Article

Separation of Co(II) and Ni(II) Using an Analog of Glycine-Betaine Based on Task-Specific Ionic Liquids

Lamia Boulafrouh, Stéphanie Boudesocque, Aminou Mohamadou [ORCID] and Laurent Dupont *

Institut de Chimie Moléculaire de Reims (ICMR), Université de Reims Champagne-Ardenne, CNRS UMR 7312, UFR des Sciences Exactes et Naturelles, Bâtiment 18 Europol'Agro, BP 1039, CEDEX 2, F-51687 Reims, France; aminou.mohamadou@univ-reims.fr (A.M.)
* Correspondence: laurent.dupont@univ-reims.fr

Abstract: A series of salts based on ethyl ester glycine-betaine derivatives, viz tri(*n*-pentyl)[2-ethoxy-2-oxoethyl]ammonium bromide, have been synthesized. These cations generate hydrophobic ionic liquids (ILs) with bis(trifluoromethylsulfonyl)imide (Tf_2N^-) or dicyanamide (Dca^-) anions. These new analogues of glycine-betaine-based ionic liquids (AGB-ILs) were characterized using spectroscopic methods (IR, ^1H, and ^{13}C NMR) and elemental analysis. These AGB-ILs were used for the selective separation of Ni(II) and Co(II) in saline media using pure ILs phase or ILs diluted in organic solvent. Interestingly, extraction of Co(II) and Ni(II) in Dca-based AGB-ILs can be enhanced using salts with chaotropic anions such as $NaNO_3$ (E > 90% for Co(II) and E = 85% for Ni(II)). Tf_2N^--based ionic liquids do not extract Ni(II) or Co(II) even in NaCl 4M. Dca^--based ILs lead to a quasi-quantitative extraction of Co(II), while extraction of Ni(II) is limited to a few percent (17%) leading to separation factors higher than 100, ensuring a good separation of both metals. Cobalt could be back-extracted from the ionic liquid phase with water or with an aqueous solution of Na_2SO_4, which limits the release of the AGB cation in aqueous media, thus preserving its integrity. Results obtained by AGB-ILs diluted in organic solvent were comparable to those obtained with the pure AGB-ILs phase, indicating that this strategy can be deployed on systems working continuously out of equilibrium since the extraction mechanisms involve fast equilibria.

Keywords: cobalt; nickel; task specific ionic liquid

1. Introduction

The production of Li-ion batteries has been increasing rapidly in recent years, as key raw materials for cathode materials of this technology, nickel and cobalt, have now acquired the status of strategic metals, with a demand for high purity (>99.99%) materials [1–4]. Today, high-purity Ni(II) and Co(II) products are mainly produced by hydrometallurgical processes from primary resources. However, as lithium-ion batteries have a limited lifetime, it becomes essential to focus [5] on the recycling of used batteries to recover these two metals to supplement the market and also avoid environmental pollution [6,7]. One of the problems encountered in the development of high-purity Ni(II) and Co(II) materials is that these two metals cannot be separated in a clean and efficient manner due to their similar ionic radii, oxidation states, and coordination numbers. Solvent extraction is the most widely used method for separating these metals [8], but it has some limitations. The extractants commonly used [9–13] do not allow the achievement of separation coefficients greater than 10, and the conditions for implementing this technology call for high concentrations of mineral acids, particularly in the stripping stage.

Therefore, the separation of Ni(II) and Co(II) from used batteries cannot be achieved in a clean, efficient, and low-consumption way. It is therefore essential to develop a breakthrough methodology to separate these two metals. Hence, it is important to find new types of extractants and new extraction methodologies that limit the massive use of mineral acids.

In recent years, ionic liquids (ILs) have attracted great interest in the field of metal extraction as an alternative medium to molecular solvents in liquid-liquid extraction processes or as new extractants [13–15]. Previous reports have highlighted the potential of room-temperature hydrophobic ionic liquids (RTILs) for the separation of cationic divalent metal ions and the recovery of precious metals in liquid-liquid extraction processes [16–35]. The modularity of ILs allows their design to be adapted to meet the needs of specific applications. Thus, several extraction strategies can be implemented, depending on the nature and coordinating properties of the metals to be extracted.

