

CHAPTER IV

EXPERIMENT

CHEMICAL REAGENTS

Metal

Cupric Nitrate $\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ (Fluka Chemika, AR)

Cupric sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AJAX Chemicals, AR)

Cupric chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker Analyzed, AR) *Organic Solvent*

Kerosene (The Bangchak Petroleum Public Co.Ltd.)

Carrier

Di(2-ethylhexyl) phosphoric acid (D2EHPA) (Sigma Chemical Co.)

Surfactant

Span 80 (Fluka Chemika)

Acid

Hydrochloric acid (HCl) 35.4% (BDH, AR)

Sulfuric acid (H_2SO_4) 96.6% (Baker Analyzed, AR)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

EXTERNAL PHASE (FEED PHASE)

The external phase or feed phase is 100 ppm. copper solution, prepared by dissolving chosen copper salt in distilled water and adjusted acidity (pH) of the prepared copper solution with hydrochloric acid solution (HCl).

MEMBRANE PHASE

The water-in-oil (w/o) emulsion was prepared by a stirring a mixture of one part of organic liquid membrane phase (kerosene+surfactant+carrier) and one part of hydrochloric acid using high speed homogenizer (model T25, IKA Labortechnik) at 8000 rpm. The organic liquid membrane phase consisted of kerosene as the solvent, D2EHPA as the carrier, and SPAN 80 as the surfactant. The conditions of membrane preparations were varied follow the scope of this study.

INTERNAL PHASE (STRIPPING PHASE)

The solution for use as the internal phase or stripping phase for the extraction of copper must have an acidic pH. In this study, hydrochloric acid solution was used.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

EXTRACTION EQUILIBRIUM

Experimental procedure

Experiments on the extraction equilibrium of copper was carried out by mixing 50 ml. of organic membrane phase and 50 ml. of the aqueous phase and then stirred by stirrer in organic membrane phase and stirred by magnetic stirrer in aqueous phase for 8 hours at room temperature. The organic membrane phase was prepared by dissolving D2EHPA and SPAN 80 in kerosene. The pH in the aqueous phase was maintained between 2 to 6 with hydrochloric acid. The membrane phase contains 0.0310 to 0.4650 M. D2EHPA and the aqueous phase was 1.5737 M copper. The two phases were separated after allowing to settle in a separatory vessel. The concentration of copper in the membrane phase was determined from the difference of copper concentrations between initial and final stages. Copper concentrations were measured by atomic absorption technique (Atomic absorption/Flame Emission Spectrophotometer. AA-670 Shimadzu, Graphic printer PR-4 Shimadzu.). The pH of the aqueous phase was also measured both at initial and final stages by a pH meter (Denver Instrument).

BATCH OPERATION

Experimental Procedure.

The stirring vessel used is 85 mm. inside diameter, 110 mm. in height with four baffles of 8 mm. width. Stirring was carried out by a marine type impeller of 40 mm. diameter, located at 55 mm. measured from the bottom of the vessel. The extraction time for each example was started from the time that emulsion phase was poured into the vessel. Samples of external aqueous copper solution (feed solution) was taken periodically during the experiment. After 60 minutes of operation, the emulsion phase was separated from the external phase. The volume of each

phase was measured and the concentrations of copper in the external phase that was taken periodically were measured by atomic absorption method (Atomic absorption/Flame Emission Spectrophotometer. AA-670 Shimadzu, Graphic printer PR-4 Shimadzu.). The pH of external phase solution as also measured using a pH meter (Denver Instrument). The process diagram of batch operation of emulsion liquid membrane is shown in Figure 4-1.

