Liquid-Liquid Extraction of Mercury (II) with Dicyclohexano-18-crown-6 and its Application to Industrial Wastes

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Abstract:

An innovative region specific method is essential to improve an environmentally and economically viable process to address the iron oxide waste problem. One such choice is to create high purity metal oxides for use in pigment, electronic and catalyst manufacturing. Currently, approaches based on liquid-liquid extraction has arisen as a novel and exclusive method for the separation and recovery of metal ions from mineral sources as well as from industrial waste streams in place of the customary pyrometallurgical methods for the reason that of its simplicity, versatility, easy recovery and ready adaptability to scaling up of the procedure. The present work purposes to investigate novel solid waste remediation procedure through resource recovery (metal values) and its reintegration as value added state-of- art products by employing liquid-liquid extraction method.

Keywords — **Extraction of Mercury (II), Industrial wastes, EDTA, Chlor-Alkali industry, DC18C6 complex.**

1. INTRODUCTION

The discovery that crown ethers selectively complex alkali and alkaline earth metals led to numerous studies of their use in liquid-liquid extraction procedures. Early workers noted that a match amongst the cavity size of the crown ether and the ionic diameter of the metal ion occasioned in high extraction selectivity. Thus, suitably sized crown ethers could be chosen to attain the selective extraction of a specific cation of interest. The nature of the substituent group on the macro cyclic ring is another significant factor that impacts the selectivity of crown ethers. Macrocyclic polyethers are chemically stable and can be effortlessly redeveloped.

Numerous studies have been carried out on the extraction of mercury (II) using crown ethers comprising N - and S - donor atoms. Associated with these, the methodical study of extraction including crown ethers comprising oxygen donor atom is sparse. This provoked to inductee a methodical study on the extraction behaviour of mercury (II) using oxygen comprising macrocyclic polyethers and their solicitation to the retrieval of mercury from the industrial waste streams. In the current chapter, the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using dicyclohexano-Ix-crown-e (DC18C6) in 1,2-dichloroethane as an extractant has been examined with a view to explicate the nature of the developments extracted into the organic phase. For association,

extraction studies have also been carried out with 18-crown-6 (18C6), benzo-15 crown-5 (B18C6) and dibenzo-18-crown-6 (DB18C6) (Fig. 1.1). The potential of DC18C6 for the retrieval of mercury from the brine-sludge of a Chlor-Alkali industry has also been inspected.
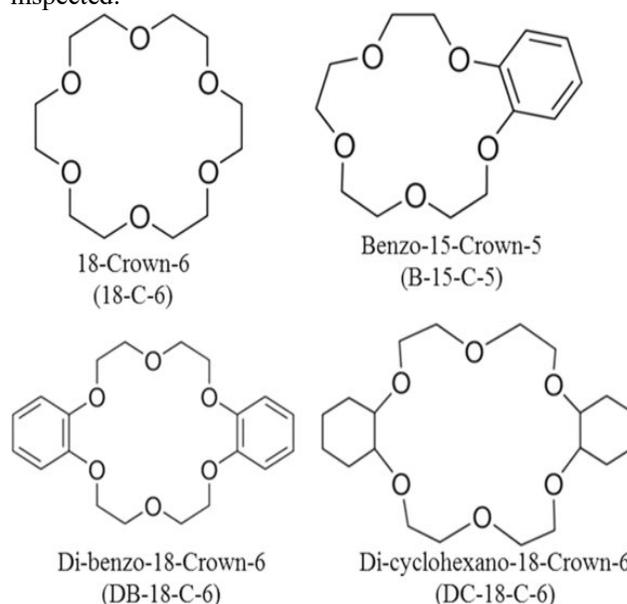
Fig. 1.1 Structures of crown ethers employed for mercury (II) extraction studies.

