CHAPTER 2

LITERATURE REVIEW

This chapter presents the literatures on liquid membranes that are of direct relevance to this work.

Liquid membranes are generally considered to be thin layers of liquid interposed between two fluid phases (gas-gas, gas-liquid, liquid-liquid). Liquid membranes can be classified according to the configuration of the membrane phase which can be either supported liquid membrane (SLM) or unsupported liquid membrane or emulsion liquid membrane (ELM). The supported liquid membrane has membrane area of 100-200 m^2/m^3 of equipment volume, whilst emulsion liquid membrane has surface areas of 1,000-3,000 m^2/m^3 (Marr and Kopp, 1982).

Supported Liquid Membrane (SLM).

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 (Takeuchi et al., 1987). 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 2.1.

Extraction occurs because of the difference in chemical potential (concentration) that exists between the two aqueous phases.

To obtain large interfacial areas for mass transfer, various types of supports have been used, i.e. ultrafiltration membrane cartridges, and semi-permeable membranes used in reversed osmosis. The most popular solid supports used are generally microporous polymeric films made of polypropylene , e.g. Celgard 2400 (Sugiura and Yamaguchi, 1983), polysulfone, or other hydrophobic materials. Typical dimensions are, a membrane thickness of 25-50 μm, with pore sizes between 0.02-1.0 μm (Danesi, 1984-1985).

Compared to emulsion liquid membrane, supported liquid membrane has an advantage in that there is no need for an emulsification and a demulsification stages. However, one of the main disadvantages is that SLM has a much lower specific surface area for

Feed Phase   **Stripping Phase**

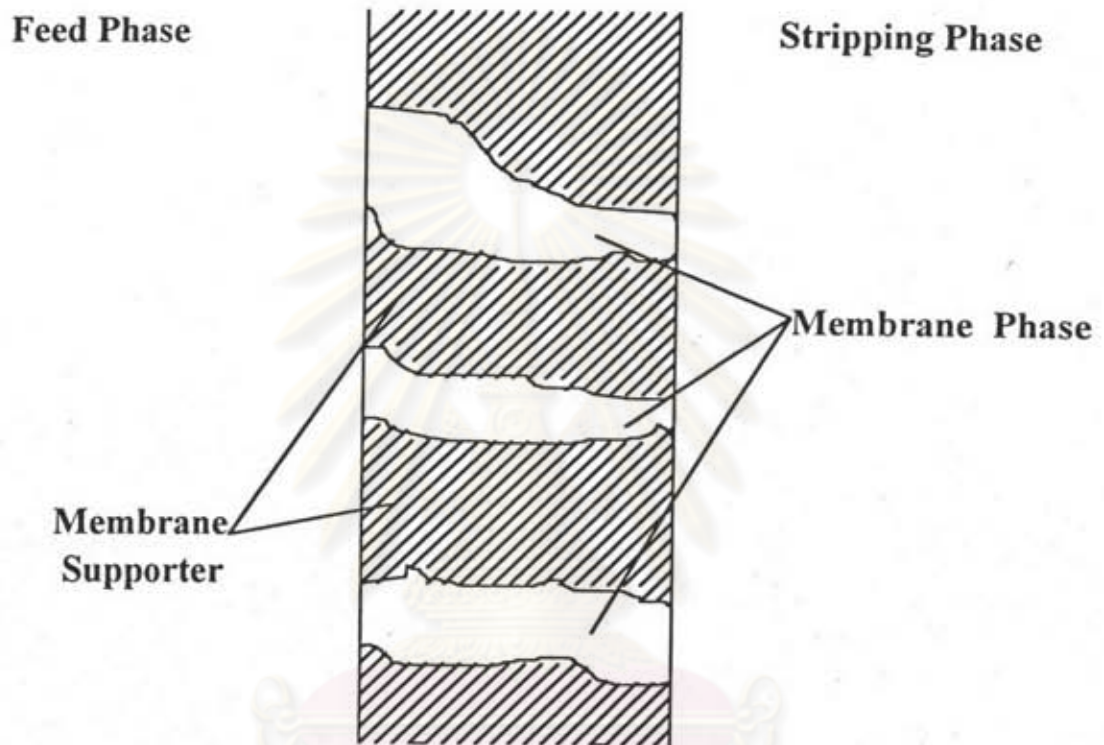Membrane Phase

Membrane
Supporter

Figure 2.1   Schematic Diagram of a Supported Liquid Membrane.

mass transfer and the membrane is much thicker. This requires a much larger equipment capacity in order to achieve the same separation. The other disadvantages include the necessity for frequent charging of the membrane liquid due to the washout of the immobilized membrane phase from the support pores (Danesi et. al., 1987) and also a low solute flux.

