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Ion-Exchange Chromatography of Metal Ions with Ethanolamine Eluents*

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Summary

Copper, nickel, zinc, cadmium and four other metals were separated on cation-exchange resins, using as eluents solutions of mono-, di- and triethanolamine with their chloride and nitrate salts. Column chromatography was used, also chromatography on resin-impregnated paper. Under suitable conditions Cu(II) is not retained by the resin at all; this fact is attributed to the formation of uncharged hydroxy-complexes. This may also occur with Ag(I).

INTRODUCTION

In our studies of ligand exchange chromatography (1, 2) we noticed that the distribution of small amounts of metal ions between a cation-exchange resin and an ammonium salt solution was affected by the addition of ethylenediamine. Adding the amine displaced the metal into the resin. For example, the distribution ratio for 0.2 mmole of Ni(II) between 2.5 meq of sulfonated polystyrene resin and 65 ml of 0.3 M ammonium nitrate, made to pH 9.5 with ammonia, was multiplied by 2.5 when 2 mmole of ethylenediamine was added. The distribution of Cu(II) and Ag(I), on the other hand, was little affected. From these

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results and others it seemed that new ion-exchange separations of metals might be achieved by using amine solutions as eluents. A promising reagent for such separations was ethanolamine, since it forms uncharged complexes with copper(II) at pH 9 and above (3, 4, 5), and might or might not form similar complexes with other metals. Diethanolamine and triethanolamine were other promising reagents. Triethanolamine has been shown to form a negatively charged hydroxy-complex with copper (3).

EXPERIMENTAL

Two kinds of experiments were performed, one for exploratory purposes using ion-exchange-resin-impregnated paper, the other using columns. A resin of the polystyrene sulfonic acid type was used in each case. The procedures were as follows:

Paper Chromatography

The paper used was Reeve Angel SA-2, containing 50% by weight of the resin Amberlite IR-120, initially in the sodium form. It was cut into strips about 1 cm by 25 cm and lightly marked with pencil lines to indicate the starting and finishing positions of the solvent front and the starting position of the metal salt. The strips were hung in stoppered test tubes with the lower end dipping in the solvent. The solvent was allowed to move up each strip about 5 cm before the spot of metal salt

TABLE 1
R_F Values in Chloride Solutions

	Base							
	Monoethanolamine				Diethanolamine			
Molar concentrations:								
BH ⁺ Cl ⁻	1	1	2	2	1	1	2	2
B	0.5	2	1	2	0.5	2	1	2
Metal:								
Cu	0.74	0.85	0.80	0.98	1.0	1.0	1.0	1.0
Cd	0.22	0.22	0.72	0.71	0.27	0.36	0.84	0.87
Zn	0.21	0.30	0.50	0.60	0.10	0.27	0.34	0.54
Hg	0.28	0.29	0.89	0.80	0.29	0.49	0.50	0.74
Pb	0.16	0.30	0.49	0.50	0.11	0.35	0.45	0.59
Ni	0.08	0.12	0.31	0.32	0.05	0.09	0.18	0.28

TABLE 2
R_F Values in Nitrate Solutions

	Base					
	Monoethanolamine		Diethanolamine		Triethanolamine	
Molar concentrations:						
BH ⁺ NO ₃ ⁻	2	2	2	2	2	2
B	1	2	1	2	1	2
Metal:						
Ag	0.63	0.67	0.97	1.0	0.85	0.75
Cu	0.95	0.91	1.0	1.0	0.81	0.74
Cd	0.29	0.28	0.19	0.31	0.15	0.25
Zn	0.38	0.43	0.27	0.47	0.11	0.21
Hg	0.26	0.27	0.22	0.48	0.46	0.38
Pb	0.30	0.38	0.34	0.47	0.14	0.23
Ni	0.22	0.25	0.20	0.27	0.12	0.29

