# CHAPTER 3

# Experimental Method & Analytical Techniques

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# EXPERIMENTAL MEHTODS AND ANALYTICAL PROCEDURES

This Chapter describes the general experimental methodology and analytical procedures adopted for extraction of various solutes into Emulsion Liquid Membranes (ELMs) in this work using Type I and Type II facilitation

Materials used in this Study are listed followed by emulsion membrane formulation methodology, emulsion characterization, experimental set-up, extraction procedure and analytical methods for concentration determination and ancillary parametric measurements.

## 3.1 MATERIALS AND REAGENTS

**Membrane material:** Virgin kerosene having boiling range of 152°C to 271°C containing n-paraffins 27.08%, naphthenes 55.92%, aromatics 16% and olefins 1% was used as the membrane material for most extraction runs. It has a density ( $\rho_{15}$ ) of 821.3 kg/m$^3$ and was supplied by Indian Oil Corporation limited, Gujarat Refinery, Vadodara.

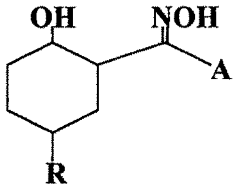
Some runs were also carried out using Hydro cracker Diesel also supplied by IOCL Gujarat Refinery, Vadodara having following specifications: Boiling range 144$^0$C to 382$^0$C, composition n-paraffins 46%, naphthenes 43%, aromatics 11% and density ($\rho_{15}$) 829.7 kg/m$^3$. Sulfur free AR grade Toluene (supplied by BDH) was the other membrane material used.

**Emulsifier:** Sorbitan monooleate (Span 80), a non ionic surfactant, having molecular weight 428 was used as the emulsifier. The emulsifier had saponification value ranging from 145 to 160, water content less than 1% and was supplied by S.D. Fine chemicals Ltd. A proprietary polymeric (Acrylate resin 505) surfactant supplied by Zydex industries was also used for some runs.

**Carrier/ Extractant:** Four different carriers were used for metal extraction studies. The carriers were used directly as supplied by the vendors. The carriers and some of their essential features are listed below:

- **LIX 84 I ®:** LIX 84 I is a water insoluble ketoxime. It is supplied worldwide by Cognis Inc. Chemically it is known as 2- hydroxy- 5- nonylacetophenone oxime. It was supplied by Cognis Ireland (Lot No 03841004) in a mixture with a high flash point hydrocarbon diluent. It forms water insoluble complexes with various metallic cations. It is an amber coloured liquid with specific gravity at 25°C of 0.90 – 0.92 and maximum copper loading capacity of 4.7 to 5.0 gm/lit of copper.
- **LIX 84 ®:** LIX 84 is essentially a mixture of a ketoxime (which is a moderate copper extractant) and a small amount of salicylaldoximes (which is a strong copper extractant). This particular formulation contains 2-hydroxy-5-nonyl acetophenone oxime (90% vol) and 5- dodecylsalicylaldoxime (10% vol) in a high flash point hydrocarbon diluent needed for handling. This extractant was supplied by Cognis Ireland (Lot No.0284001)
- **LIX 984 NC:** Its is an equivolume mixture of LIX 860N IC (5-nonyl salicylaldoxime) and LIX 84 IC (2-hydroxy-5-nonyl acetophenone oxime) in a high flash point hydrocarbon diluent needed for handling purposes. It is a viscous amber colored liquid. Reported specific gravity is 0.945 to 0.965 at 25°C and maximum copper loading of 5.1 to 5.4 gm/lit Cu. This extractant was supplied by Cognis Ireland (Lot No.03984 NC 05)

The general chemical structure of hydroxy oximes used in the above extractants is given below. It must be noted that none of the reagents used contained any modifiers except for the diluent needed for handling purpose.

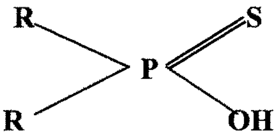


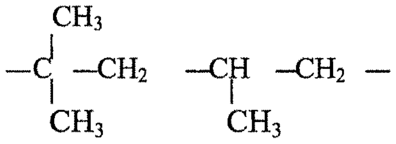
**Salicylaldoximes A = H**

**Ketoximes A = $C_6H_5$ $CH_3$**

**R = $C_9H_{19}$ or $C_{12}H_{25}$**

- **CYANEX 302®:** CYANEX 302 is the trade name of mono thio phosphinic acid produced and supplied by Cytec Canada Inc. The active component of CYANEX 302 is bis (2,4,4-trimethyl pentyl) mono thio phosphinic acid, having molecular weight of 306 with an assay of 84%. It is a pale yellow liquid, having a faint odour of hydrogen sulfide. Reported specific gravity is 0.93 at 24°C and viscosity of 195 cp at 24°C. It has a water solubility of 3mg/lit at 50°C. The chemical structure of the bis (2,4,4-trimethyl pentyl) mono thio phosphinic acid is given below:





