CHAPTER V

RESULTS AND DISCUSSION

Effect of Carrier Concentration

The objective of this section is to find a suitable concentration of carrier that for copper separation by emulsion liquid membrane. Di(2-ethylhexyl) phosphoric acid (D2EHPA) is used as a carrier. The suitable concentration of carrier is evaluated by conducting experiments with variation of carrier concentrations, from 0% to 20% by volume D2EHPA. The results of this study were shown in Figure 5-1 and 5-2, indicating that the remaining amount of copper in the feed solution (external phase) depends on concentration of the carrier.

Figure 5-1 shows the effect of carrier concentration on the copper transport. As the carrier concentration exceeded 10%(v/v), additional significant increase in carrier concentration did not yield significant increase in the final external copper concentration. It, however, resulted in significant enhancement in initial flux rates. This demonstrated that changing the carrier concentration did not change the final equilibrium condition of the system, but it affected how fast the equilibrium was reached. Since the carrier is the most expensive agent among the components of the membranes, its concentration must be chosen conservatively. Therefore, the 10%(v/v) carrier concentration seemed to be optimal for this system.

Figure 5-2 shows the effect of carrier concentration on copper transport under the same condition, to confirm the result of previous study shown in Figure 5-1, except surfactant concentration. The surfactant concentration was changed from 5% to 7% by volume Span 80. The results in Figure 5-2 were relatively the same trend as those in Figure 5-1.

Therefore, the optimum concentration of carrier maintained 10% by volume D2EHPA.

Figure 5-3 shows the concentration of copper in the internal phase during the extraction of copper at various carrier concentrations. It was found that 15% of D2EHPA offered the highest concentration of copper in the internal phase which was approximately twenty folds of the concentration of copper in the external phase.

Figure 5-4 shows the initial rate at various carrier concentrations. The maximum initial rate occured when 15% of D2EHPA was used but the initial rate at 10% of D2EHPA was not significantly lower than that of the 15% of D2EHPA. The initial rates were 19.767 and 19.258 ppm./min., respectively.

Figure 5-5 shows the effect of the carrier concentration on swelling in the emulsion liquid membrane. At the end of the extraction time, the swelling percentages of emulsion were varied from 20% to 40%. These results can be explained that the carrier, D2EHPA, is a cation exchanger which is insoluble in the aqueous phase. It has both a hydrophobic and hydrophilic group. That is, the structure of D2EHPA seems to be similar to a surfactant. Since D2EHPA in its hydrated form has the possibility of transporting water. Therefore, the increase of the carrier concentration made the molecules of water transport into the internal phase increase so the volume of internal phase was increased. But the effect of the carrier concentration on swelling was not significant because there were small differences of the percentages of swelling at various D2EHPA concentrations.

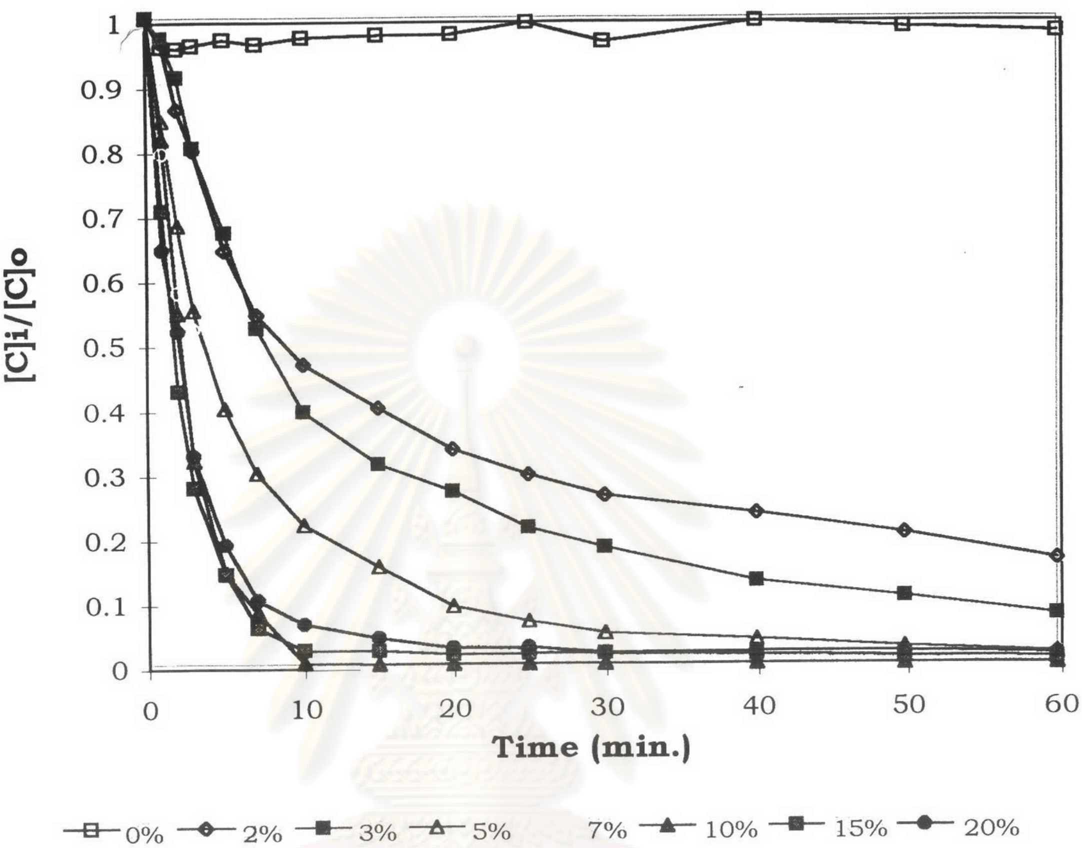

Figure 5-1 Effect of carrier concentration on extraction of 100 ppm. copper ions by emulsion liquid membrane at 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	depends on carrier concentration
	carrier (D2EHPA)	various concentration
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

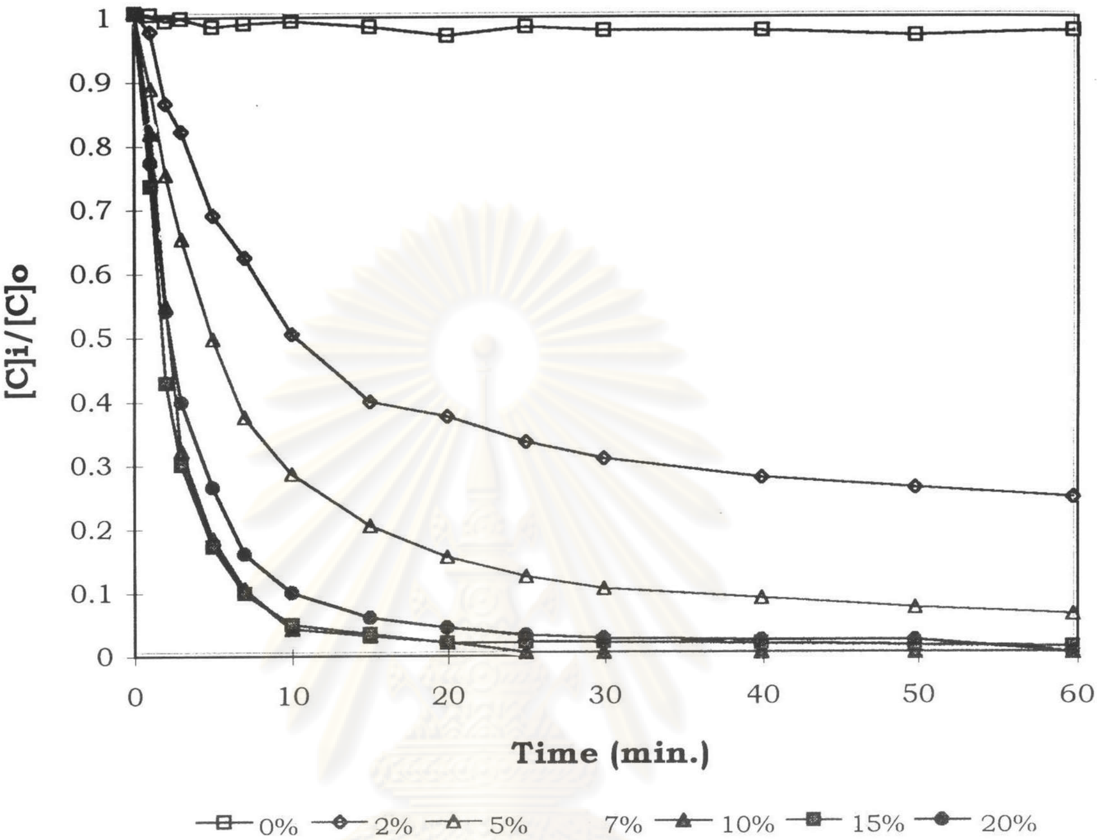

Figure 5-2 Effect of carrier concentration on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	depends on carrier concentration
	carrier (D2EHPA)	various concentration
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

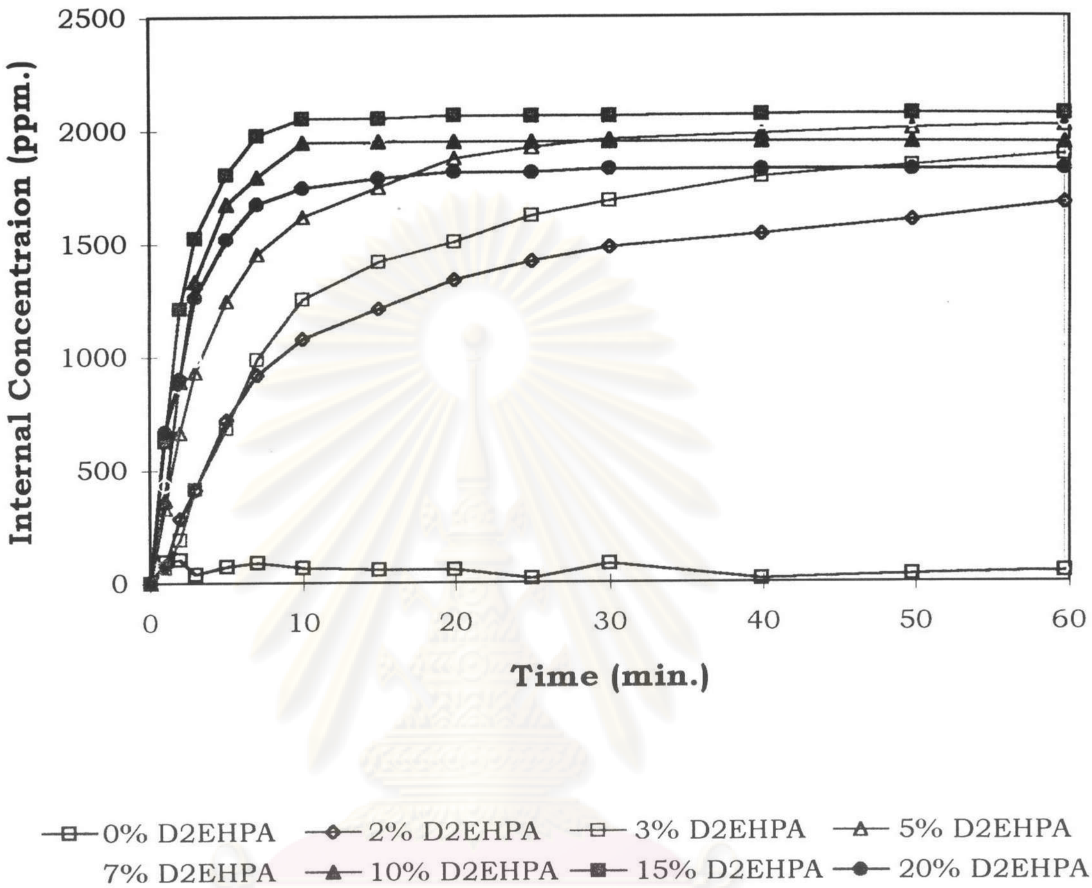

Figure 5-3 Concentration of copper in the internal phase during extraction of copper at various carier concentration

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	
		depends on carrier concentration
	carrier (D2EHPA)	various concentration
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

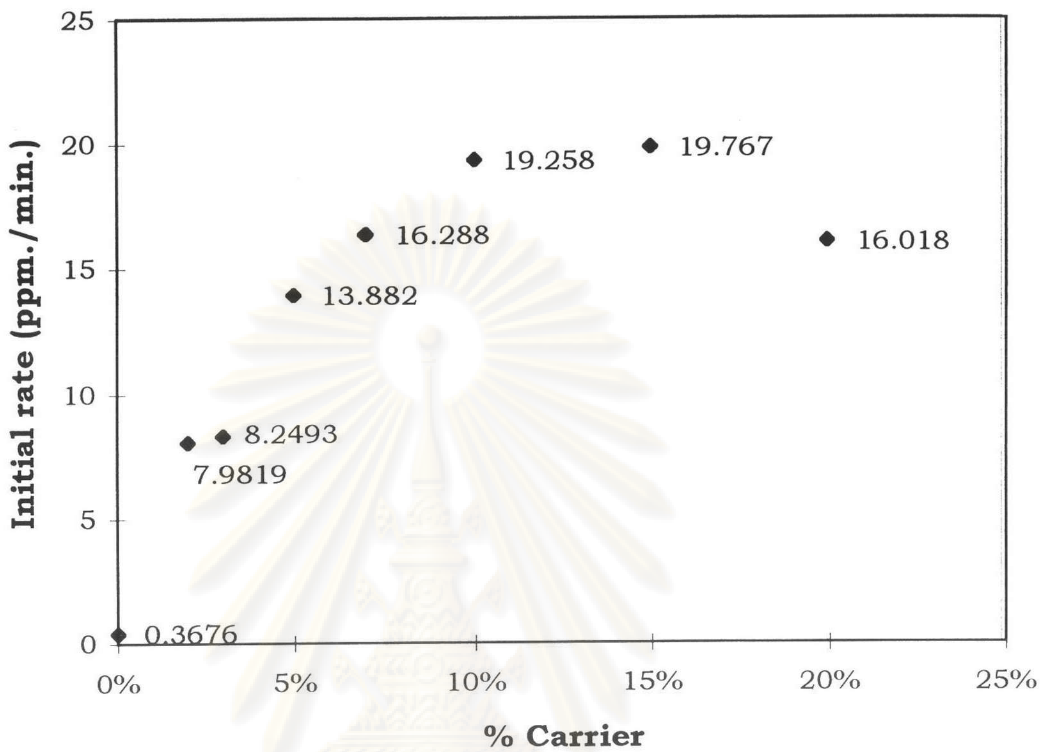

Figure 5-4 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various carrier concentration (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	depends on carrier concentration
	carrier (D2EHPA)	various concentration
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

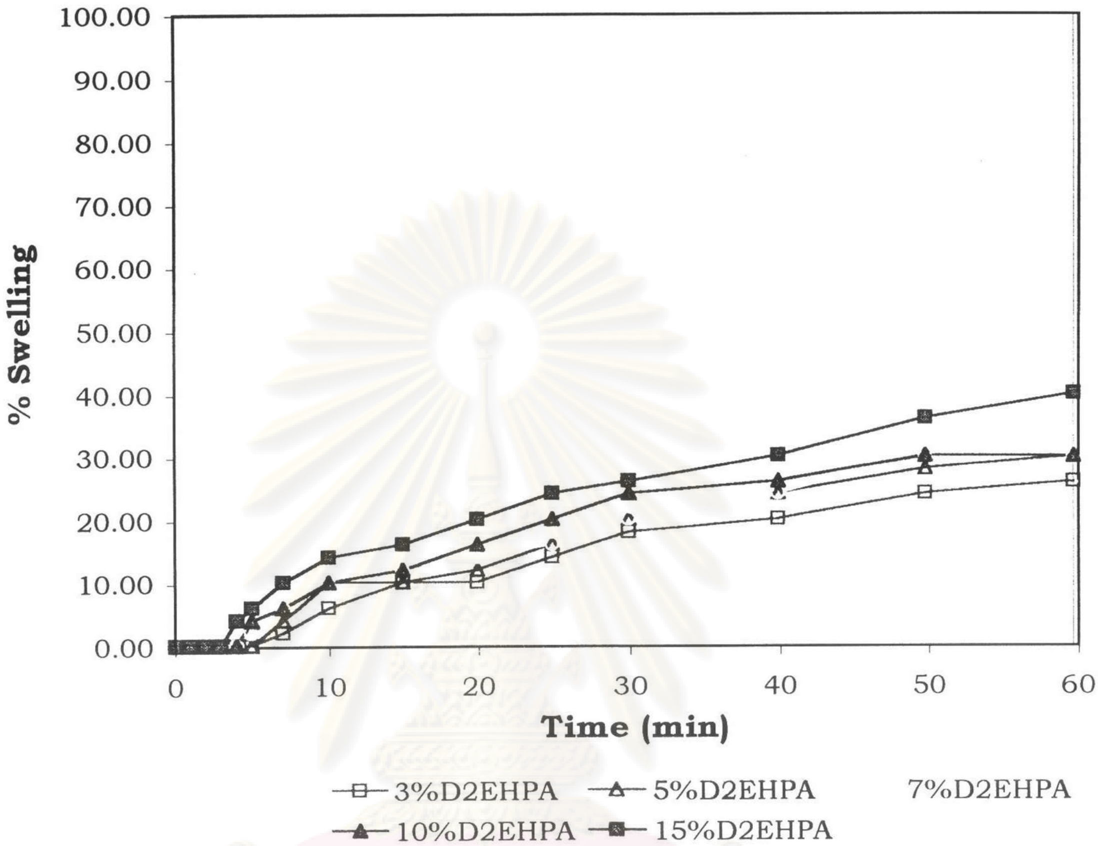

Figure 5-5 Effect of carrier concentration on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	
	depends on carrier concentration	
	carrier (D2EHPA)	various concentration
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

Effect of Surfactant Concentration

The objective of this section is to find a satisfactory concentration of surfactant for copper separation by emulsion liquid membrane. These experiments were conducted at room temperature and atmospheric pressure. Span 80 was used as a surfactant. The satisfactory concentration of surfactant was evaluated by conducting experiments with variation of surfactant concentration from 0% to 15% by volume Span 80. The results of this study are shown in Figure 5-6 and 5-7, indicating the effect of surfactant quantity on the remaining copper in the feed solution.

Figure 5-6 shows the effect of surfactant concentration on the copper transport. As the surfactant concentration was increased from 0% to 5% by volume of Span 80, the copper transport rate increased. Inversely, the copper transport rate decreased when the surfactant concentration was further increased from 5% to 15% by volume Span 80. This phenomenon can be explained that the increase of surfactant confered higher viscosity of oil phase which enhanced mass transfer resistance. For this reason, when the Span 80 was increased from 5% to 15% by volume, the copper transport rate decreased. On the other hand, when the Span 80 concentration was very low, the emulsion became unstable. Consequently, though the amount of copper transported through the membrane actually increased, the amount of copper leakage due to breakage of emulsion also increased. The resulting total amount of copper that transported, did not increase. In this particular system, a Span 80 concentration of 5% by volume seemed optimal.

Figure 5-7 shows the effect of surfactant concentration on copper transport to confirm the result of previous study shown in Figure 5-6 under the same condition, except carrier concentration. The carrier concentration was changed from 10% to 7% by volume D2EHPA. The results were relatively the same trend as those in Figure 5-6. Therefore, the optimum concentration of surfactant maintained 5% by volume Span 80.

Figure 5-8 shows the concentration of copper in the internal phase during the extraction of copper at various surfactant concentrations. It was found that at the 5% of Span 80, the extracted copper concentration can be maximized up to twenty folds of the concentration of copper in the external phase.

Figure 5-9 shows the initial rate at various surfactant concentrations. The highest initial rate was 19.258 ppm./min. when 5% by volume of Span 80 was used.