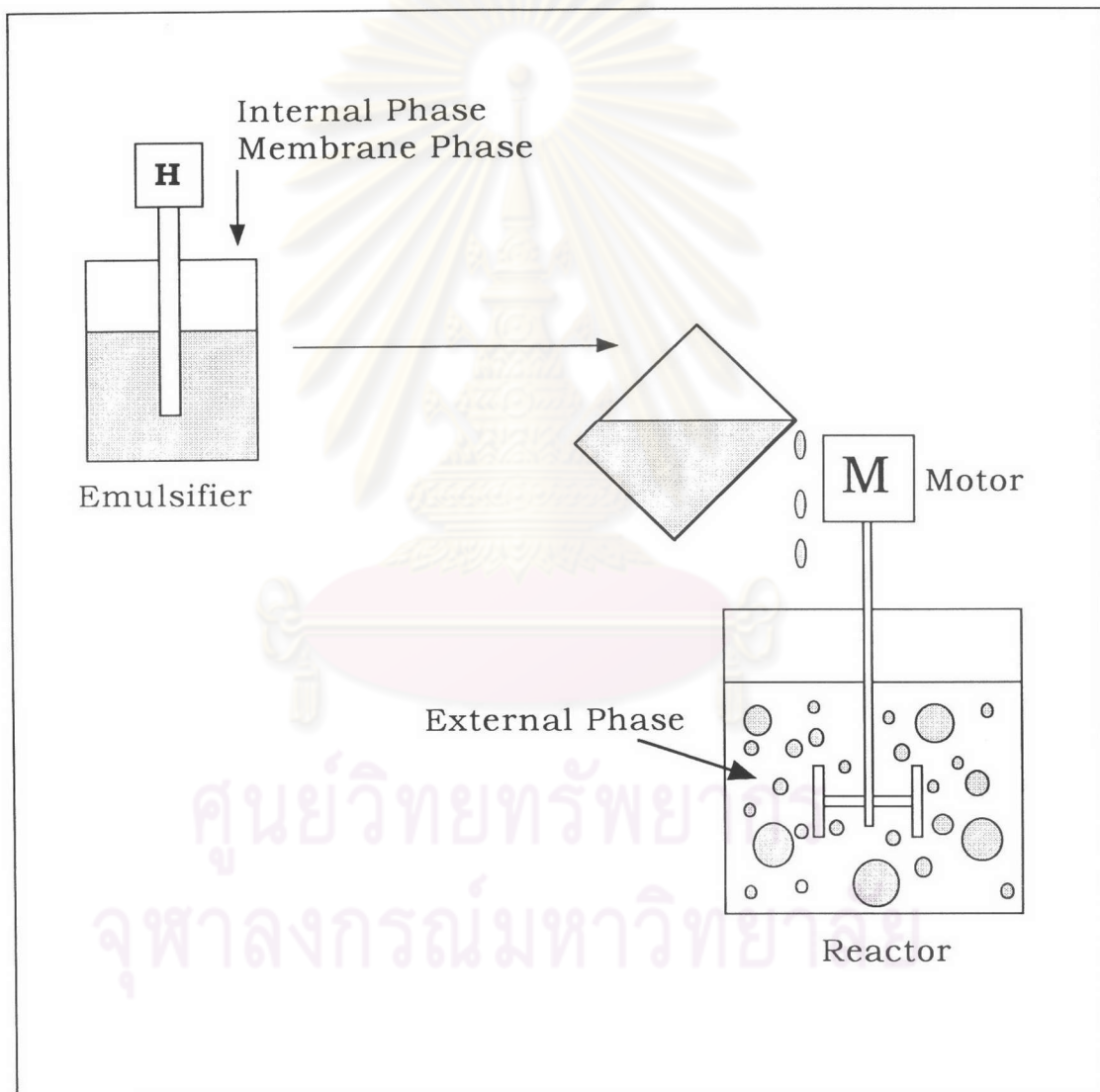


Figure 4-1 Schematic diagram of batch operation experimental apparatus

CONTINUOUS OPERATION

Experimental Procedure.

