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Separation of cobalt, nickel and copper with task-specific amido functionalized glycine-betaine-based ionic liquids

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ABSTRACT

Task Specific Ionic Liquids (TSILs) were generated by association between a cationic amido functionalized analogues of glycine-betaine (AGB) and coordinating anions such as dicyanamide (Dca^-), 4-chlorosalicylate ($ClSal^-$), saccharinate (Sac^-) and weak coordinating one such as bis(trifluorosulfonyl)imide (Tf_2N^-). Extraction of Cu(II), Ni(II), Co(II), from pure water and salt media was performed with these AGB-ILs at room temperature. The obtained results show that in pure water Clsal based AGB-ILs have a high extraction efficiency towards these metals, whereas dicyanamide based AGB-ILs may extract efficiently Cu(II). In some cases, extraction can be improved by using simple chaotropic salts or intermediate anion such as NO_3^- or Cl^-. Co(II) may be quantitatively extracted by Dca based AGB-ILs in NaCl 4 $mol.L^{-1}$. The rational use of background salts can improve the selectivity of the extraction process and allow the separation and the recovery of the three metals separately from a mixture containing two or three divalent metals. The metal could be back-extracted from the ionic liquid phase with aqueous solution of Na_2SO_4, limiting the release of ionic liquid cation in aqueous media, thus preserving its integrity. The metal extractability by the Dca based ionic liquids after the stripping is quasi-equivalent to that of the fresh AGB-IL showing that it can be reused for three or four extraction and stripping cycles. A regeneration of Dca based ionic liquids after several

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extraction cycles is made possible by adding a solution of NaDca which restore their extractive capacity.

Keywords: analogues of glycine-betaine, ionic liquid, liquid-liquid extraction, extraction mechanism, copper(II), nickel(II), cobalt(II).

Introduction

In recent years, ionic liquids (ILs) have attracted significant interest in the field of metal extraction as an alternative medium in liquid-liquid extraction processes. ILs are salts composed of asymmetric organic cations, with melting point below than 100°C. The proposal of ILs as environmentally friendly media to replace volatile organic solvents for liquid-liquid extraction, has been widely studied with the aim to develop "greener" extraction processes [1,2]. Hydrophobic ionic liquids form biphasic systems with aqueous effluents and constitute an extracting phase for metals. However, conventional ionic liquids are constituted by weak chelating moieties, and have a low capability to dissolve metal salts. The use of chelatants [3-6] or the design of Task-Specific Ionic Liquids (TSILs) [7-12] by the introduction of chelating functions on the organic cation or the use of coordinating anions [13-15] can greatly increase the metals affinity for the IL phase, providing much greater extraction yields than those found with conventional molecular solvents. However, the development of green processes requires particular attention on metal extraction mechanisms, which must limit as much as possible the release of organic species into the aqueous effluent [16-20]. Indeed, the release of organic cations in the aqueous phase alters the quality of the effluents as well as the integrity of the ionic liquid, reducing its recyclability [21,22]. In other words, the process must limit the cation exchange reactions, and exclusively favours ion-pairs extraction mechanisms. To reach this objective, extraction experiments in saline media were performed. The addition of an indifferent

electrolyte favors the neutral extraction and increase the extraction yields of metals. The extraction in salt media is a credible path for the implementation of extraction process limiting the release of ionic liquids species in aqueous solutions, showing also a real environmental benefit. The use of saline environments has already been successfully proposed in combination with hydrophilic ionic liquids to generate aqueous biphasic systems (ABS) for the extraction and separation of strategic metals [23-27]. Previous studies have shown that saline media can be combined with hydrophobic ionic liquids to enhance metal extraction and to carry out selective metal separation [28-30]. The addition of a background electrolyte is also an effective way to erase the influence of the anion of the metal salt, in the extraction process. The nature of the electrolyte plays an important role in improving extraction efficiency. In a previous work [30], we highlighted the predominant role of the counter anion of the copper salt in the extraction process of Cu(II), by comparing the extraction yields of several copper salts with tetraalkylammonium dicyanamide salts. Copper sulfate is not extracted by ionic liquid phase whereas copper perchlorate is fully extracted. As it was already reported in our previous works [30] and those of Janssen et al. [31], the influence of the anion is closely correlated to its position in the Hofmeister series. The sulfate ion is located on the left side of the Hofmeister series and has a high hydration energy, estimated at -1080 kJ mol^{-1} [32,33]. This anion interacts strongly with water molecules acting as a structuring agent, leading to “salting out” effect. For these reasons, sulfate ions are called kosmotropic, and will have a limited role in the extraction process. On the other hand, nitrate and perchlorate anions are positioned on the right side of the Hofmeister series [34]. These anions present a weak energy of solvation equal to -314 and -219 $kJ.mol^{-1}$ [32], respectively. Therefore, they are easily co-extracted with the metal cation in the ionic liquid phase which favors the extraction process by ion-pairing. These anions, which lead to “salting in” effect are called “chaotropic”, and allow the obtaining of high extraction yields. Here, we report the ability of task-specific ionic liquids, designed through association of

cationic analogues of glycine-betaine (AGB-ILs) with coordinating anions (Figure 1), to selectively extract Cu(II), Co(II) and Ni(II) in saline media. Therefore, the emphasis had been placed on the efficient separation of the mixture copper, nickel and cobalt.

The separation of Co(II) and Ni(II) is of industrial concern because of their presence in several electronic devices such as portable electronic products and electric vehicles. They are often present as nickel-metal hybride (Ni-MH) batteries, due to their high electrochemical performances. Considerable attention has been given to the recycling of used Ni-MH batteries because their random discharge can lead to serious environmental pollution [35,36]. In this work, we propose to investigate the influence of chaotropic and kosmotropic electrolytes in extraction and stripping properties of ionic liquids to develop extraction and recovery processes of these metals.

The choice of the betaine derivatives is justified by their accessibility via simple synthetic route, the cost of starting materials, and its structural modularity, which allows the control of the hydrophobicity of cation by varying the alkyl chain length bound to either the ammonium group or carboxylate group [37,38]. The choice of the anions is based on its hydrophobic and chelating nature. The saccharinate and chlorosalicylate anions [39,40] are known for their complexing capacity towards heavy and first row transition metals. The dicyanamide anion, good chelator of metal ions [41-43], is among the cheapest anion commonly used to generate ILs.

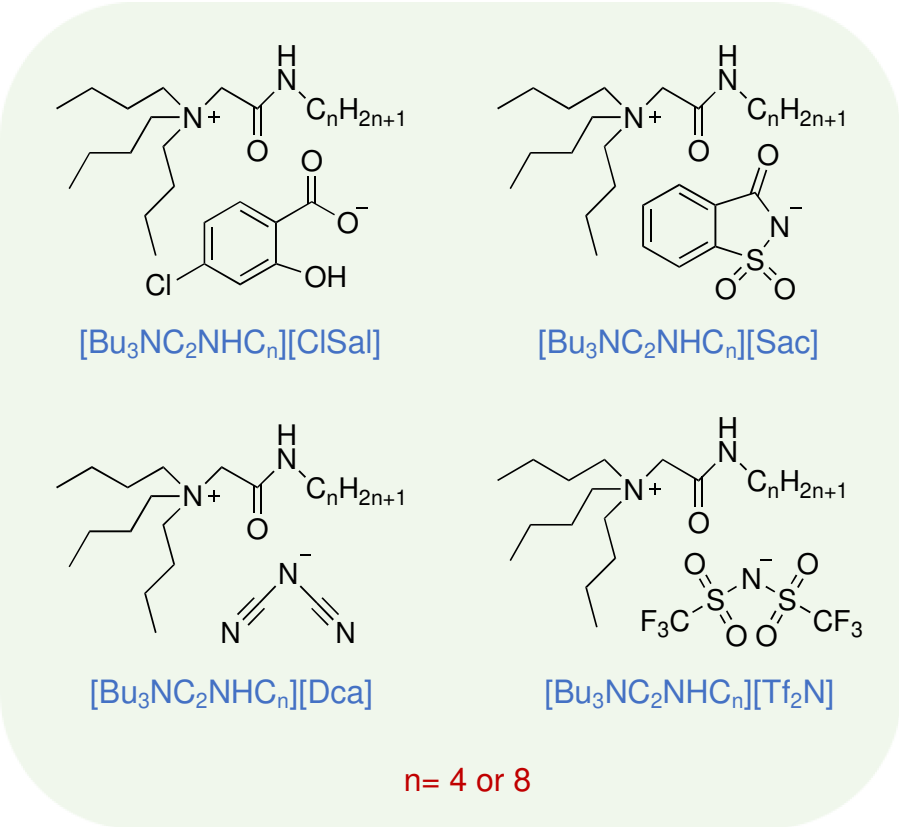

Figure 1: Structure of the synthesized AGB-ILs.

