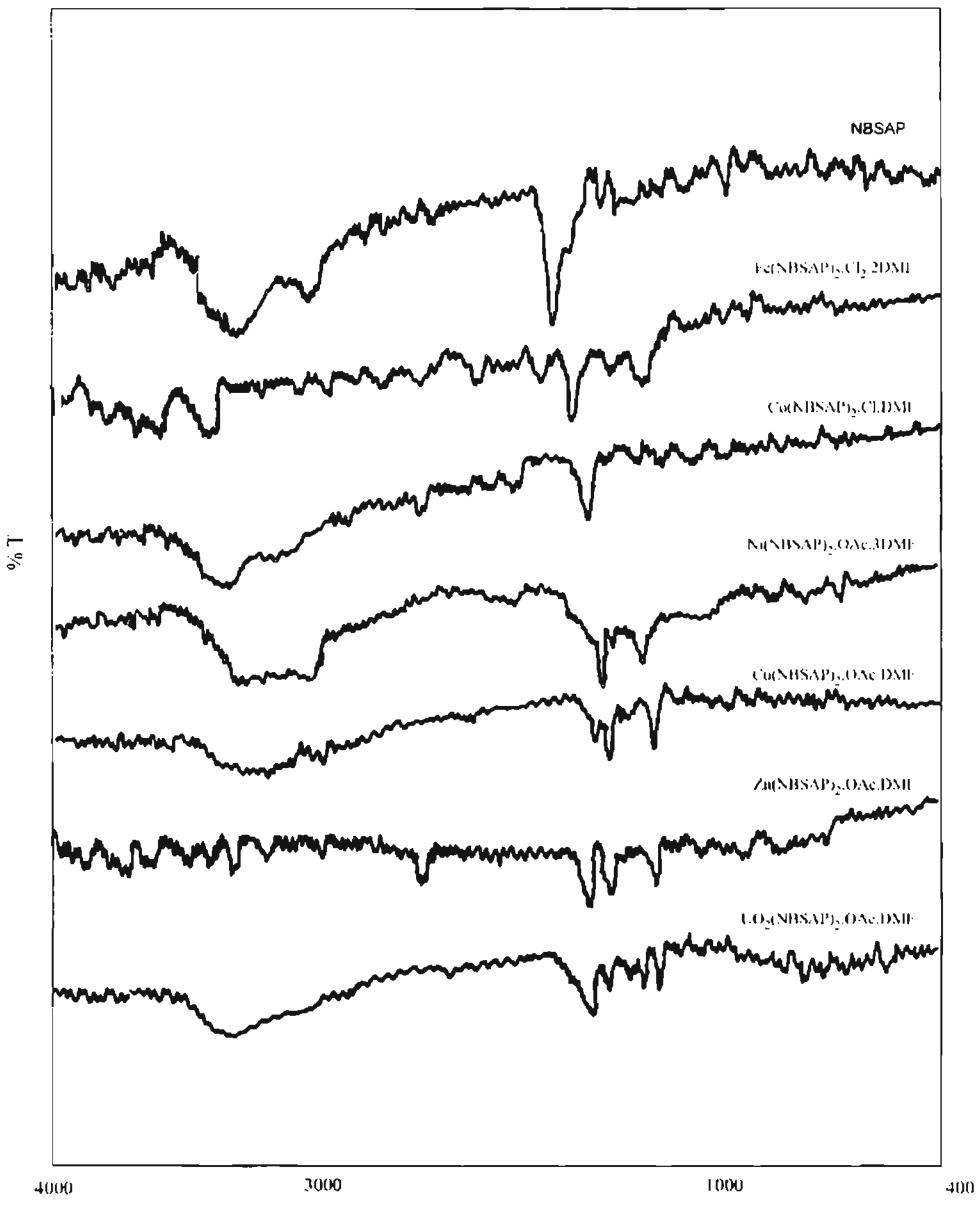


Figure 10: IR spectra of NBSAP and its complexes

