PREPARATION AND ANALYTICAL APPLICATION OF A NEW CHELATING ION EXCHANGE RESIN CONTAINING THIOGLYCOLIC ACID

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Starting from copolymerization of acrylonitrile and divinylbenzene by emulsion polymerization technique, a macroporous, crosslinked polyacrylonitrile copolymer was synthesized. The nitrile groups on the copolymer resin were converted into carboxylic acid groups by hydrolysis with strong alkaline solution of sodium hydroxide to obtain the resin matrix with carboxylic acid groups. A new chelating ion exchange resin containing alkylthioglycolate was prepared by esterification of carboxylic acid groups on the resin matrix and thioglycolic acid with 1,6-hexanediol as binding part. After studies of the basic characters, ion exchange ability, exchange rate and acidity of the medium, it was found that the new resin obtaind was highly selective for silver(I), mercury(II), gold(III) and bismuth(III) in acidic-aqueous solution. Separation of these metal ions from each other and concentration of these metal ions from very dilute solution were studied by liquid chromatography using a short column of this new resin. The analytical applications of this new resin are reported.

INTRODUCTION

The recovery of metal ions from effluents and tailings of mining industry has become of increasing concern to both industry and government during the past few years[1,2]. One technique of metal recovery which had many attractive features was selective ion exchange using crosslinked polymer resins[3,4]. The syntheses and application of various resins have been studied by many research groups since the early 1950[5,6,7]. The chemical behavior of an ion exchange resin is determined by the nature of the functional groups that are attached to the hydrocarbon skeleton. So the chelating ion exchange resins can be synthesized that are highly selective for certain groups of metal ions by adoption of appropriate ligand group attached to the matrix resin. Studies have shown that sulfur-containing ligands are more selective toward the noble and heavy metals than their oxygen and nitrogen analogues[8]. The hexylthioglycolate resin developed by Moyers and Fritz[9] has been shown to be specific for silver (I), mercury (II), bismuth (III) and gold (III) in acidic aqueous solution. This resin is a diester formed by stepwise reactions of 1,6-hexane-diol and thioglycolic acid with carboxylic acid group on Rohm and Haas XAD-4 resin, a macroporous styrene-divinylbenzene copolymer. Their work suggests us a new type of chelating ion exchange resin containing alkylthioglycolate could be synthesized if we prepare a macroporous crosslinked polyacrylonitrile by adoption of Vernon and Eccles's method[10], then convert nitrile group on the resin into carboxylic acid by hydrolysis and apply Moyers and Fritz's method to attach alkylthioglycolate to the matrix resin.

Our research work is undertaken to synthesize a new chelating ion exchange

resin containing alkyl-thioglycolate and to study about its basic characteristics and analytical application.

EXPERIMENTAL

Instrument:

All pH of the solutions were measured by Radiometer Titrator equipped with Saturated Calomel (Type K 401) and glass (Type G 202B) electrodes. The pH values were calibrated against Beckman standard *buffer solutions of pH 4.00 and 7.00.*

A Hitachi model 624 digital spectrophotometer connected with Hitachi model QD$_{13}$ recorder and 10 mm quartz cells were used for all absorbance measurements.

Infrared spectra were recorded on a Perkin-Elmer model 580 infrared spectrophotometer.

Reagents:

Analytical reagent grade chemicals were used throughout. The stock solution of silver and platinum ions were standardized by the Volhard method and gravimetric method, respectively. The stock solutions of all other metal ions were standardized by EDTA titrations.

Synthesis of Resin:

A chelating ion exchange resin containing alkylthioglycolate was synthesized according to the following steps.

A) Preparation of acrylonitrile-divinylbenzene copolymer: A macroporous, crosslinked copolymer was prepared by the reaction of acrylonitrile and divinylbenzene according to the procedure proposed by Vernon and Eccles[10].

B) Preparation of matrix resin with carboxyl groups: The above copolymer was air dried, then ground and sieved.

