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Selective extraction of cobalt ions through polymer inclusion membrane containing Aliquat 336 as a carrier

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ABSTRACT

This study reports the selective separation of Co (II) from mixtures of cobalt and nickel solutions using cellulose tri-acetate (CTA)-based polymer inclusion membranes, which incorporated the commercial extractant trioctylmethylammonium chloride (Aliquat 336). Tributylphosphate (TBP) was used as a modifier, and 2- nitro phenyl pentyl ether (2-NPPE) was applied as the plasticiser to prepare the membranes. Several important transport parameters such as the plasticiser concentration, carrier type, carrier concentration, pH of acid, stirring speed, stripping solution type and concentration, complexing reagent (NH_4SCN) concentration and synergistic effect of the modifier were discussed. At the optimum conditions, following results were found: plasticiser concentration 0.2 mL, feed solution pH 4, feed phase stirring speed 900 rpm, stripping solution 1 M NH_3 + 1 M TEA, complexing reagent (NH_4SCN) concentration 0.5 M and modifier TBP 25% w/w. Effective extraction was carried out under these conditions. The recovery factor of the cobalt ions was 100% for 4 h.

Keywords: Polymer inclusion membranes; Aliquat 336; Plasticiser; Stripping solution

1. Introduction

Cobalt and its alloys are widely used in industry and technology. Cobalt is a necessary element for special alloys in high-speed and high-temperature steels and a catalyst for hydrocarbon refining. In general, it is obtained as a by-product from the extraction of nickel, copper, zinc and lead compounds and their ores. The separation of cobalt and nickel from sulphate and chloride media is of concern to many researchers because cobalt is a vital component in several products [1].

Many researchers have focused on the separation of cobalt and nickel to provide highly pure compounds, which the industry requires, because they have similar physical and chemical properties and are most commonly found in the same ore. Precipitation, cementation, solvent extraction, adsorption, ion exchange, emulsion liquid membranes, supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) are common separation processes [2–7].

In recent years, PIMs have attracted attention [8]. PIMs are preferred to SLMs because of their effective

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carrier immobilisation, easy preparation, versatility, stability, better mechanical properties and good chemical resistance [9]. Because SLMs cannot be reused and must be reimpregnated, SLM-based processes have not been industrially used. To overcome this problem, PIMs are an attractive alternative in the separation processes.

Industry supports PIMs usage because the system provides a large surface-area-to-volume ratio, which offers the possibility of use in large-scale nuclear and harmful metal waste remediation. PIMs contain a polymer to provide mechanical strength, a carrier molecule that efficiently secures and transports ions over the membrane, and a plasticiser for elasticity, which acts as a solvent and to which the carrier molecule can diffuse [10]. PIMs are formed using a thin, flexible but stable film, which is created by casting a solution with a carrier (extractant), a plasticiser and a base polymer, such as cellulose tri-acetate (CTA) or poly (vinyl chloride) (PVC) [11].

The exploration of how different components extract and transport the target species is integral to select the membrane with the best constituents for the most effective separation performance. PVC and CTA are the most common polymers that create a gel-like network to capture the carrier and plasticiser/modifier [12–15]. For example, metallic (e.g. Cd (II) and Cu (II)) [16] and non-metallic (e.g., thiocyanate [17]) ionic species have been transported using this type of membrane, which contains only PVC and Aliquat 336. Furthermore, Konczyk et al. created a PIM system that used Aliquat 336 as a plasticiser and removed Cr(III) using D2EHPA as the carrier [18].

In earlier studies, SLM systems with Alamine 308 dissolved in chloroform and modified with Tributyl phosphate (TBP) to investigate the transportation of both Co (II) and Ni (II) [7]. Alamine 308 could be used as the extractant. Because the ammonium structure has a permanent positive charge, Aliquat 336 forms salts with different anions over a wider pH range than the primary, secondary and tertiary amines (Alamine 336, Alamine 308). For that study, CTA, TBP and Aliquat 336 presented a basis for the formation of PIMs that transported Co (II) from the feed solutions to the stripping solutions.

This study is the first exploration of PIMs that uses trioctyl methylammoniumchloride as an ion carrier and considers removing Co ions from acidic media and transferring them to an NH_4SCN aqueous solution.

