CHAPTER IV

RESULTS AND DISCUSSION

Batch Experiments

The reaction of cobalt with D2EHPA is expressed by:

$$Co^{2+} \quad + \quad 2\,\overline{RH} \quad \underset{K_{st}}{\overset{K_{ex}}{\rightleftharpoons}} \quad \overline{CoR_2} \quad + \quad 2\,H^{+} \qquad \text{............} \quad (4.1)$$

where RH is a molecule of extractant, D2EHPA. Hence, the extraction equilibrium is expressed by:

$$K_{ex} = \frac{\left[\overline{CoR_2}\right]\cdot\left[H^{+}\right]^2}{\left[Co^{2+}\right]\cdot\left[\overline{RH}\right]^2} \qquad \text{............} \quad (4.2)$$

and the stripping equilibrium is expressed by:

$$K_{st} = \frac{\left[Co^{2+}\right]\cdot\left[\overline{RH}\right]^2}{\left[\overline{CoR_2}\right]\cdot\left[H^{+}\right]^2} \qquad \text{............} \quad (4.3)$$

Since the driving force of this process is the concentration gradient of the cation H^+, the H^+ concentration in a feed solution should be as low as possible in order to be capable of loading up with the permeable hydronium ions. Therefore, despite the feed pH about 4, the feed pH about 6 was studied. In the experiment in which the initial pH of feed solution were about 6, some amount of sodium hydroxide solution was added in order to adjust the pH. In spite of a large amount of sodium hydroxide solution was added; the pH did not exceed the value of 7.0, but a large amount of precipitate occurred. This is because cobalt (II) hydroxide exists in two allotropic forms: a blue α-$Co(OH)_2$, and a pink β-$Co(OH)_2$. The hydroxide is usually prepared by precipitation from a cobaltous-salt solution by an alkali hydroxide such as sodium hydroxide. When the alkali is in excess, the pink β-form is produced. On the contrary, the blue α-form is produced when the cobalt salt is in excess. Both the hydroxide is insoluble in water and in bases, but highly soluble in mineral and organic acids [Considine, 1976]. In all the experiments, the cobaltous ion was in excess; therefore, the blue α-form was produced when some excess amount of sodium hydroxide was added.

The equilibrium constants, extraction factors (EF) and recovery factors (RF) for the batch experiments were summarized in Table 4-1 below.

Table 4-1 The results and the analyzed data for the batch experiments

Batch	I (Oxalic acid)	II (HCl)	III (HCl)
Data	pH about 4	pH about 4	pH about 6
$[Co^{2+}]$ extracted (ppm)	572.5	363.0	1,464.0
$[Co^{2+}]$ recovered (ppm)	246.6	138.1	1,143.0
Extraction factor (%)	5.68	3.04	12.30
Recovery factor (%)	2.46	1.13	9.62
K_{ex} (-)	7.6×10^{-7}	2.9×10^{-7}	5.6×10^{-6}
K_{st} (-)	8611.3	7365.9	7369.2
Difference in $[Co^{2+}]$ (%)	3.24	1.91	2.68
Difference in $[H^+]$ (%)	-0.26	1.92	-3.13

Note: See Appendix C for the definition of Extraction factor, Recovery factor, and Difference.

From the extraction factors and the equilibrium constants at the different pH values, namely the second batch at pH 4 approximately and the third batch at pH 6 approximately; it was found that pH was an influencing factor in the extraction of cabalt with D2EHPA serving as a carrier. The higher the pH value was, the more the cobaltous ions were extracted; as pH was increased from 4 to 6 approximately, the extraction factor was enhanced four times. This is because as the forward reaction, i.e. extraction process, occurs; hydronium ions are produced – referring to Equation

(4.1). If the feed solution initially contains some amount of hydronium ion, namely at low pH, the capacity of receiving the hydronium ions – a product of the reaction – is reduced. Thus, the amount of cobaltous ion which are extracted also reduced due to the equilibrium of reaction.

It was also found that when the oxalic acid solution was employed as a strip solution, the crystalline cobalt oxalates were obtained. While the hydrochloric acid solutions were employed, there was no crystalline cabalt salt. In the second and the third batches, if the feed solutions had been first prepared in a double volume with the same concentration of cobaltous ion and carried on the extraction experiment, then split this solution into two equal parts for each stripping experiment, the identical extraction factors would have been achieved. But in these two experiments, the feed solutions were prepared and each experiment was carried on separately. Nevertheless, the extraction factors were resulted similarly. One main error might be caused by the unequally initial concentrations of cobaltous ion (refer to Table 3-3). Therefore, the recovery factors and the percent differences were also similar. Moreover, the equilibrium constants which were calculated based on these values were in the same order of magnitude. In other words, the types of acid serving as strip solutions had no effects on this system.

In comparison with the cobalt recovery method invented by Ohtsuka (1990), more than 80% of cobaltous ion were extracted, from feed solution containing cobalt and nickel, by employing D2EHPA as an extractant and oxalic acid as a strip solution. However, in his experiments, the pH of feed solution was maintained within the range of 4.5-5.0 for the best result of separating cobalt from nickel, and the experiments were carried out at the constant temperature of 45 °C. As a result, his system shows the better performance than this system.

