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Selective Separation of Cobalt and Nickel using a Stable Supported Ionic Liquid Membrane

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Abstract

The selective separation of cobalt from nickel is of major importance for the recovery of cobalt from primary or secondary sources, as well as for analytical purposes. In this paper, the extraction of cobalt from the mixtures was examined using a supported liquid membrane employing the undiluted hydrophobic ionic liquid, namely tri(hexyl)tetradecyl phosphonium chloride ($[P_{66614}][Cl]$), as a carrier and polyvinylidene difluoride (PVDF) as a membrane material.

In the preliminary study, the efficiency of this supported ionic liquid membrane (SILM) for the cobalt extraction was evaluated by conventional static mode sorption experiments. Up to 86% of cobalt can be recovered under optimal conditions (by contacting SILM with 9.8 cm² in 5 mL of aqueous phase for 1 hour at 100 rpm, with 9 mol.L⁻¹ HCl in the aqueous phase).

Next, metal ion transport through a flat sheet SILM was investigated with pure water as a receiving phase. Permeation coefficients values of 2.2×10^{-6} m.s⁻¹ and 8.0×10^{-6} m.s⁻¹ were obtained with a hydrophobic and a hydrophilic membrane, respectively. The SILM showed selectivity for cobalt over nickel with separation factors as high as 218. Membrane stability was proven to be excellent, since the same SILM was used three times without losses of performances.

Keywords: Cobalt; Nickel; Selective separation; Supported ionic liquid membrane; Acid recovery.

Introduction

Cobalt is a widely used metal for numerous applications, from alloys to rechargeable lithium-ion batteries (close to 50% of the world's cobalt supplied today) [1], [2], [3]. Cobalt demand is expected to rise strongly with the growth of the rechargeable battery market for electric vehicles ([3], [4]) that could result in a significant increase in the supply risk for this transition metal in the years to come [5].

To meet this growing demand, extraction and separation of cobalt from primary ([6]) and secondary sources ([7], [8]) has attracted much attention. The recycling of spent lithium-ion batteries and permanent magnets in view of cobalt recovery has been extensively studied recently ([9],[10],[11],[12],[13],[14],[15]). Separation and microextraction of divalent cobalt ion are also an important issue for analytical chemistry purposes ([16], [17], [18], [19]).

In most of the reports, the hydrometallurgical road used implies to extract the target metal ion from aqueous solutions and to recover it with the highest purity as possible. The separation of cobalt from nickel is still a challenging task due to their proximity in the Periodic Table of the Elements and, subsequently, their similar aqueous chemical behavior.

Various techniques were reported to separate cobalt from nickel and other impurities such as iron, aluminum, and magnesium. Ion exchange resins ([20], [21], [22]), and solvent extraction ([23], [24], [25]) are among the most studied ones. However, ion exchange resins lack selectivity for cobalt and are more suitable for nickel extraction [20]. The extracting molecule *bis*(trimethylpentyl)phosphinic acid is particularly indicated for the extraction of cobalt from sulfuric acid media [24].

In hydrochloric acid media, several studies enlightened the possibility to form the lipophilic anionic complex of cobalt, CoCl_4^{2-} , which can then be extracted by amine type ligands diluted in hydrocarbon solvents ([26], [27], [28], [29]). Since divalent nickel does not form anionic complexes with chloride anions, high separation factors between these two metals can be obtained. However, solvent extraction implies to use large volumes of organic solvents that generates secondary streams of wastes.

Recently, Binnemans *et al.* used the undiluted commercial hydrophobic room-temperature ionic liquid (IL), namely tri(hexyl)tetradecyl phosphonium chloride for the cobalt-nickel separation [30], [31]. This IL allowed to obtain a highly selective extraction with Co/Ni separation factor about 50 000. Even though this phosphonium-based IL could not be declared non-toxic, its toxicity is lower than ILs incorporating fluorinated anionic parts ([32], [33], [34]). Moreover, it possesses low aqueous solubility (20-80 ppm, [35]).

Using ionic liquids as diluents offers several advantages due to their unique physicochemical properties such as low flammability and negligible vapor pressure ([36], [37]). However, their application for the solvent extraction of metals is compromised since the volume of reagents needed is still very large. Another important issue is the high viscosity of the ILs, which increases the energy needed to mix the organic and aqueous phase.

