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Synergistic extraction of cobalt and nickel ions by supported liquid membranes with a mixture of TIOA and TBP

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ABSTRACT

In this work, the selective separation of cobalt from acidic media, containing both equimolar and non-equimolar mixtures of cobalt and nickel by supported liquid membranes (SLMs), was investigated using Alamine 308 (tri-isooctylamine, TIOA) as the carrier. The liquid membrane consisted of the desired concentration of an extractant (Alamine 308), a modifier (TBP), and a diluent (chloroform). The membrane support was microporous hydrophobic polypropylene Celgard 2500. Parameters, such as the feed solution pH, modifier (TBP) concentration, temperature, stirring speeds, extractant (Alamine 308) concentration, stripping solution type, and the complexing reagent (NH_4SCN) concentration were experimentally studied and the optimum conditions were determined. The permeation coefficients (P) and initial fluxes of cobalt were calculated. A separation factor of cobalt over nickel was calculated from the experimental measurements.

Keywords: Supported liquid membranes; Cobalt-nickel separation; Alamine 308; Solvent extraction

1. Introduction

The fact that cobalt and nickel usually appear together in ores, the similar physical and chemical properties of these metals and the high purity degree required in their applications, have led to the development of a remarkable amount of work on cobalt-nickel separation. The separation of cobalt from nickel in aqueous solution has always been a problem for hydrometallurgists. Their adjacent positions in the transition metal series in the periodic table results in aqueous chemical behaviour that is too similar for the development of easy separation routes.

There are various separation methods, such as precipitation, cementation, solvent extraction, adsorption, and ion exchange [1–4]. Among them, solvent extraction is a well established technology that is used for the production of metals from relatively concentrated feed. However, industrial diluent effluents pose an important challenge as solvent extraction technique is not cost effective for the separation of metals from the dilute solution [5].

Recently, supported liquid membrane (SLM) extraction is emerging as an alternative to conventional solvent extraction due to its advantages, such as high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent

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discharge, and combination of extraction and stripping into one single unit [6,7].

The extraction chemistry is basically the same as that found in solvent extraction, but the transport process is governed by kinetic rather than equilibrium parameters, i.e. under non-equilibrium conditions during liquid membrane transport [8,9]. Amines were used to extract the metal ions. The amine extraction chemistry of thiocyanate complexes was investigated by Sanuki and co-workers, [10]. The applications of SLM for metal ions have been studied [11,12]. We used tributylphosphate (TBP) to reach maximum extraction efficiency. The development of SLM has reached significant importance for use in separation, purification or analytical applications in areas such as biomedical technology or water treatment [13–16].

They consist of an organic carrier solution immobilized in a thin macroporous polymer film separating two aqueous phases. The organic layer which plays the role of a membrane is held in the pores by capillary forces and surface tension. Among the above membranes, the SLM are known to show a high efficiency for cation separation owing to the molecular recognition process and require only a small amount of solubilized organic carriers. However, the SLM presented some difficulties for industrial applications, such as low fluxes, poor mechanical properties, and leaching of carriers at membrane interfaces which limit the long-term stability of the membranes [17,18].

The same SLM cannot be used again and has to be re-impregnated [19]. As a result, SLM-based processes have not been exploited industrially. As a means of overcoming this problem, polymer inclusion membranes represent an attractive option for separation processes [20].

Cobalt and its compounds, and alloys, are important from an industrial and technological point of view. They are used in special alloys in high-speed and high-temperature steels, in cutting tools and magnets, in jet engines and ordnance products, and as a catalyst for hydrocarbon refining. Cobalt is obtained mainly as a by-product from the extraction of nickel, copper, zinc, and lead from their ores. The separation of cobalt and nickel from sulphate and chloride media has been of practical interest for researchers [11,12,21].

2. Materials and methods

2.1. Chemicals and reagents

NH_3, TEA (triethanolamine), and NH_4SCN are of analytical grade (Fluka). TBP, $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, acetic acid, NaOH, chloroform, xylene, and n-decanol were purchased from Merck in Darmstadt, Germany. All the stock solutions for cobalt and nickel are prepared by dissolving the salts in distilled water. The extractant Alamine 308 (tri-isooctylamine, TIOA) is from Cognis Corp., Germany. The supports used for the liquid membranes are microporous hydrophobic polypropylene Celgard 2500 (Celgard Inc., USA, 25 µm thick, 0.209 µm × 0.054 µm pore size and 55% porosity).

2.2. Experimental procedure

Competitive transport of the equimolar or non-equimolar mixture of Co^{2+} and Ni^{2+} ions across the SLM from the aqueous solutions was studied using a two compartment permeation cell, which was made from a Pyrex glass, with flat-sheet membranes of 12.56 cm^2 area (A), as shown schematically in Fig. 1.