Where, **R** = $CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_2-$

**Organic Solutes:** Extraction studies were carried out for four phenols namely phenol, o-cresol, p-cresol and 2-chlorophenol. The materials as supplied by the vendors were used directly to prepare the synthetic waste- waters containing phenols. The material specification of these compounds are as mentioned below:-

- Phenol was Qualigens make with minimum assay of 99.5% having freezing point of 40-41°C.
- o-cresol was S.D. Fine Chemicals ltd make with minimum assay of 99%; freezing point 29-31°C with maximum 1% other isomers.
- p-cresol was S.D. Fine Chemicals ltd make with minimum assay of 98%; with freezing point 33-35°C.
- 2-Chlorophenol for synthesis was of Merck make and certified pure.

**Metal Solutes:** Extraction studies were carried out in sulfate media the metal salts used were:

- Copper was used in the form of cupric sulfate $CuSO_45H_2O$ of Qualigens make, Excelar grade and 99.5% purity.
- Nickel was used in the form of nickel sulfate of Ranbaxy make having assay of 23% Nickel.

**Tracer:** Lithium hydroxide monohydrate supplied by National Chemicals having assay of 99% was used as tracer for drop breakage studies.

**Ancillary reagents and chemicals:**

- Sulfuric acid was Ranbaxy make AR grade with assay 98%.
- Hydrochloric acid was Merck make with assay of minimum 35%.
- Sodium hydroxide was Ranbaxy make with assay 96% containing 2% $Na_2CO_3$.
- Ammonia solution was Ranbaxy make, assay 25%, specific gravity 0.91.
- Oxalic acid (N/10 standard) ampoules was Qualigens make.
- n-Heptane, Qualigens make AR grade was used as diluent for particle size analysis using Malvern Mastersizer 2000.
- Standard pH buffers of 4 pH, 7 pH and 9.2 pH of Qualigens make were used.
- Certified Atomic Absorption Spectroscopy standards of SRL make were used.

## 3.2 EMULSION LIQUID MEMBRANE FORMULATION METHODOLOGY

The ELMs were formulated by mixing the membrane phase with a small amount of emulsifier to which the internal stripping phase of the emulsion was slowly added under conditions of agitation. Membrane formulations were essentially different for the two types of separations studied. In Type I separations the membrane phase consists only the oil solvent and the emulsifier since the solutes are soluble in the oil phase while for Type II separations the membrane phase also contains a carrier to bind, solubilize and shuttle the targeted metal solute from bulk phase to the inner droplet phase of the emulsion.

Emulsion membranes for the transport of solutes by Type I mechanism were prepared by initially mixing kerosene with Span 80 (1- 7.5 % wt of the membrane phase) followed by gradual addition of aqueous phase while agitating the mixture with a blender at 12,000 rpm. 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 intermittent gaps. The total time for emulsification was six minutes including the gaps. The emulsions obtained were of milky white colour and largely stable during the course of extraction runs.

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. An appropriate carrier was incorporated in the membrane phase (5 to 20 %vol) when solute transport by Type II mechanism was studied. Emulsions were prepared with fixed volumes of membrane phase and inner phase. However, in order to change 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. Variation of the internal phase volume fraction ($\phi$) of the emulsion ranged from 0.4 to 0.69.

## 3.3 EMULSION CHARACTERIZATION

The Water in Oil (W/O) emulsion is the key constituent in the ELM process necessitating the characterization of such emulsions produced. The W/O emulsions prepared in this study were characterized based on density, viscosity, 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 LVDVIII + CP using CPE 42 and CPE 52 cone spindles. The relevant details of the spindle size cone angle and shear rates at different rotating speeds are given below in Table 3.1. From the data given it is apparent that at 10 rpm with CPE – 42 viscosities are obtained at shear rate of 38.4 $s^{-1}$, to obtain the same shear rate with CPE – 52 a speed of 19.2 rpm in the rheometer.

**Table 3.1: Specifications of cone spindles and shear rates**

| Cone Spindle | Cone angle (degrees) | Radius (cm) | Sample size (ml) | Shear rate ($s^{-1}$) |
|---|---|---|---|---|
| CPE - 42 | 1.565 | 2.4 | 1.0 | 3.84 x N |
| CPE - 52 | 3.0 | 1.2 | 0.5 | 2.0 x N |

Since LVDV-III + rheometer has the flexibility to operate at variable speeds, viscosity data could be conveniently obtained using both spindles under identical shear rates. The viscosity data was collected in the direction of increasing shear rates over a wide range of shear rates in order to quantify the rheological behavior of emulsions..