The advantages and disadvantages of SLM versus ELM are also summarized in table 2.1 (Lee, Evans and Cussler, 1978).

Table 2.1 Advantages and Disadvantages of SLM versus ELM.

Advantages	Disadvantages
1) Very small volume of organic phase and carrier.	1) Costs for the support material.
2) Favorable hydrodynamics, intensive mass transfer (without back mixing).	2) Pressure loss for small hollow fiber diameters and high packing densities.
3) Low release of organic phase to the aqueous feed solution.	3) Relatively clean feed solution necessary (otherwise pre-filtration occurs).
4) No surfactants.	4) Chemical cleaning of the polymer membrane, necessary from time to time.
5) No membrane instability.	5) The interface tension between the liquid membrane and the aqueous feed solution must be higher than 15 nM/m.
6) Selective re-extraction possible.	
7) Suitable for the separation of gases.	

The use of supported liquid membrane has mainly been applied to the separation of metal ions. Further details on this application can be found in work by Danesi (1984-1985, 1987), Danesi and Rickert (1986). Other species separated by supported liquid membrane include phenol and acetic acid (Sengupta et. al., 1988), and amino acids (Molinari, Bartolo and Drioli ,1992; Deblay, Minier and Reron ,1990).

Emulsion Liquid Membrane (ELM).

1. <u>General Description of Emulsion Liquid Membrane.</u>

The emulsion liquid membrane process has been used for about 25 years since first developed by Li in 1968. There are two types of emulsion liquid membrane systems water/oil/water (w/o/w) and oil/water/ oil (o/w/o). The emulsion liquid membrane system consists of three phases. In case of w/o/w system, the oil phase act like a membrane between the internal aqueous phase and the external aqueous phase. The external phase is the feed solution and the internal phase is the concentrated product solution.

In order to form an emulsion liquid membrane, the internal phase is emulsified at a high shear into a solvent or membrane phase, typically, the resulting emulsion has a mean internal phase droplet diameter of 1-10 μm. It is stabilized by addition of a surfactant to the organic phase. After emulsification, the emulsion is dispersed into the continuous external phase under mild agitation, forming a dispersion of 0.1-2 mm in diameter, the size depends on physical properties of the continuous and dispersed-phases and agitation speed.

As shown in Figure 2.2, the ELM system consists of three phases (Itoh et.al., 1990),

a) an internal phase (water phase) which is encapsulated by a membrane phase,

b) a membrane phase (oil phase) which forms a w/o (water in oil) emulsion with the internal phase, and

c) an external phase (continuous phase) in which the emulsion globules are dispersed. As a result, an emulsion in water dispersion is formed and the internal phase never directly contacts the external phase.

A solute of interest can be transported from the external aqueous phase to the internal phase by one of several mechanisms depending on chemical nature of the solute including facilitated transport and simple diffusional transport. Different solutes have different
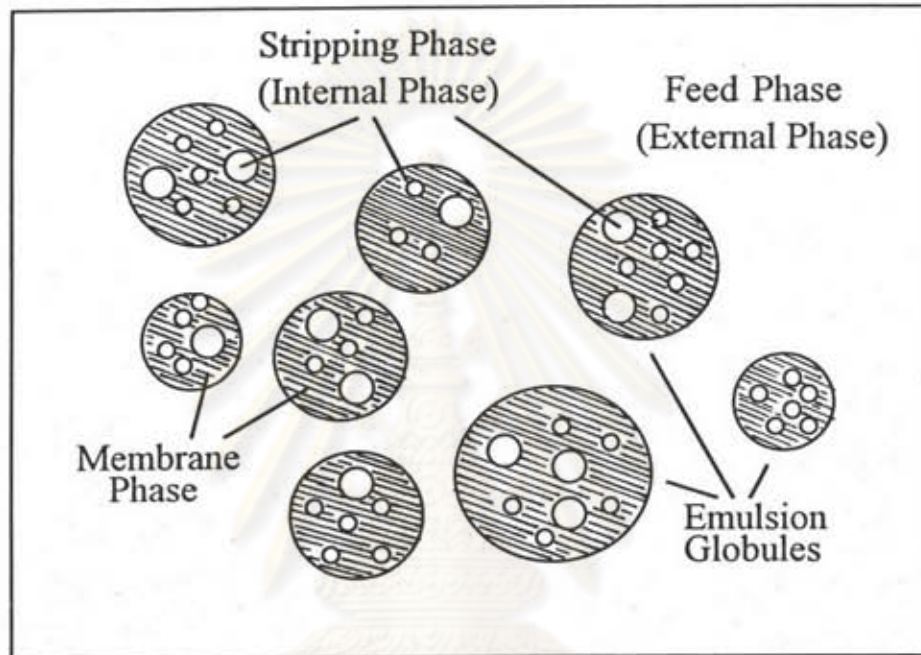
Figure 2.2 Schematic Diagram of an Emulsion Liquid Membrane.

solubilities and diffusion coefficients in the membrane.

