# CHAPTER II

# SOLVENT EXTRACTION PROCESSES

There are two extraction mechanisms in the solvent extraction process, that is the extraction of the specified spicies based on the solubility or a conventional solvent extraction process and the extraction with chemical reaction. These two mechanisms are also the fundamentals of liquid membrane processes.

## A Conventional Solvent Extraction Process

If there are two immiscible phases and there is a solute dissolved in the first phase, the solute can be distributed into the second phase when these two phases are brought into contact with each other on condition that the solute is preferably dissolved in the second phase. This basic concept is applied to conventional solvent extraction processes in which the solutes are selectively extracted from the one liquid phase to the other by the solubitity. The second phase is so-called the solvent in which the solute is preferably soluble. This second phase is very important for selectively extracting or separating only the species needed in case that the feed contains various species of solute. A schematic diagram of solvent extraction process is shown in Figure 2-1.

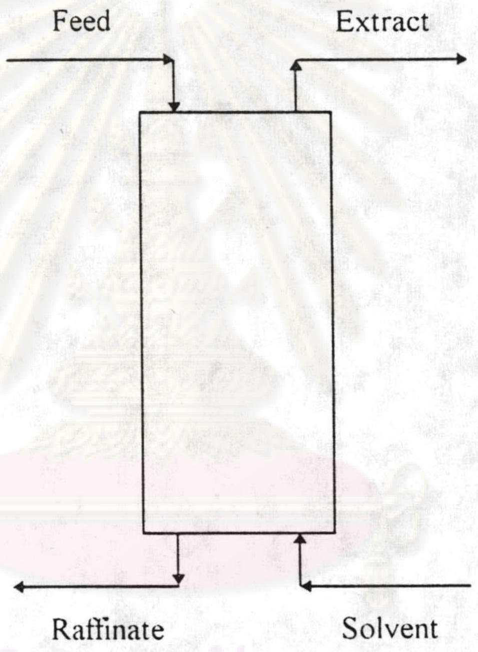

Figure 2-1 Schematic countercurrent flow diagram in a solvent extraction column

There are numerous mechanically agitated columns typically used in industries for solvent extraction processes in order to increase the rate of mass transfer between both phases. The examples of these well-known columns are Scheibel column, Rotating Disc Contactor (RDC), and Oldshue-Rushton column. The Rotating Disc Column is shown as an illustration in Figure 2-2.

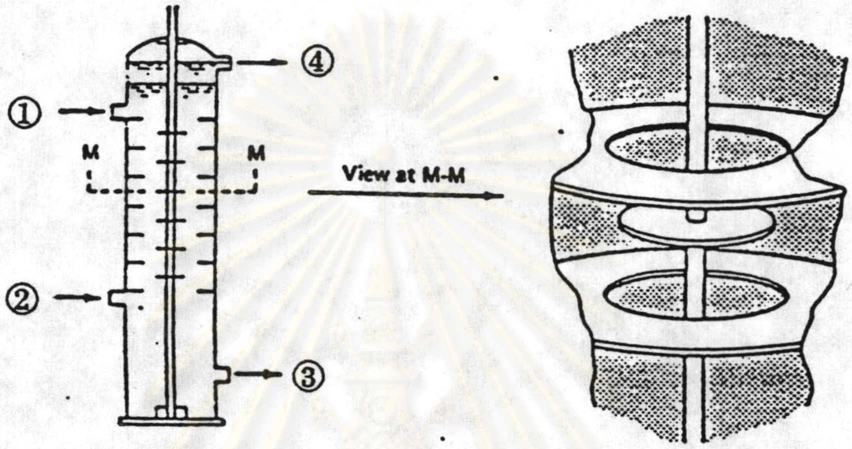

Figure 2-2 A mechanically agitated column typically used in industrial solvent extraction processes – the Rotating Disk Column where ① feed inlet, ② solvent inlet, ③ raffinate outlet, and ④ extract outlet

In General, the degree of extraction for the conventional solvent extraction process is primarily limited by the solvent-to-feed volume ratio and the distribution ratios of the solute in the feed to that in the solvent. Unfortunately, this process is not suitable to separate the solutes dissolved in a feed solution due to the low selectivity. That is, if there are a lot of species in the feed solution which are able to be dissolved in the solvent, more than one species are extracted into the solvent. Furthermore, this process is not applicable for separation of a metal ion from the aqueous solution since metal ions merely exist in aqueous slution. However, the separation selectivity can be enhanced by using an extraction with a chemical reaction which needs an extracting reagent.

