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Elution Behavior of Metal Ions with Mixed Glycine–Nitric Acid Eluents in Dowex 50W-X8 Column: Separation of Th(IV), Ce(IV), Bi(III), Fe(III), and Al(III)

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Abstract

Distribution coefficients (*K*) determined by the batch technique in acidic glycine media using Dowex 50W-X8 cation exchanger (H^+-form, 100–200 mesh size) revealed that this medium can effectively be employed to separate a number of tetravalent and trivalent metal ions from bivalent metal ions. In fixed glycine (0.40 *M*) and varying concentration of nitric acid (0.10 to 1.0 *M*), a number of mixtures containing two or three metal ions were resolved on columns using about 8 g of exchanger. In 0.40 *M* glycine–1.0 *M* HNO_3 medium, Th(IV)/Ce(IV) were separated from Al(III)/Fe(III)/Bi(III)/Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Hg(II)/Pb(II)/Ag(I) and also Al(III)/Bi(III) from a number of divalent metal ions. In 0.40 *M* glycine–0.50 *M* HNO_3 medium, the resolution of following ternary mixtures were also achieved: Th(IV)/Ce(IV)–Al(III)/Bi(III)–Fe(III)/Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Hg(II)/Pb(II)/Ag(I). Th(IV)/Al(III)/Fe(III)/Bi(III) were also separated from other divalent metal ions in 1.60 *M* glycine–0.50 *M* HNO_3 medium. The values of *K*, elution characteristics of metal ions, elution curves, and the results of the resolution of a number of mixtures of metal ions along with standard deviations are reported.

INTRODUCTION

Aminoacetic acid (glycine) offers an effective medium for achieving separation of metal ions in chromatography (*1*–*5*). Chelating exchanger was employed by Hering (*6*) to study the separation possibilities of Fe(III). Co, Ni, Cu(II), Zn, Ca, Hg, and K ions in glycine medium, while Winget (*7*) used

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it for the separation of rare earths at high temperature. The majority of works reporting the use of glycine (*8–10*) are limited in their scope and deal with a few elements. This called for a detailed and systematic study, and this work is an attempt toward that end. The following metal ions were examined individually by the batch technique: Al(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Pb(II), Bi(III), Ce(IV), Th(IV), and UO_2(VI) in HNO_3–glycine media.

The H^+-form of the cation exchanger Dowex 50W-X8, 100–200 mesh size, was employed. The following separations were achieved by column chromatography under the conditions and eluents predicted from batch experimentation data: Th(IV)/Ce(IV) was separated from binary mixtures with Co(II)/Ni(II)/Cu(II)/Zn(II)/Ag(I)/Cd(II)/Hg(II)/Pb(II)/Al(III)/Fe(III)/Bi(III) in 0.40 *M* glycine–1.0 *M* HNO_3 medium, Al(III)/Bi(III) from Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Ag(I)/Hg(II)/Pb(II)/Fe(III) in 0.40 *M* glycine–0.50 *M* HNO_3 medium, and Th(IV)/Al(III)/Bi(III)/Fe(III) from Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Ag(I)/Hg(II) in 1.60 *M* glycine–0.50 *M* HNO_3 medium.

Ternary mixtures, Th(IV)/Ce(IV)–Al(III)/Bi(III)/Fe(III)/–Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Ag(I)/Hg(II)/Pb(II), could be separated in 0.40 *M* glycine–0.50 *M* HNO_3 medium.

EXPERIMENTAL

Materials

Ion-Exchange Resin. Dowex 50W-X8 of 100–200 mesh size in the H^+-form was employed for the batch and columnar studies. The capacity and water content of the resin were 3.36 meq/g and ~ 12%, respectively.

Metal Ion Solutions. Standard 0.06 to 0.20 *M* stock solutions of Al(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II), Hg(II), Bi(III), Ce(IV), Th(IV), and UO_2(VI) nitrates (reagent grade) in nitric acid were used.

