

COPPER REMOVAL FROM DILUTE AQUEOUS SOLUTION BY  
EMULSION LIQUID MEMBRANE METHOD

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By                                 Miss Sirilak Intarawicha  
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Copper extraction from dilute aqueous solution by emulsion liquid membrane method was studied. The membrane phase was consisted of LIX 984N as extractant and Span 80 as surfactant in kerosene. Internal aqueous phase was sulfuric acid solution. The effects of parameters such as feed pH, extraction temperature, stirring speed, surfactant concentration, extractant concentration, internal stripping phase concentration and feed phase concentration were investigated. The experimental data were presented as plots of the ratio of the instantaneous copper concentration to the initial copper concentration versus time and tabulated as the percentage of copper removal with time. The optimum condition for this study was found to be at feed pH of 5, which was a predominant factor. The process was most efficient at 30°C with stirring speed of 400 rpm, 3 wt% of surfactant, 4 wt% of extractant and 2 M sulfuric acid. More than 99.7% of copper could be removed from the feed phase within 14 minutes when the optimum condition was used. Addition of 1 wt% of ethylene-propylene copolymer as viscosity improver was found to reduce membrane leakage at high speed of agitation. The third reusability of the membrane phase could be achieved with more than 97% copper removal.

Field of Study : Petrochemistry and Polymer Science

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## LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometer
$C_e$	Instantaneous concentration of copper in the feed phase
$C_{e0}$	Initial concentration of copper
$C_e/C_{e0}$	Ratio of the instantaneous concentration to initial concentration of copper
ELM	Emulsion liquid membrane
M	Molar, mol/L
min	Minute (s)
ml	Milliliter (s)
O/W/O	Oil-in-water-in-oil
ppm	Part per million
rpm	Rotation per minute
W/O/W	Water-in-oil-in-water
$^{\circ}\text{C}$	Degree Celsius
%	Percent

# **CHAPTER I**

## **INTRODUCTION**

Copper has played a significant part in the history of mankind because it is a ductile, malleable metal with excellent electrical and thermal conductivity. Most of copper is used for various industries such as electronic part industry, printed circuit board industry, electroplating industry, fertilizer industry, hydrometallurgical industry and also petrochemical industry. This basically means that more and more copper ends up in the wastewater from those industries. Therefore, it is necessary to remove and recover copper ion from wastewater due to economical reason and its degree of toxicity.

At present, there are many methods for removing and recovering copper ions from wastewater such as chemical precipitation, electrolytic process, ion exchange, reverse osmosis and solvent extraction. But there are some disadvantages and limits in each of the methods mentioned above. In the case of chemical precipitation, the main disadvantages are the addition of a great volume of chemical reagents, the generation of an enormous amount of sludge that is not easy to dispose and the redissolution of many precipitates. Electrolytic process, although applicable to the recovery of many heavy metals, the process is not generally effective for the treatment of acidic solution. Ion exchange process has disadvantages due to the necessity to regenerate the resin after desorption of metals from the loaded resins, which is complex. The method also suffers from low removal rate, which is determined by the diffusion rate of ions through the solid, ion exchange membrane. Reverse osmosis produces good water quality but requires a high operating pressure, which results in a high cost. Solvent extraction process is technical alternatives which present many difficulties, among them is the requirement of a huge inventory of expensive solvent, large scale plants to obtain the desired separation and the process generally requires multi-stage operation to achieve a high enrichment factor. Moreover, during the solvent extraction process there are many difficulties, especially with regard to solvent loss due to crud formation by presence of suspended solid particles at the aqueous/organic interface, or



by the entrainment of the organic phase into the aqueous phase, or by volatilization and degradation of the organic reagents, as indicated by Valenzuela *et al.* (1997).

Membrane processes have been applied in applications such as concentration and purification of molecular solution in the chemical and pharmaceutical industry, removal and recovery of various solutes from industrial effluents. The membrane processes offer a possibility for economical processing because they need less energy and are specially useful for thermosensitive substances. Emulsion liquid membrane (ELM) process, which is interesting method for this work, is a specific class of membrane processes.

Emulsion liquid membranes was first invented by Li (1968), for separating and concentrating heavy metal ions from aqueous effluent streams. Thereafter, this method has been widely used in many varieties of separations and has become interesting in many fields such as biochemistry, biomedicine, pharmaceutical, environmental and hydrometallurgical industry. In comparison to solvent extraction, ELMs has more advantages for separation and concentration of heavy metal because the method is capable of achieving higher concentration of metals in a single stage and can maintain the high selectivity of solvent extraction.

ELM method is unique and different from the other membrane methods. The method uses surface forces to maintain a thin layer to be stable in immiscible membrane. ELM system consists of three phases of the two types, water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). For the W/O/W system, aqueous droplets are dispersed in an oil phase, which is then dispersed in a continuous aqueous phase. For the O/W/O system, oil droplets are dispersed in an aqueous phase, which is dispersed in a continuous oil phase. The most common and the most studied double emulsions are W/O/W since they have many applications in food, cosmetic, pharmaceuticals and also hydrometallurgy processes.

The emulsion liquid membrane method has more advantages than the other methods for various reasons, such as:

1. Combination of extraction and stripping processes in a single stage, therefore the product can be separated and concentrated at the same time.
2. Reduction of metal concentration in the feed stream to very low levels and the possibility of effective extraction from very low concentration stream.

3. Providing very fast transfer rates because of high specific surface areas.
4. The method needs low energy consumption and minimal downstream unit operation.
5. Decreasing the inventory of the organic solvent and metal extractant.

One of the disadvantages of the system is the swelling of the membrane phase due to water transport from the external feed phase to the internal aqueous phase, resulting in instability of the membrane and a decrease in the degree of concentration of the solute achieved inside the membrane phase.

From advantages and disadvantage of ELM method, it is interesting to use this method to minimize releasing of heavy and toxic metal ions to our environment. Therefore, this study will be focused on the separation of copper ions by ELMs.

Considering the advantages of ELM method, it was worthwhile to investigate the application of this method to recover copper ion from very dilute concentration (10 – 100 ppm) feed phase and improve the extraction with addition of ethylene - propylene copolymer in the membrane phase.

## 1.1 Objectives

The aims of this study are to explore the possibility of extracting copper from dilute aqueous solution by ELM process and find the optimum condition for effective extraction according to the following details;

1. To study the extraction of copper by ELM process using Ketoxime - Salicylaldoxime compound as a carrier.
2. To study the optimum condition for the extraction by ELM process.
3. To study the effect of the variables to the extraction of copper by ELM process.
4. To study the improvement of extraction process with addition of the polymer.

5. To study the effect of extraction, removal, recovery and swelling to the extraction.

6. To study the reusability of the membrane phase to the extraction, the effect of carrier to the extraction.

## 1.2 Scope of This Study

The extraction of copper from very dilute aqueous solution by ELM process was investigated under the conditions shown in Table 1.1.

**Table 1.1** Experimental conditions of copper extraction by ELMs

Parameters	Conditions
Surfactant concentration (Span 80)	0, 1, 2, 3, 4 and 5% by weight
Carrier concentration (LIX 984N)	0, 3, 4, 5 and 6% by weight
Stirring speed	200, 400, 600 and 800 rpm
Internal phase concentration (H <sub>2</sub> SO <sub>4</sub> )	1.0, 1.5 and 2.0 molar
pH of the feed phase	1, 2 and 5
Initial feed phase concentration (Cu <sup>2+</sup> )	10, 20, 40, 50 and 100 ppm
Extraction temperature	30, 40 and 50°C
Polymer concentration	1 and 2% by weight

The results are presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_t/C_{e0}$ ) versus time and tabulated as the percentage of copper removal with time.

The optimum condition for effective copper extraction from very dilute feed concentration will be summarized. The copper concentration in the aqueous feed phase will be monitored to the level of the toxic limit (1.5 ppm, WHO) or lower with the optimum condition of this study.

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

At present time, water contamination by traces of heavy metal ions is a major problem of hazardous environment. There are many toxic metals, such as aluminum, cadmium, cobalt, copper, iron, nickel, zinc and etc., released into the environment especially into water. The heavy metals present in effluent must be removed and recovered due to economical and environmental reasons.

There are many separation methods which are used in the hydrometallurgical field such as solvent extraction method which is inadequate for removing metals from dilute solution, resin ion exchange method which is not selective enough to be cost efficient for the recovery of metals from dilute solution. Liquid membrane method is superior to other metal extraction methods since it can selectively remove metals from solution that contains metals in the parts per million levels.

Liquid membrane processes, in principle, are a solvent extraction process in which the extraction and stripping operations are performed simultaneously. The liquid membrane process is based on the interposition of a membrane of an immiscible liquid between two, usually miscible phases. The feed phase is the solution containing the solute which is extracted after passing through the membrane. Transfer of solute occurs selectively through this membrane from one phase into the other (Li and Calo, 1992).

Liquid membranes can be classified into 2 types by configuration of the membrane phase, there are supported liquid membrane and emulsion liquid membrane. Supported liquid membrane have membrane areas around  $100\text{-}200\text{ m}^2/\text{m}^3$  of equivalent volume, whereas emulsion liquid membranes have surface areas of  $1000\text{-}3000\text{ m}^2/\text{m}^3$  (Marr and Kopp, 1982).

A supported liquid membrane is usually in the form of a porous solid film with an organic solvent, which is held in place by capillary forces that exists within the pores. The membrane separates an aqueous phase, initially containing the desirable

solutes, from another aqueous phase into which the solutes are extracted, the stripping phase. Extraction occurs because of the difference in chemical concentration that exists between the two aqueous phases. There are many advantages of supported liquid membrane than other separation methods such as lower capital and operating costs, low energy consumption, small quantity of membrane liquid is required for filling the pores, possibility of achieving high separation factor, possibility of concentrating the recovered species during the separation and lower maintenance cost due to fewer moving parts (Tavlarides, Bae and Lee, 1987). A major reason that supported liquid membranes have not been applying for larger scale industrial processes is the limited lifetime of the liquid membrane due to the dissolution of the organic solvent in aqueous solution.

Compare to emulsion liquid membrane, supported liquid membrane has advantages in that there are no emulsion to be prepared and to be broken in order to recover the product. However, one of the main disadvantages is that supported liquid membrane has a much thicker porous membrane sheet, while affects in a much larger equipment capacity to achieve the same separation. The other disadvantages include the necessity for frequent charging of the membrane liquid due to the wash out of the immobilized membrane phase from the supported pores (Denesi *et al.*, 1987) and also a low solute flux.

## **2.1 Emulsion Liquid Membranes**

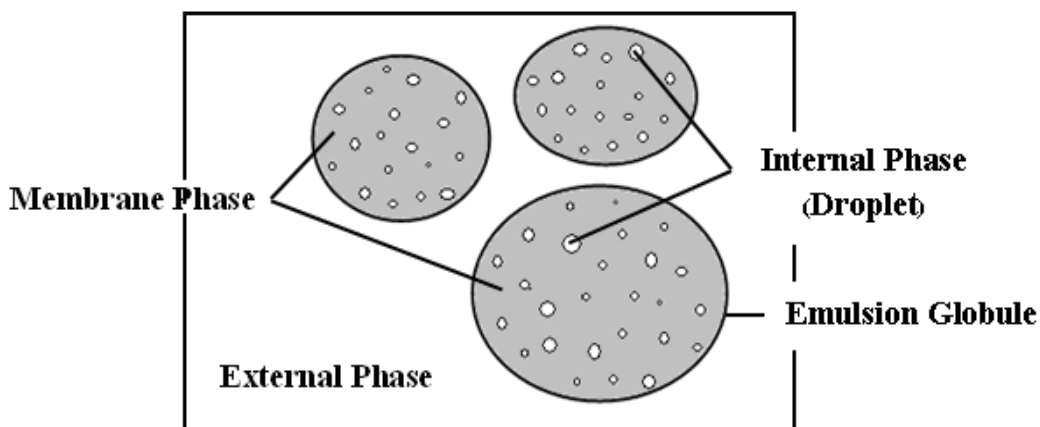
Emulsion Liquid Membranes, ELMs first invented by Li (1968), has been widely used for water treatment including the removal of metal cations and anions from aqueous streams. Initially, Li's work was concentrated on the separation of hydrocarbons with emulsion liquid membranes and later, on the removal of dissolved constituents (phenols, phosphoric acid, sodium nitrate and ammonia) from aqueous solutions. ELMs has also been used for biochemical and biomedical application such as extraction of L-lysine and extraction of alkaloid from herbs.

The emulsion liquid membranes is a liquid phase involving an emulsion configuration. ELMs, also called surfactant liquid membrane or liquid surfactant

membrane, are essentially double emulsion, i.e., water/oil/water (W/O/W) system or oil/water/oil (O/W/O) system. For the W/O/W system, the oil phase is the liquid membrane and separated from the two aqueous phases. For the O/W/O system, the aqueous phase is the liquid membrane that is separated from the two oil phases. The most common and the most studied double emulsions are of W/O/W since they have higher potential to become commercial products in food, cosmetic and pharmaceuticals systems (Garti and Lutz, 2004).

The emulsion consists of a continuous membrane phase and an internal droplet phase, which is usually the recipient of the solute that permeates from external feed phase through the membrane while the emulsion is dispersed in the feed by appropriate agitation (Li and Calo, 1992).

Most double emulsions are prepared in two steps. At first, a high shear homogenization or blending is applied on the system containing aqueous, oil phase and hydrophilic emulsifiers. High shear and prolonged homogenization is needed in order to obtain small submicronal aqueous droplets and stable W/O emulsion. In the second step, the pre-prepared W/O emulsion is gently and slowly added to an external aqueous phase containing the hydrophobic emulsifiers. Slow and stepwise addition under moderate stirring without any high-shear homogenization should be applied for the emulsion globules to be formed. The membrane phase consists of the liquid phase that separates the encapsulated, internal droplets in the emulsion from external, continuous phase, as shown in Figure 2.1. In general, the internal, encapsulated phase and the external, continuous phase are miscible. However the membrane phase must not be miscible with either of these two phases in order to be stable. Therefore, the emulsion is the W/O type if the external phase is water, and it is O/W type if the external phase is oil. To maintain integrity of the emulsion during the extraction process, the membrane phase generally contains some surfactant and additive as stabilizing agents, and it also contains a base material that is a solvent for all the other ingredients.



**Figure 2.1** Schematic of Emulsion Liquid Membrane System

The sizes of the aqueous droplets and emulsion globules depend on the fluid properties, the composition of the membrane, the viscosity of the emulsion and the stirring speed. Normal diameters are 20-40  $\mu\text{m}$  for the aqueous droplet and 200  $\mu\text{m}$  to 2 mm for the two-phase globule. A proper choice of the diameters is important. If the aqueous droplets are too small, too many of them are packed into each organic globule and consequently the liquid membrane becomes too thin and ruptures easily. Large aqueous droplets, on the other hand, result in poor efficiency because of a low surface-to-volume ratio. Thus, a very large number of emulsion globules can be formed easily to produce a very large mass transfer area adjacent to the external phase. Each emulsion globule contains many internal droplets. Thus, the internal mass transfer surface area, typically  $10^6 \text{ m}^2/\text{m}^3$ , is even much larger than the external mass transfer surface area. A rapid mass transfer in emulsion liquid membrane process can occur from either the external phase to the internal phase or from the internal phase to the external phase. Therefore considerable attention has been devoted to the choice of membrane composition and emulsion preparation conditions (Patnaik, 1995).

Separation of mixtures can readily be achievable by selective diffusion of components through the membrane phase into the receiving phase of lower equivalent concentration. Surfactant and additive included in the membrane phase can control the selectivity and permeability of the membrane. An individual component can be trapped and concentrated in the internal phase for later disposal or recovery. After

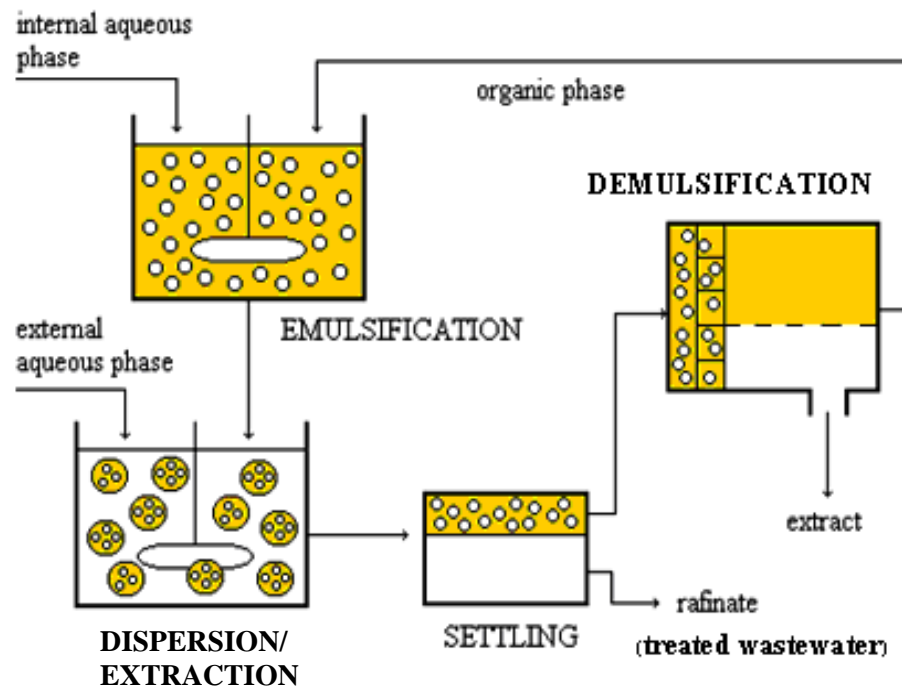
extraction, the emulsion and external phases are separated, usually by setting in a separating funnel until it divides into two distinct phases. The extracted component can be recovered from loaded internal phase of the emulsion by breaking the emulsion, such as heating, centrifugation, ultrasonification, solvent dissolution, high shearing and an electrostatic coalescence (Wang and Zhang, 1988; Marr, Bart and Draxler, 1990). The recovered membrane phase can be recycled to the emulsification step for the preparation of the emulsion with a regenerated or fresh reagent phase.

## **2.2 Emulsion Liquid Membrane Process**

A schematic representation of continuous ELM process is shown in Figure 2.2. This process consists of four steps;

1. Emulsification,
2. Dispersion of the emulsion in contact with the external feed phase for extraction,
3. Settling to separate the emulsion from the external phase which is the raffinate if the internal phase becomes the extract,
4. Demulsification for breaking of the emulsion to recover the internal phase as the extract and the membrane phase for recycle.





**Figure 2.2** Schematic of a continuous emulsion liquid membrane process

### 2.2.1 Emulsification

Emulsion liquid membranes can be adjusted to use with requirements of different separations, thus can offer versatile processes capable of separating a wide range of liquid mixtures. On the other hand, this versatility sometimes brings about difficulties in the design of membrane formulation. Choosing the appropriate membrane formulation for a particular separation is often quite complex. There are 3 components that have to be considered.

#### 1. Membrane solvent

The solvent is the main membrane component in which both of extractant and surfactant are dissolved. Although the solvent is normally regarded as an inert component, it does not affect the membrane properties. An ideal solvent for emulsion liquid membranes should have the following properties;

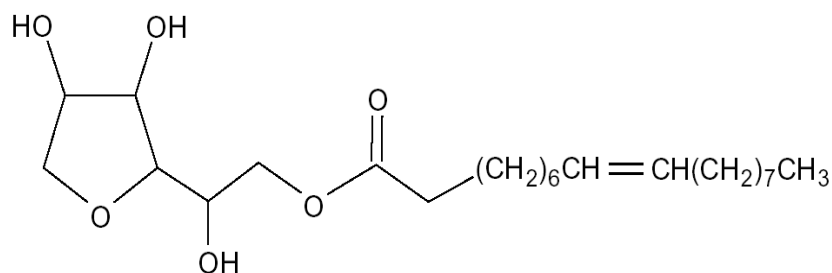
- Having low solubility in the internal and external aqueous phase so as to minimize the solvent loss.
- Being compatible with extractant and surfactant without forming a new phase.

- Having a moderate viscosity because in solvent extraction, an as-low-as possible viscosity is desired for the solvent for fast mass transfer. For emulsion liquid membranes, however, a much lower solvent viscosity would reduce the membrane strength, resulting in membrane instability.
- Having a sufficient density difference from the aqueous phase for the fast settling operation.
- Being both cheap and reliability, available for a number of alternative sources and also having low toxicity and high flash point for safety.

From the above reasons, an aliphatic diluents are preferred as the membrane solvent because of their lower solubility in water, such as cyclohexane, kerosene, shellsol A (a paraffin containing xylene) and S100N (a high molecular weight isoparaffin), etc (Seong *et al.*, 1992).

## 2. Surfactant

The surfactant is a key component for formulating a stable emulsion. Surfactant is characterized on the basis of the hydrophilic/lipophilic balance of the molecule or HLB scale. On this scale, species with high hydrophilic character which is a good oil in water emulsifier are assigned high HLB values. In order to get water in oil emulsion, low HLB surfactants are chosen. Due to the membrane has become commercialized, its applications have required more of surfactant than their major contribution to membrane stability such as chemical resistance, bacterial resistance, thermal resistance and etc. In addition, the selected surfactant should be cheap and non-toxic for economic and environmental reasons.



**Figure 2.3** Chemical structure of Span 80

Span 80, Sorbitan monooleate, is a non-ionic surfactant with a molecular weight of 428 and a HLB value of 4.3, a fairly good W/O emulsifier, is widely used in ELMs. During extraction operation, the membrane consisted of Span 80 shows less resistance for mass transfer than those with other surfactants. Span 80, however, suffers from some disadvantages. Since it is a good carrier for water molecules it favors the osmotic swelling of emulsion. Span 80 as an emulsifier is its poor chemical stability especially when NaOH is used for an internal phase (Hirato *et al.*, 1990).

The concentration of selected surfactant should be minimum to maintain stability for the whole time of extraction separation. Too much surfactant will increase the mass transfer resistance at the interface between the external and the membrane phases. It will also lead to more stable emulsion which will be harder to break (Draxler and Marr, 1986).

### 3. Carrier Species (Extractant)

The carrier species are used only in facilitated transport to enhance solute solubility and selectivity. There are two types of carrier species, charged and uncharged. The common principles for both are the extractant and their complex formed must be insoluble in the external and internal phases, as any leakage from the membrane phase decreases the efficiency of the process. The other important point is the affinity of the solute for the carrier, if the solute-carrier complex is very strong, then a stable complex is formed and the solute cannot be released to react with the chemical reagent in the internal phase (Cussler and Evans, 1974). Precipitation is also

not allowed to happen either within the membrane or at the interfaces, otherwise the membrane process will fail.

The classification is based on the type of extractants which can be simply identified into three groups. These are acidic extractants, basic extractants, and solvating extractants. Although most extractants have been identified, there is a great deal of effort to produce new reagents.

Chelating extractants are those which contain donor groups capable of forming bidentate complexes with metal ions. Commercially available chelating extractants are, at present, under the name LIX reagents which produce by Cognis. The extractants have general structures which can be subdivided into two distinct classes based on their structures and properties: the ketoximes, which are normally copper extractants of moderate strength and the salicylaldoximes, which are very strong copper extractants. There are some commercial copper solvent extraction LIX reagents shown in Table 2.1. The compositions of some hydroxy oxime copper extraction reagents from Cognis are listed in Table 2.2.