## A Solvent Extraction Process with a Chemical Reaction

The selectivity of a conventional solvent extraction process can be improved by using an extracting reagent (an extractant, or a carrier) to react selectively with the particular species. This process is known as the solvent extraction with chemical reaction. Generally, metal ions are dissolved in an aqueous solution. Therefore, in a metal production process, the feed solution is always an aqueous solution. The solvent which is the organic phase and now contains an extractant is thus called the organic solution. In order to be dissolved in the organic solvent, this chemical reactant has to be an organic substance too. Dissolved in the organic solution, the extractant reacts with the ions forming a metal ion-extractant complex. Hence, the certain metal ions can be reacted selectively with a selected extractant. However, the metal ion-extractant complex is not the general form of metal that can be used widely.

Therefore, the additional stage of metal recovery known as stripping is required to produce a useful form of metal ions. Moreover, the stripping of metal ions allows the organic solution to be reused. Normally, in an industrial solvent extraction process, there are two columns; namely an extraction column for the extraction step and a stripping column for the stripping step. A schematic process diagram of solvent extraction with chemical reaction is shown in Figure 2-3.

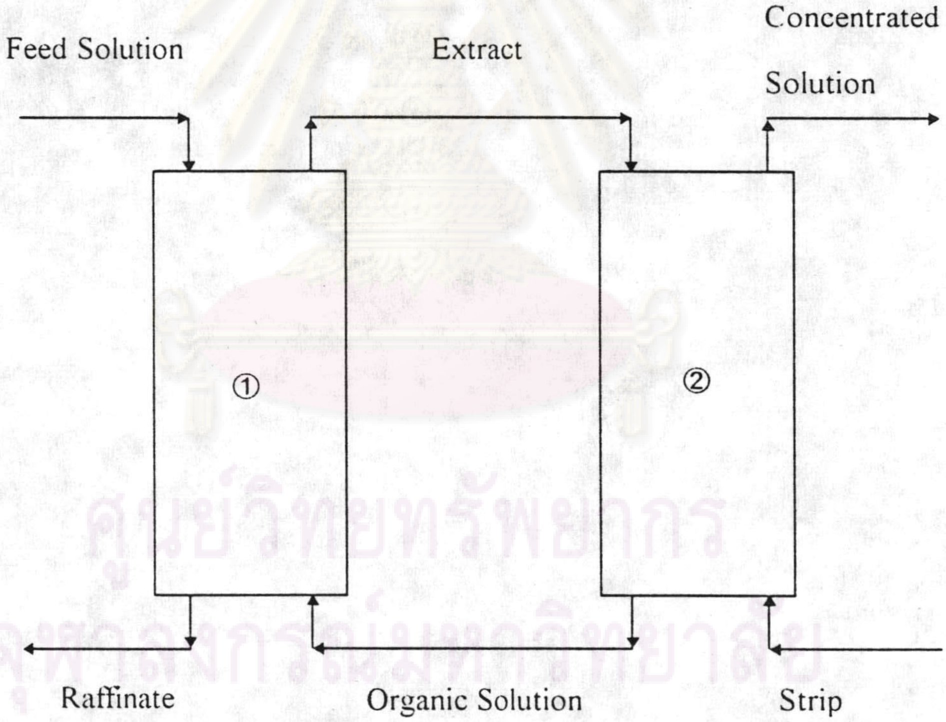

Figure 2-3 Schematic process diagram of solvent extraction with reaction: (1) an extraction column, (2) a stripping column

Even though the selectivity is enhanced by employing the reaction, the chemical reactant may be quite expensive. Furthermore, a large amount of solvent or solution is necessary for the solvent extraction because of solvent losses. Thus, an expensive, tailor-made extractant is scarcely used in this process. The extraction column has also suffered from the insufficient surface area for mass transfer. In addition, the solvent extraction processes are limited by either the physical or the chemical equilibrium. To solve these problems, the use of liquid membranes in which the extraction and stripping occur simultaneously has been proposed as an alternative to solvent extraction for selective extracting and concentrating metal ions from dilute aqueous solution.