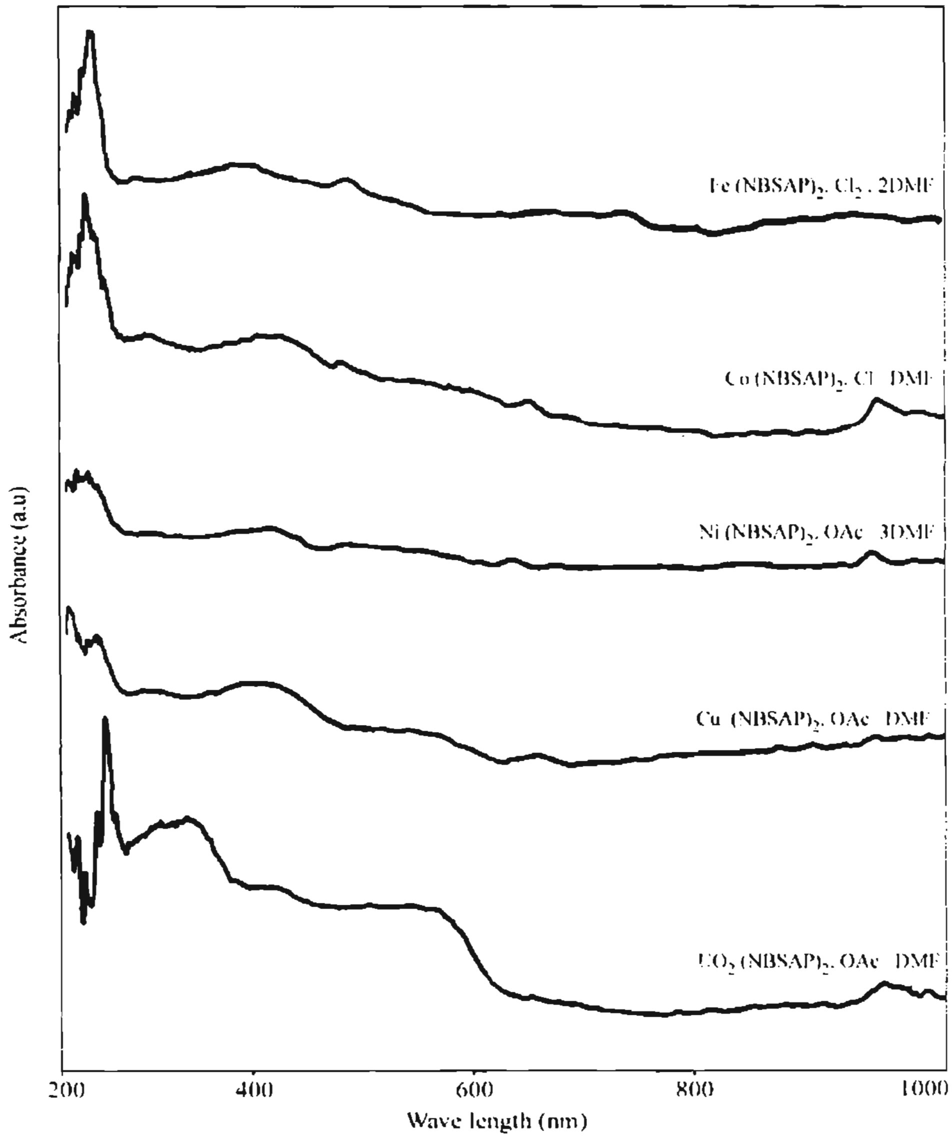
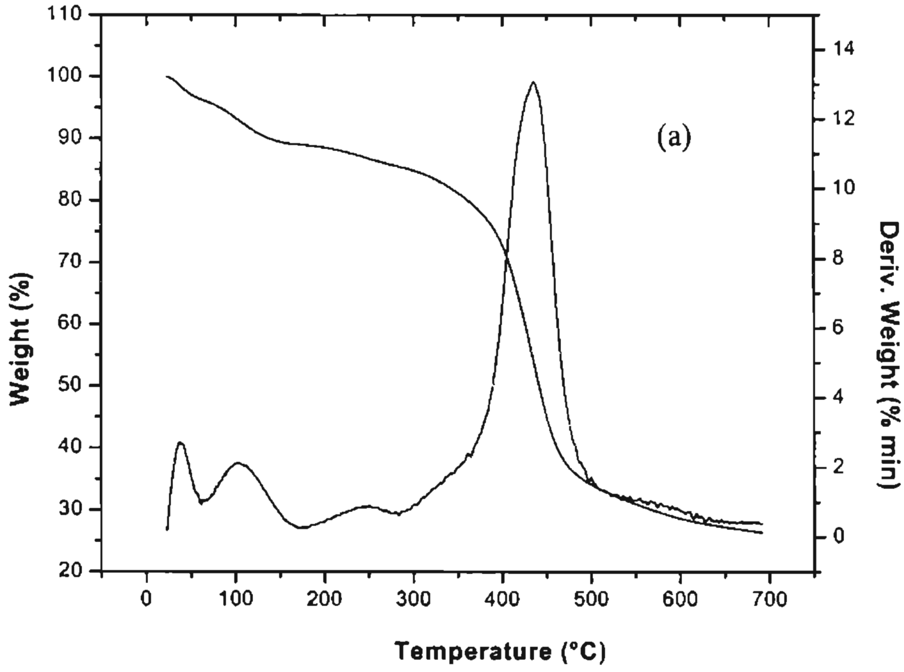