**Table 2.1** Commercial copper extraction LIX reagents from Cognis (MCT Readbook)

<b>Category/Extractant</b>	<b>Features</b>
<b>Ketoximes, LIX 84-I</b>	<ul style="list-style-type: none"> <li>• good physical performance under a wide variety of conditions, especially with respect to aqueous solution</li> <li>• good chemical stability under conditions</li> <li>• a moderately strong copper extractant</li> </ul>
<b>Salicylaldoximes</b>	<ul style="list-style-type: none"> <li>• rapid copper transfer kinetics and high extractive strength</li> <li>• strong copper extractants</li> </ul>
<b>Ketoxime-Salicylaldoxime Mixtures, LIX 984 and LIX 984N</b>	<ul style="list-style-type: none"> <li>• extractive strength and fast kinetics of the salicylaldoximes combined with the proven, excellent physical performance and stability of the ketoximes</li> <li>• a universal reagent for acid sulfate copper leach solutions</li> </ul>
<b>Modified Ketoxime-Salicylaldoxime Mixtures, MAK<sup>TM</sup> Reagents</b>	<ul style="list-style-type: none"> <li>• consist of ketoxime-salicylaldoxime mixtures to a small amount of equilibrium modifier</li> <li>• good copper transfer and selectivity</li> </ul>

**Table 2.2** Composition of some copper extraction reagents from Cognis (MCT Readbook)

<b>Extractant/Category</b>	<b>Composition</b>
LIX <sup>®</sup> 84-I /Ketoxime	A mixture of 2-hydroxy-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent needed for handling purposes.
LIX <sup>®</sup> 84-IC / Ketoxime	The concentrated version of LIX 84-I
LIX <sup>®</sup> 860-I /Salicylaldoxime	A mixture of 5-dodecylsalicylaldoxime in a high flash point hydrocarbon diluent needed for handling purposes.
LIX <sup>®</sup> 860N-I /Salicylaldoxime	A mixture of 5-nonylsalicylaldoxime in a high flash point hydrocarbon diluent needed for handling purposes.
LIX <sup>®</sup> 984N /Mixture	An equal volume mixture of LIX 84-I with LIX 860N-I.
LIX <sup>®</sup> 973 /Mixture	A 7 / 3 volume blend of LIX 860-I with LIX 84-I.
LIX <sup>®</sup> 937N / Mixture	A 3 / 7 volume blend of LIX 860N-I with LIX 84-I
LIX <sup>®</sup> 622N / Modified Salicylaldoxime	A mixture of 5-nonylsalicylaldoxime and tridecanol in a high flash point hydrocarbon diluent.
LIX <sup>®</sup> 622N-LV / Modified Salicylaldoxime	A mixture of 5-nonylsalicylaldoxime and a proprietary low viscosity alcohol in a high flash point hydrocarbon diluent
LIX <sup>®</sup> 612N-LV/ Modified Salicylaldoxime	A mixture of 5-nonylsalicylaldoxime and a proprietary low viscosity modifier in a high flash point diluent.
LIX <sup>®</sup> 616N-LV/ Modified Salicylaldoxime	A mixture of 5-nonylsalicylaldoxime and a proprietary low viscosity modifier in a high flash point diluent.

#### 4. Internal Stripping Phase

In emulsion liquid membrane process, the internal phase contains the chemical reagent which reacts with the solute to form a compound which is insoluble in the membrane phase. The chemical reagent in the internal phase is usually an acid or base (Li *et al.*, 1973). When choosing the chemical reagent for the internal phase, the chemical compatibility of the surfactant with the reagent must be considered.

Generally, the selection of the internal phase reagent is based on the thermodynamic and kinetic considerations. Thermodynamically, the selected internal phase reagent must be able to partition the solute from the membrane phase into the internal phase.

An acidic solution (sulfuric acid solution) is usually used as the internal phase reagent. The capacity of the internal phase for the solute being extracted depends on the initial concentration of such reagent.

To prepare a stable emulsion, the mean diameter of the dispersed internal phase droplets should be as small as 1-3  $\mu\text{m}$ , which requires a high input of energy density to the W/O system for emulsification. In general, emulsion is usually made by high speed agitation with stirring speed up to 20,000 rpm using commercially available emulsifiers such as Tekmar Homogenizer (Itoh *et al.*, 1990), Waring Blender (O'Brien and Senske, 1989) and ultrasonic emulsifier (Shere and Cheung, 1998).

#### **2.2.2 Dispersion/ Extraction**

The separation by an emulsion liquid membrane process includes dispersion, from which the coupled extraction/stripping is achieved, and settling, which realizes the phase separation between the loaded emulsion and the aqueous raffinate because of their density difference. Before dispersing the emulsion into the feed, the pretreatment of the feed is required as in most separation processes and is typically done by the use of 1-10  $\mu\text{m}$  filters, sometimes includes flocculation and sedimentation steps before filtration. During the dispersion operation, the emulsion is dispersed by agitation in the external feed phase and many small globules of emulsion

are formed. Normally, the size of emulsion globules is controlled in the range of 0.1-2.0 mm in diameter. Each emulsion globule contains many tiny encapsulated droplets with a typically size of 1-3  $\mu\text{m}$  in diameter. Such a large number of emulsion globules together with the numerous pre-encapsulated droplets provide large interfacial areas for both extraction and stripping.

### **2.2.3 Settling**

After the extraction is completed, phase separation of the loaded emulsion from the external raffinate takes place in the settler. The settling is similar to that for conventional solvent extraction.

### **2.2.4 Demulsification**

After emulsion liquid membrane extraction, the membrane phase must be recycled repeatedly, and the enriched internal phase is usually recovered. Therefore, demulsification of the loaded emulsion is unavoidable for the use of this separation process, with a few exceptions for the use of this technology without breaking the emulsion in some special cases (Dines, 1982).

Two principle approaches for the demulsification of the loaded emulsion are chemical and physical treatments. Chemical treatment involves the addition of a demulsifier to a membrane. This method seems to be very effective. However, the addition of demulsifier will change the properties of the membrane phase and thus prohibit its reuse. In addition, the recovery of the demulsifier by distillation is rather expensive. Therefore, chemical treatment is usually not suitable for breaking liquid membrane emulsion. Physical treatment methods include heating, centrifugation, ultrasonic, solvent dissolution, high shear and the use of high voltage electrostatic fields are alternatively employed.

## **2.3 Mechanism and Driving Force for ELMs**

In a liquid membrane separation system, there are two types of mechanisms for transporting solute across the membrane phase. They are unassisted transport and facilitated transport



### **2.3.1 Unfacilitated Transport**

This is the simplest case of solute transport through the membrane phase and is a diffusion process. This type uses a stripping agent in the internal phase to entrap the solute and maximize the mass transfer rate. No carrier is added into the membrane phase. The selectivity of solute separation depends on the partition coefficient of the solute. The solute is initially in the bulk of the external phase and diffuses to the interface of the membrane phase. Here it partitions into the membrane and diffuses across to the interface of the internal phase into which it partitions. The driving force of the transport is the concentration gradient, concentration difference of the solute across the membrane phase. In order to sustain a larger concentration gradient over a length of time, the transported solute must be converted in the receiving aqueous droplets into a form which cannot diffuse back.

The driving force can be manipulated by the inclusion in the internal phase, a chemical reagent which reacts with the solute. This has a two-fold effect, first the solute is now in a different chemical form and cannot diffuse back if it is insoluble in the organic solvent. Second, because the solute is now in a different form, the concentration of the transportable species in the internal phase, is effectively zero and the concentration gradient is maximized as mentioned above, thus enhancing mass transfer.

While unfacilitated transport mechanism is simple and inexpensive, its selectivity and efficiency are not always good. Moreover, as the separation proceeds, the neutralizing or anchoring compound in the internal phase gets depleted earlier in the droplets close to the surface of a globule, hence the solute has to diffuse further and further inward before being released and neutralized. Therefore, as time progresses the process becomes diffusion limited and slows down. To overcome this limitation a carrier is added into the membrane phase in order to increase the speed and selectivity.

### **2.3.2 Facilitated Transport**

This form of transport is of greater importance in any potential liquid membrane separation. Its application is for membrane-insoluble materials, such as charged species, metal ions and organic acids. By introducing a water-insoluble

carrier molecule into the membrane phase, the solute solubility is increased by the reversible formation of a membrane-solute carrier-solute complex. This results in higher mass transfer rates and solute selectivity due to the specific formation of the carrier-solute complex by while the solute is transported across the membrane (Cussler, 1984; Lobarch and Marr, 1987).

There are three advantages to show the benefits of using a carrier in ELM method (Richard and Koval, 1989).

1. High fluxes are possible. By combining the advantages of high-diffusion coefficients in liquid with the added carrying capacity of the carrier, larger fluxes will be obtained than those in unfacilitated transport.

2. Very selective separations are possible. The selective nature of the complexation reaction provides much better separations than those that can be obtained based solely on relative solubility and diffusion.

3. Solutes, especially ions, can be concentrated. Coupled transport allows one to pump ions against their concentration gradient.

There are two possible ways of carrier mechanism: counter-transport mechanism and co-transport mechanism.

### **2.3.2.1 Counter Transport**

The main point of counter transport is the fluxes of the two permeating ions move counter to each other across the membrane. The solute is transported across the membrane by the formation of complex as follow.

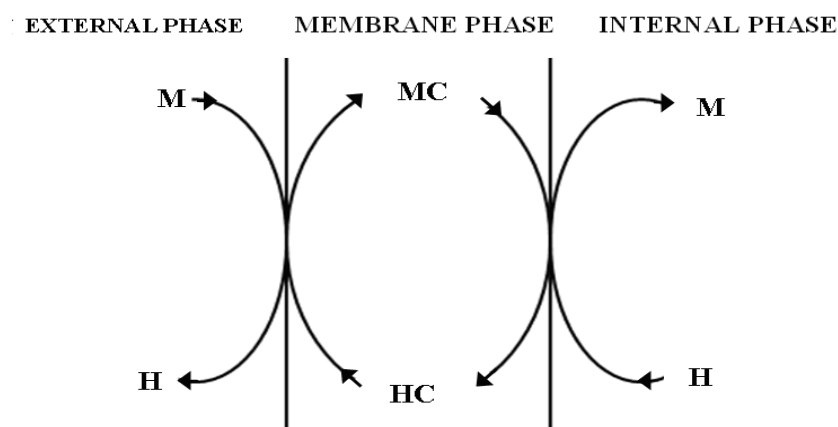
1. At the interface between the external phase and the membrane phase the solute M, reacts with the carrier HC, forming the complex MC, and liberates H<sup>+</sup> into the external phase. This complex is insoluble in either aqueous phases but is soluble in the membrane phase

2. The carrier-solute complex, MC, diffuses across the membrane to the interface between the membrane and the internal phase.

3. At this interface of 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  $H^+$  in the internal phase. Hence the solute  $M$  is released into the internal phase reagent.

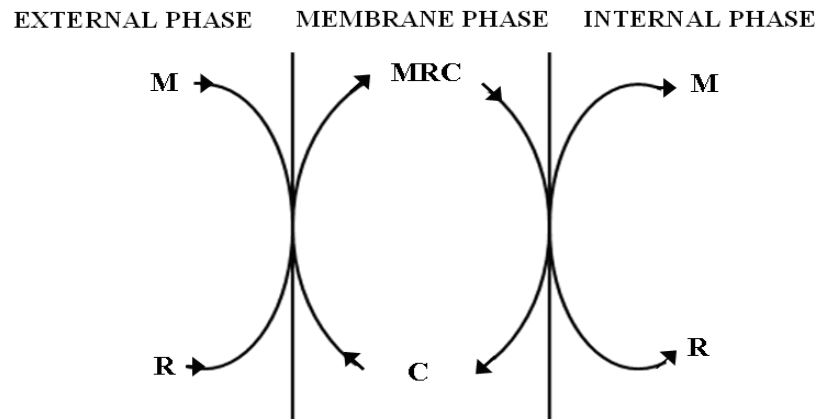
4. The carrier anion reacts with the counter-ion to form the carrier molecule,  $HC$ , which then diffuses back through the membrane to the exterior interface where the counter-ion is released, hence completing the process. The schematic diagram of counter transport is showed in figure 2.4.



**Figure 2.4** Schematic of Counter Transport

### 2.3.2.2 Co-transport

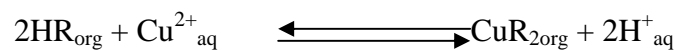
In co-transport, the less common mode of facilitated transport, the carrier molecule must be protonated before it can form a neutral complex with the anion to be transported. The mechanism is the carrier,  $C$ , reacting reversibly with the solute,  $M$ , and other component,  $R$ , and transporting them in one direction across the membrane. The free carrier diffuses back across the membrane, therefore, two coupled fluxes exist across the membrane in the same direction (Cussler, 1984). The schematic diagram of counter transport is showed in figure 2.5.



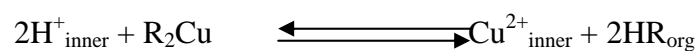
**Figure 2.5** Schematic of Co-Transport

## 2.4 Transport Mechanism of Metal Ion

General mechanism for metal transport in ELM process has been proposed (Sengupta *et al.*, 2006) for copper extraction it is the facilitated counter transport mechanism. The copper ions present in the feed phase react with the carrier ( $\text{HR}_{\text{org}}$ ) at the interface of the emulsion globule and the external feed phase. The chemical reaction that takes place at the interface can be described as:



The resulting copper complex ( $\text{CuR}_{2\text{org}}$ ) diffuses through the organic membrane phase and on contact with the internal stripping phase, then copper ion gets stripped from the carrier by the following chemical reaction:



The stripped copper ion is effectively encapsulated within the internal droplets of the emulsion globules, while the carrier shuttles back to scavenge more

copper ions from the feed phase to deposit in the internal stripping phase of the emulsion.

## 2.5 Advantages and Disadvantages of Emulsion Liquid Membranes

The main advantages of emulsion liquid membrane method are summarized as follow:

1. The specific surface area of emulsion liquid membrane is very high, giving rise to very fast extraction rates, because of the small droplet sizes.

2. Liquid membrane extraction is ideal for the separation of products, which are in low concentration in fermentation broth because the concentration difference is always maximized.

3. The solute can be simultaneously separated and concentrated by making the internal phase reagent sufficiently concentrated and ensuring that the internal phase reagent is sufficiently concentrated.

4. In comparison to conventional solvent extraction, extraction and stripping steps 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 effective 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 to be easily be scaled up to an industrial scale operation and for continuous processes.

7. Emulsion liquid membrane separations are little affected by solids, this suggests the application of this process as a primary separation step without the requirement of filtration.

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

Two disadvantages of emulsion liquid membrane method are emulsion formation and membrane breakage. There are two phenomena associated with the

operation of emulsion systems which can have a detrimental effect on the overall separation. They are leakage and swelling.

### **1. Leakage**

In emulsion liquid membrane process, some of extracted solute can leak back into the external phase. This phenomenon is accompanied by leakage of the internal phase reagent which can then transform the solute into a non-extractable form. 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 membrane leakage or breakdown is important in assessing the stability of liquid membranes. Membrane leakage in emulsion liquid membrane systems includes the rupture of the emulsion, leading to the short circuiting of the reagent and extracted solute in the internal phase to the external phase. As a result, the leakage causes a decrease of the driving force of mass transfer and an increase of the external concentration thus lowering the extraction efficiency. The main factors governing membrane stability include the membrane formulation, the method of emulsion preparation and the condition under which the emulsions are contacted with the feed solution. The leakage rates are quite different, ranging from 0.2-10 % (Zhang *et al.*, 1988; Shere and Cheung, 1988; Thien and Hatton, 1988).

### **2. Swelling**

Membrane swelling that increases the internal phase volume is a troublesome problem associated with the use of emulsion liquid membranes. It is a process by which water is transferred from the external aqueous phase into the internal droplet phase. The water transfer will dilute the solute that has been concentrated in the internal droplets, thus preventing a highly concentrated solute solution from being obtained and reduces the driving force for solute extraction (Draxler and Marr, 1986; Yan, Huang and Shi, 1987), making the membrane thinner, thereby leading to a less stable emulsion, causing a change in the rheological properties of emulsion transport and phase separation. Swelling is considered to take place via a hydrated surfactant which traverses back and forth across the membrane. Reverse micelles can accommodate both solute and water molecules; this inference is

based on data that the charged solutes are transported across the membrane without carriers, especially when micelle-promoting surfactants such as sorbitan monooleate are used (Patnaik, 1995).

Some of the possible mechanisms for swelling (Cerro and Boey, 1988) are as follow:

1. Emulsification of the external phase. This is more likely when excess surfactant is used and a high external phase to internal phase ratio is used.
2. Occlusion of part of the external phase through droplet coalescence.
3. Osmosis brought about as a result of the relatively high concentrations of reagent required for stripping.

The effect of swelling is that the transferred water dilutes the solute that was concentrated in the inner droplets, the driving force is reduced, productivity (per unit volume) is reduced since the membrane occupies a larger fraction of the emulsion volume and also the membrane becomes less stability. Swelling can be reduced by careful use of the surfactant concentration in the organic phase. On the other hand, swelling may be controlled by adding certain hydrocarbons or anion exchangers.

## **2.6 Literature Reviews**

### **2.6.1 Emulsion Liquid Membrane Applications**

#### **1. Metal Applications**

In 1987, Frankenfeld and Li reviewed the applications of ELMs for removal of toxic substances such as chromium, cadmium and copper 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). Their work was focus on phenol removal.

In 1989, Draxler, Furst and Marr reviewed ELM applications for the separation of metal ions out of waste water in a pilot plant. Their report showed that zinc, cadmium and lead can easily be separated down to concentrations which are below the limits of most environment protection agencies. The problem was reported as the co-transport of water caused by the concentration of the effluent and the dilution of the inner phase concentration.

In 1996, Kongkapetchawan studied copper separation from aqueous solution using ELM method. The membrane phase consisted of D2EHPA as a carrier and span 80 as a surfactant. An internal aqueous phase was hydrochloric solution. The ratio between the membrane phase and the internal aqueous phase was used was 1:1 by volume. The separation was operated at room temperature. The effect of carrier concentration, surfactant concentration, external feed solution acidity, initial acid concentration in the internal phase, ratio between emulsion phase to feed phase, and agitation speed was investigated. He also studied the equilibrium of copper. The results showed that the optimum pH for the extraction was 3. The optimum condition was 5% span 80, 10% D2EHPA by volume and 1 N of hydrochloric acid. Optimum speed agitation for extraction was 400 rpm. More than 99% of copper were extracted in 5 minutes under the optimum condition. He also reported the extraction equilibrium of copper to be  $8.20 \times 10^{-4} \text{ dm}^3/\text{mol}$ .

In 2000, Chakravarti, Chowdhury and Mukherjee studied the liquid membrane multiple emulsion process for separation of copper from waste waters. The carriers used in the system were LIX 622 and LIX 84. The surfactant was span 80 and the internal stripping phase was sulfuric acid. The extraction was performed at  $28 \pm 2^\circ\text{C}$ . The effect of variation such as oil membrane components, sulfuric acid concentration, pH and feed concentration was studied. They also studied interferences of other metal ions such as lead, cadmium, zinc, cobalt and nickel on the extraction of copper ion. The result showed that LIX 622 was more effective carrier than LIX 84 under the same conditions. The presence of other ions caused slower transport of copper ion.

In 2005, Valenzuela *et al.* reported the removal of copper ions from a residual mine water using ELM method. LIX 860 was used as a carrier and Span 80 was used as a surfactant. The ratio of organic phase and internal stripping phase was 1:1 by volume. The ratio 1:6 by volume between W/O emulsion and copper feed solution



was used. The temperature was kept at 30°C. The variances on copper transport through the membrane, such as the carrier concentration, the stirring time and the stirring speed of double emulsion, were studied. They observed that the use of excessively high content of surfactant produced lower metal extraction since it gave rise to higher interfacial resistance. Their result showed the potential for removal of valuable or toxic metals from dilute mine solutions.

In 2006, Sengupta, Sengupta and Subrahmanyam studied the extraction of copper from aqueous sulfate media into ELMs using the extractant LIX 984N-C. The effect of stirring speed, surfactant concentration, pH of the external continuous phase, carrier concentration, internal phase stripping acid concentration and initial copper concentration was studied. The components of emulsion were LIX 984N-C as a carrier, Span 80 as a surfactant and 1.5 M of sulfuric acid as an internal aqueous stripping phase. The ratio of organic phase and internal stripping phase was 1:1 by volume. The ratio 1:6 by volume of W/O emulsion and copper feed solution was used. The extraction temperature was 30°C. They found that LIX 984N-C efficiently extracted copper at low pH values (1-2) typical of leach solutions. They also found that LIX 984N-C could extract copper ion up to 80% from aqueous solutions at pH value of 1. They had concluded that the carrier could open up new avenues for extraction of copper into emulsion ELMs, not only from dilute solutions, but also from sulfuric acid leach solutions.

In 2006, Sengupta, Sengupta and Subrahmanyam focused on process intensification of copper extraction using ELMs. The emulsion components were consisted of LIX 84 as a carrier, Span 80 as a surfactant, kerosene as a membrane and sulfuric acid as an internal aqueous stripping phase. Extraction was carried out at 30°C. The influential parameters such as the internal phase volume fraction, surfactant concentration, internal phase stripping acid concentration, carrier concentration, pH, initial solute concentration and treat ratio were studied. The results showed that the best ratio between emulsion phase and feed phase was 1:6 by volume. The extraction was favorable above pH 2. Swelling was always observed after 30 minutes of contact with feed phase.

In 2007, Gameiro *et al.* reported the extraction of copper from ammoniacal medium by emulsion liquid membrane. The LIX 54 and LIX 84-I were selected as the

carrier for their experiments. They used ECA 4360J as the surfactant and Span 80 was used in a few experiments. Sulfuric acid aqueous solution was used as internal stripping phase. A volume ratio of 2:1 by volume was maintained for organic phase to the internal stripping phase. The ratio between emulsion phase and feed phase was not mentioned. All extractions were maintained the temperature at 25°C. The extraction of copper was investigated under various experimental conditions such as stirring speed, treatment ratio, solute concentration in feed phase, carrier concentration in membrane phase and stripping agent concentration. They also studied the modeling of solute permeation. Their studies indicated that the effects of various experimental condition could be simulated using the parameter  $k' = 1.2 \times 10^{-7} \text{ ms}^{-1}$ , which was the apparent rate constant of stripping reaction. This parameter was found to be directly proportional to the sulfuric acid concentration in the internal phase.

In 2007, Sengupta, Bhaknar and Sengupta studied extraction of copper from ammoniacal solutions into ELMs using LIX 84-I as a carrier and Span 80 as a surfactant. Emulsion was formulated with equal volume of organic phase and stripping phase. All extractions were carried out at 30°C. They found that the extraction process was very fast and almost quantitative extraction was observed in just two minutes contact between the feed and the emulsion phase for most cases. The suitable pH for the extraction was found to be at 8.1. They concluded that high carrier concentration and treat ratio led to faster recoveries.

In 2008, Venkatesan and Meera Sheriffa Begum conducted the experiment to remove copper and zinc from aqueous solution and industrial effluents using ELM technique. D2EHPA was a carrier and span 80 was a surfactant. An aqueous solution of 1 N sulfuric acid was used as internal aqueous phase. The ratio 1:1 by volume between organic phase and 1 N sulfuric acid solution was used. The effects of surfactant concentration, carrier concentration, emulsification speed, emulsification time, internal phase stripping agent concentration and W/O emulsion ratio were studied. It was found that 84% of copper and 86% of zinc were removed from aqueous solution with pH 5. They also compared the extraction of synthetic and electroplating effluent. It was found that the copper recovery of the plating effluent was 8-17% less than that of the synthetic effluent.

## 2. Bioseparation Applications

In 1982, Terry, Li and HO studied the separation of phenols and cresols from waste water. In addition to being able to separate these contaminants from waste water, they also found that unfacilitated transport (simple diffusion) for ELMs could also be used for the separation of acetic and propionic acids. Their study indicated that ELMs was particularly good at separating acetic acid from dilute solutions.

In 1987, Boey *et al.* studied the recovery of citric acid by ELM method. The membrane consisted of Alamine 336 and Span 80 as a surfactant, dissolved in Sllsol A. Sodium carbonate was used as the internal phase reagent. Their work focused on the batch extraction of model and real fermentation broth. The results showed that very fast extraction of citric acid could be achieved and over 80% of citric acid was removed in 5 minutes. Membrane swelling was also observed in their study.

In 1994, Panich reported the extraction of phenylalanine and tryptophan by using ELMs. The membrane phase consisted of D2EHPA as a cation carrier and Span 80 as a surfactant dissolved in n-dodecane. The internal aqueous phase was 1 N hydrochloric acid solution. The extraction was set up at 25°C. He studied the extraction equilibrium of mixtures and batch extraction of single dilute phenylalanine, dilute tryptophan and mixtures of both amino acids. He also studied factors of the extraction. The results showed that the extraction equilibrium constant of phenylalanine and tryptophan were found to be 0.167 and 0.11 dm<sup>3</sup>/mol, respectively. Tryptophan had a higher flux than phenylalanine. The results also showed that the extraction rate at pH 5 and 3 was higher than at pH 2. For the extraction of binary mixtures solution of tryptophan and phenylalanine, tryptophan did not have significant effect on the transport rate of phenylalanine.

