# LIQUID-LIQUID EXTRACTION AND SEPARATION OF MERCURY FROM INDUSTRIAL WASTES

THESIS SUBMITTED TO THE
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF

**DOCTOR OF PHILOSOPHY**

IN CHEMISTRY UNDER THE FACULTY OF SCIENCE

*By*
**Tania Francis**

UNDER THE SUPERVISION OF
Dr. M. L. P. Reddy

ION-SPECIFIC SEPARATION SCIENCE AND TECHNOLOGY GROUP
**REGIONAL RESEARCH LABORATORY (CSIR)**
THIRUVANANTHAPURAM - 695 019, KERALA, INDIA.

August 2002

# DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"LIQUID-LIQUID EXTRACTION AND SEPARATION OF MERCURY FROM INDUSTRIAL WASTES"** is the result of the investigations carried out by me in the Ion-specific Separation Science and Technology Group of Regional Research Laboratory (CSIR), Thiruvananthapuram, under the supervision of Dr. M. L. P. Reddy and the same has not been submitted elsewhere for any other degree.

***Tania Francis***

Thiruvananthapuram
August, 2002

REGIONAL RESEARCH LABORATORY (CSIR)
GOVERNMENT OF INDIA
TRIVANDRUM - 695 019, INDIA

**Dr. M. L. P. Reddy**
Scientist EII

Tel : 91-471-515 259, Fax : 91-471-491 712

## CERTIFICATE

This is to certify that the work embodied in the thesis entitled "**LIQUID-LIQUID EXTRACTION AND SEPARATION OF MERCURY FROM INDUSTRIAL WASTES**" is the result of the investigations carried out by Mrs. Tania Francis under my supervision in the Ion-specific Separation Science and Technology Group of Regional Research Laboratory (CSIR), Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

Thiruvananthapuram
August, 2002

M. L. P. Reddy
(Thesis Supervisor)

Email : mlpreddy@yahoo.co.uk, reddy@csrrltrd.ren.nic.in

# ACKNOWLEDGEMENTS

*It gives me great pleasure to place on record my deep sense of gratitude to my supervising teacher, Dr. M. L. P. Reddy, for his guidance, keen interest, constructive criticism and valuable suggestions throughout the course of these investigations.*

*I am grateful to Prof. Javed Iqbal, Director, RRL(T) and the former Director, Dr. G. Vijay Nair, for extending the necessary facilities for carrying out the research work.*

*I owe my special thanks to*

- *Dr. G. D. Surender, Head, Process Science and Engineering Division, RRL, for his constant encouragement towards my research work.*
- *Dr. T. R. Ramamohan, Deputy Director, RRL, for his help to carry out the mathematical modeling of the experimental data.*
- *Dr. T. Prasada Rao, Deputy Director, RRL, for the valuable suggestions during the course of my work.*
- *The staff of the R & D Section of T.C.C., Cochin, for the analytical part of the work.*
- *Ms. Soumini Mathew for $^1$H NMR spectra, Mr. P. Mukundan for the help received in IR spectra, Mr. T. R. Sureshkumar for the neat drawings, Ms. Meera R. and Ms. Shermily P. R. who have helped in various stages of the experimental work.*
- *Cytec Canada Inc., for providing free samples of CYANEX reagents.*
- *Members of Ion-specific Separation Science & Technology Group, RRL, for their invaluable support and co-operation.*
- *Library and other supporting staff of RRL for the help rendered.*
- *All other friends and colleagues of RRL for their support.*

*I acknowledge the Ministry of Environment and Forests, New Delhi and the Council of Scientific and Industrial Research, New Delhi, for their financial assistance in the form of research fellowships.*

*I take this opportunity to record my respect, regard and gratitude to all my teachers for the help, guidance and motivation that I have received during the course of my student life.*

*Above all, I bow my head to almighty God for blessing me with my beloved parents, a loving husband, inspiring sisters and in-laws for their patience and moral support shown to me, which enabled me to complete this task.*

*Thiruvananthapuram* *TANIA FRANCIS*
*August, 2002*

# *LIST OF PUBLICATIONS*

1. Cyanex 471 X as extractant for the recovery of Hg(II) from industrial wastes, **Tania Francis**, T. P. Rao and M. L. P. Reddy, *Hydrometallurgy*, **57(3)**, 263-268 (2000).

2. Studies on the liquid-liquid extraction of mercury(II) from acidic chloride solutions using Cyanex 923, R. Meera, **Tania Francis** and M. L. P. Reddy, *Hydrometallurgy*, **61(2)**, 97-103 (2001).

3. Solvent extraction of mercury (II) with dicyclohexano-18-crown-6 and its application to industrial wastes, **Tania Francis**, R. Meera and M. L. P. Reddy, *Sep. Sci. Technol.*, **36(10)**, 2341-2353 (2001).

4. Liquid-liquid extraction of Hg(II) from acidic chloride solutions using bis-2-ethylhexyl sulphoxide, **Tania Francis**, T. R. Ramamohan, and M. L. P. Reddy, *J. Chemical Tech. & Biotech.*, **76(7)**, 737-742 (2001).

5. Recent advances in the solvent extraction of mercury (II) with calixarenes and crown ethers, M. L. P. Reddy and **Tania Francis**, *Solvent Ext. Ion Exch.*, **19(5)**, 839-863 (2001).

6. Radiochemical extraction of mercury(II) from acidic chloride solutions using dialkylsulphides, **Tania Francis** and M. L. P. Reddy, *J. Radioanal. Nucl. Chem.* **252(1)**, 99-104 (2002).

7. Thiosubstituted organophosphinic acids as selective extractants for mercury(II) from acidic chloride solutions, **Tania Francis** and M. L. P. Reddy, *Solvent Extr. Ion Exch.*, 2002 (In press).

# CONTENTS

**Chapter 1**

**Chapter 2**

## Chapter 3

## Dialkyl Sulphoxides as Extractants for Mercury......................49-70

## Chapter 4

## Extraction and Separation of Mercury(II) from Industrial Wastes with Thiosubstituted Organophosphinic Acids............71-89

# *PREFACE*

The Thesis entitled "***LIQUID-LIQUID EXTRACTION AND SEPARATION OF MERCURY FROM INDUSTRIAL WASTES***" embodies the results of investigations carried out on the extraction of mercury(II) from acidic chloride solutions using various oxo - and sulphur donors as extracting ligands, with a view to develop selective liquid-liquid extraction procedures for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry. The thesis is comprised of five chapters.

The introductory chapter highlights the significance of the control and removal of mercury from industrial waste streams with special emphasis on the use of liquid-liquid extraction and separation technique as a tool. A general introduction to the extraction chemistry followed by an exhaustive literature review on the recent developments on the liquid-liquid extraction and separation of mercury(II) has also been incorporated.

The second chapter deals with studies on the liquid-liquid extraction of mercury(II) from dilute hydrochloric acid solutions with dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane as an extractant. For comparison, extraction studies have also been carried out using 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and dibenzo-18-crown-6 (DB18C6). The solid $HgCl_2$.DC18C6 complex prepared has been characterised by elemental analysis, IR and $^1H$ NMR spectral studies. The developed extraction procedure for mercury using DC18C6 has been applied for the separation of mercury from the brine-sludge of a Chlor-Alkali industry.

Chapter 3 reports on the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using bis-2-ethylhexyl sulphoxide (B2EHSO) as an extractant. For comparison, studies have also been carried out with dioctyl sulphoxide (DOSO) and an aryl sulphoxide, diphenyl sulphoxide (DPhSO). The extraction behaviour of mercury(II) has also been compared with trialkylphosphine oxide (TRPO). The dependence of extraction on the nature of the diluent has been investigated and correlated with the dielectric constants. The developed liquid-liquid extraction procedure has been applied for the extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry using B2EHSO or TRPO in kerosene as an extractant.

The fourth chapter embodies results on the extraction behaviour of mercury(II) from acidic chloride solutions with mono - and di - sulphur analogs of bis-(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), namely, bis-(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302 = CY302)and bis-(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301 = CY301). The developed liquid-liquid extraction procedure has been applied for the selective extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry using CY301 in kerosene as an extractant.

Chapter 5 incorporates the results on the selective extraction and separation of mercury from the waste streams of a Chlor-Alkali industry by employing triisobutylphosphine sulphide (TIBPS) as an extractant. For comparison, studies have also been performed with dialkyl sulphides, such as, dibutyl sulphide (DBS) and dioctyl sulphide (DOS). IR spectral studies have been employed to further clarify the nature of the extracted complexes into the organic phase. The loading and recycling capacity of TIBPS has also been determined. The effect of other metal ions such as, calcium(II), magnesium(II) and barium(II) on the extraction efficiency of mercury(II) has also been investigated with a view to develop a selective liquid-liquid extraction procedure for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry.

The conclusions of the work and the relevant literature are provided towards the end of the thesis.

# Chapter 1

# Liquid-Liquid Extraction of Mercury(II) : An Overview

Mercury is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota. Today, both inorganic and organic mercury compounds are produced in industrial processes in Chlor-Alkali, agriculture, paper and pharmaceutical industries and they are responsible for the vast majority of the present anthropogenic contamination of our environment with this toxic metal [1,2]. Mercury is a contaminant of concern, which is known to bioaccumulate through the food web, owing to its affinity to the sulphydryl groups in biological systems. Methylation of inorganic mercury in aquatic environment and their subsequent bioaccumulation in fish through the food chain is a major human health and environmental concern due to the toxicity of methylmercury. Methylmercury is a neurotoxin; causing blockage of binding sites in enzymes, interfering in protein synthesis and impeding thymidine incorporation into DNA [3]. Reports of methylmercury poisoning have come from many parts of the world. Particularly disastrous were the widespread methylmercury compound poisoning cases of Minamata Bay, Japan [4]. Thus, the control and removal of mercury have received considerable attention in recent years.

For many years, the Chlor-Alkali industry all over the world has been a matter of grave concern because of the potential pollution hazards due to the presence of mercury in the waste streams. In India, there are about 24 Chlor-Alkali plants operating based on the mercury cell process. The major culprit, "the brine-sludge" is responsible for most of the mercury loss in the Chlor-Alkali industry. Hence, the mercury content in the brine-sludge must be brought down to parts per billion levels for safe disposal. Conventional mercury treatment technologies include precipitation [5-10], carbon adsorption [11-13], ion-exchange [14-17], cementation [18-20] and roasting [21-23]. Nowadays, hydrometallurgical routes [24-29] are also being considered as economic alternatives for mercury(II) recovery from industrial waste streams. Tecnicas Reunidas, SA, Spain [30] and Baba *et al.* [31] have developed liquid-liquid extraction based processes for the recovery of mercury from waste streams of a Chlor-Alkali industry.

The conventional mercury treatment processes are generally non-selective and only roasting or retorting recovers pure mercury. The other methods involve an additional purification step for the complete recovery and all generate secondary waste. It is well known that separation processes based on the ion-exchange technique yield high purity compounds. However, these processes are time consuming and inherently expensive. Methods based on liquid-liquid extraction emerged as novel and unique technique for the separation of metal ions owing to its simplicity, versatility and ready adaptability to scaling up of the process. Recycling of the spent solvent is yet another attractive feature of this technique. Hence, in the present work the liquid-liquid extraction technique has been explored using various extraction reagents to develop selective separation procedures to recover mercury(II) from the brine-sludge of a Chlor-Alkali industry.

## 1.1 LIQUID-LIQUID EXTRACTION: GENERAL

Liquid-liquid extraction highlights the usefulness of phase distribution and is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents. In liquid-liquid extraction, a solute distributes itself between two immiscible liquids. According to Gibbs phase rule,

$$P + V = C + 2 \qquad (1.1)$$

where P is the number of phases, V the variance or degrees of freedom and C the number of components. The distribution of a solute between two immiscible solvents is univariant at constant temperature and pressure. That is, if we choose the concentration of the solute in one phase, its concentration in the other phase is fixed.

The distribution law, stated by Berthelot and Jungfleisch [32] and thermodynamically elaborated by Nernst [33] in 1891, states that at a particular temperature for a solute 'X' distributing between two immiscible solvents 1 and 2, at equilibrium, the ratio of concentrations of the two phases is a constant, provided the nature of the species is the same in both the phases.

$$D = [X]_1/[X]_2 \qquad (1.2)$$

The constant, D, is known as the distribution or extraction coefficient. The chemical potential of the solute is the same in each phase at equilibrium, provided temperature and pressure are constant, *i.e.*

$$\mu_1 = \mu_2 \qquad (1.3)$$

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions of $\mu$,

$$\mu_1^\circ + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^\circ + RT \ln m_2 + RT \ln \gamma_2. \qquad (1.4)$$

where $\mu^\circ$ represents the chemical potential of the solute in a hypothetical ideal 1 molal solution, where, $m$ represents the solute concentration in molality and $\gamma$ the molal activity coefficient. Then, the molal distribution coefficient, D, can be represented as:

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\mu_2^\circ - \mu_1^\circ)/RT} \qquad (1.5)$$

For a system in which the two solvents are completely immiscible under all circumstances the exponential term is a constant, K′, so that

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K' \qquad (1.6)$$

Thus, D depends on the activity coefficients of the solute in each of the phases. When the activity coefficients approach unity, *i.e.* at low concentrations, D becomes constant. The distribution coefficient is related to the percentage extraction, E, by the Eq. (1.7).

$$E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \qquad (1.7)$$

where $V_{aq.}$ and $V_{org}$ are the volumes of the aqueous and organic phases, respectively. The separation factor, S.F., is given by

$$S.F. \quad = \quad D_1/D_2 \qquad (1.8)$$

where $D_1$ and $D_2$ are the distribution coefficients for elements 1 and 2, respectively.

## 1.2 LIQUID-LIQUID EXTRACTION SYSTEMS

The nature of the extractable metal species is of fundamental importance in metal extraction systems. Based on these facts, Ritcey and Ashbrook [34] classified the extractants into three classes as indicated below:

(1) Those which involve compound formation
(2) Those which involve ion association
(3) Those which involve solvation of metal ion

### 1.2.1 Extractants involving compound formation

This class of extractants can be further divided into two sub-classes, namely acidic extractants and chelating extractants. The former are those having reactive groups such as –COOH, >P(O)OH, $-SO_3H$, while the latter are those which chelate with metal ions.

**A. Acidic extractants**

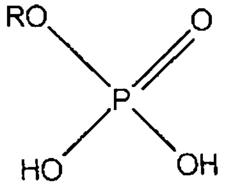
Acidic extractants or cationic liquid ion exchangers, extract metals by a cation exchange mechanism, in which hydrogen ions of the extractant are exchanged for metal ions. Basically, the general mechanism is as shown in Eq. (1.9).

$$M^{n+}_{aq} + n\,HA_{org} \rightleftharpoons MA_{n\,org} + n\,H^{+}_{aq} \qquad (1.9)$$

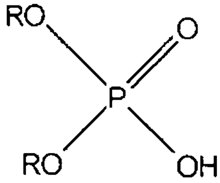
The metal extractants of the acidic type used in commercial operations are organic derivatives of phosphorus acids and monocarboxylic acids.

### *Acidic organophosphorus extractants*

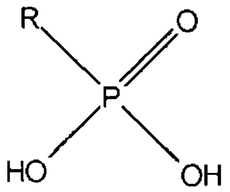
This type of extractants include the following:



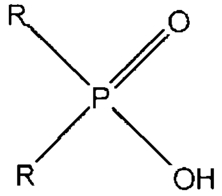
1. Monoalkyl phosphoric acid



2. Dialkylphosphoric acid



3. Monoalkyl phosphonic acid



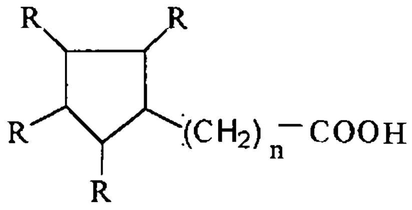
4. Dialkylphosphinic acid

*Fig. 1.1* Structures of some organophosphorus acid extractants.

where R can be alkyl or aryl substituents. Of these, alkyl phosphoric acids have proved to be most versatile, especially di-(2-ethylhexyl) phosphoric acid (DEHPA). It has been used commercially for many metals including uranium [35] and rare earths [36]. Among the esters of phosphonic acid, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) has been widely used for the extraction and separation of rare earths [37]. Various dialkyl phosphinic acid extractants such as bis-(2,4,4-trimethylpentyl) phosphinic acid (CYANEX 272) has been proved to be an important extractant for rare earth separations [38].

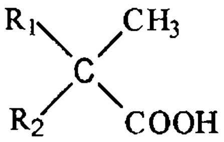
*Carboxylic acids*

Carboxylic acids such as Naphthenic acid and Versatic acids have been used commercially for the separation of metal ions.



Naphthenic acid

**5**



Versatic acid 911

($R_1, R_2 = C_4{-}C_5$)

**6**

*Fig. 1.2* Commercially available carboxylic acid extractants.

Reviews on the use of carboxylic acids in solvent extraction processing of metal ions and their applicability in this field are available in the literature [39,40].

## B. Chelating extractants

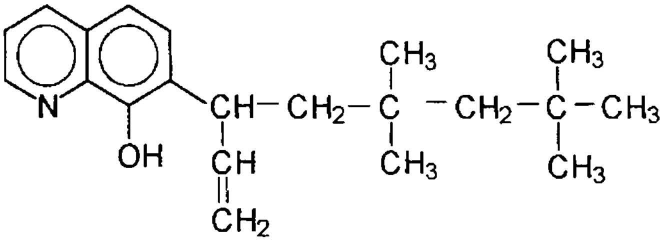
Chelating extractants contain donor atoms such as nitrogen, sulphur or oxygen as the basic atom capable of forming bidentate complexes with metal ions. Examples of some chelating reagents are dithizone, cupferron, acetylacetone, 2-thenoyltrifluoroacetone, 4-acyl-5-pyrazolones and derivatives of 5-isoxazolones. Commercially useful chelating extractants are of two types: a series of substituted 2-hydroxybenzophenone oximes produced by Henkel Corporation under the name LIX reagents and the substituted 8-hydroxyquinolines produced by Sherex (Ashland

Chemical Company) and marketed under the name Kelex. Most of these extractants were developed for the specific extraction of copper from acidic leach liquors and from alkaline solutions [41,42].

$CH_3(CH_2)_3\ CH(C_2H_5)\ C(=NOH)\ CH(OH)\ CH(C_2H_5)\ (CH_2)_3\ CH_3$

5,8-diethyl-7-hydroxy-6-dodecanone oxime

7



7-[3-(5,5,7,7-tetramethyl-1-octenyl)]-8-hydroxyquinoline (Kelex 100)

**8**

*Fig. 1.3* Chelating extractants

### 1.2.2 Extractants involving ion association

Quaternary ammonium compounds with high molecular weights such as tricaprylmethylammonium chloride commercially known as Aliquat 336 behave chemically as strong base anion exchangers and require lower concentrations of salting out reagents. Processes have been developed which employ primary ($RNH_2$) [43], secondary ($R_2NH$) [44], tertiary ($R_3N$) [45] amines and quaternary ammonium salts ($R_4N^+$) [46]. The usefulness of amines as extractants depends essentially on the ability of ions to form anionic species in the aqueous phase, which are extracted by amines in an anion exchange process. In order to achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with the metal species.

$$R_3N_{org} + HX_{aq} \rightleftharpoons R_3NH^+X^-_{org} \qquad (1.10)$$

$$R_3NH^+X^-_{org} + MY^-_{aq} \rightleftharpoons R_3NH^+MY^-_{org} + X^-_{aq} \qquad (1.11)$$

One important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which is determined by the nature of the diluent.

$$\underset{\text{Monomer}}{R_3N^+HX^-} \rightleftharpoons \underset{\text{Dimer}}{(R_3N^+HX^-)_2} \rightleftharpoons \underset{\text{Polymer}}{(R_3N^+HX^-)_n} \qquad (1.12)$$

Another factor influencing metal extraction is the nature of carbon chain and also the number of carbon atoms in the chain. Some of the metal species which have been reported to be extracted by quaternary ammonium halides (Aliquat 336) are $CuCl_2^-$, $CuCl_4^{2-}$, $FeCl_4^-$ and $CdCl_4^{2-}$ [47].

### 1.2.3 Extractants involving solvation

Oxygenated organic solvents such as alcohols (C-OH), ketones, ethers and esters show some basicity because of the lone pair of electrons on the oxygen atom and can therefore directly solvate protons and metal ions and bring about their extraction. Alcohol solvate better than ketones or ethers.

Esters of organophosphorus acids ≡P=O and a number of related compounds are a class of organic solvents which show remarkable solvating properties, whose essential functional group is the semipolar P=O bond with the oxygen atom having good steric availability. Tri-*n*-butyl phosphate (TBP) has been used in liquid-liquid extraction and may be taken as a typical example of compounds containing P=O bond The difference in degree of extraction of elements is utilised for their mutual separation using TBP [48]. The basicity and hence extractability of organophosphorus compounds is in the order: phosphates < phosphonates < phosphinates < phosphine oxides. Among trialkylphosphine oxides, tri-*n*-octylphosphine oxide (TOPO) has been used for the recovery of vanadium from phosphate liquors [49,50]. CYANEX 923, supplied by Cytec Canada Inc., belongs to the new class of extractants consisting of a mixture of trialkylphosphine oxides. Neutral bifunctional extractants such as di-hexyl-N,N,-diethylcarbamoylmethylphosphinate (DHDECMP) is used for actinide purification [51, 52].

Sulphoxides are pyramidal molecules with a lone pair of electron on both the sulphur and oxygen atoms, capable of donation. A correlation of basicity with extracting power clearly establishes the position of sulphoxides between ketones and phosphine oxides. Thus, the sulphoxides find their place as promising extractants for a number of metals [53, 54].

## 1.3 LIQUID-LIQUID EXTRACTION STUDIES OF MERCURY(II): LITERATURE REVIEW

The liquid-liquid extraction of mercury(II) has been investigated using various kinds of amines and organophosphorus extractants. However, these extractants containing nitrogen or oxygen as donor atom have only poor selectivity for mercury(II) over other metals. On the other hand, it is well known that metal ions classified into so called 'soft acids' such as gold(III), silver(I), mercury(II), palladium(II) *etc.* can be selectively and effectively extracted by extraction reagents containing sulphur as the donor (soft base) atom [55]. In recent years, various sulphur containing reagents have been used for the extraction of mercury(II) from hydrochloric acid solutions. The main aim of this literature review is to highlight the most remarkable advances achieved after 1991 on the liquid-liquid extraction of mercury from aqueous solutions using various extraction systems. The liquid-liquid extraction reagents explored in the extraction studies of mercury(II) can broadly be classified under three heads, namely,

1. Extraction by Oxo - donors
2. Extraction by N -donors and
3. Extraction by S - donors

based on the donor atom in the extractant

### 1.3.1 Extraction by Oxo - donors

Despite not having a sulphur atom in its structure, tri-*n*-butyl phosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO) have been reported as efficient extractants for mercury(II) [56]. Earlier, Sato and Nakamura [57] established the stability constants of the aqueous chloro-complexes of mercury using liquid-liquid extraction with TOPO by employing non-linear least square analysis. Mercury extraction from acidic aqueous solutions by the TRUEX process solvent, a mixture of *n*-octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and TBP in *n*-dodecane was investigated by Brewer *et al.* [58] and Herbst *et al.* [59] and reported the extraction equilibrium as:

$$\mathrm{HgCl}_{x\,aq}^{y} + a\,\mathrm{E}_{org} \rightleftharpoons \mathrm{HgCl}_2.\mathrm{E}_{a\,org} + (x\text{-}2)\,\mathrm{Cl}^{-}_{aq} \qquad (1.13)$$

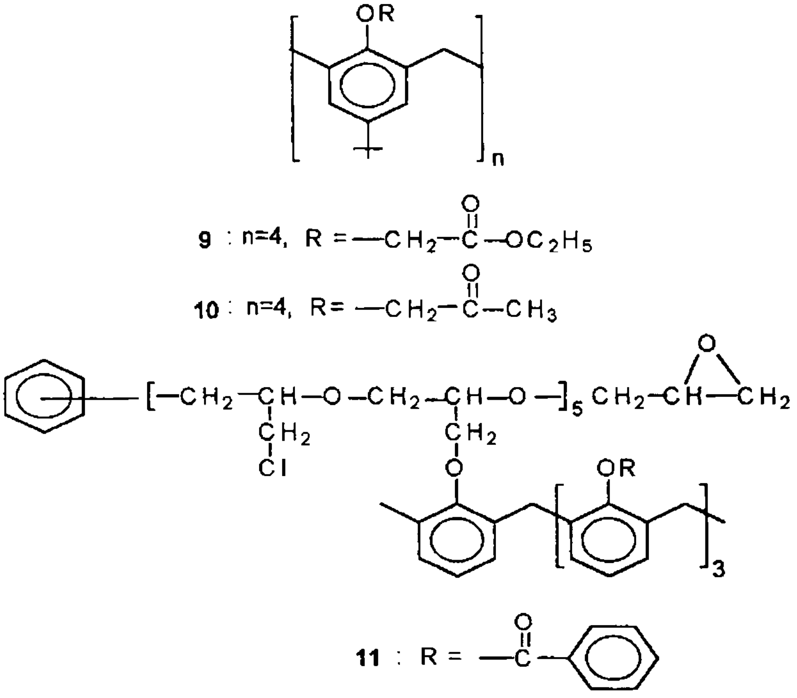
where x = 2 or 4, y = 0 or -2, E = CMPO or TBP and 'a' denotes the number of CMPO or TBP molecules. Podands containing phosphoryl fragments have been employed to study the extraction behaviour of mercury(II) from hydrochloric acid solutions [60].

The complexes of crown ethers with $HgX_2$ (X = Cl, CN) species adopt rotaxane like structures due to the covalent character of the $HgX_2$ compound [61], in particular, in the organic medium. When estimating the theoretical size of the macrocyclic which permits complex formation, the size of the substituent X in $HgX_2$ has to be considered, not only the ionic radius of the metal. In this respect, formation of complexes with $Hg(CF_3)_2$ requires the use of larger macrocyclics (20 membered ring) than with other $HgX_2$ species such as $HgCl_2$ or $Hg(CN)_2$ (18 membered rings). Paige and Richardson [62] have reported that $HgCl_2$ form 1 : 1 complex with 18-crown-6 (18C6). The metal coordination is hexagonal bipyramidal with $Cl^-$ atoms strongly coordinated in the axial positions and the 18C6 in the equatorial plane.

Recently, Giovannetti *et al.* [63] have investigated the extraction of mercury(II) from hydrochloric acid solutions (1 - 7 mol/dm$^3$) with DB18C6 (L) into benzene in the presence of $Li^+$, $K^+$, $NH_4^+$ and $Ca^{2+}$ chlorides and reported that mercury(II) was extracted prevalently as $HgCl_4^{2-}$ by forming ion-pair compounds of $[(L_2M_2)^{2+}HgCl_4^{2-}]$ (where M = $Li^+$, $K^+$ or $NH_4^+$) or $[LM^{2+}\ HgCl_4^{2-}]$ (M = $Ca^{2+}$) and $[LH^+(HHgCl_4)^-]$. It was seen from the results that the extractability of mercury(II) in the presence of these cations decreased in accordance with their ionic diameter.

The most recent studies on the liquid-liquid extraction of mercury(II) deeply rely on the use of macrocyclic ligands such as calixarenes derivatives with different number of atoms and several structural modifications. Calixarenes are macrocyclic compounds synthesised by condensation of phenol derivatives with formaldehyde in the alkaline medium. The most common calixarenes are those containing four, six or eight phenolic units and several compounds possessing different substituent groups either on the aromatic rings or on the phenolic oxygens [64]. As the number of phenolic units increase, these types of compounds exhibit significant number of conformations, affording different unique cavities with particular sizes and shapes [65-67]. Although each phenol unit can rotate according to the oxygen-through-the annulus rotation mechanism, they favourably adopt a cone conformation because of the stabilisation by intramolecular hydrogen bonding interactions and –OH groups [68,69]. Therefore, the *p-tert*-butylcalix[4]arene adopts $C_{4v}$ symmetry and has a $\pi$-basic cavity in the upper rim [70,71].

Deligoz and Yilmaz [72] have studied the extraction behaviour of transition metal ions from picrate solutions into chloroform using a series of *p-tert*-butylcalix[4]arenes in which ester and ketone groups **9-10** (Fig. 1.4) are attached to the lower rim and a polymeric calixarene **11**. The polymeric calixarene **11** was selective for $Ag^+$, $Hg^+$ and $Hg^{2+}$ unlike its monomeric analog.



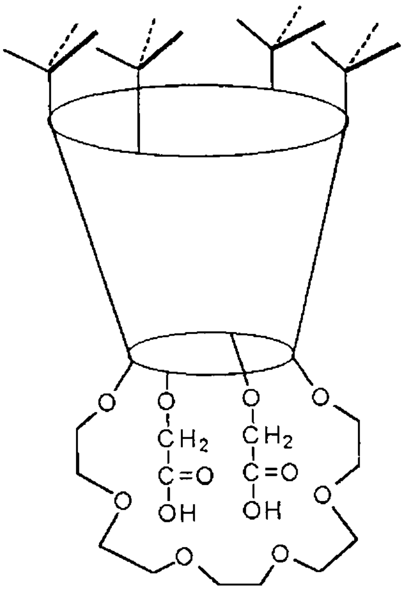
**9** : n=4, R = $-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

**10** : n=4, R= $-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

**11** : R = $-\overset{O}{\overset{\|}{C}}-C_6H_5$

*Fig. 1.4* Ester and ketone derivatives **9-10** of *p-tert*-butylcalix[4]arene and a polymeric calixarene **11** [72].

