

Separation of Co(II) and Ni(II) from thiocyanate media by hollow fiber supported liquid membrane containing Alamine300 as carrier - investigation on polarity of diluent and membrane stability

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Abstract—The separation of cobalt(II) and nickel(II) ions by HFSLM has been presented. The feed solution is 0.5 M thiocyanate containing 300 ppm each of cobalt(II) and nickel(II) ions, whereas extractant is Alamine300 and the stripping solution is ammonia. Cobalt(II) is more preferable with Alamine300 than nickel(II). The effects of pH, Alamine300 concentration and ammonia concentration were investigated. Seven diluents were used: hexane, decanol, chlorobenzene, benzene, dichloromethane, ethylene dichloride and chloroform with different polarity indexes, from 0.1–4.1. Nickel(II) ion which is unpreferable with Alamine300 was used as a tracer to determine the membrane stability. The polarity of the diluents was found to be the main factor influencing the extraction performance and stability of a liquid membrane. The decreasing of polarity of the diluent can prolong the membrane stability, but the percentages of extraction and stripping decreased. The longest lifetime, 200 minutes, was obtained by using hexane as a diluent with the polarity index of 0.1.

Key words: Cobalt, Nickel, Hollow Fiber, Liquid Membrane, Stability

INTRODUCTION

Selective separation of cobalt(II) and nickel(II) from industrial waste solutions is required in hydrometallurgical processing because of their superior properties and the similar physico-chemical properties of these metals [1,2]. It is impossible to separate the cobalt(II)-nickel(II) pair in a simple and economical way by using a well-established separation processes such as crystallization, precipitation and oxidation.

Solvent extraction seems to be the most efficient method for separation of Co(II) and Ni(II) ions from solutions, including leach liquors [3–5]. Generally, cobalt(II) is preferentially removed with a suitable carrier, leaving nickel(II) behind. However, solvent extraction has some limitations that large inventory of solvent is required and high capital cost [6].

Liquid membranes have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently, since they combine the process of extraction and stripping in a single unit operation. The extraction chemistry is basically the same as that found in solvent extraction, but the transport is governed by kinetic rather than equilibrium parameters, that is, it is governed by a non-equilibrium mass transfer [7]. The use of liquid membranes containing specific metal ion carriers offers an alternative method to the solvent extraction processes for selective separation and concentration of the metal ions from aqueous dilute solutions. Generally, liquid membranes come either in an

emulsion or a supported form. Emulsion liquid membrane (ELM) has a large transport area with a thin membrane [8]. Hence there is a fast solute extraction. There have been some previous studies on cobalt(II) and nickel(II) separation by ELM [9–11]. However, ELM is very difficult to commercialize and it suffers from swelling instability of the inner phase [12]. According to supported liquid membrane, there are several types of supported liquid membrane (SLM), including flat sheet (FSSLM), spiral (SPSLM), and hollow fiber (HFSLM). For these types, the organic phase or liquid membrane was embedded in the pores of the supporting material by capillary forces [13]. A. Sürücü et al. [14,15] studied the separation of cobalt(II) and nickel(II) by flat sheet supported liquid membrane (FSSLM) to remove metals from wastewaters. From the results, the selective separation of cobalt(II) from the solutions containing cobalt and nickel was achieved. Nevertheless, FSSLM can be utilized for laboratory scale and cannot be scaled up to industrial level because it can be operated only in a batch system. Moreover, FSSLM has low effective surface area and stability [16].

Of all the aforementioned method, a hollow fiber supported liquid membrane (HFSLM) is the most promising. It possesses several advantages over the traditional solvent extraction method, such as simultaneous one-step extraction and stripping, high selectivity, low extractant (carrier) and energy consumption, low capital and operating cost, large surface area to volume ratio, high mass transfer rate, no flooding, and easy to scale-up [17–19]. For these reasons, HFSLM has been widely investigated for application in various fields: for instance, water treatment [20], and recovery of precious metals [21], rare earth metals [22], radioactive metals [23] and biochemical substance [24]. However, most of the researches on liquid

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membranes have focused on the extraction of metal ions, the mechanisms behind the extraction, the selection of proper carriers, or the best conditions such as pH, flow rate, and concentration of feed and stripping solutions.

