

## CHAPTER VIII

### *Synthesis, characterisation and properties of a new chelating resin containing imidazolylazo group and its analytical applications*

A new chelating resin incorporating imidazolyl azo group into the matrix of polystyrene - divinyl benzene has been prepared. The exchange capacity of the resin for metal ion viz. mercury(II), silver(I) and lead(II) as a function of pH has been determined. The resin exhibits no affinity for alkali, or alkaline earth metals. The resin is highly selective for only mercury(II) and silver(I). In column operation it has been observed that Mercury(II) in trace quantity is removed very effectively from river water spiked with mercury(II) at the usual pH of natural waters.

## 1. Introduction

There has been an increasing interest in highly selective ion exchangers. These resins are, in fact, polymeric complexing and chelating compounds which, under certain experimental conditions, are characteristic of one ionic species. Skogseid<sup>1</sup> is the pioneer in the development of chemistry of these new types of complexing resin. The first such resin, a polystyrene derivative incorporating dipicrylamine group which is specific for potassium ion was described by Skogseid. Since then, the field of the chelating ion-exchange resins by incorporating a variety of chelating groups on different types of polymeric materials<sup>2</sup> has been developing steadily. The high selectivity of chelating ion-exchangers is due to their ability to form stable, often covalent, complexes of varying strength with metal ions. Kennedy and Davies<sup>3</sup> observed that the resins containing phosphoric acid functional units showed similar selectivity towards various cations, but the stability constants of resins for covalently bound cations, such as uranyl(VI) and iron(III) are greater by an order of  $10^6$  or more than that of the corresponding monomer complexes. The increase in the stability of the chelating resin complexes is attributed to a combination of various factors. e.g.

the polymer entropy effect, a lower dielectric constant of the resin matrix and also the large area of polymer having chelating functionality enhance the formation constant than those of the simple chelating agents<sup>4</sup>. Selectivity of the chelating resin depend upon the pH of the solution and can also be judged applying basic concept of hard-soft acid base concept<sup>5</sup>.

The increasing utility and application of complexing and chelating resins in transitional metals, as well as in alkali and alkaline earth metal ion separations, preconcentration and recovery of trace metal ions, catalysis, organic synthesis, nuclear chemistry, water and waste water treatment, pollution control and industrial processes including hydrometallurgy, polymer drug graft and various miscellaneous applications in analytical chemistry resulted in the development of several selective chelating ion-exchange resins<sup>6-11</sup>. A number of chelating resin containing functional groups such as iminodiacetic acid (IDA), amidoxime, aminophosphoric acid, oxime, thiols, pyridine etc. are now commonly available. A selection of commercial chelating ion-exchange resins along with the details available of their constitution, functional groups and chromophore is given in **Table VIII.1**(Appendix-1).

To synthesis a selective chelating ion exchange resin different factors have to be considered.

(a) The chelating ligand attached to a solid matrix should possess strong metal-binding properties and selectivity towards certain metal ions. The concept of 'soft' and 'hard' or 'a' and 'b' class metals can be a useful guide in this regard.

(b) The chelating group should be capable of undergoing incorporation in a polymeric network and allow the process of polymerisation or resinification; in turn, the chelating polymer should be resistant to strong acids and alkalis at elevated temperature.

(c) The chelating ligand should preferably be multidentate, permitting formation of a 1:1 chelate with a metal ion, and the chelating ion exchanger should be monofunctional as far as possible. The occurrence of mixed functional groups such as sulfonic, carboxylic or phenolic groups should be avoided.

(d) The chelating ion exchangers should possess good swelling properties and compatibility between polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking. A higher degree of cross-linking results in increased mechanical strength, but the swelling properties of

polymer are adversely affected.

For synthesizing chelating resins, the methods which are most commonly used are :

- (i) direct polymerisation and copolymerisation of monomers containing desired functional groups,
- (ii) introduction of one or more functional groups into a preformed polymer.

In method (i), the monomeric chelate forming reagent is usually the starting material. In most cases, this reagent contains one or more phenolic groups. This is condensed most often with formaldehyde or any other aldehyde in the presence of acid or alkali catalysts. The resins prepared from pyrogallol<sup>12</sup>, salicylic acid<sup>13</sup>, resorcinol<sup>14</sup>, 2,3,4-trihydroxy benzoic acid<sup>15</sup>, 2,4-dihydroxyacetophenon etc., have been described.

In method (ii), reactive groups such as chloromethyl, amino, diazo, epoxy are introduced into a polymer matrix and the product is then made to react with monomeric reagent.

Various polymeric matrices have been described in the literature, e.g. cellulose, polyvinyl alcohol, polystyrene cross linked with

divenylbenzene. Of these the styrene-divenyl benzene copolymers are most widely used, because they are chemically and mechanically very strong.

By using chloromethylated polystyrene, numerous chelate resin containing various chelating groups have been prepared. A few examples<sup>16,17</sup> are : iminodiacetate, anthranilic acid hydrazide acetylacetone etc. have been prepared.

The method involving incorporation of chelating ligands into preformed polymers or matrices to synthesize chelating ion-exchange resin is preferred to the method (i) due to the fact that the degree of incorporation of the functional group can be controlled by varying the amount of cross linking agents and the extent of modification in preformed matrices. However, the disadvantage of the method(ii) is the possibility of the contamination of the end product with by-products and intermediate products due to their incomplete conversion which is impossible to remove. Contamination of chelating ion-exchange resin adversely affects their selectivity<sup>18</sup>. In view of this, the best synthesis of a chelating ion-exchange resin can be regarded to be one which involves the minimum number of steps.

Chelating resins having N-donor centres are highly specific for transition metal ions and some resins have been designed incorporating heterocycles<sup>19</sup> viz. pyridine, imidazole, pyrazole. Polymeric matrix containing imidazole with bare pyrrolic N-H are scarce<sup>20</sup>. The (pyrrolic-N) has high affinity to class b metal ions viz. Cu(I), Ag(I), Hg(I)/(II)<sup>4</sup>. Besides, imidazole has biological importance<sup>21</sup> and has ability to form complexes with a number of metal ions<sup>22</sup>. However, there are few reports about metal complexes with imidazolyl-azo group in acidic solutions. Mercury complex with imidazolyl azo group has been reported<sup>23</sup>. Since mercury is a toxic pollutant of biological interest, its selective removal from industrial wastes, from natural waters would be of great importance. Liu<sup>20</sup> has reported the preparation of a chelating resin containing histidine and has shown that the resin is selective for silver(I), mercury(II) and few other metal ions in acidic solutions. No resin containing imidazolyl azo group has yet been reported. Herein we report the preparation and analytical applications of a resin containing imidazolyl-azo as chelating group on a polystyrene divinyl-benzene matrix.

**Experimental :****A. Materials :**

The starting material was 30-60 mesh macroreticular polystyrene di-vinylbenzene copolymer containing 8% divinylbenzene (Bird & Co., India). The metal ion solutions were prepared from corresponding analytical grade nitrates. The  $\gamma$ -active radioisotopes  $^{203}\text{Hg}$  and  $^{110\text{m}}\text{Ag}$  were supplied by Bhaba Atomic Research Centre, Trombay and were used as tracers.