## Liquid Membrane Separation Processes

The liquid membrane is composed of three layers of liquid phases, i.e. feed phase, liquid membrane itself, and strip phase, respectively, shown in Figure 2-4. Thus, the system can perform extraction and stripping simultaneously. Consequently, the equilibrium limits on both interfaces are hardly achieved.

Figure 2-4 shows a schematic example of the separation of metal ions from aqueous solution in the most common 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 acidity of the corresponding aqueous solution. The overall reaction at the interface is expressed by

$$M^{n+} + n\,\overline{RH} \rightleftharpoons \overline{MR_n} + n\,H^+ \qquad \text{..............} \ (2.1)$$

where RH is a molecule of extractant.

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

1. In the liquid phase I, a metal ion diffuses from bulk liquid to the liquid membrane surface (interface i), then reacts with the extractant forming a metal ion-extractant 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 bulk liquid phase III
4. Then the extractant diffuses back to the interface i due to its concentration gradient and repeat the phenomenon as mentioned above.

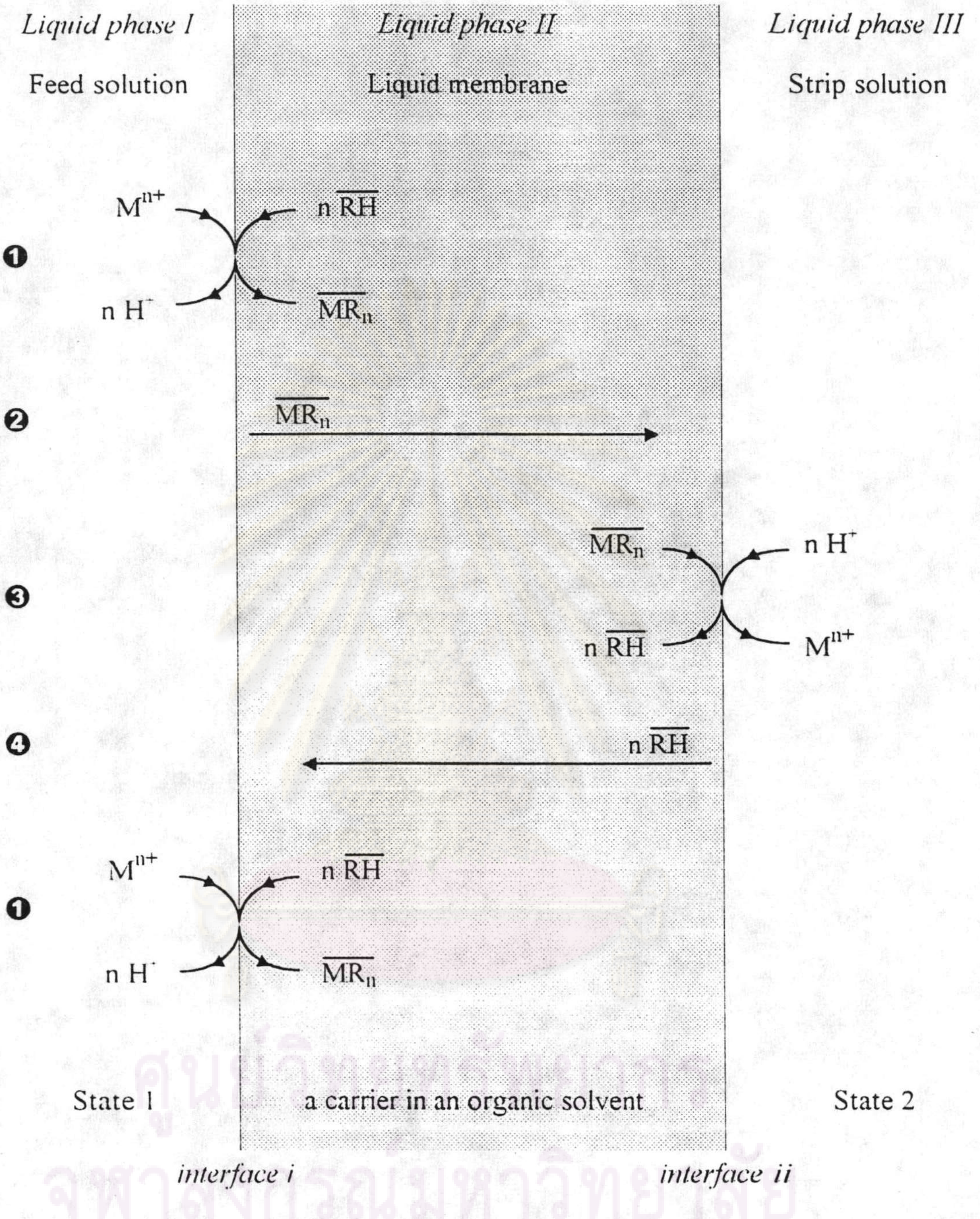

Figure 2-4 Schematic representation of the counter-transport mass transfer through a liquid membrane which ❶ is the extraction reaction, ❷ is the diffusion of a metal-carrier complex, ❸ is the stripping reaction , and ❹ is the back diffusion of the carrier

