



CHAPTER III

THEORY

There are numerous separation methods which are used in the hydrometallurgical field such as solvent extraction (also called liquid-liquid extraction), liquid membranes, and ion exchange. These methods usually deal with low concentrated process streams. In a conventional solvent extraction process, the degree of extraction is primarily limited by the solvent-to-feed ratio and the distribution ratios of the solute in the feed to that in the solvent, and the solvent to the strip. The aqueous solution initially containing all the ions that can permeate the organic solution (or the solvent) is generally referred to the feed solution. The aqueous solution present on the opposite side of the organic solution which is initially free from the permeable ions is generally referred to the strip solution. The transfer of metal ions from the feed solution to the organic solution depends on extraction with chemical reaction. The reaction is reversible; therefore, solvent recovery which allows the solvent to be reused can be accomplished by changing the chemical conditions. A large amount of organic solvent is necessary for solvent extraction. To solve this problem, the use of liquid membranes containing a carrier has been proposed as an alternative to solvent extraction to solve this problem for the selective separation and concentration of metals from dilute aqueous solution.

Liquid membrane permeation, in principle, is a solvent extraction process in which the extraction and stripping operations are performed simultaneously. The liquid phase which acts as a selective separation layer between the feed and the strip solutions is usually referred to the liquid membrane. In general, the aqueous phases - feed and strip solutions - are miscible with each other while the organic phase is immiscible with any aqueous phases. The two aqueous phases are, therefore, separated by the

membrane phase, this is so-called liquid membrane technology. Dissolved in the organic solvent, the carrier picks up the ions on the feed side of the liquid membrane and transports them by diffusion to the strip side of the membrane. The driving force is a concentration gradient of the ion-carrier complexes between both sides of the membrane. Transfer in the reverse direction from the organic phase back to the aqueous phase correspondingly requires a shift of chemical equilibrium and this process is known as “stripping.” Figure 3-1 shows the schematic example of the separation of metal ions from aqueous solution in the most common counter transport through a membrane, where the overbar denotes the species in the organic phase.

In the aqueous phase I, a metal ion diffuses to the liquid membrane surface (interface i) and reacts with two carriers forming a metal-carrier complex which diffuses through the liquid membrane driven by the existing concentration gradient. At the interface ii, the thermodynamic equilibrium is shifted and the complex is split into the carrier and the metal ion. One carrier picks up one proton and diffuses back to the feed side of the membrane while the metal ion diffuses through the interface ii to the aqueous phase III. This metal ions transport works as long as protons migrate to the opposite direction, this is so-called counter-transport. The driving force for this coupled transport is provided by the different acidities or pH values of the feed and strip solutions. In the case of a steady-state process two diffusion steps have to take place simultaneously; namely, the diffusion of metal-carrier complex from the feed side of the membrane to the strip side and the back-diffusion of the proton loaded carrier.

The separation of metal ions by the liquid membrane has attracted even greater attention. The much earlier studies by Harber and Beutner [Majumdar and Sirkar, 1992] used a thin film of oil between two aqueous phases. Two distinctly different techniques were adopted in later studies: one is the immobilized liquid membrane called supported liquid membrane

(SLM), the other is the mobilized liquid membrane called emulsion liquid membrane (ELM) or liquid surfactant membrane (LSM).

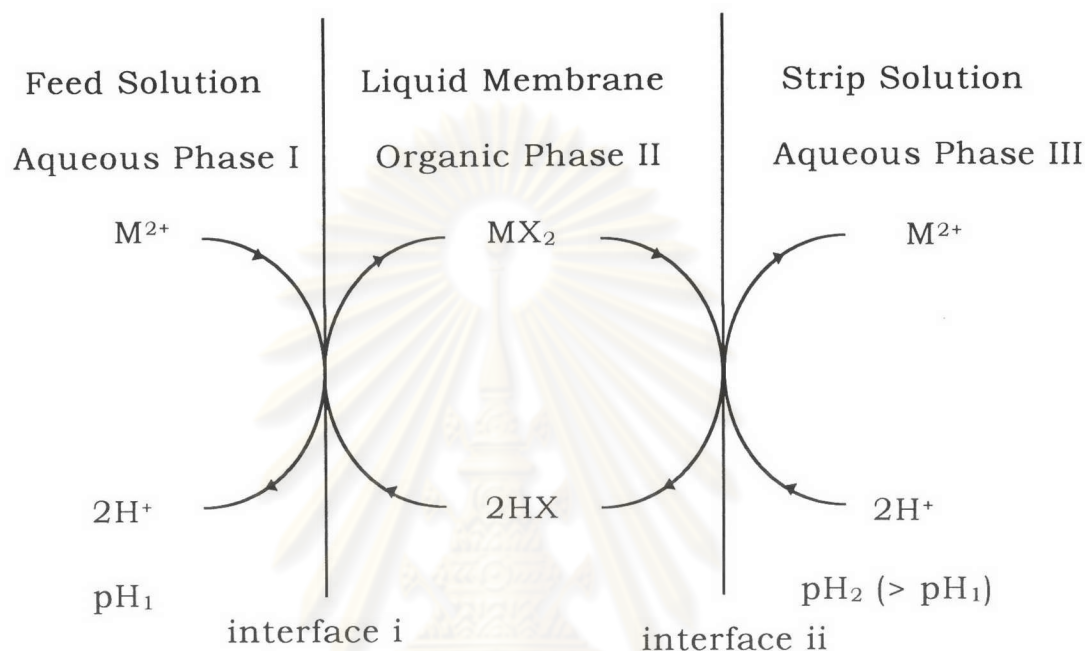


Figure 3-1 Schematic representation of the counter-transport mass transfer through a liquid membrane.

