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Ion-Exchange Behavior of Mercury(II) in Mixed Solvents: Separation from Zinc(II), Cadmium(II), Gold(III), and Thallium(III)

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Abstract

Distribution coefficients of Zn(II), Cd(II), Au(III), Hg(II), Tl(I), and Tl(III) between cation- and anion-exchangers Amberlite IR-120 and Amberlite IR-400, and aqueous solutions containing nitric or hydrochloric acid and organic solvents have been determined. The organic solvents were methanol, acetone, and tetrahydrofuran. The separation of Hg(II) from Zn(II), Cd(II), Au(III), and Tl(III) has been proposed in mixed solvents with high separation factors. Some of these separations have been actually performed using column method.

INTRODUCTION

Mercury is one of the serious pollutants of the biosphere and therefore a growing concern is being shown in the determination of its concentration in different edibles (*1, 2*) and biological samples (*3–5*). Neutron activation analysis is a potential technique for the determination of mercury at these concentration levels. Ion-exchange chromatography provides an effective and quick method for the separation of mercury activity. The cation- and anion-exchange behavior of Hg(II) in different aqueous media has been reported (*6–10*). But no systematic studies have been made on the behavior of Hg(II) in mixed solvents which in turn may provide high separation factors for its separation from Zn(II), Cd(II), Au(III), and Tl(III). The separation of Hg(II) from Zn(II) and Cd(II) is of great analytical interest as they are members of the same subgroup of the periodic table. The separation of Hg(II) from Au(III) and Tl(III) is of significance from the nuclear reaction point of view. Moreover, these separations are difficult to attain in aqueous media.

Some work (*11–13*) has already been done on the separation of Hg(II) from Zn(II) and Cd(II) in mixed solvents. But these separations can be proposed with much higher separation factors in the mixed solvents investigated by us. There is very little information (*14*) existing on the separation of Hg(II) from Au(III) and Tl(III) in mixed solvents.

The present investigation deals with the cation- and anion-exchange behavior of Zn(II), Cd(II), Au(III), Hg(II), Tl(I), and Tl(III) in a mixture of HCl or HNO_3 and methanol, acetone, or tetrahydrofuran at constant 0.6 M acid strength. Our data for Zn(II) and Cd(II) on Amberlite IR-120 is in good agreement with that of Korkisch (*15*, *16*) on Dowex-50. The separations of mercury have been proposed under the condition where the separation factor is comparatively higher. Some of these separations where the separation factor is of the order of 10^3 or greater have been actually performed using a column of 14 × 1 cm with flow rate of 1.0 ml/min.

EXPERIMENTAL

Reagents

Ion-Exchange Resins. The air-dried strongly acidic and basic, cation- and anion-exchangers, Amberlite IR-120 (20–50 mesh, hydrogen form) and Amberlite IR-400 (20–50 mesh, chloride or nitrate forms) were used for the batch and column experiments.

^{65}Zn, ^{115m}Cd, ^{198}Au, ^{203}Hg, and ^{204}Tl isotopes supplied by Bhabha Atomic Research Centre, Bombay, India, were used in suitable forms to find the distribution coefficient. The behavior of Au(III) shown in these studies is that of $(AuCl_4)^-$.

All other reagents used were of analytical grade.

Determination of Various Elements

In the case of ^{65}Zn, ^{198}Au, and ^{203}Hg, liquid counting was done on a flat 25 × 25 mm NaI(Tl) scintillation counter. An additional assembly was mounted on the crystal head to hold the beakers in a reproducible geometry. ^{115m}Cd and ^{204}Tl were counted as solid samples on a G.M. counter. The reproducibility of the counting set-up was checked in all cases.

Determination of Distribution Coefficients

The weight distribution coefficient is defined by the equation:

$$Kd = \frac{\text{Activity in 1 g of resin}}{\text{Activity in 1 ml of solution}}$$

The distribution coefficients of the different elements were determined by the batch method. Each equilibrium experiment was performed with either 20 ml of pure aqueous solution of HNO_3/HCl with varying molarity or of a mixture consisting of 0–90% of the organic solvent, 10% 6 *M* hydrochloric acid or nitric acid, containing 0.05 ml of the tracer of the element in question. To this mixture 1 g of dried resin was added and the solution was agitated on a shaking machine for 4 hr. The resin was filtered off and the activity in the filtrate was counted. The distribution coefficients were determined in duplicate and the average values are reported. The values of distribution coefficient show a precision of ±7 and ±13% for *Kd* values around 10 and 100, respectively.