Figure 11: Electronic Spectra of NBSAP complexes



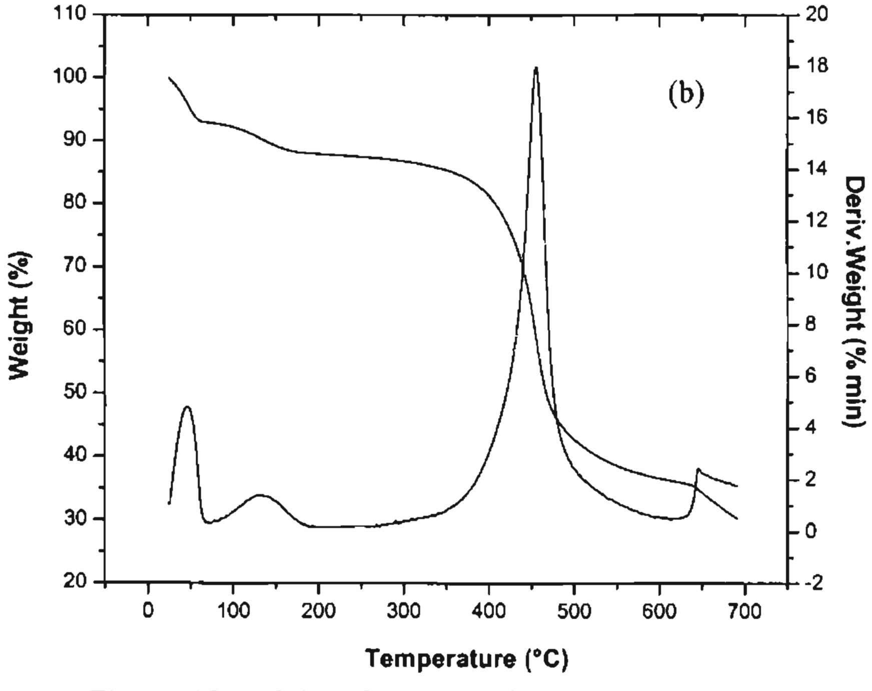


Figure 12 : TG/DTG curves of NBSAP complexes

(a) Fe, (b) Co

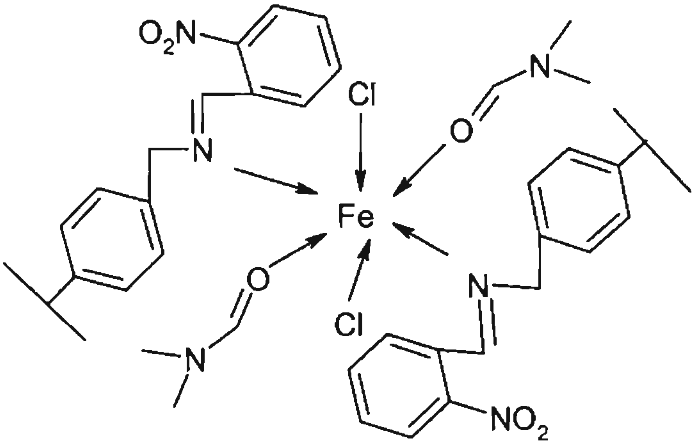


Figure 13: Structure of Fe(NBSAP)$_2$.Cl$_2$.2DMF

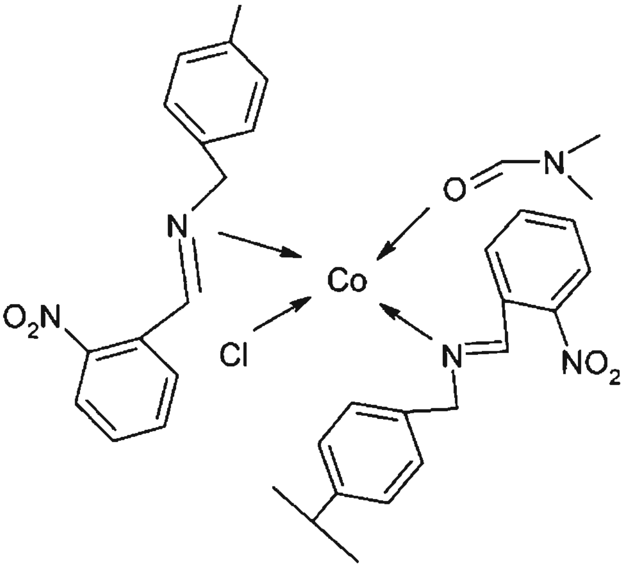


Figure 14: Structure of Co(NBSAP)$_2$.Cl.DMF