In 1995, Suetrong studied extraction of L-lysine from aqueous solution by ELMs. The membrane phase consisted of cation carrier (D2EHPA) and surfactant (Span 80) which dissolved in n-dodecane. The internal aqueous phase was hydrochloric acid solution. The extraction system was carried out at 25°C. The experimental conditions for optimum condition and extraction equilibrium of L-lysine

were studied. It was found that the extraction equilibrium of L-lysine was found to be  $0.2047 \text{ dm}^3/\text{mol}$ . The results showed that the optimum condition was 5% Span 80, 10% D2EHPA (by volume) and 1 N hydrochloric acid in internal aqueous phase. The optimum speed agitation was 420 rpm. By the optimum condition, 50% of L-lysine was extracted within 5 minutes.

In 1997, Chunsawang was conducting the experiment for alkaloid extraction from herbs by ELM process. The membrane phase consisted of n-hexane as a carrier and Span 80 as a surfactant. Hydrochloric acid solution was an internal aqueous phase. The extraction was  $25^\circ\text{C}$ . The extraction equilibrium and various conditions of extraction were studied. It was found that the suitable condition of synthetic berberine extraction was pH 11, 1% by volume of Span 80 and 0.02 M hydrochloric acid. 99% of berberine was extracted within 4 minutes with the optimum condition. The suitable condition of crude berberine extraction was pH 12, 1% by volume of Span 80 and 0.03 M hydrochloric acid. The results also showed that 70% of crude berberine was extracted in 1 minute.

In 1999, Thawisaeng studied L-lysine extraction from mother liquor by ELM method. D2EHPA was used as a carrier and Span 80 as a surfactant. Internal aqueous phase was hydrochloric acid solution. The extraction equilibrium and effects of extraction were investigated. It was observed that the extraction equilibrium constant were  $5.26 \times 10^{-4}$  and  $4.72 \times 10^{-5} \text{ dm}^3/\text{mol}$  for L-lysine in synthetic solution and in mother liquor, respectively. The experimental results showed the optimum condition for this process to be at pH 5, 2 N hydrochloric acid, 1% Span 80 by volume, 10% D2EHPA by volume with stirring speed of 360 rpm.

### **2.6.2 Swelling Studies**

In 1999, Skelland and Meng studied the non-Newtonian effect on the stability, permeability and swelling in ELM process. The extraction of benzoic acid, ammonia and phenol was chosen for studying. The extraction system was maintained at the temperature of  $25^\circ\text{C}$ . Some of the polymers such as poly-isobutylene, poly-styrene

and polybutadiene were added into the membrane phase for enhanced emulsion stability. In the case of benzoic acid extraction, the non-Newtonian membranes with 0.5 or 1.0% of poly-isobutylene provided much better performance. For extraction of phenol, the membranes made of non-Newtonian fluids with addition of 1.0 or 2.0% poly-isobutylene gave much improved stability and no reduction in mass transfer. For extraction of ammonia, the result showed that the non-Newtonian membranes with 0.5% of poly-isobutylene not only improved membrane stability but also gave a higher mass transfer rate compared to the traditional membrane.

In 2001, Yan and Pal reported the osmotic swelling behavior of globules of W/O/W ELMs. The osmotic pressure gradient between internal and external aqueous phase was induced by creating a concentration difference of D-glucose between the two aqueous phases. A Zeiss optical microscope equipped with a camera was used to observe the changes in the ELM globules. The effects of surfactant concentration and internal volume fraction of internal aqueous phase on the swelling behavior were discussed. The results indicated that the swelling ratio decreased with an increased in volume fraction of internal aqueous phase. The swelling ration generally increased with an increased in the concentration of surfactant. The permeation coefficient of water also increased with an increased in the surfactant concentration. They concluded that the mechanism of water transfer in ELMs of this experiment was reasoned by the diffusion of hydrated surfactant.

In 2002, Jiao, Rhodes and Burgess conducted the experiment to investigate the significance of inner and outer phase pressure and also interfacial film strength on W/O/W multiple emulsion stability. Many derivatives of Span 80 were used as a surfactant. The substance in the external aqueous phase was changed in each formulation. An Olympus BH-2 polarized light microscope was used to estimate size of the inner aqueous droplets. It was observed that immediately upon applying a coverslip to samples the multiple droplets deformed and there was coalescence of the inner aqueous droplets. Under certain conditions such as lipophilic surfactant concentration and internal phase osmotic pressure, the destabilized multiple emulsions formed unique metastable structures that had a dimpled appearance. They also concluded that the formation of the metastable structures correlated with the real-time instability of the W/O/W multiple emulsions investigated.

In 2007, Cheng *et al.* studied transportation of ion through the oil phase of  $W_1/O/W_2$  double emulsions. The experiment was designed to visually investigate how salt ions were transported using the capillary video microscopy technique. This study would show mechanisms of ion transport and also swelling breakdown mechanism. Sodium chloride and silver nitrate were chosen as the model reactant. It was found that both  $Cl^-$  and  $Ag^+$  could be transported through a thick oil film and  $Ag^+$  was transported faster than  $Cl^-$ . They concluded that the transport of ions mainly depended on the reverse micelle transport mechanism and that an ion with smaller Pauling radius was transported faster than an ion with larger Pauling radius.

## CHAPTER III

### EXPERIMENT

#### 3.1 Chemicals

- Cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), Analytical grade, from Fluka Chemika Co.
- LIX 984N, Ketoxime-Salicylaldoxime mixtures, equi-volume mixture of 2-hydroxy-5-nonylaceto-phenone oxime (LIX 84-I) and 5-dodecylsalicylaldoxime (LIX 860-I), Laboratory grade, from Cognis Co., Thailand
- Span 80, Sorbitan monooleate, Analytical grade from Kao Chemical Co.
- Kerosene , Industrial grade, from Exxon Mobile
- Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 96.6%, Analytical grade, from Fluka Chemika Co.
- Nitric acid ( $\text{HNO}_3$ ) 96.6%, Analytical grade, from Fluka Chemika Co.
- Ethylene-propylene copolymer, Analytical grade, from Exxon Mobile

#### 3.2 Instruments

- Blender (Model HB III, Hanabishi) for preparation of emulsification process.
- Mechanical Stirrer (Model RW20., IKA Laboratechnik) for operation in extraction step.
- pH meter (Model 744 pH meter, Metrohm) for feed pH measurement.
- Centrifuge (Model EBA 20, Hettich) for separation of the organic phase form the internal phase.

- Atomic Absorption Spectrometer (Model AAnalyst 100, Perkin Elmer) for copper analysis.
- Water bath (Model DT<sub>1</sub>, Heto Lab Equipment) for heating the extraction system.
- Brookfield cone and plate programmable Rheometer (Model DV- III, Brookfield) measured viscosity of the emulsion.
- Canon EF-S digital camera (Model EFS 60 mm Ultrasonic, Canon) for taking photo of emulsion globules.

### **3.3 Experimental**

The diagram of the experimental operation of emulsion liquid membrane process is shown in Figure 3.1. The following procedure was carried out stepwisely.

#### **3.3.1 Emulsification**

The water-in-oil (W/O) emulsion was prepared by mixing kerosene, carrier (LIX 984N) and surfactant (Span 80), the organic phase, with the internal stripping phase, sulfuric acid solution, using a blender at 12,000 rpm. The ratio between organic phase and internal stripping phase was 1:1 by volume. The compositions of the organic phase and the concentration of sulfuric acid were varied according to Table 3.1.

Viscosity of the emulsion was measured by Brookfield cone and plate programmable Rheometer, model DV-III, at different shear rates.

#### **3.3.2 Dispersion**

The copper feed solution was prepared by dissolving  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in milli Q water with addition of  $\text{H}_2\text{SO}_4$  or  $\text{Na}_2\text{CO}_3$  for pH adjustment. Concentration of the feed phase was varied from 10 -100 ppm. The emulsion was dispersed in the feed phase with 1:6 by volume of the emulsion and the feed.



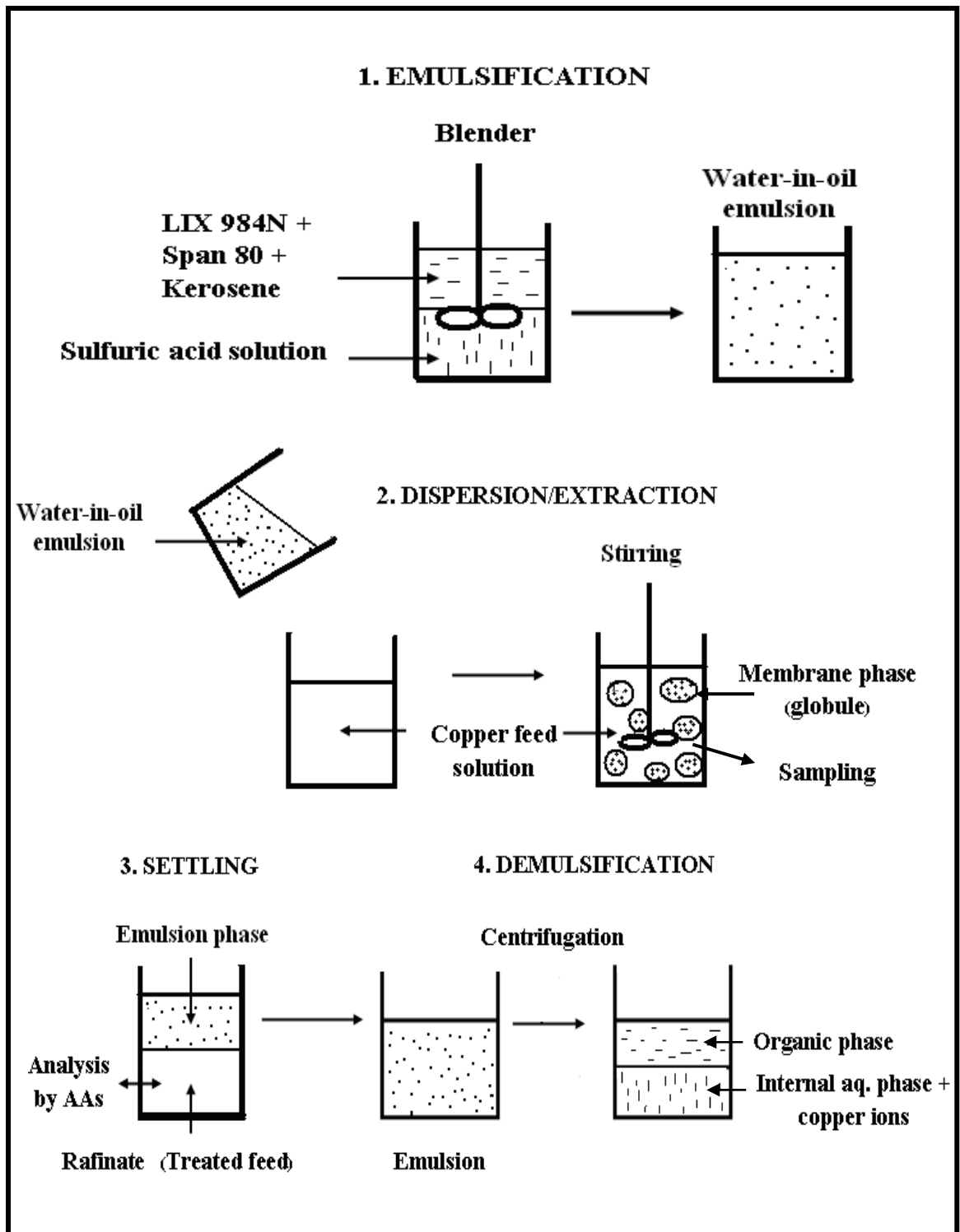
### 3.3.3 Extraction Process

- The extraction was performed in the thermostat bath with controlled temperature of  $\pm 1^{\circ}\text{C}$ . Agitation of the dispersion was achieved by mechanical stirrer with controlled speed. Samples of the feed phase solution were collected at definite time intervals (2 or 5 minutes) and analyzed for copper concentrations using Atomic Absorption Spectrometer (AAS) at the wavelength of 324 nm. The experiment was repeated 3 times for each condition.
- Size distribution of dispersed emulsion globule was investigated by photographing the dispersion with a Canon digital camera fitted with a 60 mm macro lens and a Cannon DX digital flash during the extraction process.
- Ethylene-propylene copolymer, when required, was added into the organic phase in the emulsification step.

### 3.3.4 Demulsification

The organic phase was separated from the internal phase solution by centrifugation at 2,000 rpm for 60 minutes. After 1 day settling the separation was complete.

- Recycle of the emulsion phase was done by first settling and then separating. Centrifugation was applied to separate the organic phase from the aqueous acid phase. The organic phase was collected for reuse in the latter experiment.



**Figure 3.1** Schematic diagram of experimental operation of ELM process

The extraction process was carried out by the previously mentioned steps for the conditions in Table 3.1.

**Table 3.1** Experimental conditions of copper extraction by ELMs

Parameters	Conditions
Surfactant concentration (Span 80)	0, 1, 2, 3, 4 and 5% by weight
Carrier concentration (LIX 984N)	0, 3, 4, 5 and 6% by weight
Stirring speed	200, 400, 600 and 800 rpm
Internal phase concentration (H <sub>2</sub> SO <sub>4</sub> )	1.0, 1.5 and 2.0 molar
pH of the feed phase	1, 2 and 5
Initial feed phase concentration (Cu <sup>2+</sup> )	10, 20, 40, 50 and 100 ppm
Extraction temperature	30, 40 and 50°C
Polymer concentration (ethylene-propylene copolymer)	1 and 2% by weight
Carrier reusability	2 <sup>nd</sup> and 3 <sup>rd</sup> of using

### 3.4 Data Analysis

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 collected mainly in the internal aqueous phase as an ion. Only a small portion of copper is stored in the membrane phase.

The results were presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) in the feed phase versus time.

The copper concentration in the internal phase can be calculated in the form of %Removal of copper from the equation,

$$\% \text{Removal} = \frac{\text{Initial Cu concentration} - \text{Instantaneous Cu concentration}}{\text{Initial Cu concentration}} \times 100$$

## CHAPTER IV

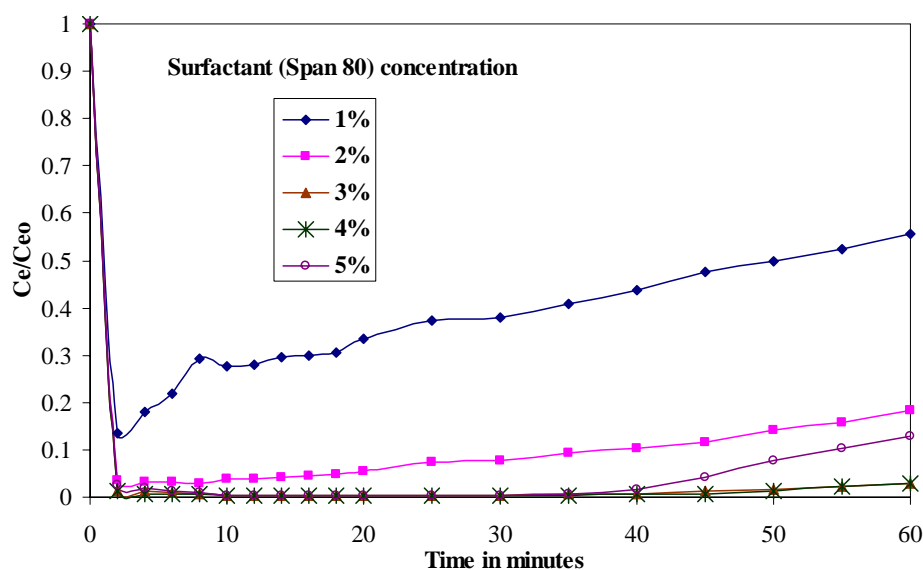
### RESULTS AND DISCUSSION

#### 4.1 Effect of Surfactant Concentration

To determine a suitable surfactant concentration for copper extraction by ELM method, the concentration of Span 80 was varied from 1 to 5% by weight. The copper concentration of the feed phase was 50 ppm. The experimental condition is listed in Table 4.1. The percentage of copper removal at various surfactant concentrations is shown in Table 4.2. The results are presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time in Figure 4.1.

**Table 4.1** The experimental condition for effect of surfactant concentration at copper 50 ppm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	various concentrations from 1 to 5%
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.1** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various surfactant concentrations  
(Cu feed concentration = 50 ppm)

**Table 4.2** Percentage of copper removal at various surfactant concentrations  
(Cu feed concentration = 50 ppm)

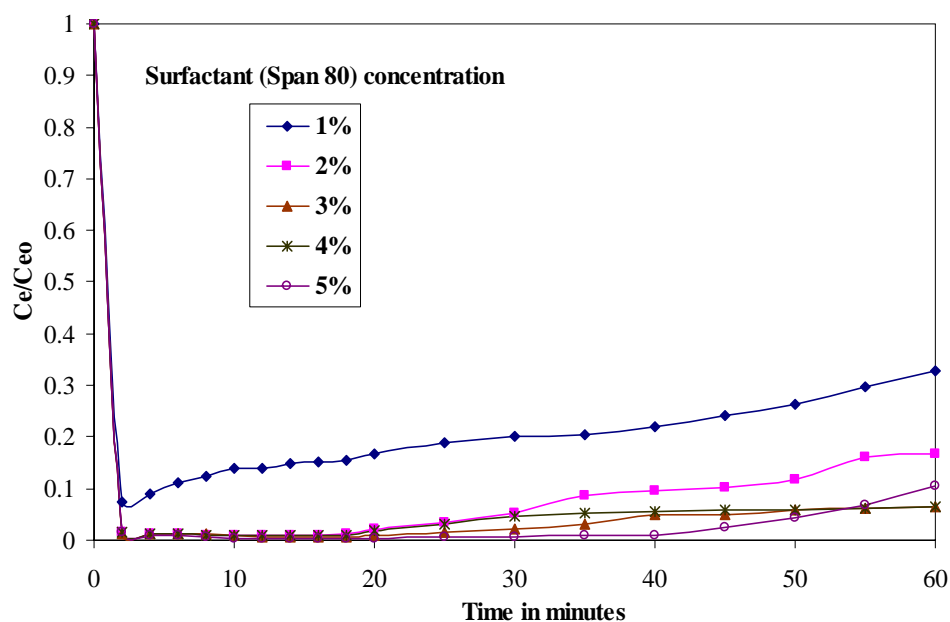
Time (min.)	% Removal of copper at various surfactant concentrations				
	1%	2%	3%	4%	5%
2 min.	86.54	96.58	98.79	98.70	97.43
4 min.	82.07	96.72	98.85	99.27	98.04
6 min.	78.07	96.86	99.14	99.33	98.85
8 min.	78.07	97.00	99.43	99.46	99.19
10 min.	72.46	96.22	99.06	99.59	99.60
12 min.	72.06	96.22	99.66	99.65	99.60
14 min.	70.46	95.73	99.77	99.65	99.73
16 min.	70.13	95.59	99.72	99.65	99.80
18 min.	69.46	95.24	99.72	99.71	99.80
20 min.	66.59	94.54	99.66	99.65	99.80
40 min.	56.25	89.75	99.37	99.40	98.31
60 min.	44.30	81.73	97.17	96.98	87.06

From Figure 4.1, it was found that less stable membrane phase was formed when 1% surfactant concentration was used and membrane leakage was observed after 2 minutes of the extraction indicated by a rise in  $C_e/C_{e0}$  versus time line. Increasing the surfactant concentration to 2%, initial extraction rate and percentage of copper removal was enhanced but the membrane leakage was also observed after 8 minutes. Sengupta *et al.* (2006) and Kumbasar (2009) reported that with 2% Span 80, the extraction rate was high but the emulsion was less stable for the total duration of 60 minutes. With 3 and 4% surfactant concentration, the membrane phase became more stable. Sengupta *et al.* (2006) found the same result with LIX 984N-C for 500 ppm of copper concentration, 1.5 M of sulfuric acid solution and stirring speed of 160 rpm. Faster initial extraction was observed (2 minutes) when 3 and 4% surfactant concentration was used. Increasing the surfactant concentration to 5%, the membrane phase was still stable with more percentage of copper removal. However, membrane leakage was found after 40 minutes, indicated by a rise in  $C_e/C_{e0}$  versus time line. Since Span 80 is a good carrier for water molecules and favors the osmotic swelling of emulsion (Hirato *et al.*, 1990), the possible mechanism is that swelling is mediated by hydrated surfactant. The surfactant solubilises water of the external phase into the membrane phase. The hydrated surfactant then diffuses to the internal phase, where the water is finally released. Thus, increasing the surfactant concentration can lead to swelling (Patnaik, 1995). With 5% surfactant concentration, low initial extraction rate was found but the maximum percentage of copper removal of 99.80% could be obtained. High surfactant concentration leads to an increase in viscosity of the membrane phase, resulting in the decrease in mass transfer of copper-carrier complex from the membrane phase to the internal stripping phase. Membrane leakage was observed for all cases indicated by a rise in  $C_e/C_{e0}$  versus time line.

The feed concentration was changed from 50 to 100 ppm and the experimental condition was listed in Table 4.3. The results of different initial concentration of copper in the feed phase and percentage of copper removal at various surfactant concentrations are shown in Figure 4.2 and Table 4.4, respectively.

**Table 4.3** The experimental condition for effect of surfactant concentration at copper  
100 ppm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	various concentrations from 0 to 5%
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	100 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.2** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various surfactant concentrations  
(Cu feed concentration = 100 ppm)



**Table 4.4** Percentage of copper removal at various surfactant concentrations

(Cu feed concentration = 100 ppm)

Time (min.)	% Removal of copper at various surfactant concentrations				
	1%	2%	3%	4%	5%
2 min.	92.69	98.39	98.56	98.52	98.52
4 min.	90.91	98.62	98.66	98.62	99.07
6 min.	88.89	98.89	98.89	98.89	99.17
8 min.	87.52	98.92	98.89	98.92	99.24
10 min.	86.08	98.99	98.99	98.99	99.52
12 min.	85.91	98.99	99.33	98.99	99.52
14 min.	85.07	99.13	99.36	99.13	99.55
16 min.	84.70	99.06	99.40	99.06	99.55
18 min.	84.57	98.79	99.26	98.92	99.55
20 min.	83.12	97.88	98.99	97.99	99.55
40 min.	77.92	90.47	95.18	94.50	99.07
60 min.	67.22	83.22	93.64	93.62	89.58

From Figure 4.2, the results were relatively the same as those in Figure 4.1, but more amount of copper in the feed phase remained. This effect is due to insufficient carrier concentration to form complex with copper. Membrane leakage was observed for all cases indicated by a rise in  $C_e/C_{e0}$  versus time line.

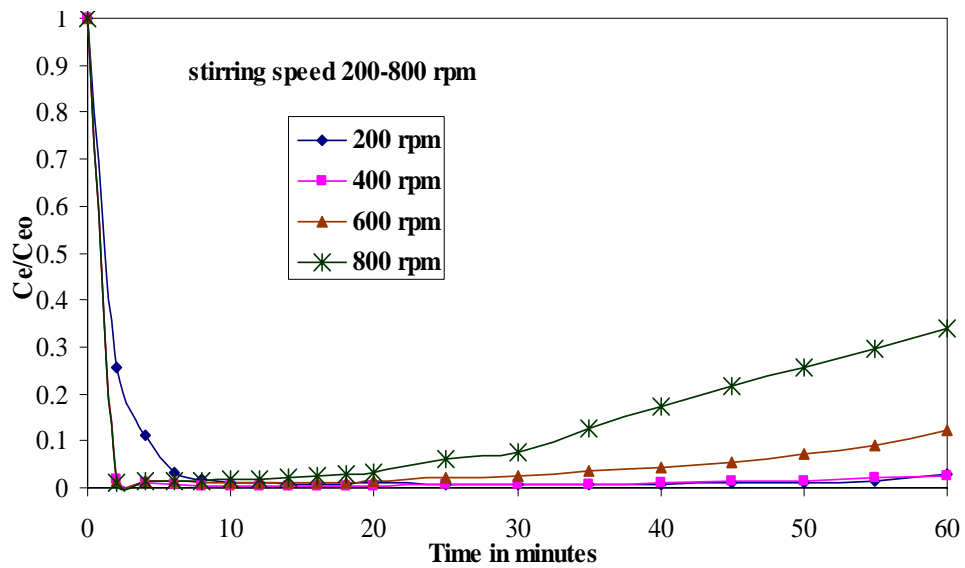
The effect of surfactant concentration on copper extraction by ELMs with stirring speed of 800 rpm was also investigated. The experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Appendix A, Table A-3 and Figure A-1, respectively. The results were relatively the same as Figure 4.2 but more amount of remaining copper in the feed phase was observed. This result is due to unstable of the membrane phase.