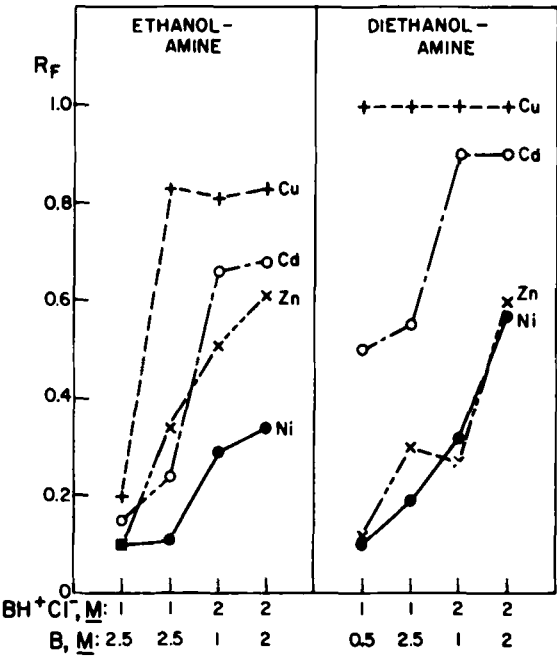


FIG. 1. Values of the migration ratio *R_F* for mixtures of monoethanolamine and diethanolamine with their chlorides.

was placed on the paper, some 3 cm behind the solvent front. Then the strip was replaced in the test tube and development continued until the solvent front reached a predetermined level. The paper was removed and dried, and the metal spot made visible by spraying with sodium sulfide solution. Zinc and cadmium spots were sprayed with 8-hydroxyquinoline solution, giving a yellow fluorescence with ultraviolet light. The amount of metal was about $0.5 \mu\text{mole}$.

The solutions for development were made by mixing known amounts of hydrochloric or nitric acid with known, excess amounts of base. (Some tests were made with ammonium chloride plus excess base, but the separations were generally poorer, and so the data are not reported.) Experiments were made with mono-, di-, and triethanolamine and with seven metals. The values of R_F are given in Tables 1 and 2. Other R_F values from a different series of experiments are shown graphically in Fig. 1.

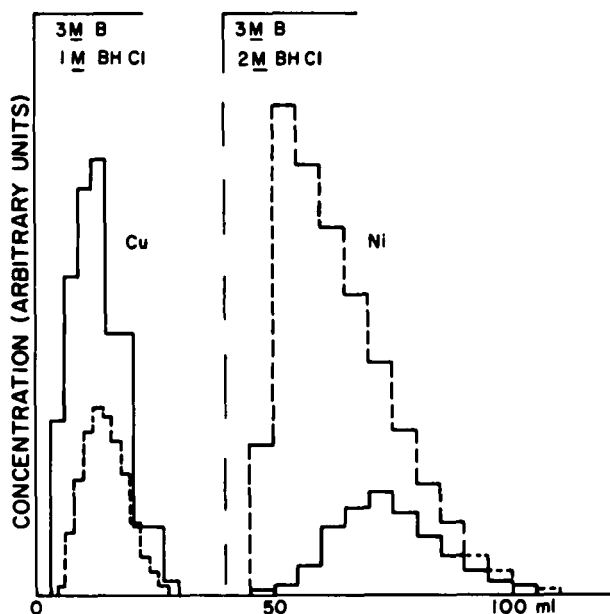


FIG. 2. Separation of copper and nickel on a column 1 cm^2 by 15 cm. Full line, 360 mg Cu, 0.36 mg Ni; dashed line, 240 mg Ni, 0.24 mg Cu.

Column Chromatography

Columns of various sizes were used; good results were obtained with 11 mm i.d. and 15 cm bed height, though 30-cm columns were also used. The resin was Bio-Rad AG-50 \times 8, 100/200 mesh. Flow rates were 1–2 cc/min. The effluents were collected in a fraction collector and the metal concentrations found by atomic absorption spectroscopy.