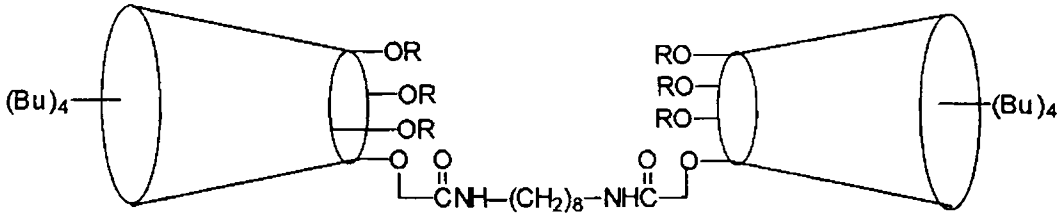
The liquid-liquid extraction behaviour of heavy metals with macrocyclic ligands based on calix[4]arenes **12** (Fig. 1.5) from weakly acidic solutions into toluene has been investigated and reported that a calixarene based compound with a crown-6-moiety **12** efficiently extracts heavy metal ions such as $Hg^{2+}$ and $Pb^{2+}$ from weakly acidic solutions due to their compatible ionic radius [73]. Further, it has also been reported quantitative extraction of $Hg^{2+}$ above pH 2.5 with the ligand containing four $-CO_2H$ groups.



**12**

***Fig. 1.5*** Macrocyclic based calix[4]arene [73].

The complexing abilities of two biscalix[4]arene **13-14** (Fig. 1.6) with $Hg^{2+}$ from picrate solutions have been studied and reported > 90% extraction [74]. Further, it has also been reported that mercury(II) is extracted in 1 : 2 metal : ligand stoichiometric ratio with **13** and in 1:1 ratio with **14**. The high complexation ability of chemically modified biscalix[4]arenes using ester and ketones as the ligating functional groups in the cone conformation show quantitative extraction towards $Hg^{2+}$. These results suggest that the ketonic groups possess considerable ionophoric properties. Memon and Yilmaz [75] reported selective extraction of $Hg^{2+}$ using 2,2-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]-arenyloxyl propanone as well as their hexaketone derivatives. These studies also reveal that the high selectivities displayed by these compounds depend on different factors such as the conformation, polarisability and the nature of the substituents on the lower rim of the biscalixarenes. The liquid-liquid extraction of alcohol, ester and ketone derivatives of biscalix[4]arene have been carried out and found the ketone derivative to be selective for $Hg^{2+}$, whereas the ester derivative was not selective and proved to be good extractant with higher affinity towards $Na^+$, $Cu^{2+}$, $Co^{2+}$ and $Hg^{2+}$. The results indicate that the ligands containing π-system functional groups and having proper conformation of calixarene cavity form novel binding sites for the complexation of metal cations.



**13** : R = $—CH_2COOC_2H_5$
**14** : R = $—CH_2COCH_3$

*Fig. 1.6* Structure of ester and ketone derivatives of biscalix[4]arene [74].

### 1.3.2 Extraction by N - donors

The amines, due to their unique anion exchange ability, have been employed to extract mercuric ions in the chloride solutions, which exist primarily as the anionic tetrachloride complex. Chapman and Caban [76] have described a liquid-liquid extraction process for the recovery of mercury(II) from dilute brine-sludge of a Chlor-Alkali plant using tri-*n*-octyl amine (TOA) as an extractant. This process involves extraction of mercuric chloride from depleted brine, from the mercury cathode cells of a Chlor-Alkali plant, of pH = 3 at temperature of 70°C, the mercuric chloride level ranging from 1-50 ppm using 0.1 mol/dm$^3$ TOA in xylene in three stages of counter current extraction with an organic to aqueous phase ratio of 0.01. The mercury from the loaded organic phase was then recovered by treating with a brine having pH = 11 at an organic to aqueous phase ratio of 100. Recently, Sato *et al.* [77] have compared the liquid-liquid extraction of mercury(II) from hydrochloric acid solutions by high-molecular weight amines such as TOA and trioctylmethylammonium chloride (TOMAC) and proposed the following equilibrium equations:

For TOA:

$$2HgCl_{2\,aq} + 2R_3NH^+Cl^-_{org} \rightleftharpoons (R_3NH)_2Hg_2Cl_{6\,org} \text{ at low acidity} \quad (1.14)$$

$$HgCl_{2aq} + 2R_3NH^+Cl^-_{org} \rightleftharpoons (R_3NH)_2.\ HgCl_{4\,org} \text{ at higher acidity} \quad (1.15)$$

For TOMAC:

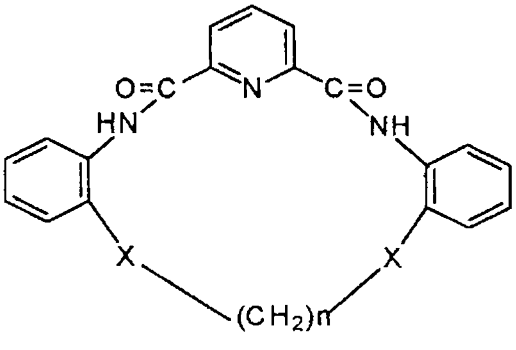
$$2\,HgCl_{3aq}^- + 2\,R_3R'N^+Cl^-_{org} \rightleftharpoons (R_3R'N)_2\,Hg_2Cl_{6\,org} + 2\,Cl^-_{aq} \quad (1.16)$$

The extraction efficiency of TOMAC was found to be higher than that of TOA. Schugerl and Gudorf [78] have described a liquid-liquid extraction process for the recovery of mercury from the waste sludge of a natural gas industry. This process involves leaching of the waste sludge with 6 mol/dm$^3$ HCl and subsequent extraction of mercury from the leach solution by employing TOA in kerosene as an extractant. The mercury was finally recovered from the loaded solvent by successive stripping in three stages using 0.1 mol/dm$^3$ NaCl and 0.05 mol/dm$^3$ NaOH, respectively. Mercury removal from water over a wide pH range has been investigated by Larson and Wiencek [79] using triisooctyl amine and tricaprylmethylammonium chloride (Aliquat 336) as liquid ion exchangers.

Cote *et al.* [80] have reported selective extraction of mercury(II) from silver nitrate solutions using Aliquat 336 after it has been complexed with a polyaminocarboxylic acid. A method for the selective extraction of mercury(II) by 2-benzylpyridine in benzene from dilute mineral acid solutions containing iodide ions has been developed and applied to the separation of mercury from environmental samples [81].

Lipophilic 8-hydroxyquinoline derivatives, such as the commercial reagent Kelex 100 [82,83] are promising extractants for metal extraction [84] and decontamination of multimetal finishing wastes [85]. Stephan *et al.* [86] synthesised a series of position isomers of 8-hydroxyquinoline and studied their extraction behaviour towards mercury(II). The higher extraction efficiency of 2-nonyl-8-hydroxyquinoline can be explained on the basis of the higher basicity of the nitrogen donor-atom as calculated through molecular modeling.

The extraction ability of various metal ions including $Hg^{2+}$ using macrocyclic compounds containing pyridine moiety **15a-e** (Fig. 1.7) has been investigated [87] and reported that the extraction efficiency for mercury(II) decreases in the order: **15b** > **15c** > **15d** > **15e**.



**15a**

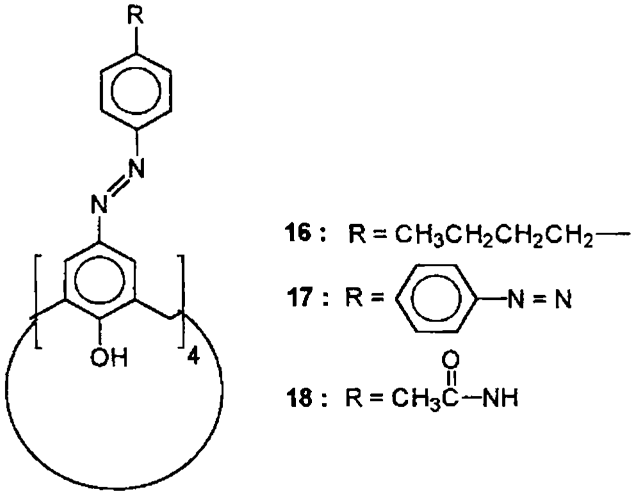
**b-e** : X=O, n=2-5

***Fig. 1.7*** Macrocyclic compounds containing pyridine moiety [87].

The liquid-liquid extraction behaviour of $Hg^{2+}$, $Hg^{+}$ and $Ag^{+}$ from picrate solutions into chloroform using calix[6]arene derivative containing azo groups has been investigated and compared with the binding properties of *p-tert*-butylcalix[6]arene and 4-phenylazo-2,6-dimethylphenol [88]. The results show that the calixarene 5,11,17,23,29,35-hexa-*p*-phenylazo-37,38,39,40,41,42-hexahydroxycalix[6]arene (*p*-phenylazocalix[6]arene) has the binding ability only to $Ag^{+}$, $Hg^{+}$ and $Hg^{2+}$, among the metal ions tested. It is clear that this extractability arises from phenylazo groups conjugated to calix[6]arene. Further, selective extractability of this compound is concerned with its specific structure which is a cyclic oligomer. In the latter studies, the characteristic nature of binding properties using *p*-(phenylazo)calix[n]arenes (n = 6 and n = 4) towards $Ag^{+}$, $Hg^{+}$ and $Hg^{2+}$ has been studied and has been explained in terms of a metal ion-induced azo-hydrazone tautomerism [89]. Liquid-liquid extraction of transition metal-ions using upper rim substituted diazo coupling derivatives (Fig. 1.8) **16-18** from picrate solutions has been investigated [90]. The compound **18** shows higher selectivity towards $Hg^{2+}$ and $Hg^{+}$ than the other compounds, which can be explained on the basis of HSAB principle. The compound **18** containing electron-donating group is a harder base and prefers the $Hg^{2+}$ cation. Choi *et al.* [91] have prepared a new azophenol type chromogenic ionophore based on *p-tert*-butylcalix[4]arene diazacrown ether which exhibited pronouncedly selective chromogenic behaviour towards $Hg^{2+}$ ions among the surveyed alkali, alkaline earth, transition and heavy metal ions in liquid-liquid extraction experiments.

Memon *et al.* [92] have reported selective complexation of $Hg^{2+}$ with biscalix[4]arene nitriles **19-21** (Fig. 1.9). The results clearly indicate that the introduction of two nitrile groups onto the lower rim of calix[4]arene showed better selectivity towards $Hg^{2+}$. This phenomenon can be explained by the HSAB principle whereby –C≡N group which is a soft base showing a stronger affinity towards soft acidic cations like $Hg^{2+}$. From these results, it is clear that mercury(II) is extracted as a 1 : 1 metal : reagent complex with **20** according to Eq. (1.17)

$$\mathrm{Hg}^{2+}_{aq} + 2\,\mathrm{Pic}^{-}_{aq} + \mathrm{L}_{org} \rightleftharpoons \mathrm{Hg(Pic)_2L}_{org} \qquad (1.17)$$

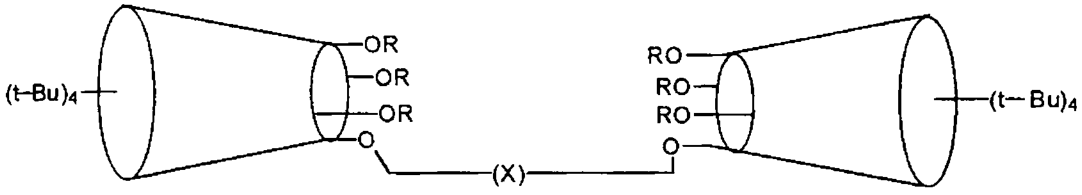


**16 :** $R = CH_3CH_2CH_2CH_2—$

**17 :** R =

**18 :** $R = CH_3C(=O)—NH$

*Fig. 1.8* Upper-rim substituted diazo-coupling derivatives of calix[4]arene [90].



**19 :** $X = CH_2CH_2OCH_2CH_2$; $R = CH_2CN$

**20 :** $X = CH_2CONH(CH_2)_2NHCOCH_2$; $R = CH_2CN$

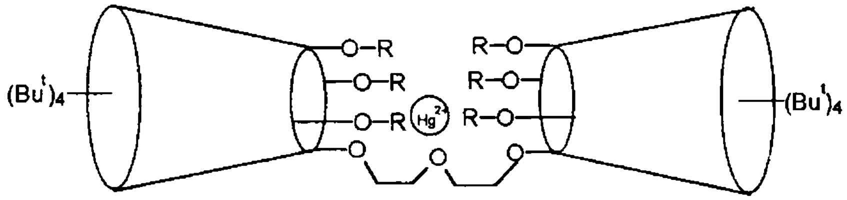
**21 :** $X = CH_2CONH(CH_2)_8NHCOCH_2$; $R = CH_2CN$

*Fig. 1.9* Structures of biscalix[4]arene nitriles [92].

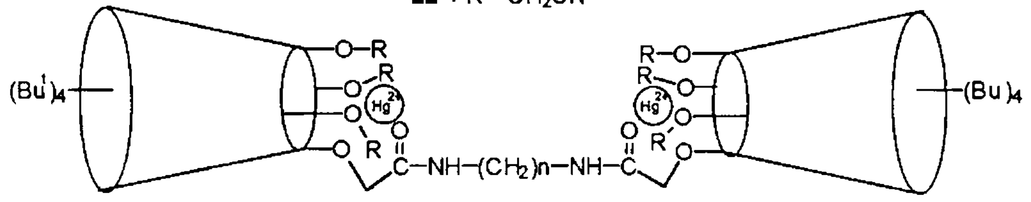
On the other hand, the extraction equilibrium of the $Hg^{2+}$ with **20** and **21** has been reported as:

$$2\mathrm{Hg}^{2+}_{aq} + 4\,\mathrm{Pic}^{-}_{aq} + \mathrm{L}_{org} \rightleftharpoons (\mathrm{Hg_2Pic_4})\mathrm{L}_{org} \qquad (1.18)$$

Further, these authors also proposed the structures of the complexes of $Hg^{2+}$ **22-24** (Fig. 1.10) formed with the calixarenes **19-21**, respectively.



**22** : R = $CH_2CN$



**23** : n = 2
**24** : n = 8

***Fig. 1.10*** Proposed structures of the complexes of $Hg^{2+}$ formed with the extractants **19-21** [92].

These authors have further investigated the binding properties of two new polymers containing pendant calix[4]arene units with nitrile functionalities on the lower rim by employing liquid-liquid extraction procedures. Both polymers exhibited good selectivity towards $Hg^{2+}$ like their precursor 5,11,17,23-tetra-*tert*-butyl-25,26,27-tricyanomethoxy-28-(2-hydroxy)ethoxycalix[4]arene [93].

### 1.3.3 Extraction by S - donors

Among the various organophosphorus extractants employed for the liquid-liquid extraction studies on mercury(II), the thiophosphorus compounds are certainly the more utilised, due to the very well known affinity between donor sulphur atoms and mercury ion, a factor which in principle, could allow a higher selectivity as a value adding to the extraction process [94]. In the recent past, triisobutylphosphine sulphide (TIBPS), marketed under the trade name of CYANEX 471X by Cytec Canada Inc., has been used for the extraction of mercury(II) from aqueous solutions [95-97]. Singh and Tandon [96] have reported a liquid-liquid extraction method for the recovery of mercury from paper industry effluent using TIBPS as an extractant. Reddy *et al.* [97] have also investigated the extraction behaviour of mercury(II) from thiocyanate solutions using TIBPS in benzene as an extractant and reported the extracted complexes as $Hg(SCN)_2$ and $Hg(SCN)_2.3TIBPS$. These results further demonstrate that mercury(II) can be selectively separated from zinc(II) and cadmium(II) at pH = 3.

Baba *et al.* [98] have described a liquid-liquid extraction process for the recovery of mercury from aqueous chloride media using dialkylmonothiophosphates ($R_1$, $R_2 = C \geq 3$, alkyl, cycloalkyl, aryl or aralkyl group) as an extractant. Brown *et al.* [99] have reported a process for the extraction of metals selected from the group consisting of zinc(II), silver(I), cadmium(II), mercury(II), nickel(II), cobalt(II) and copper(II) from aqueous solutions with dithiophosphinic acids.

Dialkyl sulphides and dialkyl sulphoxides have been considered attractive potential agents in the liquid-liquid extraction of mercury(II). Reddy *et al.* [100] have studied the extraction behaviour of mercury(II) from iodide solutions with bis-2-ethylhexyl sulphoxide (B2EHSO) in benzene as an extractant and reported the extracted complexes as $HgI_2$, $HgI_2.B2EHSO$ and $HgI_2.2B2EHSO$. Further, these authors have also discussed the separation possibilities of cadmium(II) from mercury(II). In the latter studies, Reddy and co-workers [101] have also investigated the extraction of mercury(II) from thiocyanate solutions and reported the extracted complexes as Hg(SCN)$_2$ and Hg(SCN)$_2$.2B2EHSO with the aid of chemically based models. Recently, Ishikawa and Sato [102,103] have investigated the extraction behaviour of mercury(II) from hydrochloric acid solution by employing dihexyl sulphoxide (DHSO) and reported the extracted complexes as :

$$HgCl_{2\,aq} + 2R_2SO_{org} \rightleftharpoons HgCl_2.2R_2SO_{org} \qquad (1.19)$$

$$HgCl^{-}_{3aq} + H^{+}_{aq} + 3R_2SO_{org} \rightleftharpoons HHgCl_3.3R_2SO_{org} \qquad (1.20)$$

$$HgCl^{2-}_{4aq} + 2H^{+}_{aq} + 2R_2SO_{org} \rightleftharpoons H_2HgCl_4.2R_2SO_{org} \qquad (1.21)$$

Further, when mercury(II) loading increases, the extraction equilibrium has been reported as:

$$HgCl_{2\,aq} + R_2SO_{org} \rightleftharpoons HgCl_2.R_2SO_{org} \qquad (1.22)$$

A few novel kinds of sulphur containing extracting reagents, 2-ethyl-2-(isobutylthiomethyl)butane thiol (EIBTMT), 3,3-diethylthietane (DETE) and 3,3-dibutylthietane (DBTE) have been synthesised by Inoue *et al.* [104] and utilised for the extraction of mercury(II) from acidic chloride solutions. For comparison, studies have also been performed with dihexyl sulphide (DHS), a conventional S - containing extractant. Mercury(II) was found to be extracted with DETE, DBTE and DHS according to the solvation reaction mechanism as given below:

$$HgCl^{2-}_{4aq} + 2S_{org} \rightleftharpoons HgCl_2S_{2\,org} + 2\,Cl^{-}_{aq} \qquad (1.23)$$

On the other hand, mercury(II) was found to be extracted with EIBTMT according to the following reaction:

$$HgCl^{2-}_{4aq} + 2\,HS_{org} \rightleftharpoons HgS_{2\,org} + 2H^{+}_{aq} + 4Cl^{-}_{aq} \qquad (1.24)$$

Baba *et al.* [30] have described a liquid-liquid extraction process for the extraction of mercury from industrial waste waters of soda electrolysis plants and battery industry using alkylthiol compounds as extracting reagents. Sahu and co-workers [105] have proposed a selective liquid-liquid extraction method for the recovery of mercury from industrial effluents by employing 3,4,4a,5-tetrahydro-3,3,4a-trimethyl-7-substituted-pyrimido[1,6a]benzimidazole-1-thiol (PBT). A thiol-based compound 1,3-pyridinediamidoethanethiol has been developed to bind mercury irreversibly and aid in soil remediation [106]. Nogueira *et al.* [107] devised a process for the elimination of mercury from industrial waste waters by means of liquid-liquid extraction with solvents containing an extractant from the group of thioalcohol, thiophenol or thiophene.

The extraction behaviour of mercury(II) from hydrochloric acid solutions has been investigated by Zuo and Muhammed [108] by employing a series of novel thiourea-based extractants such as: nonylthiourea (NTH), dodecylthiourea (DTH), benzylthiourea (BTH), dinonylthiourea (DNTH) and dioctylthiourea (DOTH) and reported fast kinetics of extraction for mercury(II). Further, it has also been reported the extracted complexes as $HgCl_2.DTH$ and $HgCl_2.(DTH)_3$. These authors reported that the stability constants of the extracted complexes of the various thiourea-based extractants decreases with increasing chain length. A selective extraction of mercury(II) over cadmium(II) and zinc(II) from hydrochloric acid solutions has also been established with NTH and DTH. Sandhya and Subramanian [109] have reported a simple liquid-liquid extraction procedure for the sequential separation of mercury(II) from cadmium(II) and zinc(II) using 1,3-diphenyl-2-thiourea in $CHCl_3$ as an extractant.

Liquid-liquid extraction of mercury(II) from chloride, nitrate and perchlorate medium using ω-thiocaprolactam (R) in chloroform as an extractant has been investigated by Nunez and co-workers and reported that the extraction efficiency of mercury(II) decreases in the order: $Cl^- > NO_3^- \approx ClO_4^-$ [110]. The extraction data have been analysed by both graphical and theoretical methods and reported the extracted complexes as $HgX_2.R$ and $HgX_2.R_2$ (where X = $Cl^-$, $NO_3^-$ or $ClO_4^-$). However, in concentrated hydrochloric acid solutions the extraction of mercury(II) is explained by the formation of $HgCl_3.RH$ and $HgCl_4.(RH)_2$ species.

Khan *et al.* [111] have reported the extraction of mercury(II) from mineral acid solutions using 1-naphthyl thiocarbamide in $CHCl_3$ / $Me_2CO$ (9 : 1) mixture. Comparative study on the extraction behaviour of mercury(II) using 2-(dodecylbenzenesulphonamide) thiazole and 2-(dodecylbenzenesulphonamide) benzothiazole showed that the two extracting agents can effectively extract mercury(II) at pH = 1.2 - 1.9 and 2.2 - 2.8, respectively. The extraction efficiency of the former was found to be superior to that of the latter [112]. Binding and ionophoric properties of polythioamide compounds with mercury has been investigated by Raouf *et al.* [113] and found good selectivity for mercury(II). Thiocarbamic-O-alkylesters have been reported as excellent ligands for the complexation of soft metal cations including mercury(II) from concentrated acidic solutions [114].

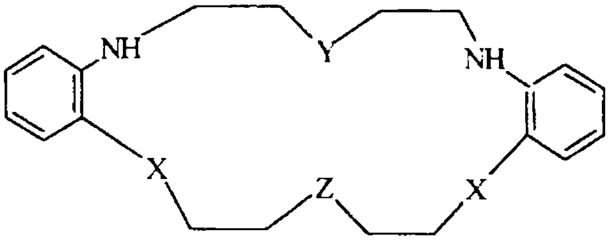
Baba and Inoue [115,116] have investigated the extraction behaviour of mercury(II) with sulphur containing carboxylic acids such as, α-butylthiolauric acid (α-BTLA ) and 2-butylthiododecanoic acid (2-BTDA) from hydrochloric acid solutions and reported that the extraction equilibrium of mercury(II) follows the solvation mechanism:

$$(RH)_{2\,org} + HgCl_{2\,aq} \rightleftharpoons (RH)_2\,HgCl_{2\,org} \qquad (1.25)$$

where RH represents α-BTLA or 2-BTDA.

Until 1992, a few studies have been carried out on the use of azathia derivatives, either cyclic or acyclic, for the extraction of metal ions [117]. Recently, Gloe *et al.* [118] have reviewed the synthesis, structure and binding properties of crown compounds and their open chain analogues containing a trithiadiazapentalene building block with soft transition metal cations. Cyclic monoazatetrathioether namely, 1-aza-4,7,11,14-tetrathiacyclohexadecane (ATCH) has been used for the extraction of many metal ions including mercury from picrate solutions [119]. ATCH extracted $Hg^{2+}$, $Ag^{+}$, $Cu^{+}$ and also $Cu^{2+}$ to some extent and other metal ions such as $Cd^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Ni^{2+}$ and $Co^{2+}$ were not found to be extracted. The metal ion binding properties of the monoazathiacrown ethers by liquid-liquid extraction was evaluated by incorporating lipophilic dodecyl and dodecanoyl group onto the monoazathiacrown ethers [120]. The liquid-liquid extraction experiments suggested that monoazathiacrown ethers have $Ag^{+}$ and $Hg^{2+}$ selectivities.

The extraction behaviour of $Ag^{+}$, $Cu^{+}$, $Cd^{2+}$, $Hg^{2+}$ and $Pd^{2+}$ has been studied over a wide range of pH using N - and S - containing analogs of DB18C6 **25** (Fig. 1.11) [121]. In the later studies, these authors [122] have reported the extracted complexes of mercury(II) as $Hg(HL)_nX_2$ ($X = Cl^-$, $NO_3^-$, picrate) in acid media and the chelate $(HgLX)_n$ species in alkaline solutions (HL = **25**). Extraction of mercury(II) from picrate solutions was investigated using azathia analog of DB18C6 and reported very high selectivity [123].



X = O, S; Y = $CH_3C_6H_4SO_2N$, S; Z=S.

**25**

*Fig. 1.11* N - and S - containing analogs of Dibenzo-18-crown-6 [121].

Due to the high affinity of thiacrowns to $Hg^{2+}$ ions, as well as the resistance to degradation under acidic conditions, crown thioethers have been well studied for the selective extraction of mercury from acidic solutions [124-126]. Small S-containing macro cycles are interesting since they have the advantage of endo-orientation of the ring S-donor atom in complexing with the metal ion. They also show unusual kinetic and thermodynamic properties [127,128]. The structure and complex formation of small 1,3-dithiol anellated thiacrown compound with silver(I) and mercury(II) from picrate solutions has been studied [129]. From the results it is clear that only 1 : 1 complexes are formed with mercury(II) in the chloride medium, whereas 2 : 1 metal : ligand complexes are formed in the nitrate medium. A series of hydrophobic tri- to hexadentate S - containing macrocyclic compounds including aromatic (benzo, a methylsulphide substituted benzo, chlorobenzo, thiophene and pyridine subunits) were synthesised **26-31** (Fig. 1.12) and tested as extractants for $Hg^{2+}$ from picrate and nitrate media, as well as for $Ag^{+}$, $Au^{3+}$ and $Pd^{2+}$ [127]. The efficiency of structurally related open chain compounds has been evaluated.

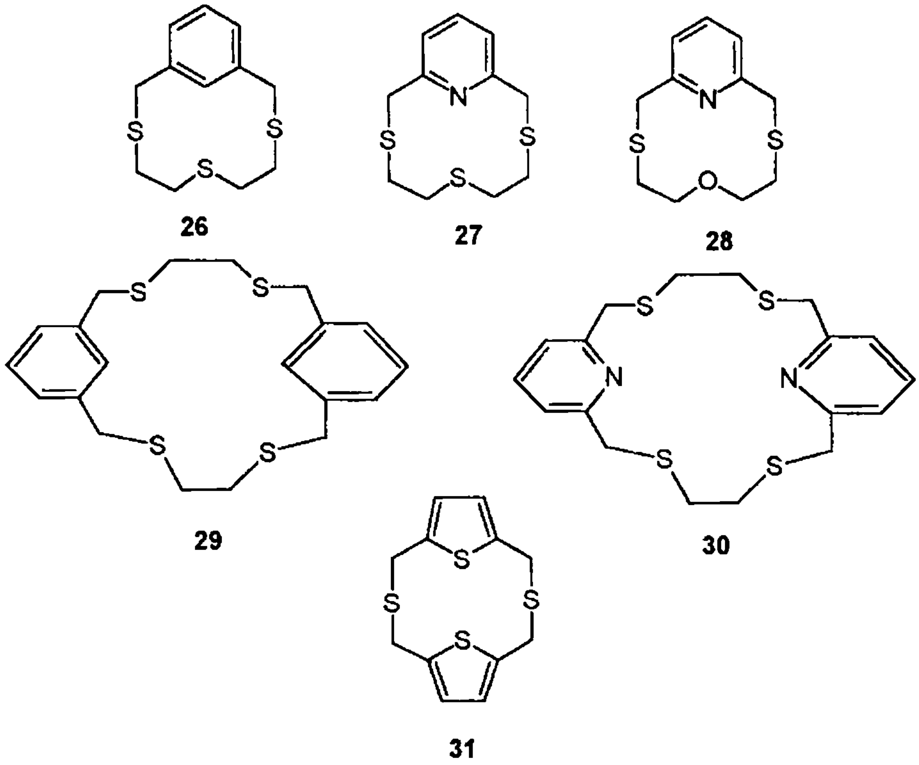
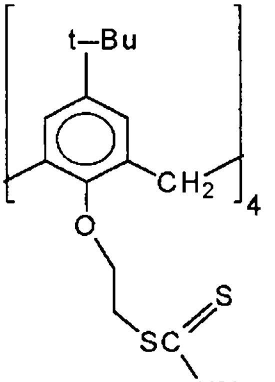
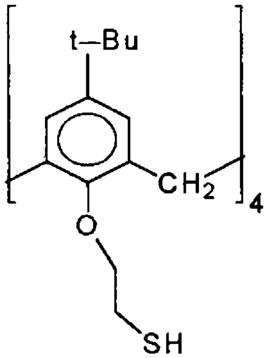


*Fig. 1.12* Tri - to hexa - dentate sulphur containing macrocyclic compounds with different substituent groups [127].

