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Preparation and properties of a new chelating resin containing imidazolyl azo groups

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

Introduction

Because of the non-biodegradable nature of metal ions their intake at certain levels is toxic [1]. Detoxification can be achieved by the use of suitable chelating agents and may be selected by applying the ideas of the hard-soft acid base concept [2, 3] and stability of the metal chelates. The design of chelating devices for the purification of water and industrial effluents etc. is a challenging area in analytical chemistry. Various methods and materials are recommended for these purposes. Exchange methods with highly selective resins [4–9] are particularly convenient. The large area of polymers with chelating functionality enhances the formation constant as against the simple chelating agents [10].

Chelating resins with N-donor centres are highly specific for transition metal ions and some resins have been designed incorporating heterocycles [11–14] viz. pyridine, imidazole and pyrazole. Polymeric matrices containing imidazole with bare pyrrolic N–H are scarce [22]. The pyrrolic-N has a high affinity to class b metal ions viz. Cu(I), Ag(I), Hg(I)/(II) [10]. Besides, imidazole has biological importance [15, 16] and has the ability to form complexes with a number of metal ions [17–20]. However, there are few reports about metal complexes with imidazolylazo groups in acidic solutions. Mahmoud et al have prepared a mercury complex with the imidazolyl azo group [21]. Since mercury is a toxic pollutant of biological interest, its selective removal from industrial wastes and natural waters would be of great importance. Liu [22] has reported the preparation of a chelating resin containing histidine and has shown that the resin is selective for silver(I), mercury(II) and a few other metal ions in acidic solutions. No resin containing the imidazolyl azo group has yet been reported. Here, we report the preparation and analytical applications of a resin containing imidazolyl azo as chelating group on a polystyrene divinylbenzene matrix.

Experimental

Apparatus and reagent. A Shimadzu UV-VIS Spectrophotometer (Model UV-190) was used for absorbance measurements. IR spectra were recorded on Shimadzu (IR-408) and Perkin-Elmer 883 spectrophotometers and pH-adjustment was made with a Sambross 335 digital pH-meter. The radioactivity was measured with a scintillation counter equipped with a well type sodium iodide crystal detector. The metal ion solutions were prepared from analytical grade nitrates. The radioisotopes ^{203}Hg and ^{110m}Ag were supplied by Bhaba Atomic Research Centre, Trombay, and were used as tracers.

Preparation of the resin. Air-dried polystyrene divinylbenzene copolymer containing 8% divinylbenzene was used as starting material. The polystyrene beads (5 g, 30–60 mesh) were swollen in chloroform, the swollen beads were removed from chloroform by suction filtration. These beads were first nitrated and reduced to the amino compound; then this product was diazotized according to the procedure described by Davies et al [23]. The diazotized product was rapidly filtered off, washed with cold distilled water until free from acid and then coupled at 0°–5 °C with a solution of imidazole in 20% aqueous sodium carbonate solution (1.8 g imidazole for 5 g of starting material), over a period of 5–6 days. This dark brown

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coloured resin was then filtered off and thoroughly washed with distilled water until free from base. The resin was air-dried and sieved, the particles of 30–60 mesh size being retained for use.

Stability of the resin. A 0.5 g portion of the resin was shaken with 100 ml of acid or alkaline solutions of various concentrations (1–6 mol l^{-1}) for 7 days, then filtered off and washed with water. After drying, the nitrogen content and exchange capacity for mercury(II) were determined with the basic form of the resin.

Water regain. Dry resin in basic form was stirred in double distilled water for 48 h, then filtered off by suction, weighed, dried at 100 °C for 48 h and reweighed.

Estimation of nitrogen and amino groups. The nitrogen content of the dried samples of the nitrated polystyrene, aminopolystyrene and the final chelating resin in the basic form was determined by the Dumas method. The amino group content of the aminopolystyrene was determined by titration in non-aqueous medium [24].

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 mol/l HCl. The resin was then filtered off, washed with water and then dried at 100 °C for 6 h to remove free HCl. The acidic hydrogen content of the acidic 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 mol l^{-1} sodium hydroxide solution for 6 h 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 the imidazolium group. In both cases, the solution was filtered under suction, and the excess of alkali was titrated with 0.10 mol l^{-1} hydrochloric acid.

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 (diameter 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 mol l^{-1} metal ion solution was added to the tube; then the mixture was shaken for a period of 24 h. 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 adsorbed on the resin was determined by measurement of the gamma activity of equal portions of the solutions, before and after the adsorption of metal ions. Lead capacity was determined by the spectrophotometric method using dithizone [25].

