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Novel Task Specific Ionic Liquids to Remove Heavy Metals from Aqueous Effluents

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Abstract: Task Specific Ionic Liquids (ILs) were generated by association between a cationic ester derivative of betaine and coordinating inorganic anions such as dicyanamide (Dca^-), chlorosalicylate (ClSal) and saccharinate (sac). Extraction of Cu(II) , Ni(II) , Co(II) , Pb(II) and Cd(II) from water was performed with these ILs at room temperature. Our results show that ionic liquid with ClSal anions have a high extraction efficiency towards Cu(II) , Ni(II) , Cd(II) , and Pb(II) , whereas dicyanamide ionic liquid may extract efficiently Cu(II) , Ni(II) Co(II) and Cd(II) . Ionic liquids with saccharinate anions are selective of Cd(II) ions. The extraction mechanism has been studied by the determination of the coextraction of the counter ion of the metal salt. Our results show that the extraction mechanism proceeds via a mixed process involving both cation exchange and ion-pairing. The proportion of which depends on the nature of the cation. The coordination of Cu(II) , Ni(II) and Co(II) in ionic liquid phase was followed by UV-vis spectroscopies. The metal could be back-extracted from the ionic liquid phase with aqueous EDTA solutions. The metal extractability of the ionic liquid after the back-extraction is equivalent to that of the fresh mixture showing that ionic liquid can be reused for several extraction and back-extraction cycles.

Keywords: ionic liquids; metal extraction; liquid-liquid extraction; back-extraction; reusability

1. Introduction

The rapid growth of industrial activities in recent years has led to a significant increase in the volume and toxicity of industrial effluents containing heavy metals. Heavy metals have a significant toxicity towards humans and the environment [1], whence the profusion of regulations governing the treatment and removal of heavy metals from industrial effluents.

Pollution reduction will, in the future, generate economic profits, because of the continuous increase in the value of metals [2]. The elimination of metals from industrial effluents may be achieved by technologies such as chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange, and adsorption [3,4]. Among them, liquid-liquid extraction is one of the most performing technologies for the recovery of metal ions, from industrial wastewaters. This technology uses extracting agents and organic solvents (kerosene, toluene, etc.) as diluent. The loss of organic diluent via volatilization, during extraction processing, generates negative environmental impact and may cause serious damage on human health. Consequently, “greener” extraction methods are being sought, and the use of ionic liquids (ILs) constitutes a possible alternative for the replacement

of traditional organic solvent [5]. In the last decade, significant works have shown that Room Temperature Ionic Liquids (RTILs) are potential substitutes for traditional solvents in liquid-liquid extraction processes, for the separation of metal ions [6–9]. Another specific advantage of ILs concerns the possibility of metal recovery by electrodeposition [10]. However, the conventional ionic liquids have a limited efficiency for metal extraction. The use of Task-Specific Ionic Liquids (TSIL) [11–19] by functionalizing organic cation with chelating moieties to increase the affinity of metals for the IL phase may overcome this problem. Ionic liquids with a coordinating anion represent another strategy to increase the recovery of metals by the IL phase. ILs with fluorinated acetylacetonate ligands have shown interesting effectiveness for the extraction of Eu(III), Nd(III), and Co. (II) [20,21]. The development of “green” extraction processes with IL requires a knowledge of the mechanisms involved, for the transfer of ions between IL and the aqueous phase, to privilege the use of ionic liquids limiting the ionic exchanges between the aqueous and organic phases [22–26]. Here, we report the ability of task-specific ionic liquids to remove heavy metals from water. The quaternary ammonium cations derivative of betaine {tri(*n*-butyl)(-ethoxy-2-oxoalkyl)ammonium (BuNC_n^+)} were associated to non-fluorinated coordinating anion such as sacharinate ($\text{Sac} = \text{C}_7\text{H}_4\text{NO}_3\text{S}^-$), chlorosalicylate ($\text{ClSal} = \text{C}_7\text{H}_5\text{O}_3^-$) and dicyanamide ($\text{Dca} = \text{C}_2\text{N}_3^-$) to generate hydrophobic ionic liquids (Figure 1), use as pure extracting phase [13,27,28]. The potential of ILs with chelating anions, as extracting agents, was investigated towards divalent toxic metals Cu(II), Cd(II), Ni(II), Co(II) and Pb(II). The choice of the betaine derivative is justified by its accessibility via simple synthetic route, by its availability, 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 the ammonium group. The choice of anions is dictated by their hydrophobic and chelating nature. The sacharinate and chlorosalicylate anions [29,30] are known for their complexing capacity towards heavy and first row transition metals, respectively. The dicyanamide anion is a cheap anion that is easy to handle to generate ILs. Its chelating ability for metal ions is well known [31,32] and the ability of the Dca^- ionic liquids to extract Cu(II) and Ni(II) from water [26,33,34] was shown in a previous study.

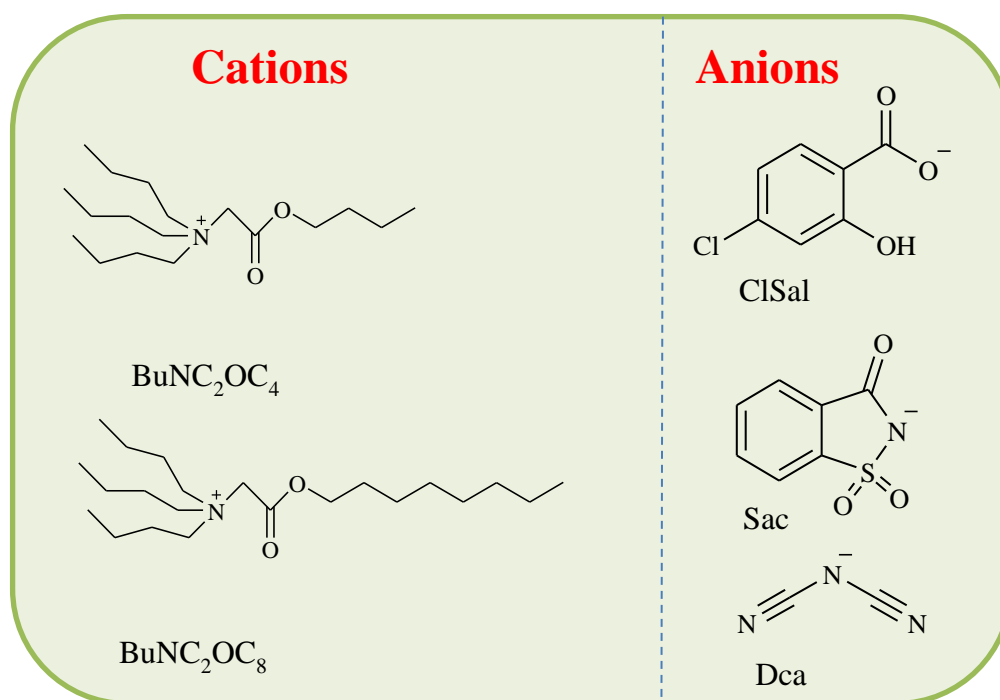


Figure 1. Structure of different analogues of glycine betaine based ionic liquids used in this study.

