

Solvent Extraction of Mercury(II) from Hydrochloric Acid Solution by High Molecular Weight Amine, Amberlite LA-1

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A selective method for the extraction of milligram amount of Hg(II) from hydrochloric acid solution with liquid anion exchanger, Amberlite LA-1 in chloroform has been proposed. The optimum concentration of hydrochloric acid is found to be 0.05 M onwards. Quantitative extraction has been achieved with the diluents like benzene, xylene, toluene, carbon tetrachloride, nitrobenzene and chloroform. Extraction of mercury is found to be quantitative with amine pretreated with HCl, even without external addition of HCl. The separation of Hg(II) from several synthetic mixtures is found to be quantitative. The probable composition of the extracted species is found to be $[(R_2NH_2^+)_2(HgCl_4)^{2-}]$. The extraction behaviour of the secondary amine, Amberlite LA-1 has been compared with that of tertiary amine like trioctylamine.

In recent years solvent extraction with high molecular weight amines and quaternary ammonium compounds has been extensively used as a promising technique for the removal of toxic elements like Zn, Cd, Hg, As, Cu, Pb, Cr etc., from industrial effluents and for the recovery with purification of fertile and fissionable materials from irradiated fuel in atomic energy centres.

The amines, due to their unique anion exchange ability, extract anionic metal complexes from the aqueous phase. Some work on liquid cation exchangers¹ has been reported from this laboratory. We have reported earlier² the extraction of zinc (II) by liquid anion exchanger. The present work reports on the selectivity of Amberlite LA-1 in chloroform for the extraction of Hg(II) from its chlorocomplex. No such work has yet been reported in the literature³⁻⁷.

The secondary amine and its salt with anionic chlorocomplex of mercury are essentially insoluble in aqueous solution but exhibit high solubility in organic solvents.

Materials and Methods

The liquid anion exchanger, Amberlite LA-1 (Rohm and Haas) was used as such. Chloroform (ICI, AR) was used as the diluent. The amine was suitably diluted with chloroform and converted into its chloride form by equilibrating with hydrochloric acid for 5 min. The molar concentration of the amine was determined as reported earlier².

A stock solution of mercury (8.2 mg/ml) was prepared by dissolving accurately weighed $Hg(NO_3)_2 \cdot H_2O$ (BDH, AR) in doubly deionised water and the solution was standardized by complexometric titration with EDTA (disodium salt) using Mg-EDTA and Eriochrome Black T indicator⁸.

All solvent extractions were carried out at $27 \pm 1.0^\circ C$.

General extraction procedure

The ratio of the volumes of aqueous phase and the organic phase was maintained at 1:1. An aqueous solution containing 8.2 mg/ml of mercury was taken and to this standard hydrochloric acid was added to maintain the required acidity (0.05 M HCl). The total volume of the aqueous phase was made upto 10 ml and equilibrated with a solution of the amine in chloroform (10 ml; 2.5% v/v) for 5 min. The two layers were allowed to settle for 5 min, the organic phase separated and to the aqueous phase was added ammonia buffer (pH 10) and Mg-EDTA. The amount of mercury present in the aqueous phase was then determined by complexometric titration. To the organic phase was added 1 M HNO_3 (10 ml) and the mixture shaken for 5 min. The two phases were allowed to settle, the organic phase separated again and the aqueous phase collected. The organic phase thus obtained was again shaken with 1 M HNO_3 (10 ml) for 5 min and the mixture allowed to settle. The organic phase was separated carefully and the aqueous phase collected. The aqueous phase (acid extract) of two successive strippings was mixed and treated with Mg-EDTA and ammonia buffer (pH 10) and the amount of mercury extracted determined as discussed earlier.

Results and Discussion

The extraction behaviour of Hg(II) with (a) amine pretreated with hydrochloric acid and (b) free amine was studied using constant concentration of metal ($4.1 \times 10^{-3} M$) and the extractant (0.045 M). It is observed that the amine pretreated with hydrochloric acid quantitatively extracts mercury without external addition of hydrochloric acid (Fig. 1). However, with

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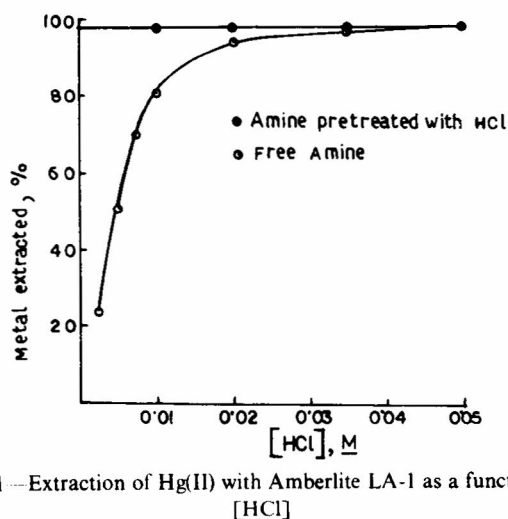