Figure 5-10 shows the effect of the surfactant concentration on swelling in the emulsion liquid membrane. At the end of the extraction time, the emulsion was 15% to 35% swelled. This phenomenon was illustrated in Chapter III. The mechanism suggested that swelling is mediated by hydrated surfactant. The surfactant solubilizes water of the external phase into the oil (membrane) phase. The hydrated surfactant then diffuses to the internal phase. Finally, the water is released in the internal phase. And the other proposed mechanism stated that water is transported by reversed micelles. The water is encapsulated by surfactant aggregates (reversed micelles) in the oil phase. The reversed micelles transport water from the external phase to the internal phase. Consequently, when the surfactant concentration increased the percentage of swelling increased.

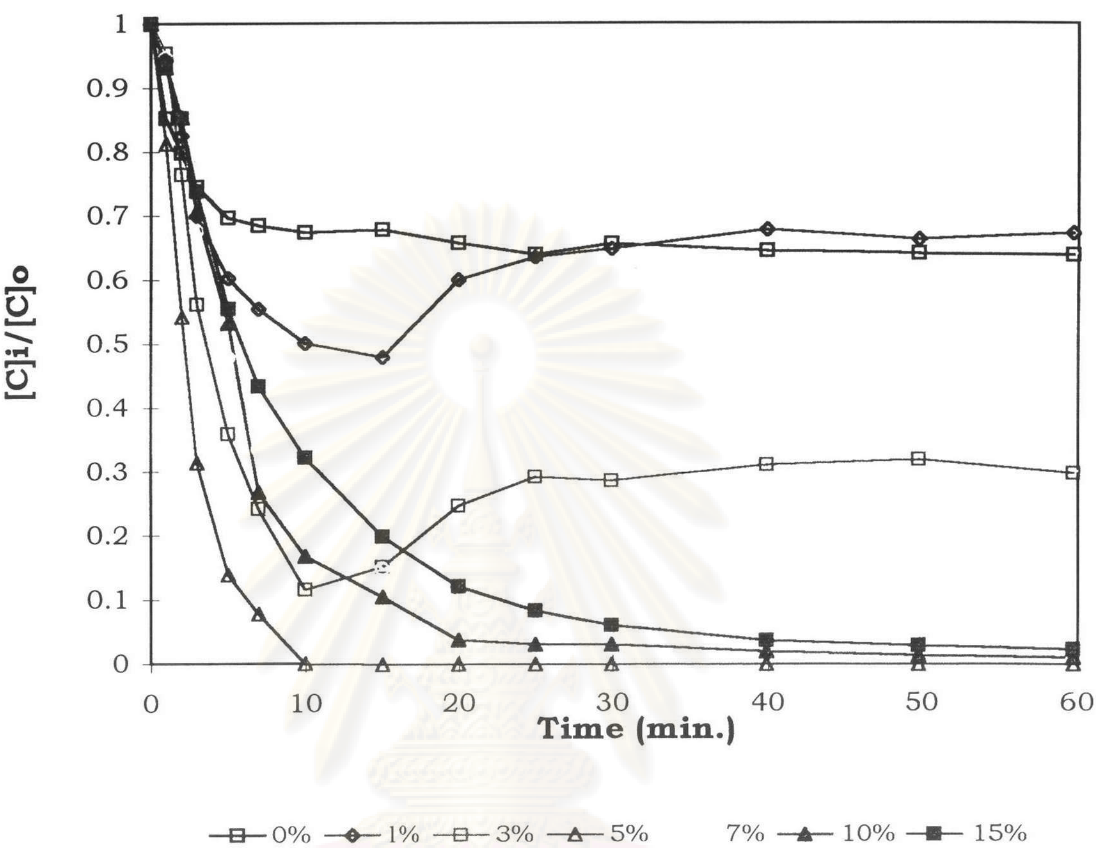

Figure 5-6 Effect of surfactant concentration on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	
		depends on surfactant concentration
	carrier (D2EHPA)	10%
	surfactant (Span 80)	various concentration
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

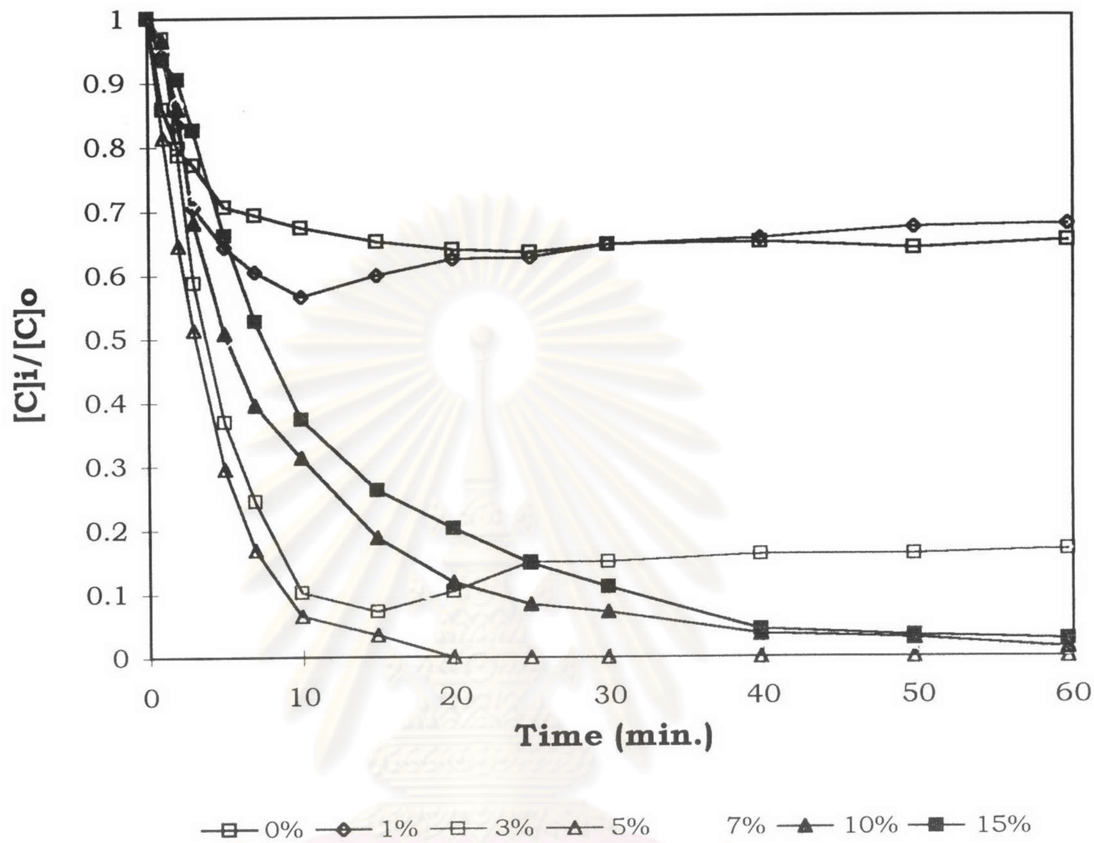

Figure 5-7 Effect of surfactant concentration on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	
		depends on surfactant concentration
	carrier (D2EHPA)	7%
	surfactant (Span 80)	various concentration
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

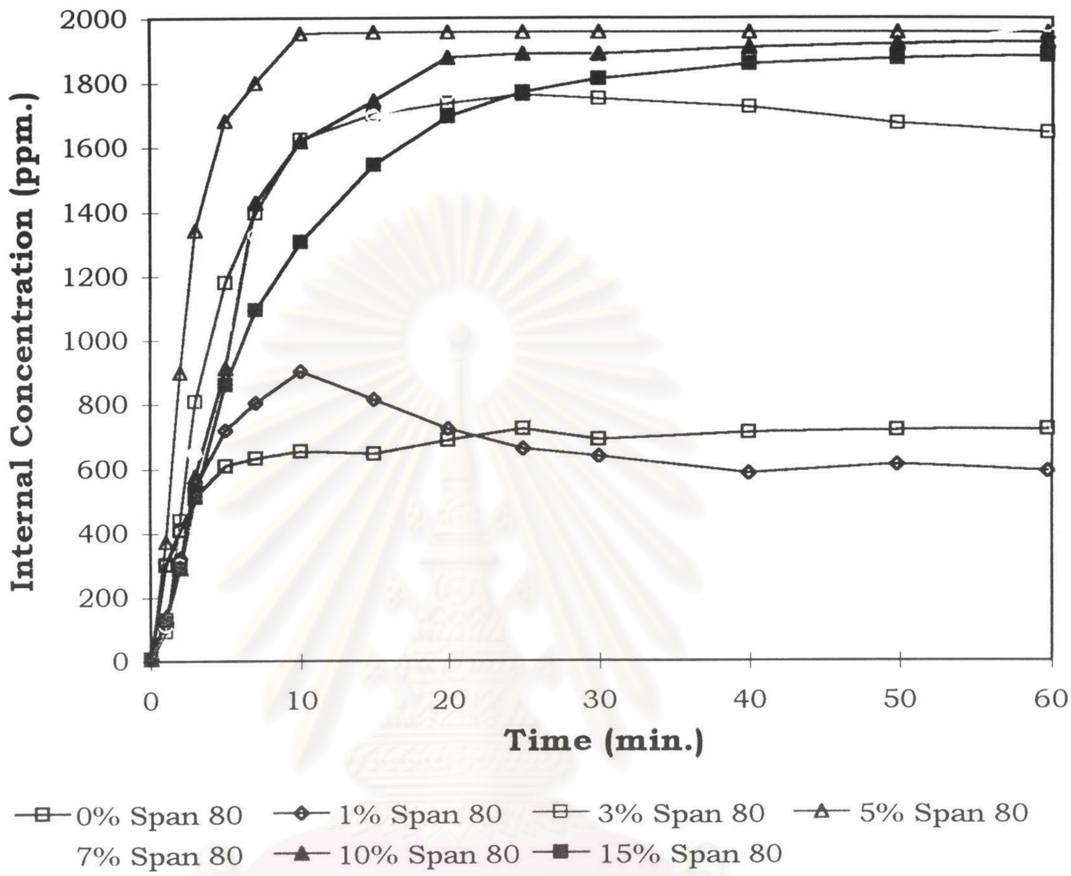

Figure 5-8 Concentration of copper in the internal phase during extraction of copper at various surfactant concentration.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	
	depends on surfactant concentration	
	carrier (D2EHPA)	10%
	surfactant (Span 80)	various concentration
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

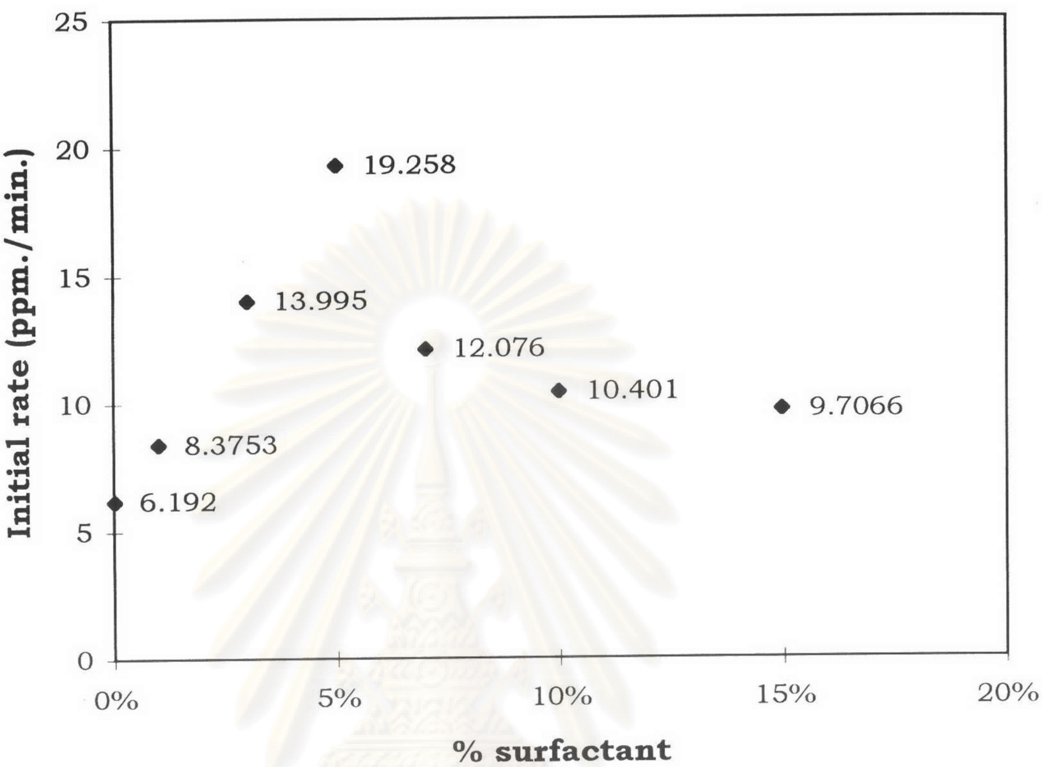

Figure 5-9 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various surfactant concentration (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	depends on surfactant concentration
	carrier (D2EHPA)	10%
	surfactant (Span 80)	various concentration
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

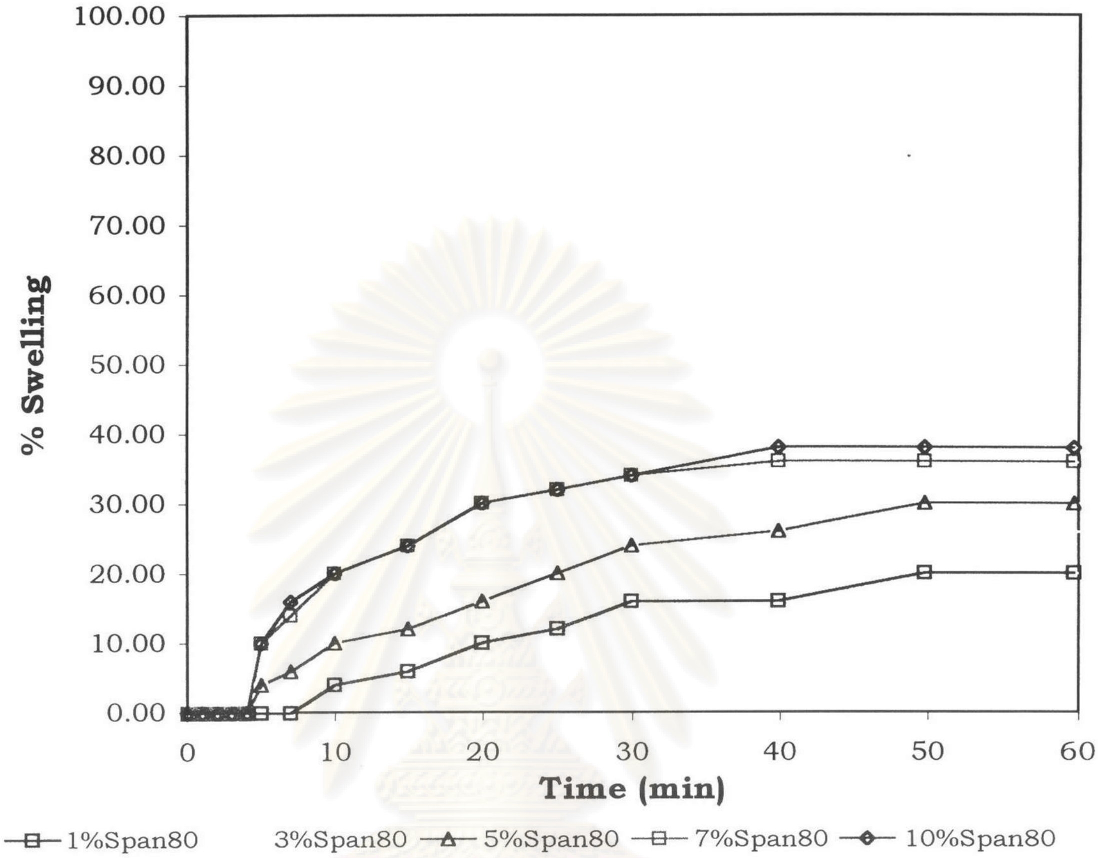

Figure 5-10 Effect of surfactant concentration on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)
Membrane phase	organic solvent (Kerosene) depends on surfactant concentration
	carrier (D2EHPA) 10%
	surfactant (Span 80) various concentration
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.
Internal phase	1N HCl acid solution
Membrane phase : Internal phase	50:50
Emulsion phase : Feed solution	50:450
Agitation speed	350 rpm.

Effect of Initial Feed Solution Acidity

The objective of this section is to find an appropriate initial feed solution acidity for copper separation by emulsion liquid membrane. Initial feed solution acidities were adjusted by hydrochloric acid. The appropriate initial feed solution acidity was evaluated by conducting experiments with variation of pH from 2 to 6. The results are shown in Figure 5-11 to 5-14. They indicate that efficiency of copper separation by emulsion liquid membrane process depended on initial feed solution acidity.

Figure 5-11 shows the effect of initial feed solution acidity on the copper transport. As the initial feed solution pH was decreased from 6 to 3, the copper transport rate increased. Inversely, the copper transport rate decreased, when pH reduced from 3 to 2. It can be illustrated that the decrease of the initial feed solution pH enhanced the solubility of copper salt in the distilled water. The less copper salt dissolved in the distilled water, the less ions it ionized. In order to facilitate the transport system, carrier was used to contribute mass transfer across the membrane. By this method, the solute must be ion form. Since the solute is transported across the membrane by reacting with carrier and forming a complex as described in chapter III. Therefore, the unionized copper can not react with the carrier. For these reasons, when the solubility of copper salt increased, the amount of ionized copper increased, thus, the mass transfer rate. On the other hand, when the initial feed solution pH was decreased from 3 to 2, the copper transport rate decreased due to the excess of hydrogen ion in the external solution at the pH 2 condition. This resulted in the small difference of hydrogen ion concentration between the internal phase and the external phase. The driving forces of the facilitated transport system of emulsion liquid membrane process is the difference of the amount of hydrogen ions between two phases. Consequently, though the solubility increased, the driving force decreased, thus, the mass transfer rate. In this particular system, initial feed solution acidity at pH 3 seemed optimal.

Figure 5-12 to 5-14 show the effect of initial feed solution acidity on copper transport to confirm the results of previous study in Figure 5-13, under the same condition, except carrier concentration and surfactant concentration. These experiments were divided into three conditions. In the first condition, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was kept constant at 5% by volume Span 80. In the second condition, surfactant concentration was changed from 5% to 7% by volume Span 80 and carrier concentration was kept constant at 10% by volume D2EHPA. And in the last condition, both of carrier concentration and surfactant concentration were changed, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was changed from 5% to 7% by volume Span 80. The results shown in Figure 5-12 to 5-14 were relatively the same trend as those in Figure 5-11 Therefore, the optimum initial feed solution acidity was at pH 3.

Figure 5-15 shows the concentration of copper in the internal phase during extraction of copper at various initial pH of external phase. It was found that at a pH of 3.0, the extracted copper concentration can be maximized up to twenty folds of the concentration of copper in the external phase.

Figure 5-16 shows the initial rate of various initial pH in external phase. This initial rate can be calculated by using the extraction of copper at time interval that copper in external phase suddenly decreases. It was found that, the highest initial rate of 15.988 ppm./min. occures when pH was 3.0.

It can be concluded that at the initial pH in external phase, 3.0 was the most appropriate for extraction of copper in this process.

The effect of initial pH of feed solution on swelling is shown in Figure 5-17. The swelling started about 4 to 5 minutes after the extraction. As pH was increased from 2 to 6, the swelling decreased. At the pH 2.0, the swelling was highest 70% in 60 minutes. Obviously, as the swelling was increased, the pH of feed solution was decreased.