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%), Tri(*n*-butyl)amine (99%), 1-butanol (99%) and ethyl bromoacetate (98%) were obtained from Sigma-Aldrich (Diegem, Belgium). Ethylenediaminetetraacetic acid disodium salt dihydrate (99%), methanesulfonic acid (99%), 1-octanol (99%), sodium saccharinate (99%) and 4-chlorosalicylic acid (99%) was purchased by Acros (Illkirsh, France).

The solutions of metals were prepared by dissolving their corresponding nitrate salt (analytical grade purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France)-Fluka Chemical (Bucharest, Romania,) in double distilled and deionized water.

2.2. Analytical 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. Routine ^1H NMR spectra were recorded in deuterated dimethyl sulfoxide $\text{C}_2\text{D}_6\text{OS}$ at room temperature with a Bruker AC 250 spectrometer. Chemical shifts (in ppm) for ^1H NMR spectra were referenced to residual protic solvent peaks. The metal analyses were performed by UV-vis spectroscopy using EDTA for Cu(II) and Ni(II) and by ICP-OES, Thermo Fisher ICAP Series for Cd(II) and Pb(II). The concentrations of NO_3^- ions in aqueous solution before and after extraction were determined by ion-HPLC with a Metrohm with a conductivity detector.

2.3. Extraction Experiments

Metals nitrate aqueous solutions were prepared in deionized water. Metal ions distribution ratios were determined by mixing 0.5 g of IL and 2 mL of aqueous phase. The mixture was shaken for 24 h to reach equilibrium and then centrifuged at 2000 rpm for 5 min. The separated organic and aqueous phases, both clear and transparent, 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 concentration of metal ions in the aqueous phase before and after extraction. The efficiency of the extraction process was evaluated by calculation of the extraction percentage (% *E*) using the following equation:

$$E = 100 * \frac{(C_{in} - C_{fin})}{C_{in}} \quad (1)$$

where C_{in} (mol L^{-1}) is the concentration in the initial aqueous solution and C_{fin} (mol L^{-1}) is the concentration in the final aqueous solution. The metal extraction percentages (% *E*) were determined at 25 °C. The initial concentration of metal solutions is fixed at $5 \times 10^{-2} \text{ mol L}^{-1}$. The experiments were made in triplicate to ensure the reproducibility of the assay, and the mean values of extraction yields were considered for each system studied. The distribution ratio (*D*) is calculated using the following formula:

$$D = \frac{(C_{in} - C_{fin})}{C_{fin}} \frac{V_w}{V_{IL}} \quad (2)$$

V_w and V_{IL} correspond to the volume of water and ionic liquid phases, respectively. The maximum *D* value measurable in this study is assumed to be 5×10^2 . The relative uncertainty on *D* is $\pm 10\%$. Experimental results done in duplicate agree within 5%.

In back-extraction experiments, the IL phase with metal extracted was contacted with 2 mL of aqueous disodium EDTA solution ($C = 10^{-1} \text{ mol}\cdot\text{L}^{-1}$ of $\text{Na}_2\text{H}_2\text{Y}$) during 4 h under stirring. The percentage of metal back extracted has been determined from the analysis of aqueous phase.

3. Results and Discussion

The preparation of different ILs was carried out by three main steps: the first step is the preparation of bromide precursor ($\text{BuNC}_2\text{OC}_2\text{-Br}$) and the second step is the preparation of the cationic ester derivative of betaine by transesterification of $\text{BuNC}_2\text{OC}_2\text{-Br}$ with butanol or octanol. The third step is the anionic metathesis reaction to generate hydrophobic ILs. The synthetic pathway is given in Figure 2.

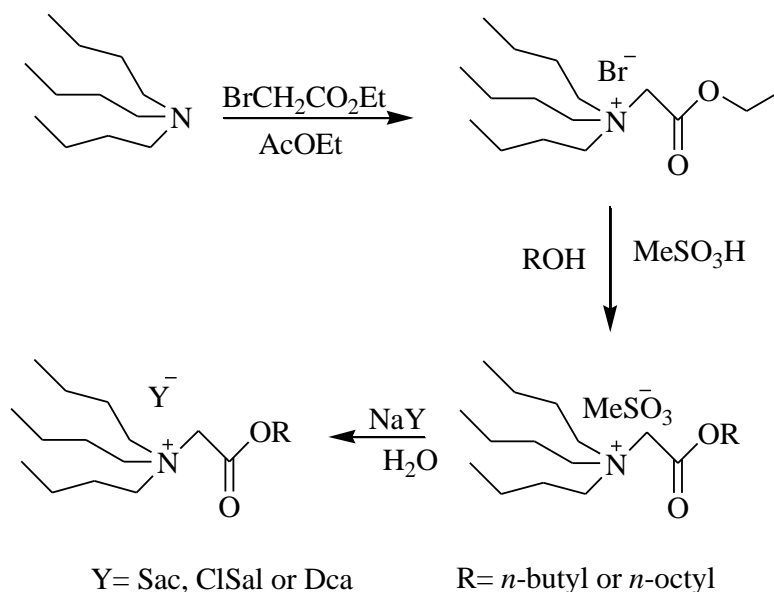


Figure 2. Synthetic route of hydrophobic ionic liquids.

The preparation of bromide salt can be considered as the least difficult step; this reaction is performed in mild conditions. The bromide salt powder was recovered through simple filtration with a quantitatively yield.

In the second step, the strategy used for the esterification reaction is to perform the reaction without any additional solvent; alcohol was also considered as solvent. Methanesulfonic acid was selected as reaction catalyst. It is the best candidate for a green synthesis route, often recyclable and less aggressive than conventional acids [35]. Anionic metathesis between the ester formed and sodium saccharinate, sodium dicyanamide and sodium chlorosalicylate is carried out in water and led in all cases to the formation of hydrophobic ILs with a good yield (>78%). All the ILs are viscous liquids at room temperature.

ILs with saccharinate and chlorosalicylate anions are slightly denser than water with values ranging from 1.040 to $1.111 \text{ g}\cdot\text{mL}^{-1}$ at 25°C (Table 1), whereas ILs with dicyanamide anion have the density less than unity. All the ionic liquids with $\text{BuNC}_2\text{OC}_4^+$ cations are denser than those of $\text{BuNC}_2\text{OC}_8^+$ cations.

At room temperature, all ionic liquids form two liquid phases when contacted with water. In biphasic system, water is the upper phase with saccharinate and chlorosalicylate based ionic liquids, and the lower phase with dicyanamide ionic liquids.

Table 1. Room temperature ionic liquids density at 25 °C.