Experimental Section

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 saccharinate (98%), sodium dicyanamide (99%), and lithium bis(trifluoromethylsulfonyl)imide were obtained from Sigma-Aldrich. Sodium hydroxide (99%), n-butylamine (99%), n-octylamine (99%) and 4-chlorosalicylic acid (98%) were purchased from Acros Organics.

Physical measurements. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer in our University. The UV-visible spectra of metal solutions were recorded using a Carry-5000 Varian spectrophotometer. The metal concentration determination was performed by spectrometry ICP-OES, Thermo Fisher ICAP. The stock

aqueous solutions of metals were prepared by dissolving the corresponding salt of the respective metals (analytical grade purchased from Sigma-Aldrich and Fluka Chemical) in double distilled and deionized water. The purity of ionic liquids was checked by elemental analysis and ^{1}H NMR. The absence of bromide ions was checked by ion chromatography.

^{1}H NMR spectrum was recorded in D_2O and DMSO-d_6 at room temperature with a Bruker AC 600 spectrometer. Chemical shifts (in ppm) for ^{1}H NMR spectra were referenced to residual protic solvent peaks. The concentrations of organic cation in aqueous phase were determined by ^{1}H NMR with an internal reference.

The metal ion distribution ratios were determined by mixing definite volume of IL and aqueous phase. The mixture was shaken during 12 h to reach equilibrium and then centrifuged (2000 g, 5 mn). The phases were then separated for analysis. The aqueous phase was analyzed by spectrophotometry ICP-OES. The efficiency of the extraction process was evaluated by the calculation of the extraction percentage (%E) using the following equation:

$$E(\%) = \frac{V_{IL}[M]_{IL}}{V_{IL}[M]_{IL} + V_{aq}[M]_{aq}} \times 100 \qquad (1)$$

The metal distribution coefficient (D) between IL and aqueous phases was calculated as follows:

$$D = \frac{[M]_{IL}}{[M]_{aq}} \times \frac{V_{aq}}{V_{IL}} \qquad (2)$$

The separation factor ($\beta_{M1/M2}$) was employed to express the selectivity of the extraction between two metals M_1 and M_2 and was calculated as:

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} \qquad (3)$$

The percentage of stripping (%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 $[M]_{IL,0}$

$$S(\%) = \left(1 - \frac{[M]_{IL}}{[M]_{IL,0}}\right) \times 100 \qquad (4)$$

The metal extraction percentages (%E) were determined at 298 K. The experiments are made in triplicate to ensure the reproducibility of the assay, and the mean values of extraction yields are considered, for each system studied.

The stripping experiments were carried out by adding 2 mL of pure water or an aqueous solution of Na_2SO_4 (1.5 mol.L^{-1}) to the recovered ionic liquid phase after extraction of the metal. The mixture was stirred 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 ^{1}H NMR spectroscopy following this method: 100 µL of an aqueous solution of DMSO previously prepared at 100 mM is introduced into a conical tube. Then 200 µL of the sample to analyze which is obtained after saturation of the aqueous phase with the ionic liquid were added. The mixture is dissolved in 700 µL of deuterated water (D_2O). For measurements after metal extraction, we use a D_2O solution with 0.1 M of NaOH to precipitate paramagnetic metal residues. The ^{1}H NMR spectrum of the DMSO solution shows a single peak at δ = 2.68 ppm that corresponds to six protons. The DMSO is an internal reference so, its signals resonate in an area which is not overlapping the different studied ionic liquids signals. From the concentration of the DMSO, the concentration of the sample can be deduced after integration of the different signals. The uncertainty range for this method is 1% [44].

Results and Discussion

Extraction of Cu(II), Ni(II) and Co(II). To examine the extraction properties of the synthesized ionic liquid towards Cu(II), Ni(II), Co(II) we determine the extraction yield (%E) from 0.05 mol.L^{-1} solutions of the nitrate salts of these metals at 298 K. The extraction yields (%E) for each IL are depicted in figure 2.

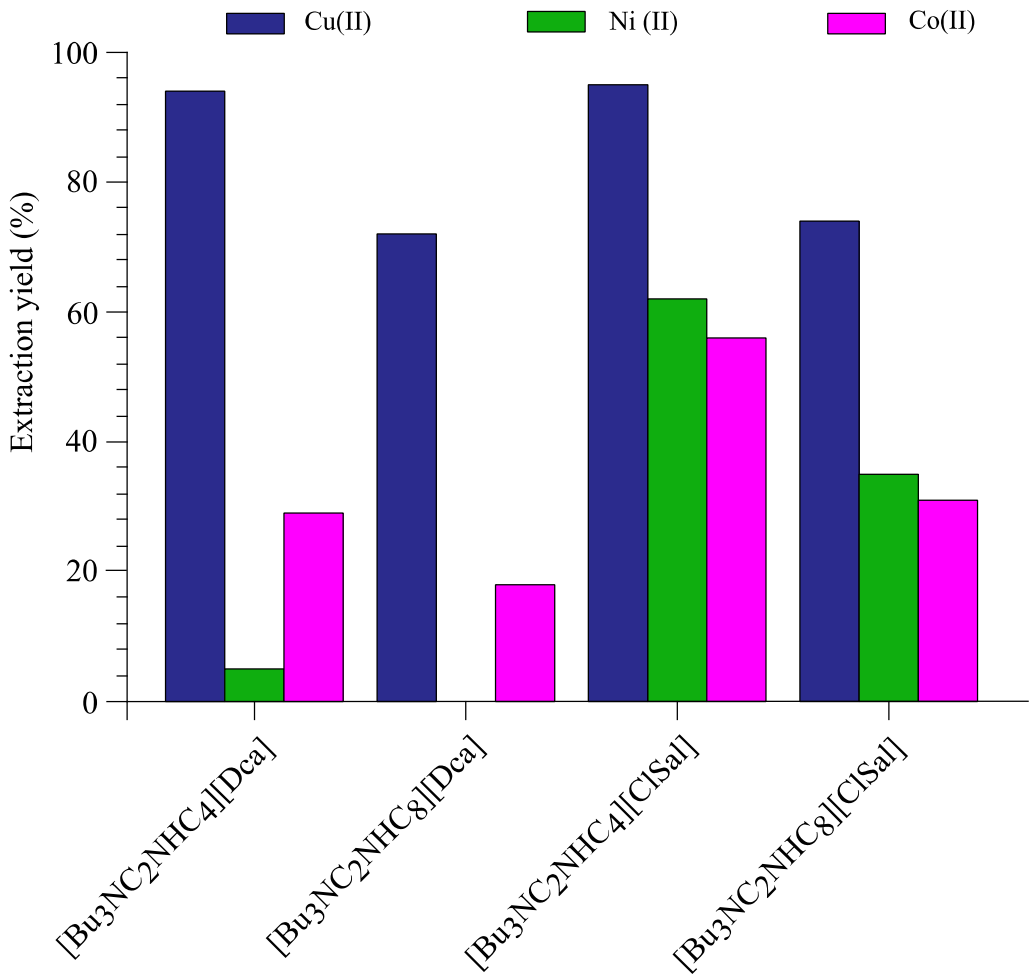

Figure 2: Extraction yields (%E) for aqueous nitrate salt with $[Bu_3NC_2NHC_n][ClSal]$ and $[Bu_3NC_2NHC_n][Dca]$. C_{metal} = 0.05 mol.L^{-1}; Vaq = 2 mL, m_{IL} = 0.5g.

The overall examination of Figure 2 shows as expected that the influence of the anion on the extraction properties of ionic liquids follows the classical trends observed in our previous works with ester analogues of glycine-betaine based ionic liquids [45]. The most efficient anion for the extraction of metal is the Clsal$^-$ anion. Indeed for all metals ions, extraction yields are higher than 50% with $[Bu_3NC_2NHC_4][ClSal]$. By comparison $[Bu_3NC_2NHC_4][Dca]$ shows weaker extraction yields for Co(II) and Ni(II). Only low extraction is observed with $[Bu_3NC_2NHC_4][Sac]$ and $[Bu_3NC_2NHC_4][Tf_2N]$ with an extraction efficiency of only a few percent for all metals. The influence of the anion is more pronounced with $Bu_3NC_2NHC_8^+$ based

ionic liquids. As already discussed in our previous works [45], the extraction of first raw metal ions (Cu(II), Co(II) and Ni(II)) by Dca^- and $ClSal^-$ based ionic liquids show that the capability of these ionic liquid to extract metal ion, is greatly correlated to the ability of the anion of the ionic liquid to form stable complexes with the metal cation. The affinity of the metals ions for DCa- and Clsal- based ionic liquids, is weak for Ni(II) and Co(II) and higher for Cu(II), and may be correlated to the relative position of these cations in the Irving-Williams series [45]. The extraction yields obtained with amide functionalized analogues of glycine-betaine are lower than those found previously with the corresponding ester. The difference is only a few percent for Cu(II) and is more marked for Ni(II) and Co(II). Indeed, extraction yields with $[Bu_3NC_2OC_4][Dca]$ is equal to 82 and 86% for Co(II) and Ni(II), respectively, whereas with $[Bu_3NC_2NHC_4][Dca]$, it is only 5 and 29% for Co(II) and Ni(II), respectively. The same trend is observed with $ClSal^-$ and $Bu_3NC_2NHC_8^+$ based ionic liquids.

