POLYHYDROXAMIC ACIDS FOR THE CHROMATOGRAPHIC SEPARATION OF METAL IONS

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CONTENTS

SUMMARY

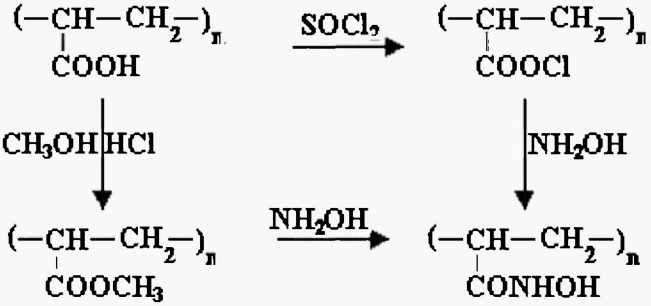
The review describes various synthetic methodologies for the synthesis of polyhydroxamic acids. Metal chelation studies of these chelating ion exchangers, especially the separation of transition metals and the actinides, have been discussed exhaustively. The miscellaneous applications of polyhydroxamic acids viz. acyl transfer agents, settling agents, iron scavengers, corrosion inhibitors etc. have also been discussed.

1. INTRODUCTION

Hydroxamic acids are bidentate chelating agents especially known for their complexing ability towards metal ions belonging to transition elements such as iron, vanadium etc. /1/. The intense colour and high stability of there metal chelates have led to the development of many sensitive and selective analytical procedures for their quantitative determination /2,3/. Much interest in the development of polyhydroxamic acids can be attributed to their occurrence in nature as trihydroxamjc acids or the siderochromes /4/. They form iron chelates of exceptional stability. This stability is due, in part to the geometry, whereby three hydroxamic acid units are spaced in such a way that they can easily orient themselves about a single iron atom and satisfy the octahedral requirements of Iron (III) complexes. The well known examples of siderochromes are ferrioxamines: which are iron chelate of linear structures having three hydroxamic acid groups spaced along the chain and ferrichromes: which consist of cyclic hexapeptides having three sides chains each bearing a hydroxamic group. The high selectivity of the siderochromes for iron is an important factor in the their use as iron transporters in biological pathways /5-6/. Desferroxamines B are used clinically for the treatment of iron poisoning. Thus many endeavors have been made to synthesize polymeric hydroxamic acids, that can be used as iron scavengers for medical purpose /38/. The interest in polyhydroxamic acids is also due to their powerful catalytic activity viz. N-methylhydroxamic acids in the hydrolysis of certain active esters /7/. Polyhydroxamic acids have also been extensively investigated for their chelating properties. Several polyhydroxamic acid ion exchangers have been successfully used for the separation of 3d transition elements and the actinides. Despite the increasing utility of polyhydroxamic acids no exclusive review on this apparently useful chelating ion exchanger has appeared though some aspects of the development of polyhydroxamic acids have been discussed by Winston /8/ and Vernon /9/. The present review is an attempt to study exhaustively the different synthetic methodologies for the synthesis of polyhydroxamic acids and their numerous applications in the field of analytical chemistry, medicine, metallurgy etc.

2. SYNTHESIS

Synthesis of polyhydroxamic acids has been mostly carried out by the treatment of hydroxylamines with either acid chlorides or esters (**scheme-I**) of the corresponding acids, though a number of other synthetic methods have also been reported. Cornaz and Deuel were first to report polyhydroxamic acids in 1954 via an acid chloride. Percentage functionalization of the product was low /10-13/ and the reason attributed was poor conversion of acids to acid chlorides. However the acid chloride method has been established as an efficient approach especially for the synthesis of N-substituted polyhydroxamic acids /14-18/. In some instances, however, the reaction of esters with hydroxylamines has been reported to give better results /19-22/. Kern and Schulz have reported the reaction of poly (methacrylate) with hydroxylamine with 80% conversion to hydroxamic acid.