On the other hand, significant viscosity of ILs is an advantage in the context of supported liquid membranes (SLMs). In this separation technique, the solvent phase composed of extractant molecules (also called the carrier) and diluent is embedded within the micropores of polymeric membrane material. Then, SLM prepared is placed between an aqueous feed and receiving phase, assuring the selective transport of the metals from one phase to another. Sustainable liquid membranes can be prepared by selecting an appropriate solvent phase embedded in the membrane, which could also help to provide a SLM with higher stability [38], [39]. The high viscosity of the ILs ensures higher capillary forces [40], which prevent them from being washed from the pores of the membrane. SLM based on highly viscous ILs were proven to improve their long term stability [41].

In this work, we developed a supported ionic liquid membrane (SILM) based on tri(hexyl)tetradecyl phosphonium chloride ($[\text{P}_{66614}][\text{Cl}]$) for the extraction of cobalt from hydrochloric acid media and its separation from nickel. Preliminary, the effect of various parameters on cobalt extraction efficiency was studied. The SILM was used as a sorbent for cobalt ions. In the second part of the present study, we used the SILM in a continuous mode,

where cobalt is selectively extracted and transported across the supported liquid membrane and then stripped to a second aqueous phase, without any stripping reagent [30].

The effect of membrane material has to be considered. For example, using a hydrophobic membrane is known to increase the thickness of the boundary layers at its interfaces [42]. Thus, the effect of membrane support hydrophilicity was investigated and was shown to have major importance on cobalt transport. Membrane stability was proven to be excellent, with the possibility to use the same SILM at least three times. Finally, we evidenced the transport of acids across the SILM, which could be used to recycle mineral acids using the SILM designed. The novelty of this work lies in the minimization of the volume of organic reagents needed to extract cobalt and separate it from nickel.

2. Materials and methods

2.1. Reagents

The room-temperature hydrophobic ionic liquid, tri(hexyl)tetradecyl phosphonium chloride (abbreviated as $[P_{66614}][Cl]$, purity > 97%, $T_m = -70^\circ C$) was purchased from Solvionic (France). The relevant physicochemical properties are displayed in Table 1.

Table 1. Physicochemical properties of the $[P_{66614}][Cl]$ IL. Values for the dry IL at room temperature, if not specified

Property	Value	Reference
Solubility in water	20-80 ppm	[43]
Viscosity	2729 cP 95 cP (water -aturated, 60°C)	[44]
Surface tension	33.6 mN.m ⁻¹	[45]
Water solubility in the IL	0.818 (mole fraction) 8.7 wt.% (water-saturated, 60°C)	[46] [30]
Density	0.88 g.mL ⁻¹ 0.90 g.mL ⁻¹ (water-saturated, 60°C)	[30]

Nickel(II) and cobalt(II) chloride salts ($NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, purity=98%) were purchased from Prolabo (France). The presence of impurities was checked by ICP-OES and was found to be negligible. Deionized water (18 MΩ.cm) was obtained with a Purelab Option Q apparatus. Hydrophobic and hydrophilic porous polyvinylidene fluoride films (PVDF, Merck or Sterlitech) were used as the liquid membrane support. This material was selected due to its resistance to harsh chemical conditions [47]. The characteristics of these films are summarized in Table 1. All of the chemicals were used as received.

Table 2. Properties of the PVDF supports used in this study.

Hydrophobic/hydrophilic	Diameter (cm)	Thickness (μm)	Nominal pore size (μm)/ porosity (%)	Supplier
Hydrophobic	2.5	150	0.45/85	Merck-Millipore
Hydrophobic	2.5	150	0.22/85	Merck-Millipore
Hydrophobic	2.5	50	0.1/-	Sterlitech
Hydrophobic	2.5	50	0.02/-	Sterlitech
Hydrophobic	5.5	125	0.45/75	Merck-Millipore
Hydrophilic	5.5	125	0.45/75	Merck-Millipore

2.2. Preparation of the SILM

The SILM was prepared at room temperature according to previously reported procedures ([48]), by immersing a virgin PVDF film in 5 mL of pure IL for at least one night. The $[P_{66614}][Cl]$ was saturated with water before use by shaking it with an equal volume of purified water for one night [30]. The excess of IL on the surface of the membrane was then left to drip for a few seconds before use. The penetration of the IL into the membrane was confirmed by weighing before and after the impregnation.

