Synthesis of a Dithiocarbamate Chelate Resin and Its Oxidized form and Their Adsorption Properties for Heavy Metal Ions

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SYNTHESIS OF A DITHIOCARBAMATE CHELATE RESIN AND ITS OXIDIZED FORM AND THEIR ADSORPTION PROPERTIES FOR HEAVY METAL IONS

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ABSTRACT

A series of macroporous dithiocarbamate chelate resins, III and V, and an oxidized resin, VI, with high adsorption capacity were prepared. The influence of various reaction conditions of amination, dithiocarboxylation, and oxidation were examined. The structure and the conversion of functional groups of resins were confirmed by IR spectra and elemental analysis. The adsorption capacities of Resin II for Hg^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} are 4.40, 2.44, 1.77, and 1.36 mmol/g, respectively. The adsorption capacities of Resins V and VI for Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{3+}, Ag^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, and Au^{3+} are 4.07-0.51 and 3.81-0.59 meq ion/g, respectively. The adsorption rate and the influence of pH on the adsorption percentage of the resins for metal ions were examined. Noble metal, transitional metal, and heavy metal ions can be quantitatively adsorbed by the resins. The adsorbed Cu^{2+}, Pb^{2+}, Cd^{2+}, Co^{3+}, and Ni^{2+} can be quantitatively eluted with $5N$ HNO_3, and the presence of large amounts of Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+} did not interfere.

INTRODUCTION

Dithiocarbamate (DTC) resins are of practical importance to water treatment, environment protection and chemical analysis, etc. This kind of chelate resins has been synthesized [1], used in collecting heavy metal ions [2], chromatographic separation, etc. [3], and produced on a commercial scale [4, 5] for the last ten years.

DTC resins with polystyrene as backbone have been reported in recent years [6, 7]. By introducing amino groups into gel-type chloromethylated polystyrene beads (Gabriel method) we have obtained DTC resins [8]. In the present work a series of macroporous dithiocarbamate chelate resins (III) and V, DTC resin) and oxidized resin (VI) had been prepared by using macroporous chloromethylated polystyrene beads, poly(vinylbenzylamine)beads, and polyethylene polyamines, according to the following reactions:
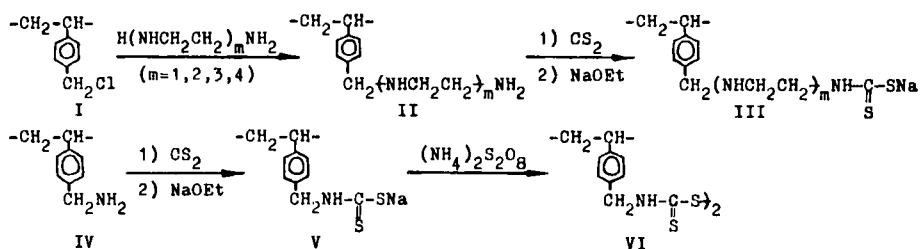
EXPERIMENTAL

1. Materials

Macroporous chloromethylated polystyrene beads: degree of crosslinking 6% (divinylbenzene), chlorine content 21.66%, specific area $13.0 \ m^2/g$. Macroporous polyvinyl benzylamine beads: degree of crosslinking 6% (divinylbenzene), nitrogen content 8.42%, weak alkali exchange capacity 5.23 mmol $-NH_2/g$.

2. Amination

After swelling in solvent, the macroporous chloromethylated polystyrene beads were treated with amine in different molar ratio and at various temperatures and reaction times with stirring.

3. Dithiocarboxylation (sodium alcoholate-ethanol method A)

The amine beads were swollen in absolute ethanol. Various molar ratios of carbon disulfide were added and reacted at 20°C for a period of time. The mixture was heated to a fixed temperature after addition of sodium ethanolate prepared with metallic sodium and ethanol.

4. Oxidation

Resin V was oxidized with an aqueous solution of ammonium persulfate by stirring at room temperature for 4 h.

5. Determination of Adsorption Properties

The concentrations of metal ions were measured by ICP (inductive coupled plasma), AAS (atomic absorption spectrometry), and titration.

RESULTS AND DISCUSSION

1. Factors Which Affect the Amination and the Quality of the Beads

We chose diethylenetriamine for amination and investigated the influence of reaction conditions. We found that the amine beads with the highest nitrogen content (12.81%) and lower residual chlorine content (0.54%) can be prepared under the A11 (see Table 1) reaction conditions: toluene as solvent, amine/chlorine mole ratio = 4, amine concentration 30 wt%, reaction at 20°C for 24 h, and then at 70°C for another 3 h.