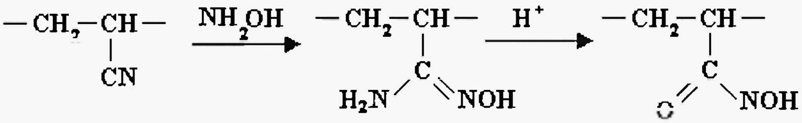


Scheme I

The general synthesis shown in scheme I has been used for the synthesis of polyacrylo and polymethacrylo hydroxamic acids by many workers /23-27/. IRC-50, a commercially available resin, has also been converted to corresponding hydroxamic acid by either of these methods /28-30/. Pillai and Mendez have incorporated N-phenyl hydroxamic acid group in styrene and maleic acid copolymer crosslinked with DVB /18/. Kamble and Patker /30/ have reported synthesis of poly(4-vinyl-2'-carboxybenzophenone) by

Friedalcraft's reaction of polystyrene and phthalic anhydride followed by conversion to hydroxamic acid via its methyl ester.

Another commonly used method to synthesize chelating ion exchange resin with pendant hydroxamic acids consists of treatment of polyacrylonitriles with hydroxyl amines followed by the hydrolysis of intermediate amidoximes /28,31-34/.The sequence of reactions carried out is depicted in **scheme II.**



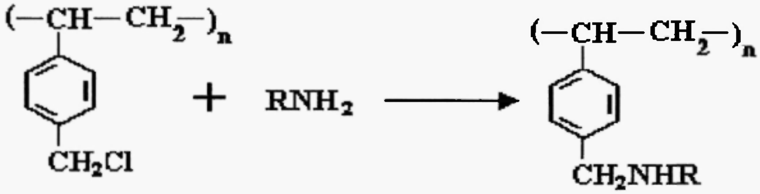
Scheme-II

Kyffins /37/ utilized this approach to convert commercial ES 346 resin containing amidoxime groups to polyhydroxamic acid resin. Marshall /38/ has described a one step reaction involving sodium hydroxide and hydroxylamine for conversion of polyacrylonitrile to polyhydroxamic acid. The resins prepared by this process possessed capacities of 1.3 and 5.5 m.mol g^{-1} for Iron(III) and Cu(II) respectively. Shah and Devi /37/ have reported the synthesis of a polyhydroxamic acid by treating a polyacrylic acid (obtained after hydrolysis of polyacrylonitrile) with various substituted hydroxylamines in the presence of sodium methoxide at 75-80°C for 18 hr. However, the desired product was not obtained when the same work was repeated by Agrawal *et al.* /25/.

One drawback of all these synthetic routes is that the chelating polymers are contaminated with free carboxylic acid groups. Various strategies used to increase the conversion to hydroxamic acids involve increasing the time of reaction and using different solvents. Acid chloride of commercial resin Zeo-Carb 226 (a crosslinked methacrylic acid) was treated with hydroxylamine at room temprature for serveral days /23/. Vrancken and Smets /29/ have reported that conversion of poly(acryloyl chloride) to corresponding hydroxamic acid can be improved when DMF was used as coupling medium. Agrawal *et al.* have reported better conversion of carboxylic acid to acid chloride by carrying out the reaction with thionyl chloride in dioxane medium /17/. The technique has also been improved upon by another approach in which an acryloyl chloride, styrene, and divinyl benzene were copolymerised by irradiation with ultra violet light and the polymers so obtained were reacted with phenyl hydroxylamine in dimethyl formamide for 14 days at 5°C /38/.

Vernon and Eccles /39/ have also reported two alternate techniques for the synthesis of polyhydroxamic acids. In the first, the hydroxamic acid group is part of the polymer chain. It was prepared by complexing phenylene dihydroxylamine (prepared from m-dinitrobenzene) with terephthaloyl chloride in dioxane in presence of sodium bicarbonate. The reaction has also been reported by an intrafacial condensation /40/. In the second p-(bromo ethyl)benzoyl phenyl hydroxylamine was anchored to poly(ethyleneimine). Substituted N-phenylbenzohydroxamic acid, ethylene dibromide, 1,4 dibromomethyl benzene and polyethyleneimine were heated in a sealed container for 24 hr at 90°C. The black rubbery substance after washing showed a capacity of 1m.mol g^{-1} for Cu (II). Agrawal and Kaur /41/ have reported the synthesis of polyhydroxamic acid by partially reducing β-nitro stryene to its hydroxylamine and then coupling it with various acid chlorides. All these polymers were free from carboxylic acid groups.