1.1 EXPERIMENTAL

1.1.1 Reagents:

The tracer solution of **203**Hg (t1/2 = 46.6 days) was attained from the Board of Radiation and Isotope Technology (BRIT), India. The crown ethers, DC18C6 (mixture of cis-syn-cis and cis-anti-cis), 18C6, B15C5 and DB18C6 were attained from Aldrich Chemical Company Inc., U.S.A. All the other chemicals engaged were of analytical reagent grade. Mercury(II) stock solution was arranged by dissolving 0.27 g of mercuric chloride in 100 ern" of distilled water. Stock solutions of calcium(II), magnesium(II) and barium(II) were organized by dissolving 0.37 g ofCaCl2H20 , 0.62 g of MgS04.7H20 and 0.61 g of BaCh correspondingly, in 25 cm^3 of distilled water. Appropriately diluted stock solutions of the above stated metal ions were used in the extraction and analytical readings. Rhodamine 6G (0.005%) solution was primed by dissolving 0.012 g in 250 cm^3 distilled water. Ammonia - ammonium chloride buffer solution of pH = 10 was prepared by dissolving 3.5 g of ammonium chloride in 28.4 cm^3 concentrated ammonia solution and diluted to 50 cm^3 with distilled water. Buffered potassium iodide solution (0.3 mol/dm^3; pH = 4) was prepared by liquefying 12.5 g of potassium iodide, 5 g of potassium hydrogen phthalate and 1 - 2 crystals of sodium thiosulphate in 250 cm^3 distilled water.

1.1.2 Apparatus:

A well type NaI(Tl) Scintillation Counter delivered by Nuc1eonix Systems, India, was used for the quantity of the gamma activity of **203**Hg radioisotope. A Hitachi 220 Double Beam Microprocessor measured Spectrophotometer was used for gauging the absorbances. Cold Vapour Mercury Analyser of Buck Scientific Model 400A, U.S.A., was engaged to determine the mercury satisfied in the brine-sludge of a Chlor-Alkali industry. A GBC Double Beam AAS, Australia, was used to decide the other related metal ions viz. calcium(II), magnesium(II) and barium(II) present along with mercury(II) in the brine-sludge of a Chlor-Alkali industry. An Ion Analyser (Orion, USA) was used for the pH quantities. A Nicolet FTIR 560 Magna Spectrometer using KBr (neat) was used to attain the IR spectrum of the mercury(II)-DC 18C6 complex. C, Hand N analysis was performed with a Perkin Elmer Series 2 Elemental Analyzer 2400. The Broker 300MHz NMR Spectrometer was used to attain the IH NMR spectra of the HgCl2DC18C6 complex. All the computer programs were inscribed in FORTRAN 77 and implemented on a 32-bit minicomputer.

1.1.3 Liquid-liquid extraction procedure:

Equal volumes of the aqueous phase containing mercury(II) (1x1O-5 mol/dnr') labelled with the radioisotope e03 Hg) and organic phase were equilibrated in a glass stoppered vial using a mechanical shaker at 303 ± I K. Initial experiments displayed that the extraction equilibrium is achieved within 30 min. The two phases were then detached and assayed radiometrically using a well kind NaI(Tl) Gamma Ray Scintillation Counter. The distribution ratio, D, was taken as the ratio of the activity of the tracer in the organic phase to that in the aqueous phase. All the extraction experimentations were accomplished in identical and the general settlement with distribution ratio values acquired was within ±5%.

1.1.4 Analytical procedure

A. Determination of mercury (II) and other associated metal ions in the brinesludge of a Chlor-Alkali industry.

The mercury (II) content in the chlorinated brine-sludge of a Chlor-Alkali industry was indomitable by Cold Vapour Atomic Absorption Spectrometric (CVAAS) method which contains of conveying Hg^{2+} from solution into an inert gaseous stream after decrease to elemental mercury with stannous chloride solution. The air stream was then passed through a cell where optical absorbance at 253.7 nm was restrained.

The mercury (II) content in the brine-sludge of a Chlor-Alkali business has also been analysed spectrophotometrically using Rhodamine 6G. To 1 cm^3 of the chlorinated brine-sludge filtrate, 5 cm^3 of potassium hydrogen phthalate (2%) solution was added along with 5 cm^3 EDTA (0.1 mol/ dm^3) solution (to mask the extra related metal ions), the pH adjusted to 40 and then 5 ern' of buttered potassium iodide solution was added trailed by 5 cm^3 Rhodamine 6G (0005%) and 1 cm^3 of 1% gelatin solution. The subsequent solution was then made up to 50 cm^3 and the absorbance were measured at 570 nm alongside a reagent blank organized under identical situations. Then the concentration of the metal ion was calculated from the regulation graph.