If each chlorine atom were replaced by one diethylenetriamine molecule, the theoretical nitrogen content of the amine beads (II, $m = 1$) would be 18.24%. The nitrogen contents (11.43-12.81%) of all prepared amine beads are much lower than this value, and the residual chlorine contents are very small. This indicates that more than one amino group per amine molecule may take part in the reaction to replace chlorine atoms, resulting in additional crosslinking.

Table 1 shows the results of amination with four different amines under the A11 reaction conditions. The nitrogen content of the amine beads increases with the number of amino groups in the amine molecule, but the conversion of functional groups decreases because of the increase of additional crosslinking.

As shown in Table 2, the amino group content of the amine beads increases

TABLE 1. Effect of Different Amines on the Amination Reaction

No.	Amine	Amino groups/ amine molecule	Elementary analysis		Conversion of functional groups,[a] mol%	Additional crosslinking,[b] %
			N, %	Cl, %		
A10	Ethylenediamine	2	11.25	0.53	69.7	30.3
A11	Diethylenetriamine	3	12.81	0.54	58.9	41.1
A12	Triethylenetetramine	4	13.34	0.71	49.1	50.9
A13	Tetraethylenepentamine	5	13.94	1.39	45.5	54.5

[a]Conversion from Cl group to $-(NHCH_2CH_2)_mNH_2$, $m = 1, 2, 3, 4$.
[b]100% − % conversion of functional group.

TABLE 2. The Results of Dithiocarboxylation with Different Amine Beads[a]

No.	Amine	N of amine beads, %	S of DTC resin, %	Conversion of functional groups,[b] mol%	Adsorption capacity of DTC resin, mmol Cu^{2+}/g
D1	Ammonia	7.51	19.59	81.4	2.10
D2	Ethylenediamine	11.25	21.19	60.9	2.14
D3	Diethylenetriamine	12.81	21.67	55.3	1.91
D4	Triethylenetetramine	13.34	22.27	55.3	1.37
D5	Tetraethylenepentamine	13.94	19.83	44.6	1.07

[a]Alcoholate-ethanol method A. CS_2/amino group 2.5 (in mol), reaction at 20°C for 24 h and then at 60°C for 12 h after adding alcoholate solution.
[b]Conversion from amino group to $>NCSSNa$ and $-NHCSSNa$.

with the number of amino group in the amine molecule. On the other hand, the additional crosslinking enhances the steric hindrance for the reaction, and a great quantity of tertiary amine is produced which is useless for the dithiocarboxylation. As a result, the molar conversion of amino to DTC group decreases progressively. These effects cause the sulfur content first to go up slowly and then to come down. The adsorption capacity for Cu^{2+} decreases progressively, except for the DTC resin corresponding to the primary amine beads, because the additional crosslinking not only limits the orientation of the ligands but also hinders the transference of the metal ions, making them difficult to place in suitable steric positions for chelation. Thus, it is concluded that ethylenediamine is the most suitable amination agent for the preparation of DTC resin with high adsorption capacity.

2. Factors in Dithiocarboxylation Affecting the Quality of DTC Resin

The sulfur contents and adsorption capacities of DTC resins prepared from ethylenediamine beads by the following methods, NaOEt-EtOH (A), NaOH-H_2O [6], NaOEt-EtOH (B) [7], without base-EtOH [11], and pyridine-isopropanol [8], were 23.22%, 2.18 mmol Cu^{2+}/g; 23.10%, 2.13; 14.35%, 1.02; 11.71%, 1.47; and 11.85%, 0.96; respectively. Thus, the DTC resin prepared by the NaOEt-EtOH method (A) had the highest sulfur content and the highest adsorption capacity for Cu^{2+}.

The NaOEt-EtOH method (A), as improved by us, differs from other methods in the heating procedure after adding alcoholate solution.

The sulfur content and the adsorption capacity for Cu^{2+} of the DTC resin does not increase any further when the CS_2/amino mole ratio is raised above 3, which is considered the optimum value, as shown in Fig. 1.

The temperature in Fig. 2 refers to the highest temperature after the alcoholate solution is added. The curves show a maximum at 65°C.

The DTC resin (III, $m = 1$) has the highest sulfur content (24.15%) and adsorption capacity for Cu^{2+} (2.33 mmol Cu^{2+}/g). This DTC resin is prepared under the following reaction conditions: CS_2/amino group mole ratio 3, reaction at 20°C for 9 h, and then at 65°C for another 9 h after EtONa-EtOH addition.