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

More than 200 droplet sizes per slide were counted. In order to ensure greater accuracy two slides were prepared for each emulsion, based on the total data of more than 400 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 photomicrographs were taken using 35 mm format with Kodak gold 200 film. All exposures were in bright field and the exposure parameters were the following:

ASA= 200, Reciprocity = 4, Exposure adjustment = 1, mode of exposure = Auto.

Internal droplet sizes evaluated by microscopic technique were also crosschecked for some samples using Malvern 2000 Mastersizer particle size analyzer. The measurements were made using n-heptane as a diluent. The diluent was selected from a list of organic solvents compatible with the instrument and was based on the proximity of its refractive index to that of kerosene the membrane phase of the emulsion. Measurements were carried out with laser obscurance ranging from10-30% and maintaining agitation in the sample cup at 1000 rpm. The analysis software recorded the average value of three measurements and particle size distribution was obtained along with value of $d_{32}$. A sample of the output is attached in Appendix A .

Stability of the emulsion was studied based on the time taken for phase separations. For almost all the runs a sample of the emulsion prepared was kept aside for observation and the time taken for phase separation was precisely recorded.

## 3.4 EXPERIMENTAL SETUP AND EXTRACTION METHODOLOGY

The experimental set-up consisted of a four baffled stirred vessel of 0.105m diameter having 1 x $10^{-3}$ $m^3$ (1 liter) capacity that functioned as a batch extractor. 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 by a dimmerstat and its speed (rpm) under operating conditions was measured using a Jaquet make tachometer. The impeller used is a six bladed disk turbine having dimensions as shown in Fig. 3.1 and Fig. 3.2.

Desired amount of feed solutions for each experimental run were prepared by precisely weighing necessary amount of the targeted solutes (phenol, o-cresol, p-cresol, 2-chlorophenol, copper sulfate, nickel sulfate) to obtain an aqueous solution of predetermined concentration in mg/lit (ppm). 600 ml. of the feed solution was charged to the extractor that filled the extractor up to a height of 7.5 cm from the bottom. The impeller is positioned at a distance of 4.5 cm from the bottom and agitation was started at constant rpm.

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.

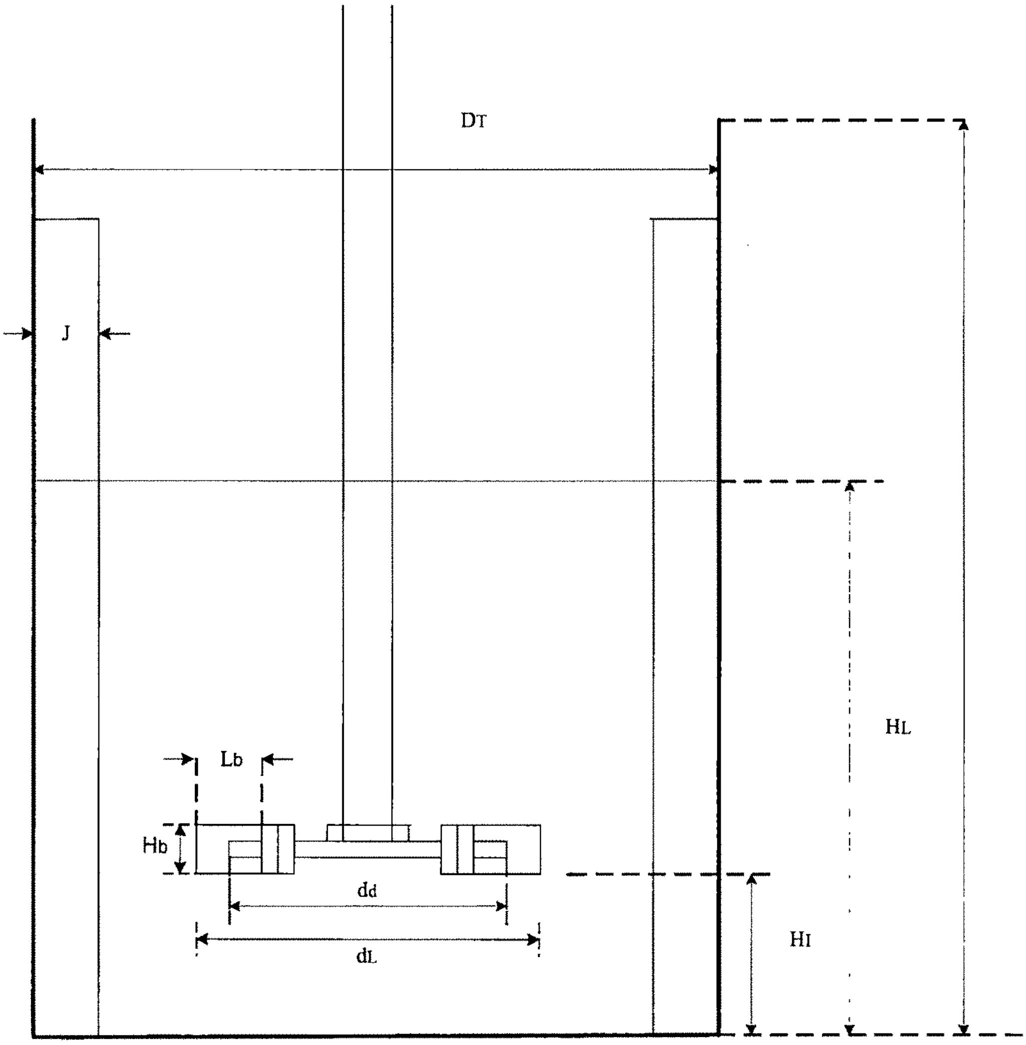
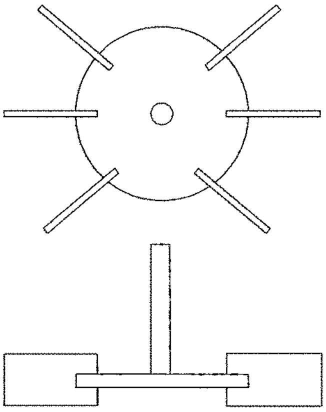