However, the development of green processes requires particular attention to metal extraction mechanisms, which must limit as much as possible the release of organic species into the aqueous effluent by ILs leaching [23,36–39]. In other words, the process should limit the cation exchange reactions and exclusively favor ion-pair extraction mechanisms [40,41]. To reach this objective, the addition of an alkaline salt in the aqueous effluent may be interesting since it limits the solubility of IL and modulates the overall extraction process to achieve the extraction by ion-pairs. The use of saline environments has already been successfully tested in combination with hydrophilic ionic liquids to generate aqueous biphasic systems (ABS) for the extraction and separation of 3d strategic metals [42–44]. Saline media can be combined with hydrophobic ionic liquids to enhance metal extraction and carry out selective metal separation [23,45–47]. The choice of the background salt is linked to the position of its constitutive anion and cation in the Hofmeister series, which defines their ability to generate "salting in" or "salting out" effects [21,47,48] in water/ionic liquid biphasic systems.

In a previous work [48], we reported the ability of dicyanamide-based ionic liquids to perform selective extraction of Co(II) and Ni(II) in saline media. The interest of the dicyanamide salt is that this dicyanamide anion has a moderate ability to coordinate metal ions [48,49] and the extraction yield of this dicyanamide-based ionic liquid can afford reversible extraction. Indeed, the extraction yield of metal ions in non-saline media is relatively low, but the extraction can be improved to become quasi-quantitative by the addition of a salt having a chaotropic anion, such as $NaNO_3$ or NaCl. The metal can be recovered by a water or an aqueous saline solution with a salt having a kosmotropic anion. The advantage of using a saline solution is that it limits the loss of ionic liquids during the back-extraction phase since a kosmotropic salt reduces the solubility of the ionic liquid. In this work, we tested the applicability of the methodology described in our previous article [48] and whether it can be applied to continuous flow systems at a semi-pilot stage to treat higher volumes of effluent. One of the requirements to develop a process on a semi-pilot scale is working outside equilibrium and, therefore, with shortened contact times between the effluent and the extracting phase. Therefore, we will work with low-viscosity phases by dissolving the ionic liquid in an organic solvent to optimize the contact time between the aqueous effluent and the extracting phase. The choice of solvent will be oriented towards solvents provided by the bioraffinery, which have more advantageous ecotoxicological properties than traditional organic solvents and will limit the use of fossil resources. One of the challenges that will have to be taken into consideration here is to know under which conditions the extractive performance of ionic liquids will be comparable to that of pure ionic liquid phases when switching the solvent medium and if the strategy that we have previously developed with pure ionic liquid phases for the separation and recovery of Co(II) to Ni(II) will work in continuous mode and in solvent media.

We report here the synthesis and characterization of the bromide (Br$^−$), bis(trifluoromethylsulfonyl)imide (Tf$_2$N$^−$), and dicyanamide (Dca$^−$)-based tri(*n*-pentyl)[2-ethoxy-2-oxoethyl] and tri(n-hexyl)[2-ethoxy-2-oxoethyl] ammonium ionic liquids (Figure 1) for the selective extraction and recovery of Co(II) and Ni(II) from saline media solution. The extraction and back extraction experiments of Co(II) and Ni(II) in dicyanamide-based AGB-ILs diluted in organic solvent will be described. The influence of several organic solvents on the extraction yield of metals will be compared, and the impact of the salt concentration and the extraction mechanism of Co(II) will be investigated. All these

experiments will be made in static mode (batch), and the results obtained will allow us to determine the applicability of this methodology to systems that work in continuous flow and to define the best possible experimental conditions for the transposition of these results at a semi-pilot scale.
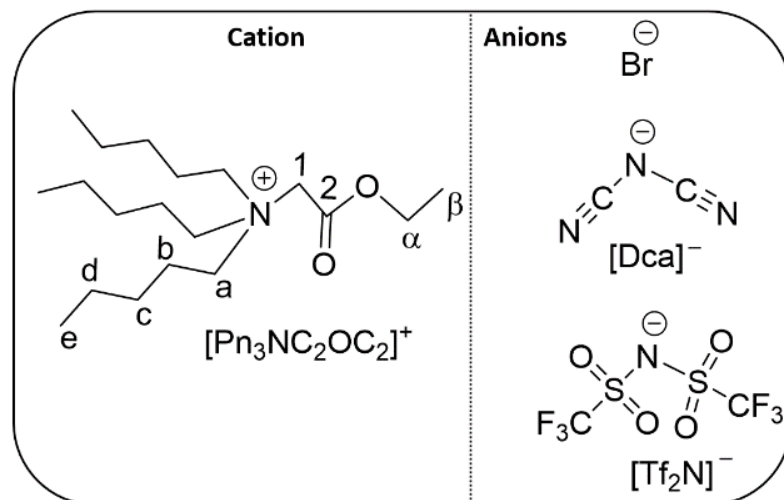
Figure 1. Chemical structure of the different tri(*n*-pentyl)[2-ethoxy-2-oxoethyl]ammonium-based AGB-ILs.

