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Column Chromatographic Separation of Hg(II), La(III), Ce(III), and In(III) from Other Metal Ions in NH_4Cl–CH_3COOH Medium by Cation Exchange

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Abstract

Cation exchange equilibrium distribution coefficients (K) with the (Dowex 50W-X8) H^+ form have been determined for 21 metal ions in media consisting of mixtures of 0.7 mol/dm^3 acetic acid and varying concentrations (0.16, 0.32, 0.48, 0.64, 0.96, and 1.28 mol/dm^3) of ammonium chloride. The distribution coefficients were determined by the batch technique for finding the conditions for the mentioned separations. The column chromatographic separations achieved were all quantitative. The results of the resolution of the synthetic binary and ternary mixtures along with the elution curves are presented.

A wide variety of anions has been used as eluting agents for the separation of metal ions on ion exchange resins. Chloride ion and acetate ion have been utilized to some extent in both anion and cation exchange. Araki et al. (*1*) separated Ca(II), Sr(II), and Ba(II) on Exchanger 1 (ZrP) using aqueous NH_4Cl, while Qureshi and co-workers (*2*) described the separation of Cd(II) from Zn(II), Ca(II), and Al(III) in NH_4Cl medium. Sitaram and Khopkar (*3*) separated Zn(II) from Cu(II) and Pb(II) on a cation exchange resin using acetic acid and sodium chloride. Kuroda and associates (*4*, *5*) separated uranium from other metal ions in acetic acid medium. Anion exchange studies in buffered aqueous solutions of acetic acid and in acetic acid–organic solvent media (*6*, *7*) were also described.

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In view of the fact that no cation exchange selectivity characteristic scales for cations in acetic acid–ammonium chloride medium are available in the literature, an investigation of the ion-exchange characterization of a large number of cations in ammonium chloride–acetic acid mixtures has been undertaken. The studies include the effect on 21 cations in mixtures of six different concentrations of ammonium chloride and 0.7 mol/dm^3 acetic acid as media.

EXPERIMENTAL

Ion Exchange Resin

Dowex 50W-X8 (H^+ form) 100–200 mesh resin was pretreated in a column successively with 0.02 mol/dm^3 EDTA solution and 2 mol/dm^3 HCl, and washed with water until neutral to litmus. After air drying the resin with suction on a sintered bed, it was stored. The capacity and the moisture content were 3.86 meq/g and ~20%, respectively.

Metal Solutions

Solutions of various metal ions (0.1–0.2 mol/dm^3) were prepared in water from their reagent grade nitrate samples. Solutions of Hg(II) (0.1 mol/dm^3) and Ce(III) (0.06 mol/dm^3) were prepared by dissolving the chlorides in water.

Ammonium Chloride Solution

A stock solution of NH_4Cl (4.0 mol/dm^3) (E. Merck) was prepared in water by direct weighing.

Acetic Acid

A stock solution of 8.0 mol/dm^3 glacial acetic acid (E. Merck) was obtained after standardization.

pH Measurements and Equilibration of the Systems

The solutions were shaken in glass-stoppered 100 cm^3 Pyrex flasks with a wrist motion Microid flask shaker (Griffin and George), and a Philips pH meter was used for pH measurements.

DISTRIBUTION STUDIES

Determination of Distribution Coefficients

For the determination of K by the batch equilibration method, 1 g portions of the resin were shaken for 1 h (it was previously ascertained that this time was adequate for the attainment of equilibrium) with suitable amounts of metal ion solutions containing different concentrations of ammonium chloride and a fixed concentration of acetic acid. The solutions were filtered and analyzed for the total metal contents, irrespective of species, titrimetrically against EDTA. The concentrations of NH_4Cl used were in the range of 0.16 to 1.28 mol/dm^3.

The K values were obtained by

$$K = \frac{\text{mol metal ion per g resin}}{\text{mol metal ion per cm}^3\text{ solution}}$$

The total volume of the aqueous phase was 25 cm^3. The experiments were performed at a room temperature of $30 \pm 2°$.

