CHAPTER 3
MATERIALS AND METHODS

The experimental and analytical methods used in this investigation for the extraction of heavy metal ions from aqueous solutions into emulsion liquid membranes is described in this Chapter. It also records the parameters used for characterization of the W/O emulsions that were used as the emulsion membrane and finally it specifies the techniques adopted to study the bonding in the extractant- metal complexes.

3.1 Materials and reagents

3.1.1 Membrane materials

- **Oil phase**

The liquid-membrane phase – the oil phase of the W/O emulsion, was formulated by incorporating a surfactant and a metal extractant in an organic diluent. Commercial kerosene was used as the membrane material, it had a boiling range 152°C – 271°C and contained n-paraffins (27.1%), naphthenes (55.9%), aromatics (16%) and olefins (1%) having density ($\rho_{15}$) of 821.3 kg / m$^3$. Kerosene was used as supplied by Indian Oil Corporation Limited.

- **Emulsifier**

Span 80 generically known as Sorbitan monooleate ($\text{C}_{24}\text{H}_{44}\text{O}_6$) having MW 428.61 was the non-ionic surfactant used for stabilizing the emulsion. It had density 986 kg / m$^3$, refractive index 1.48, flash point $>110$ ℃, saponification value from 145 to 160, water content less than 1% and was supplied by S. D. Fine Chemicals Limited. The chemical structure of Span 80 is shown in Fig. 3.1

![Chemical Structure of Span 80](image)

CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH$_2$C

OH

OH

OH

OH

Fig. 3.1 Sorbitan monooleate (Span 80)
Carrier

Carriers are metal extractants; they are in general classified on the basis of structure, acidity, extraction and stripping chemistry. The five main types of extractants commercially available for metal extraction are (1) Chelating agents, (2) Ion pair extractants, (3) Neutral or solvating extractants, (4) Organic acid extractants and (5) Ligand substitution extractants. Chelating oxime extractants and the organic acid extractants operate on a hydrogen ion cycle, extracting metals over a specific pH range and stripping at lower pH. The extraction and stripping pH isotherms for individual metals differ and this provides an opportunity for selective extraction. In the present study four different extractants were used for metal extraction as listed below.

D2EHPA

Di (2-ethylhexyl) phosphoric acid 95% minimum with Mono (2-ethylhexyl) phosphoric acid less than 2% was obtained from Fluka, Germany as well as Merck Specialties Private Limited, Germany. D2EHPA is an acidic extractant and extracts a wide range of metals. Its molecules predominate as monomers in aromatic diluents and as dimers when dissolved in aliphatic diluents. Usually aliphatic diluents are preferred for extraction processes due to their lower toxicity. Selectivity of D2EHPA for metal ions is poor, hence, careful pH control is required to achieve reasonable selectivity.

Physical data: Molecular formula: C_{16}H_{35}O_{4}P, Molecular weight: 322.4, Appearance: clear to colorless to yellow liquid, Texture: oily, Odor: odorless, Flash point: 206 °C, Lighting point: 233 °C, Solidifying point: -50 °C, Density at 25 °C: ~ 0.97 g/cm³, Viscosity: 40 mPa s.

![Diagram of D2EHPA](image_url)

Fig. 3.2 Di (2-ethylhexyl) phosphoric acid (D2EHPA)
**CYANEX 302®**

Cyanex 302 (Di (2, 4, 4,) trimethylpentyl monothiophosphinic acid) is a phosphinic derivative of phosphoric acid, where one sulfur atom replaces one of the oxygen atoms bonded to the phosphorus as shown in Fig. 3.3. The extractant was supplied by Cytec Limited, Canada, it has an active component content of 84%. Cyanex 302 is usually used in the industry for the separation of Co from Ni in feed mixtures containing cobalt and nickel. It is specific towards Co, it is known for the difficulty to strip the metal values from it which is its drawback.


![Fig. 3.3 Di (2, 4, 4,) trimethylpentyl monothiophosphinic acid (CYANEX 302)](image)

**PC 88 A®**

PC 88A generically (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) (assay 95 % minimum by weight) produced by Daihachi Chemical Industry, Japan was generously supplied by Rubamin Chemicals Pvt. Ltd. Baroda. This extractant is a phosphonic derivative and finds wide application in the refining of rare earth metals and can also be used as an extractant for extraction of other metals such as zinc, cobalt, nickel etc.

![Fig. 3.4.: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC 88A)](image)
Physical data: Molecular formula: \((\text{C}_8\text{H}_{17})_2\text{HPO}_3\), Molecular weight: 306.4, Appearance: colorless to light yellowish liquid, Texture: oily, Odor: odorless, Flash point: 170±3 °C, Lighting point: 203 °C, Solidifying point: -47 °C, Density at 25 °C:~ 0.94 – 0.96 gm/ml, Viscosity: 36±3 mPa s, refractive index: 1.4480 – 1.4520.