**Fig. 3.1:Batch extractor assembly**

Extraction runs were carried out for fixed period of time that extended up to 30 minutes for phenols and one hour for the extraction of heavy metals. The extraction runs were carried out at temperatures 30 ± 1°C. On completion of the extraction run duration the agitation was stopped, that 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 thereafter the samples collected during the experimental run were then analyzed for the solute content after necessary dilutions.



| Element | Type/size (m) |
|---|---|
| Internal Diameter ($D_T$) | 0.105 |
| Height ($H_T$) | 0.14 |
| Liquid Height ($H_L$) | 0.075 |
| Impeller Diameter ($d_I$) | 0.052 |
| Disk Diameter ($d_d$) | 0.038 |
| Type of Impeller | Flat Blade Turbine |
| No of Blades on the Impeller | 6 |
| Blade Height($H_b$) | 0.010 |
| Length of blade ($L_b$) | 0.013 |
| Height of the impeller off bottom ($H_I$) | 0.015 |
| Baffle width (J) | 0.008 |

Six Bladed Turbine Impeller Vessel and Impeller Dimensions

**Fig. 3.2: Impeller and vessel dimensions**

## 3.5 ANALYTICAL MEASUREMENTS

**Analysis of Organic Solutes:** The concentration of organics (phenols) were determined by a UV-Visual Spectrophotometer (Shimadzu make Model UV-Vis 260 ). The instrument parameters for measuring the absorbance of the samples are as follows: -

| | |
|---|---|
| ♦ Wave length range | 190-285 nm |
| ♦ Slit width = | 2 |
| ♦ Scanning speed | Fast |
| ♦ Wave length scale | 40nm/cm |
| ♦ Scan mode | Overlay |

The maximum wave length peaks found for the four different phenols are as follows:

| | |
|---|---|
| ♦ Phenol | 269.6 nm |
| ♦ o- Cresol | 270.6 nm |
| ♦ p- Cresol | 276.8 nm |
| ♦ 2-Chlorophenol | 273.8 nm |

The analysis of the respective solutes were made using these wavelengths, the calibration curves i.e. the standard *absorbance* versus *concentration* plots were prepared for each solute by measuring the absorbance of the samples of known concentrations and the data obtained were least square fitted for Beer's law:

$$\mathbf{C = kA + B}$$

where 'C' = Concentration of the solute in the sample
'A' = Corresponding Absorbance
'k and B' = Constants to be determined

The absorbance was measured in the scale of '0 to 2' where 0 refers to 0% absorbance and 2 correspond to 100% absorbance. The Beer's law constants and the regression coefficients are tabulated below:

**Table 3.2: Beers law constants for phenols**

| Solute | Beers law Constants | | Regression Coefficient $R^2$ |
|---|---|---|---|
| | k | B | |
| Phenol | 67.988 | 0.8318 | 0.9998 |
| o- Cresol | 71.464 | 3.2175 | 0.9997 |
| p- Cresol | 65.861 | 0.2531 | 0.9999 |
| 2- Chlorophenol | 68.483 | 0.8756 | 0.9999 |

The value of the regression coefficients obtained in the present study indicates that Beer's law can be used to calculate the concentration of unknown samples with high precision.