A comprehensive review of literature reveals that many *p-tert*-butylcalix[4]arene derivatives having S - containing functionalities appended to the lower rim (Fig. 1.13) and upper rim (Fig. 1.14) have been utilised for the extraction of mercury(II) from aqueous solutions [130-133] and these data have been covered in a recent review article [134].

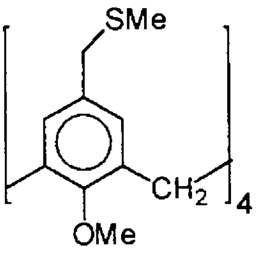


**32**

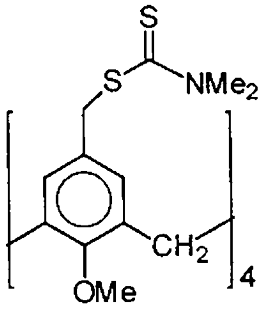


**33**

*Fig. 1.13* Calix[4]arenes with sulphur containing lower rim functionalities [130].



**34**



**35**

*Fig. 1.14* (Methylthio)methyl **35** and (N,N-dimethyldithiocarbamoyl)methyl **36** upper-rim-substituted calixarenes [131].

It is clear from the literature review that chemically modified calixarenes have been utilised for the selective extraction of mercury(II) from aqueous solutions. However, from an industrial point of view, application of calixarenes to liquid-liquid extraction process for the recovery and removal of mercury from industrial wastes is not viable due to the complexities involved in their synthesis.

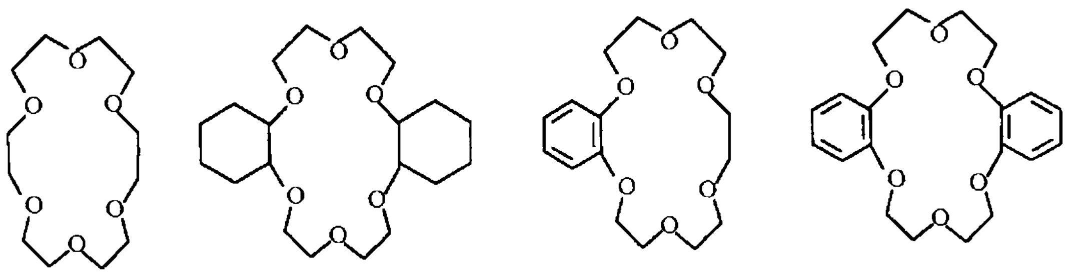
# *Chapter 2*

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

The discovery that crown ethers selectively complex alkali and alkaline earth metals [135-137] led to many studies of their use in liquid-liquid extraction processes [138-140]. Early workers noted that a match between the cavity size of the crown ether and the ionic diameter of the metal ion resulted in high extraction selectivity [141,142]. Thus, appropriately sized crown ethers could be chosen to obtain the selective extraction of a particular cation of interest. The nature of the substituent group on the macrocyclic ring is another important factor that influences the selectivity of crown ethers. Macrocyclic polyethers are chemically stable and can be easily regenerated.

Many studies have been carried out on the extraction of mercury(II) using crown ethers containing N - and S - donor atoms [118,134]. Compared with these, the systematic study of extraction involving crown ethers containing oxygen donor atom is sparse [63,143-146]. This prompted to initiate a systematic study on the extraction behaviour of mercury(II) using oxygen containing macrocyclic polyethers and their application to the recovery of mercury from the industrial waste streams.

In the present chapter, the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane as an extractant has been investigated with a view to elucidate the nature of the complexes extracted into the organic phase. For comparison, extraction studies have also been carried out with 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and dibenzo-18-crown-6 (DB18C6) (Fig. 2.1). The potential of DC18C6 for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry has also been investigated.



**18C6** **DC18C6** **B18C6** **DB18C6**

*Fig. 2.1* Structures of crown ethers employed for mercury(II) extraction studies.

## 2.1 EXPERIMENTAL

### 2.1.1 Reagents

The tracer solution of $^{203}$Hg ($t_{1/2}$ = 46.6 days) was obtained from the Board of Radiation and Isotope Technology (BRIT), India. The crown ethers, DC18C6 (mixture of cis-syn-cis and cis-anti-cis), 18C6, B18C6 and DB18C6 were obtained from Aldrich Chemical Company Inc., U.S.A. All the other chemicals employed were of analytical reagent grade.

Mercury(II) stock solution was prepared by dissolving 0.27 g of mercuric chloride in 100 cm$^3$ of distilled water. Stock solutions of calcium(II), magnesium(II) and barium(II) were prepared by dissolving 0.37 g of $CaCl_2.2H_2O$, 0.62 g of $MgSO_4.7H_2O$ and 0.61 g of $BaCl_2$ respectively, in 25 $cm^3$ of distilled water. Suitably diluted stock solutions of the above mentioned metal ions were used in the extraction and analytical studies. Rhodamine 6G (0.005%) solution was prepared 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 dissolving 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.

### 2.1.2 Apparatus

A well type NaI(Tl) Scintillation Counter supplied by Nucleonix Systems, India, was used for the measurement of the gamma activity of $^{203}Hg$ radioisotope. A Hitachi 220 Double Beam Microprocessor controlled Spectrophotometer was used for measuring the absorbances. Cold Vapour Mercury Analyser of Buck Scientific Model 400A, U.S.A., was employed to determine the mercury content in the brine-sludge of a Chlor-Alkali industry. A GBC Double Beam AAS, Australia, was used to determine the other associated 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 measurements. A Nicolet FTIR 560 Magna Spectrometer using KBr (neat) was used to obtain the IR spectrum of the mercury(II)-DC18C6 complex. C, H and N analysis was performed with a Perkin Elmer Series 2 Elemental Analyzer 2400. The Bruker 300MHz NMR Spectrometer was used to obtain the $^1H$ NMR spectra of the $HgCl_2$.DC18C6 complex. All the computer programs were written in FORTRAN 77 and executed on a 32-bit minicomputer (HCL).

### 2.1.3 Liquid-liquid extraction procedure

Equal volumes of the aqueous phase containing mercury(II) ($1 \times 10^{-5}$ mol/dm$^3$) labeled with the radioisotope ($^{203}$Hg) and organic phase were equilibrated in a glass stoppered vial using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium is attained within 30 min. The two phases were then separated and assayed radiometrically using a well type 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 experiments were performed in duplicate and the general agreement with distribution ratio values obtained was within ± 5%.

### 2.1.4 Analytical procedure

**A. Determination of mercury(II) and other associated metal ions in the brine-sludge of a Chlor-Alkali industry (obtained from Travancore Cochin Chemicals Ltd., Cochin)**

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

The mercury(II) content in the brine-sludge of a Chlor-Alkali industry has also been analysed spectrophotometrically using Rhodamine 6G [147]. 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 other associated metal ions), the pH adjusted to 4.0 and then 5 $cm^3$ of buffered potassium iodide solution was added followed by 5 $cm^3$ Rhodamine 6G (0.005%) and 1 $cm^3$ of 1% gelatin solution. The resultant solution was then made up to 50 $cm^3$ and the absorbance was measured at 570 nm against a reagent blank prepared under identical conditions. Then the concentration of the metal ion was computed from the calibration graph.

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

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

In the selectivity studies, calcium(II), magnesium(II) and barium(II) were determined by complexometric titrations using standard EDTA solution [148]. The determination of calcium(II) was carried out by the substitution titration method as described 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, 1 $cm^3$ of Mg-EDTA complex (0.1 $mol/dm^3$) was added to the above solution and titrated against standard EDTA solution (0.01 $mol/dm^3$) using eriochrome black T - potassium nitrate solid mixture (0.001 g eriochrome black T in 0.099 g potassium nitrate) as the indicator.

The complexometric titration method for magnesium(II) determination involves diluting 5 $cm^3$ of the metal ion solution to 50 $cm^3$ with distilled water followed by the addition of 2 $cm^3$ of ammonia - ammonium chloride buffer (pH = 10) and warming 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$^3$ 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) mixture 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 determined by the following method: A certain quantity of the complex was decomposed by heating in a minimum amount of $HNO_3$ : $HClO_4$ (1 : 1) solution and the excess acid was evaporated. The resultant mixture was diluted with distilled water to 25 cm$^3$ and mercury(II) was determined by EDTA titration using xylenol orange as an indicator at pH = 6 using hexamine buffer [148].

## 2.1.5 Preparation of solid mercury(II)-DC18C6 complex

$HgCl_2$.DC18C6 complex was prepared as follows: Solutions containing 0.27 g (1 mmol) $HgCl_2$ in 20 cm$^3$ 1-butanol and 0.37 g (1 mmol) DC18C6 in 20 cm$^3$ 1-butanol were heated almost to boiling and then mixed. The precipitate formed on slow cooling was filtered, dried and utilised for IR, $^1$H NMR and elemental studies.

## 2.2 RESULTS AND DISCUSSION

### Extraction of mercury(II) using crown ether (CE)

### 2.2.1 Extraction equilibrium of mercury(II)

The complex formation of mercury(II) with chloride ions can be described as follows :

$$Hg^{2+} + n\,Cl^{-} \overset{\beta_n}{\rightleftharpoons} HgCl_n^{2-n} \qquad (2.1)$$

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

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

$$K_n = [\,HgCl_n^{2-n}\,] / [HgCl_{n-1}^{3-n}]\,[Cl^{-}\,] \qquad (2.2)$$

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

$$HgCl_{2aq} + \;n\,CE_{org} \overset{K_{ex,n}}{\rightleftharpoons} HgCl_2.nCE_{org} \qquad (2.3)$$

where n = 0,1 and 2.

It can be assumed that the concentration of $Hg^{2+}$ and $HgCl^{+}$ species is very small in the ligand concentration range studied [149,101]. Then the distribution ratio, D, may be described as:

$$D = \frac{[HgCl_2]_{org} + [HgCl_2.CE]_{org} + [HgCl_2.2CE]_{org}}{[HgCl_2]_{aq} + [HgCl_3^{-}]_{aq} + [HgCl_4^{2-}]_{aq}} \qquad (2.4)$$

From Eqs. (2.2), (2.3) and (2.4), a fundamental equation for D can be described as:

$$D = \frac{K_{ex,0} + K_{ex,1}[CE]_{org} + K_{ex,2}[CE]^2_{org}}{1 + K_3[Cl^{-}\,]_{aq} + K_3K_4[Cl^{-}\,]^2_{aq}} \qquad (2.5)$$

where $[CE]_{org} = [CE]_{initial} / \{1 + (1/K_D)\}$

The values of partition coefficients ($K_D$) of the various crown ethers were obtained from the literature ($\log K_{D,18C6} = -0.04$; $\log K_{D,DC18C6} = 2.29$; $\log K_{D,B18C6} = 4.00$) [150–152]. The values of stepwise stability constants ($\log K_3 = 0.85$; $\log K_4 = 1.0$) were taken from the literature [153]. The equilibrium constants of the extracted complexes were determined by non-linear regression analysis as described below:

(1) Assume values for $K_{ex,0}$, $K_{ex,1}$ and $K_{ex,2}$;

(2) The equilibrium concentrations of the crown ether occurring in Eq. (2.5) was determined with the knowledge of initial concentration of crown ether and $K_D$ ;

(3) The distribution ratio values of D under the given conditions were calculated ($D_{cal}$) and compared with the experimental values ($D_{exp}$);

(4) The values of the assumed equilibrium constant which lead to a minimum root mean square fractional error, y, where

$$y = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{D_{cal,i} - D_{exp,i}}{D_{exp,i}}\right\}^2}$$

for all the experimental data were taken to be the equilibrium constant for the system under consideration.

## 2.2.2 Effect of hydrochloric acid concentration

The extraction of mercury(II) ($1\times10^{-5}$ mol/dm$^3$) has been investigated with varying concentrations of hydrochloric acid (0.05-0.1 mol/dm$^3$) using $2 \times 10^{-3}$ mol/dm$^3$ DC18C6 in 1,2-dichloroethane and the results are shown in

Fig. 2.2. It is clear from the results that the extraction of mercury(II) decreases continuously with increasing hydrochloric acid concentration in the aqueous phase. This may be due to the formation of species $HgCl_3^-$ and $HgCl_4^{2-}$ in the aqueous phase with increase of hydrochloric acid concentration.

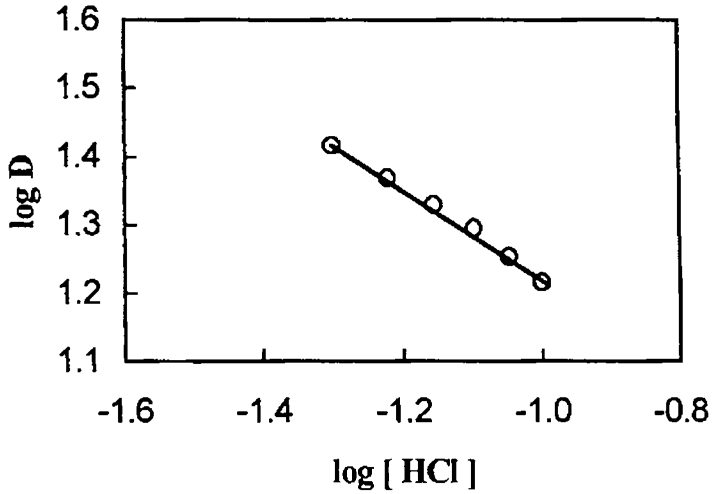


*Fig. 2.2* Effect of hydrochloric acid concentration on the extraction of mercury(II). DC18C6 = 0.002 mol/dm$^3$; mercury(II) = 1x10$^{-5}$ mol/dm$^3$.

### 2.2.3 Effect of crown ether concentration

The effect of concentration of DC18C6 (0.002 - 0.01 mol/dm$^3$) on the extraction of mercury(II) (1 x 10$^{-5}$ mol/dm$^3$) from 0.1 mol/dm$^3$ hydrochloric acid solutions has been investigated and the results are shown in Fig. 2.3. For comparison, extraction of mercury(II) has also been carried out using 18C6, B18C6 and DB18C6 as extractants. The distribution ratio, D, of mercury(II) increases linearly with increase 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 associated with the extractable complexes. On the other hand, the extraction of mercury(II) was found to be negligible when extracted with DB18C6 from dilute hydrochloric acid solutions. However, Giovannetti and co-workers [63] have reported ion-pair complexes of DB18C6 for the extraction of mercury(II) from concentrated hydrochloric acid solutions (1-7 mol/dm$^3$).

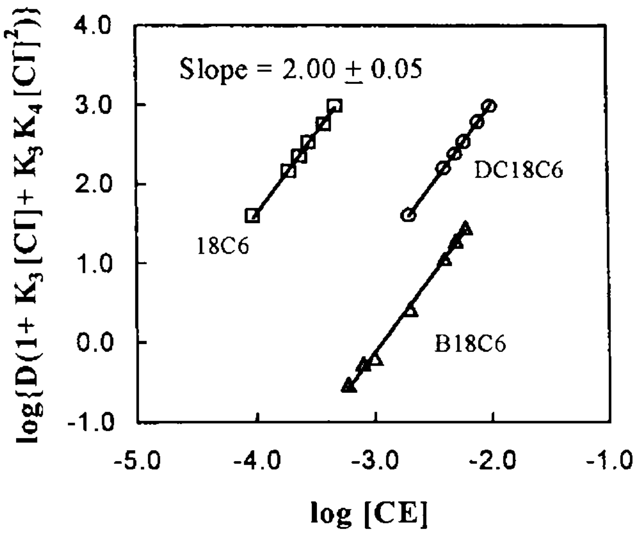


*Fig. 2.3* Effect of crown ether concentration on the extraction of mercury(II). HCl = 0.1 mol/dm$^3$; mercury(II) = 1 x 10$^{-5}$ mol/dm$^3$.

### 2.2.4 Effect of metal ion concentration

The effect of metal ion concentration (1x10$^{-5}$ - 1x10$^{-3}$ mol/dm$^3$) on the extraction process of mercury(II) has been investigated using 0.002 mol/dm$^3$ DC18C6 in 1,2-dichloroethane from 0.1 mol/dm$^3$ hydrochloric acid solutions. The log-log plot (Fig. 2.4) of the equilibrium organic phase mercury(II) concentration against the aqueous phase mercury(II) concentration is linear with a slope equal to unity, indicating the extraction of mono-nuclear species into the organic phase.

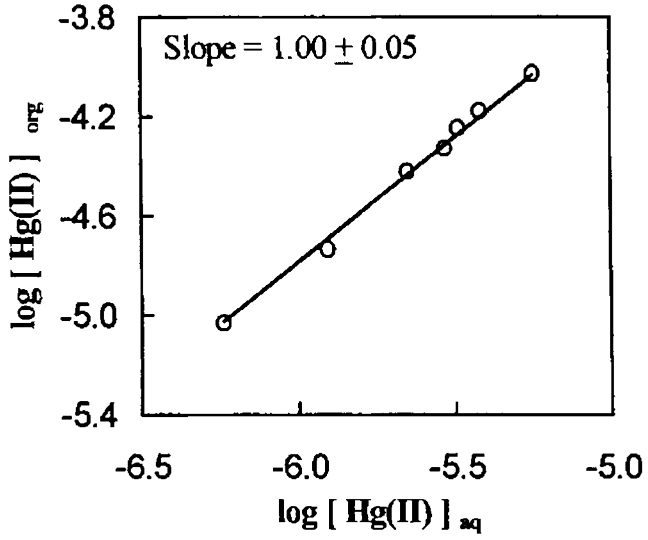


*Fig. 2.4* Effect of metal ion concentration on the extraction of mercury(II). DC18C6 = 0.002 mol/dm$^3$; HCl = 0.1 mol/dm$^3$.

These distribution data (Figs. 2.2 - 2.3) have been further analysed for confirming the stoichiometry of the extracted complexes by non-linear regression analysis using Eq. (2.5) assuming n = 0, 1 and 2. The best fit between the experimental and calculated D values was obtained only when the formation of the complex $HgCl_2.2DC18C6$ (i.e., n = 2 in Eq. (2.5)) was assumed. The values of equilibrium constants determined by non-linear regression analysis of various crown ethers are given in Table 2.1. It is clear from the Table 2.1 that the extraction efficiency of mercury(II) with various crown ethers follows the order: 18C6 > DC18C6 > B18C6, which is also the basicity sequence of these crown ethers. The sharp decrease in the extraction efficiency of mercury(II) from 18C6 to DC18C6 and B18C6 mostly reflects increasing steric effects and decreasing basicity. The higher extractability of mercury(II) with 18C6 or DC18C6 can be explained on the basis of "size-fitting effect" of these crown ethers. The 18C6 and DC18C6 with cavity size of 0.26 to 0.32 nm [154], complexes more strongly with metal ions having ionic diameter close to the cavity size such as the mercury(II) of 0.22 nm [135].

***Table 2.1.*** **Equilibrium constants of various crown ethers for the extraction of mercury(II)**

| Extractant | $\log K_{ex,2}$ |
|---|---|
| 18C6 | $9.62 \pm 0.02$ |
| DC18C6 | $6.99 \pm 0.03$ |
| B18C6 | $5.86 \pm 0.04$ |

Extending this discussion to the non-extractability of mercury(II) with DB18C6 it can be assumed that mercury(II) of 0.22 nm is too small to be stabilized by the size effect of DB18C6 (0.4 nm) [135]. For practical applications in solvent extraction, crown ethers must exhibit both high solubility in organic diluents and low distribution to the aqueous phase (high lipophilicity). Hence, for the subsequent studies on the recovery of mercury(II) from the brine-sludge of the Chlor-Alkali industry, DC18C6 has been chosen as an extractant due to its high solubility in organic diluents and its lipophilic nature in the two phase system.

### 2.2.5 Dependence of the nature of the diluent

The extraction of mercury(II) ($1 \times 10^{-5}$ mol/dm$^3$) from 0.1 mol/dm$^3$ hydrochloric acid solution using 0.01 mol/dm$^3$ DC18C6 in various diluents has been investigated and the results are shown in Table 2.2. This study clearly shows that the extraction of mercury(II) varies with the nature of the diluent. The weak hydrogen bonding between the ether oxygen of crown ethers and dichloroethane results in higher extraction efficiency of mercury(II). When chloroform is used as the diluent, low extraction of mercury(II) has been observed. This may be due to strong acid-base interaction between the basic extractant CE and the acidic diluent through hydrogen bonds. Among aromatic hydrocarbons, the extraction increases in the order: xylene > toluene > benzene.

***Table 2.2.*** **Effect of nature of the diluent on the extraction of mercury(II) 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 |

### 2.2.6 Stripping studies

Mercury(II) stripping from a loaded organic system consisting of 0.02 mol/dm$^3$ DC18C6 in 1,2-dichloroethane and 1x10$^{-5}$ mol/dm$^3$ mercury(II) has been investigated using various stripping agents and the results are given in Table 2.3. It is found that mercury(II) is stripped almost quantitatively ( > 99.9%) through a single stage with 5% $NH_4Cl$ in 1 : 10 $NH_3$ as the stripping agent.

### 2.2.7 Elemental analysis

Elemental analysis of the extracted complex gave C 38.27, H 5.61 and Hg 30.77% which compared with calculated values for $HgCl_2$.DC18C6 of C 37.3, H 5.63 and Hg 31.15%. This study clearly shows that $HgCl_2$ and DC18C6 form a 1 : 1

complex. Paige and Richardson have reported a similar 1 : 1 complex with $HgCl_2$ and 18C6 using crystallographic techniques [62].

***Table 2.3.* Stripping efficiency for mercury (II) with different reagents**

| Stripping Reagent | % Recovery of mercury(II) |
|---|---|
| 5% Thiourea (pH = 11) | 41.3 |
| 5% $NH_4Cl$ (1:10$NH_3$) | 99.9 |
| 4 mol/dm$^3$ NaCl + 0.1 mol/dm$^3$ NaOH | Negligible |
| 0.01 mol/dm$^3$ $Na_2S_2O_3$ (pH = 11) | Negligible |
| 0.2 mol/dm$^3$ EDTA (pH = 11) | Negligible |
| 2 - 3 mol/dm$^3$ Hydrochloric acid | Negligible |

### 2.2.8 IR spectral data

Infrared spectra of compounds, DC18C6 and the $HgCl_2$.DC18C6 solid complex have been recorded in the 4000 - 500 cm$^{-1}$ region. The very intense, broad and probably multicomponent $CH_2$ stretching vibration band of the free ligand has a peak at 2865 cm$^{-1}$. On complexation the intensity is much reduced and the band becomes asymmetrical with a peak at 2926 cm$^{-1}$. On the other hand, the medium intensity peak due to bending of $CH_2$ modes of the free ligand at 1349 cm$^{-1}$ is slightly downshifted to 1341 cm$^{-1}$ for the complex. Likewise, 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 likely to be found in the far infrared region.

### 2.2.9 $^1$H NMR spectral data

The $^1$H NMR spectral data for DC18C6 and $HgCl_2$.DC18C6 was obtained in $CDCl_3$. The observed chemical shifts (ppm), multiplicity and the number of protons are given in Table 2.4. The crown ether protons of the free ligand was observed as a multiplet at 3.67 ppm and the $CH_2$ protons of cyclohexane were observed as a multiplet at 1.50 ppm [135]. In the complex, the crown ether protons were observed as multiplet at 3.71 ppm and the $CH_2$ protons of cyclohexane as multiplet at 1.64 ppm. The observed NMR data confirms the formation of the complex $HgCl_2$.DC18C6.

***Table 2.4.*** **$^1$H NMR spectral data**

| Compound | Crown ether protons (ppm) | $CH_2$ protons of cyclohexane (ppm) |
|---|---|---|
| DC18C6 | 3.67 (m,20H) | 1.5 (m,16H) |
| $HgCl_2$.DC18C6 | 3.71 (m,20H) | 1.64 (m,16H) |

### 2.2.10 Selectivity studies using DC18C6

The extraction of calcium(II) ($1\times10^{-2}$ mol/dm$^3$), magnesium(II) ($1\times10^{-2}$ mol/dm$^3$) and barium(II) ($1\times10^{-2}$ mol/dm$^3$) from solutions containing 0.05 mol/dm$^3$ hydrochloric acid using 0.02 mol/dm$^3$ DC18C6 in 1,2-dichloroethane has been investigated and found that none of these metal ions are getting extracted into the organic phase. This is in good agreement with the earlier reports for the extraction of calcium(II) and barium(II) with DC18C6 [155]. On the other hand, mercury(II) was found to be quantitatively (% extracted > 99.9) extracted under the above conditions. Thus, mercury(II) can be selectively separated from the above metal ions using DC18C6 as an extractant.

## 2.2.11. Recovery of mercury from the brine-sludge of a Chlor-Alkali industry

The developed liquid-liquid extraction procedure has been applied for the removal and recovery 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 converting mercury into highly soluble mercuric chloride complexes. The chlorinated sludge was then subjected to solid-liquid separation and the filtrate was analysed for mercury(II), calcium(II), magnesium(II) and barium(II) and the results are shown in Table 2.5.

The extraction process of mercury from the brine-sludge of a Chlor-Alkali industry comprises of the following steps:

(1) Chlorination of the brine-sludge;

(2) Solid-liquid separation;

(3) Bringing the resultant filtrate liquor (pH = 1 - 2) from solid-liquid separation containing the mercury ($Hg^{2+}$ = 16 mg/$dm^3$) into contact with a substantially immiscible extractant phase, which comprises DC18C6 in 1,2-dichloroethane (0.02 mol/$dm^3$; Aq. : Org. = 1 : 1), whereupon the mercury to be separated selectively, reversibly transfers into the extractant phase (single stage extraction, % extracted > 99.9);

(4) Back-washing the extractant phase with an aqueous system consisting of 5% $NH_4Cl$ in 1 : 10 $NH_3$ to recover all the mercury contained in the extractant phase (Aq. : Org. = 1 : 1; number of stages = 1).

A schematic procedure for the extraction process is given in Fig. 2.5. Typical analysis results of the feed, raffinate and strip liquors are given in Table 2.5.