Despite its many advantages, the application of SLM on a larger scale is still very limited due to the insufficient membrane stability [25]. This application is, however, strongly conditioned by its actual life-time. Therefore, the key to successful application of SLM is to achieve the extended membrane life-time. It is well known that the type of solvent has a dominant influence on the extraction. The factors influencing the stability and life-time of SLM have been studied extensively [26-28] and include the solubility of the organic solvent in the aqueous phase, emulsion formation induced by surface shear [29], gelling of the immobilized liquid and the application of a protective coating [25]. These techniques have the potential to reduce flux unless carefully optimized.

This work is not only to investigate the separation of nickel(II) and cobalt(II) by a hollow fiber supported liquid membrane (HFSLM), but also to study the prolongation of liquid membrane stability. Seven diluents were chosen: hexane decanol, chlorobenzene, benzene, dichloromethane, ethylene dichloride and chloroform with different polarity index, from 0.1-4.1. The effect of polarity index was considered and we focused to the stability and extractability of hollow fiber supported liquid membrane system.

BACKGROUND THEORY

1. Hollow Fiber Supported Liquid Membrane (HFSLM)

The liquid membrane system consists of an aqueous feed containing metal ions and a stripping solution. The liquid membrane is between the feed and stripping phases, and contains an organic carrier which reacts with the metal ions as shown in Fig. 1. The hollow fiber module contains many hollow fibers aligned horizontally, with the liquid membrane embedded inside them. The organic phase fills the pores of the fibers by capillary force [13].

2. Separation Mechanism

The performance of liquid membrane is the selectivity to extract only the target metal. In this work, the feed solution contains two kinds of metal ion: cobalt(II) and nickel(II). The selectivity is controlled by the carrier and form of metal specie [30]. To separate cobalt(II) ion from nickel(II) ion, 0.5 M ammonium thiocyanate was added to the feed solution [31]. In acidic feed solution, cobalt(II) ions react with ammonium thiocyanate, NH_4SCN , to form the tetrahedral cobalt (II) thiocyanate complex, $\text{Co}(\text{SCN})_4^{2-}$, whereas in case

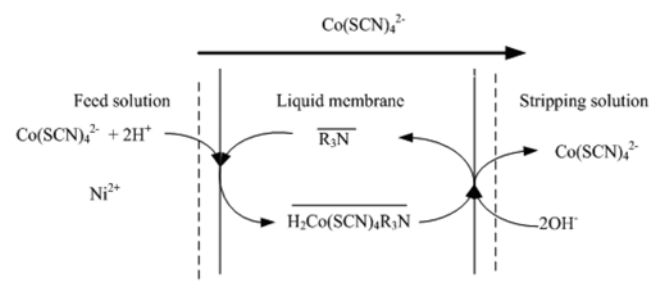


Fig. 1. Transport scheme of extraction and stripping of cobalt in a liquid membrane process using Alamine300 as a carrier.

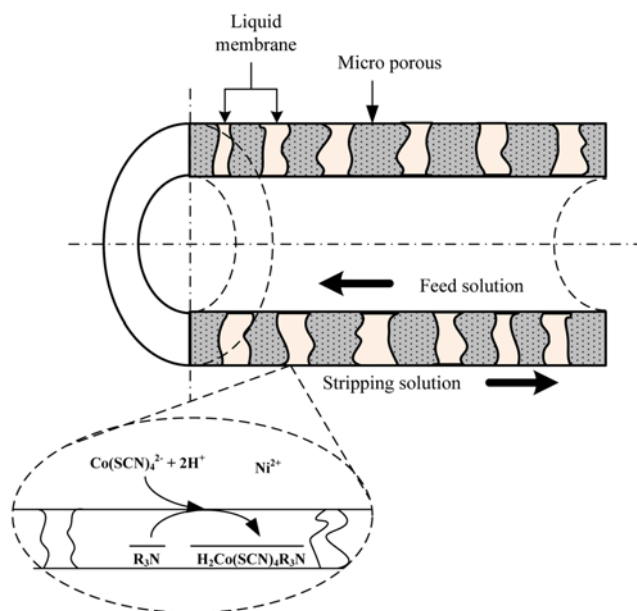


Fig. 2. Flow pattern in the hollow fiber supported liquid membrane module.