**Analysis of Metals**: The metal ion concentrations were measured using an Atomic Absorption Spectrophotometer (Chemito make Model AA – 203) equipped with Photron make hollow cathode lamps for Copper and Nickel. The instrument was fully computer controlled using software AA 203 DataStation Ver 3.2. The optimized instrument parameters for measurements of copper and nickel are as given in Table 3.3:

**Table 3.3: AAS parameters for copper and nickel**

| Parameter | Copper | Nickel |
|---|---|---|
| Wave length (nm) | 324.8 | 232.10 |
| Current (mA) | 5.0 | 9.0 |
| Slit width (nm) | 0.5 | 0.3 |
| Pmt (V) | 274.7 | 370.7 |
| Burner height (mm) | 1.0 | 1.0 |
| Fuel (litre/min) | 3.5 | 3.55 |

Copper was analyzed in a working range of 2 to 8 ppm at the specified wave length (324.8 nm) while nickel was analyzed in working range of 2 to10 ppm at the specified wave length (232.0 nm). Certified AAS standards (SRL make) were used to generate standard curves required for analysis in the above-mentioned working ranges for the different solutes. Ratio method was preferred for curve fitting. The samples of experimental runs were appropriately diluted so that they were in the specified working range for the corresponding metals the concentrations were reported in mg/dm$^3$ (ppm).

## 3.6 ANCILLARY PARAMETRIC MEASUREMENTS

**Interfacial Tension:** The interfacial tension between the emulsion phase and the solute containing aqueous phase was measured using a Du Nuoy tensiometer.

**Globule Size:** Dispersed globule size of the emulsion were determined by photographing the dispersed system using a Nikon F 60 camera fitted with a 35 – 105 mm micro lens and a Nikon SB – 80DX digital flash synchronized up to 125 frames/sec. Exposures were taken using an aperture of 11 and shutter speed of 90 frames/sec at definite time intervals covering the entire history from dispersion to final settling of emulsion globules. The pictures were processed using P 41 Kodak chemistry.

The globule sizes were measured using image analysis techniques. Care was taken to maintain correspondence of 1:1 between the photographic image and the actual visual field. Average globule size was calculated from the globule size distribution data.

**Distribution Coefficients:** Distribution coefficient of solute between the membrane phase and aqueous phase were determined by equilibrating an equal volume of kerosene with water containing pre determined amount of solutes (phenol, cresols, 2-chlorophenol) at constant temperature as that of the extraction runs. After equilibrium was attained the aqueous and organic phases were separated and the concentration of the phenols in the aqueous phase was determined using UV- Visual Spectrophotometer.

The concentration of phenols in the organic phase was determined by mass balance. Distribution coefficients were determined for solute concentrations ranging from 100 to 800 mg/lit. Identically the distribution of metals between water and carrier containing membrane phase was determined by equilibrating equal volumes of water containing known amount of solute with kerosene containing fixed percentage of carrier. These experiments were carried out with variation of pH and carrier concentration with initial solute concentration of 500 mg/dm$^3$.

**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.

**pH measurements:** Type II separations studied in this work are extremely pH sensitive, particularly with the proprietary carriers /extractants as those used in this work, pH measurements were made with Systronics make digital pH meter that was calibrated at pH of 4, 7 and 9.2 respectively using standard buffer solutions.

**Emulsion breakage:** Tracer studies were conducted to estimate the extent of leakage of the reagents contained in the internal aqueous phase of the emulsion into the continuous feed phase. The tracer chosen for study was lithium hydroxide that gave emulsions of nature identical to those prepared with sodium hydroxide in type I separations. Emulsions prepared using predetermined amount of lithium hydroxide as the internal aqueous phase were dispersed under identical conditions of agitation in water and samples of continuous phase were withdrawn at regular time intervals and analyzed for lithium content. Percent leakage was determined by material balance.

A Flame Photometer (Elico make, Model CL 361) was used to determine the lithium content of samples. Standard samples (in Beer's law range of 0 to 100 mg/lit) were prepared by reacting lithium carbonate with 1:1 HCl, these standards were used for generating the calibration curve.