

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

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IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR  
THE DEGREE OF**

**DOCTOR OF PHILOSOPHY**

**IN CHEMISTRY UNDER THE FACULTY OF SCIENCE**

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**UNDER THE SUPERVISION OF  
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**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.

Thiruvananthapuram  
August, 2002



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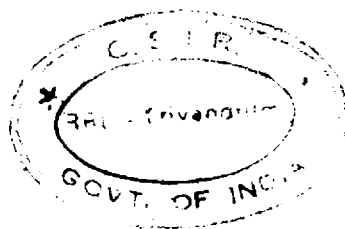
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CERTIFICATE

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  
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August, 2002*

**TANLA FRANCIS**

## 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 Extr. 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).

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## 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  $\text{HgCl}_2 \cdot \text{DC18C6}$  complex prepared has been characterised by elemental analysis, IR and  $^1\text{H}$  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*

**M**ercury 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 sulphhydryl 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,

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

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.

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

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.*

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

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

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

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:

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

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

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

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).

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

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

$$\text{S.F.} = D_1/D_2 \quad (1.8)$$

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  $-\text{COOH}$ ,  $>\text{P}(\text{O})\text{OH}$ ,  $-\text{SO}_3\text{H}$ , 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).

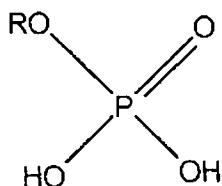


The metal extractants of the acidic type used in commercial operations are organic derivatives of phosphorus acids and monocarboxylic acids.

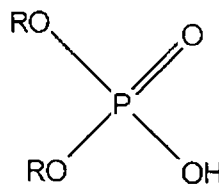


### *Acidic organophosphorus extractants*

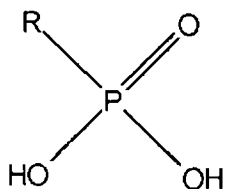
This type of extractants include the following:



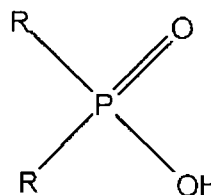
1. Monoalkyl phosphoric acid



2. Dialkylphosphoric acid



3. Monoalkyl phosphonic acid



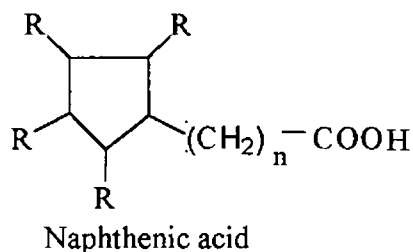
4. Dialkylphosphinic acid

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

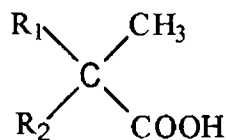
where R can be alkyl or aryl substituents. Of these, alkyl phosphoric acids have proved to be most versatile, especially di-(2-ethylhexyl) phosphoric acid (DEHPA). It has been used commercially for many metals including uranium [35] and rare earths [36]. Among the esters of phosphonic acid, 2-ethylhexyl 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.



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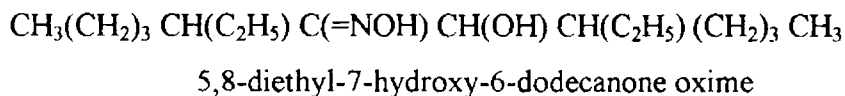
*Fig. 1.2* Commercially available carboxylic acid extractants.

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].

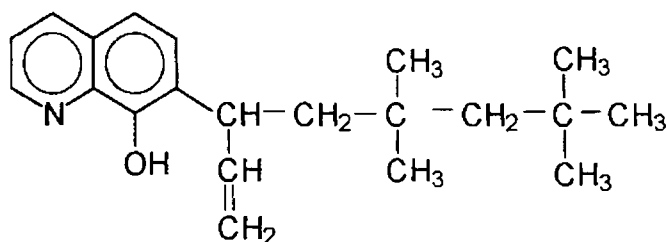
### B. Chelating extractants

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-thienyltrifluoroacetone, 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].



7



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

8

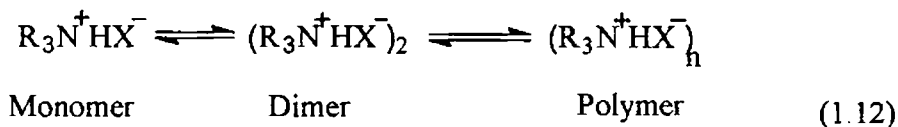
*Fig. 1.3* Chelating extractants

### 1.2.2 Extractants involving ion association

Quaternary ammonium compounds with high molecular weights such as tricaprilmethylammonium 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 ( $\text{RNH}_2$ ) [43], secondary ( $\text{R}_2\text{NH}$ ) [44], tertiary ( $\text{R}_3\text{N}$ ) [45] amines and quaternary ammonium salts ( $\text{R}_4\text{N}^+$ ) [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.



