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Synthesis and Applications of Chelating Resins of Polysaccharides Containing Hydroxamic Acid

SUNITA BOHRA, NEETA KANUNGD AND P. N. MATHUR*

Department of Chemistry, University of Jodhpur
Jodhpur-342 001, India

Chelating agents find great utility in mineral processing and in hydrometallurgical processes. Polymeric chelating agents have replaced the chelating agents. Hydroximates are useful in mineral processing as collectors for various mineral systems containing Ti,Y,La,Ce,Nb, Ta, Sn, W, Fe, Mn and Cu. Resins containing hydroxamic acid group will be more efficient. Synthesis of hydrophillic chelating resins of polysaccharide guaran incorporated with hydroxamic acids of fatty and amino acids is reported. Physicochemical characteristics of the newly synthesised resins are also reported. The amount of retention of metal by resin at equilibrium, has been determined in terms of distribution coefficient (λ_i or K_d). K_d values for Fe(II), Cu(II), Ni(II), Co(II) and U(VI) systems with the newly synthesised resins are reported.

INTRODUCTION

Chelates are frequently used for separation and concentration of metal ions. These are used in mineral processing industries as collectors and depressors. The chelates generally used in mineral processing and metal separation are usually —N—N—, —N—O—, —N—S—, —S—S—, —O—O—, type. The use of a particular chelate also depend on the nature of metal ion. In the last two decades the chelates have been replaced by chelating resins or polymeric chelates; since then the added advantages of the backbone make them more efficient. The backbone provides the large surface area, more contact period and in addition it also acts as flocculant in case of polysaccharide resins.

Polymeric chelating agents also find use in removal of toxic metals from waste and thus in water pollution control. They are also used in recovery and concentration of precious metals from sea water and lean minerals. The first chelating resin was prepared[1-3] by the ready condensation of *o*-hydroxyquinoline (oxine) with formaldehyde. Chelating resins have been used for separation and determination of traces of calcium and magnesium from concentrated solution of sodium chloride[4], lithium chloride[5] and sodium hydroxide[6]. Rare earth cations which are almost identical in their behaviour have been also separated using chelating resins.

Chelex–100 exchanger based on a styrene DVB copolymer is specific for selective sorption and separation of heavy metals and some transition elements[7,8]. An ion exchanger based on pyridine–2, 6–dicarboxylic acid[9] have been used for separation of alkaline earth metal elements[10]. Moyer's and Frtz[11] incorporated propylene diamine tetraacetic acid functional group into resin, which preferentially adsorbs polyvalent metal cations. Iminodiacetic acid[12,13], dipicrylamine[14] and imidizole[15] have been introduced in DVB styrene matrix.

Hydroxamic acid group has been introduced into a matrix containing carboxylic acid group and is specific for Fe^{3+} ion[16]. Dihydroximate[17,18] derivative of dicarboxylic acid *e.g.* malonic acid dihydroximate incorporated in DVB styrene copolymer have been used for separation of UO_2^{2+} from sea water. Cellulose dihydroximate has been reported[19] for sepaation of Cu^{2+}, Ca^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} etc.

Most polymeric chelating resins are based on petrochemical products, frequently used backbone is DVB styrene. These due to their hydrophobicity are less effective in solution compared to polysaccharide based chelating resins. Also these being petroleum products are costly and in scarce supply. The polysaccharide based chelating resins of guaran are relatively much cheaper and in abundant supply. Their hydrophilic nature helps in better separation and concentration in solution compared to the hydrophobic petro-chemical based chelating resins. We therefore incorporated hydroxamic acid of amino acid (glycine) and fatty acid (acetic acid) in guaran matrix.

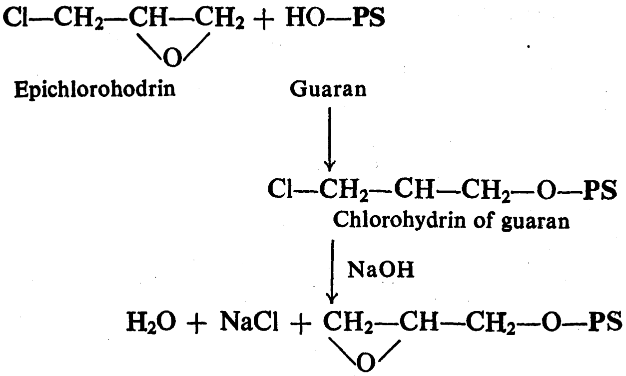
EXPERIMENTAL

Synthesis of Resins

Preparation of Epoxy Ether of Guar

1 Mole (486 g) of guaran powder (a galactomannon from the seeds of Cyanaposes tetragonalobus) was slurried with dioxane. 50% solution of aqueous NaOH was then added to make the reaction mixture alkaline. The contents of the flask were stirred magnetically at 45°C for 5 hrs, 1 mole of epichlorohydrine was then added and stirring was continued for another 4 hrs. 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).