2. Mechanisms of Mass Transfer.

In a liquid membrane process, mass transfer occurs in all three phases. In the external phase, the solute transfers across the membrane interface, then diffuses through the membrane phases. At the interface with the internal phase, the solute transfers into the small droplets of the internal phase. There are two principle mechanism of solute transport across the membrane phase (Chan and Lee, 1984) as follows:

2.1 Type I Transport.

This is the simple diffusion process in which the solute partitions into the membrane phase from the external phase, diffuses across the membrane to the dispersed interior phase droplets, and partitions into the interior phase. A reaction takes place in the internal phase which converts the solute into a species which is incapable of partitioning back into the membrane phase.

Thien et.al. (1986) pointed out that Type I Transport is applicable to uncharged solutes only, since only uncharged solutes are able to favorable partition into the membrane phase.

Removal of phenol from aqueous streams is a good example of Typed I Transport. Phenol diffuses into the organic (membrane phase) due to its solubility in this phase. At the membrane phase/internal phase interface, sodium hydroxide in the encapsulated internal phase droplets reacts with phenol to form sodium phenolate, which is impermeable in the organic phase. Since at this interface, the concentration of phenol is then effectively zero, maximum concentration gradient for phenol flux across the membrane is maintained.

The extraction of the desired solute relies entirely on its solubility or permeability in the membrane phase. Selective separations are very difficult for solutes of similar size or chemical properties. Solute diffusivity in the membrane phase and membrane viscosity are important parameters affecting the rate of extraction.

2.2 Type II or Facilitated Transport.

This transport mechanism is applied for membrane- insoluble

materials, such as charged species, e.g. metal ions., organic acids and zwitterions. This mechanism is commonly known as carrier-mediated transport. By introducing a 'carrier' molecule into the membrane phase, the solute solubility is increased by the reversible formation of a membrane-soluble carrier-solute complex. This results in faster mass transfer rates, the carrier must be insoluble in aqueous phase and be specific for the solute of interest.

There are two possible ways in which mobile carriers can work.

1) Counter-transport mechanism.

The solute is transported across the membrane by the formation of a complex and the driving force of the process is the difference between the activities of the counter-ion in the internal and external phase as follows (Lorbach and Marr, 1987):

(a) At an interface between the external phase and membrane phase, the solute A, reacts with the carrier complex BC, to form the complex AC, and liberates B in the external phase. This complex is insoluble in either aqueous phase but is soluble in the membrane phase.

(b) The carrier-solute complex (AC) diffuses across the membrane to an interface with the internal phase.

(c) At an 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 B, in the internal phase. Hence, the solute A is released into the internal phase droplets. The counter-ion is usually the non-reacting ion from the internal phase reagent.

(d) The carrier reacts with the counter-ion to form the carrier- counter ion complex BC, which then diffuses back through the membrane to an exterior interface where the counter-ion is released, hence completing the process.

2) Co-transport mechanism.

