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STUDIES ON POLYMER COMPLEXONES

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by
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CERTIFICATE

Certified that the work presented in this thesis is based on the bonafide work done by Smt.Rita Mendez under my guidance in the Department of Applied Chemistry, Cochin University of Science and Technology and no part thereof has been included in any other thesis submitted previously for the award of any degree.

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PREFACE

Ion-exchange is well established as an analytical technique in the laboratory as well as a unit operation in industry. The applications of classical "ion" exchangers have reached a point of saturation due to their non-selective character. The concept of reactive ion-exchange involving chelation has initiated a spurt of activity in the synthesis and applications of selective polymer complexones. The selectivity of such polymer complexones could be further enhanced by controlling the spatial orientation of donor atoms to an obligatory pattern demanded by the metal ions. This area has received only scanty attention from researchers.

Here the results of the studies on the behaviour of two hydroxamic acid polymer complexones derived from poly-(styrene-co-maleic acid) crosslinked with DVB are presented. They have been characterised by physical and chemicals methods and their applications in the preconcentration and separation of metal ions have been probed. The nature of the bonding between the polymer bound functionality and the metal atom has also been investigated by IR, UV-Vis and ESR spectroscopy. The thermal analysis of the resins and their metal complexes has also been carried out with a view to evaluate the influence of the metal ions on the dynamics of their degradation.

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CHAPTER I

INTRODUCTION

1.1 GENERAL INTRODUCTION

The earliest reference to the ion-exchange process is found in the Holy Bible. Moses[1] succeeded in preparing drinking water from brackish water using tree bark which probably involved ion exchange according to modern concepts. In 1830 Thompson and Way, rediscovered cation exchange in soils[2]. The materials responsible for this phenomenon were found to be zeolites, clays, glauconites and humic acids[2,3]. These discoveries led to attempts to use such materials for water softening and to synthesize new products with similar properties.

The first synthetic ion-exchanger was prepared in 1903 by Harm and Rumpler[4]. The development of synthetic organic ion-exchange resins by Adams and Holmes laid the foundation for a new industry and a new unit operation[5]. Since then there has been hectic activity in the synthesis of ion-exchange materials based on a wide variety of polymer backbones. These exchangers soon surpassed the performance of inorganic ion-exchangers because of their favourable properties. The superiority of the organic ion-exchange resins is mainly due to their better chemical and mechanical stability, higher ion-exchange capacity, faster exchange kinetics and versatality. Apart from these the ease with which their properties like porosity, particle size, nature and number of fixed ionic groups, and degree of cross-linking could be controlled during synthesis adds to their increased use. Today nearly all current industrial and laboratory applications of ion-exchange are based on such resins.

Eventhough the scale and scope of organic ion-exchangers have grown enormously, there has been a resurgence of interest in inorganic ion-exchangers especially with the development of nuclear reactors and radiochemical engineering. They have better thermal stability and resistance to radiation[6]. Ion-exchange membranes are also of interest in many areas of biological and medical research[7].

During the period of the Second World War ion-exchange chromatography was developed. The first successful use of ion exchange chromatography was in the separation of transuranium elements obtained from fission products[8]. The next triumph of ion-exchange chromatography was the separation of rare-earth elements which constitute a large part of the fission products[9]. Ion-exchange chromatography also finds application in the separation of trace impurities from pure materials.

Today, ion-exchange is firmly established as a unit operation and is a valuable supplement to filtration, distillation and adsorption. Its applications range from purification of water from spent process and effluent streams, demineralisation of water, production of ultrapure water for microelectronics industry and recovery of valuable metals from industrial wastes[10]. Ion-exchangers also find use as catalysts and molecular sieves.

Organic polymers containing chelate-forming groups as exchanging functions were found to give better selectivity than conventional cation exchangers. The selective behaviour of these resins results from the enhanced stability of metal complexes on the resin. A large number of research papers have appeared during the last fifty years on the synthesis of organic ion-exchange resins with chelating functional groups.

The idea of memory complexones was put forward by Effendiev and Kabanov[11] and this paved the way for the synthesis of highly selective resins.

1.2 FUNDAMENTALS OF ION-EXCHANGE PROCESS

1.2.1 Ion-exchange equilibria

When an ion-exchanger is placed in a solution containing two counter ions A and B of like charges there will be an equilibrium set up between the exchanger and solution phases in which A and B are distributed to different degrees. This can be represented by an equation:

$$A_s + B_r \rightleftharpoons A_r + B_s$$

$$bA_s + aB_r \rightleftharpoons bA_r + aB_s$$

where subscript 's' denotes the solution phase and 'r' the resin phase.

The equilibrium constant for each of these equilibria is:

$$K_B^A = \frac{[A]_r\,[B]_s}{[B]_r\,[A]_s}$$

$$K_B^A = \frac{[A]_r^b\,[B]_s^a}{[B]_r^a\,[A]_s^b} \qquad (1.1)$$

where the terms in brackets indicate the ion concentration in mmoles ml^{-1} for the solution phase and in mmoles g^{-1} for the resin phase. This term K_B^A which is often called the selectivity coefficient depends on the experimental conditions and gives an idea of the preference of an exchanger for ion (B) over another ion (A)[12].

1.2.2 Distribution coefficient

The weight distribution coefficient, D_g for the exchanged ion A, is given by

$$D_g = \frac{[A]_r}{[A]_s} \frac{(\text{ mmoles of } A_r)\ (\text{ml solution})}{(\text{ mmoles of } A_s)\ (\text{g resin})} \qquad (1.2)$$

Volume distribution coefficient

$D_v = D_g \rho$ where ρ is the resin bed density

$$\rho = \frac{\text{grams of dry resin}}{\text{ml of resin bed volume}}$$

Selectivity coefficient can also be written as

$$Q_s = \frac{D_g B}{D_g A} \qquad (1.3)$$

1.3 GENERAL CHARACTERISTICS OF ION EXCHANGE RESINS

Generally, ion exchange resins are characterized by (i) nature of exchanging ion (ii) capacity (iii) swelling and moisture retention capacity (iv) porosity and (v) particle size.

1.3.1 Ion exchange capacity

The total capacity of an ion exchanger is usually represented as the number of equivalents of exchangeable ions per unit weight or volume of the exchanger. When given in milliequivalents per gram of dry H^+ form or Cl^- form of the resin it is referred as weight capacity and when expressed in terms of per millilitre of swollen bed it is called volume capacity. The volume capacity depends on the water content of the exchanger and hence on the degree of crosslinking.

A more practical expression of the capacity of a resin is given in terms of its actual performance under specified conditions of pH, solution concentration etc. and is called the operating capacity. It is expressed as the number of milliequivalents of functional group on one gram of the dry resin[13].

When used in columns, the number of effective exchange sites is given by the breakthrough capacity. It is found to be less than the maximum capacity and depends on the nature of the resin, particle size, flow rate and temperature.

The best way of characterizing an ion exchanger is by giving its weight capacity and pk of ionogenic group which can be determined by pH titration.

1.3.2 Swelling and water retension capacity

When an ion-exchanger is placed in water, the counter ions as well as the matrix bearing the fixed ions get hydrated and thus swells up. Due to dissociation of ions a concentrated electrolyte solution is formed inside the resin, which causes further swelling by osmosis and in this process the matrix stretches. Equilibrium is attained when the osmotic force counterbalances the mechanical restoring force of the matrix.

The moisture retention capacity depends on various factors. Swelling is more pronounced when fixed and counter ions show high tendency for hydration. The tendency of the resin to swell decreases with increase in crosslinking since the matrix becomes more rigid.

The moisture retention capacity helps to define its hydrophilic character and to indicate effective pore size. Generally, if the equilibrium moisture retension capacity is below 50%, free diffusion into and out of the structure is limited to simple inorganic ions and above 50% much larger ions can move through the resin matrix.

1.3.3 Porosity

Porosity of an ion-exchange resin is an index of the rate of exchange of ion of limiting size which can penetrate a resin matrix. Porosity of a solid may be defined as the ratio of the volume of interstices of the material to the volume of its mass. The effective pore diameter of an ion-exchange resin can be measured by determining the exchange capacity with ions of various size.

1.3.4 Particle size

The particle size of the ion-exchange resin influences the rate of reaction. Procedures such as sieving, elutriation, density measurements and microscope measurements are commonly employed to evaluate particle size.

1.4 REACTIVE ION-EXCHANGERS

Interest in reactive ion-exchangers was aroused by the work of Helfferich[14]. In a classical ion-exchange resin the overall process is exclusively re-distribution of ions, exchanging ions retaining their identity. Reactive ion-exchange procedure comprises of one or more ion-exchange steps accompanied, preceded or succeeded by reactions resulting in the formation of different chemical species, and by consumption or transformation of initially present species. Thus every reactive ion-exchange process includes at least one ion-exchange step and one reaction which may occur in solution or at the ion exchanger boundary or inside the exchanger. Electroneutrality, Donnan effect, species size, acid-base properties of the species and the exchanger, etc. influence reactive ion-exchange. Specific interactions will affect resin selectivity for different species, the extent depends on the type of ion-exchange material. Sign and magnitude of charge are usually most important in determining ion exchange behaviour although size and specific interaction also play an important role.

Helfferich distinguished four different types of reactions taking place in reactive ion-exchangers (RIEX)[14].
Type 1: In the first type, ion-exchange takes place without resultant change in charge, e.g., reactions of metal ions with neutral chelating agents.

$$Fe^{2+} + 1,10\text{-Phenanthroline} \longrightarrow [Fe(Phen)]^{2+}$$

Type 2: Reactions resulting in an increase or decrease in the number of charges of the same sign belong to the second. e.g., Chelate formation of metal ions with ligands of low charge.

$$M^{n+} + L^{1-} \longrightarrow (ML)^{(n-1)} \qquad (n > 1)$$

Type 3: Reactions involving removal of charge resulting in neutral species and vice versa. e.g., Acid-base reactions and metal chelate formation.

$$RCOO^- + H^+ \longrightarrow RCOOH$$

$$RN(CH_2COO^-Na^+)_2 + Ni^{2+} \longrightarrow RN(CH_2COO)_2Ni + 2Na^+$$

Type 4: In the last type, the charge in the ion-exchanger is reversed. Thus charge reversal converts counter ions to co-ions or vice versa. e.g., Metal complexing with common anions.

$$Co^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-}$$

1.4.1 Objectives of RIEX

The general objectives of RIEX fall mainly in the five categories given below:

1. Isolation, concentration, or removal of individual species from diverse mixtures and matrices. Good selectivity and specificity are required to achieve successful isolation, e.g., extraction of precious metals from sea water, isolation of uranium from ore leachings and removal of mercury from waste stream.

2. Separation from one another of several very similar species. e.g., separation of lanthanides or aminoacids.

3. Total removal or concentration of groups of ionic species as in water demineralization, or ionogenic species such as weak organic acids. Here selectivity for individual species is not important.

4. Degradation of toxic chemical or biological species by transformation into innocuous species. e.g., cleavage of organophosphorous pesticide residues prior to landfill disposal.

5. Catalysis of organic reactions, e.g., acid catalyzed esterification using strong acid cation exchanger in the hydrogen form.

1.4.2 Thermodynamics of reactive ion-exchange

The free energy change (ΔG) of an ion-exchange reaction $A_{resin} + B_{solution} \rightleftharpoons A_{solution} + B_{resin}$

$$\Delta G^{B/A}_{total} = (\Delta G^{B}_{coulomb} - \Delta G^{A}_{coulomb}) + (\Delta G^{B}_{solvation} - \Delta G^{A}_{solvation})$$

$$= -RT\ln k^{B/A}$$ where k is selectivity constant.

The difference between the two coulombic terms is small hence ΔG is mainly due to the solvation term. Experiments have shown that $|\Delta G|$ for spontaneous reactions, such as chelate formation, is small compared to $|\Delta G^{B/A}_{IEX}|$. Thus ion-exchange reactions which yield an overall negative ΔG_{total} of sufficient magnitude is selected for the separation of two ions A and B.

$$\Delta G^{B/A}_{total} = \Delta G^{B/A}_{exchanger} + \sum \Delta G^{B/A}_{reaction}$$

Since $(\Delta G)_{reaction} \gg (\Delta G)_{exchanger}$

$$\Delta G^{B/A}_{total} \backsimeq \Delta G^{B/A}_{reaction}$$

From the value of $\Delta G^{B/A}_{total}$ we can predict the effectiveness of separation of two ions on a reactive ion-exchange column.

1.4.3 Kinetics of RIEX

One of the important kinetic aspects of RIEX is the rate of ion-exchange process. In classical ion-exchange process the rate is controlled by particle diffusion, film diffusion or both. The kinetics of RIEX have been treated systematically by Helfferich and grouped into four major types[15]. In type 1 process the counter ion released from the resin is consumed by chemical reaction as soon as it enters the solution.

e.g., $\overline{H}^+ + OH^- \longrightarrow H_2O$

With film diffusion the rate controlling step which is diffusion of both the counter ion and accompanying co-ion from solution phase, affects the ion-exchange kinetics to a great extent. In type 2 and 3 the counter ion originating from the solution is consumed by chemical reaction in the resin phase.

e.g. Type (2) $\overline{RCOO^-} + H^+ \longrightarrow \overline{RCOOH}$

Type (3) $\overline{Chel^{2-}Ni^{2+}} + 2H^+ \longrightarrow \overline{Chel^{2-}(H^+)_2} + Ni^{2+}$

Here the rate is controlled by diffusion through the shell surrounding the exchanger which consists of undissociated groups. This is a slow process and depends on solution concentration.

Reactions of co-ions from solution with unionized fixed inorganic groups in the resin are grouped under type 3.

e.g. $\overline{RCOOH} + OH^-, \; Na^+ \rightarrow \overline{RCOO^-Na^+} + H_2O$

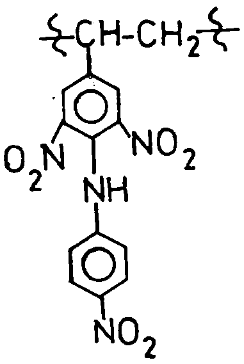
$$\overline{Chel^{2-}Ni^{2+}} + 4Na^+, \; Y4^- \; (EDTA) \longrightarrow \overline{Chel^{2-}(Na^+)}_2 + (Ni_Y)^{2-} + 2Na^+$$

Here co-ion diffusion can be the rate controlling step, and film diffusion control is ruled out. In such cases moderately slow exchange is usually observed. Thus it is found that only type 1 process is fast and all others which are by the core-shell diffusion mechanism are slow.

1.5 POLYMER COMPLEXONES - AN OVERVIEW

The poor ion selectivity of conventional ion-exchangers has led to the development of a new class of reactive ion-exchange polymers called polymer complexones. These are functionalized polymers containing chelating groups which under experimental conditions chelate with selected ionic species.

The development of polymer complexones began with the report of Erlenmeyer and Dahn[16] that mixtures of various cations could be chromatographed on a column of powdered 8-hydroxyquinoline. Griesbach's concept of selective ion-exchange by pH control[17] and the use of complexing agents were important factors which helped the development of chelating ion-exchangers. Using this concept Skogsied[18,19] succeeded in synthesizing the first potassium-specific resin. His work was based on the observation that all nitrated secondary amines selectively bind potassium ions and hence if this group could be introduced on a macromolecular framework the resulting resin would possess potassium-selective ion-exchange characteristics. Skogseid synthesized the first of such resins, a polystyrene derivative containing dipicrylamine groups[19] specific for potassium ions having the structure



This was followed by the introduction of chelating ion-exchange resins incorporating a variety of chelating groups on different polymer matrices. Mellor[20] and Gregor[21] described the preparation of several such resins containing various chelating groups.

The work on chelating ion-exchangers showed that high selectivity could be achieved if the chelating group was capable of forming a highly stable 1:1 complex with the metal ion[22]. Kennedy and Davies[23] observed that thorium(IV), iron(III) and uranyl(VI) formed relatively strong complexes with phosphates and phosphonates, whereas alkaline earth and bivalent transition metal ions and lanthanides formed either weak complexes or salts.

Many polymers with special functional groups have been prepared but they are characterized by low capacity, slow exchange rates, large volume changes and lack of expected selectivity. Bayer stressed that ligands attached to polymers show greater selectivity than in their unanchored solution form, due to their restricted geometric arrangement in the resin[24].

The synthesis of a chelating resin having iminodiacetic acid as functional group anchored on a polystyrene matrix was reported by Thomas[25]. Since then a number of publications have come out and patents were obtained for the manufacture of this chelating ion-exchanger. Dowex A-1 containing iminodiacetic acid was the first commercially available chelating resin[26]. These resins suffered from many drawbacks such as slow exchange kinetics and pronounced swelling. In spite of these drawbacks chelating resins containing iminodiacetic acid functional group have become very popular and are commercially available under different trade names. Some of the commercially available chelating resins are listed in table 1.

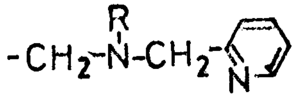
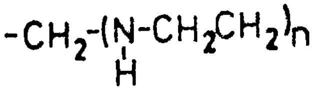
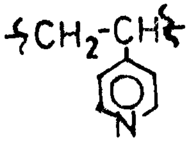
A large number of chelating ion-exchange resins incorporating a host of ligands such as amino carboxylic acids, hydroxamic acids, oximes, pyridine carboxylic acids, acid hydrazides, arsonic acids, phosphoric acids, dithiocarbamates, thiols, Schiffs bases, crown ethers and cryptands have been incorporated into organic and inorganic polymeric matrices.

1.6 SYNTHESIS OF CHELATING ION-EXCHANGE RESINS

The two important aspects of the synthesis of chelating ion-exchange resins are formation of a polymer matrix and its functionalisation. The properties of the chelating

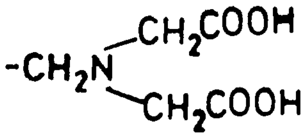
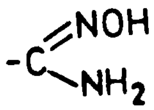
Table 1.1

Some commercially available chelating ion-exchange resins

Sl.No.	Chelating Group	Nature of chelating group	Polymer matrix	Commercial Name	Manufacturer
(1)	(2)	(3)	(4)	(5)	(6)
1.		Weakly basic group (N-alkylated picolamine)	Polystyrene-DVB	Dowex XF-4195	Dow Chemical
2.	$-CH_2NH-(C_2H_4NH)_n-H$	Basic(Polyamine)	Polystyrene-DVB	Diaion CR-20	Mitsubishi
3.	 $-CH_2-(\underset{H}{N}-CH_2CH_2)_n$	Ethylenimine	Poly(ethylene-mine)	Diaion CR-40	Mitsubishi
4.		Basic pyridine	Polyvinyl-pyridine-DVB	Sumichelate CR-2	Sumitomo

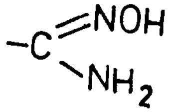
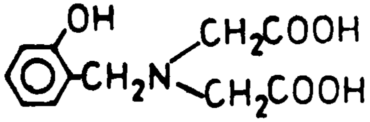
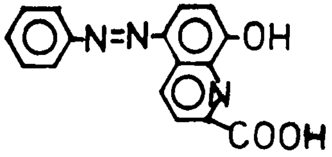
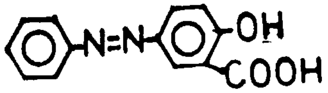
(contd...)

Table 1.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
5.	 $-CH_2N{<}^{CH_2COOH}_{CH_2COOH}$	Iminodiacetic acid	Polystyrene-DVB	1. Dowex A-1	Dow Chemical
				2. Duolite ES466	Diamond Shamrock
				3. Chelex-100	Biorad
				4. IMACSYN 101	Diamond Shamrock
				5. IRC-718(XE-318)	Rohm & Hass
				6. Wofatit MC 50	VEB Chemie-Kombinat Biterfield
				7. Permutit S-1005	Permutit Co.Ltd.
				8. TP-207	Bayer, A.G.
				9. ANKB-5D	
				10. Ligadex-1	Reanel
			Glycidylmethacrylate-ethylene dimethacrylate	11. GMA-EDMA	--
			Polyacrylic acid-DVB	12. Diaion CR-10	Mitsubishi
6.	 $-C{<}^{=NOH}_{NH_2}$	Amidoxime	Polyacrylic acid-DVB	Duolite ES 346	Diamond Shamrock

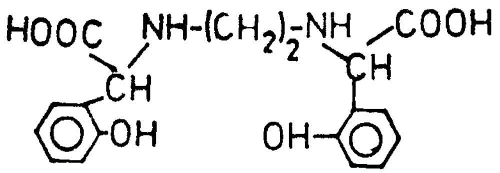
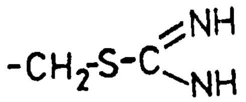
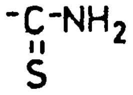
(contd...)

Table 1.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
7.		Amidoxime	Polyacrylonitrile fiber	Polyorgs VII	--
8.		O-hydroxybenzyl iminodiacetic acid	Phenol-formaldehyde	Unicellex x UR-50, UR-40, UR-30, UR-20, UR-10	Unitik Ltd.
9.		8-hydroxyquinoxaline	i) Cellulose	Hyphan cellulose	--
			ii) Poly(hydroxyethylmethacrylate-co-ethylene dimethaacrylate)	Spheron oxine 1000	Lachema, n.p.
10.		Salicyclic acid	,,	Spheron salicyl 1000	,,

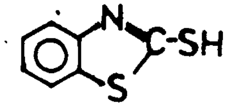
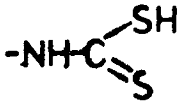
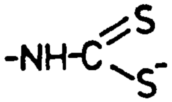
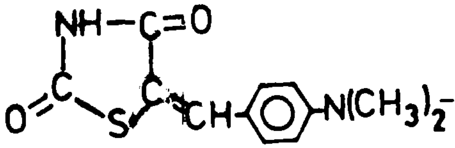
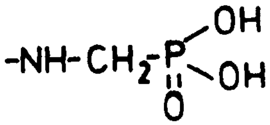
(contd...)

Table 1.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
11.			Styrene-DVB	Polystyrene-Chel-1	--
12.	 $-CH_2-S-C(=NH)-NH$	Isothioruonium	Polystyrene-DVB	i) Srafion NMRR	Ayalon
				ii)_ Ionac SR-3	Ionac, Sybrom. Chem.
				iii) Monivex	--
			Cellulose-acrylonitrile	Mtilon T	--
13.	 $-C(=S)-NH_2$	Thiosemi-carbazide	Poly(hydroxyethyl methacrylate-co-ethylene-dimethacrylate)	Spheron thiol 1000	Lachema, n.p.
14.	$-CH_2SH$	Thiol	Polyamino-phenolic condensate	Polyorys IX	--

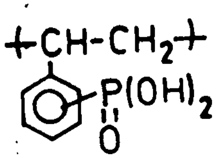
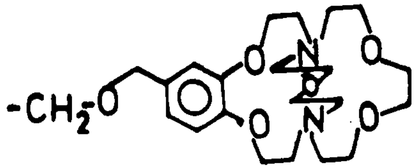
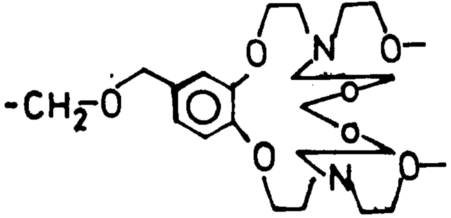
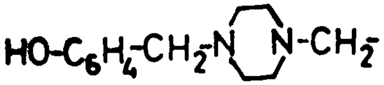
(contd...)

Table 1.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
15.	-SH	Aromatic thiol	Polystyrene-DVB	i) IMAC TMR ii) Duolite ES 465	Diamond Shamrock ,,
16.		Thiol	Polyaryl-amide	Polyorys X11	--
17.		Dithiocarbamate	--	Misso ALM 525	Nippon soda
18.		Dithiocarbamate	Polyacrylic acid	Sumichelate Q-10 R	Sumitomo
19.		--	Polystyrene-DVB	Polystyrene DMBAR	--
20.		α-aminophosphonate	Polystyrene-DVB	Duolite ES 467	

(contd...)

Table 1.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
21.	——	Aminoallyl phosphonic acid	Polystyrene-DVB	Sumichelate MC-90	--
22.		Phosphorylated dibasic polystyrene	Polystyrene	Duolite C-63	--
23.		Cryptand	Polystyrene-DVB	Kryptotix 221 B	Parish Chem.Co.
24.		Cryptand	Polystyrene-DVB	Kryptofix 222 B	,,
25.		Phenol-piperazine	--	Sirorez-Cu	Csiro, Australia

sorbent depends on the nature of polymer matrix, porosity, pore characteristics and the nature of functional groups capable of interacting with metal ions.

1.6.1 Polymer matrix

Usually two types of matrices are considered, i.e., inorganic and organic. Chelating sorbents based on inorganic supports have been reviewed[27,28]. They have high mechanical, thermal, radiation and chemical stability but have only low capacity and show poor sorption kinetics[29]. Silica is among the most extensively used inorganic supports[28]. Among the naturally occurring polymers used as supports, modified cellulose has found wide use[30,31]. Chitin (poly(N-acetyl-D-glucosamine) and its deacetylated derivative (chitosan) form important naturally occurring chelating polymers[32-35].

Most of the chelating sorbents are based on synthetic organic matrices. These matrices are obtained by either condensation or addition reactions[35-37]. Linear polystyrene has been used for the synthesis of a number of chelating sorbents, mainly polyazoderivatives. These sorbents have high sorption capacity, good kinetic properties and high selectivity. Based on this matrix, sorbents with PAR, imidazole, azorhodanine, 8-mercaptoquinoline, sulfonitroaminophenol etc. have been synthesised[38,39].

The most widely used sorbents are based on co-polymers of styrene and DVB. Their better permeability to the reaction medium facilitates the synthesis of sorbents based on them and ensures rapid sorption kinetics.

Hydrophilic macroporous co-polymers of glycidyl-methacrylate-ethylene-dimethacrylate (GMA-EDMA) as matrix and chelating groups such as iminodiacetate, ethylenediamine, mercaptomethyl etc. have found industrial applications[40,41]. Another matrix used is hydroxyethylmethacrylate-ethylene dimethacrylate with 8-hydroxy quinoline, salicyclic acid, and thiol groups. They have the advantage of high porosity and large internal surface ensuring rapid attainment of equilibrium[42,43]. Other matrices include polyethylene polyamine, polyvinyl alcohol, acrylonitrile etc.

When the synthesis of sorbent is accomplished using ligands, the polymer matrix is formed during polymerisation. Polymer complexones so obtained include polycondensation products of phenols and amines with aldehydes, chelating vinyl monomers, etc.

1.6.2 Chelating groups

The groups taking part in the formation of chelate rings include nitrogen, oxygen and sulfur atoms. Nitrogen is present in the form of primary, secondary and tertiary amines, nitro, nitroso, azo, diazo, nitrile, amide etc. Oxygen is usually in the form of phenolic, hydroxyl, carbonyl, keto and phosphonyl groups and sulphur as thiols, thioesters, thiocarbamates and disulphide groups. Chelating groups are usually capable of interacting with a large number of metals, but the stability of the chelate complex formed differs and depends on sorption conditions. This difference is used for selective extraction of metals.

1.6.3 Functionalisation of the matrix

For the incorporation of a suitable chelating group into polymer matrix, it should be capable of getting substituted in the polymer matrix, should be stable to reagents and conditions used and should be compact so that chelating ability is not hindered by polymer matrix. The co-ordinating atoms should be oriented in such a way that an unstrained chelate ring is formed. Preferably the functionalisation must be achieved in the minimum number of steps.

Functionalisation of polymer matrix is done by direct condensation of monomers containing desired functional groups, chemical modification of preformed polymers or a combination of both methods. Various methods for functionalisation by polymer modification have been reviewed[44-46].

1.6.4 Chelating sorbents by polycondensation

This is the simplest method for the synthesis of polymer complexones. They are formed from ionic organic reaction from small functionalised monomers by the elimination of alcohol or ammonia forming new C-C, C-N or C-O bond. Thus phenols and amines interact with aldehydes to form polymeric compounds containing chelating groups. Depending on the nature of the monomers used linear, branched or three dimensional structure results. These sorbent usually suffer from the disadvantage of uncertainty in their structure, insufficient selectivity, and slow sorption rate. Still polycondensation method is being used for the synthesis of new chelating sorbents[47,48].

1.6.5 Chelating sorbents by polymer modification

The method involving incorporation of chelating groups into preformed polymer is preferred to other methods, since polymers of desired characteristics can be used as starting materials.

In the case of cellulose, reactive groups are present in the polymer which form complexes with metal ions without the matrix undergoing substantial change. The reactivity of hydroxyl groups is utilized to prepare derivatives like aminobenzene, tosyl, epoxy and cyanuric cellulose which in turn react with monomeric compounds containing chelating groups. Diazotisation of cellulose aminobenzene derivatives followed by coupling with compounds containing chelating groups is also employed[49,50].

Sorbents based on linear polystyrene were synthesized from aminopolystyrene by diazotization and coupling the diazoderivatives with compounds containing chelating groups[51]. Similar reactions are used to synthesize sorbents based on styrene-DVB matrix[52-54]. Chloromethylation of these resins followed by interaction of the product with different monomeric compounds containing chelating groups is a widely used technique to produce polystyrene-based chelating resins.

1.6.6 Chelating exchanger based on derivative of polyvinylimidazole

Studies by Green and Jaskulla[55] have revealed the chelating properties of sorbents based on polyvinylimidazole. Here the donor atom is present in the matrix itself and other functional groups are introduced during polymerisation. They prepared a number of resins by treating the halomethylated copolymer of vinylimidazole and divinylbenzene with a variety of reagents containing nitrogen and sulfur atoms[56].

1.6.7 Chelating sorbents by polymerisation of vinyl compounds containing chelating groups

Vinyl pyridine sorbents have found extensive application and are synthesized by polymerizing vinyl compounds containing chelating groups like vinyl 8-hydroxyquinoline or imidazole-carboxylic acid with divinylbenzene. These sorbents are rarely used medium of synthesizing the parent vinyl compounds containing chelating groups.

1.6.8 Fibrous polymer complexones

The usual practice is to use ion-exchangers in bead form. This puts some operational constraints in their applications. Recently polymer complexones have been produced as fibres possessing large surface area with resultant faster sorption kinetics and higher capacity. Fibrous sorbents should have sufficient mechanical strength and the active groups and the matrix should be chemically stable. Fibres based on cellulose, polyvinylalcohol, polyacrylonitrile and polystyrene have been synthesized[56-58]. These fibres suffer from poor mechanical stability. Yoshioka synthesized fibrous chelating exchangers with $-N(CH_2COOH)_2$ and $-N(CH_2CH_2COOH)_2$ groups attached to polystyrene-polyproylene matrix[59]. These chelating resins have high mechanical strength and can be converted to filament, cut fibre, fabric, felt or chip.

1.6.9 Memory complexones

Of special interest are methods of synthesizing sorbents pre-designed for a metal ion of interest. Effendeiv et al synthesized a polymer complexone with macromolecular pre-arrangement of monomer residue favourable for selected ions[59,11]. Their method involved complexation of the desired metal ion with the functionalised linear polymer. The macromolecules still mobile enough, take conformation favourable for interaction with the ion. The metal ion bound-linear polymer is fixed at the optimum conformation by crosslinking. On removing the template ion the polymer preserves its ability to chelate selectively the metal ion that was used as template before crosslinking. Studies have shown that in all cases the sorbents exhibited high selectivity with respect to metal ions for which they were prearranged[60,61]. A memory complexone of this type was synthesized using diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) as monomers and N,N-methylene diacrylamide as crosslinking agent which was selective towards copper ions.

1.7 PHYSICOCHEMICAL PROPERTIES OF POLYMERIC COMPLEXONES

Polymer complexones are characterised by their physicochemical properties like acidic and basic functionalities, sorptive capacity and selectivity under various operating conditions. Other important properties to be considered are swelling, chemical and mechanical stability and possibility of regeneration for repeated use.

1.7.1 Acidic and basic properties

Polymeric chelating sorbents are usually polyfunctional and contain residual ion-exchange groups apart from the chelating groups. The acidic and basic properties of the functional groups of the exchanger affect the sorption properties and selectivity. The acidic and basic groups are characterised by their dissociation constant and the chelating groups by their number in unit mass.

1.7.2 Sorption capacity

Polymeric complexones sorb metal ions from solution by chelate formation. Since ion-exchange groups are also present metal uptake by exchange also takes place. Polymeric complexones are characterized by sorption capacity which gives the extent of chelate formation with the metal ion. It depends on the number of chelating groups, nature of polymer matrix, structural peculiarities of the matrix, and experimental conditions. Sorption capacity is expressed as milligram or millimoles or milliequivalents of the metal per gram of the sorbent.

1.7.3 Complexing properties and selectivity

The ability of a chelating resin to form complex with metals depends on the nature of the ligating groups in the sorbent and the metal ion. The complexing groups interact with metal ions via co-ordinating bonds. Spectroscopic studies using IR, UV-Vis and ESR spectroscopy have shown that the co-ordination of metal ion with donor atoms results in the formation of chelate rings[62,63]. The complex formation can be written as a competitive reaction.

$$M^{n+} + nHL \rightleftharpoons MLn + nH^{+}$$

where M and L represent the metal and ligand respectively. Since the equilibrium involves H^+ ions the degree of complex formation can be controlled by pH. The stability of metal-ligand complex increases with increasing basicity of the ligand.

The stability of complexes formed in a chelating sorbent phase is characterised by its stability constant which is useful for estimating the selectivity of the sorbent and its potential in bringing about separations. It is difficult to evaluate the stability constant K_{MR} of a reaction

$$M^{2+} + H_2R \rightleftharpoons MR + 2H^{+}.$$

An alternative is to employ the stability constant of the complex in aqueous solution (K_{ML}) with a model ligand having the same functional groups as on the resin[64,65]. Two methods widely used for measurement of K_{MR} are (i) ligand competition method which involves competition for the metal ion by the resin and a suitable ligand in solution under alkaline condition and (ii) the proton competition method. This is based on the competing reactions of metal ions and protons for the resin in acid solution of pH 2 to 4[66,67].

The difference in the stability of complexes formed during sorption is reflected in their selectivity with respect to individual metal ions. This difference in selectivity serves as the basis for the selective concentration and separation of metal ions. The selectivity of chelating exchangers for different ions is quantitatively expressed as the ratio of their stability constants. It depends on the conditions of sorption, pH of solution, concentration and speciation of metal ions in solution which is controlled by the presence of salts and ligands in solution. Chelating sorbents preserve their selectivity to a metal ion in presence of other ions and hence are often used to extract microelements from complex solutions. The selectivity of chelating sorbents for metal ions can be enhanced by the presence of other complexing agents and hence can be advantageously used in the separation of metal ions.

1.7.4 Kinetic properties

Application of polymeric sorbents especially in the separation of metal ions depends to a considerable extent on their kinetic characteristics. For clean and rapid separations apart from high selectivity and sufficient sorption capacity, complexones should have fast sorption kinetics.

The sorption kinetics depends mainly on the nature and properties of polymeric matrix. Complexones made of polymeric matrices of high porosity and hydrophilicity possess improved kinetics. Special techniques have been used to synthesize sorbents having good kinetic properties[44,68].

1.8 APPLICATION OF POLYMER COMPLEXONES

Polymer complexones find wide applications in analytical chemistry and in industry. High selectivity of chelating sorbents together with advantageous sorption kinetics enable the extraction of trace metals from their complex solutions and preconcentration from large volumes of lean solutions. They are also used for the separation of metal ions by ion-exchange chromatography.

The possibility of selective concentration of metals from mixtures is based on the difference in the stability of the complexes formed by them with the chelating polymer. For achieving selectivity one has to choose sorbents with specific chelating groups as well as optimum conditions regarding pH, temperature and the presence of complexing agents.

Preliminary concentration with the help of chelating sorbents raises the sensitivity and reliability of determining elements in various samples. Chelating sorbents retain their selectivity even in presence of high concentrations of alkali and alkaline earth metals. Hence they have been used for the concentration of micro-elements from sea, river and mineral waters[69]. Polymer complexones with different chelating groups are used to determine toxic metals in natural waters. Sorbents with dithiocarbamate and mercapto groups have been used to concentrate traces of Hg(II). Hydrophillic glycolmethacrylate gel with thiol group have been used for the separation of Hg, Ag, Sb and Bi from mineral acid solutions[70-72].

Many methods have been used for controlling pollutants in industrial effluents. Polymer complexones are effective for the removal of toxic metals like Hg(II), Cd(II), Pb(II) and As(III) even in $\mu g\ ml^{-1}$ level and find promising applications in applied analysis. Methods have been developed for the extraction of precious metals like Au, Pt and Pd from sea and natural waters and hydrometallurgical process streams. Analysis of elements in alloys have also been successfully achieved using chelating sorbents. Elements exhibiting high affinity to the chelating group of sorbents are separated by successive elution of sorbed metals with acids and complexing agents.