Ionic Liquid	Density (g·mL ^{−1})
BuNC ₂ OC ₄ -Sac	1.11
BuNC ₂ OC ₈ -Sac	1.04
BuNC ₂ OC ₄ -ClSal	1.10
BuNC ₂ OC ₈ -ClSal	1.02
BuNC ₂ OC ₄ -Dca	0.96
BuNC ₂ OC ₈ -Dca	0.96

The solubility of the ionic liquids in water were measured by NMR for dicyanamide based ionic liquids, or spectrophotometry UV-vis for chlorosalicylate or saccharinate based ionic liquid. The solubility of BuNC₂OC₄-ClSal and BuNC₂OC₈-ClSal are equal to 0.3 and 0.005%, respectively and are comparable with those of BuNC₂OC₄-Dca and BuNC₂OC₈-Dca equal to 0.35 and 0.26%, respectively. Ionic liquids with saccharinate anion are more soluble than those with dicyanamide and chlorosalicylate anions with the percentage values of 2.85 (BuNC₂OC₄-Sac) and 1.24% (BuNC₂OC₈-Sac), respectively.

3.1. Extraction of Cu(II), Ni(II), Cd(II), Co(II) and Pb(II) from Aqueous Solutions

We compare the extraction properties of six ionic liquids with a complexing anion, towards a panel of five metal cations, Cu(II), Ni(II), Cd(II), Co(II) and Pb(II). These cations are chosen for their presence in industrial discharges.

The percentage of extraction (%E) is determined with solutions of the nitrate salts of each metal at 0.05 mol·L^{−1} and at 25 °C. The extraction yields (%E) for each IL are depicted in Figure 3. The corresponding distribution ratio are given in Table 2.

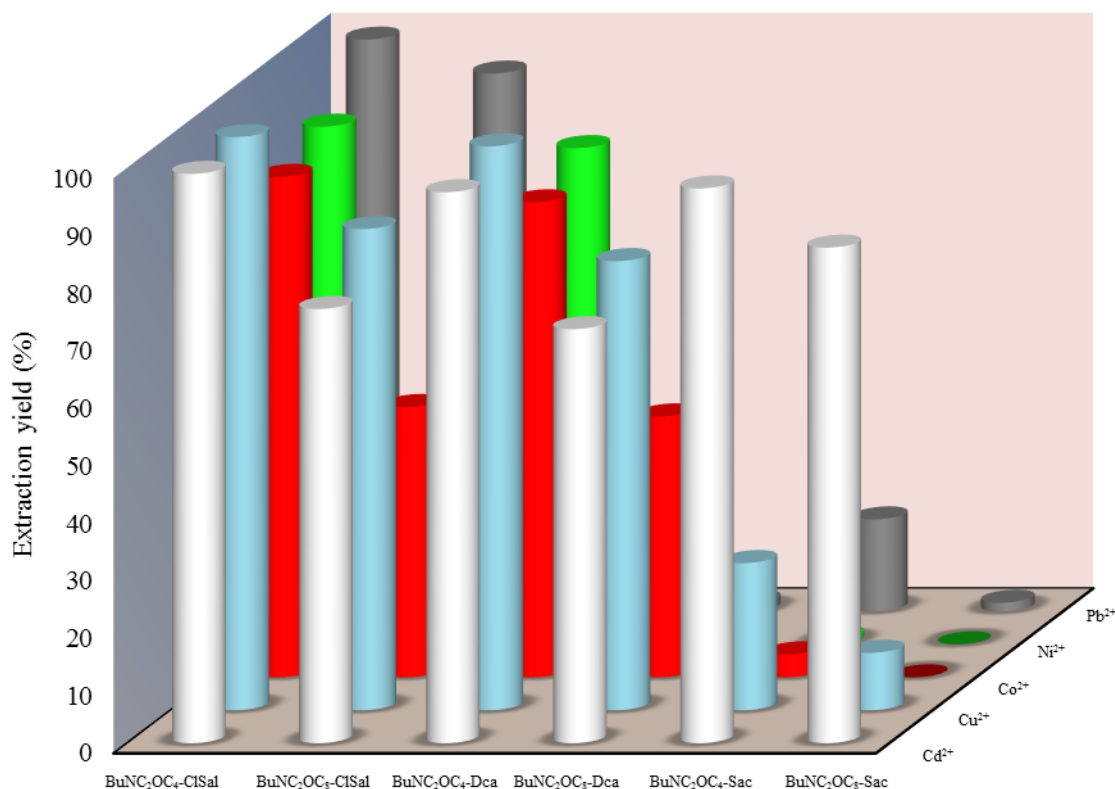


Figure 3. Extraction yields (%E) for metal aqueous nitrate salt with BuNC₂OC₄ (C8)-Sac, BuNC₂OC₄(C8)-ClSal and BuNC₂OC₄(C8)-Dca. C_{metal} = 0.05 mol L^{−1}; V_w = 2 mL; m_{IL} = 0.5 g.

3.2. Influence of the Anion of the Ionic Liquid

The overall examination of Figure 3 shows that the most efficient anion for the extraction of metals is the ClSal anion. Indeed, for all metallic cations, extraction yields are higher than 75% with BuNC₂OC₄-ClSal. By comparison, BuNC₂OC₄-Dca shows slightly weaker extraction yield, and BuNC₂OC₄-sac shows interesting extraction properties only towards Cd(II). The influence of the anion is more pronounced with ionic liquids containing BuNC₂OC₈ cation. Indeed, BuNC₂OC₈-ClSal and BuNC₂OC₈-Dca exhibit similar extraction yield with Cu(II), Cd(II) and Co.(II), but the extraction of Ni(II) does not exceed a few percent with BuNC₂OC₈-Dca, while it is close to 50% with BuNC₂OC₈-ClSal. Moreover, Pb(II) is totally extracted with BuNC₂OC₈-ClSal, whereas the extraction does not exceed a few percent with BuNC₂OC₈-Dca.

Table 2. Distribution ratio (*D*) for metal aqueous nitrate salt with BuNC₂OC₄(C₈)-Sac, BuNC₂OC₄ (C₈)-ClSal and BuNC₂OC₄ (C₈)-Dca; $C_{\text{metal}} = 0.05 \text{ mol L}^{-1}$; $V_w = 2 \text{ mL}$; $m_{\text{II}} = 0.5 \text{ g}$.

Ionic Liquid	Cu(II)	Cd(II)	Pb(II)	Ni(II)	Co.(II)
BuNC ₂ OC ₄ -Sac	1.5	120.0	0.8	0.1	0.2
BuNC ₂ OC ₈ -Sac	0.4	25.4	0.1	-	-
BuNC ₂ OC ₄ -ClSal	1301.4	439.6	735.6	40.0	29.7
BuNC ₂ OC ₈ -ClSal	21.30	12.8	59.9	4.5	3.7
BuNC ₂ OC ₄ -Dca	192.5	178.5	0.1	24.1	18.1
BuNC ₂ OC ₈ -Dca	13.7	1.8	0.1	0.3	3.2

The results reported in Figure 3 and in Table 2 show that the capability of ionic liquids to extract a metal ion is greatly correlated to the ability of the anion of the ionic liquid, to form stable complexes with the metal cation. The extraction of first row transition metal (Cu(II), Co.(II), Ni(II)) by Dca or ClSal based ionic liquids show that the affinity of the metal ions for ionic liquid phase is weak for Ni(II) and Co.(II) and higher for Cu(II). Such a trend may be related to the formation constants of complexes of these metals with the anions of the ionic liquids.