Fig. 1—Extraction of Hg(II) with Amberlite LA-1 as a function of [HCl]

free amine extraction per cent increases with increase in hydrochloric acid concentration and the extraction is quantitative at hydrochloric acid concentration $>0.05 M$ (Fig. 1). This observation clearly points the difference in the extraction behaviour of free amine and amine pretreated with hydrochloric acid (i.e. R_2NH and $R_2NH_2^+Cl^-$). The distribution ratio is calculated from the extraction data using the relation:

$$D = \frac{V}{V'} \left(\frac{x}{100-x} \right)$$

where V and V' are the respective volumes of the aqueous phase and organic phase and x is the percentage of mercury extracted^{9,10}.

The extraction of Hg(II) has also been carried out using a tertiary amine, trioctylamine (Fluka AG) under identical conditions. Trioctylamine showed improved extraction at lower acid concentration in comparison to Amberlite LA-1 though at optimum acid concentration, the extraction of metal is almost equal in the two cases (see Table 1).

In order to evaluate the probable reaction mechanism of Hg(II) with chloride ion, the extraction experiments were carried out with free amine using

Table 1—Extraction of Mercury(II) as a Function of Hydrochloric Acid Concentration with Free Amine in Chloroform

[HCl] M	Extraction (%) of Hg(II)	
	Amberlite LA-1	Trioctylamine
2.5×10^{-3}	24.4	27.7
5×10^{-3}	51.3	58.6
7.5×10^{-3}	70.0	77.9
1.0×10^{-2}	81.2	85.6
2.0×10^{-2}	93.9	95.5
3.5×10^{-2}	97.5	97.5
5.0×10^{-2}	98.5	98.5
1.0×10^{-1}	98.5	98.5

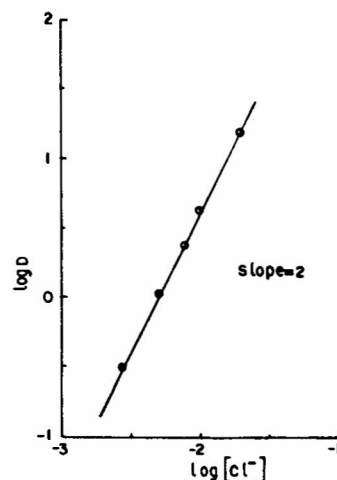
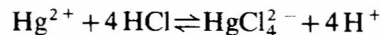
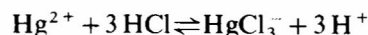
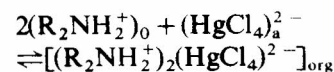


Fig. 2—Plot of $\log D$ against $\log [Cl^-]$ at constant [amine]

varying concentrations of hydrochloric acid at constant ionic strength of $0.15 M$, maintained by adding sodium sulphate. However, nearly same extraction results are obtained with or without maintaining constant ionic strength. Plot of $\log D$ against $\log [Cl^-]$ is linear (Fig. 2) with slope = 2, indicating the formation of $(HgCl_4)^{2-}$ in the aqueous phase. At lower chloride concentration, the formation of $(HgCl_3)^-$ is also expected. Therefore, the reaction mechanism in the aqueous phase is proposed to be:



At constant concentration of mercury ($4.1 \times 10^{-3} M$) and hydrochloric acid ($0.1 M$), the extraction of Hg(II) as a function of amine concentration in chloroform was studied. The extraction of Hg(II) is quantitative provided the amine:mercury molar ratio is ≥ 2 . Plot of $\log D$ against $\log [amine]$ is linear with slope = 2. Hence the reaction mechanism of Hg(II) is proposed to be:



The Hg (II)-amine ratio in the extracted species is 1:2. This result is further supported when the experiments are conducted using varying concentrations of metal. The ratio of metal to amine concentration in organic phase is again found to be 1:2, thereby corroborating the proposed stoichiometry of the extracted species.