of nickel(II) ions they hardly form the thiocyanate complex [32]. In addition, cobalt(II) is extracted as the tetrahedral anion, $\text{Co}(\text{SCN})_4^{2-}$, while nickel(II) forms an octahedral complex, $\text{Ni}(\text{SCN})(\text{H}_2\text{O})_5^{2+}$ [33]. Therefore, cobalt(II) is more preferably extracted with Alamine300 than nickel(II) into the liquid membrane phase, and the selectivity of cobalt(II) with respect to nickel(II) was reasonably high. Alamine300 is dissolved in organic diluent as a liquid membrane which is embedded by capillary force in the hydrophobic microporous hollow fiber module. A schematic diagram explaining the coupled transport between cobalt(II) ions in the feed solution and hydrogen ions in the stripping solution is shown in Fig. 2. $\text{Co}(\text{SCN})_4^{2-}$ reacts with Alamine300 (R_3N) at the interface between the feed and liquid membrane to form complex species according to Eq. (1):



After that, the complex species, $\text{H}_2\text{Co}(\text{SCN})_4\text{R}_3\text{N}$, diffuse across the organic liquid membrane to react with the stripping reagent, NH_3 , at the opposite interface. Then, cobalt(II) ions are stripped into the stripping phase by Eq. (2) and $\text{H}_2\text{Co}(\text{SCN})_4\text{R}_3\text{N}$ releases R_3N and $\text{Co}(\text{SCN})_4^{2-}$ to the liquid membrane phase and stripping phase, respectively. Finally, R_3N diffuses back to reacts with $\text{Co}(\text{SCN})_4^{2-}$ at the feed phase, in a new cycle where the cobalt(II) ion can once again be extracted and stripped.

EXPERIMENTAL

1. Feed and Stripping Solution Preparation

The feed solution was made by dissolving $\text{Co}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ in 0.5 M thiocyanate solution [31]. 300 ppm of cobalt(II) and nickel(II) were prepared. Hydrochloric acid was used to adjust pH, and acetic acid/sodium acetate buffer was added to maintain the desired feed pH. Ammonia (NH_3) solution was used as the stripping phase.

Table 1. Properties of the hollow fiber module [34]

Properties	Description
Materials	Polypropylene
Fiber i.d.	240 mm
Fiber o.d.	300 mm
Pore size	0.05 mm
Porosity	30%
Contact area	1.39 m ²
Area per unit volume	29.3 cm ² /cm ³
Module diameters	6.3 cm
Module length	20.3 cm

2. Liquid Membrane Preparation

The extractant, Alamine300 (tri-n-octylamine), was dissolved in benzene as the diluent. However, in this work, the diluent was changed from benzene to several diluents: hexane decanol, chlorobenzene, benzene, dichloromethane, ethylene dichloride and chloroform. All chemicals were analytical grade and purchased from Merck Co. Ltd.

3. Apparatus

- A Liqui-Cel® Laboratory Liquid/Liquid Extraction System (composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges) was used.

- A Liqui-Cel® Extra-Flow module (Celgard, Charlotte, NC; formerly Hoechst Celanese) was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into fabric and wrapped around a central tube feeder that supplies the shell-side fluid. The woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The properties of the hollow fiber module are shown in Table 1 [34]. The fibers are potted into a solvent-resistant polyethylene tube sheet with a polypropylene shell casing.

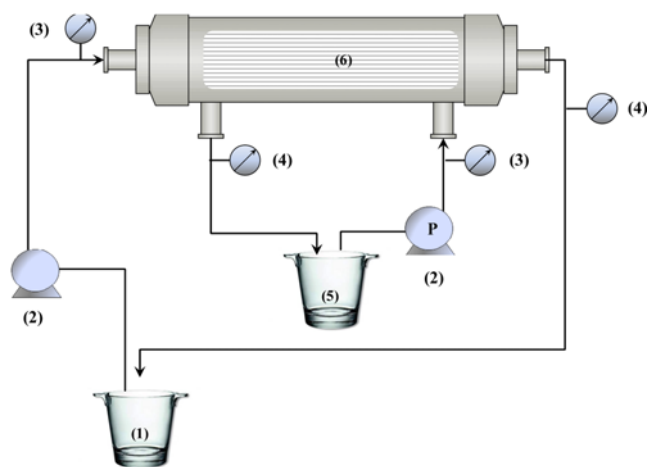
- Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)