**B. Physical Measurements :**

The elemental analysis, UV-VIS, IR and TGA were carried out as in chapter I. pH adjustment was made with a Sambross 335 digital pH-meter. The radioactivity was measured with a scintillation-counter equipped with a well type NaI Crystal detector.

**C. Synthesis of Resin :**

The resin was synthesized from chemically modified macroreticular polystyrene-divinyl benzene copolymer containing 8% divinyl benzene and 30-50 mesh size by four steps :

- i) Nitration of polystyrene,



ii) Reduction of nitrated copolymer i.e. amination of the nitrated product.

iii) Diazotization of the aminated product.

iv) Coupling of diazotied resin with imidazole.

The above three steps upto diazotization have been performed following the procedure described by Davies et al<sup>24</sup> and all the steps are shown in scheme **VIII.1**.

i) *Nitration of Polystyrene* :

Styrene-divinylbenzene polymer of macroreticular shape (5g) were swollen in  $\text{CHCl}_3$  for 30 min. The solvent was then removed by filtration using suction. The swollen beads were charged in portions over a period of 1 hr. into a stirred mixture of sulphuric acid (25 ml, specific gravity, 1.84) and nitric acid (10 ml, specific gravity, 1.5) at  $60^\circ\text{--}70^\circ\text{C}$  over a water bath. After completion of addition of these resin beads, stirring was continued at this temperature for further half an hour. The reaction mixture was then poured into ice water and the nitrated polymer was washed repeatedly with water until free from acid.

ii) *Conversion of Nitropolymer into Aminopolymer* :

The wet nitrated product obtained as above was mixed with ~40 gm

$\text{SnCl}_2$ , 50 ml conc. HCl and 50 ml ethanol. The mixture was refluxed for 10-12 hrs. over a oil-bath. The aminopolystyrene-tin complex thus obtained was filtered off, washed with water and treated with excess NaOH (2.0 M) which helped to get the free aminopolystyrene.

iii) *Diazotization of Aminopolystyrene into polystyrene diazonium chloride :*

The aminopolystyrene obtained from above was converted to the hydrochloride by washing with 2N-HCl followed by distilled water to remove the excess acid. The hydrochloride was added to ice water (~250 ml) and diazotized by alternative additions of 1 ml portions of 1 M-HCl and 1 M- $\text{NaNO}_2$ . Completion of the reaction after the addition of about 40 ml of  $\text{NaNO}_2$  solution was indicated by the permanent blue coloration of starch-iodide paper spotted with the reaction mixture. The product was filtered off washing with distilled water immediately.

iv) *Coupling imidazole with diazotized resin matrix :*

The diazotised product was made free from acid, washing with cold double distilled  $\text{H}_2\text{O}$  and then it is poured into the solution of imidazole (1.0g imidazole for 5.0g of the starting material) in 20% aqueous  $\text{Na}_2\text{CO}_3$  solution and stirred over a period of 6-7

days at 0°-5° C. The resin was then filtered off and thoroughly washed with distilled water until free from base. Finally, it was washed with dilute HCl and then with double distilled water until free from acid. The dark-brown coloured resin was washed with ethanol, dried in desiccator and stored.

#### **D. Characterisation of Resin :**

The resin is insoluble in water, alcohol and also in moderately concentrated acids, alkalis and common organic solvents.

The resin was characterised by its water regain value, elemental analysis, IR spectra, TGA and stability towards acids and bases,  $\gamma$ -radiation, and exchange capacity of metals and equilibrium rate have been studied.

##### **i.) Water regain :**

The imidazolylazo resin was immersed in double distilled H<sub>2</sub>O for 3-4 days. Then the resin was filtered, air-dried and weighed. The swollen resin was then dried at 100°-110° C for 24-30 hr. and weighed after cooling in desiccator again. Water regain value was calculated from the difference in these two weights as stated as follows in **Table VIII.2.**

Table : VIII.2

*Determination of waterregain value of the resin.*

Wt. of swollen air dried resin (in g)	Wt. of swollen resin after heating at 100-110°C (in g)	Wt. of water molecule absorbed in the resin (in g)	Water regain value of the resin (in g)
1.3550	1.0234	0.3316	0.3240
1.0534	0.7951	0.2583	0.3249
1.0856	0.8201	0.2655	0.3237

The average water regain value of the resin is 0.3242 g/g of the resin i.e. 18 mmols/g of the resin and it is of moderate order<sup>24</sup>.

ii.) *Elemental Analysis :*

*Determination of nitrogen :*

Small amount of the air dried sample of the nitrated polymer, aminated polymer and imidazolylazo resin (all belonging to the same batch) were dried by heating at 100° C for 24 hrs. and then kept in a desicator over fused CaCl<sub>2</sub>. Nitrogen in each case was determined by micro Duma's method. The results are given in **Table VIII.3.**

Table : VIII.3

*Elemental analysis for nitrogen*

Sample	Nitrogen (in mmole/g)
Nitropolymer	5.68
Aminopolymer	6.26
Imidazolylazo resin	8.61

*Estimation of amino group in aminopolymer :*

The amino group content of the aminated polymer was determined by titration in non-aqueous medium<sup>25</sup>. An accurately weighed amount of the aminated product (0.25 g) was mixed with a standard solution of perchloric acid in glacial acetic acid (25.0 ml, 0.1N) solution and glacial acetic acid (50 ml) in a stoppered conical flask. The mixture was kept in an air oven at 90°-100° C for 2-3 days. The resin was filtered off and washed with hot glacial acetic acid. To the combined filtrate and washing, 2-3 drops of 0.5% solution of crystal violet in glacial acetic acid were added. Then the solution was titrated with 0.1 N sodium acetate solution in glacial acetic acid till the green colour change to blue.

Perchloric acid solution in glacial acetic acid (strictly non aqueous, containing acetic anhydride to avoid/a drop of water)  
even

was standardised by sodium acetate solution in glacial acetic acid (also contain acetic anhydride to remove water).

iii.) *Stability of the resin :*

*Stability of the resin toward common acids and bases :*

The resin was kept immersed in 25 ml of acid or alkali solution of various concentrations (1N - 6N) for 7 days, filtered, washed with doubly distilled water and dried in air. Nitrogen content and sorption capacity of the resin for Ag(I) and Hg(II) at pH 6.0 were recorded. The results are in **Table VIII.4**.

**Table VIII.4**  
*Stability of resin (period of study : 7 days)*

Acid/ alkali	Strength	Nitrogen (in mmol g <sup>-1</sup> )		Sorption capacity of Hg(II) at pH 6.0 (mmol g <sup>-1</sup> )	
		I	II	I	II
H <sub>2</sub> SO <sub>4</sub>	1 <u>N</u>	8.61	8.60	0.62	0.62
	2 <u>N</u>		8.58		0.61
	3 <u>N</u>		8.49		0.61
	4 <u>N</u>		8.30		0.58
	5 <u>N</u>		8.10		0.50
	6 <u>N</u>		8.10		0.50
HCl	1 <u>N</u>	8.61	8.61	0.62	0.62
	2 <u>N</u>		8.59		0.60
	3 <u>N</u>		8.59		0.58
	4 <u>N</u>		8.53		0.58
	5 <u>N</u>		8.50		0.57
	6 <u>N</u>		8.41		0.57
HNO <sub>3</sub>	1 <u>N</u>	8.61	8.59	0.62	0.62
	2 <u>N</u>		8.55		0.58
	3 <u>N</u>		8.52		0.58
	4 <u>N</u>		8.41		0.49
	5 <u>N</u>		8.32		0.48
	6 <u>N</u>		8.00		0.48

Table VIII.4 (Contd.)

