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 HgCl₂·2CE (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
Conclusions

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 HgCl2.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/dm³ DC18C6 in 1,2-dichloroethane; Phase ratio Org. : Aq. = 1 : 1) and stripping (5 % NH₄Cl in 1 : 10 NH₃; 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 HgCl₂₃R₂SO, where R₂SO represents the sulfoxide. The extraction efficiency of mercury(II) with the various sulfoxides increases in the order: DPhSO < B₂EHSO < DOSO. Among the dialkyl sulfoxides, the extraction efficiency of branched chain sulfoxide, B₂EHSO, is slightly lower than the straight chain sulfoxide, 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 sulfoxides which again can be explained on the basis of steric factors. The extraction efficiency of mercury(II) with the dialkyl sulfoxides 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: K₉₉.TRPO = 8.5; K₉₉.DOSO = 0.42). The greater basicity of the P→O group in TRPO compared to that of the S→O group in the sulfoxide 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 HgCl₂₃TRPO 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:

\[
HgCl_{2aq} + 2 HX_{org} \rightleftharpoons \frac{K_{ex2}}{} HgCl_2 \cdot 2HX_{org}
\]

where HX represents the thiophosphinic acid extractants.
Conclusions

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/dm³, calcium(II) 3.88 g/dm³, magnesium(II) 0.58 g/dm³ and barium(II) 4.56 mg/dm³ using a substantially immiscible extractant phase, which is comprised of CY301 in kerosene (0.05 mol/dm³; 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 HgCl₂.2TIBPS, with TIBPS. On the other hand, mercury(II) is extracted as HgCl₂.2DBS/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$_2$S$_2$O$_3$ (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.