2. Materials and methods

2.1. Chemicals and reagents

The CTA and 2-nitro phenyl pentyl ether (2-NPPE) of analytical grade were purchased from Fluka; tributylphosphate, dichloromethane, cobalt (II) chloride hexahydrate, nickel (II) chloride hexahydrate, acetic acid, sodium hydroxide, ammonium, triethanolamine, ammonium thiocyanate and trioctylmethylammonium chloride from Merck were used in the present study.

2.2. Membrane preparation

2.2.1. Preparation of PIM

PIM membranes were prepared according to the casting solution. First, 2-NPPE (0.2 mL) was added to 70 mL of dichloromethane, where CTA (480 mg) was dissolved at room temperature. Aliquat 336 and TBP were added after the solution was mixed, which was followed by 2 h of mixing to obtain a uniform solution. To slowly evaporate the solvent of the mixed solution, a glass square container (24 cm × 24 cm) was used and maintained at room temperature overnight. Then, a few drops of cold water (at room temperature) were placed and mixed on the top of the polymer film twice [9], which resulted in the formation of a membrane. The membrane was removed from the container and had an average thickness of 25 μm, according to a digital micrometer (Salu Tron Combi-D3).

2.3. PIM transport experiment

This membrane, which is known as the polymeric film, was placed between two glass cells. A two-compartment permeation cell made of Pyrex glass using flat-sheet membranes of 12.56 cm^2 area (A) was used to study the transporting process of metal ions from the aqueous solutions through the PIM.

Equal volumes (250 mL) of the feed and strip phase were used in permeation cell. First, the cobalt and nickel salts were dissolved in distilled water to create the stock solutions for cobalt and nickel. To select cobalt from the mixture with nickel, the feed mixture was mixed with ammonium thiocyanate (NH_4SCN). One M acetic acid/1 M sodium acetate buffer was used to adjust the pH of the feed solution. For the stripping phase, $1\,M\,NH_3 + 1\,M\,TEA$ were selected to make the stripping solution. During the PIM transport experiment, the metal concentration was determined using an atomic absorption spectrometer (Shimadzu AA6701F).

3. Results and discussion

3.1. Plasticiser concentration

Plasticisers can penetrate among the polymer strands and neutralise the existing polar groups with their own polar group, which weakens their inherent intermolecular forces [8]. The plasticisation softening action occurs because the plasticisers can decrease the intermolecular attraction forces among the polymer chains. Consequently, there is an assumption that when the plasticisers are used with PIMs, they can affect the membrane mobility, how much the membrane constituents interact and the features of the polymeric medium [19].

The most commonly used plasticiser in PIMs is 2-Nitro-phenyl octyl ether (2-NPOE) because of its high dielectric constant, which enhances the membrane permeability [8]. PIMs do not require the addition of a plasticiser if ammonium salts and phosphoric acid esters are the carrier ingredients, such as in quaternary, because they already have plasticising properties [8,20]. Stiff and brittle membranes can result from low plasticiser concentration, so such concentration is not recommended [8]. The amount of plasticiser depends on the type of plasticiser and the base polymer. A volume of up to 0.2 mL (27% w/w) is appropriate for CTA; however, a larger concentration reduces the mass transport function (Fig. 1). Two factors determine this limit. It has been suggested that the permeability may increase when the plasticiser concentration increases because of the NPPE plasticisation effect, which makes the membrane more capable of plasticising and carrier movement. An increase in the amount of plasticiser increases the mobility in the membrane. To understand the reduction in permeability when the plasticiser content increases, the reduction in viscosity of the medium should be explained [8].

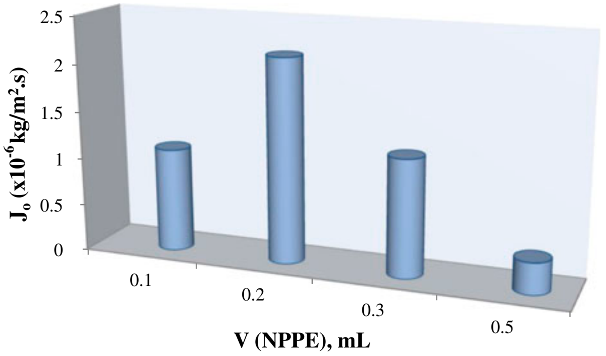

Fig. 1. Effect of plasticiser volume on cobalt flux.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

The dielectric constant of the plasticiser is notably important to the diffusion process. Ion pairs can effortlessly dissociate in high dielectric constant media [8], which leads researchers to prioritise both NPPE ($\varepsilon = 24$) [21] and NPOE ($\varepsilon = 23.9$) [9] for their high dielectric constants.

