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Ligand-Exchange Chromatography of Aromatic Amines on Resin-Bound Cobalt Ion

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ABSTRACT

The use of cobalt metal for the selective separation of aromatic amines is completed with a chemically bonded diamine and glyoxime functional groups onto *Lycopodium clavatum*. Oximes and amines are excellent complexing agents for transition metal ions. Cobalt(II) metal ions can easily be immobilized on bis-diaminoethyl-glyoximated sporopollenin (bDAEG-sporopollenin). The ligand-exchange behavior of modified *Lycopodium clavatum* with respect to aromatic amines was investigated. This will permit the evaluation of bDAEG-sporopollenin ligand exchangers for their utilization as sorbents in the recovery, pollution control, and elimination of amines from wastewater.

INTRODUCTION

Aromatic amines are very toxic atmospheric and water pollutants, particularly in the workplace because they may cause urethral track cancer in exposed individuals (1). Their presence in wastewater is harmful to aquatic life. The sources of such *N*-base containing wastewaters are dye manufacturing industries, coal gasification, rubber chemicals, and other chemicals (2). Amines that possess pairs of free electrons are capable of displaying electron-donating properties and of functioning as ligands.

Many kinds of ion exchangers and adsorption resins have been synthesized, and several methods have been described in the literature for the removal of toxic amines (3–10).

The process of ligand exchange can be applied to any amines. Any compounds that form labile coordination complexes with transition elements can be separated by the ligand-exchange method. The use of transition metal ions, such as Cu(II), Ni(II), Co(II), and Cd(II), for the achievement of high selectivity of amines has been popular in column liquid chromatography (LC). Helfferich introduced the ligand-exchange chromatography (LEC) procedure which involves separation based on the exchange of ligands with metal ions immobilized on a stationary phase (11–13).

Extensive reviews of this subject by Walton have appeared (14, 15). Aromatic amines have been separated on several metal-exchanger combinations. Recent work with metal-loaded exchangers bonded to the acrylic resin Bio-Rex 70 has given better resolution for the separation of amphetamine drugs (14).

Ligand exchangers have the particular advantage of combining high sorption capacity with high selectivity for the ligand. The selectivity for the ligand is high when the complexes with the metal ion are strong. Coordinatively saturated complexes are formed in the resin even when the ligand concentration in the external solution is very low. Various classes of amines are separable on weak acid cation cellulosic exchangers. Polystyrene resins have high affinity for aromatic amines (15).

This paper reports comparisons between chelating resins and the chromatography of some aromatic amines using Co^{2+}-loaded bDAEG-sporopollenin. Sporopollenin is a natural polymer obtained from *Lycopodium clavatum* which is highly resistant to chemicals, has a constant chemical structure, occurs naturally as a component of spore walls, and exhibits very good stability after even prolonged exposure to mineral acids and alkalies. Sporopollenin is generally considered to be a biopolymer and has been found to have the empirical formula $C_{90}H_{144}O_{27}$ (16–19). In these experiments, chromatographic separations of aromatic amines on the Co^{2+}-loaded ligand complex prepared using the reaction of glyoximes with diaminoethane were realized.

The primary objectives of this paper are: to present a special chelating natural polymer as the metal host for a ligand-exchange process involving aromatic amines; to prepare other types of new metal–ligand complexes of sporopollenin; and to utilize these complexes as sorbents for pollution control.

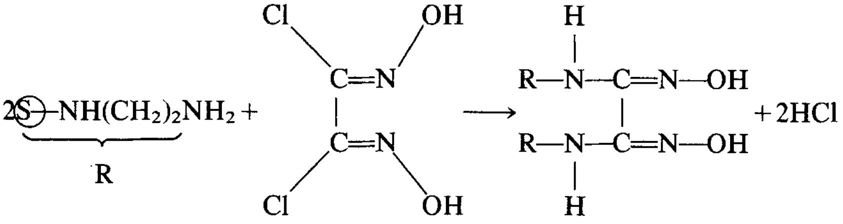
EXPERIMENTAL

Chemicals and Reagents

Lycopodium clavatum was purchased from B.D.H. All chemicals were purchased from Merck and were reagent grade. Solutions were prepared using deionized water.