LIX 84-I®

LIX 84 I chemically known as 2-hydroxy-5 nonylacetophenone oxime was supplied by Cognis Inc. Ireland. LIX 84 I is a water soluble ketoxime. It is a commercial extractant used in copper hydrometallurgy. It can function with acid and ammoniacal leach solutions and is more selective than other extractant classes. Although kinetically slower than ion pair extractants, LIX 84 I has good physical properties in terms of phase separation, low aqueous solubility, and chemical stability.

Physical data: Appearance: Fluid amber liquid, Texture: oily, Odor: of mineral oil, Flash point: > 160 °F, approximate density at 25 °C: 0.90 - 0.91 g/cm³, Viscosity (kinematic) at 40 °C: 2.71 mPa/s

![Diagram of Ketoxime and Salicyladoxime](image)

Fig. 3.5 2-hydroxy-5 nonylacetophenone oxime (LIX 84I)

3.1.2 Metal Solutes

Extraction studies were carried out in sulphate media and ammoniacal media. The metals salts and the ancillary reagents and chemicals used in this study are listed below:-

- Cupric Sulphate (\(\text{CuSO}_4\cdot5\text{H}_2\text{O}\)) of excelar grade having 99.5% purity supplied by Qualigens was the copper source.

- Nickel sulphate (\(\text{NiSO}_4\cdot6\text{H}_2\text{O}\)) having assay of 23% nickel supplied by Ranbaxy laboratories Ltd. was the nickel source.

- Zinc Sulphate (\(\text{ZnSO}_4\cdot7\text{H}_2\text{O}\)) of excelar grade having minimum 99.5 % purity supplied by Merck Specialties Pvt. Ltd. was the zinc source.
3.1.3 Ancillary reagents and chemicals

Sulfuric acid of AR grade with assay 98% was of Ranbaxy make.

Sodium Hydroxide with assay 98% was of Ranbaxy make.

Ammonium Solution (25%) having specific gravity 0.91 was of Ranbaxy make.

Standard pH buffer of 4 pH, 7 pH and 9.2 pH of Qualigens make were used.

Certified Atomic absorption spectroscopy standards of SRL make were used to generate standard curves for metal analysis.

3.2 Emulsion Liquid Membrane Formulation

The W/O emulsions were formulated by mixing the membrane phase and the aqueous stripping phase (sulfuric acid, concentration ranging from 0.5 M – 1.5 M), using a high speed blender at 12,000 rpm. The oil membrane phase of the emulsions was primarily kerosene (membrane material) which was mixed with the emulsifier Span 80 and the carrier such as D$_2$EHPA, PC88A, LIX 84I etc. In most cases Span 80 concentration was 3 % wt of the membrane phase while the carrier concentrations ranged from 2 - 20 % volume of the membrane phase.

The emulsion was prepared in a 600-ml long form beaker kept in a chilled water bath so as to dissipate the heat liberated due to intense mixing. Good emulsion formulation practices suggest that on a laboratory scale intermittent mixing is favorable for stable emulsion formulation. Hence, blending was carried out with pause at regular time intervals. The total time for emulsification was 450 seconds. The emulsions obtained were of milky white color and largely stable during the course of extraction experimentations. The emulsion prepared was not immediately used but was allowed to cure for thirty minutes so that internal morphological rearrangements could take place resulting in a more stable emulsion.

Emulsions were prepared with fixed volumes of membrane phase and inner phase. Usually volume ratio of one was opted however, to enhance the stoichiometric capacity of the internal stripping phase of the emulsion without altering the concentration of the internal reagent phase, the internal phase volumes were varied in such a manner that the internal phase volume fraction (\(\phi\)) of the emulsions ranged from 0.5 to 0.64.
3.3 Emulsion Characterization

The water in oil (W/O) emulsion is the key constituent in the ELM process necessitating characterization of these emulsions. The W/O emulsions prepared in this investigation were characterized based on density, viscosity, interfacial tension, internal droplet sizes and stability.

Densities of the emulsions were measured using a certified density bottle at the temperature of extraction. Viscosities of the emulsion were measured using Brookfield Cone and Plate Rheometer model LVDV III+CP using CPE 52 cone spindle. The cone angle was 3 degree, the spindle radius was 1.2 cm and the sample volume used was 0.5ml. Since LVDV-III + rheometer has the flexibility to operate at variable speeds, viscosity data could be conveniently obtained at varying shear rates. The viscosity data was collected in the direction of increasing shear rates over a wide range of shear rates to quantify the rheological behavior of emulsions.

