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,

\[ P + V = C + 2 \]  \hspace{1cm} (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.

\[ D = \frac{[X]_1}{[X]_2} \]  \hspace{1cm} (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, \( i.e. \)

\[ \mu_1 = \mu_2 \]  \hspace{1cm} (1.3)

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions of \( \mu \),
\[ \mu_1^\circ + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^\circ + RT \ln m_2 + RT \ln \gamma_2. \]  \hspace{1cm} (1.4)

where \( \mu_1^\circ \) 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:

\[ D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-\frac{(\mu_2^\circ - \mu_1^\circ)}{RT}} \]  \hspace{1cm} (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

\[ D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K' \]  \hspace{1cm} (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).

\[ E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \]  \hspace{1cm} (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

\[ S.F. = \frac{D_1}{D_2} \]  \hspace{1cm} (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 $-\text{COOH}$, $>\text{P(O)OH}$, $-\text{SO}_3\text{H}$, 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).

$$M_{aq}^{n+} + n\text{HA}_{org} \longleftrightarrow M\text{A}_{org} n + n\text{H}^+_{aq} \quad (1.9)$$

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

\[ \text{RO} \quad \text{P} \quad \text{OH} \]

2. Dialkylphosphoric acid

\[ \text{RO} \quad \text{P} \quad \text{OH} \]

3. Monoalkyl phosphonic acid

\[ \text{RO} \quad \text{P} \quad \text{OH} \]

4. Dialkylphosphinic acid

\[ \text{RO} \quad \text{P} \quad \text{OH} \]

*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.

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]

\[
\text{CH}_3(\text{CH}_2)_3 \text{CH}((\text{C}_2\text{H}_5) \text{C}(=\text{NOH}) \text{CH(OH)} \text{CH(C}_2\text{H}_5)(\text{CH}_2)_3 \text{CH}_3
\]

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

![Chemical structure of 7-diethyl-7-hydroxyquinoline](image)

7-

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

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$_2$NH) [44], tertiary (R$_3$N) [45] amines and quaternary ammonium salts (R$_4$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.

\[
R_3NH^+X_{\text{org}} \rightleftharpoons R_3N_{\text{org}} + X_{\text{aq}} \quad (1.10)
\]

\[
R_3NH^+X_{\text{org}} + MY_{\text{aq}} \rightleftharpoons R_3N_{\text{org}}^+MY^{-} + X_{\text{aq}} \quad (1.11)
\]

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\(^{-}\), CuCl\(_4\)\(^{2-}\), FeCl\(^{-}\) 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-<i>n</i>-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-\textit{n}-butyl phosphate (TBP) and tri-\textit{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 \textit{n}-octyl(phenyl)-\textit{N},\textit{N}-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and TBP in \textit{n}-dodecane was investigated by Brewer \textit{et al.} [58] and Herbst \textit{et al.} [59] and reported the extraction equilibrium as:

\[
\text{HgCl}^{y}_{x \text{aq}} + a \text{E}_{\text{org}} \rightleftharpoons \text{HgCl}_{2} \text{E}_{\text{org}} + (x-2) \text{Cl}^{-\text{aq}} \quad (1.13)
\]

where \(x = 2\) or 4, \(y = 0\) or -2, \(E = \text{CMPO}\) 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 HgX₂ (X = Cl, CN) species adopt rotaxane like structures due to the covalent character of the HgX₂ 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 HgX₂ has to be considered, not only the ionic radius of the metal. In this respect, formation of complexes with Hg(CF₃)₂ requires the use of larger macrocyclics (20 membered ring) than with other HgX₂ species such as HgCl₂ or Hg(CN)₂ (18 membered rings). Paige and Richardson [62] have reported that HgCl₂ 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/dm³) with DB18C6 (L) into benzene in the presence of Li⁺, K⁺, NH₄⁺ and Ca²⁺ chlorides and reported that mercury(II) was extracted prevalently as HgCl₄⁻ by forming ion-pair compounds of [(L₂M₂)²⁺HgCl₄⁻] (where M = Li⁺, K⁺ or NH₄⁺) or [LM²⁺HgCl₄⁻] (M = Ca²⁺) and [LH⁺(H₂HgCl₄)⁻]. 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 \(-\text{OH}\) groups [68, 69]. Therefore, the \textit{p-}tert-\textit{butylcalix}[4]arene adopts \(C_4\), 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 \textit{p-}tert-\textit{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.

\[
\text{Fig. 1.4 Ester and ketone derivatives 9-10 of } p\text{-}tert\text{-butylcalix}[4]\text{arene and a polymeric calixarene 11 [72].}
\]
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 \(-\text{CO}_2\text{H}\) groups.

![Fig. 1.5](image)

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

The complexing abilities of two biscalix[4]arenes 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 \( \text{Hg}^{2+} \) 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 \( \text{Hg}^{2+} \), 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.