Synthesis of Chelating Resins

DAE-sporopollenin, which was obtained as before (16), was placed in a reaction vessel, and a slurry of dichloro-antiglyoxime was added to this resin. The ligand-exchange resin was treated with Co^{2+} ion which is fixed to the resin matrix. The reaction can be represented as follows.



bis-diaminoethylglyoxime-sporopollenin
(bDAEG-sporopollenin)

Chromatography on Cobalt-bDAEG Sporopollenin

The resin was washed with water until the effluent was free of Co^{2+} ions. Then the column was packed by the slurry packing technique into a column (30 × 1 cm, borosilicate) and washed with water. The solution containing aromatic amines was passed through the ligand-exchange column which was filled with the Co^{2+}-loaded bDAEG ligand exchanger in the complexing metal–ligand form. Alcohol–ammonia–phosphate tampon solutions served as the eluants. Chromatographic separations were followed by a continuously recording UV spectrophotometer (Schimadzu UV160 A). On entering the column, the aromatic amines displace the ligands from the coordinated metal ions.

RESULTS AND DISCUSSION

The sorption of aromatic amines as ligands on bDAEG-sporopollenin resin bound cobalt-ion has been studied. The aromatic amines used included *p*-anisidine, *p*-toluidine, *m*-nitroaniline, and *p*-chloroaniline.

Coordinating polymers are polymers with covalently bound side chains which contain a donor atom that is able to form a coordinate bond to a metal ion. The interaction between metals and selective ligand exchangers depends upon properties of the metal, the solution, and the polymer itself (14). Since amines contain a lone pair of electrons, they are expected to act as electron donors with cobalt-loaded bDAEG-sporopollenin as an electron acceptor (15).

By introducing a glyoxime complex onto an aminated-sporopollenin and then attaching Co^{2+} ions, we produced an effective ligand exchanger which could be used for chromatography of aromatic amines with buffered phosphate–alcohol–ammonia eluants.

The chromatograms for *p*-anisidine: *p*-toluidine and *p*-chloroaniline: *p*-toluidine are shown in Figs. 1 and 2, respectively. All the mixtures of aromatic amines separated with bDAEG-sporopollenin are listed in Table 1. Good separations were obtained with a 20:60 (v:v) alcohol:ammonia solution in phosphate buffer as the mobile phase. By using lower linear velocities, some overlapping was reduced and aromatic amines were completely separated in 1 hour. Both adsorption and complexation occur in the ligand-exchange reaction. These combined processes cause tailing because of their different rates. Unequal rates of formation and dissociation of the cobalt–amine complex could also be a cause for peak asymmetry.

The increase in retention time on the bDAEG-sporopollenin ligand exchanger is probably caused by donor–acceptor complex formation between cobalt and the aromatic amines. Cobalt should act as an electron donor.

When mixtures of aromatic amines were introduced into a column containing the cobalt-loaded ligand exchanger and a 20:60 (v:v) alcohol:ammonia solution in phosphate buffer was passed, the amines moved along the column at different rates, with those forming more stable complexes having electron-donor substituents remaining behind while those forming

