



Selective Cobalt over Nickel separation using neat and confined ionic liquids

Stéphanie Boudesocque, Lydie Viau, Laurent Dupont

► To cite this version:

Stéphanie Boudesocque, Lydie Viau, Laurent Dupont. Selective Cobalt over Nickel separation using neat and confined ionic liquids. *Journal of Environmental Chemical Engineering*, 2020, 8 (5), pp.104319. 10.1016/j.jece.2020.104319 . hal-02991527

HAL Id: hal-02991527

<https://hal.science/hal-02991527>

Submitted on 6 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Selective Cobalt over Nickel separation using neat and confined ionic liquids

Stéphanie BOUDESOCQUE,^a Lydie VIAU,^b Laurent DUPONT^{a *}

^a Université de Reims Champagne-Ardenne, Institut de Chimie Moléculaire de Reims (ICMR), CNRS UMR 7312, UFR des Sciences Exactes et Naturelles, Bâtiment 18 Europol'Agro, BP 1039, F-51687 Reims Cedex 2, France.

^b Institut UTINAM, UMR CNRS 6213, 16 Route de Gray, Université de Bourgogne Franche-Comté, 25030 Besançon, France

*laurent.dupont@univ-reims.fr

Abstract

Task Specific Ionic Liquids (TSILs) generated by association between tetraalkylammonium cations and coordinating anions such as dicyanamide (Dca⁻) and thiocyanate (SCN⁻) were used for the selective separation of Ni(II) over Co(II). SCN-based TSIL presents higher extraction efficiency than the Dca-based one towards Co(II) ($E = 85.4\%$ vs 54.6%) and Ni (II) ($E = 22\%$ vs 0.5%) but lower separation factors ($\beta_{\text{Co/Ni}} = 21$ vs 239). Interestingly, extraction of Co(II) and Ni(II) in Dca-based TSIL can be enhanced using salts with chaotropic anions such as NaNO₃ ($E > 90\%$ for Co(II) and $E = 85\%$ for Ni(II)). The use of NaCl allows, moreover, the efficient separation of both ions with $\beta_{\text{Co/Ni}} > 1000$. The metal can be recovered from the IL phase using Na₂SO₄ aqueous solution to limit the release of the IL and to ensure a good recyclability of this latter. The confinement of TSIL in silica –matrix ionogel constitutes a valuable method to improve the handling of the IL. Indeed, the extraction properties of the ionogel containing [THN][Dca] IL are very close to those obtained using the same neat IL with

an efficient separation of Co(II) over Ni(II) in NaCl 4 mol.L⁻¹ ($\beta_{\text{Co/Ni}} > 1000$). Finally, the recyclability of the ionogel was studied and found comparable to that of neat IL.

Keywords: TSIL, Ionogel, Nickel, Cobalt, Recyclability

1. Introduction

Cobalt and Nickel are considered strategic metals because of their high industrial use. The status of cobalt could change over the next few years to that of a critical metal because of the strong demand linked to its use in the manufacture of batteries for electric vehicles, which is a fast-growing market [1]. In 2015, the cost of a ton of Co and Ni was estimated at 26.7 and 11.5 k€. Selective separation of these two metals from aqueous solutions has always been a problem in hydrometallurgy due to their similar physical and chemical properties and the high degree of purity required in their applications [2]. The separation of cobalt from nickel in mixture is of industrial concern for the recycling of batteries [3]

Liquid-liquid extraction is an important technique scale for metal recovery, with low operational costs that was extensively applied for the separation of Co(II) and Ni(II) from aqueous effluents [3,4]. In most cases, separation occurs by strong partitioning of Co(II) in organic phase, Ni(II) ions remaining in the aqueous phase [4-8]. This methodology requires the volatile and flammable organic solvents, for which the use in industrial processes is becoming increasingly controversial due to European Union directives aimed at reducing these solvents for health and safety reasons (VOC Directive 1999/13/EC; Directive 2002/3/EC). This is why, in recent years, a large number of researchers, mainly from universities, have focused on finding alternatives to the use of organic solvents in order to improve the sustainability of this method. In this context, Ionic liquids (ILs) have attracted significant interest in the field of liquid-liquid

extraction due to their non-flammability and their low vapour pressure [9,10]. The separation of cobalt from Ni uses ammonium or phosphonium extractants commercially available under the following names: Cyphos, Cyanex Aliquat [11-15]. The separation process is based on the strong interaction between halogenated complexes of Co(II) (CoCl_3^- or CoCl_4^{2-}) and ammonium and phosphonium cations which facilitates the transfer of hydrophobic $(x-2)\text{R}_4\text{N}(\text{P})^+-\text{CoCl}_x^{(x-2)-}$ ion-pair from the aqueous phase to the organic phase by anionic exchange [7,11]. Successful Co/Ni separation by liquid-liquid extraction has been performed using diluted ionic liquid in organic phase [4-8], undiluted hydrophobic ionic liquid [12] or aqueous biphasic systems (ABS) [13-15]. The major drawback of these studies is that, to be efficient, Co/Ni separation requires acidic conditions ($\text{pH} < 0$) and a high concentration of chloride ions ($> 6 \text{ mol.L}^{-1}$) in order to ensure the complete formation of halogenated complex [16].

In previous work, we have shown that the use of amido functionalized glycine-betaine-based ionic liquids can be used to achieve performant Co/Ni separation without pH control and in less chloride-concentrated media ($\text{NaCl } 4 \text{ mol.L}^{-1}$) [17]. The hydrophobic task-specific ionic liquids were designed through association of cationic analogues of glycine-betaine (AGB-ILs) with dicyanamide anion ($\text{Dca}^- = (\text{CN})_2\text{N}^-$). The extraction mechanism was based on the formation of an ion-pair between the cationic moiety and a mixed anionic complex of cobalt with Dca and chloride anions $\text{Co}(\text{dca})_x\text{Cl}_{(4-x)}$. This result points out that the synergy between the chloride ions and the coordinating anion of the ionic liquid can be a relevant factor to improve the extraction of Co(II) ions.

In this survey, we used hydrophobic TSILs designed by combining long alkyl chains cationic tetraalkylammonium and coordinating anions such as dicyanamide and thiocyanate, for selective extraction of aqueous solutions of Co(II) over Ni(II) in saline media. Compared to glycine-betaine analogues, tetraalkylammonium-based ionic liquids are more hydrophobic and

less viscous, ensuring better handling and better preservation of the integrity of the ionic liquid during extraction experiments [18].

One aspect of this work was also to propose an easy-to-implement system for the separation and recovery of strategic metals. To this aim, the confinement of the IL in silica-based ionogels was developed. In recent years, sol-gel silica materials doped with functional ILs were used for recovery of alkaline and transition metals, the recovery and separation of lanthanides and yttrium and the removal of Pb(II) and Cr(VI) from aqueous effluents [19–28]. It has been observed that the immobilization of an IL on/inside a solid support increases the adsorption efficiency towards metal ions compared to silica sorbents without ILs and affords many advantages relative to classical liquid–liquid extraction [29–32]. Compared to other immobilization methods such as solid-support grafting, the confinement of ILs in an ionogel has many advantages. First, the physical properties of the IL are maintained [33–35] while allowing easier separation of the aqueous and IL phases, similar to what is obtained with supported ILs. Moreover, no chemical modification of the IL is required, whereas grafting requires the incorporation of functional groups into the IL structure to allow the formation of a covalent bond [33].

Therefore, in this study, the extraction of Co(II) and Ni(II) by pure [THN][Dca] and [TON][SCN] phase was performed in batch experiments both in the absence and in the presence of salt to determine (1) the extraction efficiency of these ionic liquids and (2) the most suitable system to achieve separation of these two metals. The recyclability of the IL was then estimated from several cycles of extraction-stripping experiments. In the second part of this work, the metal extraction experiments were then carried out with monolithic ionogels under the same conditions as those used with pure ILs. The data, in terms of metal extraction efficiency, recovery and recyclability, are compared to the results obtained with pure ILs to assess the applicability of ionogels to metal extraction. However, a question arose regarding the

accessibility of the metal to the coordination sites of the IL and its influence on extraction kinetics. Consequently, extraction tests were also carried out on ground ionogels.

2. Experimental Section

2.1 Chemicals and reagents

All chemical and reagents used in this study were used as received without further purification. Sodium nitrate (99%) sodium chloride (99%), sodium dicyanamide (99%), and sodium thiocyanate were obtained from Sigma-Aldrich (Diegem, Belgium). Tetrahexylammonium and tetraoctylammonium bromide (98%), tetramethylorthosilicate (TMOS) and methyltrimethoxysilane (MTMS), were purchased from Acros Organics (Geel, Belgium). The nitrate metal salts had a purity of 99% or better and were purchased from Acros Organics (Geel, Belgium) or Sigma-Aldrich (Diegem, Belgium).

Stock aqueous solutions of metals were prepared by dissolving the corresponding salt of the respective metals (analytical grade purchased from Sigma-Aldrich-Fluka Chemical) in double distilled and deionized water.

