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Separation of Mercury(II) as Chloride from Zinc(II), Cadmium(II), Gold(III), and Thallium(III) by Extraction in High-Molecular-Weight Amines*

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Abstract

The extraction behavior of Zn(II), Cd(II), Hg(II), Au(III), and Tl(III) has been studied at different HCl molarities in some commercially available liquid anion exchangers. The effect of such variables as the type of amine, molarity of HCl, amine concentration, and organic diluent on extraction has been explored to suggest the best conditions of separation of Hg(II) from Zn(II), Cd(II), Au(III), and Tl(III).

INTRODUCTION

In recent years much interest has been shown in the determination of mercury in different edibles (*1*, *2*) and biological samples (*3–7*) because mercury is one of most serious pollutants of the biosphere. In these analyses, if mercury has to be separated from other associated elements, liquid–liquid extraction and ion-exchange chromatography provide the two most important techniques. In the recent past a number of separations (*8–11*) of mercury(II) from other elements have been proposed from our laboratory using these two techniques. Generally, many of the advantages of these

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two techniques combine in liquid ion exchangers to make them more suitable for carrying out the separations. It was therefore thought worthwhile to explore the commercially available liquid anion exchangers for this purpose.

The present investigation deals with the separation of Hg(II) from Zn (II), Cd(II), Au(III), and Tl(III) from hydrochloric acid solutions employing various types of high-molecular-weight amines. The importance of these separations of Hg(II) was pointed out in an earlier publication (*8*). All possible variables such as the type of amine, molarity of HCl, amine concentration, and organic diluent have been explored to suggest the best conditions for these separations. Interestingly enough, for some of the separations suggested herein, the separation factors are better than those reported previously. Some earlier workers (*12–15*) also studied the extraction behavior of these elements in some of these amines, but the data were not sufficient to indicate the best conditions for the separation.

EXPERIMENTAL

Materials

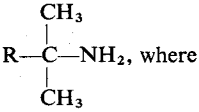
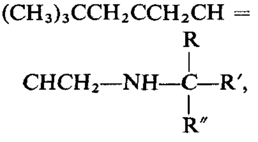
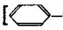
The liquid anion exchangers used in this study are listed in Table 1. They were practical grade materials and were used without further purification. The only exception was tribenzylamine, which was B.D.H., reagent grade. Chloroform and benzene used as diluents were of analytical reagent grade. ^{65}Zn, ^{115m}Cd, ^{203}Hg, ^{198}Au, and ^{204}Tl radioisotopes, supplied by Bhabha Atomic Research Centre, Bombay, India, were used as tracers. All other chemicals used were of analytical purity.

Procedure

The amine solution was made up 0.1 *M* (or any other concentration as required) in chloroform or benzene. The metal solutions ($\simeq 2.5 \times 10^{-4} M$) consisted of metal chlorides in hydrochloric acid solutions of the appropriate concentration. A small countable amount of ^{65}Zn, ^{115m}Cd, ^{203}Hg, ^{198}Au, or ^{204}Tl activity in the form of chloride was added to each of the respective metal ion solution. Equal volumes of organic amine solution and the aqueous metal ion solution were mixed together in a separatory funnel and shaken on a mechanical shaker for 5 to 10 min to ensure complete equilibration of the two phases. Equal aliquots of each phase were removed, after allowing the mixture to stand for some time, and the activity was counted by following the method described earlier (*8*). The

TABLE 1

Description of Amines

Compound	Amine type	Structure	Source
Primene JM-T	Primary	 $R{-}\overset{CH_3}{\underset{CH_3}{C}}{-}NH_2$, where R = 15 to 19 carbon atoms	Rohm and Haas
Amberlite LA-1	Secondary	 $(CH_3)_3CCH_2CCH_2CH = CHCH_2{-}NH{-}\overset{R}{\underset{R''}{C}}{-}R'$, where R + R′ + R″ = 12 to 14 carbons	Rohm and Haas
Amberlite LA-2	Secondary	Same as LA-1 except more basic	Rohm and Haas
Tribenzyl amine	Tertiary	[$-CH_2]_3N$	B.D.H.
Alamine 336	Tertiary	Tricaprylyl tertiary amine	General Mills
Aliquat 336	Quaternary	Methyl tricapyrylyl ammonium chloride	General Mills

distribution ratio (D_m), percent extraction (%E), and separation factor (S) were determined by the usual method.