3. The Properties of DTC Resin III ($m = 1$)

Under the experimental conditions, the adsorption of Cu^{2+}, Cd^{2+}, or Zn^{2+} by this resin is as high as 98-100% over a wide pH range (2-7.5).
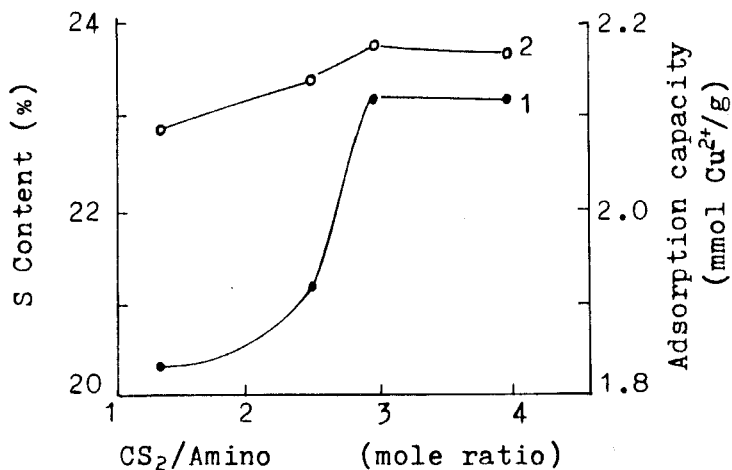
FIG. 1. Influence of the CS_2/amino group mole ratio on the dithiocarboxylation reaction. (1) S content, (2) adsorption capacity. Reaction condition as in Table 2.
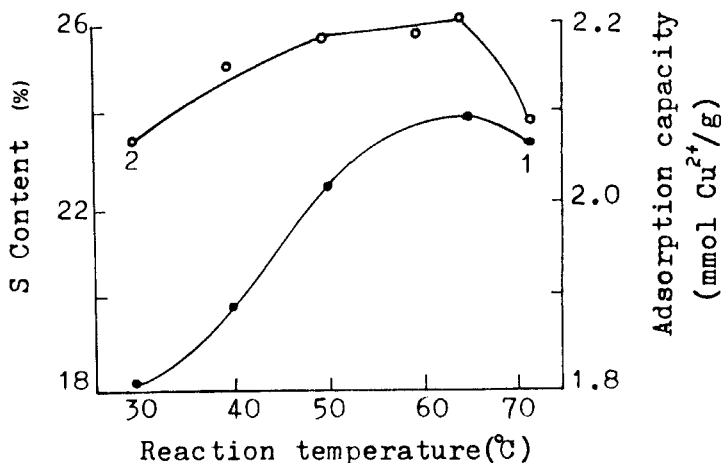

FIG. 2. Influence of temperature on dithiocarboxylation. (1) S content, (2) adsorption capacity. CS_2/amino group mole ratio = 3. Other reaction condition as in Table 2.

The adsorption capacity of the resin for Hg^{2+} is over 4 mmol/g at pH 4-5.5, but decreases rapidly below pH 4. The adsorption amount of Cu^{2+} by this resin in 1 h reaches 50% of the adsorption capacity and in 24 h is 95.5%.

We synthesized the DTC resin III ($m = 1$) under the optimum condition, so that the adsorption capacities for heavy metal ions are very high. The adsorption capacities of the DTC resin for Hg^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} are 4.40, 2.44, 1.77, and 1.36 mmol ion/g, respectively.

4. The Synthesis and Structure of Resin V and Resin VI

In our previous reports [8, 9] the conversion from $-NH_2$ to $-NHCSSNa$ was only 25.1% by using gel-type chloromethylated polystyrene beads. Dingman [10] also reported that the sulfur content of the DTC resin prepared by the dithiocarboxylation of polyethyleneimine ($-NH-CH_2CH_2-)_n$ was only 9.5%, i.e., only a quarter of the $-NH-$ groups was converted to $>N-CSSH$. In the present work we use macroporous chloromethylated polystyrene beads and an improved dithiocarboxylation method, so that the conversions of the functional group $-NH_2$ to $-NHCSSNa$ and $-NHCSS\rightarrow$ are 85.1 and 59.5%, respectively.

A problem should be mentioned here. Industrially, Resin II ($m = 0$) was prepared by the hydrolysis of poly(vinyl benzyl phthalimide) in hot concentrated aqueous NaOH. Thus, the degree of hydrolysis is lower than that of conventional hydrazinolysis. The weak alkali-exchange capacity is 5.23, as determined by the titration method, and the content of functional group (calculated from N content) is 6.01 mmol N/g, so that the degree of hydrolysis is 87%, and 13% N still exists in the form of phthalimido groups in Resin II ($m = 0$).

