CHAPTER II

LITERATURE REVIEWS

Since the pioneering work, in the 1940's, of the nuclear-materials industries in the U.S. and Britain; the hydrometallurgist or the chemical engineer have been encouraged by the successful initial uses of liquid-liquid extraction for both the separation of uranium from its ore, and the subsequent treatment of spent reactor fuel to separate plutonium from uranium and its fission products. Generally, the extractive metallurgist turned towards the less valuable; nevertheless, important, transition metals such as zinc, copper, cobalt, and nickel. Then, by 1965, the commercial processing of ores containing these transition metals was proposed. Along with these developments, manufacturers of the commercial organic extractants had been active. By 1974, the liquid-liquid extraction of copper on a large scale was a reality, and the growing values of metals on the world market suggested that even zinc could be economically recovered by hydrometallurgical routes involving solvent.

After Li's pioneering studies in 1968 on liquid membrane extraction as an alternative to solvent extraction, there have been many studies on fundamental and applied aspects of this technology. The separation of mixtures using semipermeable membranes has been the subject of continuing interest. However, this concept has not much succeeded in industrial applications since the polymeric membranes in common use have suffered from low flux rates and low selectivities in general. Thus, area and staging requirements become too great for any large-scale process. An alternative is to use liquid films for membranes. In general, such liquid films possess much higher selectivities than polymeric membranes, thereby remarkably reducing staging requirements. However, membrane systems based on thin liquid films have not been able to overcome the costs

associated with achieving sufficient area to make a significant impact in the separation area. Liquid membranes, invented in 1968 by Li, overcome this liability by generating the necessary surface area without the need for mechanical support. Therefore, these devices offer a more effective means for the separation of mixtures in an efficient manner. The large number of membranes with different formulations render this an extremely versatile process useful for a variety of applications, including hydrocarbon separations, mineral recovery, wastewater treatment, and a number of biochemical and biomedical applications.

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.

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. Zinc, Cadmium and Lead can easily be separated down to concentrations which are below the limits of most environment protection agencies.

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.

Mori, Tanigaki and Eguchi dealt with the recovery of chromium from a waste water containing sulfuric acid by both batch and continuous liquid surfactant membrane (LSM) operations, and investigate the proper condition of LSM process, the possibility of recycle use of the organic phase as the liquid membrane phase, and the prediction of the chromium concentration by a proposed transport model. Chromium in the external feed solution was successfully transported and concentrated into the internal stripping solution containing lithium hydroxide through the organic phase of kerosene with 2-ethylhexyl alcohol and polyamine (Exxon Chem., ECA4360J) with out any extractant. The recycle of the organic phase did not change the function of LSM, and the continuous operation using mixer-settler type extractors worked as a LSM process together with the developed continuous demulsifier by a/c. high electrostatics field. A model for the chromium transport was presented, in which extraction of chromium, leakage of stripping phase, entrainment of feed phase, and permeation of water were taken into account. the experimental result on the model with the experimental parameters from the batch data.

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.

Nakashio has reported a typical example, the mechanism of copper extraction by emulsion liquid membrane is illustrated in Figure 2-1, where a derivative of hydroxime (commercial name LIX 65N, abbreviated as HR) is used as a carrier of copper. As shown in Figure 2-1, copper (M^{2+}) in the external aqueous solution is selectively extracted by LIX 65N (HR) at the external interface of the emulsion globules, to form the oil-soluble complex (MR_2) by the following extraction reaction.

$$M^{2+}_{aq} + 2\ HR_{org} \rightleftharpoons MR_{2\ org} + 2\ H^{+}_{aq} \qquad (2\text{-}1)$$
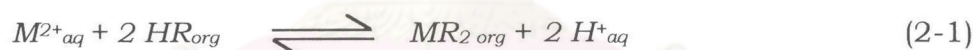
The complex of MR_2 extracted in the organic membrane phase diffuses into the interface of the internal water droplets, where copper is reversibly extracted with acid of the stripping reagent according to the backward reaction of Eq.(2-1). By keeping a higher concentration of protons in the internal aqueous solution than that in the external aqueous solution, copper ion in the external solution is pumped up in the internal aqueous solution with copper-carrier (LIX 65N).

Itoh have reported on water transport (swelling through emulsion liquid membrane). The disadvantages of swelling for an emulsion liquid membrane separation system are the dilution of the separated product in the internal phase, the increase of membrane rupture (breakage), and the increase of agitation power required to disperse the emulsion. There are two possible mechanism for swelling in emulsion liquid membrane processes. The first mechanism suggests that swelling is mediated by hydrated

surfactant, i.e. the surfactant solubilizes water of the external phase into the oil (membrane) phase. The hydrated surfactant then diffuses to the internal phase. Finally, the water is released to the internal phase. This phenomenon is driven by the difference in osmotic pressure between the external phase and the internal phases. The other proposed mechanism states that water is transported by reversed micelle. In this case, water is encapsulated by surfactant aggregated (reversed micelles) in the oil phase. The reversed micelles transport water from the external phase to the internal phase. Both mechanisms can be supported by the data of several workers and the actual mechanism seems to depend on the solutes and the composition if the membrane. Because swelling determines the efficiency if an emulsion liquid membrane process, the mechanism of water transport and its effects should be studied.