2.3. Extraction experiments of cobalt under static conditions

The aqueous feed phases were prepared by dissolving the metal chloride salts into deionized water. The exact mass of metal salt was weighed with a Sartorius BP 221S balance (precision ± 0.01 mg), while the deionized water (resistivity = $18.2 \text{ M}\Omega\cdot\text{cm}$) was obtained with a Purelab Option Q apparatus. The pH was measured by a pH meter (Eutech Instruments, pH2100x apparatus, precision ± 0.01). The extraction equilibria were studied by the conventional (batch) method at room temperature. So, a sample of the freshly prepared SILM (surface area = 9.8 cm^2) was immersed in a known volume (10 mL if not otherwise specified) of the aqueous feed solution and agitated at 100 rpm. The concentration of metal ions in the aqueous phase before (C_{before}) and after extraction (C_{after}) was determined by ICP-OES (Varian 720 ES apparatus). The extraction efficiency of the metal (E , %) is calculated with the following equation:

$$E = \frac{C_{\text{before}} - C_{\text{after}}}{C_{\text{before}}} \times 100 \quad (1)$$

The volume variation of the aqueous phase before and after extraction was checked by removing the aqueous phase after extraction with micropipettes and was found to be negligible (less than $30 \text{ }\mu\text{L}$ of variation). The cobalt content used is $15 \text{ }\mu\text{mol}$ dissolved in 10 mL of the aqueous phase, except for the variation of cobalt initial content (were cobalt initial

content is varied in the range 5-60 μmol). The aqueous HCl concentration was fixed at 9 mol.L^{-1} except for the experiment of the variation of the HCl concentration (varied in the range from 0 to 9 mol.L^{-1}). Hydrophobic PVDF membranes were used, except for the experiment in which hydrophilic and hydrophobic polymers are compared. The pore size of the membranes is 0.45 μm , except for the variation of the pore size of the membrane (where membranes having a pore size of 0.02, 0.1, 0.22 and 0.45 μm were used). The extraction time is 60 minutes (except for the contact time experiment where the contact time is varied in the range of 0-60 minutes).

The stripping from the liquid membrane phase was studied by immersing the cobalt-loaded membrane in deionized water (20 mL) for one hour at 100 rpm.

The stripping efficiency (S , %) is calculated with the following equation:

$$S = \frac{C_{\text{after stripping}}}{C_{\text{before}} - C_{\text{after}}} \times 100 \quad (2)$$

where $C_{\text{after stripping}}$ is the metal concentration in the aqueous solution used for the stripping from the loaded SILM. The operation is repeated several times with fresh deionized water until cobalt is completely removed from the liquid membrane. The complete removal is checked by a mass balance between the amount of cobalt extracted in the liquid membrane and the amount of cobalt recovered in the stripping solution. The extraction and stripping step are schematized in the following figure:

Figure 1. Scheme of the extraction (top) and stripping (down) procedures.

2.4. Membrane transport experiments

A metal ion transport experiment was carried out using a glass experimental device (Verlabo) described in the previous study ([48]). The SILM (the effective area of 17.8 cm²) was placed between the two independent compartments for the feed and receiving aqueous phases (250 mL of each), which were agitated at 50 rpm with glass agitators placed in each compartment, during 25 hours. Small aliquots from both aqueous solutions were withdrawn from the two aqueous phases at regular time intervals and the metal concentrations were determined by ICP-OES. The amount of cobalt recovered in the receiving phase at the time ("t") is calculated as follows:

$$Co_{\text{receiving phase}} = \frac{[Co]_{\text{receiving},t}}{[Co]_{\text{feed},0}} \quad (3)$$

Where $[Co]_{\text{feed},0}$ is the initial cobalt concentration at the start of the experiment, while $[Co]_{\text{receiving},t}$ is the cobalt concentration in the receiving phase at time "t".

The plot of the variation of the cobalt concentration in the feed phase against time allow us to calculate the permeation ratio (P, m.s⁻¹) [49].

$$\ln \frac{[Co]_{\text{feed},t}}{[Co]_{\text{feed},0}} = - \frac{A}{V} \times P \times t \quad (4)$$

where A is the membrane effective area and V the volume of the aqueous phase. The initial flux (J_0 , mol.m⁻².s⁻¹) is calculated according to the following equation [49]:

$$J_0 = P \times [Co]_{\text{feed},0} \quad (5)$$

The separation factor (SF) is calculated between cobalt and nickel is calculated as follows [50]:

$$SF = \frac{J_0(Co)}{J_0(Ni)} \quad (6)$$

All of these experiments were repeated at least three times at ambient temperature (25±2°C). Each experiment is run for 25 hours.

Results and discussion

3.1. Cobalt(II) extraction studies with SILM by static mode

3.1.1. Impregnation of the membranes

First, we studied the impregnation of various PVDF membranes with [P₆₆₆₁₄][Cl] IL. The results are displayed in Table 3.

Table 3. Mass of IL impregnated in the PVDF membranes.