The 60-100 $mesh$ fraction was used for the synthesis after washing with 12 M HCl, water and acetone. The copolymer (200 g) was stirred at 80° with 1000 ml 37% NaOH until no ammonia evolution. The hydrolysed polymer was cooled to room temperature, then collected by suction filtration and washed with 12M HCl, water and acetone.

C) The first esterification: The carboxylic acid resin (200 g) was mixed with 600 g of melted 1,6-hexanediol (m. p. 41°) containing 40 ml of 18 M H$_2$SO$_4$ as catalyst. The mixture was kept at 70° for 30 $hours$ for esterification. The product was collected by a hot suction filtration using boiling methanol as washing solution.

D) The second esterification: The above product (200 g) was added to 460 ml of thioglycolic acid containing 40 ml of 18 M H$_2$SO$_4$. The mixture was reacted at 70° for 30 $hours$. The final product was collected by filtration with suction and washed with 12 M HCl, water and acetone.

Characterization of Resin:

In order to verify the presence of alkylthioglycolate group in the synthesized resin, the infrared spectra of the resin was obtained with KBr pellets after each step in the synthesis. Fig. 1a was the spectrum of the matrix resin, polyacrylonitriledivinylbenzene copolymer. It exhibited IR absorption bands at 2260-2240 cm^{-1} (C≡N). The IR spectrum of hydrolyzed product of copolymer shown in Fig. 1b exhibited absorption bands at 3500-2500, 1720, and 920 cm^{-1} (-COOH). Fig. 1c was the spectrum of the diol ester intermediate. It exhibited IR absorption
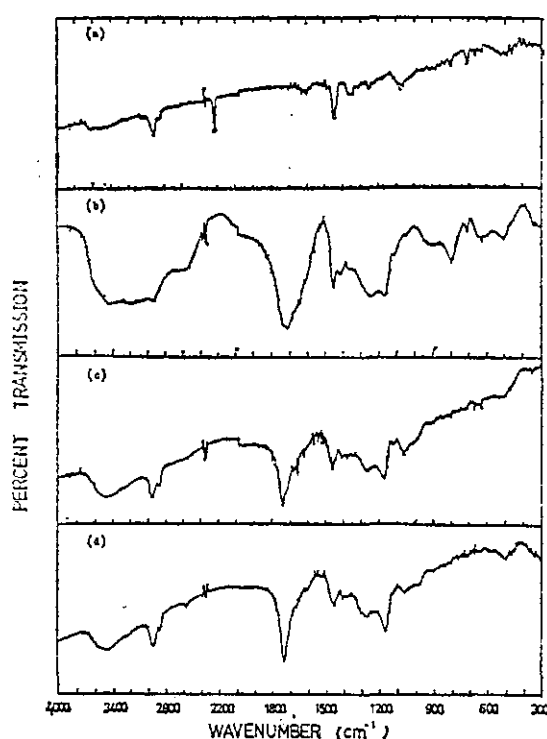
Fig. 1. Infrared spectra (a) Polyacrylonitrile-
DVB resin (R), (b) RCOOH inter-
mediate, (c) RCOO(CH₂)₂OH inter-
mediate, (d) Resin containing thiogly-
colic acid.

the synthesized resin were determined and the results were shown in Table I. The weight distribution coefficients of the metal ions, defined by the equation,

$$D = \frac{mmole \text{ of metal}/g \text{ of resin}}{mmole \text{ of metal}/ml \text{ of solution}}$$

were determined by using the batch equilibrium method. Each equilibrium experiment was performed with 35 ml of a mixture consisting of various amount of 6 M perchloric acid and 1 $mmole$ of the metal ion in question. To this mixture, 0.3 g of resin was filtered off and the metal ion determined in the filtrate. The results were shown in Table II.

bands at 3450 (-OH) and 1735, 1163 and 1064 cm^{-1} (-COOR). Fig. 1d was the spectrum of the final product of the -SH resin. It exhibited IR absorption bands at 2580 (-SH) and 1735, 1163 and 1064 cm^{-1} (-COOR).