Figure 3.6 shows the effect of shear rate on the viscosity of the emulsions prepared using the three organophosphorous acids (having Cc = 10% v/v, surfactant concentration 3%wt of oil phase and internal phase acid concentration 1.5M) at volume fractions of 0.5 and 0.64. It is observed the viscosities were very sensitive to the internal phase volume fraction. At $\phi = 0.5$, D2EHPA emulsions are more viscous at all shear rates in comparison to the emulsions with PC 88A and Cyanex 302, but as $\phi$ is increased to 0.64 the Cyanex 302 emulsion become much more viscous than the emulsions with D2EHPA and PC 88A. The viscosity of
D2EHPA and PC 88A at $\phi = 0.64$ were identical such similarity was observed in the viscosities of PC 88A and Cyanex 302 at $\phi = 0.5$. In the range of shear rates studied the emulsions showed shear thinning behavior and obeyed the power law model.

Internal drop size of the emulsion, a very important characterization parameter, was determined microscopically by Olympus microscope model BH-2 attached with a Olympus photo micrographic system model PM-10 AD. A small volume of emulsion was diluted 15 times in an appropriate solvent (kerosene or liquid paraffin). A drop of diluted emulsion was placed in the center of the slide and covered with a cover slip. Internal drop sizes were measured quickly using an ocular and stage micrometer (Erma make) at magnification of 600 X and 1500 X. more than 300 droplet sizes per slide were counted.

To ensure greater accuracy two slide’s were prepared for each emulsion based on the total data of more than 600 measurements the average value of $d_{32}$ was calculated for each case. Photomicrography of the internal droplets of the emulsion was carried out using the Olympus photomicrography system model PM-10AD attached with an exposure control unit to the microscope at magnifications of 600 X.

The interfacial tension between the emulsion phase and the solute containing aqueous phase was measured using Du Nuoy tensiometer using a ring made up of platinum – iridium. Ring method allows interfacial tension readings to be made in very short time period of 15-30 seconds with reproduced accuracy within $\pm 0.05$ dyne/cm. Table 3.1 lists the effect of the carrier concentration on the emulsion characterization parameters.

**Table 3.1:** Effect of D2EHPA concentration ($C_c$) on viscosity, interfacial tension between emulsion and feed phase, density and internal drop size of emulsions.

<table>
<thead>
<tr>
<th>Parameter measured (\text{(Emulsion formulated with } W_{\text{surf}}=3\text{wt}%, \phi=0.5,\ C_{io}=1.5 \text{ M and } C_{eo}=1000 \text{ mg/L of zinc)}).</th>
<th>Variation in carrier (D2EHPA) concentration % (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 %</td>
</tr>
<tr>
<td>Viscosity at (20 \text{ s}^{-1}) (µ) – cP</td>
<td>30.38</td>
</tr>
<tr>
<td>Interfacial Tension ((\gamma)) – mN/m</td>
<td>14.1</td>
</tr>
<tr>
<td>Density ((\rho)) - kg/m(^3)</td>
<td>903.6</td>
</tr>
<tr>
<td>Internal drop size - µm</td>
<td>5.13</td>
</tr>
</tbody>
</table>
3.4 Experimental Set up and Extraction methodology

The experimental set-up consisted of a four baffled stirred vessel 0.105 m diameter having 1000-ml (1 liter) capacity that functioned as a batch reactor. The agitator assembly consisted of a single phase variable speed 1/12 hp motor of Remi make, model no. RU-56-2G. The motor speed was regulated using a dimerstat and its speed under actual operating conditions was measured using a Jaquet make tachometer. The projected view of reaction vessel is shown in Fig. 3.7, the impeller used was a six blade disk turbine having dimensions as shown in Fig. 3.8.

Ammoniacal feed solution for extraction was prepared by dissolving metal sulphate (copper, zinc and nickel) and ammonium sulphate (50 g/L) in deionised water. The feed pH was adjusted to the desired value using ammonium hydroxide. Feed solutions for zinc extraction using organophosphorous acids were prepared by precisely weighing and dissolving the necessary amount of zinc in deionised water. The pH of the feed was adjusted using H$_2$SO$_4$ or Na$_2$CO$_3$. These feed solutions were charged to the extractor that filled the extractor up to a height of 7.5 cm from the bottom. The impeller was positioned at a distance of 4.5 cm from the bottom and then the agitation was started at a constant rate.

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Fig. 3.7 Projected views of impeller and reaction vessel
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The cured W/O emulsion was quickly poured in the extractor in necessary amount to get the desired emulsion to feed ratio (Treat ratio). As soon as the emulsion was poured in the agitated feed phase it got dispersed in the form of fine globules 1 to 3 mm in diameter within ~ 30 seconds. Samples of the aqueous phase were withdrawn at specific time intervals without stopping the agitation. Since sampling was carried out from continuous phase, where the emulsion was finely dispersed, it was necessary to plug the tip of the sampler so that the movement of emulsion globules was inhibited and only the aqueous phase was sampled.