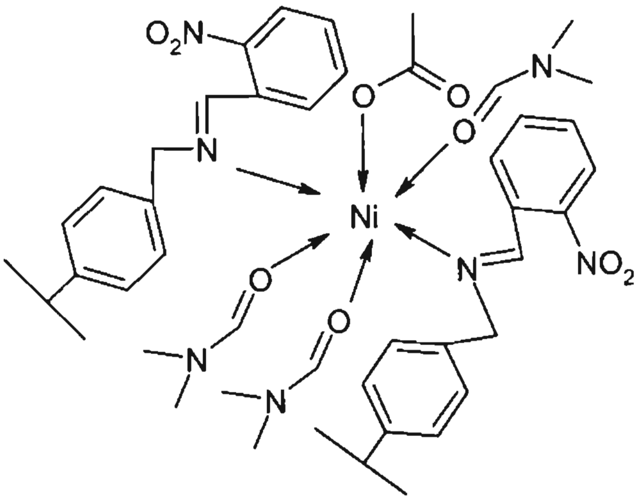


Figure 15: Structure of Ni(NBSAP)$_2$.OAc.3DMF

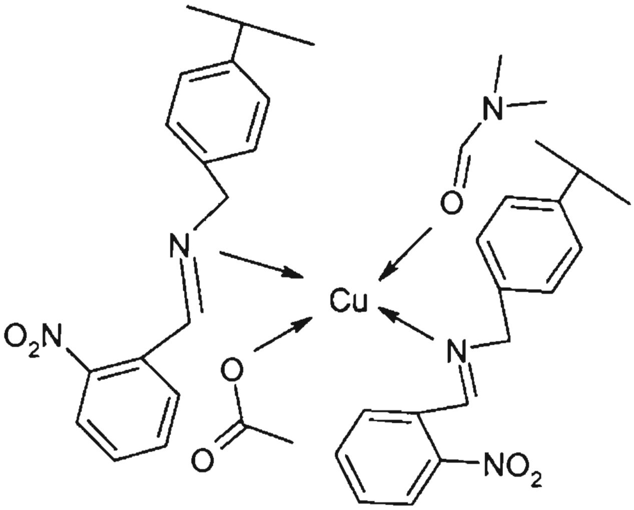


Figure 16: Structure of Cu(NBSAP)$_2$.OAc.DMF

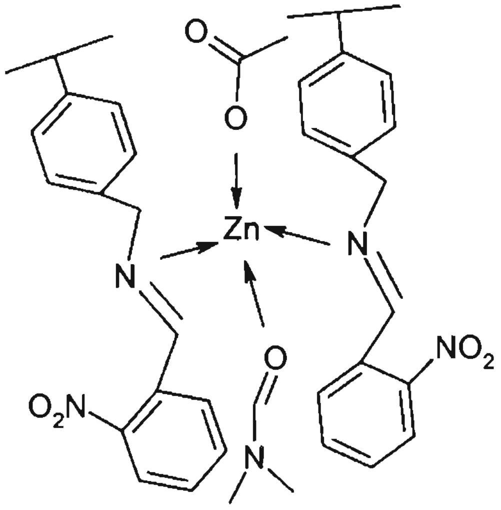


Figure 17: Structure of Zn(NBSAP)$_2$.OAc.DMF

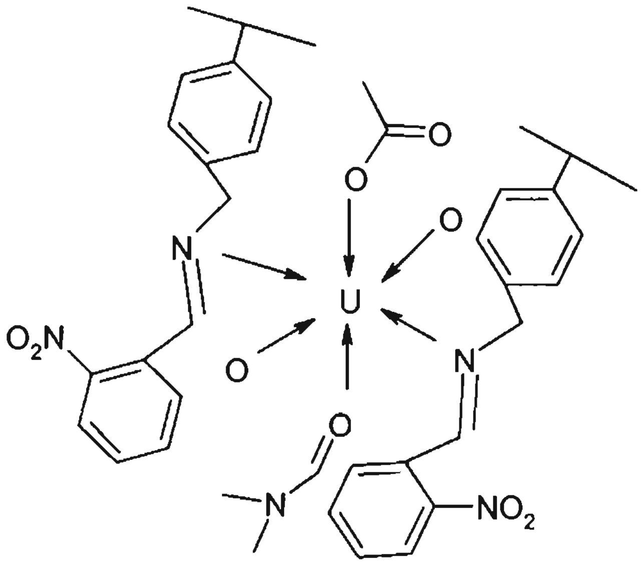


Figure18: Structure of UO$_2$(NBSAP)$_2$.OAc.DMF