*Stability of resin (period of study : 7 days)*

Acid/ alkali	Strength	Nitrogen (in mmol g <sup>-1</sup> )		Sorpton capacity of Hg(II) at pH 5.0 (mmol g <sup>-1</sup> )	
HClO <sub>4</sub>	1 <u>N</u>	8.61	8.58	0.62	0.60
	2 <u>N</u>		8.52		0.57
	3 <u>N</u>		8.47		0.51
	4 <u>N</u>		8.38		0.48
	5 <u>N</u>		8.05		0.48
	6 <u>N</u>		7.95		0.43
NaOH	1 <u>N</u>	8.61	8.60	0.62	0.62
	2 <u>N</u>		8.56		0.61
	3 <u>N</u>		8.49		0.58
	4 <u>N</u>		8.40		0.55
	5 <u>N</u>		8.32		0.52
	6 <u>N</u>		8.30		0.50

I ⇒ Before treatment with acid or alkali;

II ⇒ After treatment with acid or alkali.

The results showed that no appreciable change in nitrogen content and sorption capacities of Ag(I) and Hg(II) metals at pH 6.0 occurred after treating the resin with 6 N strength of common



acids and alkali. Hence this can be concluded that the resin is stable in moderately concentrated acids and alkali.

*Stability towards thermal energy :*

TG and DT analysis :

50 mg of the imidazolylazo resin was taken for thermogravimetric and differential thermal analyses, rate of heating was 10° C/min upto 500° C temperature. The resin was found to be stable upto 150° C. After which decomposition of the functional group occurs and 25.1% weight loss of the resin was determined. The experimental curve is given in **Fig. VIII.A**

*Stability towards gamma radiation :*

Four sets of the imidazolylazo resin were irradiated by  $\gamma$ -ray of varying strengths for different time. The sets were exposed to 1000 rad  $\gamma$ -radiation for 4 hrs., 12 hrs., 48 hrs. and 144 hrs. Sorption capacity of these four sets were determined and found to remain unchanged in case of first three sets of the resin. But for the fourth one, the sorption capacity of Hg(II) was found to be reduced by 15%. This indicates that the resin is stable at least upto 1000 rad for 48 hrs.

D.iv. *IR spectra* :

Infrared spectra of the chelating resin in KBr disc was recorded to confirm the presence of the imidazolyl azo group in the resin. IR spectra of monomer, arylazo imidazole was also recorded in the same way and compared with the above. The insertion of imidazole into the resin matrix through coupling have been confirmed from **Fig. VIII.B** and some selected IR stretching of chelating resin is given in **Table VIII.5**.

**Table : VIII.5***Selected IR Stretching for chelating resin (in cm<sup>-1</sup>)*

$\sqrt{N-H}$	:	3424 and 1677
$\sqrt{C=N}$	:	1600
$\sqrt{N=N}$	:	1516
For imidazole unit	:	1460(w), 1340(m), 1160(w), 1110(w), 1015(w), 855(s), 830(m), 700(m), 660(s)

w  $\Rightarrow$  weak, m  $\Rightarrow$  medium and s  $\Rightarrow$  strong.

D.v. *Hydrogen ion capacity* :

A 0.5 g sample of the resin in its basic form was first converted into its acid chloride by treating with 6 M HCl. The resin was then filtered off, washed with water and then dried at 100° C

for 6 hrs. to remove free HCl. The acidic hydrogen content of the acid form of the resin was then determined by back titration. The acidic form of the resin was equilibrated with 20.0 ml of 0.10 M sodium hydroxide solution for 6 hrs. at room temperature with stirring to determine the total acidic hydrogen content. Similarly, another sample of the resin in acidic form was equilibrated with sodium bicarbonate solution instead of sodium hydroxide for the determination of the hydrogen ion content of the resin from imidazolium group. In both cases, the solution was filtered under suction, and the excess of alkali was titrated with 0.10 M hydrochloric acid.

D.vi. *Metal ion capacity as a function of pH :*

A batch technique was used, metal ion being in excess to the resin, capacities were determined in the pH range 1.0 - 6.0. To a glass stoppered centrifuge tube (diam. 2.0 cm) containing 100 mg of the dry resin in basic form, 9.0 ml of the perchloric acid of desired concentration (adjusted to pH 1.0 - 6.0) was added. After equilibration of this mixture, 1.0 ml of 0.2 M metal ion solution was added to the tube; then the mixture was shaken for a period of 24 hr. The pH of the equilibrating solution was adjusted either by the addition of sodium hydroxide or perchloric acid

throughout the equilibrating period until it remained constant at the desired level. Mercury and silver capacities were obtained by using the tracer technique. The amount of each metal ion absorbed on the resin was determined by measurement of the gamma activity of equal portions of the solutions, before and after the absorption of metal ions. Lead capacity was determined by spectrophotometric method using dithizone<sup>26</sup>.

D.viii. *Desorption of metal ions :*

The resins (0.1 g) containing absorbed metal ions of maximum capacity were shaken with 10 ml of various desorbents for 1 hr. After filtration the amounts of metal ions in the filtrate were determined.

D.ix. *Equilibration rates :*

Equilibration rates for the metal ions mercury(II) and silver(I) were studied at pH 6.0 for the resin. A 10.0 ml portion of metal ion solution containing appropriate amount of the metal ion (maximum exchange capacity : 0.062 mmol for Hg(II) and 0.075 mmol for Ag(I)) and its respective tracer was equilibrated with 0.1g of the resin as described before. 1.00 ml aliquote of the

supernatant solution was withdrawn at interval of time (10 mins initially, after one hour on the hour) to determine its gamma activity. After the measurement of the activity, the aliquote was again transferred into the equilibrating solution and the equilibration of the metal ion with the resin continued. The removal of the 1.00 ml aliquote and its activity measurement was finished within a span of 1 min. The time taken for 50% uptake of the metal ions was determined from the **Fig. VIII.C.**

*D.x. Column operations :*

A 100×5mm glass column was packed with 2.0g (dried resin) of the basic form of the resin in fully swollen form, the resin bed was equilibrated with ten bed volumes of perchloric acid at pH6.0.

The sorption and recovery characteristic for mercury(II) and silver(I) in the presence of various metal ions were thoroughly studied. A 100 ml portions of the mixture of the test metal ion spiked with appropriate tracer and the foreign metal ions was allowed to flow through the resin column at a flow rate of 0.5 ml min<sup>-1</sup>. The metal ions not sorbed by the resin were completely washed out using perchloric acid at pH 6.0. The sorbed mercury(II) and silver(I) were completely eluted with about 50 bed volumes of 5% thiourea in 0.1 M HClO<sub>4</sub> and determined by

tracer technique.