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.



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  $\equiv P=O$  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

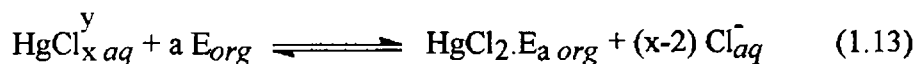
hydrochloric acid solutions. The main aim of this literature review is to highlight the most remarkable advances achieved after 1991 on the liquid-liquid extraction of mercury from aqueous solutions using various extraction systems. The liquid-liquid extraction reagents explored in the extraction studies 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:



where  $x = 2$  or  $4$ ,  $y = 0$  or  $-2$ ,  $E = \text{CMPO}$  or  $\text{TBP}$  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].

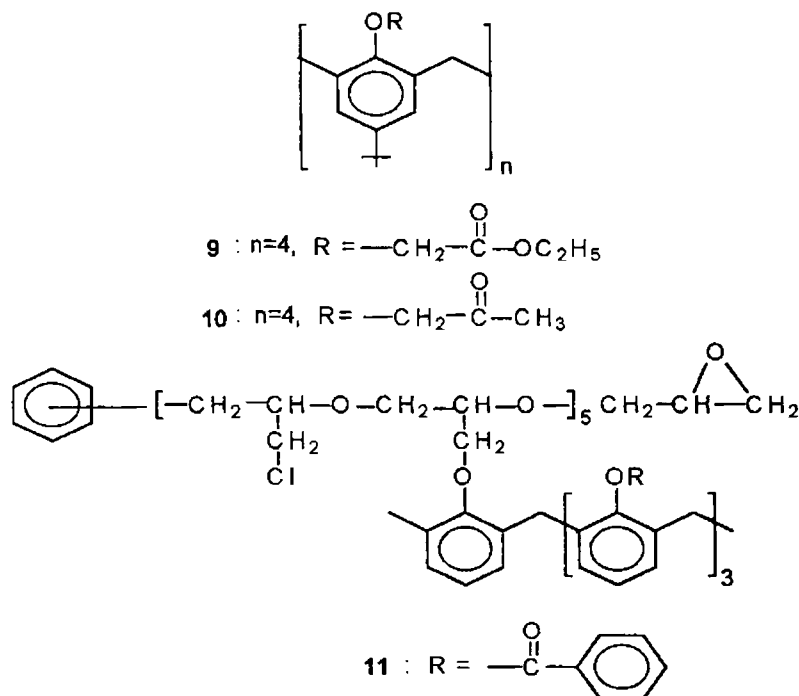
The complexes of crown ethers with  $\text{HgX}_2$  ( $X = \text{Cl}, \text{CN}$ ) species adopt rotaxane like structures due to the covalent character of the  $\text{HgX}_2$  compound [61], in particular, in the organic medium. When estimating the theoretical size of the macrocyclic which permits complex formation, the size of the substituent  $X$  in  $\text{HgX}_2$  has to be considered, not only the ionic radius of the metal. In this respect, formation of complexes with  $\text{Hg}(\text{CF}_3)_2$  requires the use of larger macrocyclics (20 membered ring) than with other  $\text{HgX}_2$  species such as  $\text{HgCl}_2$  or  $\text{Hg}(\text{CN})_2$  (18 membered rings). Paige and Richardson [62] have reported that  $\text{HgCl}_2$  form 1 : 1 complex with 18-crown-6 (18C6). The metal coordination is hexagonal bipyramidal with  $\text{Cl}^-$  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<sup>3</sup>) with DB18C6 (L) into benzene in the presence of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  chlorides and reported that mercury(II) was extracted prevalently as  $\text{HgCl}_4^{2-}$  by forming ion-pair compounds of  $[(\text{L}_2\text{M}_2)^{2+}\text{HgCl}_4^{2-}]$  (where  $\text{M} = \text{Li}^+$ ,  $\text{K}^+$  or  $\text{NH}_4^+$ ) or  $[\text{LM}^{2+}\text{HgCl}_4^{2-}]$  ( $\text{M} = \text{Ca}^{2+}$ ) and  $[\text{LH}^+(\text{HHgCl}_4)^-]$ . 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].