In these batch experiments, however, the pH and the temperature of feed solutions were not maintained in order to use these results as the references for the experiments on HFSLM. Nevertheless, the effects of maintaining pH of feed solution on cobalt extraction were studied in HFSLM experiments.

Hollow Fiber Supported Liquid Membrane Experiments

1. Effects of Cobaltous-Ion Concentration in Feed Solution

The feed solutions with the different cobalt concentrations (5,000, 8,000, and 10,000 ppm) at the same pH (about 4) were studied. The other parameter was the acidity in feed solutions. These experiments were carried out at the volumetric flowrate of 500 ml/min with circulating mode operation. The experimental conditions and the analyzed data were summarized in Table 4-2.

Table 4-2 The experimental conditions and the analyzed data for using oxalic acid as strip solutions in HFSLM experiments

Conditions	pH about 4			pH about 6
Data	5,000 ppm	8,000 ppm	10,000 ppm	10,000 ppm
Initial pH of feed solution	3.82	3.67	3.58	6.57
Initial pH of strip solution	1.40	1.41	1.41	1.39
[Co^{2+}] extracted (ppm)	1,056	1,160	1,315	2,959
Extraction factor (%)	23.01	13.23	12.23	27.63
[Co^{2+}] recovered (ppm)	2.811	3.803	3.594	14.75
Recovery factor (%)	0.06	0.04	0.03	0.14
Difference in [Co^{2+}] (%)	22.95	13.19	12.20	27.49

At pH about 4, the amount of cobaltous ions which were extracted increased as the initial cobalt concentration increased. But in view of extraction factor, the extraction factors decreased as the initial cobalt concentration increased. This is because at this pH, the amounts of cobaltous ion extracted were limited at about 1,000 ppm according to the chemical equilibrium. Referring to Equation (4.2), the equilibrium constant decreased as the initial cobalt concentration increased. Therefore, the amount of cobaltous ion remained in the raffinate increased as the increasing initail concentration of cobaltous ion. As a consequence, the extraction factor decreased as the initial cocentration of cobaltous ion increased.

However, in the stripping process, the amounts of cobalt recovered were very low. This is because the crystalline cobalt oxalates were accumulated at the shellside of fibers due to its insolubility in the aqueous strip solution. Therefore, in comparison with the batch experiment using oxalic acid solution as a strip solution, the extraction factor at 10,000 ppm of cobaltous ion in feed solution was increased approximately twice due to the continuous flowing of feed solution for 5 hours. Whereas the recovery factor was very low owing to the accumulation of cobalt oxalates on hollow fibers.

2. The Types of Strip Solution

Hydrochloric acid solutions – as strip solutions – would then be studied since the cobalt chloride was miscible in the acidic solution. In order to compare with oxalic acid, the experiments using hydrochloric acid as strip solutions with the same acidicity were carried out. The initial cobaltous-ion concentrations were 5,000 and 10,000 ppm with pH about 4. Again, at the same cobaltous-ion concentration of

10,000 ppm; the feed solutions with different acidicities, i.e. pH about 4 and 6, were studied. The experimental conditions and the analyzed data were shown in Table 4-3.

Table 4-3 The experimental conditions and the analyzed data for using hydrochloric acid as strip solutions in HFSLM experiments

Conditions / Data	pH about 4		pH about 6
	5,000 ppm	10,000 ppm	10,000 ppm
Initial pH of feed solution	3.89	3.55	6.98
Initial pH of strip solution	1.44	1.42	1.40
[Co^{2+}] extracted (ppm)	1,070	1,266	2,537
Extraction factor (%)	21.53	11.31	21.23
[Co^{2+}] recovered (ppm)	692.50	697.85	1,367.30
Recovery factor (%)	13.94	6.24	11.44
Difference in [Co^{2+}] (%)	7.60	5.08	9.74
Difference in [H^+] (%)	-0.88	-3.43	1.88

These experiments confirmed the effects of initial cobalt concentration that at the same pH, the extraction factor decreased as the initial concentration of cobaltous ion in feed solution increased because of the equilibrium of reaction. Furthermore, it was seen clearly that the recovery factors depended mainly on the extraction factors; that is, about half of the cobaltous ions which were extracted from the feed solutions were recovered from the liquid membrane by using hydrochloric acid solution. Some amount of cobaltous ions remained in the liquid membranes owning to the limitation of chemical equilibrium.

Referring to the results in the batch experiments, the systems with oxalic acid and with HCl performed similarly. In contrast, a little amount of cobalt was recovered in strip solutions as using oxalic acid. Furthermore, the accumulation of crystalline cobalt oxalates at the shellside of fibers were high because the cobaltous ions that diffused through the liquid membrane formed the crystalline cobalt oxalates which were not miscible in the oxalic acid solution. Consequently, the membrane clogging had occurred at the shellside which made the hollow fiber module reddish. Therefore, the oxalic acid was not suitable to be used as a strip solution in this system.