SCHEME 1

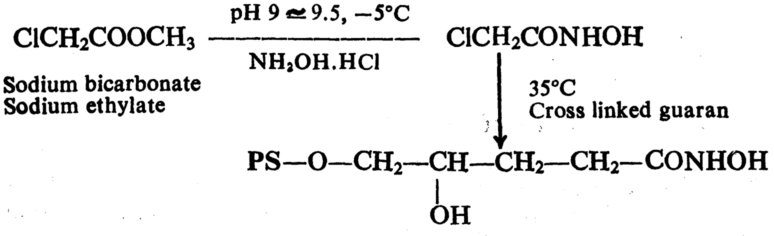


Scheme 1. Synthesis of Epoxy ether of guaran

Synthesis of Hydroxamic Acid of Acetic Acid Incorporated in Guaran (HAG)

The hydroxamic acid of acetic acid was prepared by treating 8.7 ml of chloromethyl acetate with 0.1 M hydroxylamine hydrochloride at pH 9 ≃ 9.5 adjusted by sodium bicarbonate and sodium ethylate and stirred for 5 hrs at −5°C. To 1.5 g of the so prepared hydroxamic acid of acetic acid, 0.01 M epoxy ether of guaran was added at 35°C while stirring, the stirring continued for another 3 hrs. The resin formed was treated with N/10 HCl, N/10 NaOH and N/10 HCl respectively. Finally the resin was washed with absolute alcohol and dried in vacuum (Scheme 2).

SCHEME 2



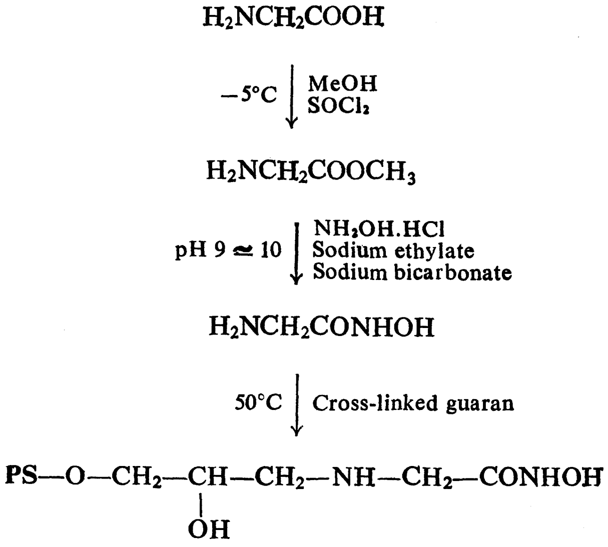
Scheme 2. Synthesis of Hydroxamic acid of acetic acid incorporated in guaran

Synthesis of Guaran Glycine Hydroximate (GGH)

First methyl ester of glycine was prepared by adding methyl alcohol and thionyl chloride.

The hydroxamic acid of glycine was next prepared by treating 0.1 mole methyl ester with methanolic solution of 0.1M hydroxylamine hydrochloride at pH 9.2 ≃ 9.3 adjusted by sodium carbonate and sodium ethylate. The hydroxamic acid of glycine formed was filtered and washed with 80% ethanol solution. To 0.02 mole of glycine hydroximate, 0.01 mole of epoxy ether of guaran was added while stirring at 50°C for 5 hrs. The product formed was filtered and treated with N/10 HCl, N/10 NaOH and N/10 HCl respectively. Finally the product was washed with absolute alcohol and dried in vacuum. The product was free flowing powder (Scheme 3).

SCHEME 3



$$\mathrm{H_2NCH_2COOH}$$

$$\Big\downarrow \; -5^{\circ}\mathrm{C} \quad \mathrm{MeOH},\ \mathrm{SOCl_2}$$

$$\mathrm{H_2NCH_2COOCH_3}$$

$$\Big\downarrow \; \mathrm{pH}\ 9 \simeq 10 \quad \mathrm{NH_2OH.HCl},\ \text{Sodium ethylate},\ \text{Sodium bicarbonate}$$

$$\mathrm{H_2NCH_2CONHOH}$$

$$\Big\downarrow \; 50^{\circ}\mathrm{C} \quad \text{Cross-linked guaran}$$

$$\mathrm{PS{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}NH{-}CH_2{-}CONHOH}$$

Scheme 3. Synthesis of Guaran Glycine Hydroximate

RESULTS AND DISCUSSION

In the spectra of hydroxamic acid derivatives of guaran, a band at 3450 $\mathrm{cm^{-1}}$ is assigned to ν(N—H), a C–O stretch of hydroxamic acid is seen at 1640 $\mathrm{cm^{-1}}$. The C=O stretch of carboxylic acid at 1580 $\mathrm{cm^{-1}}$ and the C=O stretch of ester at 1725 $\mathrm{cm^{-1}}$ disappeared.

The moisture content, bulk density, specific bulk volume and nitrogen contents of UAG and GGH are given in Table 1.