## 4.2 Effect of Stirring Speed

Experiments were performed at stirring speed of 200, 400, 600 and 800 rpm. The feed phase was 50 ppm. The experimental condition is listed in table 4.5. The results are presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time in Figure 4.3. The percentage of copper removal at various stirring speed is shown in Table 4.6.

**Table 4.5** The experimental condition for effect of stirring speed at copper 50 ppm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	various speed condition from 200 to 800 rpm



**Figure 4.3** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various stirring speed  
(Cu feed concentration = 50 ppm)

**Table 4.6** Percentage of copper removal at various stirring speed  
(Cu feed concentration = 50 ppm)

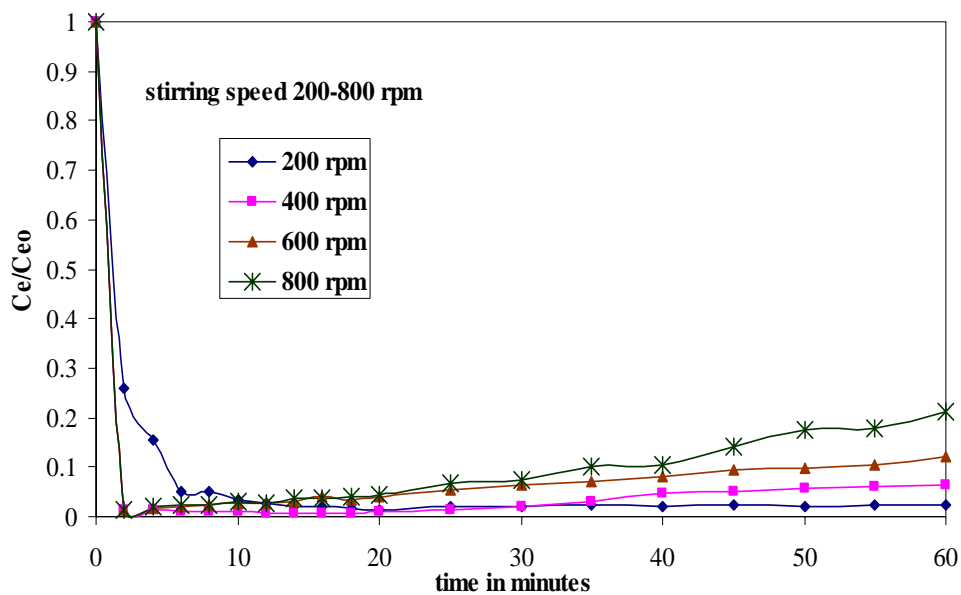
Time (min.)	% Removal of copper at various stirring speed			
	200 rpm	400 rpm	600 rpm	800 rpm
2 min.	74.35	98.79	98.60	98.89
4 min.	88.76	98.85	98.72	98.70
6 min.	96.91	99.14	98.72	98.64
8 min.	98.31	99.43	98.79	98.58
10 min.	98.76	99.06	98.98	98.33
12 min.	98.95	99.66	98.85	98.21
14 min.	99.27	99.77	98.85	97.96
16 min.	99.14	99.72	98.79	97.47
18 min.	99.14	99.72	98.66	97.22
20 min.	99.08	99.66	98.53	96.79
40 min.	99.14	99.37	95.79	83.62
60 min.	97.23	97.17	87.61	68.23

From Figure 4.3, it was found that at 200 rpm the initial extraction was slow indicated by a gradual drop of  $C_e/C_{e0}$  versus time line. When the stirring speed was increased to 400 rpm, the initial extraction was much faster. More than 99% of copper removal was obtained within 6 minutes and the maximum percentage was 99.7% in 16 minutes. After 60 minutes of the extraction, copper concentration was below the toxic limit (1.5 ppm) when stirring speed of 200 and 400 rpm were used. At 600 rpm, initial extraction was the same at 400 rpm. Almost 99% of copper concentration was removed within 10 minutes. At 800 rpm, the highest initial extraction rate was found (within 2 minutes) due to the formation of smaller emulsion globules resulting in more mass transfer. However, percentage of copper removal decreased in the long run due to membrane leakage. At 600 and 800 rpm, membrane leakage was observed after 20 and 4 minutes, respectively. Kongkapetchawan (1996) also observed similar behavior with copper extraction using D2EHPA as a carrier. The optimum agitation speed of his study was in the range of 350 to 400 rpm because more power of agitation led to more membrane breakage.

The different initial concentration of copper in the feed phase was also investigated. The feed concentration was changed from 50 ppm to 100 ppm and the experimental condition is listed in Table 4.7. The percentage of copper removal at various stirring speed and the plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Table 4.8 and Figure 4.3, respectively.

**Table 4.7** The experimental condition for effect of stirring speed at copper 100 ppm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	100 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	various speed conditions from 200 to 800 rpm



**Figure 4.4** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various stirring speed  
(Cu feed concentration = 100 ppm)

**Table 4.8** Percentage of copper removal at various stirring speed

(Cu feed concentration = 100 ppm)

Time (min.)	% Removal of copper at various stirring speed			
	200 rpm	400 rpm	600 rpm	800 rpm
2 min.	74.23	98.56	98.59	98.67
4 min.	84.50	98.66	98.22	97.87
6 min.	94.83	98.89	97.96	97.61
8 min.	95.10	98.89	97.76	97.61
10 min.	96.74	98.99	97.36	96.81
12 min.	97.42	99.33	97.26	97.18
14 min.	97.88	99.36	96.86	96.12
16 min.	97.95	99.40	95.90	96.12
18 min.	98.25	99.26	96.60	95.80
20 min.	98.52	98.99	95.81	95.58
40 min.	97.82	95.18	91.90	89.41
60 min.	97.55	93.64	87.76	78.76

From Figure 4.4, the results were relatively the same as those in Figure 4.3, but more amount of remaining copper in the feed phase was observed. This effect is due to insufficient carrier concentration to form carrier – copper complex.



**Figure 4.5** Size distribution of emulsion globule at various stirring speed

Figure 4.5 shows size distribution of emulsion globules at various stirring speed. With 200 rpm, various sizes of emulsion globules were observed with the largest of 5 mm in diameters. Increasing stirring speed to 400 rpm a fine dispersion of emulsion globules was generated. Globule sizes almost 1 mm in diameters were observed with stirring speed of 400 rpm. And at 600 and 800 rpm, even smaller size globules (less than 1 mm) were formed giving a fine dispersion. After 60 minutes at all stirring speed, globule expanded in diameters, except at 200 rpm. The results indicated that with high agitation globules were less stable emulsion globule and easier to coalesce with the other globules. It can be explained that at higher stirring speed, smaller size globules are formed leading to more surface area for mass transfer. But at the same time, higher stirring speed affects the stability of emulsion globules leading to swelling and finally membrane breakage (Sengupta *et al.*, 2006).

The effect of stirring speed on copper extraction by ELMs with 5% of surfactant concentration was also investigated. The experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C/C_{co}$ ) versus time are shown in Appendix A, Table A-6 and Figure A-2, respectively. The results are relatively the same but more membrane breakage was observed. This effect is due to excess surfactant concentration leading to osmotic swelling mediated by hydrated surfactant to the internal droplets.

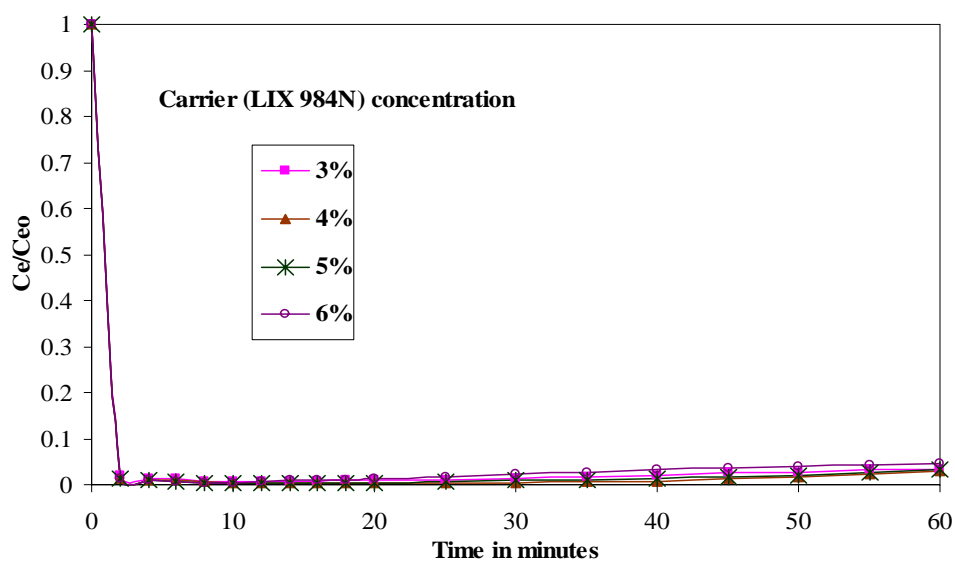


### 4.3 Effect of Carrier Concentration

The carrier concentration in the organic phase was varied from 0 to 6 % by weight. The experimental condition is listed in Table 4.9. The percentage of copper removal at various carrier concentrations is in Table 4.10. The plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Figure 4.6.

**Table 4.9** The experimental condition for effect of carrier concentration at 400 rpm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	depend on the carrier concentration
Carrier (LIX 984N)	various concentrations from 0 to 6%
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.6** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various carrier concentrations with stirring speed 400 rpm

**Table 4.10** Percentage of copper removal at various carrier concentrations with stirring speed 400 rpm

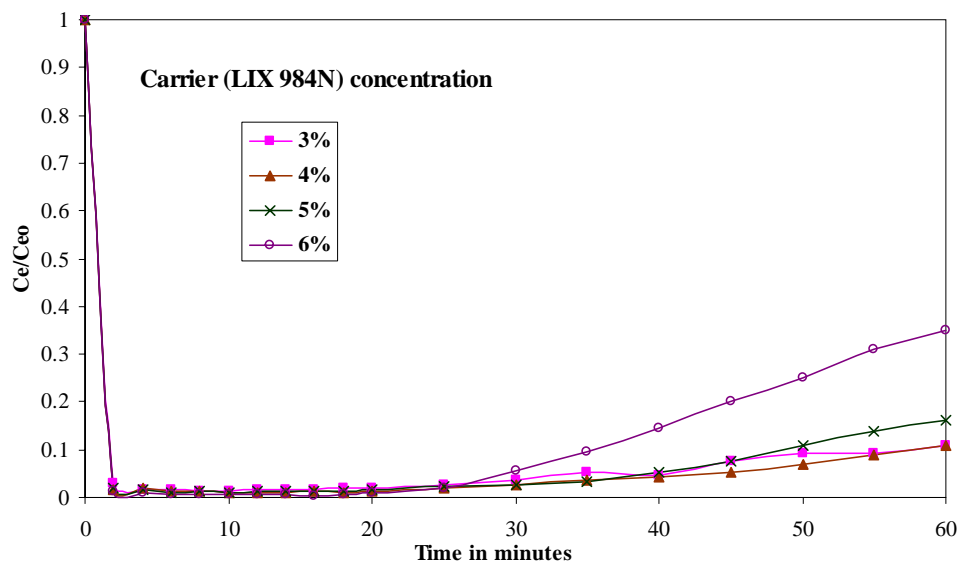
Time (min.)	% Removal of copper at various carrier concentrations			
	3%	4%	5%	6%
2 min.	97.92	98.79	98.75	98.75
4 min.	98.53	98.85	99.01	99.01
6 min.	98.63	99.14	99.34	99.45
8 min.	99.24	99.43	99.53	99.64
10 min.	99.24	99.06	99.72	99.64
12 min.	99.29	99.66	99.72	99.38
14 min.	99.29	99.77	99.79	99.13
16 min.	99.19	99.72	99.72	98.88
18 min.	99.14	99.72	99.59	98.94
20 min.	98.99	99.66	99.59	98.82
40 min.	97.97	99.37	98.75	96.86
60 min.	96.65	97.17	96.56	95.48

From Table 4.10 it was found that within 2 minutes, initial extraction rate for all carrier concentrations showed no significant difference except at 3 wt% that the lowest initial extraction rate was found. After about 12 - 14 minutes, the maximum percentage of copper removal was obtained when 3, 4 and 5% carrier concentration were used. Comparing the percentage of copper removal, 5% carrier shows slightly higher percentage. With 6% carrier concentration, the maximum percentage of copper removal was obtained within 8 minutes. Increasing carrier concentration results in more available interface for copper-carrier complexation. Membrane leakage was observed after 30 minutes extraction for all concentrations, especially with 6% of carrier concentration. Sengupta *et al.* (2007) found that about 97% copper was extracted in three minutes contact when 2, 5 and 10% LIX 84I were used as a carrier and extraction rate were found to be highest with 5% carrier concentration. His conditions were 2 - 10% LIX 84I, 3% Span 80, 1.5 M sulfuric acid solution for 500 ppm of copper in the feed phase with stirring speed of 160 rpm. Effective and economical extraction can be achieved with 4 – 5% carrier concentration.

The stirring speed was changed from 400 to 600 rpm with the experimental condition is listed in Table 4.11. The percentage of copper removal at various carrier concentrations is reported in Table 4.12. Plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_c/C_{c0}$ ) versus time are shown in Figure 4.7.

**Table 4.11** The experimental condition for effect of carrier concentration at 600 rpm

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	depend on the carrier concentration
Carrier (LIX 984N)	various concentration from 0 to 6%
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	600 rpm

**Figure 4.7** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various carrier concentrations with stirring speed 600 rpm

**Table 4.12** Percentage of copper removal at various carrier concentrations  
with stirring speed 600 rpm

Time (min.)	% Removal of copper at various carrier concentrations			
	3%	4%	5%	6%
2 min.	97.18	98.60	97.89	98.66
4 min.	98.19	98.72	98.34	99.01
6 min.	98.40	98.72	98.95	99.22
8 min.	98.60	98.79	98.95	99.36
10 min.	98.75	98.98	98.88	99.43
12 min.	98.45	98.85	98.72	99.43
14 min.	98.45	98.85	98.72	99.50
16 min.	98.34	98.79	98.72	99.36
18 min.	98.14	98.66	98.57	99.36
20 min.	97.94	98.53	98.42	99.01
40 min.	95.26	95.79	94.69	85.63
60 min.	89.08	87.61	83.82	65.10

The results of the initial extraction in Figure 4.7 were the same in Figure 4.6. There is a significant increase in membrane leakage, indicated by a rise of  $C_e/C_{e0}$  versus time lines after 30 minutes of extraction for all cases. This phenomena is due to high speed of agitation.

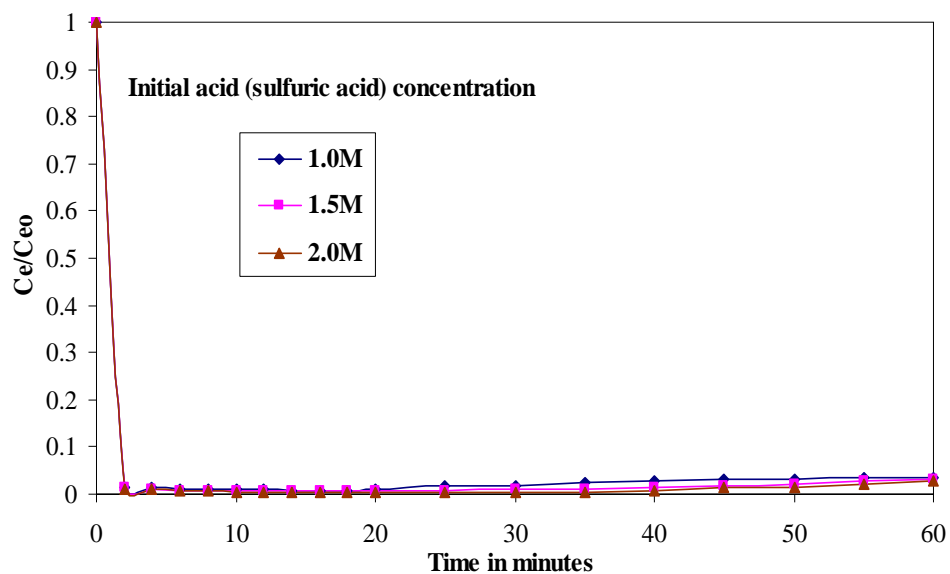
The effect of carrier concentration at stirring speeds of 200 and 800 rpm were also studied. The experimental data of remaining copper concentration in the feed phase after time intervals and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Appendix A, Table A-9, 10 and Figure A-3, 4, respectively. The results were found to be the same, but less membrane leakage was observed with 200 rpm. On the other hand, more membrane leakage was found at stirring speed of 800 rpm. This effect is due to more collision among globules leading to globule coalescence.

#### 4.4 Effect of the Initial Acid Concentration in the Internal Phase

The acid concentration in the internal aqueous phase was varied from 1.0 to 2.0 molar. The experimental condition is shown in Table 4.13. The percentage of copper removal at various acid concentrations in the internal phase is in Table 4.14. The results presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Figure 4.8.

**Table 4.13** The experimental condition for effect of initial acid concentration in the internal phase with 4% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase (sulfuric acid)	various concentrations from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.8** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various acid concentrations with 4% carrier concentration

**Table 4.14** Percentage of copper removal at various acid concentrations with 4% carrier concentration

Time (min.)	% Removal of copper at various initial acid concentrations		
	1.0 M	1.5 M	2.0 M
2 min.	98.68	98.65	98.79
4 min.	98.74	98.99	98.85
6 min.	98.81	99.13	99.14
8 min.	99.00	99.26	99.43
10 min.	99.07	99.26	99.06
12 min.	99.07	99.20	99.66
14 min.	99.20	99.33	99.77
16 min.	99.27	99.47	99.72
18 min.	99.13	99.20	99.72
20 min.	99.07	98.20	99.66
40 min.	97.23	98.44	99.37
60 min.	96.51	96.80	97.17

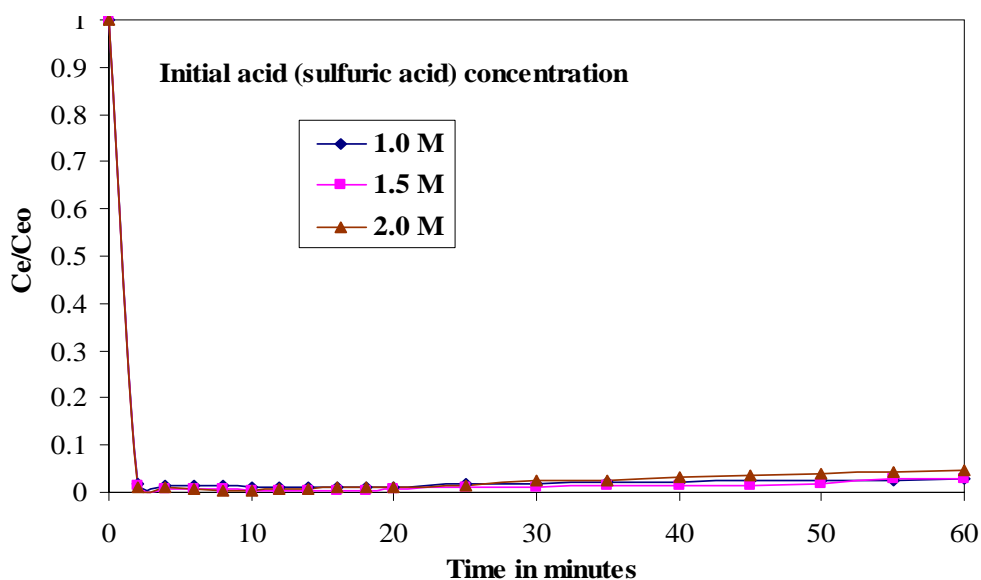
From the results, it was found that when increasing the initial acid concentration from 1 to 1.5 M, no differences of initial extraction rate in the first 2 minutes was observed. The maximum percentage was reached after 16 minutes for both cases. The initial extraction was more rapid when concentration was increased to 2 M and the total extraction of copper ions at 2 M sulfuric acid was higher, reaching the maximum percentage of copper removal within 14 minutes. The reason is from the fact (Sengupta *et al.*, 2006) that when the initial acid concentration is high, the diffusing oxime-copper complex requires to penetration no deeper within the emulsion globule to get stripped. Sengupta *et al.* (2006) found a substantial increase in extraction rates with an increase in internal phase acid concentration from 1 to 2 M. His conditions were 10% of LIX 84 for 500 ppm of copper extraction. Valenzuela *et al.* (2009) also found that when a 1.02 mol/L sulfuric acid solution was used, most of copper disappears from the feed solution and was transferred to the inner strip liquor and even better result was achieved with 2.04 and 2.65 mol/L acid solutions in a short time.

The effect of initial acid concentration in the internal phase was also studied for 6% of carrier concentration, with experimental condition is listed in Table 4.15. The percentage of copper removal at various acid concentrations is shown in Table 4.16. Plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_t/C_{e0}$ ) versus time are in Figure 4.9. From the results, it was found that increasing the acid concentration from 1 to 1.5 M the initial extraction rate was increased. This result is different from the previous experiment with 4% LIX 984N. This could be explained by the masking effect of high carrier concentration upon the internal phase acid (Sengupta *et al.*, 2007). Sengupta *et al.* (2007) also observed similar behavior. His conditions were 5 - 10% LIX 84I, 0.5 - 1.5 M sulfuric acid solution for 500 ppm of copper in the feed. Shorter time was required for 6% carrier concentration (10 minutes) to obtain the maximum percentage of copper removal when 1.5 and 2 M sulfuric acid concentration was used.



**Table 4.15** The experimental condition for effect of initial acid concentration in the internal phase with 6% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase (sulfuric acid)	various concentrations from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.9** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various acid concentrations with 6% carrier concentration

**Table 4.16** Percentage of copper removal at various acid concentrations  
with 6% carrier concentration

Time (min.)	% Removal of copper at various initial acid concentrations		
	1.0 M	1.5 M	2.0 M
2 min.	98.34	98.56	98.75
4 min.	98.50	99.19	99.01
6 min.	98.61	99.32	99.45
8 min.	98.66	99.45	99.64
10 min.	98.88	99.64	99.64
12 min.	98.93	99.64	99.38
14 min.	98.99	99.64	99.13
16 min.	98.99	99.64	98.88
18 min.	98.99	99.64	98.94
20 min.	99.10	99.45	98.82
40 min.	97.90	98.56	96.86
60 min.	97.20	97.22	95.48

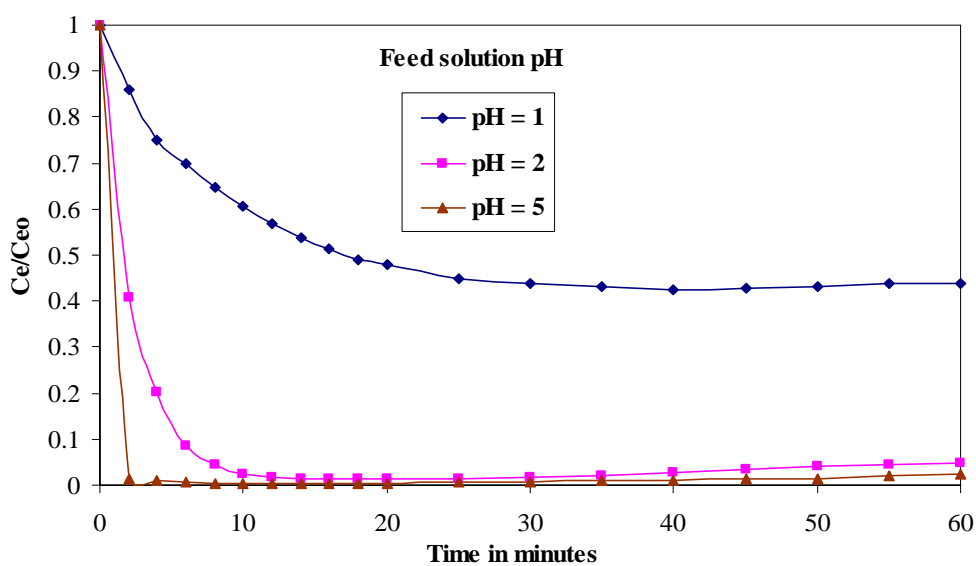
The effect of the internal acid concentration on copper extraction by ELMs with carrier concentration of 3 and 5% was also investigated. The experimental data of remaining copper concentration in the feed phase after time intervals and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time were shown in Appendix A, Table A-13, 14 and Figure A-5, 6, respectively. The results were relatively the same as when 4 and 6% of carrier concentration were used.