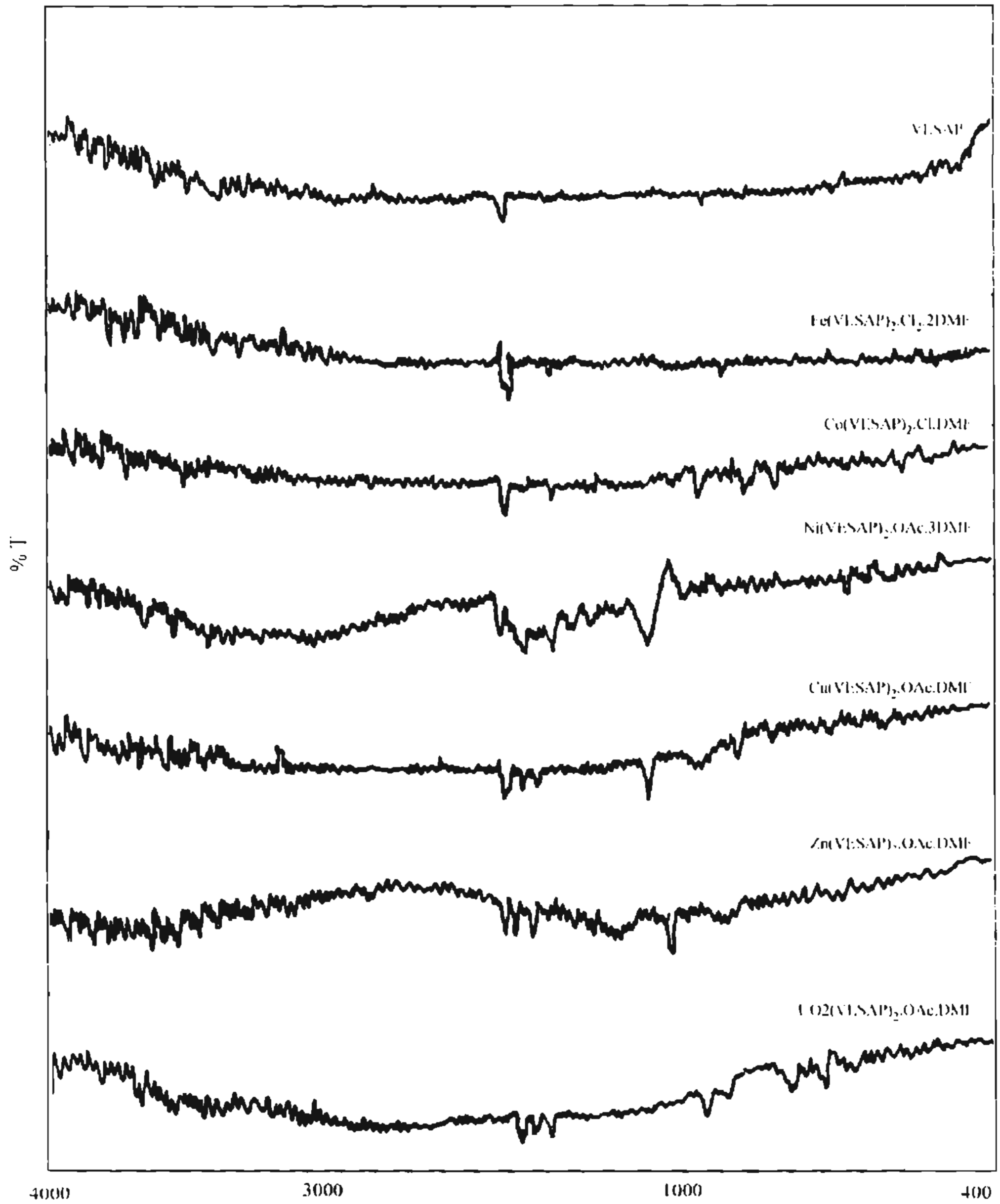


Figure 19: IR Spectra of VESAP and its complexes

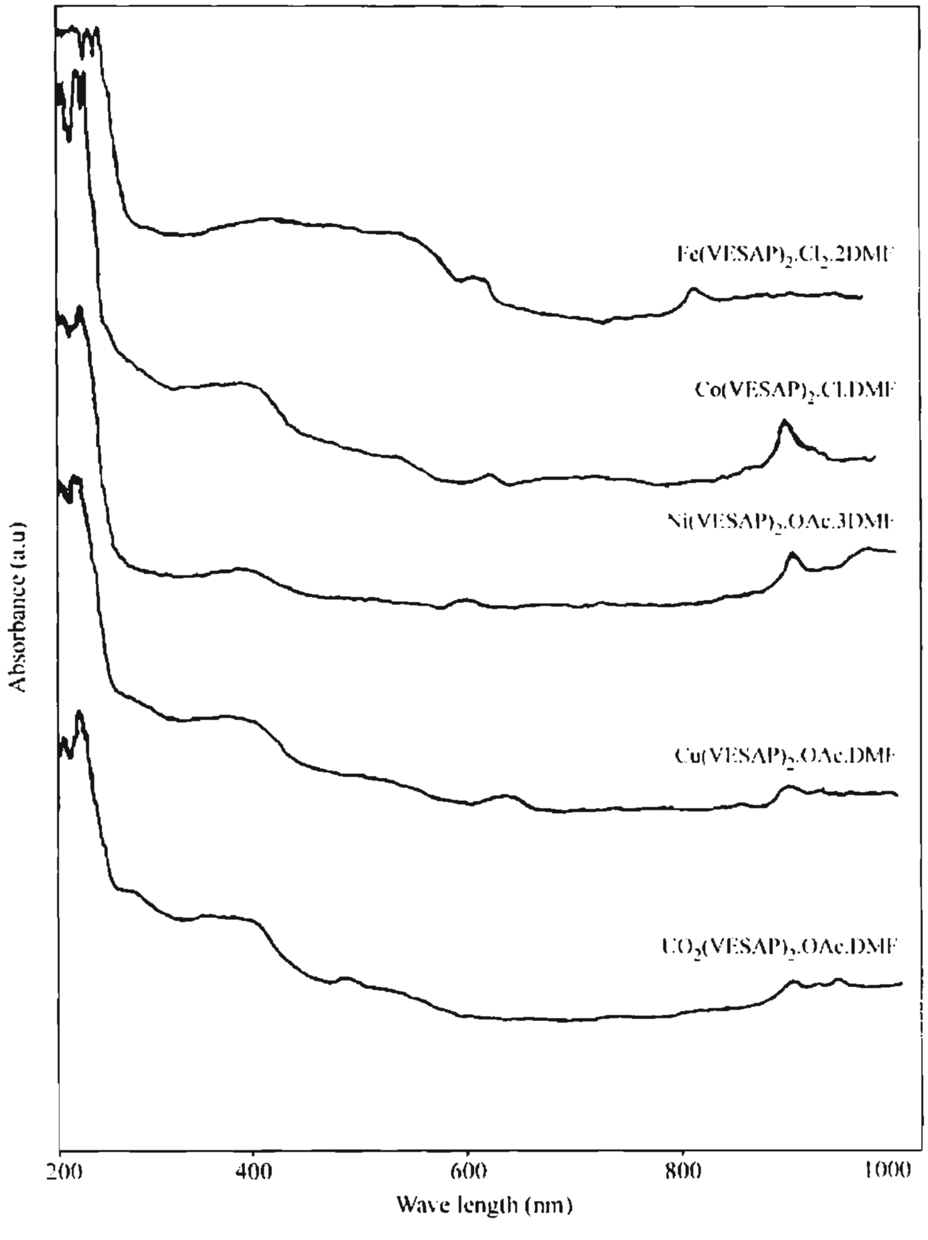


Figure 20: Electronic spectra of VESAP complexes

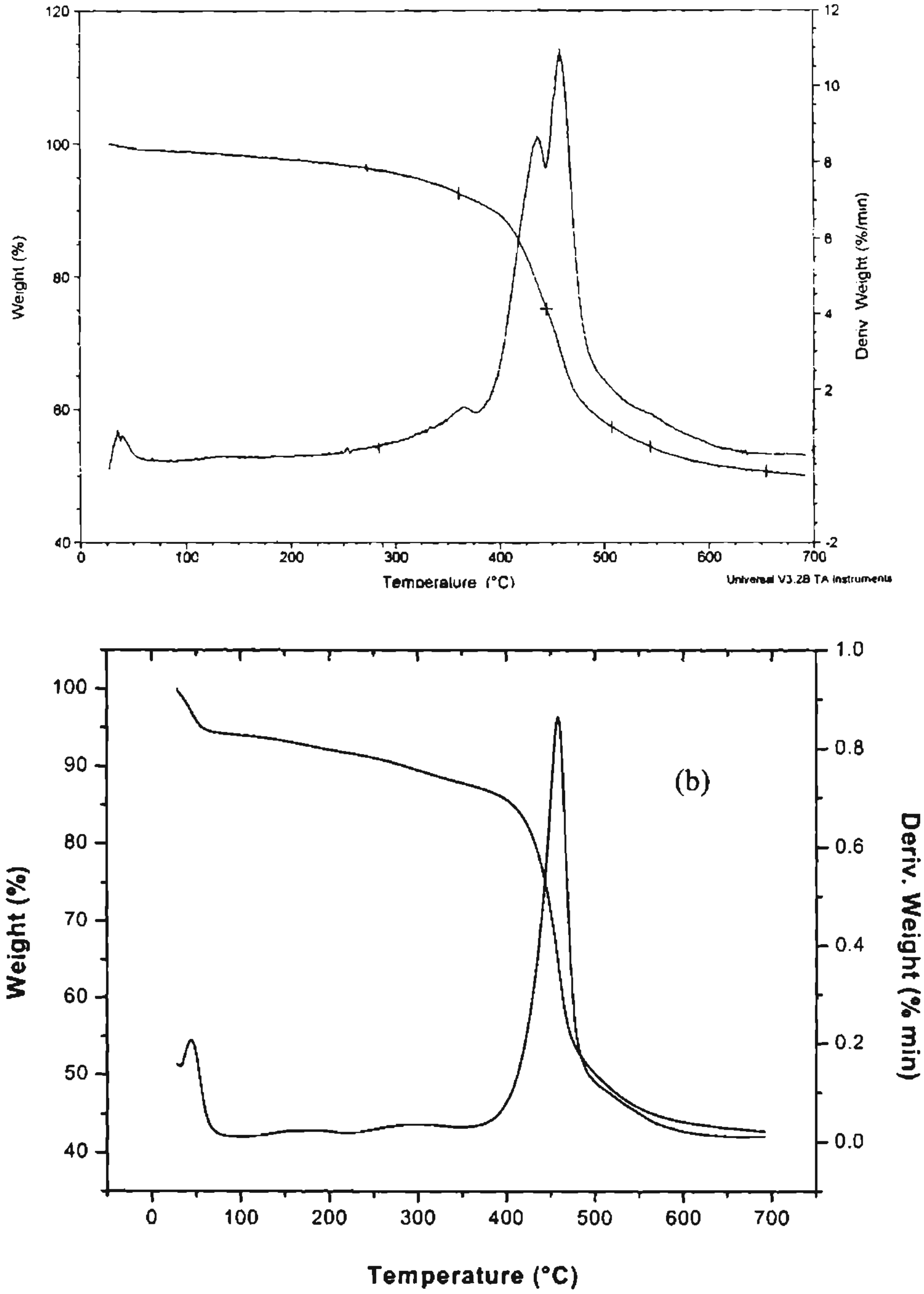


Figure 21 TG/DTG Curves of VESAP complex

(a) Cu, (b) Fe

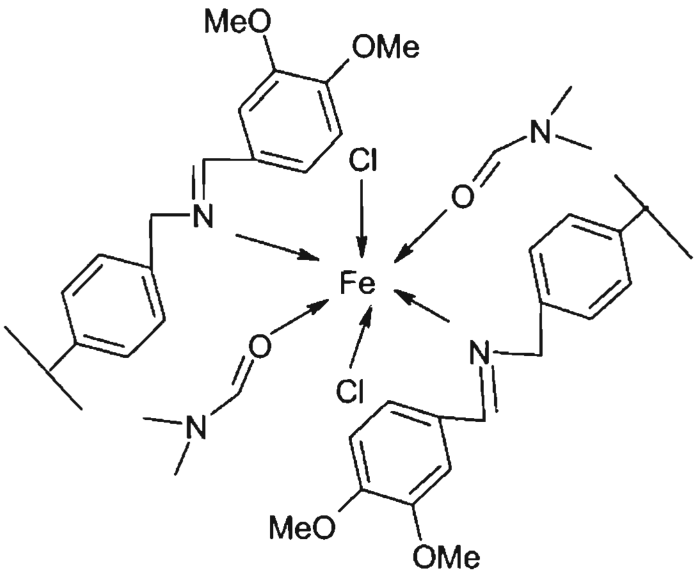