The nitrogen content of the original copolymer, the sulfur content, the hydrogen capacity, the metal ions (Ag(I), Hg(II), Au(III), Pt(IV), and Bi(III)) capacities at pH=1, and the acid ionization constants of

Table I. Physical and chemical characteristics of the thioglycolic acid resin

Percent cross linking	5.8 %
Sulfur content	1.56 mmole/g
Hydrogen capacity	2.3 mmole/g
Particle size	60-100 mesh
pK_{a_1} (—COOH)	6.2
pK_{a_2} (—SH)	8.0
Bismuth capacity (pH=1)	0.25 mmole/g
Gold capacity (pH=1)	0.58 mmole/g
Mercury capacity (pH=1)	0.80 mmole/g
Silver capacity (pH=1)	1.52 mmole/g
Platinum capacity (pH=1)	0.03 mmole/g

Note: Nitrogen content of the original poly-
acrylonitrile-divinylbenzene copolymer was
25.0%.

Table II. Distribution coefficients in perchloric acid of varied molarity

Ion	Final HClO₄ concentration, M									
	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
Ag	97.9	122.8	152.2	261.2	272.7	253.6	222.0	182.2	—	—
Au	48.2	85.3	106.1	113.9	125.9	155.3	161.7	154.8	136.1	119.0
Bi	39.1	59.0	59.0	76.9	64.8	57.2	50.5	—	—	—
Hg	63.4	68.2	70.3	91.9	64.1	64.1	64.2	64.1	—	—

Column capacities of the resin were determined for gold (III) in 0.0 to 8.0 M hydrochloric acid media using 0.3 g of the resin in a gravity flow column. The resin sample was conditioned by passing 50 ml of the acid through the column at 0.5 ml/min. Then, 0.1 M gold (III) in the acid solution was passed through the resin until saturation was reached. The column was then washed with 50 ml of the acid to remove excess metal. Elution was carried out with 40 ml of $10^{-3}M$ thiourea-pH 3.0 of HCl. All solutions used in this study contain 2 drops of 0.01% bromine water per 100 ml to prevent gold reduction on the resin. The content of gold was determined spectrophotometrically at 256 $m\mu$ as the thiourea complex. Table III showed the result of this experiment. The calibration curve was shown in Fig. 4. Because the complex formation was found to be kinetically slow and therefore, its kinetic data was shown as Fig. 3.

Column capacities of the resin for other metal ions (Ag(I), Hg(II), Pt(IV) and Bi(III)) may be determined in the same manner, using appropriate quantitative analysis of each metal ion. The contents of these metal ions were determined spectrophotometrically as the chloride complex. The calibration curves were shown in Fig. 5 and 6.

On the basis of equilibrium batch experiment, the following sequence of selectivity of the resin is observed; Ag>Hg>Au>Bi>Pt. The experiment results also show that the resin readily retains Ag(I), Hg(II), Au(III), and Bi(III) from

Table III. Capacity of resin for gold(III)

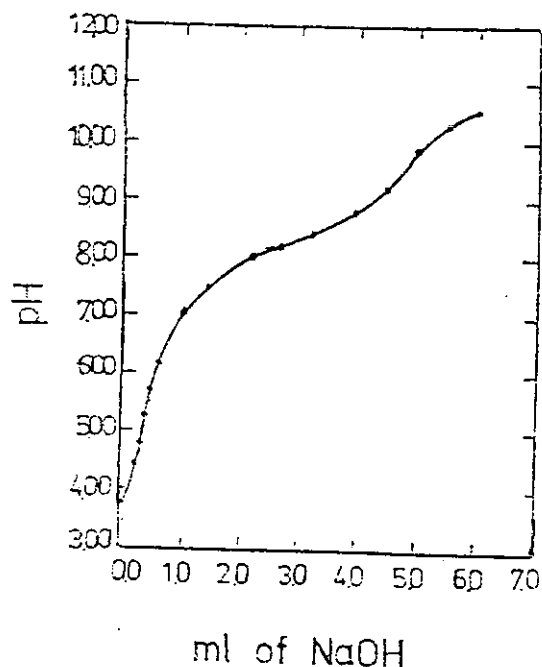| M HCl	$\mu mole$ Au^{3+}/g resin	M HCl	$\mu mole$ Au^{3+}/g resin
0.0	1.68	4.0	91.5
0.5	50.2	5.0	95.3
1.0	62.5	6.0	91.2
2.0	67.1	7.0	80.2
3.0	74.2	8.0	70.1