This assumption is corroborated by the values of the stability constants of M(II)-salicylate complexes for Cu(II), Ni(II) and Co.(II). The salicylate moieties may form stable relatively complexes by bidentate coordination giving a five membered rings species with metal ions. The first stability constant of M(II)-salicylate complexes ($\log\beta_1$) for Ni(II) and Co.(II) are 8.65 and 8.09, respectively. This reflects a similar affinity of these two metals for the salicylate anion [31,36]. The higher extraction yields of Cu(II) compared to Ni(II) and Co.(II) is in agreement with a higher stability constant for Cu(II) with a $\log\beta_1$ of 10.65 [31]. The high extraction yields of heavy metals (Cd(II) and Pb(II)) by ClSal based ionic liquids are equally in relation with the high stability constants of salicylate-Cd(II) (or Pb(II)) complexes [36,37]. The selectivity factor (SF) which represents the ratio between the distribution ratio of two metals for a given ionic liquid, indicates the selectivity of the ionic liquid towards the two metals gives useful information about the efficiency of the separation. The selectivity factors of Cu(II) towards Ni(II) ($SF_{\text{Cu/Ni}}$) or Co.(II) ($SF_{\text{Cu/Co.}}$) for BuNC₂OC₄-ClSal are between 30 and 50, respectively, whereas for BuNC₂OC₈-ClSal it is only between four and six, respectively. It seems that BuNC₂OC₄-ClSal is more selective than BuNC₂OC₈-ClSal for the separation of the first row transition metals.

The coordination of metal in the IL phases was investigated on the basis of the spectrophotometric analysis of the ionic liquid phase after extraction of Co.(II), Cu(II) and Ni(II). The electronic spectra of Ni(II) in BuNC₂OC₈-ClSal are characteristic to Ni(II) in an octahedral environment (Figure 4). The two bands with the λ_{max} located at 1145 and 700 nm are assigned to the $^3A_{2g} \rightarrow ^3T_{2g}$ and $^3A_{2g} \rightarrow ^3T_{1g}$ (F) transitions, respectively [38]. A third band with the λ_{max} located around 400 nm and partially masked by an intense transfer charge band is attributed to a $^3A_{2g} \rightarrow ^3T_{1g}$ (P) transitions. The spectrum is shifted to weaker energy by comparison to the spectrum of Ni(H₂O)₆²⁺ in aqueous solutions. This evidences the coordination of Ni(II) by oxygen atoms of the ClSal anion.

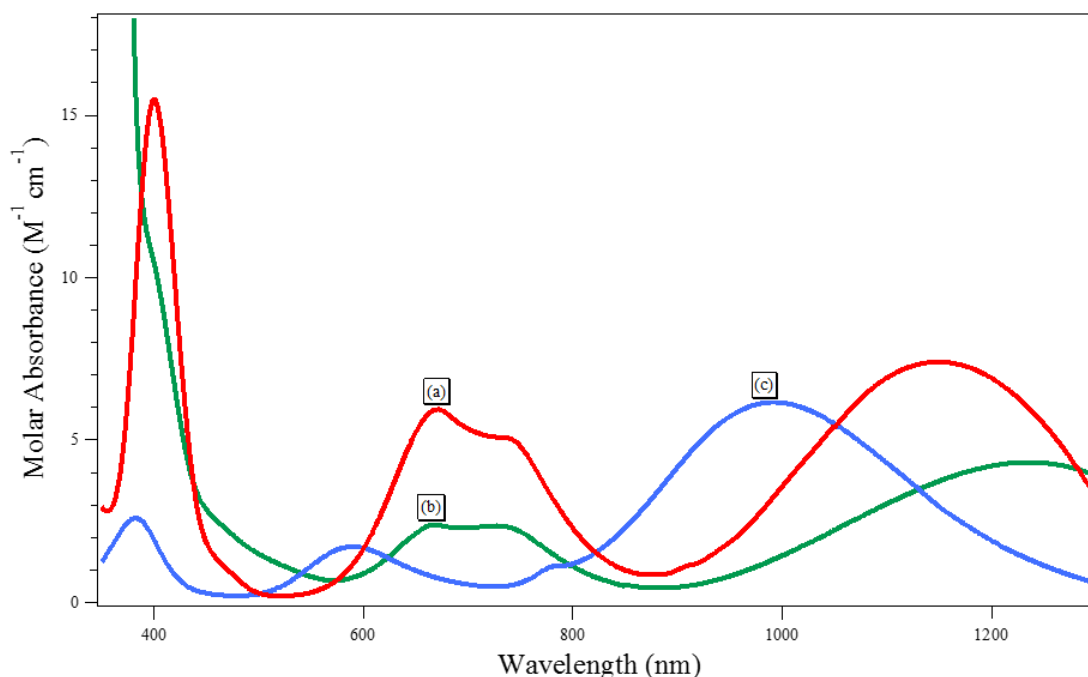


Figure 4. UV-Vis spectra of $\text{Ni}(\text{NO}_3)_2$ in ILs (a) $\text{BuNC}_2\text{OC}_4\text{-ClSal}$ phase; (b) $\text{BuNC}_2\text{OC}_4\text{-Dca}$ and (c) aqueous phase. $C_{\text{metal}} = 0.05 \text{ mol L}^{-1}$; $V_w = 2 \text{ mL}$; $m_{\text{IL}} = 0.5 \text{ g}$; UV-vis spectra are recorded in ethylacetate for ionic liquid (IL) phase.

UV-visible spectra of $\text{Cu}(\text{II})$ in IL phases are depicted Figure 5. The spectrum of $\text{BuNC}_2\text{OC}_8\text{-ClSal}$ after extraction of copper shows one single d-d transition in the visible region with a maximum wavelength at 745 nm. The relatively broad shape of the band and the value of molar extinction coefficient would be indicative of an octahedral copper complex. The higher molar absorbance of $\text{Cu}(\text{II})$ in IL phase indicates that the $\text{Cu}(\text{II})$ complex is more distorted than the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ species.

