CHAPTER III

THEORY

Liquid membrane technology has attracted increasing attention for its potential in the field of separations, and it has been demonstrated to be an effective tool in many applications such as resource recovery, pollutant removal and bioseparations. Liquid membrane extraction is a process for transporting a solute from a low concentration solution through a liquid membrane to a high concentration solution while maintaining high selectivity. An active chemical carrier is usually added into the liquid membrane to help the transport.

This chapter provides some background necessary for understanding liquid membrane extraction process.

3.1 Liquid Membrane Extraction Process

The liquid membrane is composed of three layers of liquid phase, i.e. feed phase, liquid membrane phase and stripping phase, respectively, shown in Figure 3.1. Thus, the system can perform extraction and stripping simultaneously. Consequently, the equilibrium limits on both interfaces are hardly achieved.

Figure 2.1 show a schematic example fo the separation of metal ions from aqueous solution in the most counter-transport through a membrane, wherein the overbar denotes the species in the organic phase. The direction of the interface reaction is controlled by the acidicity of the corresponding aqueous solution. The overall reaction at the interface is expressed by

$$M^{n+} + n\overline{RH} \Leftrightarrow \overline{MR_n} + nH^+$$

Where RH is a molecule of extractant.

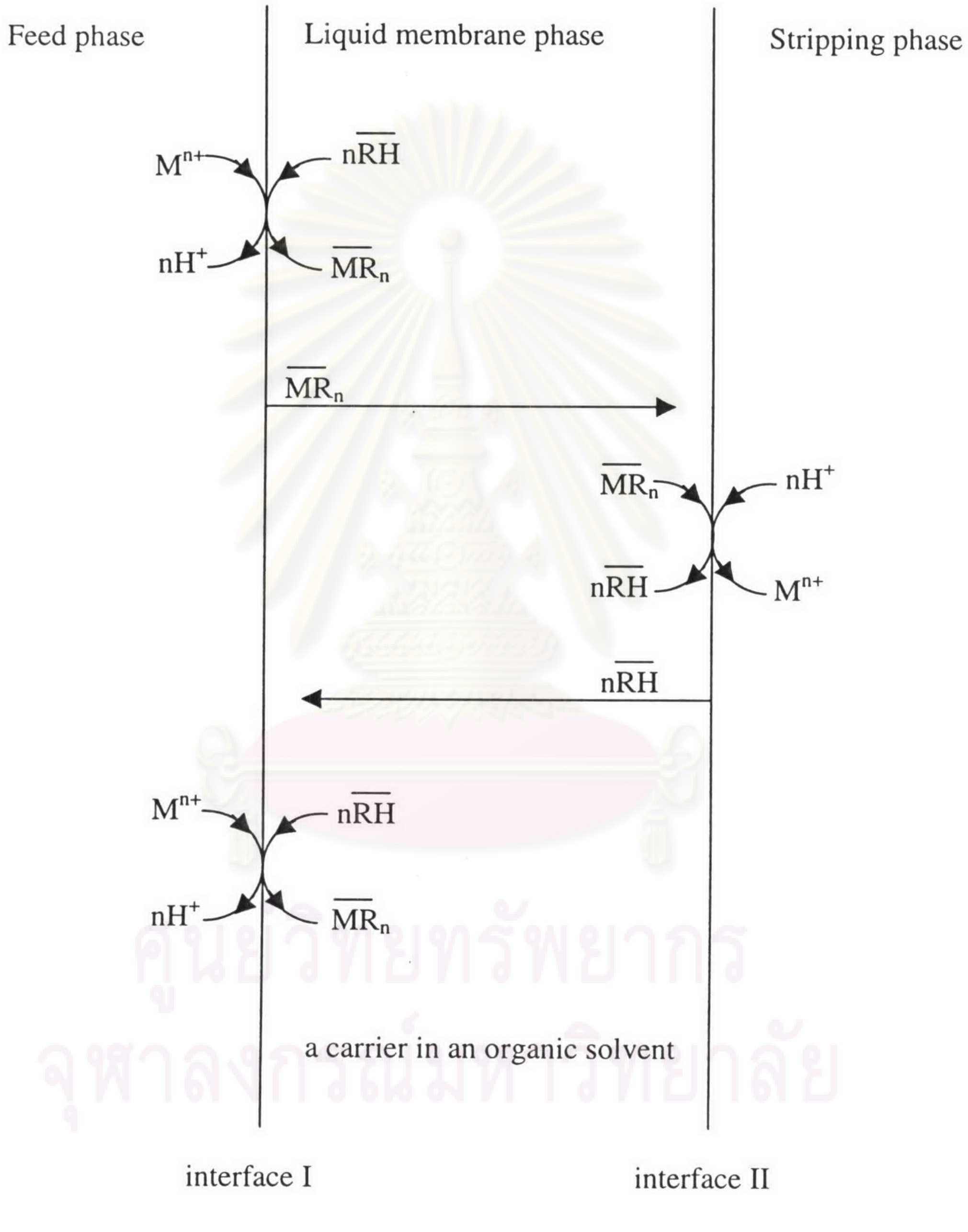


Figure 3.1 Schematic representation of mass transfer through a liquid membrane

The mechanisms of mass transfer in liquid membrane process can be described as the followings.

1. In the feed phase, a metal ion diffuses from bulk liquid to the liquid membrane surface (interface I), then reacs with the extractant forming a metal ion complex
2. Then the complex diffuses from interface I to interface II according to its concentration gradient
3. At the interface II, the state is suitable for the reverse reaction, then the complex is split into the metal ion and the extractant. The metal ion diffuses from the interface II to the stripping phase.