Supported liquid membrane

The supported liquid membrane technique uses a porous membrane as a support for the organic phase incorporating the carrier. A supported liquid membrane can be achieved by impregnating a porous solid film with an organic solvent, which is held in place by capillary forces that exist within the pores. The membrane separates an aqueous phase, initially containing the solute of interest, from another aqueous phase into which the solute is extracted, the stripping phase, as shown in Figure 3-2. Porous support membranes are available as flat sheet, hollow fiber, or spiral type. Hollow fiber membranes are preferred because of their higher packing densities, favourable hydrodynamics and other advantages.

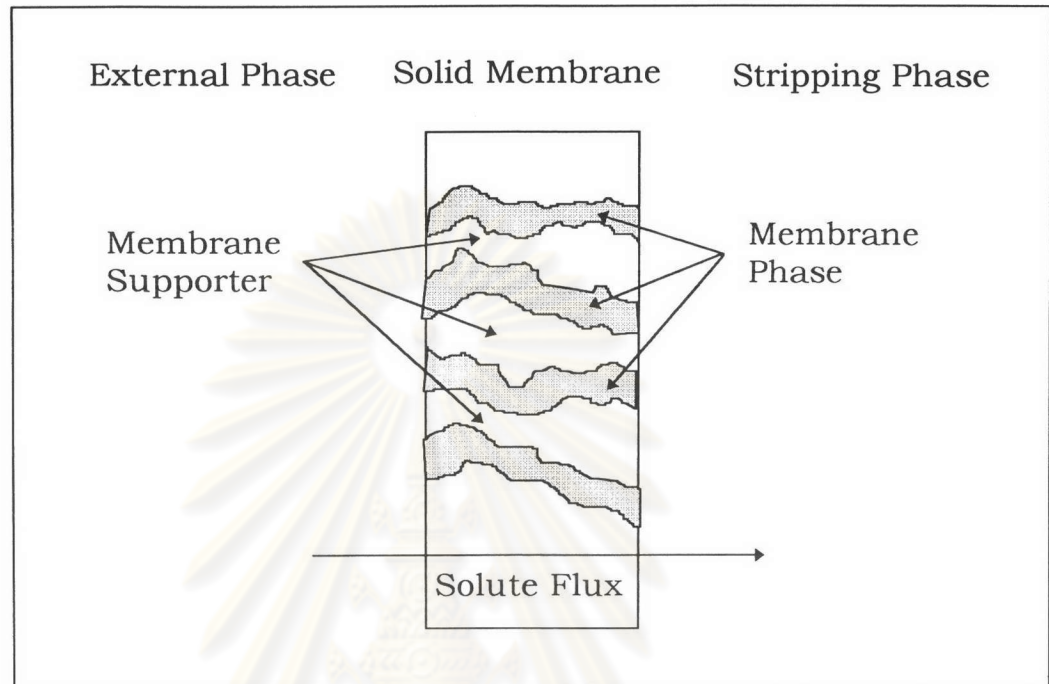


Figure 3-2 Schematic Diagram of a Supported Liquid Membrane.

Hollow fibers are produced by means of neutron bombardment and subsequent etching to produce cylindrical pore with a very narrow distribution of diameters (about 0.01 to 10 μm) in polymer films of thickness 15 to 100 μm . The porosity of this type of polymer film is 40 to 80% [Marr and Kopp, 1982]. Hollow fiber modules are manufactured in such a way that a bundle of parallel fibers are potted with synthetic resin at the front sides of a cartridge. The hollow fibers are opened at the front sides, as shown in Figure 3-3. In a module the wall of the hollow fiber membranes are impregnated with the organic solvent containing the liquid ion-exchanger. In general, the feed solution flows through the lumen (the tube side) of the hollow fibers and the aqueous strip solution circulates on the shell side of the fibers. If the feed solution is passing only once through the hollow fiber, the amount of metal recovered is not enough. The feed solution has to be circulated continuously through the module. This recycling mode operation can be realized in one- or multi-circuit processes.

The organic liquid is stabilized in the pores of the microporous membrane by capillary or surface forces and then interposed between two aqueous solutions. At the interface between the feed solution and the membrane, the solute is extracted into the membrane liquid, it then diffuses by itself or in a complex form to the other side of the membrane where the strip aqueous solution flows. At the strip solution/membrane interface, the solute is back-extracted into the strip solution. Using counter-transport or co-transport, the metal or solute species could also be concentrated in the strip solution.