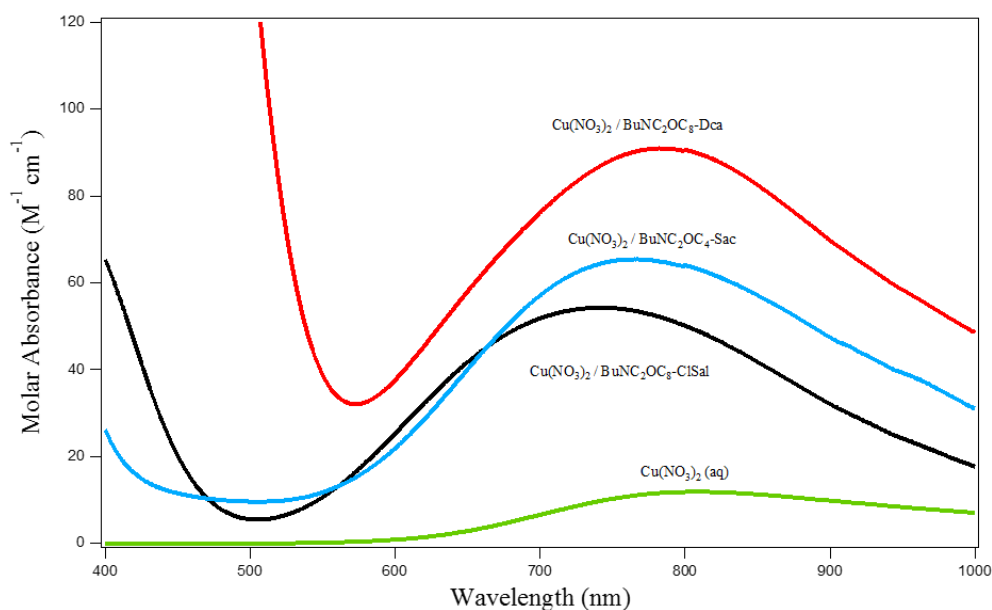


Figure 5. UV-Vis spectra of $\text{Cu}(\text{NO}_3)_2$ in aqueous and in ionic liquid phase. $C_{\text{metal}} = 0.05 \text{ mol L}^{-1}$; $V_w = 2 \text{ mL}$; $m_{\text{IL}} = 0.5 \text{ g}$; UV-vis spectra are recorded in ethylacetate for IL phase.

Figure 6 represents the spectra of Co^{2+} in the different IL phases. The spectrum of Co(II) in $\text{BuNC}_2\text{OC}_8\text{-ClSal}$ shows in the visible region, similar features than the spectrum of $\text{Co(NO}_3)_2$ in aqueous phase, with a band at 530 nm and with a shoulder at 480 nm. This band as well as its shoulder correspond to the two following transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$. The molar absorption coefficient of IL phase at 530 nm is equal to $33 \text{ cm mol}^{-1} \text{ l}$. All these features are indicative of a Co(II) in octahedral environment. It is interesting to note that the spectrum of Co(II) in $\text{BuNC}_2\text{OC}_8\text{-ClSal}$ is shifted towards lower energy compared to those recorded in aqueous media.

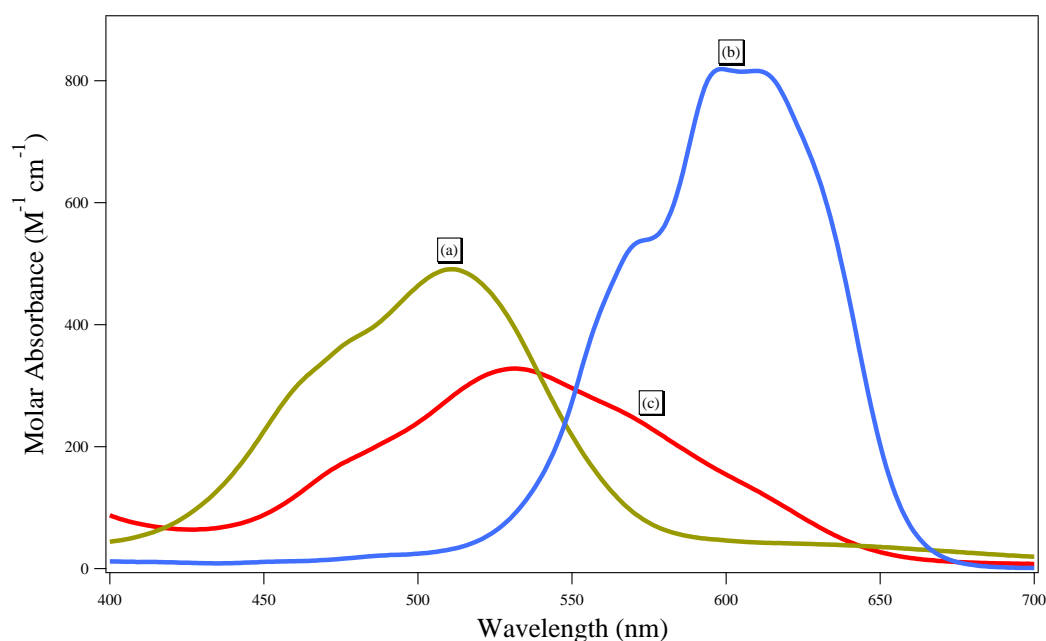


Figure 6. UV-Vis spectra of $\text{Co(NO}_3)_2$ in (a) $\text{BuNC}_2\text{OC}_8\text{-Dca}$ phase; (b) aqueous phase step up 100 times and; (c) $\text{BuNC}_2\text{OC}_8\text{-ClSal}$ phase step up 10 times. $C_{\text{metal}} = 0.05 \text{ mol L}^{-1}$; $V_w = 2 \text{ mL}$; $m_{\text{IL}} = 0.5 \text{ g}$; UV-vis spectra are recorded in ethylacetate for IL phase

In previous works, we pointed out the properties of $\text{tri}(n\text{-butyl})[2\text{-ethoxy-2-oxoethyl}]\text{ammonium}$ ($\text{BuNC}_2\text{OC}_2^+$) dicyanamide (Dca) and $\text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$ (Tf_2N^-) ionic liquids with for the extraction of metal cations [26,29,30]. Tf_2N^- is a non-coordinating anion currently used to generate ionic liquid. $\text{BuNC}_2\text{OC}_2\text{-Dca}$ extracts quantitatively Cu(II) , Ni(II) , Cd(II) and Pb(II) from 0.05 mol L^{-1} aqueous solutions. By comparison, for the same metal concentration, $\text{BuNC}_2\text{OC}_2\text{-Tf}_2\text{N}$ provides only weak extraction with extraction yield less than 10% [30]. Similar observations have been made with ionic liquid based tetraalkylammonium cation associated with Dca^- and Tf_2N^- anions [29]. Although it has high extraction yields, $\text{BuNC}_2\text{OC}_2\text{-Dca}$ does not allow considering applications in the field of the purification of industrial effluents because of its solubility in water ($\approx 6\%$), that is why we focused on the development of more hydrophobic ionic liquids, to reduce the releasing of organic cations in aqueous phase. The high extraction properties of Dca^- based ionic liquids are ascribed to the ability of dicyanamide anion to interact with metallic cations through the formation of metal complexes via their nitrogen atoms [33,34]. The examination of the structure of metal complexes in which the dicyanamide anion acts as a ligand, shows that this anion behaves as a monodentate or bridging ligand [33,34]. It is reasonable to think that the higher extraction yields observed for Cu(II) and Cd(II) compared to those of Ni(II) , Co(II) and Pb(II) are related to their higher affinity for Dca^- anion, which favors their transfer from aqueous to ionic liquid phases. However, the lack of thermodynamic data from the literature does not allow corroborating this affirmation. The only published data show that the affinity of the dicyanamide ligand for Cd(II) ions is higher than for Pb(II) with a $\log\beta_1$ values of 3.11 for Cd(II) [39] against 2.1 for Pb(II) [40]. These values also show that the affinity of