For Resin II ($m = 0$) containing 13% unhydrolysed phthalimido group, the conversion of functional groups from $-NH_2$ to $-NHCSSNa$ reaches 93.3%, and the overall conversion of functional groups from $-NH_2$ to $-NHCSS\rightarrow$ reaches 64.5% (Table 3).

The structures of Resins V and VI are confirmed not only by elementary analysis but also by IR spectra. The peak at 1505 cm^{-1} shows the existence of unhydrolysized imido group in Resins V and VI.

Furthermore, the S/N atomic ratio of Resins V and VI should be same if the oxidation of Resin V to Resin VI according to the above-mentioned scheme is complete. But the fact is that the S/N atomic ratio of Resin V is 1.70 and that of Resin VI is only 1.19. Thus it is clear that about 18% of the CSSH groups of Resin V have been lost during the oxidation with $(NH_4)_2S_2O_8$. The acidity of an aqueous solution of $(NH_4)_2S_2O_8$ may in-

TABLE 3. Functional Group Content and Conversion[a]

Resins[b]	Elementary analysis		Content of functional group (mmol functional group/g)		Conversion of functional groups, %
	N, %	S, %	Calc from % N	Calc from % S	
PS–CH$_2$NH$_2$	8.42		5.23 NH$_2$		
PS–CH$_2$NH–C(=S)–SNa	5.43	21.13	3.37 NHCSSNa + NH$_2$	3.30 NHCSSNa	93.3
PS–CH$_2$NH–C(=S)–S)	6.34	17.25	3.94 NHCSSNa + NH$_2$	2.69 NHCSSNa	64.5

two stepwise method

[a]Polyvinyl amine beads containing 13.0% unhydrolyzed phthalimido group.
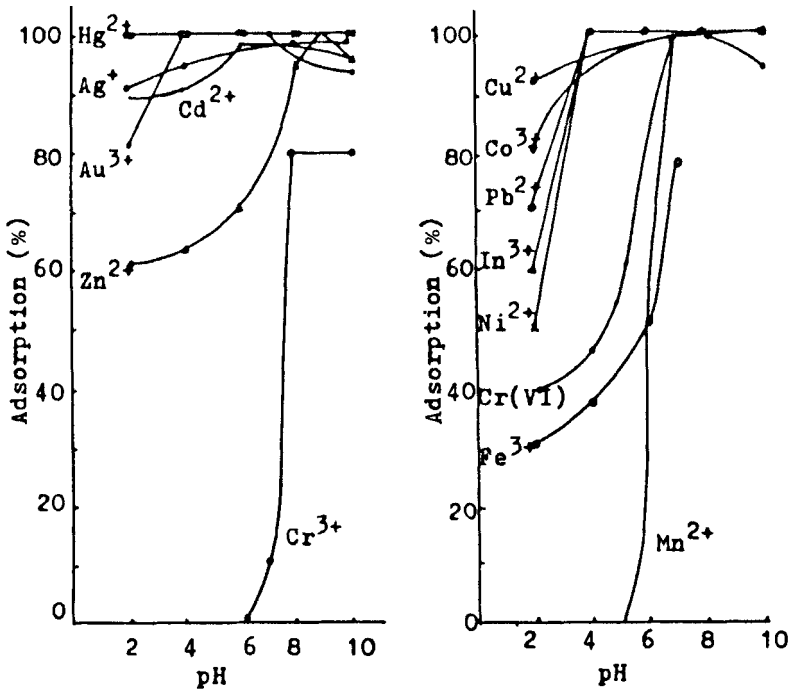[b]PS = polystyrene.

FIG. 3. Effect of pH on the adsorption of Resin V (SNa type) for different metal ions.

duce the dedithiocarboxylation reaction. The $-CS-SS-CS-$ group is more stable than the $-NH-CS-SH$ group.

5. The Properties of Poly(Vinylbenzylaminodithiocarboxylate) (Resin V, SNa type) and Its Oxidation Product (Resin VI, SS type)

(1) The Effect of pH on the Adsorption of Resins V and VI for Metal Ions

Figures 3 and 4 show that metal ions can be adsorbed quantitatively by Resins V and VI over a specific pH range.