The ester or amide analogue of glycin betaine are non-coordinating and are only involved in ion exchange reactions in the global extraction mechanism. It is reasonable to correlate the lower extraction yield obtained with the amide analogue of glycine-betaine to their lower solubility in water. Indeed, the solubilities of $[Bu_3NC_2NHC_4][ClSal]$ and $[Bu_3NC_2OC_4][ClSal]$ in water are 0.62% and 2.43%, respectively, whereas those of $[Bu_3NC_2NHC_8][Dca]$ and $[Bu_3NC_2OC_8][Dca]$ are 0.2% and 0.33%, respectively.

The figure 3 shows that dicyanamide based ionic liquids may be able to perform selective extraction taking into account the great difference of extraction yield of Cu(II) compared to those of Ni(II) and Co(II). Indeed, the separation factors $\beta_{Cu/Co}$ and $\beta_{Cu/Ni}$ (table 1), estimated from extraction experiments with single metal solution are equal to 38 and 298 with $[Bu_3NC_2NHC_4][Dca]$. The values obtained with $[Bu_3NC_2NHC_8][Dca]$ are equal to 12 and 800, respectively. The separation factors obtained with $[Bu_3NC_2NHC_n][Clsal]$ (n = 4 or 8) do not exceed 15 meaning that 4-chlorosalicylate based ionic liquids, although exhibiting higher

extraction yield, are less efficient to perform selective separations. To confirm the trends obtained with single metal solution, extraction experiments with multiple metal solutions were performed. The figure 4 depicts the extraction yields of Cu(II), Co(II) and Ni(II) with dicyanamide based ILs from Cu(II)/Co(II) and Cu(II)/Ni(II) equimolar solutions. The separation factors $\beta_{Cu/Co}$ and $\beta_{Cu/Ni}$ are equal to 180 and 620 with $[Bu_3NC_2NHC_4][Dca]$, respectively, and 140 and 432 with $[Bu_3NC_2NHC_8][Dca]$.

The higher values of the separation factors determined on binary or ternary metal solutions comparatively to those of simple metal solutions confirm the effectiveness of the dicyanamide based ILs for the separation of Cu(II) from Co(II) and/or Ni(II) (figure 3 and 4).

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

Ionic liquids	**Extraction yields (%)**			**Separation factors**	
Single metal solution					
	Co(II)	Cu(II)	Ni(II)	$\beta_{Cu/Ni}$	$\beta_{Cu/Co}$
$[Bu_3NC_2NHC_4][Dca]$	19	97	5	614	138
$[Bu_3NC_2NHC_8][Dca]$	10	90	0	>1000	81
Mixture of Cu(II) and Co(II) or Cu(II) and Ni(II) solutions					
$[Bu_3NC_2NHC_4][Dca]$	16.2	97.2	-	>1000	180
$[Bu_3NC_2NHC_4][Dca]$	-	97.4	5.7	620	-
$[Bu_3NC_2NHC_8][Dca]$	4.6	87	-	-	140
$[Bu_3NC_2NHC_8][Dca]$		89	2	432	-
Mixture of Cu(II), Co(II) and Ni(II) solutions					
$[Bu_3NC_2NHC_4][Dca]$	18.7	96.9	5.33	555	136
$[Bu_3NC_2NHC_8][Dca]$	10.5	89.7	0.1	>1000	74

$[Bu_3NC_2NHC_8][Dca]$ is the most efficient ionic liquid for the separation of Cu(II) from the other two metals when the experiment is carried out with a feed solution composed by Co(II),

Cu(II) and Ni(II) (figure 4). At the first extraction process the composition of aqueous phase is the following: Ni(II) = 0.1 mmol, Co(II) = 0.09 mmol and Cu(II) = 0.01 mmol. The IL phase composition is Co(II) = 0.01mmol and Cu(II) = 0.09 mmol.

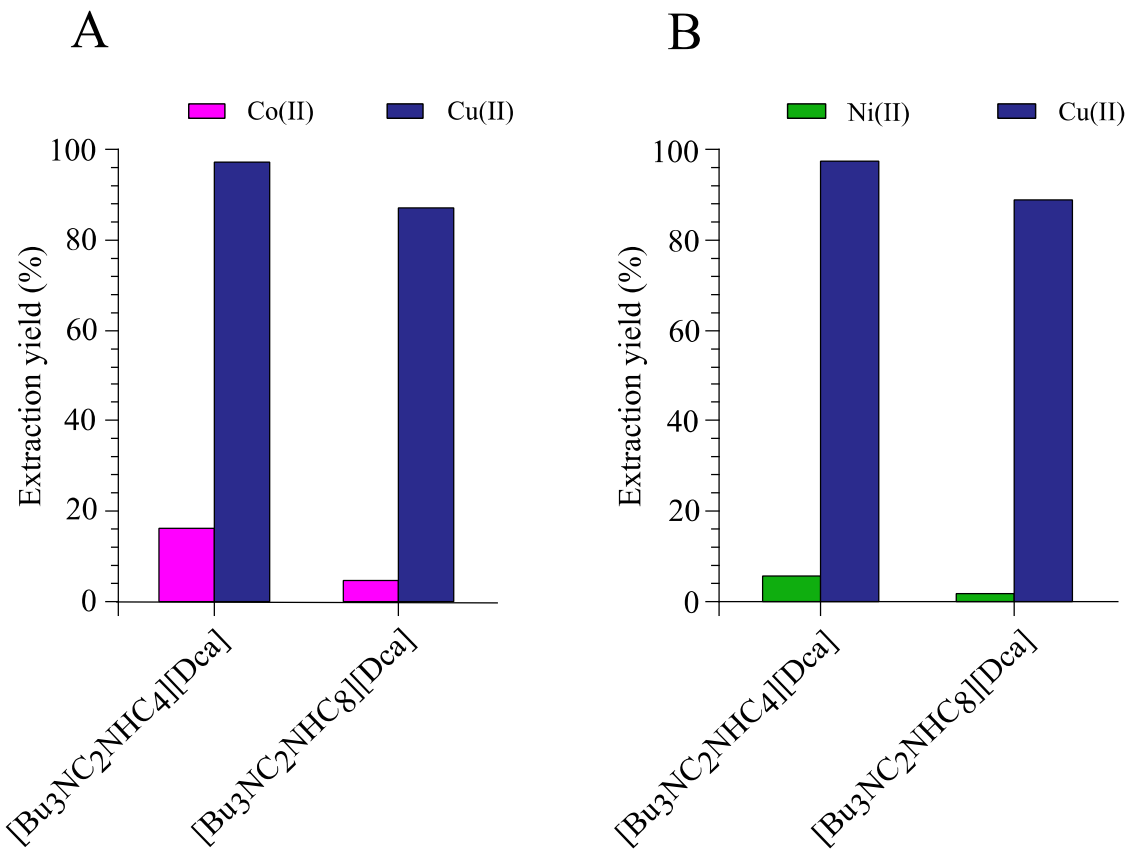

Figure 3: Extraction yields (%E) of aqueous nitrate salt of multiple metal solution with $[Bu_3NC_2NHC_n][Dca]$; (A) Cu(II)/Co(II), (B) Cu(II)/Ni(II); C_{metal} = 0.05 mol.L-1 ; V_{aq} = 2 mL, m_{IL} = 0.5g.

After separation of the IL phase and the aqueous phase, the second step is the stripping of metals from the IL phase with 2 mL of Na_4EDTA salt. This step allows the total recovery of the IL through an efficient separation of the Cu(II) and the IL phase [46].

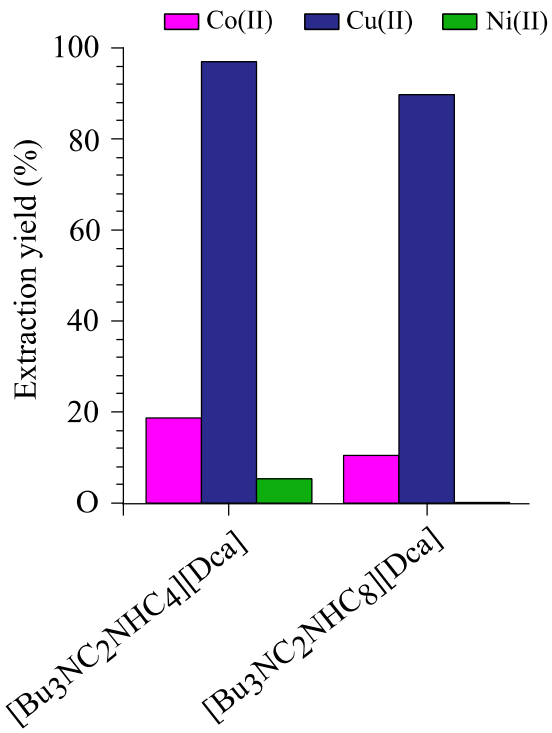

Figure 4: Extraction yields (%E) of multiple metal solution Cu(II), Co(II) and Ni(II) with $[Bu_3NC_2NHC_n][Dca]$. Condition: $C_{metal} = 0.05$ mol.L^{-1}, $V_{aq} = 2$ mL, $m_{IL} = 0.5$g.