Three distinct liquid membrane configurations have been reported: the first is an emulsion liquid membrane (ELM) or liquid surfactant membrane (LSM), the second is a supported liquid membrane (SLM) or immobilized liquid membrane, and the third one is an electrostatic pseudo-liquid membrane (ESPLIM).

## 1. Emulsion Liquid Membrane

An emulsion is a mobile liquid membrane which is composed of an internal phase and a membrane. When two immiscible solution are agitated by using a high-speed homoginizer, emulsions are formed. But these emulsions are usually not stable. Therefore, in order to maintain the integrity of emulsion during the operation, these two immicisible phases are agitated with a selected surfactant which is usually known as an emulsifier [Marr and Kopp, 1982]. Hence, this process is also called liquid surfactant membrane (LSM). Figure 2-5 illustrates an actual liquid membrane globule and a simplified model which is useful for discussion the principles of mass transfer. The aqueous phase which forms the emulsion with the membrane is called the encapsulated or internal phase.

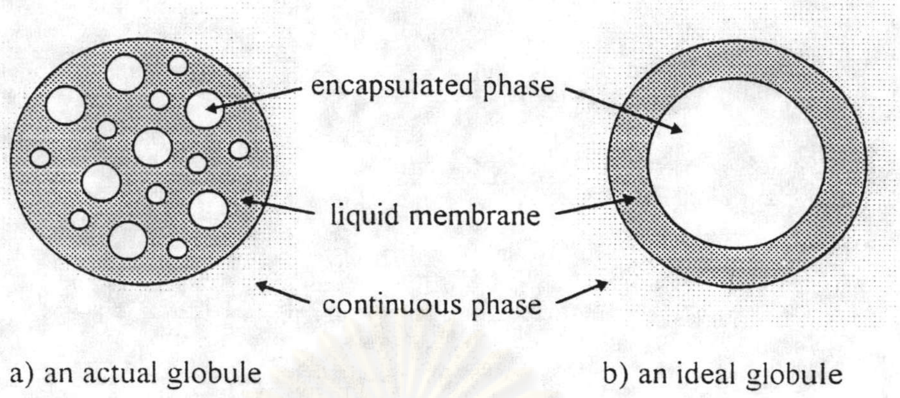

Figure 2-5 The illustrations of an emulsion liquid membrane: a) an actual globule, and b) an ideal globule

The emulsion liquid membrane is still divided into two types [Ho and Li, 1992; Marr and Kopp, 1982]; 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 emulsions.

In an industrial process, the two phases forming the emulsion are the strip solution and the organic solution containing an extractant [Gu, Ho, and Li, 1992].