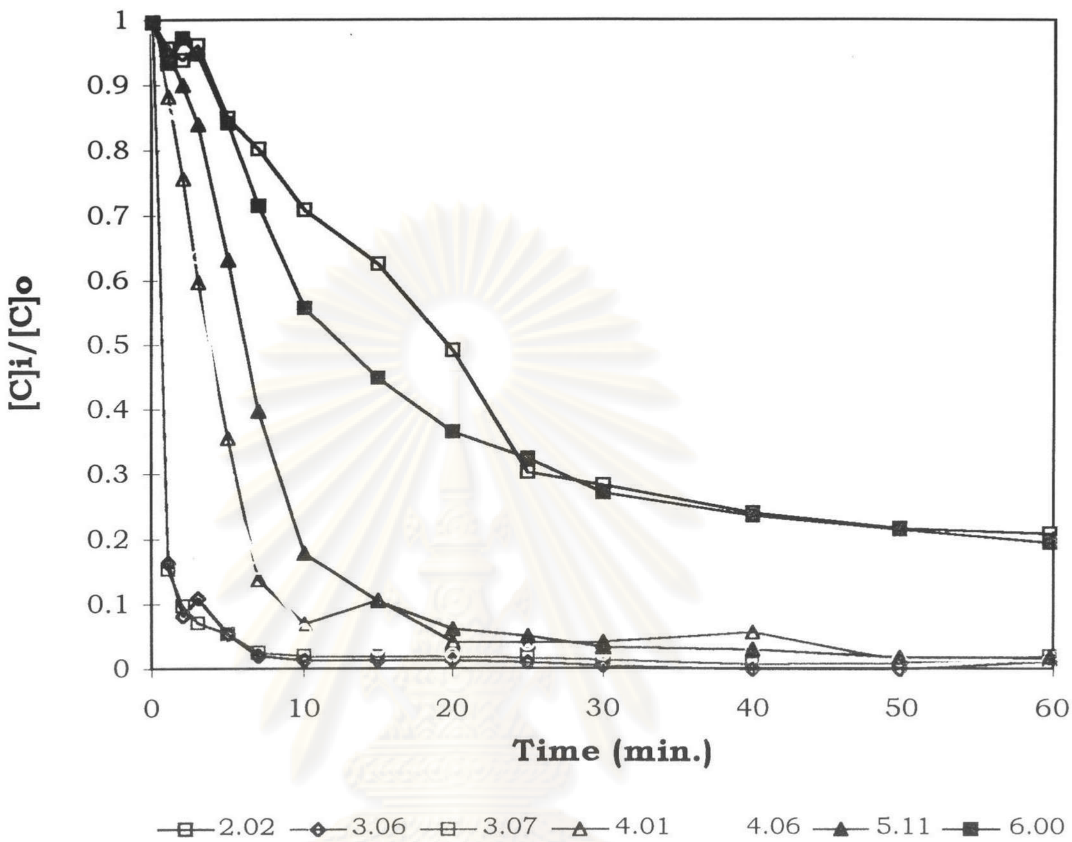

Figure 5-11 Effect of pH of feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

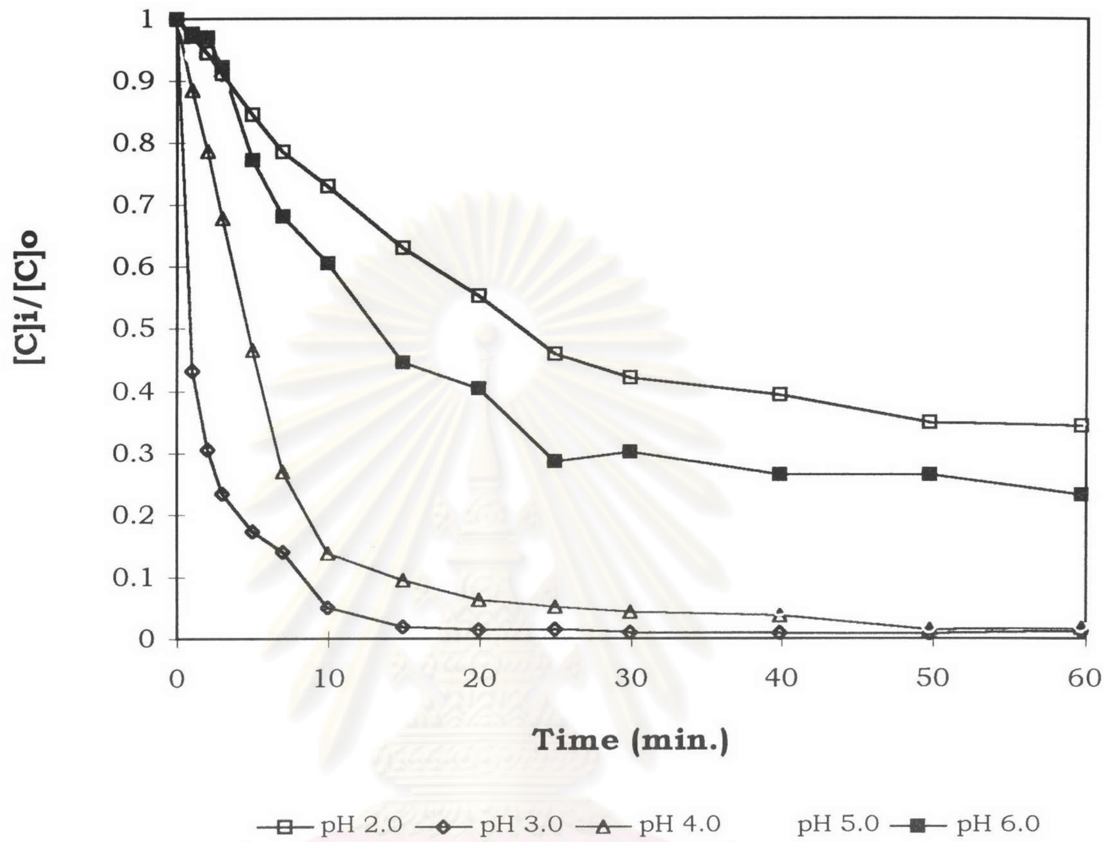

Figure 5-12 Effect of pH of feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	88%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

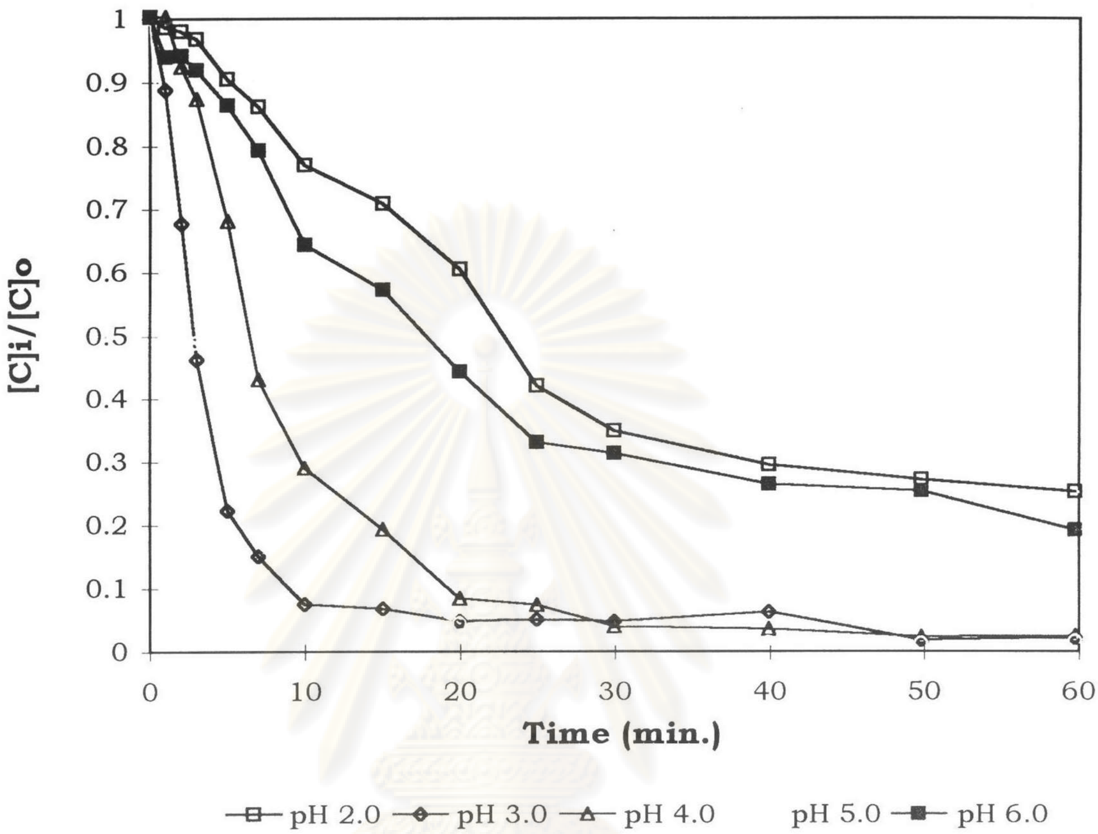

Figure 5-13 Effect of pH of feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	86%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

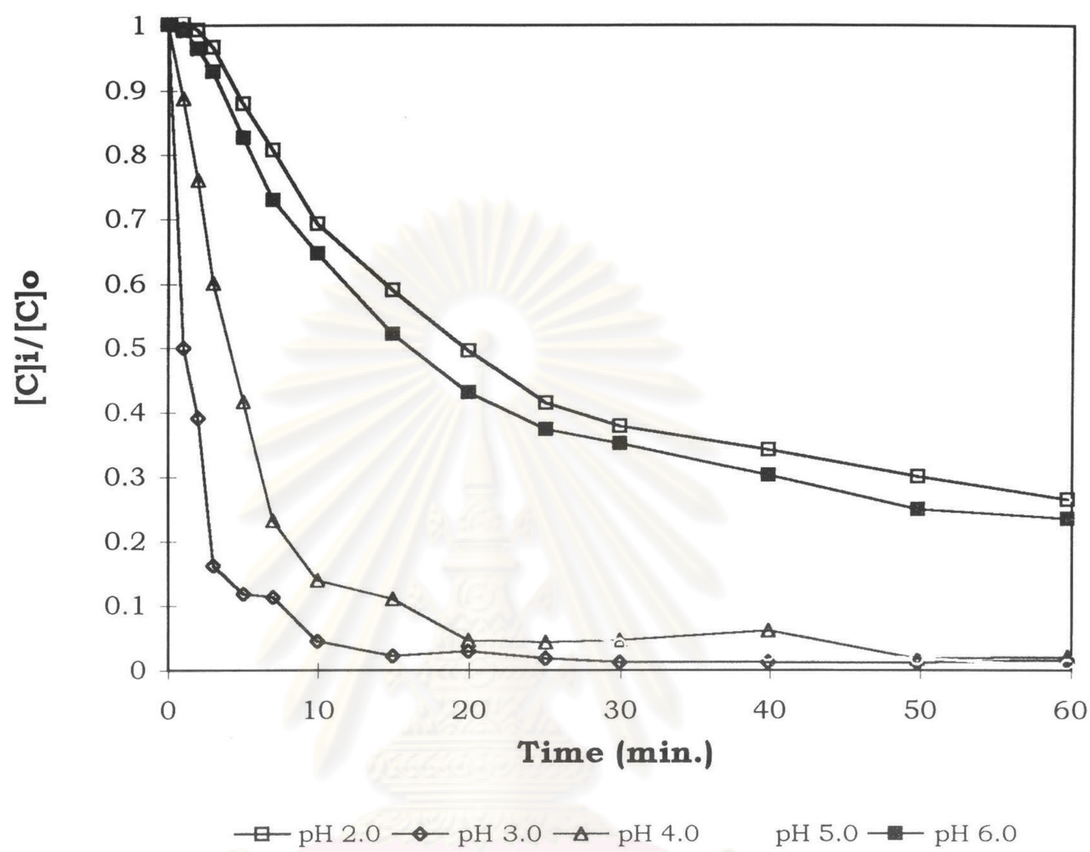

Figure 5-14 Effect of pH of feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	83%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

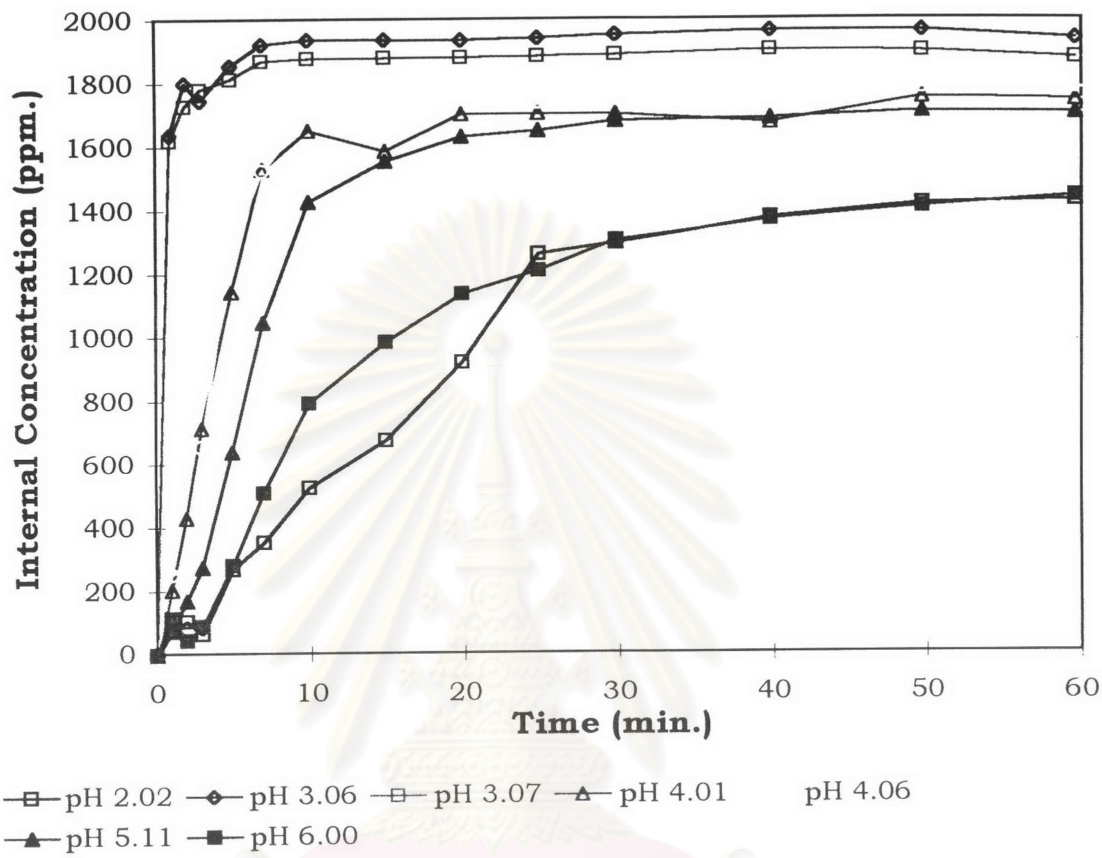

Figure 5-15 Concentration of copper in the internal phase during extraction of copper at various pH of feed solution.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

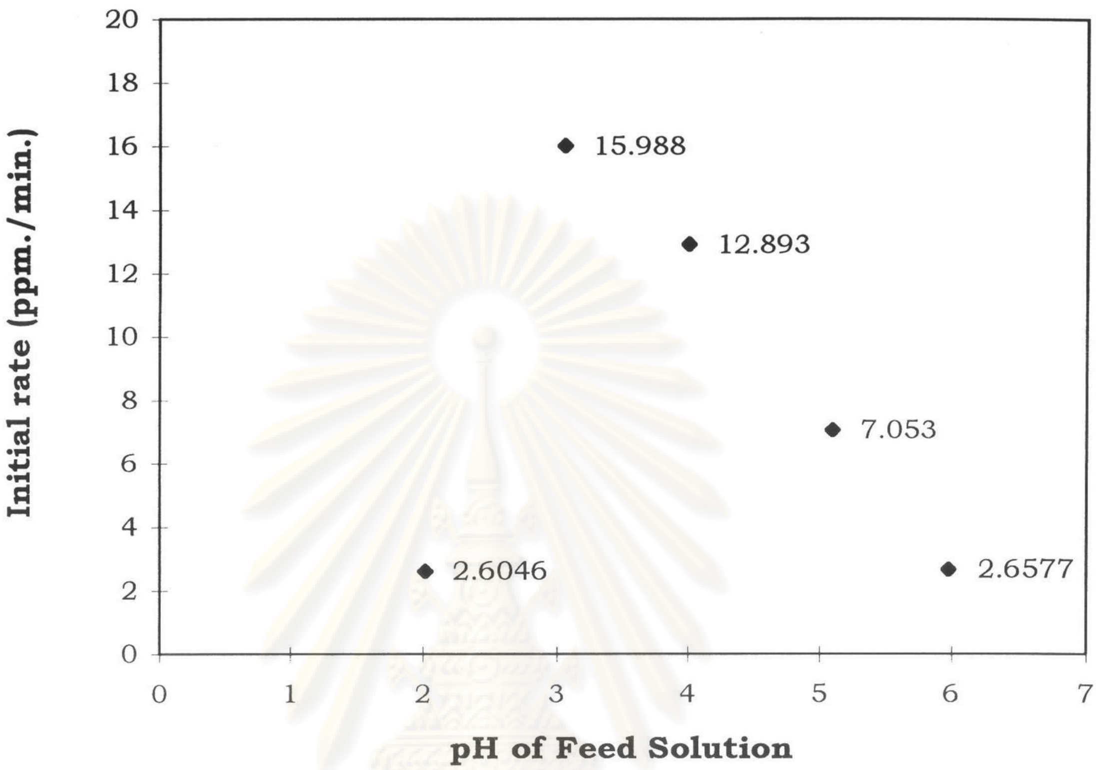

Figure 5-16 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various pH of feed solution (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

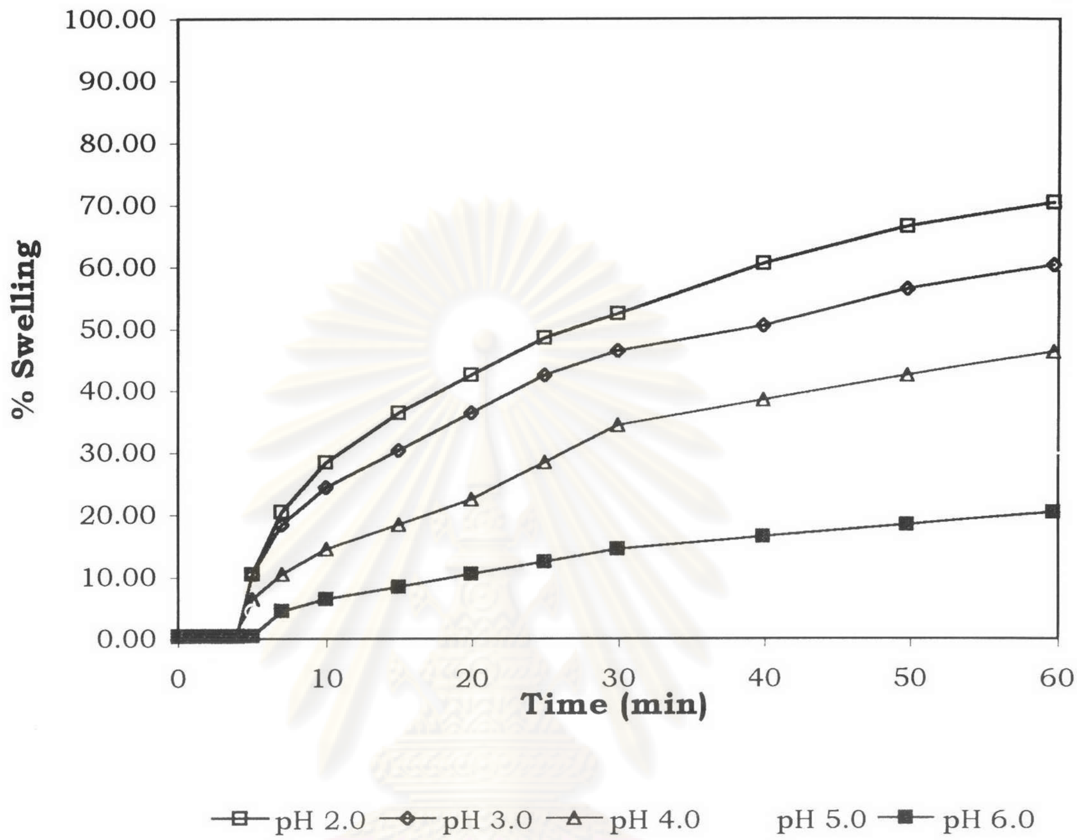

Figure 5-17 Effect of pH of feed solution on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. various pH condition (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

Effect of the Initial Acid Concentration in the Internal Phase

The objective of this section is to find a optimum initial acid concentration in the internal phase for copper separation by emulsion liquid membrane. Hydrochloric acid solution was used as the internal phase. The optimum initial acid concentration was evaluated by conducting experiments with variation of initial acid concentrations from 0.01 N to 3.0 N hydrochloric acid. The results are shown in Figure 5-18 to 5-21. They indicated that the remaining copper in the feed solution (external phase) was dependent of initial acid concentration.