Effect of salt concentration: To measure the influence of a salt media on the enhancement of extraction properties on ionic liquid phase, we performed extraction experiments of Ni(II) and Co(II) with $[Bu_3NC_2NHC_n][Dca]$ in salt media at high concentration (2 and 4 mol.L^{-1}). We used, as background electrolyte, three sodium salts with kosmotropic, intermediate and chaotropic anion: Na_2SO_4, NaCl and $NaNO_3$. This allows to examine more deeply "salting out" and "salting in" effect on the extraction properties of ionic liquid phase towards divalent metal. Although cations of the electrolyte salt contribute to "salting in" and "salting out" effect, it is currently admitted that their influence is relatively limited compared to those of anions [33,34], consequently we limit our work to the study of the influence of sodium electrolytes.

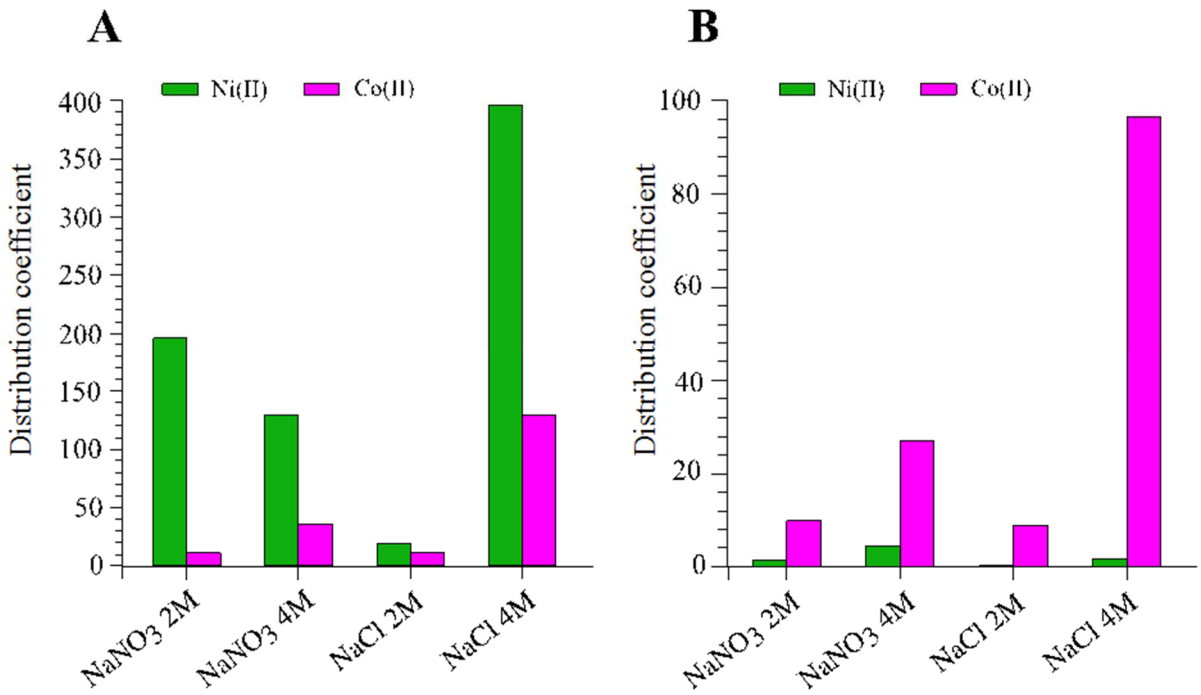

Figure 5: Effect of salt concentration on Ni(II) and Co(II) extraction with $[Bu_3NC_2NHC_4][Dca]$ (A) and $[Bu_3NC_2NHC_8][Dca]$ (B). Vaq = 2 mL; m_{IL} = 0.5g; C_{metal} = 0.05 mol.L^{-1}.

As expected, the addition of Na_2SO_4 has no effect on the extraction rate of copper. As seen previously sulfate ions are too hydrophilic to be extracted with the divalent cation in the ionic liquid phase even at high concentration, and the "salting out" effect expected by the addition of Na_2SO_4 has no benefit on the extraction yields of Ni(II) and Co(II).

The figure 5 depicts the extraction of Ni(II) and Co(II) with $[Bu_3NC_2NHC_n][Dca]$ under the influence of increasing concentrations of sodium chloride or sodium nitrate. As expected, the addition of chloride or nitrate salt leads to an increase of extraction rate. Below 2 mol.L^{-1}, the higher influence of $NaNO_3$, on the extraction yields of Ni(II) and Co(II), is clearly related to the better affinity of NO_3^- ions for ionic liquid phase compared to chloride ions. Thus, the neutral extraction on the metals by "salting in" effect is favored. Indeed, in pure water, the copper nitrate is more efficiently extracted than the copper chloride. This is in accordance with

the relative position of the two ions in the Hofmeister series. At 4 mol.L^{-1}, the results show that NaCl is more efficient than $NaNO_3$ to extract Ni(II) and Co(II). This is clearly the case for both ions with $[Bu_3NC_2NHC_4][Dca]$, and only for Co(II) with $[Bu_3NC_2NHC_8][Dca]$.

The higher influence of NaCl compared to $NaNO_3$ at 4 mol.L^{-1} can be ascribed to a specific interaction of nitrate anions with the organic cations of the ionic liquid. The nitrate anions may form stable ion-pairs by anionic metathesis leading to a partial exchange between nitrate and dicyanamide anion following the equilibrium (a).

$$[Bu_3NC_2NHC_4][Dca]_{IL} + NO_3^-(aq) \rightleftharpoons [Bu_3NC_2NHC_4][NO_3]_{IL} + Dca^-(aq) \qquad \textbf{(a)}$$

The use of a high concentration of nitrate ions, may lead to a release of Dca^- anion in aqueous phase, which can decreases the efficiency of the extraction process as seen in the case of the extraction of Ni(II) with $[Bu_3NC_2NHC_4][Dca]$ and thus alters the green side of the process. The weaker interaction of Cl^- anions with the organic cation limits the anionic exchange in the case of NaCl and allows the obtaining of higher extraction yields.

The spectrum of Co(II) in $[BuNC_2NHC_n][Dca]$ after extraction from $NaNO_3$ media shows in the visible region a band at 600 nm with a shoulder at 570 nm (figure 6). The molar absorption coefficient at 600 nm is equal to 1100 cm^{-1} .mol^{-1}.L Such features are characteristic of a Co(II) in tetrahedral environment [47], meaning a change of coordination of the metal during the extraction process to form $Co(Dca)_4^{2-}$ complexes following the equilibrium (eq. b) :

$$4[Bu_3NC_2NHC_4][Dca]_{IL} + Co^{2+}_{(aq)} + 2NO_3^-{}_{(aq)} \rightleftharpoons 2[Bu_3NC_2NHC_4][NO_3]_{IL} + [Bu_3NC_2NHC_4]_2[Co(Dca)_4]_{IL} \qquad \textbf{(b)}$$

