CHAPTER 2

LITERATURE REVIEW

Liquid membranes are the thin layers of liquid interposed between two fluid phase. By configuration of the membrane phase can be classified liquid membrane process into two types: supported liquid membrane and emulsion liquid membrane. 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 emulsion liquid membrane system consist of three phases which the membrane phase will formed an emulsion that dispersing in the external phase while extraction occur. The major advantage of an emulsion liquid membrane has a much higher specific area for mass transfer.

Since Li 's pioneering studies in 1968 on liquid membrane extraction as an alternative to solvent extraction. There has been many studies on fundamental and applied aspects of the technology. The liquid membrane process was developed, first using emulsion, and applied to hydrometallergy, oil recovery, waste water treatment and, biomedical engineering; new applications in biotechnology are reported and concern whole cell or enzymatic encapsulation and enzymatic hydrolysis (P.Deblay et al., 1989)

Whereas those studying the use of liquid emulsion membranes for metal recovery as well as the studies of Terry et.al. focused on the separation of solute from dilute streams, Thein et.al. pointed out that the economic use of liquid emulsion

membranes as a biochemical downstream processing operation requires not only separation of the effects of the following process parameters on separation and concentration; agitation speed, initial internal chloride concentration, carrier and surfactant concentration, the presence of completing ions in the external phase, the chemical nature of the counterion, and the chemical nature of the solute.

General Applications

Draxler, Furst, and Marr (1989) review the applications of emulsion liquid membranes for the separation of metal ions in a pilot plant. As can be seen in Table 2-1, zinc, copper, cadmium and lead can easily be separated down to concentrations which are below the limits of most environment protection agencies.

Table 2-1 Separation of Various Metals in a Pilot Plant.

Element	Throughput (l / hr)	Initial concentration (mg / l)	Final concentration (mg / l)
Zinc	30	4500	4
Zinc	30	500	0.8
Zinc	70	150	0.5
Copper	20	8000	27
Copper	40	800	3
Nickel	20	2200	360
Cadmium	60	14	0.01
Lead	60	8	0.01
Chromium	40	1500	4

A very detailed review of the applications of liquid membranes has been given by Frankenfeld and Li (1987). This review includes the use of emulsion liquid membranes for the removal of toxic substances from waste water, separations in hydrometallurgy and as heterogeneous catalysts. The use of emulsion liquid membranes in water treatment was reported by Li and Shier (1972), who focused on phenol removal.

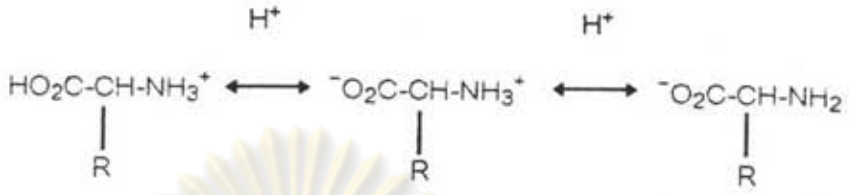
R.E.,Terry, N.N.,Li, and W.S.,HO (1982) focused on the separation of phenols and cresols from wastewater. In addition to being able to separate these contaminants from wastewater, they also found that Unfacilitated Transport liquid emulsion membrane (simple diffusion) could also be used for the separation of acetic and propionic acids. Then study indicated that liquid emulsion membranes were particularly good at separating acetic acid from dilute solutions.

Bioseparation Applications

M.P. Thien and T.A. Hatton (1988) discussed the potential for liquid emulsion membrane system in biochemical applications and their advantages over conventional systems. Examples are cited where liquid emulsion membrane has been used to successfully separate organic acids, amino acids, and antibiotics. Liquid emulsion membrane used for immobilize cells and enzyme to synthesize antibiotics and amino acid as well as decontaminate biology waste streams.

An application of liquid emulsion membranes to biochemical separations has been the separation of biochemical zwitterions from fermentation broth. A zwitterion is a compound possessing both a positive and a negative functional group at neutral

pH. Typically, as in the case of amino acids these functional groups are ionizable and can vary in charge as a function of pH:



Several important categories of biochemical can be classified as zwittrions: phospholipid, aminoacids, and β-lactam antibiotics. Due to the overpresent charge on these compounds, their solubility is greatly decreased in conventional organic solvents; traditional solvent extraction cannot be used to recover these small bioproducts from fermentation broth. As an alternative to the currently used techniques of derivitization followed by extraction or ion exchange, liquid emulsion membranes have been examined for the economical recovery of these compounds from fermentation broth.

While carrier-facilitated transport of amino acids across buoyant liquid membranes was first investigated, the first detailed study of amino acid transport in liquid emulsion membranes was carried out by Thein et.al. who examined the separation and concentration of L-phenylalanine in a liquid emulsion membrane system.