the dicyanamide ligand for the metal cations is lower than in the case of the chlorosalicylate ligand, which is consistent with the lower extraction yields observed with dicyanamide based ionic liquids compared to the chlorosalicylate one. The dicyanamide based ionic liquids are equally less selective for the first row transition metals than their analogous with ClSal anions. The selectivity factors $SF(Cu/Ni)$ and $SF(Cu/Co)$ are equal to 8 and 10.6 for $BuNC_2OC_4$ -Dca and with $BuNC_2OC_8$ -Dca, $SF(Cu/Co)$ is equal to 4.29. The main exception is the relatively high selectivity of Cu(II) towards Ni(II) with $BuNC_2OC_8$ -Dca, compared to other systems, with a selectivity factor of 53 due to a low percentage of Ni(II) extracted. It is to be noticed the low affinity of dicyanamide based ionic liquids for Pb(II) ions which makes it possible to use them effectively to separate metals from Pb(II) ions. With $BuNC_2OC_8$ -Dca, the selectivity factors $SF(Cu/Pb)$ and $SF(Cd/Pb)$ are equal to 230 and 170.

The UV spectrum of Ni(II) in $BuNC_2OC_8$ -Dca exhibit the same features as the spectrum of $Ni(H_2O)_6^{2+}$ in aqueous solution, and is characteristic to Ni(II) in an octahedral environment. The shift towards weaker energies indicates a change in the nature of donor atoms bound to the metal center related to the implication of nitrogen atoms in the coordination sphere of the metal [38].

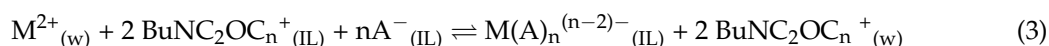
The UV-visible spectrum of Cu(II) in $BuNC_2OC_8$ -Dca show the same features as in $BuNC_2OC_8$ -ClSal in the visible region, except that the shift of the d-d transition is less marked than with $BuNC_2OC_8$ -ClSal with a maximum at 780 nm. In the UV region, the spectrum shows a supplementary transition centered at 390 nm (not shown here). This transition is ascribed to an LMCT (or MLCT) transition characteristic of the Dca coordination to Cu(II) cation. The spectrum of Co(II) in $BuNC_2OC_4$ (C₈)-dca shows in the visible region a band at 600 nm with a shoulder at 570 nm. The molar absorption coefficient at 600 nm is equal to 810 cm mol^{-1} . The spectral features of Co(II) spectra in Dca ionic liquids are characteristic of a Co(II) in tetrahedral environment, meaning a change of coordination of the metal during the extraction process. The band is assigned to a $A_2(F) \rightarrow T_1(P)$ transition [38].

The saccharinate anion behaves as monodentate ligand through its nitrogen atom or as a bidentate through N,O coordination [41]. It often act as a ternary ligand in structure of many metal complexes to achieve the coordination of metal ions [42]. No data are available in the literature concerning the formation constants in aqueous solution of divalent metal complexes with this anion, suggesting a weak coordinating ability in aqueous phase towards metal ions. One key point is that saccharin ionic liquids have a high affinity only for Cd(II), and may also be efficient to separate cadmium from other divalent cations. Indeed, the lowest selectivity factors for cadmium towards other divalent cations ($SF_{(Cd/M)} = D(Cd(II))/D(M(II))$) is that with Cu(II) ions. They are equal to 63 and 80 for $BuNC_2OC_8$ -Sac and $BuNC_2OC_4$ -Sac, respectively.

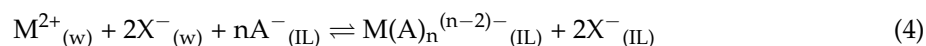
3.3. Influence of the Cation of the Ionic Liquid

Figure 3 shows that the cation of the ionic liquid has a significant influence on the extraction of metal cation. Indeed, the extraction yield is significantly higher with $BuNC_2OC_4^+$ than with $BuNC_2OC_8^+$ cations. This trend is related to (i) the more hydrophilic character of the tetrahexylammonium cation which may favor the transfer of the metal in the ionic liquid phase via cationic exchange process, and (ii) the fact that the concentration of anion, in the ionic liquid phase, is higher in $BuNC_2OC_4^+$ ILs than with $BuNC_2OC_8^+$ ILs. Indeed, as an example taking into account the molar mass of $BuNC_2OC_4$ -Dca and $BuNC_2OC_8$ -Dca, the mole number contacted with the aqueous phase in an extraction sample is respectively of 1.3 mmol for $BuNC_2OC_4$ -Dca and 1.1 mmol for $BuNC_2OC_8$ -Dca, respectively. Such a difference may be taken into account to explain partially the better extraction properties of $BuNC_2OC_4$ -Dca, which contains a higher concentration of extractant. To investigate if ion exchange occurs during extraction, coextraction of nitrate ion was followed by ion-chromatography. When a cation exchange occurs, the metal ion in the aqueous phase is exchanged

with a cation of the ionic liquid. The metal ion is then extracted into the ionic liquid, while the cation of the IL moves to the aqueous phase following the equilibria:



If extraction proceeds only via ion-pairing, the counter anion of the metal salt is co-extracted into the ionic liquid phase, so that the ratio between the metal and the counter-ion extracted should be equal to one considering the following equilibria:



The determination of the co-extraction rates of nitrate ion gives an indirect insight of the amount of cation released in the aqueous phase and allow to investigate the extraction mechanism of metal cation. Figure 7 depicts the ratio R between the extraction rate of nitrate ion and those of metal.

Ion-pairing is the dominant mechanism with $\text{BuNC}_2\text{OC}_8^+$ cation. Indeed, for all systems, except for $\text{Cu(II)/BuNC}_2\text{OC}_8\text{-ClSal}$, the ratio $E(A^-)/E(C^+)$ values are close and even may exceed 1 (Figure 7). A value higher than 1 means that the anions of the metal salt are more efficiently extracted than metal itself and suggests the possibility of anion exchange between the anion of the ionic liquid and the nitrate ions. This may take place during the extraction of Co(II) in $\text{BuNC}_2\text{OC}_8\text{-Dca}$ ($R = 1.3$) and to a small extent with $\text{BuNC}_2\text{OC}_8\text{-ClSal}$ ($R = 1.1$).