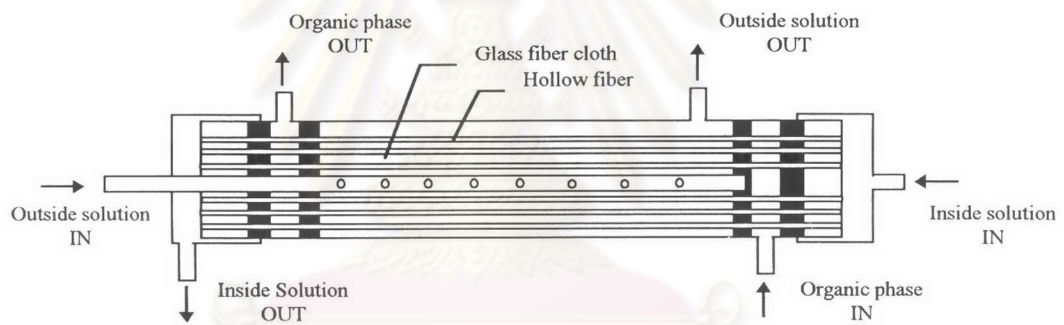


Figure 3-3. Schematic countercurrent flow in a hollow fiber cartridge

Danesi has suggested that the advantages of supported liquid membrane over other traditional separation technologies are: (a) lower capital and operating cost, (b) low energy consumption, (c) economical use of expensive, tailor-made extractants and solvent because only an extremely small quantity of membrane liquid is required for filling the pores, (d) possibility of achieving high separation factor, (e) possibility of concentrating the recovered species during the separation, and (f) lower maintenance costs due to fewer moving parts [Tavlarides, Bae, and Lee, 1987]. Despite such advantages, supported liquid membranes have not been adopted for larger scale industrial processes. A major reason is the limited lifetime of the

liquid membrane due to the dissolution of the organic solvent in aqueous solutions.

Emulsion Liquid Membrane

The emulsion liquid membrane is a liquid phase involving an emulsion configuration. Emulsion liquid membranes, also called surfactant liquid membrane or liquid surfactant membranes, are essentially double emulsions, i.e., water/oil/water (W/O/W) systems or oil/water/oil (O/W/O) systems. For the W/O/W systems, the oil phase separating the two aqueous phases is the liquid membrane. For the O/W/O systems, the aqueous phase is the liquid membrane that separating the two oil phases.

General Description of Emulsion Liquid Membrane

Emulsion liquid membranes are usually prepared by first forming an emulsion between two immiscible phases, and then dispersing the emulsion in a third phase by agitation for extraction. The membrane phase is the liquid phase that separates the encapsulated, internal droplets in the emulsion from external, continuous phase, as shown in Figure 3-4. In general, the internal, encapsulated phase and the external, continuous phase are miscible. However the membrane phase must not be miscible with either of these two phases in order to be stable. Therefore, the emulsion is of the W/O type if the external phase is water, and it is O/W type if the external phase is oil. To maintain integrity of the emulsion during the extraction process, the membrane phase generally contains some surfactant and additive as stabilizing agents, and it also contains a base material that is a solvent for all the other ingredients.

Typically, the encapsulated, internal droplets in the emulsion are 1 to 3 μm in diameter to provide a good emulsion stability for emulsion liquid membrane extraction. When the emulsion is dispersed by agitation in the external phase during the extraction process, many small globules of the

emulsion are formed. The size of the globules depends on the characteristics and concentration of the surfactant in the emulsion, the viscosity of the emulsion, and the intensity and mode of mixing. Usually the globules size is controlled in the range of 100 to 2000 μm in diameter. Thus, a very large number of emulsion globules can be formed easily to produced a very large mass transfer area adjacent to the external phase. Each emulsion globules contains many 1 to 3 μm internal droplets. Thus, the internal mass transfer surface area, typically $10^6 \text{ m}^2/\text{m}^3$, is even much larger than the external mass transfer surface area. Therefore, a rapid mass transfer in the emulsion liquid membrane process can occur from either the external phase to the internal phase or vice versa.

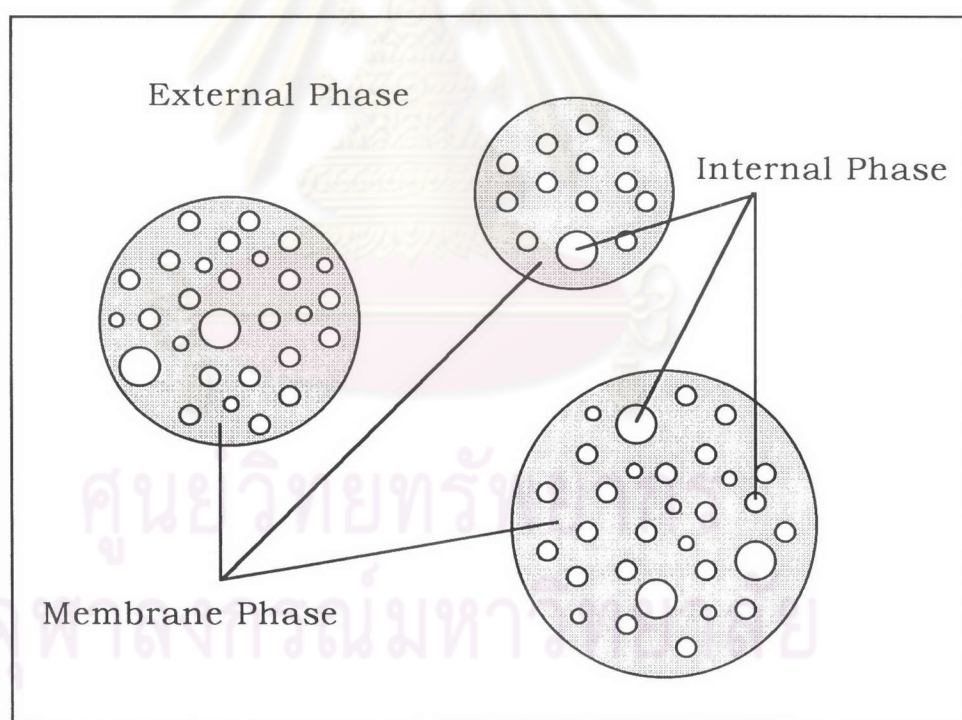


Figure 3-4. Schematic of an Emulsion Liquid Membrane System.