Calcium (II), magnesium (II) and barium (II) present along with mercury (II) in the brine-sludge of a Chlor-Alkali business were dogged by Atomic Absorption Spectrophotometer at 422.7, 285.2 and 553.6 nm, correspondingly.

B. Complexometric determination of calcium (II), magnesium (II) and barium (II)

In the discernment studies, calcium (II), magnesium (II) and barium (lI) were resolute by complexometric titrations using normal EDTA solution. The determination of calcium (II) was agreed out by the substitution titration method as labelled below: To 5 cm^3 aliquots of calcium (II) solution, 2 cm^3 of

ammonia - ammonium chloride buffer solution (pH = 10) was added and diluted to 25 cm^3 with distilled water. Then, I cm^3 of Mg-EDTA complex (0.1 mol/ dm^3) was added to the above solution and titrated contrary to standard EDTA solution (0.01 mol/ dm^3) by means of eriochrome black T - potassium nitrate solid mixture (0.001 geriochrome black T in 0.099 g potassium nitrate) as the indicator. The complexometric titration technique for magnesium (II) determination includes diluting 5 cm^3 of the metal ion solution to 50 cm^3 with distilled water shadowed by the addition of 2 cm^3 of ammonia - ammonium chloride buffer (pH = 10) and reheating the solution to 40°C before titrating against standard EDTA solution (0.01 mol/ dm^3) using 0.05 g of eriochrome black T - potassium nitrate solid mixture as an indicator. To 5 cm^3 of barium ion solution, 50 cm^3 of distilled water and 5 cm' of sodium hydroxide solution (1 mol/ dm^3) was added, pH adjusted to 12 and titrated against standard EDTA solution using methylthymol blue - potassium nitrate (0.001 g methylthymol blue in 0.099 g potassium nitrate) combination as an indicator.

C. Determination of mercury in the metal-ligand complex by EDTA titration method:

Mercury (II) in the mercury (II)-crown ether complex was indomitable by the following technique: A certain quantity of the complex was putrefied by heating in a minimum amount of HN03:HCI04 (1: 1) solution and the surplus acid were vanished. The subsequent mixture was diluted with distilled water to 25 cm^3 and mercury (II) was resolute by EDTA titration by means of xylenol orange as an indicator at pH = 6 using hexamine buffer.

2.1.5 Preparation of solid mercury(II)-DCI8C6 complex

HgCl2DCI8C6 complex was equipped as follows: Solutions comprising 0.27 g (1 mmol) HgCh in 20 cm^3 l-butanol and 0.37 g (1 mmol) DCI8C6 in 20 cm^3 I-butanol were heated almost to boiling and then mixed. The precipitate molded on slow cooling was filtered, dried and utilised for IR, 1H NMR and elemental revisions.
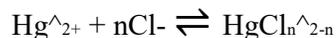
1.2 RESULTS
Extraction of mercury (II) using crown ether (CE)

2.2.1 Extraction equilibrium of mercury (II)
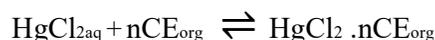The complex creation of mercury (II) with chloride ions can be labelled as follows:

$$\beta_n$$
$$Hg^{2+} + nCl^- \rightleftharpoons HgCl_n^{2-n}$$

or the stepwise formation constants (K_n) can be designated as follows:

$$K_n$$
$$HgCl_{n-1}^{3-n} + Cl^- \rightleftharpoons HgCl_n^{2-n}$$

The extraction of neutral mercury (II) complexes into the organic phase with crown ether can be designated as follows:

$$K_{ex,n}$$
$$HgCl_{2aq} + nCE_{org} \rightleftharpoons HgCl_2 .nCE_{org}$$

Where n = 0, 1 and 2.

1.2.2 Effect of hydrochloric acid concentration
The extraction of mercury (II) (1×10^{-5} mol/ dm^3) has been inspected with changing concentrations of hydrochloric acid (0.05-0.1 mol/ dm^3) using 2×10^{-3} mol/ dm^3 DC18C6 in 1,2-dichloroethane. It is clear from the consequences that the extraction of mercury(11) declines constantly with growing hydrochloric acid concentration in the aqueous phase This might be due to the formation of species $HgCl_3^-$ and $HgCl_4^{2-}$ in the aqueous phase with upsurge of hydrochloric acid concentration.