Figure 22: Structure of Fe(VESAP)$_2$.Cl$_2$.2DMF

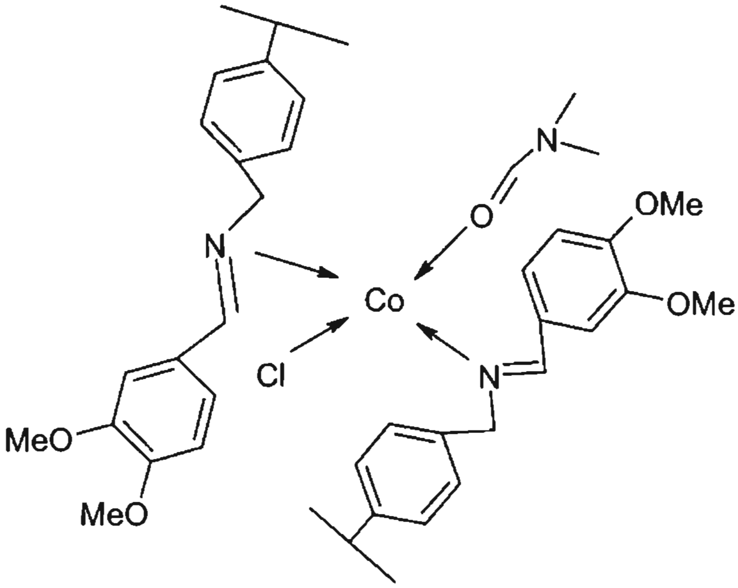


Figure 23: Structure of Co(VESAP)$_2$.Cl.DMF

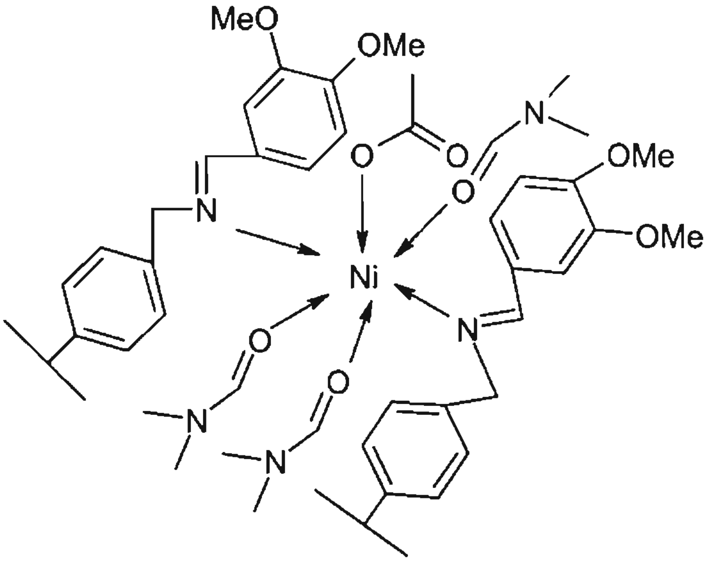


Figure 24: Structure of Ni(VESAP)$_2$.OAc.3DMF

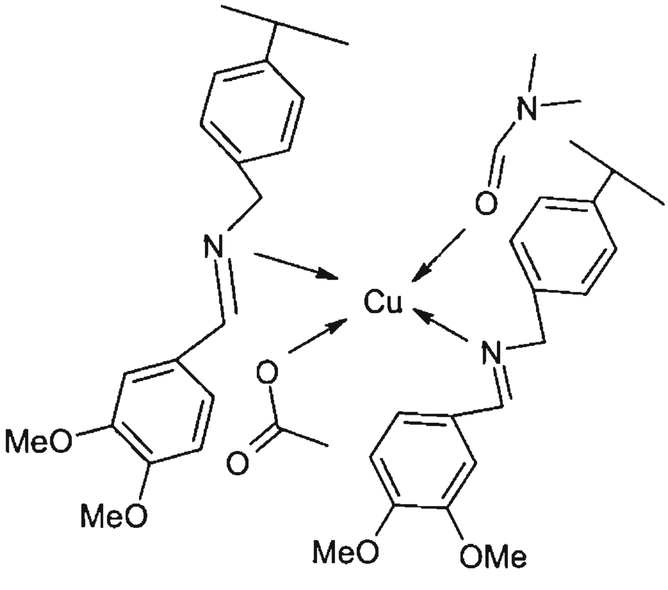


Figure 25: Structure of Cu(VESAP)$_2$.OAc.DMF