4. Then the extractant diffuses back to the interface I due to its concentration gradient and repeat phenomenon as mentioned abobe

3.2 Liquid Membrane Types

In general, liquid membrane are either unsupported or supported. Unsupported liquid membranes are in the form of double emulsion drops. While there are two generic types of membranes, five different setups have been studied in an effort to increase the efficiency of the entire liquid membrane operation. Liquid membrane setups compose of bulk liquid membrane, emulsion liquid membrane, thin sheet supported liquid membrane, hollow fiber supported liquid membrane and two hollow fiber supported liquid membrane.

3.2.1 Bulk Liquid Membrane

This setup is useful only for laboratory experiments, and is set up as follows. Following Figure 3.2, a U-tube cell is used, and some type of carrier, perhaps dissolved in CH_2Cl_2, is placed in the bottom of the tube. That is the organic membrane phase. Two aqueous phases are placed in the arms of the U-tube, floating on top of the organic membrane. With a magnetic stirrer rotating at fairly slow speeds, in the range of 100 to

300 rpm, the transported amounts of materials are determined by the concentrations in the stripping phase. Stability is maintained so long as the stirrer is not spinning too quickly.

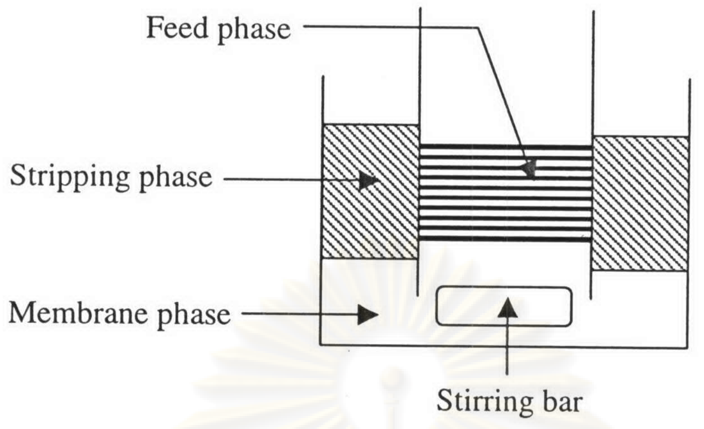


Figure 3.2 Bulk liquid membrane set up

3.2.2 Emulsion Liquid Membrane

An emulsion liquid membrane is a mobile liquid membrane that is composed of an internal phase and a membrane. When two immiscible solution are agitated by using a high homoginizer, emulsion are formed. But these emulsion are usually not stable. Therefore, in order to maintain the integrity of emulsion during the operation, these two immiscible phases are agitated with a selected surfactant that is usually known as an emulsifier (Marr and Kopp, 1982). Hence, this process is also call liquid surfactant membrane (LSM). Figure 1 illustrates an actual liquid membrane globule and simplified model that is useful foe discussion the principles of mass transfer. The aqueous phase that forms the emulsion with the membrane is called the encapsulated or internal phase.