![Structure of ester and ketone derivatives of biscalix[4]arene](image)

**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/dm³ 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:

\[ 2\text{HgCl}_2\text{aq} + 2\text{R}_3\text{NH}^+\text{Cl}^-\text{org} \rightleftharpoons (\text{R}_3\text{NH})_2\text{Hg}_2\text{Cl}_6 \text{org} \text{ at low acidity (1.14)} \]

\[ \text{HgCl}_2\text{aq} + 2\text{R}_3\text{NH}^+\text{Cl}^-\text{org} \rightleftharpoons (\text{R}_3\text{NH})_2\text{HgCl}_4 \text{org} \text{ at higher acidity (1.15)} \]

For TOMAC:

\[ 2\text{HgCl}_3\text{aq} + 2\text{R}_3\text{R'}\text{N}^+\text{Cl}^-\text{org} \rightleftharpoons (\text{R}_3\text{R'}\text{N})_2\text{Hg}_2\text{Cl}_6 \text{org} + 2\text{Cl}^-\text{aq} \text{ (1.16)} \]

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/dm³ 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/dm³ NaCl and 0.05 mol/dm³ 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 \textit{p-}\textit{}\textit{tert-}\textit{butylcalix}[6]arene and 4-phenylazo-2,6-dimethylphenol [88]. The results show that the calixarene 5,11,17,23,29,35-hexa-\textit{p-phenylazo}-37,38,39,40,41,42-hexahydroxycalix[6]arene (\textit{p-}\textit{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 \textit{p-}\textit{(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 \textit{et al.} [91] have prepared a new azophenol type chromogenic ionophore based on \textit{p-}\textit{}\textit{tert-}\textit{butylcalix}[4]arene diazaerown 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 \textit{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 \(-\text{C}≡\text{N}\) 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)

\[
\begin{align*}
\text{Hg}^{2+}_{\text{aq}} + 2 \text{Pic}^-_{\text{aq}} + \text{L}_{\text{org}} & \rightleftharpoons \text{Hg} (\text{Pic})_2 \text{L}_{\text{org}} \\
(1.17)
\end{align*}
\]

![Diagram](image)

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

![Diagram](image)

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

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

\[
\begin{align*}
19 : \ X = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2; \ R = \text{CH}_2\text{CN} \\
20 : \ X = \text{CH}_2\text{CONH(CH}_2)_2\text{NHCOCH}_2; \ R = \text{CH}_2\text{CN} \\
21 : \ X = \text{CH}_2\text{CONH(CH}_2)_3\text{NHCOCH}_2; \ R = \text{CH}_2\text{CN}
\end{align*}
\]
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.

\[
2 \text{Hg}^{2+} \text{aq} + 4 \text{Pic}^- \text{aq} + \text{L}_{\text{org}} \rightleftharpoons (\text{Hg}_2\text{Pic}_4)\text{L}_{\text{org}} \quad (1.18)
\]

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 (R₁, R₂ = C ≥ 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 sulfoxides 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 HgI₂, HgI₂·B2EHSO and HgI₂·2B2EHSO. 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:

\[
\text{HgCl}_2^{aq} + 2\text{R}_2\text{SO}_{org} \rightleftharpoons \text{HgCl}_2.2\text{R}_2\text{SO}_{org} \quad (1.19)
\]

\[
\text{HgCl}_3^{aq} + \text{H}^+ + 3\text{R}_2\text{SO}_{org} \rightleftharpoons \text{HHgCl}_3.3\text{R}_2\text{SO}_{org} \quad (1.20)
\]

\[
\text{HgCl}_4^{2-} + 2\text{H}^+ + 2\text{R}_2\text{SO}_{org} \rightleftharpoons \text{H}_2\text{HgCl}_4.2\text{R}_2\text{SO}_{org} \quad (1.21)
\]

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

\[
\text{HgCl}_2^{aq} + \text{R}_2\text{SO}_{org} \rightleftharpoons \text{HgCl}_2.\text{R}_2\text{SO}_{org} \quad (1.22)
\]

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:

\[
\text{HgCl}_4^{2-} + 2\text{S}_{org} \rightleftharpoons \text{HgCl}_2\text{S}_2\text{org} + 2\text{Cl}^-_{aq} \quad (1.23)
\]

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

\[
\text{HgCl}_4^{2-} + 2\text{HS}_{org} \rightleftharpoons \text{HgS}_2\text{org} + 2\text{H}^+_{aq} + 4\text{Cl}^-_{aq} \quad (1.24)
\]
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 o-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: $\text{Cl}^- > \text{NO}_3^- \approx \text{ClO}_4^-$ [110]. The extraction data have been analysed by both graphical and theoretical methods and reported the extracted complexes as $\text{HgX}_2.R$ and $\text{HgX}_2.R_2$ (where $X = \text{Cl}^-, \text{NO}_3^-$ or $\text{ClO}_4^-$). However, in concentrated hydrochloric acid solutions the extraction of mercury(II) is explained by the formation of $\text{HgCl}_3.R\text{H}$ and $\text{HgCl}_4.(\text{RH})_2$ species.

Khan et al. [111] have reported the extraction of mercury(II) from mineral acid solutions using 1-naphthyl thiocarbamide in CHCl$_3$ / Me$_2$CO (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, $\alpha$-butylthiolaric acid ($\alpha$-BTLA) and 2-butylthiododecanoic acid (2-BTDA) from hydrochloric acid solutions and reported that the extraction equilibrium of mercury(II) follows the solvation mechanism:

$$\text{(RH)}_2_{\text{org}} + \text{HgCl}_2_{\text{aq}} \rightleftharpoons (\text{RH})_2 \text{HgCl}_2_{\text{org}} \quad (1.25)$$

where RH represents $\alpha$-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)$_n$X$_2$ (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].
Due to the high affinity of thiacrowns to $\text{Hg}^{2+}$ 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 macrocycles 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 $\text{Hg}^{2+}$ from picrate and nitrate media, as well as for $\text{Ag}^+$, $\text{Au}^{3+}$ and $\text{Pd}^{2+}$ [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 \textit{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].
Fig. 1.13 Calix[4]arenes with sulphur containing lower rim functionalities [130].

Fig. 1.14 (Methylthio)methyl 35 and (N,N-dimethylthiocarbamoyl)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.