Separation of mixtures can be achievable by selective diffusion component through the membrane phase into the receiving phase of lower equivalent concentration. Surfactant and additive included in the membrane phase can control the selectivity and permeability of the

membrane. An individual component can be trapped and concentrated in the internal phase for later disposal or recovery. Once separation is achieved, the emulsion and external phases are separated, usually by settling as in conventional solvent extraction. The extracted component can be recovered from “loaded” internal phase of the emulsion by breaking the emulsion, usually by the use of an electrostatic coalescer (Wang and Zhang, 1988; Marr, Bart and Draxler, 1990). From breaking the emulsion, the membrane phase recovered can then be recycled to emulsification step for the preparation of the emulsion with a regenerated or fresh reagent phase.

Liquid Membrane Extraction : A Form of Solvent Extraction

Liquid-liquid extraction is a separation technology which has found wide application in the separation of metals. This has mainly involved organic/aqueous systems, but more recently, aqueous-aqueous extraction is becoming more widespread. This operation relies on the partitioning of the required solute between an aqueous and organic phase. The equilibrium governing this phenomenon can be related by means of the distribution coefficient, D^+

$$D^+ = \frac{C_2}{C_1} \quad (3.1)$$

where C_2 is the concentration of the solute in the extracting solvent phase which is usually an organic liquid. C_1 is the concentration in the aqueous product stream. After the solute has partitioned into the organic solvent, the phases are separated and the solute is usually re-extracted or stripped back into an aqueous phase.

An analogy may be drawn between emulsion liquid membrane extraction and solvent extraction (del Cerro and Boey, 1988). The emulsion phase can be considered to be an extracting solvent phase. Extraction and stripping occur simultaneously on both sides of the membrane and under non-equilibrium conditions.

In solvent extraction, the value of K_{oi} can be increased by alteration of conditions such as pH, or by the introduction of an extractant into the organic phase, which increases the solute solubility in the organic phase (Likidis and Schugerl, 1987). These improvements in solvent extraction can be applied to liquid membrane extraction, to enhance extraction efficiency and improve selectivity.

Liquid membrane extraction has several advantages over solvent extraction. As the liquid film is very thin and high specific interfacial areas are available for mass transfer, separation is fast. As only one extraction stage is required, with respect to solvent extraction there is a reduction in equipment and solvent requirements. Two obvious disadvantages of liquid membrane extraction are the requirement for an emulsion breakage operation to recover the extracted product (Chaudhuri, 1990).

Principles of Separation

In a liquid membrane process mass transfer occurs in all three phases. In the external phase the solute transfers across the interface with the membrane, then diffuses through the membrane phase. At the interface with the internal phase the solute transfers into the small droplets of the internal phase. Any reaction at this interface is usually assumed to be instantaneous because of the high specific interfacial area of the small droplets, so it is unlikely that mass transfer will be limited by the solute/reagent reaction (Ho et al., 1982). As mentioned above, the membrane phase confers selectivity on liquid membrane processes and consequently the mechanism of solute transport across this phase is of prime importance. There are two principle modes of transport across the membrane phase (Matulevicius and Li, 1975; Chan and Lee, 1984).

Unfacilitated Transport

This is the simplest case of solute transport through the membrane phase and is a diffusion process. The solute is initially in the bulk of the external phase and diffuses to the interface with the membrane

phase. Here it partitions into the membrane and diffuses across to the interface with the internal phase into which it partitions, the driving force for transport is the chemical potential difference in the solute across the membrane phase.

The driving force can be manipulated by the inclusion in the internal phase a chemical reagent which reacts with the solute. This has a two-fold effect; first, the solute is now in a different chemical form which if it is soluble in the organic solvent, cannot back-diffuse. Second, because the solute is now in a different form, the concentration of the transportable species in the internal phase, is effectively zero and hence the concentration gradient is maximized, thus enhancing mass transfer.

Thein et.al.(1985) point out that unfacilitated transport is only applicable to uncharged solutes, as charged species will be insoluble in the non-polar membrane solvent.



Figure 3-5. Schematic of two facilitated mechanism:

- (a) Type I facilitation and
- (b) Type II facilitation.

Facilitated transport

This form of transport is of greater importance in any potential liquid membrane separation. Its application is for membrane-insoluble

materials, such as charged species, e.g. metal ions, organic acids and zwitterions. By introducing a 'carrier' molecules into the membrane phase, the solute solubility is increased by the reversible formation of a membrane-solute carrier-solute complex. This results in faster mass transfer rates, selectivity is introduced into the extraction as the carrier-solute reaction can be selective(Cussler,1984). The carrier must be insoluble in water and must be also be specific for the solute of interest. The solute is transport across the membrane by the formation of a complex as follows(Lobarch and Marr, 1987).