The increasing demand for ultrapure water for the electronic industry has necessitated the use of these sorbents for the extraction of metal ions from water and for the upgrading of low grade ores and industrial scraps.

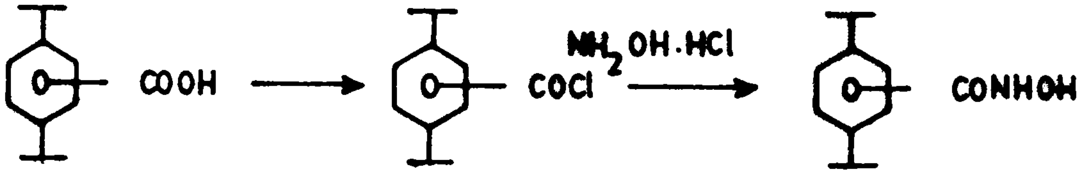
Other important applications of polymer complexones are in the separation of micro-elements from geological and biological samples, removal of metal ions from salt, acid and alkaline solutions, organic solvents and purification of reagents. Their commercial popularity is evidenced by the list of trade mark products available to various manufacturers (Table 1).

1.9 POLYMERIC HYDROXAMIC ACID RESINS

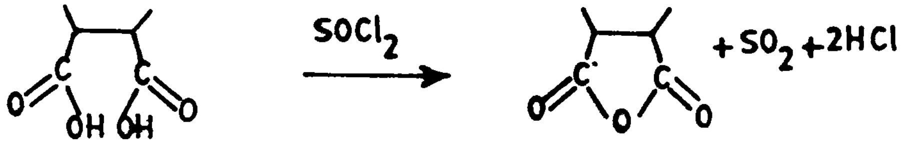
With the current interest in adapting functionalized polymers, hydroxamic acid polymers by virtue of the uniqueness of the functional group, find important applications.

Most of the developments in polymeric ligands incorporating hydroxamic acids can be attributed to the stability of the chelate complexes formed by them[73-76].

The work on polymeric hydroxamic acids was pioneered by Deuel and his coworkers. They prepared hydroxamic acid derivatives of Amberlite IRC-50 (carboxylated copolymer of styrene and divinylbenzene) and poly(methacrylic acid) resins by conversion of the carboxyl groups to acid chloride[77,78] followed by hydroxylaminolysis. The resulting polymers contained a high concentration of carboxylic acid groups, because of the poor conversion of the carboxylic acid groups to acid chloride. This was mainly due to the formation of anhydride bridges between adjacent carboxy groups. The acid chloride method was also used by Vrancken and Smets[79] by treating poly(acryloylchloride) with hydroxylamine in DMF. Petrie, Locke and Meloan described the preparation of a hydroxamic acid derivative of Amberlite IRC-50 via acid chloride--methyl ester and hydroxamic acid[80]. The product showed increased retention of V(V), Fe(II,III), Mo(VI), Hg(II), Cu(II), U(VI) and Ce(IV). These authors made no reference to the earlier work of Deuel et al in this area.



Scheme 1 Conversion of acid to hydroxamic acid



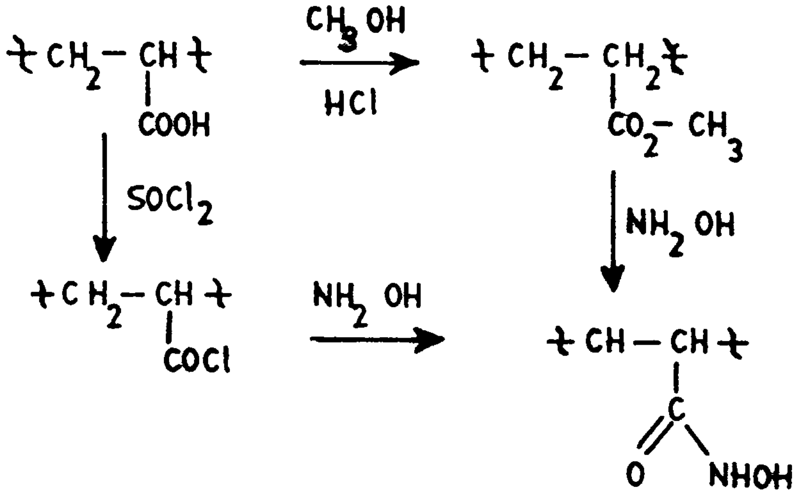
Scheme 2 Formation of acid anhydride

The co-polymerisation of various hydroxamic acid-substituted phenols and catechols into resins is also reported to give ion-exchange resins selective to heavy metals[81].

Polymeric hydroxamic acids have been prepared by converting the carboxylic acid to ester and the reaction of ester with hydroxylamine[82-84]. Of particular note is the work of Kern and Schulz[83], who converted a linear poly-(methylmethacrylate) to a poly(hydroxamic acid) with 80% efficiency and found that Fe(III), Cu(II), Ag(I), Zn(II), Hg(II), Al(III) and Pb(II) gave precipitates with the polymeric ligand. The complex formed with Fe(III) was compared with Fe(III) complex of isobutyro-hydroxamic acid and found that the polymer showed marked tendency for the formation of a 3:1 (hydroxamic acid: Fe(III) complex) which is not observed in the monomer.

Schouteden described the synthesis of poly(hydroxamic acids) from poly(acrylonitrile) by reaction with hydroxylamine followed by mild hydrolysis of intermediate amidoxime to give a chelating resin with pendant hydroxamic acid groups[85,86]. The use of this procedure for the metallation of acrylic fabrics has also been explored[87,88]. The same approach made by Kyffin[90] to convert amidoxime polymers into crosslinked poly(hydroxamic acids) by a one stage hydrolytic oximation of the acrylonitrile polymer by hydroxylamine and studied the sorption capacities for several metal ions over a wide range of pH. Several applications using this resin were studied including extraction of metals from sea water and from wet ashed sea-weed samples. He also converted a commercial ion-exchange resin having amidoxime functionality (Duolite ES 346, Diamond Shamrock) on a polyacrylic matrix to poly(hydroxamic acid) by keeping it in contact with acid solution[90].

Scheme 3: Conversion of carboxylic acid resins to hydroxamic acid resins



Marshal[91] adopted a different approach for synthesizing polyhydroxamic acids by a one stage reaction involving sodium hydroxide and hydroxylamine to convert poly(acrylonitrile) fibres to a chelating exchanger having capacities 1.3 and 5 mmol g^{-1} for Fe(III) and Cu(II) respectively.

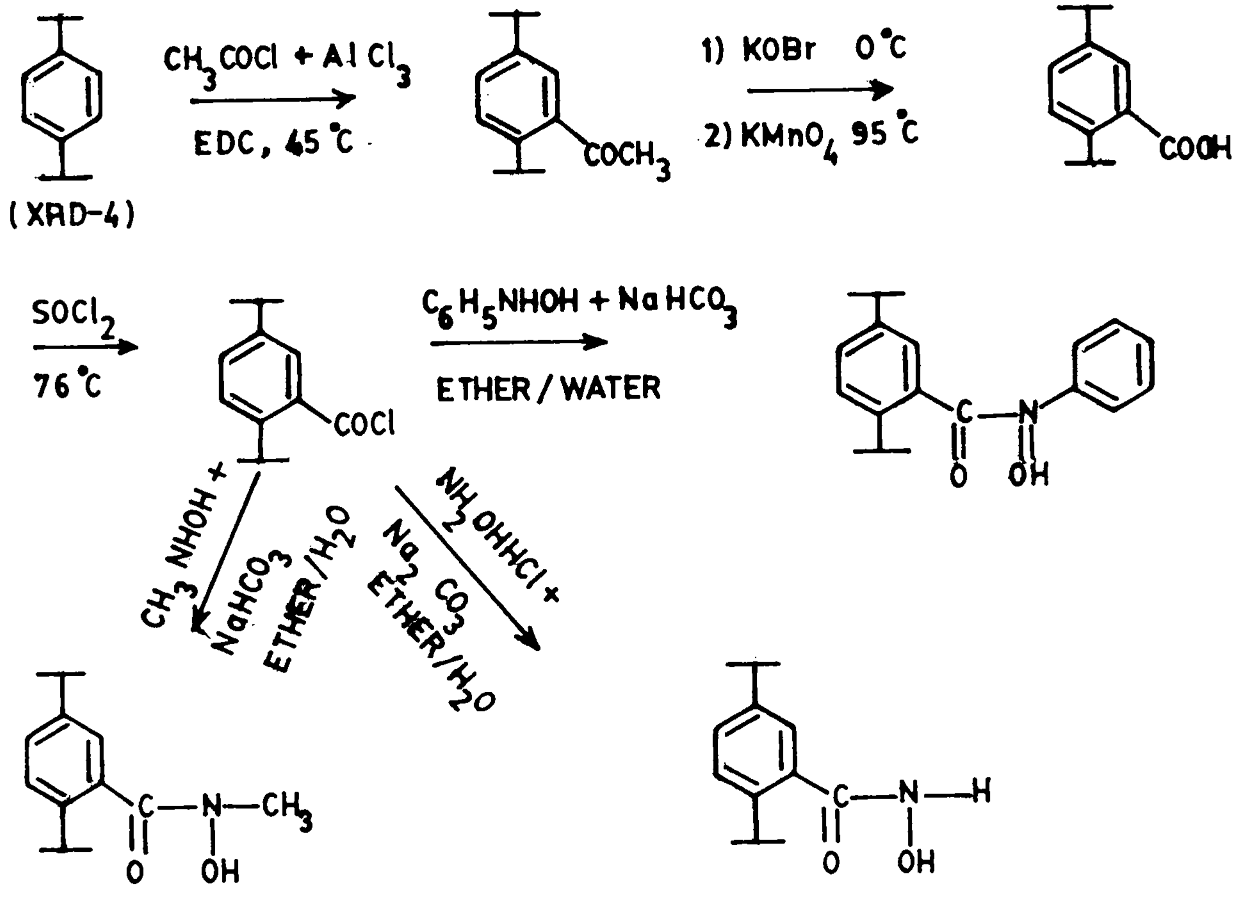
Vernon and Eccles[92,93] prepared two chelating ion-exchangers containing N-substituted hydroxylamine functional groups. One chelating ion-exchanger contained N-benzoyl-N-phenylhydroxylamine prepared by condensation of phenylene dihydroxylamine and terephthaloyl chloride and the other was prepared by reaction between p-(bromoethyl) benzoyl-phenylhydroxylamine with poly(ethyleneimine). The chelating properties of these polymers towards iron, cobalt, copper, vanadium and uranium and the effect of a complexing ligand on the resin capacity were studied.

Vernon and Eccles[94,95] synthesized a crosslinked poly(hydroxamic acid) resin by polymerising an acrylonitrile-DVB mixture, subjecting the resulting granular polymer to hydrolysis in 50% H_2SO_4 and reacting the polyamide with hydroxylamine.

Poly(hydroxamic acid) resins obtained by the conversion of polymeric carboxylic acids are unstable towards concentrated acids and bases and undergo rearrangement during regeneration. The crosslinked resins were found to be superior to the hydroxamic acid resins previously reported. They were stable towards 5 M HCl or H_2SO_4 and also to 1 M NaOH. Further they showed high selectivity for Fe(II), V(V) and Hg(II). The resin was used to separate Fe(III) from Cu(II) at pH 1.5 and Cu(II) from Co(II) and Ni(II) at pH 3.5. In addition recovery of Fe(III) and U(VI) from sea water were carried out with 97-99% efficiency.

Wan Yunus succeeded in synthesizing a crosslinked poly(hydroxamic acid) exchanger in the form of a macroporous microbead which had better capacity and sorption kinetics for metal ion. It was prepared by polymerising an acrylonitrile-ethylacrylate-DVB mixture containing 20% ethylacrylate and 5% crosslinking[96]. Vernon and Wan Yunus[97] evaluated columns of this polyhydroxamic resin for the recovery of gold and silver at trace levels and found quantitative recovery of silver from neutral to 1 M acid solutions. Separation of silver and gold was achieved by selective desorption of silver with dilute nitric acid. Gold was removed using potassium cyanide as eluent. Wan Yunus[97] and Noichaya[98] studied the properties of the resin with many metals. It was possible to separate Fe(III) and Al(III) from Ca(II) and Mg(II) and from each other. A study of these poly(hydroxamic acid) resins revealed that metal ions such as Fe(III), Ti(IV), Zr(IV), V(V) and Mo(VI) form very stable complexes with them and sorb them from acid solutions.

A patent by Fetscher et al[99] describes the preparation of several poly(hydroxamic acid) resins by the hydrolysis of polyamidoximes having $-CH(CN)CH_2CH[C{=}(NOH)NH_2]CH_2-$ repeat units. A poly(hydroxamic acid) sodium salt of this resin has been used for water sofening. Phillips and Fritz[100,101] described synthetic methods for anchoring N-phenyl and N-methyl hydroxamic acid groups to a macroporous polystyrene-DVB copolymer by the acetylation of a commercial resin XAD-4 (Rohm and Hass) followed by its oxidation to carboxy XAD. Chloroformyl XAD-4 was obtained by treating the carboxy XAD-4 with $SOCl_2$ which on treatment with N-methylhydroxylammonium chloride and N-phenylhydroxylammonium chloride gives the required polymer. Use of hydroxylammonium chloride leads to the synthesis of N-substituted hydroxamic acid resins.



Scheme 4 Conversion of XAD-4 to N-Phenyl and N-methyl hydroxamic acids

The extraction of 19 metal ions using this resin was studied as a function of pH and several analytical applications including purification of chemical reagents, concentration of trace metal ions and chromatographic separation of metal ion mixtures were demonstrated. The effect of N-substitution was studied by comparing the N-phenyl, N-methyl and unsubstituted hydroxamic acid resins.

A hydroximated cellulose powder with low concentration of hydroxamic acid groups has been prepared from carboxycellulose. Hydroxamic cellulose fibres with a high content of hydroxamic acid group have also been reported[102]. This hydroxamic cellulose has a sorption capacity of 2.1 mmol g^{-1} and is useful in trace analysis.

A new chelating ion-exchange resin named "hydroximised sephadex" (H-sephadex) was prepared by treating carboxymethyl sephadex with hydroxylamine. Lead(II), Cu(II), Cd(II), Hg(II), Zn(II) and Mn(II) were concentrated from micromolar solution of their salts over different pH ranges[103].

Shah et al[104] have described the synthesis of a number of hydroxamic acid resins by reacting poly(acrylic acid) with different hydroxylamines to get meta and para

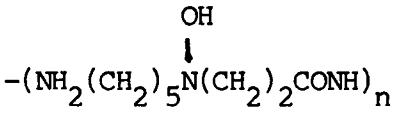
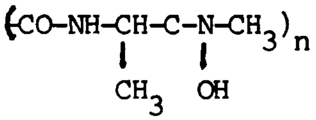
Table 1.2

Chelating sorbents with hydroxamic acid functional group

Sl.No. (1)	Chelating Group (2)	Structure (3)	Matrix (4)	Species Sorbed (5)	Reference (6)
1.	Hydroxamic acid	-CONHOH	i) Poly(methacrylic acid)	Fe(III), Zn(II),	77,78,113
			ii) Amberlite IRC-50	Cu(II)	
2.	Hydroxamic acid	-CONHOH	Poly(methylmethacrylate)	Cu(II), Zn(II), Hg(II), Al(III), Pb(II), U(VI)	83
3.	Hydroxamic acid	$-CH(CN)CH_2CH-(C=(NOH)NH_2)CH_2$	Poly(amidoximes)	Pu, U, Th	99,114
4.	Hydroxamic acid	-CONHOH	Amberlite IRC-50	Fe(II,III),V(V),Mo(VI), Ti(IV),Hg(II),Cu(II), U(VI), Ca(IV)	80
5.	Hydroxamic acid	$O-,m-,p-HOC_6H_4CONHOH$	HCHO	Zr(IV), Nb(III), Fe(II)	81
6.	3,5-resorcyclo-hydroxamic acid	--	"	"	81
7.	Hydroxamic acid	-CONHOH	i) Poly(methyl-α-chloro-acrylate)	Cu(II)	115
			ii) Poly(Me-acrylate)		

(contd...)

Table 1.2 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
8.	Hydroxamic acid	-CONHOH	Polyacrylonitrile-DVB	Fe(III)	87
9.	Hydroxamic acid	-CONHOH	Butyl acrylate	..	116
10.	Hydroxamic acid	-CONHOH	Acrylonitrile-DVB	Cu,Fe,U,V	92-95
11.	Desferoxamine-B	 $-(NH_2(CH_2)_5\overset{OH}{\overset{\mid}{N}}(CH_2)_2CONH)_n$	Poly(acrolein)	Fe(III)	108,109
12.	Hydroxamic acid	-CONHOH	Poly(acrylonitrile)	Fe(III), Cu(II)	96
13.	Hydroxamic acid	 $(CO-NH-\underset{CH_3}{\underset{\mid}{CH}}-C-\underset{OH}{\underset{\mid}{N}}-CH_3)_n$	Ethyl acrylate	Fe(III)	110,111
14.	,,	-CONHOH	Polyacrylonitrile	Cu(II),U(VI),Fe(III)	117
15.	,,	,,	Duolite ES-346	U(VI)	96
16.	,,	,,	Acrylonitrile-ethyl acrylate-DVB	Cu(II),U(VI), Ag(I), Au(III)	97
17.	,,	,,	,,	Fe(III),Ti(III),Zr IV Mo(VI),V(V)	98

(contd...)

Table 1.2 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
18.	N-Phenyl,N-methyl	$-COC_6H_5NOH, -COCH_3NOH$	Amberlite IRC-50	19 metal ions	100
19.	Hydroxamic acid	-CO-NHOH	,,	,,	101
20.	Hydroxamic acid	-CONHOH	Cellulose	Pb(II),Cu(II),Cd(II), Hg(II),Zn(II), Mn(II)	102,103
21.	Hydroxamic acid	$R'C(O)N(OH)R^2$ R'-Meph,$4NO_2C_6H_4$ $4MeC_6H_4$,4-$MeOC_6H_4$ R_2=Me,Ph,$4MeC_6H_4$,$4C_6H_4$	--	Fe(III)	112
22.	,,	$R'CON(OH)R^2$ R'=Ph,ansiyl, tosyl R^2 = $PhCH_2$, tosyl,Ph,Me	—	Fe(III)	118
23.	,,	$-C_6H_4CH_2CH(CONHOH)_2$	Polystyrene-alkyl malonate	U(VI)	106

(contd...)

Table 1.2 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)
24.	Hydroxamic acid	$-CONHOH$	Acryloyl or methacryloyl	Fe(III)	119,120 121
25.	,,	$-CONHOH$	Poly(acrylic acid)	Cd(II),Co(II),Pb(II) Cu(II)	104,105
26.	,,	$-CONHOH$	,,	Fe(III),Ga(III),In(III), Cu(II),Zn(II)	107
27.	,,	$-CH_2CH_2CONHOH$	--	Cu(II),Ca(II),Ni(II)	122
28.	,,	$-CONHOH$	Polystyrene-DVB-diethyl malonate	U(VI)	123
29.	,,	$-CONHOH$	Acrylonitrile-DVB-diethylenetriamine	Ga(III), U(VI)	124
30.	,,	$-CONHOH$	Cellulose	Ag(I),Al(III),Bi(III), Cd(II),Cr(III),Hg(II), Mn(II),Ni(II),Pd(II), Ti(III),U(VI),Zr(IV)	102

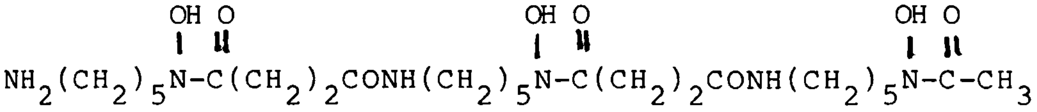
substituted phenyl hydroxamic acid resins. The effect of substitution at the nitrogen on the metal sorption capacities were also studied. These resins were used for the quantitative separation of lead and copper from industrial effluent samples using different eluting agents[105].

A patent filed by Agency of Science and Technology[106] describes the synthesis of a crosslinked polystyrene having the hydroxamic acid residue $-C_6H_4CH_2CH(CONHOH)_2$ as side chain. The resin is used to remove trace amounts of metals. e.g., uranium from sea water and waste water.

Yokoyama synthesized a hydroxamic acid by treating acrylic acid-DVB copolymer beads with ethyl chloroformate followed by treatment with hydroxylamine. The sorption capacity for metal ions were Fe(III) $>$ Ga(III) $>$ In(III) Cu(II) $>$ Zn(II). The selective separation of Ga(III) and In(III) from acid solutions containing large amount of Zn(II) are described[107].

1.10 STRUCTURE-PROPERTY RELATION IN HYDROXAMIC ACID RESINS

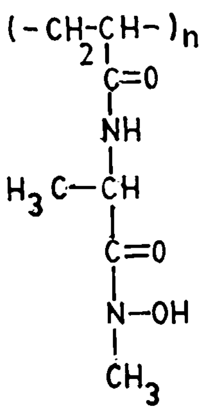
Very few efforts have been done to study the structure-property relations in chelating polymers. Ramirez and Andrade[108]. grafted trihydroxamic acid (deferoxamine B) to several polymers through the free amino group. Reaction of poly(acrolein) with desferoxamine B, produced a polymer which had high affinity for iron[109].

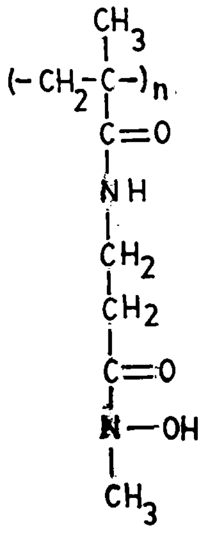


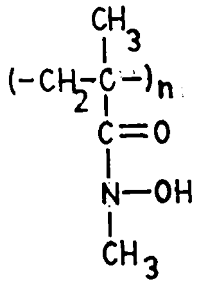
$$NH_2(CH_2)_5\overset{\overset{OH}{|}}{N}-\overset{\overset{O}{\|}}{C}(CH_2)_2CONH(CH_2)_5\overset{\overset{OH}{|}}{N}-\overset{\overset{O}{\|}}{C}(CH_2)_2CONH(CH_2)_5\overset{\overset{OH}{|}}{N}-\overset{\overset{O}{\|}}{C}-CH_3$$

Qualitative iron sorption was demonstrated for this polymer, which was proposed for the treatment of iron poisoning. Attempts were made to prepare the synthetic analogues of deferoxamine B whose chelation with Fe(III) would rival that of deferoxamine B.

In 1975 and 1976, Winston and coworkers[110,111] developed polymers bearing hydroxamic acid groups having high affinity for Fe(III) by the formation of high stability octahedral Fe(III) complex utilising neighbouring hydroxamic acid groups.







Polymer II formed very stable complexes whereas polymer I was less stable. Very unsatisfactory results were obtained with Polymer III. The iron binding stabilities of these were compared with desferoxamine B having hydroxamic acid group separated by 11 atoms. Polymer I, II and III have hydroxamic acid groups separated by 9, 11 and 3 atoms respectively. The order of stability is DFO > II > I > III respectively. From these studies it was concluded that the spacing of hydroxamic acid units is significant in designing a polymer having exceptional affinity for iron.

Christina et al studied the influence of carbon and nitrogen substituents in hydroxamic acid ligands[112]. Thermodynamic and kinetic parameters investigated for the information of high spin Fe(III) complexes by 12 bidentate hydroxamic acids viz., $R'C(O)N(OH)R^2$ where

R'-Me,Ph,$4NO_2C_6H_4MeC_6H_4$, $4\text{-}MeOC_6H_4$ and

R^2-Me,Ph,$4MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}IC_6H_4$,

$4MeCOC_6H_5$.

CHAPTER II

SYNTHESIS AND CHARACTERISATION OF POLY(STYRENE-CO-MALEIC HYDROXAMIC ACID) RESIN (SMPH)

2.1 INTRODUCTION

Polymeric hydroxamic acids have been prepared by the hydroxylaminolysis of various derivatives of poly(acrylic acid) as described in Section 1.9. The reactions of these resins with several metal ions have been studied qualitatively and a few quantitative separations have been achieved[94-98]. However, the investigations on polymeric hydroxamic acids is far from complete. The favourable geometry of vicinal dihydroxamic acids for metal binding has not been explored and it is worthwhile to investigate the properties and applications of vicinal dihydroxamic acid resins.

In this chapter the synthesis and characterization of poly(styrene-co-maleic hydroxamic acid) resin crosslinked with DVB (SMH resin) are described. Studies on the nature and sorption characteristics of the resin towards Cu(II), Fe(III), Co(II), Mn(II), Cr(III), Ni(II), Zn(II), V(V), U(VI) and Mo(VI) by both batch and column techniques are described.

2.2 EXPERIMENTAL

2.2.1 Synthesis of the resin

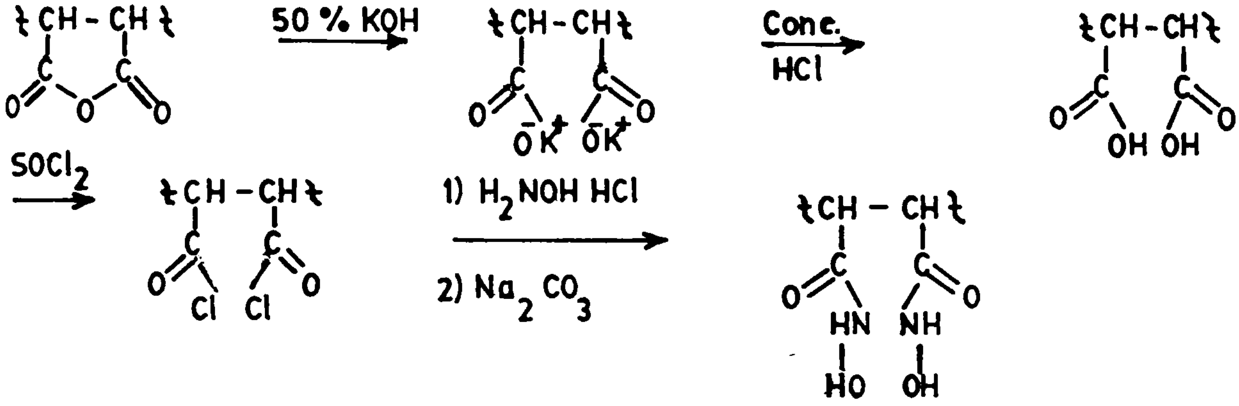
Poly(styrene-co-maleic hydroxamic acid) resin (SMH) was synthesized from styrene-maleic acid co-polymer crosslinked with divinylbenzene, by a modification of the method of Dhandhukia et al[125].

Maleic anhydride was purified by vacuum sublimation and dissolved in acetone under reflux. The maleic anhydride and styrene were taken in different mole ratios, and mixed with 0.75% divinylbenzene and benzoyl proxide (0.75 w/w% of the styrene-divinylbenzene content). The mixture was refluxed on a boiling water bath and when gelling had taken place (2 h) the polymer was transferred to a beaker. Acetone was evaporated and the polymer was cured in an oven at 80-100°C for 8 h. Samples were prepared by varying the divinylbenzene content keeping the maleic anhydride-styrene mole ratio (1:1) constant. The dry resin was ground in a mortar and sieved through ASTM standard sieves.

The copolymers were hydrolysed by refluxing with excess of 10 M potassium hydroxide for 10 h, followed by acidification with concentrated hydrochloric acid. The product was washed with water, dried in an oven at 100°C for 10 h, then refluxed with excess of thionyl chloride on a boiling water-bath for 3 h, with intermittent stirring. The excess of thionyl chloride was distilled off under reduced pressure.

To 1 g of the acid chloride were added 2.1 g of powdered sodium carbonate, 1.4 g of hydroxylammonium chloride, 10 ml of diethyl ether and 2.5 ml of water. The mixture was stirred for 2 h, then the product was filtered off, washed with water until the washings were neutral, then with methanol and finally dried in an oven at 80°C for 8 h.

The scheme for the conversion of the copolymer into the hydroxamic acid resin is shown below.



SCHEME 5 CONVERSION OF CO-POLYMER TO HYDROXAMIC ACID RESIN

2.2.2 Resin characterization

The resin was characterized by determining its nitrogen content, carboxyl content, porosity, stability towards acids and alkalies, water regain, sorption capacity, distribution coefficient and kinetics of sorption for selected metal ions.

(a) Determination of nitrogen content

Nitrogen was determined by the micro-Kjeldhal method[126]. A sample of dry resin (50 mg) was accurately weighed and transferred into the digestion flask. A digestion mixture consisting of 10 g potassium bisulfate and 20 ml of concentrated sulphuric acid and a pinch of copper sulphate were added. The contents were digested by boiling for 4 h, cooled, diluted with water and quantitatively transferred to a 250 ml standard flask and made upto the mark with water.

Aliquots (20 ml) of this solution were transferred to the distillation tube of the Kjeldhal apparatus. About 20 ml of 50% sodium hydroxide solution was used to generate ammonia. Ammonia was steam distilled and collected in a solution of boric acid and was titrated with 0.05 N hydrochloric acid to methyl red-methylene blue end point.

(b) Determination of carboxylic acid content

The carboxylic content of the starting material (styrene-maleic acid copolymer crosslinked with DVB) as well as that of the hydroxamic acid resin was determined.

About 500 mg of dry resin was accurately weighed into a 250 ml beaker and 40 ml of 0.5 M sodium carbonate were added and kept for 6 h. The resin was filtered, the filterate was titrated with 0.5 M hydrochloric acid using methyl orange as indicator. The amount of acid corresponding to the sodium carbonate consumed by the sample was found out by substracting the sample titre from the titre obtained for blank containing 40 ml of 0.5 M Na_2CO_3. Free carboxylic acid content of the resin

$$= \frac{(V_1-V_2)N_{HCl}}{W} \text{ (in m equiv } g^{-1}\text{)}$$

where

V_1, titre for the blank Na_2CO_3 in ml

V_2, titre for the sample + Na_2CO_3 in ml

W, weight of the resin taken in g.

(c) Determination of pore volume and pore size distribution of the resin

A Carlo-Erba sorptomatic series 1800 model 1810 (Italy) Sorptometer was used. The method employed to determine the pore volume and pore size distribution is similar to that devdeloped by Barret et al[127]. The relationship between nitrogen desorption isotherms at liquid nitrogen temperature and the distribution of pore volume with respect to pore radius is based on Wheeler's theory of combined physical adsorption and capillary condensation.

(d) Stability of the resin in acid and alkaline media

Weighed samples of the dry resin were separately soaked for 24 h in 0.1 M sodium hydroxide, concentrated hydrochloric acid and 0.1 M nitric acid. The resin sample was then filtered off using sintered-glass funnel, washed with distilled water and dried in an oven at 80°C for 8 h. The resin showed no significant weight loss even after repeated cycles of treatment. A comparison of the sorption capacities of the samples of treated resin and control resin for Cu(II) was made to see whether any loss of functional group occurred by the above treatment.

(e) Determination of water regain

Weighed amounts of the resin were kept immersed in deionised water for 24 h. The resin was then filtered by suction and dried by pressing between filter paper folds. Weighed amounts of the swollen resin were then dried at 80°C for 48 h and reweighed. The water taken up (in g) by one gram of the dry resin was calculated.

$$\text{Water regain (\%w/w)} = \frac{\text{Weight of water absorbed} \times 100}{\text{weight of dry resin}}$$

2.2.3 Procedures used in metal ion sorption studies

Stock solutions of metal ions were prepared using the following salts.

1.	Ammonium molybdate	$(NH_4)_6[MO_7O_{24}]4H_2O$	Qualigens Fine Chemicals
2.	Ammonium metavandate	NH_4VO_3	Merck
3.	Ammonium nickel sulphate	$(NH_4)_2SO_4.NiSO_4.6H_2O$	Qualigens Fine Chemicals
4.	Cobaltous chloride	$CoCl_2.6H_2O$	,,
5.	Copper sulphate	$CuSO_4.5H_2O$	Merck
6.	Ferric ammonium sulphate	$NH_4Fe(SO_4)_2.12H_2O$	,,
7.	Manganese sulphate	$MnSO_4.5H_2O$	,,
8.	Potassium dichromate	$K_2Cr_2O_7$	,,
9.	Uranyl nitrate	$UO_2(NO_3)_2.6H_2O$	,,
10.	Zinc sulphate	$ZnSO_4.7H_2O$	,,

All chemicals used, including the solvents were of guaranteed purity. Metal solutions were prepared by dissolving the salts in doubly distilled water. Stock solutions of 2000 mg l^{-1} were prepared for each metal and the metal ion content were checked by standard procedures. pH of the solutions were adjusted using 0.1 M ammonium citrate, 1 M citric acid or 0.1 M ammonium acetate glacial acetic acid until the desired pH was attained.

The sorption characteristics for various metal ions were studied by batch and column methods. The resin was powdered in a mortar and sieved through standard sieves. Resin particles of 74 to 150 μm) (100-200 mesh ASTM) were used for sorption studies. The resin was washed with distilled water and dried in vacuum at 80°C for 24 h before use. In all cases capacities and related parameters are expressed in terms of dry weight of the resin. It was found that the resin prepared using styrene and maleic anhydride in the ratio 1:1 and with 0.75 mole % of DVB gave the best results. Hence this resin was used for detailed studies.

(a) Batch technique

Sorption capacity, distribution coefficient and sorption kinetics were studied by batch technique.

(i) Sorption capacity

The batch capacity of the resin for copper(II), zinc(II), iron(III), cobalt(II), nickel(II), manganese(II), chromium(III), vanadium(V), uranium(VI) and molybdenum(VI) was determined in the pH range 1-7 adjusted with 0.1 M solutions of hydrochloric acid, sodium hydroxide, ammonium acetate/acetic acid or ammonium citrate/citric acid. Portions of the resin (0.1 g) were taken in stoppered conical flasks and shaken with 20 ml aliquots of the metal ion solution (400 μg ml^{-1}) for 8 h on a mechanical shaking table kept in water bath at 28±1°C. The residual concentration of metal ion in the solution was determined by withdrawing the supernatent liquid using a filter stick fitted with a G-4 sintered glass disc. The amount of metal sorbed was calculated in terms of the difference between the original and residual concentrations in the solution phase.

(ii) Distribution coefficient

For the determination of distribution coefficient (K_D) the concentration of metal ion in the solution (C_s) and resin phase (C_r) after equilibration was determined. K_D values were calculated from the relation $K_D = C_r/C_s$.

(iii) Sorption kinetics

A 0.1 g portion of the resin was shaken for 2 h with 20 ml of 400 μg ml^{-1} metal ion solution at the pH of maximum sorption capacity and the metal ion concentration in the aqueous phase was measured at different time intervals.

(iv) Effect of monomer ratio on batch capacity for copper(II) and iron(III)

Resin samples were synthesized by varying the ratio of styrene and maleic anhydride in the following ranges: (0.25:1; 0.50:1; 0.75:1; 1:1; 2:1; 3:1). Portions (0.1 g) of the resin (100-200 mesh) were shaken with 20 ml aliquots of solutions of copper(II) (at pH 5) and iron(III) (at pH 2) for 2 h and the sorption capacities were determined.

(v) Effect of varying divinylbenzene content on batch capacity for copper(II) and iron(III)

Resin samples were prepared by varying the divinylbenzene content. Styrene and maleic anhydride were taken at equimolar ratio and divinylbenzene content was varied from 0.5 to 1.5 mole %. The batch capacities for copper(II) and iron(III) were determined using different samples of the resin as described in section 2.2.3(a)(i).

(b) Column technique

A glass column (15.0 cm length and 0.6 cm i.d.) fitted with threaded plexiglass joints was used for column operations. Polyethylene tubes (2 mm i.d.) were used for interconnections. Resin particles (75-150 μm, 1.5 g) were allowed to swell in the buffer for 2 h and then slurry-packed by applying suction from a water pump. The resin bed was conditioned by the passage of appropriate buffers. The solution was fed by gravity flow and flow rate was adjusted using a sliding clip.

Breakthrough studies were carried out using copper(II), iron(III), nickel(II), manganese(II), cobalt(II), chromium(III), uranium(VI), vanadium(V), molybdenum(VI) and zinc(II). The procedures used is given below.

(i) Copper(II)

The column packed with the resin was preconditioned by running 50 ml of ammonium acetate-acetic acid buffer of pH 4. Copper(II) solution of concentration 100 μg ml^{-1} at pH 4 was allowed to pass through the column at a flow rate of 0.2 ml min^{-1}. The effluent was collected in 2 ml lots and the amount of Cu(II) determined spectrophotometrically using diethyldithiocarbamate[128].

(ii) Iron(III)

The column was pre-conditioned with 0.01 M HCl. Iron(III) (100 μg ml^{-1}) at pH 2.2 was run through the column at a flow rate of 0.2 ml min^{-1}. Two millilitre fractions were collected and concentration of iron(III) was determined spectrophotometrically using potassium thiocynate[129].