Membrane	Pore size (μm)	Diameter (cm)	Mass of IL immobilized (mg)
Hydrophobic PVDF	0.02	2.5	57.0±4.5
Hydrophobic PVDF	0.1	2.5	51.5±2.9

Hydrophobic PVDF	0.22	2.5	51.2±6.6
Hydrophobic PVDF	0.45	2.5	55.1±6.7
Hydrophobic PVDF	0.45	5.5	741±34
Hydrophilic PVDF	0.45	5.5	760±43

The mass of IL found in the membranes is obviously higher when the diameter of the membranes is higher (5.5 cm against 2.5 cm). The mass found is also close to whatever the hydrophilic or hydrophobic character of the polymer. For membranes of identical diameter (2.5 cm), the mass of IL is similar within the uncertainties, whatever the pore size of the membrane. This observation is different from what was previously reported for other ILs [48]. However, in this case, the IL is much more viscous and an external layer of IL will be deposited at the surface of the membrane. This external layer was evidenced with SEM images for various ILs ([51]) and is thicker with more viscous ILs.

3.1.2. Effect of the contact time

We investigated the effect of the contact time between a sample of SILM prepared using hydrophobic PVDF (pore size = 0.45 μm) and tri(hexyl)tetradecyl phosphonium chloride ($[\text{P}_{66614}][\text{Cl}]$) and the cobalt solution in the hydrochloric acid. The kinetics results of cobalt removal from the aqueous solution are shown in Figure 2.

Figure 2. E_{Co} depending on the contact time between $[\text{P}_{66614}][\text{Cl}]$ based SILM and aqueous cobalt solution in HCl in the membrane extraction. Aqueous phase: CoCl_2 (1.5 mmol. L^{-1}) in HCl (9 mol. L^{-1}). Membrane: hydrophobic PVDF (pore size = 0.45 μm). Membrane area = 9.8 cm^2 , volume of aqueous solution=10 mL

As can be seen, the prepared SILM is able to extract cobalt. The amount of cobalt extracted from HCl solution in the SILM is increasing with an increase of the contact time until it

reaches a plateau for contact times higher than 30 minutes under the experimental conditions used. Cobalt extraction increases from 49% with a contact time of 10 minutes to 67% with a contact time of 60 minutes. The kinetics of this membrane extraction process is close to the time needed to extract cobalt with $[P_{66614}][Cl]$ using as extracting solvent (*i.e.* in liquid-liquid extraction), which is the time necessary to reach equilibrium [30]. A contact time of 1 hour is retained for further experiments to ensure that the extraction equilibrium is reached whatever the chemical conditions prevailing in the aqueous phase.

3.1.3. Effect of aqueous HCl concentration

The most important experimental parameter for the extraction of cobalt under its chlorocobalt complex is the concentration of chloride anion in the aqueous phase. The effect of the initial HCl concentration in the aqueous phase on the cobalt extractability with a sample of SILM based on $[P_{66614}][Cl]$ by the membrane extraction is evidenced in Figure 3.

Figure 3. E_{Co} depending on the initial HCl concentration in the aqueous phase. Aqueous phase: $CoCl_2$ (1.5 mmol. L⁻¹) in HCl (variable). Membrane: hydrophobic PVDF (pore size = 0.45 μ m). Membrane area = 9.8 cm², volume of aqueous solution=10 mL. The contact time is 1 h

The amount of cobalt extracted from the aqueous HCl solution is linearly increasing with the initial concentration of HCl. Negligible extraction of cobalt is evidenced at $[HCl] = 0$ M in the aqueous phase. The extraction of cobalt increases and can reach values about 70% with 9 mol.L⁻¹ of HCl in the aqueous phase. This rate is explained by the high amount of chloride anion in the aqueous phase needed to form the anionic complex $CoCl_4^{2-}$ and to allow its extraction by the phosphonium-based ionic liquid [52], [53]. Cobalt is extracted at the liquid membrane interface according to the following equation [30]:

where the subscripts “SILM” and “feed” refer to the SILM and aqueous feed phase, respectively. The aqueous initial concentration of HCl was fixed at 9 mol.L⁻¹ for further experiments.

3.1.4. Effect of the pore size of the membrane

Next, the effect of the membrane pore size was investigated (Figure 4).