Glycine. Standard 2.0 *M* stock solution of glycine (E. Merck, G.R.) was prepared in water.

Nitric Acid. Standard 5.0 *M* stock solution of HNO_3 was prepared in water.

Eluting Agents:

(a) 1.0 *M* HNO_3–0.40 *M* glycine mixture
(b) 0.50 *M* HNO_3–0.40 *M* glycine mixture
(c) 0.50 *M* HNO_3–1.60 *M* glycine mixture
(d) 2.5 and 6.0 *M* HNO_3
(e) 2.5 *M* HCl

All experiments were carried out at a room temperature maintained at 30 ± 2°C.

Procedure

Distribution Studies. The distribution coefficients of individual metal ions were determined by the batch equilibration technique.

Two sets of experiments were carried out:

(a) Glycine was fixed at 0.40 *M* and nitric acid concentration was varied from 0.10 to 1.0 *M*
(b) Glycine was varied from 0.04 to 1.60 *M* and nitric acid concentration was fixed at 0.50 *M*

One gram (air dried) of the conditioned resin (H^+-form) was added to a flask containing the required amounts of metal ion, nitric acid, and glycine. To ensure complete equilibration, the metal ions were kept to about 30% of the total exchange capacity of the resin. The flask containing metal ion, acid, and glycine (total volume 25 mL) was shaken for 1 h and the metal content was determined in the aqueous phase by complexometry [except for UO_2(VI) which was determined gravimetrically as oxinate] (*11–13*).

Distribution coefficients (K) = meg metal ion per g resin/meg metal ion per mL of solution

The relative experimental error in the determination of the K values was between ±2 and ±5%. The values of K are shown in Tables 1 and 2.

On Column Separation

Preparation of Resin Column and Its Preconditioning. A slurry of well-washed and purified cation exchanger was made in deionized water and transferred to a clean graduated chromatographic column (about 65 cm length and 0.85 cm bore). The height of the resin bed was about 8.0 cm. The bed was treated with 0.50 *M* HNO_3–0.40 *M* glycine or 1.0 *M* HNO_3–0.40 *M* glycine mixture, as needed.

Preparation of Feed. For the separation of Ce(IV) or Th(IV) from other metal ions, the feed was prepared in 1.0 *M* HNO_3–0.40 *M* glycine mixture by mixing aliquots of the metal ion solutions to be separated. For separating Al(III) or Bi(III) from other metal ions [except Ce(IV) or Th(IV)] and for ternary separations, the feed was prepared in 0.50 *M* HNO_3–0.40 *M* glycine mixture. The feed was prepared in duplicate in 25 mL.

Sorption of Feed. Feed was passed through the preconditioned resin

TABLE 1

Distribution Coefficients in Varying (0.10 to 1.00 *M*) Nitric Acid at Fixed (0.40 *M*) Glycine Concentration

	Concentration of nitric acid (*M*)					
Metal ion	0.00	0.10	0.30	0.50	0.80	1.00
pH	6.21	2.77	1.79	0.86	0.45	0.26
Al(III)	[a]	[a]	292.0	107.0	39.0	33.1
Fe(III)	—	471.0	52.0	27.6	18.2	14.0
Co(II)	1560	174.0	46.3	27.0	15.2	11.0
Ni(II)	1790	198.0	46.7	27.0	14.8	11.6
Cu(II)	235.0	101.0	40.8	23.3	12.7	9.0
Zn(II)	1170	184.0	41.9	23.6	13.3	9.8
Ag(I)	—	43.5	19.7	13.8	9.3	6.7
Cd(II)	2030	191.0	45.0	23.8	11.0	10.5
Hg(II)	—	268.0	161.0	59.2	18.8	10.8
Pb(II)	1680	183.0	38.3	17.9	9.4	7.9
Bi(III)	[a]	[a]	8059	150.0	41.2	35.5
Ce(IV)	[b]	[b]	[b]	[b]	201.0	88.1
Th(IV)	8.3	116.0	[a]	[a]	2090	1030
U(VI)	—	2950	40.5	28.7	11.9	15.4

[a] Very high value.