(iii) Chromium(III) and Nickel(II)

The column was pre-conditioned at pH 5.0 using ammonium acetate-acetic acid. Chromium(III) solution (100 µg ml^{-1}) at pH 5.0 was passed through the column at a flow rate of 0.2 ml min^{-1}. Eluate fractions were collected and the amount of chromium determined spectrophotometrically using diphenylcarbazide[133].

Similarly nickel(II) solution was run under identical conditions and analysed spectrophotometrically using dimethylglyoxime[130].

(iv) Cobalt(II), Zinc(II), Manganese(II)

The column was pre-conditioned by running ammonium acetate-acetic acid buffer at pH 6. Solutions of cobalt(II), zinc(II) and manganese(II) (100 µg ml^{-1}) were passed through the column at flow rate of 0.2 ml min^{-1}. Eluate fractions were collected. Cobalt(II) and manganese(II) were analysed spectrophotometrically using ammonium thiocynate and periodate respectively[131,132] and zinc(II) by a.a.s.

(v) Vanadium(V), Molybdenum(VI) and Uranium(VI)

Breakthrough studies on vanadium(V), molybdenum(VI) and uranium(VI) were carried out using solutions containing 100 μg ml^{-1} of each metal at pH 4.0, 3.0 and 4.5 respectively. The column was conditioned using the buffers, and metal ion solutions run through the column at 0.2 ml min^{-1}. Concentrations of metal ions in the eluate were determined spectrophotometrically[134-136].

2.2.4 Methods used for determining metal ion concentration

The following metal ions are determined spectrophotometrically and the methods used are summarised in Table 2.1.

Table 2.1

Spectrophotometric determination of metal ions

Metal ion	Reagent	λ max (nm)	Reference
Copper(II)	Sodium diethyldithiocarbamate	435	128
Iron(III)	Potassium thiocyanate	480	129
Nickel(II)	DMG/Br_2-Water	445	130
Cobalt(II)	Ammonium thiocyanate/ amylalcohol ether	612	132
Manganese(II)	Potassium periodate	545	131
Chromium(III)	Diphenyl carbazide	540	133
Vanadium(V)	Sodium tungstate/ phosphoric acid	410	134
Molybdenum(VI)	Potassium thiocyanate/ amylalcohol	465	135
Uranium(VI)	Arzenazo III	655	136

Zn(II) was determined by atomic absorption spectrophotometry.

Instruments used

1. pH was measured using Model 1400 pH meter (E.S.Research, Madurai). A combination electrode system consisting of a glass electrode and Ag/AgCl/Sat.KCl electrode was used. Routine adjustments like slope and asymmetric corrections were done whenever necessary.

2. Model 200-20 UV-Visible Spectrophotometer, Hitachi, Japan was used for spectrophotometric measurements. Slit width was adjusted at 2 nm. Matched fused silica cuvettes were used as sample cells.

3. Model 2380 Perkin Elmer atomic absorption spectrophotometer was used for the quantitation of zinc. The analytical wavelength used and other instrumental settings were as per the manufacturers manual.

2.3 RESULTS AND DISCUSSION

SMH is a porous resin. The skeletal structure of the resin contains poly(styrene co-maleic acid) crosslinked with divinylbenzene. Hence the resin has sufficient mechanical strength to withstand the flow velocities encountered in analytical work. It has a water regain of ∼ 50%.

The nitrogen content of the dry resin was found to be 2.68 mmol g^{-1}. The carboxylic acid content of the starting material, i.e., poly(styrene co-maleic acid) crosslinked with DVB was found to be 6.1 m equiv g^{-1}, and that of SMH 3.7 m equiv g^{-1}. This indicates that only 47% of carboxylic acid in the starting material is converted to hydroxamic acid. The hydroxamic acid resin reported by Phillips and Fritz was synthesized from Amberlite XAD-4 by the acid chloride route[101]. They obtained 64% conversion of the acid groups to hydroxamic acid, but their resin had a nitrogen content of only 1.08 mmol g^{-1} resulting in relatively poor capacity compared to SMH resin reported here.

2.3.1 Porosity of the resin

SMH typically contains ∼ 28% micropores (< 20Å) and ∼ 71.6% mesopores (20-500 Å) calculated from the pore size distribution curve and has a pore volume of 0.01 ml g^{-1} as determined by the nitrogen sorption method.

2.3.2 Stability of the resin

The resin is insoluble in acid and alkali. It shows excellent chemical stability. It is not degraded by concentrated hydrochloric acid, 0.1 M nitric acid and 0.1 M sodium hydroxide. However, the hydroxamic acid group undergoes oxidative degradation in concentrated nitric acid. The sorption capacity of the resin for Cu(II) was not affected by treatment with these reagents (table 2.2). The resin prepared

Table 2.2

Sorption capacity of acid- and alkali-treated SMH resin for Cu(II)

Amount of SMH resin 0.1 g, volume of Cu(II) solution 20 ml, amount of Cu(II) 4.0 mg, shaking time 8 h, temperature 28±1°C, treatment time 24 h

Treatment given	Capacity (mmol g^{-1})
Neat	1.145
0.1 M HCl	1.145
0.5 M HCl	1.144
2 M HCl	1.144
0.1 M NaOH	1.145
0.1 M HNO_3	1.143

by Fritz was stable to 2 M HCl and 1 M NH_3, whereas the hydroxamic acid synthesized by Vernon[137] having acrylonitrile-DVB matrix showed a decrease for Cu(II) capacity even in 0.1 M HCl. The polyacrylamide-DVB based resin showed very poor stability towards nitric acid losing its functional group in contact with 0.1 M HNO_3 for 24 h.

2.3.3 Effect of pH on metal ion uptake

The extraction of several metal ions by SMH resin as a function of pH was studied by batch technique. Since most of the metal ions are prone to precipitation at higher pH, studies were limited to pH 7. The results are given in tables 2.3-2.12 and Fig.2.1.

The sorption capacity for Cu(II) increases with increase in pH and reaches a maximum of 1.14 mmol g^{-1} at pH 5.5. The breakthrough capacity for Cu(II) for the hydroxamic acid resin reported by Fritz was 0.4 mmol g^{-1} at pH 4 and the extraction of Cu(II) by batch method at the same pH was 99.5%. SMH resin extracted 90.7% of Cu(II) at pH 5.5 (Fig.2.1). A direct comparison of the sorption capacity of the resin for metal ions is not possible with other hydroxamic acid resins reported in literature because of the difference in experimental conditions.

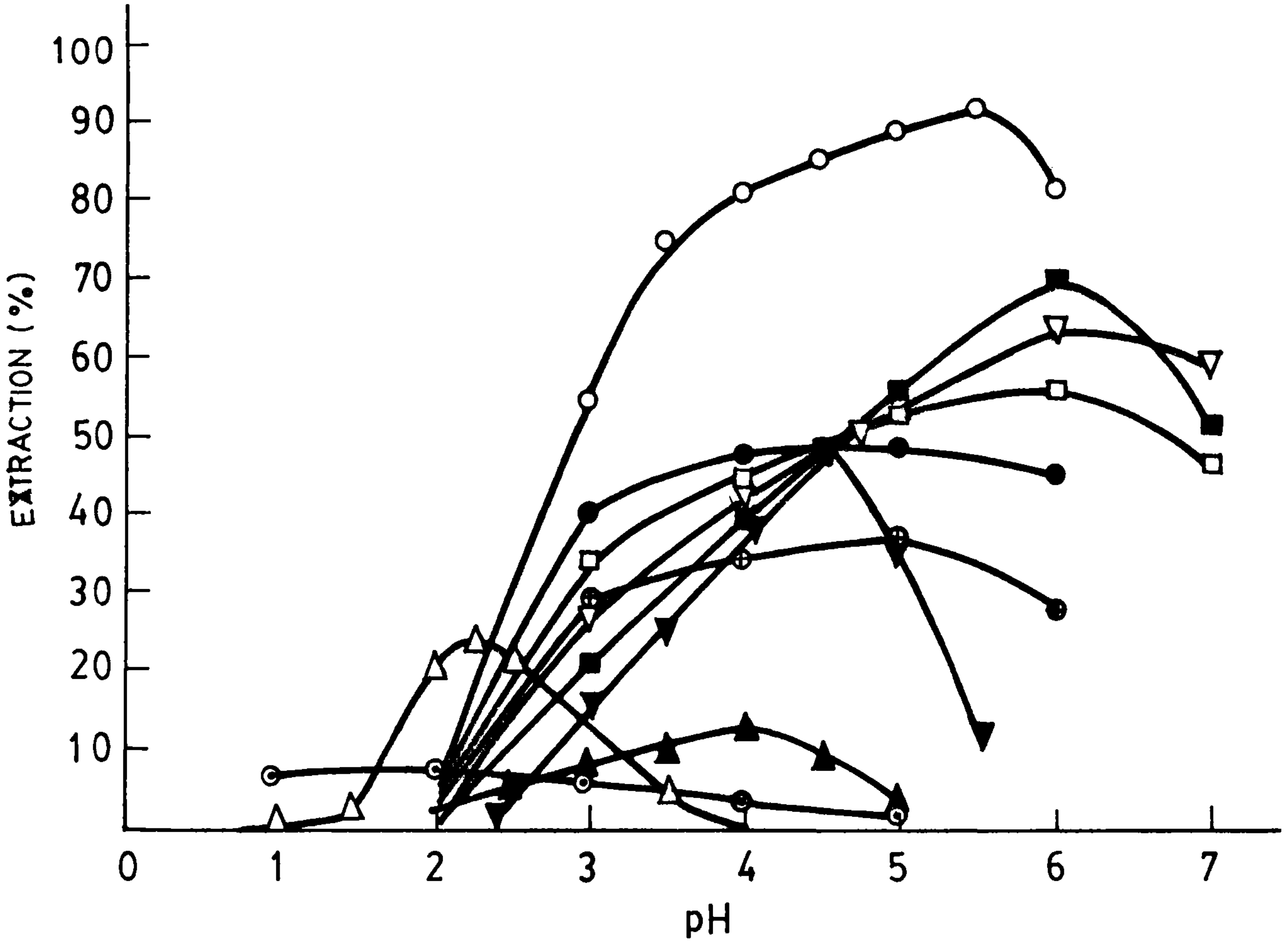


Fig.2.1 Effect of pH on the uptake of metal ions by SMH resin. Amount of resin 0.1 g, particle size 75-150 um, volume of solution 20 ml, concentration of metal ion 400 µg ml^{-1}, shaking time 8 h, temperature 28±1°C. ○, Cu(II); ●, Ni(II); ▽, Co(II); □, Mn(II); ⊕, Cr(III); △, Fe(III); ■, Zn(II); ▲, V(V); ▼, U(VI); ⊙, Mo(VI).

The sorption capacity of Fe(III), was found to increase from 0.03 mmol g^{-1} at pH 1.5 to 0.33 mmol g^{-1} at pH 2.3. The capacity reaches a maximum of 0.33 mmol g^{-1} at pH 2.3 with only 23.2% extraction (Fig.2.1). Further increase in pH produces a sharp decrease in capacity. The sorption capacity of SMH resin for Fe(III) is considerably lower than that for most of other metal ions studied. Also Fe(III) is retained from more acidic solutions compared to other metal ions studied. Most of the hydroxamic acid resins reported in the literature are found to form highly stable Fe(III) complexes[96,111,187]. The hydroxamic acid reported by Fritz showed 100% extraction for Fe(III) at pH 2.0. High sorption capacity for Fe(III) has been reported for hydroxamic acid resins derived from acrylonitrile-co-ethylacrylate by Wan Yunus[96] and Vernon[137]. The resin reported by Wan Yunus has a sorption capacity of 3.5 mmol g^{-1} at pH 5 for Fe(III) and 3.0 mmol g^{-1} at pH 3 for Cu(II). In the case of the resin synthesized by Vernon, capacity of Cu(II) at pH 4 was 4.0 mmol g^{-1} and for Fe(III) at pH 3 was 3.5 mmol g^{-1}.

SMH resin reported here has a lower capacity for Fe(III) than Cu(II). This is in contrast to the observations made on other hydroxamic acid resins mentioned. The high selectivity for Cu(II) shown by SMH could be due to the vicinal position of the hydroxamic acid groups which are favourably poised for co-ordination with the Cu(II) of planar geometry. Similar results have been reported by Eccles[94] and Kyffin[95] on hydroxamic acid polymers based on acrylonitrile-DVB. The capacities reported by Eccles for their resin is 3.2 mmol g^{-1} for Cu(II) at pH 6 and 1.3 mmol g^{-1} for Fe(III) at pH 3. Kyffin has also reported a high capacity for Cu(II) (2.1 mmol g^{-1}) and a lower capacity for Fe(III) (1.7 mmol g^{-1}) at pH 3.

In the case of Ni(II) the sorption capacity increases with pH and reaches a maximum of 0.69 mmol g^{-1} with 51.2% extraction at pH 4.5-5.0. Cr(III) also shows maximum sorption at pH 4.8-5.0. The capacity for Cr(III) at pH 5.0 is 0.57 mmol g^{-1} with 37.2% extraction.

For Zn(II), Co(II) and Mn(II) the pH of maximum sorption is 6.0 with capacities of 0.86, 0.85 and 0.84 mmol g^{-1} respectively. The percentage extraction at the pH of maximum sorption is 70, 62.5 and 57.5% respectively.

SMH resin has a capacity of 0.21 mmol g^{-1} at pH 4 for V(V) and 0.17 mmol g^{-1} for U(VI) at pH 4.5. Mo(VI) is not sorbed to any significant extent on the resin over a wide range of pH and has a maximum capacity of only 0.07 mmol g^{-1} at pH 1.5-2.5.

2.3.4 Distribution coefficient

The dependence of distribution coefficient (K_D) on pH is indicated in tables 2.3-2.12 and Fig.2.2. The K_D values at pH of maximum sorption is in the order Cu(II) $\gg$ Zn(II) $>$ Co(II) $>$ Ni(II) $>$ Mn(II) $>$ U(VI) $>$ Cr(III) $>$ Fe(III) $>$ V(V) $>$ Mo(VI). Table 2.13 gives the capacities and K_D values of the metal ions at the pH of maximum sorption. It is seen that the K_D value of Cu(II) is very high compared to those of other metal ions. Hence Cu(II) is preferentially sorbed in presence of other metal ions and can be pre-concentrated in presence of other metal ions which co-occur in natural and industrial contexts. Eventhough the K_D values of Fe(III) and other metal ions are low, the K_D values are very much pH dependent and the difference in the K_D values at the pH of maximum sorption makes the resin suitable for the separation of these metal ions from their mixtures.

2.3.5 Sorption kinetics

For the efficient separation of metal ions on an ion-exchange column, rapid sorption is important. The sorption kinetics for various metal ions on SMH resin is given in tables 2.14-2.16 and Figs.2.3-2.4. The half-time for saturation at the pH of maximum sorption which is a measure

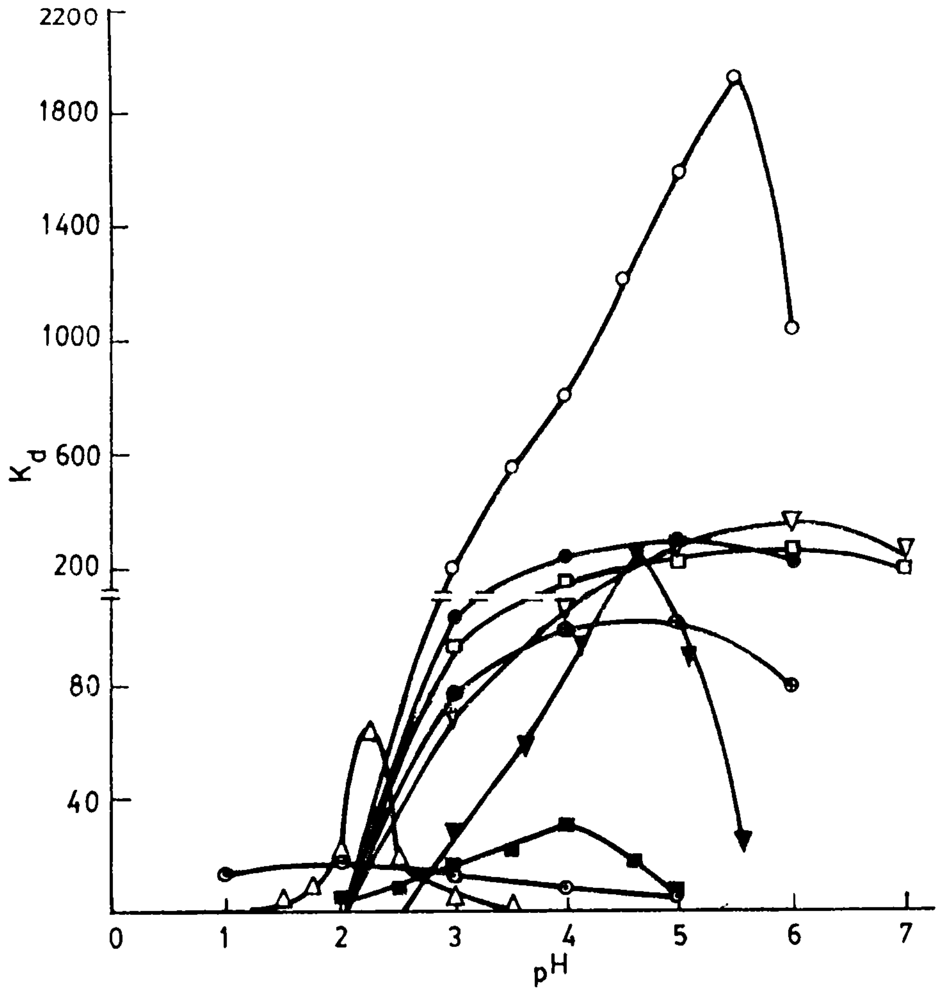


Fig.2.2 Distribution coefficient K_D for various metal ions at different pH using SMH resin.
Weight of resin 0.1 g, particle size 75-150 μm; volume of solution 20 ml, amount of metal ion 4.0 mg, shaking time 8 h, temperature 28±1°C.
○, Cu(II); ■, Zn(II); ▽, Co(II); □, Mn(II); ●, Ni(II); ⊕, Cr(III); △, Fe(III); ▲, V(V); ▼, U(VI); ⊙, Mo(VI).

Tables 2.3 to 2.12 Sorption of metal ions on SMH resin as a function of pH

Amount of SMH resin 0.1 g, particle size 75-150 μm, volume of solution 20 ml, amount of metal ion 4.0 mg, shaking time 8 h, temperature 28±1°C.

$$K_D = \frac{\text{mg of metal ion per g of resin}}{\text{mg of metal ion per ml of solution}}$$

Table 2.3

Copper (II)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0.04	3.1	7
3.0	0.70	55.3	248
3.5	0.95	75.6	621
4.0	1.02	81.3	874
4.5	1.07	85.3	1168
5.0	1.12	89.2	1460
5.5	1.14	90.7	1948
6.0	1.02	81.0	852

Table 2.4

Nickel(II)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0.01	0.3	1.0
3.0	0.58	42.5	147
4.0	0.68	50.0	200
5.0	0.69	51.2	291
6.0	0.66	50.0	200

Table 2.5

Iron(III)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
1.54	0.03	2.1	4.5
1.77	0.04	2.8	5.8
2.10	0.16	11.4	25.7
2.29	0.33	23.2	66.7
2.50	0.14	10.0	22.3
3.00	0.03	2.0	4.4

Table 2.6

Manganese(II)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0.01	0.6	1.2
3.0	0.38	36.9	116.8
4.0	0.67	46.3	172.0
5.0	0.78	53.8	232.4
6.0	0.84	57.5	270.6
7.0	0.71	48.8	190.2

Table 2.7

Cobalt(II)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.1	0	0	0
3.0	0.37	27.5	75.9
3.9	0.56	41.3	140.4
4.9	0.68	50.0	200
6.0	0.85	62.5	333
7.0	0.75	55.0	244

Table 2.8

Zinc(II)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0	0	0
3.0	0.27	21.9	56.0
4.0	0.50	40.9	139.5
5.0	0.72	58.7	286.7
6.0	0.86	70.0	472.3
7.0	0.63	51.5	214.8

Table 2.9

Chromium(III)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0	0	0
3.0	0.47	29.7	89.5
4.0	0.53	34.4	106.2
5.0	0.57	37.2	118.4
6.0	0.44	28.4	79.5

Table 2.10

Vanadium(V)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
2.0	0.05	3.2	6.7
3.0	0.12	7.8	16.8
3.5	0.15	9.3	20.3
4.0	0.21	13.3	30.5
5.0	0.06	3.8	7.8

Table 2.11

Uranium(VI)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
3.0	0.04	10.6	23.8
3.5	0.08	24.4	64.5
4.0	0.13	37.5	120.0
4.5	0.17	50.0	200.0
5.0	0.13	37.5	120.0
5.5	0.04	10.6	23.8

Table 2.12

Molybdenum(VI)

pH	Capacity mmol g^{-1}	Percentage extracted	K_D
1.0	0.06	7.8	16.8
2.0	0.07	8.3	18.0
3.0	0.06	7.8	16.8
4.0	0.03	3.5	7.3
5.0	0.02	2.8	5.7

Table 2.13

Metal sorption properties of SMH resin

Metal ion	pH for maximum sorption	Capacity mmol g^{-1}	K_D	Approximate time for 50% of maximum sorption (min.)
Copper(II)	5.5	1.14	1948·0	2
Zinc(II)	6.0	0.86	472.3	4
Cobalt(II)	6.0	0.85	333.0	2
Nickel(II)	5.0	0.69	291.0	3
Manganese(II)	6.0	0.84	270.6	4
Chromium(III)	5.0	0.57	118.4	3
Iron(III)	2.3	0.33	66.7	4
Vanadium(V)	4.0	0.21	30.5	4
Uranium(VI)	4.5	0.17	200.0	4
Molybdenum(VI)	2.0	0.07	18.0	4

Table 2.14

Sorption kinetics of metal ions on SMH resin

Amount of resin 0.1 g, particle size 75-150 µm, volume of metal ion solution 20 ml, amount of metal ion 4.0 mg, temperature 28±1°C, pH: Cu(II) 5.5, Ni(II) 5.0, Fe(III) 2.25. Buffer used: 0.1 M ammonium acetate/glacial acetic acid.

Time	Capacity (mmol g^{-1})		
	Cu(II)	Ni(II)	Fe(III)
5	1.0	0.43	0.16
10	1.08	0.57	0.22
15	1.14	0.65	0.27
20	1.14	0.69	0.31
30	1.14	0.69	0.33
60	..	0.69	0.33

Table 2.15

Sorption kinetics for metal ions on SMH resin

Conditions same as table 2.12

pH:Mn(II) 6.0, Co(II) 6.0, Zn(II) 6.0

Time	Capacity (mmol g^{-1})		
	Mn(II)	Co(II)	Zn(II)
5	0.45	0.58	0.69
10	0.62	0.85	0.73
15	0.75	0.85	0.79
20	0.84	0.85	0.84
30	0.84	..	0.86
60	0.84	..	0.86

Table 2.16

Sorption kinetics for metal ions on SMH resin

Conditions same as table 2.12

pH:Cr(III) 5.9, V(V) 4.0, U(VI) 4.5, Mo(VI) 2.0

Time	Capacity (mmol g^{-1})			
	Cr(II)	U(VI)	V(V)	Mo(V)
5	0.33	0.09	0.12	0.04
10	0.38	0.13	0.19	0.05
15	0.44	0.14	0.21	0.06
20	0.56	0.15	0.21	0.06
30	0.57	0.17	0.21	0.06
60	0.57	0.17	..	..

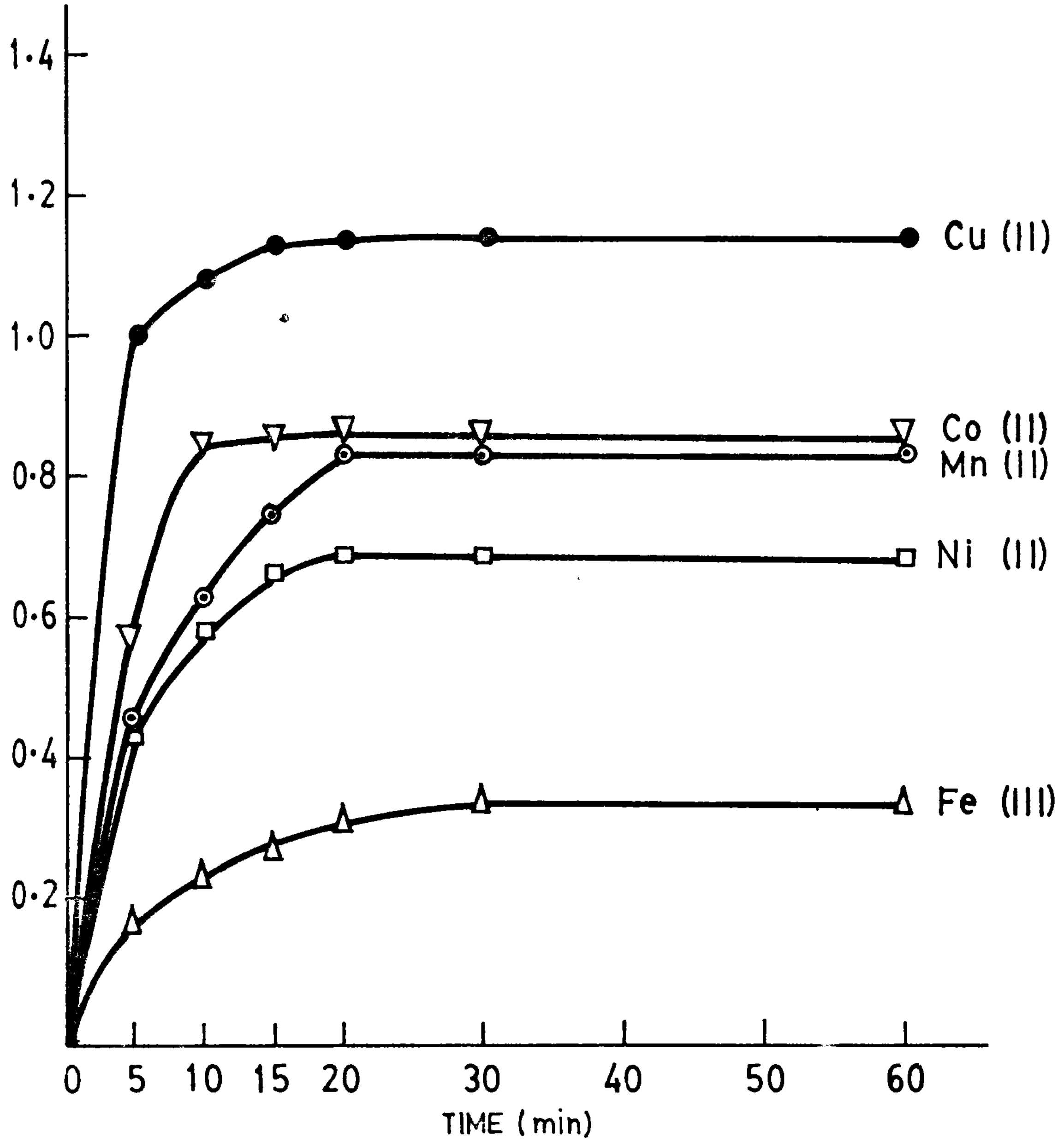


Fig.2.3 Kinetics of sorption of metal ions on SMH resin. Amount of resin 0.1 g, particle size 75-150 µm, volume of solution 20 ml, amount of metal ion 4.0 mg, temperature 28±1°C, buffer 0.1 M ammonium acetate/glacial acetic acid.
pH; Cu(II) 5.5, Ni(II) 5.0, Fe(III) 2.25, Mn(II) 6.0, Co(II) 6.0.
▲ , Fe(III); ● , Cu(II); ⊕ , Mn(II); ■ , Ni(II); ▽ , Co(II).

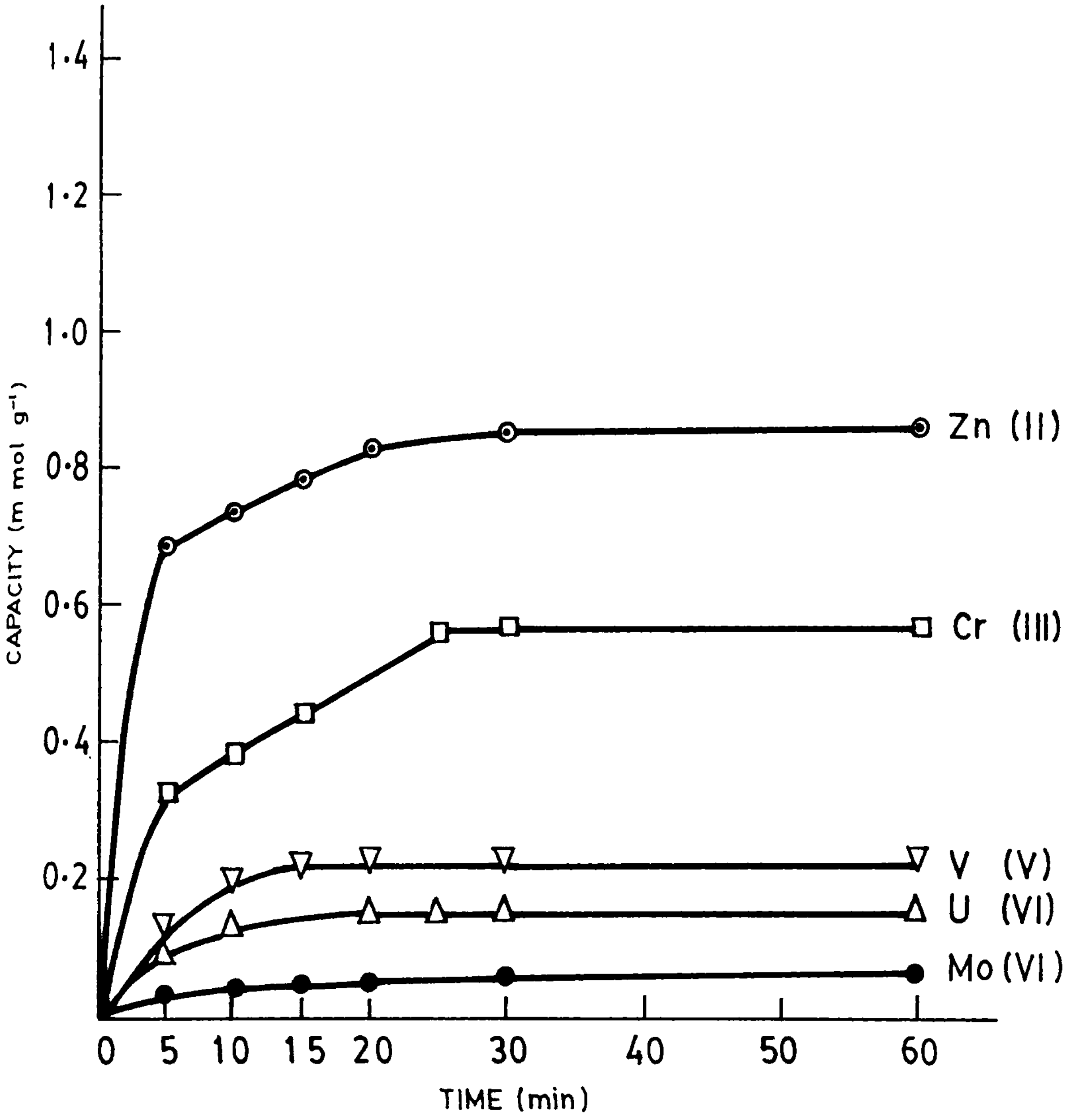


Fig.2.4 Kinetics of sorption of metal ions on SMH resin. Conditions same as in Fig.2.3.
pH: Zn(II) 6.0, Cr(III) 5.0, V(V) 4.0, U(VI) 4.5, Mo(VI) 2.0.
⊙ , Zn(II); ● , Mo(VI); □ , Cr(III); △ , U(VI); ▽ , V(V).

of the rate of uptake of various metal ions is given in table 2.13. The half-times are less than 5 minutes in all cases showing that the sorption of metal ions on this medium is sufficiently rapid. The SMH resin gives a greatly improved sorption kinetics compared to the hydroxamic acid resins reported earlier. The resins reported by Wan Yunus[96], Eccles[94] and Kyffin[95] have $t^{\frac{1}{2}}$ of 8, 43 and 102 minutes although these resins have higher capacities for the metal ions. Phillips and Fritz synthesized the resin with $t^{\frac{1}{2}}$ of <5 minutes at the cost of reduced capacity.

The change in capacity with pH, coupled with the favourable kinetics makes this resin suitable for the analytical separation of these metal ions under carefully selected conditions.

2.3.6 Effect of monomer ratio and divinylbenzene content on the batch capacity

To evaluate the influence of monomer ratio and DVB content on the sorption characteristics of the resin, Cu(II) and Fe(III) were used as typical probes. Figure 2.5 gives the batch capacities of the resin for Cu(II) and Fe(III) for different mole ratios of maleic anhydride-styrene at constant DVB content. The batch capacities for both metal

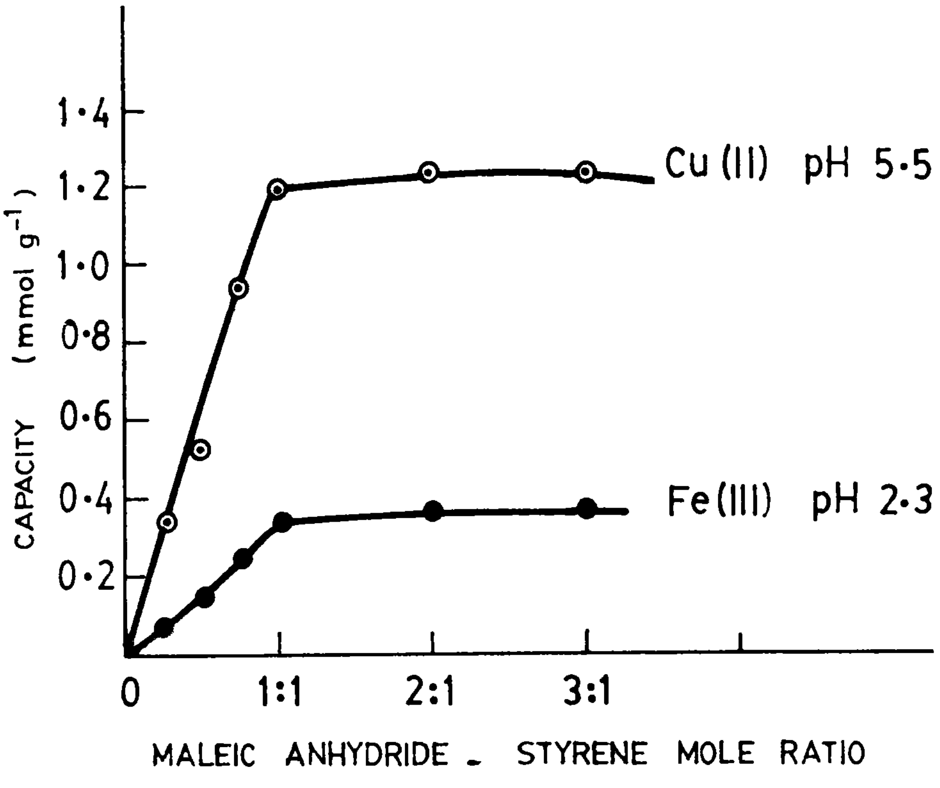


Fig.2.5 Effect of varying maleic anhydride-styrene mole ratio in SMH resin on the batch capacity for Cu(II) and Fe(III).
Weight of resin 0.1 g, particle size 75-150 µm, shaking time 8 h, volume of solution 20 ml, amount of metal ion 4.0 mg, buffer 0.1 M, ammonium acetate/glacial acetic acid.