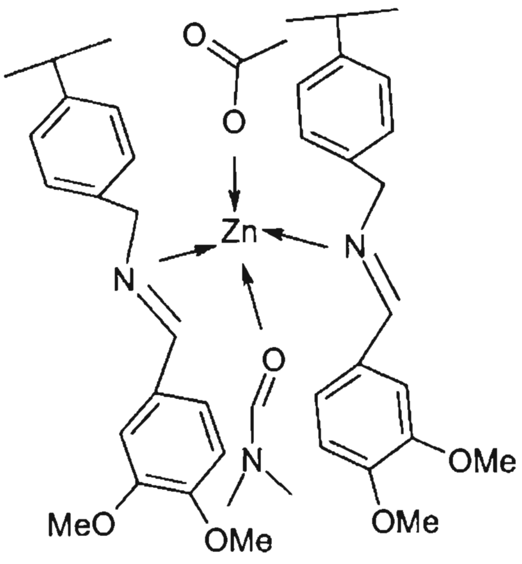


Figure 26: Structure of Zn(VESAP)$_2$.OAc.DMF

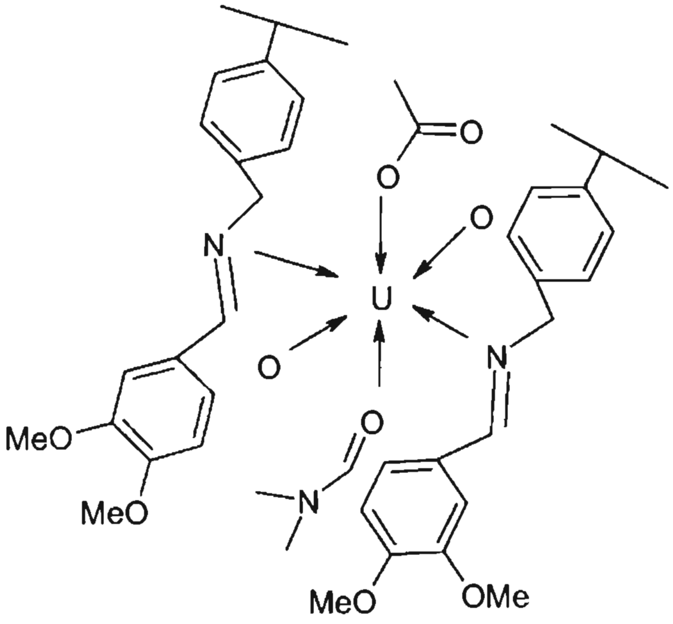


Figure 27: Structure of UO$_2$(VESAP)$_2$.OAc.DMF

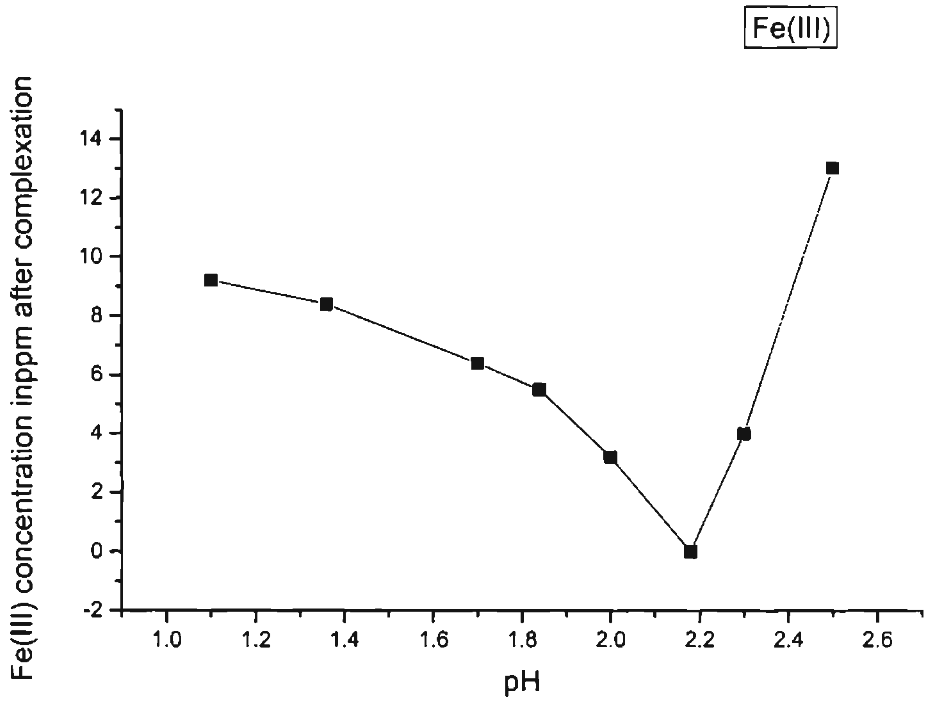


Figure 28: Effect of pH on the removal of Fe(III) using salicylaldehyde schiff base supported on amino methylated polystyrene