***Table 2.5.*** **Selective separation of mercury(II) from the brine-sludge of a Chlor-Alkali industry using DC18C6 in 1,2-dichloroethane as an extractant**

| Metal Ion | Amount of metal ion | | |
|---|---|---|---|
| | Feed | Raffinate | Strip liquor |
| Mercury(II) | 16.00 mg/dm$^3$ | 1.60 μg/dm$^3$ | 15.998 mg/dm$^3$ |
| Calcium(II) | 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. |

*N.D.= not detectable

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

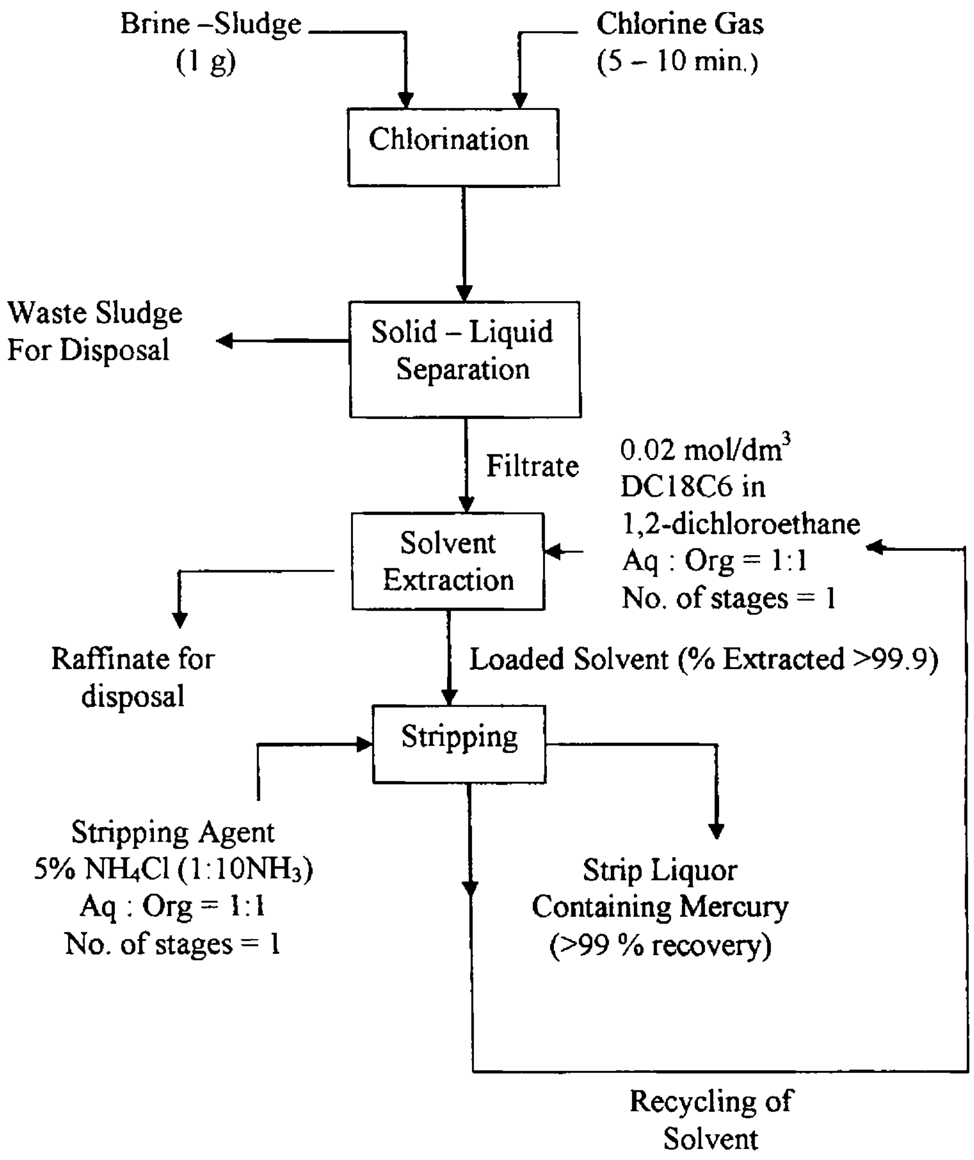


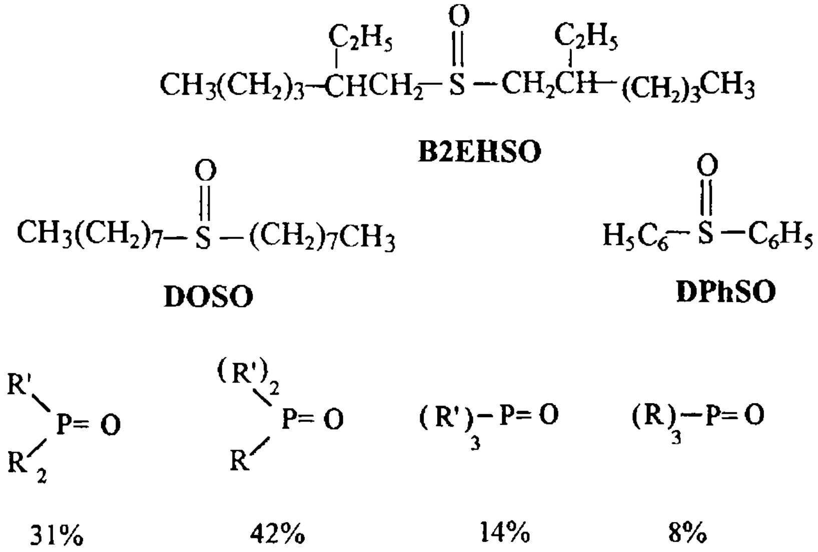
***Fig. 2.5*** Selective liquid-liquid extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.

# *Chapter 3*

# *Dialkyl Sulphoxides as Extractants for Mercury*

Dialkyl sulphoxides, $R_2SO$, containing the S=O functional group are powerful extractants, possessing high selectivity and chemical stability. Their other advantages include good thermal stability, low toxicity, potential abundance, economic supply, noncorrosivity, nonvolatility and good coordination ability. Among the dialkyl sulphoxides, a novel sterically hindered branched chain extractant, bis-2-ethylhexyl sulphoxide (B2EHSO) offers distinct advantages over other analogs owing to its unrestricted solubility in an alkane diluent.

The present chapter reports on the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using various sulphoxides namely, di-*n*-octyl sulphoxide (DOSO), bis-2-ethylhexyl sulphoxide (B2EHSO) and an aryl sulphoxide, such as diphenyl sulphoxide (DPhSO). For comparison, extraction studies also have been carried out with trialkylphosphine oxide (TRPO). The extraction data have been analysed by both graphical and theoretical methods taking into account aqueous phase speciation and all plausible complexes extracted into the organic phase. The selectivity of these extractants for the separation of mercury(II) from other metal ions such as calcium(II), magnesium(II) and barium(II) has also been investigated. The developed liquid-liquid extraction procedure has been applied for the extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.



where R = hexyl and R' = octyl

**TRPO(CYANEX 923)**

*Fig. 3.1* Structure of extractants used in the present study.

## 3.1 EXPERIMENTAL

### 3.1.1 Reagents

Bis-2-ethylhexyl sulphoxide (B2EHSO) obtained from Lancaster, England, was used as such for the extraction studies. DPhSO supplied by Aldrich-Chemie, Germany, was used without purification. The trialkylphosphine oxide (TRPO) commercially available under the trade name CYANEX 923 supplied by Cytec Canada Inc., contained about 93% of trialkylphosphine oxides including dioctylhexylphosphine oxide (40-44%), dihexyloctylphosphine oxide (28-32%), trihexylphosphine oxide and trioctylphosphine oxide [156]. Xylene of analytical reagent quality obtained from Merck, India, was used as the diluent in the present study. All other chemicals employed were of analytical reagent grade. DOSO was synthesised in our laboratory according to the procedure described below:

**Synthesis of di-*n*-octyl sulphoxide**: The reactions involved in the synthesis of DOSO are as follows:

$$ROH + HBr \longrightarrow RBr + H_2O \qquad (3.1)$$

$$2RBr + Na_2S \longrightarrow R_2S + 2NaBr \qquad (3.2)$$

$$R_2S + H_2O_2 \longrightarrow R_2SO + H_2O \qquad (3.3)$$

where R = *n*-octyl group

*n*-octyl bromide was prepared by refluxing *n*-octanol and a mixture of hydrobromic acid (48%) and concentrated sulphuric acid for 2.5 hours. The bromide layer was separated, washed once with cold concentrated sulphuric acid, then with water and finally with dilute sodium carbonate solution. The crude bromide was dried over anhydrous calcium chloride and distilled. The *n*-octyl bromide was then converted to di-*n*-octyl sulphide by refluxing with an alcoholic solution of sodium sulphide for 12 hours on a steam cone. The mixture was then cooled to room temperature and poured into a 25% solution of sodium chloride. The di-*n*-octyl sulphide, which formed the upper layer was removed, dried over anhydrous sodium sulphate and further purified by distilling under reduced pressure. For oxidation to di-*n*-octyl sulphoxide, di-*n*-octyl sulphide was dissolved in distilled acetone. Slightly more than the calculated amount of 30% (by weight) of hydrogen peroxide was added gradually to the sulphide solution. The mixture was stirred for about an hour and then kept aside for 24 hours. The acetone was evaporated slowly at room temperature. The di-*n*-octyl sulphoxide formed was then recovered and recrystallised from petroleum ether (60-80°C) and was characterised by its melting point (m.p. = 71°C), molecular weight and infrared spectra.

### 3.1.2 Liquid-liquid extraction and analytical procedure

The liquid-liquid extraction procedure and analytical methods followed for the determination of metal ions were the same as described in Chapter 2. Preliminary experiments showed that extraction equilibrium is attained within 5 min. for all the extraction systems.

### 3.1.3 Preparation of mercury(II)-B2EHSO / TRPO complex

The mercury(II)-B2EHSO / TRPO complex was prepared by following the general procedure: The loading of B2EHSO (0.5 mol/dm$^3$) and TRPO (0.2 mol/dm$^3$) in xylene with 5 x 10$^{-3}$ mol/dm$^3$ mercury(II) from 0.05 mol/dm$^3$ hydrochloric acid solutions were carried out by repeated contacts with fresh portions of metal solutions for 15 min. The loaded organic phase was then separated and utilised for IR spectral studies. The KBr (neat) containing a film of the metal complex solution was put under an IR lamp to evaporate xylene completely. For comparison, the IR spectra of pure B2EHSO and TRPO were also taken.

## 3.2 RESULTS AND DISCUSSION

### 3.2.1 Effect of hydrochloric acid concentration on the extraction of mercury(II)

The effect of hydrochloric acid concentration (0.05 – 0.1 mol/dm$^3$) on the extraction of mercury(II) (1 x 10$^{-5}$ mol/dm$^3$) has been investigated using 0.5 mol/dm$^3$ B2EHSO or 0.05 mol/dm$^3$ TRPO in xylene as an extractant and the results are shown in Fig. 3.2. It is clear from the results that the extraction of mercury(II) decreases linearly with increasing hydrochloric acid concentration.

This may be due to the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ species in the aqueous phase with increasing chloride ion concentration. A similar trend has been observed by Brewer *et al.* [58] in the extraction of mercury(II) from hydrochloric acid using *n*-octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and TBP in *n*- decane.

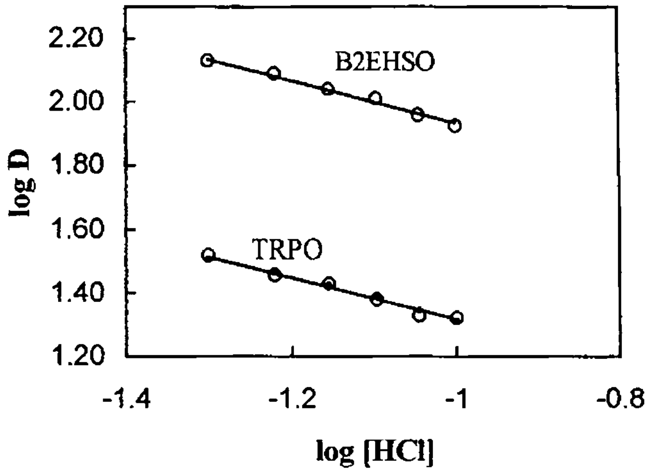


*Fig. 3.2* Effect of hydrochloric acid concentration on the extraction of mercury(II). B2EHSO = 0.5 mol/dm$^3$; TRPO = 0.05 mol/dm$^3$; mercury(II) = 1x10$^{-5}$mol/dm$^3$.

### 3.2.2 Effect of extractant concentration

The effect of concentration of various sulphoxides namely, B2EHSO (0.1 – 0.5 mol/dm$^3$), DOSO (0.1 - 0.4 mol/dm$^3$) and DPhSO (0.2 - 0.9 mol/dm$^3$) on the extraction of mercury(II) from 0.1 mol/dm$^3$ of hydrochloric acid solutions has been investigated and the results are shown in Fig. 3.3. For comparison, the extraction of mercury(II) has been investigated using TRPO (0.02 - 0.05 mol/dm$^3$)

as an extractant. The distribution ratio, D, of mercury(II) increases linearly with increase in the concentration of the extractant in the organic phase and from the slope of the log–log plots it is clear that three molecules of B2EHSO / DOSO / DPhSO / TRPO are associated with the extracted complexes. A similar solvation number has been reported by Reddy *et al.* [157] for the extraction of mercury(II) from thiocyanate solutions using di-*n*-pentyl sulphoxide or di-*n*-octyl sulphoxide. Zuo and Muhammed [108] have also observed a solvation number of three for the extraction of mercury(II) using dodecylthiourea.

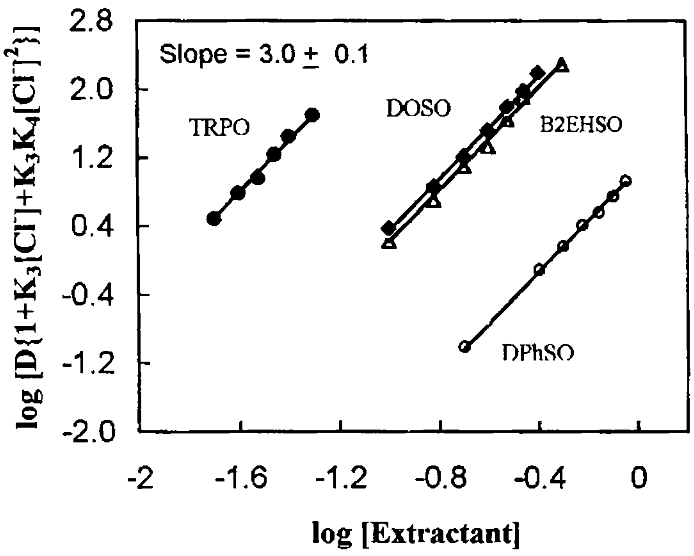


*Fig. 3.3* The effect of extractant concentration on the extraction of mercury(II). HCl = 0.1 mol/dm$^3$; mercury(II) = 1x10$^{-5}$ mol/dm$^3$.

### 3.2.3 Effect of metal ion concentration

The effect of metal ion concentration (1x10$^{-6}$–1x10$^{-4}$ mol/dm$^3$) on the extraction process of mercury(II) has been investigated from 0.1 mol/dm$^3$

hydrochloric acid solutions using 0.2 mol/dm$^3$ B2EHSO or 0.03 mol/dm$^3$ TRPO in xylene as an extractant. The extraction efficiency of mercury(II) was found to be independent of initial aqueous phase metal ion concentration under the present experimental conditions. The log–log plots depicted in Fig. 3.4 of the equilibrium organic phase metal ion concentration against the aqueous phase metal ion concentration is linear with a slope equal to unity, indicating that only mononuclear species seem to be extracted into the organic phase.

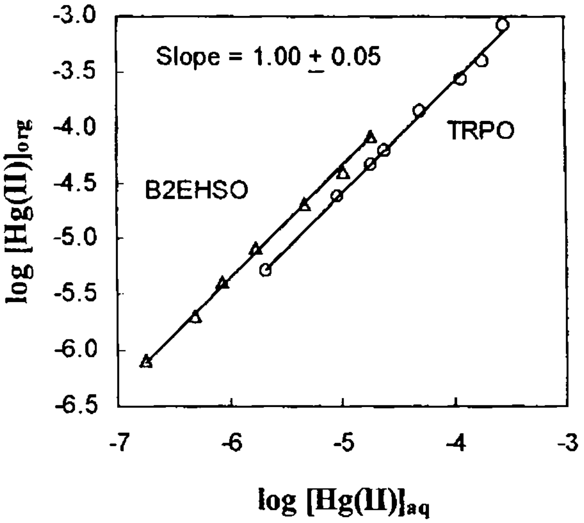


*Fig. 3.4* Effect of metal ion concentration on the extraction of mercury(II). B2EHSO = 0.2 mol/dm$^3$; TRPO = 0.03 mol/dm$^3$; HCl = 0.1 mol/dm$^3$.

### 3.2.4 Extraction equilibrium of mercury(II)

The complex formation of mercury(II) from acidic chloride solutions can be described as follows :

$$Hg^{2+} + n\,Cl^- \overset{K_n}{\rightleftharpoons} HgCl_n^{2-n} \qquad (3.4)$$

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

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

$$K_n = [\,HgCl_n^{2-n}\,] \,/\, [HgCl_{n-1}^{3-n}]\,[Cl^-] \quad (3.5)$$

The extraction of neutral mercury(II) complexes with solvating extractants like sulphoxides ($R_2SO$) or trialkylphosphine oxide (TRPO) may be described as follows:

$$HgCl_{2aq} + n\,E_{org} \overset{K_{ex,n}}{\rightleftharpoons} HgCl_2.nE_{org} \qquad (3.6)$$

where n = 0, 1, 2 and 3; and E denotes the extractant.

It can be assumed that the concentration of $Hg^{2+}$ and $HgCl^+$ species is very small in the ligand concentration range studied [149]. Furthermore, it has also been assumed that the extraction of charged ion species into xylene containing small amounts of the neutral solvating extractant is almost negligible. Then, the distribution ratio may be described as:

$$D = \frac{[HgCl_2]_{org} + [HgCl_2.E]_{org} + [HgCl_2.2E]_{org} + [HgCl_2.3E]_{org}}{[HgCl_2]_{aq} + [HgCl_3^-]_{aq} + [HgCl_4^{2-}]_{aq}} \qquad (3.7)$$

From Eqs. (3.5), (3.6) and (3.7), a fundamental equation for D can be described as:

$$D = \frac{K_{ex,0} + K_{ex,1}[E]_{org} + K_{ex,2}[E]_{org}^2 + K_{ex,3}[E]_{org}^3}{1 + K_3[Cl^-]_{aq} + K_3K_4[Cl^-]_{aq}^2} \qquad (3.8)$$

The values of the stepwise stability constants ($\log K_3 = 0.85$; $\log K_4 = 1.0$) were taken from the literature [153].

The stoichiometry of the extracted complexes has been further confirmed by analysing the extraction data presented in Figs. 3.2 and 3.3 using Eq. (3.8) (n = 0, 1, 2 and 3). The best fit between the experimental and calculated D values was obtained only when the formation of the species $HgCl_2.3E$, was assumed. The equilibrium constants of the above extracted complexes have been determined by non-linear regression analysis as described earlier and are given in Table 3.1.

***Table 3.1.*** **Equilibrium constants and shifts of the OH frequency of coordinated water bonded to different sulphoxides**

| Extractant | $\Delta\nu_{OH}$ | log $K_{ex,3}$ |
|---|---|---|
| TRPO | 270 | $5.59 \pm 0.03$ |
| DOSO | 210 | $3.34 \pm 0.02$ |
| B2EHSO | 200 | $3.21 \pm 0.02$ |
| DPhSO | 160 | $1.06 \pm 0.03$ |

It is believed that the infrared frequency of the phosphoryl group could serve as a measure of its basicity in neutral organophosphorus extractants. In sulphoxides, the S=O stretching frequency in different compounds was observed to be nearly constant and thus could not be a guide to measure its basicity. Reddy and co-workers [158] have developed a method for assessing the basicity of sulphoxides and trialkylphosphine oxide based on the IR shift of the symmetric stretching frequency of OH group of water on coordination with the donor and the observed IR shifts are given in Table 3.1. The increase in the values of $\Delta\upsilon_{OH}$ (difference in IR shifts between OH frequency of uncoordinated water and coordinated water on extraction) clearly indicates the increase in the donor strength of the solvating reagent as: DPhSO < B2EHSO < DOSO < TRPO. It is clear from Table 3.1 that the equilibrium constants of different extractants increase with the donor strength ($\Delta\nu_{OH}$ value) of the reagent as: DPhSO < B2EHSO < DOSO < TRPO. The sharp decrease in the extraction efficiency of mercury(II) from TRPO to DOSO reflects the decreasing basicity of these extractants (Nitric acid uptake constant: $K_{H, TRPO} = 8.5$; $K_{H, DOSO} = 0.42$). The greater basicity of the P→O group in TRPO compared to that of the S→O group in the sulphoxides would account for the high extraction efficiency of mercury(II) [158]. Among dialkyl sulphoxides, the extraction efficiency of branched chain sulphoxide, B2EHSO, is slightly lower than the straight chain sulphoxide, DOSO, which can be attributed to the steric effects. Further, it is also very clear that the extraction efficiency of arylsulphoxide, DPhSO, is found to be significantly lower than dialkyl sulphoxides which can again be attributed to the steric factors. Though the extraction efficiency of mercury(II) is found to be higher with DOSO than with B2EHSO among the various sulphoxides tried, the solubility limitations of DOSO and commercial availability of B2EHSO influenced the choice of extractant for further experiments. The commercial availability and high extraction efficiency of TRPO influenced the choice of this extractant for further investigations for the extraction and separation of mercury(II) from the brine-sludge of a Chlor-Alkali industry.

### 3.2.5 Loading capacity of B2EHSO and TRPO

Aliquot of 10 $cm^3$ of 0.5 $mol/dm^3$ B2EHSO in kerosene and 0.2 $mol/dm^3$ TRPO in xylene has been repeatedly extracted at $303 \pm 1$ K for 10 min. with the same volume of aqueous solution containing mercury(II) ($1 \times 10^{-2}$ $mol/dm^3$ in the case of B2EHSO and $5 \times 10^{-3}$ $mol/dm^3$ in the case of TRPO) and 0.05 $mol/dm^3$ hydrochloric acid to determine the loading capacity of the solvent. After equilibration, the phases were disengaged and analysed for mercury content in the aqueous phase. The plot of cumulative [Hg(II), g]$_{org}$ per 100 g of B2EHSO versus the number of stages of contact is given in Fig. 3.5. It is clear from the figure that most of the mercury existing in the aqueous phase is extracted into the organic phase up to the 5th contact in the case of B2EHSO and 20th contact in the case of TRPO. Further, the loading capacity of TRPO (Fig. 3.6) has been found to be significantly higher (12.88 g mercury(II) per 100 g of TRPO) than that of B2EHSO which has a loading capacity of 0.33 g mercury(II) per 100 g of B2EHSO.

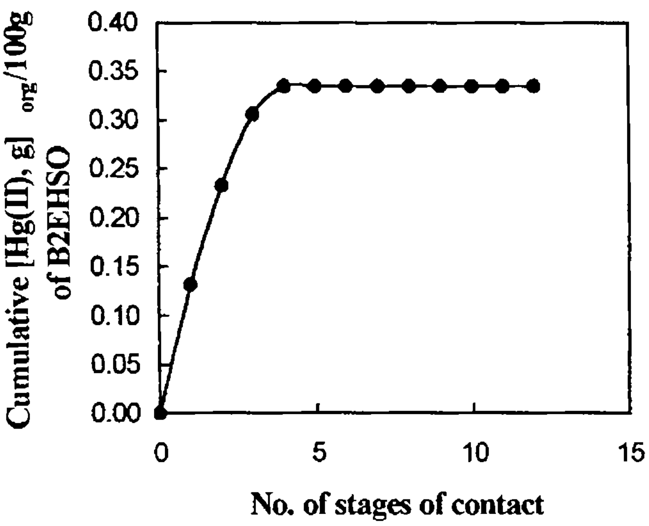


*Fig. 3.5* Loading capacity of B2EHSO by mercury(II) from 0.05 mol/dm$^3$ HCl solutions.

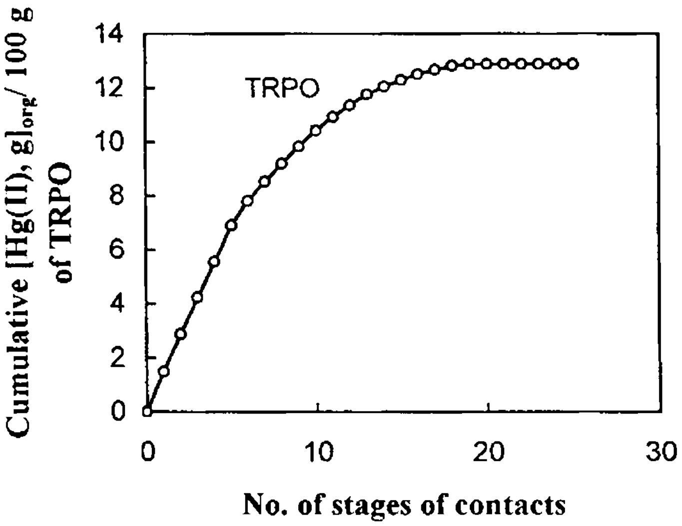


*Fig. 3.6* Loading capacity of TRPO by mercury(II) from 0.05 mol/dm$^3$ HCl solutions.

### 3.2.6 Dependence of extraction of mercury(II) on the nature of the diluent

The extraction of mercury(II) from 0.1 mol/dm$^3$ hydrochloric acid solution using 0.2 mol/dm$^3$ of B2EHSO in various diluents has been studied and the results are shown in Table 3.2. This study clearly indicates that extraction of mercury(II) varies with the nature of the diluent. When chloroform is used as the diluent, very little extraction of mercury(II) has been observed. This may be due to strong acid – base interaction between basic extractant, B2EHSO and acidic diluent, chloroform, through hydrogen bonding. Among the aromatic hydrocarbons employed as diluents the extraction efficiency increases in the order: benzene < toluene < xylene (It is to be noted that benzene is carcinogenic). The results also clearly demonstrate that diluents such as kerosene (boiling range 160-200°C ) and cyclohexane having low dielectric constants show high extractions for mercury(II). Further, this may be due to the weak interaction between the extractant and the diluent. On the other hand, diluents having higher dielectric constants, such as chloroform gave poor extraction. However, in the present work, methylisobutyl ketone (MIBK), having a high dielectric constant shows high extraction for mercury(II). This can be attributed to the synergistic effect of the mixed-ligand system (B2EHSO + MIBK).

***Table 3.2.*** **Dependence on the nature of diluent on the extraction of mercury(II) from HCl solutions (0.1 mol/dm$^3$ in the case of B2EHSO; 1 mol/dm$^3$ in the case of TRPO) by B2EHSO (0.2 mol/dm$^3$) and TRPO (0.1 mol/dm$^3$)**

| Diluent | Dielectric constant | Distribution ratio (B2EHSO) | Distribution ratio (TRPO) |
|---|---|---|---|
| MIBK | 13.11 | 36.20 | 543 |
| Chloroform | 4.90 | 0.04 | 0.01 |
| Benzene | 2.28 | 3.09 | 1.64 |
| Xylene | 2.26 | 4.84 | 3.26 |
| Toluene | 2.22 | 4.59 | 2.06 |
| Cyclohexane | 2.02 | 11.03 | 94 |
| Kerosene (160-200°C) | 2.00 | 48.00 | 426 |

Studies on the dependence of the nature of the diluent on the extraction of mercury(II) using TRPO (0.1 mol/dm$^3$) from 1 mol/dm$^3$ hydrochloric acid solutions show a similar trend as that of B2EHSO. In view of the higher extraction efficiency of mercury(II) by B2EHSO or TRPO in kerosene, further studies for the recovery of mercury(II) from the brine-sludge have been carried out using kerosene as the diluent.

### 3.2.7 Stripping studies

In any extraction process it becomes almost imperative to back-extract the metal from the loaded organic phase. Mercury stripping from a loaded organic solvent system consisting of 0.5 mol/dm$^3$ B2EHSO in kerosene (containing 1 x 10$^{-5}$ mol/dm$^3$ mercury(II)) has been investigated using various stripping agents of different concentrations and the results are shown in Table 3.3.

***Table 3.3.* Stripping studies for mercury with various stripping reagents from a loaded B2EHSO (0.2 mol/dm$^3$) system**

| Stripping agent | % Recovery |
|---|---|
| 1% thiourea in 1%HCl | 99.9 |
| 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH | 99.9 |
| 0.01 mol/dm$^3$ $Na_2S_2O_3$ pH = 4.09 | 95.8 |
| 2.0 mol/dm$^3$ HCl | 62.0 |
| 0.01 mol/dm$^3$ NaCl; pH = 10.45 | 26.5 |
| 2 mol/dm$^3$ $NH_4Cl$ | 30.5 |
| 5% $NH_4Cl$ in 1:10 $NH_3$ | 99.4 |

As the D values of mercury(II) were found to be high in a range of hydrochloric acid concentrations, stripping was impractical with hydrochloric acid solution alone. Among the many strippants tried, a mixture of 1% thiourea in 1% HCl and 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH were found to be effective (% recovery > 99.9%) stripping agents for mercury in a single stage with a phase ratio equal to unity.

Mercury(II) stripping from a loaded organic system consisting of 0.1 mol/dm$^3$ TRPO in kerosene has been investigated using various stripping agents and the results are shown in Table 3.4. The results indicate that mercury has been stripped almost quantitatively with 0.01 mol/dm$^3$ sodium thiosulphate or 5% thiourea in 1% HCl in a single stage with a phase ratio equal to unity.

***Table 3.4*. Stripping studies of mercury(II) with various stripping reagents from a loaded 0.1 mol/dm$^3$ TRPO in kerosene**

| Stripping agent | Phase Ratio Aq. : Org. | % Recovery |
|---|---|---|
| 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH | 1:2 | 16.2 |
| 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH | 1:1 | 28.8 |
| 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH | 2:1 | 75.0 |
| 2-5 mol/dm$^3$ HCl | 1:1 | Negligible |
| 5 mol/dm$^3$ $HNO_3$ | 1:1 | 40.6 |
| 5% thiourea in 1% HCl | 1:1 | 99.0 |
| 0.01 mol/dm$^3$ sodium thiosulphate (pH = 5.5) | 1:1 | 99.5 |

### 3.2.8 Recycling capacity of B2EHSO or TRPO

The recycling capacity of B2EHSO or TRPO has been systematically investigated first by loading mercury(II) and then by stripping using 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH in the case of B2EHSO and 0.01 mol/dm$^3$ sodium thiosulphate in the case of TRPO. The results (Fig. 3.7) revealed practically insignificant change in the extraction efficiency of the extractants, B2EHSO (> 99.9%) or TRPO (> 99.9%) even after ten cycles of extraction.

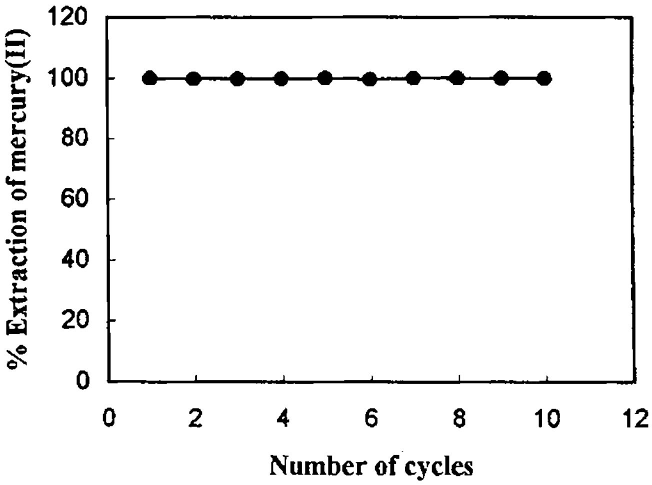


*Fig. 3.7* Recycling capacity of B2EHSO / TRPO extractants. B2EHSO = 0.5 mol/dm$^3$; TRPO = 0.1 mol/dm$^3$; HCl = 0.1 mol/dm$^3$.