1. Organic Acids

Terry et.al. (1982) have reported the extraction of acetic and propionic acids using emulsion liquid membranes. Both acids can be produced by bacterial fermentation. This work was concerned with the removal of contaminants from waste water, and shows that these solutes can be removed from aqueous solutions.

The recovery of citric acid has been studied by Boey et.al. (1987). The emulsion liquid membrane consists of Alamine 336 and Span 80 dissolved in Shellsol A. Sodium carbonate was used as the internal phase reagent. This work looked at the batch extraction of both model and real fermentation broth. 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 of 4.5% citric acid from fermentation broth showed the similar extraction profile. Significant emulsion swelling was also observed in this study, the volume of the internal phase was more than doubled.

2. Amino Acids

The extraction of phenylalanine using emulsion liquid membrane was carried out by Thien et.al.(1986;1988). In this study, the carrier used was Aliquat 336 (anionic carrier of tri-capryl quateryammonium salt), in Solvent 100N (paraffinic solvent), established by the surfactant Paranox 100 (nonionic emulsion stabilizing) and decyl alcohol (co-surfactant for the carrier molecule). The internal phase was the 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.(1990) studied the separation of phenylalanine by emulsion liquid membrane. In this case the membrane was not the same as Thien et.al.'s 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 1.6M 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 microorganisms are usually negatively changed and could result in the fouling of the membrane interface.

Boyadzhiev and Atanassova (1991) have been explored the possibility of L-lysine recovery from its dilute aqueous solutions applying a liquid membrane and studied the transport mechanism of the three-phases liquid system. They used 5% (v/v) D2EHPA as an a cationic carrier and used n-decane as an intermediate. The extraction occurs in the two compartment glass cell as shown in figure 2-1.

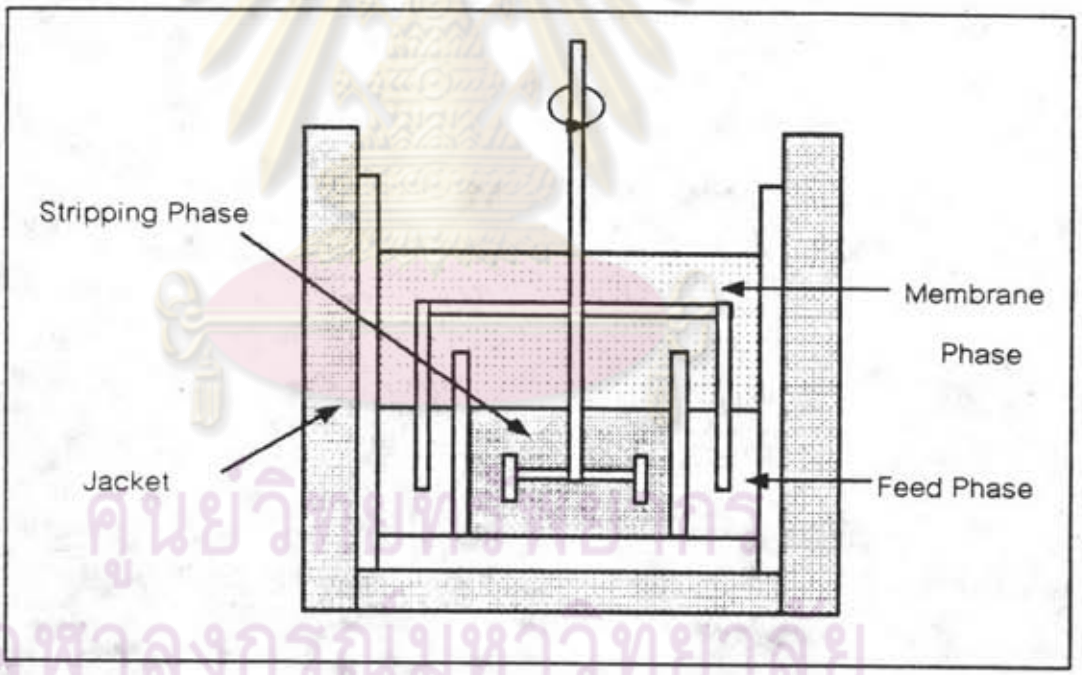


Figure 2-1. Schematic Diagram of Two Compartments Vessel for Extraction.

Noppaporn Panich (1994) has been studied the extraction of two essential amino acids, L-phenylalanine and L-tryptophan, by emulsion liquid membrane from dilute solution. In this case, it has been studied the equilibrium extraction of mixtures and batch extraction of single dilute phenylalanine, dilute tryptophan and mixture of both amino acids. The membrane phase consists of cation carrier D2EHPA and the surfactant Span 80 dissolved in n-dodecane. The internal aqueous phase was 1N HCl solution. It was found that tryptophan had a higher flux than phenylalanine. The extraction rate at pH 5 and 3 was higher than at pH 2. In the extraction of binary mixtures solution of tryptophan and phenylalanine, tryptophan did not have significant effect on the transport rate of phenylalanine.