Then the emulsion is dispersed in the feed phase from which the metal ions have to be removed shown in Figure 2-6. 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 demulsified in order to reuse the organic solution and to recover the strip solution for further treatment. Finally, this system can produce the concentrated strip solution. However, the emulsions may swell during the operation leading to breaking of emulsion.

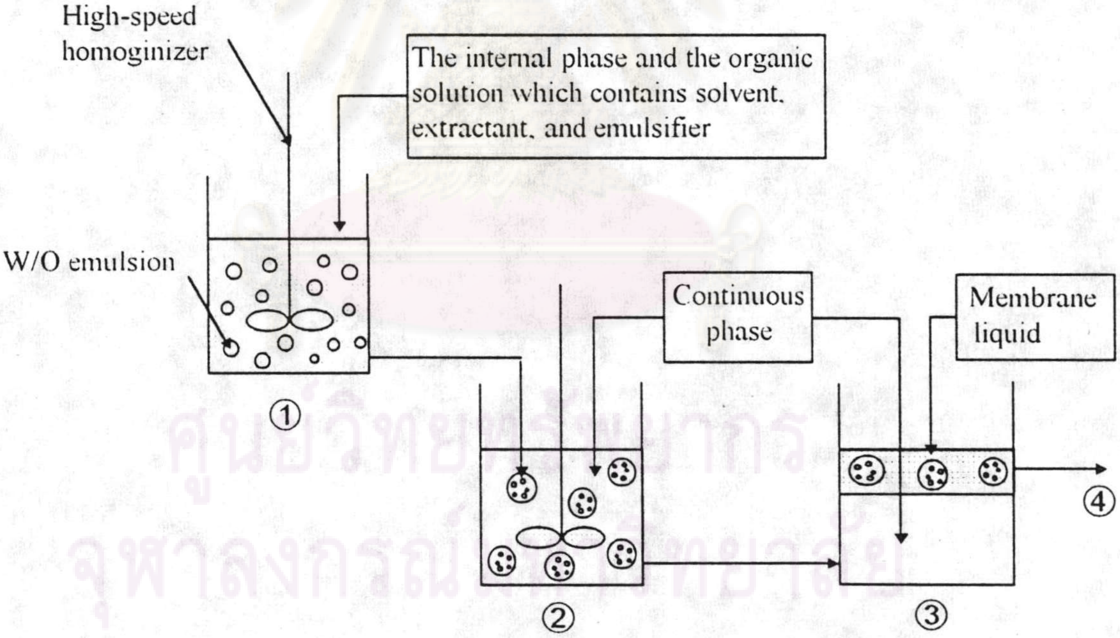

Figure 2-6 Schematic diagram of an emulsion liquid membrane process; ① emulsification, ② dispersion and permeation, ③ mixer settler, and ④ demulsification

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 viscousity of solutions which form emulsion, and the nature and concentration of the emulsifier [Ho and Li, 1992]. 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.

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 results 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 formation 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 further 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, that is chemical and physical treatment. The chemical treatment involves the addition of a demulsifier to the emulsion. This 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 strip solutions and a reduction of extraction efficiency.

### 2. Supported Liquid Membrane

The supported liquid membrane technique uses a porous membrane as a support for the organic phase incorporating the extractant. Porous support membranes are available as a flat sheet, a hollow fiber module, or a spiral-wound module. Hollow fiber membranes are preferable because of their higher membrane-area-to-volume ratio. However, in case that membrane clogging may occur in hollow fibers of very small diameter, especially due to fine solid particles; the spiral-wound module can be used instead of the hollow fiber module [Teramoto, et al., 1987].

In a hydrophobic hollow fiber module as shown in Figure 2-7, the membrane must be prepared first by impregnating the walls of hollow fiber membrane with an organic solution which contains a selected extractant. This organic solution is impregnated into the micropores inside the hollow fiber by electron affinity and held in the micropores by capillary force [Marr and Kopp, 1982]. The simultaneous extraction and stripping process occurs when the feed and the strip solution flows in each side of the fibers. However, during the operation, the differential pressure across the membrane may not exceed the breakthrough pressure. Otherwise, the aqueous solution along with the membrane liquid will be driven through the pores into the other aqueous stream.