[b] Precipitation.

TABLE 2

Distribution Coefficients in Varying (0.04–1.60 *M*) Glycine at Fixed (0.50 *M*) Nitric Acid Concentration

	Concentration of glycine (*M*)						
Metal ion	0.04	0.12	0.28	0.40	0.64	1.00	1.60
pH	0.40	0.45	0.58	0.77	1.60	2.24	2.65
Al(III)	201.0	121.0	—	107.0	69.3	73.8	112.0
Fe(III)	259.0	65.2	29.2	27.5	33.4	143.0	259.0
Co(II)	35.5	32.2	29.6	27.1	20.7	19.0	23.8
Ni(II)	40.0	36.0	29.0	27.4	19.0	20.7	23.7
Cu(II)	34.5	33.1	26.7	23.3	18.6	17.2	10.4
Zn(II)	33.9	33.1	26.7	23.3	18.0	17.5	21.7
Ag(I)	15.7	—	14.4	13.5	12.6	12.6	14.7
Cd(II)	36.0	32.8	29.1	24.0	20.1	11.6	14.1
Hg(II)	30.7	—	48.1	59.2	67.9	35.9	22.2
Bi(III)	284.0	209.0	179.0	150.0	126.0	117.0	135.0
Th(IV)	[a]	[a]	[a]	[a]	[a]	[a]	[a]
U(VI)	32.0	29.3	27.3	—	23.5	22.2	41.3

[a] Very high value.

bed at a flow rate of 1.5 ± 0.5 mL/min and the feed effluent was collected in 5 mL fractions from the beginning of the sorption step.

Elution. After sorption the elution was done by different eluting agents to achieve quantitative separations.

RESULTS

Fixed Glycine (0.40 *M*)-Varying Acid (0.10–1.0 *M*) System

The affinity of cation exchanger in the H^+-form is more for the metal ions than when it is in the Na^+-form, as seen from the higher K values. In general, the K value decreases with increasing HNO_3 concentration (0.10–1.0 *M*). At 1.0 *M* HNO_3 the K values are only slightly lower than those obtained with 1.0 *M* HNO_3 alone (*14*), indicating that the decreases in K values are largely due to the effect of nitric acid rather than of glycine. Ce(IV) and Th(IV) have the highest K values with mixtures using 1.0 *M* HNO_3, probably due to weak complexation and a higher charge on the metal ion. The K values show that the order of sorption is M(IV) > M(III) > M(II) > M(I).

On the basis of the results of Tables 1 and 2, some separation possibilities are indicated and columnar separations were worked out. For the resolution of the binary mixtures containing Ce(IV)/Th(IV) and one of the other metal ions, the breakthrough of weakly held Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), Hg(II), Pb(II), Bi(III), or Al(III) was early. These were therefore eluted with 1.0 *M* HNO_3–0.40 *M* glycine mixture eluent and were completely recovered with about 100 mL of eluent [except Al(III) and Bi(III) which required 135 mL]. The elution characteristics of individual metal ions are reported in Table 3. The breakthrough of strongly retained Ce(IV) or Th(IV) was not observed even after passing 150 or 200 mL of the same eluent, and therefore they were stripped off with 70 mL of 2.5 *M* HCl and 70 mL of 6.0 *M* HNO_3, respectively. The results of binary separations along with the values of standard deviations are reported in Table 4. Only some of the typical separations are shown in Fig. 1.

For separating binary mixtures containing Al(III) or Bi(III) and one of the other metal ions, the breakthrough of strongly retained Al(III) or Bi(III) was not observed by passing about 150 mL of the eluent 0.50 *M* HNO_3–0.40 *M* glycine mixture whereas other metal ions were quantitatively recovered with less than 150 mL of the same eluent (Table 3). Al(III) and Bi(III) were finally eluted with about 140 mL of 1.0 *M* HNO_3–0.40 *M* glycine mixture.

