

## Synthesis of new chelating ion exchange resins derived from guaran and divinylbenzene styrene copolymer for selective adsorption of metal ions

Kalpa Mandal<sup>1</sup>, Sameer Vyas<sup>2</sup>, Swati Vyas<sup>3</sup>

<sup>1</sup>Department of Chemistry, Dyal Singh College, University of Delhi-110003, India

<sup>2</sup>Central Soil and Materials Research Station, New Delhi -110016, India

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**Abstract:** New chelating ion exchange resin containing hydroximate of 5 amino salicylic acid was synthesized by incorporating it in divinylbenzene styrene (DVBS) copolymer. Hydrophilic polysaccharidematrix of guaran was also used to incorporate hydroximate of 5 amino salicylic acid in it. The resin characteristics were studied by determining its bulk density, specific bulk volume, moisture content, degree of substitution and ion exchange capacity. The resin was characterized by means of IR spectra, Nitrogen content and pH titration. The distribution coefficient values of different metal ions namely Fe(II), Cu(II), Zn(II), Cd(II), Co(II), Ni(II), Ca(II), U(VI), Cr(VI) & W(VI) was carried out on these resins as a function of pH. Metal analysis was done by Atomic Absorption Spectrophotometer. The hydroximate derivative of guaran is found to be more selective than that of diving benzene co-polymer.

**Key Words:** Adsorption, Coefficient, DVB Styrene, Distribution, Guar gum,

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### I. Introduction:

The chelating ion exchange resins have wide range of application in different areas. Their application based on their synthesis containing different functional groups and reagents. The functionalized polymers containing specific functional groups have wide spread applications.<sup>1-2</sup> They have been used in biological systems, synthesis of penicillin<sup>3</sup>, immobilization enzyme<sup>4</sup>, application of dyes<sup>5</sup>, ion exchange as substrate carrier<sup>6</sup>, as protecting group<sup>7</sup>, in isolation or removal of interfering ions, separation of electrolytes from non-electrolytes ion and in the preparation of high purity water etc.

Chelating resins from chelate complexes with metal ions instead of undergoing ion exchange process. They have been reported for their extensive use in separation and concentration of metal ions<sup>8-12</sup>. They are useful in mineral processing industries as float aids, depressants, flocculants and collectors. Chelax 100 has been reported to be extensively used. Chelax 100 resin (styrene divinylbenzenecopolymer containing iminodiacetic acid) is used for preconcentration and separation of rare earth and heavy metals in pH range of 6-8 but they exhibit the disadvantage that the affinity of resins for alkaline earth metal is similar to that of transition ions.

Chelax 100 and Dowex A-1 are also used for collection of trace element Cd, Zn, Pb, Co, Cu, Fe, Mn, U, V and Au from sea water<sup>13</sup>. All these amino poly carboxylic acid containing chelating resins are not enough selective and that their efficiency is reduced due to their ability to form stable complexes with alkaline earth metals. With the aim of synthesizing selective chelating resins which require no pretreatment of the sample for concentration, which do not form stable complexes with alkaline earth metals and also useful in hydrometallurgical process specially in mineral processing as float acids. We tried to synthesize chelating resins containing hydroximates of amino hydroxyl carboxylic acid, 5 amino salicylic acid hydroximate in DVB styrene and in guar have been synthesized.

### II. Experimental:

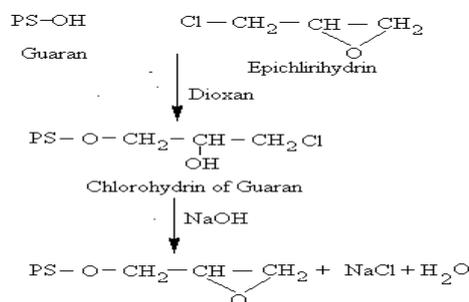
All chemicals used were of A R grade. Guar powder (200 mesh size) was obtained from local guar gum industry. Chloromethylated DVBS with 4% crosslinking was procured from Thermax Pvt. Ltd. 5 amino salicylic acid, epichlorohydrin and hydroxylamine hydrochloride were obtained from Sisco chemical industries, Bombay were solvents were distilled before use. Infrared spectra of the synthesized resins were recorded on Shimadzu IR-400 spectrophotometer using KBr pellets. Kjeldahl method was used for analysis of Nitrogen. Metal ions were estimated using Perkin elmer-2380 atomic absorption spectrophotometer.