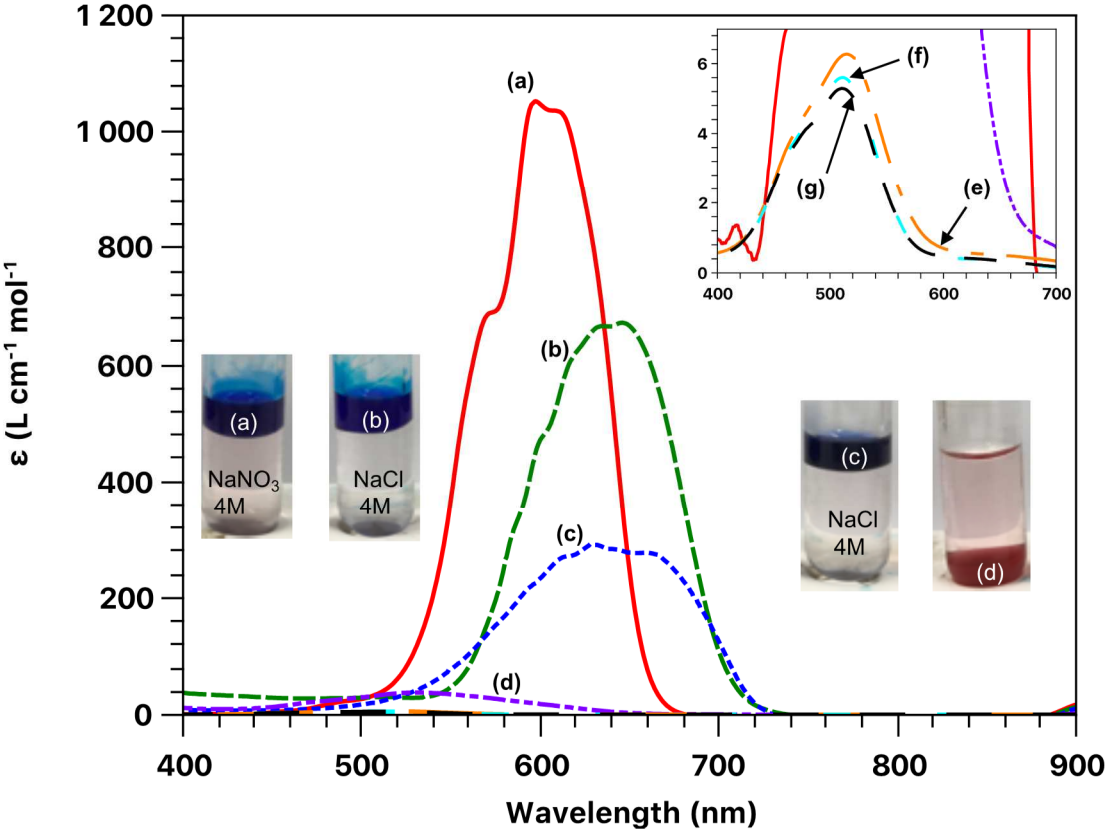

Figure 6: UV-Vis spectra of Co(II) (a) in $[Bu_3NC_2NHC_4][Dca]$ from $NaNO_3$ 4 mol.L^{-1}, (b) in $[Bu_3NC_2NHC_4][Dca]$ from NaCl 4 mol.L^{-1}, (c) in $[Bu_3NC_2NHC_4][ClSal]$from NaCl 4 mol.L^{-1} (d) in $[Bu_3NC_2NHC_4][ClSal]$ from $NaNO_3$ 4 mol.L^{-1}, (e) in water from NaCl 4 mol.L^{-1}, (f) in water (g) in water from $NaNO_3$ 4 mol.L^{-1}.

The bands are assigned to a $^4A_2(F) \rightarrow {}^4T_1(P)$ transition. It is interesting to note that the spectrum of Co(II)) extracted from NaCl medium is shifted to higher wavelength compared to that of Co(II) extracted from $NaNO_3$ medium. This shift is indicative of the implication of weaker donor atom than the nitrogen of dicyanamide in the coordination sphere of Co(II) and can be ascribed to the formation of mixed complexes $Co(Dca)_{(4-x)}(Cl)_x$. The UV-visible spectrum of the aqueous solution of Co(II) in NaCl 4 mol.L^{-1} is close to those of Co(II) in water (see insert

figure 6). The involvement of Cl^- anions in the coordination sphere of Co(II) is concomitant with the extraction of Co(II) in the ionic liquid phase (eq. c).

$$(4\text{-}x)[Bu_3NC_2NHC_4][Dca]_{IL} + Co^{2+}_{(aq)} + xCl^-_{(aq)} \rightleftharpoons (2\text{-}x)[Bu_3NC_2NHC_4]^+_{(aq)} + [Bu_3NC_2NHC_4]_2[Co(Dca)_{4-x}Cl_x]_{(IL)} \quad \textbf{(c)}$$

The influence of a salt media on the extraction properties of $[Bu_3NC_2NHC_n][Clsal]$ phase is similar to that described for $[Bu_3NC_2NHC_n][Dca]$ (results not shown here). Quantitative extraction can even be achieved for Ni(II) and Co(II) in $NaNO_3$ 4 mol.L^{-1}. In the case of $[Bu_3NC_2NHC_n][Clsal]$, $NaNO_3$ remains more efficient than NaCl for metal extraction whatever the concentration used. This is related to the higher hydrophobicity of $Clsal^-$ anion compared to Dca^- anion which limits the anionic exchange between NO_3^- and $ClSal^-$ and thus preserves the extraction capacity of the ionic liquid phase even in high concentration of salt. The spectrum of $[BuNC_2NHC_n][ClSal]$ after Co(II) extraction from $NaNO_3$ 4 mol.L^{-1} (figure 6) shows in the visible region a band at 530 nm with a shoulder at 480 nm. The molar absorption coefficient at 530 nm equal to 33 cm^{-1}.mol^{-1}.L is indicative of Co(II) in octahedral environment [47]. This band as well as its shoulder correspond to the following transitions: $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$. Spectroscopic analysis of $[BuNC_2NHC_n][ClSal]$ phase after Co(II) extraction from NaCl 4 mol.L^{-1} evidenced a change of coordination mode of Co(II), from octahedral to tetrahedral environment, during the transfer from aqueous to ionic liquid phase [47]. It is pertinent to ascribe this change of coordination mode to the formation of complex with a mixed ligands $Co(ClSal)_{(4-x)}Cl_{(x)}$ in ionic liquid phase.

It is interesting to note that salt media does not enhance Co(II) and Ni(II) extraction yields with $[Bu_3NC_2NHC_n][Sac]$ and $[Bu_3NC_2NHC_n][Tf_2N]$. The extraction yields of both these metals do not exceed few percent, even at 4 mol.L^{-1} of NaCl or $NaNO_3$. The Sac^- and Tf_2N^- anions are

weakly coordinating towards Cu(II), Co(II) and Ni(II). This study shows that the systems that will benefit most from the use of saline environments are those incorporating an anion with at least a moderate complexing power. The formation of stable complexes in ionic liquid medium can be seen as a driving force which allows overcoming the metal dehydration process constituting a brake on the transfer of metal from the aqueous phase to the ionic liquid phase.

These results evidenced that the Hofmeister series can be an exploitable tool to control the extraction-stripping properties of ionic liquid phase in saline environments without use of additional extractant. The use of chaotropic and kosmotropic salt in successive extraction and stripping steps would be performed to implement selective metal separation processes with a limited release of cation or anion of the ionic liquid in aqueous media. An aqueous solution constituted by a salt with a chaotropic anion will improve extraction efficiency of the ionic liquid phase. The role of chaotropic anions cannot be seen as a purely “salting-in” effect, like those that contributes to increase the solubilization of proteins in water. The influence of chaotropic anions is due to their properties to easily form ion-pairs with the hydrophobic organic cations of ionic liquids. Such ion-pairs are insoluble in water and therefore chaotropic anions are coextracted with metal cation in the ionic liquid phase, thus enhancing metal extraction by ion-pairing. A kosmotropic anion will be able to surround itself with a solvation sphere and will have a structuring effect on the solvent molecules, which leads to a decrease of the fraction of the free solvent molecule, and therefore a decrease of the solubility of ionic liquid in aqueous phase [34]. Another interpretation of the Hofmeister effect was given by M. Kobrak and coworkers on the basis of their investigations on the behaviour of copper mining with protic trialkylammonium hexa(octa or deca)noate salts [31,48]. They evidenced that the presence of copper salt in the IL phase increases water absorption and induces a change in the structure of hydrophilic/hydrophobic nanodomains inside the IL phase. The role of the counter anion of the metal lies in its ability to stabilize the hydrophilic/hydrophobic nanodomain interfaces and is

related to its relative position in the Hofmeister series. Although we based our interpretations on the nature of the interaction between the organic cation and the anion of the electrolyte. Their conclusions could be relevant to aprotic ionic liquids such as those described in this work. However, the study of the formation of nanodomain in aprotic analog of glycine-betains based ionic liquids requires further investigations that are beyond the scope of this study.

In stripping step, a kosmotropic anion limits the release of an ion of the ionic liquid in aqueous solution and thus preserve its integrity. The solubility of $[Bu_3NC_2NHC_4][Dca]$ in Na_2SO_4 1.5 $mol.L^{-1}$ is equal to 2×10^{-3} $mol.L^{-1}$ which is twenty one times lower than in pure water (43×10^{-3} $mol.L^{-1}$). The solubility of $[Bu_3NC_2NHC_4][Dca]$ in Na_2SO_4 1.5 $mol.L^{-1}$ is fifty times lower (10^{-4} $mol.L^{-1}$) than in water (5×10^{-3} $mol.L^{-1}$).