In all experiments, the supports used for the liquid membranes were microporous hydrophobic polypropylene Celgard 2500 (Celgard Inc., USA), 25 µm thick, and 55% porosity. The support was soaked for 18 h in a membrane solution of the desired composition, then left to drip for few seconds before being placed in the SLM cell. TBP was used as a modifier to improve the membrane performance. The volumes of both aqueous feed and strip phases were 250 mL. Various feed solutions were prepared by adding both cobalt and nickel salts to study the effect of feed composition. Ammonium thiocyanate (NH_4SCN) was added into the feed mixture to increase the selectivity of cobalt against nickel. 1 M Acetic acid/1 M Sodium acetate buffer used was essential for cobalt-nickel separation to maintain the desired feed pH, which was very critical and held constant. The feed and stripping phases were mechanically stirred at the desired mixing speed of 20 ± 1°C to avoid concentration polarization

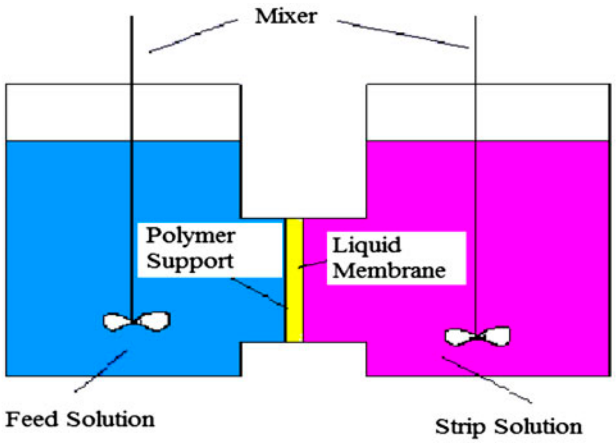

Fig. 1. Schematic diagram of experimental apparatus.

conditions at the membrane interfaces and in the bulk of the solutions.

2.3. Analysis

During the SLM system transport experiments, the samples of feed and strip phases (about 1 mL) were periodically removed for the determination of Co^{2+} and Ni^{2+} concentration by atomic absorption spectroscopy. The Shimadzu AA6701F model atomic absorption spectrometer was used in this study. Cobalt was determined by flame-acetylene media. The cobalt wavelength was 240.7 nm with a slit width of 0.2 nm and Nickel wavelength was 232 nm with a slit width of 0.2 nm.

The feed phase pH measurements were determined with a Schott model CG840 pH meter (Germany). Membrane permeabilities were determined by monitoring cobalt and nickel concentrations in the feed phase as a function of time.

2.4. Permeation model in flat sheet SLM

The permeation coefficient (P) and initial flux (J_o), from concentration–time (C–t) curve, were calculated from Eqs. (1) and (2):

$$\ln\frac{C}{C_o} = -\frac{A\varepsilon}{V_F}Pt \tag{1}$$

$$J_o = -\left(\frac{dC}{dt}\right)_o\left(\frac{V_F}{A\varepsilon}\right) \tag{2}$$

where V_F is the volume of the feed phase, ε is the porosity of membrane support, C and C_o are the concentrations of cobalt in the feed phase at elapsed time and time zero, respectively, and t is the elapsed time. $(dC/dt)_o$ is the slope at $t = 0$. A is the membrane area.

Amines are the general reagents among the extractants which form ion pairs and are known as basic extractant types, and extract metal ions according to the ion association principle. The chemistry of amine extraction of thiocyanate complexes was investigated by Sanuki and co-workers, [10] in detail. For this extraction system, the extraction reaction of cobalt can be given by Eq. (3):

$$2R_3N(o) + 2H^+(aq) + Co(SCN)_4^{2-}(aq) \rightarrow [(R_3NH^+)_2\, Co(SCN)_4^{2-}](o) \tag{3}$$

The stripping reaction for the cobalt (II) thiocyanate complex with an alkaline solution is expressed by Eq. (4):

$$[(R_3NH^+)_2\, Co(SCN)_4^{2-}](o) + 2OH^-(aq) \rightarrow 2R_3N(o) + Co(SCN)_4^{2-}(aq) + 2H_2O \tag{4}$$