3. Effects of Acidity of Feed Solution

The feed solutions of 10,000 ppm cobaltous ion with two different pH values (about 4 and 6) were studied. The results were shown in Table 4-2 and 4-3 using oxalic acid and hydrochloric acid as strip solutions, respectively. Like the batch experiments; it was found that the extraction factor was increased as the pH of feed solution increased due to the increasing capacity of loading hydronium ions in feed solution. Therefore, the amount of cobaltous ion extracted increased as the amount of hydronium ion transferred increased resulting in higer extraction factor.

In comparison with the batch experiments using HCl as strip solutions, it was found that the extraction factor was enhanced four times at pH about 4, and it was enhanced twice at pH about 6 by the simultaneous extraction and stripping process.

Even though each experiment was carried out until the steady state was reached, the extraction did not accomplish. This suggested that the extraction not depend on the steady state. Moreover, as reaching the steady state, the amount of cobalt extracted and recovered became almost constant. Conversely, at the beginning of each experiment, i.e. high pH of feed solution the extraction and stripping factors were very high. That means if the pH of feed solution was still high throughout the experiment, the extraction factors and recovery factors would be high. Therefore, in the next experiment, it was predetermined that the pH of feed solution was kept constant at 6. The experimental conditions for this experiment are expressed below.

Feed solution:	5,000 ppm of cobaltous ion with pH 6.64
Strip solution:	Hydrochloric acid solution with pH 1.53
Volumetric flowrate:	500 ml/min
Basic solutions:	0.01M NaOH for the first 135 minutes, and 2M NaOH for the others