Ramirez and Andrade /42/ grafted trihydroxamic acid, desferroxamine B to several polymers through the free amino groups. The reaction carried out for attaching desferroxamine to chloromethylated polystryene, XAD-2 and XAD-4 is depicted in scheme III

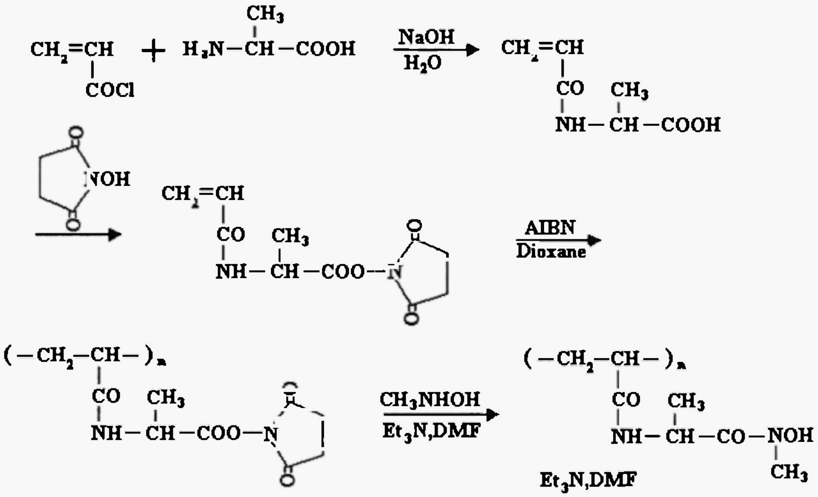


Where R is deferroxamine -B

Scheme-III

Winston and co-workers /44-49/ have prepared a number of polyhydroxamic acids using naturally occurring trihydroxamic acids as models and with such spacers that could imitate the arrangement of octahedral Fe(III) complex of naturally occurring hydroxamic acids. They have also shown that the hydroxamic acid can be prepared by activating the acid group by first synthesizing its N-hydroxy succimide ester (**Scheme IV**).

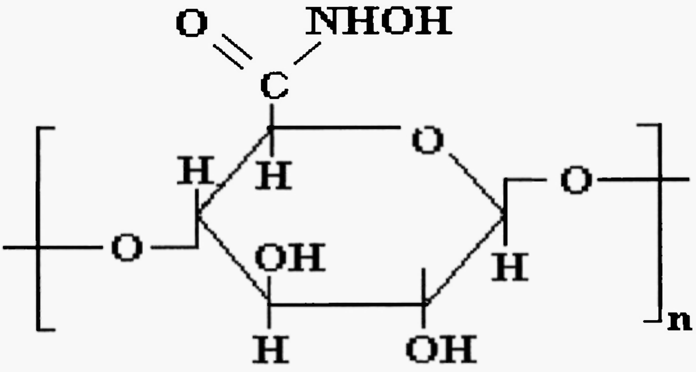
Larger surface area, greater pore size, greater physical strength and ease of equilibration prompted Phillips and Fritz /15,16/ to incorporate hydroxamic acid groups into macroporous polystyrene divinylbenzene copolymers. The commercial XAD-2 and XAD-4 resins were first acetylated followed by oxidation to carboxylic acids. The carboxy polymers were then transformed to hydroxamic acids through acid chloride method shown in scheme I. Polymers showed several analytical applications.