The emulsion liquid membrane is still divided into two types(Ho and Li,1992); that is , a water-in-oil (abbreviated as W/O) emulsion if the encapsulated phase is an aqueous solution, and an oil-in-water(O/W) emulsion providing that the encapsulated phase is an organic solution. Once a W/O emulsion is dispersed in the other aqueous phase- the continuous phase, a system with the phase sequence of W/O/W is obtained. Analogously, from an O/W emulsion, an O/W/O system is obtained with the phase sequence of oil(I)-water(II)-oil(III). Thus, based on the two types of emulsion, there are two types of surfactant; that is a hydrophilic surfactant for O/W emulsions, and a hydrophobic surfactant for W/O emulsion.

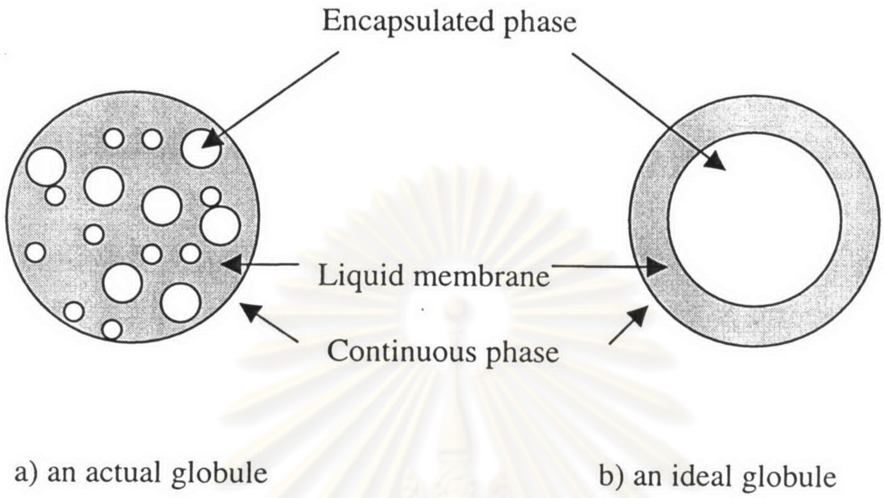


Figure 3.3 The illustrations of an emulsion liquid membrane: a) an actual globule, and b) an ideal globule

In an industrial process, the two phases forming emulsion are the strip solution and the organic solution containing an extractant. Then the emulsions dispersed in the feed phase from which the metal ions have to be removed. When the metal ions are extracted from the feed solution, the system is then settled in order to disengage the raffinate and the emulsion. The raffinate can be discharged instantly as the effluent while the emulsion which loads up with the metal ions has to be broken or demulsilied in order to reuse the organic solution and the recover the strip solution for future treatment. Finally, this system can produce the concentrated strip solution. However, the emulsion may swell during the operation leading to breaking of emulsion.

Typically, the encapsulated droplets in the emulsion are within 1 to 3 μm in diameter to provide a good stability during the extraction operation, and the size of emulsion globules is controlled in the range of 0.1-2.0 mm in diameter. The size depends strongly on the mode and the intensity of agitating, the viscosity of solutions which form emulsion, and the nature and concentration of the emulsifier. It is noted that the smaller the diameter, the larger the mass transfer area. Therefore, a rapid mass transfer in the emulsion liquid membrane process can be accomplished from either the external phase to the internal phase or vice versa.

