

CHAPTER 1

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Emulsion liquid membranes separation technique was invented by N.N.Li in 1968. Since then this technique has demonstrated considerable potential as an effective tool for an increasingly wide variety of separations that include the following:

- ◆ Removal of trace contaminants from wastewater
- ◆ Recovery and enrichment of heavy metal ions
- ◆ Removal of organic and inorganic acids from water
- ◆ Recovery of bio chemicals including separation of amino acids, antibiotics and phospholipids from fermentation broths.
- ◆ Fractionation of hydrocarbons

In addition to the above, certain esoteric biomedical applications including blood oxygenation, preparation of artificial blood cells, extraction of cholesterol from blood, treatment of chronic uremia, treatment of drug overdose and slow release of drugs are being developed. Emulsion liquid membranes (ELMs) also have potential utility as membrane reactors for controlling the heterogeneous catalytic oxidation of ethylene to acetaldehyde over PdCl_2 and CuCl_2 catalyst system also for carrying out catalytic reactions using enzymes (Ho and Li 1992).

Three separations using emulsion liquid membranes have been commercialized:

- ◆ Recovery of zinc from rayon plant effluents in Austria.
- ◆ Recovery of phenol from wastewater at a plastics plant in China.
- ◆ Treatment of cyanide containing wastewater from gold mining in China.

In addition to these three commercial applications, ELMs have been used as a well-control fluid for preventing well blowout and sealing loss zones in oil and gas wells since 1985. ELMs are still in its nascent stage of development, which is evident from the passing reference to it for the first time in Perry's Chemical Engineers Handbook 7th edition (1997).

ELMs are usually prepared by first forming an emulsion between two immiscible phases and then dispersing this emulsion in a third (continuous) phase by agitation. The liquid membrane phase is that which separates the encapsulated phase in the emulsion from the external continuous phase. In general, internal phase droplets are small having diameter up to 10 μm , whereas the dispersed phase globules are about 0.1 to 2.0 mm in diameter. Therefore an immensely large surface area for mass transfer is generated that leads to very rapid removal of targeted solutes.

At the end of extraction run, the emulsion and aqueous feed phase are separated by settling and the reacted internal phase can be recovered if desired by breaking the emulsion. Surfactants and other additives are normally added to the membrane phase to provide stability to the emulsion also to control the diffusivity and/ or selectivity of the transporting species in the membrane.

The effectiveness of the liquid membrane process can be enhanced by resorting to facilitated transport mechanisms in the emulsion membranes. There are two types of facilitated transport mechanisms, which are named Type I and Type II transports. In Type I transport, the concentration gradient of permeate is maximized by reacting the solute in the receiving phase irreversibly, thereby maintaining permeate concentration effectively zero in this phase. It is desirable that reaction products formed be incapable of diffusing back. In Type II facilitation, a carrier is incorporated in the membrane phase. This carrier works as a shuttle to transport the solute species from the external phase to the internal phase.

Although much has been reported on the extraction of various solutes in ELMs, very few investigators focused on the nature of emulsion used and the nature of interrelation between emulsion morphology and extraction behavior. ELMs make use of transient entities like emulsions as extracting agents. Unless and until the emulsions are properly prepared and characterized it is impossible to achieve repetitive reproducible results that is demanded by the chemical industry.

More over commercial success will also depend on suppression / elimination of certain features associated with ELMs such as emulsion swelling and emulsion breakage. It is

necessary to appropriately quantify these aspects along with extraction kinetics using ELMs. These are the areas of weakness in ELM studies. These aspects are not amenable to theoretical analysis and modeling in absence of data, and can be addressed only when large volume of data are gathered and critically analyzed. There is very limited information on continuous extraction using ELMs. Attention on this aspect needs to be focused. Similarly, aspects of demulsification also needs to be addressed

Further in the flux of development, it is often observed that much of the information acquired tends to become obsolete in a short span of time. One such example concerning ELMs is the substantial information gathered for copper extraction using carriers of earlier genre like LIX 63, LIX64 N etc. remain only of academic interest, and stand unusable in the industry because these carriers are no longer available commercially. Hence, it is necessary to keep on constantly building up on the information levels available to remain contemporary.

Many mathematical models for solute transport in liquid membranes have been proposed. The advancing front model of Ho *et al.* (1982) is regarded as a standard model for Type I transport. This model though widely quoted has been actually tried out with very limited data and that too obtained under a rather narrow range of variation. The efficacy of this model predictions need to be established against experimental data obtained with wide variation of parametric conditions. Bunge and Noble (1984) developed the reversible reaction model in which the reaction between the solute and internal reagent is a reversible one. The predictions of this model also need to be assessed with adequate experimental data.

In view of the state of the Art mentioned above, this investigation was undertaken to address the following:

- i. To prepare formulations of W/O emulsions that could be used effectively as ELMs with high order of reproducibility.
- ii. To adequately characterize the emulsions prepared on the basis of drop size distribution, viscosity and surface tension etc.
- iii. To study the dispersion characteristics of the emulsions prepared.
- iv. To test the W/O emulsions for extraction of solutes using Type I and Type II facilitated transport mechanisms.

- v. To obtain substantial data on extraction of phenols with wide ranging variations in emulsion and process parameters in order to buildup on the existing data on phenol.
- vi. To obtain experimental data of extraction of other phenols such as o-cresol, p-cresol and 2-chlorophenol.
- vii. To make an attempt to relate qualitatively the extraction kinetics with membrane properties and thereby obtain a general picture of phenol extractions.
- viii. To obtain experimental data with new commercial extractants introduced for copper extraction, particularly to study the extraction of copper using ELMs at $\text{pH} \leq 2$.
- ix. To study the suitability of copper extraction using ELMs in ammoniacal conditions.
- x. To check the possibility of use of chelating extractants for nickel extraction using ELMs.
- xi. To test the efficacy of the Advancing front model of Ho *et al.* and the Reversible reaction model of Bunge and Noble against widely varying experimental data.
- xii. To critically analyze experimental data in order to identify the dominant parameters affecting extraction for Type I transport and Type II transport and also to investigate the main factors contributing to membrane instability.