The stirring vessel used is the same with used in batch operation, 85 mm. in inner diameter, 110 mm. in height with four baffles of 8 mm. in width. Stirring was carried out by a marine type impeller of 40 mm. diameter, located at 55 mm. from the bottom of the vessel. The first, the emulsion was prepared by a high speed homogenizer (model T25, IKA Labortechnik) at 8000 rpm. using one part of the organic liquid membrane phase (kerosene with carrier and surfactant), and one part of the stripping solution (Hydrochloric acid). The organic liquid membrane phase consisted of kerosene as the solvent, D2EHPA as the carrier, and SPAN 80 as the surfactant. The condition of membrane preparation was used the optimum condition that found from batch operation study. The feed solution (external aqueous solution, 100 ppm. copper which already adjusted pH by HCl acid) was fed into the vessel by diaphragm pump (Chem-Feed, Blue-White Industries). Stirring was carried out in range 350-400 rpm. And set inlet volumetric flow rate of feed solution as equal as outlet volumetric flow rate of raffinate solution. The extraction time for each example was started from the time that emulsion phase was fed into the vessel. The flow rate of feed solution was set follow the scope of this study and the volumetric flow rate of emulsion phase was kept constant at 0.2 l/hr. Samples of external aqueous copper solution (feed solution) was taken periodically during the experiment. After 240 minutes of operation, the concentrations of copper in the external phase that was taken periodically were measured by atomic absorption method (Atomic absorption/Frame Emission Spectrophotometer. AA-670 Shimadzu, Graphic printer PR-4 Shimadzu.). And the pH of external phase solution were also measured by a pH meter (Denver Instrument). The process diagram of emulsion liquid membrane is shown in Figure 4-2