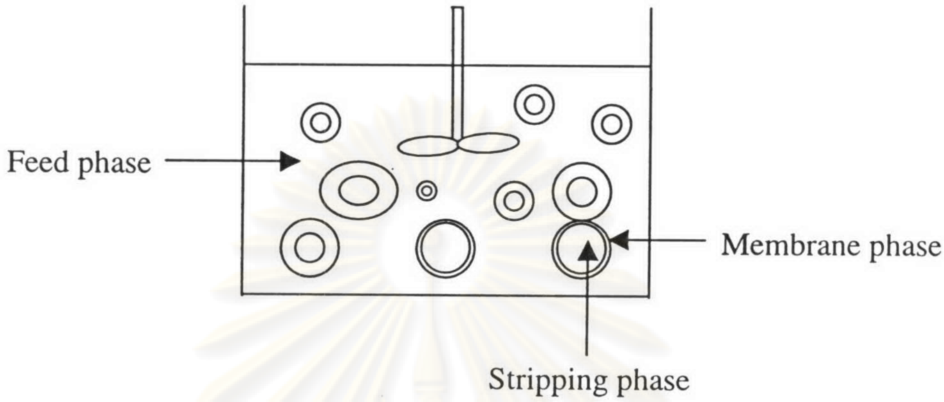


Figure 3.4 Emulsion liquid membrane set up

Although the emulsion liquid membrane process presents a novel approach for separation of dilute metal solutions, there are problems existing in this method. The addition of emulsifier result in the two additional procedures which make the process complicated, that is emulsification and demulsification (Gu, 1992). Moreover, the flux is lower due to the emulsifier formulation at the interfacial film. In spite of high the mass transfer area to volume ratio, the mass transfer from or to the encapsulated solution is limited due to the surfactant. One major problem is to break the emulsion after it is fully loaded up with metal ions to recover the internal phase for future treatment. The membrane solution is then re-emulsified with fresh strip solution and reused for extraction. There are two principal approaches for the demulsification of the loaded emulsion, which is chemical and physical treatment. The chemical treatment involves the addition of a demulsifier to the emulsion. The method seems to be very effective; nevertheless, the demulsifier added will change the properties of the membrane liquid and thus prohibit its reuse. The physical treatment usually involves the use of high-voltage electrostatic fields that is the most efficient, economic way for demulsification. However, the apparatus is rather complicated. The need for intermittent demulsifying and forming of the membrane is clearly disadvantageous. Any breakdown of the emulsion results in loss of organic and strips solutions and reduction of extraction efficiency.

Advantages and disadvantages of emulsion liquid membrane

The advantages of the emulsion liquid membrane can be listed as follows:

1. The specific surface area is very high, given rise to very fast transfer rate.
2. The liquid membrane extraction is ideal for the separation process because the concentration difference is always maximized.
3. The feed phase do not pre-treatment.
4. The emulsion Liquid membrane process is little affected by solids, which suggests application of this process as a primary separation step without the requirement of filtration.
5. In the emulsion liquid membrane process, extraction and stripping can be carried out in one stage therefore the capital and operating cost are reduced.
6. The emulsion liquid membrane process can easily scaled up to an industrial scale operation and/or a continuous process.
7. The emulsion liquid membrane extraction is more economical as much smaller quantities of expensive extraction are required.

Disadvantages

The emulsion liquid membrane has two main disadvantages that are leakage and swelling.

1. Leakage

Leakage is the emulsions break down from the external phase to the internal phase or opposite direction. 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.

2. Swelling

Swelling occurs in the emulsion liquid membrane due to water transport from the external phase to the internal phase. This causes swelling of the internal phase and subsequently dilution of the internal phase contents. Additionally, the apparent viscosity of the emulsion increases and can lead to the emulsion breakage.

3.2.3 Thin sheet Supported Liquid membrane

The most simplistic in design, the thin sheet supported liquid membrane can be utilized for laboratory scale, but cannot be scaled up for industrial use. Essentially, this is just a porous polymer membrane whose pores are filled with the organic liquid and carrier, set in between your source phase and your receiving phase, which are being gently stirred. See Figure 3.5.