3.2. Effect of the carrier type

Although quaternary ammonium compounds (e.g. Aliquat 336) do not contain an ion–electron pair at the nitrogen atom, several researchers [22–24] consider them the basic carriers based on the similarity in the extraction mechanism that use amines and fully substituted quaternary ammonium compounds [8]. Güell et al. have showed that a PIM that uses a higher Aliquat 336 concentration can noticeably increase the membrane conductivity and dielectric constant and decrease the membrane area resistance [25].

Because the carrier is incorporated into a polymeric material gel network, the viscosity of the membrane liquid phase increases and prevents the components from moving to the adjacent aqueous phases [26].

Each carrier was evaluated in terms of the cobalt flux. The carriers selected for this study were: Alamine 336, Alamine 308 and Aliquat 336 (Fig. 2). The best cobalt flux was obtained using Aliquat 336, which created salts with different anions over a larger pH range than the primary, secondary and tertiary amines because the ammonium structure has a permanent positive charge [27,28].

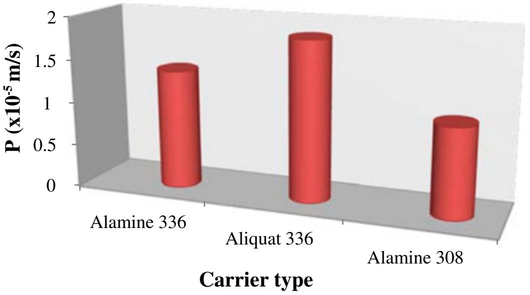

Fig. 2. Effect of carrier type on cobalt permeation coefficient.
Note: Modifier (TBP): 15% w/w; plasticiser (2-NPPE): 0.2 mL; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

3.3. Effect of the Aliquat 336 concentration

For the PIM system, the amount of carriers affects the Co (II) ion transport through the membrane. An increase in carrier concentration results in the extraction capacity, but it is necessary to avoid using carriers because carriers are generally notably expensive. The required concentration of Aliquat 336 to transport Co (II) was in the range of 0–30% (w/w), and the best recovery factor was 25% (w/w), which resulted in the most optimal solution. Fig. 3 illustrates that an increase of the carrier concentration from 0 to 30% made the flux increase from 1.14×10^{-6} to 2.27×10^{-6} kg/m^2 s and subsequently decrease to 1.54×10^{-6} kg/m^2 s. The cobalt flux increases with the extractant concentration. The extractability is increased 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, which increases the membrane resistance. The quality of the Co (II)–Aliquat 336 complex formation at the feed/membrane interface may clarify this result. A higher Aliquat 336 concentration may result in the membrane saturation of the Co (II)–Aliquat 336 complex, because the Co (II)–Aliquat 336 complex creation was enhanced when the carrier concentration increased [9]. High viscosities in the membrane prevent the diffusion of the ion-carrier complex in the membrane [29]. Saturation of the carrier in the membrane causes it to deposit on the membrane surface, which may decrease the activity and transport characteristics of the membrane by deteriorating the homogeneous structure of the membrane surface [30].

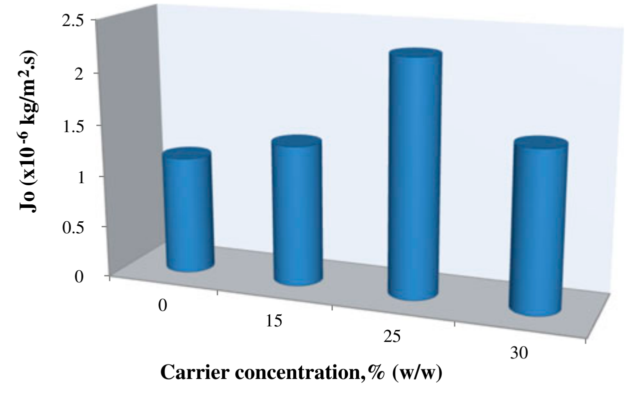

Fig. 3. Effect of Aliquat 336 concentration on cobalt flux.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; pH: 4; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

3.4. Effect of pH

It was observed that only Co (II), which is an anionic species at pH 4, could be extracted into the membrane. In the literature, one study explored the use of PIMs for Co (II) removal [18].