Fig. 2. Titration curve of acid form of chelating resin.
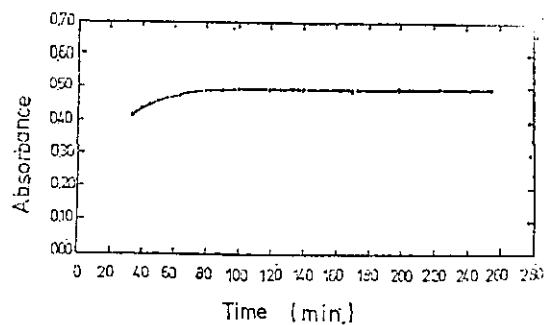(titrant: 0.1 N NaOH) μ=0.1 M

Fig. 3. Gold-Thiourea complex.
[Au^{3+}]=7.0×10^{-5}M
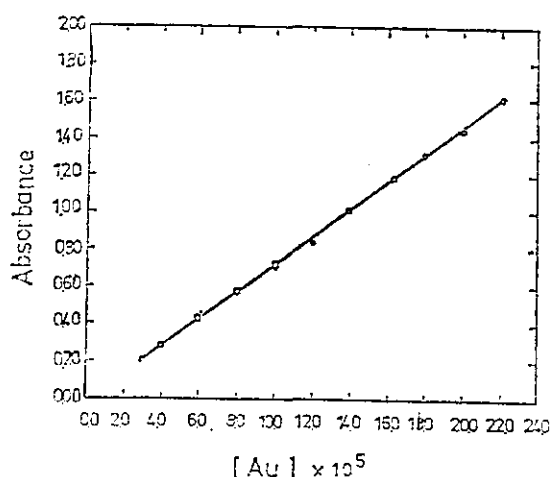[thiourea]=1.0×10^{-3}M
pH=3.0 in HCl
λ=256 $m\mu$

Fig. 4. Validity of Beer's law.
[thiourea]$=1.0\times10^{-3}M$
$pH=3.0$ in HCl
$\lambda=256\,m\mu$

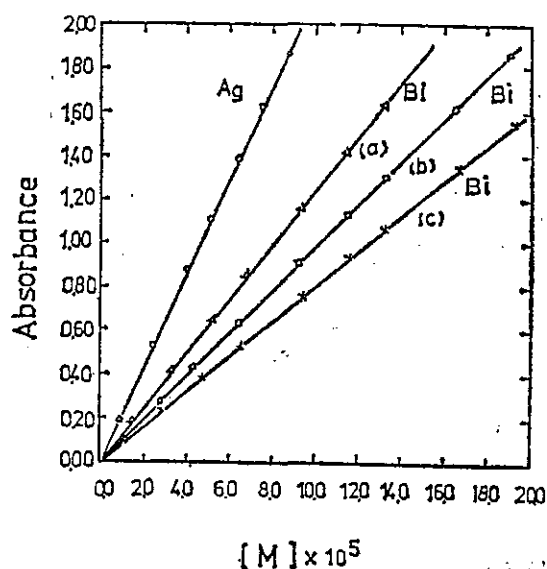Fig. 5. Validity of Beer's law.
(a) Bi^{3+}: in $2\,M$ HCl ($\lambda=325\,m\mu$)
(b) Bi^{3+}: in $1\,M$ HCl ($\lambda=321\,m\mu$)
(c) Bi^{3+}: in $0.5\,M$ HCl ($\lambda=317\,m\mu$)
Ag^+: in $2\,M$ HCl ($\lambda=215\,m\mu$)

either $0.1\,M$ HClO$_4$ or $0.1\,M$ HCl.