Preparation and Pretreatment of Resin Bed

The resin bed was prepared by transferring a slurry (~5 g of resin) to the column to obtain a bed 7.5 ± 0.3 cm long. The feed of 25 cm^3 of 0.16 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid was prepared by mixing measured volumes of Hg(II) and one of the other metal ions to be separated. The mixture was passed through the resin at a flow rate of 1.0 ± 0.3 cm^3/min. Hg(II) passed into the effluent, while the other metal ions were sorbed on the resin bed. The effluent was collected in 5 cm^3 fractions.

Chromatographic Separation

The column with the sorbed cations was washed with 40–50 cm^3 of 0.16 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid and the effluent was collected in 5 cm^3 fractions. The total (65–75 cm^3) eluant volume (25 cm^3 feed + 40–50 cm^3 of washing solution) was found to be sufficient for the quantitative recovery of Hg(II). Thereafter Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Al(III), Cr(III), or In(III) were eluted with 1.28 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid. The most strongly retained elements, Y(III), La(III), Ce(III), Pr(III), Gd(III), and Sc(III), were desorbed with 3–4 mol/dm^3 HNO_3.

RESULTS AND DISCUSSION

A decrease in the *K* values was observed with a corresponding increase in the amount of NH_4Cl at a fixed concentration of acetic acid in all the metal ions investigated (Table 1). The major effect resulting from the addition of acetic acid to water, which may affect the adsorbility, is the lowering of the dielectric constant ($E_{H_2O} = 80.3$, $E_{HAc} = 6.2$) which results in an increase of the attractive forces between the ions of unlike charge and therefore favors association or complex formation (*8*). This enhances the decrease in *K* values with an increase of NH_4Cl concentration.

To facilitate a choice of eluting conditions, *K* for a wide range of eluting agent concentrations was determined using mixtures of varying concentrations of NH_4Cl (0.16 to 1.28 mol/dm^3) and 0.7 mol/dm^3 acetic acid.

A remarkable decrease in the distribution coefficient values of Hg(II) in all the media was noted. This anomalous behavior is due to the strong complexing tendency of Hg(II) with acetic acid and with ammonium

TABLE 1

Values of Distribution Coefficients (*K*) in NH_4Cl–0.7 mol/dm^3 CH_3COOH

	Ammonium chloride concentration (mol/dm^3)					
Metal ion	0.16	0.32	0.48	0.64	0.96	1.28
Mg(II)	100.0	80.6	60.2	30.0	10.2	4.3
Ca(II)	132.0	58.3	30.6	25.0	10.2	5.3
Sr(II)	181.2	82.6	52.3	30.5	20.0	11.9
Ba(II)	465.0	138.8	73.0	57.4	25.3	10.0
Mn(II)	191.3	88.0	55.2	38.4	15.1	4.9
Fe(III)	120.3	55.6	30.0	18.3	9.2	2.1
Co(II)	223.6	74.5	30.3	24.7	12.1	4.3
Ni(II)	197.9	62.2	36.9	20.0	13.2	5.9
Cu(II)	140.9	52.7	26.9	16.5	6.07	2.6
Zn(II)	88.6	30.5	16.6	10.8	2.0	0.25
Cd(II)	135.0	99.2	70.0	40.2	15.8	5.0
Hg(II)	0.65	0.35	0.35	0.25	0.25	0.25
Al(III)	612.5	438.2	178.1	137.5	48.5	6.2
La(III)	812.5	812.5	720.0	625.2	285.6	85.5
Ce(III)	1120	980.5	777.0	552.5	325.0	137.5
Cr(III)	320.0	225.0	110.2	57.2	20.0	4.2
In(III)	125.0	85.2	68.7	40.0	20.0	7.1
Y(III)	1600	1176	318.7	295.0	158.3	100.5
Pr(IV)	1475	1320	1275	820.0	625.0	235.0
Gd(III)	1725	1225	587	320.0	281.2	179.1
Sc(III)	1225	1000	585	225.0	153.5	105.2

chloride. At 0.16 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid, Hg(II) can be separated from its binary mixtures with the other metal ions investigated.