D.xi. *Removal of mercury(II) from river water polluted with mercury (II) :*

Natural river water (pH 5.6)<sup>27</sup> was spiked with mercury(II) and <sup>203</sup>Hg, so that the concentration of mercury become 2.0 µg/ml in the river water. The above mixture was passed through the 100 × 5 mm glass column containing 2.0 g of the resin at a flow rate of 0.5 ml min<sup>-1</sup>. The break through of mercury(II) was observed after 125 ml of the mixture has been allowed to pass through. The concentration of mercury(II) in the effluent before the break through point were determined by tracer technique.

D.xii. *Studies with resin blanks :*

To confirm that imidazolylazo group is involved in metal ion sorption, the diazotized amino polystyrene in sodium carbonate solutions was boiled for several hours to replace the diazo group by hydroxyl group. The mercury(II) exchange capacity of the resin thus formed was examined at pH 6.0. The exchange capacity was found to be almost zero.

## Results and discussions :

### *A. Synthesis and characterisation of resin :*

The resin was synthesized from 30-60 mesh macroreticular styrene-divinylbenzene copolymer beads through the steps shown in experimental section.

The nitrogen content of the compound II was 7.95% (5.68 mmol of nitro resin  $\text{g}^{-1}$ ). After reduction, the total nitrogen in compound(III) was found to be 8.76%. The estimation of amino group in amino resin was 3.4 mmol  $\text{g}^{-1}$ , which gives about 55% conversion from step II to III. The nitrogen content of the final resin (compound IV) was found to be 12.05% or 8.61 mmol  $\text{g}^{-1}$  of the resin. A rough estimate of the composition of the final product may be obtained by considering that diazotization is cent per cent but the subsequent coupling reaction is not. The unreacted diazonium ion will ultimately decompose leaving the corresponding phenolic compound. One should also keep in mind that the phenol thus formed may not form any azophenol by binding with another diazonium ion, only because the phenolic -OH is firmly attached to the resin matrix and may not find another fixed diazonium ion nearby. Calculations based on this consideration, show that conversion efficiency from step III to

IV is about 50%. The final product, therefore, may contain 1.5, 2.5 and 1.5 mmol g<sup>-1</sup> of imidazolylazo, unconverted nitro and phenolic -OH resin respectively. The hydrogen ion capacity of the imidazolium ion and the total hydrogen ion capacity of the resin were found to be 1.48 and 2.85 mmol g<sup>-1</sup> respectively, which further strengthens our hypothesis about the composition of the final product. The maximum exchange capacity of the resin for silver(I) was found to be 0.75 mmol g<sup>-1</sup> **Table VIII.7**. If the resin metal complexes are 1:1 complexes (which is most likely) the maximum exchange capacity should be 1.48 mmol g<sup>-1</sup>. Steric factors are probably responsible for lower exchange capacities. The infrared spectrum of the resin showed bands at 3424 cm<sup>-1</sup>, 1677 cm<sup>-1</sup> for N-H stretching, 1600 cm<sup>-1</sup> for C=N and 1516 cm<sup>-1</sup> for N=N stretching. Other vibrations due to imidazole skeleton are observed at **Table VIII.5** and is the indication of imidazole incorporation into the polymeric matrix.



Table : VIII.6

*Physical and chemical characteristics of imidazoly azo resin*

Bead size	30 - 50 mesh
Water regain	18 mmol g <sup>-1</sup>
Nitrogen content	8.61 mmol g <sup>-1</sup>
Hydrogen ion capacity (imidazolium group)	1.48 mmol g <sup>-1</sup>
Total hydrogen ion capacity	2.85 mmol g <sup>-1</sup>
Equilibration rate (t <sub>1/2</sub> ) (for Ag(I) and Hg(II))	45 min

The chemical stability of the resin in 1.0 - 6.0 M hydrochloric acid, perchloric acid and sodium hydroxide solutions was examined. No significant changes in nitrogen content was observed and the exchange capacities for silver(I) and mercury(II) were not reduced. From these facts, it is clear that the resin is sufficiently stable in both acid and alkali medium. Thermogravimetric analysis showed that it is stable upto 150° C.

The time required for 50% uptake of the maximum capacity for mercury(II) and silver(I) was found to be 45 mins. This shows that

the resin is suitable for column operation under a low flow rate. The water regain value of the resin ( $18 \text{ mmol g}^{-1}$ ) is also quite satisfactory for column operation.

**B. Sorption and desorption of metal ions :**

The sorption behaviour of mercury(II), silver(I) and lead(II) on the resin by batch method is shown in **Fig. VIII.D** and the maximum exchange capacity for the metal ions is given in **Table VIII.7**. It is observed that the resin has high exchange capacity only for mercury(II) and silver(I) viz. **Table VIII.7**.

The effects of different eluents on the desorption of metal ions absorbed is given in **Table VIII.8**. Complete desorption of mercury(II) and silver(I) took place with eluents containing complexing agents viz. 5% thiurea in  $0.1 \text{ M HClO}_4$ .

**Table : VIII.7**

*Maximum exchange capacities for the metal ions  
(as a function of pH (in mmol/g))*

<b>pH</b>	<b>Ag (I)</b>	<b>Hg (II)</b>	<b>Pb (II)</b>
1.0	0.39	0.50	0.00
2.0	0.54	0.59	0.01
3.0	0.63	0.61	0.06
4.0	0.70	0.62	0.01
5.0	0.75	0.62	0.00
6.0	0.75	0.62	0.00

**Table : VIII.8**

*Desorption of mercury(II), silver(I) and lead(II) by different eluents*

<b>Eluent</b>	<b>Recovery of Hg (II) (%)</b>	<b>Recovery of Ag (I) (%)</b>	<b>Recovery of Pb (II) (%)</b>
4M HCl	40	--	--
6M HCl	60	--	--
1M HClO <sub>4</sub>	--	60	100
6M HClO <sub>4</sub>	60	60	--
5% Thiourea in 0.1M HClO <sub>4</sub>	100	100	--

In column operation, as shown in **Table VIII.9** the presence of macro amount of diverse metal ions such as copper(II), cobalt(II) nickel(II), iron(II), manganese(II), calcium(II), barium(II), magnesium(II) and sodium(I) did not interfere with the sorption and desorption of mercury(II) and silver(I). Thus it is observed that the resin has a high selectivity only for Hg(II) and Ag(I). The non-interference of alkali and alkaline earth metal ions is of interest for the application of the resin in the concentration and removal of mercury(II) from highly saline solutions (industrial wastes, sea water) and river water. The break through curve for the removal of mercury(II) from river water<sup>27</sup> spiked with mercury(II) is shown in **Fig. VIII.E**. No mercury(II) was detected in the effluent from the column till the break through point is reached.