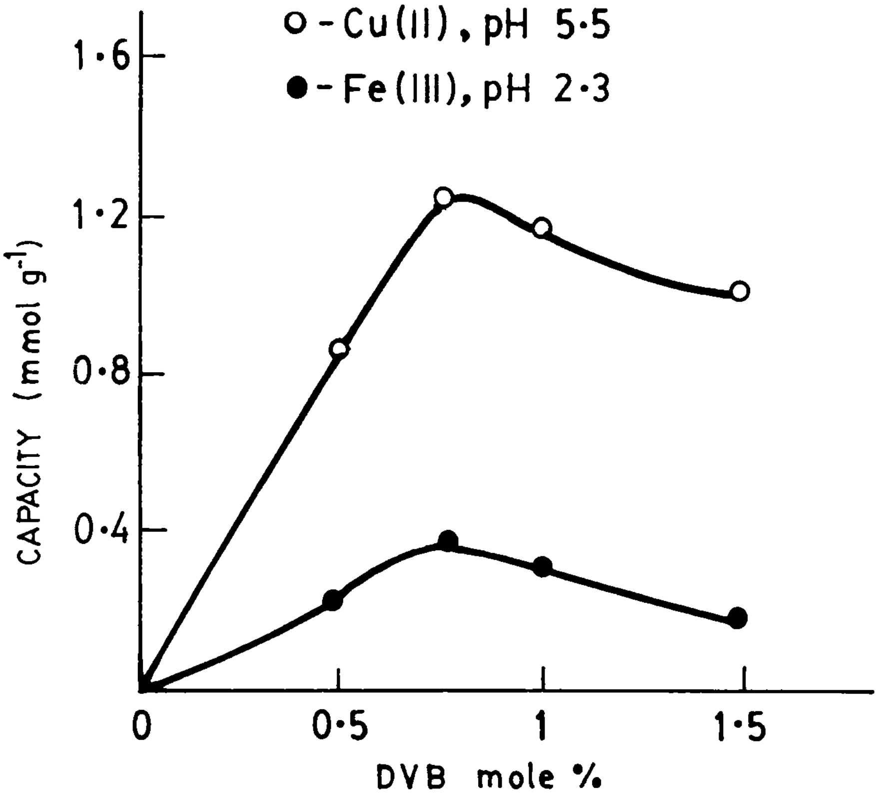


Fig.2.6 Effect of varying mole % of DVB in SMH resin on the batch capacity for Cu(II) and Fe(III). Conditions same as in Fig.2.5.

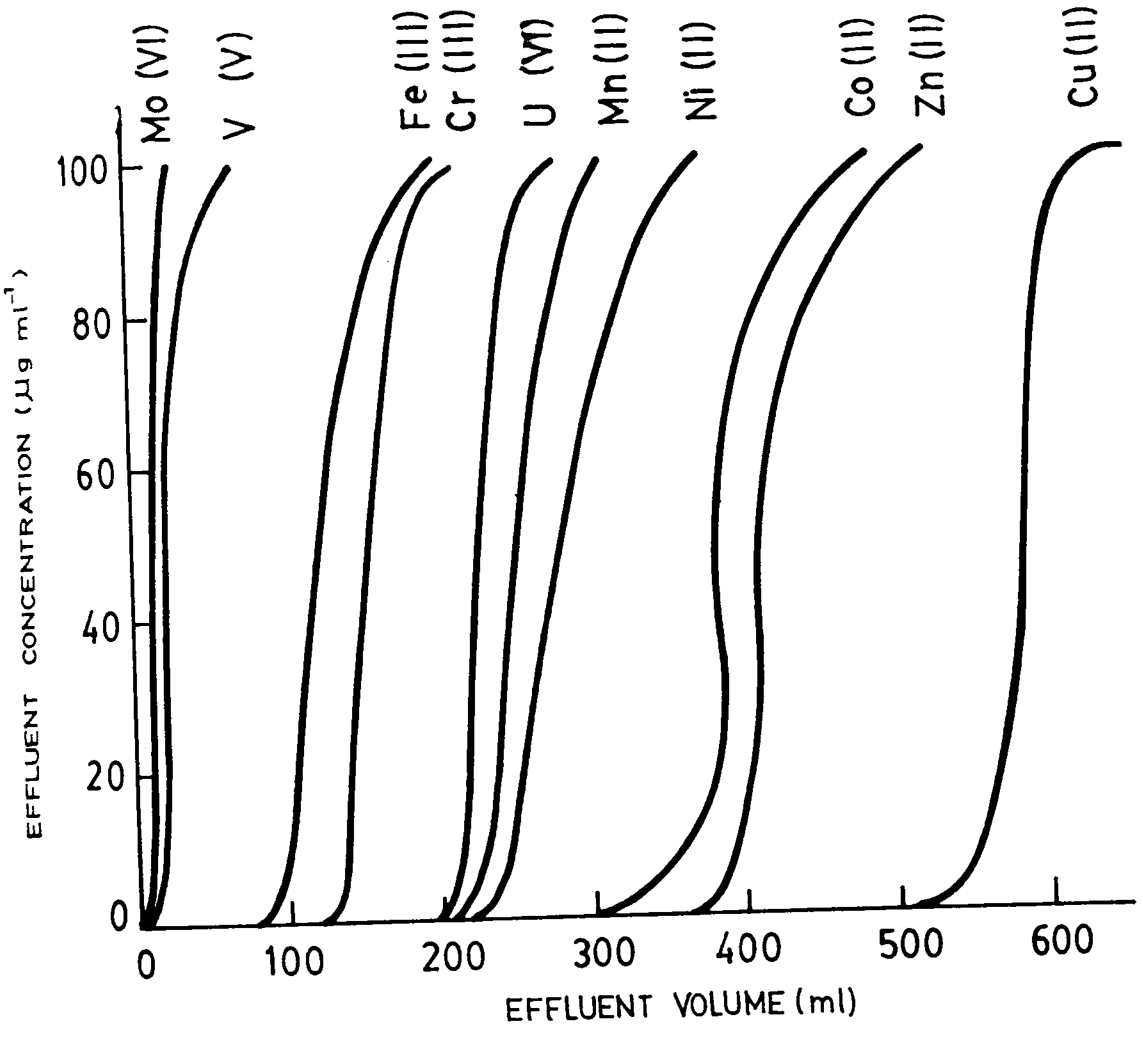


Fig.2.7 Breakthrough curves for metal ions on SMH resin. Column dimensions 15 cm length and 0.6 cm i.d., amount of resin packed 1.5 g, particle size 75-150 µm, flow rate 0.2 $ml\ min^{-1}$, concentration of metal ion solutions 100 $\mu g\ ml^{-1}$. pH of solutions: Cu(II) 5.5, Ni(II) Fe(III) 2.2, Mn(II) 6.0, Co(II) 6.0, Zn(II) 6.0, Cr(III) 5.0, V(V) 4.0, U(VI) 4.5, Mo(VI) 2.0.

CHAPTER III

APPLICATIONS OF SMH RESIN

ions increase as the maleic anhydride content increases and becomes a maximum at equimolar ratio. Further increase in maleic anhydride content does not improve the capacity.

Similarly the batch capacities of Cu(II) and Fe(III) were found to increase with the DVB content at equimolar monomer ratio. The capacities reach a maximum at 0.75 mole % of DVB. Further increase in DVB content produces a decrease in the capacities (Fig.2.6).

2.3.7 Breakthrough studies

The breakthrough curves for different metal ions at the pH of maximum sorption at a flow rate of 0.2 ml min^{-1} are given in Fig.2.7. All the breakthrough curves are steep at the breakthrough point. Mo(VI) and V(V) reach their breakthrough points very close without any significant retention on the column, whereas other metal ions reach their breakthrough points at different times indicating the possibility of separating those metal ions from their mixtures. The breakthrough curve for Cu(II) suggests the possibility to pre-concentrate Cu(II) from very dilute solution.

3.1 METAL ION SORPTION

Studies on the pH dependent sorption, distribution coefficient and breakthrough capacity for various metal ions have indicated the possibility of separating metal ion mixtures using SMH resin. Accordingly the following metal ions were separated and quantitated as typical cases.

3.1.1 Experimental

Column set up was exactly the same as that in section 2.2.3(b).

(a) Nickel(II)-copper(II) separation

Solutions containing various proportions of Ni(II) and Cu(II) were prepared and pH was adjusted at 5 using ammonium acetate and acetic acid. The column was pre-conditioned using the same buffer. Aliquot of the mixture was introduced and the flow rate was adjusted at 0.5 ml min^{-1}. Nickel(II) was eluted using ammonium citrate-citric acid buffer (pH 5) and Cu(II) using 0.1 M HCl. The eluents were collected in 5 ml fractions and concentration of the metal ions determined spectrophotometrically[128,130].

(b) Cobalt(II)-copper(II) separation

The column was conditioned with ammonium-acetate acetic acid buffer (pH 5). Synthetic mixtures of Co(II) and Cu(II) were prepared, and the pH of solutions were adjusted using ammonium acetate and acetic acid to pH 5. Aliquots of the mixture (1 ml) were introduced and the flow rate was adjusted to 0.5 ml min^{-1}. Both Co(II) and Cu(II) were sorbed on the column. Cobalt(II) was first eluted using 0.001 M HCl followed by elution of Cu(II) using 0.1 M HCl. Both metal ions were quantitated spectrophotometrically[128,131].

(c) Manganese(II)-copper(II) separation

Manganese(II) and copper(II) in various proportions were prepared and pH was conditioned at 5. One millilitre aliquot of the mixture was introduced after preconditioning the column using the same buffer. Manganese(II) and copper(II) in various proportions were prepared after preconditioning the column using same buffer and eluted. Both Mn(II) and Cu(II) were sorbed on the column. Mn(II) was first eluted using 0.001 M HCl followed by elution of Cu(II) with 0.1 M HCl. Fractions of eluent collected were analysed for the metal ion content[128,132].

(d) Copper(II)-iron(III) separation

Synthetic mixtures of Cu(II) and Fe(III) of various proportions were prepared using 0.01 M HCl. The column was preconditioned with 0.01 M HCl. Aliquot (1 ml) of the mixture was introduced at the top of the column through the sample introduction port. The flow rate was adjusted to 0.5 ml min^{-1}. Copper(II) was eluted using 0.1 M HCl and fractions of 5 ml were collected and analysed for Cu(II) spectrophotometrically[128]. Iron(III) was eluted subsequently using 0.2 M HCl at the same flow rate. The concentration of Fe(III) in the fractions were determined spectrophotometrically[129].

(e) Nickel(II)-iron(III) separation

Mixtures containing various proportions of Ni(II) and Fe(III) were prepared in 0.01 M HCl. One millilitre of the mixture was introduced after conditioning the column with 0.01 M HCl at a flow rate of 0.5 ml min^{-1}. Elution of Ni(II) was achieved using 0.01 M HCl. Fe(III) was retained on the column and subsequently eluted using 0.2 M HCl. Concentration of metal ions in the fractions were determined spectrophotometrically[129,130].

(f) Vanadium(V)-iron(III) separation

Solutions containing various amounts of V(V) and Fe(III) were prepared in 0.01 M HCl. The column was preconditioned using 0.01 M HCl and 1 ml of the mixture introduced. Vanadium(V) was eluted using 0.01 M HCl and the metal ions in the fractions were quantitated[134]. Iron(III) was subsequently eluted using 0.2 M HCl and determined spectrophotometrically[129].

(g) Iron(III)-nickel(II)-copper(II) separation

Solutions containing various amounts of Fe(III), Ni(II) and Cu(II) were prepared, the pH being adjusted using ammonium citrate-citric acid of pH 4. The column was conditioned with the same pH and 1 ml of the mixture was introduced into the column. Iron(III) was eluted at pH 4. Ni(II) and Cu(II) retained on the column were eluted using 0.01 M and 0.1 M HCl respectively. The eluate were collected in 5 ml lots and metal ion concentration was determined[128-130].

3.1.2 Results and discussion

From the pH-capacity curves (Fig.2.1) breakthrough capacities and sorption kinetics (table 2.13) of SMH resin for various metal ions, it is evident that the resin has different selectivities for the transition metal ions studied.

It is observed that SMH resin is highly selective towards Cu(II) and hence it is possible to separate the other metal ions from their mixtures with Cu(II). The pH of maximum sorption for these metal ions is in the order Zn(II) = Co (II) = Mn(II) > Cu(II) > Ni(II) = Cr(III) > U(VI) > V(V) > Fe(III) > Mo(VI). Eventhough the pH of maximum sorption of Cu(II), Co(II), Mn(II) and Ni(II) is around pH 6 their sorption capacities are different. Hence it is possible to separate Ni(II), Co(II) and Mn(II) from Cu(II) using different eluting agents. Ni(II), Co(II) and Mn(II) can be eluted using 0.01 M HCl whereas Cu(II) is eluted only by 0.1 M HCl.

In all cases different proportion of the constituents were tried to check the validity of separation in different range of concentration. Analysis were replicated and standard deviation calculated. The results are presented in tables 3.1 to 3.3 and Figs.3.1 to 3.2.

Table 3.1

Nickel(II)-copper(II) separation on SMH resin

Column dimension 15 cm length and 0.6 cm i.d., weight of resin 0.5 g, particle size 74-150 µm, flow rate 0.5 ml min^{-1}. Eluent for Ni(II), ammonium citrate-citric acid pH 5; eluent for Cu(II), 0.1 M HCl.

Amount loaded (µg)		Amount recovered * (mean value) (µg)	Eluent volume (ml)	Error mean value (%)	Standard deviation (µg)
Mn(II)	100	97.0	60	-3.0	0.16
Cu(II)	100	97.8	20	-2.2	0.10
Ni(II)	50	49.7	50	-0.6	0.18
Cu(II)	100	99.3	20	-0.6	0.15
Ni(II)	100	98.0	60	-2.0	0.10
Cu(II)	50	49.0	15	-1.0	0.20

* Mean of 6 values.

Table 3.2

Cobalt(II)-copper(II) separation on SMH resin

Column conditions same as in table 3.1. Eluent for Co(II) 0.001 M HCl, eluent for Cu(II) 0.1 M HCl

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Co(II) 100	99.7	25	-0.3	0.20
Cu(II) 100	99.9	35	-0.1	0.17
Co(II) 50	49.1	20	-1.8	0.11
Cu(II) 100	100.0	35	0	0.15
Co(II) 100	100.3	25	0.3	0.20
Cu(II) 50	49.7	30	0.6	0.18

* Mean of 6 values.

Table 3.3

Manganese(II)-copper(II) separation on SMH resin

Eluent for Mn(II) 0.001 M HCl, eluent for Cu(II) 0.1 M HCl. Other conditions same as in table 3.1

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Mn(II) 100	99.8	20	-0.2	0.09
Cu(II) 100	100	15	0	0.05
Mn(II) 50	49.7	15	-0.6	0.07
Fe(III) 100	99.9	15	-0.1	0.04
Mn(II) 100	100	20	0	0.10
Fe(III) 50	49.9	20	-0.2	0.03

* Mean of 6 values.

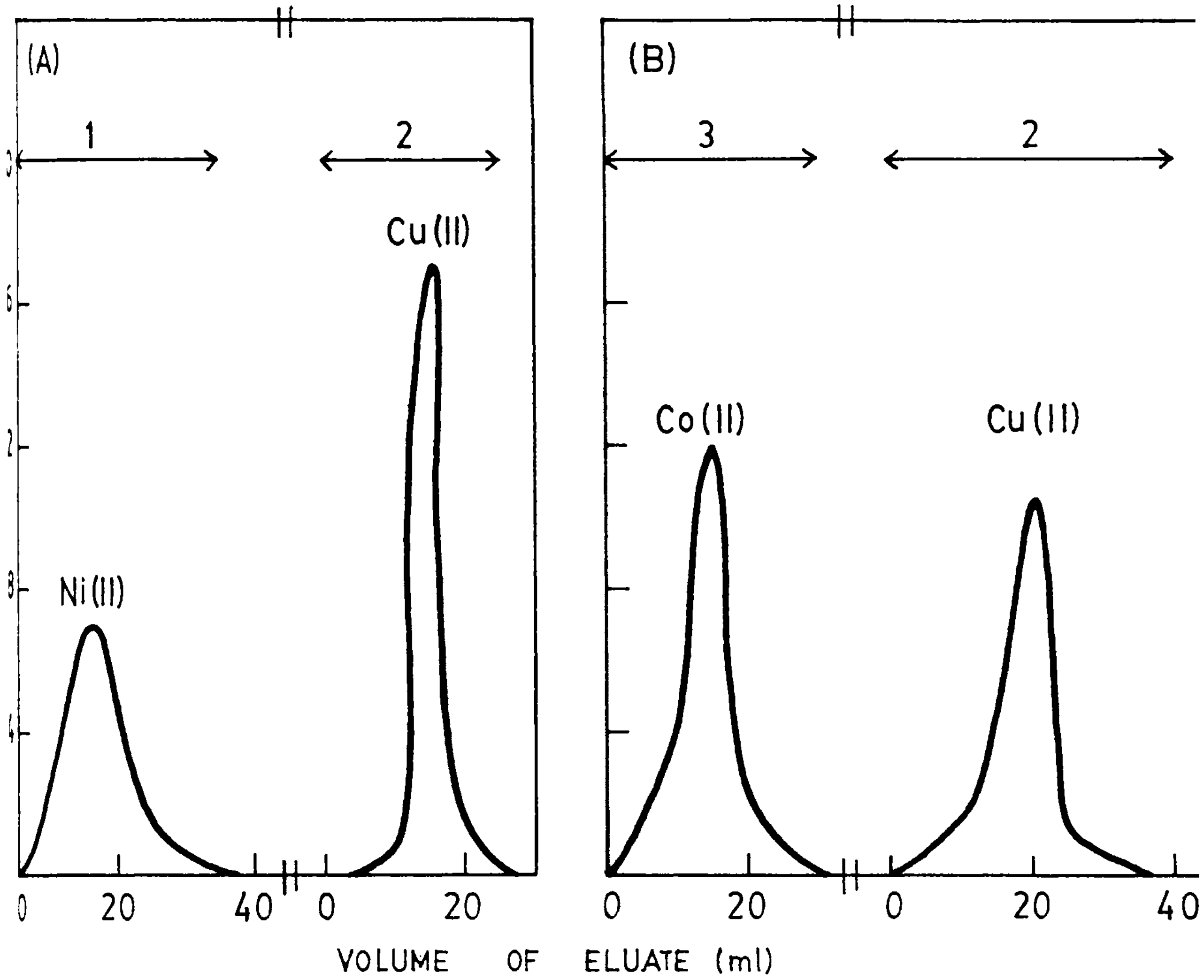


Fig.3.1 Elution curves for (A) Ni(II)-Cu(II), (B) Co(II)-Cu(II).

1) Citrate buffer pH 5, eluent for Ni(II)
2) 0.1 M HCl, eluent for Cu(II)
3) 0.001 M HCl, eluent for Co(II)

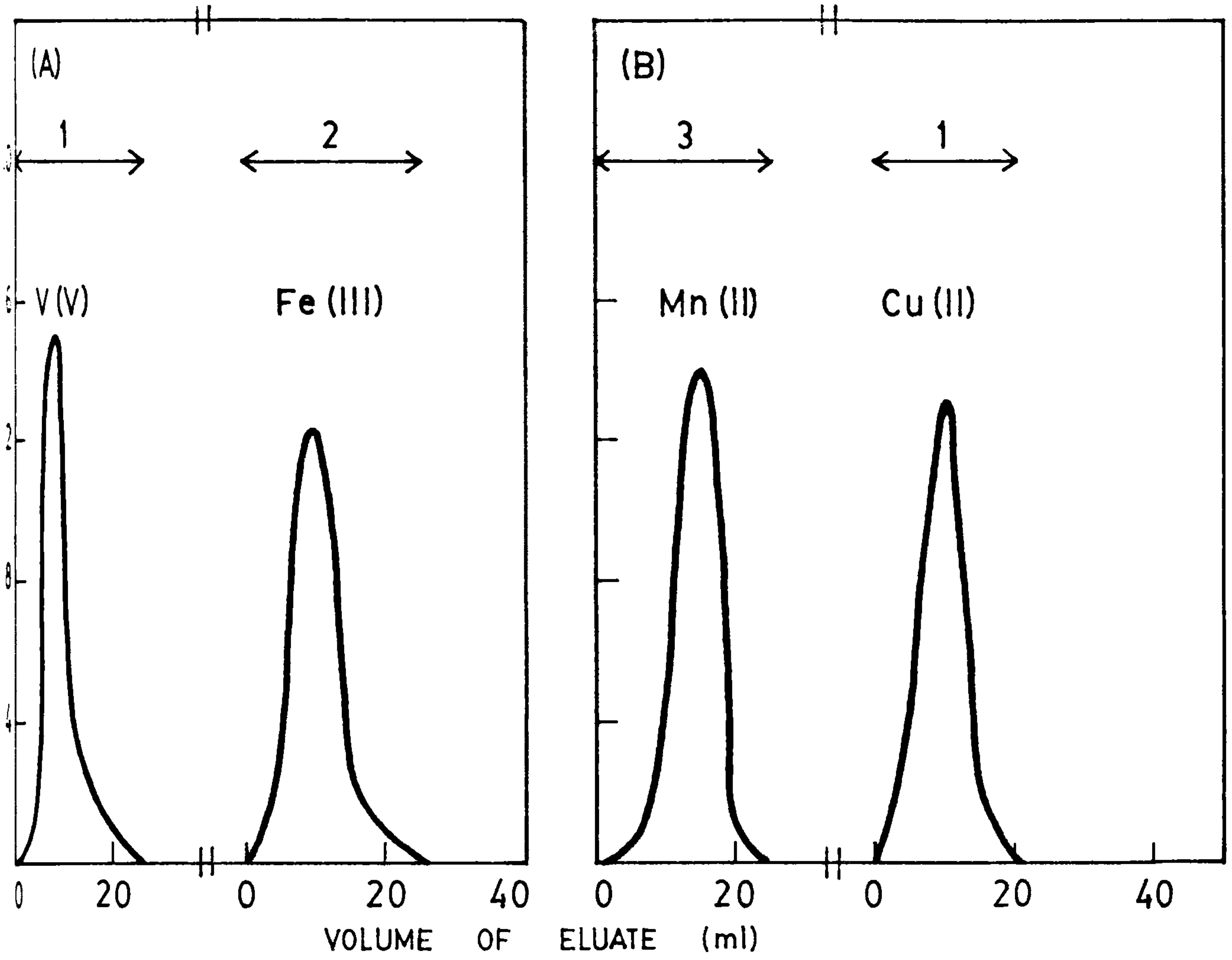


Fig.3.2 Elution curves for (A) V(V)-Fe(III), (B) Mn(II)-Cu(II).

1) 0.01 M HCl, eluent for V(V)
2) 0.2 M HCl, eluent for Fe(III)
3) 0.001 M HCl, eluent for Mn(II)
4) 0.1 M HCl, eluent for Cu(II)

The pH of maximum sorption for Fe(III) is low compared to Cu(II), Ni(II), Co(II), Mn(II) and V(V) (table 2.13). Separation of Cu(II)-Fe(III), Ni(II)-Fe(III), V(V)-Fe(III) were achieved from these mixtures using different eluents. Cu(II), Ni(II) and V(V) were not sorbed on the resin and were easily separated from Fe(III).The results are presented in tables 3.4 to 3.6, and Figs.3.2 to 3.3. It can be seen that the standard deviation for the recovery is low and the elution curves show well separated peaks indicating clean separations.

The wide difference in the K_D values of the resin for the different metal ions, makes the resin suitable for the separation of ternary mixtures. As a typical case separation of constituents in Fe(III)-Ni(II)-Cu(II) mixture was carried out. The results are presented in table 3.7 and elution curves given in Fig.3.4. The separations are well defined and also the standard deviation for the recoveries are low.

Earlier workers have made only scanty reports on the separation of transition metals from their mixtures using hydroxamic acid resins. These results shed more light on the possible application of hydroxamic acid resins in the analytical separation of metal ions from different matrices.

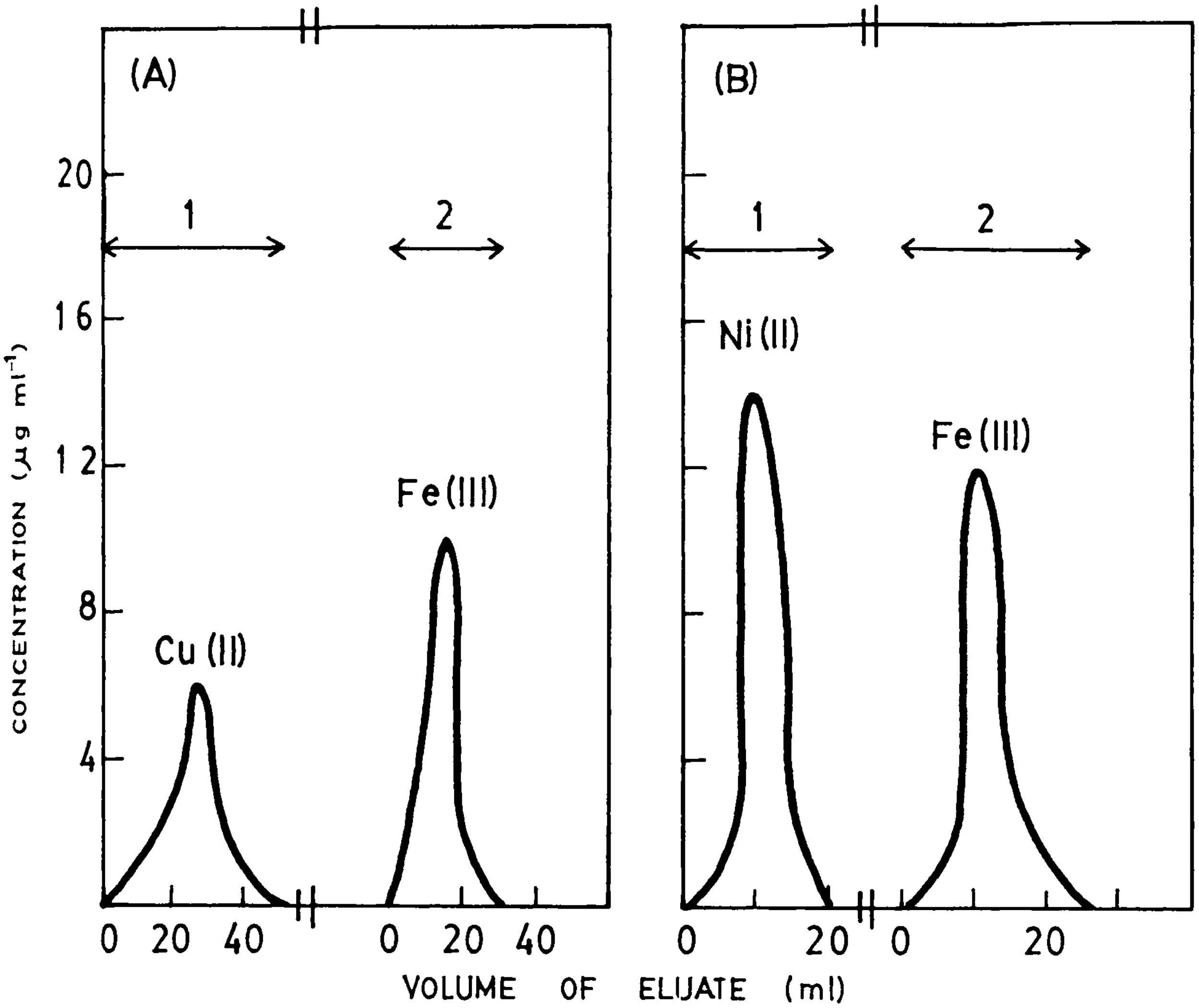


Fig.3.3 Elution curves for (A) Cu(II)-Fe(III), (B) Ni(II)-Fe(III).
1) 0.1 M HCl, eluent for Cu(II)
2) 0.2 M HCl, eluent for Fe(III)
3) 0.01 M HCl, eluent for Ni(II)

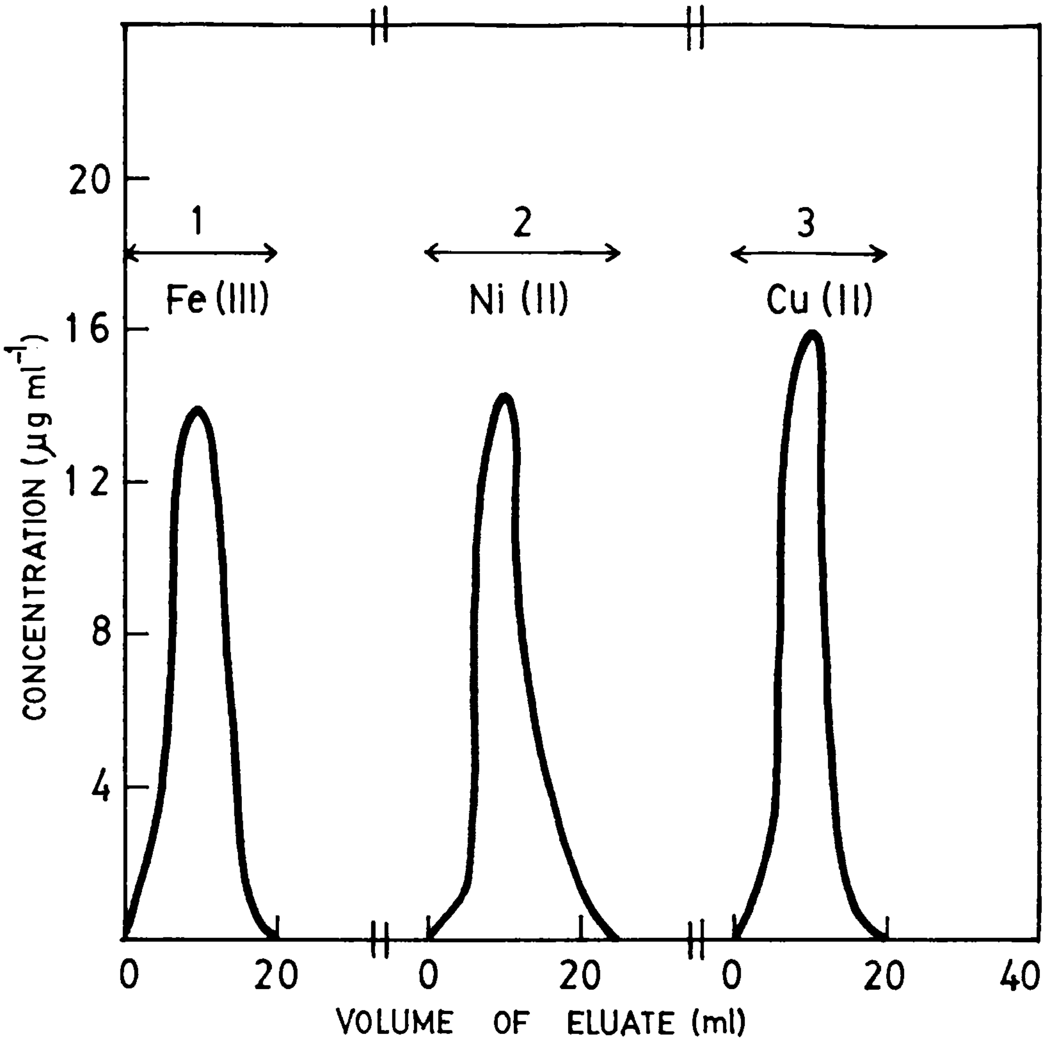


Fig.3.4 Elution curves for Fe(III)-Ni(II)-Cu(II)
1) Citrate buffer (pH 4), eluent for Fe(III)
2) 0.01 M HCl, eluent for Ni(II)
3) 0.1 M HCl, eluent for Cu(II)

Table 3.4

Copper(II)-iron(III) separation on SMH resin

Eluent for Cu(II), 0.1 M HCl, eluent for Fe(III) 0.2 M HCl. Other conditions same as in table 3.1

Amount loaded (μg)	Amount recovered (mean value)* (μg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (μg)
Cu(II) 100	100.6	50	0.6	0.09
Fe(III) 100	99.9	25	-0.1	0.05
Cu(II) 50	50.2	25	0.4	0.06
Fe(III) 100	99.9	25	-0.1	0.07
Cu(II) 100	100.3	50	0.3	0.11
Fe(III) 50	49.8	25	-0.4	0.08

* Mean of 6 values.

Table 3.5

Nickel(II)-iron(III) separation on SMH resin

Eluent for Ni(II) 0.01 M HCl, eluent for Fe(III) 0.2 M HCl.
Other conditions same as in table 3.1

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Ni(II) 100	99.8	15	-0.2	0.09
Fe(III) 100	100.1	20	0.1	0.18
Ni(II) 50	49.7	15	-0.6	0.15
Fe(III)100	100.3	20	0.3	0.12
Ni(II) 100	99.7	15	0.3	0.12
Fe(III) 50	50.2	15	0.4	0.20

* Mean of 6 values.

Table 3.6

Vanadium(V)-iron(III) separation on SMH resin

Eluent for V(V) 0.01 M HCl, eluent for Fe(III) 0.2 M HCl. Other conditions same as in table 3.6

Amount loaded (μg)	Amount recovered (mean value)* (μg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (μg)
V(V) 100	98.9	20	-1.1	0.15
Fe(III) 100	101.2	25	1.2	0.09
V(V) 50	49.3	15	-1.4	0.17
Fe(III) 100	50.3	20	0.3	0.11
V(V) 100	99.1	20	-0.9	0.20
Fe(III) 50	49.4	20	-1.2	0.15

* Mean of 6 values.

Table 3.7

Iron(III)-nickel(II)-copper(II) separation on SMH resin

Eluent for Fe(III) citrate buffer (pH 4), eluent for Ni(II) 0.01 M HCl, eluent for Cu(II) 0.1 M HCl. Other conditions same as in table 3.1

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Fe(III) 100	100	15	0	0.17
Ni(II) 100	99.7	20	-0.3	0.15
Cu(II) 100	99.3	15	-0.7	0.03
Fe(III) 100	100.1	15	0.1	0.07
Ni(II) 50	49.7	10	-0.6	0.11
Cu(II) 50	49.1	10	-1.8	0.04
Fe(III) 50	49.9	10	-0.2	0.09
Ni(II) 50	49.7	10	-0.6	0.10
Cu(II) 100	99.8	15	-0.2	0.05

* Mean of 6 values.

3.2 PRE-CONCENTRATION OF COPPER FOR DETERMINATION BY ATOMIC ABSORPTION OR EMISSION SPECTROPHOTOMETRY

3.2.1 Introduction

Determination of trace or ultratrace levels of metal ions in natural waters is often preceded by a concentration step to increase the analyte concentration to levels that can be reliably measured by the instrument. For example, the optimum concentration of copper that can be determined by a.a.s is 2 $\mu g\ ml^{-1}$. Hence it is necessary to raise the concentration of the metal in the analyte by a pre-concentration procedure for analysis by a.a.s.

An ideal method for the preconcentration of trace metals from natural waters should have the following characteristics:

1. It should simultaneously allow isolation of the analyte from the matrix and yield a favourable enrichment factor.

2. The procedure must be simple and clean requiring the introduction of a minimum of reagents in order to eliminate their interference, hence producing a low sample blank and a corresponding lower detection limit.

3. And it should produce a final solution that readily matches with the matrix solution used to generate the analytical calibration curve. One commonly used method is to pass a large volume of sample through a column of cation-exchange or chelating exchange resin which will retain the trace metal. The metal ion is then be recovered into a small volume, which gives a pre-concentration factor equal to the ratio of the volume of sample to the volume of eluate. This is typically done before determination of elements which do not have low enough detection limits to be directly determined by a.a.s. Other atomic spectrometric techniques like electrothermal a.a.s. and plasma atomic emission can also benefit from pre-concentration from interfering matrices.

The studies presented in chapter II show that SMH resin is highly selective for Cu(II). Hence the pre-concentration of copper from natural waters was studied using SMH resin.

3.2.2 Experimental

Standard Cu(II) solution was prepared using copper sulphate ($CuSO_4.5H_2O$) and diluted to give concentrations of 1.00 μg ml^{-1}, 0.200 μg ml^{-1} and 0.020 μg ml^{-1}. The pH of the solutions were adjusted to 5 using ammonium acetate-acetic acid.

The glass column was packed with SMH resin of particle size 75-150 µm and conditioned with acetate buffer of the same pH. Five hundred millilitres of Cu(II) solution were passed through the column at 0.5 ml min^{-1}. The sorbed Cu(II) on the resin was eluted with 0.1 M HCl. The metal ion in the eluate was determined by a.a.s.

3.2.3 Results and discussion

The high capacity and K_D value for Cu(II) (Fig.2.2) compared with the other metal ions studied make the resin applicable for the pre-concentration of Cu(II) from very dilute solutions. The method is simple and involves pH adjustment followed by running the solution over the resin and elution into a small volume of 0.1 M HCl. Table 3.8 gives the results of pre-concentration of Cu(II) with quantitative recovery. At lower concentrations the recovery became less quantitative perhaps due to relatively high losses due to adsorption on the glass surface[138].

Table 3.8

Pre-concentration of copper(II) on SMH resin

Concentration of Cu(II) (µg ml^{-1})	Amount of Cu(II) loaded* (µg)	Eluent volume** (ml)	Amount recovered (µg)	Percentage recovery	Error of mean value
1000	500.0	20	498.1	99.62	-0.38
200	100.0	20	97.9	97.9	-2.1
20	10.0	15	9.4	94.0	-6.0

* 500 ml of copper solution passed through the column.