2.2 Ionic liquid synthesis and elaboration of organo-silica ionogel

[THN][Dca] and [TON][SCN] ILs were synthesized according to our previous paper [30] and their synthesis is reported in SI.

Organo-silica ionogels were prepared according to the following procedure. In a Teflon vial, the IL [THN][Dca] (360 mg, 0.85 mmol) was dissolved under stirring in an ethanol/water solution (0.9 mL/0.25 mL) for 5 min before adding 0.5 mL of a TMOS/MTMS mixture (50/50 v/v). The synthesis was performed by using 3.44 mmol of silica precursor and using the following molar ratio: 0.5 TMOS/0.5 MTMS/0.25 IL/4 H₂O/4.5 EtOH. The resulting solution was stirred at room temperature for 5 min. Gelation occurred within 24 hours. The Teflon vial

was kept closed for 48 h and then opened. The aging process was followed by the weight loss over time and complete aging was reached when no more weight variation was noticed (around 15 days were found to be necessary).

2.3 Physical measurements

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer in Reims University. The UV-visible spectra of metal solutions were recorded using a Carry-5000 Varian spectrophotometer. The metal analyses were performed by UV-Vis spectroscopy using EDTA for Co(II) and Ni(II) and by ICP-OES, Thermo Fisher ICAP Series. Thermogravimetric analyses (TGA) were carried out on a TA Instrument SDT Q600 by using platinum crucibles under an air flow, with a heating rate of 5 °C/min up to 850°C.

The nitrogen adsorption–desorption isotherms at 77 K were measured, after IL extraction, using a Micrometrics ASAP 2420 surface area and porosity analyzer on monolith pieces degassed under vacuum at 120 °C for 12 h. The mesopore size distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method applied to the desorption branch of the N₂ adsorption-desorption isotherm.

Quantitative ²⁹Si solid-state NMR was performed on ground samples on a Bruker Avance II 300WB spectrometer and using a 4 mm probe. Spectra were acquired using a $\pi/6$ single pulse with proton decoupling and a 80s recycling delay. Samples were spun in ZrO₂ rotors at 4 kHz. Condensation degrees C_T and C_Q were calculated separately for T and Q units using the following equations 1 and 2 [36]:

$$C_T = \frac{\sum i\%Ti}{300} \quad (1) \quad \text{and} \quad C_Q = \frac{\sum i\%Qi}{400} \quad (2)$$

where i represents the number of siloxane bonds per unit.

Percentages of silicon environments were estimated using DMFIT 2019 [36]. ^{29}Si chemical shifts are reported relative to tetramethylsilane (TMS).

Infrared spectra were recorded with a 2 cm^{-1} resolution on a Bruker Vertex70 FTIR spectrometer with the use of a Platinum ATR accessory equipped with a diamond crystal.

2.4 Extraction experiments

Batch experiments

The metal ion distribution ratios were determined by mixing 0.5 g of IL and 2 mL of aqueous metal phase. The mixture was stirred overnight and then centrifuged (2000 g, 5 min). The phases were then separated for analysis. The aqueous phase composition was analyzed by spectrophotometry UV-Vis or by ICP-OES. The metal ion concentration in the IL phase was deduced from the difference between the initial concentration of metal ions in the aqueous phase and the concentration of metal ions after extraction. The efficiency of the extraction process was evaluated by the calculation of the extraction percentage (%E) using the following equation 3:

$$E = 100 * \frac{(C_{in} - C_{fin})}{C_{in}} \quad (3)$$

Where C_{in} (mol.L^{-1}) is the metal concentration in the initial aqueous solution and C_{fin} (mol.L^{-1}) is the metal concentration in the final aqueous solution.

The metal distribution coefficient (D) between IL and aqueous phases was calculated according to equation 4 (V_{aq} and V_{IL} correspond to the volume of water and ionic liquid phases, respectively):

$$D = \frac{[M]_{IL}}{[M]_{aq}} \times \frac{V_{aq}}{V_{IL}} \quad (4)$$

The separation factor ($\beta_{M1/M2}$) was employed to express the selectivity of the extraction between two metals $M1$ and $M2$ and was calculated as follows (equation 5):

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} \quad (5)$$

The stripping percentage (% S) was established as the amount of metal back-extracted from IL-rich phase to the total amount of metal in IL before the stripping $[M]_{IL,0}$ (equation 6)

$$\%S = \left(1 - \frac{[M]_{IL}}{[M]_{IL,0}} \right) \times 100 \quad (6)$$

The metal extraction percentages (% E) were determined at 298 K. The concentration of metal solutions lies in the range 10^{-3} to 10^{-1} mol.L⁻¹. The experiments are made in triplicate to ensure the reproducibility of the assay, and the mean value of extraction yields are considered, for each system studied.

Stripping experiments were performed by addition of 2 mL of pure water or a solution of Na₂SO₄ (1.5 mol.L⁻¹) to the ionic liquid phase recovered, after metal extraction. The mixture was shaken for 4 hours and centrifuged. The aqueous and ionic liquid phases were then separated for analysis.

The concentrations of ionic liquid cations in the aqueous phase were determined using quantitative ¹H NMR spectroscopy. To achieve this, 100 μ L of an aqueous solution of DMSO previously prepared at 100 mM is introduced into a conical tube. Then 200 μ L of the sample to analyze which is obtained after saturation of the aqueous phase with the ionic liquid were added. All this is dissolved in 700 μ L of deuterated water (D₂O). For measurements after paramagnetic metal extraction, a D₂O solution with 0.1 M of NaOH was used to precipitate metal residues. The ¹H NMR spectrum of the DMSO solution shows a single peak at $\delta = 2.68$ ppm and

corresponds to six protons. The DMSO is considered as an internal reference. Its peaks do not overlap with those of the ionic liquids studied. Knowing its concentration, the concentration of the sample can be calculated after integration of the peaks. The uncertainty range for this method is 1% [37].

Metal extraction experiments with [THN][Dca] confined in ionogel

The metal extraction experiments with ionogel were performed in similar conditions as those used in batch experiments. The mass of [THN][Dca] contained in the ionogel is about 350 mg for a total weight of 600 mg. Consequently, to ensure the same $[\text{IL}]/[\text{M}^{2+}]$ ratio as in batch experiments, the ionogel was contacted with 1.5 mL of the aqueous metal solution and placed under stirring for 6 hours. The solution and the ionogel were then separated by sedimentation, and the aqueous phase was analyzed to determine the residual metals concentration.

Experiments are also carried out with crushed ionogels. The ionogel is ground in a ceramic mortar for a few minutes until an homogeneous powder is obtained. Under these conditions, the ionogel is weighed before extraction and the volume of the metal solution to be used is adjusted to ensure the same ratio $[\text{IL}]/[\text{M}^{2+}]$ as for the batch experiments. The metal solution is brought into contact with the ionogel for the time necessary to reach equilibrium. Then, the ionogel was separated from the aqueous phase by centrifugation. The characteristics of the ionogels used are given in table 1.

Table 1: Characteristics of ionogel

Ionogel	Ionic liquid	m_{ionogel} (g)	m_{IL} (g)	% IL
1	[THN][Dca]	0.550	0.358	65
2	[THN][Dca]	0.621	0.365	59

As the characteristics of ionogels 1 and 2 are very close, the results obtained with these two ionogels will be discussed indistinctly.

3. Results and Discussion

3.1 Synthesis of task-specific ionic liquids

The association of tetraalkylammonium cations with Dca^- and SCN^- anions by anionic metathesis generates hydrophobic ILs $[\text{THN}][\text{Dca}]$ and $[\text{TON}][\text{SCN}]$ in good yields, higher than 70% (Fig. 1).

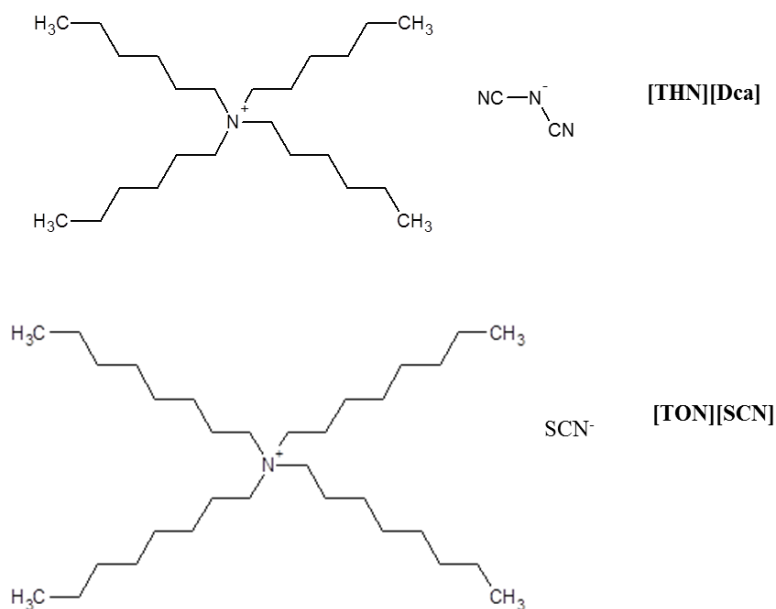


Figure 1: Structure of the tetraalkylammonium-ILs

The solubilities of these ILs in water were determined by ^1H NMR. The values, expressed in weight percents, are 0.05% for $[\text{THN}][\text{Dca}]$ and 0.17% for $[\text{TON}][\text{SCN}]$, respectively. In all cases, the leaching of ionic liquid, in aqueous phase during extraction will not exceed 0.5%,

which makes them viable for the extraction. The density of [THN][Dca] and [TON][SCN] are close to those of water and respectively equal to 0.95 and 0.91.