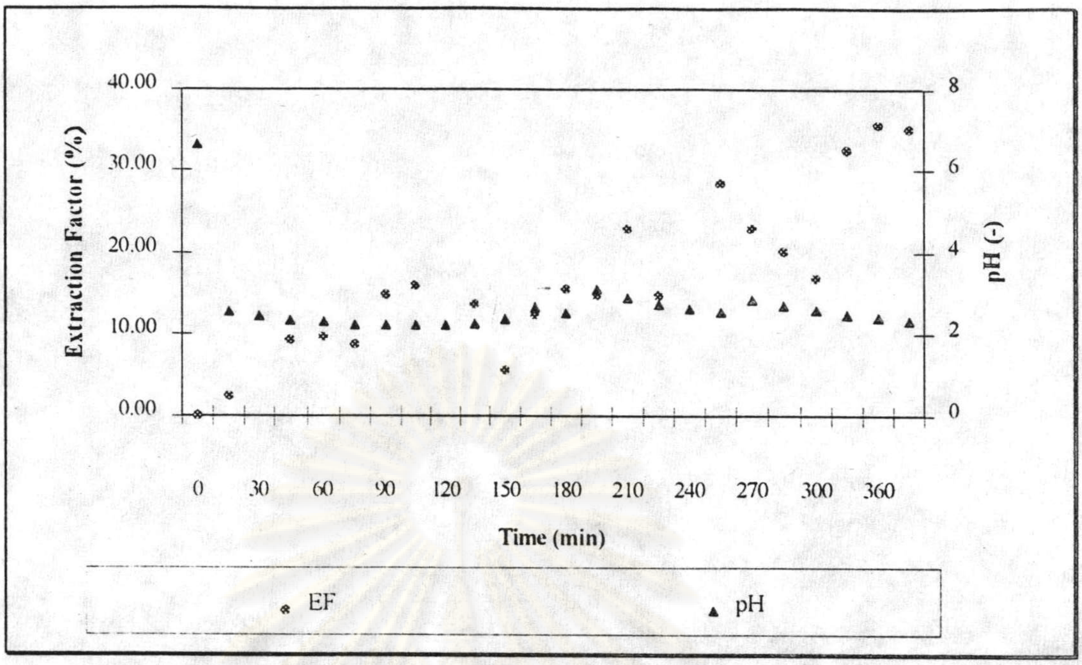

Figure 4-1 The extraction factors for the experiment on the pH of feed solution

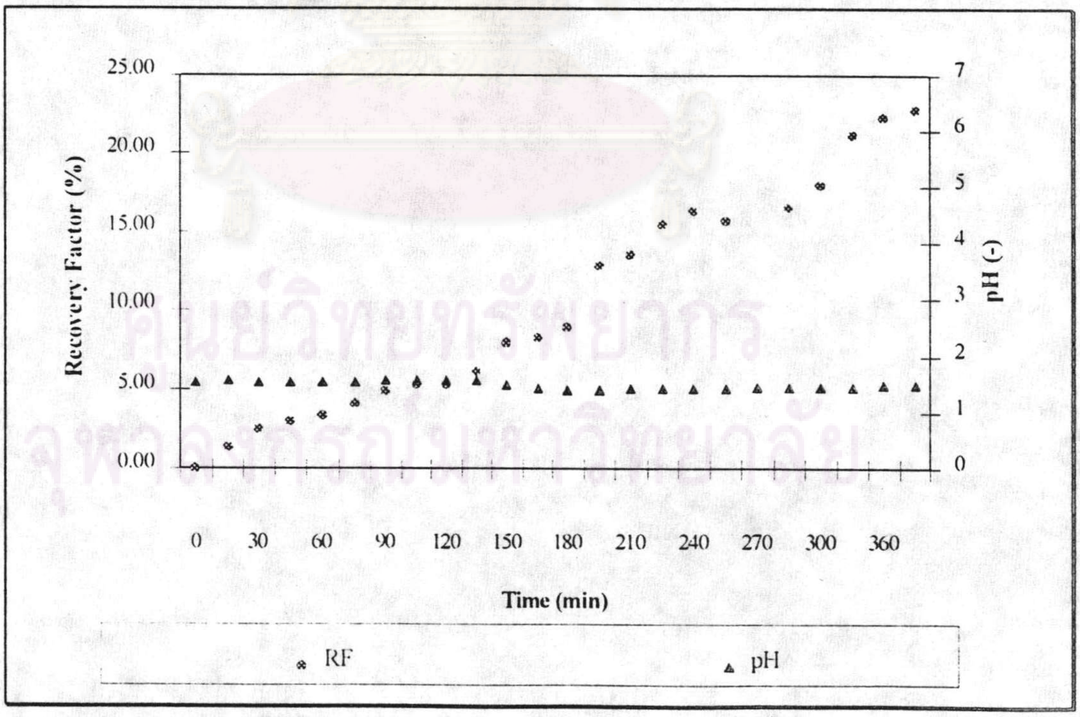

Figure 4-2 The recovery factors for the experiment on the pH of feed solution

The feed and the strip solutions were sampled periodically to measure the pH. Some amount of basic solution was added when the pH of feed solution dropped below 2.5. Whereas 10 ml of 0.01M HCl was added when the pH of strip solution exceeded 1.55. From this experiment it was found that both the extraction and the recovery factors increased as time passed due to the maintained pH of both feed and strip solution. Therefore, the extraction and stripping processes were not limited by the chemical equilibrium. Especially, in the extraction process – referring to Equation (4.1) – the forward reaction occurred continuously due to the disappearance of hydronium ions during the operation. In comparison with the experiments on HFSLM using HCl as strip solutions, it was found that the extraction and recovery factors were enhanced as the acidities, especially the pH of feed solution, were maintained.

However, the pH of feed solution dropped so largely and quickly that sodium hydroxide prepared was not concentrated enough to adjust the pH to 6. The amount of sodium hydroxide solution added should not so much; otherwise, the cobal concentration in feed solution might be diluted by the large amount of basic solution added. After the feed solution passed the liquid membrane module, the raffinate then loaded up with plenty of hydronium ions which made the acidity dropped largely. As a result, for a circulation-mode operation, the pH in feed reservoir dropped according to the drastically decreased pH of the circulated raffinate. If the raffinate was not circulated into the feed reservoir, the extraction would increase. Otherwise, a pH controller might be employed to adjust the pH in feed reservoir.

Therefore, the further experiments were once-through-mode operation for both feed and strip solutions. Still, the strip solutions were hydrochloric acid solutions with pH about 1.

4. The Mode of Operation

Alternatively, the experiments were carried out by once-through-mode operation. The pH of the exit feed solution was then adjusted to 6 by adding some amount of sodium hydroxide solution and, again, pumped into the tubeside of the hollow fiber in the same manner.

Experimental conditions

Volumetric flowrates:	500 ml/min
Feed soltuions:	5,000 ppm of cobaltous ion with pH about 6.5
Strip solutions:	Hydrochloric acid solution with pH about 1
Organic solutions:	20 V/V% D2EHPA in toluene

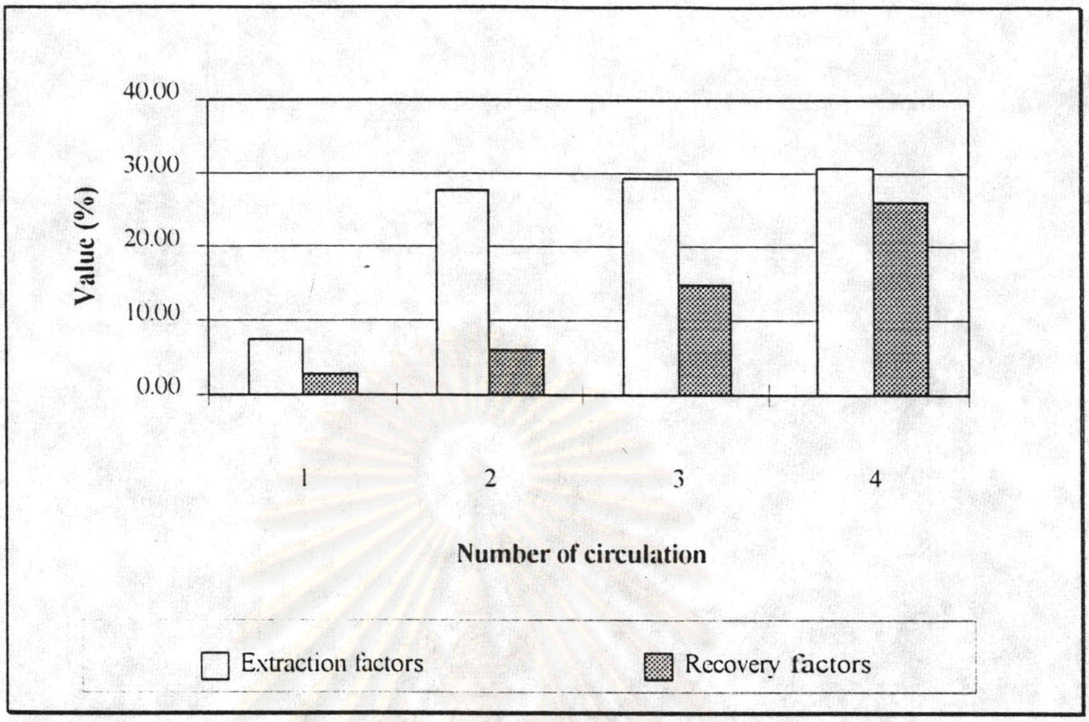

Figure 4-3 The effects of number of circulation at the volumetric flowrate of 500 ml/min