Fig. 4 shows the effect of pH on the flux of metal ions that were extracted with the membrane. Fig. 4 further illustrates the function of low pH on the absorption of cobalt (II) against nickel (II), which suggests that it has significantly high complexation ability for cobalt (II). The Co (II) > Ni (II) sequence describes the selectivity of cobalt against nickel with the membrane [7]. Because of the ion exchange character of the quaternary alkyl ammonium salt, the complex $[(A^+)_2 \cdot Co(SCN)_4^{-2}]$ was found in the membrane phase (Eq. 1). A^+ represents methyl tri-octyl ammonium cation [31].

However, in the stripping reaction in Eq. (2), the complex in the basic medium can easily deteriorate. A decrease in pH difference causes a decrease in transport speed, which shows that the driving force in the transport of cobalt ion in the present study is the pH difference. Therefore, it is possible to say that the pH difference significantly affects the extraction and stripping reaction. The highest cobalt extraction efficiency was found at pH 4 (Fig. 4). Therefore, the stability of pH 4 should be maintained constant. Sodium acetate–acetic acid tampon was used to maintain the feed solution stable.

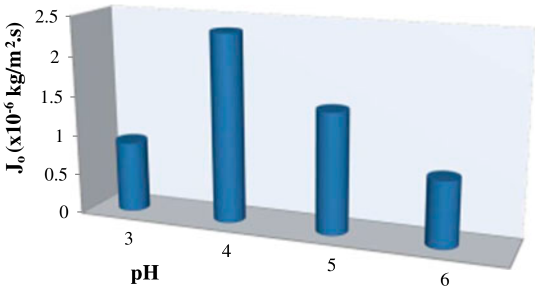

Fig. 4. Effect of feed pH on cobalt flux.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

Feed-membrane side reaction of cobalt can be given by Eq. (1):

$$2R_4N^+Cl^-_{(org)} + Co(SCN)^{2-}_{4(aq)} \rightarrow (R_4N^+)_2Co(SCN)^{2-}_{4(org)} + 2Cl^- \quad (1)$$

Stripping-membrane side reaction and membrane reaction are expressed, respectively, by Eq. (2) and Eq. (3):

$$(R_4N^+)_2Co(SCN)^{2-}_{4(org)} + 2OH^-{}_{(org)} \rightarrow 2R_4N^+OH^-_{(org)} + Co(SCN)^{2-}_{4(aq)} \quad (2)$$

$$2R_4N^+OH^-_{(org)} + 2H^- + 2Cl^- \rightarrow 2R_4N^+Cl^-_{(org)} + 2H_2O \quad (3)$$

3.5. Effect of the stirring speed

The mixing speed of the feed solution ranged between 600 and 1,500 rpm. The highest extraction speed was obtained at 900 rpm. This state increased the extraction speed of cobalt as a result of a decrease in thickness of the boundary layer of the liquid phase adjacent to the feed–membrane interface, which was caused by the increase in mixing speed of the feed solution. An increase in mixing speed results in an increase in flux trend. However, Fig. 5 shows that the flux decreases again when the mixing speed was higher than 900 rpm, when the permeability decreases because of the turbulence caused by stirring.

3.6. Effect of the stripping solution type and concentration

The membrane/stripping interface should have basic characteristics to extract Co from the membrane to the stripping solution because the amine group protonated in the membrane/stripping interface must release proton to make the carrier release Co (II), which depends on the pH value of the medium. Because the pH of the stripping phase is nearly stable throughout the experiment, ammoniac-TEA was used in the stripping phase. However, another reason to use ammoniac-TEA was to prevent metals from precipitating as hydroxides in the transport experiments.

Furthermore, NH_3, TEA and Na_2CO_3, which were the essential aqueous solutions, were also tested as stripping reagents. It was concluded that the optimal stripping phase combination was 1 M NH_3 + 1 M TEA (Fig. 6).

In this study, it was observed that an ammonia concentration over 1.0 M made the NH_3 molecules in the strip solution permeate through the membrane pores to the feed phase, which diminished the cobalt flux because of an increase in pH of the feed solution. Consequently, ammoniac and TEA mixtures were used in various concentrations, and the optimal conditions were obtained using 1 M NH_3 + 1 M TEA mixture for the stripping solution. Fig. 7 reveals the effect of the stripping solution concentration on the permeation coefficient.