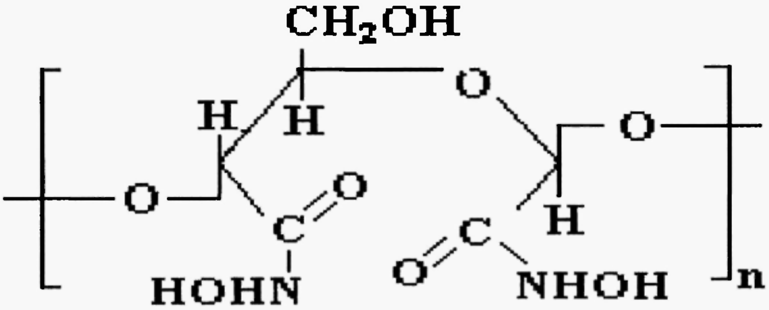
Scheme-IV

Increasing awareness of the necessity to control environmental pollution has prompted scientists to synthesize biodegradable ion exchanging resins. Naturally occurring cellulose has been explored as a viable polymer support. A hydroximated cellulose powder (I) with low content of hydroxamic groups has been prepared from a starting material of carboxy cellulose containing about 6wt % of carboxylic group /50/.

Cellulose hydroxamic acids have also been reported by Tolmachev *et al.* /53,54/. Maekawa and coworkers /55/ have prepared a cellulose derivative with increased percentage of hydroxamic acid group (II) after modifying cellulose molecule by mild oxidation.



(I)



(II)

A chelating resin named "Hydroximised Sephadex" has been prepared by treating carboxymethyl Sephadex with H-exchange capacity of 4.27 m.mol. g^{-1} with hydroxylamine /55/. Iminodiacetic acid resins have also been modified to hydroxamic acid resins. Winston *et al.* /48/ have reported conversion of commercial resin chelex-100 to polyhydroxamic acid by first reacting with ethyl chloroformate followed by reaction with hydroxylamine. Imino acid hydroxamates have also been incorporated into polymers containing saturated aliphatic hydrocarbon main chains through acid chloride formation. The acid chlorides were prepared with $SOCl_2$ in dichloroethane in presence of phase transfer catalyst $PhCH_2Et_3NCl$ at 90°C for 8 hr., subsequently heating in $NH_2OH/EtOH$ at 70°C for 48 hr. Polymers showed selective absorption for Mo(VI) and Fe(III) at pH 2 and V(V) and Cu(II) at pH 8 /67/.

Amino acid hydroxamates of Guaran have been reported by Ahuja, Audesh and Mathur /56/. They have also reported anchoring of hydroxamic acids of glycine, anthranilic acid, malonic acid and iminodiacetic acid on styrene divinyl benzene copolymers /57/. Michael addition has also been used as a convenient method for the synthesis of polydroxamic acids /58/. Characterization of polyhydroxamic acids has been done mainly by IR spectroscopy and estimation of nitrogen content.

3. APPLICATIONS

3.1 Analytical applications

The incessant need to measure accurately pico and nano quantities of metal ions has led to the development of many advanced techniques in analytical chemistry. Most of these techniques are not only expensive but also highly sensitive to matrix interferences. A viable alternate is first to separate and pre-concentrate the metal ion using highly selective chelating resins. Polyhydroxamic acids are easier to synthesize compared to Dowex A-I (commercial chelating resin). The equilibration rates, swelling and other properties of these are also comparable. Higher selectivity of polyhydroxamic acids compared to Dowex A-I makes them more versatile ion exchangers for analytical analysis. Polyhydroxamic acids also have the ability to separate multivalent ions such as Fe(III) from Cu(II) {pH = 1.5}, Ca(II) from Co(II) {pH = 3.5}, where Dowex A-I resins are useful only for the blanket extraction of these resins at pH>5 /27/.The numerous analytical applications of polyhydroxamtc acids have been summarized in Table-I.

3.1.1. Sorption and Chromatographic Separation Studies of Transition Metals

Polyhydroxamic acids have oxygen donor atoms that belong to the hard acid category. So they can bind strongly with transition elements especially the 3d series, which are all hard bases. Sorption of Cu(II), Pd(II),Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Fe(II), Fe(III), V(V) along with Hg(II), Au(II), Ag(I) has been reported (Table- I) . Literature shows that N-substituted polyhydroxamic acid has been found to be more efficient in separation of mixtures compared to unsubstituted ones. Various parameter like effects of pH on metal-ion uptake, elution, distribution co-efficient, the effect of electrolytes on metal sorption in break through studies have been extensively investigated and based on these studies separation of many binary, ternary and quaternary mixtures have been reported. The effect of different crosslinks and degree of crosslinking on metal sorption has been studied by Lee and Hong /67,68/. Some of the mixtures separated on polyhydroxamic acids are illustrated here.