4. Procedure

The organic solution (the mixture between Alamine300 and a diluent) was circulated in the tube and shell sides of the hollow fiber membrane for 20 minutes in order to become embedded in the pores. After that, the experiment was started by flowing feed solution into the tube side. Simultaneously, stripping solution was countercurrently pumped into the shell side, and circulating mode operation was performed. A schematic illustration of the process is shown in Fig. 3. The flow rates of both the feed and stripping solutions were 100 mL/min. To ensure that the system was at steady state, after 90 minutes the samples (2 mL) were taken at the final time from the raffinate and stripping phases and the concentrations of cobalt(II) and nickel(II) ions were measured by ICP-AES. The percentages of extraction and stripping were calculated by using Eqs. (3) and (4), respectively.

$$\% \text{extraction} = \frac{C_{i,\text{feed}} - C_{i,\text{raf}}}{C_{i,\text{feed}}} \times 100 \quad (3)$$

$$\% \text{stripping} = \frac{C_{i,\text{st}}}{C_{i,\text{feed}}} \times 100 \quad (4)$$

**Fig. 3. Schematic diagram of the experimental set-up of a hollow fiber supported liquid membrane process.**

- | | |
|---------------------------|----------------------------|
| (1) Feed reservoir | (4) Outlet pressure gauges |
| (2) Gear pumps | (5) Strip reservoir |
| (3) Inlet pressure gauges | (6) hollow fiber module |

where $C_{i,\text{feed}}$, $C_{i,\text{raf}}$ and $C_{i,\text{st}}$ are the concentrations of feed, raffinate and outlet stripping of component i , respectively.

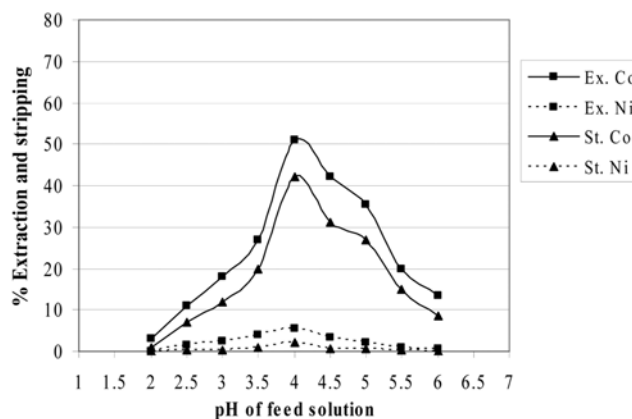
5. Analytical Instrument

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) Perkin Elmer, Optima 4300 DV) was used to determine the concentrations of cobalt(II) and nickel(II) ions. The wavelengths for cobalt(II) and nickel(II) ions are 228.616 nm and 231.604 nm, respectively. The method was proposed by Henk J. van de Wiel [35].

RESULTS AND DISCUSSION

1. Effect of pH of the Feed Solution

The pH of the feed solution is a main factor governing the extraction behavior. The effect of pH of feed solution on the percentage of cobalt(II) extraction and stripping was examined in the range of

**Fig. 4. The influence of pH of feed solution on the percentages of extraction and stripping: 2% by volume of Alamine300, 300 ppm Co(II) and Ni(II) in the feed solution, and 0.5 M ammonia in the stripping solution. Flow rates of the feed and stripping solutions were 100 mL/min.**

2.0-6.0, as shown in Fig. 4. The pH of feed solution was adjusted by using acetic acid/sodium acetate buffer. When the pH of the feed solution decreased from 6.0 to 4.0, the percentage of cobalt(II) extraction and stripping increased due to the higher availability of protons for the reaction in Eq. (1). However, when the pH of the feed solution further decreased from 4.0 to 2.0, the percentage of cobalt(II) extraction and stripping decreased. This can be explained by the fact that the concentration of protons in the feed solution will form a species, $H_2Co(SCN)_4$, which may not ionize completely to form a complex with Alamine300. Hence, the extraction will decrease with the increase in acid concentration. Therefore, the maximum cobalt(II) extraction occurred at pH 4.0 and it was used in the following experiments.