In the case of γ-counting the values of percent extraction showed a precision of approximately ±1% at 60% extraction, while the precision was about ±2% for β-counting. Each experiment was run in duplicate and the average values are reported. The effect of metal ion concentration on the distribution ratio was found to be insignificant. All the distribution studies were done at room temperature (25 ± 3 °C).

RESULTS AND DISCUSSION

In almost all the amines the extraction of Hg(II) increases with decreasing molarity of hydrochloric acid and reaches a limiting value around 0.2 *M* HCl (Fig. 1). The extraction in Aliquat 336 is an exception to this and is more or less quantitative over the entire acid range. The behaviors of Zn(II) and Cd(II) are similar, with broad maxima around 2 *M* HCl (Figs. 2 and 3). The curves for the extraction of Zn(II) and Cd(II) in Primene JM-

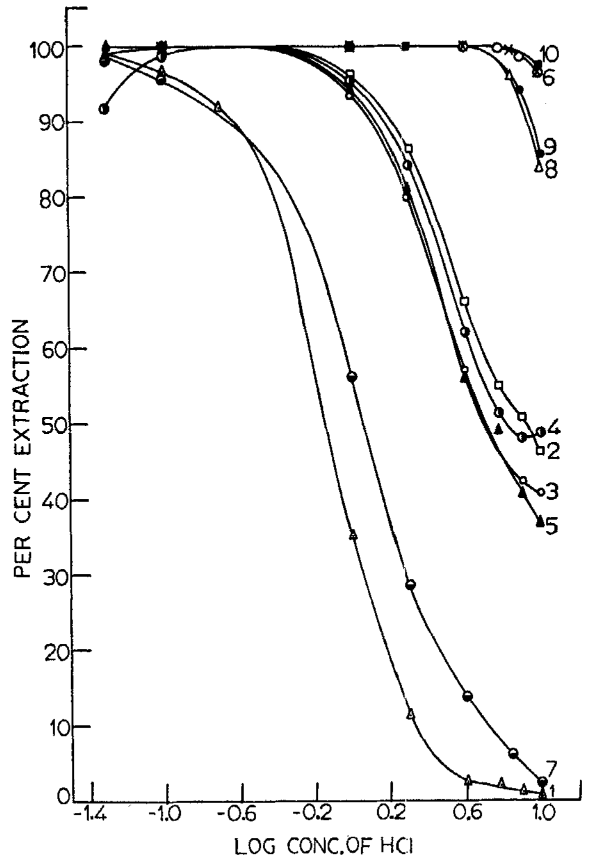


FIG. 1. Extraction of Hg(II) from HCl solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Primene JM-T; (2) Amberlite LA-1; (3) Amberlite LA-2; (4) tribenzylamine; (5) Alamine 336; (6) Aliquat 336. Benzene solvent: (7) Primene JM-T; (8) Amberlite LA-1; (9) Amberlite LA-2; (10) Alamine 336 and Aliquat 336.