RESULTS AND DISCUSSION

The results of distribution coefficients of all the metal ions are given in Tables 1–16. In Tables 1–4, distribution coefficients are given in pure aqueous media with hydrochloric acid or nitric acid. The distribution coefficient values in mixed solvents are reported in Tables 5–16. The points of separation of mercury from other elements with high separation factors are listed in Table 17. Those marked with an asterisk have been actually performed (Figs. 1–4).

Ion-Exchange Behavior of Zn(II), Cd(II), Au(III), Hg(II), Tl(III), and Tl(I)

HCl–Cation-Exchanger. As expected, Au(III), Hg(II), and Tl(III) show a negligible adsorption in pure acid medium over the entire molarity range investigated. The addition of THF or acetone to the acid solution causes insignificant changes in the distribution coefficients of these three elements. But in methanol, Au(III) and Hg(II) show a maxima and

TABLE 1

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of HCl

Ion	HCl concentration (*M*)			
	0.1	0.6	1.0	4.0
Zn(II)	925	45	13	3.2
Cd(II)	295	8.2	2.1	0.6
Au(III)	0.2	0.5	0.6	0.7
Hg(II)	0.1	1.2	0.9	0.4
Tl(III)	3.5	6.0	2.4	1.4
Tl(I)	347	33	8.0	1.8

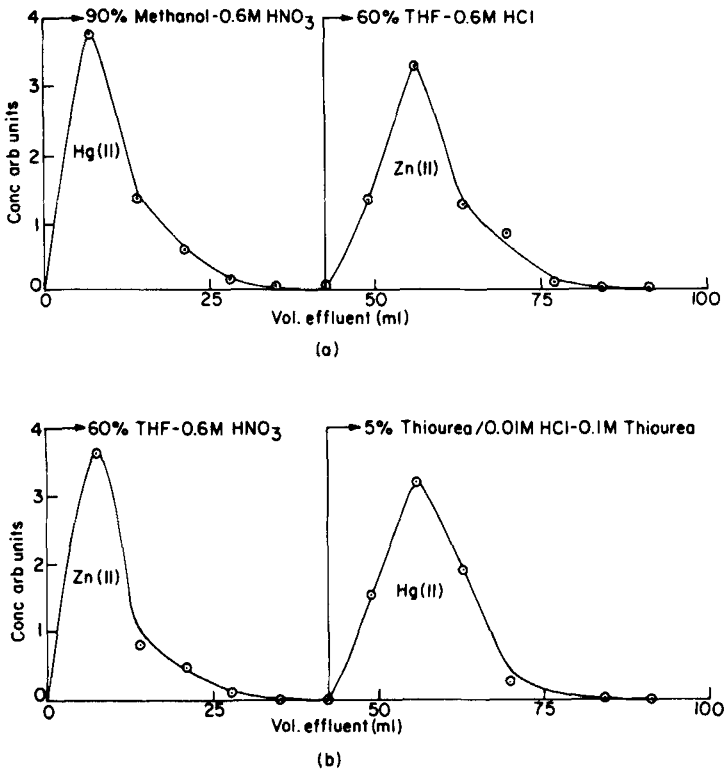

FIG. 1. Separation of mercury(II) from zinc(II): (a) Amberlite-120 (H^+), (b) Amberlite-400 (NO_3^-).

TABLE 2

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of HCl

Ion	HCl concentration (M)			
	0.1	0.6	1.0	4.0
Zn(II)	75	138	2021	2251
Cd(II)	692	1810	2502	3257
Au(III)	5257	5232	6721	6822
Hg(II)	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Tl(III)	166	221	$>10^4$	$>10^4$
Tl(I)	4.1	40	112	1921

TABLE 3

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of HNO_3

Ion	HNO_3 concentration (M)			
	0.1	0.6	1.0	4.0
Zn(II)	8571	40	21	8.2
Cd(II)	6411	43	21	9.1
Au(III)	61	61	23	20
Hg(II)	482	24	22	15
Tl(III)	342	30	32	3.2
Tl(I)	346	56	13	10

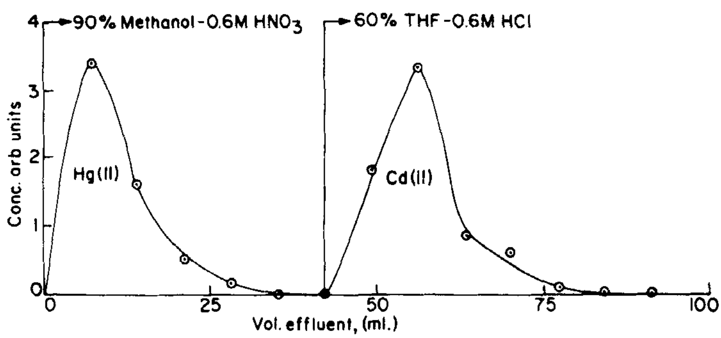

FIG. 2. Separation of mercury(II) from cadmium(II), Amberlite-120 (H^+).