2. Effect of Alamine300 Concentration

The carrier, Alamine300, concentration in the liquid membrane plays a vital role in the overall extraction behavior. To study this effect, the concentration of Alamine300 in benzene was varied in the range of 1-5% by volume while the other operating conditions were constant. The results are shown in Fig. 5. When Alamine300 concentration was increased from 1-5% by volume, the percentage of the extraction and stripping of cobalt(II) ions rose abruptly. Nevertheless, when the Alamine300 concentration exceeded 5% by volume, both extraction and stripping efficiency slightly decreased because the increase of membrane phase viscosity as the extractant concentration increases in this phase. Higher viscosity generates a lower diffusion speed of the species and affects the mass transfer process [36]. As a result, a concentration of 5% by volume was selected as the optimal carrier concentration.

3. Effect of Ammonia Concentration in the Stripping Solution

Another parameter that affects the transport of cobalt(II) ion is the stripping agent and its concentration. Since the extraction and stripping reactions in SLM are performed simultaneously, it is important to explore the effect of reagent concentration in the stripping solution in order to enhance effective cobalt(II) transport by making efficient stripping reaction at the interface of the membrane and the stripping solution [37].

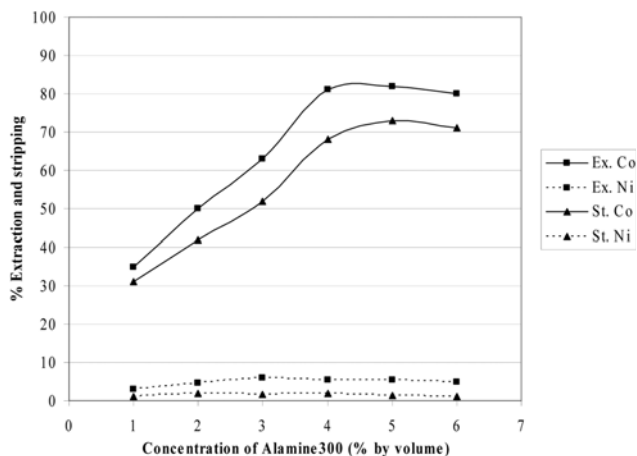


Fig. 5. The influence of Alamine300 concentration in benzene on the percentages of extraction and stripping: pH of feed solution was 4.0, 300 ppm Co(II) and Ni(II) in the feed solution, and 0.5 M ammonia in the stripping solution. Flow rates of the feed and stripping solutions were 100 mL/min.

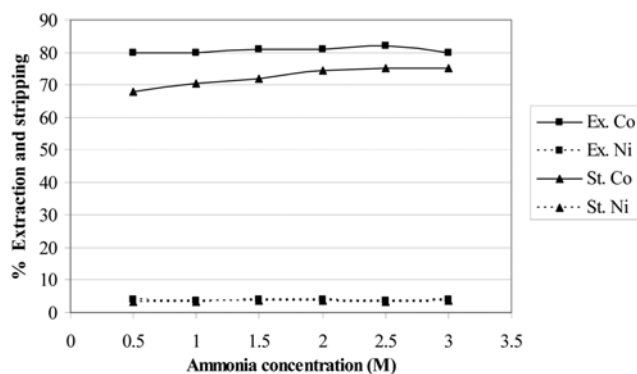


Fig. 6. The influence of concentration of ammonia in the stripping solution on the percentages of extraction and stripping: pH of feed solution was 4.0, 5% by volume of Alamine300 in benzene, 300 ppm Co(II) and Ni(II) in the feed solution and flow rates of the feed and stripping solutions were 100 mL/min.

The stripping reaction equation is shown in Eq. (2). Ammonia concentration in the stripping solution ranged from 0.5-3.0 M; the results obtained are shown in Fig. 6. When ammonia concentration increased, the percentages of extraction were practically constant but percentages of stripping slightly increased. The stripping of cobalt(II) ions by Alamine300 was expressed in Eq. (2). According to Le Chatelier's principle, as the number of hydroxide ions increases, more cobalt(II) ions are stripped into the stripping solution. However, when the ammonia concentrations are higher than 2.5 M, the percentage of stripping is constant due to the limitation of mass transfer area of hollow fiber [38].