1. At the interface between the external phase and membrane phase the solute M^{2+} , reacts with the carrier complex HR, to form the complex MR_2 , and liberates H^+ in the external phase. This complex is insoluble in either aqueous phase but is soluble in the membrane phase.
2. The carrier-solute complex (MR_2) diffuses across the membrane to the interface with the internal phase.
3. At the interface with the internal phase the reverse reaction occurs, brought about by a shift in the reaction equilibrium due to the higher concentration of a counter-ion H^+ , in the internal phase. Hence the solute M^{2+} is released into the internal phase reagent.
4. The carrier reacts with the counter-ion to form the carrier-counter-ion complex HR, which then diffuses back through the membrane to the exterior interface where the counter-ion released, Haunch completing the process.

Although Lobarch and Marr(1987) state that the driving force of the difference between the activities of the counter-ion in the internal and external phase, it is more process is known as counter transport (Figure 3-6).

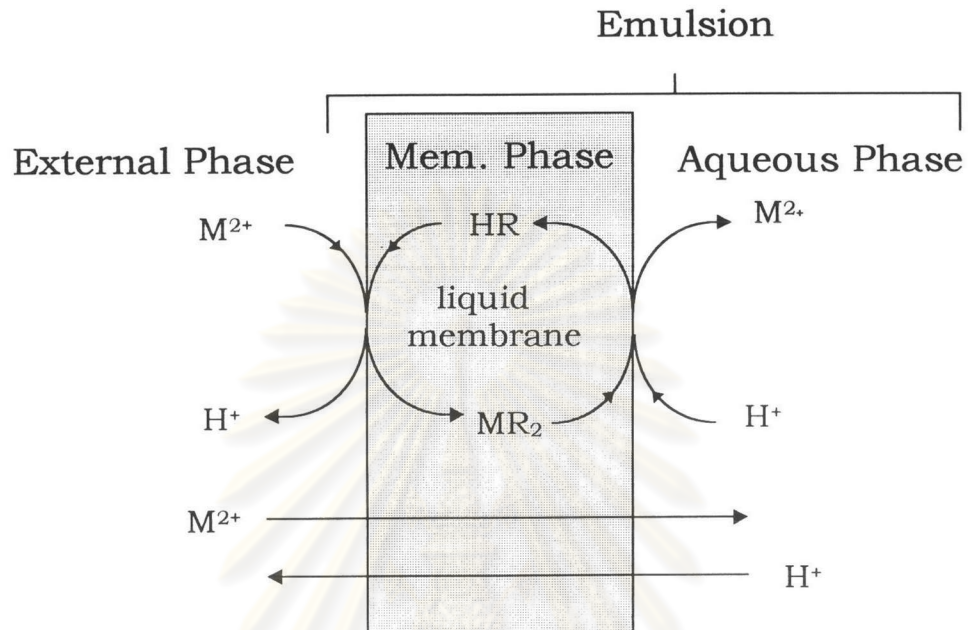


Figure 3-6. Schematic of Counter Transport of Solute M^{2+} by Carrier HR .

The second, less common mode of facilitated transport is known as co-transport (Figure 3-7). This is characterized by the carrier (C) reacting reversibly with the solute A, and a second species B, and transporting them in one direction across the membrane. Therefore two coupled fluxes exist across the membrane in the same direction (Cussler, 1984).

Process Considerations

An emulsion liquid membrane process includes three steps

- 1) emulsification
- 2) dispersion/extraction/settling
- 3) demulsification (breaking of emulsion)

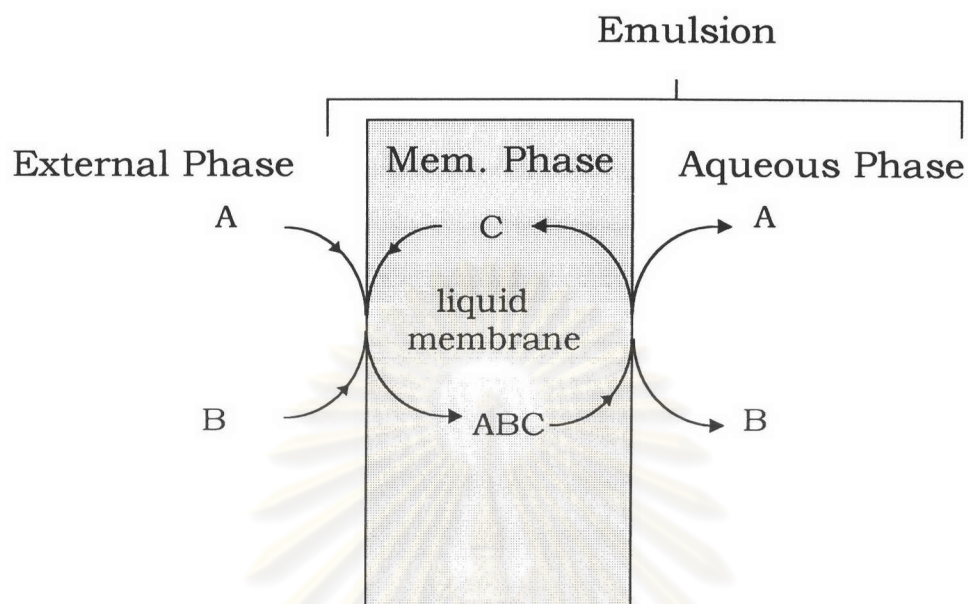


Figure 3-7. Schematic of Co-Transport of Solute A and B by the Carrier C.