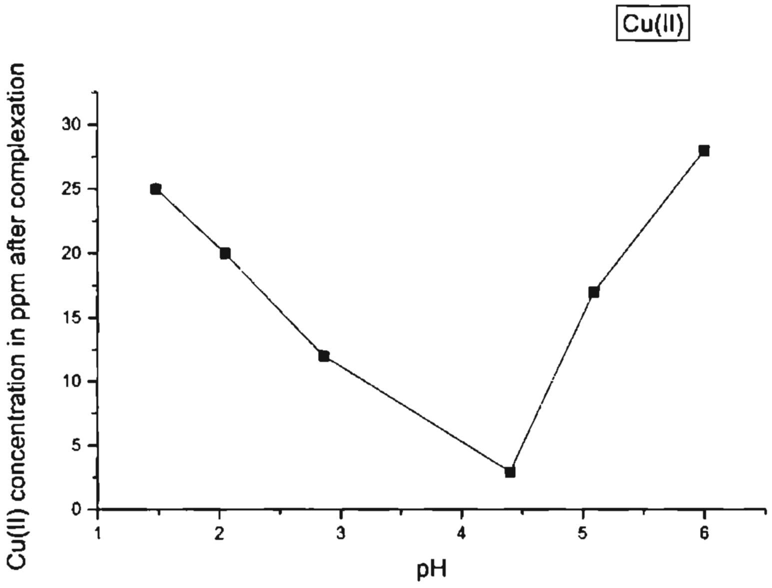


Figure 29: Effect of pH on the removal of Cu(II) using 2-nitro benzaldehyde schiff base supported on amino methylated polystyrene

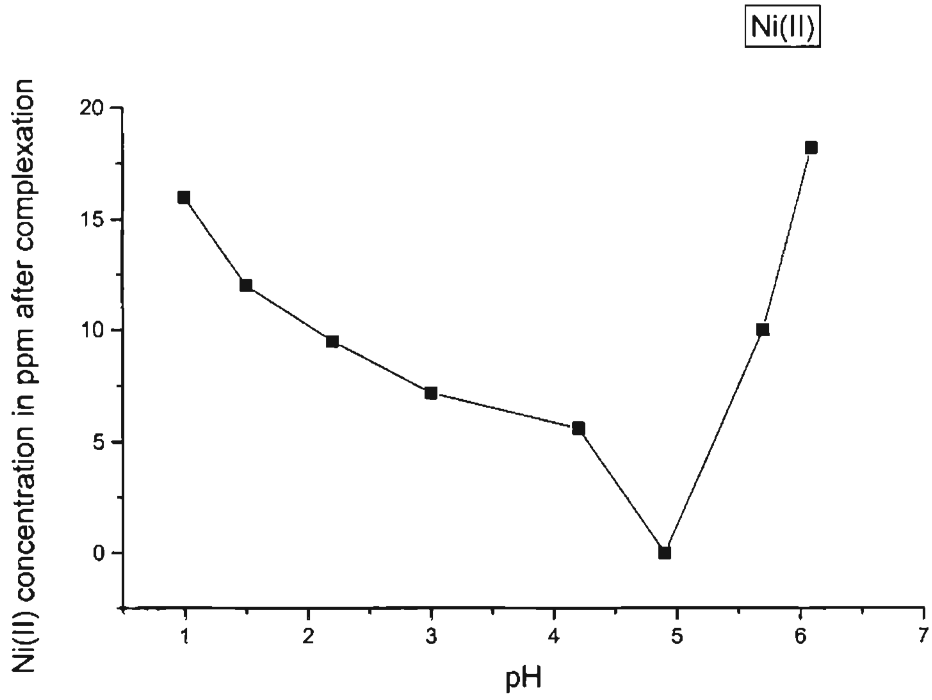


Figure 30: Effect of pH on the removal of Ni(II) using vanillin schiff base supported on amino methylated polystyrene

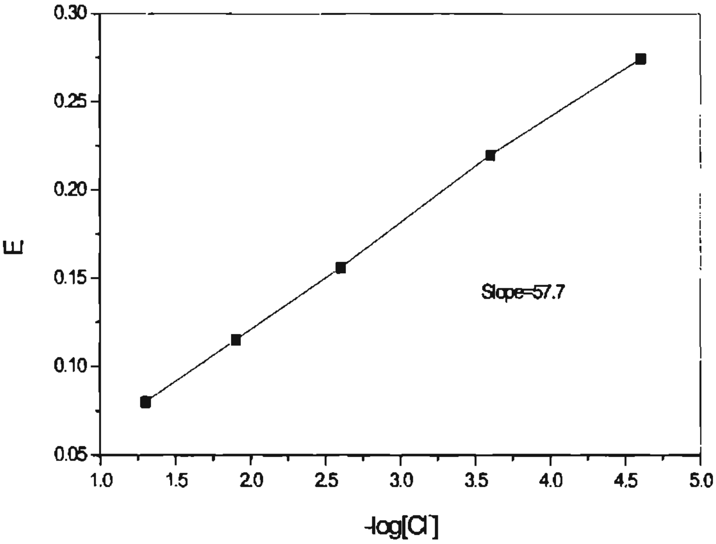


Figure 31: Plot of -log[Cl⁻] vs E

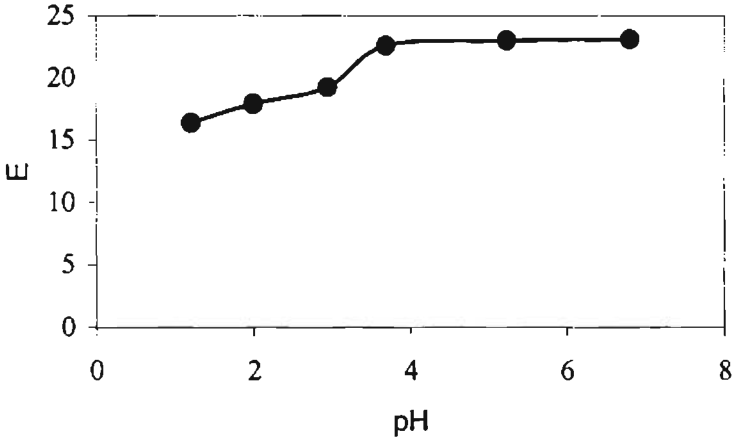


Figure 32: Plot of pH vs E

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