Determination of Distribution Coefficient

The molar distribution coefficients 'K_d' of metals Cu(II), Ni(II), Co(II), Fe(II) and U(VI) showing pronounced adsorption on these

TABLE 1

Resin	Moisture content %	Bulk density g/cm^3	Specific Bulk volume cm^3/g	Nitrogen content %
HAG	18.3	0.823	1.21	0.74
GGH	3.3	0.735	1.36	1.67

chelating resins were determined by batch method. Portions of different chelating resins in hydrogen form were placed in glass stoppered conical flasks, containing 1 ml of metal solution corresponding to 1 mg metal ion and a known volume of appropriate buffer of 0.2M sodium acetate and 0.2M acetic acid for pH adjustments. The contents were stirred magnetically and equilibriated overnight in some cases where slow exchange takes place. Two phases were separated after equilibration using Whatman 42 filter paper and an aliquot of filtrate was analysed for metal concerned. The calibration curves for different metals were plotted, by analysing a series of standard solutions of metal ions using atomic absorption spectrophotometer.

Estimation of U(VI) was done by thiocyanate method using U.V. spectrophotometer at 380 nm.

The distribution coefficient was calculated using the formula,

$$K_d \text{ or } \lambda_1 = \frac{\text{amt. of metal ion in resin phase/gm of dry resin}}{\text{amt. of metal ion in soln./ml of solutions}}$$

The perusal of the results shows that the distribution coefficient value first increases and then decreases wilh increasing pH.

Sorption studies of various metal ions with GGH resin shows that Fe(II) has maximum adsorption at pH 5.5, Cu(II) and Co(II) at pH 5, U(VI) and Ni(II) shows maximum adsorption at pH 6. The values of distribution coefficient for Fe(II), Cu(II), Ni(II), Co(II) and U(VI) at the pH of their maximum adsorption are 1851, 932, 467, 597 and 875 respectively.

At the pH of maximum adsorption, distribution coefficient values for these metal ions are in the following order:

$$\text{Fe(II)} > \text{Cu(II)} > \text{U(VI)} > \text{Co(II)} > \text{Ni(II)}$$

In the case of sorption studies with HAG resin Fe(II), Co(II) and U(VI) shows maximum adsorption at pH 5.5, Ni(II) shows good adsorption at pH 6 and Cu(II) shows highest value of distribution coefficient at pH 5.

TABLE 2

AMOUNT OF DRY HAG RESIN TAKEN—0.0967 g

S. No.	pH	K_d values				
		Fe(II)	Cu(II)	Ni(II)	Co(II)	U(VI)
1.	4.0	203	158	4	81	53
2.	4.64	—	209	—	93	—
3.	5.0	439	325	54	104	79
4.	5.5	900	—	518	236	416
5.	6.0	432	254	610	136	128
6.	7.0	—	202	537	98	88

TABLE 3

AMOUNT OF DRY GGH RESIN TAKEN — 0.0817 g

S. No.	pH	K_d values				
		Fe(II)	Cu(II)	Ni(II)	Co(II)	U(VI)
1.	4.0	339	152	25	187	107
2.	4.64	—	310	—	230	–
3.	5.0	985	932	63	597	115
4.	5.5	1851	351	222	472	135
5.	6	812	210	467	426	975
6.	7	565	—	437	—	230

The values of distribution coefficients for Fe(II), Cu(II), Co(II), Ni(II) and U(VI) at the pH of their maximum adsorption are 900, 325, 236, 610 and 416 respectively. At the pH of their maximum adsorption distribution coefficient values for these metal ions are in the following order:

$$\mathrm{Fe(II)} > \mathrm{Ni(II)} > \mathrm{U(VI)} > \mathrm{Cu(II)} > \mathrm{Co(II)}$$

In order to compare the effectiveness of the two resins K_d values for different metal ions at pH's of their maximum adsorption and at the same pH were compared. Table 4 gives K_d values of various metal ions at pH's of their maximum adsorption and at the same pH=5 for the two resins.

TABLE 4

Metal Ions	HAG		GGH	
	K_d	pH	K_d	pH
Fe(II)	439	5·0	985	5.0
	900	5.5	1851	5.5
Co(II)	104	5.0	597	5.0
	236	5.5	472	5.5
Ni(II)	54	5.0	63	5.0
	518	5.5	222	5.5
U(VI)	79	5.0	115	5.0
	128	6.0	875	6.0
Cu(II)	325	5.0	932	5.0

It is seen from the Table 4 that GGH is more efficient than HAG except in case of nickel where the fatty acid hydroximate is more efficient than the amino acid hydroximate. The higher efficiency of amino acid hydroximates is due to decreased electron density on the co-ordinating oxygen atoms because of the presence of nitrogen of the amino group present in them. This may also be due to the additional coordination site available in the form of nitrogen of the amino acid.

Distribution coefficient values also reveals that separation of mixtures of metal ion can also be achieved by these resins.

Data of distribution coefficient on GGH resin for Fe(II) and U(VI) shows that a mixture of Fe(II) and U(VI) can be separated at pH 5.5 (K_d—Fe(II)—1851, U(VI)—135). Iron can also be separated from a mixture of Fe(II) and Ni(II) at pH 5 (K_d—985 and 63 respectively).

The work on separation of mixture of metal ion is in progress.

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