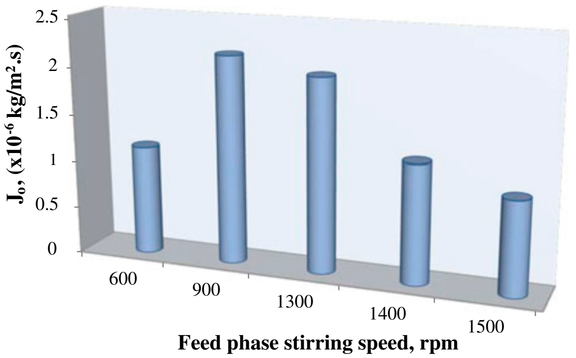

Fig. 5. Effect of feed phase stirring speed on cobalt flux.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; pH: 4; plasticiser (2-NPPE): 0.2 mL; extractant concentration: 25%; solvent: dichloromethane; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

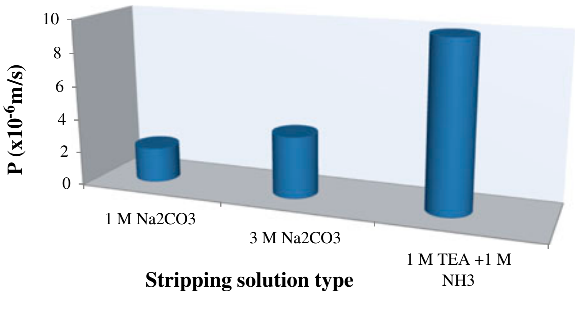

Fig. 6. Effect of stripping solution type on cobalt permeation coefficient.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

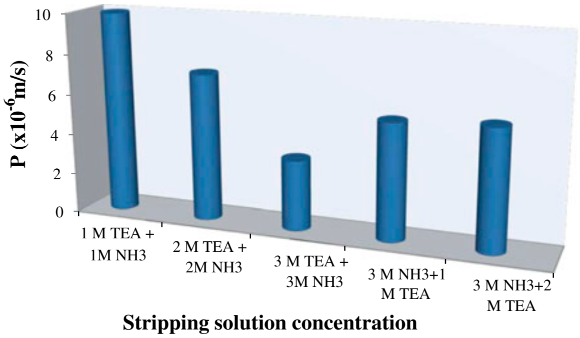

Fig. 7. Effect of the stripping solution concentration on the cobalt permeation coefficient.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA; membrane thickness: 25 μm.

3.7. Effect of complexing reagent (NH_4SCN) concentration

The effect of the NH_4SCN concentration in the feed solution on the extraction speed or extraction efficiency was studied. To use NH_4SCN in this study, the cobalt ions in the acidic feed solutions react with the excess NH_4SCN to form the pink colour tetrahedral cobalt (II)–thiocyanate complex $Co(SCN)_4^{2-}$, whereas they hardly form the thiocyanate complex with nickel ions. Fig. 8 reveals the change of the NH_4SCN concentration with the effect of the initial mass flux. When the NH_4SCN concentration ranged between 0.0 and 1.00 M, the highest extraction efficiency was obtained at 0.5 M NH_4SCN.

3.8. Synergistic effect of modifier

TBP was selected to obtain the maximum extraction efficiency value. It was found that the modifiers increased the extraction effectiveness.

In the membrane phase, the synergistic effect of the modifier was explored in the range of 0–30% (w/w). It was found that the cobalt flux was augmented by increasing the TBP concentration (Fig. 9). However, Marcus and Kertes [32] explained that an adduct between the complex of Eq. (4) and a neutral ligand such as TBP could also be formed in the SLM [33]. Biswas and Basu [34] also reported this conclusion. Finally, De Haas et al. [35] suggest that the extraction and stripping reactions for TBP are Eqs. (4) and (5), respectively.

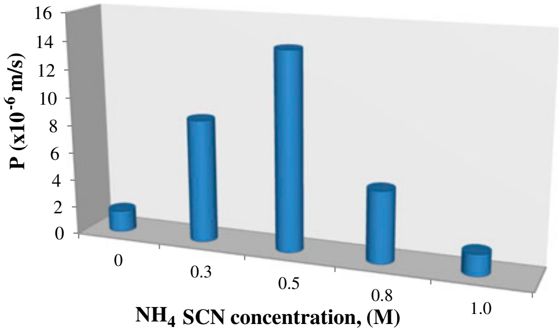

Fig. 8. Effect of the complexing reagent (NH_4SCN) concentration on the cobalt permeation coefficient.
Note: Modifier (TBP): 15% w/w; extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; polymer type: CTA; membrane thickness: 25 μm.