1.2.3 Effect of crown ether concentration:
The effect of concentration of DC18C6 (0.002 - 0.01 mol/ dm^3) on the extraction of mercury (II) ($l \times 10-5$ mol/ dm^3) from 0.1 mol/ dm^3 hydrochloric acid solutions has been studied. For evaluation, extraction of mercury (II) has also been carried out using 18C6, B15C5 and DB 18C6 as extractants. The distribution ratio, D, of mercury(II) upsurges linearly with upsurge in the concentration of crown ethers and from the slope of the log-log plot it is clear that two molecules of DC18C6 or 18C6 or B18C6 are connected with the extractable complexes. On the other hand, the extraction of mercury (II) was found to be insignificant when extracted with DBI8C6 from dilute hydrochloric acid solutions. Though, Giovannetti and eo-workers have stated ion-pair complexes of DB18C6 for the extraction of mercury (II) from concentrated hydrochloric acid solutions (1-7 mol/ dm^3).

1.2.4 Effect of metal ion concentration:
The effect of metal ion concentration ($lxlO-5 - lxlO-3$ mol/ dm^3) on the extraction procedure of mercury(II) has been inspected using 0.002 mol/ dm^3 DCI8C6 in 1,2-dichloroethane from 0.1 mol/ dm^3 hydrochloric acid solutions. The log-log plot of the equilibrium organic phase mercury(II) concentration against the

aqueous phase mercury(lI) concentration is linear with a slope equal to union, specifying the extraction of mono-nuclear species into the organic phase.

1.2.5 Dependence of the nature of the diluent:

The extraction of mercury (II) (lxl0-s mol/ dm^3) from 0.1 mol/ dm^3 hydrochloric acid solution using 0.01 mol/ dm^3 DC18C6 in numerous diluents has been examined and the outcomes are shown in Table 2.2. This study obviously shows that the extraction of mercury (II) differs with the nature of the diluent. The weak hydrogen bonding amongst the ether oxygen of crown ethers and dichloroethane outcomes in higher extraction efficacy of mercury (ll). When chloroform is used as the diluent, low extraction of mercury (II) has been perceived. This might be due to strong acid-base interaction amongst the basic extractant CE and the acidic diluent through hydrogen bonds. Amongst aromatic hydrocarbons, the extraction upsurges in the order: xylene> toluene> benzene.

Table 2.1: Effect of nature of the diluent on the extraction of mercury(ll) using 0.01 mol/ dm^3 DC18C6

Diluent	D
Benzene	1.51
Toluene	5.34
Xylene	7.10
Chloroform	1.98
1,2-dichloroethane	398.00

1.2.6 Stripping studies:

Mercury (II) stripping from a loaded organic system contain mg of 0.02 mol/ dm^3 DCI8C6 in 1,2-dichloroethane and IxlO-5 mol/ dm^3 mercury(II) has been inspected using numerous stripping agents and the outcomes are given in Table 2.3. It is found that mercury (II) is stripped nearly quantitatively (> 99.9%) over a single stage with 5% NH4Cl in 1: 10 NH3 as the stripping agent.

Stripping Reagent	% Recovery of mercury(II)
5% Thiourea (pH = 11)	41.3
5% NH4CI (1:10NH3)	99.9
4 mol/ dm^3 NaCI + 0.1 mol/ dm^3 NaOH	Negligible
0.01 mol/ dm^3 Na2S20 3(pH = 11)	Negligible
0.2 mol/ dm^3 EDTA (pH = 11)	Negligible
2 - 3 mol/ dm^3 Hydrochloric acid	Negligible

Table 2.2: Stripping efficiency for mercury (II) with different reagents

1.2.7 Elemental analysis:

Elemental analysis of the extracted complex gave C 38.27, H 5.61 and Hg 30.77% which matched with calculated values for HgCh.DCI8C6 of C 37.3, H 5.63 and Hg 31.15%. This study evidently shows that HgCh and DC 18C6 form a 1:1 complex. Paige and Richardson have stated a similar 1:1 complex with HgCh and 18C6 using crystallographic methods.