It was found that, in one-through-mode operation with repeated circulating the feed solution after its pH was adjusted to about 6, the extraction and the recovery factors increased as the increasing number of circulation. Furthermore, in the first pass through the module, the extraction factors were much greater than the recovery factors. Since the liquid membrane was ready for extracting cobaltous ions in the feed solution; as soon as the feed solution was brought into contact with the liquid membrane, the extraction of cobaltous ions occurred. However, the stripping reaction did not started simultaneously since the diffusion of metal ion-extractant complexes from interface i to interface ii took a period of time. In other words, if both feed and strip solutions was pumped simultaneously into the module countercurrently, both solutions would reach the half way of module at the same time. The extraction had already occurred as the feed solution passed that half way of the module, while the stripping would occurr as the strip solution passed the remained half way. Therefore, in the first pass through the module, the extraction reaction had occurred already while the stripping reaction just started up. But the next circulations, the stripping reaction occurred immediately since the liquid membrane already loaded up with the cobalt complex. For once-throgh-mode operation together with adjusting the pH of feed solution to about 6 for each circulation, 30% of initial cobalt was extracted and cobalt recovery could be high as 25% within the fourth circulation.

Along with effects of number of circulation, effects of volumetric flowrates of both feed and strip solution were studied.

5. Effects of Volumetric Flowrate

The experimental conditions were the same as those of studying effects of number of circulation, but the flowrates were varied from 100 ml/min, 100 ml/min with the circulated strip solution, and 500 ml/min The results were shown in Figure 4-4.