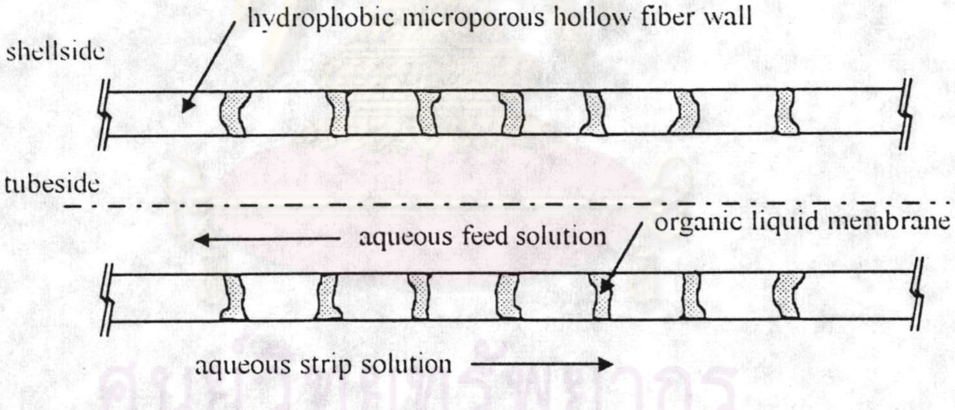

Figure 2-7 Immobilized phase interfaces in a SLM for a hydrophobic hollow fiber substrate, aqueous feed and strip solutions, and organic liquid membrane

In general, the feed solution flows through the fiber lumen (the tubeside) of the hollow fibers and the aqueous strip solution circulates on the shellside of the fibers since a high degree of solute extraction from the feed stream which flows in the shellside cannot be achieved in a hollow fiber module due to significant bypassing and backmixing flows in the shellside [Prasad and Sirkar, 1990]. The operation mode can be realized in once-through mode or continuously circulation mode. The flow pattern is also divided into countercurrent and cocurrent flows.

Conversely, for a hydrophilic hollow fibers, the membrane liquid which is held in the pores is an aqueous solution, see Figure 2-8. Like the O/W emulsion, a system with the phase sequence of oil(I)–water(II)–oil(III) is obtained. Then, if there are two organic solutions flowing on both sides of the membrane, the aqueous/organic interface will be immobilized at the pore mouths of the membrane and the aqueous phase will not be dispersed in the organic phases and vice versa. Solute extraction and back-extraction can be achieved through the aqueous/organic interface at the pore mouths.

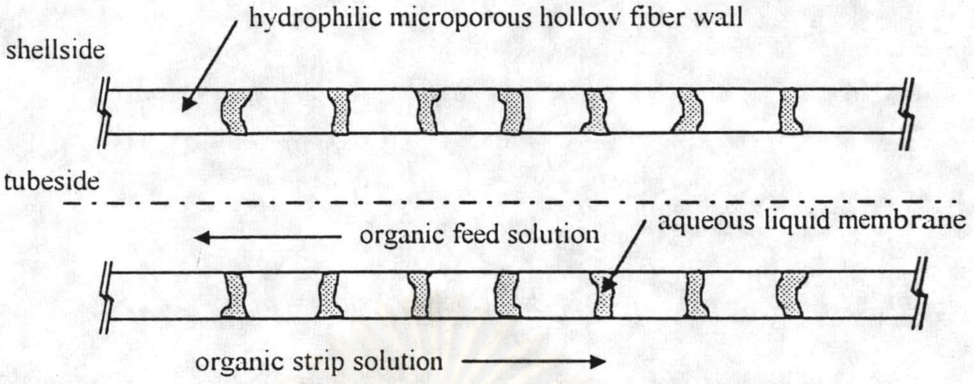

Figure 2-8 Immobilized phase interfaces in a SLM for a hydrophilic hollow fiber substrate, organic feed and strip solutions, and aqueous liquid membrane

A considerable amount of academic and industrial researches have been focused on developing hollow fiber for metal separation [Loiacono, Drioli, and Molimari, 1986; Prasad and Sirkar, 1990; Tanigaki, et al., 1988]. The advantages of supported liquid membrane over other traditional solvent extraction processes are [Tavlarides, Bae, and Lee, 1987; and Schulz, 1988]:

1. low capital and operating costs
2. low energy consumption
3. economical use of expensive, tailor-made extractants and solvents because only an extremely small quantity of membrane liquid is required for filling the pores.