4. Effect of Concentration of Cobalt and Nickel in Feed Solution

The concentrations of cobalt(II) and Nickel(II) in the feed solution were varied in the range of 100 to 500 ppm in the feed solution. Fig. 7 indicates that an increase in the concentration of cobalt(II) and nickel(II) ions decreases the percentages of extraction and strip-

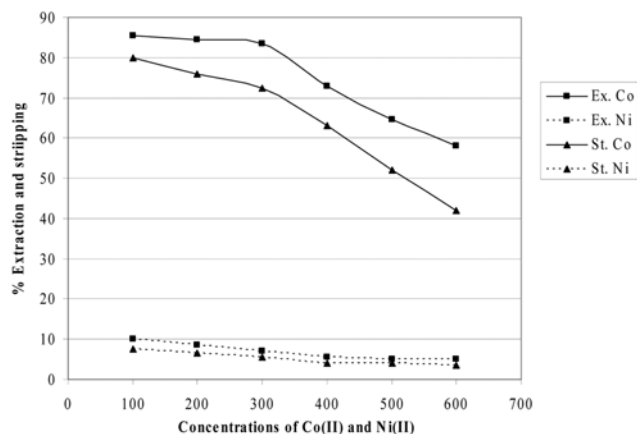


Fig. 7. The influence of concentrations of cobalt(II) and nickel(II) in feed solution on the percentages of extraction and stripping: pH of feed solution was 4.0, 5% by volume of Alamine300 in benzene, 2.5 M ammonia in the stripping solution and flow rates of the feed and stripping solutions were 100 mL/min.

ping. However, it does not mean that the extractability decreases with the increasing of metal concentration in feed solution. When the concentration of metal ion in the feed solution is higher, the amount of metal ion that transport across liquid membrane must increase. It can be checked by the 'average metal ion flux' across the liquid membrane by Eq. (5).

$$\text{Flux} = \frac{C_{i, \text{st}} V}{A t} \quad (5)$$

where $C_{i, \text{st}}$ is the concentration of component i in the stripping tank at final time, V is the volume of stripping tank, A is the mass transfer area and t is the operating time.

The flux of cobalt(II) and Nickel(II) is shown in Fig. 8; it is observed that the increase in the concentration of feed solution from 100 to 500 ppm generally increased the metal flux. The results correspond to the theoretical model proposed by Rovira and Sastre [39] that the flux of metal ions in a supported liquid membrane is proportional to the concentration of metal ions in the feed solution when the concentration is low. It should be noted that a measurement in percentage value is not appropriate when the concentration of the feed solution increased.

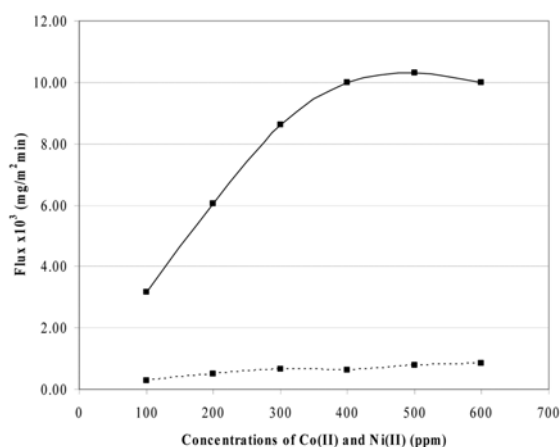


Fig. 8. The relationship between the concentrations of cobalt(II) and nickel(II) in feed solution and the separation flux: pH of feed solution was 4.0, 5% by volume of Alamine300 in benzene, 2.5 M ammonia in the stripping solution and flow rates of the feed and stripping solutions were 100 mL/min.

5. Selectivity

The experimental data of cobalt(II) and nickel(II) separation from binary mixtures are shown in 1-4. Clearly, there is a significantly greater cobalt extraction than nickel under these conditions. The selectivity (α) is very important for the multi-component separation, which can be calculated by Eq. (6).

$$\alpha = \frac{\text{Concentration of desired product in stripping solution}}{\text{Concentration of undesired product in stripping solution}} \quad (6)$$

The values of selectivity with different variables are shown in Table 2. The data indicate that some conditions bring a very high selectivity, e.g., at pH of 5.5 or 6.0 and low concentration of Alamine300. However, these conditions are unusable because the percentages of stripping are not high enough. The effective conditions should provide both high mass transfer efficiency and high selectivity. Therefore, the recommended conditions are pH feed of 4.0, 3-6% by volume of Alamine300, 2 M ammonia in stripping phase and 400 ppm each of cobalt(II) and nickel(II) in the feed solution.