At higher concentrations of NH_4Cl (0.96–1.28 mol/dm^3) the K values of La(III), Ce(III), Y(III), Pr(III), Gd(III), and Sc(III) are comparatively higher than those of the other metal ions. These metal ions can hence be separated from their binary mixtures with other metal ions, e.g., In(III), Fe(III), Al(III), and Cr(III).

The values of the separation factors with respect to Hg(II) for all the cations in 0.16 mol/dm^3 NH_4Cl–0.7 mol/dm^3 acetic acid are given in Table 2.

Among the systems where columnar separations were carried out, the conditions predicted from batch experiment data were found to be true. Hg(II)/La(III)/Ce(III)/Y(III)/Pr(III)/Gd(III)/Sc(III) could be separated from other metal ions. The elution characteristics of metal ions are shown in Table 3.

The following general procedure may be employed for these binary separations.

Pass the feed, 0.16 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid containing Hg(II) and one of the other metal ions to be separated, through the

TABLE 2

Separation Factors ($\alpha^{M^{n+}}_{Hg(II)}$) in 0.16 mol/dm^3 NH_4Cl–0.7 mol/dm^3 CH_3COOH

Separated cations	$\alpha^{M^{n+}}_{Hg(II)}$
Mg(II)–Hg(II)	154
Ca(II)–Hg(II)	203
Sr(II)–Hg(II)	278
Ba(II)–Hg(II)	715
Mn(II)–Hg(II)	294
Fe(III)–Hg(II)	185
Co(II)–Hg(II)	344
Ni(II)–Hg(II)	304
Zn(II)–Hg(II)	136
Cu(II)–Hg(II)	217
Cd(II)–Hg(II)	208
Al(III)–Hg(II)	942
La(III)–Hg(II)	1250
Ce(III)–Hg(II)	1723
Cr(III)–Hg(II)	492
In(III)–Hg(II)	192
Y(III)–Hg(II)	2461
Pr(IV)–Hg(II)	2269
Gd(III)–Hg(II)	2654
Sc(III)–Hg(II)	1885

TABLE 3

Elution Characteristics of Metal Ions

Metal ions	BTV[a]	VEP[b]	TEV[c]	Eluting agent
Mg(II)	5	20	90	1.28 mol/dm^3 NH_4Cl–0.7 *M* CH_3COOH
Ca(II)	10	40	85	"
Sr(II)	5	25	100	"
Ba(II)	10	35	95	"
Mn(II)	5	15	75	"
Fe(III)	5	20	80	"
Co(II)	5	20	80	"
Ni(II)	5	20	90	"
Cu(II)	5	30	80	"
Zn(II)	5	15	75	"
Cd(II)	5	15	60	"
Hg(II)	5	15	65	0.16 mol/dm^3 NH_4Cl–0.7 *M* CH_3COOH
Al(III)	5	30	70	1.28 mol/dm^3 NH_4Cl–0.7 *M* CH_3COOH
La(III)	150	—	—	"
Ce(III)	150	—	—	"
Cr(III)	5	15	60	"
In(III)	10	35	70	"
Y(III)	100	—	—	"
Pr(IV)	200	—	—	"
Gd(III)	200	—	—	"
Sc(III)	200	—	—	"

[a]Breakthrough volume.
[b]Volume elution peak.
[c]Total elution volume.

column pretreated with 0.16 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid. Hg(II) accompanies the feed effluent and may subsequently be eluted by continuing the elution with 0.16 mol/dm^3 NH_4Cl, whereas other metal ions, except La(III), Ce(III), Y(III), Pr(III), Gd(III), and Sc(III), are retained on the resin and stripped off by eluting with 1.28 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid.