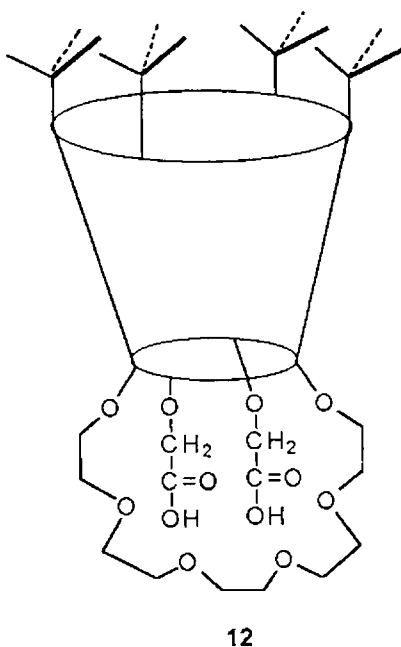
Deligoz and Yilmaz [72] have studied the extraction behaviour of transition metal ions from picrate solutions into chloroform using a series of *p-tert*-butylcalix[4]arenes in which ester and ketone groups 9-10 (Fig. 1.4) are attached to the lower rim and a polymeric calixarene 11. The polymeric calixarene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



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



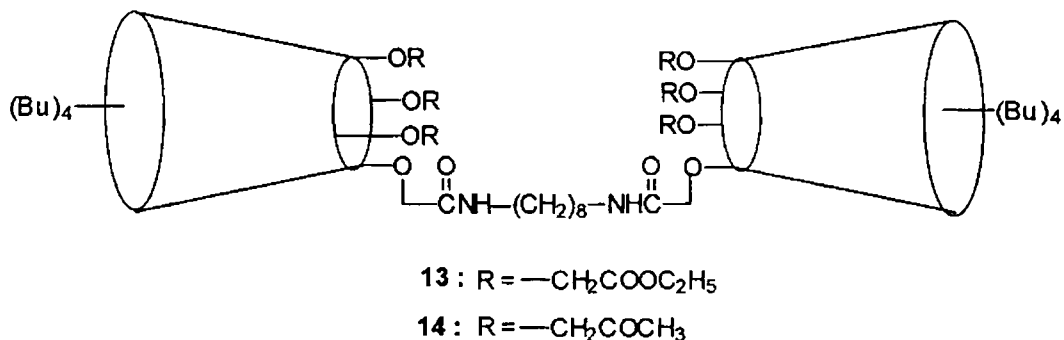
The liquid-liquid extraction behaviour of heavy metals with macrocyclic ligands based on calix[4]arenes **12** (Fig. 1.5) from weakly acidic solutions into toluene has been investigated and reported that a calixarene based compound with a crown-6-moiety **12** efficiently extracts heavy metal ions such as  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  from weakly acidic solutions due to their compatible ionic radius [73]. Further, it has also been reported quantitative extraction of  $\text{Hg}^{2+}$  above pH 2.5 with the ligand containing four  $-\text{CO}_2\text{H}$  groups.



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

The complexing abilities of two bis-calix[4]arene **13-14** (Fig. 1.6) with  $\text{Hg}^{2+}$  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 bis-calix[4]arenes using ester and ketones as the ligating functional groups in the cone conformation show quantitative extraction towards  $\text{Hg}^{2+}$ . These results suggest that the ketonic groups possess considerable ionophoric

properties. Memon and Yilmaz [75] reported selective extraction of  $\text{Hg}^{2+}$  using 2,2-bis-[5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix[4]-arenyloxy] 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 bis-calixarenes. The liquid-liquid extraction of alcohol, ester and ketone derivatives of bis-calix[4]arene have been carried out and found the ketone derivative to be selective for  $\text{Hg}^{2+}$ , whereas the ester derivative was not selective and proved to be good extractant with higher affinity towards  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Hg}^{2+}$ . The results indicate that the ligands containing  $\pi$ -system functional groups and having proper conformation of calixarene cavity form novel binding sites for the complexation of metal cations.



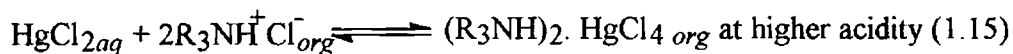
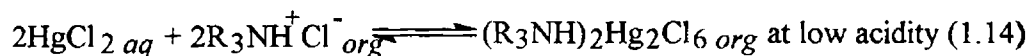
**Fig. 1.6** Structure of ester and ketone derivatives of bis-calix[4]arene [74].

