STUDIES ON EMULSION LIQUID MEMBRANES

SUMMARY OF THE
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By

BINA R. SENGUPTA

Guided By

PROF. N. SUBRAHMANYAM

CHEMICAL ENGINEERING DEPARTMENT
FACULTY OF TECHNOLOGY AND ENGINEERING
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
BARODA

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SUMMARY

Emulsion liquid membrane separation (ELMs) 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

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

Emulsion liquid membrane separation is achieved by preparing an emulsion between two immiscible phases and then dispersing the emulsion formed into a third (continuous) phase by agitation so as to extract a solute from the continuous phase into the inner phase of the emulsion or vice-versa The membrane phase is the liquid that separates the encapsulated internal droplets within the emulsion from the external continuous phase

When the emulsion is dispersed with mild agitation in the external continuous water phase, many small globules of the emulsion are formed The size range of these globules vary from 0 1 mm to 3mm, globule size largely depends on mode and intensity of agitation, emulsion viscosity, constituents and composition of the emulsion A large surface area for mass transfer is generated because of the small size of the emulsion globules formed Further the internal encapsulated droplets within the emulsion globules are just 1 to '0 μm in diameter; that leads to an enormously large internal mass transfer area typically of the order of 10^6 m^2/m^3. The net result being that a very rapid mass transfer takes place in ELM process irrespective of the transfer being from the continuous to the inner encapsulated phase or vice-versa

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

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* 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 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 pH ≤ 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.

The Thesis is presented in seven chapters Chapter 1 is devoted to the introduction just presented above

Chapter (2) presents the Literature Survey with respect to the essential features of emulsion liquid membranes which include literature on membrane materials and surfactants used for emulsion preparation, emulsion morphology, swelling, leakage, and various other aspects of emulsion stability. Aspects of dispersion behaviour and dropsize distributions are also incorporated. This chapter also reviews the transport mechanism into ELMs that may be broadly classified as Type I facilitated transport and Type II facilitated transport Type I transport involves a chemical reaction inside the internal droplets of the emulsion that leads to a maximization of driving force for solute transfer While Type II transfer involves the use of a carrier in the membrane phase that binds molecules or ions, which are otherwise insoluble in the membrane, and shuttles it inside the membrane to the internal phase present within the emulsion globules. ~~This is the~~ mechanism for transport of heavy metals in ELMs A comprehensive review of various solutes investigated using these two types of transport processes is also presented

Chapter (3) Experimental methods and analytical procedures describes the emulsion membrane formulation methodology , emulsion characterization, experimental Setup, extraction procedure, analytical methods for concentration determination and ancillary measurements

Chapter (4) Results and Discussions Extraction of Phenols, include the relevant details about characterization of emulsions based on internal drop sizes, rheological properties of emulsions, interfacial tension between extracting emulsions and aqueous solutions, dispersion behavior of emulsion, prediction of globule sizes, effective diffusivity etc

Batch Extraction of four phenols namely phenol, o-cresol, p-cresol and 2-chlorophenol using well characterized membranes are reported The effect of various emulsion parameters such as internal phase volume fraction, surfactant concentration etc and the effect of process parameters such as stirring speed emulsion to feed ratio etc are studied Finally an integral view of separation of phenols are presented wherein any points of similarities and differences between the extraction behavior of these solutes are presented It would be presumptuous to expect that all phenols will show identical behavior, however investigations reveal that dominant parameters which influences Type I separations are the molar ratio of the internal reagent to the solute in feed and the solute distribution coefficient between the membrane and water phase.

Chapter (5) Results and Discussions· Extraction of copper and nickel, also includes the relevant details about the emulsions used for the extraction of these two metals Three commercial chelating extractants namely LIX 84, LIX 84 I and LIX 984 NC were used as carrier in the membranes for facilitated transport of copper from acidic media Effect of various emulsion and process parameters was investigated Extraction under highly acidic conditions was also performed Investigations revealed that LIX 984 NC was an excellent carrier even in highly acidic conditions were most other extractants failed to perform satisfactorily

Extraction of nickel and copper individually also in combination was also studied in ammoniacal conditions. Copper transport was found to be very fast however nickel transport was hindered due to the slow stripping kinetics of nickel

Chapter (6) Transport of solutes into emulsion liquid membranes Modeling and Simulation, discusses the various approaches to modeling of the solute transport in ELMs. The advancing front model (AFM), which is the standard model for Type 1 transport, is reviewed and utilized to predict extraction profiles using experimentally determined parameters It is found that at high solute concentration the AFM predicts concentration profiles reasonably well but fails to do so at low solute concentration This behaviour is attributed to the idea of reaction irreversibility that is built in the advancing front model

The reversible reaction model proposed by Bunge and Noble was also used to predict concentration profile for situations where the AFM did not work, it was found that in some situations the fit between experimental and predicted profiles was quite good

Chapter (7) presents the summary and conclusions of the present work. It may be summarized that the main hindrance to the commercial growth of the ELMs technology lies in the lack of appropriate and extensive data of various separations using properly characterized emulsions that would assure the industry of reproducibility of results These aspects need to be continually addressed in order to have a strong case for the adoption of ELM techniques on a commercial scale In the present work an attempt has been made in this direction by presenting extraction data with adequately characterized membranes that also helped in obtaining a deeper insight on the extraction behaviour of ELMs

The success of ELM technique will largely depend on the stability and consistency of the membranes hence, it is necessary to aggressively pursue research to develop more stable W/O emulsions to strengthen the case for Emulsion liquid membrane separations