The R value is much less than one with $\text{BuNC}_2\text{OC}_4^+$ cation, meaning that the mechanism for extracting metal ions is a mixed process that includes both cation exchange and ion-pair extraction. The R value represents the extent of ion-pair extraction. It is clearly seeing from Figure 7 that with $\text{BuNC}_2\text{OC}_4\text{-ClSal}$, the extraction of metal proceeds mostly via cation-exchange, especially, in the case of the extraction of Ni(II) . In the case of $\text{BuNC}_2\text{OC}_4\text{-Dca}$, the two mechanisms are operant, nearly to the same extent.

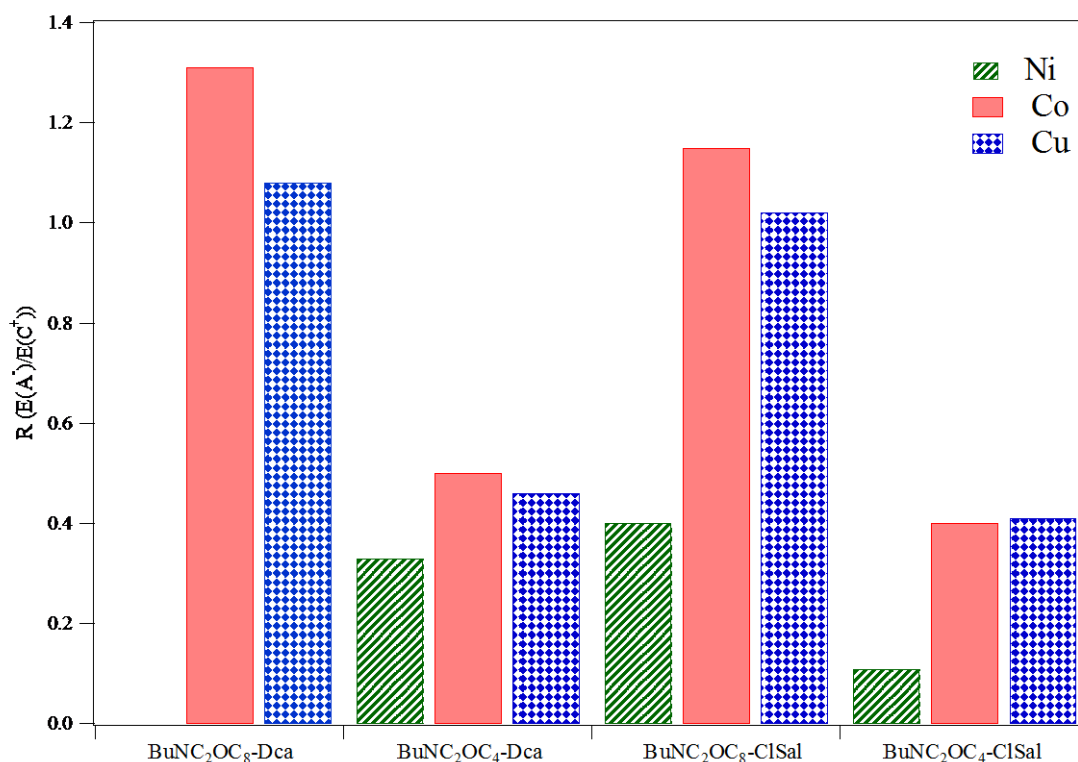


Figure 7. Ratio (A^-/C^+) between the extraction rate of anion and those of Cu(II) , Co(II) and Ni(II) , for the different salt used at different concentration.

All the results show that $\text{BuNC}_2\text{OC}_4^+$ based ionic liquids are more efficient to extract metal ions than that of $\text{BuNC}_2\text{OC}_8^+$. The disadvantage is that their higher solubility leads to the extraction with a large proportion of cationic exchange resulting in a significant release of organic cations in the aqueous phase. In comparison, $\text{BuNC}_2\text{OC}_8^+$ based ionic liquids, despite their lower performance, favor exclusively ion-pair extraction and allow the development of more eco-compatible extraction processes. These results may suggest that the $\text{BuNC}_2\text{OC}_4^+$ based ionic liquids would be less viable in large-scale use. However, it is also necessary to conceive a possible use in media with high salinities, which corresponds to most liquid industrial effluents. As we have shown in previous work [26], high salinity causes an increase in extraction efficiency, promotes ion pair extraction and thus limits the release of organic cations during extraction processes.

3.4. Back-Extraction of Metal Ions and Recyclability of Ionic Liquid

The back-extraction process will be based on exchange ligand reaction and would be suitable by using a hydrophilic ligand with stronger affinity for metal cations than the anions of ionic liquid. To verify this hypothesis, we carried out the experience of back-extraction with aqueous disodium EDTA solution at 0.1 mol L^{-1} contacted with ionic liquid phases previously loaded with metal. EDTA is a hexavalent ligand that forms stable 1:1 complexes with divalent metals; the stability constants of the complexes formed are often higher than 12 (in logarithmic units). In this case, the back-extraction process would involve a replacement of M(II) by Na^+ ions in the ionic liquid phase, or the back-extraction of NO_3^- ions previously extracted in the ionic liquid phase, or both of them.

Figure 8 shows that EDTA is an efficient ligand to recover metal ions from the ionic liquid phase. Cu(II) is back extracted from $\text{BuNC}_2\text{OC}_n\text{-ClSal}$ with recovery percentages close to 100% and higher than 80% with $\text{BuNC}_2\text{OC}_n\text{-Dca}$. The efficiency is observed for the recovery of Ni(II) Cd(II) and Co(II) from these two ionic liquids. Cd(II) is also fully back extracted from $\text{BuNC}_2\text{OC}_n\text{-Sac}$ with a back extraction percentage exceeding 90%.