Emulsification.

Membrane Formulation.

Emulsion liquid membranes can be "tailor made" to meet the requirements of different separations, and thus they can offer versatile processes capable of separating a wide range of liquid mixtures. On the other hand, this versatility sometimes brings about difficulties in the design of membrane formulation. Choosing the appropriate membrane formulation for a particular separation task is often quite complex. For unfacillitated transport, the membrane phase consists only of a diluent and a surfactant to stabilize the primary emulsion. No extractant is needed for unfacillitate transport because the solute transport across the membrane is accomplished through its physical solubility and then diffusion in this membrane. However, for facilitation transport, an extractant and its associated stripping agent must be incorporate into the membrane and internal phase, respectively, in order to achieve a coupled extraction/stripping process.

Extractants/ Stripping Agents.

When choosing extractants, the selected extractant and its complex must be soluble in the membrane phase, but insoluble in the external and internal phase. Precipitates are also not allowed to form either within the membrane or at the interfaces. Otherwise, the membrane process will fail.

Generally, the selection of the extractant/stripping agent system is based on the thermodynamic and kinetic considerations. Thermodynamically, the selected extractant should favor the distribution of the solute from the external phase to the membrane phase.

A thermodynamic condition exists under which the liquid membrane process can be operated while solvent extraction cannot. A solvent extraction process need a high distribution ratio for extraction so as to increase the extraction ability. The non-equilibrium feature of emulsion liquid membranes allows the selected extractant to have a lower distribution ratio for extraction than solvent extraction.

Kinetically, The selected extractant and stripping agent should usually exhibit fast reactions for both extraction and stripping . But it is interesting to note that because its much higher interfacial area for stripping than that for extraction, and emulsion liquid membrane process is capable of coping with the situation in which the extractant has relatively fast extraction kinetics but the stripping agent has extremely low stripping kinetics.

The classification is based on the type of extractants. There are three principal groups which can be identified. These are acidic extractants, the basic extractants, and the solvating extractants. Although most extractants were identified, there is a great deal of effort to produce new reagents.

Acidic Extractants. This class of extractants can be further divided into two subclasses, namely acidic extractants and chelating extractants. The former are those having reactive groups such as $-\text{COOH}$, $> \text{P}(\text{O})\text{OH}$, $-\text{SO}_3\text{H}$, while the latter are those which chelate with metals. Metal cations can react with organic acids and acidic chelating agents to form neutral complexes that are preferentially dissolved by the organic phase:



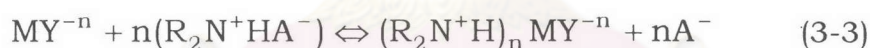
Here the overbar denotes species in the organic phase. The above equation describes a cation exchange reaction wherein hydrogen ions are exchanged for the metal cation, so the degree of extraction of metal ions depends on the pH of the aqueous phase. The degree of extraction of the metal ions will also vary with nature of the metal.

Extractants of the acidic type which have been found useful, or promising, as metal extractants in commercial operations are organic derivatives of phosphorous acids and monocarboxylic acids. Of these, alkylphosphoric acid have proven to be the most versatile, especially di-2-ethylhexyl phosphoric acid (D2EHPA). Some particular advantages of the use of D2EHPA in solvent extraction processing are its chemical stability; generally good kinetics of extraction; good loading and stripping characteristics; low solubility in the aqueous phase; versatility in the extraction of many metals including uranium, cobalt, and nickel, rare earths, and vanadium; and its availability in commercial quantities.

Chelating extractants are those which contain donor groups capable of forming bidentate complexes with metal ions. Commercially available chelating extractants are, at present, limited to two types: (a) a series of substituted 2-hydroxy benzophenone oximes produced by Henkel Corporation (General Mill Inc.) under the name LIX reagents, the Acorga reagents by Imperial Chemical, and the SME extractants of Shell

Chemical; and (b) the substituted 8-hydroxyquinoline produced by Sherex (Ashland Chemical Company) and marketed under the name Kelex. The general properties and extraction mechanism of these acid extractants have been reviewed by Ashbrook, Flett, Danesi, Whewell, Hudson, Preston and Ritcey et al. and will not be repeated here.

Basic Extractants Basic extractants (anion exchangers) are organic reagents which can easily form a salt while in contact with an aqueous acid solution. In commercial solvent extraction processing basic extractants are limited to amines and quaternary ammonium halides. Processes have been developed which employ primary (RNH_2), secondary (R_2NR), tertiary (R_3N) amines and quaternary ammonium salts (R_4N^+). The usefulness of amines as extractants is usually considered to depend essentially on the ability of metal ions to form anionic species in the aqueous phase, which are extracted by amines in an anion-exchange process:



In order to achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with metal species:



that is, amine extracts an acid to form an amine salt or polar ion-salt, $R_3N^+HA^-$, in the organic phase. On contacting this solvent with an aqueous solution containing an ionic metal species, MY^{-n} , exchanges occur like equation (3-3). Thus the amine salt should be considered as being the extracting agent and not the free amine. One important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which depends on the properties of the diluent and the nature of ammonium cation and anion:



Third phase formation, that is the splitting of the organic phase into two parts, is common in these systems and occurs through solubilities problems relating to aggregation. this problem can be eliminated by addition of diluent modifiers such as long-chain aliphatic alcohols.