In the resolution of ternary mixture, Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), Hg(II), or Pb(II) was first eluted with 0.50 *M* HNO_3–0.40 glycine mixture eluent. The second step was the elution of Al(III) or

TABLE 3

Elution Behavior of Metal Ions on Dowex 50W-X8 (H^+-form, 100–200 mesh) Using 0.40 *M* Glycine–1.0 *M* HNO_3 and 0.40 *M* Glycine–0.50 *M* HNO_3 as Eluents[a]

	0.40 *M* Glycine–1.0 *M* HNO_3			0.40 *M* Glycine–0.50 *M* HNO_3		
Metal ions	BTV (mL)	VEP (mL)	TEV (mL)	BTV (mL)	VEP (mL)	TEV (mL)
Ag(I)	4	15	55	10	45	100
Co(II)	4	20	90	10	60	140
Ni(II)	4	25	90	10	65	140
Cu(II)	4	15	80	10	40	130
Zn(II)	4	15	90	10	35	140
Cd(II)	3	20	75	10	45	125
Hg(II)	4	15	80	—	—	—
Pb(II)	4	10	95	10	25	140
Fe(III)	4	15	75	10	35	125
Al(III)	25	65	135	>150	—	—
Bi(III)	28	70	135	>150	—	—
Ce(IV)	>150	—	—	—	—	—
Th(IV)	>200	—	—	>150	—	—

[a] BTV = breakthrough volume. VEP = volume elution peak. TEV = terminal elution volume.

TABLE 4

Results of the Separation of Th(IV)/Ce(IV)/Al(III)/Bi(III) from Fe(III)/Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Hg(II)/Pb(II)/Ag(I) in Fixed Glycine (0.40 *M*)–Varying Nitric Acid (0.10–1.0 *M*) Media[a]

			Found	
Metal ion	Taken (mg)	N	mg ($\bar{x}$)	σ
Fe(III)	18.60	8	19.00	0.15
Co(II)	29.76	8	29.40	0.10
Ni(II)	29.53	8	29.50	0.14
Cu(II)	32.09	10	32.20	0.12
Zn(II)	32.89	8	32.80	0.08
Cd(II)	56.77	8	56.60	0.08
Hg(II)	100.90	12	103.50	0.13
Pb(II)	104.60	12	105.40	0.09
Ag(I)	56.63	12	56.70	0.15
Al(III)	8.50	24	8.63	0.12
Bi(III)	67.93	30	69.18	0.08
Ce(IV)	35.73	30	36.01	0.10
Th(IV)	60.33	30	61.00	0.14

[a] $\bar{x}$ = mean, N = number of determinations. σ = standard deviation.

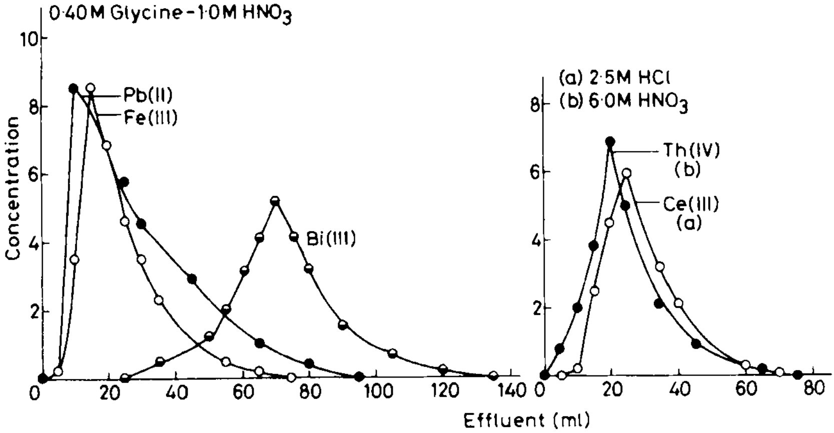

FIG. 1. Elution curves of Pb(II)/Bi(III)/Fe(III) and Th(IV)/Ce(IV). The concentration is represented in terms of milliliters of 0.01 *M* EDTA.