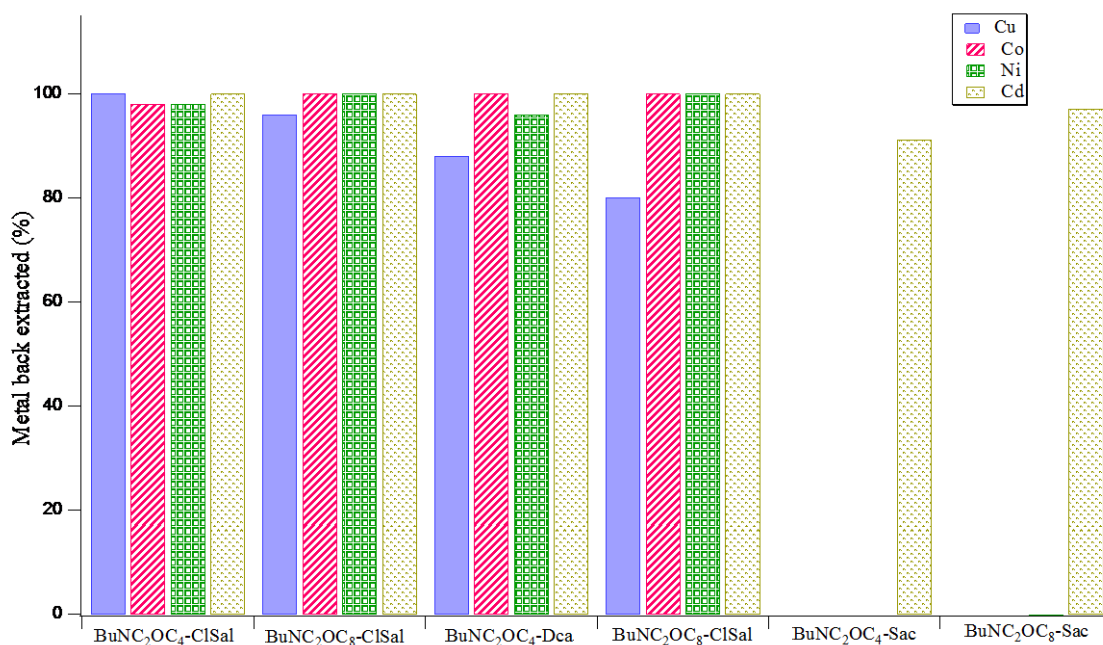


Figure 8. Extraction and back-extraction yield (%E) for M(II) .

After the back-extraction process, it is important to check if the ionic liquid would be able to be reused for the extraction of metal from aqueous solution. To check the recyclability of the ionic

liquids, several cycles of extraction-back extraction were carried-out on the same ionic liquid phase, following the same experimental conditions as those reported previously.

After each cycle, the metal concentration was determined in the aqueous phase, and the extraction and back-extraction yields have been determined by taking into account the total concentration of metal present in the ionic liquid phase. Figure 9 reports the extraction and back-extraction yields for Cu(II) and Co(II) with $\text{BuNC}_2\text{OC}_n\text{-Sal}$ ionic liquid.

The results show that the efficiency of extraction and back-extraction remained similar over three cycles. The extraction yields are nearly constant over the three cycles, whereas the back-extraction yields are higher than 95%. Therefore, these results confirm that the ionic liquid can be regenerated in the back-extraction process with EDTA solution and can be reused for metal extraction; the release of ionic liquid remains sufficiently limited to not alter the performance of the latter. These results may be generalized for all the systems studied in this work.

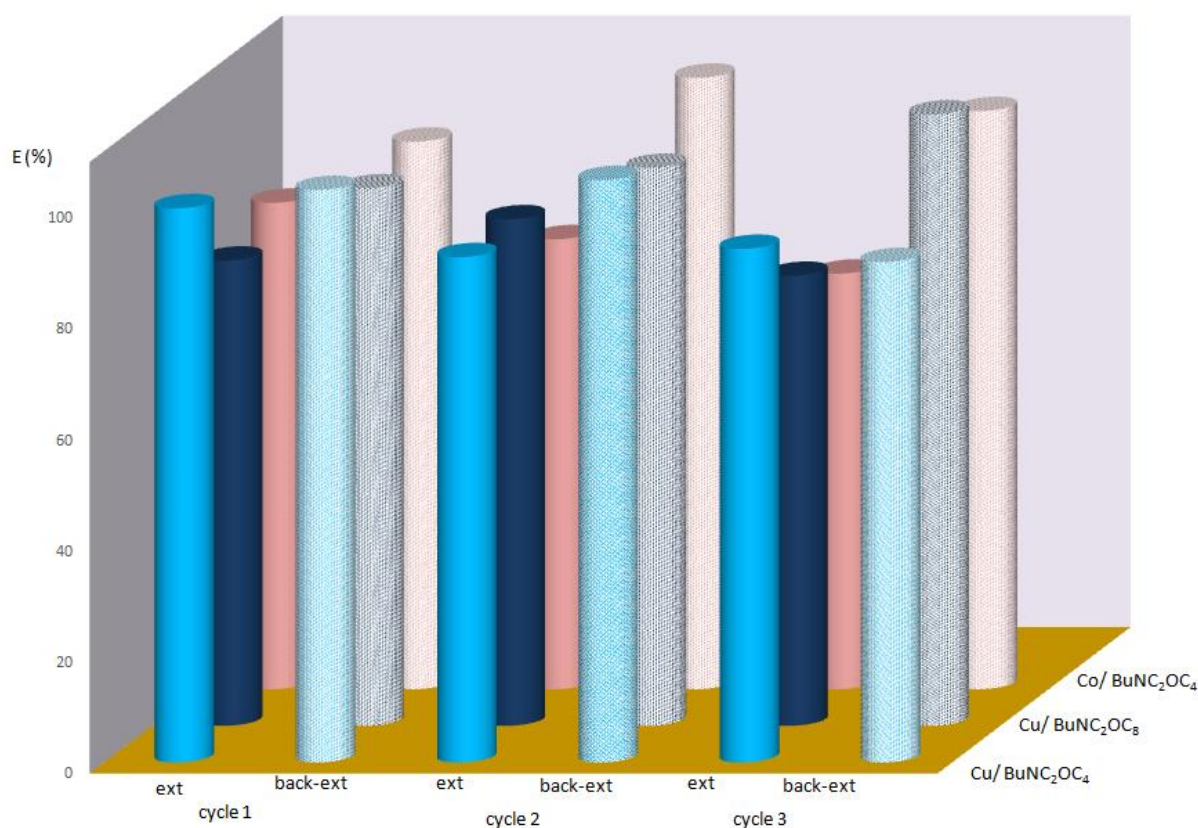


Figure 9. Reusability of ionic liquid phase for copper and cobalt extraction using $\text{BuNC}_2\text{OC}_n\text{-ClSal}$.

4. Conclusions

Our results report the possibility of designing in a simple way hydrophobic ILs able to extract efficiently metallic cations by liquid-liquid extraction. The ionic liquids use as negative pole common coordinating anions, such as dicyanamide, chlorosalicylate and saccharinate, instead of fluorinated compounds. Our first results show that chlorosalicylate based ionic liquids have a high extraction efficiency towards Cu(II), Ni(II), Cd(II), and Pb(II), whereas dicyanamide based ionic liquids may extract efficiently Cu(II) and Cd(II). Ionic liquids with saccharinate anions are selective of Cd(II) ions. The UV-vis investigations of the first row transition metals show the coordination of the metal with the anion of ionic liquids.

The extraction process is reversible with all the ionic liquids, and the metal ions can be recovered by aqueous solutions of disodium EDTA. In order to conceive environmentally-friendly systems for

industrial applications, a workable way is to privilege the ionic liquids with the $\text{BuNC}_2\text{OC}_8^+$ cation, which are less soluble. The ionic liquids with the $\text{BuNC}_2\text{OC}_4^+$ cation nevertheless remain interesting for the development of liquid-liquid extraction processes, but their extraction properties must be studied in higher salinity environments which favor extraction by ion pair. These results show that the strategy of designing ionic liquids with coordinating anions with low hapticity giving moderately stable complexes in the ionic liquid phase is a promising route for the extraction of aqueous metal ions. In this case, the metals can be easily recovered in the aqueous phase with water-soluble ligands with high hapticity.

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