## 4.5 Effect of Feed pH

The pH of the feed phase was adjusted from 1 – 5 by sulfuric acid. The experimental condition is listed in Table 4.17. The percentage of copper removal at various the feed phase pH is reported in Table 4.18. Plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_c/C_{e0}$ ) versus time are in Figure 4.10.

**Table 4.17** The experimental condition for effect of feed pH with 4% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 ml
External phase	50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase	60:360 ml
Stirring speed	400 rpm



**Figure 4.10** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various feed pH with 4% carrier concentration

**Table 4.18** Percentage of copper removal at various feed pH with 4% carrier concentration

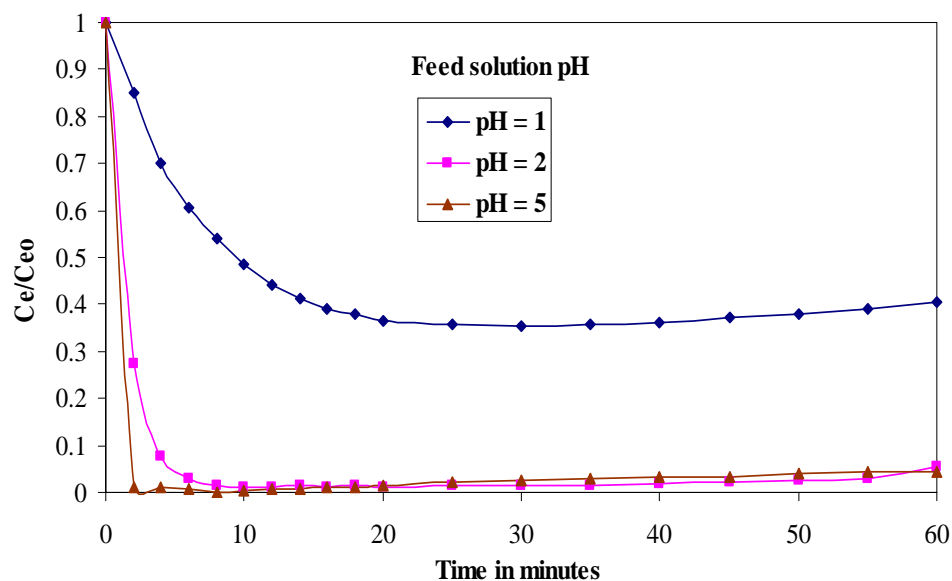
Time (min.)	% Removal of copper at various feed pH		
	pH = 1	pH = 2	pH = 5
2 min.	14.09	59.30	98.79
4 min.	25.05	79.76	98.85
6 min.	30.13	91.54	99.14
8 min.	35.38	95.62	99.43
10 min.	39.37	97.55	99.06
12 min.	43.20	98.30	99.66
14 min.	46.22	98.60	99.77
16 min.	48.62	98.54	99.72
18 min.	50.96	98.22	99.72
20 min.	52.21	98.48	99.66
40 min.	57.46	97.37	99.37
60 min.	56.04	95.27	97.17

From the results, it was observed that at pH 1, the extraction rate was very low and after 20 minutes,  $C_e/C_{e0}$  line became constant. The maximum percentage of copper removal was only 57%. The excess of hydrogen ion in the feed phase at pH 1 could lead to back-extraction, whereby the initially extracted copper in the membrane phase diffuses back to the feed phase. When increasing the feed pH to 2, the extraction rate was enhanced and quantitative copper recovery was obtained. The highest extraction rate was found when the pH was 5. Within 14 minutes, the maximum percentages of copper removal were 98.6% and 99.7% when the feed pH was 2 and 5, respectively.

The effect of feed pH with carrier concentration changed from 4 to 6% by weight was also studied. The experimental condition is listed in Table 4.19. The percentage of copper removal at various feed phase pH is shown in Table 4.20. Plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are in Figure 4.11.

**Table 4.19** The experimental condition for effect of feed pH with 6% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.11** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various feed pH with 6% carrier concentration

**Table 4.20** Percentage of copper removal at various feed pH with 6% carrier concentration

Time (min.)	% Removal of copper at various feed pH		
	pH = 1	pH = 2	pH = 5
2 min.	14.96	72.53	98.75
4 min.	29.93	92.21	99.01
6 min.	39.29	97.03	99.45
8 min.	45.85	98.35	99.64
10 min.	51.59	98.77	99.64
12 min.	55.76	98.84	99.38
14 min.	58.83	98.77	99.13
16 min.	60.88	98.77	98.88
18 min.	62.05	98.70	98.94
20 min.	63.34	98.70	98.82
40 min.	63.69	98.01	96.86
60 min.	59.65	94.38	95.48

From Figure 4.11, the results were relatively the same as those in Figure 4.10, but more percentage of copper removal was obtained in a shorter time. This effect is due to high carrier concentration

The effect of feed pH was also studied with different carrier concentration (3 and 5%). The experimental data of remaining copper concentration in the feed phase after time intervals and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Appendix A, Table A-17, 18 and Figure A-7, 8. The results show no differences. Sengupta *et al.* (2006) and Valenzuela (2009) also observed similar phenomena. Their conditions were 10% LIX 84, 3% Span 80, 1.5 M of sulfuric acid and 500 ppm copper in the feed phase for Sengupta's work and 3% LIX 860 N-IC, 2% Span 80, 2.04 M of sulfuric acid and 250 ppm copper in the feed phase for Valenzuela's work. Below and above pH 5, copper extraction was found to decrease. At pH 1, the maximum extent of copper recovery was just 28% when LIX 84 was a carrier. In comparison between LIX 84 and LIX 984N, more amount of copper was obtained with the latter. This result is due to features of its components. LIX 984N consists of salicylaldoxime compound which is a strong extractant for copper even at low pH values of 1 to 2.

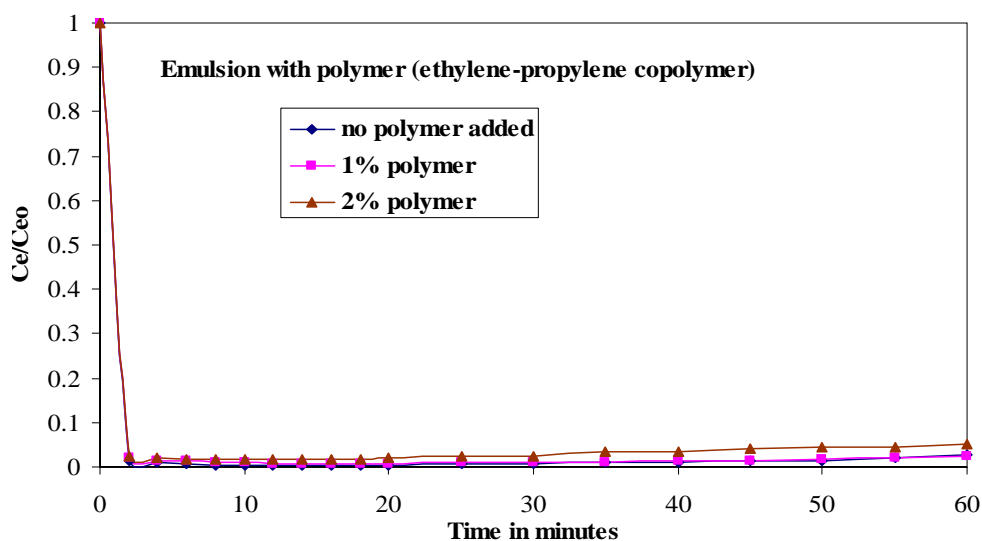
## 4.6 Effect of Polymer in the Membrane Phase

To study the effect of polymer in the membrane phase, 1 - 2% ethylene-propylene copolymer was added into the organic phase. The experimental condition is listed in Table 4.21. The percentage of copper removal at various polymer concentrations is shown in Table 4.22. The results presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Figure 4.12.

**Table 4.21** The experimental condition for effect of polymer concentration with stirring speed 400 rpm

<b>Experimental conditions:</b>	
Membrane phase (no polymer added)	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Membrane phase (1 – 2% polymer added)	
Organic solvent (Kerosene)	depend on the polymer
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Polymer (ethylene propylene copolymer)	1 - 2% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm





**Figure 4.12** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various polymer concentrations with stirring speed 400 rpm

**Table 4.22** Percentage of copper removal at various polymer concentrations with stirring speed 400 rpm

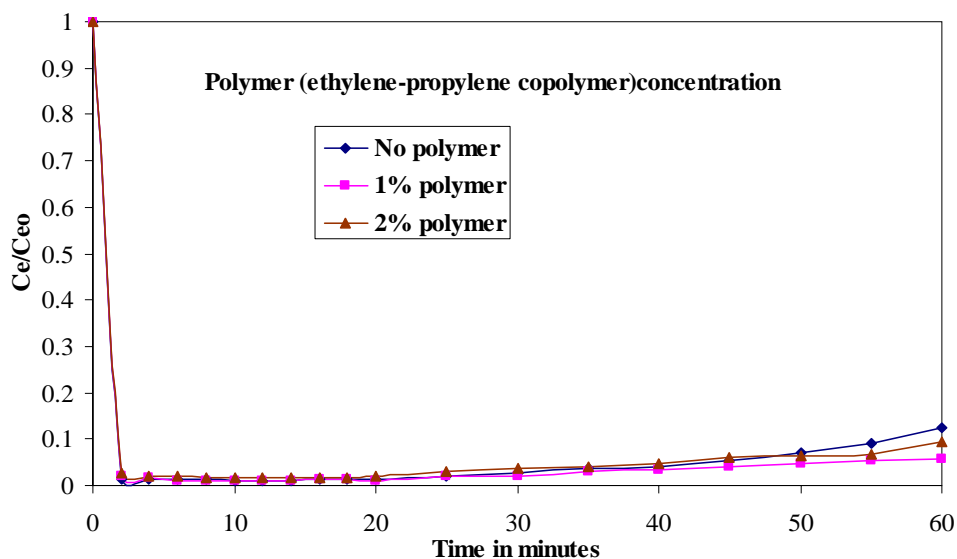
Time (min.)	% Removal of copper at various polymer concentrations		
	No polymer	1% polymer	2% polymer
2 min.	98.79	98.07	97.72
4 min.	98.85	98.73	98.09
6 min.	99.14	98.73	98.15
8 min.	99.43	98.85	98.15
10 min.	99.06	99.04	98.20
12 min.	99.66	99.22	98.31
14 min.	99.77	99.28	98.42
16 min.	99.72	99.16	98.42
18 min.	99.72	99.16	98.36
20 min.	99.66	99.16	97.99
40 min.	99.37	98.67	96.43
60 min.	97.17	97.64	94.82

From the results it was observed that polymer addition into the membrane phase led to a decrease in initial extraction rate at first 2 minutes. This effect is due to an increase in viscosity of the membrane phase resulting in low mass transfer. In 14 minutes, 99.7%, 99.2% and 98.4% of copper were removed from the feed phase when the membrane was not added with polymer and with 1 and 2% polymer addition, respectively. Less membrane breakage was observed when no polymer and 1% polymer were added into the membrane phase. With 2% polymer concentration, membrane breakage was more obvious after 20 minutes, indicated by a rise in  $C_e/C_{e0}$  ratio line.

The stirring speed was changed from 400 to 600 rpm. The experimental condition is listed in Table 4.23. The percentage of copper removal at various polymer concentrations is shown in Table 4.24. The plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are in Figure 4.13. From the results it was found that after 10 minutes, membrane leakage was decreased when the membrane was added with 1% polymer indicated by more percentage remained. At 60 minutes of extraction, the percentage of copper removal of membrane without polymer and 1% polymer was 87% and 94%, respectively. This result is different from the copper extraction with stirring speed 400 rpm. It could be explained that adding 1% polymer led to a decrease in membrane breakage when the extraction was performed at stirring speed higher than 400 rpm. With 2% polymer, the maximum percentage of copper removal was less than that with no polymer and with 1% polymer. This result is due to excess of polymer concentration. Skelland and Meng (1999) studied effect of addition of polyisobutylene, polybutadiene and polystyrene into the membrane phase for benzoic acid extraction by ELMs. They found that the non-Newtonian membrane with 0.5 or 1% PIB and 2% Span 80 provided much better performance at 500 rpm, long term extraction efficiency was easily maintained with better than 90% benzoic acid and no reduction in mass transfer rate.

**Table 4.23** The experimental condition for effect of polymer concentration with stirring speed 600 rpm

<b>Experimental conditions:</b>	
Membrane phase (no polymer added)	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Membrane phase (1 - 2% polymer added)	
Organic solvent (Kerosene)	depend on the polymer
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Polymer (ethylene propylene copolymer)	1 - 2% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	600 rpm



**Figure 4.13** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various polymer concentrations with stirring speed 600 rpm

**Table 4.24** Percentage of copper removal at various polymer concentrations with stirring speed 600 rpm

Time (min.)	% Removal of copper at various polymer concentrations		
	No polymer	1% polymer	2% polymer
2 min.	98.60	98.03	97.14
4 min.	98.72	98.28	97.94
6 min.	98.72	98.96	98.04
8 min.	98.79	98.89	98.15
10 min.	98.98	99.08	98.15
12 min.	98.85	99.08	98.15
14 min.	98.85	99.02	98.20
16 min.	98.79	98.77	98.25
18 min.	98.66	98.77	98.30
20 min.	98.53	98.83	98.04
40 min.	95.79	96.68	95.25
60 min.	87.61	94.22	90.45

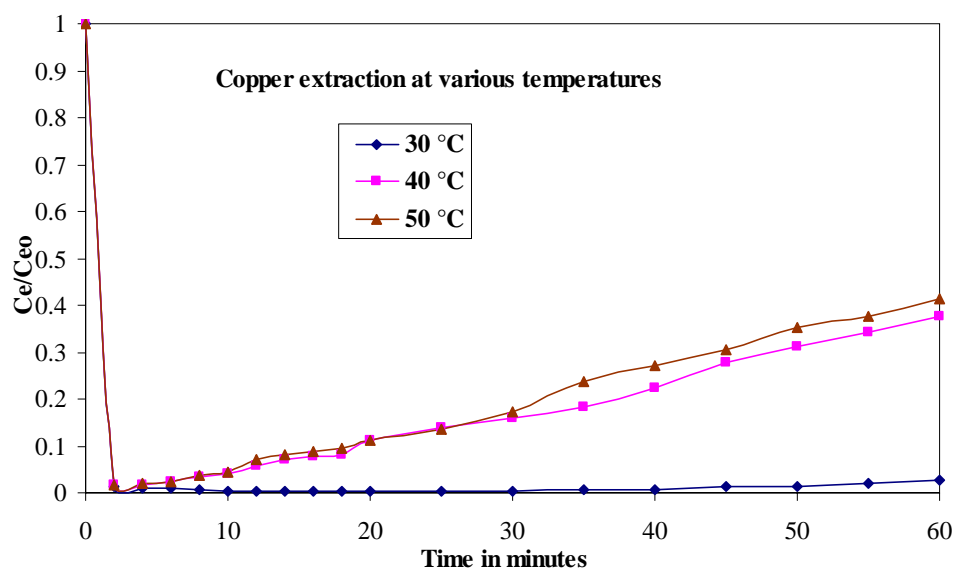
Further more, the effect of polymer concentration on copper extraction by ELM method with stirring speed at 800 rpm was also investigated. The experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_t/C_{e0}$ ) versus time are showed in Appendix A, Table A-21 and Figure A-9. The results were relatively the same as stirring speed of 600 rpm. This effect is due to addition of polymer.

## 4.7 The Effect of Extraction Temperature

The extraction temperature was varied from 30 – 50°C. The experimental condition is listed in Table 4.25. The percentage of copper removal at various extraction temperatures is reported in Table 4.26. Figure 4.14 shows the plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time.

**Table 4.25** The experimental condition for effect of extraction temperature with 4% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm
Extraction temperature	various from 30 – 50°C



**Figure 4.14** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various extraction temperatures with 4% carrier concentration

**Table 4.26** Percentage of copper removal at various extraction temperatures with 4% carrier concentration

Time (min.)	% Removal of copper at various extraction temperatures		
	30°C	40°C	50°C
2 min.	98.79	98.27	98.26
4 min.	98.85	98.22	97.98
6 min.	99.14	97.70	97.47
8 min.	99.43	96.56	96.41
10 min.	99.06	95.88	95.52
12 min.	99.66	94.39	92.85
14 min.	99.77	92.97	92.01
16 min.	99.72	92.34	91.12
18 min.	99.72	91.88	90.50
20 min.	99.66	88.92	88.89
40 min.	99.37	77.45	72.94
60 min.	97.17	62.28	58.66

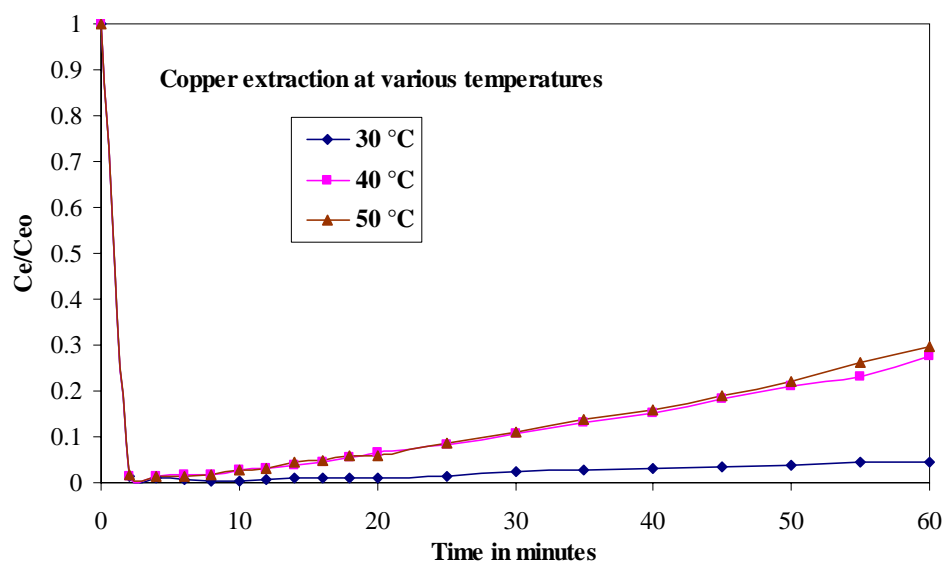
As seen from the results, for all temperatures initial extraction are efficient. About 98% of copper was obtained within 2 minutes. At 30°C the extraction rate was stable for 50 minutes and the maximum percentage of copper removal was 99% within 14 minutes. When increasing temperature from 30 to 50°C, the membrane became less stable and membrane leakage was observed after 2 minutes. The results indicated that the stability of emulsion is reduced when temperature is higher than 30°C due to a decrease in viscosity by increasing temperature.

Effect of extraction temperature was also studied with 6% carrier concentration the experimental condition is in Table 4.27. The percentage of copper removal at various extraction temperatures is shown in Table 4.28. The plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are in Figure 4.15.

**Table 4.27** The experimental condition for effect of extraction temperature with 6% carrier concentration

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm
Extraction temperature	various from 30 – 50°C





**Figure 4.15** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various extraction temperatures with 6% carrier concentration

**Table 4.28** Percentage of copper removal at various extraction temperatures with 6% carrier concentration

Time (min.)	% Removal of copper at various extraction temperatures		
	30°C	40°C	50°C
2 min.	98.75	98.73	98.36
4 min.	99.01	98.53	98.76
6 min.	99.45	98.40	98.69
8 min.	99.64	98.14	98.29
10 min.	99.64	97.29	97.22
12 min.	99.38	96.90	96.75
14 min.	99.13	96.31	95.54
16 min.	98.88	95.40	95.27
18 min.	98.94	94.48	94.07
20 min.	98.82	93.37	94.00
40 min.	96.86	84.75	84.14
60 min.	95.48	72.54	70.47

Similar results were found. However, at 30°C membrane leakage was observed after 25 minutes. With 6% carrier concentration, the extraction at 40 and 50°C, more percentage of copper removal was obtained when comparing with 4% carrier concentration. This result could be attributed to the increase in carrier concentration while led to an increase in viscosity of the membrane.

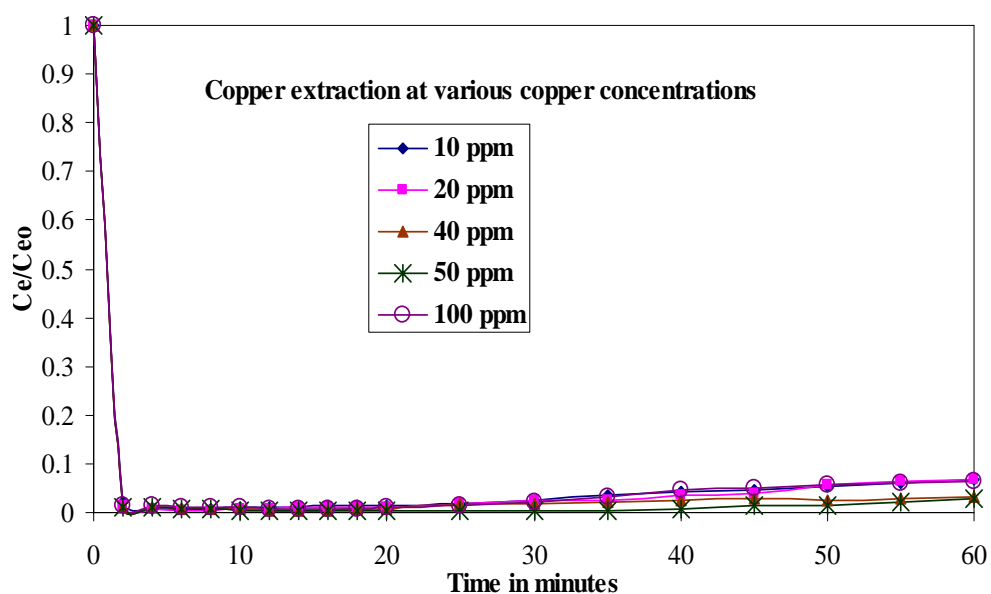
The effect of extraction temperature was also studied with 3 and 5% of carrier concentration. The experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds and plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are shown in Appendix A, Table A-24 and Figure A-10. The results were found to be the same.

## 4.8 The Effect of Copper Concentration in the Feed Phase

Copper concentration was varied in the range of 10 ppm to 100 ppm. The experimental condition is listed in Table 4.29. The percentage of copper removal at various copper concentrations is shown in Table 4.30. Plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_e/C_{e0}$ ) versus time are in Figure 4.16.