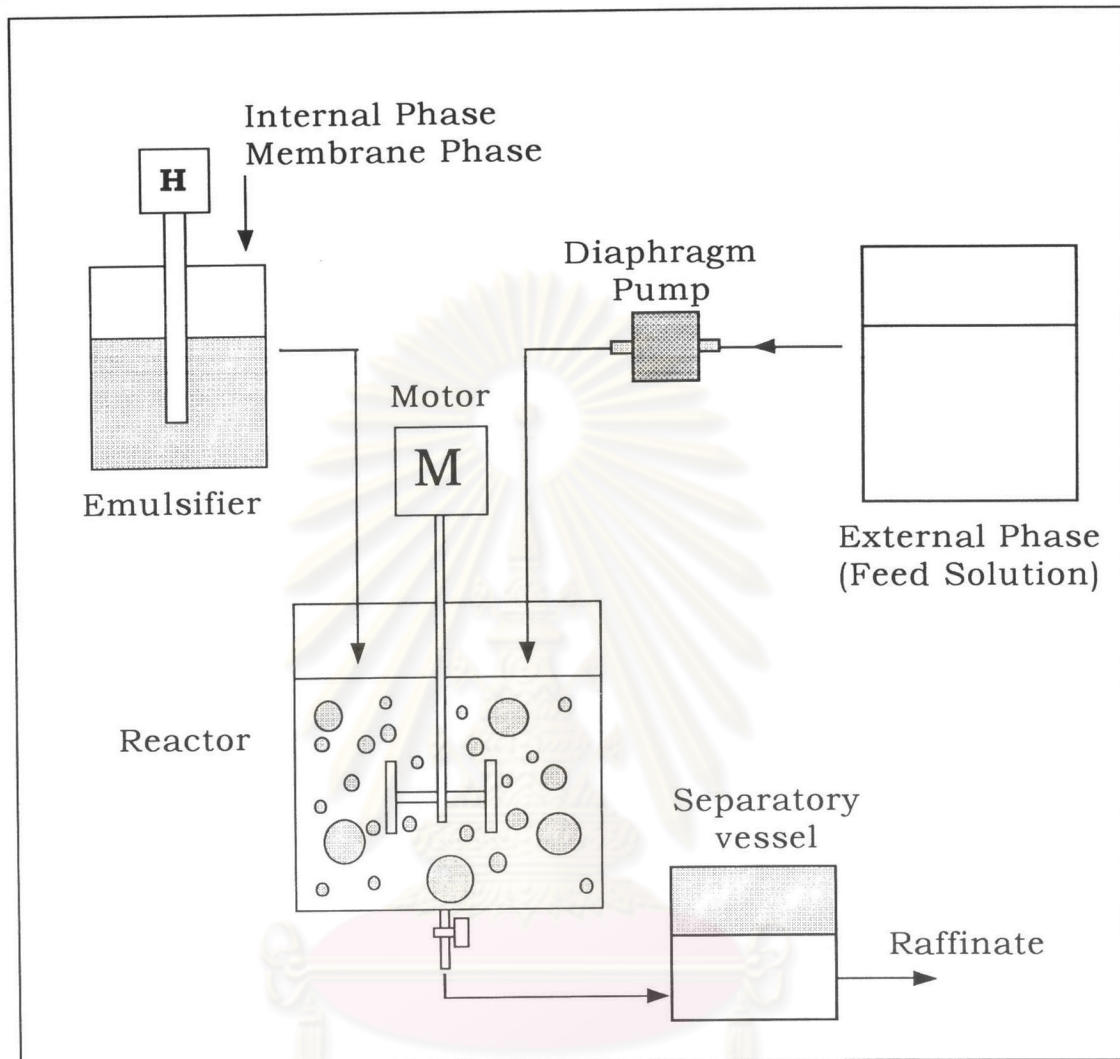


Figure 4-2 Schematic diagram of continuous operation experimental apparatus

EXTRACTION IN TWO COMPARTMENT VESSEL

Experimental procedure

A 100 ppm. copper (Fluka, AR) in distilled water was used as the donor phase. The membrane liquid, as already mentioned, was a solution of di(2-ethylhexyl) phosphoric acid (D2EHPA) (pure, Fluka AR) in kerosene. On the basis of preliminary tests it was found that 10% by volume is a reasonable concentration of carrier in the solvent used. When this

experimental technique was used, lower concentration of D2EHPA, although preferable from economical and ecological points of view, lead to a considerable slowdown of the process. a 1N. solution of Hydrochloric acid was used as a receiving phase.

The experimental studies were carried out by applying simple bulk liquid membrane technique: a two compartment cell equipped with four baffles, show in Figure 4-3, was used. The receiving phase was stirred by magnetic stirrer, the membrane phase was stirred by marine type impeller, and the donor phase was circulated by diaphragm pump. In order to keep both interface areas (a) constant, the rotation speed of the stirrer was limited up to 60 rpm. The volume of donor phase was 300 ml., the volume of receiving and that of membrane phase were 100 ml. The Copper concentration in both aqueous phase were measured by atomic absorption method. All experiments were carried out at room temperature.