### 3.2.9 IR spectral studies of mercury(II)-B2EHSO or TRPO complex

The IR spectra of the extracted mercury(II)-B2EHSO complex shows a shift of the S=O characteristic peak at 1029 to 1036 cm$^{-1}$ (Fig. 3.8). A frequency shift of the S=O stretch towards the higher frequency indicate coordination of the B2EHSO molecule to mercury through sulphur of the S=O group. A similar behaviour has been observed by Shukla *et al.* [159] in the extraction of palladium(II) from nitric acid by B2EHSO.

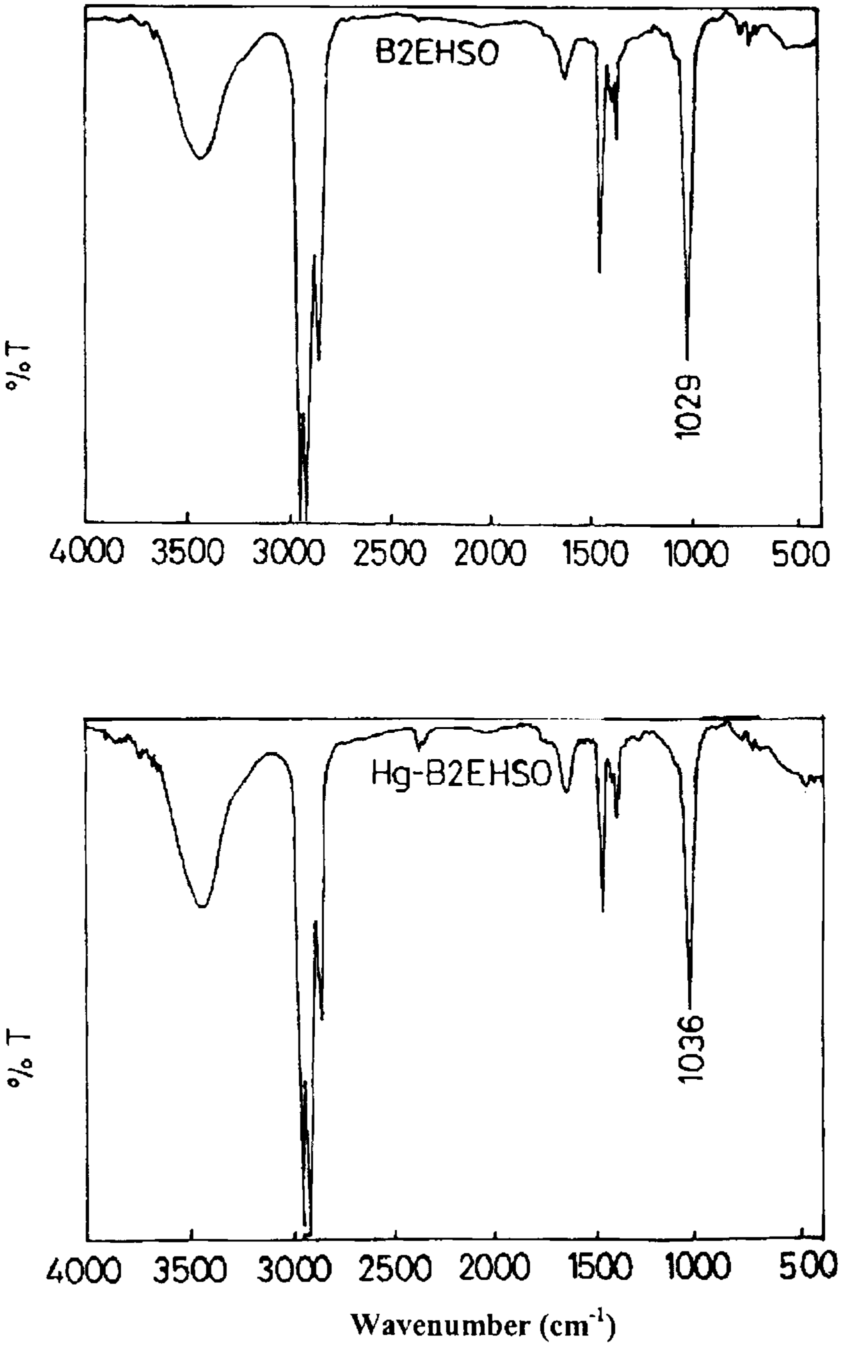


*Fig. 3.8* IR spectra of B2EHSO and mercury(II)-B2EHSO complex.

The IR spectra of the extracted complex show that the stretching frequency of P=O in TRPO has shifted from 1146 cm$^{-1}$ to 1116 cm$^{-1}$ in $HgCl_2.3TRPO$ complex (Fig.3.9). This indicates that there is strong interaction between the oxygen of the phosphine oxide and mercury, which is also evident from the extraction data.

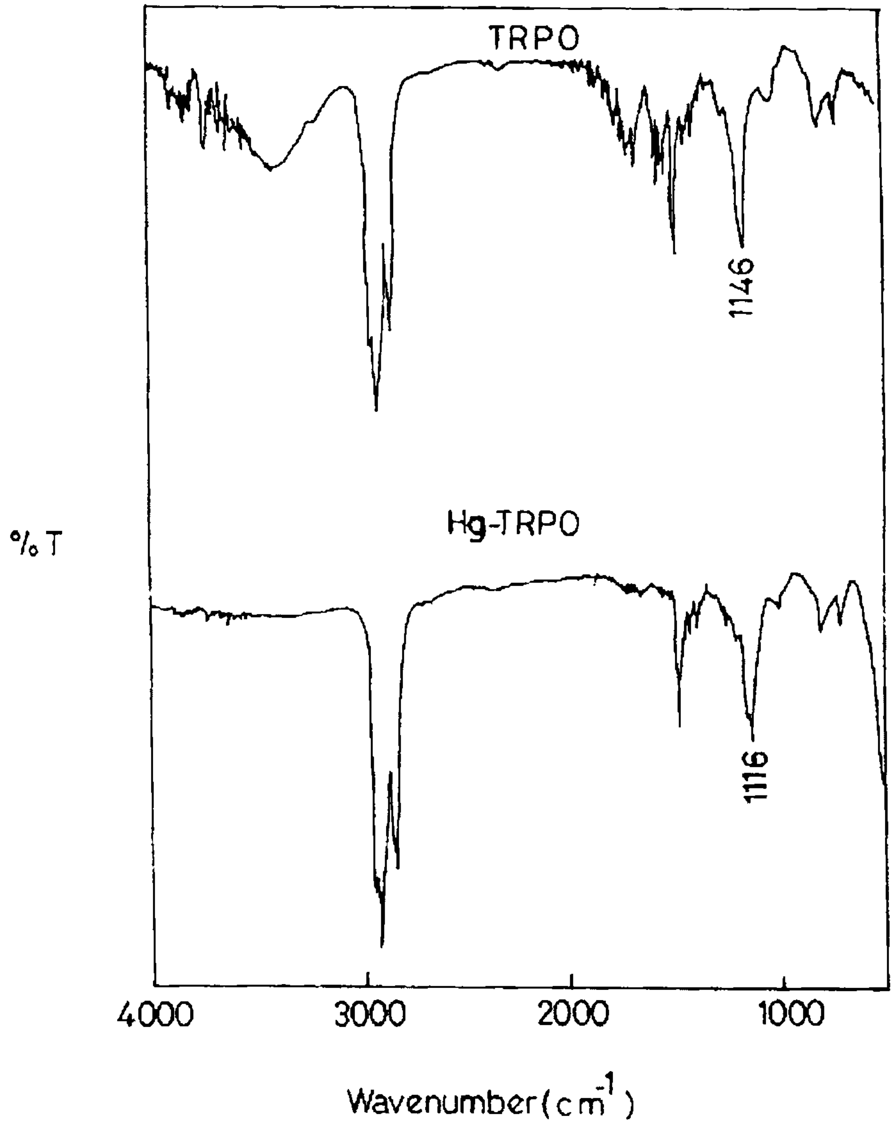


*Fig. 3.9* IR spectra of TRPO and mercury(II)-TRPO complex.

### 3.2.10 Selectivity studies

The effect of other metal ions such as, calcium(II) (0.01mol/dm$^3$), magnesium(II) (0.01 mol/dm$^3$) and barium(II) (0.01mol/dm$^3$) from solutions containing 0.05 mol/dm$^3$ hydrochloric acid using B2EHSO (0.5 mol/dm$^3$) and TRPO (0.2 mol/dm$^3$) in kerosene on the extraction process of mercury(II) has been studied and found that none of these metal ions are getting extracted into the organic phase. On the other hand, mercury(II) was found to be quantitatively extracted (% extracted > 99.9) under the above conditions. Thus, mercury(II) can be selectively separated from the above metal ions associated with it in the brine-sludge of a Chlor-Alkali industry using B2EHSO or TRPO in kerosene as an extractant.

### 3.2.11 Liquid-liquid extraction and separation of mercury from the brine-sludge of the Chlor-Alkali industry

The developed liquid-liquid extraction procedure for the extraction of mercury using B2EHSO or TRPO in kerosene has been applied for the removal and recovery of mercury from the brine-sludge of a Chlor-Alkali industry. Brine-sludge (1 g) in 10 cm$^3$ of 0.05 mol/dm$^3$ of HCl was chlorinated for 5–10 min. for converting mercury into highly soluble mercuric chloride complexes. The chlorinated sludge was then subjected to solid-liquid separation and the filtrate was analysed for mercury(II), calcium(II), magnesium(II) and barium(II) and the results are given in Table 3.5.

The extraction process of mercury from the brine-sludge comprises the steps of:

(1) chlorination of the brine-sludge (1 g in 10 cm$^3$ of 0.05 mol/dm$^3$ HCl chlorinated for 5 - 10 min.),

(2) solid-liquid separation,

(3) bringing the aqueous liquor (pH between 1 – 2) containing mercury (16 mg/dm$^3$) into contact with a substantially immiscible extractant phase (phase ratio : Org. : Aq. = 1 : 1) which comprises B2EHSO (0.5 mol/dm$^3$) or TRPO (0.2 mol/dm$^3$) in kerosene, whereupon mercuric chloride to be separated, selectively and reversibly transfers into the extractant phase (single stage extraction, % extracted = > 99.9),

(4) back-washing the loaded extractant phase with an aqueous system containing 4 mol/dm$^3$ NaCl in 0.1 mol/dm$^3$ NaOH (Single stage in the case of B2EHSO; Phase ratio Org.:Aq. = 1:1) and 0.01 mol/dm$^3$ sodium thiosulphate solution (Four stages in the case of TRPO; Phase ratio Org.:Aq. = 1:1) to recover all mercury (% recovery > 99.9 %).

***Table 3.5.*** **Selective separation of mercury(II) from the brine-sludge of a Chlor-Alkali industry using B2EHSO / TRPO in kerosene extractants**

| Metal Ion | Amount of metal ion | | |
|---|---|---|---|
| | Feed | Raffinate | Strip liquor |
| Mercury(II) | 16.00 mg/dm$^3$ | 1.60 μg/dm$^3$ | 15.998 mg/dm$^3$ |
| Calcium(II) | 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. |

*N.D.= not detectable

A schematic flow diagram of the above laboratory scale process is shown in Fig. 3.10. The investigations reveal that B2EHSO or TRPO can be used as a selective liquid-liquid extraction reagent for the recovery of mercury from the brine-sludge of a Chlor–Alkali industry.

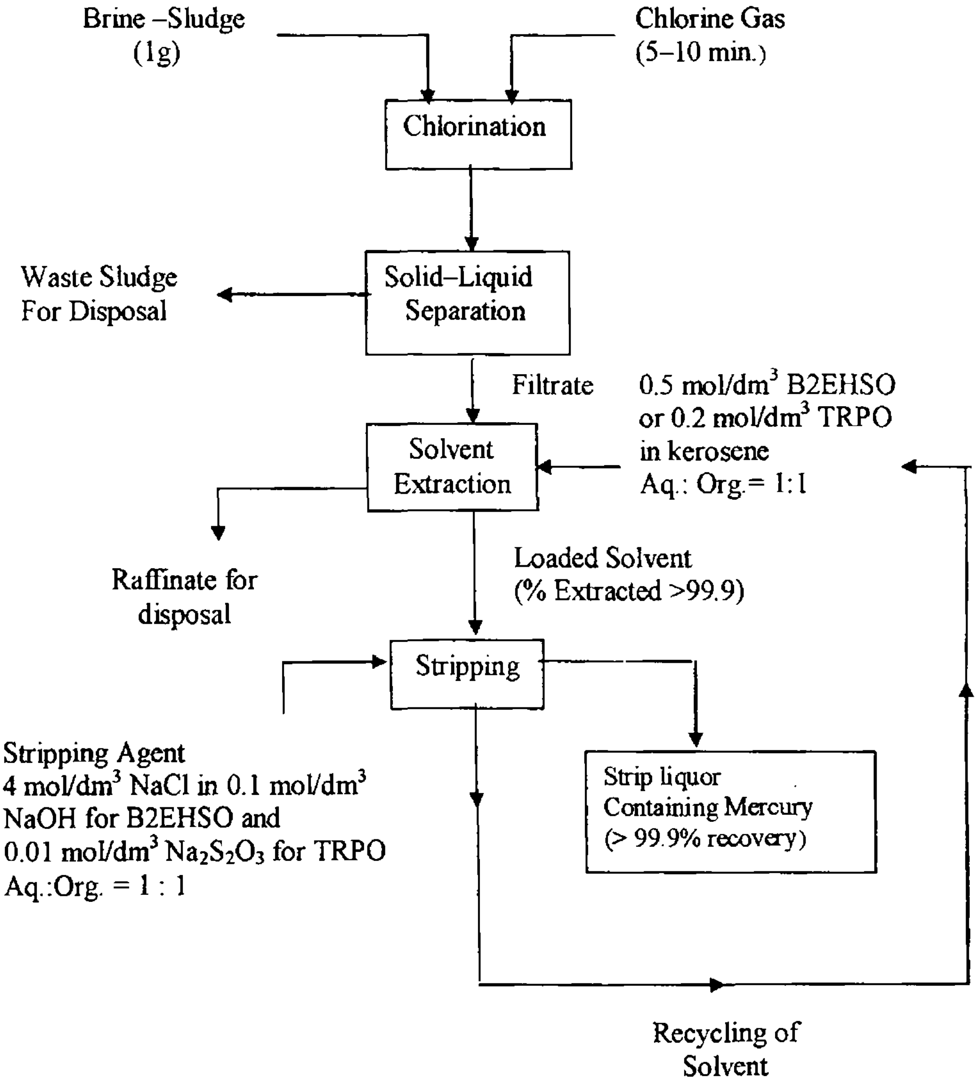


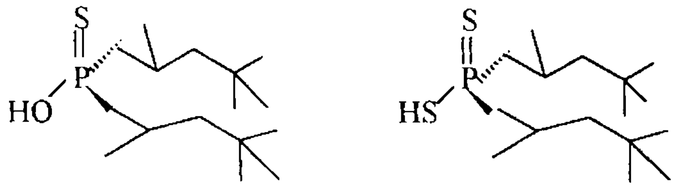
*Fig. 3.10* Selective liquid-liquid extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.

# Chapter 4

# Extraction and Separation of Mercury(II) from Industrial Wastes with Thiosubstituted Organophosphinic Acids

Over the last few decades organophosphorus acids have been widely studied concerning the liquid-liquid extraction of several metal ions, but less is known about the phosphinic and especially the thiophosphinic acids, where one or two oxygen atoms of the acidic group have been replaced by sulphur atoms. The commercial availability of certain extractants containing dialkyl oxothio - and dithiophosphinic acids namely, bis-(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302 = CY302) and bis-(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301 = CY301), has further expanded the accessible range of properties of this broad class of extractants. These extractants have received considerable attention both for their ability to extract soft transition metal ions [160-162] and for their unparalleled ability to differentiate between chemically similar trivalent lanthanides and actinides [163,164]. However, no reports have appeared in the literature on the extraction behaviour of mercury(II) using the above thiophosphinic acids.

This prompted to investigate the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using CY302 and CY301 in kerosene as extractants with the aim to develop a selective liquid-liquid extraction process for the separation of mercury from the waste streams of a Chlor-Alkali industry. The structures of the extractants relevant to this work and their abbreviations are given in Fig. 4.1.



CY302 CY301

*Fig. 4.1* Structure of thiophosphinic acids.

## 4.1 EXPERIMENTAL

### 4.1.1 Reagents

The extractants CY302 and CY301 supplied by Cytec Canada Inc. were purified by the precipitation of the cobalt salt [165] and ammonium salt methods [166], respectively.

**Purification of CY302:** CY302 was purified by the cobalt salt precipitation method as described below [165]: An approximately 0.5 mol/dm$^3$ solution of CY302 in hexane was prepared and added to half its volume of a saturated sodium sulphate solution, in which an amount of sodium hydroxide equivalent to CY302 plus a 20% excess has been dissolved. The phases were mixed vigorously for 10 min. and then allowed to separate. The organic phase containing the sodium salt of CY302 was separated and contacted with 0.5 mol/dm$^3$ solution of cobalt sulphate whereby the organic phase became saturated with the cobalt salt of CY302. The precipitated cobalt - CY302 complex was washed with ice cold acetone, filtered and air dried. The complex was decomposed with a mixture of 4 mol/dm$^3$ $H_2SO_4$ and diethyl ether and the impurities were removed by evaporation in a rotary evaporator. The purity of CY302 was determined by the potentiometric titration in 75% iso-propanol with 0.1 mol/dm$^3$ N-tetrabutylammonium hydroxide and was found to be > 99% pure.

**Purification of CY301:** 52 g of CY301 (0.13 mol) was dissolved in 200 cm$^3$ benzene and heated to 70°C while being stirred. After adding 14 g of ammonium carbonate the solution was left to react at this temperature for about an hour. The solution was filtered and kept overnight in a refrigerator (10°C). The crystallised ammonium salt was filtrated and recrystallised twice from benzene. A white crystalline product (40 g) was obtained after drying, which was gathered in 300 cm$^3$ petroleum ether (40-60°C) and shaken twice with 300 cm$^3$ of 4 mol/dm$^3$ HCl. The organic phase was then separated, washed twice with distilled water and finally dried with 20 g anhydrous sodium sulphate. The solvent was then removed at 30°C using a rotary evaporator and characterised by GC-MS.

### 4.1.2 Liquid-liquid extraction and analytical procedure

The liquid-liquid extraction procedure and analytical methods followed for the determination of metal ions were the same as described in Chapter 2. Preliminary experiments revealed that the extraction equilibrium is attained within 10 min. for all the extraction systems.

### 4.1.3 Preparation of mercury(II)–CY301 complex

The mercury(II)-CY301 complex was prepared by following the liquid-liquid extraction procedure as described in Chapter 3. The loaded organic phase was then separated and utilised for IR spectral studies. The KBr (neat) containing a film of the metal complex solution was put under an IR lamp to evaporate xylene completely. For comparison, the IR spectrum of purified CY301 was also taken.

## 4.2 RESULTS AND DISCUSSION

### 4.2.1 Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration (0.5 - 1.0 mol/dm$^3$) on the extraction of mercury(II) has been investigated using 3 x 10$^{-4}$ mol/dm$^3$ CY301 or CY302 in kerosene as an extractant and the results are depicted in Fig. 4.2. The results show that the extraction of mercury(II) decreases continuously with increasing hydrochloric acid concentration in the aqueous phase. This decrease may be attributed to the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ species with the increase in chloride ion concentration in the aqueous phase. Fig. 4.3 shows the result on the effect of hydrogen ion concentration (0.1 - 0.6 mol/dm$^3$) on the extraction process of mercury(II) at constant chloride ion (0.55 mol/dm$^3$), metal ion (1 x 10$^{-5}$ mol/dm$^3$) and extractant (3 x 10$^{-4}$ mol/dm$^3$) concentrations. It is clear from the figure that the extraction of mercury(II) is independent of hydrogen ion concentration under the present experimental conditions. This clearly highlights that CY301 and CY302 do not behave as cation-exchangers. This may be due to the strong affinity of the sulphur atom of the extractant to the soft metal ion like mercury(II). A similar behaviour has been observed by Baba and Inoue [115] in the extraction of mercury(II) from hydrochloric acid solutions using α-butylthiolauric acid as an extractant.

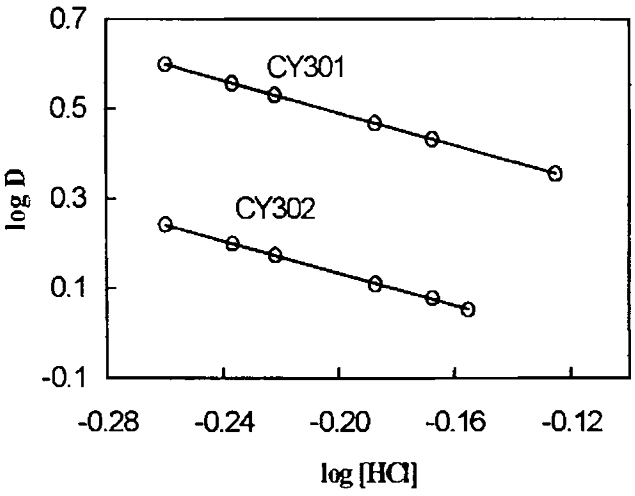


*Fig. 4.2* Effect of hydrochloric acid concentration on the extraction of mercury(II). CY301 / CY302 = $3 \times 10^{-4}$ mol/dm$^3$ in kerosene; mercury(II) = $1 \times 10^{-5}$ mol/dm$^3$.

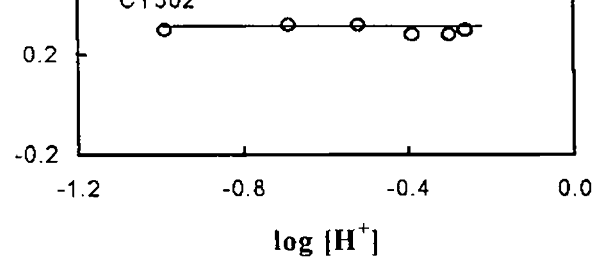


*Fig. 4.3* Effect of hydrogen ion concentration on the extraction of mercury(II). CY301 /CY302 = $3 \times 10^{-4}$ mol/dm$^3$ in kerosene; mercury(II) = $1 \times 10^{-5}$ mol/dm$^3$.

### 4.2.2 Effect of extractant concentration

The effect of concentration of CY301 (1 x $10^{-4}$- 3 x $10^{-4}$ mol/dm$^3$) or CY302 (1 x $10^{-4}$- 5 x $10^{-4}$ mol/dm$^3$) on the extraction of mercury(II) from hydrochloric acid (0.55 mol/dm$^3$) solution has been studied by keeping the metal and acid concentrations constant and the results are given in Fig. 4.4. It is clear from the figure that the extraction efficiency of mercury(II) increases linearly with increasing concentration of the extractant. From the slope of the plot of log $\{D(1+K_3[Cl^-]+K_3K_4[Cl^-]^2)\}$ vs. log [HX] it is inferred that two molecules of CY301 or CY302 are involved in the extracted complexes of mercury(II).

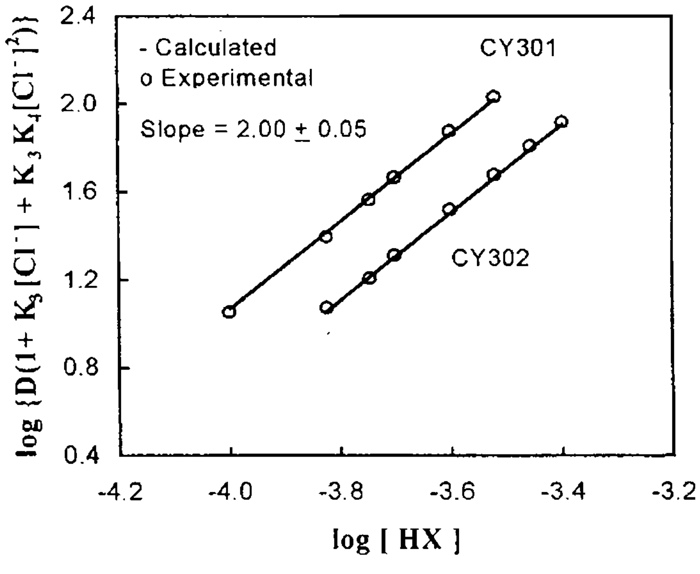


*Fig. 4.4* Effect of extractant concentration on the extraction of mercury(II). HCl = 0.55 mol/dm$^3$ and mercury(II) = 1x$10^{-5}$ mol/dm$^3$.

### 4.2.3 Effect of metal ion concentration

The effect of metal ion concentration on the extraction process of mercury(II) has been investigated using $3x10^{-4}$ mol/dm$^3$ CY302 or CY301 in kerosene as an extractant from 0.55 mol/dm$^3$ hydrochloric acid solutions. The extraction efficiency of mercury(II) is found to be independent of initial aqueous phase metal ion concentration ($1x10^{-6}$ - $1x10^{-5}$ mol/dm$^3$). The log-log plot (Fig. 4.5) of the equilibrium organic phase metal ion concentration against the aqueous phase metal ion concentration is linear with a slope equal to 1.0, indicating that only mononuclear species seem to be extracted into the organic phase.

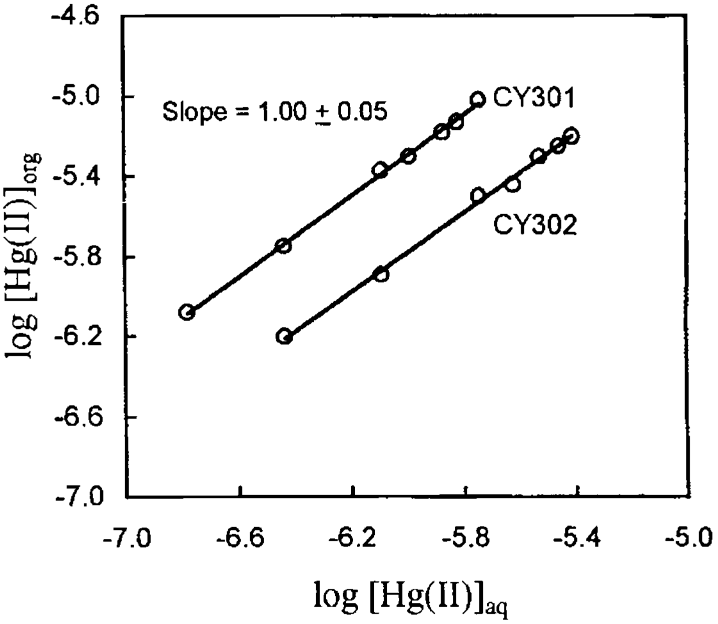


*Fig.4.5* Effect of metal ion concentration on the extraction of mercury(II). CY301 / CY302 = $3x10^{-4}$ mol/dm$^3$ in kerosene; HCl = 0.55 mol/dm$^3$.

### 4.2.4 Extraction equilibrium of mercury(II)

Owing to the strong affinity of the sulphur atom of the thiophosphinic acids to mercury(II), as evident from the present work, the extraction equilibrium of mercury(II) with thiophosphinic acids may be described as follows:

$$HgCl_{2\,aq} + n\,HX_{\,org} \overset{K_{ex,n}}{\rightleftharpoons} HgCl_2 \,.\, nHX_{org} \qquad (4.1)$$

where n = 0,1 and 2 and HX represents the extractants.

It has been reported elsewhere that these thiophosphinic acids exist as monomers in diluents like kerosene under low concentrations of the reagent with the support of vapour phase osmometry [167], neutron scattering experiments [168] and IR spectroscopy [169].

The complex formation of mercury(II) from acidic chloride solutions can be described as follows :

$$Hg^{2+} + n\,Cl^{-} \overset{\beta_n}{\rightleftharpoons} HgCl_n^{\,2-n} \qquad (4.2)$$

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

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

$$K_n = [\,HgCl_n^{\,2-n}\,] \,/\, [HgCl_{n-1}^{\,3-n}]\,[Cl^{-}] \qquad (4.3)$$

It can be assumed that the concentration of $Hg^{2+}$ and $HgCl^{+}$ species is very small in the ligand concentration range studied [149]. Then the distribution ratio, D, may be represented as:

$$D = \frac{[HgCl_2]_{org} + [HgCl_2.HX]_{org} + [HgCl_2.2HX]_{org}}{[HgCl_2]_{aq} + [HgCl_3^{\,-}]_{aq} + [HgCl_4^{\,2-}]_{aq}} \qquad (4.4)$$

From Eqs. (4.1), (4.3) and (4.4), a fundamental equation for D can be described as

$$D = \frac{K_{ex,0} + K_{ex,1}[HX]_{org} + K_{ex,2}[HX]^2_{org}}{1 + K_3[Cl^-]_{aq} + K_3K_4[Cl^-]^2_{aq}} \quad (4.5)$$

The values of the stepwise stability constants (log $K_3$ = 0.85; log $K_4$ =1.0) are taken from the literature [153].