**Table 4.29** The experimental condition for effect of copper concentration in the feed phase

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	various from 10 - 100 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.16** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at various copper concentrations

**Table 4.30** Percentage of copper removal at various copper concentrations

Time (min.)	% Removal of copper at various copper concentrations				
	10 ppm	20 ppm	40 ppm	50 ppm	100 ppm
2 min.	97.76	98.63	98.75	98.79	98.56
4 min.	99.13	99.41	98.75	98.85	98.66
6 min.	99.13	99.61	99.15	99.14	98.89
8 min.	99.13	99.64	99.25	99.43	98.89
10 min.	98.45	99.41	99.45	99.06	98.99
12 min.	98.79	99.22	99.75	99.66	99.33
14 min.	98.79	99.02	99.65	99.77	99.36
16 min.	98.45	98.83	99.65	99.72	99.40
18 min.	98.45	99.02	99.45	99.72	99.26
20 min.	98.45	98.83	99.25	99.66	98.99
40 min.	95.69	96.49	97.45	99.37	95.18
60 min.	93.28	93.19	96.95	97.17	93.64

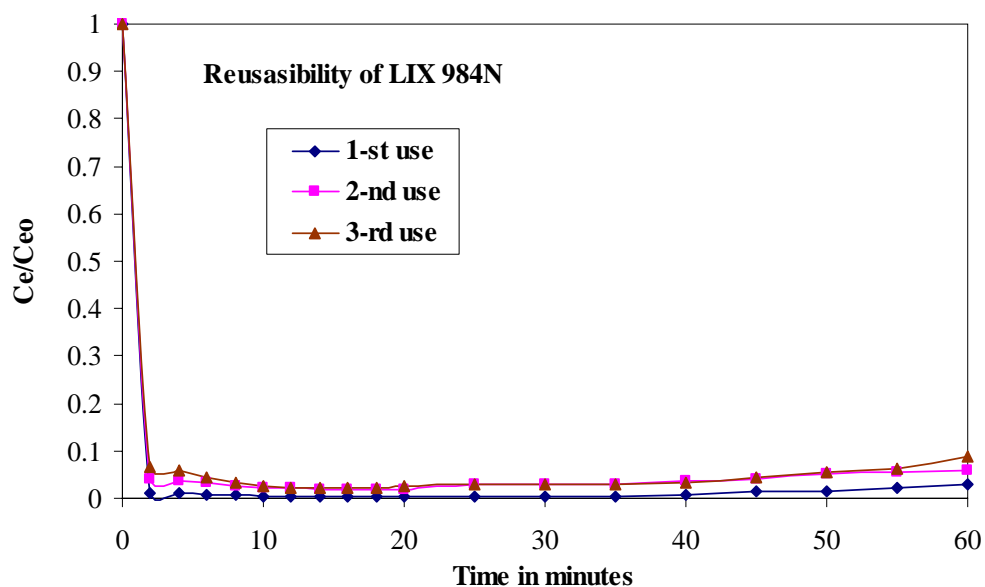
It was found that initial extraction rate (within 2 minutes) of all cases were the same and the lowest initial extraction rate was found when copper concentration in the feed phase was 10 ppm. Membrane leakage was observed for every case and obvious for 10, 20 and 100 ppm indicated by a rise in  $C_e/C_{e0}$  versus time line. The maximum percentage of copper removal for 10, 20, 40, 50 and 100 ppm was found after 4, 8, 12, 14 and 16 minutes respectively. Within 6 minutes, 99% of copper was removed for all cases, except for 100 ppm, 98% of copper was removed. This could be due to the limited amount of carrier to form copper-carrier complex. Membrane leakage was observed after about 25 minutes for all cases, especially for feed concentration of 10 and 100 ppm indicated by a rise in  $C_e/C_{e0}$  line. Sengupta *et al.* (2006) also studied effect of initial feed concentration. Copper concentration was in the range of 497 mg/L to 1900 mg/L. The membrane phase consisted of 3% Span 80, 10% LIX 84 and 2 M sulfuric acid. The extraction rate was increased when initial feed concentration decreased.

## 4.9 The Carrier Reusability

The collected carrier was reused for copper extraction for the second and third times. The experimental condition is shown in Table 4.31. Percentage of copper removal is in Table 4.32. The results presented as plots of ratio of instantaneous copper concentration to initial copper concentration ( $C_c/C_{c0}$ ) versus time are in Figure 4.17.

**Table 4.31** The experimental condition for carrier reusability

<b>Experimental conditions:</b>	
Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2 M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm



**Figure 4.17** Plots of ratio of instantaneous copper concentration to initial copper concentration versus time at carrier reusability

**Table 4.40** Percentage of copper removal at carrier reusability

Time (min.)	% Removal of copper at various carrier reusability		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
2 min.	98.79	95.83	93.25
4 min.	98.85	96.19	94.23
6 min.	99.14	96.85	95.52
8 min.	99.43	97.44	96.50
10 min.	99.06	97.62	97.55
12 min.	99.66	97.80	97.73
14 min.	99.77	98.22	97.79
16 min.	99.72	98.16	97.73
18 min.	99.72	98.10	97.67
20 min.	99.66	98.10	97.49
40 min.	99.37	96.31	96.69
60 min.	97.17	94.41	91.17

From the results it was found that initial extraction rate at first 2 minutes was higher for the first use than the second and third times. The maximum percentage of copper removal was reached within 14 minutes for all cases. The values of copper removal were 99.7%, 98.2% and 97.7% for the first, second and third uses respectively. Membrane leakage was more obvious in both second and third time use.



## CHAPTER V

### CONCLUSION AND FURTHER STUDY

#### 5.1 Conclusion

From the previous chapters, there were many parameters which had an effect to copper extraction by ELMs. The first predominant parameter was feed pH. Copper extraction had the highest initial rate and maximum percentage of copper removal (99.7%) when the feed pH was 5. Extraction temperature also had a major effect to ELM process. At the temperature higher than room temperature (30°C), the membrane phase was less stable leading to a decrease in initial extraction rate and an increase in membrane leakage. Surfactant concentration was another vital factor for copper extraction by ELM method. High percentage of copper removal was obtained when surfactant concentration was in the range of 3 - 5% by weight. The membrane became unstable when less surfactant concentration was used. At stirring speed of 200 and 400 rpm, more than 99% of copper removal was obtained but bigger size globule was found at 200 rpm resulting in slower mass transfer. The suitable ranges of carrier and internal acid concentration are found to be 3 - 6% by weight and 1 - 2 M, respectively.

Optimum condition of copper extraction by ELMs for low feed concentration (10 - 100 ppm) is suggested in the list of Table 5.1. Under the condition copper extraction was found to be very efficient and the copper concentration in the aqueous feed phase could be monitored to the level of the toxic limit of 1.5 ppm.

**Table 5.1** The optimum condition for 50 ppm copper extraction by ELMs

Parameters	Optimum Conditions
Feed pH	pH = 5.0
Extraction temperature	30°C
Span 80	3% by weight
Stirring speed	400 rpm
LIX 984N	4% by weight
Sulfuric acid	2.0 molar

More than 99% of copper could be separated from the dilute feed solution by one batch ELM operation within 14 minutes using the optimum condition. Sengupta (2006) results on copper extraction using LIX 984N-C as a carrier was less than 90% after 15 minutes for 500 ppm copper feed solution using their optimum condition. Ethylene-propylene copolymer, 1% by weight, could reduce membrane swelling and membrane leakage when the extraction was operated at high stirring speed (600 – 800 rpm) with a decrease in initial extraction rate. The maximum percentage of 99% was obtained which was more than the that (90%) found by Skelland and Meng (1999) when PIB was used. Reusability of LIX 984N as a carrier indicated that more than 97% of copper could be removed by ELMs even for the third use. ELM process evidently offers a green chemical method for copper extraction with low consumptions of energy, organic solvent and extractant.

## 5.2 Further Study

1. The optimum condition may be applied for copper recovery from actual industrial waste.
2. Suitable condition found for copper may be applied for other metal ion extraction.
3. The use of other surfactants (Tween 80) and carriers (D2EHPA) for copper extraction by ELM method may be carried out.

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## **APPENDICES**

## APPENDIX A

### EXTRACTION EXPERIMENTAL DATA

#### Part I : Surfactant Concentration Variable

##### Experimental condition:

Membrane phase	depend on the surfactant concentration
Organic solvent (Kerosene)	4% by weight
Carrier (LIX 984N)	various concentration from 0 to 5%
Surfactant (Span80)	2M sulfuric acid solution
Internal phase	120:120 by volume
Organic phase : Internal phase	50 ppm of Cu at pH 5.00
External phase	60:360 by volume
Membrane phase : External phase	400 rpm
Stirring speed	

**Table A-1** Experimental data of remaining copper concentration in the feed phase after time intervals at various surfactant concentrations

Time (min.)	Copper concentration (ppm.)				
	1% Span 80	2% Span 80	3% Span 80	4% Span 80	5% Span 80
0	49.78±0.05	49.02±0.04	49.44±0.06	49.53±0.06	49.52±0.05
2	6.69±0.06	1.67±0.04	0.59±0.05	0.64±0.05	1.27±0.06
4	8.92 ±0.08	1.60±0.05	0.56±0.05	0.35±0.05	0.96±0.05
6	10.91±0.05	1.53±0.06	0.42±0.05	0.32±0.04	0.56±0.08
8	14.60±0.05	1.46±0.05	0.28±0.04	0.26±0.05	0.39±0.05
10	13.70±0.06	1.84±0.05	0.19±0.04	0.20±0.05	0.19±0.05
12	13.90±0.09	1.84±0.05	0.16±0.04	0.17±0.04	0.19±0.04
14	14.70±0.05	2.08±0.07	0.10±0.04	0.17±0.05	0.13±0.05
16	14.87±0.05	2.15±0.05	0.13±0.04	0.17±0.04	0.09±0.05
18	15.20±0.07	2.33±0.05	0.13±0.05	0.13±0.04	0.09±0.05
20	16.63±0.05	2.67±0.05	0.16±0.04	0.17±0.04	0.09±0.04
25	18.59±0.02	3.64±0.05	0.19±0.05	0.20±0.05	0.09±0.05
30	18.82±0.05	3.77±0.08	0.22±0.05	0.20±0.05	0.09±0.05
35	20.28±0.04	4.53±0.05	0.25±0.05	0.23±0.05	0.36±0.05
40	21.78±0.04	5.02±0.07	0.30±0.06	0.29±0.06	0.83±0.05
45	23.74±0.05	5.74±0.05	0.71±0.05	0.39±0.05	2.11±0.06
50	24.73±0.05	6.95±0.06	0.73±0.05	0.70±0.05	3.85±0.05
55	26.03±0.06	7.74±0.05	1.08±0.08	1.08±0.04	5.03±0.05
60	27.72±0.06	8.95±0.04	1.39±0.05	1.49±0.05	6.40±0.06



**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	various concentration from 0 to 5%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	100 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-2** Experimental data of remaining copper concentration in the feed phase after time intervals at various surfactant concentrations

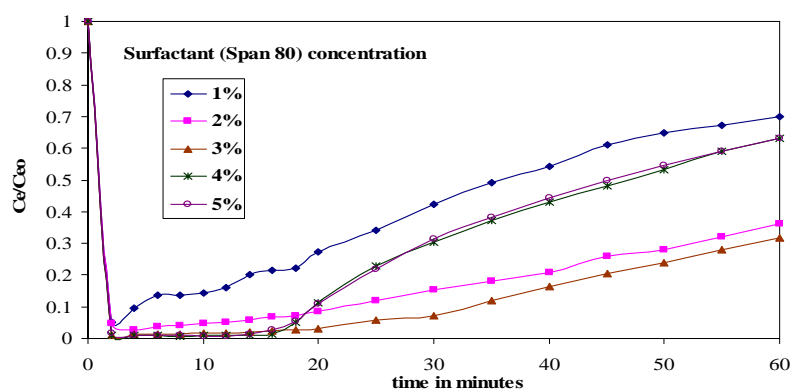
Time (min.)	Copper concentration (ppm.)				
	1% Span 80	2% Span 80	3% Span 80	4% Span 80	5% Span 80
0	98.37±0.06	98.37±0.08	98.54±0.06	98.37±0.05	98.23±0.05
2	7.19±0.1	1.58±0.06	1.41±0.05	1.44±0.06	1.45±0.06
4	8.94±0.06	1.34±0.05	1.31±0.05	1.34±0.05	0.90±0.06
6	10.92±0.06	1.08±0.07	1.08±0.05	1.08±0.05	0.80±0.05
8	12.27±0.1	1.05±0.08	1.08±0.05	1.05±0.05	0.73±0.05
10	13.69±0.06	0.98±0.08	0.98±0.06	0.98±0.06	0.46±0.06
12	13.85±0.06	0.98±0.05	0.65±0.06	0.98±0.06	0.46±0.06
14	14.68±0.05	0.85±0.06	0.62±0.06	0.85±0.06	0.43±0.06
16	15.04±0.05	0.92±0.05	0.59±0.0	0.92±0.07	0.43±0.07
18	15.17±0.05	1.18±0.06	0.72±0.07	1.05±0.05	0.43±0.09
20	16.59±0.06	2.07±0.06	0.98±0.07	1.97±0.05	0.43±0.06
25	18.54±0.06	3.49±0.05	1.51±0.06	3.16±0.06	0.56±0.1
30	19.76±0.07	5.14±0.05	2.17±0.06	4.48±0.06	0.60±0.06
35	20.22±0.09	8.61±0.05	3.13±0.05	5.31±0.06	0.84±0.06
40	21.71±0.06	9.36±0.05	4.74±0.06	5.40±0.06	0.90±0.05
45	23.66±0.06	10.09±0.06	4.98±0.05	5.80±0.06	2.53±0.06
50	25.97±0.05	11.67±0.06	5.73±0.06	5.73±0.06	4.29±0.06
55	29.23±0.05	15.87±0.05	5.97±0.07	5.97±0.06	6.63±0.05
60	32.24±0.05	16.49±0.06	6.26±0.06	6.26±0.04	10.23±0.06

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	various concentration from 0 to 5%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	800 rpm

**Table A-3** Experimental data of remaining copper concentration in the feed phase after time intervals at various surfactant concentrations

Time (min.)	Copper concentration in the feed phase (ppm.)				
	1% Span 80	2% Span 80	3% Span 80	4% Span 80	5% Span 80
0	50.62±0.05	48.02±0.05	50.55±0.05	50.26±0.06	50.12±0.06
2	2.54±0.05	2.24±0.05	0.55±0.05	0.58±0.07	0.92±0.06
4	4.86±0.05	1.34±0.05	0.65±0.06	0.47±0.06	0.57±0.06
6	6.85±0.04	1.83±0.06	0.68±0.06	0.45±0.06	0.53±0.04
8	6.88±0.07	1.93±0.06	0.71±0.06	0.42±0.08	0.44±0.04
10	7.32±0.05	2.28±0.04	0.84±0.04	0.45±0.06	0.41±0.06
12	8.13±0.06	2.45±0.06	0.90±0.06	0.50±0.06	0.34±0.06
14	10.25±0.05	2.83±0.06	1.02±0.06	0.50±0.04	0.60±0.07
16	10.85±0.05	3.24±0.06	1.27±0.05	0.67±0.06	1.43±0.07
18	11.29±0.05	3.42±0.06	1.40±0.05	2.64±0.06	2.71±0.1
20	13.85±0.06	4.07±0.06	1.62±0.06	5.68±0.06	5.53±0.06
25	17.22±0.06	5.70±0.05	2.93±0.06	11.52±0.05	11.01±0.06
30	21.43±0.08	7.29±0.05	3.65±0.05	15.32±0.05	15.69±0.08
35	24.89±0.08	8.61±0.06	5.96±0.05	18.78±0.06	19.22±0.06
40	27.39±0.06	10.06±0.06	8.27±0.05	21.65±0.06	22.26±0.06
45	30.89±0.06	12.38±0.06	10.34±0.05	24.20±0.06	24.99±0.05
50	32.77±0.06	13.49±0.05	12.12±0.06	26.80±0.06	27.33±0.05
55	34.02±0.05	15.39±0.06	14.12±0.05	29.63±0.06	29.67±0.05
60	35.33±0.06	17.29±0.06	16.05±0.05	31.65±0.05	31.62±0.05

**Figure A-1** Effect of surfactant concentration on extraction of 50 ppm copper ions by emulsion liquid membrane at 4% LIX 984N

**Part II : Stirring Speed Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	various speed condition from 200 to 800 rpm

**Table A-4** Experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds

Time (min.)	Copper concentration (ppm.)			
	200 rpm	400 rpm	600 rpm	800 rpm
0	49.04±0.05	49.44±0.06	49.39±0.05	50.55±0.05
2	12.57±0.06	0.59±0.05	0.69±0.06	0.55±0.05
4	5.51±0.06	0.56±0.05	0.62±0.08	0.65±0.06
6	1.51±0.05	0.42±0.05	0.62±0.05	0.68±0.06
8	0.82±0.07	0.28±0.04	0.59±0.06	0.71±0.06
10	0.60±0.07	0.19±0.04	0.50±0.06	0.84±0.04
12	0.51±0.05	0.16±0.04	0.56±0.05	0.90±0.06
14	0.35±0.05	0.10±0.04	0.56±0.04	1.02±0.06
16	0.41±0.05	0.13±0.04	0.59±0.05	1.27±0.05
18	0.41±0.06	0.13±0.05	0.65±0.06	1.40±0.05
20	0.45±0.06	0.16±0.04	0.72±0.06	1.62±0.06
25	0.38±0.06	0.19±0.05	1.00±0.08	2.93±0.06
30	0.41±0.05	0.22±0.05	1.29±0.08	3.65±0.05
35	0.38±0.06	0.25±0.05	1.85±0.06	5.96±0.05
40	0.41±0.05	0.30±0.06	2.07±0.06	8.27±0.05
45	0.54±0.05	0.71±0.05	2.64±0.04	10.34±0.05
50	0.51±0.06	0.73±0.05	3.49±0.06	12.12±0.06
55	0.66±0.06	1.08±0.08	4.41±0.06	14.12±0.05
60	1.35±0.05	1.39±0.05	6.11±0.1	16.05±0.05

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	100 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	various speed condition from 200 to 800 rpm

**Table A-5** Experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds

Time (min.)	Copper concentration (ppm.)			
	200 rpm	400 rpm	600 rpm	800 rpm
0	97.09±0.05	98.54±0.06	99.72±0.06	100.49±0.06
2	25.01±0.06	1.41±0.05	1.40±0.06	1.33±0.05
4	15.04±0.05	1.31±0.05	1.76±0.05	2.13±0.06
6	5.01±0.05	1.08±0.05	2.03±0.05	2.39±0.06
8	4.75±0.06	1.08±0.05	2.23±0.06	2.39±0.06
10	3.15±0.06	0.98±0.06	2.62±0.05	3.19±0.05
12	2.50±0.06	0.65±0.06	2.72±0.05	2.83±0.05
14	2.04±0.07	0.62±0.06	3.12±0.05	3.89±0.05
16	1.98±0.07	0.59±0.0	4.07±0.06	3.89±0.05
18	1.69±0.06	0.72±0.07	3.38±0.04	4.21±0.06
20	1.42±0.08	0.98±0.07	4.17±0.06	4.43±0.06
25	1.91±0.05	1.51±0.06	5.49±0.06	6.81±0.06
30	1.95±0.06	2.17±0.06	6.35±0.08	7.54±0.04
35	2.14±0.04	3.13±0.05	7.04±0.08	10.13±0.06
40	2.11±0.06	4.74±0.06	8.07±0.06	10.64±0.06
45	2.14±0.06	4.98±0.05	9.42±0.07	14.25±0.07
50	1.91±0.06	5.73±0.06	9.85±0.07	17.57±0.06
55	2.24±0.05	5.97±0.07	10.51±0.10	18.08±0.06
60	2.37±0.05	6.26±0.06	12.19±0.08	21.33±0.06

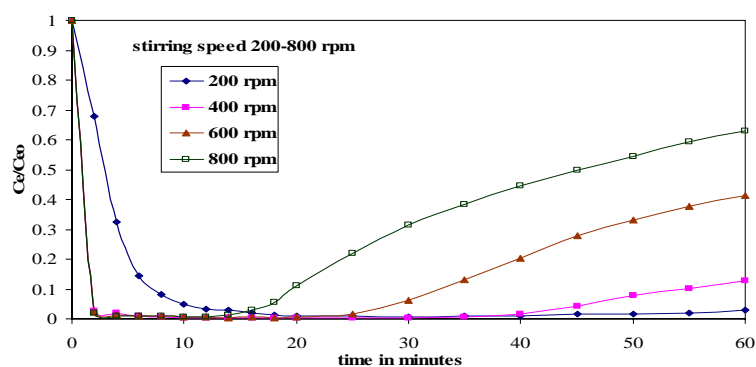
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	5% by weight
Internal phase	
Organic phase : Internal phase	2M sulfuric acid solution
External phase	120:120 by volume
Membrane phase : External phase	50 ppm of Cu at pH 5.00
Stirring speed	60:360 by volume
	various speed condition from 200 to 800 rpm

**Table A-6** Experimental data of remaining copper concentration in the feed phase after time intervals at various stirring speeds

Time (min.)	Copper concentration (ppm.)			
	200 rpm	400 rpm	600 rpm	800 rpm
0	49.85±0.05	49.52±0.05	48.33±0.06	50.12±0.06
2	33.84±0.05	1.27±0.06	1.07±0.06	0.92±0.06
4	16.19±0.06	0.96±0.05	0.64±0.06	0.57±0.06
6	7.14±0.06	0.56±0.08	0.45±0.05	0.53±0.06
8	4.04±0.04	0.39±0.05	0.45±0.05	0.44±0.04
10	2.49±0.06	0.19±0.05	0.28±0.05	0.41±0.04
12	1.70±0.05	0.19±0.04	0.32±0.05	0.34±0.04
14	1.40±0.07	0.13±0.05	0.22±0.05	0.60±0.06
16	1.04±0.07	0.09±0.05	0.25±0.05	1.43±0.06
18	0.61±0.04	0.09±0.05	0.19±0.04	2.71±0.05
20	0.51±0.06	0.09±0.04	0.35±0.04	5.53±0.05
25	0.51±0.06	0.09±0.05	0.81±0.04	11.01±0.06
30	0.38±0.06	0.09±0.05	2.96±0.06	15.69±0.06
35	0.48±0.05	0.36±0.05	6.41±0.06	19.22±0.05
40	0.54±0.06	0.83±0.05	9.76±0.07	22.26±0.06
45	0.74±0.05	2.11±0.06	13.54±0.06	24.99±0.06
50	0.87±0.06	3.85±0.05	16.02±0.06	27.33±0.06
55	0.94±0.05	5.03±0.05	18.30±0.06	29.67±0.06
60	1.40±0.05	6.40±0.06	20.02±0.1	31.62±0.1

**Figure A-2** Effect of stirring speed on extraction of 50 ppm copper ions by emulsion liquid membrane at 4% LIX 984N and 5% Span 80



**Part III : Carrier concentration Variable****Experimental conditions:**

Membrane phase	Organic solvent (Kerosene)	depend on the carrier concentration
	Carrier (LIX 984N)	various concentration from 0 to 6%
	Surfactant (Span80)	3% by weight
Internal phase		2M sulfuric acid solution
Organic phase : Internal phase		120:120 by volume
External phase		50 ppm of Cu at pH 5.00
Membrane phase : External phase		60:360 by volume
Stirring speed		400 rpm

**Table A-7** Experimental data of remaining copper concentration in the feed phase after time intervals at various carrier concentrations

Time (min.)	Copper concentration (ppm.)			
	3% LIX 984N	4% LIX 984N	5% LIX 984N	6% LIX 984N
0	50.04±0.05	49.44±0.06	49.58±0.06	50.21±0.06
2	1.03±0.05	0.59±0.05	0.64±0.06	0.62±0.06
4	0.73±0.05	0.56±0.05	0.48±0.06	0.49±0.06
6	0.68±0.06	0.42±0.05	0.32±0.04	0.27±0.05
8	0.37±0.06	0.28±0.04	0.23±0.04	0.18±0.05
10	0.37±0.06	0.19±0.04	0.13±0.04	0.18±0.05
12	0.35±0.06	0.16±0.04	0.13±0.04	0.30±0.05
14	0.35±0.06	0.10±0.04	0.10±0.04	0.43±0.05
16	0.40±0.06	0.13±0.04	0.13±0.04	0.56±0.06
18	0.42±0.06	0.13±0.05	0.19±0.04	0.52±0.06
20	0.50±0.04	0.16±0.04	0.19±0.04	0.59±0.05
25	0.55±0.04	0.19±0.05	0.29±0.04	0.75±0.06
30	0.70±0.04	0.22±0.05	0.48±0.05	1.19±0.06
35	0.86±0.06	0.25±0.05	0.48±0.05	1.35±0.06
40	1.01±0.06	0.30±0.06	0.61±0.05	1.57±0.06
45	1.36±0.06	0.71±0.05	0.87±0.06	1.73±0.06
50	1.36±0.06	0.73±0.05	0.93±0.06	1.98±0.06
55	1.57±0.07	1.08±0.08	1.28±0.06	2.17±0.06
60	1.67±0.07	1.39±0.05	1.70±0.06	2.26±0.06