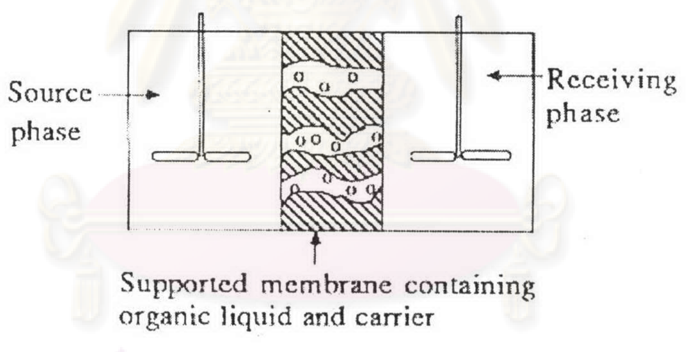


Figure 3.5 Thin sheet supported liquid membrane set up

In this system, can probably guess that the way to instability is to somehow get rid of the carrier or organic liquid in the pores of that supporting membrane. There are two possible ways for this to occur. One is through carrier or solvent evaporation, and the other is by creating a large pressure differential across the membrane, effectively pushing the fluid out.

3.2.4 Hollow Fiber Supported Liquid membrane

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 exists within a pore. The membrane separated an aqueous phase, initially containing the solute of interest, from another aqueous phase into which the solute is extracted, the stripping phase, as shown figure 3.6. Extraction occurs because of the difference in chemical potential (concentration) that exists between the two aqueous phases.

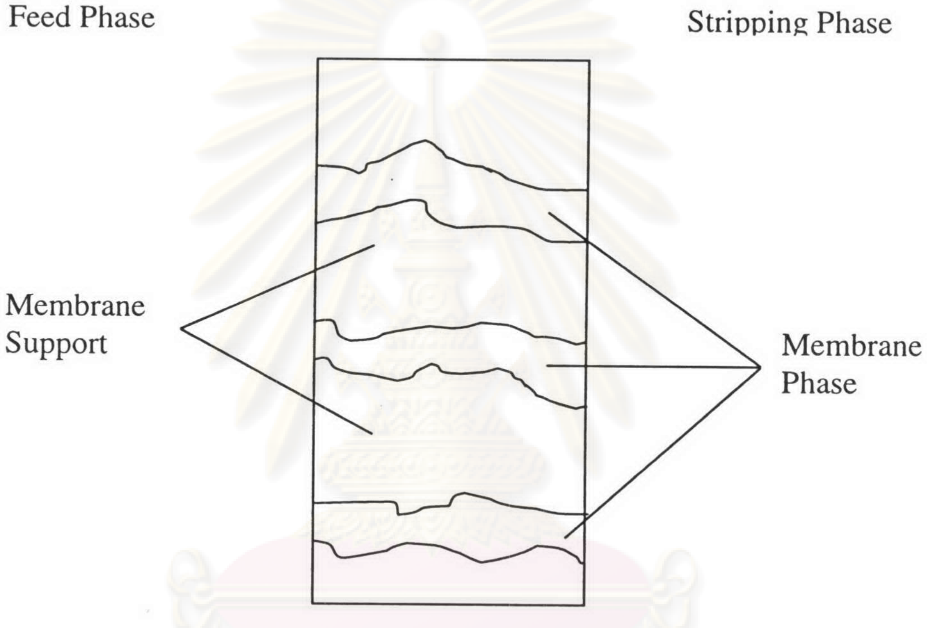


Figure 3.6 Schematic diagram of supported liquid membrane

The design of the hollow fiber supported liquid membrane is akin to a large electrical cable.Which is a single nonporous material, through which the materials inside cannot be transported. Inside that shell, there are many, many thin fibers running the length of the shell, all in nice, neat rows. What occurs is that the source phase is piped through the system from top to bottom, and the pores in the fibers themselves are filled with the organic phase. The carriers in that phase then transport the source across to the receiving phase, and then the receiving phase is forced out through the sides of the shell. Figure 3.7 represents this system.