Since La(III), Ce(III), Y(III), Pr(III), Gd(III), and Sc(III) have higher K values at a higher concentration (1.28 mol/dm^3) of NH_4Cl, their separation from other cations may also be achieved at this concentration of NH_4Cl. For their separation, on passing the feed of 1.28 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid, the other metal ions [Mg(II), Ca(II), Sr(II), Ba(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Al(III), Cr(III), and In(III)] accompanied the feed effluent and were eluted by continuing the elution with 1.28 mol/dm^3 NH_4Cl in 0.7 mol/dm^3 acetic acid. The strongly retained La(III), Ce(III), Y(III), Pr(III), Gd(III), and Sc(III) were stripped off by eluting with 3 mol/dm^3 HNO_3.

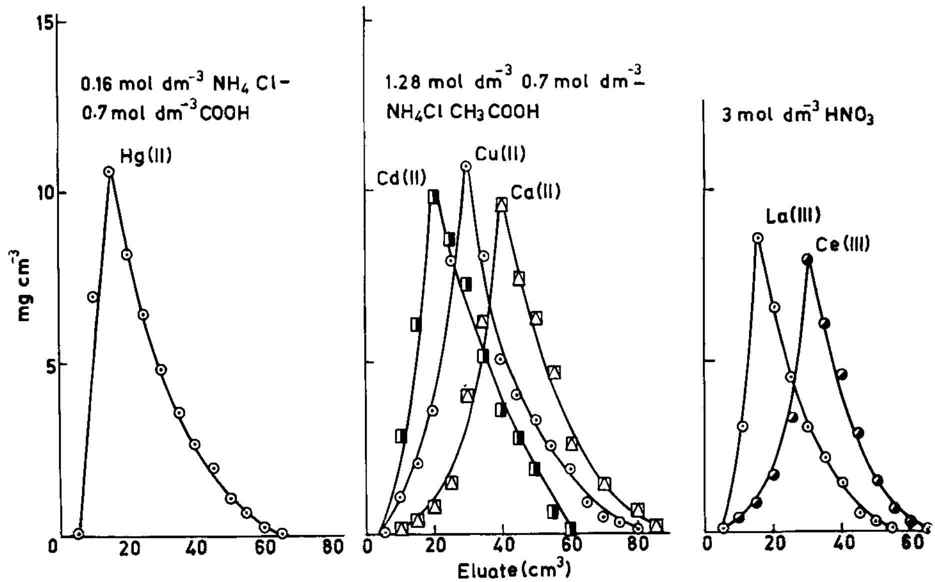

FIG. 1. Elution curves of Hg(II)–Ca(II)/Cu(II)/Cd(II)–La(III)/Ce(III).

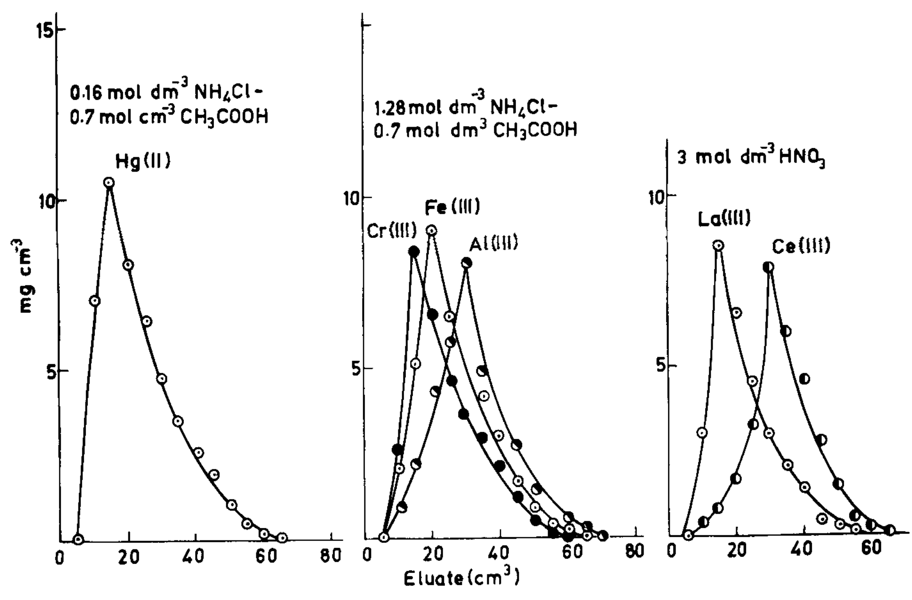

Fig. 2. Elution curves of Hg(II)–Fe(III)/Al(III)/Cr(III)–La(III)/Ce(III).