This mechanism is less common than the counter-transport one. It 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. The free carrier then diffuses back
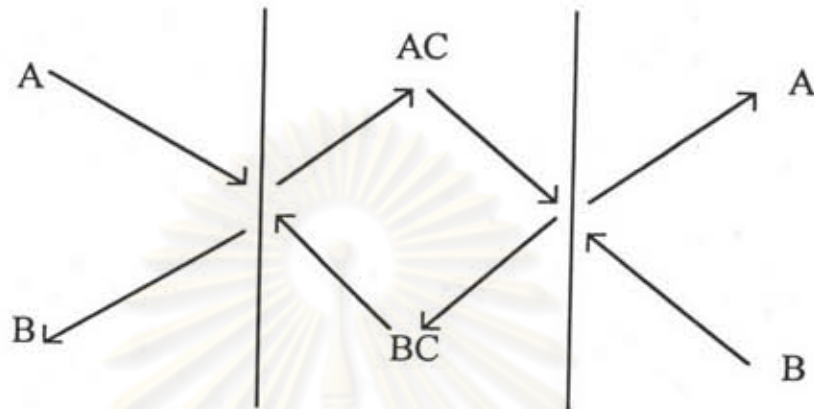
Figure 2.3 Counter-Transport of Solute A by the Carrier C.
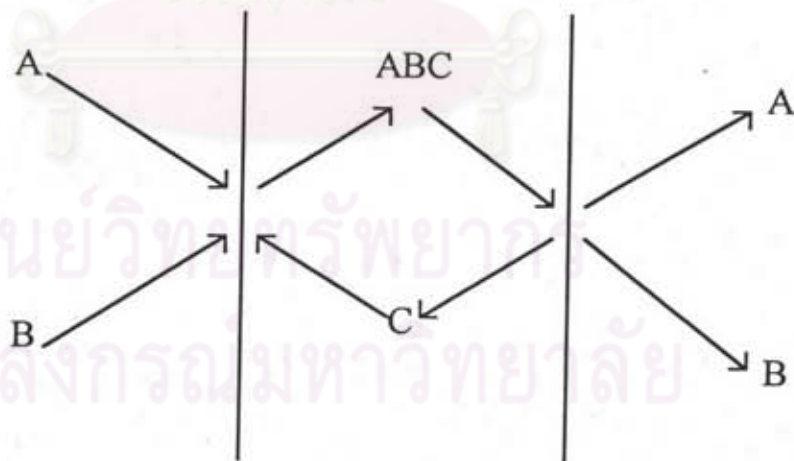

Figure 2.4 Co-Transport of Solute A and B by the Carrier C.

across the membrane. Therefore, two coupled fluxes exist across the membrane in the same direction (Cussler, 1986).

3. Process Consideration.

The effectiveness of emulsion liquid membranes relies on the formulation and preparation of emulsions with good extractive properties and stability. Such characteristics can be achieved by careful selection of membrane solvent, surfactant, carrier and stripping agents.

3.1 Choice of Membrane Phase Components.

Generally, the membrane phase is made up of three components: membrane solvent, surfactant and carrier species.

(a) Membrane Solvent.

In case of water in oil emulsion, the membrane solvent shall be an organic solvent. In principle, any organic solvent can be used to prepare water in oil emulsions. However, the long chain aliphatic hydrocarbon and alcohols are preferred because of their low toxicity particularly if the extracted solute is to be marketed as a consumable product (Dadgar and Foutch, 1985).

(b) Surfactant.

Surfactant is a major contributor to stabilization of the emulsion. Surface active agents reduce the interfacial tension between an organic and an aqueous phase, therefore reducing the energy required to disperse one into the other. Surfactants are characterized on the basis of the hydrophilic/ lipophilic balance of the molecule or HLB scale. On this scale, species with high hydrophilic character and which are good oil in water emulsifiers, are assigned high HLB values. In order to get water in oil emulsions, surfactants with a low HLB are generally chosen. In this work the non-ionic surfactant Span 80 (sorbitan monoleate) which has a HLB value of 4.3, was used. Span 80 has been widely used to form water in oil emulsion in liquid membrane research because the HLB value is close to the optimum HLB value of 5.0 for a water in oil emulsifier (Boey et. al., 1987; Draxler, and Marr, 1986).

(c) Carrier Species.

A carrier is incorporated in the membrane phase for Type II or Facilitated Transport. Solutes that are insoluble or only slightly soluble in the membrane phase can be solubilised by forming complexes, salts, or ion pairs with the carriers. There are two classes of carrier molecule, charged and uncharged, but common criteria for both are that the carrier and its complexes must be insoluble in the aqueous phase.

Examples of carrier that have been used in biochemical systems are shown in table 2.2.

Table 2.2 Examples of Carriers Used in Liquid MembraneExtraction.

Carrier	Solute	Reference
Alamine 336 (a mixture of trioctyl and tridecyl amine)	Citric acid	Boey, Garcia Del Cerro, and Pyle, 1987.
	Lactic acid	Scholler, Chaudhuri, and Pyle, 1993.
Aliquat 336 (Quaternary ammonium salt)	L-phenylalanine	Thien, Hatton, and Wang, 1986.
D2EHPA [di-(2-ethylhexyl) phosphoric acid]	L-phenylalanine	Itoh et. al., 1990.
	L-tryptophane L-phenylalanine	Teramoto et. al., 1991.

3.2 Choice of Internal Phase Reagent.

An acidic or alkaline solution is usually the internal phase reagent. The capacity of the internal phase for the solutes to be extracted depends on the initial concentration of such reagents.