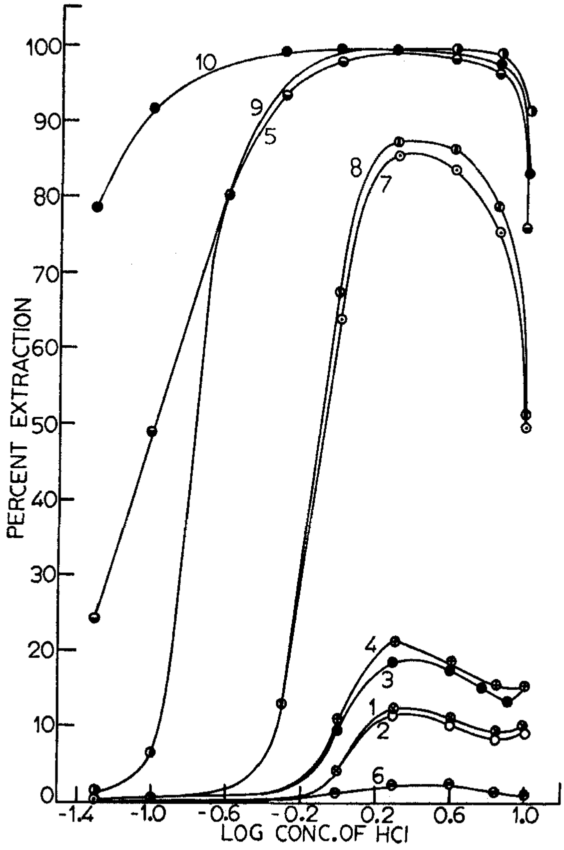


FIG. 2. Extraction of Zn(II) from HCl solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Amberlite LA-1; (2) Amberlite LA-2; (3) tribenzylamine; (4) Alamine 336; (5) Aliquat 336. Benzene solvent: (6) Primene JM-T; (7) Amberlite LA-1; (8) Amberlite LA-2; (9) Alamine 336; (10) Aliquat 336.

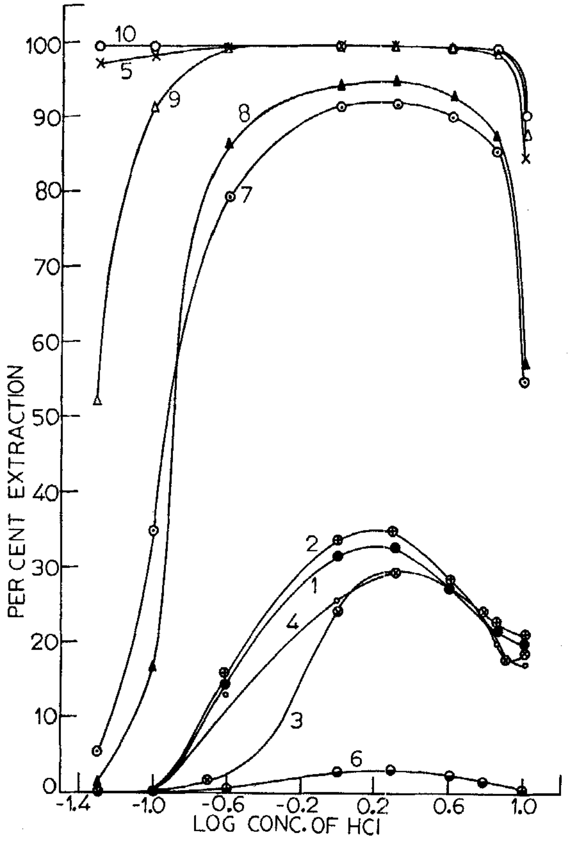


FIG. 3. Extraction of Cd(II) from HCl solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Amberlite LA-1; (2) Amberlite LA-2; (3) tribenzylamine; (4) Alamine 336; (5) Aliquat 336. Benzene solvent: (6) Primene JM-T; (7) Amberlite LA-1; (8) Amberlite LA-2; (9) Alamine 336; (10) Aliquat 336.

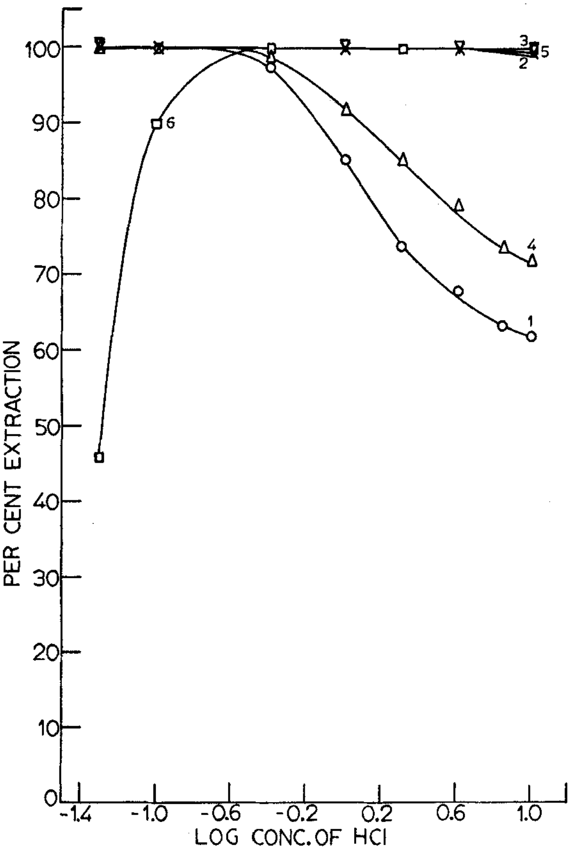


FIG. 4. Extraction of Au(III) from HCl solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Primene JM-T; (2) Amberlite LA-1; (3) tribenzylamine, Alamine 336, and Aliquat 336. Benzene solvent: (4) Primene JM-T; (5) Amberlite LA-1; (3) Alamine 336; (6) Aliquat 336.