As mentioned above, the difference in hydrogen concentration between the external and internal phases is the driving force in this emulsion liquid membrane process. The copper transported at various hydrochloric acid concentrations in the internal phase is shown in Figure 5-18. As hydrochloric acid concentration was increased, the copper transport rate increased. In the first period (at first 5 minutes) there were, however, almost no differences between the results of 0.1 N and 2.0 N hydrochloric acid concentrations. As hydrochloric acid concentration was increased to 3.0 N, the agitation rarely occured because the membrane was subjected to high swelling resulting in a high viscosity membrane and high mass transfer resistance. As hydrochloric acid concentration was increased, the osmotic pressure difference between the internal phase and the external phase increased providing a significant driving force for water transport across the membrane. The water transported to the internal phase via a hydrated surfactant.

Figure 5-19 to 5-21 show the effect of initial acid concentration in the internal phase on copper transport to confirm the result of previous study in Figure 5-18, under the same condition, except carrier concentration and surfactant concentration. These experiments also were divided into three conditions. In the first condition, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was kept constant at 5% by volume Span 80. In the second condition, surfactant concentration was changed from 5% to 7% by volume Span 80 and carrier concentration was kept constant at 10% by volume D2EHPA. And in the last condition, both of carrier concentration and surfactant concentration were changed, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was changed from 5% to 7% by volume Span 80. The results illustrated in Figure 5-18 to 5-21 are relatively the same trend as those in Figure 5-20. Therefore, the optimum initial acid concentration in the internal phase was 1.0 N hydrochloric acid.

Figure 5-22 shows the concentration of copper in the internal phase during the extraction of copper at various internal hydrochloric acid concentrations. There was almost no difference of the concentration of copper in the internal phase over 0.5 N hydrochloric acid which was approximately twenty folds of concentration of copper in the external phase.

Figure 5-23 shows the initial rate at various internal hydrochloric acid concentrations. The maximum initial rate of 19.258 ppm./min. occured when 1.0 N hydrochloric acid was used.

Figure 5-24 shows the effect of the internal hydrochloric acid concentration on swelling in the emulsion liquid membrane. At the end of the extraction time, the swelling of emulsion at 0.5 N and 1.0 N hydrochloric acid was 20% and 30%, respectively, it was not significantly different but the swelling at 2.0 N was 80% which is significantly different while compared with the lower concentrations. This effect occured because the internal pH was decreased while the internal hydrochloric acid concentration increased. The decrease of pH in the internal phase enhanced the system driving force. While the copper ions was transferred from the external phase to the internal phase the molecules of water can also be transferred.

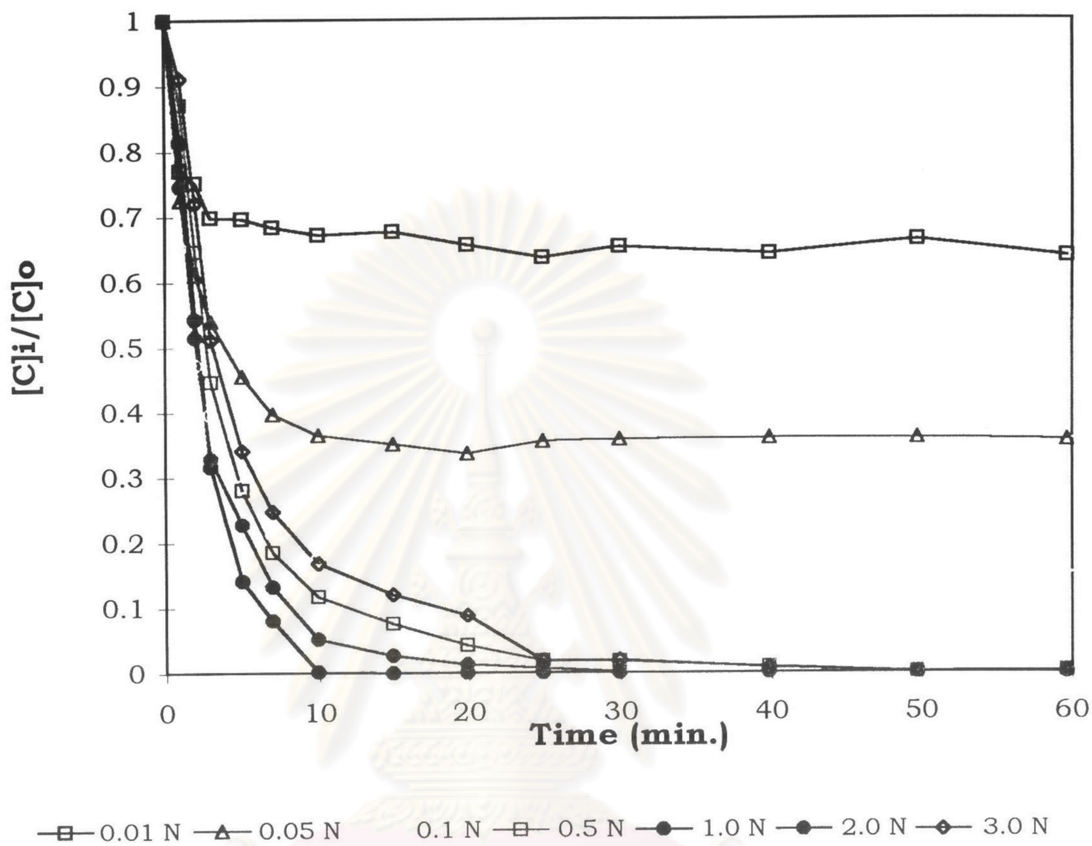

Figure 5-18 Effect of internal phase concentration on extraction of 100 ppm.copper ions by emulsion liquid membrane at 10% D2EHPA and 5% Span 80

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

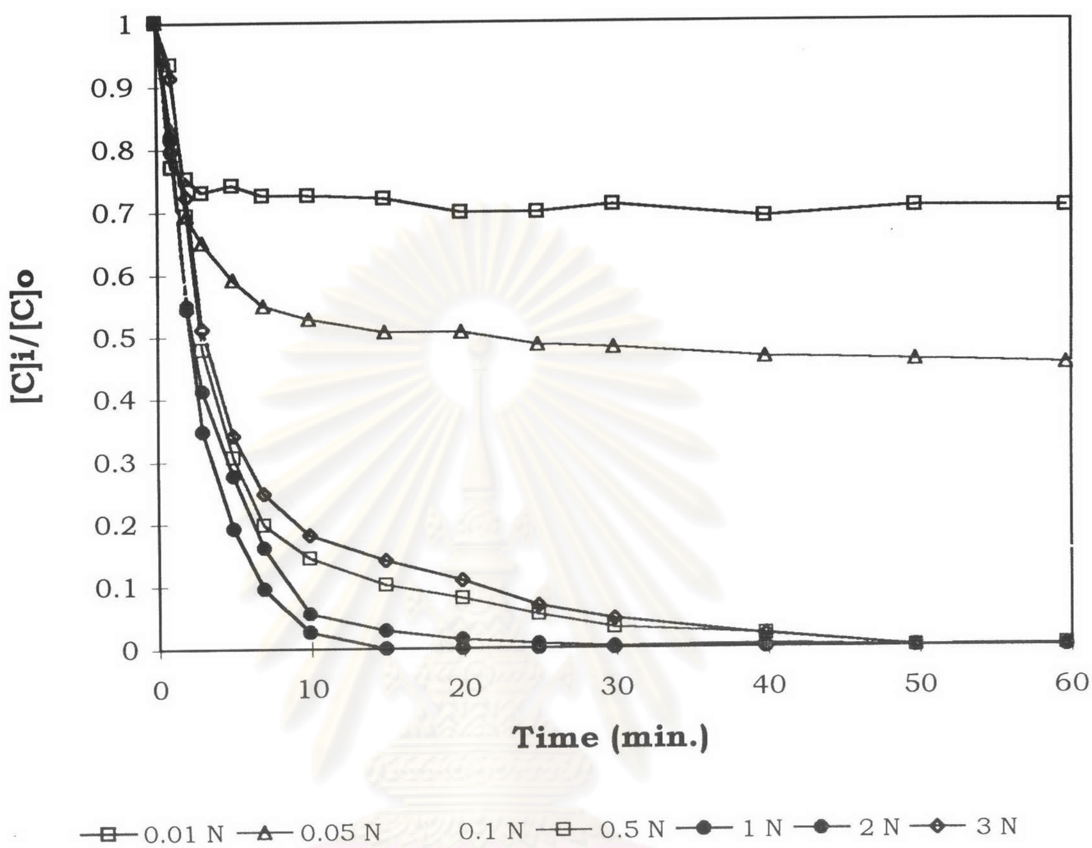

Figure 5-19 Effect of internal phase concentration on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	88%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various acid concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

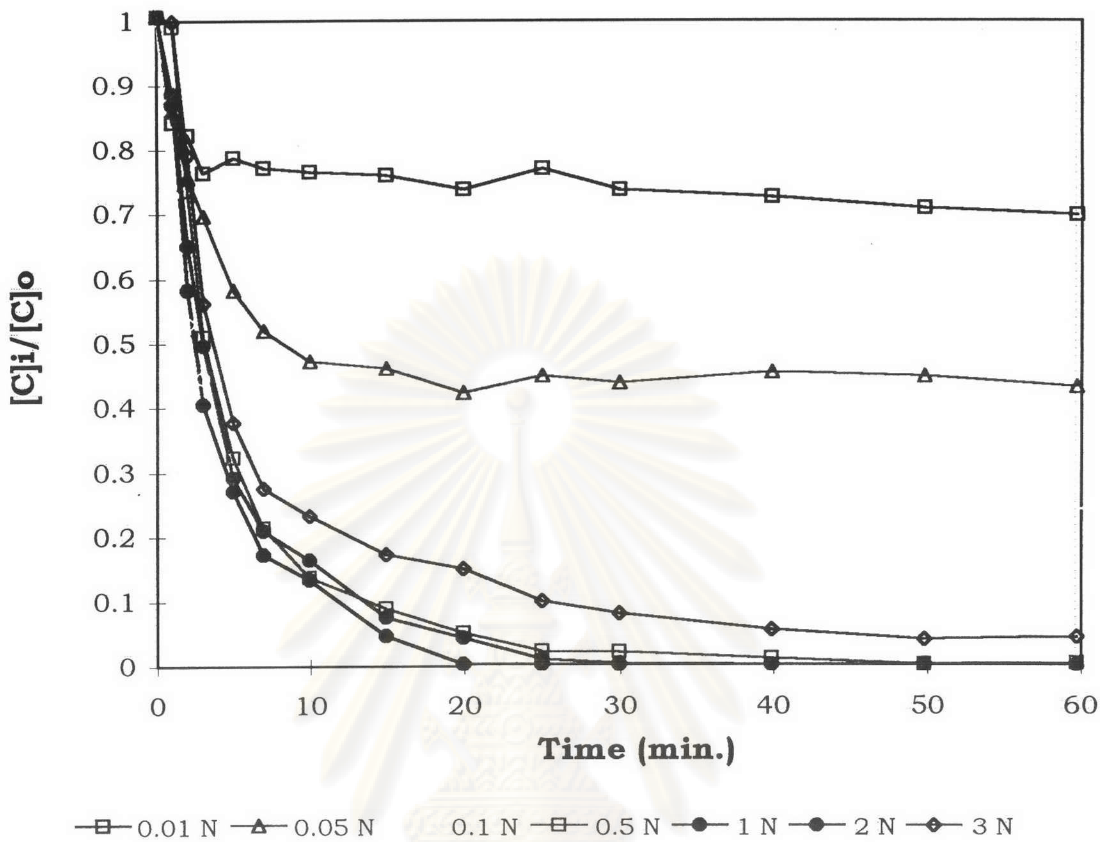

Figure 5-20 Effect of internal phase concentration on extraction of 100 ppm.copper ions by emulsion liquid membrane at 7% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	86%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various acid concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

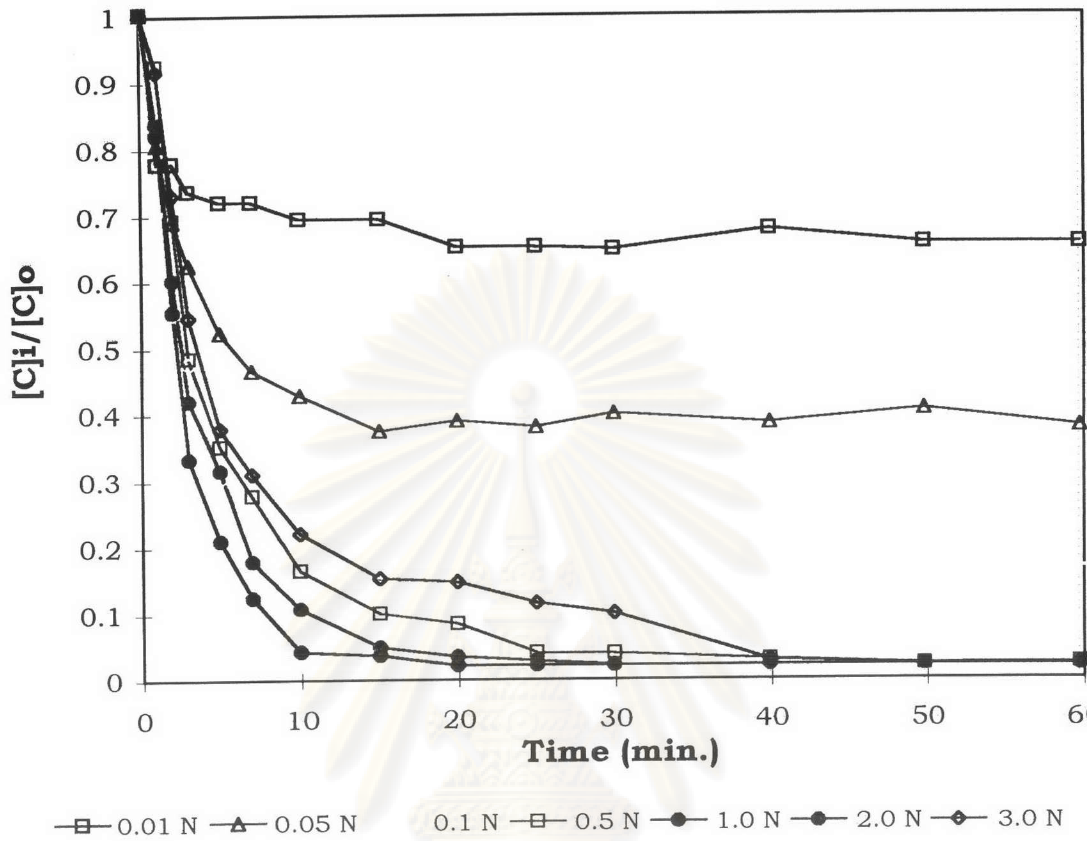

Figure 5-21 Effect of internal phase concentration on extraction of 100 ppm.copper ions by emulsion liquid membrane at 10% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	83%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various acid concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

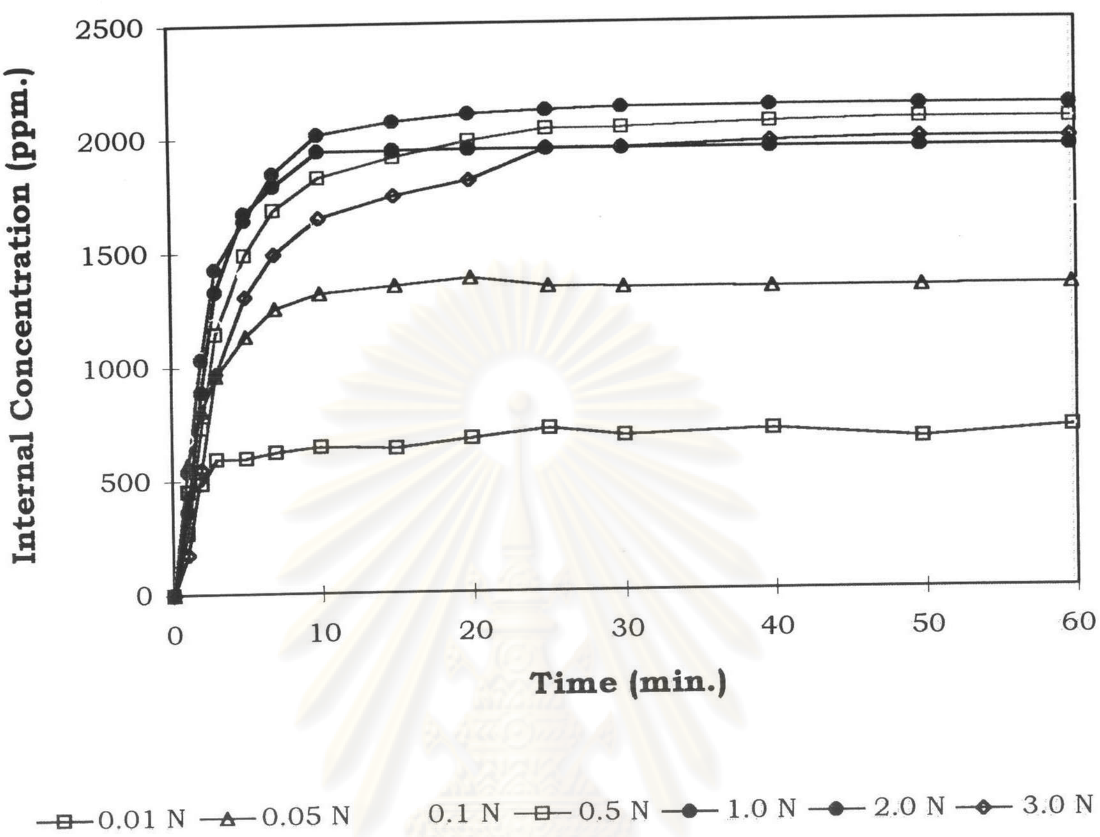

Figure 5-22 Concentration of copper in the internal phase during extraction of copper at various internal phase concentration