The figure 7 compares the mole number of Co(II) from extraction and stripping yields in NaCl and $NaNO_3$ at 4 $mol.L^{-1}$. For clarity, the mole number of Co(II) extracted in pure water is reported and corresponds to the upper part of the right column. The lower part of the column corresponds to the difference between the extractions in saline and in aqueous media. The interest is to compare the efficiency of the stripping process in relation to the intrinsic extraction properties of the ionic liquid in aqueous medium. For a totally reversible process, the stripping yields must correspond to the difference between the extraction yields in a saline media and those in aqueous medium. It can be seen that it is more or less the case with Co(II)/$[Bu_3NC_2NHC_n][Dca]$ even if the stripping yield is always slightly higher than the difference between the extraction rate in saline and in aqueous media. The difference is 13% with $[Bu_3NC_2NHC_4][Dca]$ in $NaNO_3$ and $[Bu_3NC_2NHC_8][Dca]$ in NaCl, 9% with $[Bu_3NC_2NHC_8][Dca]$ in $NaNO_3$ 8% for $[Bu_3NC_2NHC_4][Dca]$ in NaCl. The difference may be ascribed either to a difference of ionic strength between extracting or back extracting phase or to an anionic exchange reaction between the dicyanamide anion and the counter anion of the salt which may slightly modify the composition of the ionic liquid phase after the stripping

stage, affecting thus the integrity of the ionic liquid. The most relevant ionic liquid for the development of a reversible green extraction system will be based (i) on the metal extraction rates obtained in a saline environment which should be as high as possible, and (ii) on the difference between the extraction and stripping rates which should be as low as possible. Considering these 2 parameters, the most relevant system for the recovery of Co(II) seems to be $[Bu_3NC_2NHC_8][Dca]/NaNO_3$ and $[Bu_3NC_2NHC_8][Dca]/NaCl$.

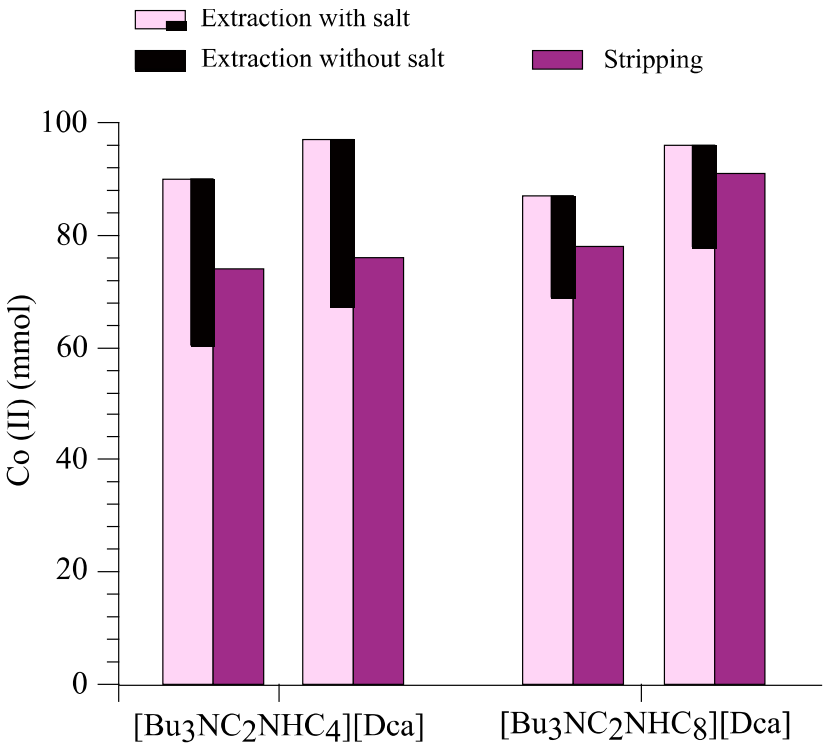

Figure 7: comparison of Co(II) molar number from extraction and stripping process with $[Bu_3NC_2NHC_n][Dca]$ in saline media. $V_{aq} = 2$ ml; $m_{IL} = 0.5$g; $C_{metal} = 0.05$ mol L^{-1}.

$Clsal^-$ based ILs have a higher affinity for Co(II) than those with dicyanamide anion, leading to higher extraction yields (see SI). However this higher affinity limits the recovery of Co(II) by stripping which remains lower than that obtained with dicyanamide salts. Consequently, $Clsal^-$ based ILs are less suitable candidates for the development of green processes.

One of the aspects that must be addressed concerns the release of the organic cation into the aqueous phase during the extraction-stripping processes. Table 2 gives the concentration values of the organic cation measured in aqueous phase after stripping by quantitative ^{1}H NMR. Stripping steps were performed in pure water or in aqueous Na_2SO_4 medium. In both cases, stripping yields are similar (difference less than 2% which is common with the experimental errors).

Table 2: Concentration of organic cation in aqueous phase determined by quantitative ^{1}H NMR; V_{aq} = 2 ml; M_{IL}= 0.5 g

ILs	M	%E $NaNO_3$ 2 mol.L^{-1}	C^+_{aq} (10^{-3} mol.L^{-1})	Stripping	%S	C^+_{aq} (10^{-3} mol.L^{-1})
$[Bu_3NC_2NHC_4][Dca]$	Co(II)	74	9.7	H_2O	80	50.0
$[Bu_3NC_2NHC_4][Dca]$	Co(II)	74	9.7	Na_2SO_4 (1.5 mol.L^{-1})	80	1.5
$[Bu_3NC_2NHC_8][Dca]$	Ni(II)	71	9.4	H_2O	87	55.1
$[Bu_3NC_2NHC_8][Dca]$	Ni(II)	18	1.3	Na_2SO_4 (1.5 mol.L^{-1})	86	1.2

As seen in table 2, the use of Na_2SO_4, instead of water limits the release of the cation of the ionic liquid, due to "salting-out" effect, and preserves the integrity of ionic liquid phase.

Separation of Co and Ni in mixture: the separation factors are determined from single, equimolar binary Co(II), Ni(II) metal solutions. From the values of separation factor (β) given in table 3, the systems chosen to perform selective separation of Co(II) and Ni(II) is $[Bu_3NC_2NHC_8][Dca]$/NaCl 4 mol.L^{-1}. The value of $\beta_{Co/Ni}$ is close to those described by Schaeffer *et al*. [24] and Onghena *et al.* [25] in ABS made from $[P_{44414}][Cl]$ in HCl/NaCl mixture. This value ($\beta_{Co/Ni}$ = 75) ensure an efficient separation of Co(II) from Ni(II) as seen in

figure 8. The recovery of Co(II) is effective by stripping in water or in Na_2SO_4 solutions (figure 9).

Table 3: Extraction yields (%). Separation factors (β) calculated from multiple metal extractions in saline media. Condition: C_{metal} = 0.05 mol.L^{-1} ; V_{aq} = 2 mL, m_{IL} = 0.5g.

Ionic liquids	Extraction yields (%)		Separation Factors (β)
Single metal solutions			
$NaNO_3$ 4 mol.L^{-1}	Co(II)	Ni(II)	$\beta_{Co/Ni}$
$[Bu_3NC_2NHC_4][Dca]$	97	90	3.6
$[Bu_3NC_2NHC_8][Dca]$	87	53	5.9
NaCl 4 mol.L^{-1}	Co(II)	Ni(II)	$\beta_{Co/Ni}$
$[Bu_3NC_2NHC_4][Dca]$	97	99.8	0.32
$[Bu_3NC_2NHC_8][Dca]$	96	31	53.41
Mixture Co(II) and Ni(II) solutions			
$NaNO_3$ 4 mol.L^{-1}	Co(II)	Ni(II)	$\beta_{Co/Ni}$
$[Bu_3NC_2NHC_4][Dca]$	99.1	98.8	1.3
$[Bu_3NC_2OC_8][Dca]$	78.7	33.5	7.3
NaCl 4 mol.L^{-1}	Co(II)	Ni(II)	$\beta_{Co/Ni}$
$[Bu_3NC_2NHC_4][Dca]$	98.5	88.6	8.4
$[Bu_3NC_2NHC_8][Dca]$	94.3	18	75.3