Figure 4. E_{Co} depending on the pore size of the polymeric membrane support. Aqueous phase: CoCl₂ (1.5 mmol. L⁻¹) in HCl (9 mol.L⁻¹). Membrane: hydrophobic PVDF. Membrane area = 9.8 cm², volume of aqueous solution = 10 mL. The contact time is 1 h

No significant differences in the cobalt extraction efficiency can be seen with the change in the support's pore size. Whatever the nominal pore size, the extractability of cobalt from aqueous solution was in the range of 65-70%. With this liquid membrane, the [P₆₆₆₁₄][Cl] ionic liquid is responsible for the extraction of the metal ion (no extraction occurs neither with the virgin hydrophobic polymer nor with the virgin hydrophilic polymer). It seems that cobalt is extracted at the interface between the SILM and the aqueous phase by the IL located at the interface. The IL being highly viscous, there is always an external layer of IL left on the membrane surface, whatever the impregnation method used [54]. Thus, the amount of IL available at the membrane interface is probably similar whatever the pore size of the membrane support, which could explain the similar extraction rates obtained.

3.1.5. Effect of initial cobalt content

A membrane pore size of 0.45 μm was retained to study the effect of the cobalt content. To do so, the volume of the aqueous phase was varied in the range from 5 to 60 mL with the same cobalt concentration (1.5 mmol.L⁻¹) and a constant membrane area (Figure 5).

Figure 5. E_{Co} depending on the amount of cobalt (μmol) in the aqueous phase. Aqueous phase: CoCl_2 (variable) in HCl (9 mol.L^{-1}). Membrane: hydrophobic PVDF (pore size= $0.45 \mu\text{m}$). The membrane area is 9.8 cm^2 . The contact time is 1 h

The cobalt extraction efficiency is highly dependent on the volume of the aqueous phase placed in contact with the SILM sample. With a low volume of the aqueous phase (5 mL), cobalt extraction efficiency can reach values up to 86%. However, extraction efficiency decreases from 86% to 19% when the volume of the aqueous phase is increased from 5 mL to 40 mL. The amount of IL in the SILM being low (around 50 mg), it is probably saturated with cobalt complexes, making it unable to accumulate more cobalt. The appearance of the membrane after extraction is shown in Figure 6.

Figure 6. Picture of a porous membrane film before impregnation (left), after impregnation (middle), and of a piece of the SILM after extraction of cobalt from hydrochloric acid media (right).

The membrane turns from white to translucent after its impregnation with the IL, which indicates that membrane pores and surface are filled with the IL. After the extraction step,

the membrane color turns to blue, probing the extraction of cobalt chloride complex from the aqueous phase to the SILM by the $[P_{66614}][Cl]$ IL.

3.1.6. Selectivity, stripping and SILM re-usability studies

Recently, the selectivity of the $[P_{66614}][Cl]$ IL for cobalt(II) over nickel(II) was proven to be unprecedently high [30] using solvent extraction. In the present study, the selectivity for cobalt and nickel was evaluated with the SILM incorporating the $[P_{66614}][Cl]$ IL (Figure 7). As a matter of comparison, results are shown with a hydrophobic as well as a hydrophilic polymer, in the same conditions.

Figure 7. E_{Co} and E_{Ni} with an aqueous phase made of $CoCl_2$ and $NiCl_2$ (41.5 mmol.L^{-1} of each) in HCl (9 mol.L^{-1}). Membrane: hydrophobic or hydrophilic PVDF (pore size = $0.45 \text{ }\mu\text{m}$). Membrane area = 9.8 cm^2 , volume of aqueous solution = 10 mL . The contact time is 1 h

Starting with an equimolar mixture of cobalt and nickel chlorides (1.54 mmol.L^{-1}), it can be seen that around 70% of the initial cobalt is extracted to the membrane phase, while the amount of nickel removed from the aqueous is indiscernible. The selectivity of the SILM is excellent since the phosphonium-based IL is only able to extract the anionic metallic species, while divalent nickel doesn't form anionic complexes in chloride media [55]. Fig. 7 shows that the selectivity is similar whatever the membrane used since no extraction of nickel occurs with neither with a hydrophilic nor with a hydrophobic polymer. It can also be seen that no significant differences in the extraction efficiency of cobalt were observed since E_{Co} values are close whatever a hydrophilic or hydrophobic polymer is used. To remove cobalt from the membrane phase and to potentially re-use the SILM, the stripping and re-usability studies were performed (Figure 8 and Figure 10).

Figure 8. Amount of Co stripped from the membrane after extraction (1.5 mmol.L⁻¹ in HCl 9 mol.L⁻¹, V=10 mL). Stripping solution: deionised water (V=20 mL). Membrane: hydrophobic PVDF (pore size = 0.45 μm). Membrane area = 9.8 cm². The contact time is 1 h

Cobalt can be stripped from the SILM using pure water, according to Eq. (8) [30].

The subscript “stripping” refers to the aqueous stripping phase. However, a large volume of water is necessary. Three successive contacts with 20 mL of fresh water are necessary to remove completely the extracted cobalt from the membrane. The re-usability of the membrane was evaluated by using the same membrane over three cycles of extraction-stripping (Figure 9).