(a) Separation of Binary Mixtures

Vernon *et al.* have reported the separation of binary mixture of Fe(III) and Cu(II) by passing the mixture through the column at pH 1.5. Copper was not retained and washed out by buffer solution of same pH and Fe(III) was eluted out using 4M HCl /27/. Mendez and Pillai has reported the separation of same mixture along with that of Cu(II) and Fe(III); Ni(II) and Fe(III); Ni (II)and Cu(II), Mn(II) and Cu(II) by gradient elution using HCl /59/. Agrawal *et al.* have reported complete separation of binary mixture of Cu(II)-Pb(II), Cu(II)-Ni(II),Zn(II) - Pb(II) and Co(II)-Fe(III) by selective elution using 0.5 M H_2SO_4 for Cu and Zn, 0.5 M HNO_3 for Pb ,1 M tartaric acid for nickel and 4M HCl for the elution of iron(III) /25/. Vernon has also reported separation of gold from silver and copper by eluting with 0.5 % KCN, 0.5 M HNO_3 and 0.5 M HCl respectively /60/. Separation of a mixture of Hg(II) and Pb(II) has been reported by passing the mixture at pH 1.5. At this pH lead was not retained and washed out by appropriate buffer solution, where as Hg(II) was eluted using 6M CH_3COOH /23/.

(b) Separation of Ternary Mixtures

Mandez and Pillai have reported the separation of a ternary mixture of Fe(III)-Ni-Cu by gradient elution using HCl for Ni ,Cu and citrate buffer for Fe(III) /18/. Agrawal *et al.* have reported separation of several ternary mixtures such as Cu-Pb--Ni, Ca-Ni-Pb, Zn-Ni-Pb, Co-Ni-Pb and Fe-Pb-Ni using selective eluting agents /25,26/. Separation of a ternary mixture of Cu-Co-Ni has been reported by passing the mixture through the resin column equilibrated at pH 2. Cobalt was not retained and 0.25M tartaric eluted nickel and copper acid /80/.

Table - 1

Analytical Applications of Polyhydroxamic Acids

Sr. No.	polyhydroxamic acid	Metal ions studied	Metal ions separated	Eluants	Ref.
1	N-phenyl substituted polyhydroxamic acid	Cu, Pb, Ni	Cu-Pb-Ni; Cu-Pb; Cu-Ni.	Cu-0.5 M H_2SO_4 Pb-0.5 M HNO_3 Ni -1 M tartarate	25
2	Polyhydroxamic acid of ethyl acrylate-co-DVB polymer	Co, Fe, V, U	---	---	55
3	GOPUR - 3000 containing hydroxamic acid and amidoxime groups	U	Separation from mineral waste	---	64
4	Poly(4-vinyl-2'-carboxy benzophenone hydroxamic acid)	Fe(III), Cu, Ni	---	---	30
5	Calixarene-4-hydroxamic acid supported on XAD-4	Fe(III), Co, Pb,Cd, Mn, Ni, Zn, Cu, V	---	---	79