#### 2.1 Synthesis of Resins

##### 2.1.1 Preparation of epoxyether of guaran.

486 g of guaran powder (a galctomannon from the seeds of cyanaposestetragonalobus) was slurried with dioxine. 50% aqueous sodium hydroxide was added to guaran gradually to render the reaction mixture alkaline. The contents of the flask was slurried magnetically at 45°C for 2 hours. One more of

epichlorohydrin was added to the flask with continuous stirring. The pH of reaction mixture was adjusted between 9-10, and stirring continued for another 4 hours at 45°C. The compound was filtered on vacuum pump and washing was done with 80% aqueous methanol containing nitric acid. This epoxy ether of guaran was further used for derivatisation (scheme 1)



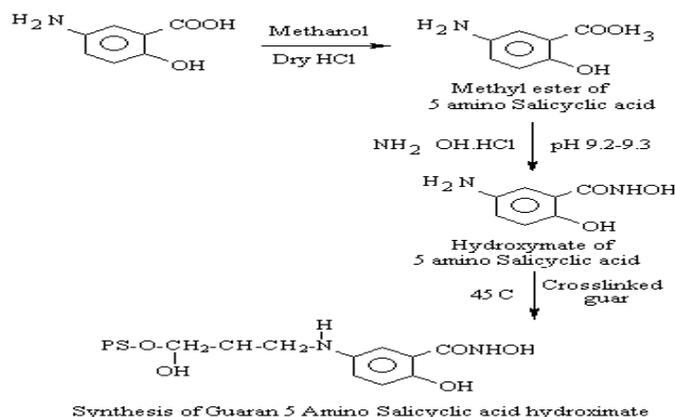
Synthesis of epoxy ether of Guarán

### Scheme-1

#### 2.1.2 Synthesis of Guarán 5 amino Salicylic acid Hydroximate:

This was done in three steps

- Preparation of methyl ester of 5- Amino salicylic acid: 15.3 g (0.1 mole) of 5 Amino salicylic acid was taken in a 250 ml round bottom flask to the acid excess methanol was added then dry HCL gas was passed till the saturation was complete. The reaction mixture was refluxed for 3 hours on mantle. The methyl ester of 5 Amino salicylic acid was formed.
- Synthesis of hydroximate of 5 Amino salicylic acid.:8.35 g (0.05 mole) of methyl ester of 5 Amino salicylic acid and methanolic solution of 3.49 g (0.05 mole) hydroxylamine hydrochloride were stirred on magnetic stirrer for 5 hours in a round bottom flask at 30°C. The Ph of reaction mixture was adjusted by sodium methylate to Ph 9.2-9.3. The hydroxamic acid of 5 amino salicylic acid was formed which was filtered on Buchner funnel and washed with 80% methanol solution.
- Incorporation of hydroxamate of 5 Amino salicylic acid in guar.: 3.36 g (0.02 mole) of hydroxamic acid of 5 Amino salicylic acid was taken in 10 ml methanol and stirred at 45°C for 5 hour. During the process of stirring 4.86 g (0.01 mole) of epoxy ether of guaran was added. The product formed was filtered and the resin formed was successively treated with 0.1N HCL, 0.1N NaOH and 0.1N HCL. The resin was finally washed with absolute alcohol and dried in vacuum (scheme 2).