Figure 9. Amount of Co extracted over three consecutive cycles (60 minutes each) of extraction/stripping with the same SILM membrane. Aqueous phase: $CoCl_2$ (1.5 mmol. L^{-1}) in HCl (9 mol. L^{-1}). Membrane: hydrophobic PVDF (pore size= $0.45 \text{ }\mu\text{m}$). Membrane area= 9.8 cm^2 , volume of solution= 10 mL . Stripping is conducted with three successive contacts with deionized water ($V=20 \text{ mL}$ of fresh water at each contact).

While the extraction of cobalt is sufficiently high after the first extraction cycle (67%), the extraction efficiency for cobalt is only about 26% on the second cycle. The complete stripping of the metal (checked by mass balance) is done before each new run. Negligible extraction was obtained in the third cycle of extraction. The membrane performances are degraded after several cycles of extraction. After each extraction-stripping step, a slight amount of IL is leached from the membrane surface because of aqueous solubility of IL. When the amount of IL in the SILM becomes too low, it affects the extraction efficiency.

3.2. Metal extraction using SILM and effect of membrane hydrophobicity

The SILM based on $[P_{66614}][Cl]$ ionic liquid can be used in a continuous mode with a membrane contactor, allowing to extract cobalt from a feed phase and to strip it in a receiving phase. Pure water was selected as a receiving phase since it allows the recovery of cobalt from the IL phase (Figure 8). The time evolution of cobalt ion concentrations in both aqueous phases is displayed in Figure 10.

Figure 10. Time courses of cobalt ion concentration in the aqueous feed and receiving phases during IL-based SLM operation. Feed phase: CoCl_2 (1.7 g.L^{-1}) in HCl (9 mol.L^{-1}). Receiving phase: deionized water. Membrane phase: $[\text{P}_{66614}][\text{Cl}]$ in hydrophobic PVDF. Pore size= $0.45 \text{ }\mu\text{m}$. Effective area= 17.8 cm^2

It can be seen that cobalt concentration in the feed phase is gradually decreasing, indicating that cobalt is extracted at the feed/liquid membrane interface according to Eq. (7). [30]

Meanwhile, the cobalt content in the receiving phase is increasing. However, cobalt is not entirely stripped from the SILM phase, since the addition of cobalt concentration in the feed + receiving phase is not equal to the initial amount of cobalt introduced in the feed phase. The affinity of cobalt for the IL is too strong and a significant amount of cobalt accumulates in the membrane phase.

However, an interesting phenomenon was observed with the IL embedded in the hydrophobic polymer. As evidenced in Figure 11, the pH of the aqueous receiving phase is gradually decreasing, which proves that acid protons are transported through the SILM.

Figure 11. Time evolution of pH in the aqueous receiving phase. Feed phase: CoCl_2 (1.7 g.L⁻¹) in HCl (9 mol.L⁻¹). Receiving phase: de-ionised water. Liquid membrane: $[\text{P}_{66614}][\text{Cl}]$ in hydrophobic PVDF.

It is well known that the ILs are hygroscopic and can incorporate in their structure a large amount of water and acid. Using SILMs based on these highly hygroscopic ILs, dynamic clusters, and water micro-environments can be formed inside the IL [56]. These micro-environments constitute a potential path to transport water-soluble compounds. In our case, it could constitute a way to recycle and purify the acid used in the feed phase. To further confirm this effect, we studied the evolution of the pH in the feed and receiving phases. The feed phase is made of hydrochloric acid, the receiving phase is made of de-ionised water. To confirm that the acid is not contaminated with metals in the receiving phase, we added nickel in the feed phase. The results are displayed in the following figure.

Figure 12. (a) Evolution of pH in the feed and receiving phases. (b) Evolution of nickel concentration in the feed and receiving phases. Feed phase: $NiCl_2$ (10 mg.L⁻¹) in HCl (0.1 mol.L⁻¹). Receiving phase: de-ionised water. Liquid membrane: $[P_{66614}][Cl]$ in hydrophobic PVDF.

As evidenced in Fig. 12 (a), the pH of the feed phase is decreasing over time, which could be related to the diffusion of protons from the feed to the receiving phase. Fig. 12 (b) shows that nickel ions remain in the feed phase since there is no extraction of nickel with the IL. The concentration of nickel found in the receiving phase is below the detection limit (0.1 mg.L⁻¹) during the experiment.