TABLE 4

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of HNO_3

Ion	HNO_3 concentration (*M*)			
	0.1	0.6	1.0	4.0
Zn(II)	10	10	11	12
Cd(II)	0.8	0.8	0.9	0.9
Au(III)	646	601	600	582
Hg(II)	114	43	35	35
Tl(III)	86	82	84	79
Tl(I)	0.9	2.1	9.2	22

TABLE 5

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of THF in 0.6 *M* HCl

Ion	THF concentration (%)					
	0	20	40	60	80	90
Zn(II)	45	31	10	3.1	1.1	1.1
Cd(II)	8.2	2.1	0.9	0.7	0.8	0.5
Au(III)	0.5	4.1	3.1	0.9	0.8	0.6
Hg(II)	1.2	1.1	1.4	0.9	2.1	0.9
Tl(III)	6.0	4.1	2.1	1.3	1.3	1.5
Tl(I)	33	19	13	1.2	3.2	0.9

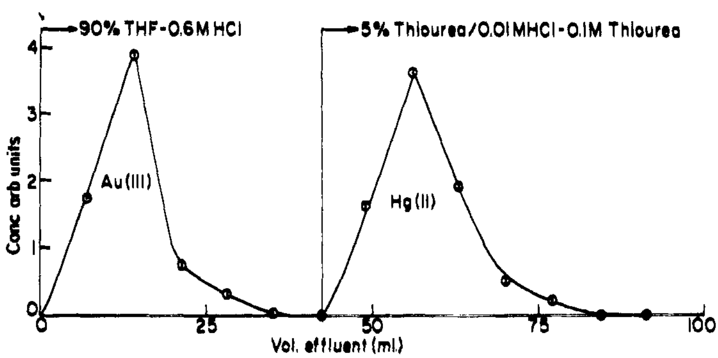

FIG. 3. Separation of mercury(II) from gold(III), Amberlite-400 (Cl^-).

TABLE 6

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of THF in 0.6 *M* HCl

Ion	THF concentration (%)					
	0	20	40	60	80	90
Zn(II)	138	514	872	356	170	171
Cd(II)	1810	1932	4567	1025	975	703
Au(III)	5232	4308	241	2.6	2.0	0.1
Hg(II)	$>10^4$	370	368	282	201	200
Tl(III)	221	183	107	51	0.1	0.1
Tl(I)	40	141	328	421	0.2	0.2

TABLE 7

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of Acetone in 0.6 *M* HCl

Ion	Acetone concentration (%)					
	0	20	40	60	80	90
Zn(II)	45	37	2.2	1.1	0.9	0.8
Cd(II)	8.2	2.4	2.2	1.7	1.5	1.2
Au(III)	0.5	3.1	1.1	0.9	0.8	0.8
Hg(II)	1.2	1.1	1.2	0.9	0.8	0.7
Tl(III)	6.0	5.8	5.9	3.9	2.4	1.2
Tl(I)	33	40	45	43	31	5.7

TABLE 8

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of Acetone in 0.6 *M* HCl

Ion	Acetone concentration (%)					
	0	20	40	60	80	90
Zn(II)	138	691	693	571	343	232
Cd(II)	1810	1841	1945	747	517	241
Au(III)	5232	421	418	200	69	42
Hg(II)	$>10^4$	962	460	432	421	187
Tl(III)	221	1.1	1.2	1.1	1.2	0.9
Tl(I)	40	4.1	2.8	1.1	32	42

TABLE 9

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of Methanol in 0.6 *M* HCl

Ion	Methanol concentration (%)					
	0	20	40	60	80	90
Zn(II)	45	35	30	9.1	0.9	0.8
Cd(II)	8.2	7.1	6.1	6.2	3.1	2.9
Au(III)	0.5	19	29	18	10	2.9
Hg(II)	1.2	21	90	51	19	0.2
Tl(III)	6.0	119	207	257	952	959
Tl(I)	33	38	72	35	27	7.1