6	N-phenyl polyhydroxamic acid of poly(styrene-co-maleic acid)	Cu, Fe(III), Ni, Ca, Mn, Zn, Pb, Mo, V, U	Cu - Fe Ni - Fe Ni - Cu Mn - Cu Fe - Ni - Cu	Gradient elution using HCl and citrate buffer	18,59
7	Poly(acrylo hydroxamic acid)resin derived from polyacrylonitrile	Cu, Zn, Pb, Cd, Co, Ni, Mg, Ca	Zn - Cd [5] Cu - Co - Ni Cu - Ni	Cd, Zn - 0.5M HCl Cu,Ni - 0.25M tartaric acid Co - no chelation	80,81
8	Polyhydroxamic acid from Zafran and Acriliam	Pu, U, Co, Th	---	---	65,66
9	Crosslinked hydroxamic acid resin(containing amidoxime or hydroxamic acid groups)	Ga, Al	---	---	82
10	Cellulose hydroxamic acid	Fe(III), Cu, Zn, Co, Ni, UO_2	Fe - Cu Cu - Others	---	53,54
11	Polyhydroxamic Acid Resin	Mg, Ca, Fe(III), Cu, Co, Zn, Ni	---	---	83
12	Endocyclic hydroxamate	Ni, Fe	---	---	84

Table- 1 (continued)

Analytical Applications of Polyhydroxamic Acids

Sr. No.	**polyhydroxamic acid**	**Metal ions studied**	**Metal ions separated**	**Eluants**	**Ref.**
13	Poly(acrylo, methacrylo/ N-methyl methacrylo hydroxamic acid) with amino acid spacers	Fe	---	---	43-49
14	N-methyl hydroxamic acid XAD-4	Mg, Ca, Mn, Co, Ni, Zn, Cr, La, Lu, Eu, Cu, U, Al, Sc, Th, Fe	---	---	15
15	N-hydroxy-N-phenyl carbamoyl XAD-4	V, Cu, Al, Fe, Th, Zr, Ti, U, Mo, Mg, Ca, Pb, Hg, As, Nb, Sn, U, Sb, Bi	---	Th - 1 M HCl Al, Fe - 0.1 M Zr - oxalic acid Cu, V - 0.1 M HCl Ti - 0.3 M HF Mo - 1 M NH_3 W - 0.1M Sodium tartarate	16

16	Poly(acrylo hydroxamic acid) resin	Fe(II), Fe(III), Cd, Ni, Cu, V, UO_2, Hg, Pb	V - Fe[2.0] U - Fe[8.2] Cu - Co - Ni Fe - Cu [1.5]	---	27,89
17	Poly(styrene-DVB-acrylo hydroxamic acid) resin	Ag, Al, Au. Co, Cu, Fe(III), Mn, Ni, V, Ti, Mo, V, Pb, Bi, Th, Zr	U - Mg U - Mn, Pb, Cu, Fe, Ti, Mo, V,Th, Bi, Zr		9
18	Polyhydroxamic acid of Chelex -100	Fe	---	---	46
19	N-phenyl hydroxyl amine of styrene - DVB-acryloyl phenyl hydroxylamine copolymer	Fe(III), Fe(II), Cu, V, Ni, Hg, Co, Pb from acetate media	Hg - Pb [1.5]	Cu,Co,Ni - 2 M H_2SO_4 Hg,Pb - 6M CH_3COOH V -4 M H_2SO_4	23
20	N-benzoyl-N-phenyl hydroxylamine polymer	Cu, Co, V, Fe(III), UO_2	---	---	39
21	Hydroxamicacid of Polyethylene imine resin	Cu, V, Fe, UO_2	---	---	39
22	Cellulose hydroxamic acid polymer	Cu, Fe.,Co,Mn Ca,Cd, Ni, Zn,	---	---	51,52

Table- 1 (continued)
Analytical Applications of Polyhydroxamic Acids

Sr. No.	polyhydroxamic acid	Metal ions studied	Metal ions separated	Eluants	Ref.
23	Poly(sulphohydroxamic acid)	Cu , Ni	---	---	85
24	Poly(acrylo- α- chloro acrylo hydroxamic acid)	Cu	---	HCl	20
25	Polyhydroxamic acid of styrene-maleic anhydride copolymer	Cu, Fe, Co, Cd, U	---	HCl	86
26	Poly(methacrylo hydroxamic acid) resin	Fe,Cu,Zn	---	----	13
27	Poly (acrylo hydroxamic acid)	Na, Cu, Ag, Mg, Ca, Sr,Ba, Zn, Cd, Ag, Al, Ti, Pb,Bi, Mn, Fe, Fe(III), Co, Ni, Ce(III) Ce(IV),U	---	----	21
28	Polyhydroxamic acid resin derived from polyacrylonitrile	Cu, Au, Ag,	Au - Ag, Au - Cu Ag - Cu, Au-Fe	Au - 0.5% KCN Ag - 0.5M HNO_3 Cu - 0.5M HCl , Fe - 2M HCl	60