3.2 Extraction of Co(II) and Ni(II) by ionic liquids [THN][Dca] and [TON][SCN]

Agitated contact between the aqueous metal solution and the ionic liquid phase causes an immediate color change of both phases, indicating that the transfer of metal cations from the aqueous to the IL phase is a fast, almost instantaneous process. To examine the extraction properties of the TSILs with respect to Ni(II) and Co(II), the extraction percentages (%E) were determined from metal nitrate solutions at 0.05 mol.L^{-1} . The experiments were carried out at 298 K. The extraction efficiencies (%E) for each IL are shown in Figure 2.

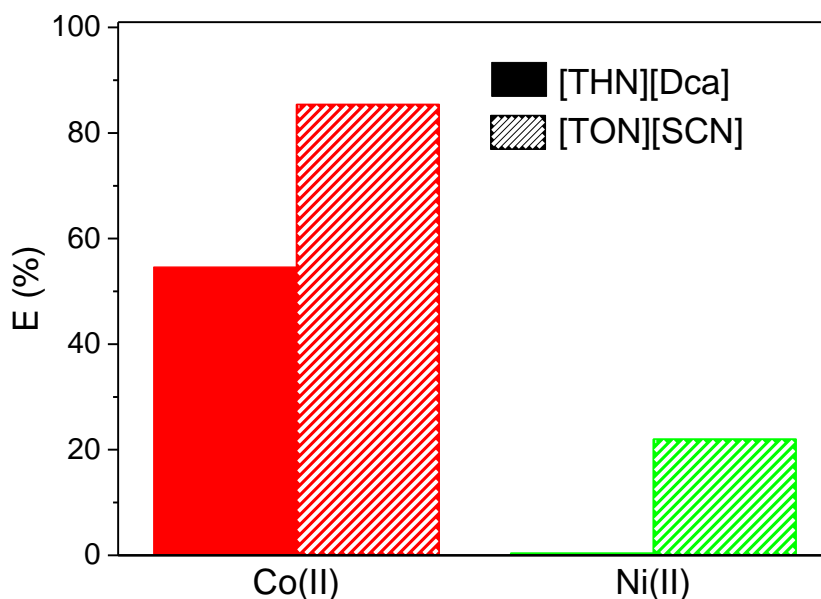


Figure 2: Extraction yields (%E) for aqueous nitrate salts with [THN][Dca] and [TON][SCN].

$C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$, $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{IL}} = 0.5 \text{ g}$.

The overall examination of Figure 2 shows that the most efficient IL for metal extraction is [TON][SCN], with extraction yields higher than 80% for Co(II), whereas with [THN][Dca] the extraction yields are equal to 54%, respectively. Only weak extraction is observed for Ni(II) with both TSILs. Indeed, the extraction yield is about 22% with [TON][SCN] and no extraction is detected with [THN][Dca]. The relative affinity of the first row transition metal (Co(II) and Ni(II)) for the IL phase is strongly correlated with the ability of the anion of the IL to form stable complexes with the metal cation. SCN⁻ is an anion which has the ability to bind Co(II) and Ni(II) metal ions to form complexes with a relatively low stability constant in aqueous medium (β_1 less than 3) [16].

According to a recent study, the Dca⁻ anion [38] has been shown to have a low coordination capacity in aqueous medium towards 3d metals and a good coordination capacity in IL medium. No value of stability constant has been determined in aqueous and non-aqueous media, so it is relevant to consider that the Dca⁻ anion has a lower coordination capacity than the SCN⁻ anion. Interestingly, despite lower extraction yields obtained with [THN][Dca], the values of separation coefficients given in Table 2 show that [THN][Dca] allows more efficient separations than [TON][SCN]. This study thus highlighted that the thiocyanate anion is, from this point of view, an anion with a too high coordinating ability. We thus performed our other studies with [THN][Dca]. However, the extraction efficiencies for Co(II) and Ni(II) obtained with [THN][Dca] were too low to generate efficient extraction systems. We thus further study the possibility of using saline media in two-phase systems to improve the extraction properties of the [THN][Dca] phase and to achieve efficient separation of Co(II) and Ni(II).

Table 2: Extraction yields (%) and separation factors (β) calculated from single metal extraction. Conditions: $C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$; $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{IL}} = 0.5\text{g}$.

Ionic liquids	E (%)		$\beta_{\text{Co/Ni}}$
	Co(II)	Ni(II)	
[THN][Dca]	54.6	0.5	239
[TON][SCN]	85.4	22	21

3.3 Extraction of Co(II) and Ni(II) in NaDca, NaCl and NaNO₃

Extraction experiments of Ni(II) and Co(II) with [THN][Dca] were performed in NaNO₃ and NaCl at concentrations of 0.5 and 4 mol.L⁻¹ and in NaDca at concentrations of 0.2 and 0.5 mol.L⁻¹ (Figure 3). As expected, the addition of chloride or nitrate salt results in an increase of the extraction yields for Ni(II) and Co(II) extraction. Extraction efficiencies for Co(II) are 44% and 99.4% in 0.5 mol L⁻¹ and 4 mol L⁻¹ in NaCl, and 90 and 98.3% in NaNO₃ at the same concentration. At 0.5 mol.L⁻¹, the greater influence of nitrate on extraction is consistent with its higher chaotropic nature. The lower influence of NaNO₃ compared to NaCl at 4 mol.L⁻¹ has already been observed with ionic liquids based on glycine betaine [17] and can be attributed to a specific interaction of nitrate with organic cations, which can form stable ion pairs by anionic metathesis leading to a partial exchange between nitrate and dicyanamide anion, following the equilibrium (7) :



The use of a high concentration of nitrate ions, while promoting cobalt extraction, may lead to a release of Dca⁻ anion in aqueous phase, which can affect the extraction capacity of the ionic liquid. Moreover, the ability of chloride ions to coordinate Co(II) may favor its co-extraction in the ionic liquid phase and explain the higher efficiency of NaCl for Co(II) extraction at 4 mol.L⁻¹. The most remarkable effect is obtained with sodium dicyanamide which allows a quantitative extraction of Co(II) for electrolyte concentrations lower than 0.5 mol.L⁻¹. This effect can be

explained both by the hydrophobicity of the dicyanamide anion, which gives it a chaotropic character and, also, by its coordinating ability towards 3d metals.

As shown in Figure 3, the extraction of Ni(II), which does not exceed a few percent in aqueous solution, can be largely improved by the addition of NaNO₃ or NaDca. With NaNO₃, the extraction yield is 26% at 0.5 mol.L⁻¹, 85% at 4 mol.L⁻¹ and reaches 91.5% in 0.5 mol.L⁻¹ NaDca. However, unlike the results obtained with Co(II), the addition of NaCl has no effect on the extraction of Ni(II) even at a concentration as high as 4 mol.L⁻¹.

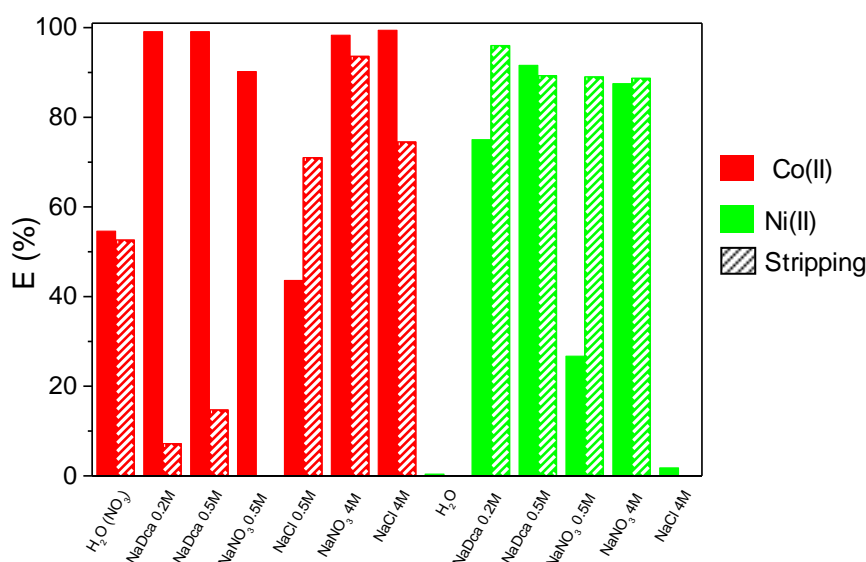


Figure 3: Effect of salt concentration on Ni(II) or Co(II) extraction in [THN][Dca]. $V_{aq} = 2$ mL; $m_{IL} = 0.5$ g; $C_{metal} = 0.05$ mol.L⁻¹

Figure 3 also compares stripping yields of Co(II) from IL phase in all the systems studied. The stripping phase is constituted of 2 mL of a 1 mol.L⁻¹ Na₂SO₄ solution. The stripping yields are expressed in relation to the initial concentration of metal in the IL phase. Our results indicate that extractions in NaNO₃ and NaCl are reversible and the metal can be recovered in a single step. In our conditions, the stripping yield of Co(II) from IL phase previously contacted with NaNO₃ is 93% compared to 75% for ionic liquid phase previously contacted with NaCl. In the

latter case, the complete recovery of Co(II) may be achieved by using 5 mL of stripping solution. On the other hand, the use of NaDca, as background electrolyte, enhances Co(II) extraction but leads to a non-reversible process. Indeed, the stripping yields of Co(II) does not exceed few percents. In the same conditions, the stripping of Ni(II) is higher than 85%.