Since the positively charged compounds are not transported across the membrane and the anionic complexes are poorly stripped from the membrane, the acid could be recovered in the receiving phase and decontaminated from the metals. This SILM process could be an alternative to processes based on expensive electrodialysis and anion exchange membranes frequently reported for the purification and recovery of mineral acids ([57], [58], [59], [60],

[61]). However, the recovery of acids is out of the scope of this study and it was not studied further.

While the extraction of cobalt ions (Eq. 73) is efficient with the hydrophobic polymer, its stripping is complex. To improve the stripping, water has to be available to wash the excess of chloride anion in the IL at the SILM/receiving phase interface according to Eq. (8).

This reaction is not favored with a hydrophobic polymer since it does not let penetrate water, and consequently limits the stripping of cobalt. By switching from hydrophobic PVDF to hydrophilic one, the stripping of cobalt is now complete, as evidenced in Fig. 13.

Figure 13. Time courses of cobalt and nickel ion concentration in the aqueous feed and receiving phases. Feed phase: CoCl_2 (230 mg.L^{-1}) and NiCl_2 (210 mg.L^{-1}) in HCl (9 mol.L^{-1}). Receiving phase: de-ionised water. Liquid membrane: $[\text{P}_{66614}][\text{Cl}]$ in hydrophilic PVDF.

The initial aqueous feed solution contained a mixture of cobalt and nickel chlorides. The concentration of cobalt ions is gradually decreasing in the feed phase and gradually increasing in the receiving phase. After 25 hours of SILM operation, the totality of the initial cobalt placed in the feed solution was found in the receiving solution. It seems that cobalt is transported across the membrane in a solution diffusion-mechanism, characterized by stable complexes [62]. The IL-cobalt complexes ($[\text{P}_{66614}^+][\text{CoCl}_4^{2-}]$) migrates from the feed to the receiving phase, while the IL ($[\text{P}_{66614}^+][\text{Cl}^-]$) migrates through the membrane in the opposite direction. As can be seen in Fig. 13, nickel ion concentration in the feed phase remains almost constant throughout the experiment. However, a slight amount of nickel is recovered in the receiving phase after 25 hours (11.5 mg.L^{-1} , representing 5.6% of the initial nickel placed in the feed solution). Since nickel is not extracted by the IL, the transport of low concentrations of nickel could be related to the micro-environments of water inside the SILM. These micro-environments constitute non-selective paths in which water-soluble compounds such as nickel ions can be transported across the polymeric support. These micro-environments are presumably more pronounced with hydrophilic support.

The comparison between hydrophobic and hydrophobic membrane for cobalt transport was made. The results are displayed in Table 4.

Table 4. Comparison of the results obtained with hydrophilic or hydrophobic membranes. Feed phase: CoCl_2 (230 mg.L⁻¹) and NiCl_2 (210 mg.L⁻¹) in HCl (9 mol.L⁻¹). Receiving phase: de-ionised water. Liquid membrane: $[\text{P}_{66614}][\text{Cl}]$ in hydrophilic PVDF.

Membrane	P (m.s ⁻¹)	J ₀ (mol.m ⁻² .s ⁻¹)	SF Co/Ni
Hydrophobic PVDF	$2.2 \times 10^{-6} \pm 2.2 \times 10^{-7}$	$5.0 \times 10^{-6} \pm 4.2 \times 10^{-7}$	-
Hydrophilic PVDF	$8.0 \times 10^{-6} \pm 5.4 \times 10^{-7}$	$1.4 \times 10^{-5} \pm 1.2 \times 10^{-6}$	218±8

The permeation ratio values obtained are $2.2 \times 10^{-6} \pm 2.2 \times 10^{-7}$ m.s⁻¹ and $8.0 \times 10^{-6} \pm 5.4 \times 10^{-7}$ m.s⁻¹ for the hydrophobic and the hydrophilic polymer, respectively. The metal ion flux value is $1.4 \times 10^{-5} \pm 1.2 \times 10^{-6}$ mol.m⁻².s⁻¹ for the hydrophilic polymer while the value obtained for the hydrophobic polymer is $5.0 \times 10^{-6} \pm 4.2 \times 10^{-7}$ mol.m⁻².s⁻¹. It can be concluded that both permeation (P) and initial metal ion flux (J₀) of cobalt is higher when using a hydrophilic polymer rather than a hydrophobic one. This effect could be related to the higher thickness of the boundary layers with hydrophobic membranes [42]. It should also be mentioned that the stripping of the metal is not complete when using hydrophobic membranes. The separation factor for Co over Ni reaches values up to 208 when using a hydrophilic polymer. As already mentioned, this separation is better with a hydrophobic membrane, since no transport of nickel is obtained, which makes impossible to calculate the separation factor.