The stoichiometry of the extracted complexes has been further confirmed by analysing the extraction data presented in Figs. 4.2 and 4.4 using Eq. (4.5) (n = 0,1 and 2). The best fit between the experimental and calculated D values was obtained only when the formation of the species $HgCl_2.2HX$ (HX = CY302 or CY301) was assumed. Based on the preceding studies, the extraction equilibrium of mercury(II) with thiophosphinic acids when extracted from hydrochloric acid solutions may be represented as:

$$HgCl_{2aq} + 2\,HX_{org} \xrightleftharpoons{K_{ex,2}} HgCl_2 \,.\, 2HX_{org} \quad (4.6)$$

The equilibrium constants of the above extracted complexes have been determined by non-linear regression analysis and are given in Table 4.1.

***Table 4.1.* Equilibrium constants of Thiophosphinic acids for the extraction of mercury(II)**

| Extractant | log $K_{ex,2}$ |
|---|---|
| CY302 | 8.71 ± 0.03 |
| CY301 | 9.06 ± 0.03 |

It is clear from the Table 4.1 that the extraction efficiency of CY301 is higher than that of CY302. Further, according to the Hard-Soft-Acid-Base (HSAB) principle, the extraction ability of bis-(2,4,4-trimethylpentyl)phosphinic acid; CYANEX 272

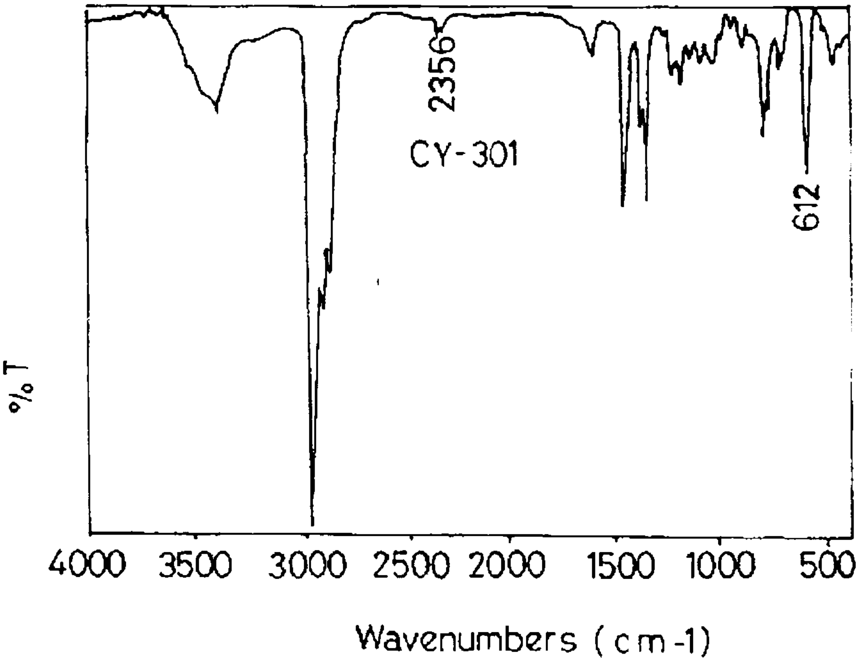
(Hard), bis-(2,4,4-trimethylpentyl)monothiophosphinic acid; CY302 (Intermediate soft) and bis-(2,4,4-trimethylpentyl)dithiophosphinic acid; CY301 (Soft), towards soft metal ions like mercury(II) should increase gradually. This is consistent with our observation that mercury(II) do not extract with CYANEX 272 from hydrochloric acid solutions. On the other hand, the extraction efficiency of mercury(II) increases gradually from CY302 to CY301. In view of the higher extraction efficiency of mercury(II) with CY301, it has been employed for the extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.

### 4.2.5 IR spectral studies of mercury(II)-CY301 complex

The IR spectrum of CY301 shows a -P=S stretching frequency band at 612 $cm^{-1}$ and -S-H stretching band at 2356 $cm^{-1}$. In the extracted complex, the -P=S band was shifted to lower frequency from 612 $cm^{-1}$ to 579 $cm^{-1}$ (Fig. 4.6). This indicates the participation of the sulphur atom of the -P=S with mercury(II) in the complex through coordination. Further, the position of the -S-H stretching frequency has not been disturbed. This confirms that CY301 does not behave as a cation-exchanger as it is evident from the extraction data.

### 4.2.6 Loading capacity of CY301

Aliquot of 10 $cm^3$ of 5 x $10^{-3}$ mol/$dm^3$ CY301 in kerosene diluent was repeatedly extracted at 303 $\pm$ 1 K for 30 min. with an equal volume of aqueous phase containing 0.02 g/$dm^3$ of mercury(II) and 0.1 mol/$dm^3$ HCl. The aqueous



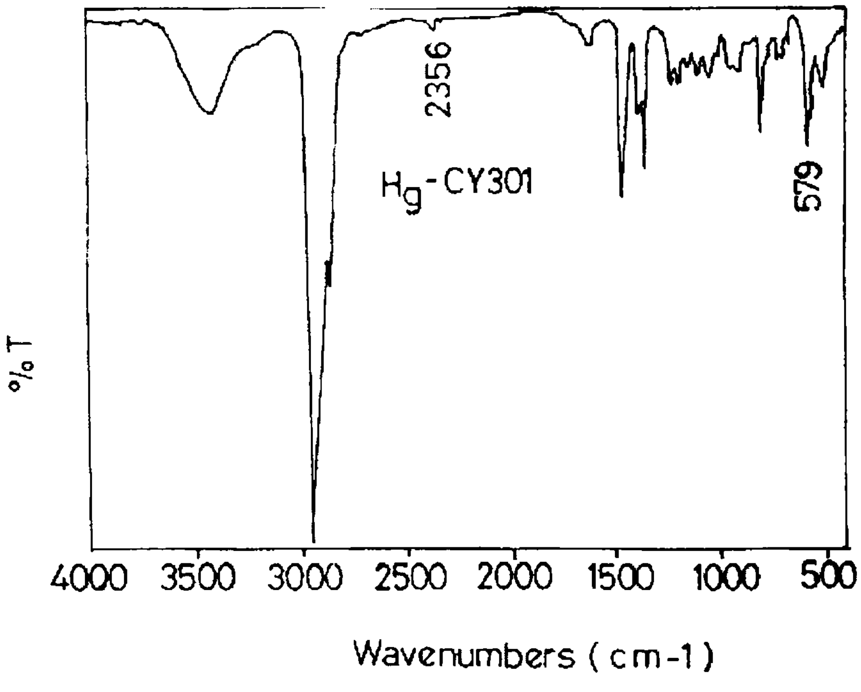


*Fig. 4.6* The IR spectra of CY301 and mercury(II)-CY301 complex.

phases were analysed for mercury(II) after each stage of extraction and the cumulative mercury(II) content transferred into the organic phase was calculated. The plot of cumulative $[Hg(II), g]_{org}$ per 100 g of CY301 vs. number of stages of contact is presented in Fig. 4.7. It is clear from the figure that the loading capacity of CY301 in kerosene is 17.64 g mercury(II) per 100 g of the extractant.

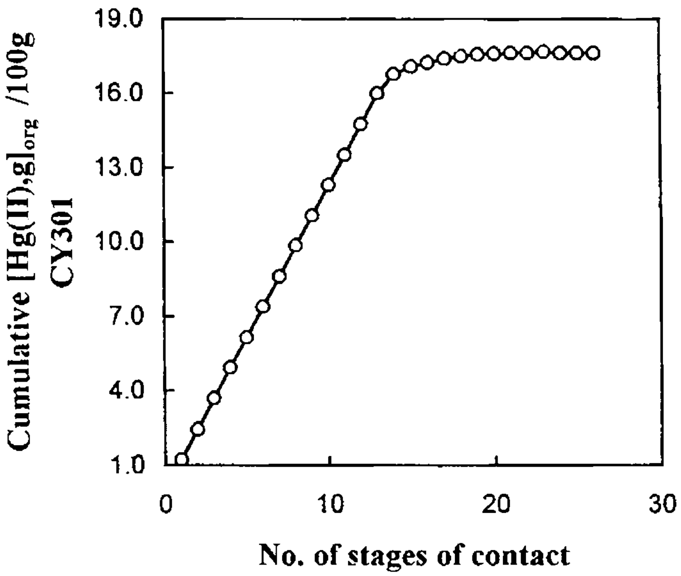


*Fig. 4.7* Loading capacity of CY301 in kerosene by mercury(II) from 0.1 mol/dm$^3$ HCl solutions.

### 4.2.7 Dependence of the nature of the diluent

The extraction of mercury(II) from 0.55 mol/dm$^3$ hydrochloric acid solutions using 3 x 10$^{-4}$ mol/dm$^3$ CY301 in various diluents has been studied and the results are shown in Table 4.2. The study clearly shows that the extraction of mercury(II) varies with the nature of the diluent. The results indicate that diluents such as kerosene having low dielectric constant show high extraction for mercury(II). This may be attributed to the weak interactions between the extractant and the diluent. Among the aromatic hydrocarbons, extraction increases in the order: xylene < toluene < benzene (it is to be noted that benzene is carcinogenic).

***Table 4.2.*** **Dependence of the nature of the diluent on the extraction of mercury(II) using $3x10^{-4}$ mol/dm$^3$ CY301 in kerosene**

| Diluent | Dielectric constant | $D_{CY301}$ |
|---|---|---|
| Kerosene | 2.00 | 4.10 |
| Benzene | 2.28 | 3.33 |
| Toluene | 2.22 | 2.93 |
| Xylene | 2.26 | 0.87 |
| Chloroform | 4.90 | 3.24 |
| Cyclohexane | 2.02 | 2.05 |
| Methylisobutyl ketone | 13.11 | 1.83 |

In view of the higher extraction efficiency of mercury(II) by CY301 in kerosene, further studies for the recovery of mercury from the brine-sludge have been carried out using kerosene as the diluent.

### 4.2.8 Stripping studies

Various stripping agents of different concentrations and phase ratios were examined to recover the metal ion from the loaded organic phase (5 x $10^{-3}$ mol/dm$^3$ CY301 in kerosene containing 1 x $10^{-4}$ mol/dm$^3$ mercury(II)) in a single stage and the results are given in Table 4.3. It is clear from the results that mercury(II) can be recovered > 99% in a single stage stripping (Phase ratio of Org. : Aq. = 1 : 2), when concentrated hydrochloric acid was used as the stripping agent. Further, preliminary experiments reveal that mercury(II) can be quantitatively recovered from the loaded organic phase in two stages of stripping using concentrated hydrochloric acid as a stripping agent with a phase ratio of Org. : Aq. = 2 : 1.

***Table 4.3.* Stripping efficiency for mercury(II) with different reagents**

| Stripping Reagent | % Recovery of mercury(II) | Phase Ratio (Org. : Aq.) |
|---|---|---|
| 1-4 mol/dm$^3$ HCl | Nil | 1 : 1 |
| 8 mol/dm$^3$ HCl | 16.0 | 1 : 1 |
| 8 mol/dm$^3$ HCl | 31.0 | 1 : 2 |
| HCl (11.3 mol/dm$^3$) | 96.0 | 1 : 1 |
| HCl (11.3 mol/dm$^3$) | 97.0 | 2 : 1 |
| HCl (11.3 mol/dm$^3$) | 99.7 | 1 : 2 |
| 0.01 mol/dm$^3$ $Na_2S_2O_3$; pH = 3.5 | Nil | 1 : 1 |
| 5% thiourea in 1% HCl | Nil | 1 : 1 |
| 4 mol/dm$^3$ NaCl ; pH=2.0 | 2.0 | 1 : 1 |

### 4.2.9 Recycling capacity of CY301 in kerosene

The recycling capacity of CY301 has been systematically investigated first by loading mercury(II) and then by stripping the loaded organic phase using concentrated hydrochloric acid in five stages. The results reveal practically insignificant change in the extraction efficiency of CY301 even after ten cycles of extraction.

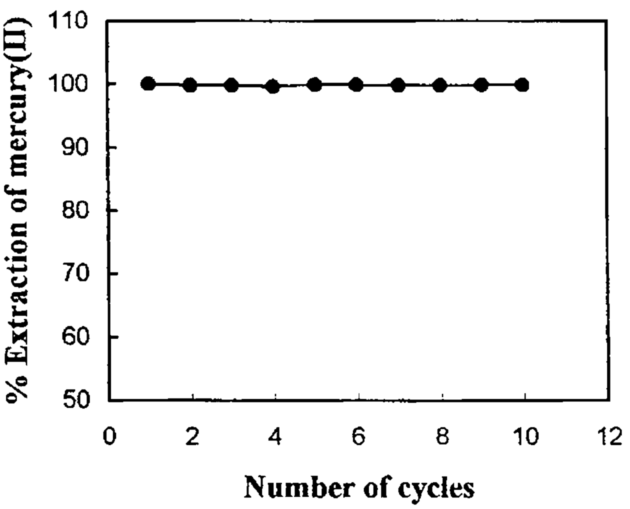


*Fig. 4.8* Recycling capacity of CY301 in kerosene. CY301 = 0.05 mol/dm$^3$; HCl = 0.2 mol/dm$^3$.

## 4.2.10 Selectivity studies

The extraction behaviour of calcium(II) (0.01 mol/dm$^3$), magnesium(II) (0.01 mol/dm$^3$) and barium(II) (0.01 mol/dm$^3$), which are associated with mercury(II) in the waste streams of the Chlor-Alkali industry has been investigated using 0.05 mol/dm$^3$ CY301 in kerosene as an extractant from 0.05 mol/dm$^3$ hydrochloric acid solutions as the aqueous phase. It was found that none of these metal ions were co-extracted along with mercury(II) into the organic phase. Thus, mercury(II) can be selectively separated from the above metal ions through the use of CY301 in kerosene as an extractant.

### 4.2.11 Recovery of mercury from the brine-sludge of a Chlor-Alkali industry

The developed liquid-liquid extraction procedure for the selective extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry was applied using CY301 in kerosene as an extractant. Brine-sludge sample (5 g) in 10 $cm^3$ of 0.2 mol/$dm^3$ hydrochloric acid was chlorinated for 5-10 min. for converting mercury into highly soluble mercuric chloride complexes. The chlorinated sludge was then subjected to solid-liquid separation and the filtrate was analysed for mercury(II), calcium(II), magnesium(II) and barium(II) and the results are shown in Table 4.4.

The extraction process of mercury from the brine-sludge of a Chlor-Alkali industry (Fig. 4.9) is comprised of the following steps:

(1) Chlorination of the brine-sludge;

(2) Solid-liquid separation;

(3) Selective extraction of mercury(II) in a single stage from the feed solution (chlorinated brine-sludge filtrate; pH = 1 - 2 ), consisting of mercury(II) 27.5 mg/$dm^3$, calcium(II) 3.88 g/$dm^3$, magnesium(II) 0.58 g/$dm^3$ and barium(II) 4.56 mg/$dm^3$ using a substantially immiscible extractant phase, which is comprised of CY301 in kerosene (0.05 mol/$dm^3$; Phase ratio of Org. : Aq. = 1 : 1), whereupon mercury reversibly transfers into the extractant phase (% extraction of mercury(II) > 99.99);

(4) Mercury was then recovered from the loaded organic phase by stripping with concentrated hydrochloric acid in 5 stages at an organic to aqueous phase ratio of 1 : 2.

A schematic flow diagram of the above laboratory scale process is shown in Fig. 4.9. Typical analysis results of the feed, raffinate and strip liquors are given in Table 4. 4.

***Table 4.4.* Selective separation of mercury(II) from the brine-sludge of a Chlor-Alkali industry using CY301 in kerosene**

| Metal Ion | Amount of metal ion | | |
|---|---|---|---|
| | Feed | Raffinate | Strip liquor |
| Mercury(II) | 27.50 mg/dm$^3$ | 2.75 µg/dm$^3$ | 27.497 mg/dm$^3$ |
| Calcium(II) | 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. |

*N.D.= not detectable

The investigations reveal that > 99.9% mercury can be recovered selectively through a single stage extraction and five stages of stripping process from the brine-sludge of a Chlor-Alkali industry using CY301 (0.05 mol/dm$^3$) in kerosene as an extractant.

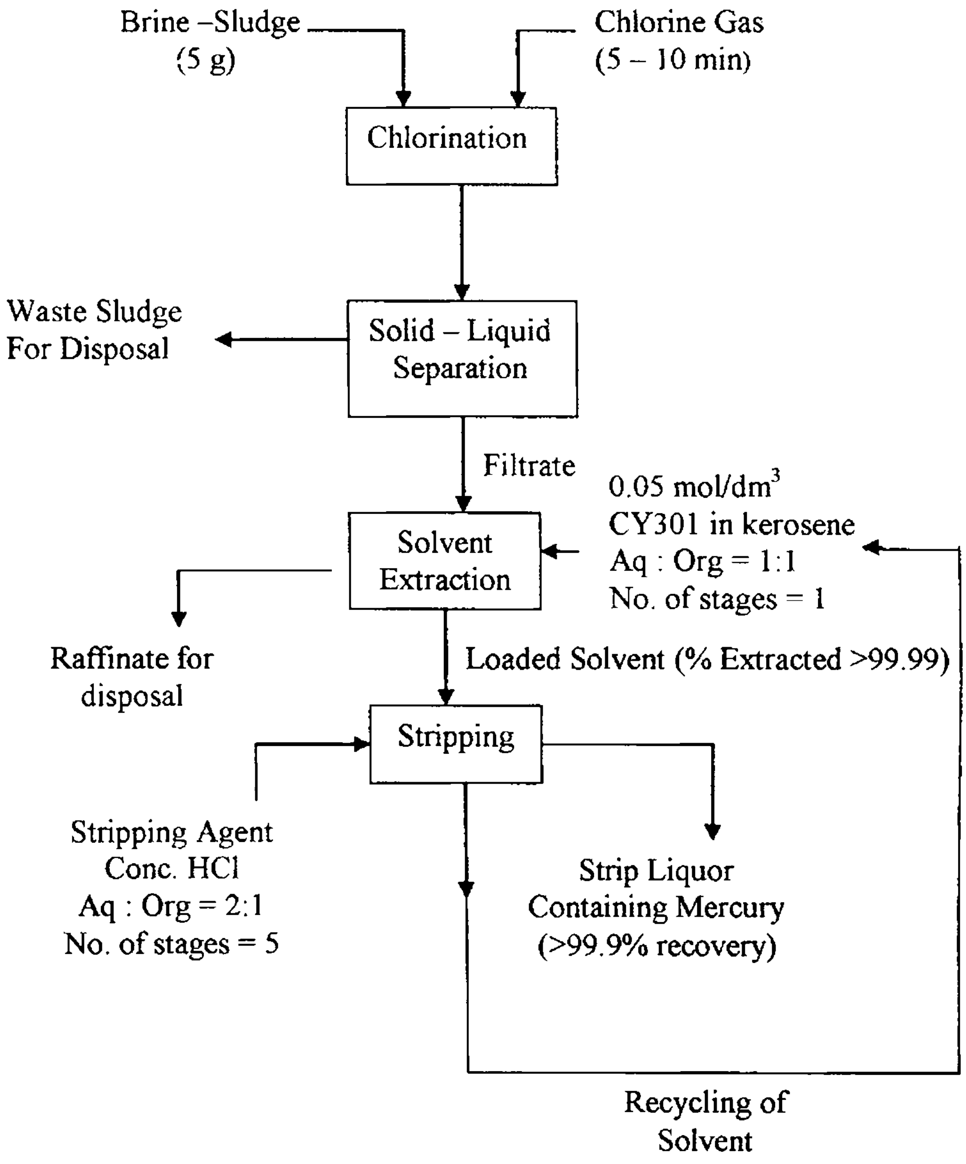
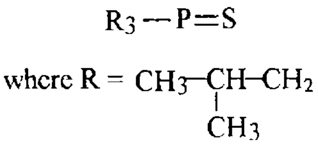


***Fig. 4.9*** Selective liquid-liquid extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry using CY301 in kerosene.

# *Chapter 5*

# *Triisobutylphosphine Sulphide as an Extractant for the Recovery of Mercury from the Brine-Sludge of a Chlor-Alkali Industry*

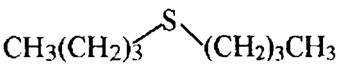
In the recent past, triisobutylphosphine sulphide (TIBPS) marketed under the trade name CYANEX 471X by Cytec Canada Inc., has been suggested as a potential extractant for many soft metal ions [170-172]. Due to its lower pKa value, it may be possible to extract metal ions at a higher acidity than trialkylphosphine oxide. Moreover, the branching in the chain may introduce selectivity in the extraction. However, systematic extraction studies on mercury(II) involving TIBPS are very limited [95-97]. Hence, in the present study TIBPS has been explored as a potential extractant for the selective extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry. For comparison, studies have also been performed with dialkyl sulphides such as, dibutyl sulphide (DBS) and dioctyl sulphide (DOS).

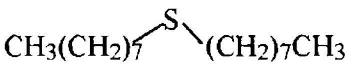


$$R_3-P=S$$

$$\text{where } R = CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2$$

**TIBPS (CYANEX 471X)**





**DBS** **DOS**

*Fig. 5.1* Structure of extractants used in the present work.

## 5.1 EXPERIMENTAL

### 5.1.1 Reagents

TIBPS, commercially available under the trade name of CYANEX 471X supplied by Cytec Canada Inc., was used without further purification for the extraction studies. Dibutyl sulphide (DBS) and dioctyl sulphide (DOS) obtained from Fluka Chemika, Switzerland, were employed as such for the comparative extraction studies. All the other chemicals employed were of analytical reagent grade.

### 5.1.2 Liquid-liquid extraction and analytical procedure

The liquid-liquid extraction procedure and analytical methods followed for the determination of metal ions were the same as described in Chapter 2. Preliminary experiments showed that the extraction equilibrium is attained within 5 min. for all the extraction systems.

### 5.1.3 Preparation of mercury(II)-TIBPS complex

The mercury(II)-TIBPS complex was prepared according to the procedure described in Chapter 3. The KBr (neat) containing the film of the metal complex solution was put under the IR lamp to evaporate the xylene completely. For comparison, the IR spectrum of pure TIBPS was also taken.

## 5.2 RESULTS AND DISCUSSION

### 5.2.1 Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration (0.18 - 0.4 mol/dm$^3$) on the extraction of mercury(II) has been investigated using 5 x 10$^{-3}$ mol/dm$^3$ TIBPS in xylene as an extractant and the results are depicted in Fig. 5.2. It is clear from the results that the extraction efficiency of mercury(II) decreases with increasing hydrochloric acid concentration in the aqueous phase. This may be due to the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ species with increasing chloride ion concentration in the aqueous phase. A similar trend has been observed for the extraction of mercury(II) with dialkyl sulphides such as, DBS and DOS (Fig. 5.3).

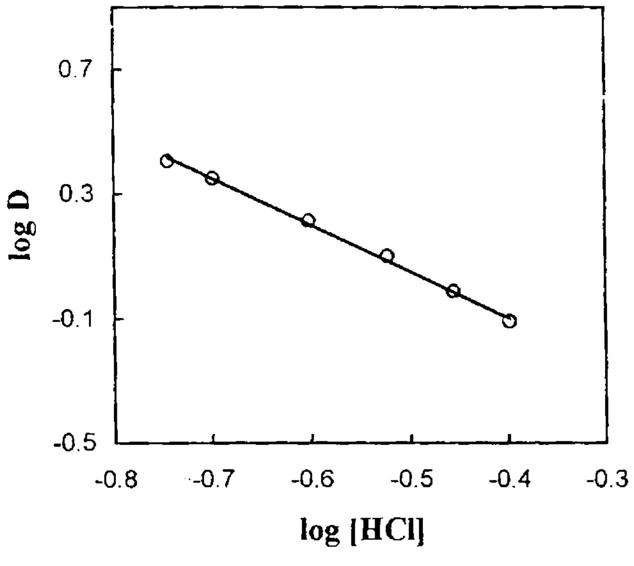


***Fig. 5.2*** Effect of hydrochloric acid concentration on the extraction of mercury(II) using 5 x 10$^{-3}$ mol/dm$^3$ TIBPS in xylene as an extractant. mercury(II) = 1 x 10$^{-5}$ mol/dm$^3$.

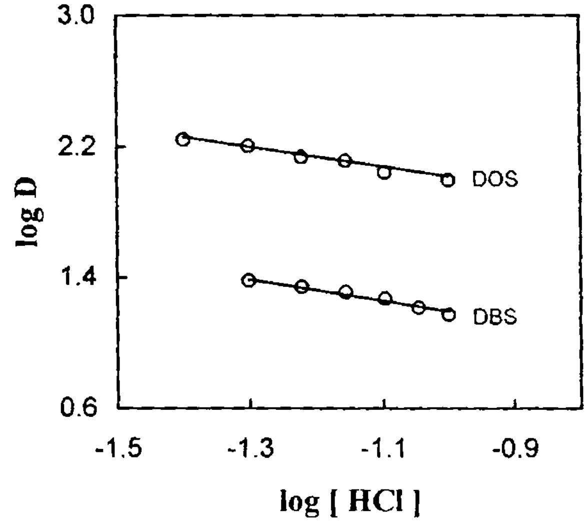


*Fig. 5.3* Effect of hydrochloric acid concentration on the extraction of mercury(II) using dialkyl sulphides. DBS = 2 x $10^{-3}$ mol/dm$^3$; DOS = 0.2 mol/dm$^3$; mercury(II) = 1 x $10^{-5}$ mol/dm$^3$.

### 5.2.2 Effect of extractant concentration

The effect of TIBPS concentration (4 x $10^{-3}$ - 1 x $10^{-2}$ mol/dm$^3$) on the extraction of mercury(II) from 0.2 mol/dm$^3$ hydrochloric acid solutions has been studied and the results are shown in Fig. 5.4. It is clear from the figure that the extraction of mercury(II) increases linearly with increasing TIBPS concentration and from the slope of the log-log plot it is clear that two molecules of TIBPS are involved in the extracted complex. For comparison, the effect of DBS and DOS in xylene on the extraction efficiency of mercury(II) has also been investigated and the results are given in Fig. 5.5. The extraction efficiency of mercury(II) increases linearly with increasing concentrations of the dialkyl sulphides and from the slope of the log-log plots it is clear that two and three molecules of the dialkyl sulphides are involved in the extracted complexes of mercury(II).

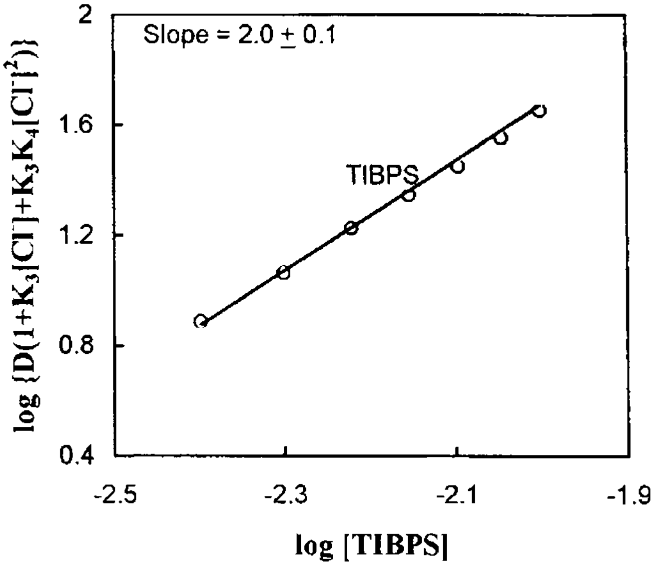


*Fig. 5.4* Effect of TIBPS concentration on the extraction of mercury(II). HCl = 0.2 mol/dm$^3$; mercury(II) = 1 x 10$^{-5}$ mol/dm$^3$.

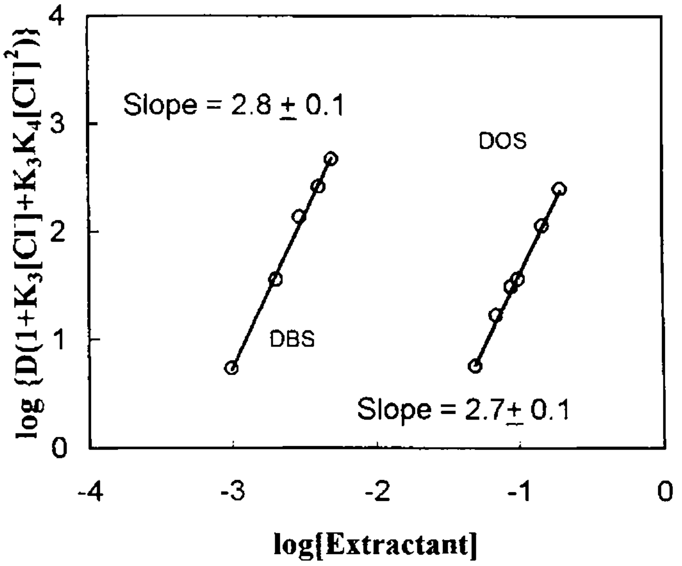


*Fig. 5.5* Effect of dialkyl sulphide concentrations on the extraction of mercury(II). HCl = 0.1 mol/dm$^3$; mercury(II) = 1 x 10$^{-5}$ mol/dm$^3$.