6. Effect of Polarity of Diluent and Investigation of Liquid Membrane Stability

Organic diluents influence the performance of liquid membrane systems. The role of the diluent is not only to improve the physical properties of the liquid membrane system, but also to improve the interaction product. This needs to be taken into account in the choice of diluents [36]. As known from liquid membrane theory, the main factor of liquid membrane stability is the type of diluent [40,41]. In

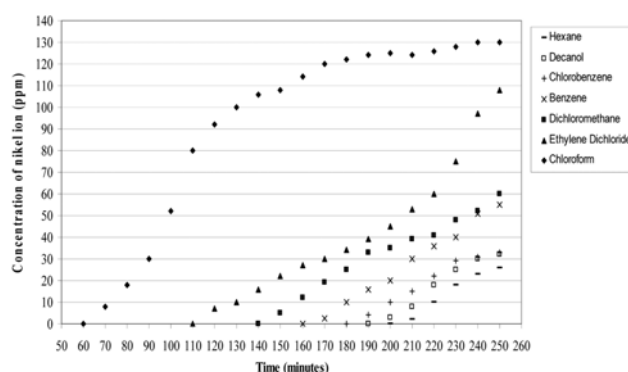


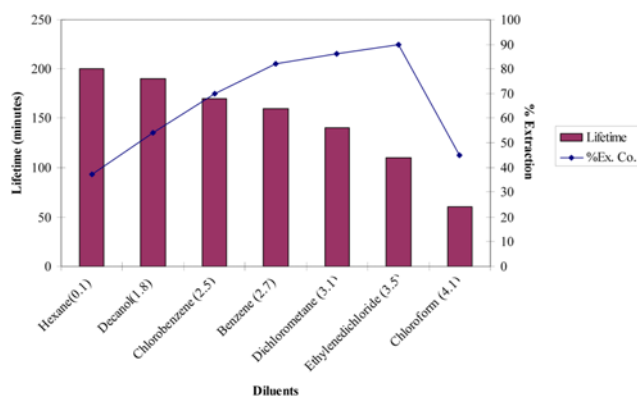
Fig. 9. Relationship between type of diluent and the concentration of nickel ion in stripping solution at different times.

Table 2. Values of selectivity for different conditions compared to the percentage of stripping

Feed solution pH	% Strip of Co(II)	$\alpha_{\text{Co}}(-)$	$\alpha_{\text{Ni}}(-)$	Extractant conc. (% volume)	% Strip of Co(II)	$\alpha_{\text{Co}}(-)$	$\alpha_{\text{Ni}}(-)$	NH ₃ conc. (M)	% Strip of Co(II)	$\alpha_{\text{Co}}(-)$	$\alpha_{\text{Ni}}(-)$	Feed conc. (ppm)	% Strip of Co(II)	$\alpha_{\text{Co}}(-)$	$\alpha_{\text{Ni}}(-)$
2.0	0.8	8.0	0.125	1.0	31.1	31.0	0.032	0.5	73.4	24.3	0.041	100	79.4	10.6	0.093
2.5	7.0	35.0	0.028	2.0	42.3	21.0	0.047	1.0	74.5	21.3	0.046	200	76.0	11.6	0.085
3.0	12.1	60.0	0.017	3.0	52.5	32.5	0.031	1.5	75.8	19.0	0.052	300	72.5	13.1	0.075
3.5	20.0	20.0	0.05	4.0	68.0	34.0	0.029	2.0	77.3	25.8	0.038	400	63.0	15.7	0.063
4.0	42.3	21.0	0.047	5.0	73.4	52.1	0.019	2.5	78.0	17.3	0.057	500	52.2	13.0	0.076
4.5	31.2	62.0	0.016	6.0	71.0	71.0	0.014	3.0	79.2	14.3	0.069	600	41.7	12.0	0.083
5.0	27.0	54.0	0.018												
5.5	14.8	75.0	0.013												
6.0	8.5	85.0	0.011												

Table 3. Lifetime and performance of liquid membrane with diluents different polarities

Diluents	Hexane	Decanol	Chlorobenzene	Benzene	Dichloromethane	Ethylendichloride	Chloroform
Polarity (–)	0.1	1.8	2.5	2.7	3.1	3.5	4.1
Lifetime(min)	200	190	170	160	140	110	60
%Extraction	37	57	70	82	86	90	45
%Stripping	28	42	63	75	76	83	30