3.4 Selective separation of Co other Ni.

The extraction yields of Co(II) and of Ni(II) allow the determination of separation factors $\beta_{\text{Co/Ni}}$ to select the most efficient electrolyte for the separation of these two metals. In Table 3 are reported the values of extraction yields and separation factors for Ni(II) and Co(II) extraction. An efficient Co/Ni separation is considered to be achieved for $\beta_{\text{Co/Ni}}$ values higher than 50 combined with extraction yields higher than 80% for Co(II) and less than 20% for Ni(II) [12,13, 17]. Looking at the values in Table 3, the most efficient electrolyte to perform selective separation of Co(II) and Ni(II) and which meets all criteria is NaCl 4 mol.L⁻¹. The value of separation factor obtained with multimetal Co(II)/Ni(II) solution confirms the efficiency of this electrolyte for Co(II)/Ni(II) separation. Indeed, with this salt media, $\beta_{\text{Ni/Co}}$ values estimated from experiments using single and multimetal solutions, are greater than 1000.

The values obtained for D_{Co} and $\beta_{\text{Co/Ni}}$ show that [THN][Dca]/NaCl (4 mol.L⁻¹) is suitable for efficient separation of Co and Ni by liquid-liquid extraction with biphasic system. The efficiency of [THN][Dca]/NaCl is similar to the one reported for P₆₆₆₁₄Cl in conditions close to our study. D_{Co} and $\beta_{\text{Ni/Co}}$ values are higher than those found by Schaeffer *et al.* [13] and Onghena *et al.* [14] for ABS made from [P₄₄₄₁₄][Cl] in HCl/NaCl mixture and those found for commercial extractant such as Cyanex 272 and 301. The here reported values are equally higher to the values reported with glycine-betaine-based ILs [17] in our previous work.

Table 3: Extraction yields (%) and separation factors ($\beta_{\text{Co/Ni}}$) calculated from single or multimetal (*) solution in salt media for [THN][Dca]. Conditions: $C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$; $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{IL}} = 0.5\text{g}$.

Salt media	Extraction yields (%)		Separation factors
	Co(II)	Ni(II)	$\beta_{\text{Co/Ni}}$
NaCl 4 mol.L ⁻¹	99.5	1.8	> 1000
NaNO ₃ 0.5 mol.L ⁻¹	90.2	26.7	25.3
NaNO ₃ 4 mol.L ⁻¹	98.3	87.5	8.3
NaDca 0.5 mol.L ⁻¹	99.1	91.6	10.1
NaCl 4 mol.L ⁻¹ *	99.5	7.2	> 1000

In a previous paper, we pointed out that the most efficient ILs for performing selective extraction were constituted of anions with moderate coordinating power [17]. Experiments performed with [THN][Dca] confirm this trend. The efficiency of NaCl to separate Ni(II) and Co(II) is related to the enhanced coordination of Cl⁻ with Co(II) ions and the ability of this ligand to enter the cobalt coordination sphere to form mixed complexes with Dca⁻ ion in the ionic liquid phase. This has been evidenced in our previous study [17]. The extraction of Co(II) ions obeys the following equilibrium (8):

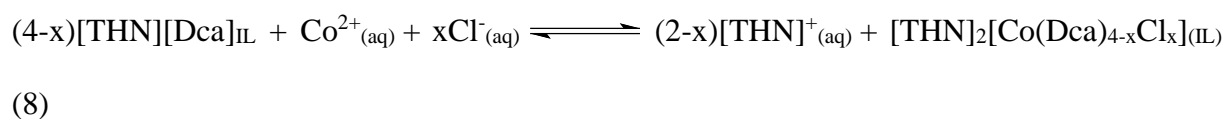


Table 4: comparison of distribution coefficient of Co (D_{Co}) and Ni (D_{Ni}) and separation factors ($\beta_{\text{Co/Ni}}$) of Co over Ni of system described in literature for liquid-liquid extraction for the recovery of strategic metals

System	Solvent/extractant	media	D_{Co}	D_{Ni}	$\beta_{Co/Ni}$	ref
biphasic system IL/aq	[THN][Dca]	NaCl 4 mol.L ⁻¹	790	0.073	> 1000	This study
biphasic system IL/aq	[Bu ₃ NC ₂ NHC ₈][Dca]	NaCl 4 mol.L ⁻¹	96	1.8	53	[17]
biphasic system O/A	Kerosene/ R ₄ NSCN Kerosene/ R ₄ NCl Kerosene/ R ₄ NSO ₄	pH 5	-	-	600 1 0.5	[5]
biphasic system O/A	kerosene/Cyanex 301	HCl 6 mol.L ⁻¹ HCl 4 mol.L ⁻¹	9.10 7.62	0.17 0.06	53.5 127	[4]
biphasic system IL/aq	Cyphos 101 /Cyanex 272	pH 5	0.74	0.0108	69	[7]
biphasic system IL/aq	Cyphos 101	HCl 8M	>100	0.06	-	[3]
biphasic system O/A	toluene /cyanex 272 toluene /Cyphos 104 toluene /Cyphos 101	0.6M/HCl	0.02 3.22 5.05	0.00 0.21 0.00	14	[6]
biphasic system O/A	Octane/INET 3	pH 5.8	23.9	0.08	498	[8]
biphasic system IL/Aq	P ₆₆₆₁₄ Cl	8 mol.L ⁻¹ HCl	460	0.0088	52 000	[11]
ABS P ₄₄₄₁₄ Cl-HCl (NaCl)-H ₂ O	P ₄₄₄₁₄ Cl	30% HCl	-	-	50	[13]
ABS P ₄₄₄₁₄ Cl -NaCl- H ₂ O	P ₄₄₄₁₄ Cl	11% NaCl	100	0.1	500	[14]

3.5 Recyclability of [THN][Dca]

After the stripping process, the IL must be reusable for metal extraction experiments. The loss of [THN][Dca] during the extraction and stripping processes is negligible owing to its low

aqueous solubility. Indeed, the solubility of [THN][Dca] in Na_2SO_4 1 mol.L^{-1} , determined by ^1H NMR measurements, is equal to 0.025%, two times less than in aqueous media. To check the recyclability of the IL, several cycles of extraction-stripping were performed in the same experimental conditions than those used for extraction and stripping experiments. The recyclability of [THN][Dca] was compared in NaCl and NaNO_3 media.

Figure 4 shows the extraction and stripping yields for Co(II) extraction. The stripping yields were determined by considering the total concentration of metal present in the IL phase.

The results show that the efficiency of the extraction and stripping processes remains similar over 2 to 3 cycles in NaNO_3 medium. The extraction efficiency remains above 90% after the third cycle. Metal stripping remains effective throughout the cycle and ensures metal recovery of more than 90%. The same trend is observed with NaCl, but with less efficient stripping than that obtained with NaNO_3 .