TABLE 10

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of Methanol in 0.6 *M* HCl

Ion	Methanol concentration (%)					
	0	20	40	60	80	90
Zn(II)	138	620	656	858	933	939
Cd(II)	1810	1901	9345	9421	9621	9677
Au(III)	5232	362	27	25	13	11
Hg(II)	$>10^4$	238	41	34	71	80
Tl(III)	221	219	207	257	952	960
Tl(I)	40	102	407	1121	1223	1224

TABLE 11

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of THF in 0.6 *M* HNO_3

Ion	THF concentration (%)					
	0	20	40	60	80	90
Zn(II)	40	49	142	675	955	1122
Cd(II)	43	49	172	881	1225	6421
Au(III)	61	24	20	20	20	18
Hg(II)	24	8.1	3.2	4.3	4.1	4.2
Tl(III)	20	58	122	170	263	321
Tl(I)	56	61	90	96	96	113

TABLE 12

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of THF in 0.6 *M* HNO_3

Ion	THF concentration (%)					
	0	20	40	60	80	90
Zn(II)	10	1.0	0.8	0.1	3	2.1
Cd(II)	0.8	4.2	9.1	14	29	25
Au(III)	601	101	119	132	133	142
Hg(II)	43	44	82	89	104	135
Tl(III)	82	86	89	91	85	83
Tl(I)	2.1	0.8	0.6	0.6	0.4	0.3

TABLE 13

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of Acetone in 0.6 *M* HNO_3

Ion	Acetone concentration (%)					
	0	20	40	60	80	90
Zn(II)	40	71	134	401	993	1621
Cd(II)	43	80	161	551	1951	4213
Au(III)	61	25	22	22	22	20
Hg(II)	24	30	35	38	51	96
Tl(III)	20	30	35	42	50	96
Tl(I)	56	60	241	423	441	908

TABLE 14

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of Acetone in 0.6 *M* HNO_3

Ion	Acetone concentration (%)					
	0	20	40	60	80	90
Zn(II)	10	1.1	1.0	0.9	6.2	5.6
Cd(II)	0.8	2.2	5.1	3.8	12	23
Au(III)	601	101	119	122	125	130
Hg(II)	43	106	180	180	204	801
Tl(III)	82	84	86	91	88	83
Tl(I)	2.1	3.1	2.3	8.1	8.2	8.4

TABLE 15

Variation of Cation-Exchange Distribution Coefficients with Changing Concentration of Methanol in 0.6 *M* HNO_3

Ion	Methanol concentration (%)					
	0	20	40	60	80	90
Zn(II)	40	64	66	131	299	601
Cd(II)	43	55	96	217	397	721
Au(III)	61	31	21	19	13	6.2
Hg(II)	24	24	90	51	19	0.2
Tl(III)	20	31	41	78	147	89
Tl(I)	56	54	66	121	180	327

Tl(III) shows a continuous increase with increasing methanol content. Zn(II), Cd(II), and Tl(I) show increases in adsorption with decreasing acid concentration. The addition of organic content causes decreases in the *Kd* values of Zn(II) and Cd(II) but a maxima is obtained in 40% methanol or acetone in the case of Tl(I).

HCl–Anion-Exchanger. Au(III), Hg(II), and Tl(III) are strongly adsorbed at the entire molarity range of the acid investigated, and with

TABLE 16

Variation of Anion-Exchange Distribution Coefficients with Changing Concentration of Methanol in 0.6 *M* HNO_3

Ion	Methanol concentration (%)					
	0	20	40	60	80	90
Zn(II)	10	1.8	3.1	3.4	4.2	4.5
Cd(II)	0.8	1.0	0.9	0.6	0.7	25
Au(III)	601	69	92	99	98	98
Hg(II)	43	48	59	69	115	201
Tl(III)	82	84	86	94	87	84
Tl(I)	2.1	0.9	0.8	0.7	1.1	2.2