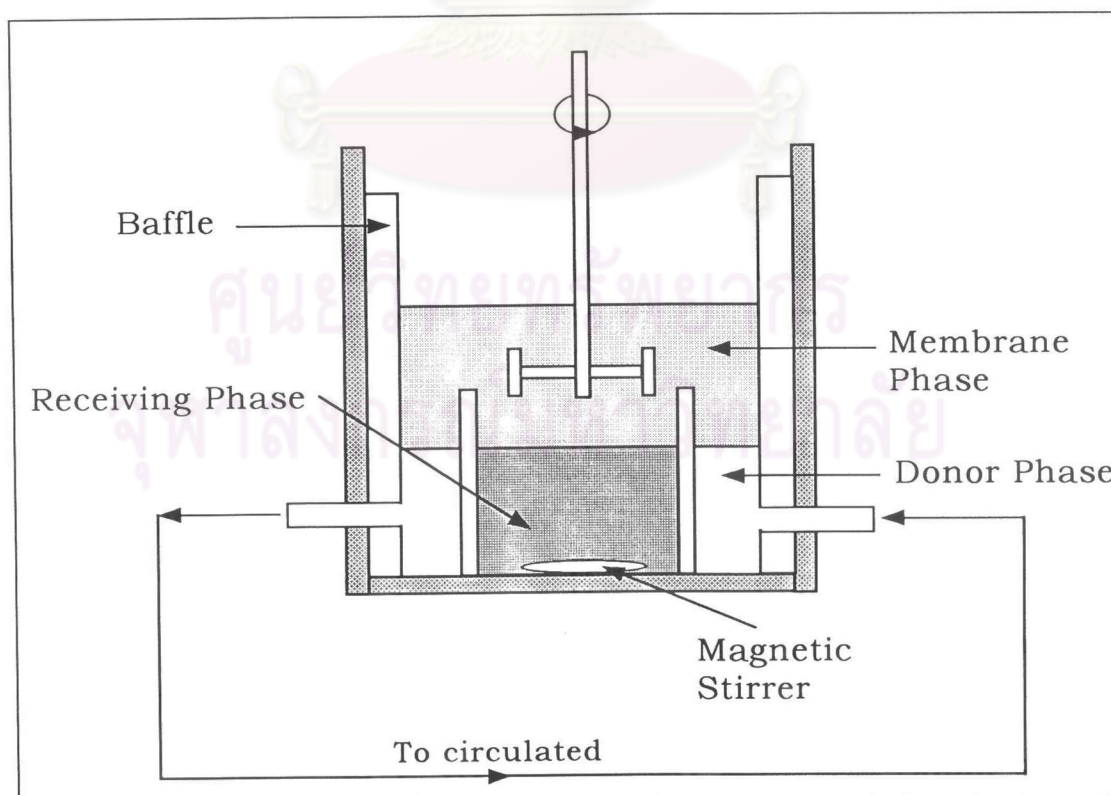


Figure 4-3 Schematic Diagram of Two Compartments Vessel for Extraction

Calculation of Swelling in the Internal phase

The measurement of emulsion swelling can be done by measuring the volume of the emulsion phase and the external phase after each extraction by using a mass balance. The percentage of emulsion swelling can be then calculated using the following equation

$$\begin{aligned}
 \% \text{ Swelling} &= \frac{(\text{Internal Phase Volume}-\text{Initial Internal Phase Volume}) \times 100}{\text{Initial Internal Phase Volume}} \\
 &= \frac{(\text{Internal Phase Volume}-25) \times 100}{25} \\
 &= \frac{(\text{Membrane Phase Volume}-\text{Organic Phase Volume}-25) \times 100}{25} \\
 &= \frac{(\text{Membrane Phase Volume}-25-25) \times 100}{25} \\
 &= \frac{(\text{Membrane Phase Volume}-50) \times 100}{25}
 \end{aligned}$$

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Calculation of Copper concentration in the Internal phase.

In this study, the concentration of Copper in the external phase was measured. On the other hand, the concentration of Copper in the internal phase was calculated using material balance based on the assumption that in the emulsion liquid membrane process, the membrane phase functions as a transfer vehicle, and the Copper is stored mainly in the internal aqueous phase as an ion. Only a small portion of the Copper is stored in the membrane phase, depending on the equilibrium between the external, membrane and internal phases. The example of calculation of concentration of Copper in the internal phase is shown in the following example:

Initial concentration of Copper in the external phase or $[Cu^{2+}] = 100$ ppm.

From the experimental results, the concentration of Copper in the external phase after 1 minute extraction = 85 ppm.

Consequently, the amount of copper that penetrated into the internal phase

$$= 100 - 85 \text{ ppm.}$$

$$= 15 \text{ ppm.}$$

Since the volume of external phase = 450 ml.

From the experimental results, the volume of the internal phase = 25 ml.

Therefore, the concentration of Copper in the internal phase $[Cu^{2+}]_i$;

$$= \frac{15\text{ppm.} \cdot 450\text{mL.}}{25\text{mL.}}$$

$$= 270 \text{ ppm .}$$