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

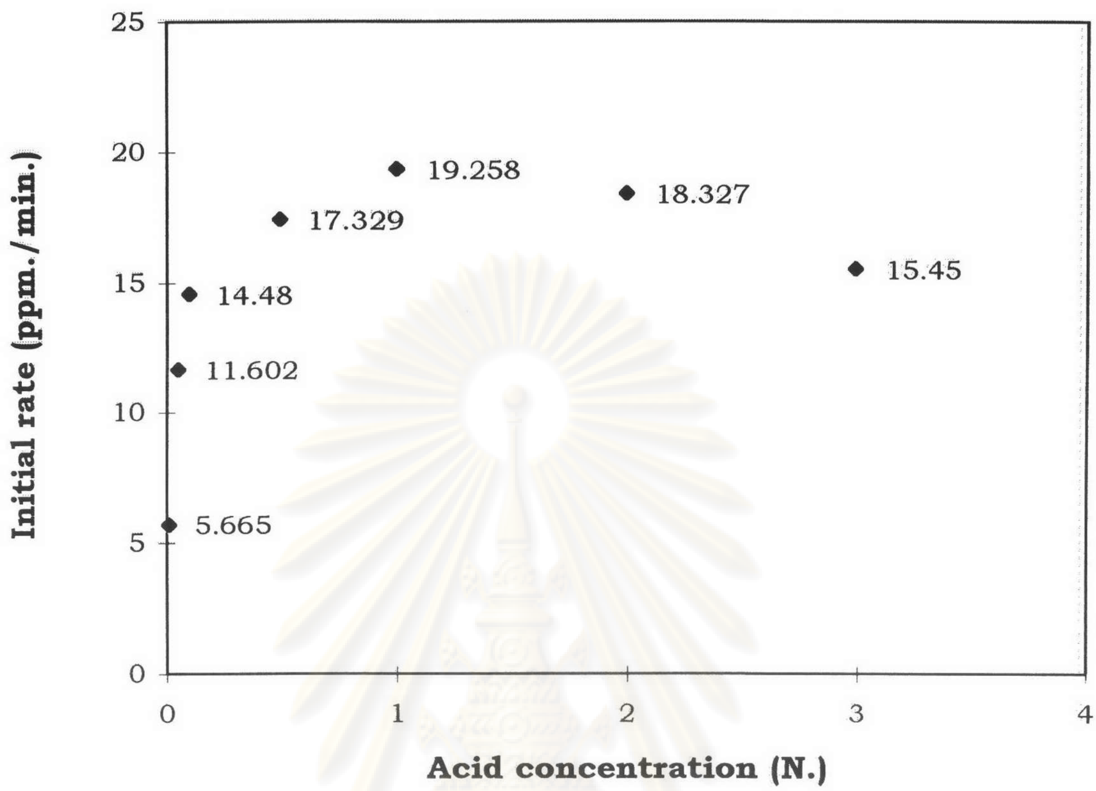

Figure 5-23 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various internal phase concentration (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

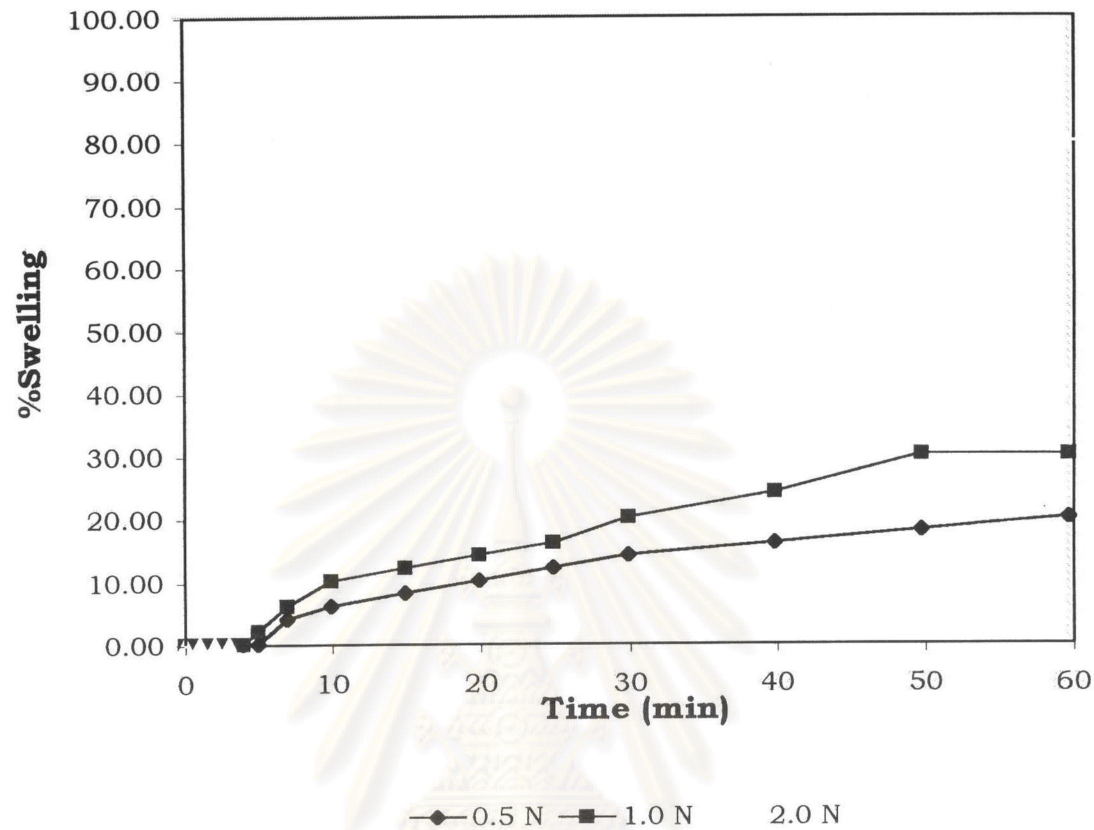

Figure 5-24 Effect of internal phase concentration on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	HCl acid solution	various concentration
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	350 rpm.	

Effect of Emulsion Phase to External Phase Ratio

The objective of this section is to find an appropriate ratio of emulsion phase to external phase (feed solution) for copper separation by emulsion liquid membrane. The appropriate ratio of emulsion phase to external phase (feed solution) was evaluated by conducting experiments with variation of ratios, from 1:1 to 1:19. The results are shown in Figure 5-25 to 5-28. They indicated that the ratio of emulsion phase to external phase (feed solution) affected the efficiency of copper separation by emulsion liquid membrane process.

The effect of the emulsion phase to external phase ratio on the copper transport rate is shown in Figure 5-25. When the emulsion phase to external phase ratio was decreased from 1:1 to 1:9, there were almost no differences in the copper transport rate. But at the higher ratios, the swelling phenomenon occur more easily more than at the lower ones. At the ratio of 1:1, the swelling phenomenon occurred almost 100%. When the ratio decreased, the swelling also decreased. When it was further decreased from 1:9 to 1:19, the copper transport rate significantly decreased. In this range swelling occurred less than 20%, but the breakage phenomenon highly occurred instead. And the systems with higher emulsion phase to external phase ratios were more viscous and require more agitation to produce small dispersed phase globules.

Figure 5-26 to 5-28 show the effect of emulsion phase to external phase ratio on copper transport to confirm the result of previous study in Figure 5-25 under the same condition, except carrier concentration and surfactant concentration. These experiments also were divided into three conditions. In the first condition, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was kept constant at 5% by volume Span 80. In the second condition, surfactant concentration was changed from 5% to 7% by volume Span 80 and carrier concentration was kept constant at 10% by volume D2EHPA. And in the last condition, both of carrier concentration and surfactant concentration were changed, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was changed from 5% to 7% by volume Span 80. The results of this study in Figure 5-26 to 5-28 were rather the same trend as those in Figure 5-25. Therefore, the optimum ratio of emulsion phase to external phase was 1:9.

Figure 5-29 shows the concentration of copper in the internal phase during extraction of copper at various emulsion phase to external phase ratio. It was found that at a emulsion phase to external phase ratio was 1:9, the concentration of copper in the internal phase can be maximized up to twenty folds of its concentration in the external phase.

Figure 5-30 shows the initial rate of various ratios of emulsion phase to external phase. This initial rate can be calculated by using the extraction of copper at the first time interval that copper in external phase suddenly decreases. It was found that the ratio of 1:3 offered the highest initial rate of 19.819 ppm./min. But it can be concluded from the results that the emulsion phase to external phase ratio of 1:9 was the most satisfactory condition for extraction of copper for this process. In addition, the initial rate was up to 19.258 ppm./min at this ratio

Figure 5-31 shows the effect of emulsion phase to external phase (feed solution) ratio on swelling in the emulsion liquid membrane. At the end of the extraction time, the swelling of emulsion was 25% to over 95%. When the emulsion phase to external phase ratio decreased, the total amount of copper transported across the membrane decreased and so did the amount of water transported. Therefore, the swelling decreased.

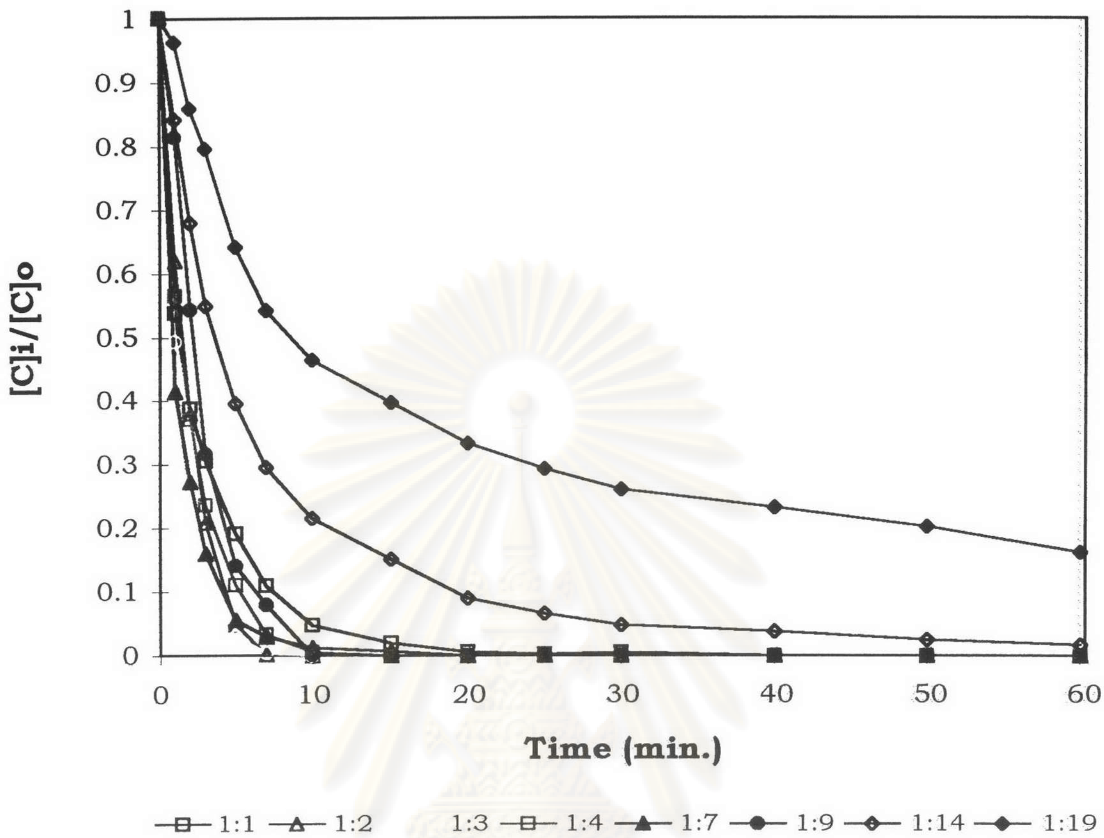

Figure 5-25 Effect of ratio of emulsion phase to feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

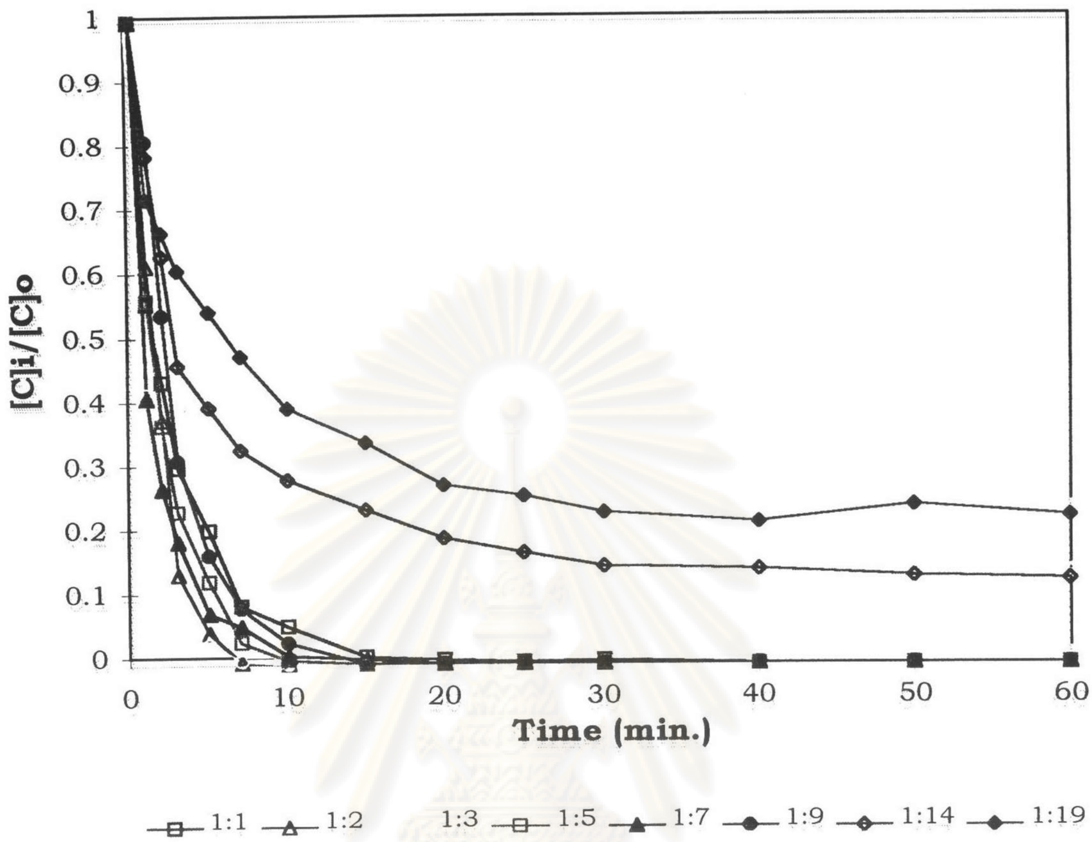

Figure 5-26 Effect of ratio of emulsion phase to feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	88%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

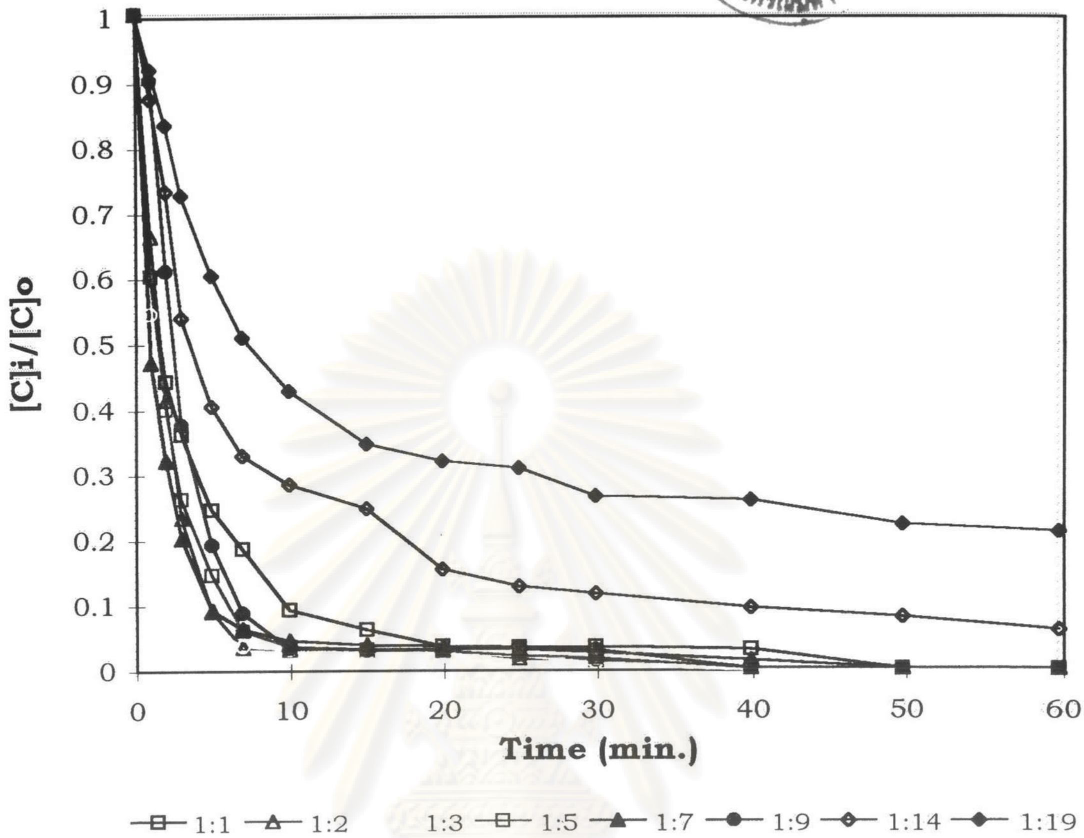

Figure 5-27 Effect of ratio of emulsion phase to feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	86%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

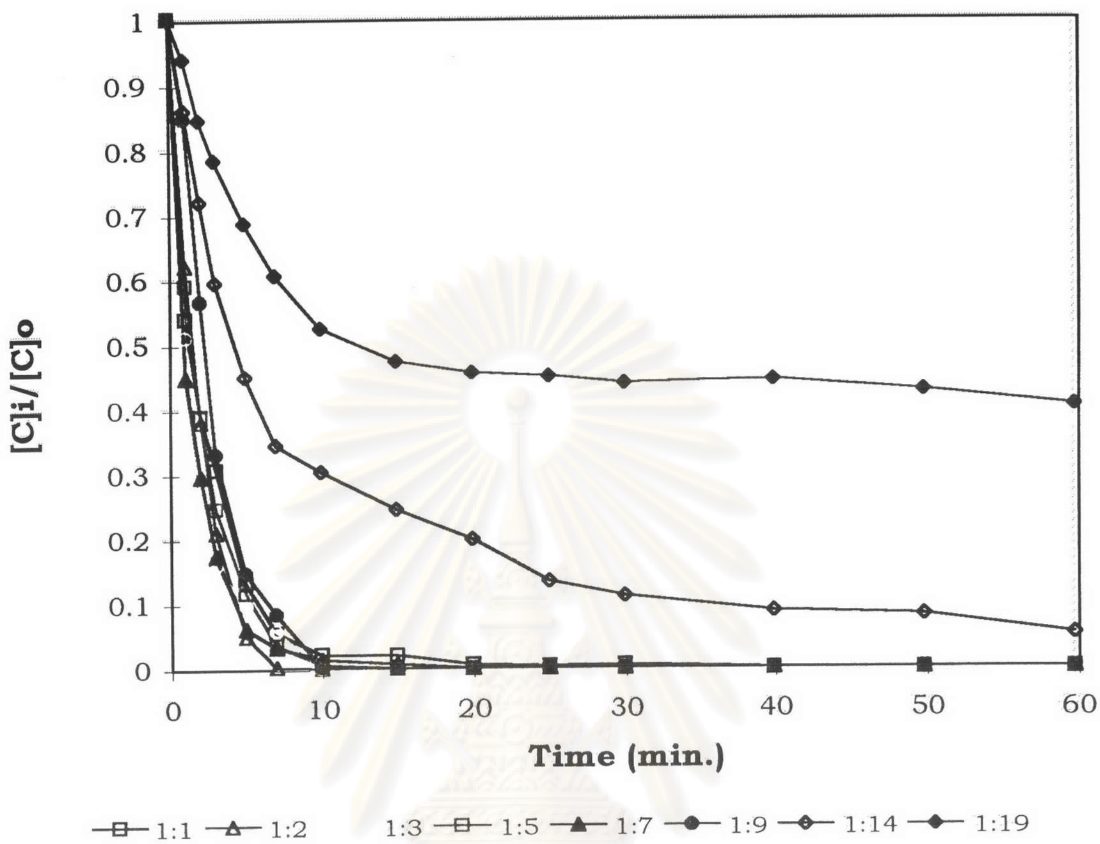

Figure 5-28 Effect of ratio of emulsion phase to feed solution on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	83%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