**Table : VIII.9**

*Separation of Hg(II), 2 ug ml<sup>-1</sup> and Ag(I), 2 ug ml<sup>-1</sup> from several binary mixtures with other metal ions in a sample volume of 100 ml at pH 6.0.*

<b>Foreign metal ion</b>	<b>Amount of Foreign metal ion (ug)</b>	<b>Hg(II) found (ug), with% of recovery in parenthesis</b>	<b>Ag(I) found (ug), with% of recovery in parenthesis</b>
Cu(II)	2,000	190 (95%)	195 (97%)
Co(II)	2,000	200 (100%)	200 (100%)
Ni(II)	2,000	200 (100%)	200 (100%)
Fe(III)	2,000	195 (97%)	200 (100%)
Mn(II)	2,000	200 (100%)	200 (100%)
Ca(II)	2,000	200 (100%)	200 (100%)
Ba(II)	2,000	200 (100%)	200 (100%)
Mg(II)	2,000	200 (100%)	200 (100%)
Na(II)	2,000	200 (100%)	200 (100%)

### **C. Epilogue :**

The results show that the resin containing imidazolylazo group is very selective for mercury(II) and silver(I). The high selectivity of the resin to mercury(II), silver(I) may be due to the soft basic pyrrolic N-H of the imidazole azo matrix. The bare N-H play the key role in binding and may be followed by

chelation via azo-N. This resin has immense potential to be used effectively for the preconcentration and removal of mercury (II) from natural water or industrial wastes.

**References :**

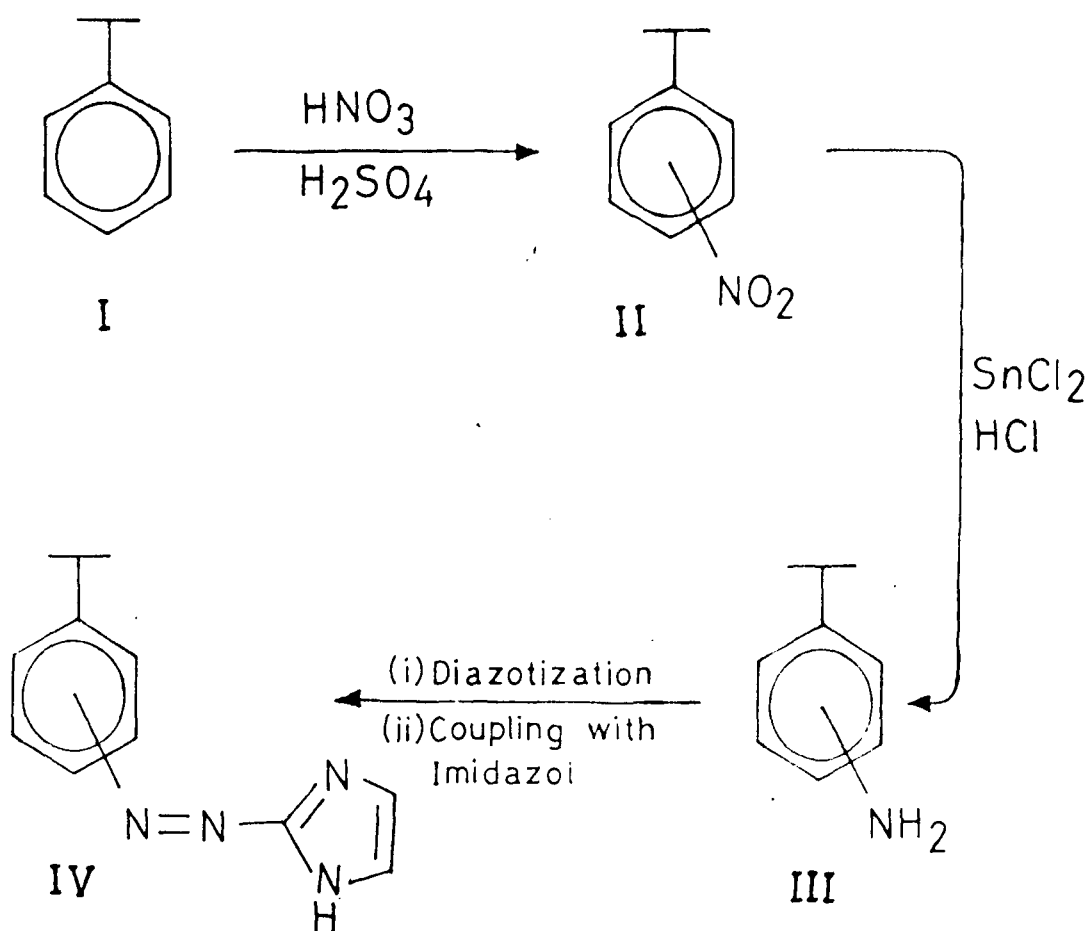
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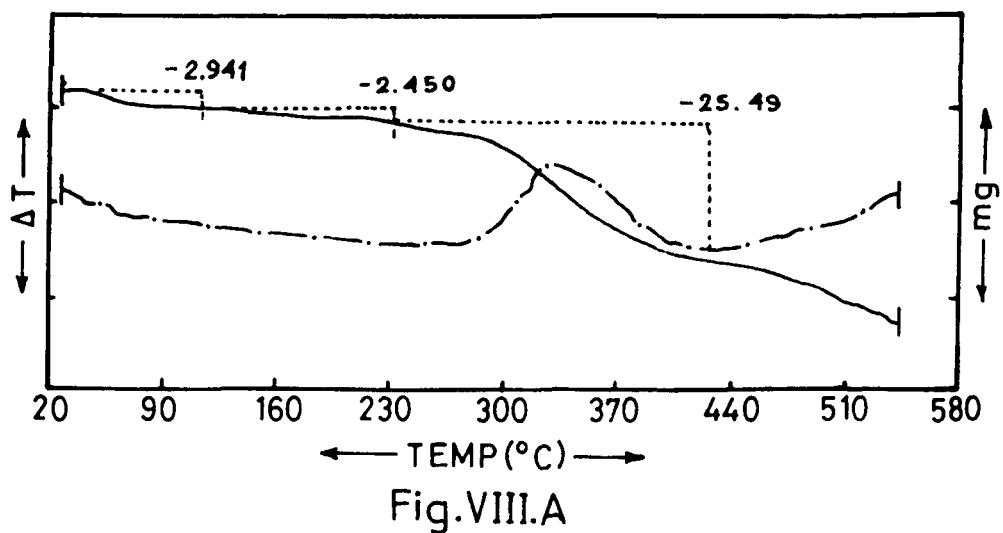
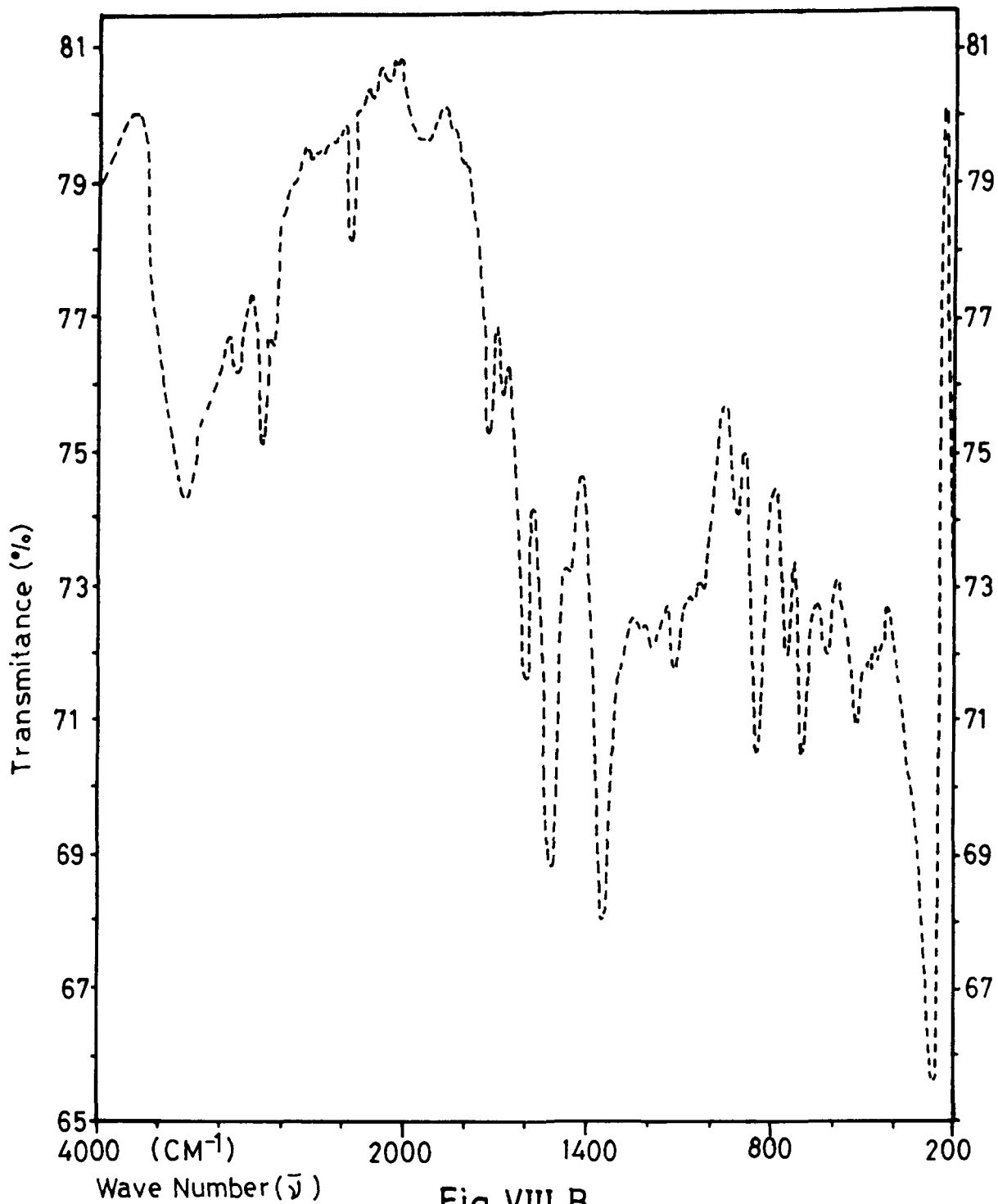