Boyadzhiev and Bezenshek were conducting the experiment to extraction of mercury(II) cation from low-pH aqueous solutions by means of a double emulsion technique was studies in a laboratory scale, 2 turbine agitator. A 10% solution of long-chain fatty acid (oleic and linolic) in normal paraffins (C_{11}- C_{15}) was used as the intermediate phase. The optimal operational conditions for fast and complete removal of mercury, providing a 1000 fold concentration increase of the metal in the receiving, encapsulated phase, were obtained.

The commercial product of SPAN 80 contains some impurities, such as dioleate and trioleate (Goto et al. 1987; Nakashio et al. 1988). SPAN 80 is a fairly good emulsifier, so it is widely used in emulsion liquid membrane studies. During extraction operations , the membranes incorporated with SPAN 80 show less resistance to mass transfer than those with other surfactants. (Draxler and Marr 1986; Strzelbicki and Schlosser 1989; Lee and Chan 1990).
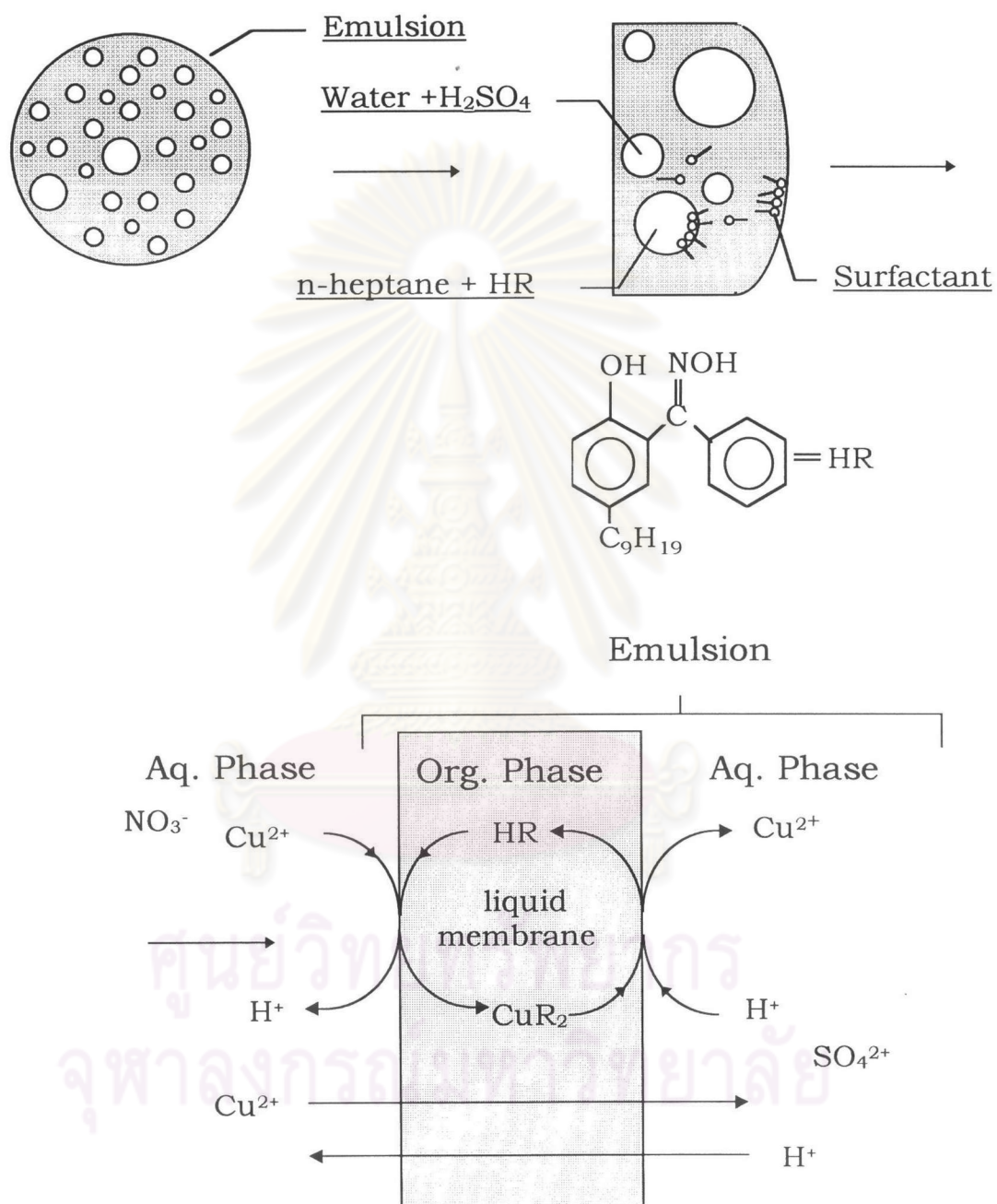
Figure 2-1 Mechanism of copper separation with emulsion liquid membrane.