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the carrier concentration
Carrier (LIX 984N)	various concentration from 0 to 6%
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	600 rpm

**Table A-8** Experimental data of remaining copper concentration in the feed phase after time intervals at various carrier concentrations

Time (min.)	Copper concentration (ppm.)			
	3% LIX 984N	4% LIX 984N	5% LIX 984N	6% LIX984N
0	49.39±0.09	49.39±0.05	49.79±0.06	50.42±0.05
2	1.39±0.06	0.69±0.06	0.93±0.06	0.67±0.04
4	0.89±0.05	0.62±0.08	0.82±0.06	0.49±0.04
6	0.79±0.05	0.62±0.05	0.51±0.05	0.38±0.04
8	0.69±0.05	0.59±0.06	0.51±0.05	0.31±0.04
10	0.61±0.05	0.50±0.06	0.55±0.05	0.28±0.04
12	0.76±0.05	0.56±0.05	0.63±0.05	0.28±0.04
14	0.76±0.06	0.56±0.04	0.63±0.06	0.24±0.04
16	0.81±0.05	0.59±0.05	0.63±0.05	0.31±0.04
18	0.91±0.06	0.65±0.06	0.70±0.06	0.31±0.05
20	1.01±0.06	0.72±0.06	0.78±0.06	0.49±0.04
25	1.34±0.07	1.00±0.08	1.16±0.06	0.91±0.06
30	1.81±0.07	1.29±0.08	1.39±0.07	2.82±0.06
35	2.61±0.06	1.85±0.06	1.65±0.06	4.80±0.06
40	2.34±0.04	2.07±0.06	2.64±0.06	7.24±0.06
45	3.76±0.06	2.64±0.04	3.77±0.06	10.14±0.06
50	4.49±0.06	3.49±0.06	5.44±0.05	12.61±0.07
55	4.56±0.05	4.41±0.06	6.88±0.05	15.61±0.08
60	5.39±0.06	6.11±0.1	8.05±0.05	17.59±0.08

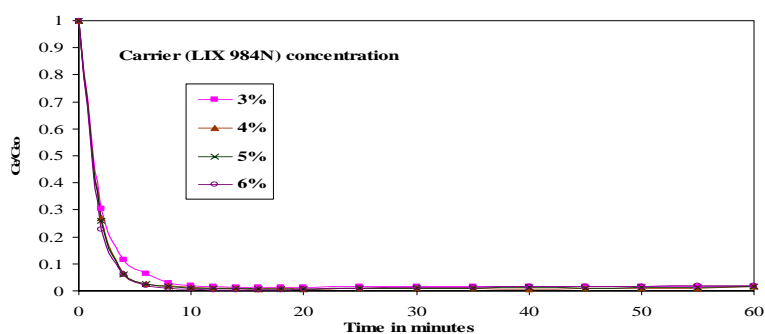
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the carrier concentration
Carrier (LIX 984N)	various concentration from 0 to 6%
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	200 rpm

**Table A-9** Experimental data of remaining copper concentration in the feed phase after time intervals at various carrier concentrations

Time (min.)	Copper concentration (ppm.)			
	3% LIX 984N	4% LIX 984N	5% LIX 984N	6% LIX984N
0	50.04±0.07	49.04±0.05	49.58±0.06	50.21±0.06
2	15.25±0.08	12.57±0.06	12.82±0.06	11.44±0.06
4	5.80±0.06	5.51±0.06	3.05±0.06	3.02±0.06
6	3.22±0.06	1.51±0.05	1.288±0.06	1.00±0.06
8	1.39±0.06	0.82±0.07	0.80±0.06	0.49±0.06
10	0.96±0.05	0.60±0.07	0.45±0.06	0.24±0.06
12	0.73±0.05	0.51±0.05	0.42±0.06	0.11±0.06
14	0.68±0.05	0.35±0.05	0.42±0.06	0.11±0.06
16	0.65±0.06	0.41±0.05	0.39±0.06	0.08±0.06
18	0.68±0.06	0.41±0.06	0.35±0.06	0.14±0.06
20	0.68±0.04	0.45±0.06	0.35±0.06	0.27±0.06
25	0.80±0.07	0.38±0.06	0.42±0.06	0.43±0.06
30	0.73±0.06	0.41±0.05	0.48±0.06	0.62±0.06
35	0.73±0.05	0.38±0.06	0.48±0.06	0.71±0.06
40	0.75±0.05	0.41±0.05	0.61±0.06	0.78±0.06
45	0.75±0.05	0.54±0.05	0.55±0.06	0.81±0.06
50	0.78±0.05	0.51±0.06	0.61±0.06	0.81±0.06
55	0.80±0.05	0.66±0.06	0.71±0.06	0.90±0.06
60	0.80±0.05	1.35±0.05	0.87±0.06	1.00±0.06

**Figure A-3** Effect of carrier concentration on extraction of 50 ppm copper ions by emulsion liquid membrane at 200 rpm





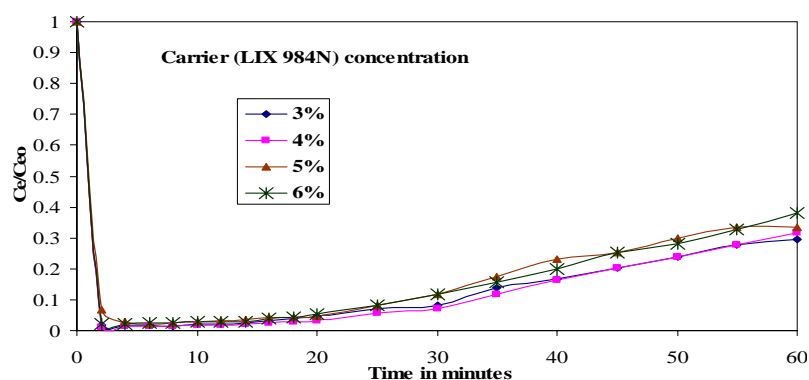
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the carrier concentration
Carrier (LIX 984N)	various concentration from 0 to 6%
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	800 rpm

**Table A-10** Experimental data of remaining copper concentration in the feed phase after time intervals at various carrier concentrations

Time (min.)	Copper concentration (ppm.)			
	3% LIX 984N	4% LIX 984N	5% LIX 984N	6% LIX984N
0	49.33±0.06	50.55±0.05	49.63±0.06	48.72±0.06
2	0.93±0.06	0.55±0.05	3.30±0.06	1.10±0.06
4	0.90±0.06	0.65±0.06	1.48±0.06	1.03±0.06
6	0.90±0.06	0.68±0.06	1.14±0.06	1.17±0.06
8	0.78±0.06	0.71±0.06	1.26±0.06	1.21±0.06
10	0.98±0.06	0.84±0.04	1.39±0.06	1.31±0.06
12	1.05±0.06	0.90±0.06	1.54±0.06	1.31±0.06
14	1.25±0.06	1.02±0.06	1.70±0.06	1.45±0.06
16	1.65±0.06	1.27±0.05	2.07±0.06	1.90±0.06
18	1.88±0.06	1.40±0.05	2.16±0.06	2.03±0.06
20	2.27±0.06	1.62±0.06	2.34±0.06	2.62±0.06
25	3.57±0.06	2.93±0.06	4.01±0.06	3.93±0.06
30	4.09±0.06	3.65±0.05	5.74±0.06	5.76±0.06
35	6.91±0.06	5.96±0.05	8.61±0.06	7.55±0.06
40	8.16±0.06	8.27±0.05	11.42±0.06	9.65±0.06
45	9.98±0.06	10.34±0.05	12.53±0.06	12.24±0.06
50	11.70±0.06	12.12±0.06	14.81±0.06	13.76±0.06
55	13.62±0.06	14.12±0.05	16.60±0.06	15.93±0.06
60	14.59±0.06	16.05±0.05	16.66±0.06	18.55±0.06

**Figure A-4** Effect of carrier concentration on extraction of 50 ppm copper ions by emulsion liquid membrane at 800 rpm



**Part IV : Initial acid concentration in the internal phase Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	various concentration from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-11** Experimental data of remaining copper concentration in the feed phase after time intervals at various acid concentrations

Time (min.)	Copper concentration (ppm.)		
	1.0 molar	1.5 molar	2.0 molar
0	50.93±0.08	50.82±0.07	49.44±0.06
2	0.67±0.05	0.68±0.05	0.59±0.05
4	0.63±0.05	0.51±0.05	0.56±0.05
6	0.60±0.05	0.44±0.04	0.42±0.05
8	0.50±0.05	0.37±0.04	0.28±0.04
10	0.47±0.04	0.37±0.04	0.19±0.04
12	0.47±0.04	0.40±0.04	0.16±0.04
14	0.40±0.04	0.33±0.04	0.10±0.04
16	0.37±0.04	0.26±0.04	0.13±0.04
18	0.43±0.04	0.40±0.04	0.13±0.05
20	0.47±0.04	0.40±0.04	0.16±0.04
25	0.80±0.04	0.44±0.04	0.19±0.05
30	0.90±0.04	0.57±0.04	0.22±0.05
35	1.17±0.05	0.61±0.04	0.25±0.05
40	1.40±0.06	0.78±0.04	0.30±0.06
45	1.60±0.06	0.96±0.05	0.71±0.05
50	1.64±0.06	1.13±0.06	0.73±0.05
55	1.77±0.06	1.44±0.06	1.08±0.08
60	1.77±0.06	1.62±0.06	1.39±0.05

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase	various concentration from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-12** Experimental data of remaining copper concentration in the feed phase after time intervals at various acid concentrations

Time (min.)	Copper concentration (ppm.)		
	1.0 molar	1.5 molar	2.0 molar
0	50.70±0.05	50.59±0.06	50.21±0.06
2	0.84±0.05	0.72±0.05	0.62±0.06
4	0.75±0.05	0.40±0.04	0.49±0.06
6	0.70±0.05	0.34±0.04	0.27±0.05
8	0.67±0.06	0.27±0.04	0.18±0.05
10	0.56±0.06	0.18±0.04	0.18±0.05
12	0.53±0.06	0.18±0.04	0.30±0.05
14	0.51±0.05	0.18±0.04	0.43±0.05
16	0.51±0.05	0.18±0.04	0.56±0.06
18	0.51±0.05	0.18±0.04	0.52±0.06
20	0.45±0.04	0.27±0.04	0.59±0.05
25	0.89±0.04	0.46±0.04	0.75±0.06
30	0.92±0.06	0.56±0.05	1.19±0.06
35	1.17±0.06	0.69±0.05	1.35±0.06
40	1.06±0.06	0.72±0.05	1.57±0.06
45	1.25±0.06	0.79±0.05	1.73±0.06
50	1.19±0.06	0.98±0.05	1.98±0.06
55	1.25±0.06	1.40±0.06	2.17±0.06
60	1.41±0.06	1.40±0.06	2.26±0.06

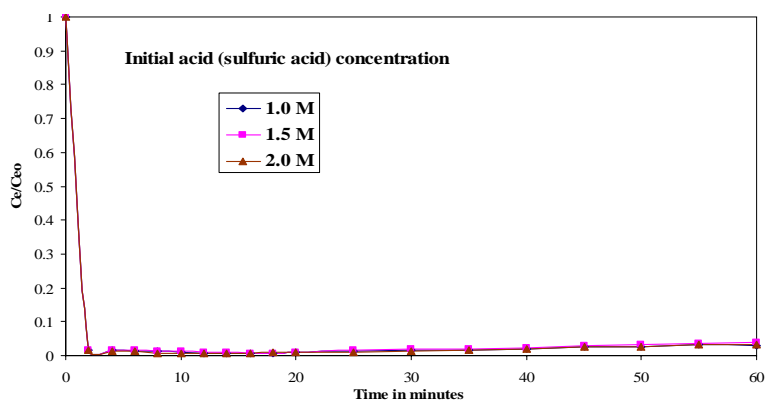
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	94% by weight
Carrier (LIX 984N)	3% by weight
Surfactant (Span80)	3% by weight
Internal phase	various concentration from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-13** Experimental data of remaining copper concentration in the feed phase after time intervals at various acid concentrations

Time (min.)	Copper concentration (ppm.)		
	1.0 molar	1.5 molar	2.0 molar
0	50.54±0.08	48.53±0.05	50.04±0.05
2	1.21±0.05	1.16±0.05	1.03±0.05
4	0.74±0.05	0.77±0.05	0.73±0.05
6	0.67±0.05	0.71±0.05	0.68±0.06
8	0.60±0.05	0.68±0.05	0.37±0.06
10	0.50±0.04	0.59±0.05	0.37±0.06
12	0.40±0.04	0.50±0.05	0.35±0.06
14	0.40±0.04	0.41±0.04	0.35±0.06
16	0.37±0.04	0.35±0.04	0.40±0.06
18	0.37±0.04	0.35±0.04	0.42±0.06
20	0.47±0.04	0.53±0.04	0.50±0.04
25	0.60±0.04	0.80±0.04	0.55±0.04
30	0.77±0.05	0.95±0.05	0.70±0.04
35	0.87±0.05	1.01±0.05	0.86±0.06
40	1.04±0.05	1.13±0.05	1.01±0.06
45	1.27±0.05	1.44±0.05	1.36±0.06
50	1.34±0.05	1.56±0.05	1.36±0.06
55	1.58±0.06	1.77±0.05	1.57±0.07
60	1.54±0.06	1.89±0.08	1.67±0.07

**Figure A-5** Effect of acid concentration on copper extraction by ELM



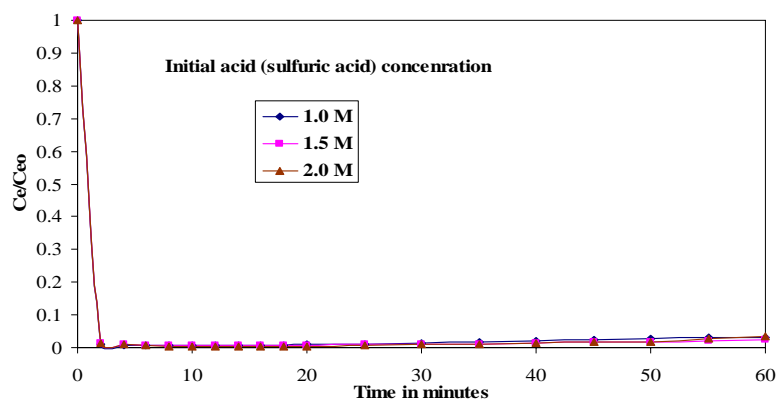
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	92% by weight
Carrier (LIX 984N)	5% by weight
Surfactant (Span80)	3% by weight
Internal phase	various concentration from 1.0 to 2.0 molar
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5.00
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-14** Experimental data of remaining copper concentration in the feed phase after time intervals at various acid concentrations

Time (min.)	Copper concentration (ppm.)		
	1.0 molar	1.5 molar	2.0 molar
0	50.54±0.07	50.16±0.06	49.58±0.06
2	0.54±0.05	0.60±0.05	0.64±0.06
4	0.40±0.05	0.48±0.04	0.48±0.06
6	0.40±0.05	0.38±0.04	0.32±0.04
8	0.33±0.04	0.35±0.04	0.23±0.04
10	0.33±0.04	0.35±0.04	0.13±0.04
12	0.33±0.04	0.26±0.04	0.13±0.04
14	0.33±0.04	0.29±0.04	0.10±0.04
16	0.33±0.04	0.32±0.04	0.13±0.04
18	0.37±0.04	0.32±0.04	0.19±0.04
20	0.47±0.04	0.35±0.04	0.19±0.04
25	0.60±0.04	0.45±0.04	0.29±0.04
30	0.77±0.05	0.51±0.04	0.48±0.05
35	0.87±0.06	0.54±0.04	0.48±0.05
40	1.04±0.06	0.63±0.04	0.61±0.05
45	1.27±0.06	0.79±0.05	0.87±0.06
50	1.34±0.06	0.92±0.06	0.93±0.06
55	1.58±0.07	1.01±0.06	1.28±0.06
60	1.54±0.05	1.26±0.06	1.70±0.06

**Figure A-6** Effect of acid concentration on copper extraction by ELM



**Part V : The feed phase pH Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-15** Experimental data of remaining copper concentration in the feed phase after time intervals at various feed pH

Time (min.)	Copper concentration (ppm.)		
	pH = 1	pH = 2	pH = 5
0	50.79±0.05	49.56±0.08	49.44±0.06
2	43.63±0.05	20.17±0.07	0.59±0.05
4	38.06±0.08	10.02±0.06	0.56±0.05
6	35.48±0.06	4.19±0.06	0.42±0.05
8	32.82±0.06	2.16±0.06	0.28±0.04
10	30.79±0.08	1.21±0.06	0.19±0.04
12	28.84±0.07	0.83±0.06	0.16±0.04
14	27.31±0.07	0.69±0.06	0.10±0.04
16	26.09±0.07	0.72±0.05	0.13±0.04
18	24.90±0.06	0.72±0.05	0.13±0.05
20	24.26±0.05	0.75±0.05	0.16±0.04
25	22.73±0.05	0.75±0.05	0.19±0.05
30	22.24±0.05	0.83±0.05	0.22±0.05
35	21.83±0.05	1.09±0.06	0.25±0.05
40	21.60±0.05	1.30±0.06	0.30±0.06
45	21.74±0.05	1.73±0.06	0.71±0.05
50	21.83±0.05	1.96±0.06	0.73±0.05
55	22.26±0.06	2.13±0.06	1.08±0.08
60	22.32±0.06	2.34±0.06	1.39±0.05

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-16** Experimental data of remaining copper concentration in the feed phase after time intervals at various feed pH

Time (min.)	Copper concentration (ppm.)		
	pH = 1	pH = 2	pH = 5
0	50.28±0.05	50.44±0.06	50.21±0.06
2	42.75±0.05	13.85±0.07	0.62±0.06
4	35.23±0.05	3.92±0.07	0.49±0.06
6	30.52±0.06	1.49±0.06	0.27±0.05
8	27.22±0.07	0.82±0.06	0.18±0.05
10	24.34±0.07	0.61±0.05	0.18±0.05
12	22.24±0.05	0.58±0.05	0.30±0.05
14	20.69±0.06	0.61±0.05	0.43±0.05
16	19.66±0.06	0.61±0.05	0.56±0.06
18	19.08±0.05	0.65±0.05	0.52±0.06
20	18.42±0.05	0.65±0.05	0.59±0.05
25	17.91±0.06	0.72±0.06	0.75±0.06
30	17.74±0.06	0.68±0.05	1.19±0.06
35	18.01±0.05	0.79±0.06	1.35±0.06
40	18.25±0.05	1.00±0.06	1.57±0.06
45	18.67±0.05	1.14±0.06	1.73±0.06
50	19.15±0.05	1.25±0.06	1.98±0.06
55	19.66±0.05	1.46±0.07	2.17±0.06
60	20.28±0.05	2.83±0.06	2.26±0.06

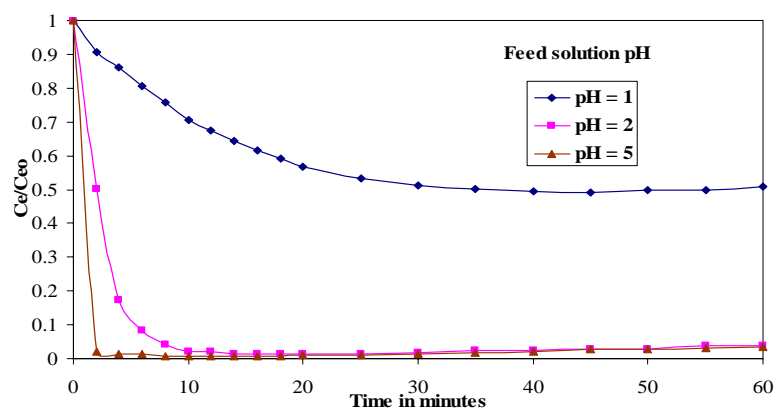
**Experimental conditions:**

Membrane phase		
Organic solvent (Kerosene)		94% by weight
Carrier (LIX 984N)		3% by weight
Surfactant (Span80)		3% by weight
Internal phase		
		2M sulfuric acid solution
Organic phase : Internal phase		120:120 by volume
External phase		50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase		60:360 by volume
Stirring speed		400 rpm

**Table A-17** Experimental data of remaining copper concentration in the feed phase after time intervals at various feed pH

Time (min.)	Copper concentration (ppm.)		
	pH = 1	pH = 2	pH = 5
0	49.49±0.08	50.40±0.06	50.04±0.05
2	44.78±0.08	25.37±0.05	1.03±0.05
4	42.68±0.06	8.71±0.05	0.73±0.05
6	39.87±0.07	4.22±0.05	0.68±0.06
8	37.42±0.07	2.06±0.04	0.37±0.06
10	35.00±0.06	1.11±0.04	0.37±0.06
12	33.45±0.05	0.98±0.05	0.35±0.06
14	31.91±0.05	0.64±0.05	0.35±0.06
16	30.40±0.05	0.61±0.04	0.40±0.06
18	29.21±0.05	0.61±0.04	0.42±0.06
20	28.15±0.05	0.67±0.04	0.50±0.04
25	26.43±0.05	0.74±0.04	0.55±0.04
30	25.31±0.05	0.91±0.04	0.70±0.04
35	24.78±0.06	1.15±0.05	0.86±0.06
40	24.40±0.05	1.15±0.05	1.01±0.06
45	24.26±0.05	1.35±0.05	1.36±0.06
50	24.57±0.06	1.35±0.07	1.36±0.06
55	24.71±0.05	1.89±0.05	1.57±0.07
60	25.14±0.05	1.99±0.01	1.67±0.07

**Figure A-7** Effect of acid concentration on copper extraction by ELM





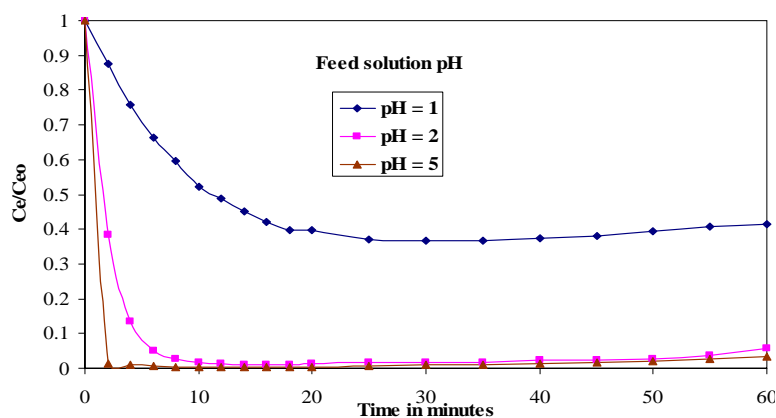
**Experimental conditions:**

Membrane phase		
Organic solvent (Kerosene)		92% by weight
Carrier (LIX 984N)		5% by weight
Surfactant (Span80)		3% by weight
Internal phase		
		2M sulfuric acid solution
Organic phase : Internal phase		120:120 by volume
External phase		50 ppm of Cu at various pH from 1 to 5
Membrane phase : External phase		60:360 by volume
Stirring speed		400 rpm

**Table A-18** Experimental data of remaining copper concentration in the feed phase after time intervals at various feed pH

Time (min.)	Copper concentration (ppm.)		
	pH = 1	pH = 2	pH = 5
0	49.39±0.08	49.67±0.05	49.58±0.06
2	43.25±0.08	19.05±0.05	0.64±0.06
4	37.49±0.06	6.67±0.05	0.48±0.06
6	32.84±0.06	2.52±0.05	0.32±0.04
8	29.49±0.06	1.28±0.05	0.23±0.04
10	25.75±0.06	0.88±0.04	0.13±0.04
12	24.04±0.06	0.63±0.04	0.13±0.04
14	22.27±0.06	0.57±0.04	0.10±0.04
16	20.85±0.06	0.51±0.04	0.13±0.04
18	19.64±0.05	0.57±0.04	0.19±0.04
20	19.61±0.05	0.63±0.04	0.19±0.04
25	18.28±0.05	0.75±0.04	0.29±0.04
30	18.12±0.05	0.88±0.04	0.48±0.05
35	18.09±0.05	0.91±0.04	0.48±0.05
40	18.47±0.05	1.13±0.06	0.61±0.05
45	18.76±0.05	1.19±0.06	0.87±0.06
50	19.52±0.05	1.28±0.06	0.93±0.06
55	20.18±0.06	1.90±0.06	1.28±0.06
60	20.53±0.06	2.80±0.06	1.70±0.06