Pt(IV) is partially retained by the resin from either tartrate and HClO$_4$ or HCl media.

On the other hand, the resin shows no affinity for alkaline earth, manganese (II), iron (III), cobalt (II), nickel (II), copper (II),
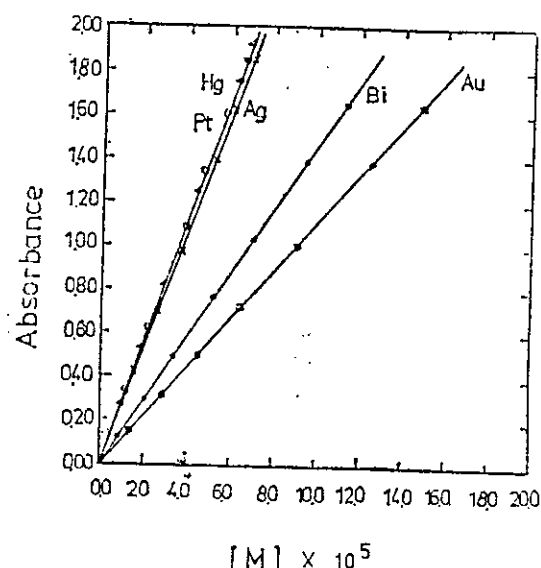

Fig. 6. Validity of Beer's law.
Ag^+ in $6\,M$ HCl ($\lambda=215\,m\mu$)
Au^{3+} in $6\,M$ HCl ($\lambda=313\,m\mu$)
Bi^{3+} in $6\,M$ HCl ($\lambda=327\,m\mu$)
Hg^{2+} in $6\,M$ HCl ($\lambda=229\,m\mu$)
Pt^{4+} in $6\,M$ HCl ($\lambda=262\,m\mu$)

zinc (II), cadmium (II), and lead (II) in $0.1\,M$ acid. Tin (IV) and antimony (V) are also not retained in the medium containing $0.0002\,M$ sodium hydrogen tartrate and $0.1\,M$ acid. These facts indicate that column chromatographic separation and concentration of metal ions (Ag(I), Hg(II), Au(III), Bi(III)) are possible by using this resin.

Chromatographic Application:

In the present work, batch distribution coefficients are used as guides to the selection of conditions for column separation. Separation of Ag(I), Au(III), Bi(III) and Hg(II) in their mixture may be done as follows; The resin column is conditioned with $30\,ml$ of $0.1\,M$ HClO$_4$, and $0.0002\,M$ tartrate at $0.5\,ml/min$. A sample containing 0.4-$3.0\,\mu mole$ is introduced into the column. Allowing the liquid level to drop down to the top of resin bed, rinse the wall of the reservoir with $0.1\,M$ HClO$_4$ and $0.0002\,M$

Table IV. Silver, Gold, Bismuth and Mercury Recovery in the Presence of Other Metals

Metal ion	Metal added (μmole)	Metal found[*] (μmole)	Recovery (%)	Molar ratio				
				Cu/M	Fe/M	Pb/M	Sn/M	Sb/M
Ag	0.450	0.451	100.2	18	30	1	2	2
Au	0.450	0.452	100.4	40	1	1	2	2
Bi	0.398	0.391	97.3	70	10	1	2	2
Hg	0.450	0.453	100.7	10	1	1	2	2

[*] Average of 2 or 3 individual results.

tartrate to wash down any foreign metal ions through the column. The retained Bi(III), Ag(I) and Hg(II) are sequently eluted with 1.0, 2.0, and 6.0 M HCl and determined spectrophotometrically at 321, 215, 229 $m\mu$ as their chloride complexes, respectively. Au(III) which is retained by the resin during this process is eluted by $10^{-3}M$ thiourea-pH 3.0 in HCl and is determined spectrophotometrically at 256 $m\mu$ as the thiourea complex. The effect of the presence of other metal ions on the recovery of Ag, Au, Bi and Hg is shown in Table IV. Samples containing gold (III) and various foreign metal ions were separated on the column. Quantitative separation and recovery of gold (III) was obtained in all cases (see Table V). The separation curve of a four-component mixture is shown in Fig. 7.