3. Results and discussion

3.1. Effect of feed solution pH

In order to assess the role of pH during the separation of cobalt from the equimolar solution of cobalt and nickel, pH variation studies in the range of 3.0–6.0 were carried out, as indicated in Fig. 2. As seen in Fig. 2, the permeation coefficient increased from 2.6×10^{-6} to $13.5 \times 10^{-6}\,m\,s^{-1}$ with the increase of pH from 3.0 to 4.0 and then decreased to $9.0 \times 10^{-6}\,m\,s^{-1}$. The increase in proton concentration, that is a decrease in pH, will lead to increased formation of the complex, $(R_3NH^+)_2 \cdot Co(SCN)_4^{2-}$ that causes an increase in the diffusional resistance and hence a decrease in permeation coefficient [22]. On the other hand, the decrease in the coefficient with an increase of pH can be explained by the fact that the concentration of the protonated tertiary amine, R_3NH^+ decreases due to the less availability of proton and thus, the adduct, $(R_3NH^+)_2 \cdot Co(SCN)_4^{2-}$ concentration will decrease, as described by Eq. (3). As a result, the flux will decrease. Therefore, the maximum extraction was obtained at pH 4.0 and consequently, it is essential to maintain a constant pH in the feed solution using the NaAc/HAc buffer.

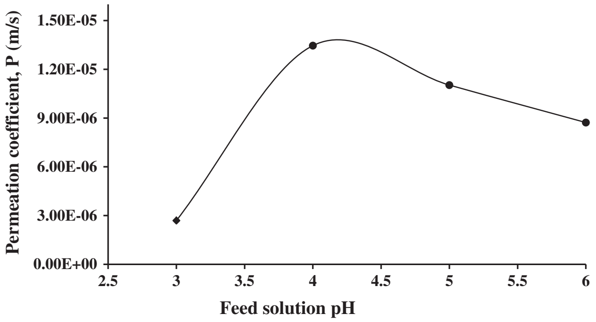

Fig. 2. Effect of feed pH on cobalt permeation coefficient.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}; 300 mg L^{-1} Ni^{2+}, feed stirring speed: 1,200 min^{-1}, strip phase stirring speed: 1,200 min^{-1}, strip solution: 1 M NH_{3+}1 M TEA, compl. reagent (NH_4SCN): 0.5 mol L^{-1}, Temp.: 20˚C, membrane support: Celgard 2500.

3.2. Synergistic effect of neutral or solvation extractant (TBP)

The combination of amines and neutral or solvation extractants was studied by a potential extracting system for metal ions [23]. TBP variation studies in the range of 0–30% w/w were carried out, as indicated in Fig. 3. Fig. 3 shows that there is a synergic effect from which the flux of cobalt, J_o is increased when carriers are used. The increase in TBP concentration increases the Co^{2+} flux since the complex diffusivity, as described by Eq. (5), during the membrane phase increases due to a decrease in the membrane viscosity [24]. According to Marcus and Kertes [25], however, an adduct between the complex of Eq. (6) a neutral ligand, like TBP, could also be formed in the SLM. This view is also supported by Biswas and Basu [26,27] who state that the nature of the extracted adduct in presence of the combined extractant can be expected to be $[(R_3NH^+)_2 \cdot CoCl_4^{2-} \cdot B]$, B representing the neutral extractant. Thus, the effect of B can be described in terms of the replacement of water molecules from $[(R_3NH^+)_2 \cdot CoCl_4^{2-} \cdot xH_2O]$. This leads to an adduct formation, which is responsible for the enhanced extraction into the organic phase. However, de Haas [28], and Kumbasar's [29] co-workers give the extraction and stripping reactions for TBP by Eqs. (6) and (7), respectively.

$$D = kT/\eta \tag{5}$$

where D: diffusion coefficient, η: viscosity, and T: temperature.

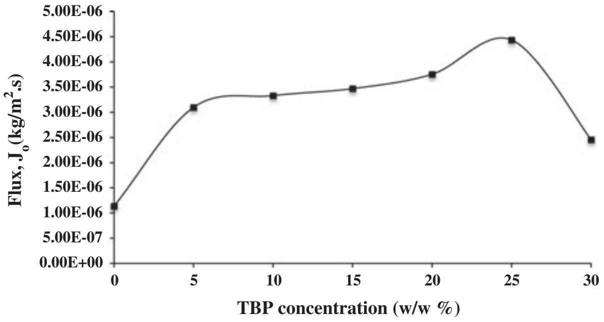

Fig. 3. Synergistic effect of neutral or solvation extractant (TBP) conc. on cobalt mass flux.
Note: Extractant: Alamine 308 (5% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}; 300 mg L^{-1} Ni^{2+}; feed soln. pH: 4.0, feed stirring speed: 1,200 min^{-1}, strip stirring speed: 1,200 min^{-1}, strip soln.: 1 M NH_{3+}1 M TEA; Compl. reagent (NH_4SCN): 0.5 M, temperature: 20˚C, membrane support: Celgard 2500.