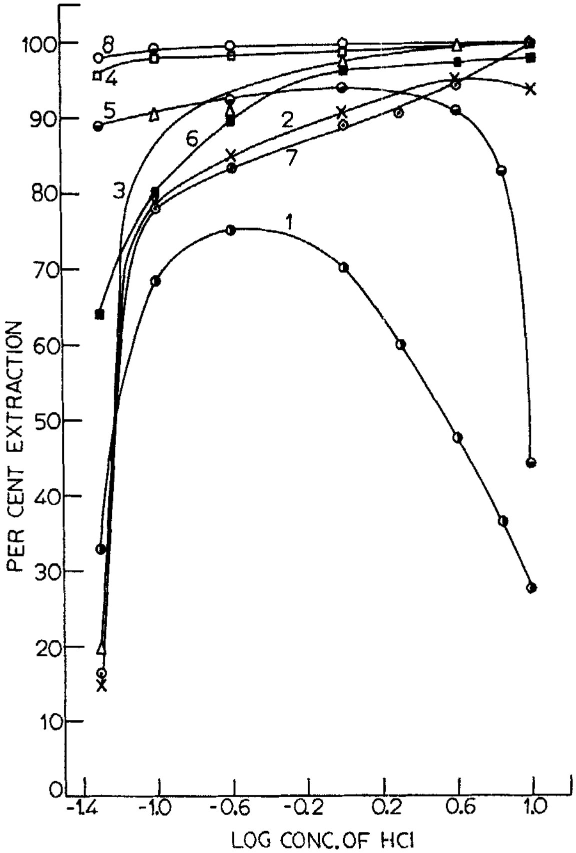


FIG. 5. Extraction of Tl(III) from HCl solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Primene JM-T; (2) Amberlite LA-1; (3) Alamine 336; (4) Aliquat 336. Benzene solvent: (5) Primene JM-T; (6) Amberlite LA-1; (7) Alamine 336; (8) Aliquat 336.

T–chloroform system are not shown because the extractions were less than 2% over the entire molarity range of hydrochloric acid. Most of the amines used quantitatively extract Au(III) at all concentrations of the acid (Fig. 4). The extraction in Primene JM-T is relatively poor at higher acid concentrations. A sharp fall is observed in Au(III) extraction at lower acid concentrations in the Aliquat 336–benzene system. The extraction of Tl(III) in various systems in shown in Fig. 5. The effect of acid concentration on the extraction of Tl(III) does not show any significant trend. However, in a number of cases there is a sharp decrease in Tl(III) extraction at lower acid concentrations.

It is apparent from the curves that the extractions in benzene are generally higher than those in chloroform. The extraction behavior of all of these elements is quite analogous to solid anion exchangers. The behavior of Hg(II) and Au(III) is also similar to the extraction behavior of these elements as chlorides in oxygenated solvents (*9*, *16*). For all of these elements the extraction efficiency of various amines follows the expected order: primary $<$ secondary $\lesssim$ tertiary $<$ quaternary.

From the data it is apparent that Hg(II) can be separated almost quantitatively from Zn(II) and Cd(II) only at very low concentrations of hydrochloric acid ($\leqslant 0.25$ *M*). These separations can be carried out in chloroform or benzene solutions of Primene JM-T, Amberlite LA-1, and Amberlite LA-2, or chloroform solutions of tribenzylamine and Alamine 336. The best conditions for the separation of Hg(II) from Zn(II) and Cd (II) in these systems are given in Tables 2 and 3, respectively. The efficiency of separation is indicated by the separation factor (*S*). These separations are not possible in Aliquat 336 because Zn(II) and Cd(II) also show higher extractions, even at lower concentrations of hydrochloric acid. In general, chloroform is a better diluent for these separations because the extractions