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Scheme - VIII.1



# Equilibration rate

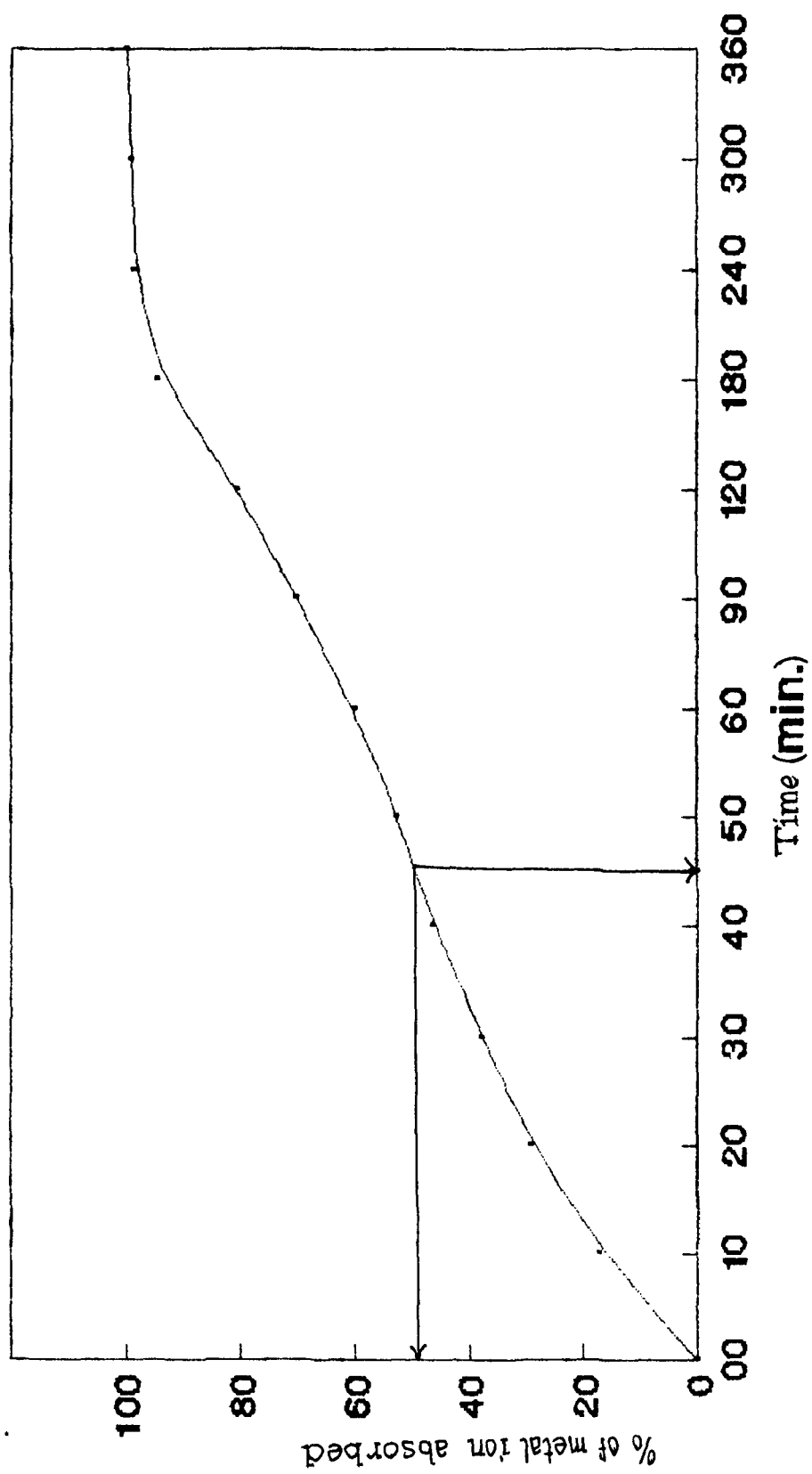


Fig. VIII.C

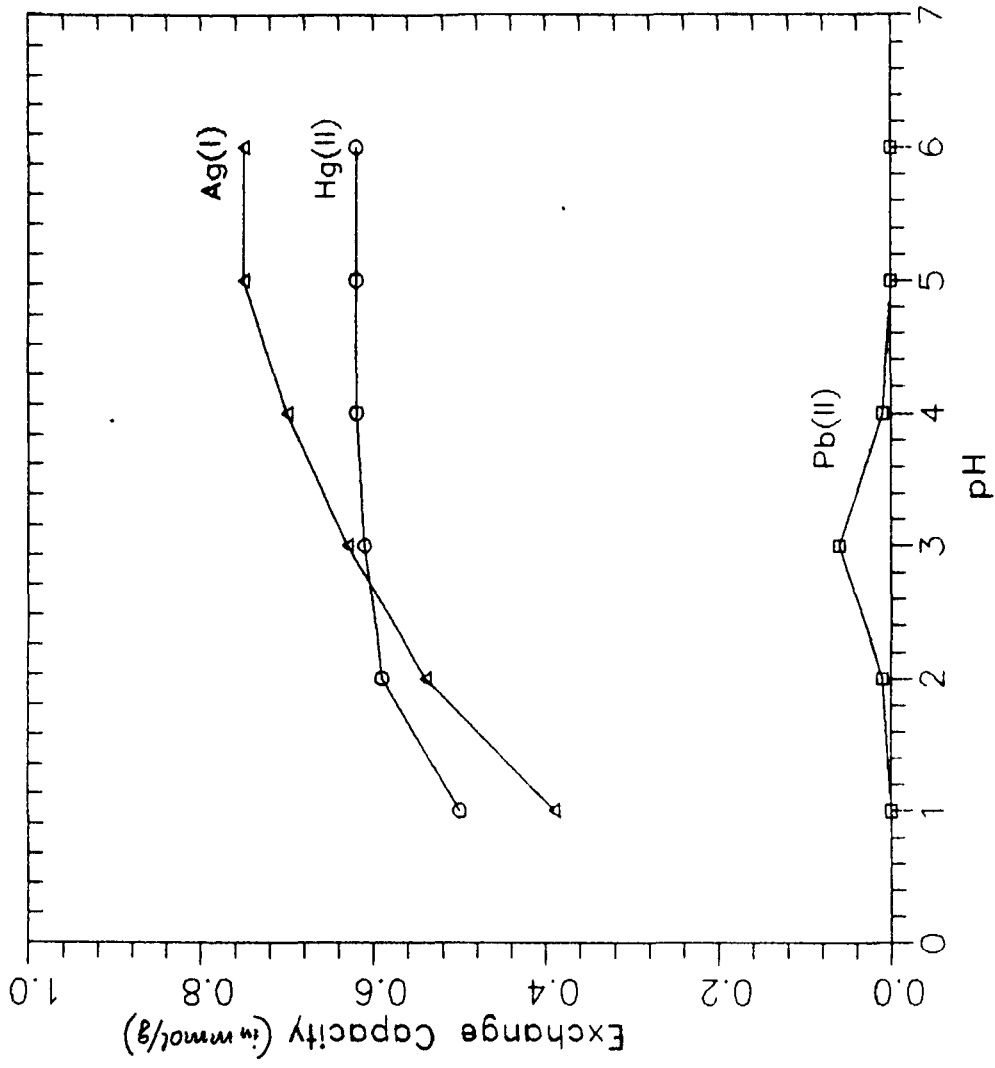


Fig.VIII.D.Exchange Capacity vs. pH

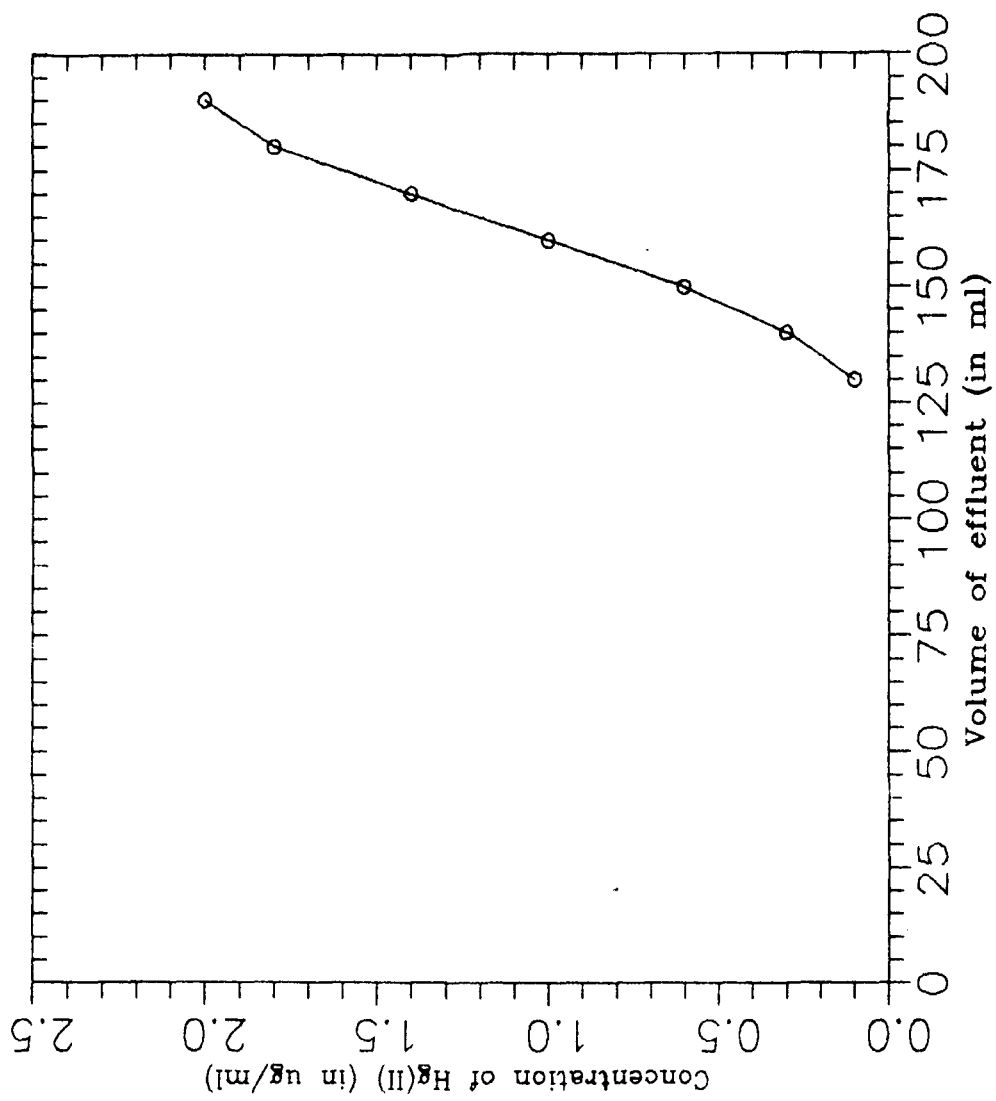


Fig.VIII.E. Breakthrough Curve.

TABLE VIII - 1  
Details of a selection of commercially available chelating ion exchange resins 8

S.No.	Manufacturer	Commercial name	Active functional or chelating group	Nature of chelating group	Donor atoms	Polymeric matrix (cross-linking)
1.	Diamond Shamrock	IMAC GT 73	Complexing (group not known) -SH	Weakly acidic	-	Polystyrene (X% DVB)
2.	Diamond Shamrock	IMAC TMR		Aromatic thiol	S	Polystyrene (X% DVB)
3.	Diamond Shamrock	IMAC SYN 101		Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
4.	Diamond Shamrock	Duolite ES 346		Amidoxime	NO	Polyacrylic (X% DVB)
5.	Diamond Shamrock	Duolite ES 465	-SH	Aromatic thiol	S	Polystyrene (X% DVB)
6.	Diamond Shamrock	Duolite ES 466		Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
7.	Diamond Shamrock	Duolite ES 467		Amino phosphonic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
8.	Dow Chemical, U.S.A.	Dowex A-1		Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
9.	Dow Chemical, U.S.A.	Dowex XF-4195 Dowex XF-4196		Weakly basic groups	N <sub>2</sub>	Polystyrene (X% DVB)
10.	Dow Chemical, U.S.A.	Dowex XFS-43084		Weakly basic group	N <sub>2</sub> O	Polystyrene (X% DVB)

(contd.)