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

Equilibration rates. Equilibration rates for the metal ions mercury(II) and silver(I) were studied at pH 6.0 for the resin. The time taken for 50% uptake of the metal ions was determined.

Column operations. A 100 × 5 mm glass column was used. The column was packed with 2.0 g (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 pH 6.0.

The sorption and recovery characteristics for mercury(II) and silver(I) in the presence of various metal ions were thoroughly studied. A 100 ml portion 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^{-1}. 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 mol l^{-1} $HClO_4$ and determined by the tracer technique.

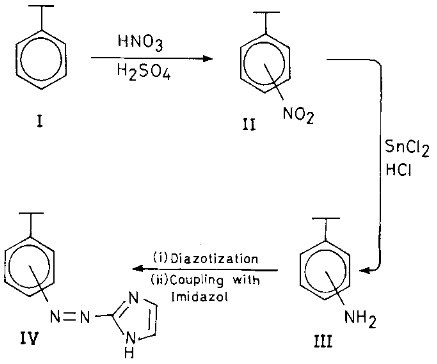
Removal of mercury(II) from river water polluted with mercury(II). Natural river water (pH 5.6) [26] was spiked with mercury(II) and ^{203}Hg, so that the concentration of mercury became 2.0 μg ml^{-1} in the river water. The above mixture was passed through the 100 × 5 mm glass column containing 2.0 g of the resin at a flow rate of 0.5 ml min^{-1}. The break-through of mercury(II) was observed after 150 ml of the mixture has been allowed to pass through. The concentration of mercury(II) in the effluent before the break-through point was determined by the tracer technique.

Studies with resin blanks. To confirm that the imidazolyl azo group is involved in metal ion sorption, the diazotized aminopolystyrene in sodium carbonate solutions was boiled for several hours to replace the diazo group by the 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 discussion

Synthesis and characterization of the resin

The resin was synthesized from 30–60 mesh macroreticular styrene divinylbenzene copolymer beads through the steps shown in Scheme 1.



Scheme 1

The nitrogen content of the compound II was 7.95% (5.68 mmol of nitro resin g^{-1}). After reduction, the total nitrogen in compound(III) was found to be 8.76%. The estimation of the amino group in the amino resin was 3.4 mmol 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 g^{-1} of the resin. A rough estimate of the composition of the final product may be obtained by considering that diazotization is complete, 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

Table 1 Physical and chemical characteristics of the imidazolyl azo resin

Bead size	30–50 mesh
Water regain	18 mmol g^{-1}
Nitrogen content	8.61 mmol g^{-1}
Hydrogen ion capacity (imidazolium group)	1.48 mmol g^{-1}
Total hydrogen ion capacity	2.85 mmol g^{-1}
Equilibration rate ($t_{1/2}$) (for Ag(I), Hg(II))	45 min
I.R. data	: 3424 cm^{-1}, 1677 cm^{-1} for N–H stretching : 1600 cm^{-1} for >C=N–stretching : 1516 cm^{-1} for –N=N–stretching 1460 w, 1340 m, 1160 w, 1110 w, 1015 w, 855 s, 830 m, 700 m, 660 s for the imidazole unit

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 1.51, 2.48 and 1.51 mmol g^{-1} of imidazolyl azo, 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^{-1}, 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^{-1} (Table 2). If the resin metal complexes are 1:1 complexes (which is most likely), the maximum exchange capacity should be 1.48 mmol g^{-1}. Steric factors are probably responsible for lower exchange capacities.

The infrared spectrum of the resin showed bands at 3424 cm^{-1}, 1677 cm^{-1} for $\nu_{(N-H)}$ stretching, 1600 cm^{-1} for $\nu_{(C=N)}$ stretching and 1516 cm^{-1} for $\nu_{(N=N)}$ stretching (Table 1). Other vibrations due to imidazole skeleton are shown in Table 1 and are the indication of imidazole incorporation into the polymeric matrix.

The chemical stability of the resin in 1.0–6.0 mol l^{-1} 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 min. This shows that the resin is suitable for column operation under a low flow rate. The water regain value of the resin (18 mmol g^{-1}) is also quite satisfactory for column operation.