4. low maintenance costs due to fewer moving parts
5. possibility of achieving high overall separation factor

The advantages of hydrophobic hollow fiber operations over emulsion liquid membrane operations are:

1. low energy consumption since only two pump sets are utilized
2. low operating cost
3. the small amount of organic solution used – only to impregnate the hollow fiber before an operation
4. no surfactant used resulting in higher fluxes – but the fiber wall itself reduces the overall mass-transfer area.

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 solution in the aqueous solutions. Ideally, the organic solvent and extractant must be soluble in neither the feed nor the strip solutions so as to increase the lifetime of the liquid membrane. In case of slightly soluble membrane liquid, both the mobile phases should be presaturated with the organic solution used in order to reduce the solubility of the membrane liquid in these solutions. Another disadvantage of this system is that the hollow fiber module is very expensive.

The requirements for the porous support structure can be summarized as follows [Schulz, 1988]:

1. high porosity – in order to increase the mass-transfer area
2. thin walls – usually up to 50 μm since the thinner the membrane, the greater the rate of mass transfer. However, if the wall is too thin, the lifetime will decrease
3. high chemical resistance material
4. small pore diameters – since the strength of capillary force depends upon the pore diameter; the larger the diameter, the weaker this force resulting in losses of membrane liquid
5. low cost

Moreover, the required properties of membrane liquid and process parameters are:

1. high-viscosity solvent – in order to reduce the loss of membrane liquid due to the shear stress in the mobile phases, resulting in longer lifetime of liquid membrane.
2. high-temperature feed solution – since the extraction reaction increase as the temperature increases. However, an increase in temperature increases the solubility of the organic phase in the feed phase.

### 3. Electrostatic Pseudo–Liquid Membrane

The electrostatic pseudo-liquid membrane is another novel liquid membrane system which was devoloped by Gu in 1988 by combining an electrostatic technique with the principle of a liquid membrane. The unique features of ESPLIM overcome some existing shortcomings in liquid membrane, such as the complicated ELM process and the instability of SLMs. This process is a nonequilibration mass transfer – like ELM and SLM – which takes place in a specially made reaction tank, as illustrated in Figure 2-9. The upper part of this tank is divided into an extraction cell and a stripping cell by a specially made baffle plate, and in the lower part are the extraction and the stripping settlers that are separated from each other by a divider. Two pairs of electrodes are mounted across the extraction and stripping cells respectively. In this system, the organic phase acts as a continuous phase.