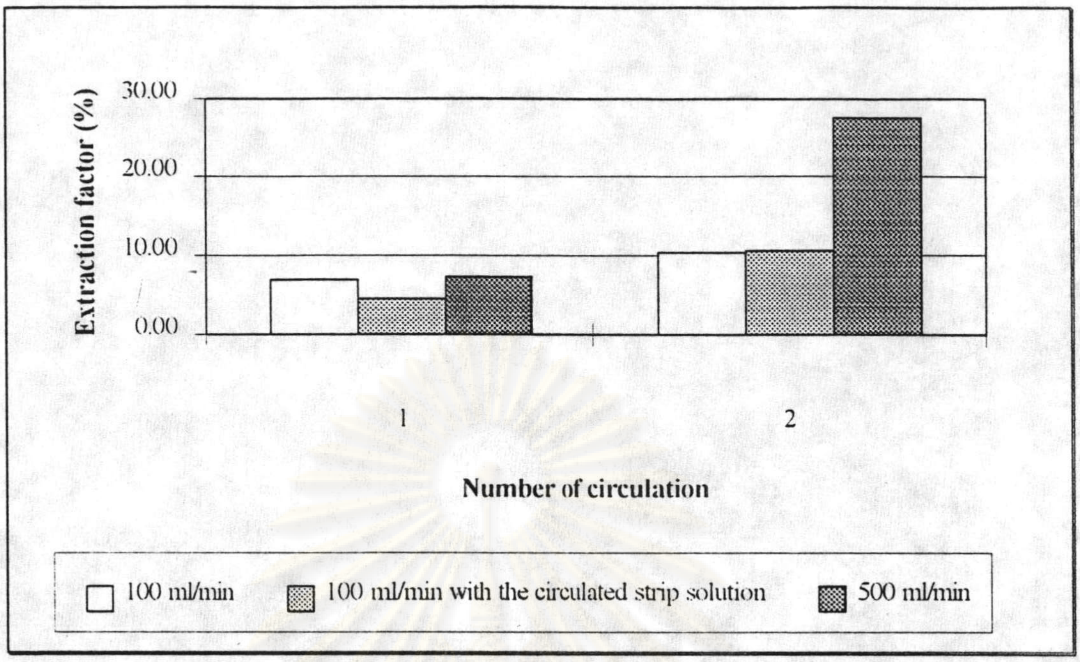

Figure 4-4 The extraction factors as a function of volumetric flowrate

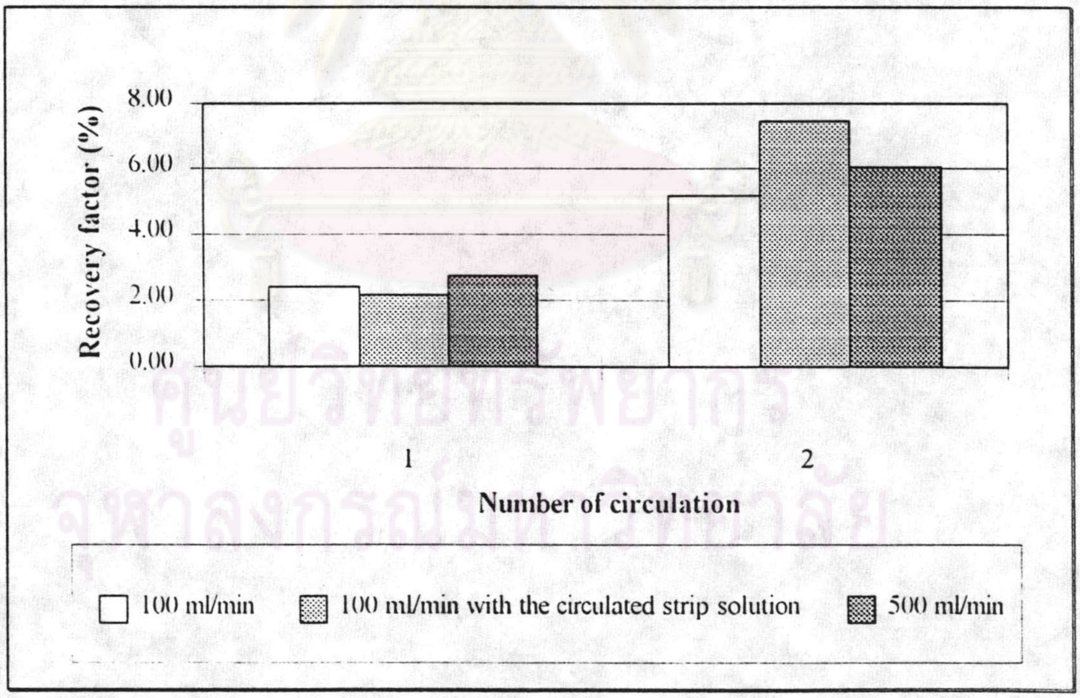

Figure 4-5 The recovery factors as a function of volumetric flowrate

It was found that in the first circulation, the extraction factors were not different significantly. But in the second circulation, as the flowrate increased from 100 to 500 ml/min, the extraction factor was enhanced approximately three times. That is as the volumetric flowrate increased, the amounts of cobaltous ion which were extracted and recovered increased. This is because the extraction reaction occurred mostly at the beginning of the module resulting in dropping of pH in feed solution. Then the reaction hardly occurred as the feed solution passed through the remained part of the module since the equilibrium was shifted along the flowing path of the module. Therefore, it was no use letting the raffinate remain in the module. Moreover, it was found that the circulated strip solution had no effects on extracting and stripping cobalt since this solution contained so much hydronium ions that the transfer of them did not affect the acidity of the strip solution.