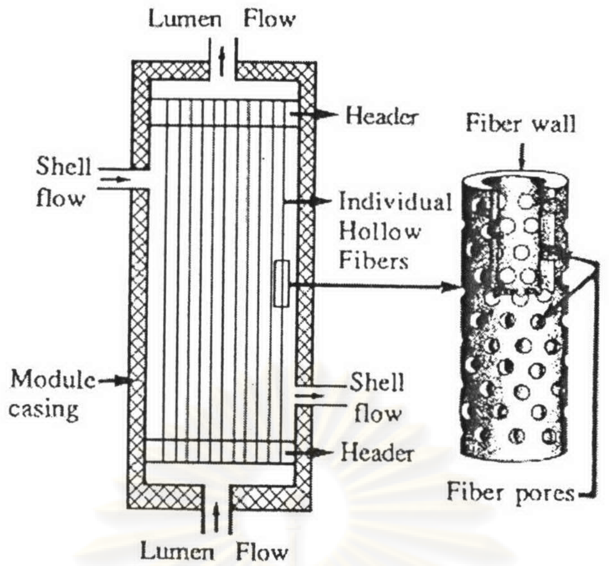


Figure 3.7 Hollow fiber supported liquid membrane

There are several inherent boons to using the hollow fiber system.

1. The surface area and membrane thickness provide rapid transportation.
2. The source/receiving phases are more easily recoverable than the emulsion system.
3. The entire source and receiving phase are not in contact with the membrane at any given instant.
4. Leakage and contamination are easily contained.

Likewise, there are a few problems associated with this system.

1. Very hydrophobic membrane solvents are required to maintain integrity.
2. Hollow Fiber System must be cleaned between uses or there will be aqueous and contaminant buildup.
3. Pore Fouling, a cousin to caking in filters, often occurs due to surface effects and particles in the system.
4. High Capital Costs.

The advantages and disadvantages of the supported liquid membrane compare to the emulsion liquid membrane.

The advantages

The advantages of the supported liquid membrane are:

1. no emulsification problem,
2. very small of the extractant,
3. low release of the extractant,
4. no surfactant,
5. no membrane instability,
6. suitable for the gas separation.

The disadvantages

The disadvantages of the supported liquid membrane are:

1. high cost for the supported material,
2. relative clean feed solution necessary,
3. chemical cleaning of the polymer membrane, necessary from time to time,
4. pressure loss for small hollow fiber diameters and high packing density.

3.2.5 Two Module Hollow Fiber Supported Liquid Membrane

In an effort to work around one of the problems found in the hollow fiber supported liquid membrane, researchers attempted another setup, one that looks something like the sketch in Figure 3.8. The way this works is that the source phase is piped in through one channel of hollow fibers, and the receiving phase in and out through another, with a stirred membrane phase in contact with both.

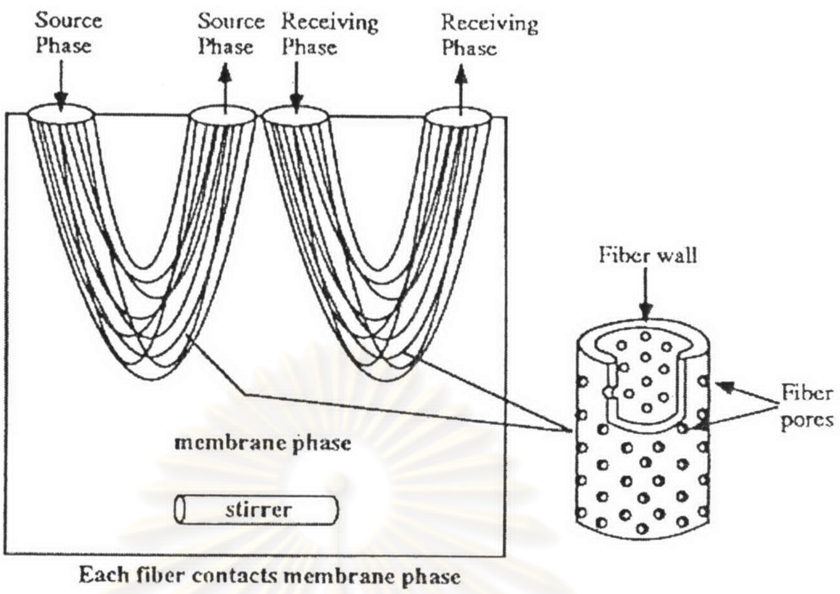


Figure 3. 8 Two modules hollow fiber supported liquid membrane

Advantages of two module hollow fiber supported liquid membrane are:

1. Solvents with lower hydrophobicities required
2. simple replacement of solvent and carrier
3. Relatively high transport rate
4. Leakage and contamination are easily contained.
5. Creation of a boundary layer slows system down as compared to either emulsion liquid membrane or hollow fiber supported liquid membrane

The disadvantages of two module hollow fiber supported liquid membrane are:

1. Transport rates dependant on amount of stirring of membrane phase
2. Fouling a problem
3. High Capital Costs

3.3 Mechanisms of Mass Transfer in Liquid Membrane Process

In a liquid membrane, mass transfer occurs in all three phases. In the feed phase, the solute transfers across the membrane interface, then diffuses through the membrane phase. At the interface between the stripping phase and the membrane phase, the solute transfer to the stripping phase. In supported liquid membrane, there are two principle mechanism of solute transport across the membrane phase as follow.

1. Counter-transport

The key feature of counter transport is that the flux of the two permeating ions moves counter to each other across the membrane. The solute is transported across the membrane by the formation of a complex and the driving force of the process is the different between the activities of the counter-ion in the feed phase and the stripping phase as follow.

(a) The solute A in the feed phase diffuses to an interface between the feed phase and membrane phase, and then reacts with the carrier complex BC, to form the complex AC, and liberated B in the feed phase. This complex is insoluble in either aqueous phase but is soluble in the membrane phase.
(b) The complex AC diffuses across the membrane to the interface with the stripping phase.
(c) At the interface with the stripping phase the reverse reaction occurs, brought about by a shift in the reaction equilibrium due to a higher concentration of the counter-ion B, in the stripping phase. Hence, the solute A diffuses to the stripping phase.
(d) The carrier reacts with the counter ion B form the carrier –counter ion complex BC, which then diffuses back through the membrane phase to an interface between membrane phase and feed phase where the counter-ion is released, hence completing the process.

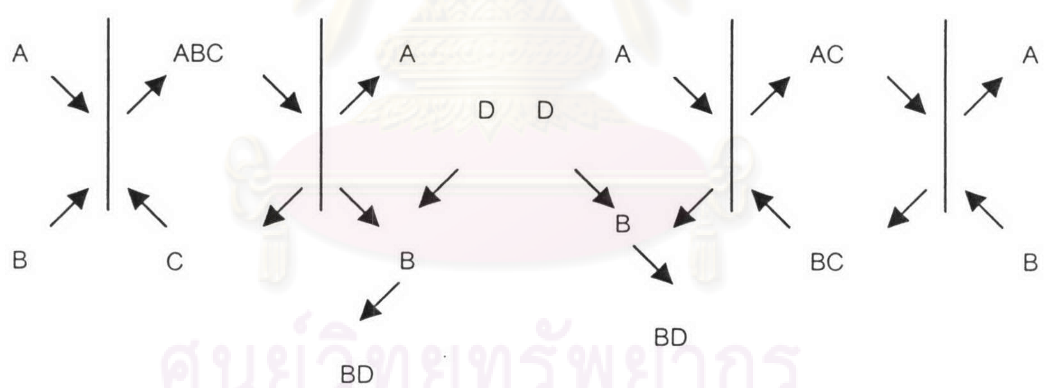
2. Co-transport

The key feature of co-transport is that the flux of the two permeating ions moves in the same direction across the membrane. This mechanism is less common than the counter transport. The mechanisms of this process are described as follow.

(a) The solute A and the co ion B in the feed phase diffuses to an interface between the feed phase and membrane phase, and then reacts with the carrier complex C, to form the complex ABC.

(b) The complex ABC diffuses across the membrane to the interface with the stripping phase. At this interface the reverse reaction occurs and then releases the solute A and the co ion B to the stripping phase and carrier C diffuses to the interface between feed phase and membrane phase.

(c) In the stripping phase, the co ion B reacts with D form the complex BD. This complex is insoluble in the membrane phase.



(a) Co-transport (b) Counter-transport

Figure 3.9 Mechanism of mass transfer in supported liquid membrane: (a) Co-transport and (b) Counter-transport.