The first tests were made with solutions of ethylene diamine with a deficiency of hydrochloric acid; the metals chosen were nickel and copper. Nickel was eluted first, but the bands were broad and overlapped somewhat. After the encouraging paper chromatography results with the ethanolamines, column tests were made with these eluents. Zinc and cadmium were separated completely on a column 6 mm in diameter and 30 cm long, with a solution 1.5 *M* in ethanolamine and 1.0 *M* in ammonium chloride; 0.3 mmole of each metal was applied; zinc emerged first with concentration peak at 30 ml, cadmium afterward with peak at 230 ml. Figure 2 shows the separation of copper and nickel, in the proportions 1000:1 and 1:1000 by weight, using monoethanolamine and a deficiency of hydrochloric acid. Elution volumes of these and other metals are given in Table 3.

TABLE 3
Peak Elution Volumes from Column of 15 ml Bulk Volume^a

	Base				
	Monoethanolamine				Diethanol- amine
Molar concentrations:					
BH ⁺ Cl ⁻ (or NO ₃ ⁻)	1	1	2	2	2
B	1	3	1	3	1
Metals:					
Ag	24*	—	—	—	—
Cu	22	20	—	—	7
Cd	87	95*	—	22	12
Zn	92	72*	25	27	75
Ni	—	—	67	42	115
Ca	—	—	87	117	>200

^a Asterisk indicates nitrate solutions; other data for chlorides. Volumes are totals in ml, uncorrected for void or dead volume.

Triethanolamine nitrate, 2 *M* salt, 1 *M* base, gave elution volume 12 ml with Cu.

RESULTS AND DISCUSSION

The chief results of analytical interest are the following:

(1) Copper(II) is transported easily by monoethanolamine and even more easily by diethanolamine. This can be understood by reference to the formation constants of the uncharged complexes $\text{CuB}(\text{OH})_2$, whose logarithms are 17.4 for monoethanolamine and 18.2 for diethanolamine, and of $\text{CuB}_2(\text{OH})_2$, whose values are 19.6 and 19.8 (3). The latter complexes predominate at the concentrations used in this work. There is little difference in their stabilities, however, and the higher R_F values found with diethanolamine could be due to stronger binding of the diethanolammonium cation by the resin. So many factors influence R_F and the partition ratio between resin and solution that only the most general theoretical conclusions can be drawn, but it does seem that of the metals studied, only copper and perhaps silver form uncharged complexes with the ethanolamines to any great extent.

Copper is easily separated from other metals by mono- or diethanolamine, and Fig. 2 shows that traces of copper can be separated quantitatively from large amounts of nickel and *vice versa*.

(2) Silver is easily separated from other metals by its high mobility in diethanolamine-nitrate solutions. It can be separated from copper in monoethanolamine-nitrate solutions that are 2 *M* in salt and 1 *M* in base; copper is more mobile than silver (Table 2).

(3) Zinc and cadmium are best separated in diethanolamine-chloride solutions 2 *M* in salt and 1 *M* in base (Table 1). This conclusion was verified by column chromatography. Cadmium moves the faster in chloride solutions, but in nitrate solutions the order is reversed and the difference is reduced. Evidently the formation of chloride complexes is important.

(4) Calcium is easily separated from zinc, nickel, and other elements in monoethanolamine-chloride solutions 2 *M* in salt and 3 *M* in base (Table 3). It is less mobile than the other metals. This suggests a general method for separating alkaline earth metals from transition and post-transition metals.

(5) Good sequential separations of several metals are indicated by paper chromatography; in diethanolamine-chloride solutions 2 *M* in salt and 2 *M* in base the sequence is Cu-Cd-Hg-Pb-Zn-Ni, and in monoethanolamine-chloride solutions 2 *M* in salt and 2 *M* in base it is Cu-Hg-Cd-Zn-Pb-Ni. In each case copper moves the fastest.

From the practical standpoint the most valuable separations are those

that permit trace quantities of one element to be separated from large quantities of other elements. Cation-exchange separations with ethanol-amine solutions seem to offer this possibility.

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