(2) The Adsorption Capacities of Resins V and VI for Metal Ions

Under the optimum pH condition, the adsorption capacities of Resin V for Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{3+}, Ag^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, and Au^{3+} are 4.07, 2.56, 2.05,
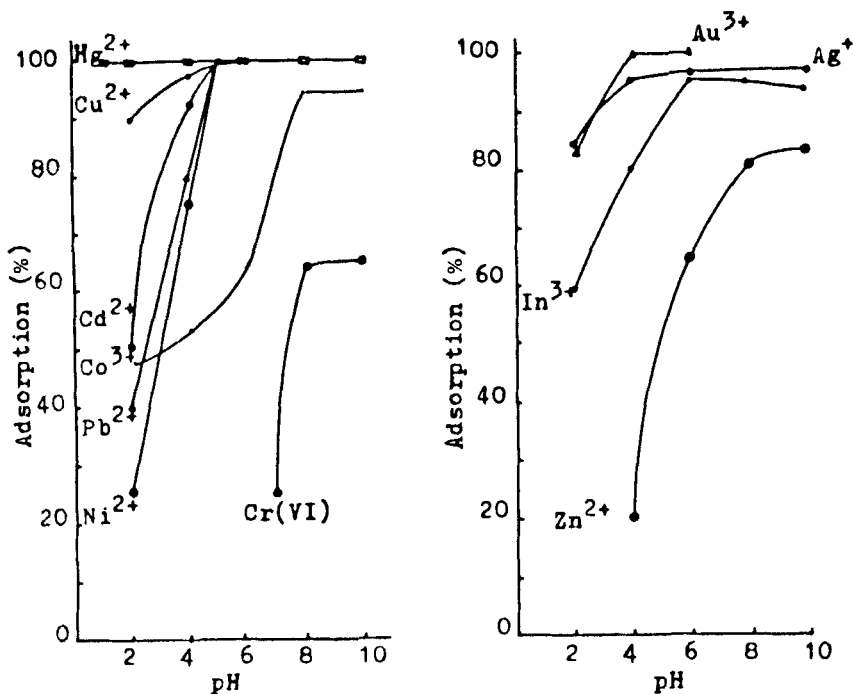
FIG. 4. Effect of pH on the adsorption of Resin VI (SS type) for different metal ions.

1.62, 1.58, 1.23, 0.79, 0.76, and 0.51 meq ion/g, respectively. The adsorption capacities of Resin VI for the same ions are 3.81, 2.71, 1.50, 1.72, 1.44, 1.08, 0.84, 0.78, and 0.59 meq ion/g, respectively.

(3) Dynamic Adsorption

Cu^{2+} and Cd^{2+} can be adsorbed quantitatively when the Resin V (or VI) bed is 8 cm deep and the flow rate is 1 mL/min. In addition, Co^{3+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} can also be adsorbed quantitatively when the Resin V bed is 8 cm deep and the flow rate is 3 mL/min.

(4) Elution and the Interference of Coexisting Ions

Cu^{2+}, Co^{3+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} adsorbed on Resin V and Cu^{2+}, Pb^{2+}, and Cd^{2+} adsorbed on Resin VI can be eluted from column quantitatively by $5\ N$ HNO_3.

TABLE 4. Effect of Coexistent Ions on Elution

Coexistent ions	Amoung added, mg	Cu^{2+}			Pb^{2+}			Cd^{2+}			Co^{2+}			Ni^{2+}		
		Amount added, μg	Recovery μg	%	Amount added, μg	Recovery μg	%	Amount added, μg	Recovery μg	%	Amount added, μg	Recovery μg	%	Amount added, μg	Recovery μg	%
Ca^{2+}	10	10.0	10.0	100	20.0	21.0	105	10.0	10.0	100	10.0	10.5	105	10.0	10.0	100
Mg^{2+}	10	10.0	10.0	100	20.0	20.6	103	10.0	10.0	100	10.0	10.0	100	10.0	10.0	100
Fe^{3+}	10	10.0	10.0	100	20.0	21.0	105	10.0	9.5	95	10.0	10.5	105	10.0	10.5	105
Al^{3+}	10	10.0	10.0	100	20.0	20.0	100	10.0	10.0	100	10.0	10.0	100	10.0	10.0	100

The data listed in Table 4 show that the presence of 1 000 times higher concentrations of coexistent ions Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+} do not interfere with the quantitative adsorption and elution of Resin V for Cu^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}.

(5) The Accuracy of the Method

The standard deviation and the relative standard deviation for recovery of Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} are in the range of 0.42, 4.4%; 0.48, 4.8%; 0.37, 3.7%; 0.35, 3.5%; and 0.83, 4.2%; respectively. These data were calculated from nine replications of the experiments and are very satisfactory.

(6) The Recoveries

The recovery percentages of Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} in four natural water samples were in the range of 95-105%.

ACKNOWLEDGMENT

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