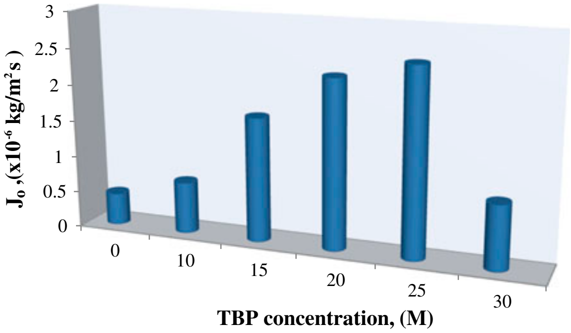

Fig. 9. Effect of the TBP concentration on cobalt flux.
Note: Modifier (TBP); extractant: Aliquat 336; plasticiser (2-NPPE): 0.2 mL; pH: 4; extractant concentration: 25%; solvent: dichloromethane; feed stirring speed: 900 rpm; strip-phase stirring speed: 900 rpm; strip solution: 1 M NH_3 + 1 M TEA; feed phase concentration: 300 mg/L; feed phase volume: 250 mL; strip solution volume: 250 mL; NH_4SCN concentration: 0.5 M; polymer type: CTA.

$$Co(SCN)_{4(aq)}^{2-} + 2TBP_{(o)} + H^{+}_{(aq)} \rightarrow (TBP)_2H_2Co(SCN)_{4(0)} \tag{4}$$

$$(TBP)_2H_2Co(SCN)_{4(O)} + 2OH^{-}_{(aq)} \rightarrow Co(SCN)_4^{2-} + 2TBP_{(0)} + 2H_2O_{(aq)} \tag{5}$$

4. Extraction and transport studies

Carriers that are basically complexing agents or ion exchangers accomplish the transport with the PIM system. The complex or ion pair formed between the metal ion and the carrier is solubilised in the membrane and facilitates the metal ion transport across the membrane. The chemical reactions that occur during the extraction and stripping of the target solutes for PIMs are basically similar to the equivalent solvent extraction systems. The desired solutes transport through the membrane is equal to the fundamental difference between the two systems. PIM research is primarily focused on maximising the membrane fluxes while maintaining the extraction efficiency and corresponding solvent extraction system selectivity [8].

4.1. Permeation model in polymer inclusion membrane

The permeation coefficient (P) and initial flux (J_o), from C–t curves, were calculated, respectively, from Eqs. (6) and (7):

$$ln\frac{c}{c_0} = -\frac{A}{V_F}\cdot P\cdot t \tag{6}$$

$$J_0 = -\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)_0\left(\frac{V_F}{A}\right) \tag{7}$$

where VF is the volume of the feed phase, C and Co are the concentrations of cobalt in the feed phase at elapsed and initial time, respectively, and t is the elapsed time. $\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)_0$ is the slope at t = 0. A is the membrane area.

4.2. Optimum conditions

The following results were obtained from examining the experimental parameters: Modifier: TBP (25% w/w); Plasticiser: NPPE (0.2 mL); Extractant: Aliquat 336 (25% w/w); Stripping solution: 1 M NH_3 + 1 M TEA; Feed solution pH: 4.0; Complexing reagent: NH_4SCN (0.5 M); Membrane thickness: 25 μm; Polymer type: CTA; Feed phase stirring speed: 900 rpm; Stripping phase stirring speed: 900 rpm.

Table 1
Recovery factor under the optimum conditions

Equimolar mixture (mg/L)	η
100 Co + 100 Ni	100
200 Co + 200 Ni	100
300 Co + 300 Ni	99.9
400 Co + 400 Ni	95
500 Co + 500 Ni	86
700 Co + 700 Ni	68.8
1,000 Co + 1,000 Ni	43.2

5. Conclusions

A polymer inclusion membrane process using Aliquat 336 to extract and separate cobalt from acidic solutions was studied. At the optimal conditions, cobalt was extracted with 100% efficiency for the equimolar feed mixtures of 100 mg/L Co^{2+} + 100 mg/L Ni^{2+} and 200 mg/L Co^{2+} + 200 mg/L Ni^{2+} within 4–6 h (Table 1).

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