SPAN 80, however, suffers from some drawbacks. It is good carrier for water molecules and therefore favors the osmotic swelling of emulsion (Martin and Davies 1977; Colonart et al. 1984; Hiroto et al. 1990). Another disadvantage of SPAN 80 as an emulsifier lies in its poor chemical stability, especially when the NaOH is incorporated into the internal phase (Zhang et al. 1988). Abou-Nemeh and Van Petegham (1990) proposed that the instability of SPAN 80 was caused by its decomposition due to hydrolysis and by microemulsion formation due to the presence of H_2O in SPAN 80 and other membrane component. In addition, SPAN 80 also suffers from its high solubility in an aqueous phase, which causes a high reagent loss (Draxler and Marr 1986; Zhang and Xiao 1989, 1990).

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.

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.

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 2-2.
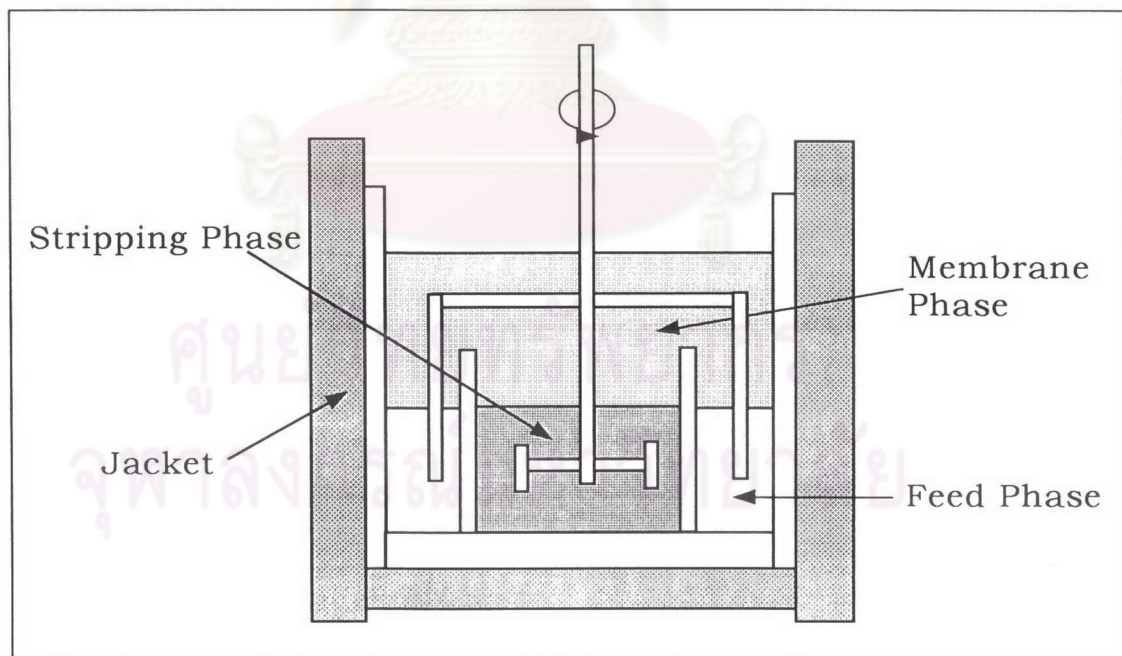

Figure 2-2. Schematic Diagram of Two Compartments Vessel for Extraction.

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.

Apirak SueTrong (1995) has been studied the extraction of L-lysine from aqueous solution by emulsion liquid membrane. In this case, it has been studied the equilibrium extraction and batch extraction of L-lysine. The membrane phase consists of cation carrier D2EHPA and the surfactant Span 80 dissolved in n-dodecane. It was found that 12 moles of L-lysine reacted with 1 mole of dimeric form of D2EHPA to form a complex in the membrane phase. The internal aqueous phase was 1N HCl solution. The extraction rate was maximum at pH 5.

Tavlarides has reported both emulsion liquid membrane and supported liquid membrane has the advantage of accomplishing the extraction and stripping operation with very high enrichment factors in a single stage. However, there are several problems which need to be overcome for the future development.

Emulsion liquid membrane, the stability of a emulsion liquid membrane is of major importance, since breakdown of the organic films will show directly as a loss in extraction efficiency as well as a loss of strip solution. Some steps can be taken to increase the stability of the organic phase by adding polymer materials or by increasing the surface viscosity. However, further studies are necessary to improve the stability of the emulsion. The solubility of the surfactant in the aqueous phase (raffinate

and strip solution) is important. Ideally surfactants totally insoluble in the aqueous phases should be used to prevent any overall loss from the system. In addition, the solvent losses or solubility from one phase to the other may also increase due to the surfactant added in the system. The process development problems, such as emulsion breakdown, iron poisoning and colloidal solids incorporation, have yet to be overcome.