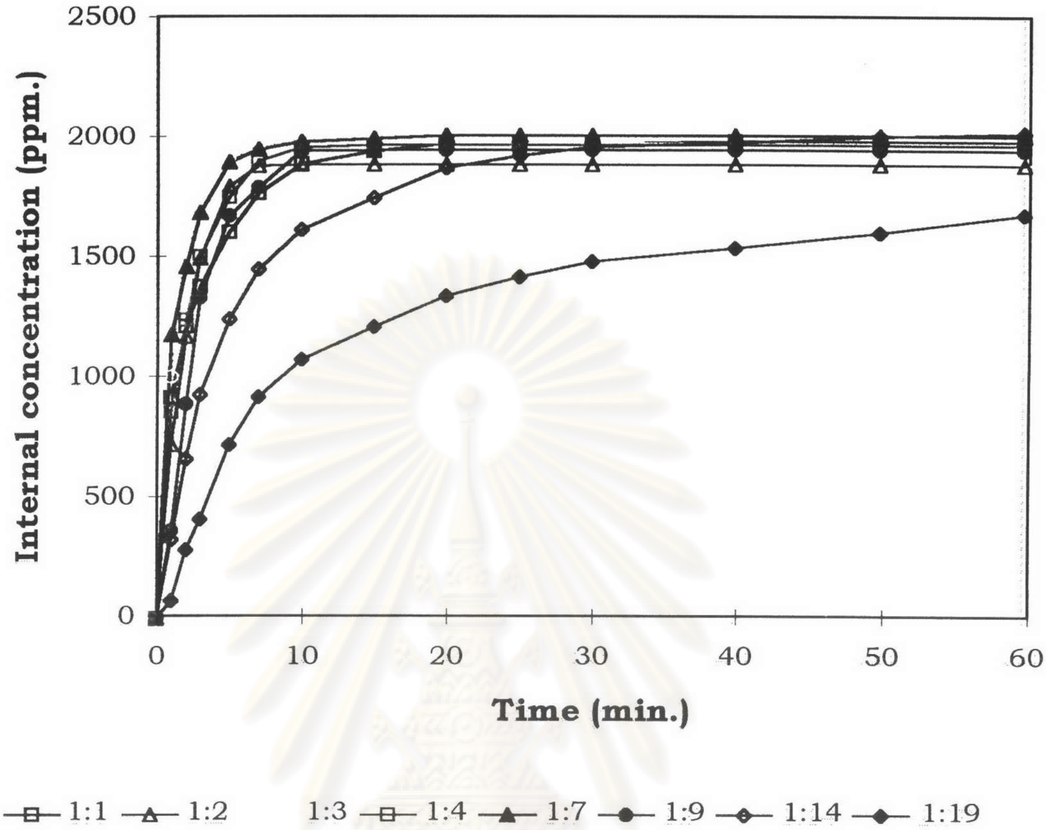

Figure 5-29 Concentration of copper in the internal phase during extraction of copper at various ratio of emulsion phase to feed solution

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

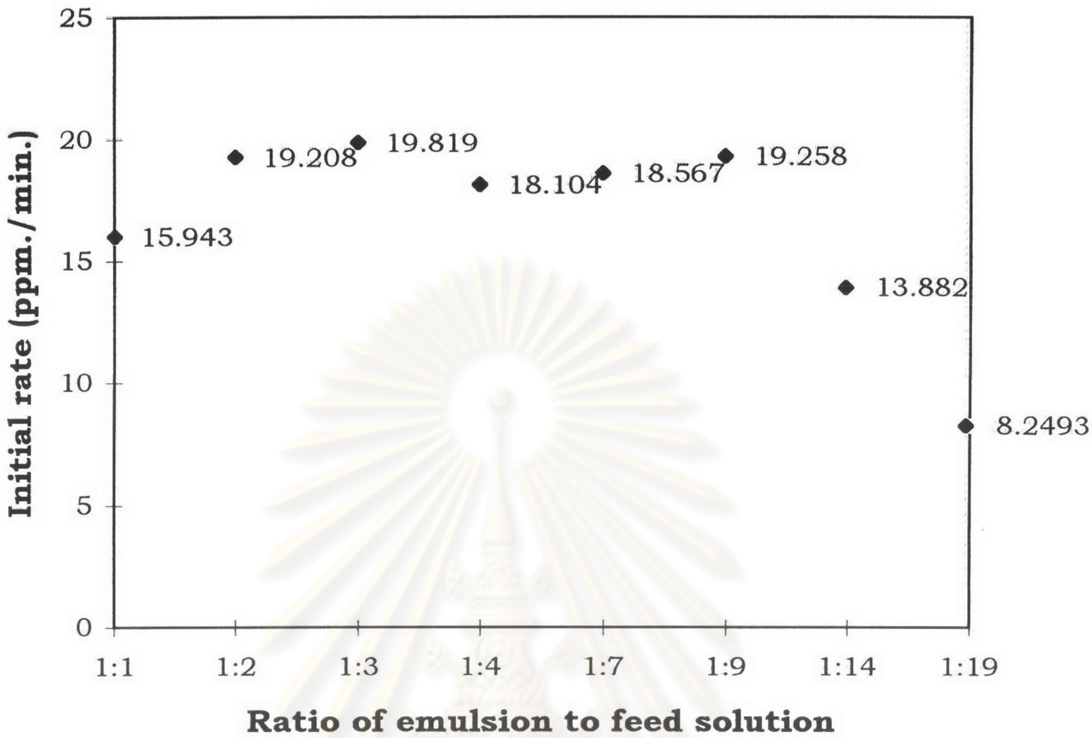

Figure 5-30 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various ratio of emulsion phase to feed solution (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

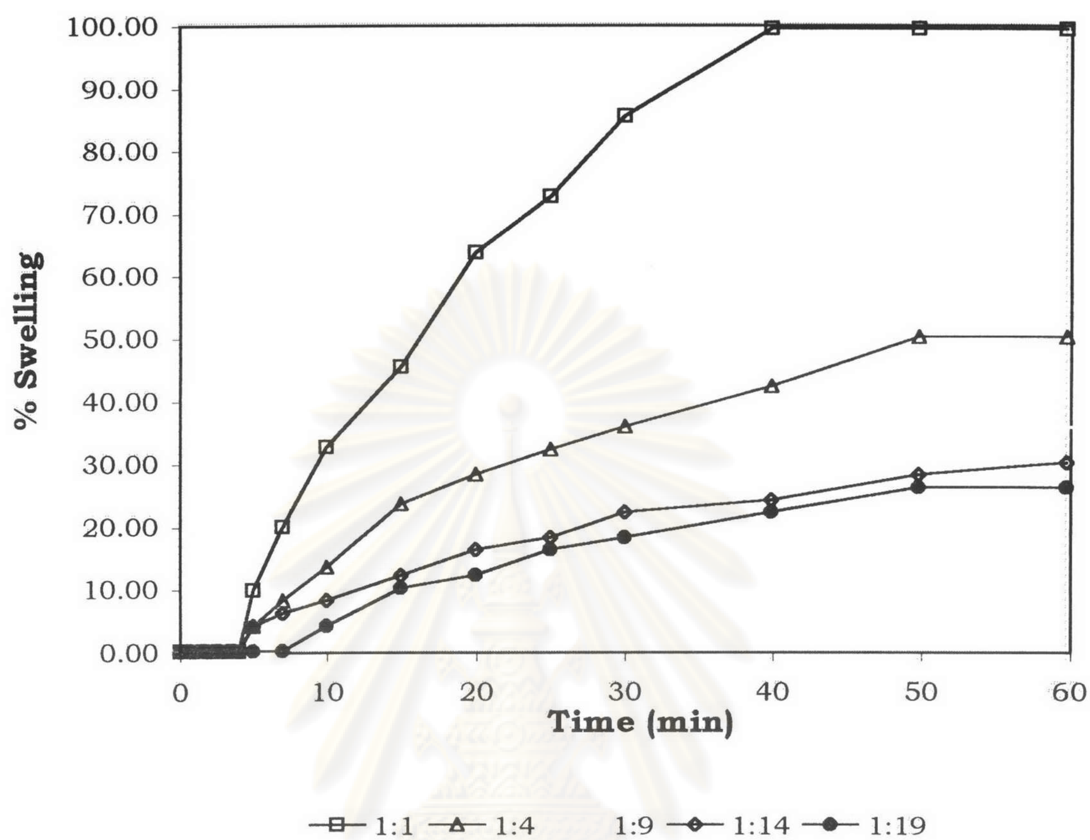

Figure 5-31 Effect of ratio of emulsion phase to feed solution on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	various ratio condition	
Agitation speed	350 rpm.	

Effect of Agitation Speed

The objective of this section is to find a proper agitation speed for copper separation by emulsion liquid membrane. The proper agitation speed was evaluated by conducting experiments with variation of agitation speeds from 200 to 700 rpm. The results of this study are shown in Figure 5-32 to 5-35. They indicated that the remaining copper in the feed solution (external phase) depended on agitation speed.

The effect of the agitation speed on the copper transport rate is shown in Figure 5-32. When the agitation speed was increased from 200 to 500 rpm., the copper transport rate was increased too but there were almost no differences in the copper transport rate for agitation over 500 rpm. As the agitation speed increased the mass transfer coefficients of the external phase film and the surface area of the emulsion globules increased. On the other hand, the breakage of the membrane also seemed to increase due to the increase in shear. The increase of the breakage seems to offset the mass transfer coefficient and the surface area. In this particular system since the external copper concentration is high and the diffusivity of the carrier/copper complex was relatively low, the effect of increasing mass transfer coefficient in the external phase appeared to be small.

Figure 5-33 to 5-35 show the effect of agitation speed on copper transport to confirm the result of previous study in Figure 5-32, the same condition was used, except carrier concentration and surfactant concentration. These experiments also were divided into three conditions. In the first condition, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was kept constant at 5% by volume Span 80. In the second condition, surfactant concentration was changed from 5% to 7% by volume Span 80 and carrier concentration was kept constant at 10% by volume D2EHPA. And in the last condition, both of carrier concentration and surfactant concentration were changed, carrier concentration was changed from 10% to 7% by volume D2EHPA and surfactant concentration was changed from 5% to 7% by volume Span 80. The results of this study were relatively the same trend as those in Figure 5-32. The agitation speed which gave the highest of percentages of extraction was 700 rpm. But the optimum agitation speed was in the range of 350 to 400 rpm because of more power of agitation requirement and the breakage of membrane.

Figure 5-36 shows the concentration of copper in the internal phase during the extraction of copper at various agitation speeds. When the agitation speed was increased, the copper concentration in the internal phase increased. At over 400 rpm, the extracted copper concentration in the internal phase can be maximized up to twenty folds of concentration of copper in the external phase.

Figure 5-37 shows the initial rate at various agitation speeds. It was found that, when the agitation speed increased, the initial rate also increased. But there were small differences of the initial rate over 500 rpm. when compared with under 500 rpm. which was significantly differences.

Figure 5-38 shows the effect of agitation speed on swelling in the emulsion liquid membrane. At the end of the extraction time, the swelling of the emulsion was between 25% to 35% in 60 minutes. As the agitation speed increased the swelling of membrane phase decreased. Itoh et.al (1989) explained the breakage of the membrane. They found that the membrane breakage seems to increased due to the increase in shear and the increase of the agitation speed. At low agitation speed, there was no breakage of membrane phase and the swelling effect was considered significant. While at high agitation speed, membrane can be broken by the increase of shear then the swelling effect was considered small because the water would be back transported into the external phase.

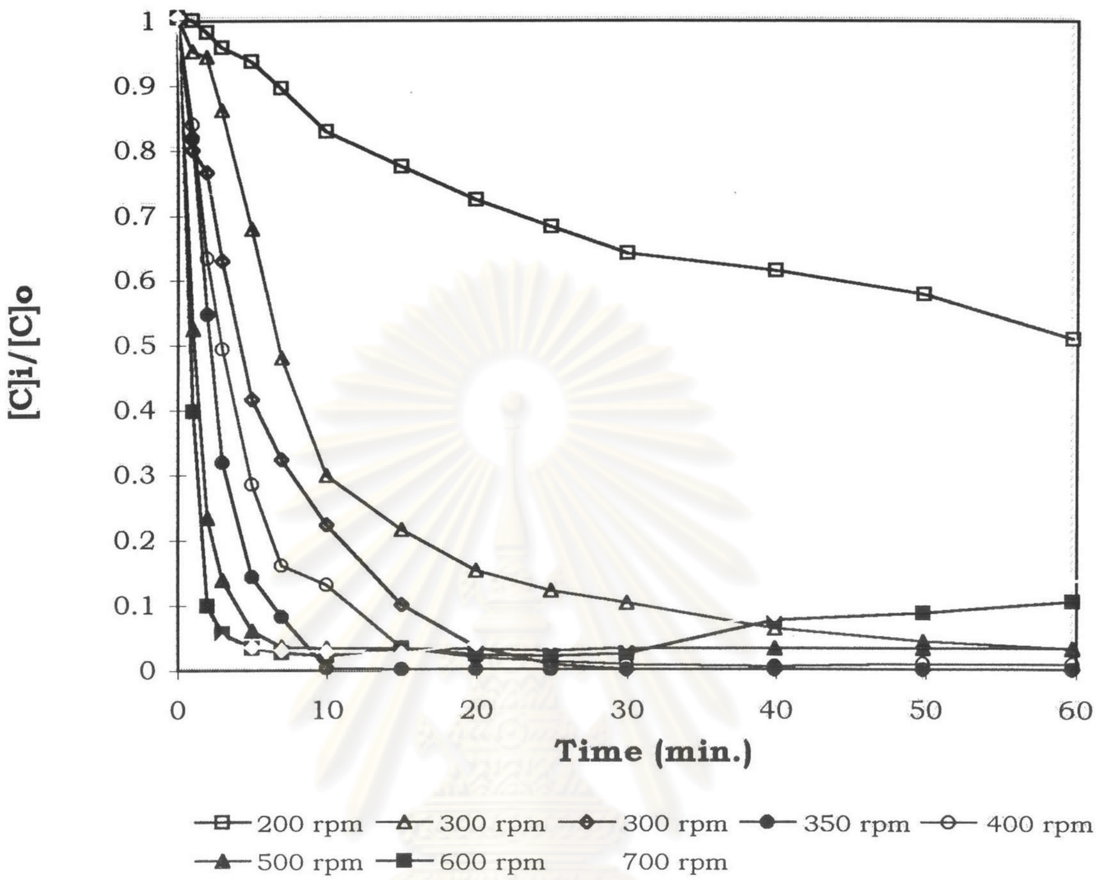

Figure 5-32 Effect of speed of agitator on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

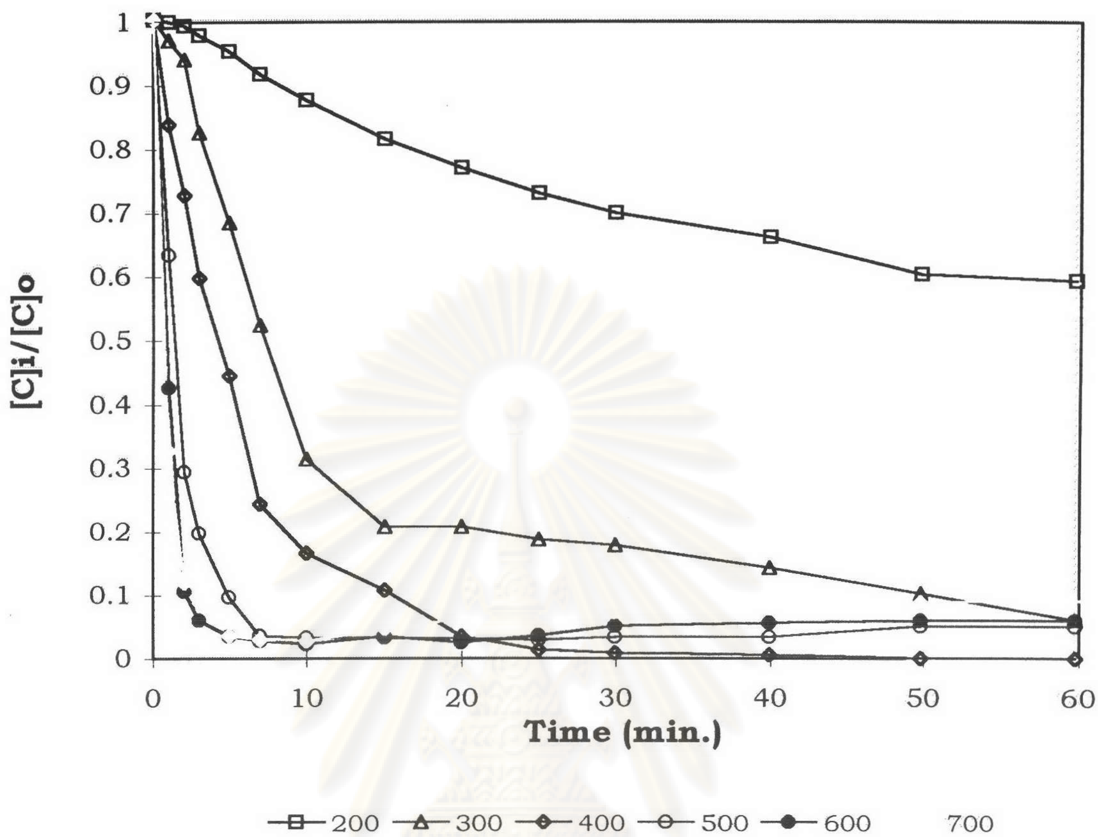

Figure 5-33 Effect of speed of agitator on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 5% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	88%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

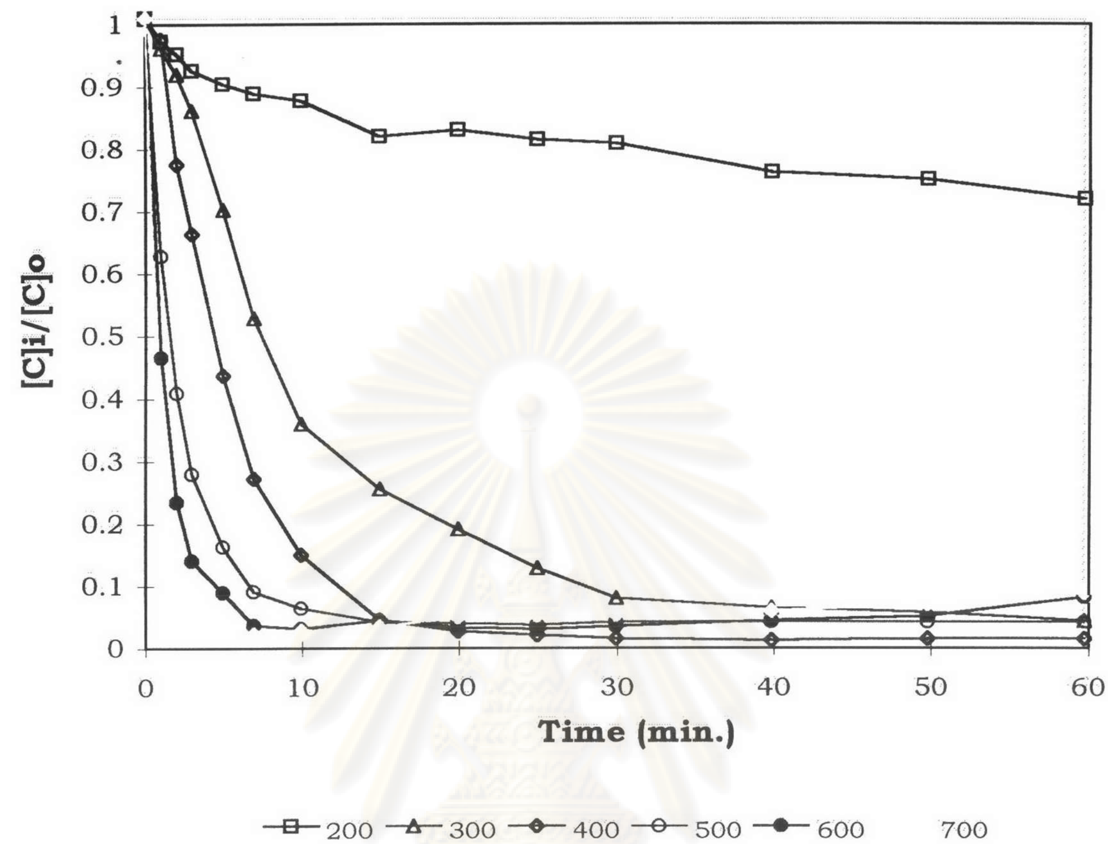

Figure 5-34 Effect of speed of agitator on extraction of 100 ppm. copper ions by emulsion liquid membrane at 7% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	86%
	carrier (D2EHPA)	7%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