** Mean of three determinations.

3.3 RECOVERY OF URANIUM(VI) FROM SEA WATER USING SMH RESIN

3.3.1 Introduction

Uranium in sea water is present at an average concentration of 2.8-3.3 $\mu g\ l^{-1}$ with many other elements. The amount of uranium dissoslved in the oceans of the world is estimated to be about 4 billion tons. The large concentration of others ions make classical cation exchange virtually useless in this context. Accordingly, the development of selective sorbents for its recovery from sea water gives unlimited prospects.

Many types of adsorbents have been tested for the effective recovery of uranium from sea water[139-142]. Chelating resins containing amidoxime group are found to be effective sorbents for uranium from sea water[143-145]. Several workers have investigated the prospects of using chelating resins with hydroxamic function for the recovery of uranium from sea water[94-97,101,137].

The studies by earlier workers and also our studies on SMH resin suggest the possibility of recovering uranium from sea water.

3.3.2 Experimental

(a) Preparation of synthetic sea water

Synthetic sea water was prepared by the method suggested by Muroi and Hamaguzhi[146]. The composition of synthetic sea water used in this study is given below.

Table 3.9

Composition of synthetic sea water

Salt	Concentration (g l^{-1})
NaCl	23.476
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.066
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF	0.003

The salts were dissolved in distilled water and diluted to 1 litre. The sea water thus prepared was spiked with aliquots of standard uranyl nitrate solution so as to get an appropriate concentration of U(VI).

(b) Breakthrough and elution studies using uranium(VI)

pH of sea water was adjusted to 4.0 using ammonium acetate and acetic acid.

The column set up was the same as that used in section 2.2.3.(b) The resin was slurry packed on the column and conditioned with ammonium acetate-acetic acid buffer of pH 4. Samples of sea water spiked with U(VI) were run through the column at a flow rate of 0.5 ml min^{-1}. Fractions of the eluate were collected and analysed for U(VI). A breakthrough run was made using U(VI) solution of 100 μg ml^{-1}.

(c) Pre-concentration of U(VI) from sea water

Synthetic sea water spiked to different concentration of U(VI) was used i.e., 0.02, 0.2 and 1 μg ml^{-1} and 100 ml of the spiked test solutions of pH 4 were separately passed through the column conditioned as described earlier at a flow rate of 0.5 ml min^{-1}. The sorbed U(VI) on the column was eluted with 0.1 M HCl. Uranium in the eluate was determined spectrophotometrically[136].

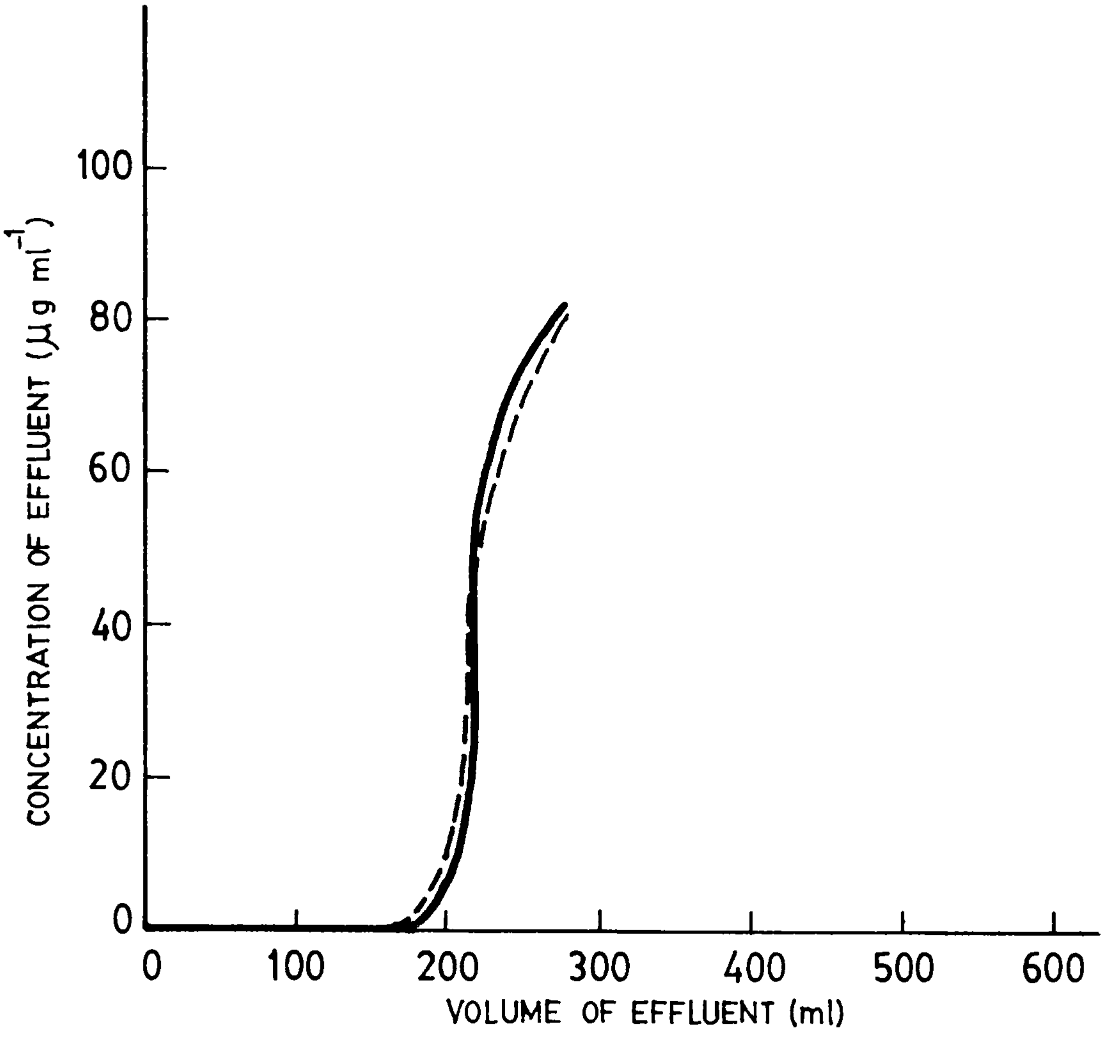


Fig.3.5 Breakthrough curves for U(VI) spiked synthetic sea water.
A——— Standard U(VI) solution (100μg ml^{-1}).
B----- Synthetic sea water spiked with U(VI) (100 μg ml^{-1})
Column dimension 15 cm length and 0.6 cm i.d., amount of resin loaded 1.5 g, pH 4, flow rate 0.5 ml min^{-1}.

3.3.3 Results and discussion

As evident from the K_D values for U(VI) (Table 2.11) and breakthrough studies (Fig.2.7) SMH resin is favourable for the pre-concentration of U(VI). A 100 µg ml^{-1} U(VI) solution passed through the column at a flow rate of 0.5 ml min^{-1} gave breakthrough curve A (Fig.3.5). Curve B in the same figure shows the breakthrough characteristic for sea water containing 100 µg ml^{-1} of U(VI). As observed from the figure the influence of other salts present in sea water have little effect on the uptake of U(VI).

The results of the recovery are presented in Table 3.10. Satisfactory recovery was obtained using 0.1 M HCl as eluent.

3.4 TREATMENT AND ANALYSIS OF CHROMIUM PLATING SHOP EFFLUENTS

3.4.1 Introduction

The discharge of industrial effluents containing toxic constituents into environment has become a serious problem. Chromate and dichromate, if ingested causes skin disorder, bleeding nose, ulceration of mucous membranes and respiratory problems. Prolonged exposure causes liver

Table 3.10

Pre-concentration of U(VI) from synthetic sea water using SMH resin

Concentration of U(VI) in sea water ($\mu g\ ml^{-1}$)	Amount of U(VI) loaded* (μg)	Eluent volume** (ml)	Amount recovered (μg)	Percentage recovery	Error of mean value
1.00	100	30	99.1	99.1	-0.9
0.200	20	30	19.4	97.0	-3.0
0.020	2	25	1.95	97.5	-2.5

* 100 ml of sea water passed through the column.
** Mean of three values.

and kidney diseases. Cr(VI) inhibits growth of algae over a concentrated range of 0.03-6.4 p.p.m. while it may stimulate growth when present at lower concentrations. The chromium(VI) concentration in the public water system should not exceed 0.05 mg l^{-1} and the limit for chromium(III) is 1.0 mg l^{-1}[147]. Rinse water from chromium plating bath which is the major part of total waste water produced in a metal plating shop a high concentration of Cr(VI) and appreciable amounts of Cr(III). Nature has no mechanism other than dilution to nullify the effect of hexavalent chromium. Various methods including ion-exchange are in use for the recovery of chromium effluents[147].

Even the most carefully conducted plating operations are plagued by the contamination of the bath solution by undesirable metals. The presence of such impurities affects the appearance, texture, ductility and activity of platings. The limited tolerance of the particular process solution to the metallic contaminants demands careful maintenance of the quality of the bath liquor. The contaminants are usually removed by selective electrolysis, reduction, oxidation or precipitation of the impurities at a favourable pH. To select the most effective method the contaminants should be identified and quantitated. The methods of analysis currently in use are based on polarography and a.a.s.

3.4.2 Experimental

The chromium bath solutions and shop floor effluents were collected from the plating shops of Sideco, Pachalam, Cochin, which is the biggest plating unit in the State.

(a) Pre-treatment of the effluent

The chromium bath solution containing Cr(VI) with Fe(III) and Cu(II) as impurities along with Cr(III) had pH $\simeq$ 1. Since the hydroxamic group is sensitive to strong oxidants the solution required pre-treatment to reduce Cr(VI) to Cr(III). This was achieved using a minimum of sodium metabisulfite (as 10% solution) and boiling of excess SO_2. Two drops of concentrated nitric acid were added and boiled for five minutes to reoxidize any Fe(II) formed. The rinse water was also given a similar pre-treatment.

(b) Separation of chromium(III), copper(II) and iron(III) in plating shop effluent

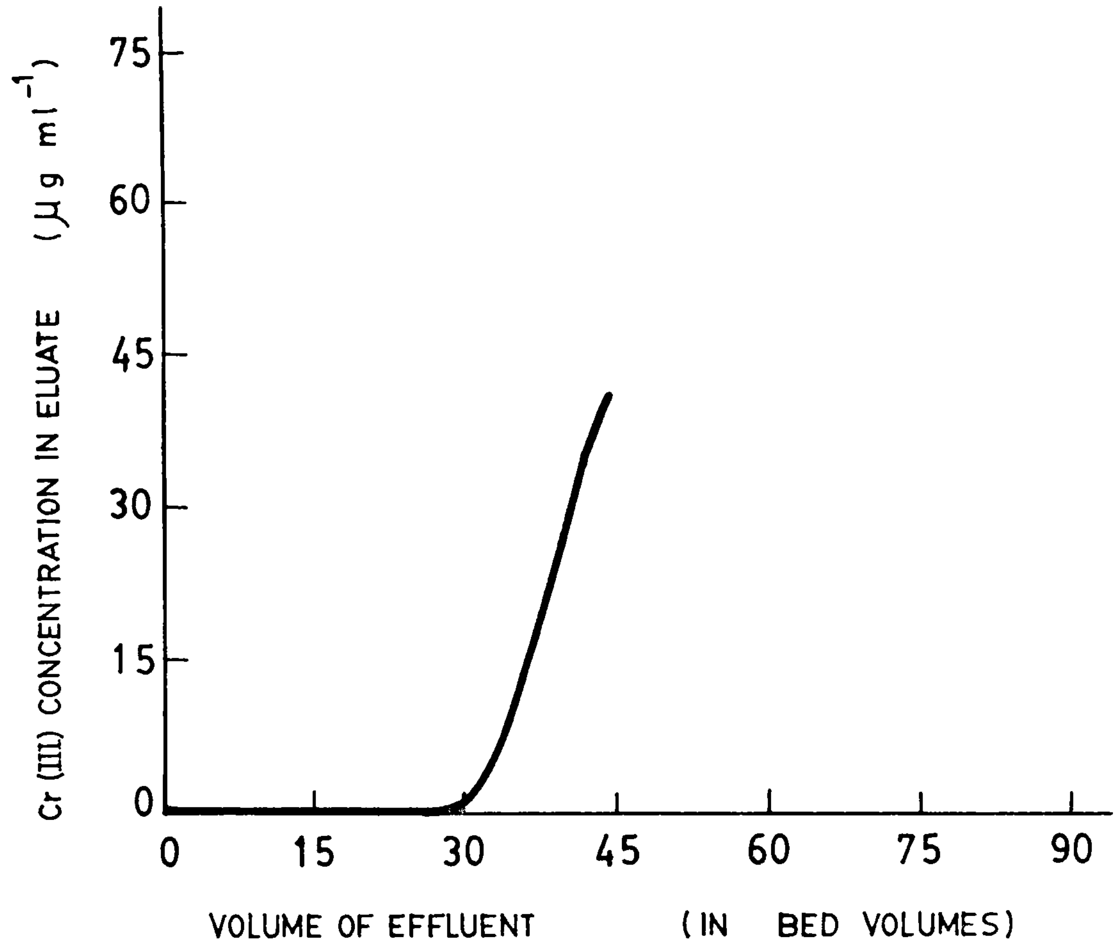
The column used was the same as that described in section 2.2.3(b) and was conditioned at pH 3 using ammonium citrate-citric acid. After conditioning the resin 1 ml of the pre-treated effluent for which pH was adjusted at 3 was introduced into the column. Chromium(III) was eluted using ammonium citrate-citric acid (pH 3) at a flow rate of 0.5 ml min^{-1}. Copper(II) and iron(III) were retained on the column. Copper(II) was then eluted with 0.1 M HCl followed by Fe(III) with 0.2 M HCl. The amount of Cr(III), Cu(II) and Fe(III) in the fractions were determined spectrophotometrically.

(c) Recovery of chromium from rinse water

The pH of the pre-treated sample was adjusted to 3 using ammonium citrate and citric acid. The solution was then passed through the column conditioned at pH 3 at a flow rate of 0.2 ml min^{-1}. Fractions were collected and concentration of Cr(III) determined.

3.4.3 Results and discussion

The chromium plating shop effluent usually contains high concentration of chromium, copper and iron. Hence it was necessary to dilute the solution before analysis. The SMH resin studied has a high degree of selectivity for Cu(II) (Fig.2.1). Hence eventhough the resin has appreciable capacity for Cr(III) at pH 5, Cr(III) could be easily eluted



ig.3.7 Breakthrough curve for Cr(III) from plating bath rinse water.
pH 3, ammonium citrate-citric acid. Other column characteristics same as in Fig.3.6.

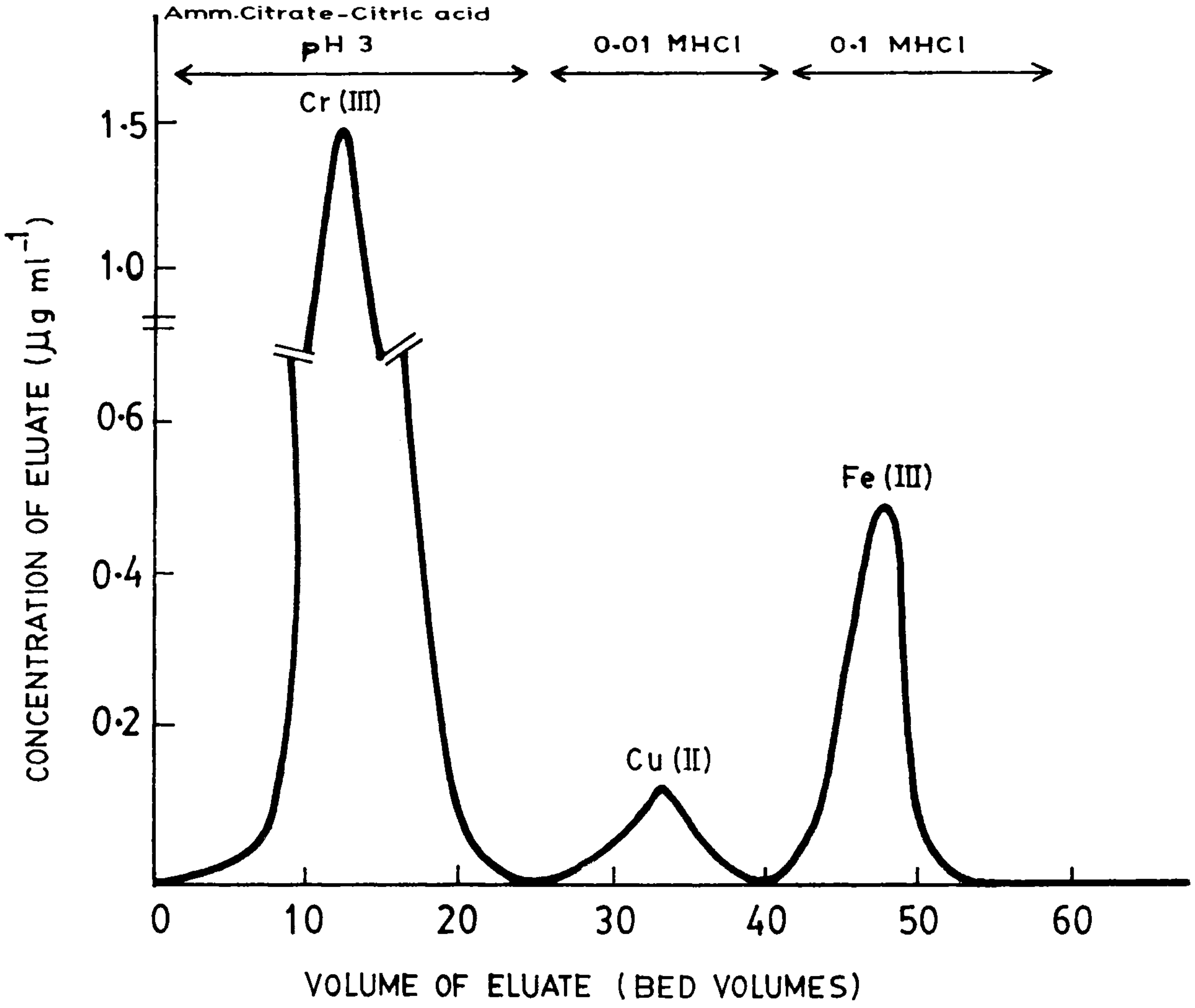


Fig.3.6 Separation of Cr(III), Cu(II) and Fe(III) from chromium plating solution.
Column dimension 15 cm length and 0.6 cm i.d., amount of resin 1.5 g, flow rate 12 bed volume/hour (bed volume 2.8 ml), eluent pH 3 - ammonium citrate-citric acid, eluent for Cr(III) 0.01 M HCl, eluent for Cu(II); 0.1 M HCl, eluent for Fe(III).

Table 3.11

Results of the analysis of plating bath solutions for the same sample at various dilutions

Plating bath solution	Metal ion	Mean of amount of metal ion recovered (μg)	Standard deviation* (μg)
1	Cr(II)	43.46	0.30
	Cu(II)	3.96	0.09
	Fe(III)	7.11	0.05
2	Cr(III)	55.8	0.50
	Cu(II)	5.07	0.10
	Fe(III)	8.86	0.05
3	Cr(III)	66.04	0.30
	Cu(II)	6.22	0.03
	Fe(III)	10.54	0.04
4	Cr(III)	90.08	0.20
	Cu(II)	8.09	0.04
	Fe(III)	14.24	0.56

* Mean and standard deviation of 5 readings given.

at lower pH. Subsequently Cu(II) was eluted with 0.1 M HCl and Fe(III) with 0.2 M HCl. The results are reproducible (Fig.3.6). Some typical results for different dilutions of the same sample are given in table 3.11.

The high breakthrough capacity obtained for Cr(III) using rinse solution (Fig.3.7) makes the resin applicable for the pre-concentration of Cr(III) from rinse solution.

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF POLY(STYRENE-CO-MALEIC N-PHENYLHYDROXAMIC ACID) RESIN (SMPH)

4.1 INTRODUCTION

The relationship between the structure and chelating properties of hydroxamic acid ligands has received much attention. Bass and Yoe studied thirtysix hydroxamic acids with various structural features for use as colorimetric reagents[147]. They concluded that color formation by these reagents is a function of pH, solvent and reagent concentration and that N-substitution does not significantly alter the characteristics.

The studies on poly(hydroxamic acid) resins reported in the literature are mostly on primary or N-unsubstituted cross-linked polyacrylic acid derivatives. Investigation by Philip et al[100,101] and Shah et al[104] have shown that N-phenyl substitution reduces the metal sorption capacity which is an expected consequence of the increase in formula weight of the repeat units. A perusal of the literature has revealed that the effect of incorporating N-phenylhydroxamic acid functions at the vicinal positions in the polymer backbone has not yet attracted the attention of researchers.

The synthesis of the N-phenylhydroxamic acid resin derived from poly(styrene-co-maleic acid) crosslinked with DVB is described in this section. The extraction of ten metal ions by the resin as a function of pH and also their sorption kinetics are reported here.

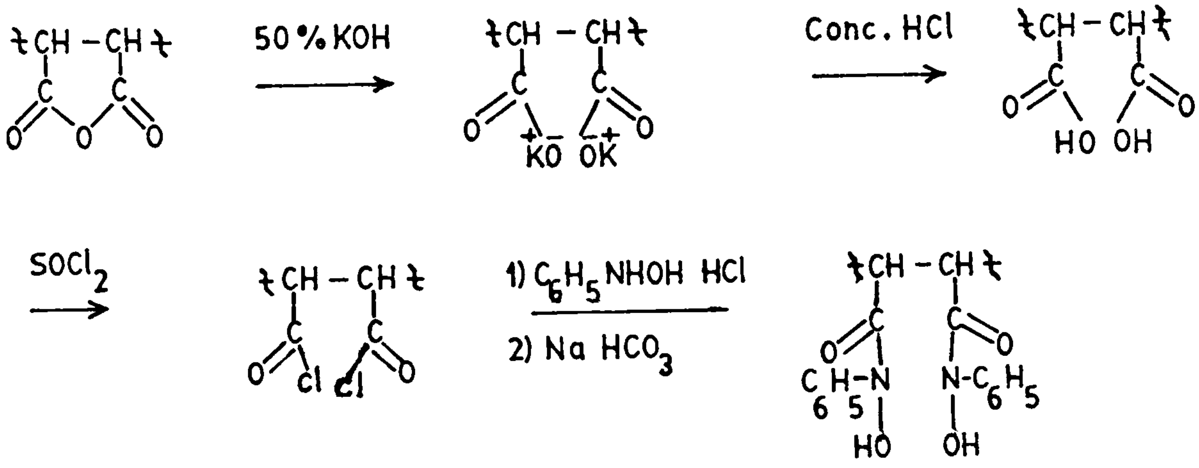
4.2 EXPERIMENTAL

4.2.1 Synthesis of the resin

Poly(styrene-co-maleic acid) crosslinked with DVB was prepared using styrene-maleic anhydride of equimolecular ratio with 0.75 mole % DVB. The copolymer so obtained was converted to the acid chloride as reported in section 2.2.1.

The acid chloride of the resin was washed with anhydrous diethyl ether and dried in a stream of dry air. To 10 g of the acid chloride were added 5 g of sodium bicarbonate, 10 ml of water and 100 ml of a solution containing 100 g of freshly prepared N-phenylhydroxylamine in diethyl ether. N-phenylhydroxylamine was prepared just before use by the reduction of nitrobenzene with zinc dust [148] The mixture was allowed to stand at room temperature with stirring for 2 h. The product was collected by filtration and washed with water and methanol. It was then dried in an air oven at 80°C for 8 h. The dry resin was ground in a mortar and seived through standard seives. Samples of particle size 74-150 µm (100-200 mesh ASTM) were used for further studies.

The synthetic routes employed is schematically shown below:



SCHEME 6 SYNTHESIS OF SMPH RESIN

4.2.2 Resin characterization

The resin was characterized by its nitrogen content, carboxyl content, stability towards acids and alkalies, water regain, sorption capacity, distribution coefficient, and sorption kinetics. The procedures used were the same as those described in section 2.2.2 for SMH resin.

i) Batch techniques

(a) Sorption capacities for metal ions

The metal sorption capacities of the resin for copper(II), iron(III), nickel(II), cobalt(II), zinc(II), lead(II), molybdenum(VI), uranium(VI), vanadium(V) and manganese(II) were determined by equilibrating 0.1 g of the resin with 20 ml of metal ion solution (400 $\mu g\ ml^{-1}$) in the pH range 1-6. Hydrochloric acid was used to adjust the pH between 1 and 2 and acetate buffer (0.1 M ammonium acetate and glacial acetic acid) in the pH range 3-6. The reactants were shaken for 8 h and the residual concentration of the metal ion was determined by withdrawing the supernatent liquid using a filter stick fitted with a G-3 sintered glass filter. The amount of metal ion sorbed was calculated from the difference between the initial and residual concentrations in the solution phase. The sorption capacities were calculated as described in section 2.2.2.

(b) Distribution coefficient

Distribution coefficient was determined as given in section 2.2.3(a)(ii).

(c) Sorption studies

The rate of uptake of various metal ions on the resin was determined by shaking 0.1 g of the resin with 20 ml of metal ion solution (400 μg ml^{-1}) the pH being adjusted to that at which sorption of the respective metal ions occurred. Aliquots of the test solutions were withdrawn at various time intervals and the residual concentration of the metal ion was determined.

ii) Column technique

A glass column, 10 cm length and 1.2 cm i.d. fitted with ground glass joints was used for the column operations. The column and feed adjustments used were same as those described in section 2.2.3(b).

Breakthrough studies were carried out using solutions of copper(II), iron(III), nickel(II), cobalt(II), manganese(II), molybdenum(VI), vanadium(V), zinc(II) and uranium(VI). The metal ion solutions after adjusting the pH were passed through the column at a flow-rate of 0.5 ml min^{-1}. The eluate fractions were collected in 5 ml portions, and analysed for the metal ion concentration spectrophotometrically as described in section 2.2.4.

4.3 RESULTS AND DISCUSSION

4.3.1 Nature of the resin

The resin is the N-phenylhydroxamic acid derivative of poly(styrene-co-maleic acid) crosslinked with DVB. The resin is porous and has a water regain of 45%.

The nitrogen content of the resin was found to be 1.56 mmol g^{-1} of dry resin, whereas poly(styrene-co-maleic acid) used as the starting material contained 6.1 m equiv g^{-1} of carboxylic acid. This indicates that only 38% of the carboxylic acid is converted to N-phenylhydroxamic acid.

The stability of the resin towards 0.1 M NaOH, 0.1 M HNO_3 and conc. HCl was investigated by soaking it in each medium separately for 24 h. The resin recovered by washing and drying showed no significant change in mass or capacity for Cu(II) by this treatment. These observations indicate that it is stable in these media (table 4.1).

Table 4.1

Sorption capacity of acid and alkali treated SMPH-resin for Cu(II)

Amount of SMPH resin 0.1 g, volume of Cu(II) solution 20 ml, amount of Cu(II) 4 mg, shaking time 8 h, temperature 28±1°C.

Treatment given	Capacity (mmol g^{-1})
Neat	1.13
0.1 N HCl	1.13
0.5 N HCl	1.129
2 N HCl	1.128
0.1 N NaOH	1.129
0.1 N HNO_3	1.129

4.3.2* Effect of pH on metal ion sorption

The extraction of several metal ions by N-phenylhydroxamic acid resin as a function of pH is shown in Figs.4.1 and 4.2 and tables 4.2 to 4.11. It can be seen that compared to other metal ions studied the resin has a high selectivity for Cu(II) reaching a maximum of 1.1 mmol g^{-1} at pH 3. This may be due to the favourable steriochemistry of Cu(II) for co-ordination with vicinally located hydroxamic acid functional group.

Iron(III) is retained from solutions of lower pH compared with the other metal ions studied. The sorption capacity reaches a maximum at pH 1.5 and decreases sharply on further increase of pH.

The sorption capacity for Pb(II) and Zn(II) increases steadily as pH is increased. In the case of Co(II), Mn(II) and Ni(II) as the pH is increased, the capacity increases, reaches a maximum and then decreases. The sorption capacity for U(VI) reaches 0.13 at pH 1.5 with 37.5% extraction. For V(V) the sorption capacity is very low, Mo(VI) is not sorbed to any significant extent.

Table 4.2 to 4.11

Sorption of metal ions on SMPH resin as a function of pH

Amount of SMPH resin 0.1 g, particle size 74-150 µm, volume of solution 20 ml, amount of metal ion 4.0 mg, shaking time 8 h, temperature 28±1°C.

$$K_D = \frac{\text{mg of metal ion per g of resin at equilibrium}}{\text{mg of metal ion per ml of solution at equilibrium}}$$

Table 4.2

Copper(II)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
2.0	0	0	0
2.25	0.34	26.87	73.5
2.5	0.61	48.75	190.2
3.0	1.13	90.5	1898.0
4.0	1.13	90.5	1898.0
5.0	1.13	90.5	1898.0

Table 4.3

Nickel(II)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
2.2	0.09	5.9	12.6
2.6	0.09	5.9	12.6
3.0	0.38	27.8	77.1
4.0	0.59	43.1	151.6
5.0	0.45	31.3	90.9
5.7	0.19	14.1	32.7

Table 4.4

Iron(III)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
1.0	0.06	4.3	9.15
1.25	0.39	27.5	75.9
1.50	0.57	40	133.3
1.75	0.22	15.3	36.2
2.0	0.05	3.4	7.1

Table 4.5

Manganese(II)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
2.2	0	0	0
3.0	0.13	9.1	19.9
3.5	0.37	25.3	67.8
4.0	0.61	41.6	142.2
5.0	0.65	44.4	159.5
6.0	0.31	21.6	55.0

Table 4.6

Cobalt(II)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
2.0	0.08	6.3	13.3
3.0	0.23	17.2	41.5
4.0	0.59	43.8	155.6
5.0	0.84	61.7	322.4
5.5	0.69	50.8	206.3
6.0	0.36	26.6	72.3

Table 4.7

Zinc(II)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
2.0	0.08	6.3	13.5
3.0	0.20	16.5	39.5
3.5	0.40	33.1	98.8
4.0	0.61	49.6	197.0
5.0	0.64	52.5	221.1
6.0	0.79	64.3	359.4

Table 4.8

Lead(II)

pH	Capacity (mmol g^{-1})	Percentage extracted
2.0	0.10	25.4
3.0	0.24	63.1
4.0	0.32	82.8
5.0	0.37	95.5
6.0	0.36	93.6

Table 4.9

Vanadium(V)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
1.0	0.06	3.8	7.8
2.0	0.07	4.8	10.0
3.0	0.13	8.0	17.4
4.0	0.12	7.5	16.2

Table 4.10

Uranium(VI)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
3.0	0	0.63	1.3
3.5	0.079	23.8	62.3
4.0	0.081	24.4	64.5
4.5	0.13	37.5	120.0
5.0	0.09	27.5	75.9
5.0	0.08	23.8	62.3

Table 4.11

Molybdenum(VI)

pH	Capacity (mmol g^{-1})	Percentage extracted	K_D
1.0	0.04	4.5	9.4
2.0	0.01	1.5	3.1
3.0	0.018	1.0	2.0
4.0	0	0	0

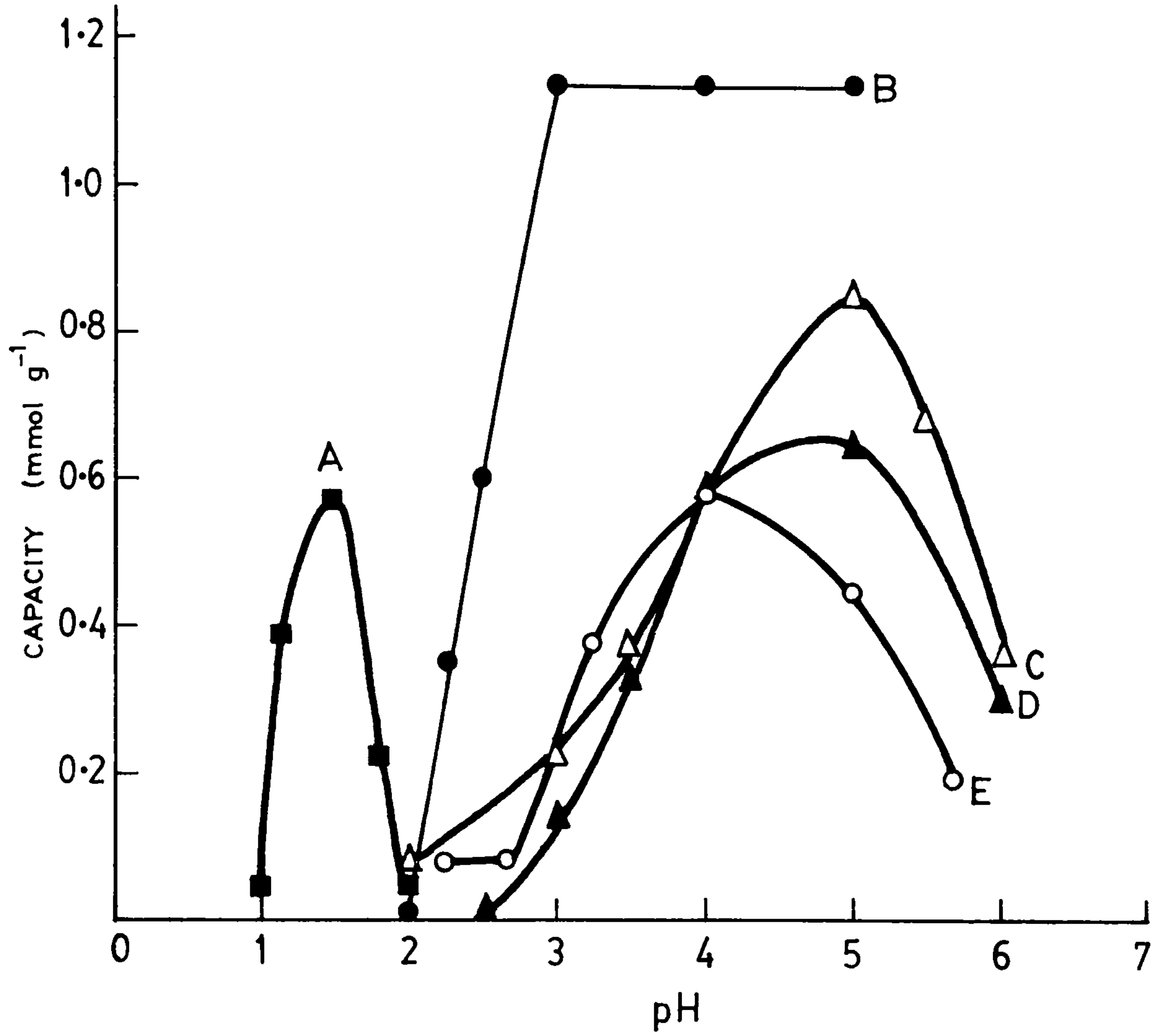


Fig.4.1 Effect of pH on the sorption of metal ions on SMPH resin. Amount of resin 0.1 g; particle size 74-150 μm; volume of solution 20 ml; concentration of metal ion solution 400 μg ml^{-1}; shaking time 8 h. A, Fe(III); B, Cu(II); C, Co(II); D, Mn(II); E, Ni(II).