Concentration procedure:

The resin is conditioned with 0.1 M HCl; then 500 ml of very dilute solution of metal ions, is passed through the column. The sorbed metal ions are eluted and determined spectrophotometrically. The results are shown in Table VI.

Table V. Separation of gold(III) from other metal ions

Metal ion	Metal added (μmole)	Au added (μmole)	Au found[*] (μmole)	Difference (μmole)
Bi (III)	10	1.56	1.69	+0.13
Cd (III)	10	1.56	1.65	+0.09
Cu (II)	10	1.56	1.52	−0.04
Fe (III)	10	1.56	1.62	+0.06
Hg (II)	10	1.56	1.58	+0.02
Pb (II)	10	1.56	1.56	+0.00
Sb (III)	10	1.56	1.59	+0.03
Sn (IV)	10	1.56	1.51	−0.05

[*] Average of 2 or 3 individual results.
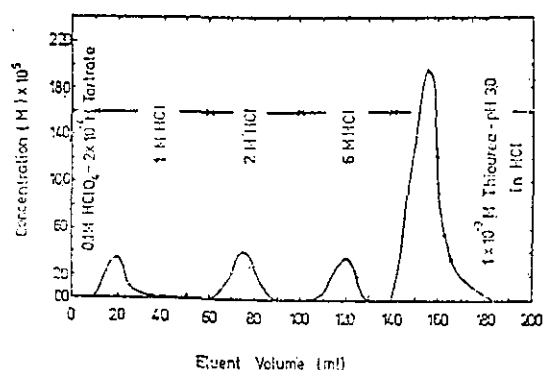
Fig. 7. Separation of Bi^{3+}—Ag^+—Au^{2+}—Hg^{2+} with the resin column.
Column: $2.5 \times 0.6\,cm$ $i.d.$
Flow rate: $0.5\,ml/min$
Metal ions adsorbed: $Bi^{3+} = Ag^+ = Hg^{2+} = 0.45\,\mu mole$
$Au^{3+} = 3.00\,\mu mole$

Table VI. The recovery of Metal Ion from Very Dilute Solution

Metal ion	Metal added (in 500 ml 0.1 N HCl) (μmole)	Eluent	Metal found (μmole)	Recovery (%)
Ag	0.450	2 M HCl	0.438	100.1
Au	1.500	$1.0 \times 10^{-3} M$ thiourea pH 3.0 in HCl	1.446	102.6
Bi	0.400	1 M HCl	0.361	101.2
Hg	0.450	6 M HCl	0.457	101.6

DISCUSSION

The results of characterization of the resin, indicate that the synthesized resin was dibasic polyacid as shown in Fig. 2. The two kinds of titrable hydrogens with pK values of 6.2 and 8.0 are assignable to the remaining carboxylic acid and the mercaptan, respectively. Accordingly, the resin capacity measurements are carried out at pH 1.0 which is sufficiently acidic to avoid any interaction of the metal ions with carboxyl groups in the synthesized resin.

In the synthesis of resin, a six carbon diol is chosen as linking agent between the resin matrix and thioglycolate group to avoid any steric hindrance from the matrix, so that the chelating ligand can be freely to assume a geometric configurations around the metal ion similar to the monomer's. Of course, the steric effect resulting from the functional groups being linked is an interesting problem. A study on the effect of the size of the linking agent between polymer matrix and functional group on the selectivity of the resin is in progress.

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