TABLE VIII.1 (contd.)

11.	Bio-rad	Chelex-100	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\   \\ -\text{CH}_2\text{N} \\   \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
12.	Mitsubishi	Diaion CR-10	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\   \\ -\text{CH}_2\text{N} \\   \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene
13.	Mitsubishi	Diaion CR-20	$-\text{CH}_2-\text{NH}-(\text{C}_2\text{H}_4\text{NH})_n-\text{H}$	Basic (polyamine)	N <sub>v</sub>	Polystyrene (X% DVB)
14.	Mitsubishi	Diaion CR-40	$\begin{array}{c} \text{H} \\   \\ -\text{CH}_2-\text{N}-\text{CH}_2\text{CH}_2- \\   \\ \text{H} \end{array}$	Ethylenimine	N <sub>v</sub>	-
15.	Nippon Soda	Misso ALM-525	$\begin{array}{c} \text{SH} \\   \\ -\text{NH}-\text{C}=\text{S} \end{array}$	Dithiocarbamic acid	NS <sub>2</sub>	-
16.	Reanal, Budapest	Ligandex E	$\begin{array}{c} \text{CH}_2 \\   \\ -\text{CH}_2-\text{N}-\text{CH}_2\text{CH}_2\text{N}-\text{CH}_2 \\   \quad   \quad   \\ \text{CH}_2\text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \quad \text{CO}_2\text{H} \end{array}$	Ethylenediamine triacetic acid	N <sub>2</sub> O <sub>4</sub>	Polystyrene (X% DVB)
17.	Reanal, Budapest	Ligandex I	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\   \\ -\text{CH}_2\text{N} \\   \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
18.	Rohm & Haas	IRC-718 (XE-318)	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\   \\ -\text{CH}_2\text{N} \\   \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
19.	Unitika Ltd., Japan	Unicellex UR-50 (also UR-40, UR-30, UR-20 & UR-10)	$\begin{array}{c} \text{OH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CH}_2\text{N} \\   \quad   \\ \text{CH}_2\text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \end{array}$	( <i>o</i> -Hydroxybenzyl)iminodiacetic acid	NO <sub>3</sub>	Phenol + formaldehyde
20.	VEB Chemiekombinat Bitterfeld, DDR	Wofatit MC 50	$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\   \\ -\text{CH}_2\text{N} \\   \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)

(contd.)



TABLE - VIII - 1 (Contd.)


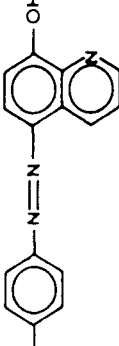
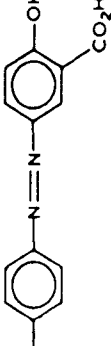
S.No.	Manufacturer	Commercial name	Active functional or chelating group	Nature of chelating group	Donor atoms	Polymeric matrix (cross-linking)
21.	Permutit Co. Ltd., England	Permutit S-1005	$-\text{CH}_2-\begin{matrix} \text{CH}_2\text{CO}_2\text{H} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{CH}_2\text{CO}_2\text{H} \end{matrix}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB)
22.	Sumitomo, Japan	Sumichelate Q-10R	$-\text{NH}-\text{C}=\text{S} \begin{matrix} \diagup \\ \text{S} \\ \diagdown \\ \text{NO} \end{matrix}$	Dithiocarbamic acid	NS <sub>2</sub>	Polyacrylic
23.	Sumitomo, Japan	Sumichelate CR-2	$-\text{CH}_2-\text{CH}-\text{C}_5\text{H}_4\text{N}$ 	Basic (poly pyridine)	N,	Polyvinylpyridine (20% DVB)
24.	Lachema, n.p., Brno	Spheron Oxine 1000		8-Hydroxyquinoline	NO	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)
25.	Lachema, n.p., Brno	Spheron Salicyl 1000		Salicylic acid	O <sub>2</sub>	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)
26.	Lachema, n.p., Brno	Spheron Thiol 1000	$-\text{OCH}_2-\text{CH}-\text{CH}_2\text{SH}$ $ $ $\text{OH}$	Thiol	S <sub>2</sub>	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)
27.	Bayer, A.G., West Germany	TP-207	$-\text{CH}_2-\begin{matrix} \text{CH}_2\text{CO}_2\text{H} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{CH}_2\text{CO}_2\text{H} \end{matrix}$	Iminodiacetic acid	NO <sub>2</sub>	Polystyrene (X% DVB) (contd.)

TABLE VIII 1 (contd.)

28.	Ayalon, Haifa Israel	Srafion NMRR		Isothiuronium	N <sub>2</sub> S	Polystyrene (X% DVB)
29.	Ionac, Sybrom Chem. Div., U.S.A.	Ionac SR-3		Isothiuronium	N <sub>2</sub> S	Polystyrene (X% DVB)
30.	Csiro, Aust- ralia	Sirorez-Cu		Phenol-pipera- zine	NO	-
31.	Parish Chem. Co., Utah, U.S.A.	Kryptofix 221B (polymer bound)		Cryptand	NO	Polystyrene (2% DVB)
32.	Parish Chem. Co., Utah, U.S.A.	Kryptofix 222B (polymer- bound)		Cryptand	NO	Polystyrene (2% DVB)

**Appendix II****Publications :****A. Relating to thesis work :**

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3. Synthesis and spectroscopic investigation of uranium(VI) complexes of pyrimidine and pyridine Schiff bases and their peroxo derivatives; P. Chattopadhyay and C. Sinha; Bulletin of Pure and Applied Sciences, 1995, 14c(1), 7-12.
4. Synthesis and characterization of uranyl complexes and their peroxo derivatives with some thioschiff bases; P. Chattopadhyay and C. Sinha; Indian J. Chem., 1996, 35A, 523-526.
5. Preparation and properties of a new chelating resin containing imidazolylazo group; P. Chattopadhyay, C. Sinha and D.K. Pal; Fresenius J. Anal. Chem. (in press).
6. Synthesis and characterization of cobalt(III) complexes of o-arylazophenolcarboxylic acids; P. Chattopadhyay, D.K. Pal and C. Sinha; Vidyasagar Univ. J. Physical Science, (in press).
7. Synthesis, structure and redox activity of cobalt(II)/(III)

complexes of 2-methoxyazophenols; P. Chattopadhyay, D.K. Pal and C. Sinha; J. Indian Chem. Soc. (accepted).

8. Synthesis and spectroscopic studies of 2,2'-dipyridylamine La(III), Ce(III), Pr(III), Th(IV), UO<sub>2</sub>(VI) complexes and peroxo derivatives of UO<sub>2</sub>(VI); P. Chattopadhyay and C. Sinha; Synth. React. Inorg. Met. Org. Chem. (accepted).
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