29	Hydroxamic acid of Amberlite IRC - 50	V, Fe, Mo, Ti, Cu, UO_2, Ca, Hg	---	---	14
30	Hydroxamic acid polymer of Amberlite IRC-50	Fe	---	---	11,12
31	Poly (hydroxamic acid) of acrylonitrile fibers	Cu, Pb	Cu -Pb [5.0]	Pb - not retained Cu - 1N HNO_3	37
32	(Anthranilic acid hydroxamate) of Guaran	Fe(II), Co, Ni, Cu, Zn, Ca, V, W	---	---	56
33	Aspartamide poly hydroxamic acid	Fe(III)	---	---	87
34	N-phenyl polymethacryl hydroxamic acid	Cu, Pb, Ni, Fe, Co, Zn	Ternary and quarternary mixtures	Ni - 1 M tartrate Fe - 4 M HCl Pb - 0.5 M HNO_3 Cu - 0.5 M H_2SO_4	26
35	Polyvinyl pyrrolidine hydroxamate	Am	---	---	95
36	Poly(styrene-p - hydroxamic acid)	Ce(IV),La,Ce, Nd,Y	Ce(IV) - Ln(III) Ce(IV) - Ce(III) La(III) - Ce(III	---	17
37	Poly(B-styryl) hydroxamic acid	U(VI)	U(VI) - La(III)	La - 0.1M EDTA U(IV) - 2M HCl	41
38	Polyhydroxamic acid	Mo, Fe(III), V(V), Cu	---	---	88

Note: M - Molarity of the solution ; [ ] - pH of the metal solution ; ( ) - Oxidation state of metal ion *(c) Separation of Quaternary and Quinary mixtures*

Separation of quaternary and quinary mixture of 3d transition elements such as Co-Pb-Fe-Ni, Zn-Pb-Fe-Ni, Co-Cu-Pb-Ni-Fe and Co-Zn-Pb-Fe-Ni on polymethacryto hydroxamic acid columns has been reported by Agrawal and co-workers /26/ using a selective elution technique.

3.1.2 Sorption and Chromatographic Separation of Actinides

Hydroxamic acid is known to be a remarkable chelating agent for $UO_2^{2+}$and so appropriately much attention has been paid to its extraction and pre-concentration on polyhydroxamic acid columns. Macroporous polyhydroxamic acid ion-exchangers have been used to recover U(VI) from $Mg(HCO_3/_2$ solution produced in magnox process. Resin columns were successfully used to strip Ti, Zr, V, Mo and Bi from U(VI) solution in HNO_3 /9/. The resins have been reported to extract 10 kg of uranium from 1500 tons of seawater /61/. Gopur-3000 containing hydroxamic acid and amidoxime groups have been used for separation of uranium from mineral waste /64/. A polyvinyl pyrrolidone hydroxamic acid prepared by heating of poly vinyl pyrrolidone with NaOH and $NH_2OH.HCl$ at 90° C for 2 days had been used for separation of Am from aqueous streams. No retention of metal was observed at pH 2 and 6 but 99% sorption was observed at pH 8 /62/. Novel tetrahydroxamic chelators for actinide complexsation have also been reported for minimization and remediation of DOE nuclear waste problems /63/.

(a) Separation of Uranium(IV) and Thorium(IV)

Phillips and Fritz have reported separation of U(IV) from Th(IV/ on N-methyl hydroxamic acid resin. Thorium was eluted with 3M HCl, whereas uranium was eluted with a mixture of 3M HCl and 0.1 M oxalic acid /16/.