Bi(III) with 1.0 *M* HNO_3–0.40 *M* glycine and finally very strongly held Ce(IV) or Th(IV) was desorbed as described earlier.

Fixed Nitric Acid (0.50 *M*)-Varying Glycine (0.04–1.60 *M*) System

At fixed 0.50 *M* HNO_3, the *K* values decrease with increasing the glycine concentration from 0.04 to 1.00 *M*, but a slight decrease in the *K* values has been observed at 1.60 *M* glycine in the case of bivalent metal ions except those of Cu(II) and Hg(II). In the case of Cu(II), the *K* values continuously decrease, but in the case of Hg(II) the *K* increased from 0.04 to 0.64 *M* glycine and then started decreasing from 1.00 to 1.60 *M* glycine. The trend of *K* values is highest for tetravalent Th(IV) as described earlier.

For the separation of Th(IV) from Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), or Hg(II), feed was prepared in a 1.60 *M* glycine–0.50 *M* HNO_3 mixture by mixing known amounts of Th(IV) and one of the other metal ions. The breakthrough of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), or Hg(II) was early, and these could be quantitatively recovered with less than 150 mL of 1.60 *M* glycine–0.50 *M* HNO_3 mixture eluent. The elution behavior of these ions is reported in Table 5. Th(IV) was strongly held by the resin and had to be finally eluted with 80 mL of 6 *M* HNO_3. The results are reported in Table 6.

The separation of Al(III), Fe(III), or Bi(III) from other metal ions [except

TABLE 5

Elution Behavior of Metal Ions on Dowex 50W-X8 (H^+-form, 100–200 mesh) Using 1.60 *M* Glycine–0.50 *M* HNO_3 as Eluent[a]

Metal ion	BTV (mL)	VEP (mL)	TEV (mL)
Ag(I)	15	40	75
Co(II)	25	60	125
Ni(II)	25	60	125
Cu(II)	18	60	130
Zn(II)	13	40	125
Cd(II)	20	50	130
Hg(II)	15	40	105
Al(III)	>150	—	—
Fe(III)	>150	—	—
Bi(III)	>150	—	—
Th(IV)	>200	—	—

[a] BTV = breakthrough volume. VEP = volume elution peak. TEV = terminal elution volume.

TABLE 6

Results of the Separation of Th(IV)/Bi(III)/Fe(III)/Al(III) from Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II)/Hg(II)/Ag(I) in Fixed Nitric Acid (0.50 M)- Varying Glycine (0.04–1.60 *M* Media[a]

			Found	
Metal ion	Taken (mg)	*N*	mg ($\bar{x}$)	σ
Co(II)	29.65	8	30.00	0.10
Ni(II)	29.65	8	30.06	0.12
Cu(II)	31.96	12	32.20	0.15
Zn(II)	32.69	8	33.00	0.08
Cd(II)	56.54	10	56.92	0.14
Hg(II)	101.31	12	102.50	0.15
Ag(I)	56.63	12	56.10	0.13
Al(III)	8.77	14	8.90	0.10
Fe(III)	19.00	16	18.90	0.06
Bi(III)	63.75	16	63.98	0.12
Th(IV)	58.01	20	58.50	0.14

[a] $\bar{x}$ = mean. *N* = number of determinations. σ = standard deviation.

Th(IV)] was achieved in 1.60 M glycine–0.50 M HNO_3. The weakly held metal ions show almost the same elution behavior as in Table 5. The strongly sorbed Al(III), Fe(III), or Bi(III) was eluted in the end with 2.5 M HNO_3.

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