### Scheme-2

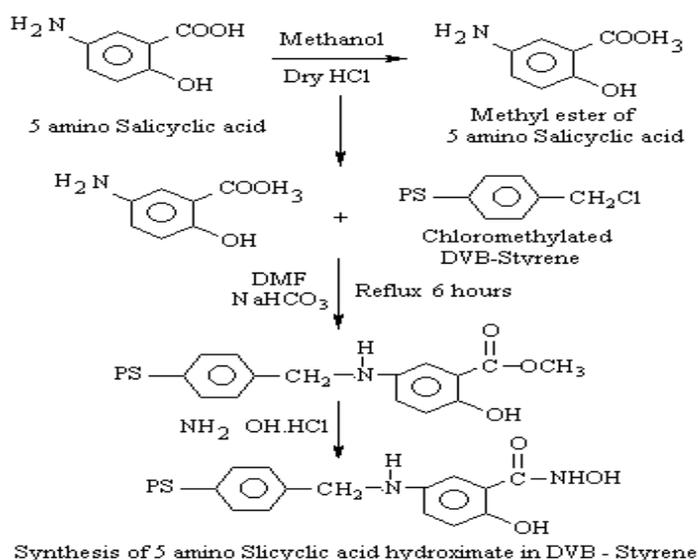
#### 2.1.3 Synthesis of 5 Amino salicylic acid hydroximate in DVB styrene:

This was also done in three steps:

- Preparation of methyl ester of 5- Amino salicylic acid: same procedure was followed as mentioned in section 1
- Incorporation of ester in DVB styrene. : 5.714 g (0.02 mole) of chloromethylated beads in DVB –styrene were taken and soaked overnight in DMF for swelling. The swelled resin was taken in a round bottom flask 16.7 g (0.1 mole) of methyl ester of 5 Amino salicylic acid and dissolved in DMF. This was added to round bottom flask containing beads to the reaction mixture 8.4 g (0.1 mole) of sodium bicarbonate was

added slowly. The reaction mixture was refluxed with water condenser on a water bath at 70°C. Few porcelain pieces were added to the reaction mixture to avoid bumping during the reaction the reaction. The reaction mixture was then refluxed for 8 hours. The product was filtered on Buchner funnel and washed with hot distilled water followed by methanol.

- (c) Synthesis of hydroxamate of 5 Amino salicylic acid: The above filtered product was taken in round bottom flask. To this methanolic solution of 6.9 g (0.1 mole) hydroxyl amino hydrochloride was added. The reaction mixture was then refluxed with water condenser on water bath for 5 hours. To this reaction mixture sodium methylate was added to adjust pH between 9.2-9.3 This was again refluxed for 5 hours. Product formed was filtered on Buchner funnel washing was done with 80% aqueous methanol containing few drops of nitric acid to remove excess alkali. The resin was successively treated with 0.1N HCL, 0.1N NaOH and 0.1N HCL. The final washing was done with methanol and product was dried under vacuum.(Scheme 3)



**Scheme-3**

### III. Determination of distribution coefficients:

The molar distribution coefficients 'Kd' of metals showing pronounced adsorption on chelating resins is Cu(II), Fe(II), Zn(II), Co(II), Cd(II), Ni(II), Ca(II), Cr(VI), W(VI), U (VI) were determined by batch method. Weighed amount of resin (1 g) in hydrogen form were placed in glass stopped conical flasks containing 1 ml of 1000 ppm metal ion solution and a known volume (40 ml) of (0.2 m) sodium acetate-acetic acid buffer of varying pH (4-7). The contents were stirred magnetically for 10 hrs at 25°C. The two phases after equilibrium were separated by filtration and an aliquot of filtration was analyzed for metal concerned by atomic absorption spectrophotometer.