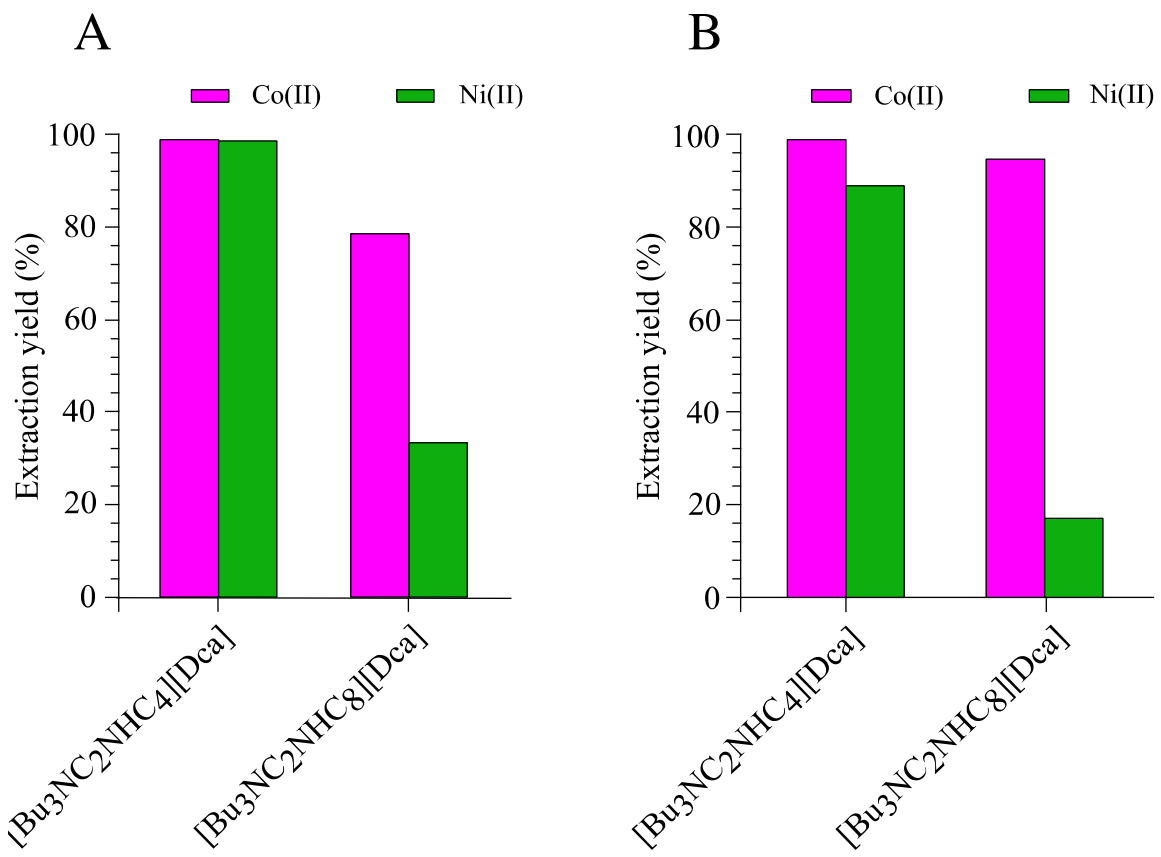

Figure 8: Extraction yields (%E) from an equimolar Co(II) and Ni(II) multi-metal solution with $[Bu_3NC_2NHC_n][Dca]$; (A) in $NaNO_3$ 4 mol.L^{-1} and (B) in NaCl 4 mol.L^{-1}; C_{metal} = 0.05 mol.L^{-1} ; V_{aq} = 2 mL, m_{IL} = 0,5 g

Before the separation, the solution is composed by 0.1 mmol of each metal. After the first extraction step, the aqueous phase composition is 0.082 mmol of Ni(II) and 0.006 mmol of Co(II). In the IL phase the composition is 0.094 mmol of Co(II) and 0.018 mmol of Ni(II). The stripping of IL phase was performed with 2 mL of water in order to recover the IL phase. The metals in IL-rich phase are also effectively recover during the stripping process. The water phase after stripping is composed by 0.093 mmol of Co(II) and 0.018 mmol of Ni(II).

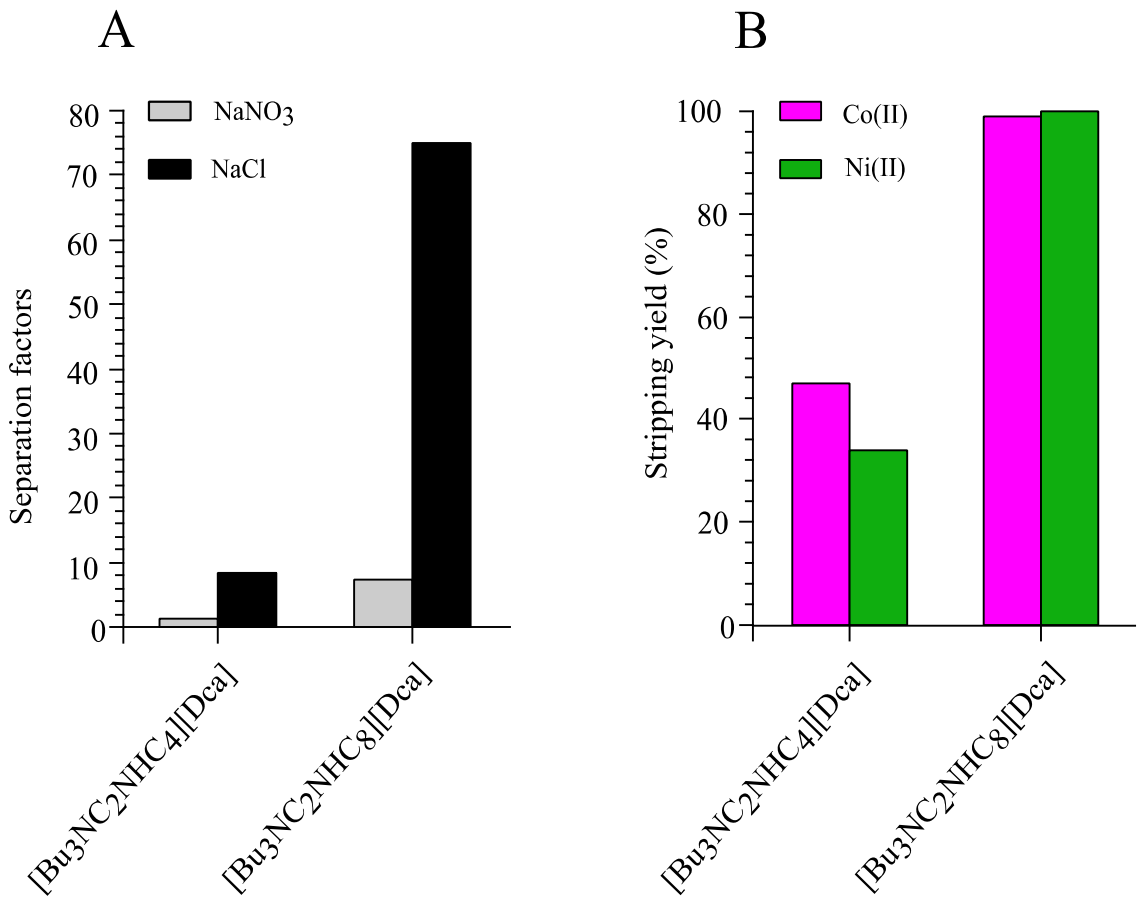

Figure 9: Separation factors (A) of an equimolar Co(II) and Ni(II) metal solution, in NaCl 4 mol.L^{-1} with [$Bu_3NC_2NHC_n$][Dca]. Conditions: C_{metal} = 0.05 mol.L^{-1}, V_{aq} = 2 mL, m_{IL} = 0.5g. Corresponding stripping yields (B) of ILs metal rich phase with water. Condition: V_{aq} = 2 mL.

Separation of Cu and Co from Cu, Co, Ni mixture: the separation of Ni(II) from Co(II) and Cu(II) mixture can be carried out with dicyanamide based ILs. The extraction was performed with a feed aqueous equimolar solution of metals at 0.05 mol.L^{-1} in NaCl 4 mol.L^{-1}. The stripping of the IL phase was done with water and the results are presented figure 10.

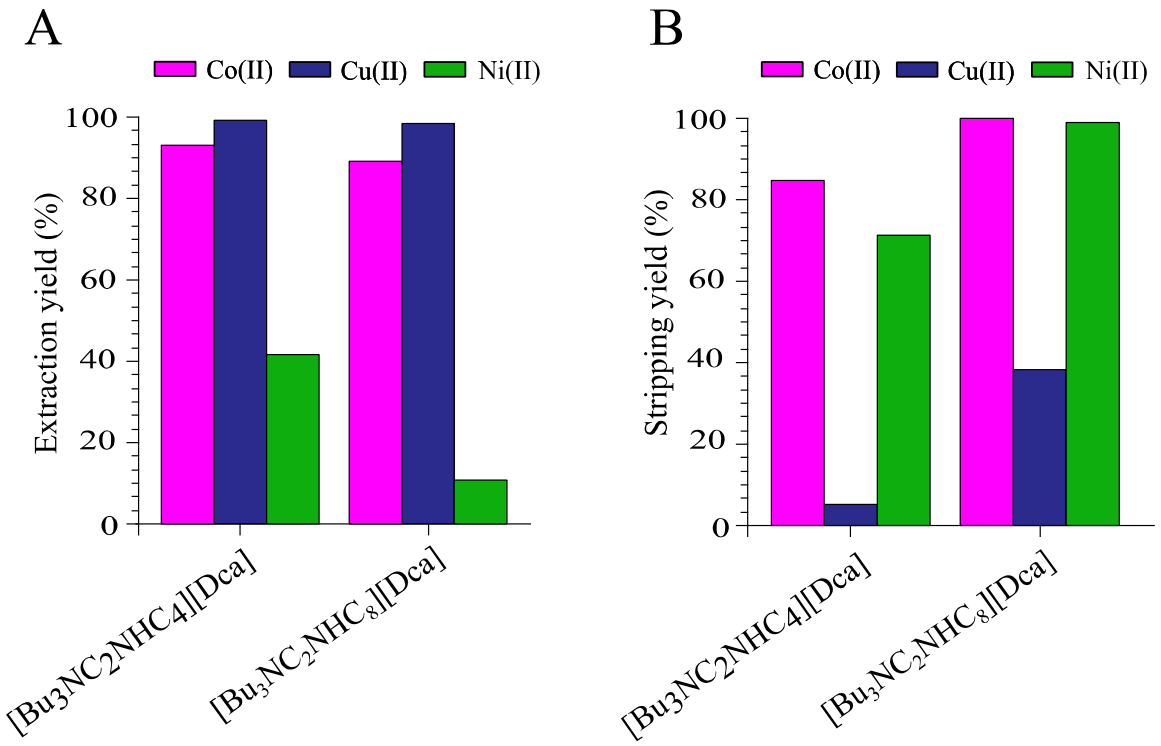

Figure 10: Extraction yields (A) from equimolar Cu(II), Co(II) and Ni(II) solution in NaCl 4 mol.L^{-1} with [$Bu_3NC_2NHC_n$][Dca]. Condition: C_{metal} = 0.05 mol.L^{-1}, V_{aq} = 2 mL, m_{IL} = 0.5g. Corresponding stripping yield (B) of ILs phase with water calculated from extracted metals. Condition: V_{aq} = 2 mL.