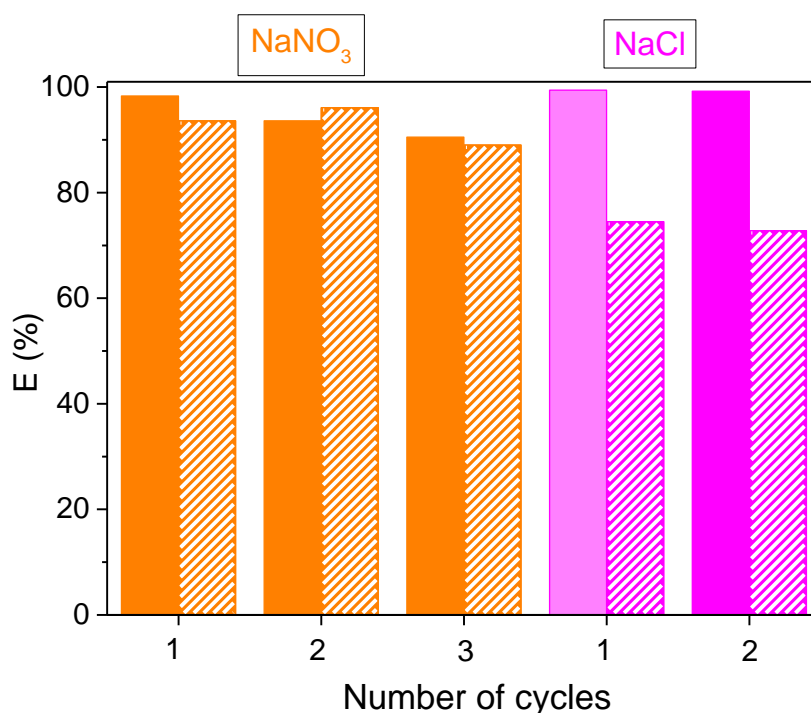


Figure 4: Reusability of the ionic liquid phase for cobalt extraction using [THN][Dca]

3.5 Extraction of Ni(II) and Co(II) by ionogels

The efficiency of [THN][Dca] for efficient Co/Ni separation being made in biphasic system, we then immobilized the IL in silica-based material called ionogels in order to determine the performance of such materials for these extractions.

a. Synthesis and characterization of ionogels

Ionogels were obtained by sol-gel reaction in the presence of [THN][Dca] using a mixture of TMOS/MTMS as silica precursor in order to render the silica surface hydrophobic. This method was proven to be efficient to obtain stable ionogels overtime in water by preventing IL leaching into the aqueous phase [39]. Different sol-gel methods have been used to prepare silica-based ionogels *i.e* the formic acid solvolysis and the hydrolytic method. It has been evidenced that, for the same cationic short alkyl chain BMIM⁺ component, the choice of the method to be used is governed by the nature of the IL anion [40]. Our attempts to use the formic acid route failed as formic acid reacts with [THN][Dca] to form a white precipitate that has not been identified. Silica ionogels containing Dca⁻ anions have been elaborated by Deng and collaborators using the aqueous route in the presence of diluted hydrochloric acid [41,42]. We thus turned out to the aqueous acidic route. Compared to our previous results, the IL [THN][Dca] is less soluble in ethanol and the volume of solvent was thus increased. The loading of the IL was determined by TGA to be around 61% (Figure 6). The IL was then removed from the ionogel by means of a Soxhlet extraction using acetonitrile for two days. The efficiency of the extraction was checked by thermal gravimetric analysis (TGA) and IR spectroscopy. Although no traces of remaining IL could be detected on the IR spectrum (Figure 5) of the washed gel, the remaining content was determined to be around 7% by TGA (Figure 6).

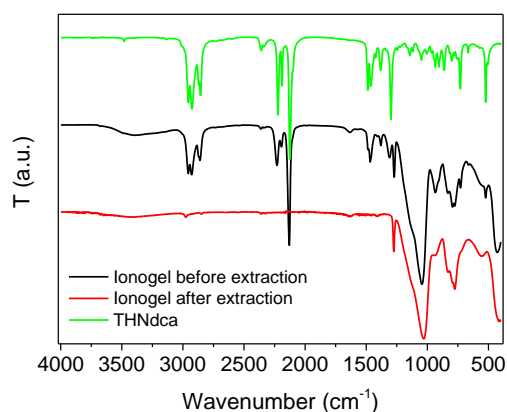


Figure 5. ATR-FTIR spectra of the IL [THN][Dca] and the ionogel before and after extraction of the IL.

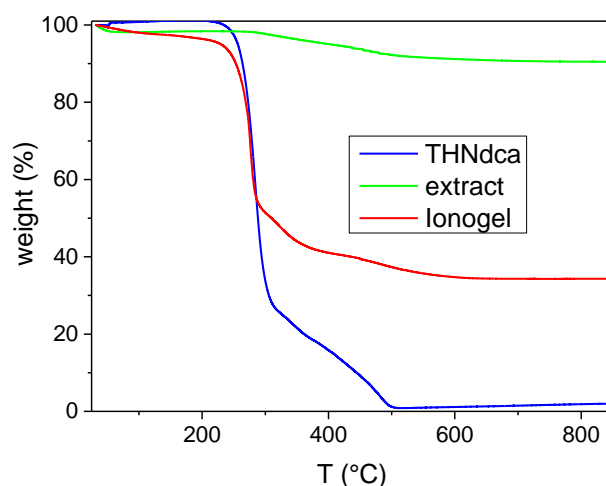


Figure 6. Thermogravimetric analysis plot of [THN][Dca], the ionogel before and after extraction

The N₂ adsorption-desorption isotherm of the ionogel after extraction of the IL disclosed a type IV isotherm characteristic of mesoporous material with H₂ hysteresis loop according to IUPAC classification (Figure 7a) and the pores size distribution is relatively narrow (Figure 7b). Pore volume, surface area and pore diameter of the ionogel obtained with [THN][Dca] are reported in Table 4. These results are compared to those obtained with other ionogels synthesized with dca-based IL containing imidazolium or S-ethyltetrahydrothiophene (Eth) cations at the same

IL loading [41]. The use of THN⁺ cation led to higher specific surface area (1021 m².g⁻¹) and pore volume (1.05 cm³.g⁻¹) but to a significant decrease of pore size. At a first glance, these two latter observations seem contradictory. The THN⁺ cation is bulkier than the imidazolium or Eth cations and should led to an increase of both pore volume and pore size. The discrepancy with the obtained results might be explained by the fact that, for a same IL, addition of MTMOS has been shown to increase the surface area but to decrease pore size [40].

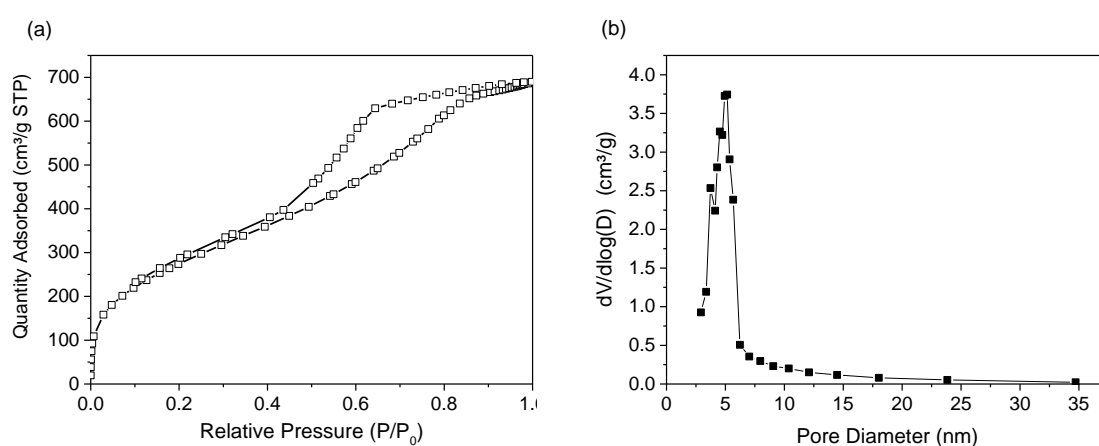


Figure 7. (a) Nitrogen adsorption-desorption isotherm of the ionogel after IL extraction and (b) pore size distribution

Table 4. Textural characteristics of the ionogel determined from adsorption/desorption isotherm at 77K.

Silica precursor	IL	IL loading (%)	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _{BJH} (nm)	Gel time
TMOS-MTMOS	[THN][Dca]	60	1021	1.05	4.6	24 h
TEOS	EMImdca ^a	60	383	0.78	7.9	
TEOS	EThdca ^a	60	420	0.76	6.8	

^a from ref 56

The condensation degrees of the Q and T units were determined by ^{29}Si single pulse NMR analysis (figure S1). The ^{29}Si NMR spectra presents four peaks at -56.1, -64.1, -101.1 and -109.9 ppm attributed to the T^2 ($\text{Si}(\text{OSi})_2(\text{OX})\text{CH}_3$, $\text{X} = \text{H}$ or CH_3), T^3 ($\text{Si}(\text{OSi})_3\text{CH}_3$), Q^3 ($\text{Si}(\text{OSi})_3(\text{OX})$, $\text{X} = \text{H}$ or CH_3) and Q^4 ($\text{Si}(\text{OSi})_4$) silicon sites, respectively [43]. The condensation degree of the T units is 92% and that of the Q unit is 96% (Table S1).

b) Co(II) and Ni(II) extraction in NaCl and NaNO_3 4 mol.L $^{-1}$

Crude ionogels are in the form of a disc of a certain thickness. They can be put directly in contact with the metal solution and placed under stirring on a shaking table. Our experimental conditions are defined to work with the same ratio $[\text{M}^{2+}]_0/[\text{IL}]$ as in batch experiments in order to be able to directly compare the data obtained with ionogels with those obtained in batch experiments. Preliminary experiments have shown that kinetics of transfer from the metal to the IL phase confined in the crude ionogel were not instantaneous contrary to what was observed in batch experiments. Several hours of contact were found necessary to reach the steady state. Therefore, the stirring time before analysis was set at a minimum of 12 hours.