TABLE 17

Separation of Hg(II) from Various Cations

Cation separated	Concentration of effluent and nature of resin	Separation factor
Zn(II)	80% THF–0.6 *M* HNO_3 (cation)	233
	90% Methanol–0.6 *M* HNO_3 (cation)	$>10^3$*
	60% THF–0.6 *M* HNO_3 (anion)	890*
	60% Acetone–0.6 M HNO_3 (anion)	200
Cd(II)	40% Methanol–0.6 *M* HCl (anion)	276
	80% THF–0.6 *M* HNO_3 (cation)	306
	90% Methanol–0.6 *M* HNO_3 (cation)	$>10^3$*
Au(III)	90% THF–0.6 *M* HCl (anion)	$>10^3$*
Tl(III)	90% Methanol–0.6 *M* HCl (cation)	$>10^3$*
	80% THF–0.6 *M* HCl (anion)	$>10^3$*
	20% Acetone–0.6 *M* HCl (anion)	962*
	90% Methanol–0.6 *M* HNO_3 (cation)	445

increasing content of THF or acetone there is a continuous decrease in their *Kd* values. The addition of methanol decreases the adsorption of Au(III) and Hg(II) and increases that of Tl(III). The adsorption of Zn(II), Cd(II), and Tl(I) increases with increases in the acid molarity. In case of Zn(II) and Cd(II), there is a maxima around 40% THF or acetone while Tl(I) gives a maxima in 60% THF. The *Kd* values of Zn(II), Cd(II), and Tl(I) increase with increasing concentrations of methanol.

HNO_3–Cation-Exchangers. The adsorption of Au(III), Hg(II), and Tl(III) decreases with increasing concentrations of the acid. With increasing organic content the adsorption of Au(III) decreases and that of Tl(III) increases. The *Kd* values of Hg(II) show a decrease in THF, an increase in acetone, and a maxima in methanol. In the case of Zn(II), Cd(II), and Tl(I), the adsorption decreases with increasing acid molarity. A continuous increase in their *Kd* values is observed by increasing organic content.

HNO_3–Anion-Exchanger. The adsorption of Au(III) and Tl(III) is not affected by varying the acid concentration. Hg(II) shows a decrease with increasing acid concentration. With the addition of organic solvent

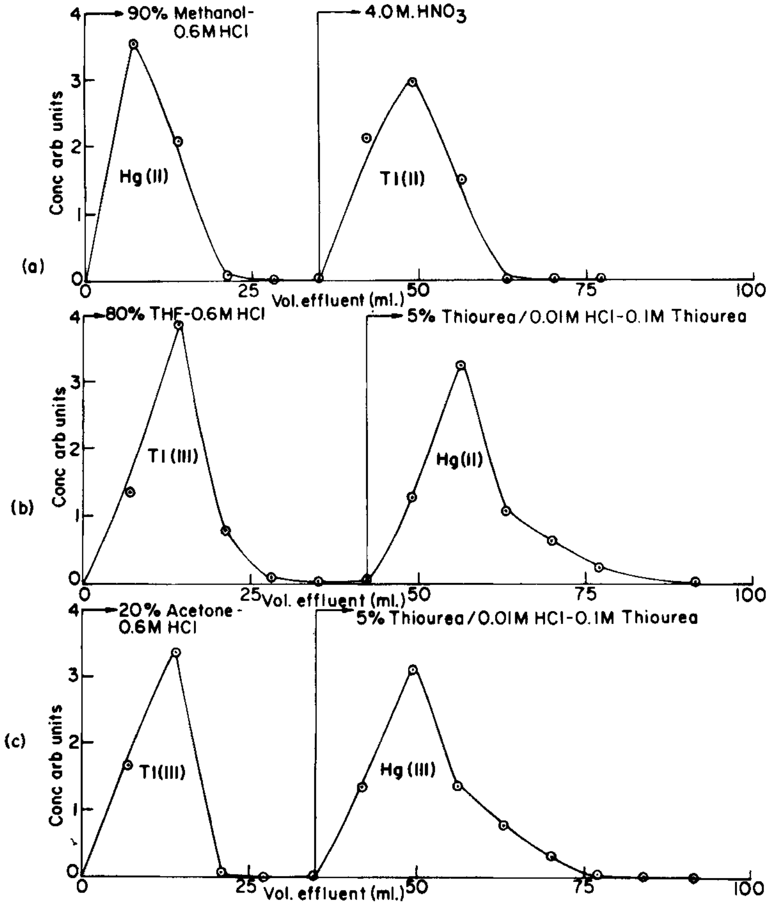

FIG. 4. Separation of mercury(II) from thallium(III): (a) Amberlite-120 (H^+), (b) and (c) Amberlite-400 (Cl^-).

the adsorption of Au(III) suddenly decreases, Hg(II) increases, and that of Tl(III) remains unaffected. The acid concentration does not affect the adsorption of Zn(II) and Cd(II) but increases that of Tl(I). The addition of organic solvents decreases the *Kd* values of Zn slightly. The adsorption of Cd(II) increases with increasing organic content, but there is no effect in the case of Tl(I).

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