### 5.2.3 Effect of metal ion concentration

The effect of metal ion concentration ($1 \times 10^{-6}$ - $1 \times 10^{-4}$ mol/dm$^3$) on the extraction process of mercury(II) has been investigated using $5 \times 10^{-3}$ mol/dm$^3$ TIBPS in xylene as an extractant from 0.2 mol/dm$^3$ hydrochloric acid solutions and found that the extraction efficiency of mercury(II) is independent of initial metal ion concentrations under the present experimental conditions. The log-log plot (Fig. 5.6) of the equilibrium organic phase metal ion concentration against the aqueous phase metal ion concentration is linear with a slope equal to unity, indicating the extraction of mononuclear species into the organic phase. A similar behaviour has been observed on the effect of metal ion concentration with dialkyl sulphides (Fig. 5.7).

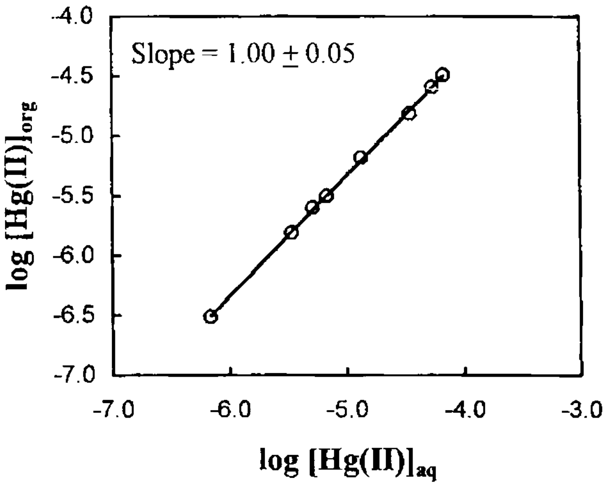


***Fig. 5.6*** Effect of metal ion concentration on the extraction of mercury(II) using TIBPS. TIBPS = $5 \times 10^{-3}$ mol/dm$^3$; HCl = 0.2 mol/dm$^3$.

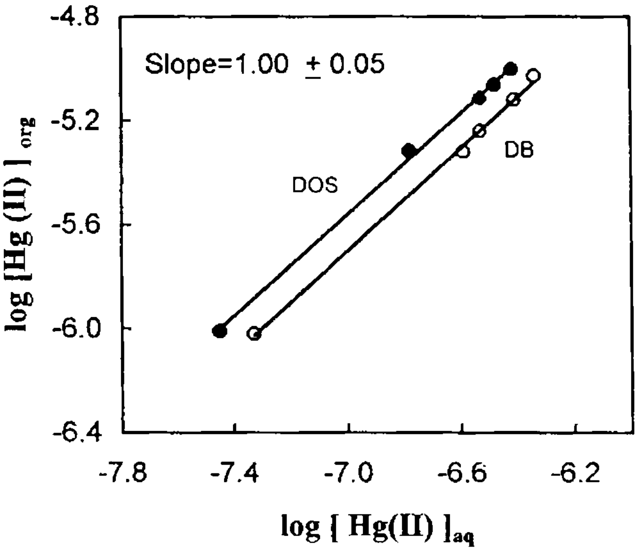


*Fig. 5.7* Effect of metal ion concentration on the extraction of mercury(II) using dialkyl sulphides. DBS = 2 x $10^{-3}$ mol/dm$^3$; DOS = 0.1 mol/dm$^3$; HCl = 0.1 mol/dm$^3$.

### 5.2.4 Extraction equilibrium of mercury(II)

Based on the preceding studies, the extraction equilibrium of mercury(II) may be described as follows :

$$HgCl_{2aq} + nS_{org} \xrightleftharpoons{K_{ex,n}} HgCl_2.nS_{org} \qquad (5.1)$$

where n = 0, 1, 2 and 3; $K_{ex,n}$ = equilibrium constant and S denotes the extractant.

Then, the distribution ratio, D, may be represented (from Eqs. (4.4) and (5.1)) as:

$$D = \frac{[HgCl_2]_{org} + [HgCl_2.S]_{org} + [HgCl_2.2S]_{org}}{[HgCl_2]_{aq} + [HgCl_3^-]_{aq} + [HgCl_4^{2-}]_{aq}} \qquad (5.2)$$

From Eqs. (5.1), (4.4) and (5.2), a fundamental equation for D can be described as:

$$D = \frac{K_{ex,0} + K_{ex,1}[S]_{org} + K_{ex,2}[S]^2_{org}}{1 + K_3[Cl^-]_{aq} + K_3K_4[Cl^-]^2_{aq}} \quad (5.3)$$

where $K_3$ and $K_4$ are the stepwise stability constants of the reactions described in the previous chapters and the values (log $K_3$ = 0.85; log $K_4$ = 1.0) were taken from the literature [153]. The equilibrium constants of the extracted complexes were determined by non-linear regression analysis as described in Chapter 2.

The stoichiometry of the extracted complexes has been further confirmed by analysing the extraction data presented in Figs. 5.2, 5.3, 5.4 and 5.5 using Eq. (5.3) (n = 0, 1, 2 and 3). The best fit between the experimental and calculated D values was obtained when the formation of the species $HgCl_2.2TIBPS$, $HgCl_2.2DBS/2DOS$ and $HgCl_2.3DBS/3DOS$ were assumed. The equilibrium constants of the above extracted complexes have been determined by non-linear regression analysis and are given in Table 5.1. It is clear from the Table 5.1 that the extraction efficiency of these extractants decreases in the order: DBS > TIBPS > DOS. Among dialkyl sulphides, the extraction efficiency of DBS is found to be significantly higher than that of DOS. This can be explained on the basis of steric factors of these extractants. The increasing alkyl chain length of the dialkyl sulphides clearly diminishes the extraction efficiency of mercury(II).

***Table 5.1.*** **Equilibrium constants of the various sulphide extractants for the extraction of mercury(II)**

| Extractant | log $K_{ex,2}$ | log $K_{ex,3}$ |
|---|---|---|
| DBS | 6.23 ± 0.02 | 9.58 ± 0.02 |
| TIBPS | 5.67 ± 0.02 | ___ |
| DOS | 3.10 ± 0.03 | 4.38 ± 0.03 |

### 5.2.5 IR spectral studies of mercury(II)-TIBPS complex

The IR spectra of mercury(II)-TIBPS complex (Fig. 5.8) shows a shift of the P=S stretching from 705 to 695 $cm^{-1}$, indicative of the participation of the sulphur of the P=S group in the complex formation through coordination.

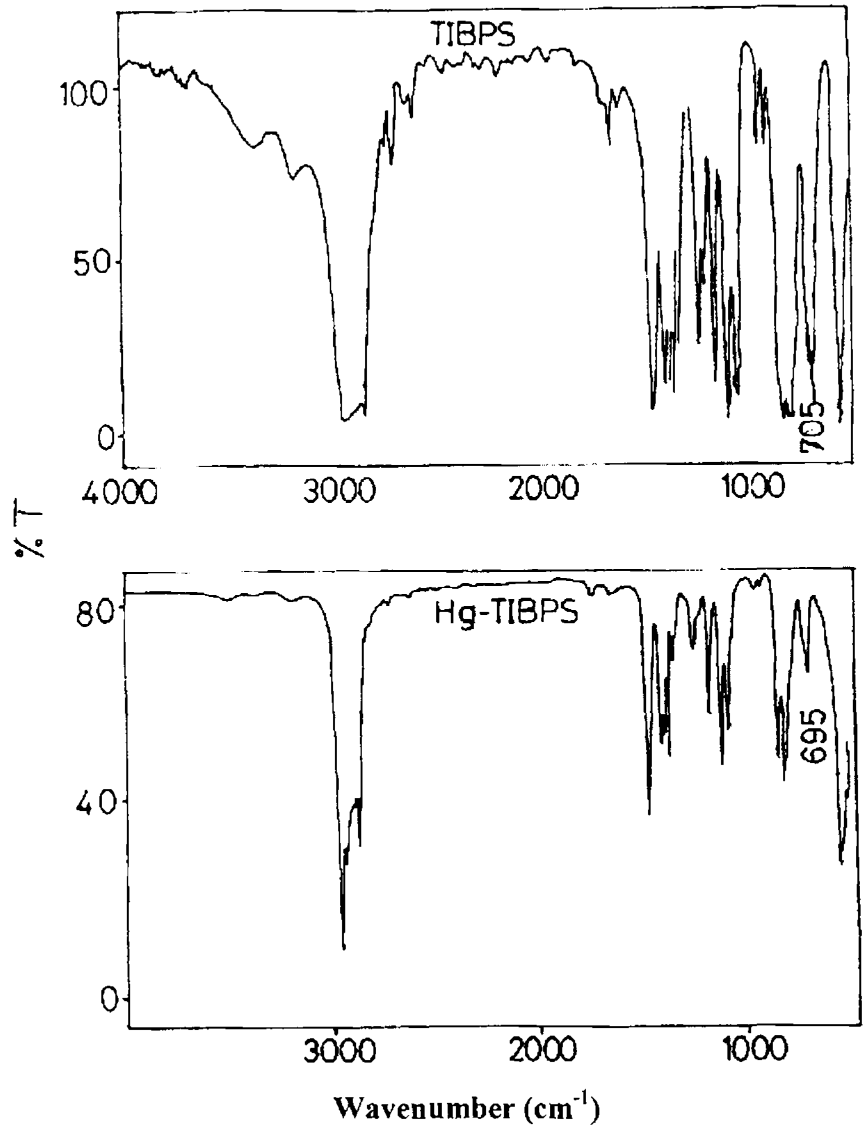


*Fig. 5.8* IR spectra of TIBPS and mercury(II)-TIBPS complex.

## 5.2.6. Loading capacity of TIBPS by mercury

Aliquot of 10 $cm^3$ of 0.05 mol/$dm^3$ TIBPS in xylene were repeatedly extracted at 303 ± 1K for 30 min. with equal volumes of aqueous solution containing 5 x $10^{-4}$ mol/$dm^3$ mercury(II) and 0.1 mol/$dm^3$ hydrochloric acid. After reaching the equilibrium, the phases were disengaged and aqueous phases analysed for mercury(II) content. The plot of cumulative [Hg(II), $g]_{org}$ per 100 g of TIBPS vs. the number of stages of contact is presented in Fig. 5.9. It is clear from the figure that the loading capacity of TIBPS for mercury(II) is 14.15 g mercury(II) per 100 g of the extractant.

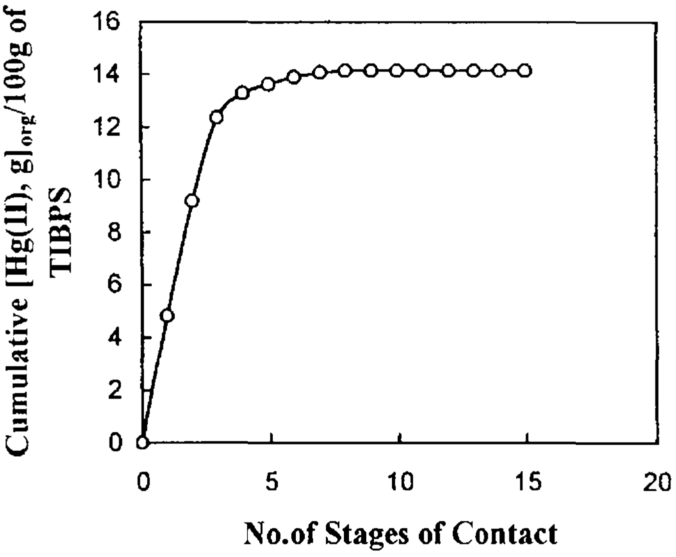


***Fig. 5.9*** Loading capacity of TIBPS in kerosene for mercury(II) from 0.1 mol/$dm^3$ HCl solutions.

### 5.2.7 Effect of the nature of the diluent

The effect of the nature of the diluent on the extraction process of mercury(II) from 0.2 mol/dm$^3$ hydrochloric acid solution using 0.01 mol/dm$^3$ TIBPS has been investigated and the results are given in Table 5.2. The study clearly shows that the extraction efficiency of mercury(II) varies with the nature of the diluent. The results clearly demonstrate that diluents such as kerosene having low dielectric constant show high extraction for mercury(II). Among aromatic hydrocarbons, the extraction efficiency decreases in the order: benzene > toluene > xylene. In view of the commercial availability and good extraction efficiency, in the subsequent studies, kerosene has been chosen as the diluent.

***Table 5.2.* Dependence on the nature of the diluent on the extraction of mercury(II) from 0.2 mol/dm$^3$ hydrochloric acid solutions using TIBPS**

| Diluent | Dielectric constant (ε) | D |
|---|---|---|
| Methylisobutyl ketone | 13.11 | 48.4 |
| Benzene | 2.28 | 16.68 |
| Toluene | 2.22 | 10.56 |
| Xylene | 2.26 | 8.65 |
| 1,2-dichloroethane | 10.45 | 50.25 |
| Chloroform | 4.90 | 10.02 |
| Cyclohexane | 2.02 | 0.65 |
| Kerosene | 2.00 | 28.08 |

### 5.2.8 Stripping studies

Mercury stripping from a loaded organic solvent system consisting of 0.1 mol/dm$^3$ TIBPS in kerosene containing 1 x 10$^{-5}$ mol/dm$^3$ mercury(II) has been investigated using various stripping agents and the results are given in Table 5.3. Among the many stripping agents studied, 5% thiourea in 1% HCl and 0.01 mol/dm$^3$ $Na_2S_2O_3$ (pH = 5.5) are found to be effective for the stripping of mercury(II) (% recovery > 99.5%) from the loaded organic phase in a single stage with the phase ratio equal to unity.

***Table 5.3*** **Stripping studies for mercury(II) with various stripping agents**

| Stripping agents | % Recovery |
|---|---|
| 5 % thiourea in 1 % HCl | > 99.9 |
| 0.01 mol/dm$^3$ $Na_2S_2O_3$ (pH = 5.5) | 99.5 |
| 0.01 mol/dm$^3$ NaCl (pH = 12.5) | 93.9 |
| 5 mol/dm$^3$ HCl | 65.8 |
| 0.01 mol/dm$^3$ $NH_4Cl$ (pH = 11.1) | 91.5 |

### 5.2.9 Recycling capacity of TIBPS in kerosene

The recycling capacity of TIBPS has been systematically investigated first by loading mercury(II) and then by stripping the loaded organic phase using 0.01 mol/dm$^3$ NaCl (pH = 12.5) in three stages. The results reveal practically insignificant change in the extraction efficiency of TIBPS even after ten cycles of extraction (Fig. 5.10).

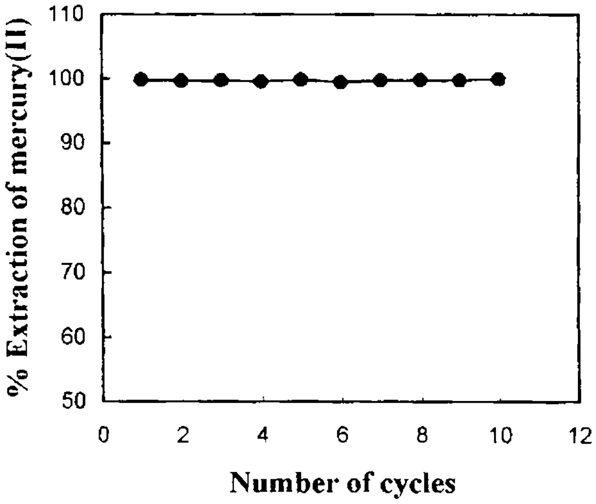


***Fig. 5.10*** Recycling capacity of TIBPS in kerosene. TIBPS = 0.1 mol/dm$^3$; HCl = 0.05 mol/dm$^3$.

### 5.2.10 Selectivity studies

The effect of other metal ions such as calcium(II) (0.01 mol/dm$^3$), magnesium(II) (0.01 mol/dm$^3$) and barium(II) (0.01 mol/dm$^3$), in 0.05 mol/dm$^3$ hydrochloric acid solutions using 0.1 mol/dm$^3$ TIBPS in kerosene on the extraction process of mercury(II) has been studied and found that none of these metal ions are getting extracted into the organic phase. On the other hand, mercury(II) is found to be quantitatively extracted (% extraction > 99.9) under the present experimental conditions. Thus, mercury(II) can be selectively separated from the above metal ions using TIBPS in kerosene as an extractant.

### 5.2.11 Extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry

The developed liquid-liquid extraction method has been utilised for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry by employing TIBPS in kerosene as an extractant. 5 g of the brine-sludge sample in 10 $cm^3$ of 0.2 $mol/dm^3$ hydrochloric acid was chlorinated (5-10 min.) for converting mercury into highly soluble mercuric chloride complexes. The chlorinated filtrate was analysed for mercury(II), calcium(II), magnesium(II) and barium(II) and the results are shown in Table 5.4.

The extraction process of mercury(II) from the brine-sludge of a Chlor-Alkali industry is comprised of the following steps:

(1) Chlorination of the brine-sludge sample (5 g);

(2) Solid-liquid separation;

(3) Selective separation of mercury(II) in a single stage from the feed solution (chlorinated brine-sludge filtrate; pH = 1 - 2), consisting mercury(II) 27.5 $mg/dm^3$, calcium(II) 3.88 $g/dm^3$, magnesium(II) 0.58 $g/dm^3$ and barium(II) 4.56 $mg/dm^3$ using a substantially immiscible extractant phase, which is comprised of TIBPS in kerosene (0.1 $mol/dm^3$; Phase ratio of Org. : Aq. = 1 : 1), whereupon mercury reversibly transfers into the extractant phase (% extraction of mercury > 99.9);

(4) Mercury was then recovered from the loaded organic phase by stripping with 0.01 mol/dm$^3$ NaCl (pH = 12.5) in three stages at an organic to aqueous ratio of 1 : 1.

A schematic procedure for the extraction and separation process is given in Fig. 5.11.

***Table 5.4.* Selective separation of mercury(II) from the brine-sludge of a Chlor-Alkali industry using TIBPS in kerosene**

| Metal Ion | Amount of metal ion | | |
|---|---|---|---|
| | Feed | Raffinate | Strip liquor |
| Mercury(II) | 27.50 mg/dm$^3$ | 2.75 μg/dm$^3$ | 27.497 mg/dm$^3$ |
| Calcium(II) | 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. |

*N.D.= not detectable

The analysis results of the feed, raffinate and strip liquors given in Table 5.4 reveal that > 99.9% mercury can be recovered selectively through a single stage extraction and three stages of stripping process from the brine-sludge of a Chlor-Alkali industry using 0.1 mol/dm$^3$ TIBPS in kerosene as an extractant.

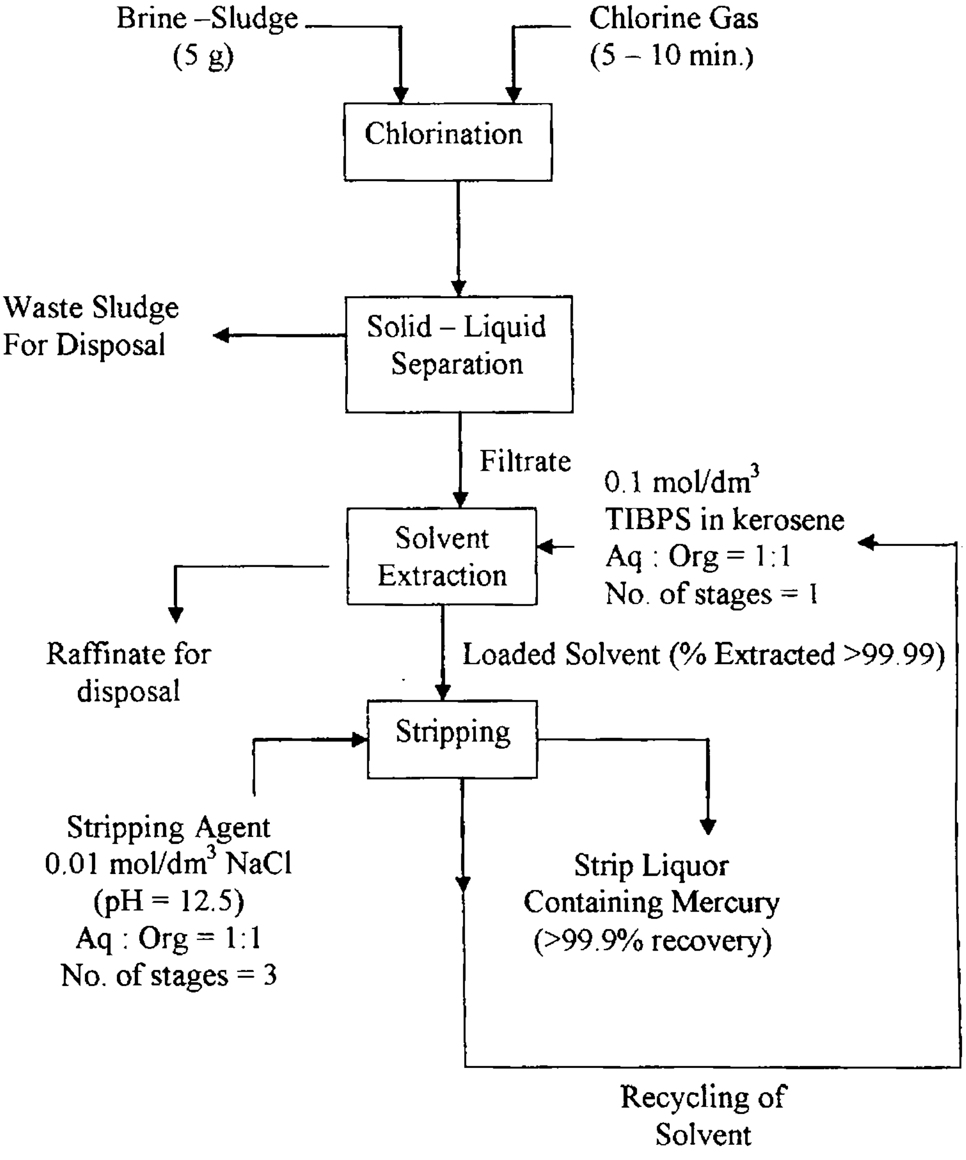


*Fig. 5.11* Selective liquid-liquid extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry using TIBPS in kerosene.

# *Conclusions*

For many years, the Chlor-Alkali industry all over the world has been a matter of grave concern because of the potential pollution hazards due to the presence of mercury in the waste streams. Thus, the control and removal of mercury from the waste streams is important. Hence, in the present work, an attempt has been made to selectively recover mercury from the brine-sludge of a Chlor-Alkali plant by employing various oxo - and sulphur donors as extracting ligands.

The extraction behaviour of mercury(II) from dilute hydrochloric acid solutions has been investigated using dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane as an extractant. For comparison, extraction studies have also been carried out with 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and dibenzo-18-crown-6 (DB18C6). The extraction data have been analysed by both graphical and theoretical methods by taking into account aqueous phase complexation of the metal ion with inorganic ligands and all plausible complexes extracted into the organic phase. The results demonstrate that mercury(II) is extracted into 1,2-dichloroethane as $HgCl_2.2CE$ (CE represents the crown ether). The equilibrium constants of the extracted complexes have been deduced by non-linear regression analysis with the aid of suitable chemically based model developed. The extraction efficiency of the various crown ethers follows the order: 18C6 > DC18C6 > B18C6, which is also the basicity sequence of these crown ethers. The sharp decrease in the extraction efficiency of mercury(II) from 18C6 to DC18C6 and B18C6 mostly reflects increasing steric effects and decreasing basicity. The higher extractability of mercury(II) with 18C6 or DC18C6 can be explained on the basis of "size-fitting effect" of these crown ethers. The solid complex of $HgCl_2.DC18C6$ has been synthesised and characterised by elemental, IR and $^1H$ NMR spectral studies. For practical application in liquid-liquid extraction, crown ethers must exhibit both high solubility in organic diluents and low distribution to the aqueous phase. Hence, for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry, DC18C6 has been chosen as an extractant. The effect of other metal ions such as, calcium(II), magnesium(II) and barium(II), which are associated with mercury(II) in the brine-sludge of a Chlor-Alkali industry has also been investigated using DC18C6 in 1,2-dichloroethane as an extractant. The results show that none of these metal ions are getting extracted into the organic phase along with mercury(II) under the present experimental conditions. Thus, mercury(II) can be selectively separated from the above metal ions by employing DC18C6 as an extractant. The developed liquid-liquid extraction process has been applied for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry. The investigations reveal that > 99.9% mercury can be selectively recovered through a single stage extraction (0.02 $mol/dm^3$ DC18C6 in 1,2-dichloroethane; Phase ratio Org. : Aq. = 1 : 1) and stripping (5 % $NH_4Cl$ in 1 : 10 $NH_3$; Phase ratio Org. : Aq. = 1 : 1) process from the brine-sludge of a Chlor-Alkali industry.

A novel sterically hindered branched chain dialkyl sulphoxide, bis-2-ethylhexyl sulphoxide (B2EHSO) has been explored as an extractant for mercury(II) from dilute hydrochloric acid solutions. For comparison, studies have also been performed with dioctyl sulphoxide (DOSO) and diphenyl sulphoxide (DPhSO). The extraction behaviour of mercury(II) with the sulphoxides have also been compared with a trialkyl phosphine oxide (TRPO), CYANEX 923, which is essentially a mixture of four trialkylphosphine oxides. The results demonstrate that mercury(II) is extracted into xylene as $HgCl_2.3R_2SO$, where $R_2SO$ represents the sulphoxide. The extraction efficiency of mercury(II) with the various sulphoxides increases in the order: DPhSO < B2EHSO < DOSO. Among the dialkyl sulphoxides, the extraction efficiency of branched chain sulphoxide, B2EHSO, is slightly lower than the straight chain sulphoxide, DOSO, which can be attributed to the steric effects. Further, it is also very clear that the extraction efficiency of arylsulphoxide, DPhSO, is found to be significantly lower than dialkyl sulphoxides which again can be explained on the basis of steric factors. The extraction efficiency of mercury(II) with the dialkyl sulphoxides is found to be considerably lower than that of trialkyl phosphine oxide (TRPO), which is in good agreement with the basicity values of these ligands extractants (Nitric acid uptake constant: $K_{H, TRPO} = 8.5$; $K_{H, DOSO} = 0.42$). The greater basicity of the $P \rightarrow O$ group in TRPO compared to that of the $S \rightarrow O$ group in the sulphoxide would account for the higher extraction efficiency of mercury(II). The IR spectral studies of the mercury(II)–B2EHSO complex show a shift of the S=O characteristic peak at 1029 to 1036 $cm^{-1}$, indicating coordination of the B2EHSO molecule to mercury through sulphur of the S=O group. On the other hand, the shift of the P=O stretching frequency in TRPO from 1146 $cm^{-1}$ to 1116 $cm^{-1}$ in $HgCl_2.3TRPO$ complex indicates that there is strong interaction between the oxygen of the phosphine oxide and mercury. The dependence of extraction on the nature of the diluent has been investigated and correlated with their dielectric constants. Diluents such as kerosene and cyclohexane, having low dielectric constants, show high extraction efficiency for mercury(II). On the other hand, diluents having higher dielectric constants, such as chloroform, gave poor extraction. In view of the higher extraction efficiency observed for mercury(II) with B2EHSO or TRPO in kerosene, further studies for the extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry has been carried out using kerosene as a diluent. Selectivity studies using B2EHSO or TRPO in kerosene proved that these extractants selectively extract mercury(II) over other metal ions such as, calcium(II), magnesium(II) and barium(II) under the present experimental conditions. The studies conducted on the recycling capacity of the extractants reveal practically insignificant change in the extraction efficiency of these extractants even after ten cycles of extraction. The loading capacity of TRPO has been found to be significantly higher (12.88 g mercury(II) per 100 g of TRPO) than that of B2EHSO which has a loading capacity of 0.33 g mercury(II) per 100 g of the extractant. The developed liquid-liquid extraction procedure has been applied for the removal and recovery of mercury from the brine-sludge of a Chlor-Alkali industry. From the above studies it can be concluded that B2EHSO or TRPO can be used as a selective liquid-liquid extraction reagent for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry.

The extraction behaviour of mercury(II) from dilute hydrochloric acid solutions has been studied using mono - and di - sulphur analogs of bis-(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), namely, bis-(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302 = CY302) and bis-(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301 = CY301), with the aim to develop a selective liquid-liquid extraction process for the separation of mercury from the waste streams of a Chlor-Alkali industry. The results clearly demonstrate that CY302 and CY301 do not behave as cation-exchange extractants but as solvating extractants, owing to the strong affinity of sulphur atom of the extractant for the soft metal ion mercury. The extraction equilibrium of mercury(II) with thiophosphinic acids when extracted from hydrochloric acid solutions may be represented as:

$$HgCl_{2aq} + 2\,HX_{org} \xrightleftharpoons{K_{ex,2}} HgCl_2 \cdot 2HX_{org}$$

where HX represents the thiophosphinic acid extractants.