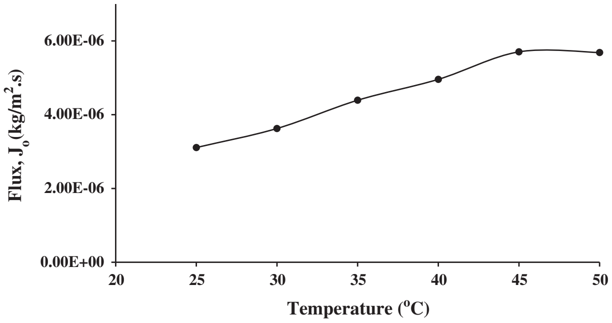

Fig. 4. Effect of temperature on cobalt flux.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}; 300 mg L^{-1} Ni^{2+}, feed soln. pH: 4.0, feed stirring speed: 1,200 min^{-1}, strip stirring speed: 1,200 min^{-1}, strip solution: 1 M NH_{3+}1 M TEA, Complex. reagent (NH_4SCN): 0.5 M, membrane support: Celgard 2500.

$$\begin{aligned} &Co(SCN)_4^{2-}(aq) + 2TBP(o) + 2H^+(aq) \\ &\rightarrow (TBP)_2\ H_2Co(SCN)_4(o) \end{aligned} \tag{6}$$

$$\begin{aligned} &(TBP)_2\ H_2(SCN)_4(o) + 2OH^-(aq) \\ &\rightarrow Co(SCN)_4^{2-}(aq) + 2TBP(o) + 2H_2o(aq) \end{aligned} \tag{7}$$

From Fig. 3, it can be seen that the value of the flux increases up to 25% w/w TBP in the membrane and then decreases. The increase in TBP concentration, in fact, causes the viscosity of the membrane solution, having TIOA as extractant, to decrease, and thus, the Co^{2+} flux increases up to a certain level at which the membrane solution becomes saturated or viscous again.

3.3. Effect of system temperature

Fig. 4 shows that the highest extraction efficiency is 75.7% at 45˚C. The extraction efficiency of the feeding phase was 68.57% at 35˚C, but at the end of the experiment, the extraction efficiency of the diffused cobalt stripping phase was 84.74% at 45˚C and 99.9% at 35˚C. Probably, the endothermic reaction is the reason for this increased temperature feed and the stripping membrane interfaces on the surface.

The cobalt flux through SLM was also examined against temperature, between 25 and 50˚C, as shown in Fig. 4. Fig. 4 illustrates that the Co^{2+} flux increases with the increase of temperature. The increase in temperature causes the complex diffusivity in the membrane phase to increase and the membrane viscosity to decrease, as given in Eq. (5), and thus, the Co^{2+} flux increases. This indicates that the diffusional resistance to mass transfer is of prime importance.

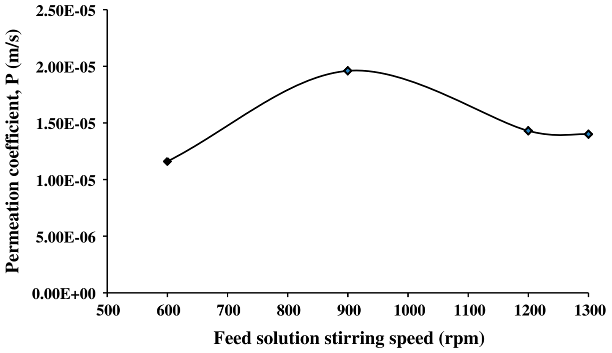

Fig. 5. Feed solution stirring speed on cobalt permeation coefficient.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}; 300 mg L^{-1} Ni^{2+}, feed soln. pH: 4.0, strip solution: 1 M $NH_{3+}1$ M TEA, compl. reagent (NH_4SCN): 0.5 M, temp.: 20°C; membrane support: Celgard 2500.

3.4. Effect of the stirring speed in the feed phase

Previous experiments were carried out to establish adequate hydrodynamic conditions. The permeability of the membrane was studied as a function of the stirring speed, which ranged between 600 and 1,300 min^{-1}, on the feed solution side and the results are shown in Fig. 5. Feed mixture of equimolar concentration were used, Co^{2+} and Ni^{2+} each being 500 mg L^{-1}, and the pH was maintained at 4.0. Fig. 5 illustrates that when the stirring speed is increased to 900 min^{-1}, the thickness of the aqueous diffusion layer at the membrane–feed interface and the aqueous resistance to mass transfer are decreased to a constant value, which results in an increase in the permeability of cobalt. Thereon, it decreased with an increase in speed due to the possible leakage of the liquid membrane out of the polymeric membrane pores as a result of the speed enhancement.

3.5. Effect of extractant (Alamine 308) concentration

The effect of Alamine 308 concentration in the membrane phase on cobalt permeation was studied in the range of 5–15% (w/w). The cobalt permeation coefficients were calculated at different Alamine 308 concentrations and are shown in Fig. 6. Cobalt flux increases with the extractant concentration. The extractability increases in the membrane phase. However, at higher extractant concentrations, the decrease in flux can be explained in terms of the increase in carrier viscosity in the membrane phase that increases the membrane resistance.