The extraction properties of the ionogel with $[\text{THN}][\text{Dca}]$ towards Ni(II) and Co(II) in salt media were examined. The extraction yields (%E) are depicted in figure 8 and a picture of the ionogel after extraction is given in figure 9.

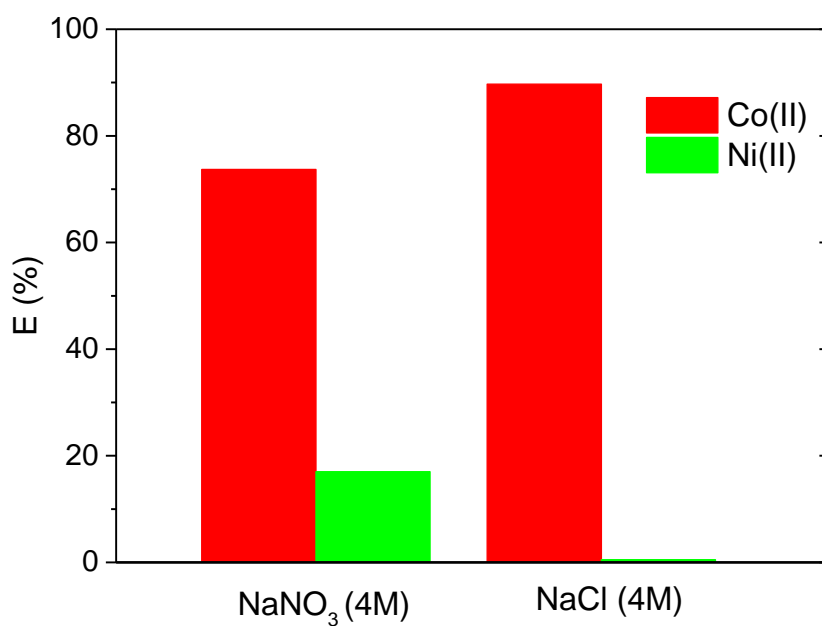


Figure 8: Extraction yields (%E) for aqueous nitrate salt with [THN][Dca]. $C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$; $V_{\text{aq}} = 1.5 \text{ mL}$, $m_{\text{Ionogel}} = 0.6\text{g}$ (0.35g of IL in ionogel).

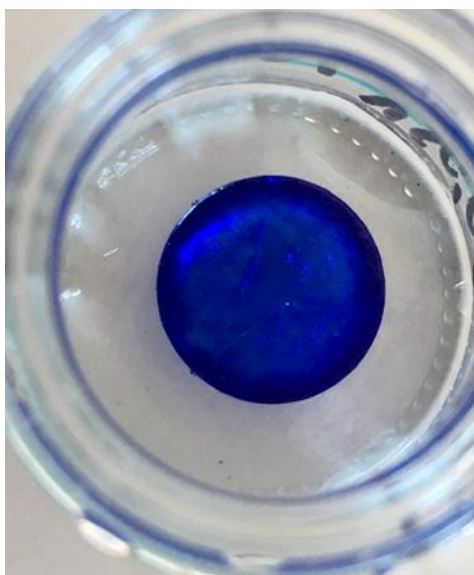


Figure 9: Snapshot of ionogel ([THN][Dca]) after Co(II) extraction. $C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$; $V_{\text{aq}} = 1.5 \text{ mL}$, $m_{\text{Ionogel}} = 0.6\text{g}$ (0.35g of IL in ionogel).

The Co(II) extraction yields obtained with [THN][Dca] confined in ionogel are 73.7% and 89.5% in NaNO₃ and NaCl, respectively. These values should be compared with the extraction yields obtained with neat [THN][Dca] respectively equal to 99.4 and 98.3 %. Although the extraction performance of the IL seems to decrease slightly due to the effect of confinement, it is still relevant for the extraction of Co(II) ions.

The spectrum of Co(II) in neat [THN][Dca] after extraction from NaCl media shows in the visible region a band at 600 nm with a shoulder at 570 nm (Figure S2). The molar absorption coefficient at 600 nm is equal to 900 cm⁻¹.mol⁻¹.L. These characteristics are close to those of the tetrahedral Co(Dca)₄²⁻ complex [44], which means that a change of the coordination of the metal during the extraction process occurred. The spectrum of Co(II) in [THN][Dca] confined in silica ionogel show two bands at 645 and 595 nm both characteristics of Co(II) in tetrahedral coordination (Figure S2). The position of these two transitions seems to indicate (i) a different coordination sphere for Co(II) in neat and confined environments (ii) the formation of at least two types of mixed complexes corresponding to a stoichiometry Co(dca)_(4-x)Cl_(x).

The confinement of [THN][Dca] greatly impacted its ability to extract Ni(II) ions in NaNO₃ medium. Indeed, the extraction efficiency of Ni(II) obtained with the ionogel was only 17% whereas it was 98.3% with the pure IL. No extraction was observed in NaCl medium.

c) Influence of ionogel grinding on extraction properties

Our first observation was that ionogel crushing significantly improved the kinetics of metal partitioning from the aqueous phase to the confined IL phase. A Co(II) solution brought into contact with a crushed ionogel became colourless in less than a few minutes, which means that the time required to reach equilibrium was less than that required for a crude ionogel. Nevertheless, to stay homogeneous with previous experiments made with the crude ionogel,

the stirring time before analysis was set at a minimum of 12 hours. Table 5 shows the extraction (E) and stripping yields (%S) obtained with [THN][Dca] in a ground ionogel for Co(II) and Ni(II) in NaCl 4 mol.L⁻¹. Experiments were carried out on a single metal solution and on a mixture of the two metals in equimolar concentration.

Table 5: Extraction (E) and stripping (%S) yields for Co(II) and Ni(II) with [THN][Dca] confined in ground ionogel from single and bimetallic solutions* (the values in brackets refer to the extraction yields obtained with the crude ionogel). C_{metal} = 0.05 mol.L⁻¹; V_{aq} = 1.5 mL.

[THN][Dca] confined in ionogel	Extraction yields (%)		Stripping yields (%)	Separation factors
	Co(II)	Ni(II)	E' (Co)	$\beta_{Co/Ni}$
NaCl 4 mol.L ⁻¹	98.5 (89.7)	0.5 (0.5)	70.3 (88.3)	> 1000
NaCl 4 mol.L ⁻¹ *	99.5	1	85.2	> 1000

The extraction yield of Co(II) in crushed ionogel is slightly higher to the one obtained with neat IL phase whereas it remains the same for Ni(II) extraction. Our experiments thus show that the most important effect of grinding is to improve the accessibility of the IL and consequently the kinetic of extraction.

Taking into account the Co(II) and Ni(II) extraction yields obtained from a mixing solution, it appears that the efficiency of [THN][Dca] confined in the ground ionogel for separating Co(II) and Ni(II) in a NaCl mixture, is comparable to that obtained with a pure IL, with a separation factor greater than 1000, a quantitative Co(II) extraction and a Ni(II) extraction yield which does not exceed 1%.

d) Recyclability of the ionogel

The leaching of [THN][Dca] confined in the crude ionogel has been measured in water and in Na_2SO_4 solution of 1 mol L^{-1} . The proportions of IL release in these phases are equal to 0.04% and 0.023%, respectively. These values are lower than the solubility of pure [THN][Dca] and guarantee a low release of the confined IL during the extraction and stripping processes. The recyclability of the monolithic ionogel was evaluated over several extraction-stripping cycles, following the same experimental conditions than those used for single extraction experiments. To improve the stripping yield, the volume of the stripping phase was set to 5 mL of 1 mol.L^{-1} Na_2SO_4 instead of the 2 mL used for single extraction experiments. The recyclability of the ionogel was compared in NaCl and NaNO_3 media.

Figure 10 reports the extraction and stripping yields for the extraction of Co(II) with [THN][Dca] ionogel with NaNO_3 or NaCl 4 mol.L^{-1} . With NaNO_3 (Figure 10a), the results show that the efficiency of the extraction decreases regularly over the extraction/stripping cycles. The extraction yield is greater than 70% in the first cycle and drops to 45% in the third cycle. The stripping yield remains nearly constant over the three cycles and higher than 80%. The loss of extraction efficiency, during the extraction-stripping cycles can be attributed to the $\text{NO}_3^-/\text{Dca}^-$ exchange which depletes the IL of the coordinating Dca^- anion.

After the third cycle, the ionogel was contacted with a 1 mol.L^{-1} NaDca aqueous solution during 12 hours and then the fourth cycle of extraction was carried out. As seen in figure 10a, treatment by Dca^- anion regenerates the extraction capability of the IL. Indeed, the extraction yield for this fourth cycle is 77%.

In NaCl medium (Figure 10b), the loss of extraction efficiency over the cycle is much less marked than in NaNO_3 , since the extraction yield of the third cycle is equal to 73%. As for NaNO_3 , the efficiency of stripping remains nearly constant over the three cycles and higher than 80%. The higher hydrophilicity of Cl^- compared to NO_3^- limits the anionic exchange with

Dca⁻ anion. NaCl medium provides a better preservation of the integrity of the ionogel than NaNO₃.