6. The Effects of Extractant Concentration

Experimental conditions

Organic solutions: 10, 15, 20, and 25 V/V% D2EHPA in toluene

Feed solutions: 500 ppm with pH about 6.5

Strip solutions: Hydrochloric acid solution with pH about 1

Volumetric flowrate: 1,000 ml/min

Operating mode: Once-through mode

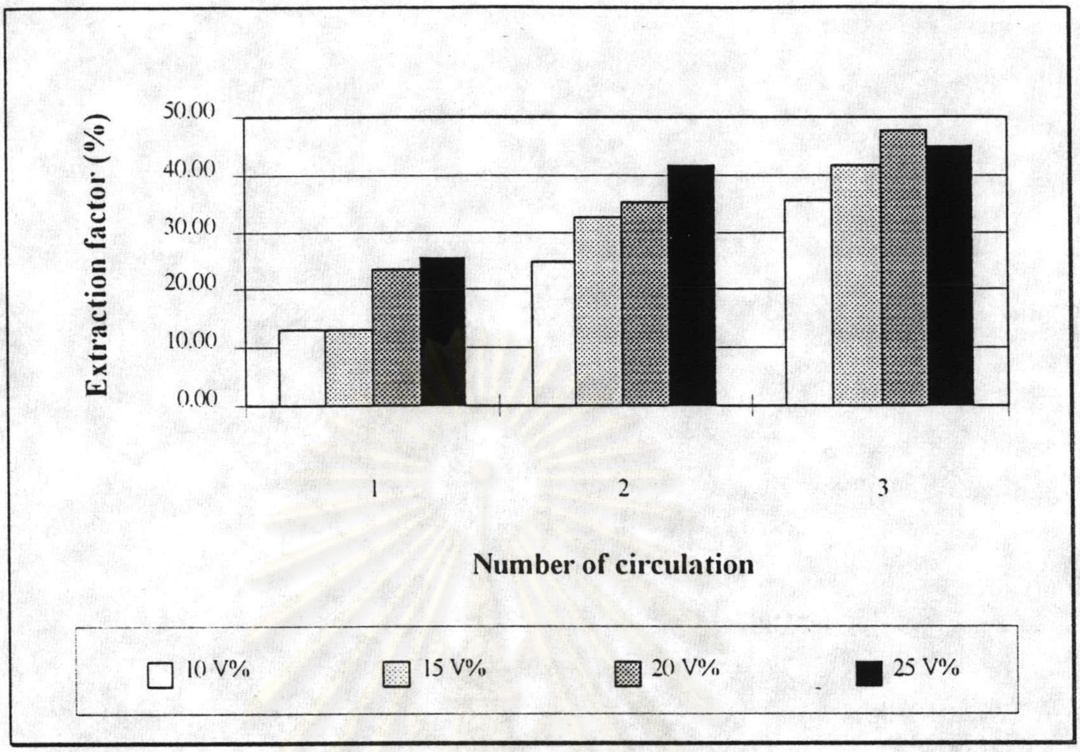

Figure 4-6 The extraction factors as a function of extractant concentration

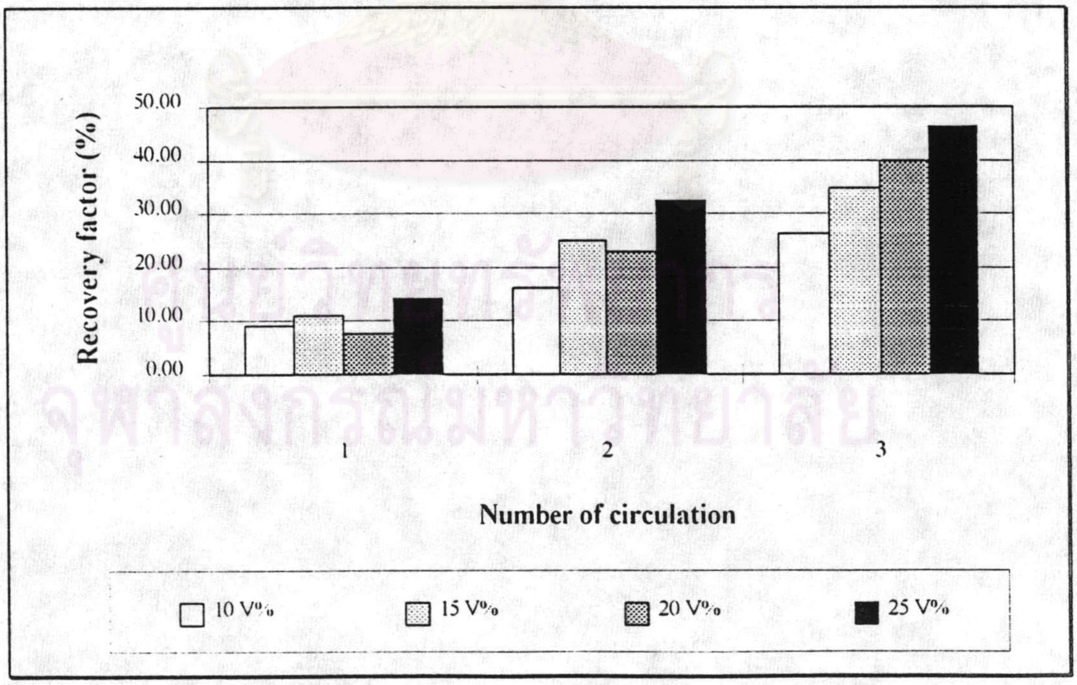

Figure 4-7 The recovery factors as a function of extractant concentration

It was found that the higher the concentration of the extractant, the larger the amount of cobalt extracted and recovered. Referring to Equation (4.1) and (4.2), since the concentration of extractant was increased, the forward reaction was enhanced resulting in increasing the equilibrium constant of extraction reaction. Also, the equilibrium constant of stripping reaction – referring to Equation (4.3) – was also enhanced. As a result, the rates of reaction at the interfaces were increased. Hence, the amounts of cobaltous ion extracted and recovered were enhanced as the increasing concentration of D2EHPA.

However, the increasing concentration of D2EHPA has limitation. Since D2EHPA is a branched, large molecule – referring to Equation (3.1), when a metal ion forms the complex with two molecules of D2EHPA, the molecule is very large. As a consequence, the molecular diffusion is abstructed by the molecules of D2EHPA.

7. Effects of Types of Solvent

Experimental conditions

Organic solutions: 20, and 25 V% D2EHPA in n-dodecane

Cobaltous ion concentration: 500 ppm, approximately

Initial pH of feed solution: 6.5, approximately

Initial pH of strip solution: 1, approximately

Volumetric flowrate: 1,000 ml/min

Operating mode: Once-through mode

The extraction factors and the recovery factors were shown in Figure 4-8 and Figure 4-9, respectively. It was noted that toluene is abbreviated to T and n-dodecane is abbrievated to D.