1.2.8 IR spectral data:

Infrared spectra of compounds, DC18C6 and the HgCh.DCI8C6 solid complex have been recorded in the 4000 - 500 cm^-1 region. The very powerful, broad and possibly multicomponent CH2 extending vibration band of the free ligand has a peak at 2865 cm". On complexation the intensity is much condensed and the band turn out to be asymmetrical with a peak at 2926 cm^-1. On the other hand, the medium intensity peak due to bending of CH2 modes of the free ligand at 1349 cm^-1 is slightly downshifted to 1341cm^-1 for the complex. Similarly, the bands at 1120 and 847 cm^-1 are shifted down to 1103 and 838 cm^-1 respectively on complexation. The metal-oxygen bands are most probable to be found in the far infrared area.

1.2.9 Selectivity studies using DC18C6:

The extraction of calcium (II) (lx10-2 mol/ dm^3), magnesium(II) (lxlO-2 mol/ dm^3) and barium(II) (lxlO-2 mol/ dm^3) from solutions comprising 0.05 mol/ dm^3 hydrochloric acid using 0.02 mol/ dm^3 DC18C6 in 1,2-dichloroethane has been examined and found that none of these metal ions are getting extracted into the organic phase. This is in good covenant with the prior information for the extraction of calcium (II) and barium (II) with DC18C6. On the other hand, mercury (II) was found to be quantitatively (% extracted> 99.9) extracted under the above conditions. Therefore, mercury (II) can be selectively parted from the above mentioned metal ions using DC18C6 as an extractant.

2.2.10: Recovery of mercury from the brine-sludge of a Chlor-Alkali industry:

The developed liquid-liquid extraction process has been applied for the removal and retrieval of mercury from the brine-sludge of a Chlor-Alkali industry using DC18C6 as an extractant. The brine-sludge sample (1 g) in 10 cm^3 of 0.05 mol/ dm^3 hydrochloric acid was chlorinated for 5-10 min. for altering mercury into exceedingly soluble mercuric chloride complexes. The chlorinated slush was then subjected to solid-liquid separation and the filtrate was analysed for mercury (II), caIcium(II), magnesium(II) and barium(II) and the outcomes are shown in Table 2.3. The extraction process

of mercury from the brine-sludge of a Chlor-Alkali industry includes of the subsequent phases:

(1) Chlorination of the brine-sludge;

(2) Solid-liquid separation;

(3) Transporting the resultant filtrate liquor (plf > 1 - 2) from solid-liquid separation comprising the mercury (Hg2+ ;: 16 mg/ dm^3) into contact with a substantively immiscible extractant phase, which includes DC18C6 in 1,2-dichloroethane (0.02 mol/ dm^3; Aq. : Org. = 1 : 1), whereupon the mercury to be separated selectively, reversibly relocates into the extractant phase (single stage extraction, % extracted> 99.9);

(4) Back-washing the extractant phase with an aqueous system containing of 5% ~CI in 1 : 10 NH3 to recuperate all the mercury confined in the extractant phase (Aq. : Org. = 1 : 1; number of stages = 1).

Typical analysis results of the feed, raffinate and strip liquors are given in Table 2.3:

Metal Ion	Amount of metal ion	Amount of metal ion	Amount of metal ion
	Feed	Raffinate	Strip liquor
Mercury(II)	16.00 mg/ dm^3	1.60 ug/ dm^3	15.998 mg/ dm^3
Calcium(ll)	3.88 g/ dm^3	3.88 g/ dm^3	N.D.
Magnesium(II)	0.58 g/ dm^3	0.58 g/ dm^3	N.D.
Barium(II)	4.56 mg/ dm^3	4.56 mg/ dm^3	N.D.

The research expose that mercury can be separated selectively and quantitatively (% recovery> 99.9) through a single stage extraction and stripping procedure from the brine-sludge of a Chlor-Alkali industry by means of 0.02 mol/ dm^3 DC18C6 in 1,2-dichloroethane as an extractant.

CONCLUSION

This paper highlighted the importance of the control and elimination of mercury from industrial waste streams with distinctive emphasis on the use of liquid-liquid extraction and separation method as a tool. A general introduction to the extraction chemistry shadowed by an exhaustive literature assessment on the recent progresses on the liquid-liquid extraction and separation of mercury (II) has also been incorporated in this paper briefly.

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