(b) Separation of Uranium(VI) from Lanthanides

Agrawal and Kaur have reported preconcentration and separation of U(VI) from Lanthanides in various samples. A solution of U(VI/ and La(III) was sorbed on to the polyhydroxamic acid column at pH 6. The La(III) was eluted with 0.1 M EDTA solution and U(VI/ with 2M HCl /41/.

3.1.3 Sorption and Chromatographic Separation of Lanthanides

Kern and Schulz /21/ have reported sorption of Ce(III) and Ce(IV) on poly acrylo hydroxamic acids. Recently Agrawal and Kaur have reported sorption and separation studies of lanthanides on poyhydroxamic acids in detail. These workers were able to separate Ce(III) from other lanthanides after oxidising former to Ce(IV) . A partial separation of La(III) from Ce(III) was achieved by selective elution using 0.5% ammonium oxalate solution. They have also reported separation of lanthanides as group from other metal ions such as Fe(III), Al(III), Cu(II), Pb(II), Mg(II), Ca(II), Be(II). Preconcentration of lanthanides and the effect of various electrolytes such as NaCl, Na_2SO_4,$NaNO_3$, and Na_2CO_3 on metal sorption have also been reported /17/.

3.2 Medicinal Applications

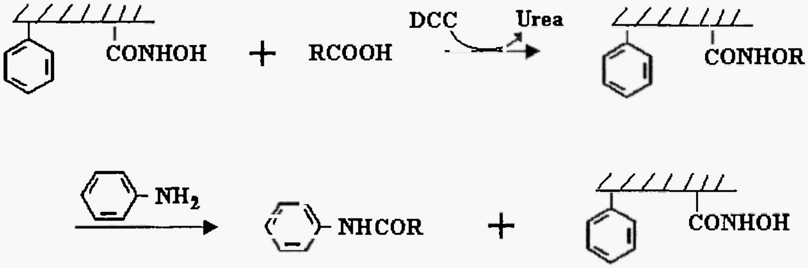
Polyhydroxamic acid has been extensively studied with an aim to find a cure for iron poisoning. Winston and coworkers have synthesised many polyhydroxamic acids in which the adjacent hydroxamic acid groups are separated by 11 to 3 atoms. The stability of the iron complexes of these polymers was compared with that of desferrioxamine B, the naturally occurring siderophore. The stability of complexes decreased with decreasing number of intervening atoms /38/. A polyhydroxamic acid has been patented for its urease inhibition activity /74/.

3.3 Industrial Applications

Polyhydroxamic acids are increasingly becoming useful in the field of metallurgy, which is manifested in the numerous patents being published. Polyhydroxamic acids derived from C_1 -C_4 alkylacrylate esters were found to be good settling agents in the treatment of slurries in Baeyer's process /75/. Clarifying of Baeyer's process alumina trihydrate slurries has also been reported by a terpolymer of acrylic acid, acrylamide and acrylohydroxamic acid units in approximate ratio of 2:1:1 /76/. Polyhydroxamic acids have also been found useful for the recovery of alkali metal carbonates from slurries containing minerals and alkali metal sesquicarbonates /77/. Certain polymers bearing hydroxamic acid groups in the pendent arms are claimed to have pigment dispersing properties for heavy metal ions and sequestering properties for alkaline earth elements /78/. Polyhydroxamic acids have also been reported as water softeners /71/, corrosion inhibitors of iron and steel alloys in contact with industrial waste /79/ and contrasting agents in nuclear magnetic imaging /80/. Polypyrrole and polycarbazole hydroxamic acids have been investigated for their conducting properties /81/. Recently metal complexes of polyhydroxamic acid have also been studied for their conducting properties /82/.

3.4 Acyl group transfer agents

Activation of a carboxylic group in hydroxamic acid has been utilized as a means of facile acyl group transfer by Narita and co-workers. Mechanism of acyl transfer has been shown in scheme **V** /19/. Recently Sophaimma and Sree Kumar synthesized a series of polystyrene supported hydroxamic acids and their dithiocarbonic anhydrides to study the effect of architecture of a polymer on the efficiency of acyl transfer reactions /83/.



Scheme-V

ACKNOWLEDGEMENT

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