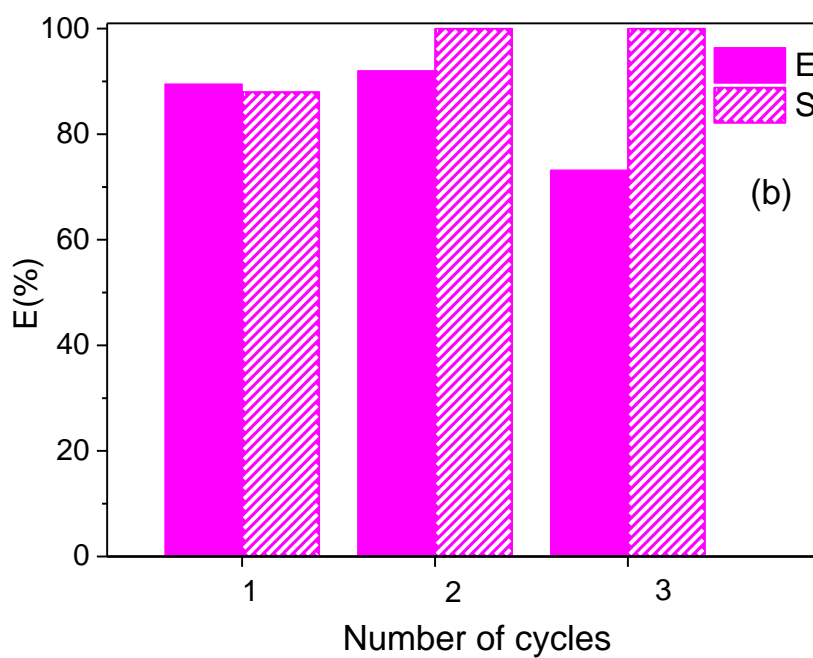
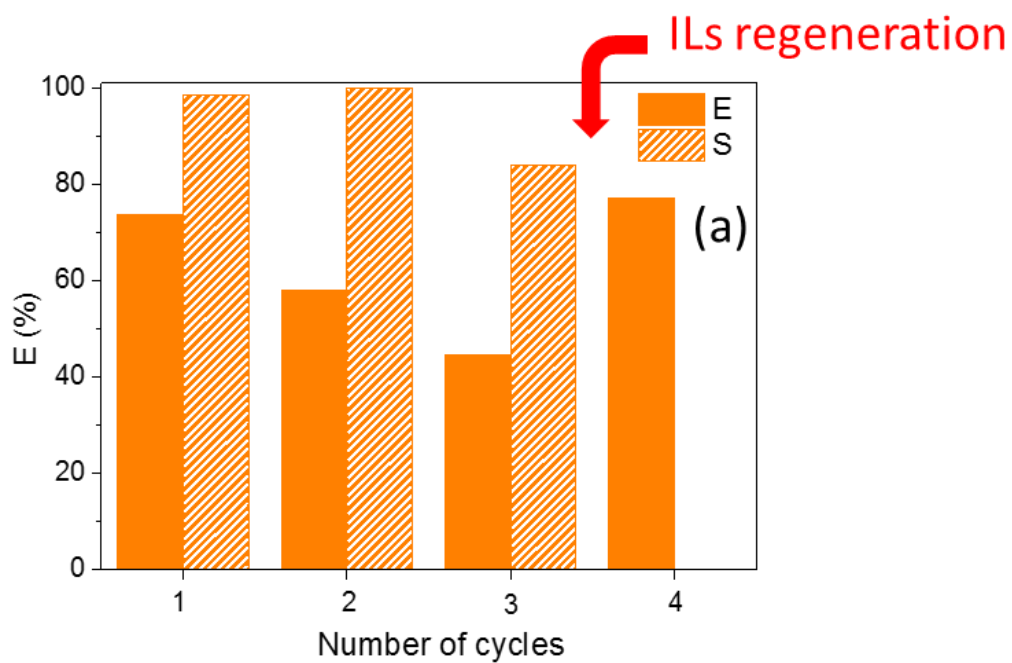


Figure 10: Reusability of [THN][Dca] confined in ionogel for cobalt extraction (a) in NaNO₃ 4 mol.L⁻¹ ; (b) in NaCl 4 mol.L⁻¹

Conclusion

In this work, we demonstrated the ability of TSILs, obtained by combining tetraalkylammonium cations with coordination anions, to remove Co(II) and Ni(II) from aqueous effluents. ILs are composed of low-cost fractions and extraction does not require the use of a chelating agent, which is a valuable advantage for process design. The thiocyanate-based IL has a high efficiency for the extraction of Co(II). The moderate efficiency of dicyanamide-based IL allows the implementation of a process for the selective extraction of Co(II) and Ni(II) by the successive use of NaCl and Na₂SO₄ with separation factors as high as the best performing systems described in the literature ($\beta_{\text{Co/Ni}} > 1000$). Under these conditions, the leaching of IL in the aqueous effluent is limited, thus preserving the integrity of the extraction phase and its reusability. The confinement of [THN][Dca] in a silica-matrix ionogel is a valuable solution to improve the handling of the IL. Indeed, the extraction properties and recyclability of the [THN][Dca] ionogel were found to be very close to those obtained with the pure IL, with efficient separation of Co(II) from Ni(II) in NaCl 4 mol.L⁻¹. In this preliminary work, we have shown that ionogels can be a credible alternative to ILs grafted on a solid matrix. Further experiments are currently performed to evaluate the upscaling of our results.

Acknowledgments

The authors are grateful to the ‘‘GDR LIPs’’ for its financial support.

Appendix A : supplementary data

References

- [1] European Commission. Study on the review of the list of Critical Raw Materials; Publications Office of the European Union: Luxembourg, 2017. <https://doi.org/10.2873/876644>.
- [2] D.S. Flett, Cobalt–nickel separation in hydrometallurgy: a review. *Chem. Sustain. Dev.* 12 (2004) 81–91.
- [3] K. Larsson, K. Binnemans, Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling, *Green Chem.* 16 (2014) 4595–4603. <https://doi.org/10.1039/C3GC41930D>
- [4] Hachemaoui A., Belhamel K. Simultaneous extraction and separation of cobalt and nickel from chloride solution through emulsion liquid membrane using Cyanex 301 as extractant, *International Journal of Mineral Processing* 161 (2017) 7–12. <http://dx.doi.org/10.1016/j.minpro.2017.02.002>
- [5] A.A. Nayl Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336, *Journal of Hazardous Materials* 173 (2010) 223–230 <http://dx.doi.org/10.1016/j.jhazmat.2009.08.072>
- [6] M. Janiszewska, A. Markiewicz, M. Regel-Rosocka, Hydrometallurgical separation of Co(II) from Ni(II) from model and real waste solutions, *Journal of Cleaner Production* 228 (2019) 746–754. <https://doi.org/10.1016/j.jclepro.2019.04.285>
- [7] D. Cholico-Gonzalez , A. Chagnes, G. Cote, M. Avila-Rodriguez, Separation of Co(II) and Ni(II) from aqueous solutions by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) as solvent, *J. Mol. Liq.* 209 (2015) 203–208. <https://doi.org/10.1016/j.molliq.2015.05.048>
- [8] Fu J., Xu W., Yub F., Wanga H., Wanga J., Evaluation of an unsymmetrical dialkylphosphinic acid INET-3 for cobalt and nickel extraction and separation from sulfate

<https://doi.org/10.1016/j.mineng.2020.106499>

[9] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry *Chem. Soc. Rev.* 37 (2008) 123–150. <https://doi.org/10.1039/B006677J>.

[10] G.J. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for “clean” liquid-liquid extraction. *Chem. Commun.* (1998) 1765–1766. <https://doi.org/10.1039/A803999B>.

[11] S. Wellens, B. Thijs, K. Binnemans, An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids, *Green. Chem.* 14 (2012) 1657–1665. <https://doi.org/10.1039/C2GC35246J>

[12] M. Gras, N. Papaiconomou, N. Schaeffer, E. Chainet, F. Tedjar, J.A.P. Coutinho, I. Billard, Ionic-Liquid-Based Acidic Aqueous Biphasic Systems for Simultaneous Leaching and Extraction of Metallic Ions. *Angew. Chem. Int. Ed.* 57 (2018) 1563 –1566. <https://doi.org/10.1002/anie.201711068>

[13] N. Schaeffer, M. Gras, H. Passos, V. Mojilireddy, C.M.N. Mendonça, E. Pereira, E. Chainet, F. Tedjar, J.A.P. Coutinho, I. Billard, N. Papaiconomou, Synergistic Aqueous Biphasic Systems: A New Paradigm for the “One-Pot” Hydrometallurgical Recovery of Critical Metals, *ACS Sustainable Chem. Eng.* 7 (2019) 1769–1777. <https://doi.org/10.1021/acssuschemeng.8b05754>.

[14] B. Onghena, T. Opsomer, K. Binnemans, Separation of cobalt and nickel using a thermomorphic ionic-liquid-based aqueous biphasic system, *Chem. Commun.* 51 (2015) 15932–15935. <https://doi.org/10.1039/C5CC06595J>.