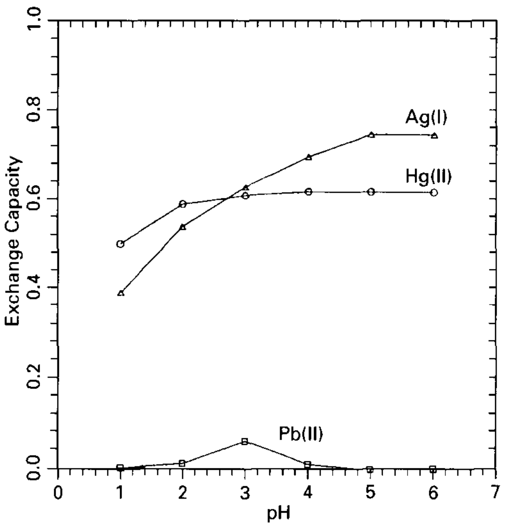


Fig. 1. Exchange capacity (mmol g^{-1}) of the resin for different metal ions vs. pH

Table 2 Maximum exchange capacities for the metal ions

Metal ion	Maximum capacity (mmol g^{-1})
Hg (II)	0.62 (pH 4.0–6.0)
Ag (I)	0.75 (pH 5.0–6.0)
Pb (II)	0.06 (pH 3.0)

Sorption and desorption of metal ions

The sorption behaviour of mercury(II), silver(I) and lead(II) on the resin by the batch method is shown in Fig. 1 and the maximum exchange capacity for the metal ions is given in Table 2. It is observed that the resin has a high exchange capacity only for mercury(II) and silver(I).

The effects of different eluents on the desorption of the metal ions adsorbed is given in Table 3. Complete desorption of mercury(II) and silver(I) took place with eluents containing complexing agents viz. 5% thiourea in 0.1 mol l^{-1} $HClO_4$.

In column operation (as shown in Table 4) the presence of macro amounts of diverse metal ions

Table 3 Desorption of mercury(II), silver(I) and lead(II) by different eluents

Eluent	Recovery of Hg (II) (%)	Recovery of Ag (I) (%)	Recovery of Pb (II) (%)
4 mol l^{-1} HCl	40	–	–
6 mol l^{-1} HCl	60	–	–
1 mol l^{-1} $HClO_4$	–	–	100
6 mol l^{-1} $HClO_4$	60	60	–
5% Thiourea in 0.1 mol l^{-1} $HClO_4$	100	100	–

Table 4 Separation of 2 μg ml^{-1} Hg (II) and 2 μg ml^{-1} Ag (I) from several binary mixtures with other metal ions in a sample volume of 100 ml at pH 6.0

Foreign metal ion	Amount of foreign metal ion (μg)	Hg (II) found (μg), with % of recovery in parenthesis	Ag (I) found (μg), with % of recovery in parenthesis
Cu(II)	2000	190(95%)	195(97%)
Co(II)	2000	200(100%)	200(100%)
Ni(II)	2000	200(100%)	200(100%)
Fe(III)	2000	195(97%)	200(100%)
Mn(II)	2000	200(100%)	200(100%)
Ca(II)	2000	200(100%)	200(100%)
Ba(II)	2000	200(100%)	200(100%)
Mg(II)	2000	200(100%)	200(100%)
Na(I)	2000	200(100%)	200(100%)

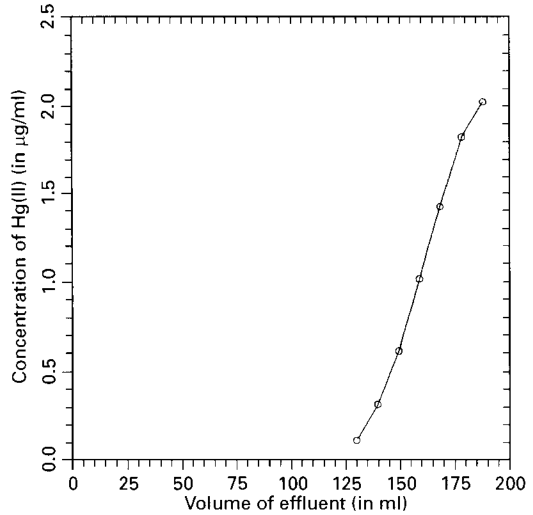


Fig. 2. Break-through curve for Hg(II) in river water spiked with Hg(II). Concentrations of Hg(II) in the sample solution: 2.0 μg ml^{-1}; resin 2 g; flow rate 0.5 ml min^{-1}

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 mercury(II) and silver(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 the mercury(II) from river water [26] spiked with mercury(II) is shown in Fig. 2. No mercury(II) was detected in the effluent from the column until the break-through point is reached.

The results show that the resin containing imidazolyl azo group is very selective for mercury(II) and silver(I). This high selectivity may be due to the soft basic pyrrolic N–H of the imidazole azo matrix. The bare N–H plays the key role in binding and may be followed by chelation via azo-N. This resin has an immense potential for the effective preconcentration and removal of mercury(II) from natural water or industrial wastes.

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