4. Advantages and Disadvantages of Emulsion Liquid Membranes.

Chandhuri (1990) has summarized the advantages and disadvantages of emulsion liquid membranes as follows:

4.1 Advantages.

The main advantages of emulsion liquid membranes are summarized below:

1) Because of the small droplet sizes, 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, liquid membrane extraction is ideal for the separation of products that are in low concentration in fermentation broths (Boey et. al., 1987).

3) The solute can be simultaneously separated and concentrated by:

(a) Making the internal phase volume smaller than that of the external phase.

(b) Ensuring that the internal phase reagent is sufficiently 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 /or 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 et. al., 1988).

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

4.2 Disadvantages.

Besides the two disadvantages of ELM ,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.

1) Leakage.

During solute extraction, some of the 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).

2) Swelling.

Water transport can occur from the external phase into 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. Significant swelling was observed during the separation of L-phenylalanine and it was shown that the water transport was caused by a hydration of L-phenylalanine as well as mediated by the surfactant (Itoh et. al., 1990).

5. Liquid Membranes in Bio-separation Process.

The purpose of this section is to summarize the current state of the application of emulsion liquid membrane in particular to the extraction of bio-products such as organic acids and amino acids.

5.1 Organic Acids.

Boey et. al.(1987) reported the extraction of citric acid by emulsion liquid membrane. The liquid membrane consists of Alanine 336 and Span 80 dissolved in Shellol A and sodium carbonate solutions were used as the internal stripping agent. Batch extraction of both model and real fermentation broths were studied. The results show that very fast extraction of citric acid can be achieved. Over 80% of a 5% (w/v) citric acid solution was removed in under 5 minutes. Experiment with 4.5% citric acid in fermentation broths showed a similar extraction profile. Significant emulsion swelling was also observed. The volume of the internal phase was more than doubled.

Various parameters of lactic acid separation from fermentation broths by emulsion liquid membrane have been optimized by the study of Reisinger and Marr (1992). Using these parameters, lactic acid can be separated up to 90%, concentrated up to 3 times and cleared of most of its by-products. Only about 1% of glucose and amino acids is permeated together with the lactic acid. With these parameters, not only lactic acid but also other monocarboxylic acids can be separated.

Scholler et. al. (1993) reported the studies on the batch extraction of lactic acid by emulsion liquid membrane. The membrane phase consists of the tertiary amine carrier, Alanine 336 and the surfactant Span 80 dissolved in n-heptane/paraffin and aqueous solutions of sodium carbonate in the internal phase. The effects of internal phase reagent, extraction temperature, and initial external phase pH on the extraction efficiency and the emulsion swelling are examined. The extraction efficiency from the fermentation broth is found to be lower as compared to aqueous solutions of pure lactic acid.

5.2 Amino Acids.

The extraction of phenylalanine by emulsion liquid membrane was carried out by Thien et. al. (1986, 1988). In this study, the membrane phase consisted of a paraffinic solvent (Solvent 100 Neutral, Exxon Chemical Company), a nonionic emulsion stabilizing surfactant (Paranox 100, Exxon Chemical Company), an anionic "carrier" of tri-capryl quaternary ammonium salt (Aliquat 336, Henkel Corporation), and a co-surfactant for the carrier molecule (decyl alcohol, Sigma Chemical). The internal phase was the basic solution of 2.0 M

KCl at pH 11. They assessed the effects of various experimental parameters on the separation of phenylalanine. Itoh et. al. (1990a, 1990b) reported the study on extraction of phenylalanine by emulsion liquid membrane. In this case the membrane was not the same as the previous study. A carrier in the membrane phase was changed to cationic carrier, D2EHPA , with Telura 619 as a paraffinic solvent and Paranox 100 as an emulsion-stabilizing surfactant. The internal phase was acidic solution of 1.6 M HCl. The main reason for using cationic carrier was that in the application of an anionic carrier for the separation of phenylalanine the removal of cells from the fermentation broth might be necessary. The surface of the micro-organisms are usually negatively changed and could result in the fouling of the membrane interface. In addition, organic acids are often seen in fermentation broth as impurities and could be transported in competition with Phe. Cation carrier thus seen to be preferable.

Teramoto et. al. (1991) reported the study of extraction of phenyalanine, tryptophan, B-phenethylamine and tryptophan methyl ester by emulsion liquid membrane containing D2EHPA as a carrier. The organic liquid membrane solution consisted of n-dodecane, D2EHPA, and an emulsifier CR-500 which is the condensation product of polyglycerol and polyricinoleic acid was used as an emulsifier. Span 80 was also used in some experiments. Experimental results on the extraction of tryptophane phenyalanine and B-phenethylamine were satisfactory simulated by the proposed permeation model.