### 1.3.2 Extraction by N - donors

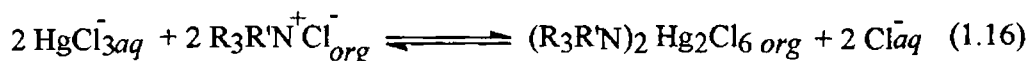
The amines, due to their unique anion exchange ability, have been employed to extract mercuric ions in the chloride solutions, which exist primarily as the anionic tetrachloride complex. Chapman and Caban [76] have described a liquid-liquid extraction process for the recovery of mercury(II) from dilute 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<sup>3</sup> 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:



For TOMAC:

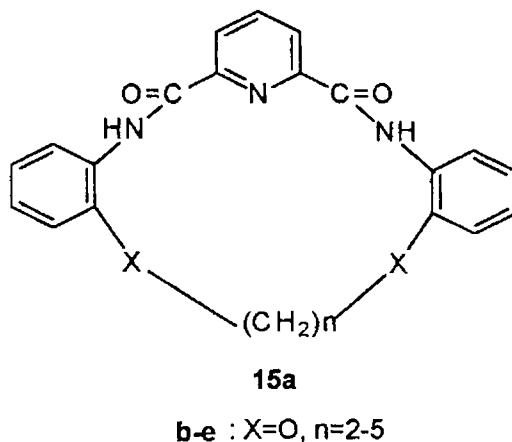


The extraction efficiency of TOMAC was found to be higher than that of TOA. Schugerl and Gudorf [78] have described a liquid-liquid extraction process for the recovery of mercury from the waste sludge of a natural gas industry. This process involves leaching of the waste sludge with 6 mol/dm<sup>3</sup> 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<sup>3</sup> NaCl and 0.05 mol/dm<sup>3</sup> 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  $\text{Hg}^{2+}$  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**.

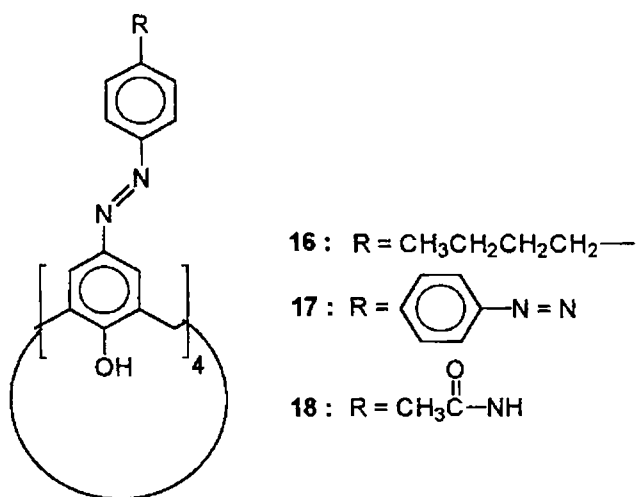
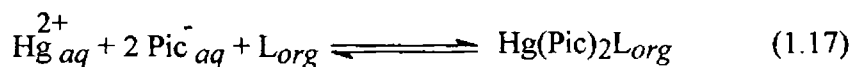


*Fig. 1.7* Macrocyclic compounds containing pyridine moiety [87].

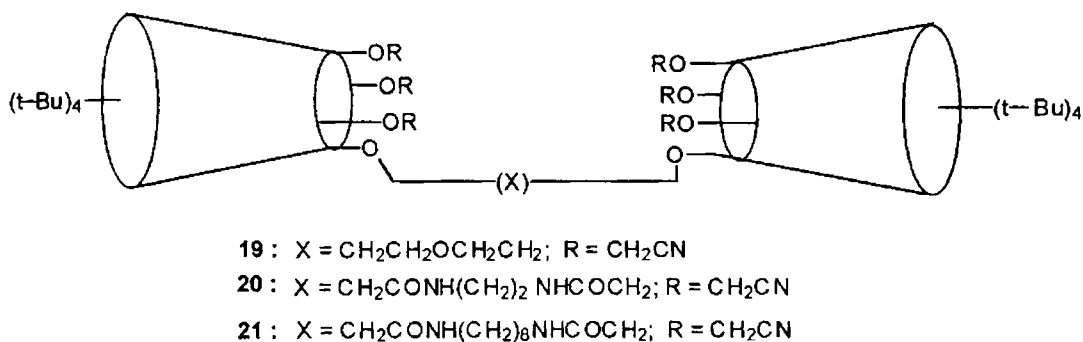
The liquid-liquid extraction behaviour of  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$  and  $\text{Ag}^+$  from picrate solutions into chloroform using calix[6]arene derivative containing azo groups has been investigated and compared with the binding properties of *p*-*tert*-butylcalix[6]arene and 4-phenylazo-2,6-dimethylphenol [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  $\text{Ag}^+$ ,  $\text{Hg}^+$  and  $\text{Hg}^{2+}$ , 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  $\text{Ag}^+$ ,  $\text{Hg}^+$  and  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  and  $\text{Hg}^+$  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  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  with bis-calix[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  $\text{Hg}^{2+}$ . This phenomenon can be explained by the HSAB

principle whereby  $-\text{C}\equiv\text{N}$  group which is a soft base showing a stronger affinity towards soft acidic cations like  $\text{Hg}^{2+}$ . 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)



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



**Fig. 1.9** Structures of bis-calix[4]arene nitriles [92].

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











































































































































































































