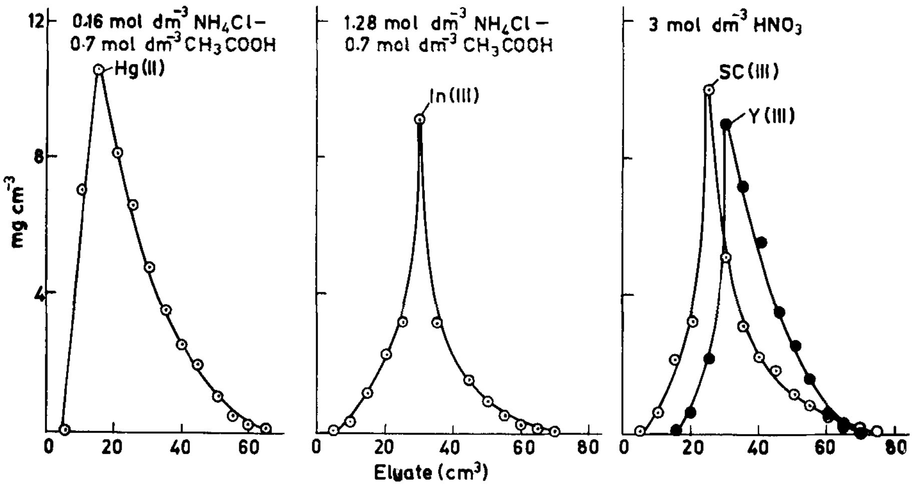

FIG. 3. Elution curves of Hg(II)–In(III)–Y(III)/Sc(III).

TABLE 4

Quantitative Separation of Synthetic Mixtures

Taken (mg)				Found (mg)		
Hg(II)	Ce(III)	Other elements		Ce(III)	Hg(II)	Other elements
94.23	62.50	Cu(II)	32.06	62.90	94.20	32.35
94.23	62.50	Cd(II)	53.95	62.65	94.35	54.05
94.23	62.50	Ca(II)	17.80	62.50	94.23	17.72
94.23	62.50	Fe(III)	27.90	62.55	94.30	27.95
94.23	62.50	Al(III)	13.45	62.95	94.00	13.60
94.23	62.50	Cr(III)	25.16	62.92	93.95	25.25
Hg(II)	La(III)	Other elements		Hg(II)	La(III)	Other elements
94.35	58.87	Cu(II)	32.06	94.25	58.95	32.25
94.35	58.87	Cd(II)	53.90	94.40	58.85	53.97
94.35	58.87	Cd(II)	17.80	94.30	58.90	17.92
94.35	58.87	Fe(III)	26.70	94.38	58.82	26.82
94.35	58.87	Al(III)	13.45	94.35	58.92	13.52
94.35	58.87	Cr(III)	26.23	94.40	58.94	26.38
Hg(II)	In(III)	Other elements		Hg(II)	In(III)	Other elements
95.25	37.52	Sc(III)	20.82	95.30	38.09	Sc(III) 20.93
95.25	37.52	Y(III)	42.60	95.28	37.83	Y(III) 43.15

In the present studies (Figs. 1–3) the column chromatographic experiments have also revealed the feasibility of a number of ternary separations, since breakthrough of La(III), Ce(III), Y(III), Pr(IV), Gd(III), and Sc(III) was not reached until after the passage of about 150 cm^3 of NH_4Cl. This volume of NH_4Cl is sufficient to complete the elution of the other metal ions. After the complete elution of the other ions as described above, these ions can be stripped off with mineral acids. The results are presented in Table 4.

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