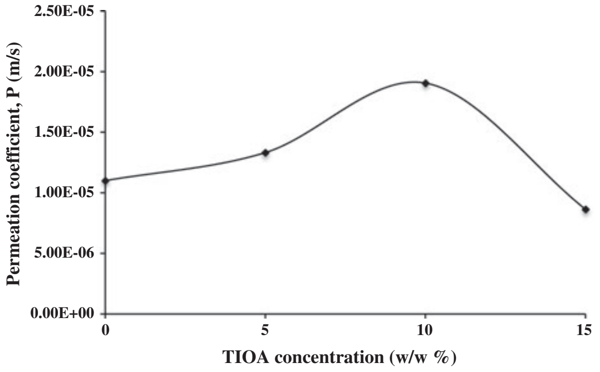

Fig. 6. Effect of TIOA concentration on cobalt permeation coefficient.
Note: Modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}, 300 mg L^{-1} Ni^{2+}, feed soln. pH: 4.0, feed stirring speed: 1,200 min^{-1}, strip phase stirring speed: 1,200 min^{-1}, strip solution: 1 M $NH_{3+}1$ M TEA, compl. reagent (NH_4SCN): 0.5 M, temp.: 20°C, membrane support: Celgard 2500.

It was observed in Fig. 6 that cobalt permeation increased from 1.10×10^{-5} to 1.91×10^{-5} m s^{-1} with an increase of Alamine 308 concentration up to 10% (w/w) and with a further increase in the extractant concentration to 15% (w/w); the cobalt permeation coefficient decreased to 8.64×10^{-6} m s^{-1}.

3.6. Effect of the stripping solution type

In general, metallic ions extracted by amines can be stripped from the protonated amine by the removal of a proton using neutral or alkaline solutions. The stripping reaction for the cobalt (II) thiocyanate

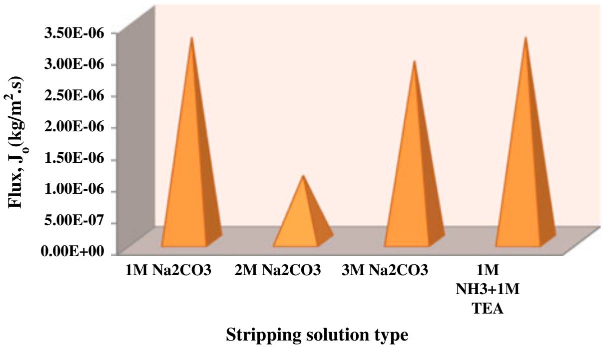

Fig. 7. Effect of stripping solution type on cobalt flux.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}, 300 mg L^{-1} Ni^{2+}; feed soln. pH: 4.0, Feed stirring speed: 1,200 min^{-1}, strip stirring speed: 1,200 min^{-1}, complex. reagent (NH_4SCN): 0.5 M, membrane support: Celgard 2500.

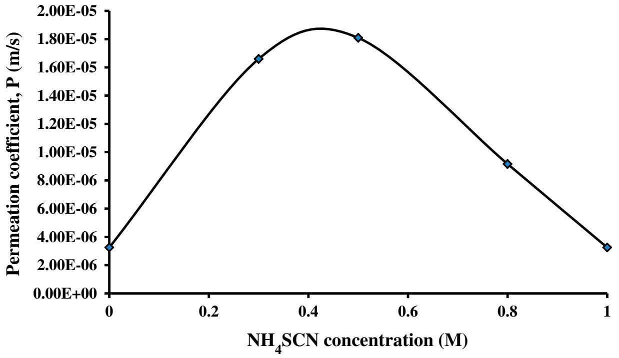

Fig. 8. The effect of the NH_4SCN concentration on the cobalt permeation coefficient.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent: chloroform, feed phase: 300 mg L^{-1} Co^{2+}, 300 mg L^{-1} Ni^{2+}, feed soln. pH: 4.0, feed stirring speed: 1,200 min^{-1}, strip stirring speed: 1,200 min^{-1}, strip solution: 1 M NH_3+1 M TEA, membrane support: Celgard 2500.

complex with an alkaline solution is expressed by Eq. (4) [30].

Ammonia and triethanol amine solution mixtures were used as reagents to strip and separate the cobalt from the membrane phase to the aqueous phase. In addition, Na_2CO_3 was also used as a stripping reagent (Fig. 7). Finally, a stripping solution containing 1 M NH_3 + 1 M TEA was selected as the stripping phase mixture.