Before the extraction with [$Bu_3NC_2NHC_8$][Dca], the composition of aqueous phase is Ni(II) 0.089 mmol, Cu(II) 0.002 mmol and Co(II) 0.011 mmol. The composition of IL phase after the extraction is: Co(II) = 0.089 mmol, Cu(II) = 0.098 mmol and Ni(II) = 0.011 mmol. After the separation of the aqueous and IL phases, the stripping of the IL phase with 2 mL of Na_4EDTA allows the total recovery of the IL with an efficient separation of the remaining Cu(II) and Ni(II) and the IL phase.

Another solution to separate Cu(II) and Co(II) from IL phase is to realize a stripping phase with water. This step allows to have in aqueous phase 0.089 mmol of Co(II), 0.011 mmol of Ni(II) and 0.037 mmol of Cu(II). The remaining Cu(II) in IL phase is removed with Na_4EDTA salts.

Recyclability of ionic liquid: after the stripping process, the ionic liquid must be reusable for metal extraction. The loss of ionic liquid during the extraction and stripping processes is negligible owing to the aqueous solubility of ILs. To check the recyclability of the ionic liquids, several cycles of extraction-stripping were performed on the same ionic liquid, with the same experimental conditions as those described above and with an aqueous Na_2SO_4 1.5 mol.L^{-1} as stripping phase. The recyclability of ionic liquid was compared in NaCl and $NaNO_3$ media. The figure 11 reports the extraction and stripping yields for the extraction of Co(II) with [$BuNC_2OC_4$][Dca]. For more clarity stripping yields are expressed in relation to the initial concentration of metal in the ionic liquid phase.

The results show that the efficiency of the extraction and the stripping processes remained similar over 3 cycles for both salt media. Indeed, the extraction yields is greater than 90% over the three first cycles, whereas the stripping yields decrease slightly but remain higher than 65%. From the fourth cycle, a significant loss in the extraction capacity of the ionic liquid phase in $NaNO_3$ 4 mol.L^{-1} was observed, with an extraction yield of 35%. In NaCl media the loss of efficiency is much less marked, since the extraction yield of the fourth cycle is equal to 89%. The loss of extraction efficiency, during the extraction-stripping cycles can be attributed to the NO_3^-/Dca^- exchange which depletes the ionic liquid in Dca^-.

After the fourth cycle, the ionic liquid phase was contacted with a NaDca solution 1 mol.L^{-1} during 12 hours, and then the fifth cycle of extraction and stripping was carried out. As seen in figure 15, for the both systems studied, this treatment regenerates the extraction capability of the ionic liquid. Indeed, the extraction yields for this fifth cycle are 97% in $NaNO_3$ media and 94% in NaCl media.

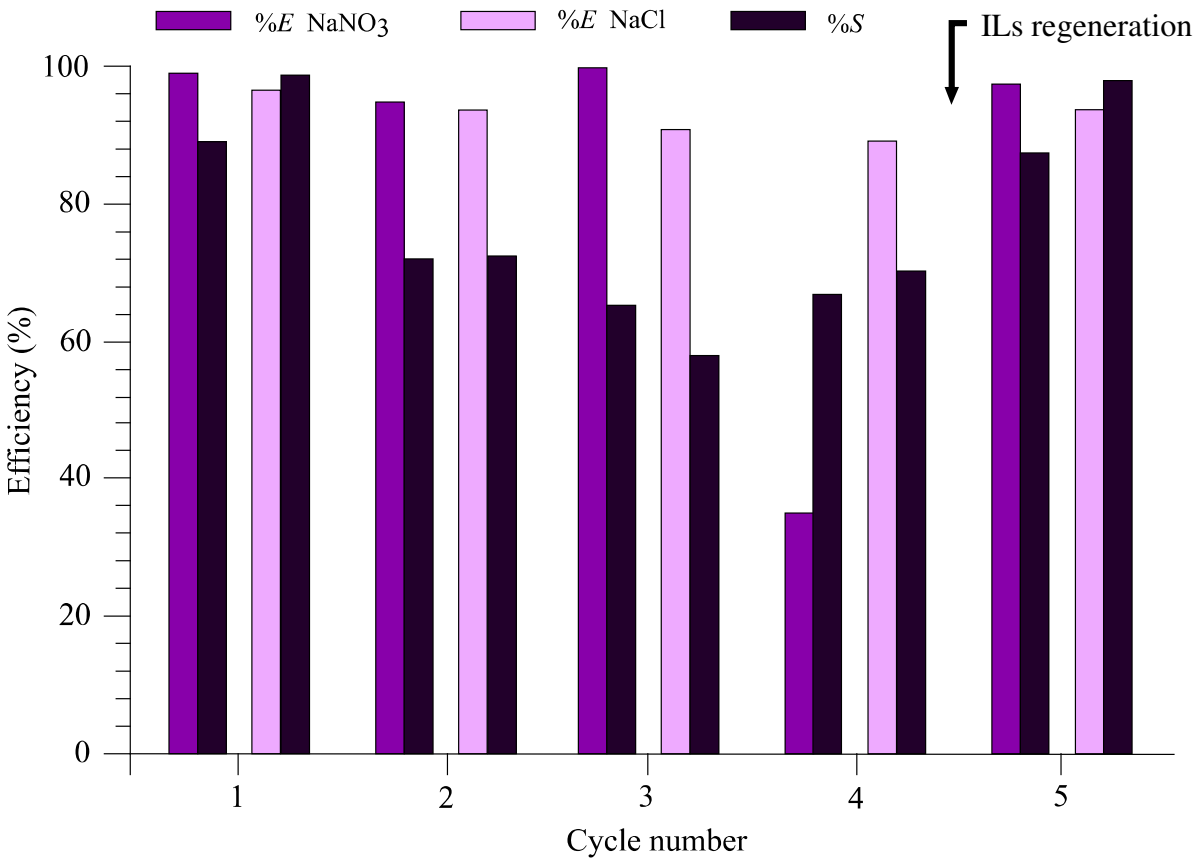

Figure 11: Reusability of ionic liquid phase for copper and cobalt extraction using [$BuNC_2NHC_4$][Dca]

Conclusion

Here, we have demonstrated the ability of task-specific ionic liquids, obtained by association of cationic analogue of glycine-betaine with coordinating anions, to remove Cu(II), Co(II) and Ni(II) from aqueous effluents and in saline media. The ILs are composed of inexpensive moieties and the extraction does not require the use of a chelating agent, which is a valuable advantage for process design.

The 4-chlorosalycilate based ionic liquids exhibit a high potential for the extraction of divalent cation of first row transition metal. The dicyanamide based ionic liquids allow the separation of Cu(II) from Ni(II) and Co(II) in aqueous effluents. The rational use of background salts, constituted by chaotropic and kosmotropic anion allows the implementation of selective

extraction process limiting the leaching of ionic liquid in the aqueous effluents and preserving the integrity of the extraction phase and its reusability. We have demonstrated that the addition of a supporting electrolyte improves the extraction capacities of ionic liquids based coordinating anions. The most effective systems for working with a saline media are dicyanamide based ionic liquids, which present a moderate complexing power anion. Under these conditions, the use of a supporting electrolyte with a chaotropic anion, like chloride or nitrate, allows to extract quantitatively Cu(II) and Ni(II) in $NaNO_3$ 4 $mol.L^{-1}$ medium, and Cu(II) and Co(II) in NaCl 4 $mol.L^{-1}$. Based on the value of separation factor, the use of NaCl allows the selective separation of Co(II) from Ni(II) in aqueous effluents. Stripping phase with a kosmotropic anion such as SO_4^{2-}, allows the quantitative recovery of Co(II) extracted.

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