- [15] S. Boudesocque, A. Mohamadou, A. Martinez, I. Dechamps, L. Dupont, L. Use of dicyanamide ionic liquids for metal ions extraction, RSC. Advances 6 (2016) 107894-107904. <https://doi.org/10.1039/C6RA18991A>
- [16] K. J. Powell, Academic software Mini SC database version 5.3, 1999.
- [17] P.D. Diabate, S. Boudesocque, A. Mohamadou, L. Dupont, Efficient separation of Cobalt, Nickel and Copper using analogues of glycine-betaine based ionic liquids. Sep. Purif. Technol. 242 (2020) 116782. <https://doi.org/10.1016/j.seppur.2020.116782>
- [18] S. Boudesocque, A. Mohamadou, A. Martinez, I. Dechamps, L. Dupont, L. Use of dicyanamide ionic liquids for metal ions extraction, RSC. Advances 6 (2016) 107894-107904. <https://doi.org/10.1039/C6RA18991A>
- [19] T. Yost, B. Fagan, L. Allain, C. Barnes, S. Dai, M. Sepaniak, Z. Xue, Crown ether- doped sol-gel materials for strontium(II) separation, Anal. Chem. 72 (2000) 5516–5519. <https://doi.org/10.1021/ac0005518>.
- [20] B. Yu, J. Bell, H. Luo, S. Dai, Ionic liquid and silica sol-gel composite materials doped with N,n',n'-tetra(n-octyl)diglycolamide for extraction of La^{3+} and Ba^{2+} , Sep. Sci. Technol. 47 (2012) 244–249. <https://doi.org/10.1080/01496395.2011.621162>.
- [21] R. Makote, H. Luo, S. Dai, M. Abraham, L. Moens, Synthesis of ionic liquid and silica composites doped with dicyclohexyl-18-crown-6 for sequestration of metal ions, Clean Solvents 819 (2002) 26–33. <https://doi.org/10.1021/bk-2002-0819.ch003>.
- [22] Tian, P. Yin, R. Qu, C. Wang, H. Zheng, Z. Yu, Removal transition metal ions from aqueous solutions by adsorption using novel hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphoric acid, Chem. Eng. J. 162 (2010) 573–579. <https://doi.org/10.1016/j.cej.2010.05.065>.
- [23] A. N. Turanova, V. K. Karandashev, N. S. Sukhinina, V. M. Masalova, G. A. Emelchenko, Adsorption of lanthanides and scandium ions by silica sol-gel material doped

with novel bifunctional ionic liquid, trioctylmethylammonium 1-phenyl-3-methyl-4-benzoyl-5-onate, *Journal of Environmental Chemical Engineering* 4 (2016) 3788–3796. <https://doi.org/10.1016/j.jece.2016.08.024>.

[24] Y. Liu, X. Sun, F. Luo, J. Chen, The preparation of sol-gel materials doped with ionic liquids and trialkyl phosphine oxides for Yttrium(III) uptake, *Anal. Chim. Acta* 604 (2007) 107–113. <https://doi.org/10.1016/j.aca.2007.10.005>

[25] Y. Liu, L. Zhu, X. Sun, J. Chen, F. Luo, Silica materials doped with bifunctional ionic liquid extractant for Yttrium extraction, *Ind. Eng. Chem. Res.* 48 (2009) 7308–7313. <https://doi.org/10.1021/ie900468c>

[26] Y. Liu, L. Guo, L. Zhu, X. Sun, J. Chen, Removal of Cr(III, VI) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials, *Chemical Engineering Journal* 158 (2010) 108–114. <https://doi.org/10.1016/j.cej.2009.12.012>.

[27] B. Ekka, L. Rout, M. K.S.A. Kumar, R. K. Patel , P. Dash, Removal efficiency of Pb(II) from aqueous solution by 1-alkyl-3- methylimidazolium bromide ionic liquid mediated mesoporous silica, *Journal of Environmental Chemical Engineering* 3 (2015) 1356–1364. <https://doi.org/10.1016/j.jece.2014.12.004>.

[28] Y. Liu, L. Guo, L. Zhu, X. Sun, J. Chen, Removal of Cr(III, VI) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials, *Chemical Engineering Journal* 158 (2010) 108–114. <https://doi.org/10.1016/j.cej.2009.12.012>.

[29] P. Forte, A. Sachse, M. Maes, A. Galarneau, D. De Vos, Selective continuous flow extractive denitrogenation of oil containing S- and N heteroaromatics using metal-containing ionic liquids supported on monolithic silica with hierarchical porosity *RSC Adv.* 4 (2014) 1045-1053. <https://doi.org/10.1039/c3ra43585g>.

- [30] E. Jean, D. Villemin, M. Hlaibi, L. Lebrun, Heavy metal ions extraction using new supported liquid membranes containing ionic liquid as carrier, *Sep. and Purif. Technol.* 201 (2018) 1–9. <https://doi.org/10.1016/j.seppur.2018.02.033>
- [31] W. Yun, Z. Youwen, F. Fuyou, L. Huimin, H. Peizhou, S. Yinglin, Synthesis of task-specific ionic liquids with grafted diglycolamide moiety. Complexation and stripping of lanthanides, *J. Radioanal. Nucl. Chem.* 299 (2014) 1213–1218. <https://doi.org/10.1039/C7DT04255H>
- [32] C. A. Hawkins, M.A. Momena, S.L. Garvey, J. Kestell, M. D. Kaminski, M. L. Dietz, Evaluation of solid-supported room-temperature ionic liquids containing crown ethers as media for metal ion separation and preconcentration, *Talanta* 135 (2015) 115–123. <https://doi.org/10.1016/j.talanta.2014.12.019>
- [33] K. Yavir, L. Marcinkowski, R. Marcinkowska, J. Namieśnik, A. Kloskowski, Analytical applications and physicochemical properties of ionic liquid based hybrid materials: A review *Analytica Chimica Acta* 1054 (2019) 1–16. <https://doi.org/10.1016/j.aca.2018.10.061>
- [34] J. Le Bideau, L. Viau, A. Vioux, Ionogels, ionic liquid based hybrid materials, *Chem. Soc. Rev* 40 (2011) 907–925. <https://doi.org/10.1039/C0CS00059K>.
- [35] I. V. Melnyk, Y. L. Zub, E. Véron, D. Massiot, T. Cacciaguerra, B. Alonso, Spray-dried mesoporous silica microspheres with adjustable textures and pore surfaces homogeneously covered by accessible thiol functions *Chem. Mater.* 18 (2008) 1368–1382. <https://doi.org/10.1039/B717133A>
- [36] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J. O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra, *Magn. Res. Chem.* 40 (2002) 70–76. <https://doi.org/10.1002/mrc.984>.
- [37] F. Malz, H. Jancke, Validation of Quantitative NMR, *J. Pharm. Biomed. Anal.* 38 (2005) 813–823. <https://doi.org/10.1016/j.jpba.2005.01.043>

- [38] M. Gras, N. Papaiconomou, E. Chainet, I. Billard, Dicyanamide Ions as Complexing Agents of Co(II): From Weak Ligands in Water to Strong Ones in an Ionic Liquid, *Solv. Extr. Ion Exch.* 36 (2018) 583-601. <https://doi.org/10.1016/j.seppur.2020.116782>.
- [39] M.A. Néouze, J. Le Bideau, P. Gaveau, S. Bellayer, A. Vioux, Ionogels, New Materials Arising from the Confinement of Ionic Liquids within Silica-Derived Networks, *Chem. Mater.* 19 (2006) 3931-3936. <https://doi.org/10.1021/cm060656c>
- [40] L. Viau, M.A. Néouze, C. Biolley, S. Volland, D. Brevet, P. Gaveau, P. Dieudonné, A. Galarneau, A. Vioux, Ionic Liquid Mediated Sol-Gel Synthesis in the Presence of Water or Formic Acid: Which Synthesis for Which Material ?, *Chem. Mater.* 24 (2012) 3128-3134. <https://doi.org/10.1021/cm301083r>.
- [41] J. Zhang, Q. Zhang, F. Shi, S. Zhang, B. Qiao, L. Liu, Y. Ma, Y. Deng Greatly enhanced fluorescence of dicyanamide anion based ionic liquids confined into mesoporous silica gel *Chem. Phys Lett*, 461 (2008) 229-234. <https://doi.org/10.1016/j.cplett.2008.07.015>.
- [42] J. Zhang, Y. Ma, F. Shi, L. Liu, Y. Deng, Room temperature ionic liquids as templates in the synthesis of mesoporous silica via sol-gel method, *Micropor. Mesopor. Mat.* 119 (2009) 97-103. <https://doi.org/10.1016/j.micromeso.2008.10.003>
- [43] C.J. Brinker, G.W. Scherer Sol-gel science. The physics and chemistry of sol-gel processing Academic, New York (1990) p. 543-558. <https://doi.org/10.1002/adma.19910031025>.
- [44] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, NY.,