3.7. Effect of the complexing reagent (NH_4SCN) concentration

The effect of the NH_4SCN concentration on the cobalt flux is shown in Fig. 8. It was found that by increasing the concentration from 0.5 to 1.0 M, the cobalt flux decreases.

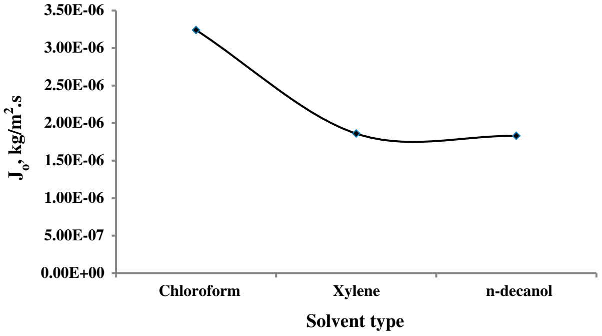

Fig. 9. The effect of the solvent type on cobalt flux.
Note: Extractant: Alamine 308 (5% w/w), modifier: TBP (15% w/w) in diluent, feed phase: 300 mg L^{-1} Co^{2+}, 300 mg L^{-1} Ni^{2+}, feed soln. pH: 4.0, complex. reagent (NH_4SCN): 0.5 M, Feed stirring speed: 1,200 min^{-1}, strip stirring speed: 1,200 min^{-1}, strip solution: 1 M NH_{3+}1 M TEA, membrane support: Celgard 2500.

The cobalt ions in the acidic feed solutions react with an excess NH_4SCN to form the pink color tetrahedral cobalt (II) thiocyanate complex, $Co(SCN)_4^{2-}$, whereas in case of nickel ions, they hardly form the thiocyanate complex [31,32].

The thiocyanate complex reacts with tertiary amines, such as tri-isooctyl or trioctyl amines dissolved in various solvents, and forms a blue color adduct, $[(R_3NH^+)_2 \cdot Co(SCN)_4^{2-}]$ [33–36]. The cobalt (II) species obtained as such is accepted to be the cobalt (II) thiocyanato complex [34,35].

On the other hand, the octahedral complex of nickel ions probably consists of $Ni(SCN)_6^{4-}$ or $Ni(SCN)_4(H_2O)_2^{2-}$ [32,37,38]. This is in agreement with the reports of Zhu [39], which state that the 7*d* electron of Co^{2+} is one of the most favored ion for the tetrahedral configuration from the viewpoint of the ligand field theory, and that the steric hindrance is the only factor that could weaken the octahedral configuration. So, cobalt is more preferably extracted into the membrane phase than nickel, and the thiocyanate complexation is significant such that the selectivity of cobalt with respect to nickel is thus increased.

3.8. Effect of diluent

Chloroform, n-decanol, and xylene were used as diluents and are shown in Fig. 9. The best cobalt permeation was obtained by using chloroform as the diluent. The polarity of the diluent is the most decisive factor. So, we selected chloroform as a solvent.

3.9. Optimum conditions

The following results were obtained from examining the experimental parameters:

- Diluent: Chloroform.
- Feed solution pH: 4.0.
- Complexing reagent (NH_4SCN) concentration: 0.5 M.
- Extractant TIOA (Alamine 308) concentration: 10% w/w.
- Neutral or solvation extractant (TBP) concentration: 25% w/w.
- Feed solution stirring speed: 900 min^{-1}.
- Stripping solution stirring speed: 900 min^{-1}.
- Temperature: 35°C.
- Stripping solution: 1 M NH_3 + 1 M TEA.
- Polymer support: Celgard 2500.

Table 1
Separation factors, $\alpha_{Co/Ni}$, of Co over Ni under the optimum conditions

Equimolar		Nonequimolar	
Mixture (mg L^{-1})	$\alpha_{Co/Ni}$	Mixture (mg L^{-1})	$\alpha_{Co/Ni}$
100 Co^{+} 100 Ni	88.1	100 Co^{+} 500 Ni	437.3
200 Co^{+} 200 Ni	151.8	200 Co^{+} 500 Ni	366.1
300 Co^{+} 300 Ni	215.2	300 Co^{+} 500 Ni	322.3
400 Co^{+} 400 Ni	∞	400 Co^{+} 500 Ni	320.8
500 Co^{+} 500 Ni	∞	600 Co^{+} 500 Ni	329.8
700 Co^{+} 700 Ni	∞	800 Co^{+} 500 Ni	378.9
1,000 Co^{+} 1,000 Ni	∞	1,000 Co^{+} 500 Ni	331.2