Another factor influencing metal extraction by amines is the nature of the carbon chain, and also the number of carbon atoms in the chain. Normally aliphatic amines are the best extractants. Amines, useful for solvent extraction purposes, are generally limited to these having molecule weight in the range 250 to about 600, normally between 250 and 400. Those with molecular weights of about 250 tend to be too soluble in water, and those of about 600 are generally too insoluble in the organic phase. Extraction systems of basic extractants and their extraction mechanism have been recently reviewed by Ritcey, Flett, Cox, Hudson, Danesi, and Miller et al. and will not be expounded upon here.

Solvating Extractants or neutral extractants are organic reagents that possess only donor groups that do not dissociating protons. Since no anionic or cationic groups are available in the molecule, the metal species are extracted from the water phase as neutral complex. The neutralizing ion is a water soluble negatively charged ligand. the extent of extraction by solvating extractants depends on the extent of complex formation in the aqueous phase, as in the case of the basic extractants. Extraction is by solvation of either the central metal atom of the complex or the proton in the case of formation of a complex acid species:



or



where S is a solvating agent. The solubility of inorganic species in the organic phase is increased by means of this solvation.

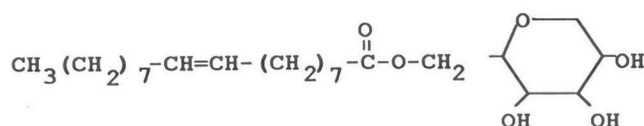
Surfactants

The surfactant is the key component for forming a stable emulsion. In emulsion liquid membranes, the overwhelming majority involves W/O/W double emulsion systems. But as membranes have become commercialized, their industrial applications have required more of the surfactants than their major contribution to membrane stability. An ideal surfactant should possess the following properties :

1. It carries virtually no water during operation so as to alleviate osmotic swelling.
2. It does not react with the extractant in the membrane phase ; if any, the reaction should promote the extraction process rather than catalyze the decomposition of the extractant.
3. It has a low interfacial resistance to mass transfer .
4. It does not inhibit demulsification.
5. It is soluble in the membrane phase but insoluble in the external and internal phase.
6. It is stable against acids , bases , and bacteria.

In addition , the selected surfactant should be cheap and nontoxic for economic and environmental considerations.

SPAN 80 (Sorbitan monooleate) is a nonionic surfactant with a molecular weight of 428. Its structure is :



Diluents

The diluent is the main membrane component in which both extractant and surfactant are dissolved. Although the diluent is normally regarded as an "inert" component, it does affect the membrane properties, such as distribution coefficient and diffusion coefficient, and can have significant impact on the effectiveness of the membrane system. From the viewpoint of industrial application, an ideal diluent should;

1. Have low solubility in the internal and external aqueous phase so as to minimize the solvent loss.
2. Be compatible with extractant and surfactant without the formation of new phases.
3. Have a moderate viscosity (In solvent extraction , an as-low-as possible viscosity is desired for the diluent for fast mass transfer. For emulsion liquid membranes, however, a much lowered diluent viscosity would reduce the membrane strength, resulting in membrane instability.)
4. Have a sufficient density difference from the aqueous phase for the fast settling operation.
5. Be both cheap and readily available from a number of alternative sources.
6. Have low toxicity and a high flash point for safety reasons.

Based on the above considerations, aliphatic diluents are generally preferred to aromatic diluents because the aliphatic diluents usually can meet most of the above mentioned requirements.

Emulsion Preparation

To prepare a stable emulsion, the mean diameter of the dispersed internal droplets should be as small as 1 to 3 μm , which requires a high input of energy density to the water-oil system for emulsification. In laboratory studies, emulsions are usually made by high speed agitators with stirring rates up to 20,000 rpm.

Dispersion/Extraction/Settling

The separation for an emulsion liquid membrane process includes dispersion, by which the coupled extraction/stripping is achieved, and settling, which realizes the phase separation between the loaded emulsion and the aqueous raffinate because of their density difference. Before dispersing the emulsion into the feed, the pretreatment of the feed is required as in most separation processes. The pretreatment is typically done by the use of 1-10 μm filters, and it sometimes includes flocculation and sedimentation steps before filtration. During the dispersion operation, the emulsion is dispersed by agitation in the external phase and many small globules of emulsion are formed. Normally, the size of emulsion globules is controlled in the range of 0.1 to 2.0 mm in diameter. Each emulsion globule contains many tiny encapsulated droplets with a typically size of 1 to 3 μm in diameter. Such a large number of emulsion globules together with the numerous pre-encapsulated droplets provides large interfacial areas for both extraction and stripping. After the separation is completed, phase separation of the loaded emulsion from the external raffinate takes place in the settler. The settling is similar to that for conventional solvent extraction.

Demulsification

After liquid membrane extraction, the membrane phase must be recycled repeatedly, and the enriched internal phase is usually recovered. Therefore, demulsification of the loaded emulsion is unavoidable for the use of this separation process, although a few exceptions use this technology without breaking the emulsion in some special cases(Dines,1982).