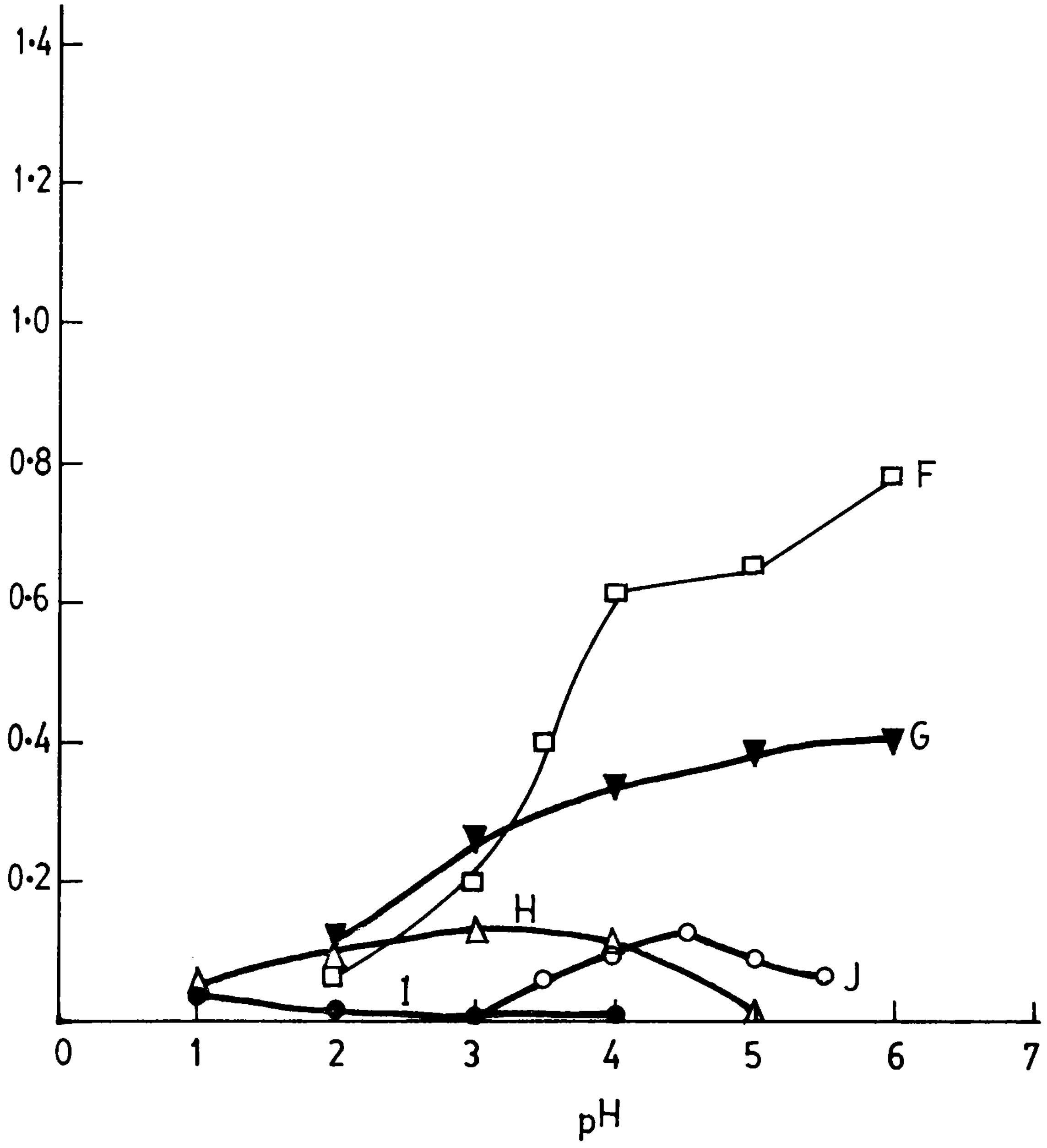


Fig.4.2 Effect of pH on the sorption of metal ions on SMPH resin. Conditions same as in Fig.4.1. F, Zn(II); G, Pb(II); H, V(V); I, Mo(VI) and J, U(VI).

Compared to the capacities of SMH resin for metal ions, it is found that there is considerable decrease in the capacity of SMPH resin for the metal ions (table 4.12). This could be due to the steric hindrance exerted by substitution of phenyl group on the introgen atom blocking the facile co-ordination of the nitrogen atoms to the metal ions.

4.3.3 Distribution coefficient

Tables 4.2 to 4.11 and Fig.4.3 give the distribution coefficients at various pH for the metal ions. The K_D values at the pH of maximum sorption vary for the metal ions studied. The K_D values for Cu(II) is exceptionally high showing that the resin has a higher affinity towards Cu(II). The capacities and K_D values at the pH of maximum sorption is given in table 4.12. The wide difference in the K_D values of metal ions makes the resin applicable for the separation of a number of binary and ternary mixtures of metal ions.

4.3.4 Sorption kinetics

The sorption kinetics for various metal ions on SMPH resin is given in tables 4.13 to 4.15 and Figs. 4.4 and 4.5. The time for reaching 50% of maximum sorption ($t^{\frac{1}{2}}$) is less than 5 minutes for all metal ions studied.

Table 4.12

Metal sorption properties of SMH and SMPH resins

Metal ion	SMH			SMPH		
	pH for maximum sorption	Capacity (mmol g^{-1})	K_D	pH for maximum sorption	Capacity (mmol g^{-1})	K_D
Copper(II)	5.5	1.14	1948.0	3.0	1.13	1898.0
Zinc(II)	6.0	0.86	472.3	6.0	0.79	359.4
Cobalt(II)	6.0	0.85	333.0	5.0	0.84	322.4
Nickel(II)	5.0	0.69	291.0	4.0	0.59	151.6
Iron(III)	2.3	0.33	66.7	1.5	0.57	133.3
Manganese(II)	6.0	0.84	270.6	5.0	0.65	159.5
Vanadium(V)	4.0	0.21	30.5	3.0	0.13	17.4
Uranium(VI)	4.5	0.17	200.0	4.5	0.13	120.0
Molybdenum(VI)	2.0	0.07	16.0	1.0	0.04	9.4

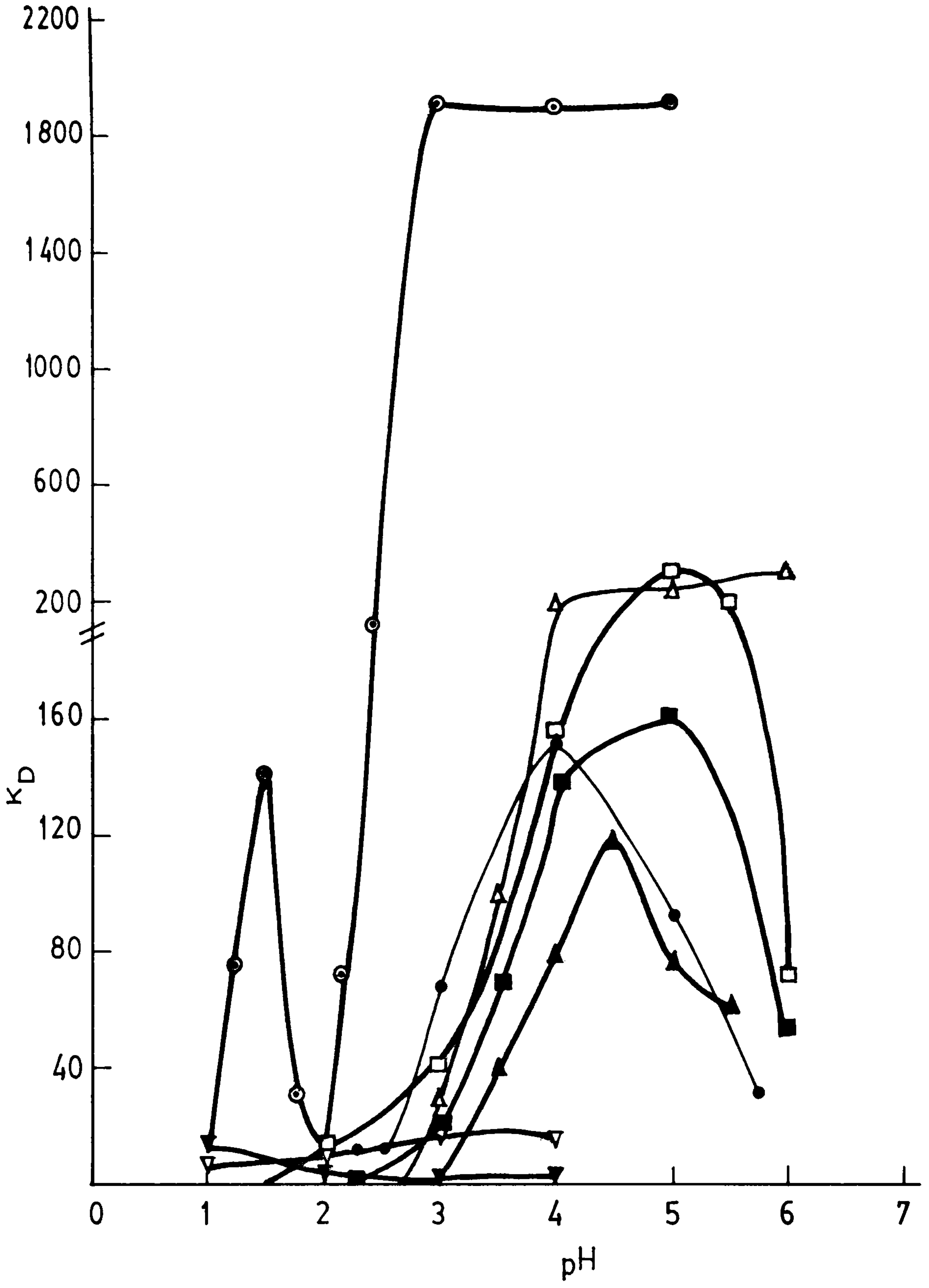


Fig.4.3 Distribution coefficient k_D for various metal ions at different pH using SMPH resin.
Conditions are same as in Fig.4.1.
○, Cu(II); ■ , Mn(II); □ , Co(II); ● , Ni(II);
⊙, Fe(III); △ , Zn(II); ▽ , V(V); ▲ , U(VI);
▼, Mo(VI).

Table 4.13

Sorption kinetics of metal ions on SMPH resin

Amount of resin 0.1 g, particle size 74-150 µm, volume of metal ion solution 20 ml, amount of metal ion 4.0 mg, temperature 28±1°C. pH: Cu(II) 3.0, Ni(II) 4.0, Fe(III) 1.5, Buffer 0.1 M ammonium acetate/glacial acetic acid.

Time (min.)	Capacity (mmol g^{-1})		
	Cu(II)	Ni(II)	Fe(III)
5	1.10	0.58	0.27
10	0.12	0.59	0.32
15	1.13	0.59	0.40
20	1.13	0.59	0.54
30	1.13	--	0.57
60	--	--	0.57

Table 4.14

Sorption kinetics of metal ions on SMPH resin

Conditions same as in Table 4.13
pH: Pb(II) 5.0, Zn(II) 6.0, Co(II) 5.0

Time (min.)	Capacity (mmol g^{-1})		
	Pb(II)	Zn(II)	Co(II)
5	0.35	0.67	0.74
10	0.37	0.70	0.80
15	0.37	0.78	0.84
20	0.37	0.78	0.84
30	--	0.79	0.84
60	--	0.79	0.84

Table 4.15

Sorption kinetics of metal ions on SMPH resin

Conditions same as in Table 4.13

pH: Mn(II) 5.0, V(V) 3.0, U(VI) 4.5, Mo(VI) 1.0

Time (min.)	Capacity (mmol g^{-1})			
	Mn(II)	V(V)	U(VI)	Mo(VI)
5	0.55	0.06	0.10	0.02
10	0.59	0.10	0.11	0.03
15	0.64	0.12	0.13	0.04
20	0.65	0.13	0.13	0.04
30	0.65	0.13	0.13	0.04
60	0.65	0.13	--	--

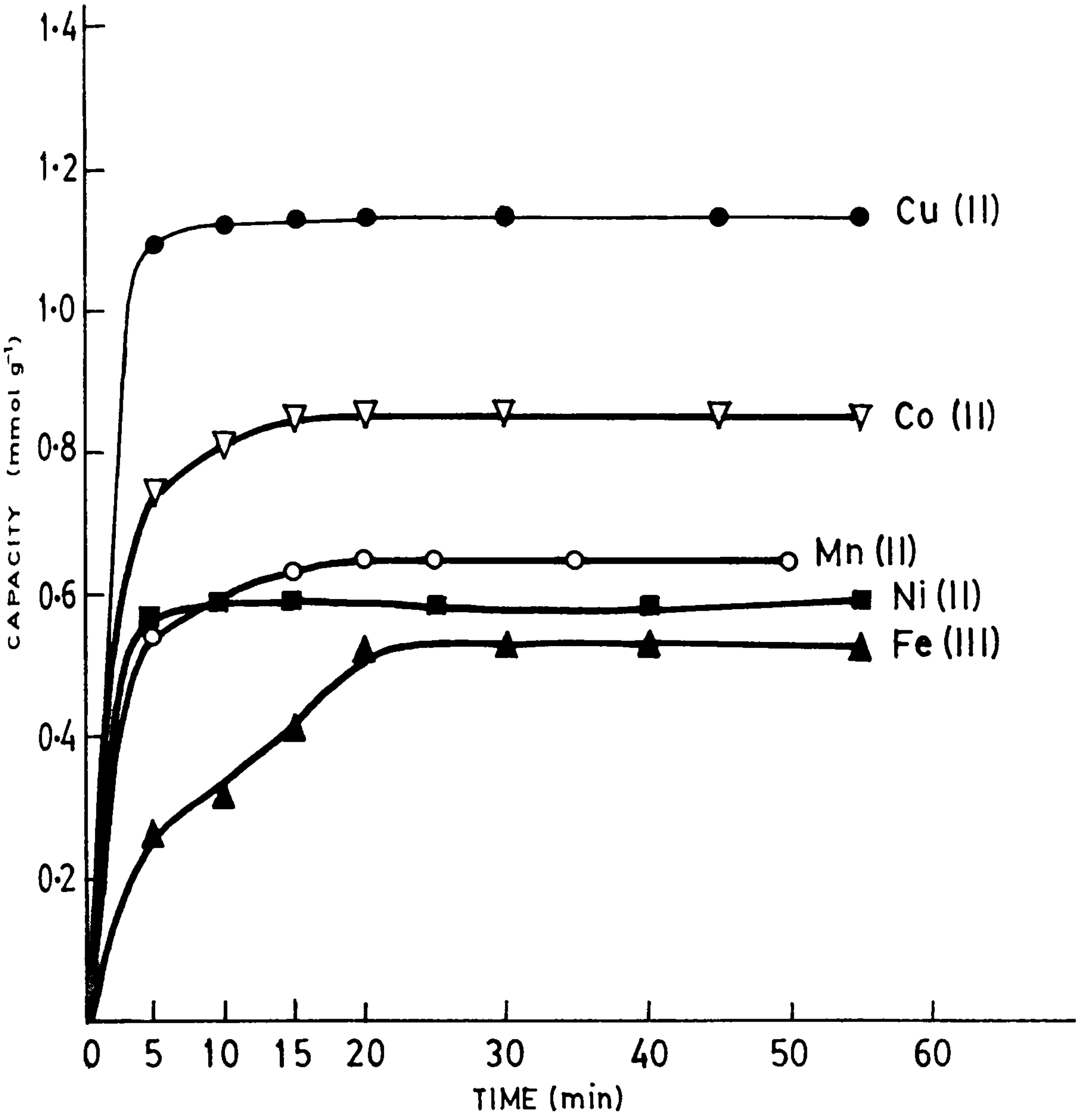


Fig.4.4 Sorption kinetics of metal ions on SMPH resins. Amount of resin 0.1 g, particle size 75-150 μm, volume of solution 20 ml, amount of metal ion 4.0 mg, temperature 28±1°C, buffer 0.1 M ammonium acetate/glacial acetic acid. pH: Cu(II) 3.0, Co(II) 5.0, Mn(II) 5.0, Ni(II) 4.0, Fe(III) 1.5.

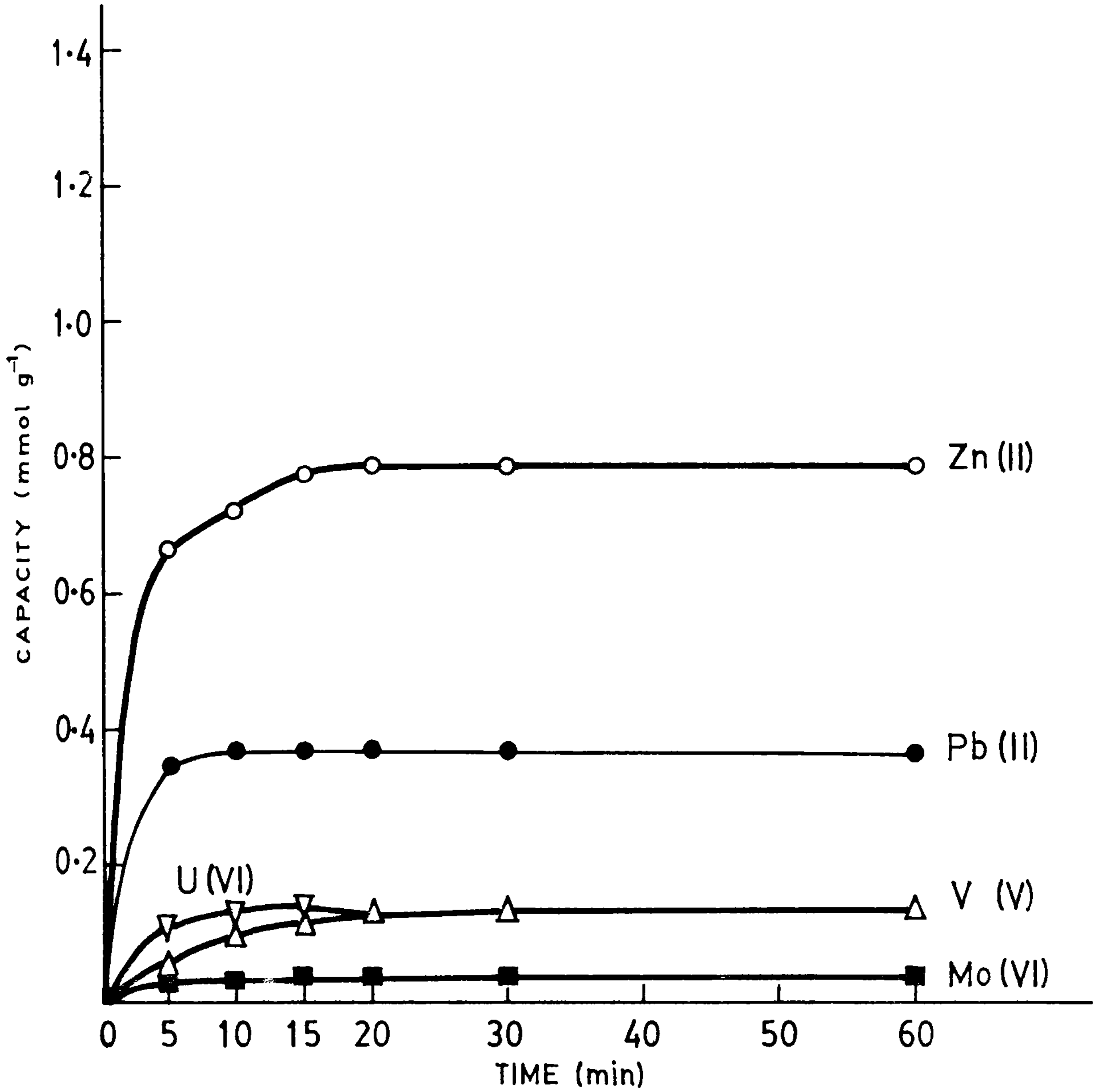


Fig.4.5 Sorption kinetics of metal ions on SMPH resin. Conditions same as that in Fig.4.4. pH: Zn(II) 6.0, Pb(II) 5.0, V(V) 3.0, U(VI) 4.5, Mo(VI) 1.0.

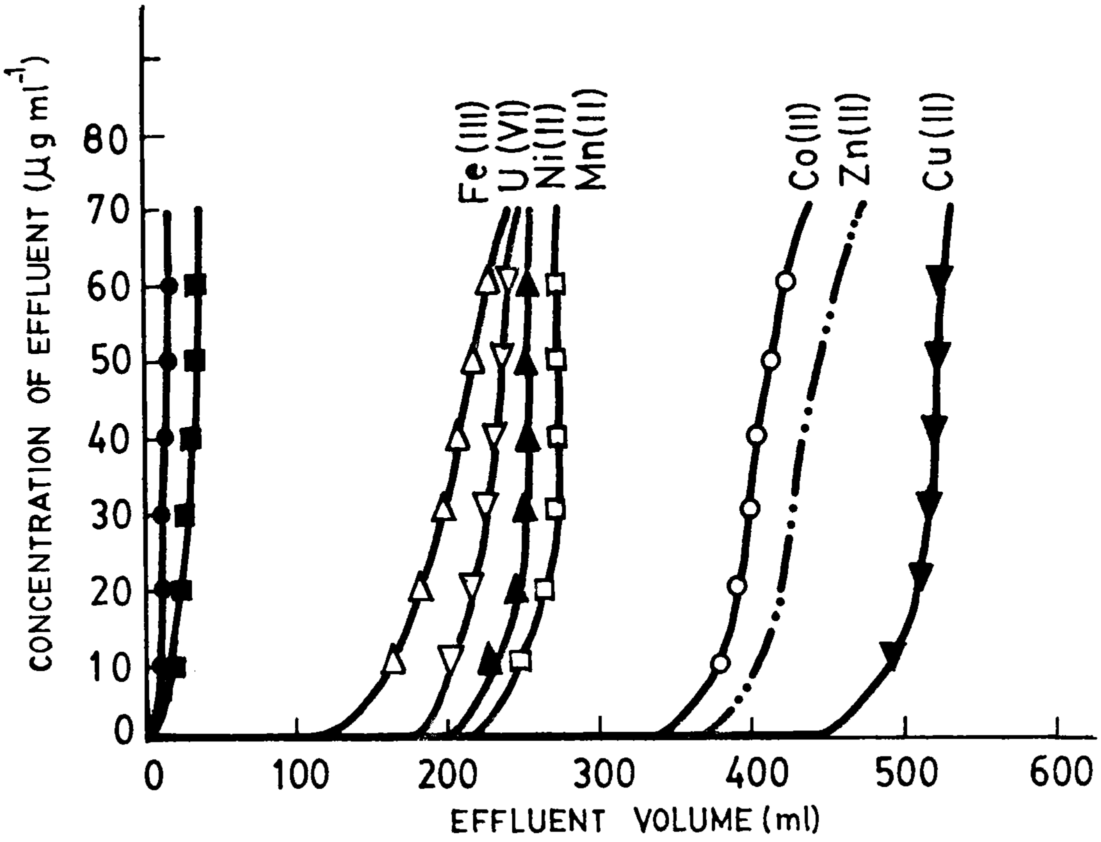


Fig.4.6 Breakthrough curves for metal ions on SMPH resin. Column dimension, 10 cm length and 1.2 cm i.d.; particle size 75-150 μm; concentration of metal ion solutions, 100 μg ml^{-1}; flow rate, 0.5 ml min^{-1}. pH of solutions Fe(III) and Mo(VI), 1.5; V(V), 3; Ni(II) and Cu(II), 4; U(VI) 4.5, Mn(II) and Co(II), 5.

The favourable sorption kinetics makes the resin useful for the ion chromatographic separation of metal ions from their mixtures.

4.3.5 Breakthrough studies

From the point of view of ion-exchange chromatography breakthrough capacities are more significant than batch capacities. The breakthrough curves for different metal ions at the pH of maximum sorption at a flow rate of 0.5 ml min^{-1} are given in Fig.4.6. The breakthrough curves are steep and the metal ions are found to breakthrough at different times. The breakthrough curves indicate the possibility of pre-concentration of metal ions from their lean sources and separation from their mixtures.

CHAPTER V

ANALYTICAL APPLICATIONS OF SMPH RESIN

5.1 INTRODUCTION

The results from batch and column extraction experiments presented in Chapter IV point to the fact that SMPH resin is a suitable medium for the separation of different metal ions studied from their mixtures. Some of the typical separations achieved are presented in this chapter.

5.2 EXPERIMENTAL

The column employed was the same as that described in section 4.2.2(ii).

(a) Copper(II)-iron(III) separation

Copper(II) and iron(III) mixtures of various compositions were prepared in 0.01 M HCl. The column was pre-conditioned with 0.01 M HCl and 1 ml aliquot of the analytical mixture was introduced into the column. Copper(II) was eluted using 0.03 M HCl followed by Fe(III) using 0.2 M HCl. Fractions were collected and concentration of metal ions determined spectrophotometrically[128,129].

(b) Nickel(II)-iron(III) separation

Mixtures of Ni(II)-Fe(III) of various compositions were prepared. The pH of the solution was adjusted to

2 using HCl. The column was pre-conditioned with 0.01 M HCl and 1 ml of the mixture introduced. Flow rate was adjusted 0.5 ml min^{-1}. Nickel(II) was eluted using 0.03 M HCl followed by elution of Fe(III) using 0.2 M HCl. Both metal ions in the eluate were quantitated spectrophotometrically[129,130].

(c) Nickel(II)-copper(II) separation

pH of the solutions containing Ni(II) and Cu(II) of various proportions were adjusted to 4 using ammonium acetate and acetic acid. The column was conditioned at the same pH. Aliquot of Ni(II)-Cu(II) mixture (1 ml) was introduced into the column. Nickel(II) was first eluted using 0.01 M HCl and quantitated spectrophotometrically. Subsequently copper(II) was eluted using 0.1 M HCl and its concentration determined.

(d) Manganese(II)-copper(II) separation

Manganese(II)-copper(II) mixtures of various ratios were prepared and pH was adjusted to 4 using ammonium acetate and acetic acid. After pre-conditioning the column at the same pH 1 ml aliquot of the mixture was introduced into the column. Ni(II) was eluted using 0.01 M HCl followed by Cu(II) with 0.1 M HCl. The fractions collected were quantitated spectrophotometrically for the metal ions[132,128].

(e) Iron(III)-nickel(II)-copper(II) separation

Ternary mixtures containing various proportions of Fe(III), Ni(II) and Cu(II) were prepared and pH was adjusted to 4 using ammonium citrate and citric acid. The column was pre-conditioned at the same pH. Aliquots of the mixture were introduced at the top of the column. Fe(III) was eluted using citrate buffer pH 4. Ni(II) was then eluted using 0.01 M HCl followed by Cu(II) using 0.1 M HCl. The metal ions in the eluate were quantitated spectrophotometrically.

5.3 RESULTS AND DISCUSSION

SMPH resin is found to have a moderate degree of selectivity for various ions as observed from the break-through curves (Fig.4.7), batch capacities and pH of maximum sorption (table 4.12). Further, the favourable sorption kinetics makes the resin useful for separating metal ion mixtures on a column of the resin. Synthetic mixtures of Cu(II)-Fe(III), Ni(II)-Fe(III), Ni(II)-Cu(II), Mn(II)-Cu(II) and Fe(III)-Ni(II)-Cu(II) were separated on a column of the resin.

From the dependence of sorption on pH (Figs.4.1 and 4.2) it is clear that Fe(III) has a comparatively low pH of maximum sorption (1.5) compared to the other metal ions, and hence can be separated from Cu(II), Ni(II), Mn(II), Co(II) etc. from acid solutions using a column of the resin. As typical examples, Cu(II)-Fe(III) and Ni(II)-Fe(III) separations were achieved from a medium of low pH. Cu(II) and Ni(II) are not sorbed on the resin at this pH and are separated from Fe(III) which is strongly sorbed on the resin. Fe(III) can be eluted only by 0.2 M HCl.

The various compositions of metal ions in the mixtures and the recovery are given in tables 5.1 and 5.2. As observed from these tables the standard deviations for the recoveries are low. The elution curves for the chromatographic separation (Fig .5.1) show well separated peaks. As in the case of SMH resin, SMPH resin also shows a high degree of selectivity towards Cu(II). The high K_D value of Cu(II) compared to those of other metal

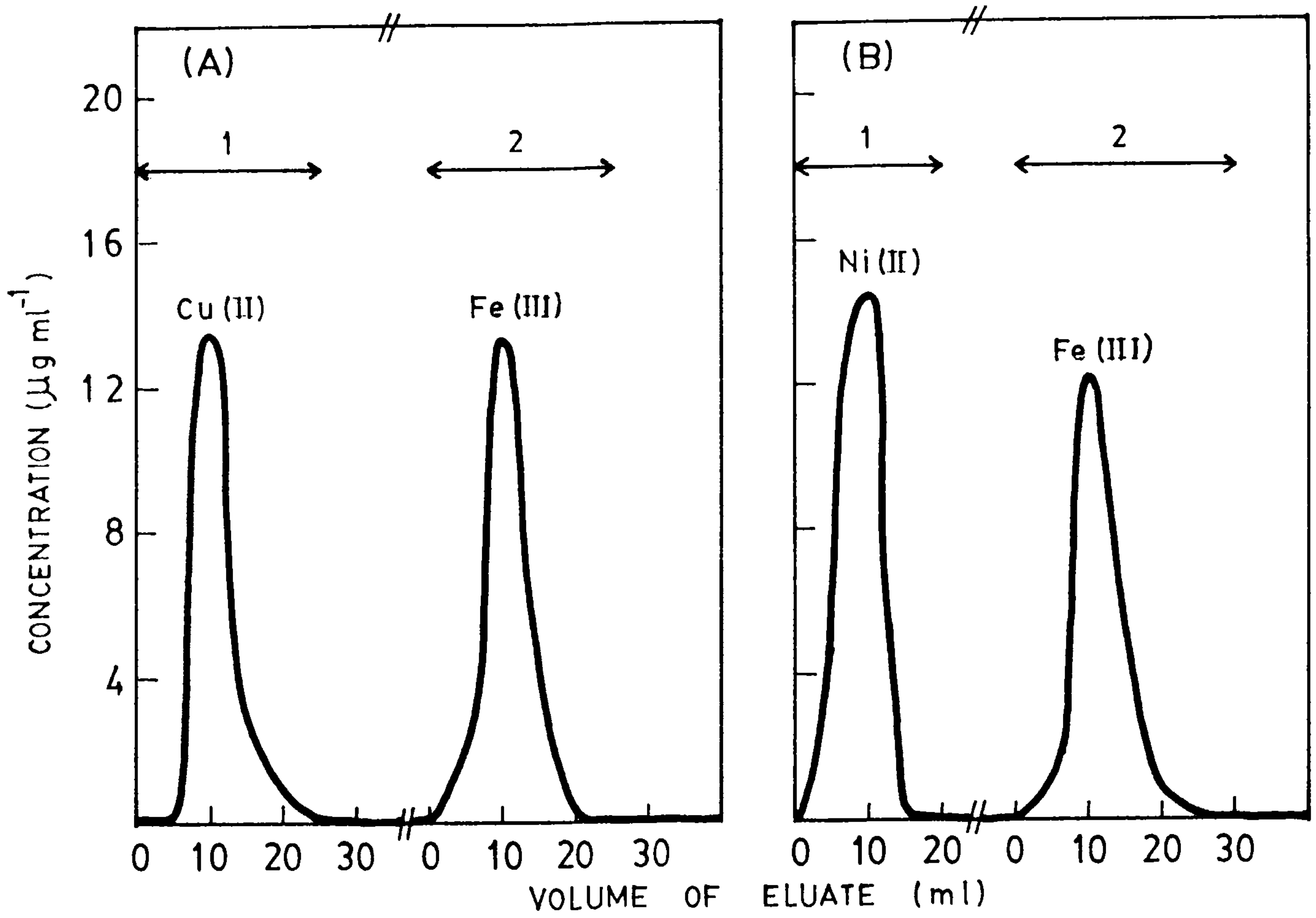


Fig.5.1 Elution curves for (A) Cu(II)-Fe(III), (B) Ni(II)-Fe(III). Column dimension 10 cm length and 1.2 cm i.d.; particle size 75-150 µg, flow rate 0.5 ml min^{-1}.
1) 0.03 M HCl, eluent for Cu(II)
2) 0.2 M HCl, eluent for Fe(III)

Table 5.1

Copper(II)-iron(III) separation on SMPH resin

Column dimension 10 cm length and 1.2 cm i.d., particle size 75-150 µm, flow rate 0.5 ml min^{-1}, eluent for Cu(II) 0.03 M HCl, eluent for Fe(III) 0.2 M HCl.

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Cu(II) 100	99.9	25	-0.1	0.21
Fe(III) 100	100.1	20	1.0	0.15
Cu(II) 100	99.8	25	-0.2	0.19
Fe(III) 50	49.8	15	-0.4	0.07
Cu(II) 50	49.7	20	-0.6	0.15
Fe(III) 100	100.2	20	0.2	0.12

* Mean of 6 values.

Table 5.2

Nickel(II)-iron(III) separation on SMPH resin

Eluent for Ni(II) 0.03 M HCl, eluent for Fe(III) 0.2 M HCl. Other conditions same as in table 5.1

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Ni(II) 100	99.7	15	-0.3	0.10
Fe(III) 100	100.3	25	0.3	0.09
Ni(II) 100	99.9	15	-0.1	0.11
Fe(III) 50	49.9	15	-0.2	0.15
Ni(II) 50	49.6	15	-0.4	0.06
Fe(III) 100	100.1	25	0.1	0.04

* Mean of 6 values.

Table 5.3

Nickel(II)-copper(II) separation on SMPH resin

Eluent for Ni(II) 0.01 M HCl, eluent for Cu(II) 0.1 M HCl. Other conditions same as in table 5.1.

Amount loaded (μg)	Amount recovered (mean value)* (μg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (μg)
Ni(II) 100	99.8	20	-0.2	0.07
Cu(II) 100	99.9	20	-0.1	0.12
Ni(II) 100	99.7	20	-0.3	0.10
Cu(II) 50	49.7	15	-0.6	0.13
Ni(II) 50	49.9	15	-0.2	0.04
Cu(II) 100	99.9	20	-0.1	0.09

* Mean of 6 values.

Table 5.4

Manganese(II)-copper(II) separation on SMPH resin

Eluent for Mn(II) 0.001 M HCl, eluent for Cu(II) 0.1 M HCl. Other conditions same as in table 5.1.

Amount loaded (µg)	Amount recovered (mean value)* (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Mn(II) 100	99.9	20	-0.1	0.20
Cu(II) 100	100.1	20	0.1	0.17
Mn(II) 100	99.7	20	-0.3	0.15
Cu(II) 50	50.1	15	0.2	0.11
Mn(II) 50	49.9	15	-0.1	0.11
Cu(II) 100	99.9	20	-0.1	0.14

* Mean of 6 values.

Table 5.5

Iron(III)-nickel(II)-copper(II) separation on SMPH resin

Eluent for Fe(III) citrate buffer pH 4, eluent for Ni(II) 0.01 M HCl. Other conditions same as in table 5.1.

Amount loaded (µg)	Amount recovered (mean value)[*] (µg)	Eluent volume (ml)	Error of mean value (%)	Standard deviation (µg)
Fe(III) 100	100.4	15	0.4	0.11
Ni(II) 100	99.7	30	-0.3	0.25
Cu(II) 100	99.9	20	-0.1	0.16
Fe(III) 100	100.1	15	0.1	0.09
Ni(II) 50	49.9	20	-0.2	0.12
Cu(II) 50	49.7		-0.6	0.15
Fe(III) 50	50.1	15	0.2	0.07
Ni(II) 50	49.8	20	-0.4	0.03
Cu(II) 100	100.1	20	0.1	0.10

* Mean of 6 values.