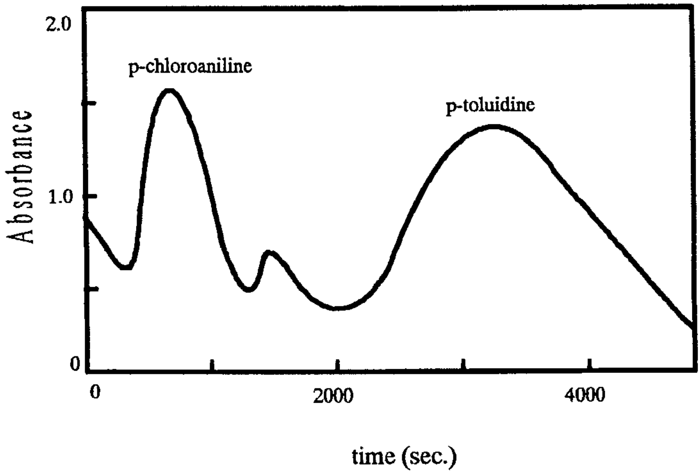


FIG. 1 Separation of aromatic amines on the Co^{2+}-loaded bDAEG-sporopollenin resin: column, 30 × 1 cm; eluant, 20:60 (v:v) alcohol:ammonia solution in phosphate buffer; flow rate, 0.90 $mL \cdot min^{-1}$; detection at 248 nm.

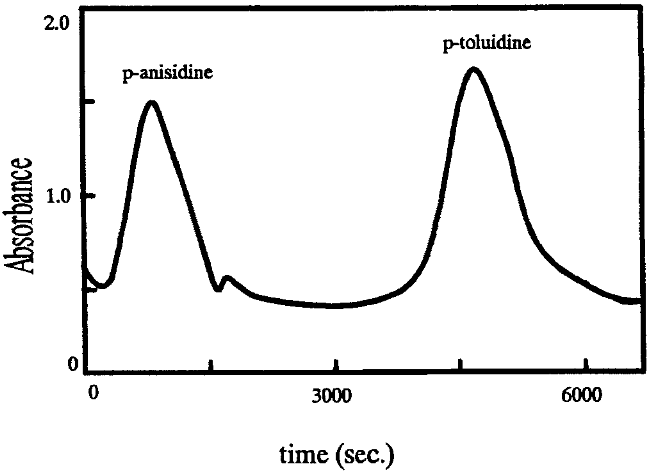


FIG. 2 Separation of aromatic amines on the Co^{2+}-loaded bDAEG-sporopollenin resin: column, 30 × 1 cm; eluant, 20:60 (v:v) of alcohol:ammonia solution in phosphate buffer; flow rate, 0.90 $mL \cdot min^{-1}$; detection at 248 nm.

weak complexes having electron-acceptor substituents moving ahead as seen in Figs. 1 and 2. Also, steric hindrance around the amino nitrogen loosens the attachment to the metal ions and causes the substance to migrate faster.

For tertiary mobile phases consisting of very weak and low concentrations of a very strong solvent (alcohol), small variations in the concentra-

TABLE 1

Retention Volumes of Aromatic Amines by Using Co^{2+}-Loaded bDAEG-Sporopollenin Eluation 20:60 (v:v) of Alcohol:Ammonia Solution in Phosphate Buffer. Sample Concentration 2.5 × 10^{-3} M

Chromatogram	Molecule	Wavelength (nm)	Amount injected (μL)	Retention time (s)	Retention volume (mL)
1	*p*-Chloroaniline	248	350	380	5.7
	p-Toluidine			3200	48.0
2	*p*-Anisidine	248	350	1230	18.4
	p-Toluidine			4850	72.8
3	*m*-Nitroaniline	248	350	3900	58.5
	p-Anisidine			5200	78.0
4	*o*-Nitroaniline	248	350	1960	29.4
	p-Toluidine			2510	37.7

tion of the more polar solvent has a significant effect on the retention of solutes. Changing the alcohol concentration in the eluant from 20 to 30% reduced the retention time of aromatic amines.

Polystyrene resins give broad, asymmetrical bands with aromatic amines in LEC (15). This may occur by the superposition of π-bonding on the metal–ligand interaction.

bDAEG-sporopollenin resin was found to last for months without any noticeable change in efficiency. Different prepared supports under identical conditions gave similar results. Cobalt-loaded bDAEG-sporopollenin may show selectivity toward different classes of compounds, and so is worthy of further study.

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