Two principle approaches for the demulsification of the loaded emulsion are chemical and physical treatments. Chemical treatment involves the addition of a demulsifier to the emulsion. This method seems to be very effective. However, the added demulsifier will change the properties of the membrane phase and thus prohibit its reuse. In addition,

the recovery of the demulsifier by distillation is rather expensive. Therefore, chemical treatment is usually not suitable for breaking liquid membrane emulsions. Physical treatment methods include heating, centrifugation, ultrasonic, solvent dissolution, high shear, and the use of high voltage electrostatic fields.

Advantages and Disadvantages

Noppaporn Panich (1994) has summarized the advantages and disadvantages of emulsion liquid membranes as follows:

Advantages.

The main advantages of emulsion liquid membranes are summarized below:

1. Because of the small droplets size, the specific surface area of emulsion liquid membranes is very high, giving rise to very fast transfer rates.

2. Because the concentration difference is always maximized, the liquid membrane extraction is ideal for the separation of products that are in low concentration in fermentation broth (Boey et.al.,1987).

3. The solute can be simultaneously separated and concentrated by making the internal phase reagent is sufficiently concentrated and ensuring that the internal phase reagent is sufficient concentrated.

4. As mentioned above, in comparison to conventional solvent extraction, extraction and stripping can be carried out in one stage, hence reducing the equipment capacity and associated capital and running costs (Boey et.al.,1987).

5. With respect to reactive extraction, liquid membrane extraction is more economical as much smaller quantities of the expensive extractant are required.

6. Emulsion liquid membrane systems are based on liquid-liquid extraction technology. This technology has been shown that it can

easily scaled up to an industrial scale operation and a continuous process (Thien and Hatton, 1987; Likidis and Schuger, 1987).

7. Liquid membrane emulsion separations are little affected by solids which suggests application of this process as a primary separation step without the requirement of filtration (Thien and Hatton, 1988).

8. Unlike chromatographic separations, emulsion liquid membranes do not require any pre-treatment of the feed phase (Thien and Hatton, 1987).

Disadvantages

Besides the two disadvantages of emulsion liquid membrane, i.e., emulsion formation and breakage, there are two other phenomena associated with the operation of emulsion system that can have a detrimental effect on the overall separation.

Leakage

During solute extraction, some extracted solute can leak back into the external phase. Usually this is accompanied by leakage of the internal phase reagent which can then transform the solutes into a non-extractable form. This is primarily an emulsion formulation problem. The emulsion is designed so that it is stable under process conditions, but is also easy to break to recover the extracted solute. The degree of emulsion breakage is small, less than 2% occurs during the initial stages of extraction (Thien and Hatton, 1987).

Swelling

Emulsion swelling is a process by which water is transferred from the external droplet phase. The water transfer will: dilute the solute that has been concentrated in the internal droplets, reduce the driving force for solute extraction, make the membrane thinner (leading to a less stable emulsion), and change the rheological properties of the emulsion to cause difficulties in emulsion transport and phase separation.

The two types of emulsion swelling that can occur are osmotic swelling which is driven by differences in the osmotic pressure between the external and internal phases and swelling attributed to the entrainment of the external aqueous phase which due to the repeated coalescence and redispersion of emulsion globules during the dispersion operation.

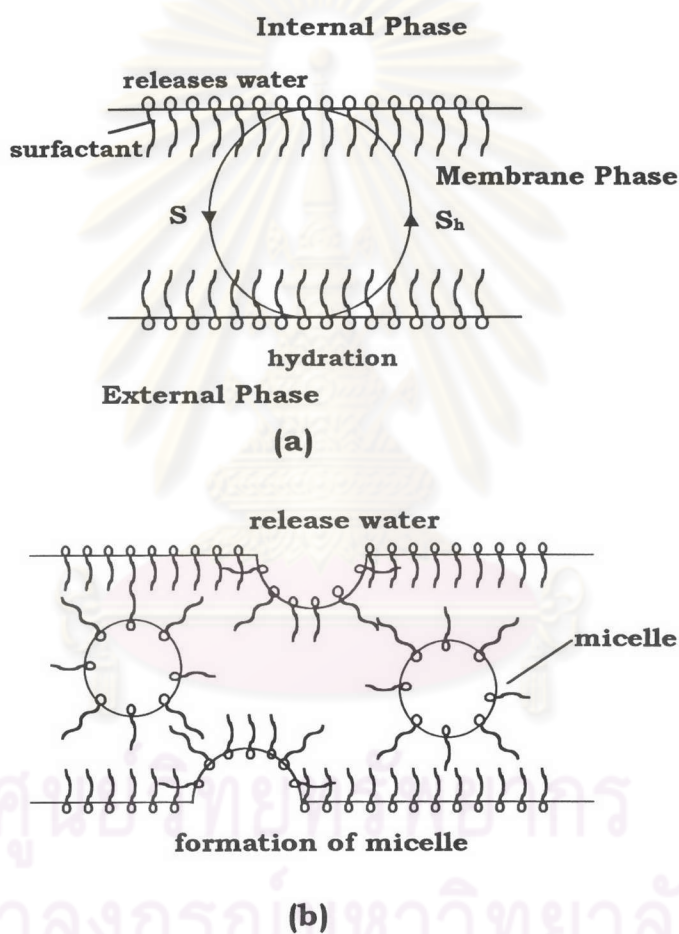


Figure 3-8. Schematic representation of water transport.

(a) Hydrated surfactant mechanism.

(b) Reversed micelle mechanism.

S: Non (or poorly) hydrated surfactant.

S_h: Hydrated surfactant.