3.10. Membrane selectivity

Under optimum conditions, the effects of feed concentration, both equimolar and non-equimolar, on the extraction rate or separation of cobalt, have been experimentally studied. The separation factors, $\alpha_{Co/Ni}$, Eq. (8), of Co^{2+} over Ni^{2+}, based on the initial feed composition, was determined for seven hours, under the optimum conditions, and shown for the both equimolar and non-equimolar feed mixtures in Table 1. Extraction efficiencies (η) were calculated in Eq. (9).

$$\alpha_{Co/Ni} = \frac{(C_{Co}/C_{Ni})_{strip}}{(C_{Co}/C_{Ni})_{feed,o}} \tag{8}$$

$$\eta = 1 - \left(\frac{C}{C_o}\right)_{feed} \tag{9}$$

As seen from Table 1, cobalt selectivity with respect to nickel was high. The system is more selective for lower initial metals concentrations.

4. Conclusions

The SLM process, using Alamine 308 (TIOA) to extract and separate cobalt from the acidic solutions, was studied. From this study the following conclusions can be drawn:

(1) The optimum conditions are determined experimentally as stated above.

(2) At the optimum conditions, the extraction of cobalt is achieved with the efficiencies of 100.0 and 62.2% for the equimolar feed mixtures of 200 mg L^{-1} Co^{2+} + 200 mg L^{-1} Ni^{2+} and 700 mg L^{-1} Co^{2+} + 700 mg L^{-1} Ni^{2+}, respectively, within seven hours, and the separation factors of Co^{2+} over Ni^{2+} are 151.8 and infinite. For nonequimolar feed mixtures of 200 mg L^{-1} Co^{2+} + 500 mg L^{-1} Ni^{2+}, and 800 mg L^{-1} Co^{2+} + 500 mg L^{-1} Ni^{2+}, the extraction efficiencies of cobalt are 100.0 and 69.4%, respectively, and the separation factors of Co^{2+} are 366.1 and 378.9 within seven hours.

(3) From the results obtained in the temperature effect, there is a significant diffusional resistance in membrane phase as shown in the results and discussion, i.e. the rate of cobalt extraction ranged from 84.7% at 45˚C to 99.9% at 35˚C.

References

[1] K. Kongolo, M.D. Mwena, A.N. Banza, E. Gock, Cobalt and zinc recovery from copper sulphate solution by solvent extraction, Miner. Eng. 16 (2003) 1371–1374.

[2] M.J.S. Yabe, E. Oliveira, Heavy metals removal in industrial effluents by sequential adsorbent treatment, Adv. Environ. Res. 7 (2003) 263–272.

[3] M. Lofti, A. Nafaa, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Sep. Purif. Technol. 26 (2002) 137–146.

[4] K. Dong Seog, The removal by crab shell of mixed heavy metal ions in aqueous solution, Biores. Technol. 87 (2003) 355–357.

[5] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction Principles and Applications to Process Metallurgy, vol. II, Elsevier, Amsterdam, 1979, pp. 279–361.

[6] B. Swain, K. Sarangi, R.P. Das, Separation of cadmium and zinc by supported liquid membrane using TOPS-99 as mobile carrier, Sep. Sci. Technol. 39(9) (2004) 2171–2188.

[7] B. Swain, K. Sarangi, R.P. Das, Effect of different anions on separation of cadmium and zinc by supported liquid membrane using TOPS-99 as mobile carrier, J. Membr. Sci. 277(1–2) (2006) 240–248.

[8] X.J. Yang, A.G. Fane, Performance and stability of supported liquid membranes using LIX 984 N for copper transport, J. Membr. Sci. 156 (1999) 251–263.

[9] G. Leon, M.A. Guzman, Kinetic study of the effect of carrier and stripping agent concentrations on the facilitated transport of cobalt through bulk liquid membranes, Desalination 184 (2005) 79–87.

[10] S. Sanuki, M. Yata, H. Majima, Stripping of silver from Primene JMT loaded with silver thiocyanate complexes, Hydrometalurgy 52 (1999) 123–135.

[11] A. Surucu, V. Eyupoglu, O. Tutkun, Selective separation of cobalt and nickel by supported liquid membranes, Desalination 250 (2010) 1155–1156.

[12] A. Surucu, V. Eyupoglu, O. Tutkun, Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier, J. Ind. Eng. Chem. 18 (2012) 629–634.