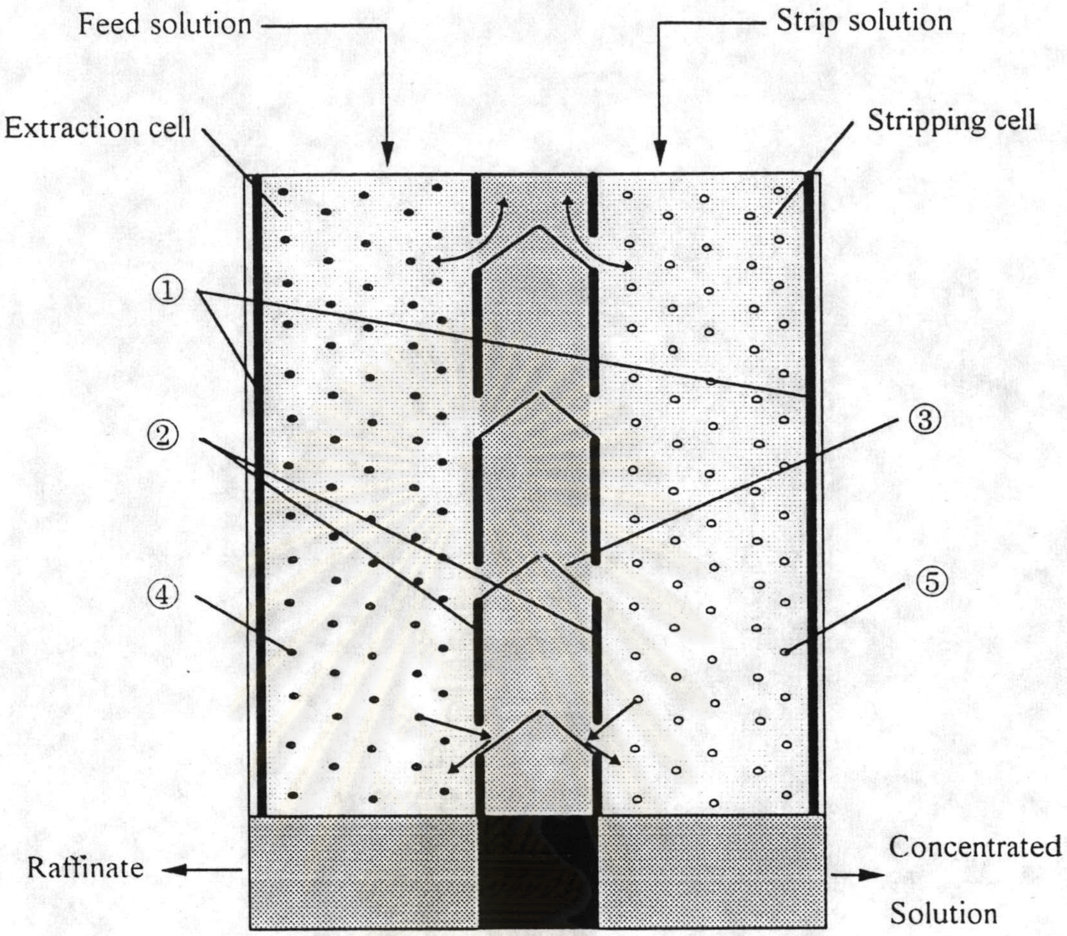

Figure 2-9 Schematic diagram of electrode-baffle structure where: ① high-voltage electrode, ② grounded electrode (baffle plate), ③ baffle, ④ feed droplets, and ⑤ strip droplets

Once a high-voltage electrostatic field which is high enough for phase dispersion is applied across the extraction and stripping cells simultaneously, the feed solution which is added to the extraction cell and the strip solution which is added to the stripping cell are dispersed into numerous droplets within the corresponding cells.

In the extraction cell, the solute in the aqueous droplets is extracted into the organic phase with the selected chemical reaction. The metal ion-extractant complex formed in the extraction cell diffuses through the perforated baffle plate, driven by its own concentration gradient, into the stripping cell. In the stripping cell, the extractant is regenerated after the solute is stripped off. Diffused back through the perforated baffle plate by its concentration gradient, the extractant starts extracting the solute in the extraction cell again. However, if the droplets of the aqueous feed or strip solution enter the holes of the baffle, those droplets coalesce together since there is no electric field. Upon gravity, these coalesced drops will slip away from the holes, back to their respective cells.

The advantages of this system are:

1. high mass-transfer area
2. well mixing which occurs as the aqueous droplets are moving across the cell due to the electric field
3. low maintenance costs owing to no moving part
4. low energy consumption

The disadvantages of this system are:

1. large volume of organic solvent and extractant are used – since the organic phase acts as the continuous phase.

2. it is possible that mass-transfer resistance is high due to the diffusion of metal ions across the baffle plate as minimum distance.
3. Steady state can be achieved much slowly.

One problem that has not yet been satisfactorily solved for the SLM process is membrane instability due to the gradual loss of membrane liquid by dissolution during the operation. Nevertheless, like all other techniques, ESPLIM has its own limitation. It is effective when the dispersed phase is an aqueous solution and the continuous phase is an organic solution with low polarity because such the organic solution shows good dielectric property. Thus, it is confined to the extraction of solutes from aqueous solutions.