TABLE 2

Separation of Hg(II) from Zn(II) at 0.1 *M* HCl with 0.1 *M* Amine Solution

Amine	Separation factor using Chloroform diluent	 Benzene diluent
Primene JM-T	$\sim 10^4$	$>10^4$
Amberlite LA-1	$>10^5$	$\sim 10^5$
Amberlite LA-2	$>10^5$	$\sim 10^5$
Tribenzylamine	$\sim 10^4$	—
Alamine 336	$>10^6$	2×10^3

TABLE 3

Separation of Hg(II) from Cd(II) at 0.1 M HCl with 0.1 M Amine Solution

Amine	Separation factor using	
	Chloroform diluent	Benzene diluent[a]
Primene JM-T	$>10^4$	$\sim 10^4$
Amberlite LA-1	$\sim 10^5$	5.5×10^2 (5×10^3)
Amberlite LA-2	$\sim 10^5$	1.5×10^3 ($\sim 10^4$)
Tribenzylamine	$>10^4$	—
Alamine 336	$\sim 10^5$	—

[a] The data within parentheses are the separation factors at 0.05 *M* HCl.

TABLE 4

Efficiency of Various Concentrations of Nitric Acid for Stripping Hg(II) from 0.1 *M* Amberlite LA-1–Chloroform System

Strippant	Hg(II) stripped (%)
Distilled water	0.4
0.2 *M* HNO_3	8.7
1 *M* HNO_3	59.8
4 *M* HNO_3	83.6
10 *M* HNO_3	89.8

of Zn(II) and Cd(II) are relatively higher in benzene systems. Mercury(II) can be readily stripped from the organic layer using 4 *M* or higher concentrations of nitric acid. The stripping efficiency of different concentrations of nitric acid for the Amberlite LA-1–chloroform system is given in Table 4.

The separation of Hg(II) from Au(II) and Tl(III) can only be attained in Primene JM-T at higher molarities of hydrochloric acid by using chloroform or benzene as the diluent. At about 10 *M* HCl, 60 to 70% of Au(III) extracts into the organic layer with practically negligible extraction ($\leqslant 2\%$) of Hg(II). Likewise, the separation of Hg(II) from Tl(III) can be carried out in the Primene JM-T–benzene system at 7 *M* HCl where about 84% of Tl(III) is extracted into the organic phase along with about 6% of Hg(II). The same separation can also be carried out in a benzene solution of Primene JM-T at 4 *M* HCl where 48% of Tl(III) is extracted with a negligible amount ($\leqslant 2\%$) of Hg(II). The best conditions for the separation of Hg(II) from Au(III) and Tl(III), along with the separation factors, are given in Table 5. These separations are best carried out in a 0.1 *M* solution of the amine. At lower amine concentration the separation factors are

TABLE 5

Separation of Hg(II) from Au(III) and Tl(III) with 0.1 *M* Solution of Primene JM-T in Benzene and Chloroform

Hg(II) separated from	Diluent	Concentration of HCl (*M*)	Separation factor
Au(III)	Benzene	10	110
	Benzene	7	90
	Chloroform	10	106
Tl(III)	Benzene	7	76
	Benzene	4	64
	Chloroform	10	24

TABLE 6

Effect of Amine Concentration on the Separation of Hg(II) from Au(III) and Tl(III) at 10 *M* HCl in Primene JM-T–Chloroform System

Hg(II) separated from	Concentration of amine (*M*)	Separation factor
Au(III)	0.05	121
	0.1	106
	0.2	96
	0.5	64
Tl(III)	0.05	29
	0.1	24
	0.2	18
	0.5	14

slightly better but the extractions of the elements concerned are low. It is apparent from the data given in Table 6 that an increase in the amine concentration reduces the separation factor. Moreover, at higher acid concentrations, concentrated solutions of the amines are degraded.

The conditions for the separation of Hg(II) from Zn(II) and Cd(II) suggested here give better separation factors than those for the oxygenated solvent–chloride system. The separation factors obtained here are comparable to solid anion exchange resin–aqueous chloride systems. However, the rapidity and convenience of liquid anion exchangers are better than those of solid anion exchangers for this purpose. For the separation of Hg(II) from Au(III) and Tl(III), the separation factors are comparable to those in oxygenated solvents. However, these two separations cannot be conveniently achieved with solid anion-exchange resins from an aqueous chloride medium.

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