Mercury was extracted with 2.5% amine solution in various diluents. The results indicate quantitative extraction of mercury with benzene, xylene, toluene, carbon tetrachloride, nitrobenzene and chloroform. Further stripping of mercury from the organic phase with $1 M HNO_3$ (10 ml) is not complete in a single stripping operation. Two successive strippings are

Table 2—Effect of Diverse on the Extraction of Hg(II) with Amberlite LA-1

[Hg(II), 8.25 mg; [HCl] = 0.1 M]			
Diverse ions	Amount added (mg)	Source	Mercury extracted (%)
Cu ²⁺	400	CaCl ₂ .2 H ₂ O	97.9
Sr ²⁺	400	SrCl ₂ .6 H ₂ O	97.9
Ba ²⁺	400	BaCl ₂ .2 H ₂ O	98.4
Mg ²⁺	300	MgSO ₄ .7 H ₂ O	97.4
Mn ²⁺	100	MnCl ₂ .4 H ₂ O	97.9
Ni ²⁺	70	NiSO ₄ .7 H ₂ O	97.4
Cr ³⁺	30	Cr ₂ (SO ₄) ₃ .6 H ₂ O	97.4
Cu ²⁺	40	CuSO ₄ .5 H ₂ O	98.4
Co ²⁺	40	CoSO ₄ .6 H ₂ O	98.4
Fe ³⁺	25	FeCl ₃ .6 H ₂ O	98.4
Al ³⁺	5	Al(NO ₃) ₃ .9 H ₂ O	97.0
*Zn ²⁺	20	Zn(Ac) ₂	97.4
*Pb ²⁺	20	Pb(NO ₃) ₂	97.4
SO ₄ ²⁻	1200	Na ₂ SO ₄ .10 H ₂ O	97.9
PO ₄ ³⁻	500	KH ₂ PO ₄	97.4

*Extracted by R₂NH₂⁺Cl⁻ without adding HCl.

Table 3—Quantitative Separation of Hg(II) from Synthetic Mixtures using Amberlite LA-1

[Hg(II) taken = 8.25 mg; [HCl] = 0.1 M]		
Sample No.	Mixture taken (mg)	Mercury extracted (%)
1	Ca ²⁺ (200) + Sr ²⁺ (200)	97.4
2	Ca ²⁺ (200) + Ba ²⁺ (200)	97.9
3	Sr ²⁺ (200) + Ba ²⁺ (200)	97.4
4	Ni ²⁺ (35) + Cu ²⁺ (20)	98.4
5	Cu ²⁺ (20) + Co ²⁺ (20)	97.9
6	Mn ²⁺ (50) + Ni ²⁺ (30)	97.9
7	Cr ³⁺ (15) + Co ²⁺ (15)	97.4
8	Fe ³⁺ (10) + Co ²⁺ (15)	97.9
9	*Zn ²⁺ (10) + Pb ²⁺ (10)	97.4
10	Ca ²⁺ (100) + Sr ²⁺ (100) + Ba ²⁺ (100)	97.9
11	Mn ²⁺ (30) + Ni ²⁺ (10) + Cu ²⁺ (10)	97.4
12	Cr ³⁺ (10) + Cu ²⁺ (10) + Co ²⁺ (10)	97.4
13	Fe ³⁺ (10) + Cr ³⁺ (10) + Co ²⁺ (10)	97.4

*Extracted by R₂NH₂⁺Cl⁻ without adding HCl.

found necessary for quantitative stripping of mercury from the organic phase. It is also observed that back extraction is complete with chloroform as the diluent. It appears that diluents also have some effect towards back extraction. The optimum time of two successive strippings for quantitative back extraction of mercury with 1 M HNO₃ from the organic phase is found to be 5 min for each stripping.

The effect of diverse ions on the quantitative extraction of Hg(II) under optimum condition is shown in Table 2. The tolerance limit for such ions like calcium, strontium, barium, magnesium, manganese, sulphate, phosphate are high and that of nickel, chromium, copper, cobalt, iron, aluminium are low above which extraction decreases. It is also found that zinc and lead can be separated by pretreated amine (R₂NH₂⁺Cl⁻) without external addition of hydrochloric acid.

Quantitative separation of mercury from some of the synthetic mixtures was attempted and the results are shown in Table 3. It has been possible to separate mercury from several ternary and quaternary mixtures.

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References

- De A K & Ray U S, *Sep Sci*, **6** (1971) 25, 443; **7** (1972) 419, 449.
- De A K, Ray U S & Parhi N, *J Indian chem Soc*, **59** (1982) 1334.
- Singh O V & Tandon S N, *J inorg nucl Chem*, **36** (1974) 439.
- Bullock J I & Tuck D G, *J inorg nucl Chem*, **28** (1966) 1103.
- Moore F L, *Sep Sci*, **7** (1972) 505.
- Moore F L, *Environ Lett*, **10** (1975) 77.
- Moore F L, *Environmental Sci Tech*, June 1972, 525.
- Pribil R, *Chelometry, basic determinations* (Chemapol, Prague) 1961, 63.
- De A K, Khopkar S M & Chalmers R A, *Solvent extraction of metals* (Van Nostrand, London) 1970, 2.
- Morrison G H & Freiser H, *Solvent extraction in analytical chemistry* (Wiley, New York) 1957, 12.