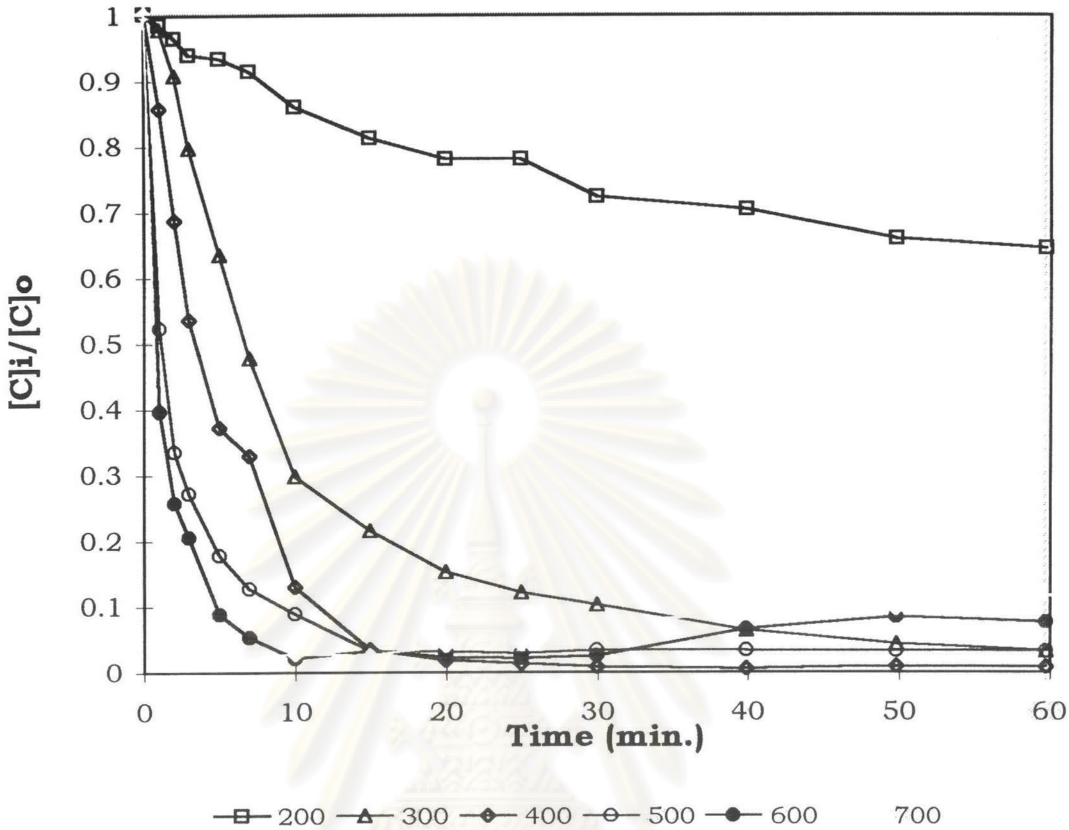

Figure 5-35 Effect of speed of agitator on extraction of 100 ppm. copper ions by emulsion liquid membrane at 10% D2EHPA and 7% Span 80.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	83%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	7%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

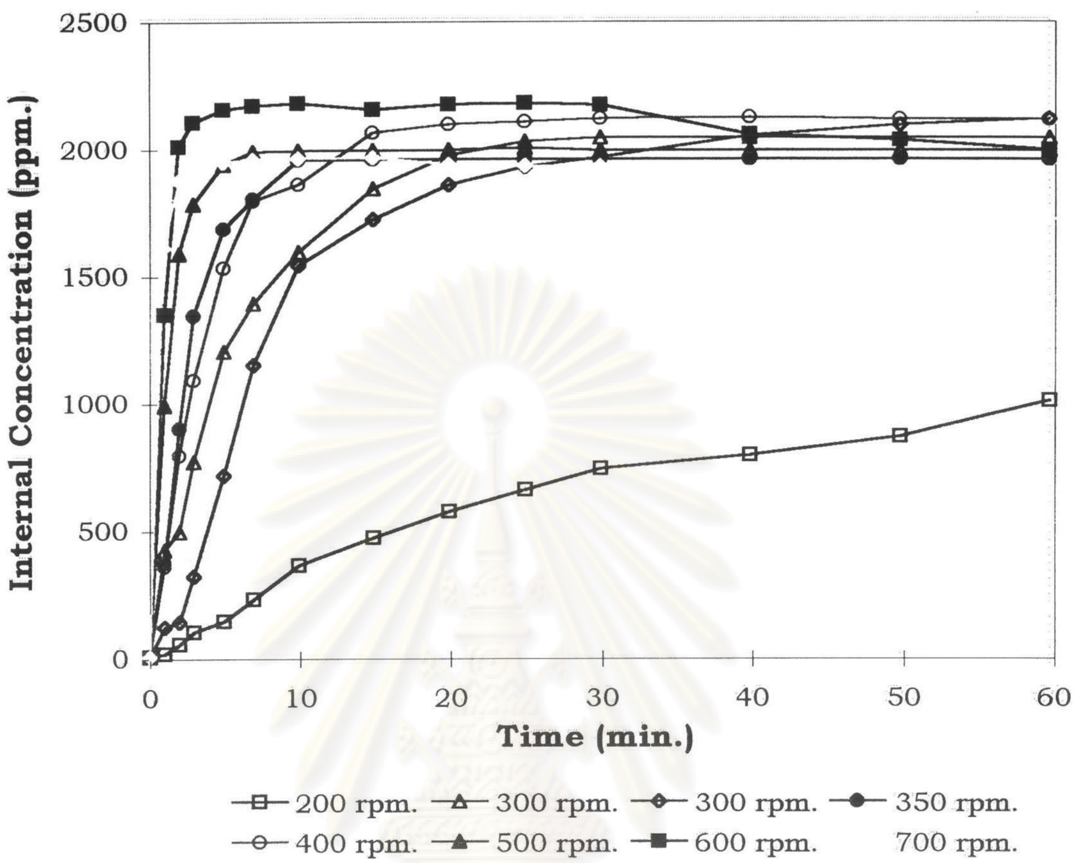

Figure 5-36 Concentration of copper in the internal phase during extraction of copper at various speed of agitator.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

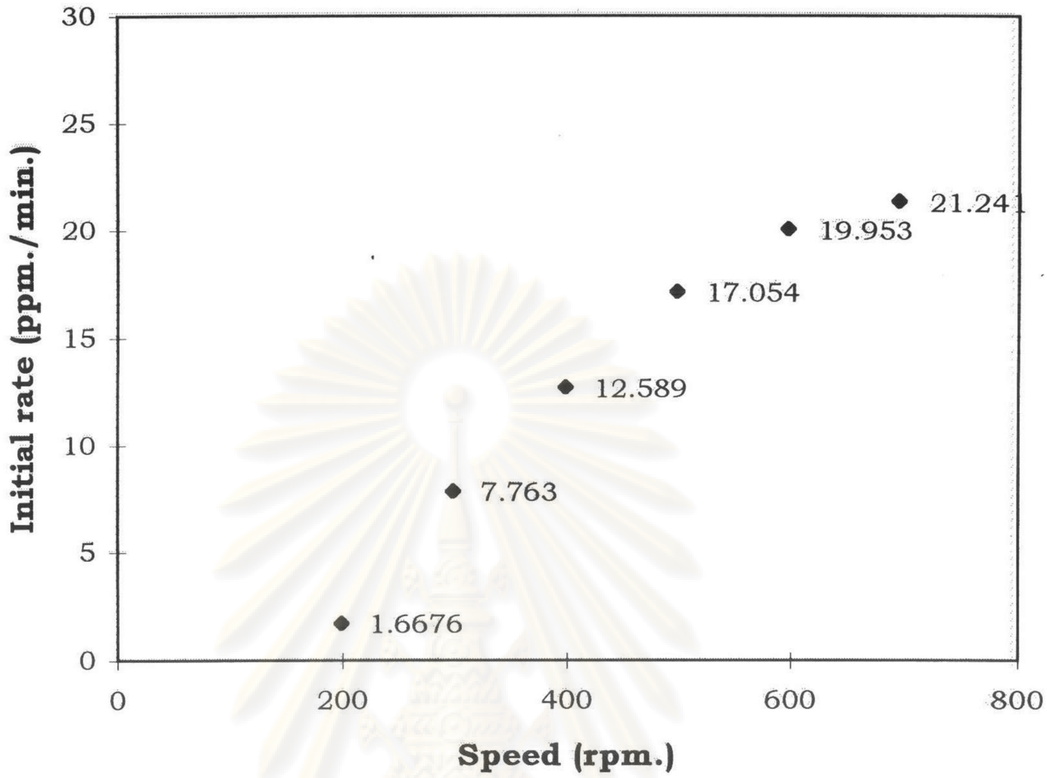

Figure 5-37 Initial rate on extraction of 100 ppm. copper ions by emulsion liquid membrane at various speed of agitator (at first 5 minute interval).

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

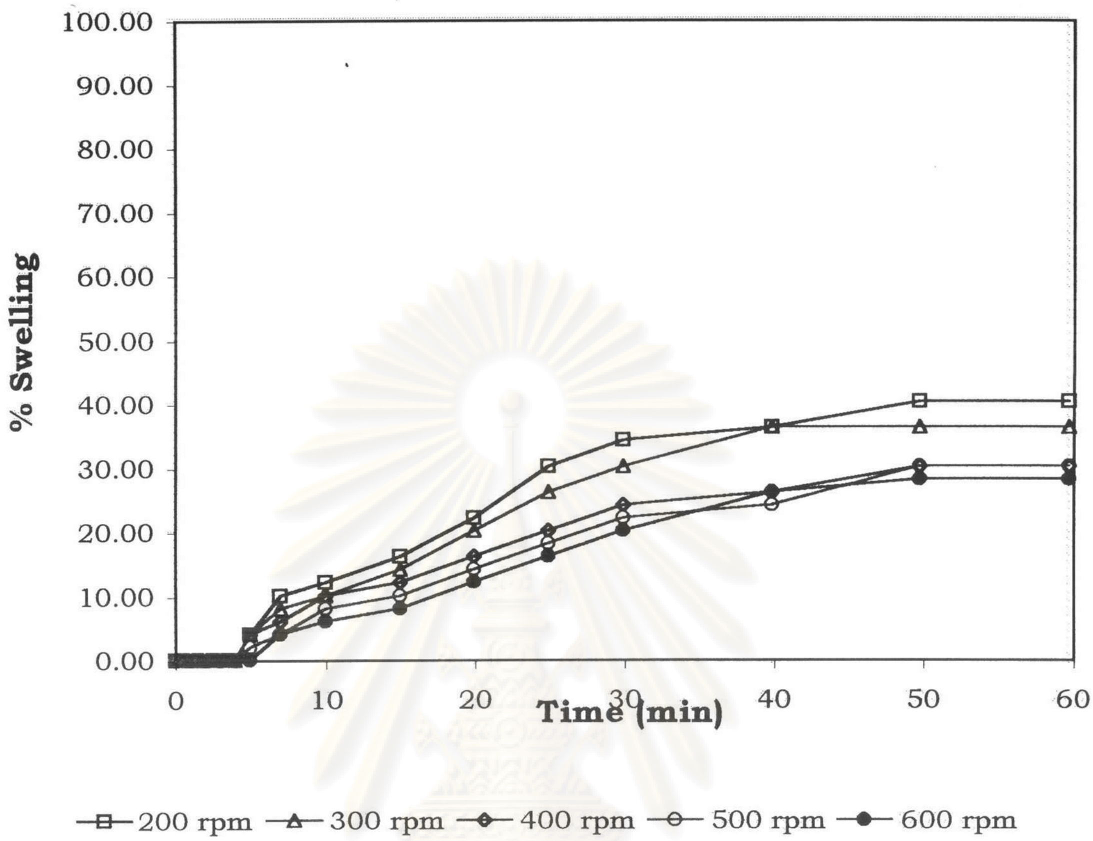

Figure 5-38 Effect of speed of agitator on % swelling on extraction of 100 ppm. copper by emulsion liquid membrane.

Experimental conditions:

External phase	100 ppm. Cu. at pH 3.00 (adjust by HCl acid solution)	
Membrane phase	organic solvent (Kerosene)	85%
	carrier (D2EHPA)	10%
	surfactant (Span 80)	5%
Membrane preparation	Homogenized at speed =8000 rpm. 10 min.	
Internal phase	1 N HCl acid solution	
Membrane phase : Internal phase	50:50	
Emulsion phase : Feed solution	50:450	
Agitation speed	various speed condition	

Continuous Operation

Figure 5-39 shows the results of the 240-minute continuous operation in one stage mixer-settler. Run A was the volumetric flow rate of feed solution at 1.8 liter/hour, which was 9 times of the volumetric flow rate of emulsion phase. Therefore, the volumetric flow rate of emulsion phase was 0.2 liter/hour. At the end of the extraction time, the average of the removal of copper from the feed solution was 76.28%. And the remaining copper concentration in the raffinate phase was higher than that of the batch operation because of smaller residence time. Run B was the volumetric flow rate of feed solution at 1.0 liter/hour, which was decreased from previous condition, but the same volumetric flow rate of emulsion phase as Run A. The remaining copper concentration in the raffinate phase eventually became less than that of Run A, as the effect of the residence time increased. For Run C which 0.5 liter/hour and Run D which 0.2 liter/hour were likely the same trend as that of Run B. That is, under constant volumetric flow rate of emulsion phase, the remaining copper concentration in the raffinate phase decreased in corresponding with the decrease of volumetric flow rate of feed solution. Therefore, extraction increase. This phenomenon can be illustrated that when the volumetric flow rate of feed solution decreased, the contacting time between feed solution and emulsion phase increased. Consequently, the extraction occurred better at lower volumetric flow rate. The table 5-1 summarizes the results of additional Runs carried out on a continuous operation experimental reactor. In all Runs, the volumetric flow rate of emulsion phase was kept constant at 0.2 l/hr.

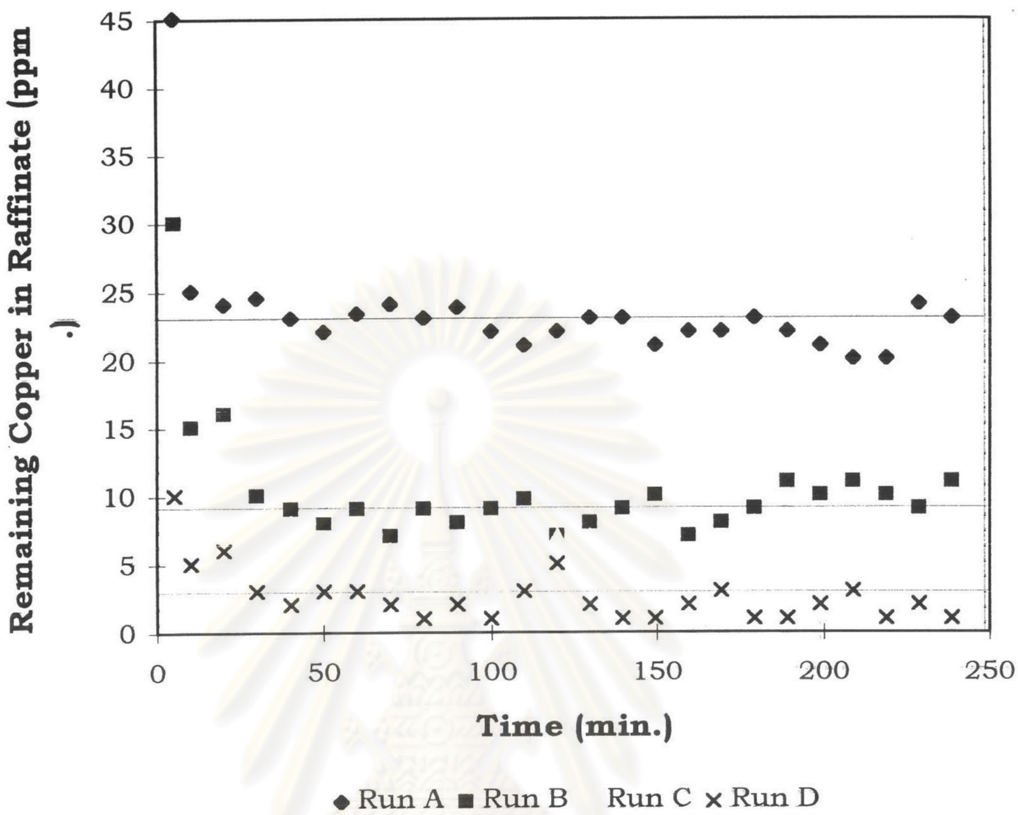

Figure 5-39 The remaing copper in the raffinate phase at various volumetric flow rate of feed solution

Conditions

Run A Volumetric flow rate of feed solution 1.8 liter/hour

Run B Volumetric flow rate of feed solution 1.0 liter/hour

Run C Volumetric flow rate of feed solution 0.5 liter/hour

Run D Volumetric flow rate of feed solution 0.2 liter/hour

Table 5-1 The remaining copper in the raffinate phase and % extration at various volumetric flow rate of feed solution

Test	Volumetric flow rate of feed solution (l/h)	Volumetric flow rate of emulsion phase (l/h)	Remaining copper (ppm.)	% Extraction
Run A	1.8	0.2	23.72	76.28
Run B	1.0	0.2	10.48	89.52
Run C	0.5	0.2	7.20	92.80
Run D	0.2	0.2	2.64	97.36

Comparison of Copper Loading Capacity between Solvent Extraction Process and Emulsion Liquid Membrane Process.

For a direct comparison of the copper loading capacities of the two processes, three sets of experiments were run to compare the solvent extraction loading capacity of copper in kerosene containing 10% active D2EHPA with the loading capacity of an emulsion containing 10% D2EHPA in the membrane phase. The emulsion tests were made using two different concentrations of hydrochloric acid in the internal phase.

In the tests, a given amount of organic phase consisting of D2EHPA in kerosene or emulsion was repeatedly contacted with an equal volume of fresh solution containing 500 ppm. copper at pH 3.0. In each step, the raffinate was drained and fresh solution was added. The experimental results are given in Figure 5-40, showing the trend in the stepwise decay of extraction for three cases.

In the case of solvent extraction (Case I), the extraction efficiency decreased drastically after just two steps. The percent copper extracted decreases from 84.7% in the second step down to 60% in the third step. In six steps the loading was completed and no further extraction took place. The total loading capacity of copper per cubic centimeter of active D2EHPA was found to be 0.069 g/cm^3 of D2EHPA.

In the case of an emulsion containing low acid internal aqueous phase (0.1 N hydrochloric acid) (Case II), the total loading capacity for copper was 0.15 g/cm^3 of D2EHPA. This was twice the loading achieved with D2EHPA in kerosene.