**Figure A-8** Effect of acid concentration on copper extraction by ELM



**Part VI : Polymer concentration Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the polymer concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Ethylene-propylene copolymer	various concentration from 0 to 2%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-19** Experimental data of remaining copper concentration in the feed phase after time intervals at various polymer concentrations

Time (min.)	Copper concentration (ppm.)		
	No polymer	1% Polymer	2% Polymer
0	49.44±0.06	50.26±0.09	50.47±0.05
2	0.59±0.05	0.96±0.05	1.14±0.05
4	0.56±0.05	0.63±0.05	0.95±0.06
6	0.42±0.05	0.63±0.05	0.93±0.06
8	0.28±0.04	0.57±0.05	0.93±0.06
10	0.19±0.04	0.48±0.04	0.90±0.05
12	0.16±0.04	0.39±0.04	0.85±0.05
14	0.10±0.04	0.35±0.04	0.79±0.05
16	0.13±0.04	0.42±0.04	0.79±0.05
18	0.13±0.05	0.42±0.04	0.82±0.05
20	0.16±0.04	0.42±0.04	1.01±0.05
25	0.19±0.05	0.45±0.04	1.17±0.05
30	0.22±0.05	0.48±0.04	1.14±0.05
35	0.25±0.05	0.48±0.04	1.77±0.06
40	0.30±0.06	0.66±0.04	1.79±0.06
45	0.71±0.05	0.72±0.05	1.98±0.06
50	0.73±0.05	0.90±0.05	2.26±0.05
55	1.08±0.08	1.03±0.05	2.17±0.05
60	1.39±0.05	1.18±0.05	2.61±0.08

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the polymer concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Ethylene-propylene copolymer	various concentration from 0 to 2%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	600 rpm

**Table A-20** Experimental data of remaining copper concentration in the feed phase after time intervals at various polymer concentrations

Time (min.)	Copper concentration (ppm.)		
	No polymer	1% Polymer	2% Polymer
0	49.39±0.05	49.15±0.07	50.21±0.05
2	0.69±0.06	0.84±0.05	1.43±0.06
4	0.62±0.08	0.96±0.05	1.03±0.06
6	0.62±0.05	0.51±0.04	0.98±0.05
8	0.59±0.06	0.54±0.04	0.92±0.05
10	0.50±0.06	0.45±0.04	0.92±0.05
12	0.56±0.05	0.45±0.04	0.92±0.05
14	0.56±0.04	0.48±0.04	0.90±0.05
16	0.59±0.05	0.60±0.04	0.87±0.04
18	0.65±0.06	0.60±0.04	0.84±0.04
20	0.72±0.06	0.57±0.04	0.98±0.04
25	1.00±0.08	0.93±0.04	1.53±0.05
30	1.29±0.08	1.02±0.05	1.90±0.05
35	1.85±0.06	1.41±0.05	2.03±0.05
40	2.07±0.06	1.62±0.05	2.38±0.05
45	2.64±0.04	1.93±0.05	3.30±0.05
50	3.49±0.06	2.35±0.06	3.25±0.08
55	4.41±0.06	2.59±0.05	3.44±0.07
60	6.11±0.1	2.83±0.06	4.79±0.08

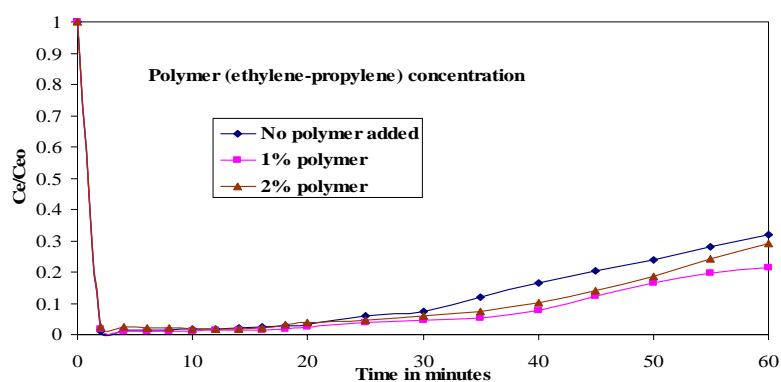
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the polymer concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Ethylene-propylene copolymer	various concentration from 0 to 2%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	800 rpm

**Table A-21** Experimental data of remaining copper concentration in the feed phase after time intervals at various polymer concentrations

Time (min.)	Copper concentration (ppm.)		
	No polymer	1% Polymer	2% Polymer
0	50.55±0.06	49.76±0.09	50.21±0.05
2	0.55±0.06	0.86±0.1	1.21±0.06
4	0.65±0.05	0.47±0.04	1.16±0.06
6	0.68±0.06	0.56±0.04	1.11±0.06
8	0.71±0.06	0.56±0.04	0.98±0.05
10	0.84±0.05	0.53±0.04	0.92±0.05
12	0.90±0.06	0.68±0.04	0.92±0.05
14	1.02±0.07	0.65±0.04	0.95±0.05
16	1.27±0.06	0.77±0.04	1.14±0.05
18	1.40±0.06	0.92±0.05	1.53±0.05
20	1.62±0.05	1.16±0.05	1.85±0.05
25	2.93±0.05	1.93±0.05	2.33±0.08
30	3.65±0.06	2.34±0.05	2.96±0.05
35	5.96±0.05	2.67±0.06	3.62±0.09
40	8.27±0.06	3.89±0.08	5.02±0.07
45	10.34±0.08	6.02±0.07	7.06±0.04
50	12.12±0.08	8.16±0.07	9.34±0.05
55	14.12±0.07	9.76±0.06	12.17±0.05
60	16.05±0.1	10.65±0.05	14.57±0.1

**Figure A-9** Effect of polymer concentration on copper extraction by ELM



**Part VII : Extraction temperature Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm
Extraction temperature	various from 30 – 50 °C

**Table A-22** Experimental data of remaining copper concentration in the feed phase after time intervals at various extraction temperatures

Time (min.)	Copper concentration (ppm.)		
	30 °C	40 °C	50 °C
0	49.44±0.06	49.38±0.09	50.51±0.1
2	0.59±0.05	0.85±0.05	0.87±0.05
4	0.56±0.05	0.87±0.05	1.01±0.06
6	0.42±0.05	1.13±0.06	1.27±0.06
8	0.28±0.04	1.69±0.06	1.80±0.06
10	0.19±0.04	2.03±0.06	2.25±0.05
12	0.16±0.04	2.76±0.06	3.61±0.07
14	0.10±0.04	3.47±0.05	4.03±0.06
16	0.13±0.04	3.78±0.05	4.48±0.06
18	0.13±0.05	4.00±0.07	4.79±0.05
20	0.16±0.04	5.47±0.05	5.61±0.06
25	0.19±0.05	6.82±0.05	6.90±0.05
30	0.22±0.05	7.83±0.05	8.76±0.05
35	0.25±0.05	9.07±0.1	11.94±0.05
40	0.30±0.06	11.13±0.05	13.66±0.08
45	0.71±0.05	13.72±0.09	15.41±0.08
50	0.73±0.05	15.47±0.05	17.86±0.08
55	1.08±0.08	16.96±0.05	18.93±0.05
60	1.39±0.05	18.62±0.05	20.87±0.06

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	91% by weight
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm
Extraction temperature	various from 30 – 50 °C

**Table A-23** Experimental data of remaining copper concentration in the feed phase after time intervals at various extraction temperatures

Time (min.)	Copper concentration (ppm.)		
	30 °C	40 °C	50 °C
0	50.21±0.06	49.40±0.07	48.10±0.06
2	0.62±0.06	0.62±0.05	0.78±0.05
4	0.49±0.06	0.72±0.05	0.59±0.05
6	0.27±0.05	0.78±0.05	0.62±0.05
8	0.18±0.05	0.91±0.05	0.81±0.05
10	0.18±0.05	1.33±0.06	1.33±0.06
12	0.30±0.05	1.52±0.06	1.56±0.06
14	0.43±0.05	1.81±0.06	2.14±0.05
16	0.56±0.06	2.27±0.05	2.27±0.04
18	0.52±0.06	2.72±0.05	2.85±0.07
20	0.59±0.05	3.27±0.07	2.88±0.05
25	0.75±0.06	4.04±0.05	4.10±0.08
30	1.19±0.06	5.23±0.07	5.23±0.08
35	1.35±0.06	6.49±0.07	6.65±0.05
40	1.57±0.06	7.52±0.05	7.62±0.05
45	1.73±0.06	9.01±0.04	9.14±0.1
50	1.98±0.06	10.36±0.08	10.65±0.05
55	2.17±0.06	11.33±0.08	12.52±0.05
60	2.26±0.06	13.56±0.08	14.20±0.1

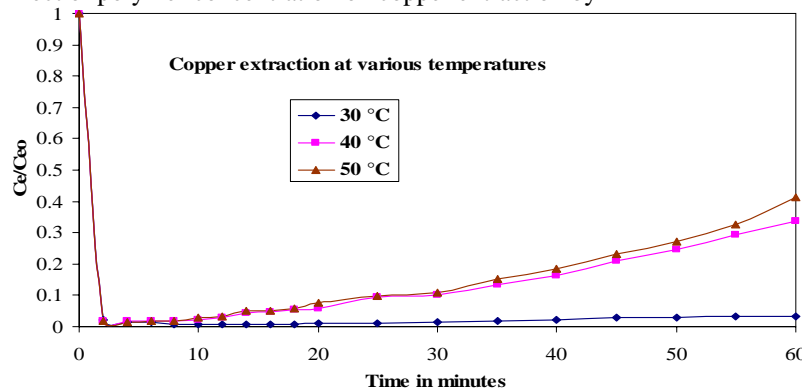
**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	94% by weight
Carrier (LIX 984N)	3% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm
Extraction temperature	various from 30 – 50 °C

**Table A-24** Experimental data of remaining copper concentration in the feed phase after time intervals at various extraction temperatures

Time (min.)	Copper concentration (ppm.)		
	30 °C	40 °C	50 °C
0	50.04±0.05	49.38±0.06	50.38±0.1
2	1.03±0.05	0.85±0.04	0.91±0.05
4	0.73±0.05	0.82±0.04	0.77±0.04
6	0.68±0.06	0.90±0.04	0.87±0.04
8	0.37±0.06	0.93±0.04	0.94±0.04
10	0.37±0.06	1.13±0.05	1.54±0.05
12	0.35±0.06	1.47±0.05	1.64±0.05
14	0.35±0.06	2.20±0.05	2.48±0.06
16	0.40±0.06	2.37±0.05	2.48±0.06
18	0.42±0.06	2.59±0.06	2.94±0.06
20	0.50±0.04	2.93±0.06	3.77±0.05
25	0.55±0.04	4.56±0.05	4.96±0.05
30	0.70±0.04	5.01±0.07	5.42±0.05
35	0.86±0.06	6.54±0.07	7.69±0.07
40	1.01±0.06	8.03±0.07	9.33±0.07
45	1.36±0.06	10.34±0.05	11.71±0.05
50	1.36±0.06	12.09±0.06	13.77±0.09
55	1.57±0.07	14.42±0.05	16.47±0.05
60	1.67±0.07	16.65±0.1	20.84±0.06

**Figure A-10** Effect of polymer concentration on copper extraction by ELM



**Part VII : Feed concentration Variable****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	various from 10 - 100 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-25** Experimental data of remaining copper concentration in the feed phase after time intervals at various feed phase concentrations

Time (min.)	Copper concentration (ppm.)				
	10 ppm	20 ppm	40 ppm	50 ppm	100 ppm
0	10.68±0.05	19.03±0.06	40.79±0.08	49.44±0.06	98.54±0.06
2	0.23±0.05	0.25±0.06	0.50±0.05	0.59±0.05	1.41±0.05
4	0.09±0.04	0.11±0.04	0.46±0.05	0.56±0.05	1.31±0.05
6	0.09±0.04	0.07±0.04	0.34±0.04	0.42±0.05	1.08±0.05
8	0.09±0.04	0.06±0.04	0.30±0.04	0.28±0.04	1.08±0.05
10	0.12±0.04	0.11±0.04	0.22±0.04	0.19±0.04	0.98±0.06
12	0.12±0.04	0.14±0.05	0.09±0.04	0.16±0.04	0.65±0.06
14	0.12±0.04	0.18±0.05	0.13±0.0	0.10±0.04	0.62±0.06
16	0.16±0.05	0.22±0.05	0.13±0.04	0.13±0.04	0.59±0.0
18	0.16±0.05	0.18±0.05	0.22±0.04	0.13±0.05	0.72±0.07
20	0.16±0.05	0.22±0.05	0.30±0.04	0.16±0.04	0.98±0.07
25	0.20±0.06	0.33±0.05	0.66±0.06	0.19±0.05	1.51±0.06
30	0.27±0.05	0.44±0.05	0.75±0.05	0.22±0.05	2.17±0.06
35	0.38±0.06	0.48±0.05	0.87±0.05	0.25±0.05	3.13±0.05
40	0.45±0.06	0.66±0.05	1.03±0.06	0.30±0.06	4.74±0.06
45	0.49±0.06	0.77±0.05	1.15±0.06	0.71±0.05	4.98±0.05
50	0.56±0.06	1.11±0.06	1.07±0.06	0.73±0.05	5.73±0.06
55	0.64±0.06	1.22±0.06	1.15±0.06	1.08±0.08	5.97±0.07
60	0.71±0.06	1.29±0.06	1.24±0.06	1.39±0.05	6.26±0.06



**Part VIII : Carrier reusability****Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	93% by weight
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	3% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
External phase	50 ppm of Cu at pH 5
Membrane phase : External phase	60:360 by volume
Stirring speed	400 rpm

**Table A-26** Experimental data of remaining copper concentration in the feed phase

Time (min.)	Copper concentration (ppm.)		
	1 <sup>st</sup> -use	2 <sup>nd</sup> -use	3 <sup>rd</sup> -use
0	49.44±0.06	50.59±0.06	49.09±0.08
2	0.59±0.05	2.10±0.06	3.31±0.06
4	0.56±0.05	1.92±0.05	2.82±0.06
6	0.42±0.05	1.59±0.05	2.19±0.06
8	0.28±0.04	1.29±0.05	1.71±0.07
10	0.19±0.04	1.20±0.06	1.20±0.07
12	0.16±0.04	1.11±0.04	1.11±0.05
14	0.10±0.04	0.90±0.04	1.08±0.05
16	0.13±0.04	0.93±0.04	1.11±0.05
18	0.13±0.05	0.96±0.04	1.14±0.05
20	0.16±0.04	0.96±0.04	1.23±0.06
25	0.19±0.05	1.44±0.06	1.44±0.06
30	0.22±0.05	1.53±0.05	1.50±0.06
35	0.25±0.05	1.50±0.06	1.50±0.06
40	0.30±0.06	1.86±0.06	1.62±0.06
45	0.71±0.05	2.13±0.06	2.13±0.07
50	0.73±0.05	2.61±0.06	2.61±0.07
55	1.08±0.08	2.82±0.07	3.12±0.06
60	1.39±0.05	2.94±0.07	4.33±0.05

## APPENDIX B

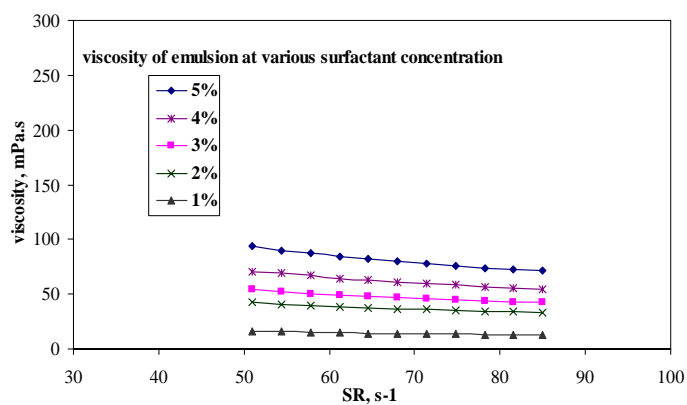
### VISCOSITY DATA

#### Part I : Surfactant Concentration Variable

##### Experimental conditions:

Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	4% by weight
Surfactant (Span80)	various concentration from 1 to 5%
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
Membrane preparation	blend at speed 12000 rpm for 4 minutes

**Figure B-1** Effect of surfactant concentration in membrane phase on the viscosity at various shear rates

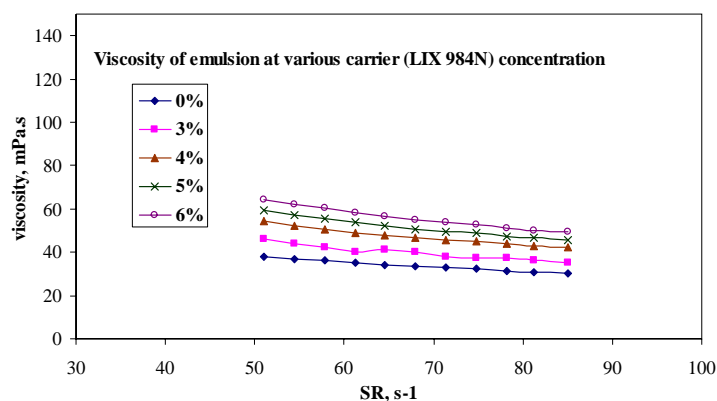


## Part II : Carrier Concentration Variable

### Experimental conditions:

Membrane phase	Organic solvent (Kerosene)	depend on the surfactant concentration
	Carrier (LIX 984N)	various concentration from 0 to 6%
	Surfactant (Span80)	3% by weight
Internal phase		2M sulfuric acid solution
Organic phase : Internal phase		120:120 by volume
Membrane preparation		blend at speed 12000 rpm for 4 minutes

**Figure B-2** Effect of carrier concentration in membrane phase on the viscosity at various shear rates

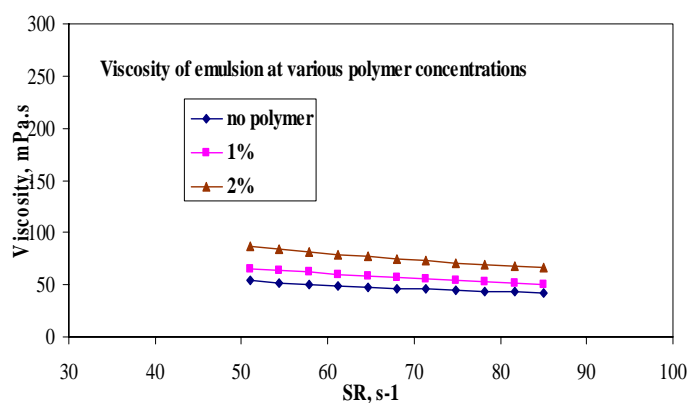


## Part III : Polymer Concentration Variable

### Experimental conditions:

Membrane phase	Organic solvent (Kerosene)	depend on the surfactant concentration
	Carrier (LIX 984N)	4% by weight
	Surfactant (Span80)	3% by weight
	Polymer concentration	various from 1 – 2% by weight
Internal phase		2M sulfuric acid solution
Organic phase : Internal phase		120:120 by volume
Membrane preparation		blend at speed 12000 rpm for 4 minutes

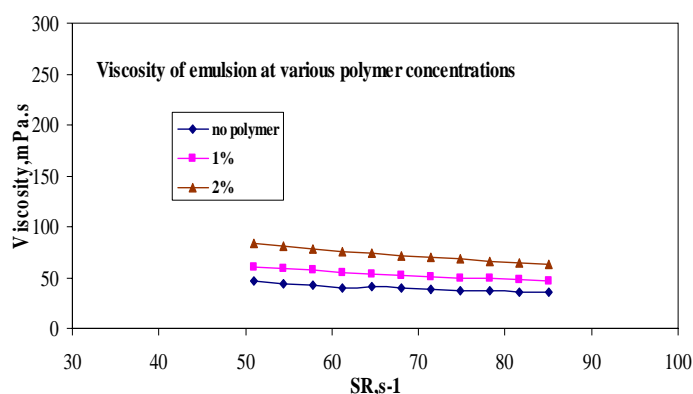
**Figure B-3** Effect of polymer concentration in membrane phase on the viscosity at various shear rates



**Experimental conditions:**

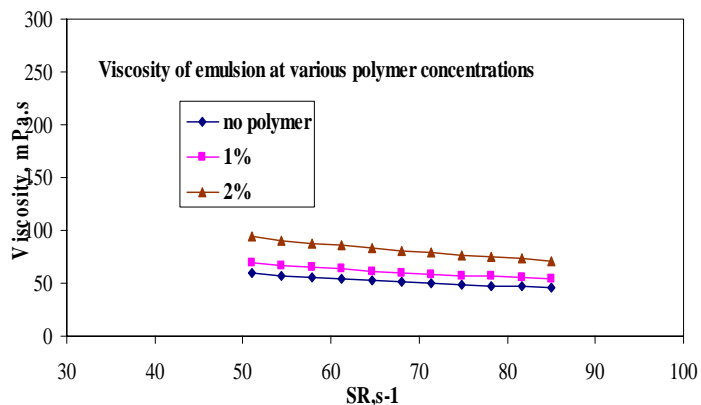
Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	3% by weight
Surfactant (Span80)	3% by weight
Polymer concentration	various from 1 – 2% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
Membrane preparation	blend at speed 12000 rpm for 4 minutes

**Figure B-4** Effect of polymer concentration in membrane phase on the viscosity at various shear rates

**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	5% by weight
Surfactant (Span80)	3% by weight
Polymer concentration	various from 1 – 2% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
Membrane preparation	blend at speed 12000 rpm for 4 minutes

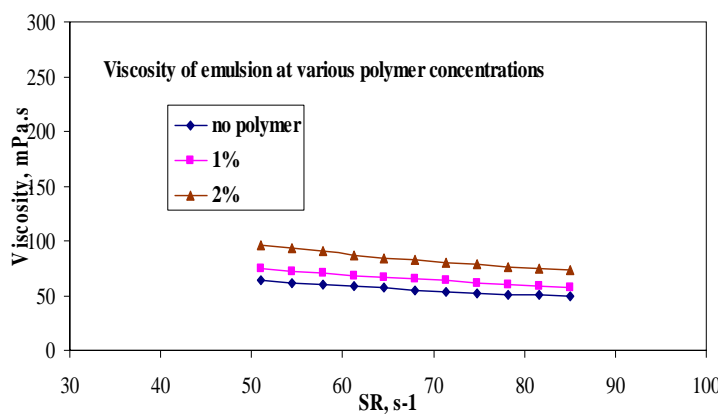
**Figure B-5** Effect of polymer concentration in membrane phase on the viscosity at various shear rates



**Experimental conditions:**

Membrane phase	
Organic solvent (Kerosene)	depend on the surfactant concentration
Carrier (LIX 984N)	6% by weight
Surfactant (Span80)	3% by weight
Polymer concentration	various from 1 – 2% by weight
Internal phase	2M sulfuric acid solution
Organic phase : Internal phase	120:120 by volume
Membrane preparation	blend at speed 12000 rpm for 4 minutes

**Figure B-6** Effect of polymer concentration in membrane phase on the viscosity at various shear rates



## VITA

Miss Sirilak Intarawicha was born on July 14<sup>th</sup>, 1982, in Thailand. She graduated in Bachelor Degree of Science in General Science from faculty of Science, Kasetsart University in 2005. Since 2006 she has been graduated student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2008.

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A part of this thesis is used to present in International Graduates Congress 2007 (3<sup>rd</sup> MPSGC) on 12<sup>th</sup> – 14<sup>th</sup> December 2007 at University of Malaya, MALAYSIA in the title “Stability and Swelling in Emulsion Liquid Membrane for Copper Extraction” and The 10<sup>th</sup> National Graduate Research Conference on 11<sup>st</sup> – 12<sup>nd</sup> September 2008 at Sukhothai Thammathirat Open University, THAILAND in the title “Factors Influencing Copper Ion Extraction from Dilute Aqueous Solution by Emulsion Liquid Membrane”