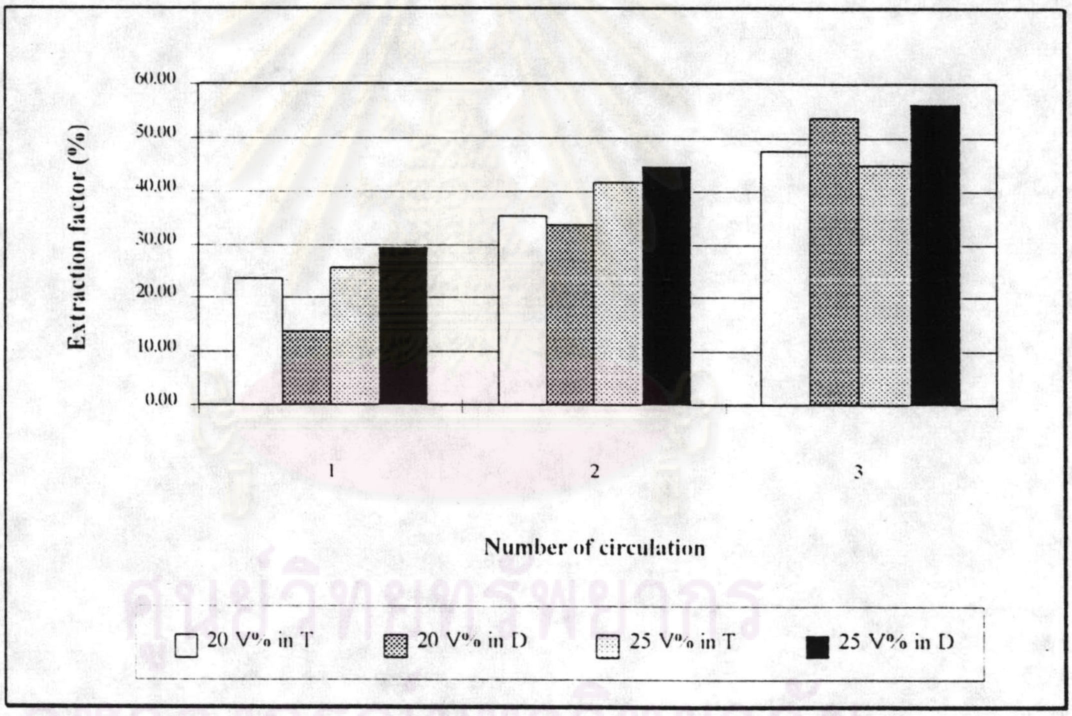

Figure 4-8 The extraction factors as a function of the types of solvent

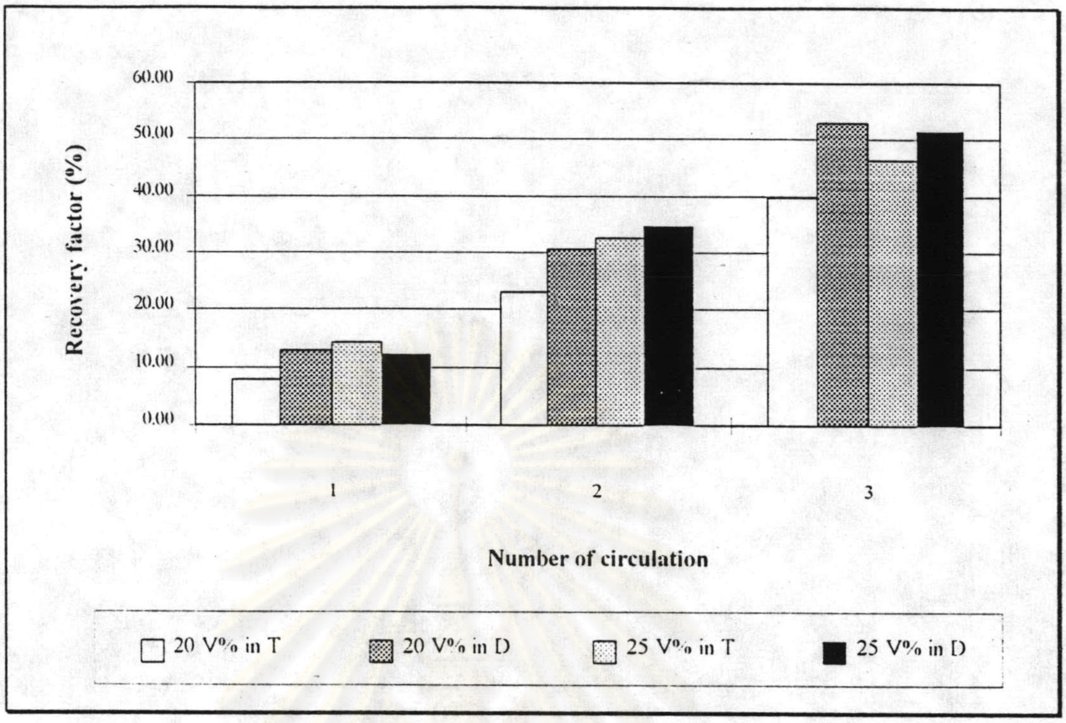

Figure 4-9 The recovery factors as a function of the types of solvent

It was found that, at the same extractant concentration, n-dodecane – as a solvent – performed better than toluene. This is because at 25 °C n-dodecane was insoluble in water whereas toluene was soluble in water as 0.0492 wt% [Stephen and Stephen 1979]. Moreover, the viscosity of n-dodecane was much higher than that of toluene; that is, 1.35 cp for n-dodecane and 0.558 cp for toluene [Weast, 1968]. Hence, the losses of solvent and extractant due to the shear stress and the solubility in the mobile phases when n-dodecane was used as solvent were less than those when toluene was used, resulting in longer lifetime of liquid membrane.