In the last case (Case III), whereas emulsion containing high acid in the internal aqueous phase (1.0 N hydrochloric acid) was used, the copper extraction was much better. Figure 5-40 give the results of 17 repeated cumulative loading tests using a high acid internal aqueous phase. The percentage copper extracted in each of the first 10 steps was more than percentage copper extracted in each of the first 10 steps was more than 90%. The extraction efficiency of copper from solution decreased gradually as the hydrochloric acid in the internal aqueous phase decreased and the copper increased. In 17 steps, the total copper extracted per cubic centimeter of D2EHPA was about 0.37 g, a value of about five times higher than that of D2EHPA in kerosene. It is expected that extraction can be continued for many more steps, beyond 17 steps. Thus, the total loading capacity would be much higher than 0.37 g. The above results indicated that the loading capacity of an emulsion was much higher than that of kerosene solvent in terms of D2EHPA utilization per unit volume of reagent.

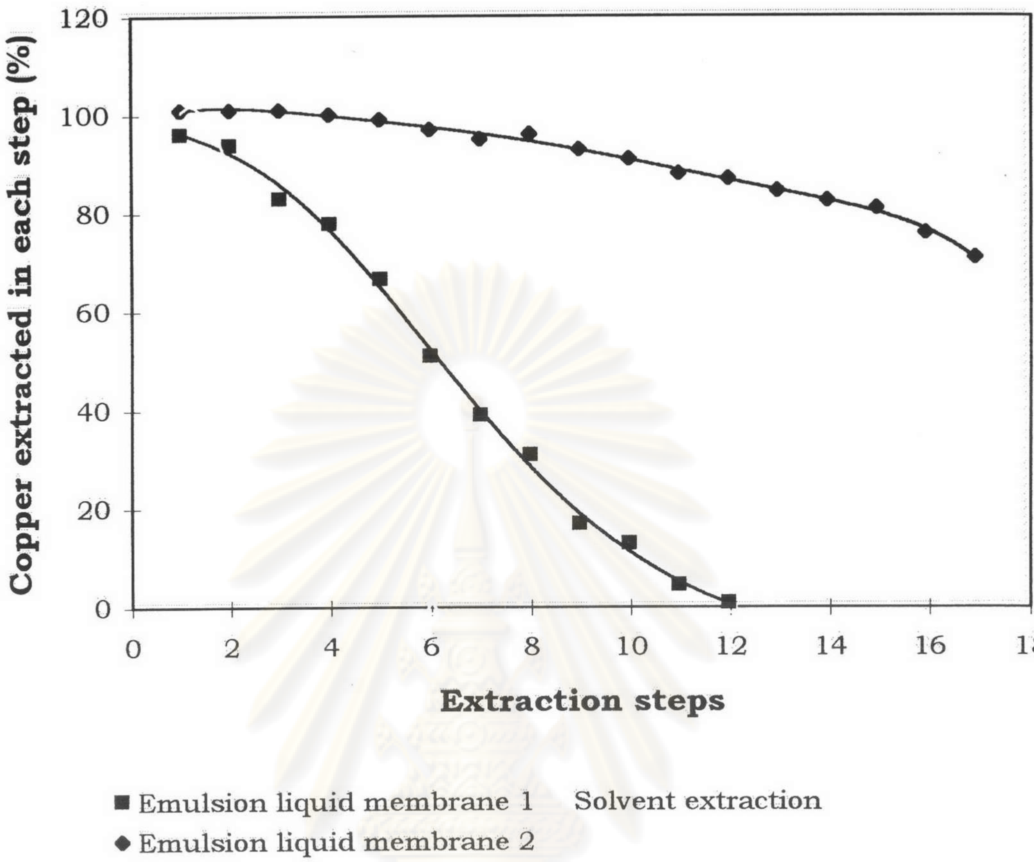

Figure 5-40 Copper extracted in each consecutive stage using Solvent extraction and Emulsion liquid membrane.

Conditions

Case I Solvent Extraction

Case II Emulsion Liquid Membrane with 0.1 N HCl

Case III Emulsion Liquid Membrane with 1.0 N HCl

Extraction Equilibrium of Copper

For the liquid equilibrium extraction of copper in the presence of D2EHPA, it was found that Cu^{2+} ions formed a complex with D2EHPA in the oil phase which existed in the dimeric form as follow:

$$Cu^{2+} + m(\overline{HR})_2 \rightleftharpoons \overline{CuR(HR)_{2m-1}} + mH^+ \quad (5\text{-}1)$$

Equilibrium constant

$$K_{ex} = \frac{[\overline{CuR(HR)_{2m-1}}]_{eq}\,[H^+]^m_{eq}}{[Cu^{2+}]_{eq}\,[\overline{HR}]^m_{eq}} \quad (5\text{-}2)$$

where $(\overline{HR})_2$ is the dimer of D2EHPA in the membrane phase and m is the stoichiometric coefficient and $\overline{CuR(HR)_{2m-1}}$ is the Cu^{2+}/carrier complex in the membrane phase.

The distribution coefficient of copper in the ion form is expressed by:

$$D^+ = \frac{[\overline{CuR(HR)_{2m-1}}]_{eq}}{[Cu^{2+}]_{eq}} \quad (5\text{-}3)$$

From equation (5-2),

$$\frac{K_{ex}[(\overline{HR})_2]^m_{eq}}{[H^+]^m_{eq}} = \frac{[\overline{CuR(HR)_{2m-1}}]_{eq}}{[Cu^{2+}]_{eq}} \quad (5\text{-}4)$$

From equation (5-3) and (5-4),

$$D^+ = \frac{K_{ex}[(\overline{HR})_2]^m_{eq}}{[H^+]^m_{eq}} \quad (5\text{-}5)$$

$$\log D^+ = \log K_{ex}[(\overline{HR})_2]^m_{eq} - \log [H^+]^m_{eq}$$

$$\log D^+ = \log K_{ex}[(\overline{HR})_2]^m_{eq} - m \log [H^+]_{eq} \quad (5\text{-}6)$$

$$\log D^+ + \log [H^+]^m_{eq} = \log K_{ex} + m \log[(\overline{HR})]_{eq}$$

$$\log(D^{+}[H^{+}]^{m}_{eq}) = \log K_{ex} + m \log[\overline{(HR)_2}]_{eq} \qquad (5\text{-}7)$$

Based on the assumption that Copper reacted with D2EHPA, the following mass balance equation can be obtained :

$$[\overline{(HR)_2}]_{eq} = [\overline{(HR)_2}]_i - m(\overline{CuR\,(HR)_{2m-1}})_{eq} \qquad (5\text{-}8)$$

$$[\overline{CuR\,(HR)_{2m-1}}]_{eq} = [Cu^{2+}]_i - [Cu^{2+}]_{eq} \qquad (5\text{-}9)$$

From the above equations, the values of K_{ex}, D^{+} and $[\overline{(HR)_2}]_{eq}$ can be calculated. Figure 5-41 to 5-42 shows the relationship between distribution coefficient of Cu^{2+},(D^{+}) and $[H^{+}]_{eq}$. It was found that graphs of initial pH varied from 2.0 to 6.0 were straight lines with the slope of -1.9873 and -1.9278 which considered here -2.0000. As can be seen from the equation (5-6), the slope of the equation (5-6) is m that is corresponding to this curve. Therefore, m in equation (5-6) is -2.0000. It was found that , when $[H^{+}]_{eq}$ was decreased, the $[D^{+}]_{eq}$ was increased.

The graphs of $\log(D^{+}[H^{+}]^{m})_{eq}$ versus $\log[\overline{(HR)_2}]_{eq}$ are shown in figure 5-43 and 5-44. According to equation (5-7) the slope of graph of $\log(D^{+}[H^{+}]^{m})_{eq}$ versus $\log[\overline{(HR)_2}]_{eq}$ is m. In this case, the value of slope or m is 2, It was found that one moles of Cu^{2+} reacted with two mole of dimer of D2EHPA to form complex in the membrane phase. Therefore, the total equation of copper extraction with D2EHPA should be

$$Cu^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{CuR_2(HR)_2} + 2H^{+} \qquad (5\text{-}10)$$

Figure 5-45 shows the calculated value of individual experiment data points and a change of the values of K_{ex} with respect to the values of $[\overline{(HR)_2}]_{eq}$. It was found that, there was a slight change in K_{ex} values.

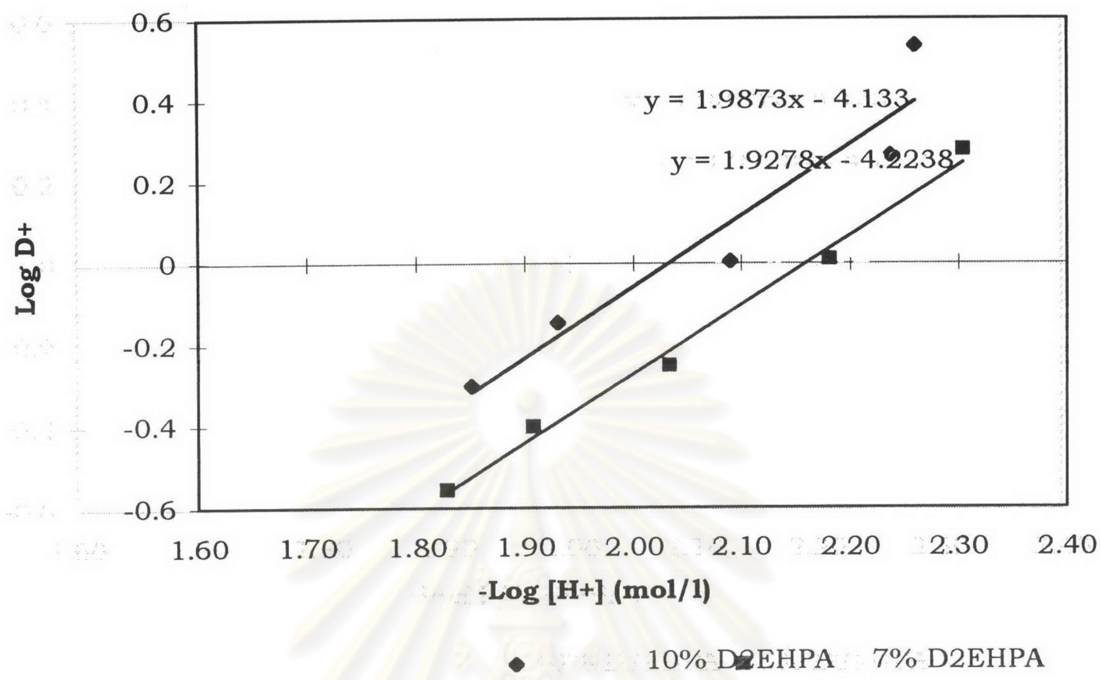

Figure 5-41 Log of Distribution Coefficient of Cu2+ vs. -Log [H+]eq.

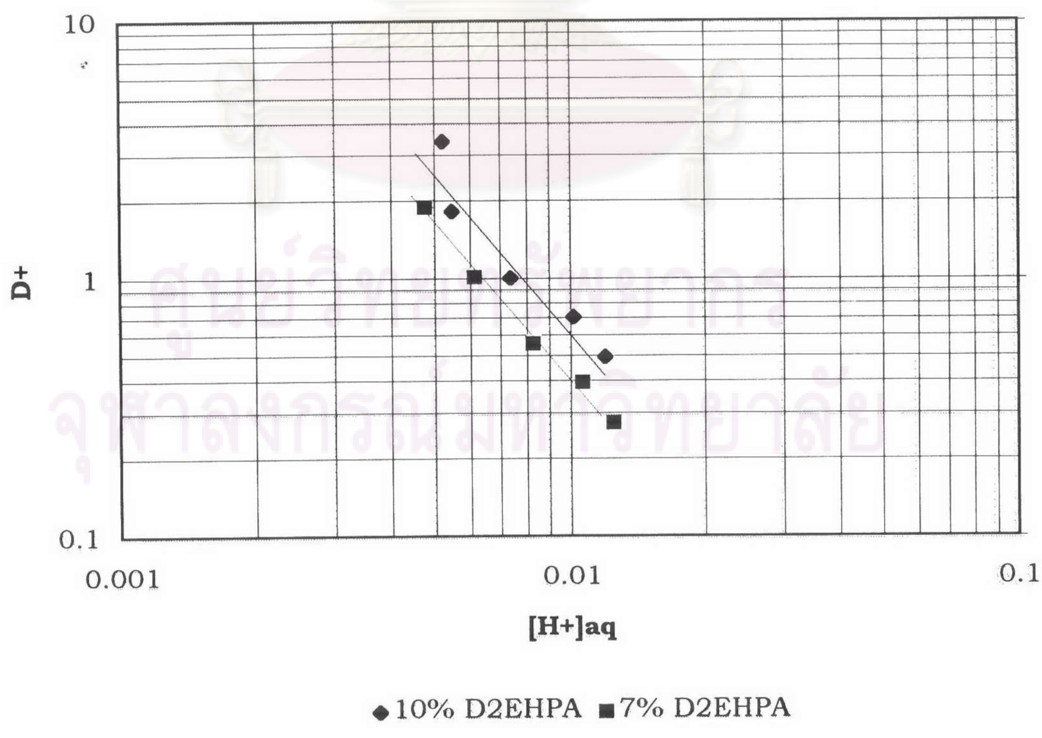

Figure 5-42 Distribution Coefficient of Cu2+ vs. [H+]eq.

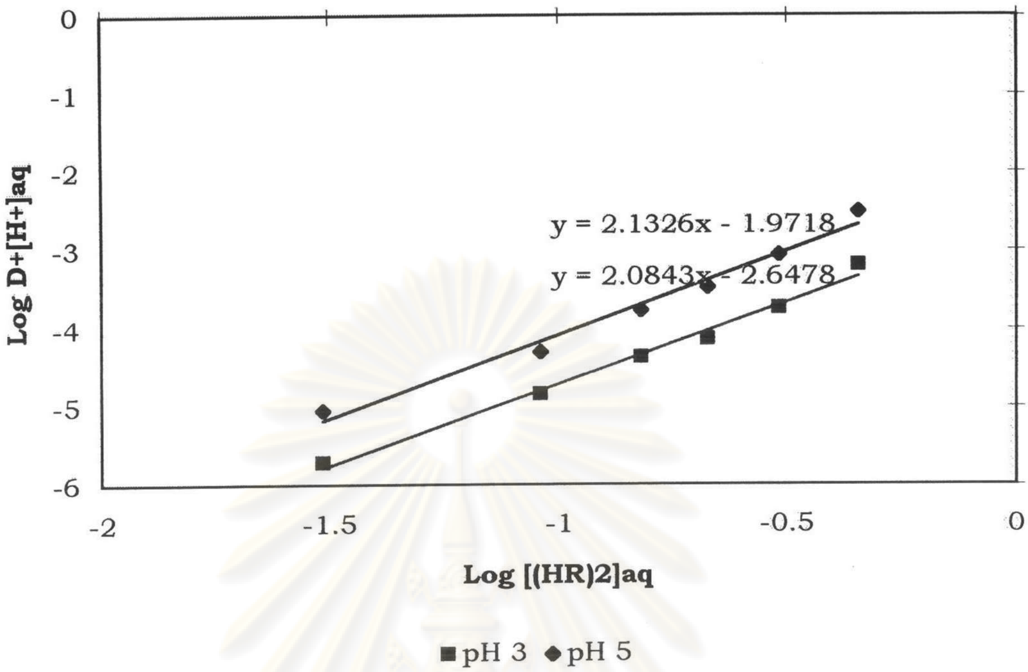

Figure 5-43 Log [D+][H+]eq vs. Log [(HR)2]eq of Copper

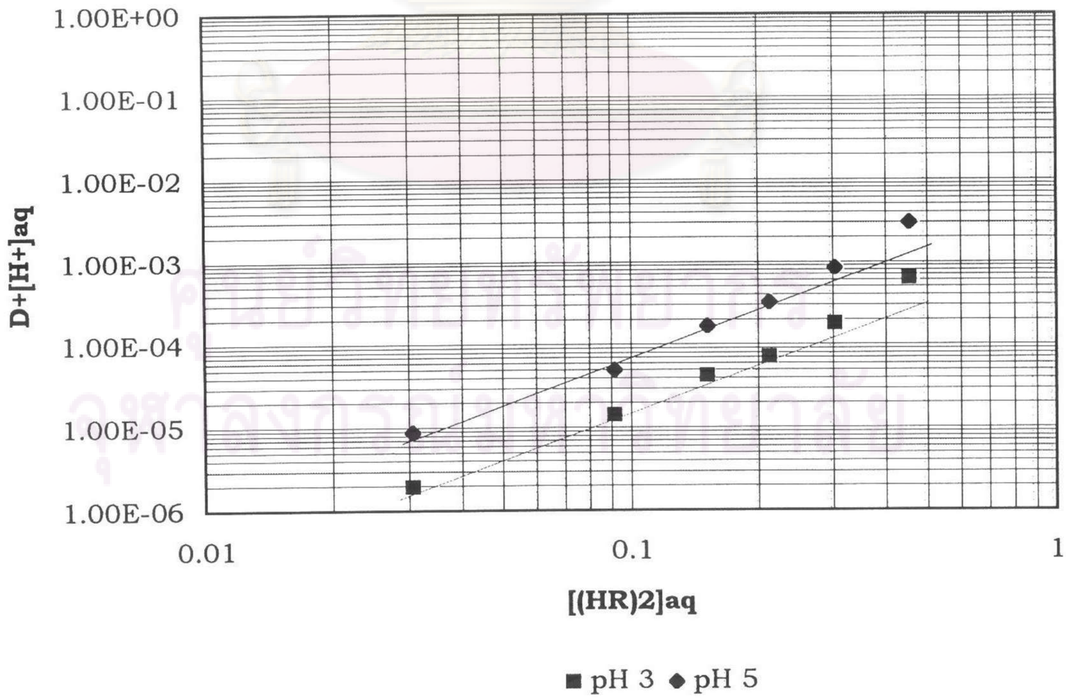

Figure 5-44 [D+][H+]eq vs. [(HR)2]eq of Copper

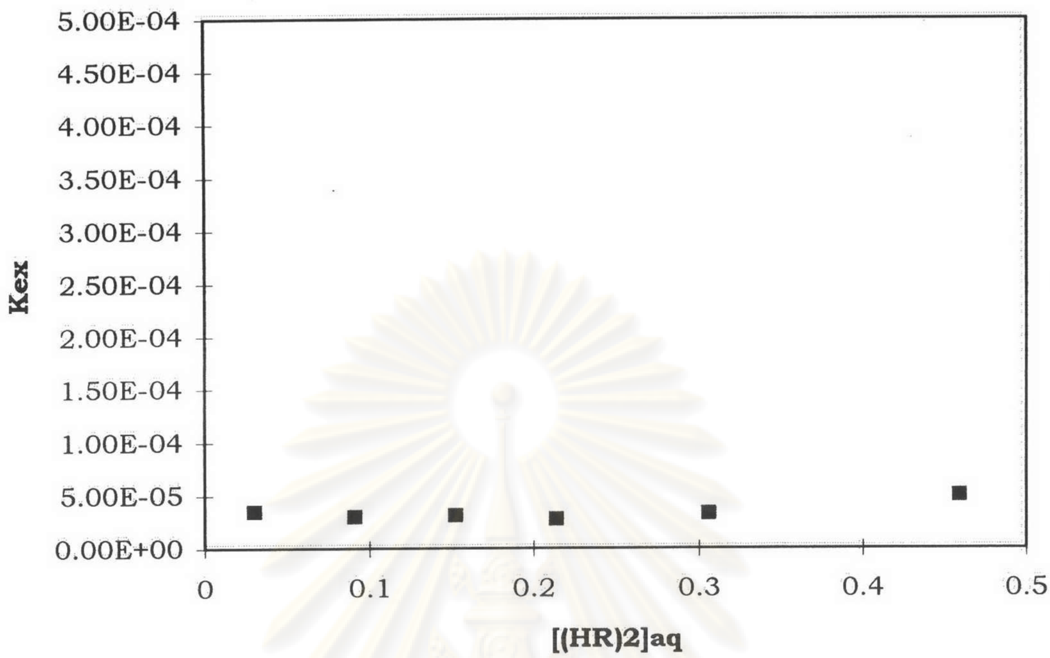

Figure 5-45 Kex of Copper vs. [(HR)2]eq