The proposed mechanism of extraction is displayed in the following figure:

Figure 14. Proposed mechanism of cobalt transport across the supported liquid membrane

The CoCl_4^{2-} complexes are extracted by the IL at the feed/liquid membrane interface and then back-extracted at the liquid/membrane/interface in a continuous process. It seems that that the facilitated transport of cobalt across the membrane is a solution diffusion-mechanism, characterized by stable complexes [62]. The IL-cobalt complexes ($[\text{P}_{66614}^+][\text{CoCl}_4^{2-}]$) migrates from the feed to the receiving phase, while the IL ($[\text{P}_{66614}^+][\text{Cl}^-]$) migrates through the membrane in the opposite direction. In this SILM system, it is clear that the high viscosity of the IL will slow down the diffusion of cobalt complexes. Therefore, ~~we could presume~~ it seems that the system is governed by mass transfer rather than chemical reactions which are often considered as fast and no rate-limiting steps [63].

The transport of cobalt through designed SILM and its selective separation from nickel can be visually illustrated by the change of color of both aqueous phases over time (Figure 15).

Figure 15. Picture of the membrane contactor initially and at various time intervals. Feed phase: CoCl_2 (2000 mg.L^{-1}) and NiCl_2 (2000 mg.L^{-1}) in HCl (9 mol.L^{-1}). Receiving phase: de-ionised water. Liquid membrane: $[\text{P}_{66614}][\text{Cl}]$ in hydrophilic PVDF.

At the start of the experiment, the aqueous feed phase (left) is blue due to the presence of the anionic cobalt species, while the receiving phase (water, right) has no color. After a few hours, the receiving phase turns to red due to the transfer of cobalt and its stripping under the form of the red CoCl_2 . With a longer time of contact, the red coloration of the receiving phase gets more and more pronounced. After 46 hours, the green color of the feed phase and the red color of the receiving phase indicates that nickel is left in the feed phase while cobalt is transported from the feed to the receiving phase.

SILM stability was evaluated by using the same membrane over several cycles of extraction, using fresh feed and receiving phases for each cycle (Table 5).

Table 5. Amount of cobalt transported from the feed phase after several cycles with the same membranes Feed phase: CoCl_2 (200 mg.L^{-1}) in HCl (9 mol.L^{-1}). Receiving phase: de-ionised water. Liquid membrane: $[\text{P}_{66614}][\text{Cl}]$ in hydrophilic PVDF.

[Co], initially (mg.L^{-1})	Cycle	Time of the cycle (hours)	Amount of Co in the receiving phase
200	1	24	100 $\pm$ 4%
200	2	24	100 $\pm$ 3%
200	3	24	100 $\pm$ 6%

It can be seen from Table 5 that complete transport of cobalt was obtained, using the same liquid membrane over three consecutive cycles of 24 hours each. The IL is surely removed from the surface of the membrane after being immersed for a long period in water. However, the long alkyl chains of the IL lead to Van der Waals's interaction with the support [64], [65]. The higher capillary forces associated with the high viscosity of the IL make the liquid membrane highly stable and the IL difficult to be forced out of the pores.

4. Conclusions

Cobalt extraction was studied using a SILM based on the undiluted room-temperature hydrophobic IL $[\text{P}_{66614}][\text{Cl}]$. The effect of several parameters on cobalt sorption was studied under static conditions and it was evidenced that up to 86% of cobalt can be extracted with high selectivity over nickel. Cobalt can be stripped with deionized water, but the re-usability was not possible since the IL at the surface of the membrane is leached to the aqueous phase. However, this sorption technique is interesting for analytical purposes since it requires low volumes of organic reagents.

The SILM was used in a continuous mode with water as a receiving phase. The effect of the hydrophobic/hydrophobic nature of the polymer was studied. Cobalt stripping was not quantitative when using a hydrophobic polymer since water is not available to wash the excess chloride from the IL. However, hydrochloric acid transport was evidenced and could be attributed to the formation of micro-environments inside the SILM. This effect could be used to recover and purify acids from aqueous phases. Complete extraction and stripping of cobalt were obtained when using a hydrophilic polymer. The permeation ratio and metal ion flux of cobalt were both higher when using a hydrophilic polymer as compared to the hydrophobic one. The selectivity for cobalt over nickel was satisfying, but the water micro-environments were suspected to create non-selective paths for the transport of metals across the SILM. The designed SILM was proven to be stable over three cycles, allowing to obtain a complete transport of cobalt.

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Graphical Abstract

[P₆₆₆₁₄][Cl] Ionic Liquid in PVDF

Co + Ni

H₂O

Ni

Co