The equilibrium constants of the extracted complexes have been deduced by non-linear regression analysis with the aid of suitable chemically based model developed. It is clear from the equilibrium constant values that the extraction efficiency of CY301 is higher than that of CY302. This is in good agreement with the HSAB concept that the extraction ability of CYANEX 272 (hard); CY302 (intermediate soft) and CY301 (soft) towards soft metal ions like mercury(II), should increase gradually. Further, this is also consistent with our observation that mercury(II) do not extract with CYANEX 272 from hydrochloric acid solutions. On the other hand, the extraction efficiency of mercury(II) increases gradually from CY302 to CY301. In view of the higher extraction efficiency of mercury(II) with CY301, it has been further explored as an extractant for the recovery of mercury from industrial waste streams. The loading capacity of CY301 has been determined and found to be 17.64 g per 100 g of the extractant. The effect of the nature of the diluent on the extraction process of mercury(II) has been investigated and correlated with their dielectric constants. The results clearly demonstrate that the extraction of mercury(II) varies with the nature of the diluent. The results indicate that diluents such as kerosene having low dielectric constant show high extraction for mercury(II). This may be attributed to the weak interactions between the extractant and the diluent. Among the aromatic hydrocarbons, extraction increases in the order: xylene < toluene < benzene. It is clear from the stripping studies for the recovery of mercury(II) from the loaded CY301 in kerosene system that high concentrations of hydrochloric acid is required for the back-extraction of the metal ion. This may be due to the strong complex formation of soft metal ion like mercury(II) with CY301. Results from the recycling capacity experiments of CY301 reveal practically insignificant change in the extraction efficiency of the extractant even after ten cycles of extraction. The extraction behaviour of calcium(II), magnesium(II) and barium(II) which are associated with mercury(II) in the brine-sludge of a Chlor-Alkali industry has also been investigated using CY301 in kerosene as an extractant. It is found that none of these metal ions are co-extracted along with mercury(II) into the organic phase. Thus, the study clearly demonstrates the usefulness of CY301 in kerosene as a selective reagent for the extraction of mercury(II) over calcium(II), magnesium(II) and barium(II) from dilute hydrochloric acid solutions (pH = 1-2). The developed liquid-liquid extraction procedure by employing CY301 in kerosene as an extractant has been applied for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry. The extraction process comprises of the following steps: (1) Chlorination of the brine-sludge; (2) Solid-liquid separation; (3) Selective extraction of mercury(II) in a single stage from the feed solution (chlorinated brine-sludge filtrate; pH = 1-2 ), consisting of mercury(II) 27.5 mg/dm$^3$, calcium(II) 3.88 g/dm$^3$, magnesium(II) 0.58 g/dm$^3$ and barium(II) 4.56 mg/dm$^3$ using a substantially immiscible extractant phase, which is comprised of CY301 in kerosene (0.05 mol/dm$^3$; Phase ratio Org. : Aq. = 1 : 1), whereupon mercury reversibly transfers into the extractant phase (% extraction of mercury(II) > 99.99); (4) Mercury was then recovered from the loaded organic phase by stripping with concentrated hydrochloric acid in 5 stages at an organic to aqueous ratio of 1 : 2. The investigations reveal that CY301 can be used as a potential extractant for the selective extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.

Owing to the strong affinity of mercury(II) towards soft ligands, investigations have been carried out on the extraction behaviour of mercury(II) from dilute hydrochloric acid solutions using triisobutyl phosphine sulphide (TIBPS) as an extractant. For comparison, studies have also been performed with dialkyl sulphides such as, dibutyl sulphide (DBS) and dioctyl sulphide (DOS). The results demonstrate that mercury(II) is extracted into xylene as $HgCl_2.2TIBPS$, with TIBPS. On the other hand, mercury(II) is extracted as $HgCl_2.2DBS/2DOS$ and

$HgCl_2.3DBS/3DOS$ with dialkyl sulphides. The extraction efficiency of the extractants decreases in the order: DBS > TIBPS > DOS. Among dialkyl sulphides, the extraction efficiency of DBS is found to be significantly higher than DOS. The increasing alkyl chain length of the alkyl sulphide clearly diminishes the extraction efficiency of mercury(II). The IR spectra of the $HgCl_2$-TIBPS complex shows a shift of the P=S stretching from 705 - 695 $cm^{-1}$ indicating the participation of the sulphur of the P=S group in complex formation through coordination. The loading capacity of TIBPS for mercury(II) is found to be 14.15 g of mercury(II) per 100 g of the extractant, which is comparable with that of CY301. The effect of the nature of the diluent on the extraction process of mercury(II) using TIBPS has been investigated. The results clearly demonstrate that diluents such as kerosene having low dielectric constants exhibit high extraction efficiency towards mercury(II). Among the many strippants tried for the back-extraction of mercury(II) from the loaded organic phase, 5% thiourea in 1% HCl and 0.01 mol/$dm^3$ $Na_2S_2O_3$ (pH = 5.5) are found to be effective stripping agents. The selectivity of mercury(II) over calcium(II), magnesium(II) and barium(II) has also been investigated and found that none of these metal ions are extracted into the organic phase along with mercury(II). The developed liquid-liquid extraction method has been utilised for the recovery of mercury from the brine-sludge of a Chlor-Alkali industry by employing TIBPS in kerosene as an extractant. The results clearly demonstrate that TIBPS can be used as a potential extractant for the selective extraction and separation of mercury from the brine-sludge of a Chlor-Alkali industry.

# *References*

1. J. E. Sanchez Uria, A. Sanz-Medel, *Talanta*, **47**, 509 (1998).
2. A. K. De, *Environmental Chemistry*, Wiley Eastern Limited, p. 75 (1989).
3. N. J. Langford, R. E. Ferner, *J. Hum. Hypertens.*, **13(10)**, 651 (1999).
4. T. Tsubaki, K. Irukayama, Eds., *Minamata Disease: Methylmercury poisoning*, Kodensha, Tokyo (1977).
5. E. R. Krishnan, P. W. Utrecht, A. N. Patkar, J. S. Davis, S. G. Pour, M. E. Foerst, *Recovery of Metals from Sludges and Wastewaters*, Noyes Data, Park Ridge, N.J. (1993).
6. W. Brooke-Devlin, *Mercury and Arsenic Wastes Removal, Recovery, Treatment and Disposal*, US Environmental Protection Agency, Noyes Data, Park Ridge, NJ, p. 6, (1992).
7. F. J. Touro, A. D. Lipps, US Patent 4,734,270 (1988).
8. A. F. Griffin, W. D. Hinchliffe, US Patent, 4,681,628 (1987).
9. M. Misra, J. A. Lorengo, US Patent, 5,599,515 (1997).
10. J. T. Malito, US Patent 6,352,675 (2002).
11. M. Grayson, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, **15**, p. 143 (1981).
12. D. K. Singh, B. Srivastava, R. K. Bharadwaj, *Pollut. Res.*, **20(2)**, 173 (2001).
13. C. A. Cody, S. J. Kemnetz, US Patent, 5,667,694 (1997).
14. N. S. C. Becker, R. J. Eldridge, *React. Polym.*, **21(1-2)**, 5 (1993).
15. N. S. C Becker, R. J. Eldridge, *React. Polym.*, **22(2)**, 131 (1994).
16. F. H. Wang, T. J. Hsu, M. Y. Chen, *Huang Ching Pao Hu*, **13(2)**, 74 (1996).
17. M. C. Diyardin, C. Caze, I. Vroman, *React. Funct. Polym.*, **43(1&2)**, 123, (2000).

18. J. M. Grau, J. M. Bisang, *J. Chem. Technol. Biotechnol.*, **62(2)**, 153 (1995).

19. A. L. Anacleto, J. R. Carvalho, *Miner. Eng.*, **9(4)**, 385 (1996).

20. W. E. Fristad, M. J. Virnig, D. K. Elliott, US Patent 5,785,935 (1998).

21. T. E Weyand, C. J. Koshinski, *Proc., Ann. Meet.- Air Waste Management Assoc.* (1996).

22. C. W. Kenney, B. J. Hansen, *Proc. Int. Conf. Incineration Therm. Treat. Technol.*, 193, (1996).

23. M. W. Loo, US Patent 4,149,879 (1979).

24. L. D. Jayaweera, R. G. Robins, *Extr. Process Treat. Minimisation Wastes 1994, Proc. Int. Symp.*, J. P. Hager Ed., Miner. Met. Mater. Soc.: Warrendale, 39 (1994).

25. M. A. Rockandel, L. G. Twidwell, US Patent 5,209,774 (1993).

26. A. C. S. Pedroso, L. E. R. Gomes, J.M.R. de Carvalho, *Environ. Technol.*, **15(7)**, 657 (1994).

27. H. H. Fulbright, M. Leaphart, V. Van Brunt, *Sep. Sci. Technol.*, **32(1-4)**, 373 (1997).

28. L. G. Twidwell, R .J. Thompson, *Journal of Metals*, **53(1)**, 15 (2001).

29. J. S. Bowers Jr., US Patent 4,957,634 (1990).

30. Tecnicas Reunidas, SA, Spain, Liquid-Liquid Extraction of Mercury from Wastewaters Results in no Waste Discharge, CS210, DOC NO: 400-018-A-209.

31. Y. Baba, K. Inoue, K. Yoshizuka, R. Yasukawa, M. Tazaki, Jpn. Kokai Tokkyo Koho JP04164817 A2 (1992).

32. M. Berthelot, J. Jungfleisch, *Ann. Chim. Phys.*, **26**, 396 (1872).

33. W. Nernst, *Z. Physik. Chem.*, **8**, 110 (1891).

34. G. M. Ritcey, A. W. Ashbrook, *Solvent Extraction: Principles and Applications to Process Metallurgy, Part I*, Elsevier Science Publishers B.V., Amsterdam, (1984).

35. K. B. Brown, C. F. Coleman, *Prog. Nucl. Energy, Series III*, **2**, 3 (1958).
36. Z. Kolarik, H. Pankova, *J. Inorg. Nucl. Chem.*, **28**, 2325 (1966).
37. Daihachi Chemical Industry Co. Ltd., Fr. Demande 2460275 (1981).
38. J. L. Sabbot, A. Rollat, E.U. Patent 156735 (1985).
39. N. M. Rice, *Hydrometallurgy*, **3**, 111 (1978).
40. A. W. Ashbrook, *Min. Sci. Eng.*, **5**, 169 (1973).
41. R. R. Swanson, D. W. Agers, "*A new reagent for the extraction of copper*" presented at the AIME meeting, New York (1964).
42. G. M. Ritcey, "*Recovery of copper concentrated solutions by solvent extraction using Kelex 100*" presented at the 2nd Annual Meeting, Canadian Hydrometal. Metall. Soc. of CIMM, Montreal, 1972; CIM Bull., **66**, 75 (1973).
43. D. R. Spink, D. N. Okuhara, *International Symposium on Hydrometallurgy*, Eds. D. J. I. Evans, R. S. Shoemaker, Pub. by AIME, New York, 497 (1973).
44. C. Bozec, J. M. Demarthe, L. Gandon, *Proc. Int. Solv. Extr. Conf.*, Lyon, Pub. Soc. Chem. Ind., London, 1201 (1974).
45. B. G. Meyburgh, *J. South African Inst. Min. Metall.*, **71**, 55 (1970).
46. C. J. Lewis, J. E. House, "*The Recovery of Molybdenum by LEE from Uranium Mill Circuits*" Presented at Annual AIME Meeting, New York (1960).
47. J. D. Miller, M. C. Fuerstenan, *Met. Trans.*, **1**, 2531 (1970).
48. V. M. Vdovenko, A. A. Lipovskii, S. A. Nikitina, *Russ. J. Inorg. Chem.*, **5**, 499 (1961).
49. E. L. Koerner, M. F. Lucid, US Patent 3, 700, 415 (1972).
50. M. F. Lucid, W. M. Leaders, US Patent 3, 734,696 (1973).
51. E. P. Horwitz, A. C. Muscatello, D. G. Kalina, L. Kaplan, *Sep. Sci. Technol.*, **16**, 417 (1981).
52. E. P. Horwitz, D. G. Kalina, H. Diamond, W. W. Schulz, *Solvent Extr. Ion Exch.*, **3**, 75 (1985).
53. M. L. P. Reddy, *Proc. Ind. Acad. Sci.(Chem. Sci.)*, **103**, 95 (1991).

54. S. R. Mohanty, A. S. Reddy, *J. Inorg. Nucl. Chem.*, **37**, 1791 (1975).
55. J. March, *Advanced Organic Chemistry, Reactions & Mechanisms and Structures*, **4th** edition, John Wiley & Sons, N.Y. (1992).
56. T. Sato, I. Ishikawa, K. Sato, *Process Metall.* **7A**, 913 (1992).
57. T. Sato, T. Nakamura, *Hydrometallurgy*, **6**, 3 (1980).
58. K. N. Brewer, R. S. Herbst, I. Y. Glagolenko, T. A. Todd, *Solvent Extr. Ion Exch.*, **16(2)**, 487 (1998).
59. R. S. Herbst, K. N. Brewer, T. J. Tranter, T. A. Todd, *Solvent Extr. Ion Exch.*, **13(3)**, 431 (1995).
60. A. N. Turanov, V. K. Karandashev, V. E. Baulin, *Solvent Extr. Ion Exch.*, **14(2)**, 227 (1996).
61. S. V. Luis, J. C. Frias, R. V. Salvador, M. Bolte, *J. Chem. Crystallo.*, **29(4)**, 403 (1999).
62. C. R. Paige, M. F. Richardson, *Can. J. Chem.*, **62**, 332 (1984).
63. R. Giovannetti, V. Bartocci, L. Petetta, *J. Chem. Res.(s)*, **299**, 1401 (1999).
64. J. Vicens, V. Bohmer, *Calixarenes.* Kluwer Academic Press : Dordrecht (1991).
65. C.D. Gutsche, *Calixarenes.* Royal Society of Chemistry: Cambridge (1989).
66. S. Shinkai, *Tetrahedron,* **49(40)**, 8933 (1993).
67. V. Bohmer, *Angew. Chem., Int.* Ed. Engl., **34**, 713 (1995).
68. C. D. Gutsche, B. Dhawan, J.A. Levine, K.H. No, L.J. Bauer, *Tetrahedron,* **39(3)**, 409 (1983).
69. K. Araki, S. Shinkai, T. Matsuda, *Chem. Lett.*, **4**, 581 (1989).
70. C. D. Gutsche, I. Alam, *Tetrahedron*, **44(15)**, 4689 (1988).
71. A. Ikedo, S. Shinkai, *Chem. Rev.*, **97(5)**, 1713 (1997).
72. H. Deligoz, M. Yilmaz, *Solvent Extr. Ion Exch.*, **13(1)**, 19 (1995).
73. N. T. K. Dung, R. Ludwig, *New J. Chem.*, **23(6)**, 603 (1999).

74. S. Memon, M. Yilmaz, *Sep. Sci. Technol.*, **35(3)**, 457 (2000).
75. S. Memon, M. Yilmaz, *Sep. Sci. Technol.*, **36(12)**, 2785 (2001).
76. T. W. Chapman, R. Caban, US Patent 3,899,570 (1975).
77. T. Sato, K. Sato, Y. Noguchi, *Solvent Extr. Res. Dev. Jpn.*, **8**, 26 (2001).
78. K. Schugerl, M. Gudorf, *Value Adding Solvent Extr., [Pap. ISEC'96]*, Eds. D.C. Shallcross, R. Paimin, L. M. Prvcic, **2**, 1525 (1996).
79. K. A. Larson, J. M. Wiencek, *Ind. Eng. Chem. Res.*, **31(12)**, 2714 (1992).
80. G. Cote, H. Lizama, S. Esteban, D. Bauer, *J. Chem. Res. Synop.*, **(5)**, 150 (1992).
81. A. Rusheed, S. Ahmed, *J. Radioanal. Nucl. Chem. Articles*, **159(1)**, 13 (1992).
82. M. J. Citores, R. M. Alonso, L. A. Fernandez, *Sep. Sci. Technol.,* **29**, 1441 (1994).
83. E. Dziwinski, G. Cote, D. Bauer, J. Szymanowski, *Hydrometallurgy,* **37**, 243 (1995).
84. D. Bauer, G. Cote, *Proc. ICHM'88* Beijing (China), International Academic Publisher 545 (1988).
85. C. S. Brooks, *Met. Finish.*, **85**, 55 (1987).
86. H. Stephan, K. Gloe, T. Kruger, C. Chartroux, R. Neumann, E. Weber, A. Mockel, N. Woller, G. Subklew, M. J. Schwuger, *Solvent Extr. Res. Dev. Jpn.*, **3**, 43 (1996).
87. S. G. Dmitrienko, N. A. Pasekova, E. D. Slyusareva, A. A Formanovskii, I. V. Mikhura, Y.A. Zolotov, *Vestn. Mosk. Univ., Ser.2: Khim.*, **31(4)**, 378 (1990).
88. E. Nomura, H. Taniguchi, S. Tamura, *Chem. Lett.,*1125 (1989).
89. E. Nomura, H. Taniguchi, Y. Otsuji, *Bull. Chem. Soc. Jpn.*, **66**, 3797 (1993).
90. H. Deligoz, E. Erdem, *Solvent Extr. Ion Exch.*, **15(5)**, 811 (1997).
91. M. J. Choi, M. Y. Kim, S. K. Chang, *Chem. Commun.*, **(17)**, 1664 (2001).
92. S. Memon, G. Uysal, M. Yilmaz, *Sep. Sci. Technol.*, **35(8)**, 1247 (2000).

93. G. Uysal, S. Memon, M. Yilmaz, *React. Func. Polym.*, **50(1)**, 77 (2001).

94. G. Cote, D. Bauer, *Rev. Inorg. Chem.*, **10(1-3)**, 121 (1989).

95. Y. Baba, Y. Umezaki, K. Inoue, *Solvent Extr. Ion Exch.*, **4(1)**, 15 (1986).

96. R. Singh, S. N. Tandon, *Talanta*, **44**, 843 (1997).

97. M. L. P. Reddy, A. D. Damodaran, M. C. S. Reddy, *Radiochim. Acta*, **76**, 109, (1997).

98. Y. Baba, K. Inoue, K. Yoshizuka, R. Yasukawa, A. Fujimoto, Jpn. Kokai Tokkyo Koho JP 03,278,802, Dec. 10 (1991).

99. T. J. Brown, W. A. Rickelton, R. J. Boyle, US Patent 4,721,605 (1988).

100. M. L. P. Reddy, S. Sujatha, T. R. Ramamohan, T. Prasada Rao, C. S. P. Iyer, A. D. Damodaran, *Radiochim. Acta*, **69**, 201 (1995).

101. M. L. P. Reddy, M. S. Reddy, A. D. Damodaran, *J. Radioanal. Nucl. Chem.* **191(2)**, 331 (1995).

102. I. Ishikawa, T. Sato, *Nippon Kagaku Kaishi*, **(11)**, 779 (2000).

103. I. Ishikawa, T. Sato, *Bunseki Kagaku*, **50(2)** (2001).

104. K. Inoue, R. Yasukawa, N. Miura, Y. Baba, K. Yoshizuka, *Solvent Extr. Ion Exch.*, **10(5)**, 769 (1992).

105. R. Sahu, S. M. Sondhi, B. Gupta, *J. Radioanal. Nucl. Chem.*, **200(6)**, 509 (1995).

106. B. S. Howerton, *Prepr. Ext. Abstr. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.*, **41(1)**, 419 (2001).

107. E. D. Nogueira, A. L. R. Abad, M. B. Muntadas, J. M. R. Vega, US Patent 4,151, 077 (1979).

108. G. Zuo, M. Muhammed, *Solvent Extr. Ion Exch.*, **13(5)**, 855 (1995).

109. D. Sandhya, M. S. Subramanian, *J. Radioanal. Nucl. Chem.*, **224(1-2)**, 53 (1997).

110. M. E. Nunez, E. Rodriguez de San Miguel, J. C. Aguilar, M. T. J. Rodriguez, J. de Gyves, *Solvent Extr. Ion Exch.*, **16(6)**, 1421 (1998).

111. A. Khan, A. Rusheed, S. Ahmed, S. Baig, *J. Radioanal. Nucl. Chem.*, **231(1-2)**, 41 (1998).

112. Y. Yang, B. Chen, X. Yu, W. Yao, *Huaxue Shijie*, **40(11)**, 609 (1999).

113. K. B. Raouf, C. Picard, P. Tisnes, L. Cazaux, *J. Inclusion Phenom. Macrocyclic Chem.*, **34(3)**, 277 (1999).

114. L. Quas, U. Schroder, B. Schroder, F. Dietze, L. Beyer, *Solvent Extr. Ion Exch.*, **18(6),** 1167 (2000).

115. Y. Baba, K. Inoue, *Solvent Extr. Ion Exch.*, **3(1&2)**, 35 (1985).

116. K. Inoue, Y. Baba, *Rev. Inorg. Chem.*, **10(1-3),** 1 (1989).

117. A. P. Paiva, *Sep. Sci. Technol.,* **28(4)**, 947 (1993).

118. K. Gloe, H. Graubaum, M. Wust, T. Rambusch, W. Seichter, *Coord. Chem. Rev.*, **222**, 103 (2001).

119. K. Chayama, A. Norio, Y. Tamari, H. Tsuji, *Bunseki Kagaku*, **42(11)**, 687 (1993).

120. M. Tanaka, M. Nakamura, T. Ikeda, K. Ikeda, H. Ando, Y. Shibutani, S. Yajima, K. Kimura, *J. Org. Chem.*, **66(21),** 7008 (2001).

121. N. G. Vanifalova, N. V. Isakova, O. M. Petrukhim, Y. A. Zolotov, *Zh. Neorg. Khim.***,** **36(3)**, 792 (1991).

122. N. G. Vanifalova, N. V. Isakova, O. M. Petrukhim, *Zh. Neorg. Khim.*, **36(3),** 804 (1991).

123. N. A. Pasekova, I. V. Pletnev, E. V.Malkhasyan, *Zh. Neorg. Khim.*, **36(11),** 2971 (1991).

124. T. F. Baumann, J. G. Reynolds, G. A. Fox, *React. Funct. Polym.*, **44(2)**, 111 (2000).

125. T. F. Baumann, J. G. Reynolds, G. A. Fox, *Chem. Eng. News*, **76(3)**, 37 (1998).

126. T. F. Baumann, J. G. Reynolds, G. A. Fox, *Chem. Commun.*, **16,** 1637 (1998).

127. O. Heitzsch, K. Gloe, H. Stephan, E. Weber, *Solvent Extr. Ion Exch.*, **12(3)**, 475 (1994).

128. H. A. Jenkins, S. J. Loeb, A. M. Riera, *Inorg. Chim. Acta*, **246(1-2)**, 207 (1996).

129. K. Gloe, T. Kruger, H. Stephan, M. Wagner, U. Drutkowski, R. M. Olk, U. Leckelt, R. Richter, E. Hoyer, *Z. Anorg. Allg. Chem.*, **624**, 152 (1998).

130. A. T. Yordanov, J. T. Mague, D. M. Roundhill, *Inorg. Chem.*, **34**, 5084 (1995).

131. A. T. Yordanov, O. M. Falana, H. F. Koch, D. M. Roundhill, *Inorg. Chem.*, **36**, 6468 (1997).

132. G. G. Talanova, H. S. Hwang, V. S. Talanov, R. A. Bartsch, *Chem. Commun.*, 1329 (1998).

133. P. Rao, O. Enger; E. Graf, M. W. Hosseini, A. D. Cian, J. Fischer, *European J. Inorg. Chem.*, **(7)**, 1503 (2000).

134. M. L. P. Reddy, T. Francis, *Solvent Extr. Ion Exch.*, **19(5)**, 839 (2001).

135. C. J. Pedersen, *J. Am. Chem. Soc.*, **89(26)**, 7017 (1967).

136. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, D. Sen, *Chem. Rev.*, **85**, 271 (1985).

137. R. M. Izatt, K. Pawlak, J. S. Bradshaw, R. L. Bruening, *Chem. Rev.*, **95**, 2529 (1995).

138. R. A. Schwind, T. J. Gilligan, E. L. Cussler, *Synthetic Multidentate Macrocyclic Compounds;* Eds.: R. M. Izatt, J. J. Christensen, Academic Press: New York, 289 (1978).

139. W. J. McDowell, *Sep. Sci. Technol.*, **23(12&13)**, 1251 (1988).

140. S. M. Khopkar, M. N. Gandhi, *J. Sci. Ind. Res.*, **55(3)**, 139 (1996).

141. *Host Guest Complex Chemistry: Macrocycles. Synthesis, Structures, Application*; F. Vogtle, E. Weber, Eds. ; Springer-Verlag : New York, (1985).

142. *Macrocyclic Compounds in Analytical Chemistry: Chemical Analysis*, Y.A. Zolotov, Ed.; Wiley : New York, 143(3) (1997).

143. E. Gracia Espana, J. Latorre, S. V. Luis, J. F. Miravet, P. E. Pozuelo, J. A. Ramirez, C. Soriano, *Inorg. Chem.*, **35**, 4591 (1996).

144. M. Kodama, E. Kimura, S. Yamaguchi, *J. Chem. Soc. Dalton Trans.*, 2536 (1980).

145. J. Rebek Jr., S. V. Luis, L. R. Marshall, *J. Am. Chem. Soc.*, **108**, 5011 (1986).

146. S. V. Luis, M. I. Burguete, R. V. Salvador, *J. Incl. Phenom.*, **10**, 341 (1991).

147. T. V. Ramakrishna, G. Aravamudan, M. Vijayakumar, *Anal. Chim. Acta*, **84**, 369 (1976).

148. A. I. Vogel, *A Textbook of Quantitative Chemical Analysis*; 5th Edn., ELBS, Longman : England, 329 (1996).

149. T. Sekine, T. Ishii, *Bull. Chem. Soc. Jpn.*, **43(8)**, 2422 (1970).

150. I. M. Kolthoff, M. K. J. Chantooni, W. Wang, *J. Chem. Eng. Data*, **38(1)**, 556 (1993).

151. R. M. Izatt, R. L. Bruening, G. A. Clark, J. D. Lamb, J. J. Christensen, *J. Membr. Sci.*, **28(1)**, 77 (1986).

152. K. Kina, K. Shiraishi, N. Ishibashi, *Bunseki Kagaku*, **27**, 291 (1978).

153. R. M. Smith, A. E. Martell, *Critical Stability constants: Inorganic Complexes*; Vol. 4, Plenum Press: New York, (1976).

154. C. J. Pedersen, *J. Am. Chem. Soc.*, **92**, 386 (1970).

155. A. H. Bond, R. Chiarizia, V. J. Huber, M. L. Dietz, *Anal. Chem.*, **71(4)**, 2757 (1999).

156. W. A. Rickelton, R. J. Boyle, *Sep. Sci. Technol.*, **23(12&13)**, 1227 (1988).

157. A. S. Reddy, M. L. P. Reddy, *J. Radioanal. Nucl. Chem., Letters*, **87(6)**, 397 (1984).

158. P. B. Santhi, M. L. P. Reddy, T. R. Ramamohan, A. D. Damodaran, *Talanta*, **41**, 9 (1994).

159. J. P. Shukla, R. K. Singh, S. R. Sawant, N. Varadarajan, *Anal. Chim. Acta.*, **276**, 181 (1993).

160. K. C. Sole, T. L. Ferguson, J. B. Hiskey, *Solvent Extr. Ion Exch.*, **12**, 1033 (1994).

161. M. S. Alam, K. Inoue, K. Yoshizuka, Y. Dong, P. Zhang, *Hydrometallurgy*, **44**, 245 (1997).

162. K. C. Sole, J. B. Hiskey, *Hydrometallurgy*, **30**, 345, (1992).

163. H. Hoshi, A. Tsuyoshi, K. Akiba, *J. Radioanal. Nucl. Chem.*, **243**, 621 (2000).

164. C. Hill, C. Madic, P. Baron, M. Ozawa, Y. Tanaka, *J. Alloys Comps.*, **159**, 271 (1998).

165. H. J. Bart, J. Reidetschagler, *Hydrometallurgy*, **26**, 389 (1991).

166. G. Modolo, R. Odoj, *J. Radioanal. Nucl. Chem.*, **228(1-2)**, 83 (1998).

167. A. Almela, M. P. Elizalde, *Anal. Proceedings*, **32**, 145 (1995).

168. M. P. Jensen, R. Chiarizia, V. Urban, *Solvent Extr. Ion Exch.*, **19(5)**, 865, (2001).

169. A. Menefee, D. Alford, C. B. Scott, *J. Chem. Phys.*, **25**, 370 (1956).

170. A. P. Paiva, M. Lemaire, *Sep. Sci. Technol.*, **31(19)**, 2599 (1996).

171. V. Salvado, M. Hidalgo, A. Masana, M. Munoz, M. Valiente, M. Muhammed, *Process Metall.*, *7B* (Solvent Extr. 1990, Part B), p. 1511 (1992).

172. J. N. Mathur, G. H. Rizvi, M. S. Murali, R. H. Iyer, D. Deshingkar, T. K. Theyyunni, **10th** Nat. Symp. on Strategic and Hi-Tech Metals Extraction and Process Characterisation, Udaipur (India), 21 - 23 March, p. 240 (1994).