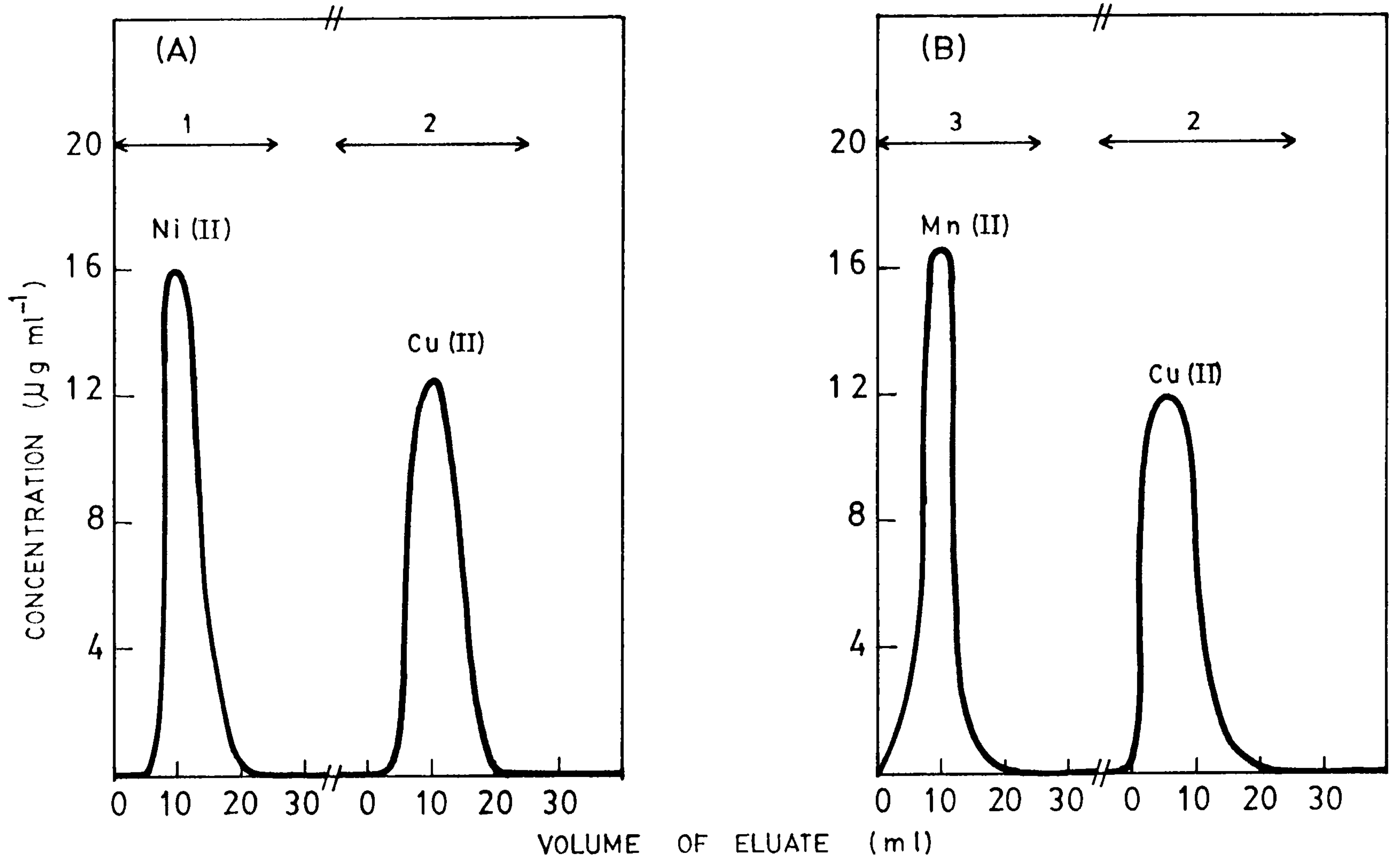


Fig.5.2 Elution curves for (A) Ni(II)-Cu(II), (B) Mn(II)-Cu(II).
Conditions same as in Fig.5.1.
1) 0.01 M HCl, eluent for Ni(II)
2) 0.03 M HCl, eluent for Cu(II)
3) 0.001 M HCl, eluent for Mn(II)

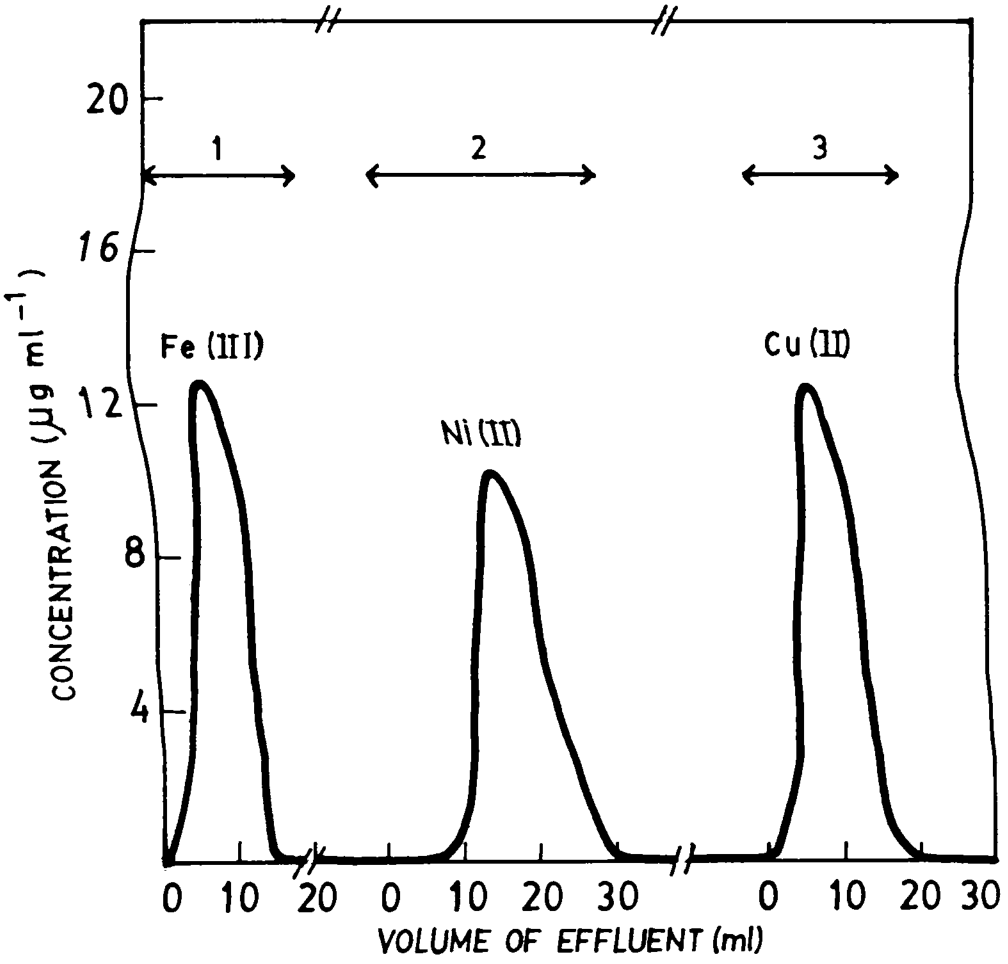


Fig.5.3 Elution curves for Fe(III)-Ni(II)-Cu(II). Conditions same as in Fig.5.1.
1) Citrate buffer pH 4, eluent for Fe(III)
2) 0.01 M HCl, eluent for Ni(II)
3) 0.1 M HCl, eluent for Cu(II).

CHAPTER VI

PHYSICO-CHEMICAL STUDIES ON SMH AND SMPH RESINS AND THEIR METAL COMPLEXES

ions lends the resin useful for the separation of these metal ions from Cu(II). The results of the separation achieved for the mixtures of Cu(II)-Ni(II) and Mn(II)-Cu(II) using different eluents are presented in tables 5.3 and 5.4. The recoveries are characterized by low magnitudes for standard deviation. Elution curves (Fig .5.2) show clean separations.

The separation and recovery of individual metals from the ternary mixture of Fe(III)-Ni(II)-Cu(II) of various compositions are presented in table 5.5. The medium used was citrate buffer pH 4 to prevent the precipitation of Fe(III). The metal ions were separated using different eluting agents. The elution curves are well defined (Fig. 5.3) and have low magnitudes for standard deviation (table 5.5).

These separations show that SMPH resin is a promising medium for the efficient separation of the transition metals.

6.1 INTRODUCTION

In the development of metal-ion specific resins, a detailed knowledge of the co-ordination geometry of the resin around the metal ions is of great importance. Physico-chemical methods mainly based on spectral and magnetic properties have been used to obtain structural information of polymer complexes[149]. Hoek and Reedijk carried out such investigation with the aid of electronic spectra and EPR on the metal complexes of commercially available chelating resin chelex-100, having styrene-DVB matrix to which iminodiacetate groups are attached[150,151]. They have also reported similar studies on the complexes of spheron oxime 1000-a chelating resin with hydroxyethyl-methacrylate and ethylene dimethacrylate matrix to which 8-quinolinol functional groups are attached. Infrared spectroscopy is another technique which has been used for characterising chelating ion-exchange resins and to locate the co-ordination sites of chelating resins in their metal complexes[152-155]. So far no work has been reported on the co-ordination geometry of bound metal ions on chelating resins with vicinal hydroxamic acid functional groups. In this chapter the results of the studies on the relationship between the geometry around the metal ion for Cu(II), Fe(III), Co(II) and Ni(II) and chelating nature of SMH and SMPH resins using electronic, ESR and FTIR spectroscopy are presented.

6.2. EXPERIMENTAL

6.2.1 Instruments used

Solid state electronic spectra of the complexes in the region 300 to 2000 nm were recorded with a Hitachi U-3410 spectrophotometer using the mull technique[156]. FTIR spectra of the resins and their metal complexes were recorded using a BOMEM DA 3.16 FTIR spectrophotometer in the region 500-4000 cm^{-1}. The ESR powder spectra was taken using a E 109 (Varian) ESR spectrophotometer at room temperature.

6.2.2 SMH resin and complexes

(a) Synthesis

Metal complexes of Cu(II), Fe(III), Co(II) and Ni(II) were prepared by shaking 1 g of SMP resin with 200 ml of the metal ion solutions of 2000 $\mu g\ ml^{-1}$ concentration at the pH of maximum sorption reported earlier in Table 2.13. The coloured complexes were suction filtered after shaking for 8 h, washed with water and dried at 80°C in vacuum for 10 h.

Table 6.1

IR absorption bands (cm^{-1}) of SMH resin and its metal complexes

SMH	SMH-Cu(II)	SMH-Fe(III)	SMH-Ni(II)	SMH-Co(II)	Assignment of relevant bands
3450 (b)	3450 (b)	3450 (b)	3450 (b)	3450 (b)	νOH (bound water) and NH
1654 (s)	1708 (v.s.)	1693 (v.s.)	1700 (v.s.)	1703 (v.s.)	νC=O (hydroxamic acid)
1562 (m)	1562 (sh)	1562 (sh)	1562 (sh)	1562 (sh)	ν N-H
1250 (s)	1230 (s)	1230 (s)	1230 (s)	1230 (s)	ν C-N
1085 (m)	1072 (m)	1072 (m)	1072 (m)	1072 (m)	ν N-O
1492 (m)	1492 (m)	1496 (m)	1496 (m)	1496 (m)	ν C-C(Ar)
1408 (m)	1408 (sh)	1408 (sh)	1408 (sh)	1408 (sh)	μ COO^-
--	1385 (w)	1385 (w)	1385 (w)	1385 (w)	ν COO^-
702 (s)	702 (s)	702 (s)	702 (s)	702 (s)	ν C-H(Ar)

Abbreviations: b - broad; s - strong; v.s. - very strong; w - weak; m - medium; sh - shoulder.

(b) Infrared spectra

The infrared spectra of Fe(III), Cu(II), Co(II) and Ni(II) complexes of the resin were compared with the spectrum of uncomplexed resin. Some of the absorption bands in the spectrum of the ligand have shifted to the lower frequency region on complexation except that of carbonyl absorption frequency which shows considerable increase in frequency after complexation.

The frequency of some of the important absorption bands are given in Table 6.1 The frequency of the band at 1085 cm^{-1} which is due to N-O absorption in uncomplexed resin has been lowered to 1074 cm^{-1} in the complexes. This decrease is attributed to the effect of co-ordination of nitrogen of the hydroxamic acid group to the metal resulting in a decrease in N-O vibration frequency. Similarly the absorption bands at 1250 cm^{-1} due to ν_{C-N} has also been lowered to 1230 cm^{-1}. This further confirms the co-ordination of the nitrogen atom.

A considerable increase for carbonyl stretching frequency from 1654 cm^{-1} in uncomplexed resin to 1708 cm^{-1} and 1693 cm^{-1} was observed in the case of the copper and iron complexes respectively. Had the co-ordination occurred

occurred through oxygen atoms of the carbonyl group, the spectra of the complexes would have shown a decrease in the carbonyl stretching frequency. Therefore the carbonyl group is not involved in co-ordination. The increase in frequency is certainly a secondary effect of the co-ordination through nitrogen atom. This can be understood from the two resonance structures (A and B) possible for the hydroxamic acid group.

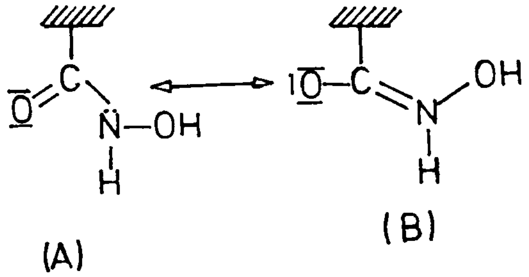


Fig. Resonance structures for the hydroxamic acid group.

The high frequency due to the carboxy group can be attributed to the contribution of resonance from A to the structure of the complexes. Such an increase in $>C=O$ frequency and a decrease in -CN frequency have already been observed in the case of urea complexes of Pd(II) and Pt(II) which are known to coordinate through the nitrogen atom[157]. A band due to ν coo$^-$ is seen at 1408 cm^{-1} in the spectra of the ligand and the complexes, which could be due to the presence of unconverted free carboxylic acid group. A new band is also seen at 1385 cm^{-1} in the spectra of all the complexes, indicating participation of some of these carboxylic groups in co-ordination to the metal.

The broad band at 3450 cm^{-1} which is due to OH and NH stretching frequencies is observed in both complexed and uncomplexed resin. Since the resin has considerable amount of bound water which cannot be driven out by the treatment given, it is difficult to utilize these data for assigning the bands. The TG studies of the complexes described in chapter VII indicate loss of weight below 100°C due to the slow loss of water bound to the resin.

(c) Electronic spectra

The Fe(III) complex shows only a shoulder band at 25400 cm^{-1} which might be due to the charge transfer transition. The absence of d-d bands suggest the complex to have a high spin octahedral structure[158]. The Co(II) complex shows a band at 19500 cm^{-1}. It also exhibits a shoulder at 8750 cm^{-1}. Similar bands have been observed in cobalt

Table 6.2

Electronic spectral data of SMH metal complexes

Substance	Absorption maxima (cm^{-1})	Tentative assignment
SMH-Fe(III) complex	25400	Charge transfer transition
SMH-Co(II) complex	19500	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	8750	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
SMH-Cu(II) complex	25000	$^2B_{1g} \rightarrow {}^2E_{1g}$
	13000	$^2B_{1g} \rightarrow {}^2B_{2g}$
	8000	$^2B_{1g} \rightarrow {}^2A_{1g}$
SMH-Ni(II) complex	27000	$^3A_{2g} \rightarrow {}^3T_{2g}$
	14800	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	8300	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$

loaded chelex-100 where it has been reported that Co(II) is octahedrally surrounded when bound to the resin[150,159]. The band at 19500 cm^{-1} can be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The other absorption band at 8750 cm^{-1} is due to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition was not observed since it is a two electron transition[159].

Octahedral Ni(II) complexes usually have three absorption bands in the region from 8000-13000 cm^{-1}, 15000-19000 cm^{-1} and 25000-29000 cm^{-1}.[159] The Ni(II) resin complex also shows three bands nearly in the same region suggesting octahedral structure. The bands at 8300 cm^{-1}, 14800 cm^{-1} and 27000 cm^{-1} can be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions respectively. Similar observations have been made on Ni(II) loaded chelax 100 whose electronic spectrum is found to be typical for octahedrally surrounded nickel[150].

The copper complex shows three bands at 8000 cm^{-1}, 13000 cm^{-1} and 25000 cm^{-1}. Normally one d-d is expected for octahedral Cu(II) complexes. The appearance of these bands may be due to square planar structure[160].

The high selectivity of the resin for Cu(II) compared to other metal ions like Fe(III) can be explained on the basis of these observations. Cu(II) has a higher tendency to form four-co-ordinated or square planar structure which is more easily formed than the octahedral structure. The donor lone pair of the ligand must be flexible enough to permit an obligatory tetrahedral or square planar structure, thus favouring chelation of Cu(II) over Fe(III). Similar observations have been made on chelating resins having pyridine derivatives as functional groups[161].

(d) ESR spectra

The ESR spectra of Fe(III), Ni(II) and Co(II) complexes are found to have many hyperfine structures and no conclusions could be drawn from these spectra. However the hyperfine structures in these cases suggest that the bonding might be through the nitrogen atom.

The ESR spectrum of copper complex shows the $H_{\perp r}$ and two $H_{\parallel}$ maxima. In this case $g_{\parallel}$ and $g_{\perp r}$ values were calculated and it was found to be 2.35 and 2.08 respectively. Further $A_{\parallel}$ value was 140G. Similar values have been reported for other chelating resins forming square planar

Cu(II) complexes[162,163]. Hence these results also suggest a square planar co-ordination for the SMH-Cu(II) complex.

6.2.3 SMPH resin and metal complexes

(a) Synthesis of SMPH metal complexes

Metal complexes of Cu(II), Fe(III), Co(II) and Ni(II) were prepared by shaking 1 g of SMPH resin with 200 ml of the metal ion solutions of 2000 µg ml^{-1} concentration at the pH of maximum sorption reported in Table 4.12. The coloured complexes were suction filtered after shaking for 8 h, washed with water and dried in vacuum at 80°C for 10 h.

(b) Infrared spectra

The infrared spectra of Fe(III), Cu(II), Co(II) and Ni(II) complexes of the resin were compared with the spectra of the uncomplexed resin. The frequencies of some of the relevant bands are given in Table 6.3. It is observed that as in the case of SMH resin, the absorption bands of the SMPH resin have shifted to lower frequency region on complexation except the carbonyl absorption frequency which shows considerable increase.

The N-O absorption band at 1080 cm^{-1} in SMH resin has been lowered to 1075 cm^{-1} in its complexes. The band

Table 6.3

IR absorption bands (cm^{-1}) of SMPH resin and its metal complexes

SMPH	SMPH-Cu	SMPH-Fe	SMPH-Ni	SMPH-Co	Assignment of relevant bonds
3420 (b)	3420 (b)	3420 (b)	3420 (b)	3420 (b)	ν O-H (based H_2O)
1580 (s)	1730 (v.s.)	1730 (v.s.)	1730 (v.s.)	1730 (v.s.)	ν C=O (hydroxamic acid)
1200 (v.s.)	1180 (s)	1180 (s)	1180 (s)	1180 (s)	ν C-N
1080 (w)	1075 (w)	1075 (w)	1075 (w)	1075 (w)	ν N-O
1490 (m)	1490 (m)	1490 (m)	1490 (m)	1490 (m)	ν C-C(Ar)
1400 (m)	1400 (w)	1400 (v.w.)	1400 (v.w.)	1400 (v.w.)	ν COO^-
--	1350 (m)	1350 (m)	1350 (m)	1350 (m)	ν COO^-
700 (s)	700 (s)	700 (s)	700 (s)	700 (s)	ν C-H(Ar)

Abbreviations: b - broad, s - strong, v.s. - very strong, w - weak, v.w - very weak, m - medium.

at 1200 cm^{-1} which is due to the ν_{COO} of the resin has alsobeen lowered to 1180 cm^{-1} in all the complexes. Therefore as in the case of SMH resin complexes here also the co-ordination of the hydroxamic acid group with the metal is via the nitrogen atom. The observed increase in carbonyl stretching frequency from 1580 cm^{-1} in uncomplexed resin to 1730 cm^{-1} in complexes can be attributed to the non-involvement of the oxygen atom of the carbonyl group in co-ordinating with metal ions.

The ν_{COO^-} band at 1400 cm^{-1} has shifted to 1350 cm^{-1}, indicating the participation of the unconverted carboxylic acid in co-ordination to the metal.

The N-H stretching frequency of hydroxamic acid group, and the O-H frequencies which are due to resin bound water are seen as a broad band at 3420 cm^{-1}. The effect of N-phenyl substitution is noticed by a decrease in the frequencies of C-N, N-O and C=O bands for SMPH samples as compared with those of SMH samples (Tables 6.1 and 6.3).

(c) Electronic spectra

The electronic spectra of the SMPH complexes show bands in the same region as those of the corresponding SMH resin complexes. The absorption maxima of the bands in the

Table 6.4

Spectral data of SMPH complexes

Substance	Absorption maxima (cm^{-1})	Tentative assignment
SMH-Fe complex	20000	Charge transfer transition
SMH-Co complex	19500	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$
	8620	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}$
SMH-Cu complex	25000	${}^{2}B_{1g} \rightarrow {}^{2}E_{1g}$
	14700	${}^{2}B_{1g} \rightarrow {}^{2}B^{2}_{g}$
	8150	${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$
SMH-Ni complex	25870	${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$
	18690	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$
	8695	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$

complexes together with the band assignments are given in Table 6.4.

The shoulder band at 20000 cm^{-1} in the spectrum of Fe(III) complex is due to charge transfer complex forming high spin octahedral complex. As in the case of SMH-Co(II) complex the absorptions is found nearly in the same regions at 19500 cm^{-1} and 8620 cm^{-1} indicating the formation of octahedral Co(II) complex. Ni(II) complex shows three bands at 25870 cm^{-1}, 18690 cm^{-1} and 8695 cm^{-1} which lie in the region generally expected for Ni(II) octahedral complex.

The three bands for SMPH-Cu complex appear at 25000, 14700 and 8150 cm^{-1} which are almost at the same regions as in SMH-Cu complex suggesting a square planar Cu(II) complex in this case also. Therefore it can be concluded that like SMH resin, SMPH resin also form octahedral complexes with Fe(III), Co(II), Ni(II) and square planar complex with Cu(II) indicating a similar geometry around the metal ion.

CHAPTER VII

THERMAL STUDIES ON SMH AND SMPH RESINS AND THEIR METAL COMPLEXES

7.1 INTRODUCTION

In this chapter the results of the thermal studies on the two polymer complexones SMH and SMPH and their metal complexes using thermogravimetry and differential thermal analysis are presented.

7.2 EXPERIMENTAL

7.2.1 Synthesis of SMH and SMPH metal complexes

The synthesis of SMH and SMPH metal complexes are described in chapter II and chapter IV respectively.

7.2.2 Instruments used

Simultaneous TG-DTG curves were recorded using a Du Pont 990 thermal analyser in conjunction with a 951 thermogravimetric analyser. DTA traces were also recorded using Du Pont differential thermal analyser. In all cases the experiments were carried out in dry nitrogen atmosphere at a flow rate of 50 ml min^{-1}. The mass of the samples used were in the range 3-6 mg. The heating rate was 10°C min^{-1}. Computational work was done on a Busybee PC, PC/XT computer (HCL Ltd.) using FORTRAN-77.

7.2.3 Mathematical analysis of TG curves

The specific rate equation for the thermal decomposition of a solid of the type

A (solid) $\longrightarrow$ B (solid) + C (gas) is derived from the kinetic equation

$$\frac{d\alpha}{dT} = kf(\alpha) \tag{7.1}$$

where $f(\alpha)$ depends on the reaction mechanism but usually takes the form $(1-\alpha)^n$, where 'α' is the degree of conversion, 't' the time, 'k' the rate constant and 'n' the order of reaction. For a linear heating rate

$$T = T_o + \phi t \tag{7.2}$$

where T_o is temperature of commencement of decomposition and ϕ is heating rate given by relation $\frac{dT}{dt} = \phi$.

$$\frac{d\alpha}{dT} = \frac{k}{\phi}(1-\alpha)^n \tag{7.3}$$

The temperature dependence of the rate constant is obtained by applying the Arrhenius equation

$$k = Ae^{-E/RT} \tag{7.4}$$

where A is the pre-exponential factor, E the activation energy and T the temperature in Kelvin. If the expression for k given by eq.(7.4) is substituted in eq.(7.3) then

$$\frac{d\alpha}{dT} = \frac{A}{\phi} e^{-E/RT}(1-\alpha)^n \qquad (7.5)$$

Various attempts have been made by several workers to obtain convenient forms of equation (7.5). In the present investigation we have used only the Coats-Redfern-equation for the evaluation of kinetic parameters.

7.2.4 The Coats-Redfern equation

The Coats-Redfern equation is obtained by the integration of equation (7.5), which is rewritten as

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\phi} e^{-E/RT}dT \qquad (7.6)$$

Rewriting equation (7.6) with limits of integration we have

$$\int_0^{\alpha} [d\alpha/(1-\alpha)^n] = \frac{A}{\phi} \int_0^{T} e^{-E/RT} \qquad (7.7)$$

If the integral on the left hand side of the equation is denoted by the function $g(\alpha)$, then

$$g(\alpha) = 1 - [(1-\alpha)^{1-n}/1-n] \quad \text{where } n \neq 1 \qquad (7.8)$$

$$g(\alpha) = -\ln(1-\alpha) \quad \text{where } n = 1 \qquad (7.9)$$

Coats and Redfern have evaluated the right hand side of equation (7.7) and the final form of Coats Redfern equation can be written as

$$\log\, [g(\alpha)/T^2] = \log \frac{AR}{\phi E} \left[\frac{1-2RT}{E} - \frac{E}{2.303RT}\right] \qquad (7.10)$$

Since $\frac{2RT}{E}$ is negligible in comparison with unity, the equation can be written as

$$\log[g(\alpha)/T^2] = \log \frac{AR}{\phi E} - \frac{E}{2.303RT} \qquad (7.11)$$

The order parameter was evaluated for the different stages of decomposition using an iteration method. Using a computer, linear plots of $\log[g(\alpha)/T^2]$ versus $1/T$ were drawn by the least-squares method, taking the 'α' and the corresponding 'T' values from the TG curve. Linear curves were drawn for different values of 'n' ranging from 0 to 2, in increments of 0.01. The value of 'n' which gave the best fit was chosen as the order parameter for each type of decomposition.

The slope $(-E/2.303R)$ obtained by plotting $\log [g(\alpha)/T^2]$ against $1/T$ is used to calculate E. Knowing E, A can be calculated from the intercept. The entropy of activation 'Δs' was calculated using the relation

$$A = \frac{kT}{h} e^{\Delta s/R}$$

where 'k' is the Boltzman constant, 'h' is the Plancks constant and 'R' is the gas constant.

7.3 RESULTS AND DISCUSSION

7.3.1 SMH - metal complexes

(a) Thermal behaviour

The TG, DTG and DTA curves for the SMH resin and its complexes with Fe(III), Co(II), Cu(II) and Ni(II) in nitrogen atmosphere are given in Figs.7.1 to 7.5.

The values of the DTG peak temperatures, values of the temperature of inception and temperature of completion for each stage of decomposition together with mass loss data are tabulated in Table 7.1. The temperature range for the DTA peaks as well as the peak temperatures are also given in the same table. It can be seen that there are four stages of decomposition for the SMH resin as well as