[13] A. Drapala, P. Wieczorek, Extraction of short peptides using supported liquid membranes, Desalination 148 (2002) 235–239.
[14] M.M. Naim, A. Monir, Desalination using supported liquid membranes, Desalination 153 (2002) 361–369.
[15] P.R. Danesi, Separation of metals species by supported liquid membrane, Sep. Sci. Technol. 19 (1984/1985) 857–894.
[16] M.L. Goyette, T.L. Longin, R.D. Noble, C.A. Koval, Selective photo facilitated transport of sodium ions through liquid membranes: Key factors in experimental design, transport results and comparison with a mathematical model, J. Membr. Sci. 212 (2003) 225–235.
[17] A. Gherrou, H. Kerdjoudj, R. Molinari, E. Drioli, Facilitated transport of Ag(I), Cu(II) and Zn(II) ions by using DB18C6 and DA18C6 as carriers: Interface behaviour on the ion transport, Sep. Sci. Technol. 36 (2001) 2289–2304.
[18] C. Hill, J.F. Dozol, H. Rouquette, S. Eymard, B. Tournois, Study of stability of some supported liquid membranes, J. Membr. Sci. 114 (1996) 73–80.
[19] N.M. Kocherginsky, Q. Yang, L. Seelam, Recent advances in supported liquid membrane technology, Sep. Pur. Technol. 53 (2007) 171–177.
[20] N. Pont, V. Salvado, C. Fontas, Selective transport and removal of Cd from chloride solutions by polymer inclusion membranes, J. Membr. Sci. 318 (2008) 340–345.
[21] F.J. Alguacil, Facilitated transport and separation of manganese and cobalt by a supported liquid membrane using DP-8R as a mobile carrier, Hydrometallurgy 65 (2002) 9–14.
[22] W. Ashraf, A. Mian, Selective separation and preconcentration studies of chromium (VI) with Alamine 336 supported liquid membrane, Toxicol. Environ. Chem. 88(2) (2005) 187–196.
[23] A.G. Gaikwad, Synergetic transport of europium through a contained supported liquid membrane using trioctylamine and tributyl phosphate as carriers, Talanta 63 (2004) 917–926.
[24] M.E. Campderros, J. Marchese, Transport of niobium (V) through a TBP-Alamine 336 supported liquid membrane from chloride solutions, Hydrometallurgy 61 (2001) 89–95.
[25] Y. Marcus, A.S. Kertes, Ion exchange and solvent extraction of metal complexes, Intersci., New York, NY 166 (1969) 1391–1392.
[26] S. Biswas, S. Basu, Synergistic extraction of cobalt (II) by tri-octylamine and neutral donors, J. Radional. Nucl. Chem. 240 (1998) 387–390.
[27] S. Biswas, S. Basu, Extraction of zirconium (IV) from hydrochloric acid solutions by tri-octylamine and neutral donors, J. Rad. Nucl. Chem. 242 (1999) 253–258.
[28] K.S. de Haas, P.A. Brink, P. Crowther, Solvent extraction of iron, cobalt and nickel from thiocyanate melts, J. Inorg. Nucl. Chem. 33(12) (1971) 4301–4309.
[29] R.A. Kumbasar, Separation and concentration of cobalt from aqueous thiocyanate solutions containing cobalt–nickel by emulsion liquid membranes using TBP as extractant, J. Membr. Sci. 338 (2009) 182–188.
[30] R.A. Kumbasar, O. Tutkun, Separation of cobalt and nickel from acidic leach solutions by emulsion liquid membranes using Alamine 300 (TOA) as a mobile carrier, Desalination 224 (2008) 201–208.
[31] M.S. Uddin, M. Kathiresan, Extraction of metal ions by emulsion liquid membrane using bi-functional surfactant equilirium and kinetic studies, Sep. Pur. Technol. 19(1–2) (2000) 3–9.
[32] R.R. Amirov, Influence of cations on the formation of cobalt (II) complexes with thiocyanate ions in solutions of nonionic micelles, Russ. J. Coord. Chem. 29 (2003) 559–563.
[33] F.J. Alguacil, M. Alonso, Separation of zinc (II) from cobalt (II) solutions using supported liquid membrane with DP-8R (di (2-ethylhexyl) phosphoric acid) as a carrier, Sep. Pur. Technol. 41 (2005) 179–184.
[34] H. Watanabe, K. Akatsuka, Extraction of cobalt (II) from aqueous thiocyanate solutions by tri-n-octylamine, Anal. Chim. Acta 38 (1967) 547–552.
[35] H. Matsuo, S. Chaki, S. Hara, Jpn. Anal. 14 (1965) 935.
[36] M. Fujimoto, Y. Nakatsukasa, Microanalysis with the aid of ion exchangers, XXI. Modifications of the resin spot test with high molecular weight amines, Anal. Chim. Acta 27 (1962) 373–376.
[37] J.S. Preston, Solvent extraction of cobalt and nickel by organophosphorus acids. 1. Comparison of phosphoric, phosphonic and phosphonic acid systems, Hydrometallurgy 9 (1982) 115–133.
[38] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, John Wiley & Sons, New York, NY, 1999.
[39] T. Zhu, Solvent extraction in China [J], Hydrometallurgy: Elsevier, 27 (1991) 231–245.