<table>
<thead>
<tr>
<th>Element</th>
<th>Type/ Size (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Diameter</td>
<td>0.105</td>
</tr>
<tr>
<td>Height (HT)</td>
<td>0.14</td>
</tr>
<tr>
<td>Liquid Height (HL)</td>
<td>0.076</td>
</tr>
<tr>
<td>Impeller Diameter (dl)</td>
<td>0.052</td>
</tr>
<tr>
<td>Disk Diameter (dd)</td>
<td>0.038</td>
</tr>
<tr>
<td>Type of Impeller</td>
<td>Flat Blade Turbine</td>
</tr>
<tr>
<td>No. of Blades on the Impeller</td>
<td>6</td>
</tr>
<tr>
<td>Blade Height (Hb)</td>
<td>0.010</td>
</tr>
<tr>
<td>Length of blade (Lb)</td>
<td>0.045</td>
</tr>
<tr>
<td>Height of the impeller off bottom (HI)</td>
<td>0.013</td>
</tr>
<tr>
<td>Baffle width (J)</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Fig. 3.8 Six bladed turbine impeller and its dimensions

Batch extraction runs were carried out for fixed period of time that extended from 3 to 10 minutes. The extraction runs were carried out at temperatures 30±1°C. On completion of the extraction run duration the agitation was stopped, this resulted in rapid separation of the emulsion phase from the aqueous phase. The total contents of the extractor were poured in a separating funnel and the emulsion phase was separated from the aqueous phase. The final volume of the emulsion phase was measured to get an estimate of emulsion swelling due to water transport. The samples collected during the experimental run were then analyzed for
the metal content after necessary dilutions using an atomic absorption spectrophotometer. Extraction data were plotted as ratio of instantaneous metal concentration to initial concentration (Ce/Ceo) versus time.

### 3.5 Analysis of Metals

The metal ion concentrations were measured using an atomic absorption spectrophotometer (Chemito Make Model AA-203) equipped with Photon make hollow cathode lamps for copper, nickel and zinc. The instrument was fully computer controlled using software AA203 data station version 3.2. The optimized instrument parameters for measurement of targeted metal ions are given in Table 3.2.

**Table 3.2 Optimized instrument parameters for measurement of targeted metal ions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Copper</th>
<th>Nickel</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>324.8</td>
<td>232.10</td>
<td>212.5</td>
</tr>
<tr>
<td>Current (mA)</td>
<td>5.0</td>
<td>9.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Slit Width (nm)</td>
<td>0.5</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Pmt (V)</td>
<td>274.7</td>
<td>370.7</td>
<td>333</td>
</tr>
<tr>
<td>Burner height (mm)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fuel (liter/min)</td>
<td>3.5</td>
<td>3.55</td>
<td>3.5</td>
</tr>
<tr>
<td>Working range (ppm)</td>
<td>2 – 8</td>
<td>2 – 10</td>
<td>0 – 2</td>
</tr>
</tbody>
</table>

Ratio method was preferred for curve fitting. The samples of the experimental runs were appropriately diluted so that they were in the specified working range for the corresponding metals the concentrations were reported in ppm.

### 3.6 Other Parametric Measurements

#### 3.6.1 pH measurement

Metal extractions studied in this work are extremely pH sensitive, particularly so with the proprietary carriers/extractants that were used in this study. The pH measurements were made using a *Systronics* make digital pH meter that was calibrated at pH values of 4 and 7 for...
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3.6.2 Swelling of emulsion

Swelling is the increase in volume of emulsion due to transport of water from continuous phase to dispersed emulsion phase. Swelling has a bearing on emulsion breakage and is an important design parameter. Swelling of emulsion was determined at the end of each extraction run by separating out the emulsion phase from the water phase and noting the change in volume of emulsion with respect to its initial volume.

3.6.3 IR Spectra

Fourier-Transform Infrared spectroscopy (FT-IR) is a useful tool to study the nature of groups present in a system. The nature of groups present, the bonding of the various groups in the extractant with the metal, the interaction between the extractant and the diluents etc. all get revealed by IR spectroscopy.

Heavy metals such as Cu, Zn, Ni and their mixtures form complexes of different nature with various metal extractants which can be revealed by FTIR spectroscopy. FTIR spectra of LIX 84I complexes with Cu, Zn and Cu+Zn were acquired using a Thermo Nicolet 6700 FT-IR spectrometer and D2EHPA, PC 88A, CYANEX 302 complexes with zinc were acquired using a Shimadzu FTIR spectrometer Model no. 8400S.