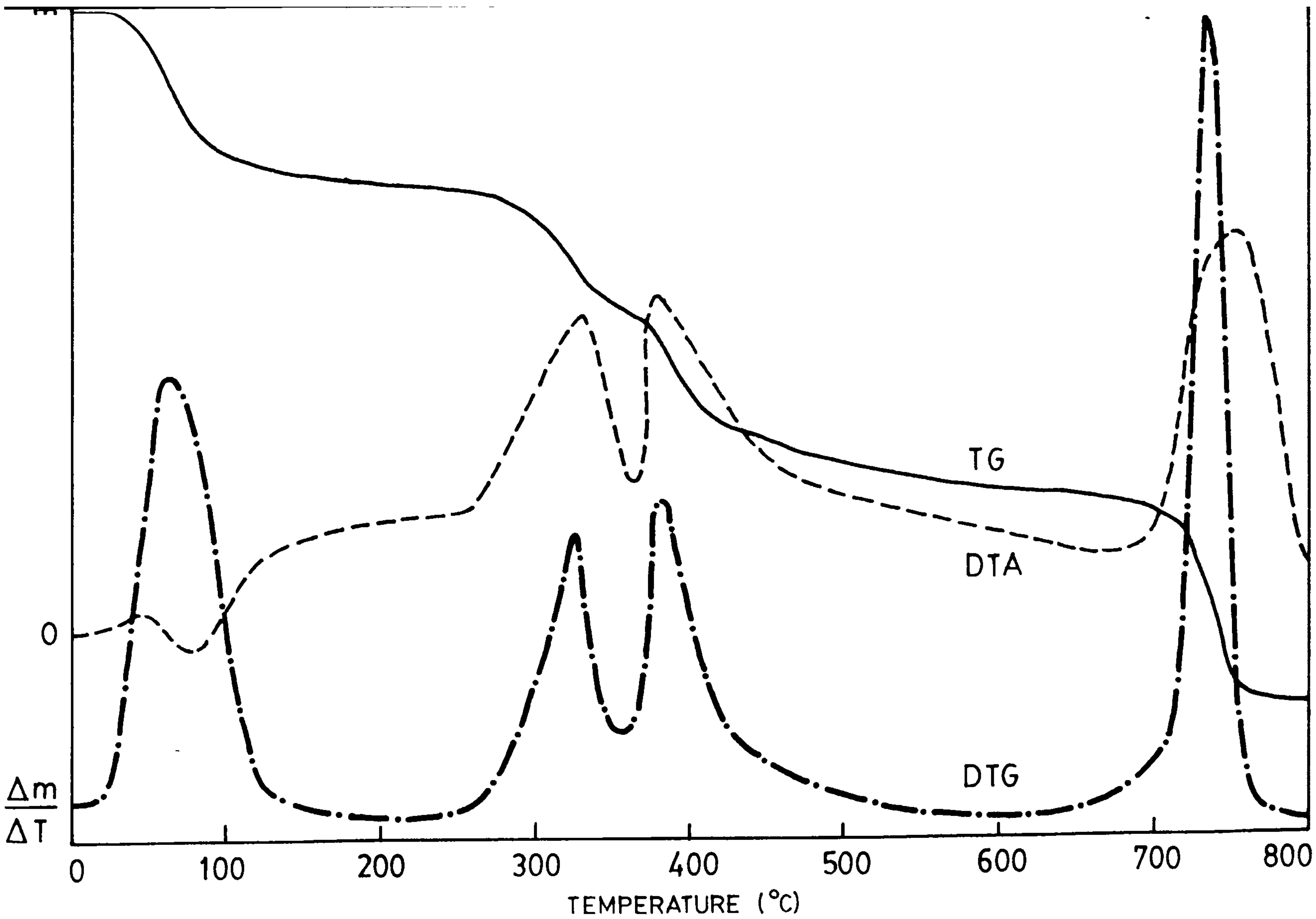


Fig.7.1 TG, DTG and DTA of SMH resin

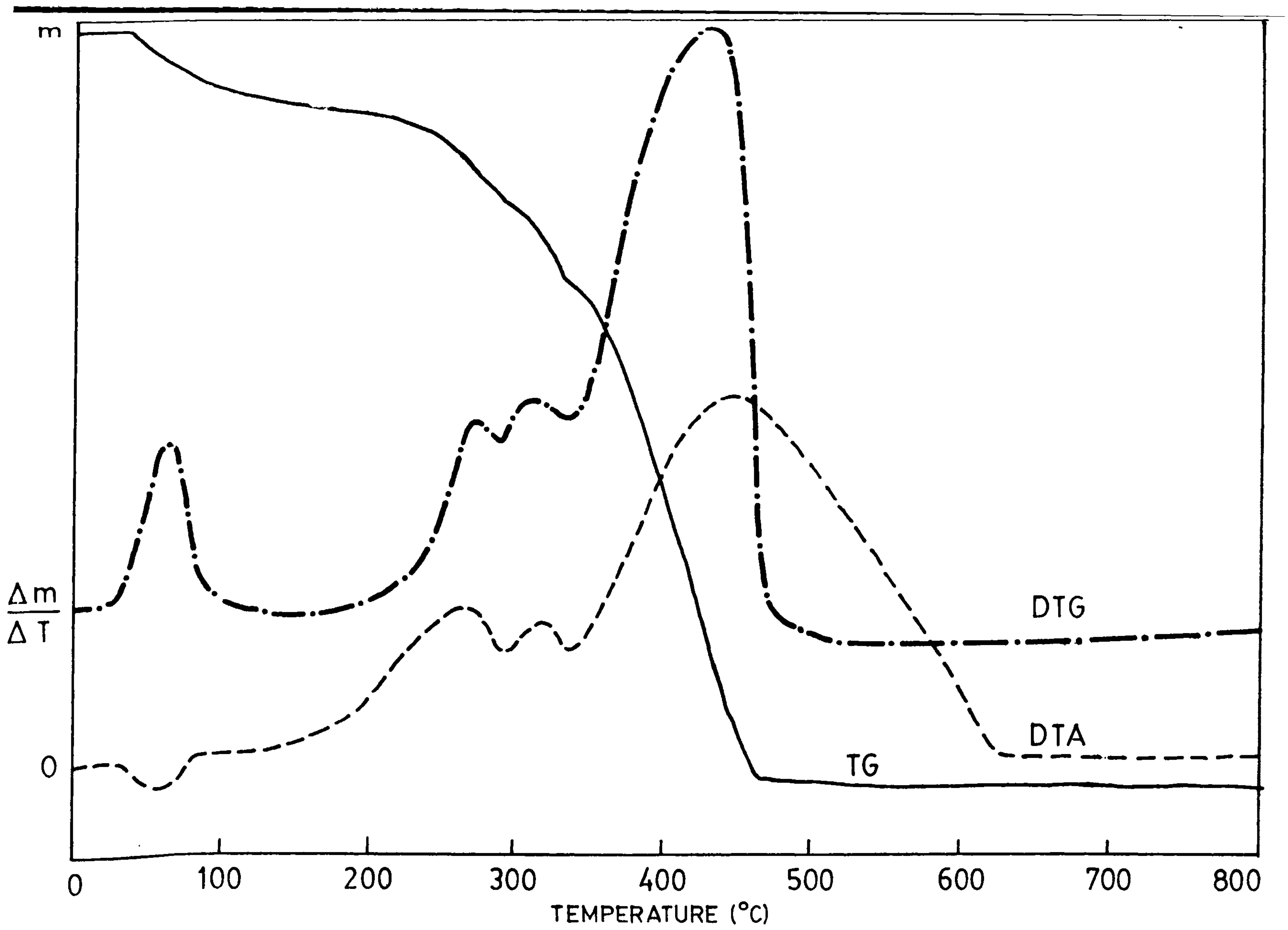


Fig.7.2 TG, DTG and DTA of SMH-Fe(III) complex

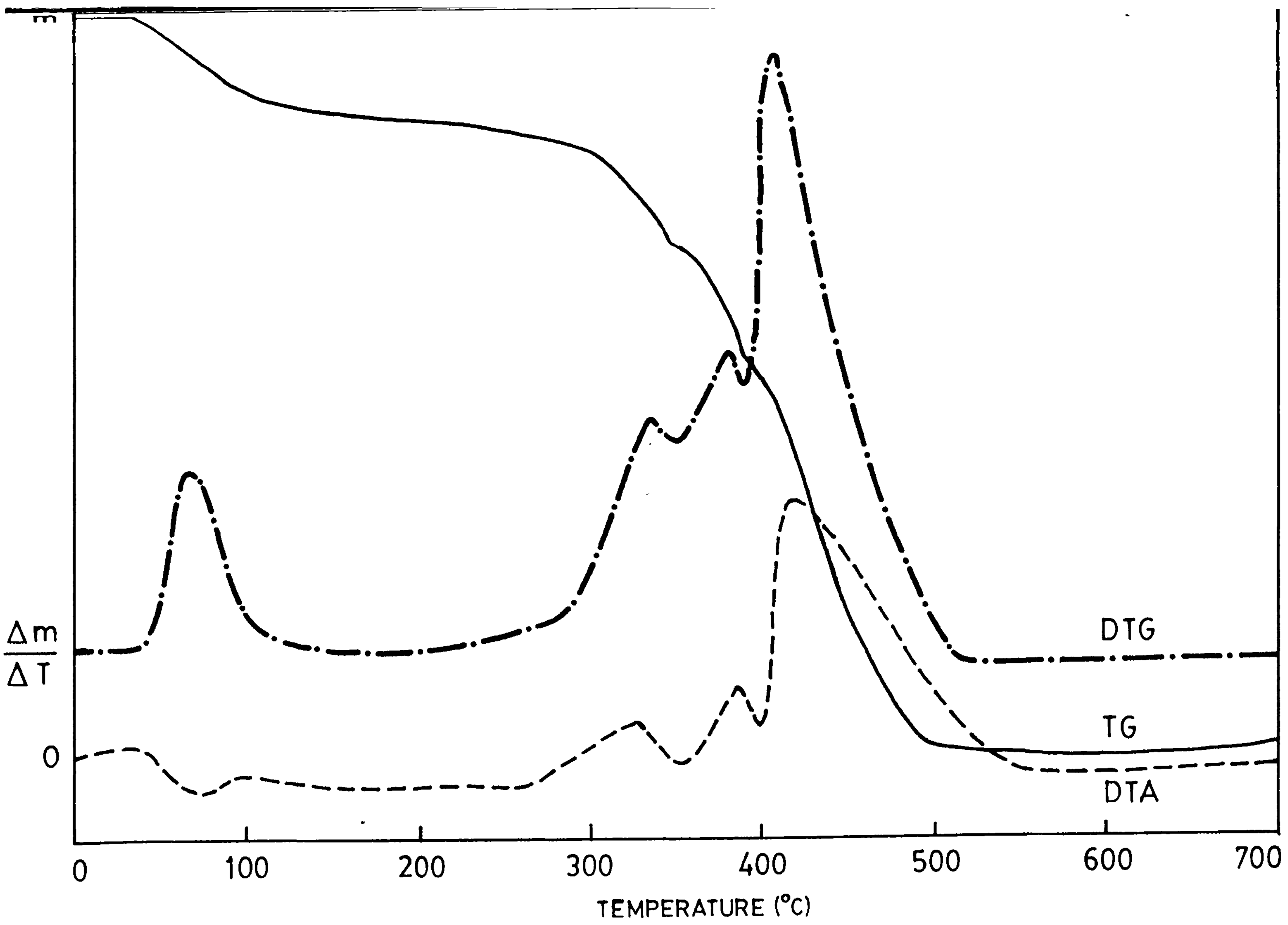


Fig.7.3 TG, DTG and DTA of SMH-Co(II) complex

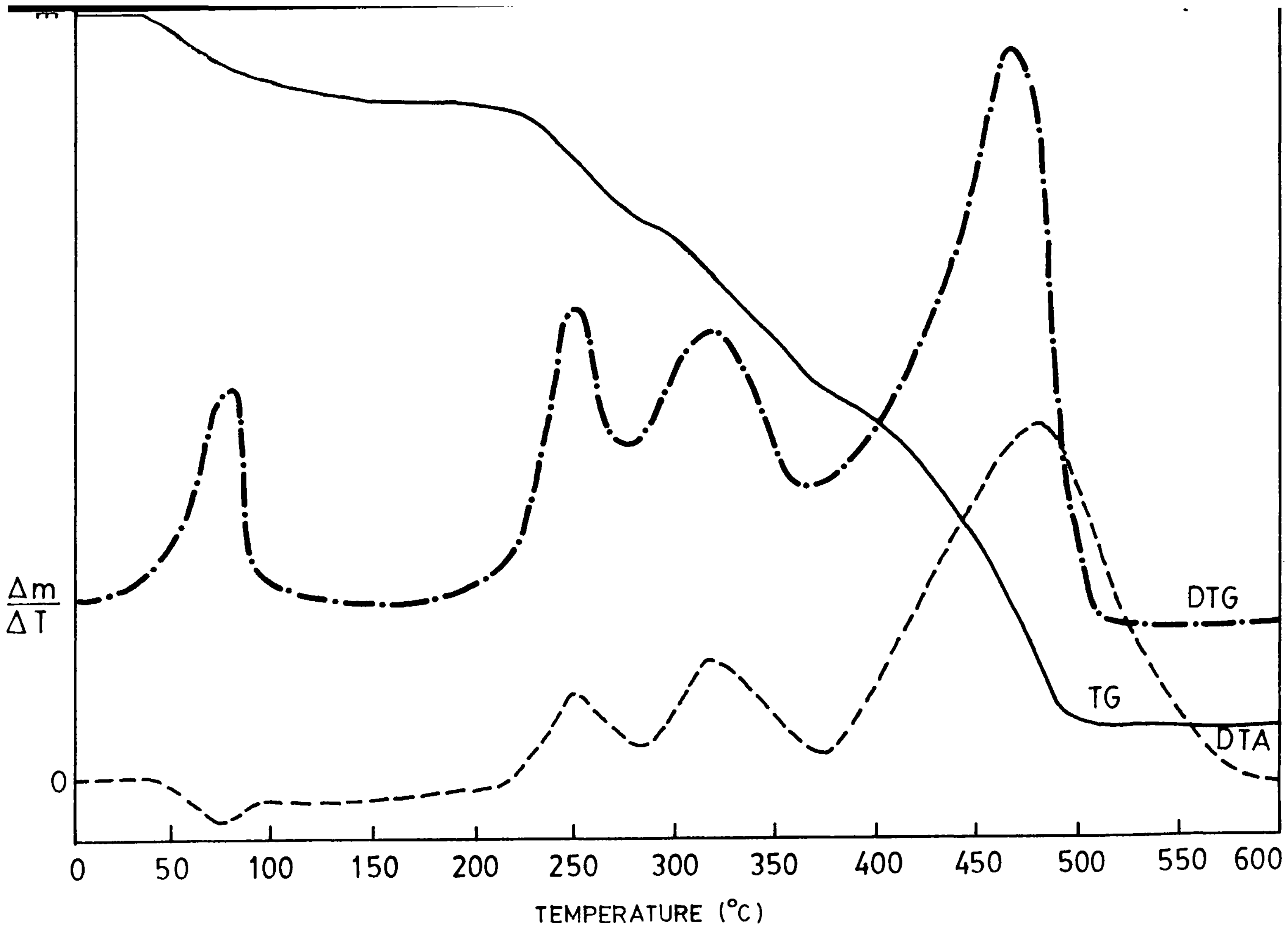


Fig.7.4 TG, DTG and DTA of SMH-Cu(II) complex

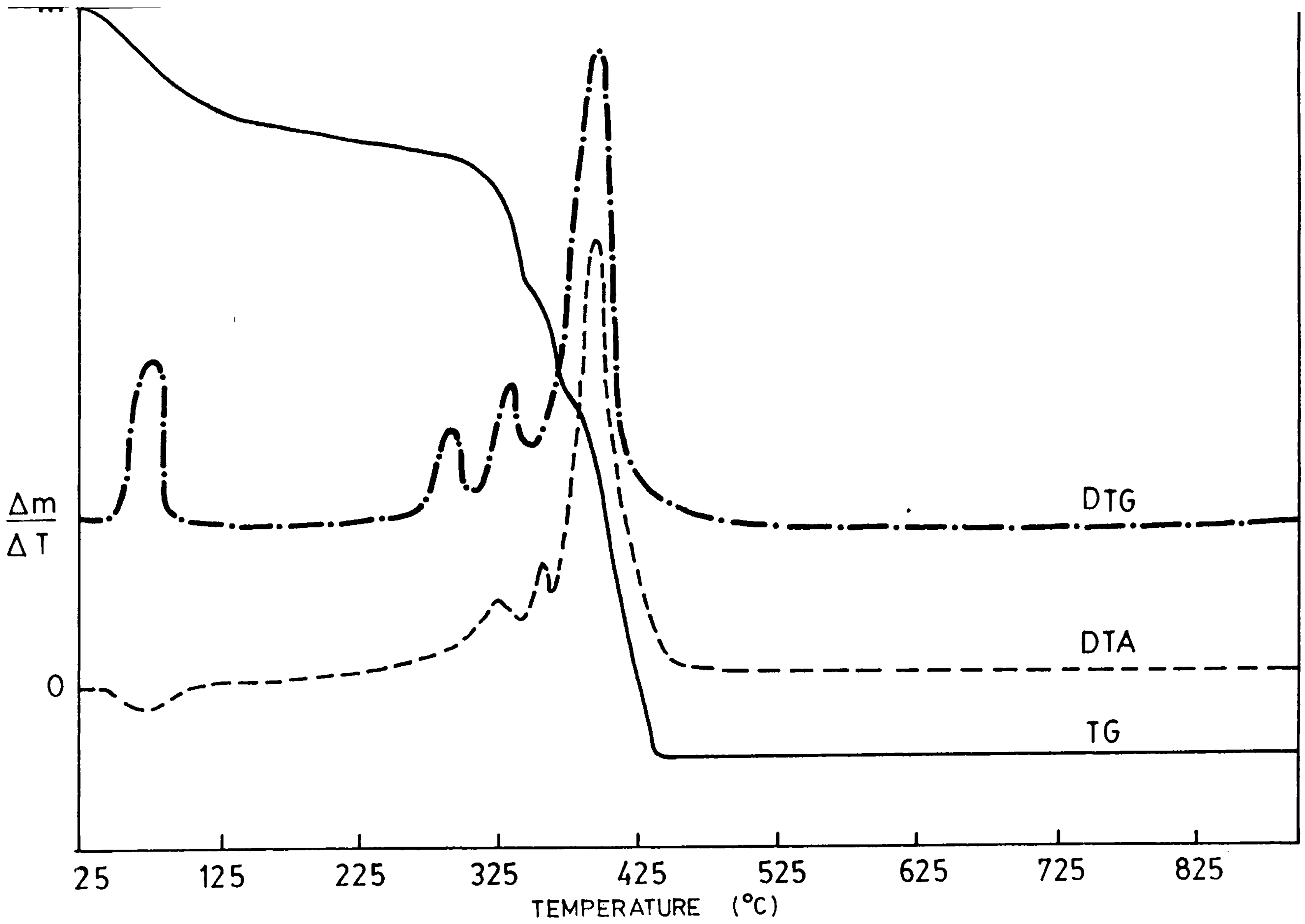


Fig.7.5 TG, DTG and DTA of SMH-Ni(II) complex

Table 7.1

Thermal decomposition data of SMH resin and its metal complexes

Substance	Peak temperature in DTA (°C)	Temperature range in DTA (°C)	Peak temperature in DTG (°C)	Temperature range in DTG (°C)	Stage of decomposition	Loss (%) from TG
(1)	(2)	(3)	(4)	(5)	(6)	(7)
SMH resin	70 endo (w)	50-90	60	30-80	I	20.00
	320 exo (m) (sh)	260-360	320	260-360	II	13.79
	385 exo (m) (sh)	360-480	385	360-480	III	16.32
	755 exo (v.s.)	700-820	740	670-770	IV	23.40
SMH-Fe complex	70 endo (w)	60-90	60	30-90	I	7.9
	265 exo (w)	200-285	270	190-290	II	10.88
	310 exo (w)	285-330	310	290-335	III	10.00
	450 exo (s)	330-620	435	335-470	IV	58.14

(contd...)

Table 7.1 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
SMH-Co complex	70 endo (w)	50-90	60	40-90	I	10.00
	330 exo (w)	275-350	340	275-345	II	12.64
	385 exo (w)	350-400	385	345-395	III	15.94
	410 exo (s)	400-560	410	395-510	IV	55.5
SMH-Cu complex	70 endo (w)	50-90	60	40-90	I	10.00
	250 exo (m)	210-280	245	210-275	II	12.38
	310 exo (m)	280-370	305	275-360	III	18.56
	485 exo (s)	370-600	465	360-500	IV	40.46
SMH-Ni complex	70 endo (v.w.)	50-90	60	40-90	I	14.00
	335 exo (v.w.)	295-350	335	300-345	II	14.7
	365 exo (w)	350-375	365	345-370	III	14.0
	395 exo (v.s.)	375-435	395	370-435	IV	40.3

Abbreviations: v.s. - very strong; s - strong; w - weak; v.w. - very weak; sh - sharp; endo - endothermic, exo - exothermic.

its metal complexes. All the compounds are seen to lose their mass even from 40°C onwards. The DTG peak corresponding to this stage of decomposition is around 60°C. This is paralleled by a weak endothermic DTA peak around 70°C. The mass loss in this stage is due to the removal of lattice water. The evidence for lattice water is present in the i.r. spectra of these samples which show a broad band in the region 3060 cm^{-1}.

The mass loss corresponding to the other three stages of decomposition as given in Table 7.1 for SMH resin and its complexes might be either due to the decomposition of the functional groups or due to the degradation of the polymer. All the DTG peaks corresponding to these stages have the parallel DTA peaks. The decomposition reactions are generally expected to be endothermic. The exothermicity of the DTA peak in the present cases might be due to some side reactions taking place (probably formation reactions) at these temperatures. The large amount of heat evolved during these reactions might have swamped the endothermicity of the decomposition reactions. Similar observations have been made during the thermal degradation of polymers and in those cases the exothermicity has been attributed to be due to oligomerisation reactions[164]. Therefore in the present cases also during the course of these reactions not only decomposition but also other reactions like oligomerisation takes place.

A comparison of the DTG peak temperatures for the last three stages in Table 7.1 shows that the incorporation of metal in the SMH resin has lowered the DTG peak temperatures for all stages. The DTG peak temperature for the final decomposition stage has been lowered from 740°C for SMH resin to 400-450°C in case of its metal complexes. This might be due to the catalytic effect of the metal ions on the decomposition of the SMH resin.

There is a residue of 14.7% for SMH resin whereas the percentage of residue in case of metal complexes has been considerably reduced to 8.5, 10, 13.9 and 12% for Fe(III), Co(II), Cu(II), Ni(II) complexes respectively. This also further lends evidence to the catalytic activity of the metal ions in bringing about a more exhaustive degradation of the polymer.

(b) Decomposition kinetics

The kinetic parameters for the different stages of decomposition have been calculated using Coats-Redfern equation and are presented in Table 7.2. The correlation

Table 7.2

Kinetic parameters for the thermal decomposition of SMH resin and its metal complexes

Substance .	Stage of decompo-sition	Order (n)	E_a (KJ mol^{-1})	$A(S^{-1})$	Δs (KJ $mol^{-1}k^{-1}$)	r
(1)	(2)	(3)	(4)	(5)	(6)	(7)
SMH resin	II	1.17	132.69	$2.59x10^9$	-70.49	0.9945
	III	3.18	329.90	$1.80x10^{24}$	212.88	0.9885
	IV	0.764	603.63	$12.124x10^{29}$	320.93	0.9929
SMH Fe complex	II	0.08	66.90	$8.20x10^3$	-174.99	0.9929
	III	1.431	257.52	$1.164x10^{21}$	152.83	0.9821
	IV	1.03	130.27	$0.389 x10^8$	-106.81	0.9914
SMH Co complex	II	0.991	175.25	$1.539x10^{13}$	1.553	0.9439
	III	1.38	298.62	$1.966x10^{32}$	175.33	0.9959
	IV	1.47	199.27	$2.626x10^{12}$	-33.50	0.9818

(contd...)

Table 7.2 (contd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
SMH Cu complex	II	1.62	185.75	5.418×10^{16}	70.86	0.9949
	III	2.27	180.93	1.217×10^{14}	19.23	0.9941
	IV	1.84	149.62	4.360×10^{8}	-87.06	0.9809
SMH Ni complex	II	1.294	274.92	0.6889×10^{22}	167.26	0.9981
	III	0.142	82.49	2.70×10^{17}	237.49	0.9986
	IV	1.01	212.18	2.08×10^{14}	22.49	0.9982

coefficient (r) are in the range 0.9900 to 0.9986 for most of the stages indicating nearly perfect fits. The order 'n' of the reaction in these cases does not provide any meaningful information about the mechanism of decomposition. However, the parameters 'E_a' and 's' may be employed for the comparison of a given decomposition process for similar compounds[165]. In the present investigation these values have been evaluated using the same equation under nearly identical experimental conditions (heating rate, furnace atmosphere and sample weight) and hence can be used conveniently for comparison.

A comparison of E_a of SMH resin with that of the SMH metal complexes for the second stage of decomposition shows that E_a increases considerably for the Co(II), Ni(II) and Cu(II) complexes indicating slower rate of decomposition at this stage. However, in the case of the Fe(III) complex the E_a value decreases indicating faster rate of decomposition probably due to the catalytic activity of the complex. This is indicated by a similar trend in entropy of activated states. The Δs value for SMH resin is negative indicating a highly ordered activated state. In the case of the Co(II), Cu(II) and Ni(II) complexes, the entropy of activation has positive values which shows that activated complexes are less ordered for this stage. For the Fe(III) complex Δs have become more negative which might be due to the chemisorption of the decomposition products[166]

The E_a and Δs values for the third stage of decomposition are found to be lower for the metal complexes compared to those for the SMH resin indicating faster rate of decomposition of the complexes at this stage. This again can be attributed to the catalytic activity of the metal for this stage of the decomposition.

For the last stage of decomposition the catalytic activity of the metal ions is most pronounced. The Δs values for the Cu(II), Co(II) and Fe(III) complexes are all negative indicating a highly ordered state. The large decrease in E_a values of the metal complexes shows that the catalytic effect of the metal ions is in the order Fe(III) > Co(II) > Cu(II) > Ni(II).

7.3.2 SMPH resin and its metal complexes

(a) Thermal behaviour

The TG, DTG and DTA curves for the SMPH resin and its complexes with Cu(II) and Ni(II) in nitrogen atmosphere are given in Figs.7.6 to 7.8. The DTA peak temperatures

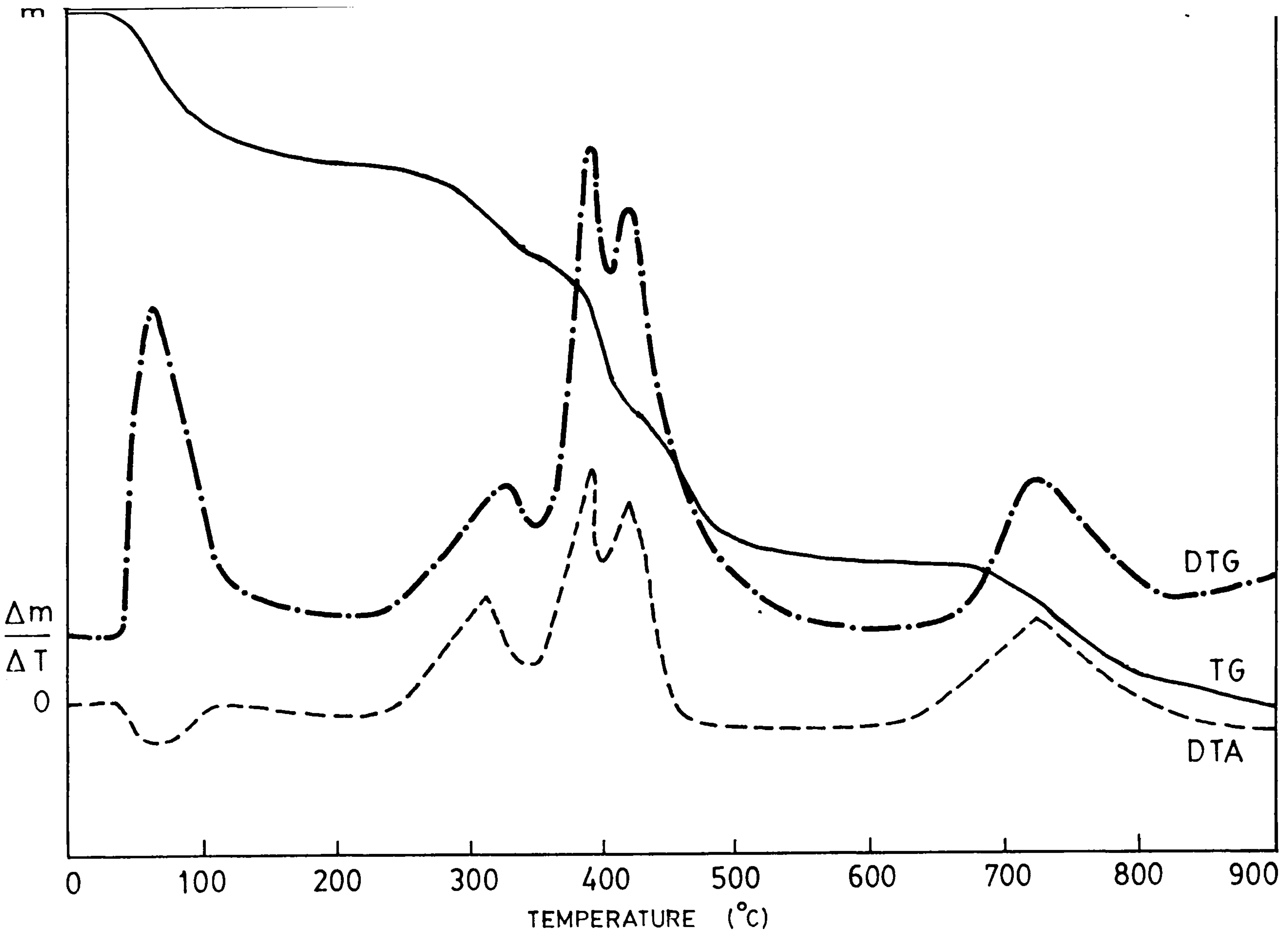


Fig.7.6 TG, DTG and DTA of SMPH resin

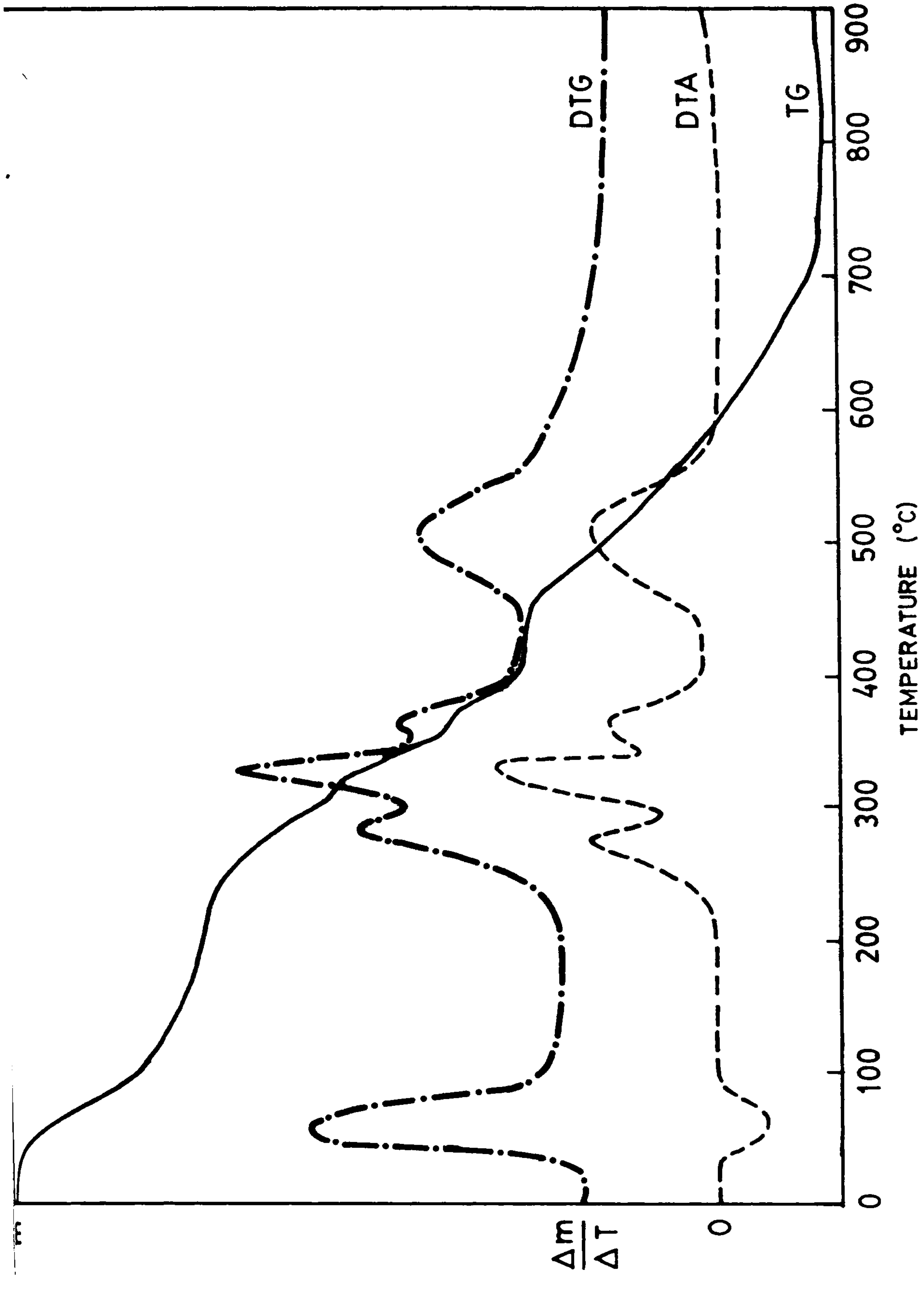


Fig.7.7 TG, DTG and DTA of SMPH-Cu(II) Complex

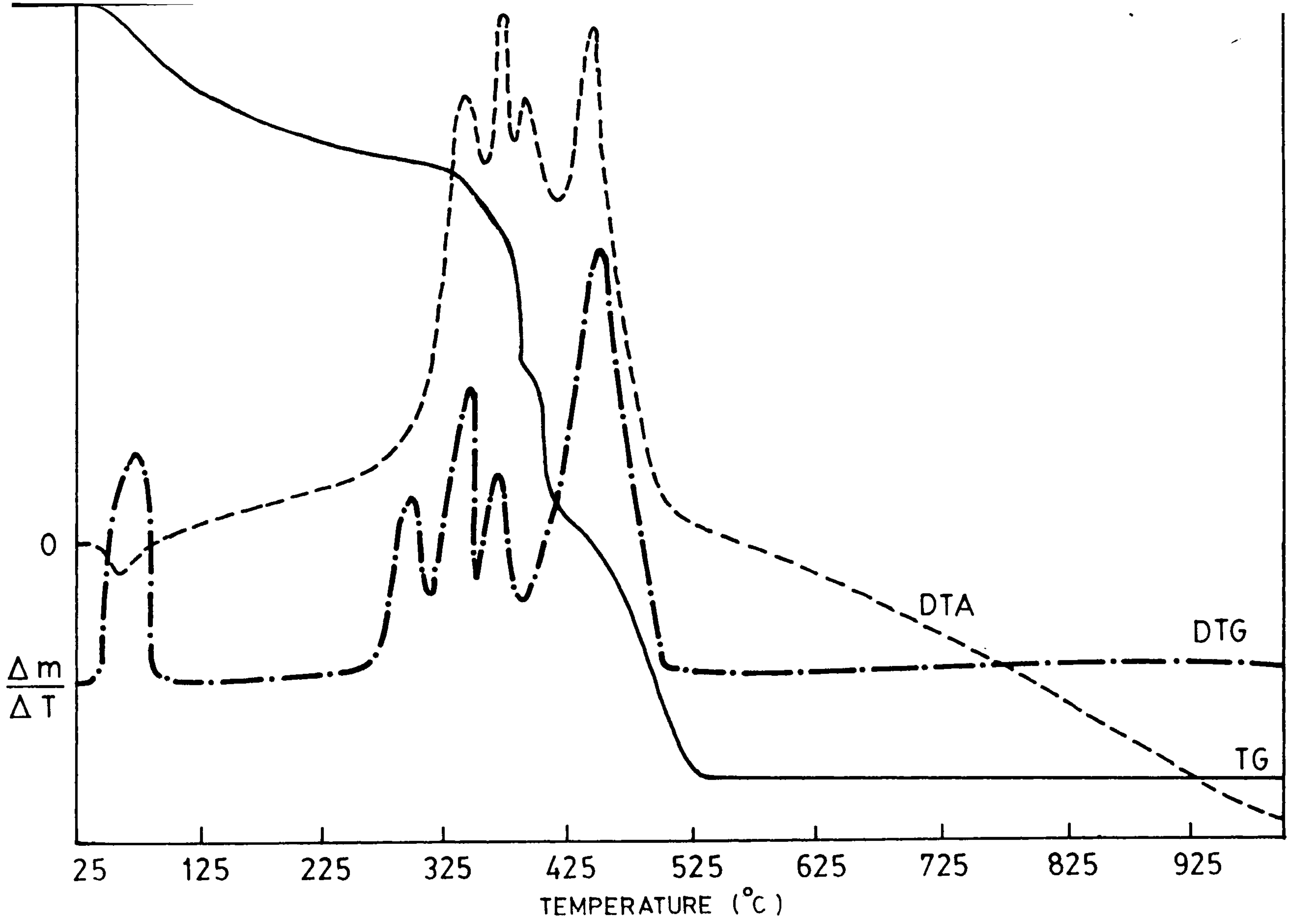


Fig.7.8 TG, DTG and DTA of SMPH-Ni(II) complex

and temperature range for the decomposition stages together with the mass loss data are tabulated in Table 7.3. The temperature range for the DTA peaks as well as the peak temperatures are also given in the same table.

The thermal decomposition pattern for the SMPH resin and metal complexes is quite similar to that of SMPH resin except for an additional stage of decomposition.

Here also the first stage of decomposition for all the three samples correspond to the removal of lattice water as evidenced from the band at 3050 cm^{-1} in the i.r. spectra. All the compounds start losing mass at 40°C. The DTG peak at 60°C is parallel with a weak endothermic DTA peak around 70°C.

The mass loss corresponding to the other four stages of decomposition is given in Table 7.3 and as in the previous case might be either due to decomposition of the functional groups or due to the degradation of the polymers. The additional stage of decomposition in these samples might be due to the removal of the phenyl group of SMPH resin which is not present in SMH resin. Here again all the DTG peaks have parallel exothermic DTA peaks in contrast

Table 7.3

Thermal decomposition data of SMPH resin and its metal complexes

Substance	Peak temperature in DTA (°C)	Temperature range in DTA(°C)	Peak temperature in DTG (°C)	Temperature range in DTG (°C)	Stage of decomposition	Loss (%) from TG
SMPH resin	70 endo (w)	50-90	60	40-90	I	15.00
	325 exo (m)	230-335	325	230-335	II	10.00
	390 exo (s)	350-405	385	350-405	III	14.54
	420 exo (m)	405-490	420	405-490	IV	17.27
	725 exo (s)	660-810	720	660-810	V	12.73
SMPH Cu complex	70 endo (w)	50-90	60	30-90	I	15.00
	280 exo (m)	210-290	280	210-300	II	13.63
	325 exo (s)	290-350	325	300-350	III	13.65
	370 exo (w)	350-400	365	350-400	IV	12.27
	495 exo (s)	460-560	490	400-530	V	18.00
SMPH Ni complex	70 endo (w)	40-90	60	30-90	I	12.00
	330 exo (m)	285-345	320	275-330	II	18.72
	360 exo (s)	345-375	350	330-365	III	16.64
	395 exo (m)	375-415	380	365-405	IV	9.98
	445 exo (s)	415-495	440	405-495	V	16.64

Abbreviations: s - strong; w - weak; m - medium; sh - sharp; endo - endothermic; exo - exothermic.

to the expected endothermic peaks indicating that the mechanism of decomposition is similar to that for SMH resin and metal complexes.

The catalytic activity of the metal ions on the decomposition of the SMPH resin is evidenced from the decrease in the DTG peak temperature for all stages in comparison with the uncomplexed resin which is most pronounced for the last stage.

The incorporation of metal ions in the SMPH resin also has the effect of bringing about a more complete degradation of the polymers. This is observed from the percentage of final residue which is 14% for SMPH resin whereas for the metal complexes the carbonaceous residue is negligible.

(b) Decomposition kinetics

The kinetic parameters evaluated for the different stages of decomposition is presented in Table 7.4. The values of the correlation coefficient indicate nearly perfect fits.

The E_a values for the second and third stages of decomposition are found to increase for metal complexes indicating slower rate of decomposition whereas for the

Table 7.4

Kinetic parameters for the thermal decomposition of SMPH resin and its metal complexes

Substance	Stage of decompo-sition	Order (n)	E_a (KJ mol^{-1})	A (S^{-1})	Δs (KJ $mol^{-1}k^{-1}$)	r
SMPH resin alone	II	0.91	86.19	0.184×10^{6}	-54.19	0.9939
	III	1.22	196.06	2.19×10^{13}	4.220	0.8251
	IV	2.75	442.25	2.398×10^{31}	349.24	0.9980
	V	1.64	340.91	2.34×10^{15}	39.32	0.9956
SMPH Cu complex	II	0.52	86.85	0.247×10^{6}	-89.79	0.9980
	III	1.31	250.60	0.618×10^{20}	128.21	0.9953
	IV	2.86	286.73	1.17×10^{21}	152.12	0.9979
	V	1.90	276.02	2.68×10^{16}	61.69	0.9905
SMPH Ni complex	II	0.80	184.23	0.482×10^{14}	11.18	0.9960
	III	1.73	511.14	1.813×10^{40}	234.26	0.9854
	IV	1.19	348.26	2.39×10^{25}	47.60	0.9977
	V	1.64	337.78	3.58×10^{22}	179.58	0.9975

last two stages, the E_a values have been lowered in the case of Ni(II) and Cu(II) complexes indicating the catalytic effect of the metal ions in bringing about faster decomposition of the polymer at these stages.

The negative values of entropy of activation for the second stage of SMPH resin and Cu(II) complex shows highly ordered activation state. The positive values for the other stages indicate a lesser ordered state for the activated states. The Δs values are found to increase for the metal complexes for the third and the last stage compared to SMPH resin; whereas for the fourth stage the complexes have lower Δs values indicating more ordered state of the activated complex.

CHAPTER VIII

CONCLUSIONS

The selectivity limitations of ion-exchangers have largely been overcome by using reactive exchangers bearing chelating functions of a high degree of selectivity. Of these, hydroxamic acids of acrylic copolymers and carboxy styrene co-polymers are shown to be promising in the selective extraction of metal values from lean sources and in the chromatographic separation of cations prior to instrumental quantitation. The selectivity characteristics and applications of hydroxamic acid polymer complexones with vicinal hydroxamic acid functions derived from styrene-maleic acid co-polymer are presented in this work. The hydroxamic acid derivatives were prepared from styrene-co-maleic acid cross-linked with DVB--one is the unsubstituted hydroxamic acid (SHM) and the other is its N-phenyl derivative (SMPH). By virtue of the spatial orientation of the donor atoms in vicinal hydroxamic acid, they can have a high degree of selectivity for metals which form square planar complexes. This is proved by the results presented here.

The ratio of the monomer residues in the co-polymer as well as the nature of substitution of the functional group in the polymer controls the metal sorption capacity of the resin. The concentration of the monomer residue which can be derivatized to form the chelating function determines the chemical characteristics of the resulting complexone. Peroxide catalysed polymerization can give a maximum maleic acid-styrene ratio of only 1:2 even if a higher ratio is employed. Conversion of the precursor polymer, i.e., styrene-co-maleic acid to the hydroxamic acid through the acid chloride route gives a maximum conversion of only 47%. The capacity of the resulting resin is much higher than that of similar resins obtained from XAD resin reported in the literature.

Poly(styrene-co-maleic acid) crosslinked with DVB presented in this work is stable in conc.HCl 0.1 M NaOH and 0.1 M HNO_3. Continued contact with these media for 24 h does not alter the capacity. The pH at which maximum sorption occurs for selected transition metals are given in table 8.1.

The kinetics of exchange of metal ions on both resins are sufficiently fast and on the average it is less than 5 min. for both SMH and SMPH resins. The k_D values which represent the tenacity of extraction of the metal at the pH of maximum sorption are in the order: Cu(II) > Zn(II) > Co(II) > Ni(II) >Mn(II) > U(VI) > Cr(III) > Fe(III) > V(V) > Mo(VI).

Table 8.1

Metal ion	pH of maximum sorption
Cu(II)	5.5
Zn(II)	6.0
Co(II)	6.0
Ni(II)	5.0
Mn(II)	6.0
Cr(III)	5.0
Fe(III)	2.3
V(V)	4.0
U(VI)	4.5
Mo(VI)	2.0

From the evaluation of exchange capacity by batch and breakthrough studies it is seen that SMH resin is useful for the separation of binary mixtures of Cu(II)-Fe(III), Co(II)-Cu(II), Ni(II)-Cu(II), V(V)-Fe(III) and Ni(II)-Fe(III). Clean separations are achieved and standard deviations for the estimations are on the favourable side. The high degree of selectivity of the resin for Cu(II) permits its preconcentration from ion rich media like sea water, process effluents and process water. Extraction of uranium from sea water was also attempted. About 99% of recovery is possible at 1 $\mu g\ ml^{-1}$ level but this falls to about 97% at 20 $\mu g\ ml^{-1}$ level.

Chromium plating baths are easily contaminated by other metals and have to be discarded frequently. Monitoring of the presence and quantity of metals like copper and iron in the bath solution and also the presence of all of them in the bath effluent is significant. Methods have been developed for the separation of Cu(II), Cr(III) and Fe(III) in chromium plating effluents and to quantitate them.

Substitution of a coordinating function by a bulky group affects its coordination characteristics. Moreover, substitution decreases the capacity of the resin. The decrease in capacity is a consequence in the increase in the formula weight of the repeat units. The study of the N-phenyl hydroxamic derivative of poly(styrene co-maleic acid) presented here supports this point. Only 38% of the carboxylic acid could be converted to the N-phenyl derivative. The pH at which maximum sorption occurs for different metal ions shows that the complex formed with iron is weaker than that with copper in near neutral media. The usefulness of SMPH in the separation and analysis of Cu(II)-Ni(II), Ni(II)-Fe(III), Mn(II)-Cu(II) and Fe(III)-Ni(II)-Cu(II) are also shown.

The infrared spectral data conclusively show that in the metal complexes studied the nitrogen atom of hydroxamic acid function is coordinated to the metal. The increase in the C=O stretching frequency in the complexes indicates that O-atoms are not involved in coordination. No conclusive information could be drawn from NH stretching frequencies since they are overlaid by OH stretching frequencies of the bound water which cannot be driven out completely by vacuum drying.

Electronic spectral data indicate that the Fe(III) complex has a high spin octahedral structure. The complexes formed by copper(III) with SMH and SMPH have square planar structure. This is because the donor atoms of the ligand are situated at positions which are flexible enough to permit the formation of an obligatory square planar structure demanded by the metal ion. The ESR spectral data also support this conclusion. Both in the SMH and SMPH complexes the participation of residual carboxylic acid function in complex formation is evident.

The thermal studies on the resins and their metal complexes show that the bound water is lost only slowly on heating. A comparison of the onset temperatures for thermal decomposition for the resins as well as their metal complexes indicates that the metal exerts a catalysing effect. A more complete degradation of the polymer residue occurs in presence of the metal. The products of the various stages of decomposition were not fully identified. Hence more quantitative information could not be drawn out of these studies. The negative entropy values associated with the second stage of decomposition suggest that the substrate has a highly ordered activation state.

The studies presented in this thesis establish the analytical usefulness of the two resins and shed some light on the bonding characteristics and thermal behaviour of the resins and the metal complexes formed by them.

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3. "Synthesis, Characterisation and Analytical Applications of a Hydroxamic Acid Resin", Rita Mendez and V.N.Sivasankara Pillai, Talanta (in press).

4. "Spectral and Thermal Decomposition Studies on Metal Derivatives of Poly(styrene-co-maleic hydroxamic acid) resin". Rita Mendez and V.N.Sivasankara Pillai (to be communicated).