The calibration curves for different metals were plotted by analyzing a series of standard solutions of metal ions. The unknown concentration was determined from these curves. The distribution coefficient value 'Kd' was completed using the formula.

$$K_d = \frac{\text{Amount of metal in resin / g of dry resin}}{\text{Amount of metal in solution / mL of solution}}$$

**Table 1:**

**Resin characteristics:**

Resin	Moisture Content (%)	Bulk Density g/cm <sup>3</sup>	Specific Bulk Volume cm <sup>3</sup> /g	Nitrogen Content (%)
ASAH-G	16.54	0.714	1.40	1.44
ASAH-DVB	8.33	0.641	1.56	1.63

**Table 2:**

**Kd value of different metal ions on G-ASAH**

pH	Fe(II)	Cu(II)	Zn(II)	Cd(II)	Co(II)	Ni(II)	U(VI)	Cr(II)	W(VI)
4	657	207	1686	598	-	194	207	1962	889
4.64	850	269	1734	613	-	230	306	2326	1483
5	1000	471	1792	624	146	301	366	3270	2553
5.5	3555	841	1761	634	556	341	666	2158	4455
6	9741	225	1757	700	385	426	841	1792	6832
6.5	899	150	1742	748	139	279	254	-	3266
7	-	-	-	691	-	-	-	-	-

**Table 3:**

**Kd values of different metal ions on ASAH-DVBS**

pH	Fe(II)	Cu(II)	Zn(II)	Cd(II)	Co(II)	Ni(II)	U(VI)	Cr(II)	W(VI)
4	1186	351	1706	596	--	222	231	2064	1025
4.64	1788	740	1786	665	--	279	333	2353	1891
5	3662	910	1824	681	363	345	648	3402	2974
5.5	8385	1405	1778	692	728	443	766	2173	6220
6	5911	648	1758	716	388	540	910	1792	6837
6.5	4722	498	1562	766	181	363	549	--	23247

**IV. Result And Discussion**

In the IR spectra of guaran 5 amino acid hydroximate resin, a band was observed at 3400 cm<sup>-1</sup> which was assigned to N-H mode while another broad band at 3000-2800 cm<sup>-1</sup> was ascribed to O-H. The C=O stretch vibration of hydroxamic acid appeared at 1670 cm<sup>-1</sup>. The C-O peak of carboxylic acid near 1580 and C=O band of ester near 1725 cm<sup>-1</sup> disappeared in spectra of dihydroxamic acid derivative.

The moisture content, bulk density, specific bulk volume and N content of G ASAH and ASAH BVB are in table 1 & 2.

**V. Conclusion**

**Sorption studies of various metal ions by the resins**

The molar distribution studies of various metal ions viz. Fe(II), Cu(II), Zn(II), Cd(II), Co(II), Ni(II), Ur(VI), Cr(VI) & W(VI) with the newly synthesized resins G-ASAH and ASAH-DVBS are given in table 2 & 3 respectively. The data indicate that the values of distribution coefficient first increases, attains a maxima and then finally decreases with increasing pH.

In case of guaran 5-amino salicylic acid hydroximate, the resin shows maximum adsorption at pH 5 for Zn(II) & Cr(VI) ions. Fe(II), Ni(II), U(VI) and W(VI) show maximum adsorption at pH 6. Cu(II) and Co(II) show maximum adsorption at pH 5.5 while Cd(II) adsorbs maximum at pH 6.5. At the pH of maximum adsorption the selectivity order of various metal ions on this resin are as follows:

Fe(II) > W(VI) > Cr(VI) > Zn(II) > U(VI) > Cu(II) > Cd(II) > Co(II) > Ni(II)  
 9741 6832 3270 1792 841 840 748 556 426

The data suggests that the resin shows good efficiency for Fe(II). The Kd value is over ten times the value for metals like Cu(II), Cd(II), Co(II) and Ni(II). So this resin can easily be used for the separation of Fe from Ni at pH 6, W(VI) from U(VI) also pH 6. With the resin 5-amino salicylic acid hydroximate DVB styrene,

the results are comparable to the Guaran counterpart. Here also the resin shows high absorbance with Fe (II) at pH 5.5.

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