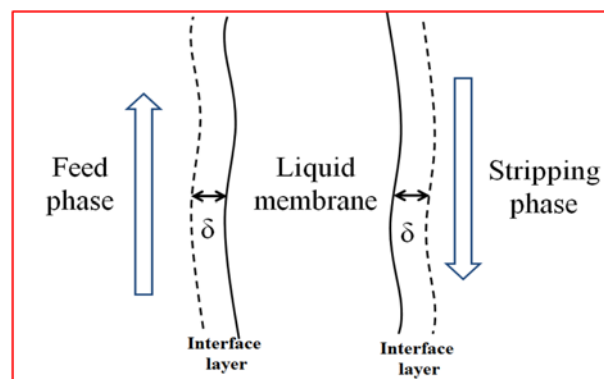
**Fig. 10. The relationship between the polarity of diluents and the percentage of extraction.**

this study, several diluents with different polarity indexes were chosen as follows: hexane, 0.1; decanol, 1.8; chlorobenzene, 2.5; benzene, 2.7; dichloromethane, 3.1; ethylene dichloride, 3.5; chloroform, 4.1 [42]. The effects of the polarity of these diluents on the lifetime of liquid membrane as well as the percentage of extraction and stripping of cobalt(II) ions were investigated.

The optimum conditions from 1-3 were used in these experiments. Because nickel(II) ion was rejected in the feed solution, we can use it as a tracer to determine the membrane stability by the fact that when nickel(II) ion is detected in the stripping side, it means that liquid membrane has been damaged and leaked out from the hollow fiber porous because nickel(II) ion were able to pass through the pores from the feed side to the stripping side.

The dependence of diluents on the stability was determined and shown in Fig. 9 in the order of hexane>decanol>chlorobenzene>benzene>dichloromethane>ethylendichloride>chloroform. The correlation between membrane lifetime and percentages of extraction and stripping with different polarity diluents are summarized in Table 3. Hexane results in the longest lifetime of 200 minutes. As a result, polarity is a single parameter correlation. When the polarity of the diluent decreases, the lifetime or stability of the liquid membrane is significantly increased.

Fig. 10 shows the relationship between the polarity of diluent and the percentage of extraction after 60 minutes for different diluents, using the optimal condition from 1-3. On the contrary, when the polarity increased, both percentages of extraction and stripping of cobalt(II) were higher. The polarity index of water is 9.0 [38]. It is known that the extraction reaction occurs at the interface feed/liquid membrane layer. When the polarity of diluent increases, the diluent becomes more soluble in the feed phase as shown in Fig. 11. Thus, the number of extraction and stripping reactions increases and it leads to a higher the percentages of extraction and stripping.

**Fig. 11. Schematic representation of interface layers at the feed side and stripping side.**

Unfortunately, the big increasing of polarity made the interface layers (δ) grew too thick and consequently the liquid membrane leaks out from the pore of hollow fiber into the feed and the stripping solutions. As a result, higher polarity of diluent brings higher extraction performance but lower stability. Especially, when the polarity of diluent exceeds 3.5, the stability was too low to be trapped in the hollow fiber porous. In this case, the percentages of extraction and stripping by using chloroform are meaningless. Therefore, in this study, benzene, which has a polarity of 2.7, is recommended as a diluent because it achieves the best balance between the extraction performance and the stability of membrane.

CONCLUSIONS

Cobalt(II) ions were selectively extracted from a cobalt(II)/nickel (II) binary mixture in thiocyanate media by using Alamine300 as carrier. The optimum conditions were pH of 4.0, 4% (v/v) Alamine 300 and 2.5 M of ammonia in stripping solution, which resulted in the highest percentages of extraction and stripping of cobalt(II) (about 82% and 75%, respectively). The increasing of feed concentration decreases the percentages of extraction and stripping but increases the metal ion flux. When the polarity of the diluent decreased, the stability increased. On the contrary, when the polarity index increased, percentages of extraction and stripping were higher. Hexane provides the longest lifetime of 200 minutes. Unfortunately, when the polarity index exceeded 3.5, both the percentages of extraction and stripping abruptly decreased because liquid membrane leaked out due to solubility being too high to be trapped in hollow fiber pores.

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