2. Materials and Methods

2.1. Materials

Tri(*n*-pentyl)amine (98%), ethyl bromoacetate (98%), methylisobutylketone (MBIK) (99%), butyl acetat (BuOAc) (>99.5%), 2-methyltetrahydrufuran (Me-THF) (>99%), sodium dicyanamide (99%), and lithium bis(trifluoromethylsulfonyl)imide were obtained from Sigma-Aldrich. Nickel(II) nitrate (99%), cobalt(II) nitrate (>99%), sodium chloride (99%), and sodium sulfate (99%) were purchased from Fisher Scientific.

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

Elemental analyses (C, H, N, and S) were carried out on the elementary CHNS thermo-electron FLASHEA 1112 series. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ at room temperature with a Brüker AC 500 MHz spectrometer. Chemical shifts (in ppm) for ^{1}H NMR spectra were referenced to residual protic peaks. IR spectra of ionic liquids were recorded on a PerkinElmer UATR Two. UV-Vis spectra were measured with Spectrometer Cary 5000 UV-Vis-NIR. The viscosity was measured with a Brookfield Viscometer DV-II + Pro. The temperature of the sample was maintained to $\pm 0.1\ °$C by an external temperature control, CPE 51. Differential Scanning Calorimetry (DSC) was performed on a DSC Q100 TA Instrument under nitrogen atmosphere. Thermogravimetric analyses were carried out using a Netzsch TG 209F3 Tarus thermogravimetric analyzer under an argon atmosphere, ranging from 30 to 600 $°$C with a heating rate of 10 $°$C min^{-1}. The mass of TGA samples used varied between 10 and 20 mg, and samples were heated from 30 to 600 $°$C. The decomposition temperatures of AGB-ILs were measured at T$_{onset}$, with the temperature corresponding to 10% mass loss.

2.2. Ionic Liquid Synthesis

N,N,N-tri(n-pentyl)[2-ethoxy-2-oxoethyl]ammonium bromide [Pn$_3$NC$_2$OC$_2$][Br]

A solution of tri(*n*-pentyl)amine (77.33 g, 0.34 mol) in ethyl acetate (300 mL) was added dropwise, and 2-bromoacetic acid ethyl ester (36.74 g, 0.22 mol) was added in 100 mL of ethyl acetate. The mixture was then stirred at room temperature for five days. Then, the solvent was evaporated, and the crude oily product obtained was washed several

times with diethylether (5 × 150 mL). The solid, yellowish product was drying at ambient temperature under vacuum.

Yield: (92%). Elemental analysis: calculated for $C_{19}H_{40}NO_2$ Br (MW = 365.32 g.mol^{-1}): C 57.8%. H 10.22% and N 3.55%. Found: C 57.54%, H 10.14%, and N 3.64%. ^{1}H NMR, δ/ppm (500 MHz, CDCl$_3$): 0,84 [t, 9 H, 3 CH$_3$(e)]; 1,27 [m, 15 H, 6 CH$_2$(d+c)] + CH$_3$(β)]; 1,70 [m, 6 H, 3 CH$_2$(b)]; 3,58 [m, 6 H, 3 CH$_2$(a)]; 4,19 [q, 2 H, [CH$_2$(1)]; 4,57 [s, 2 H, CH$_2$(α)].^{13}C NMR, δ/ppm (125.7 MHz, CDCl$_3$): 13.76 [3 CH$_3$(e)]; 13.91 [CH$_3$(β)]; 22.06, 22.18 [3 CH$_2$(d+c)]; 28.25 [3 CH$_2$(d)]; 57.62 [CH$_2$(1)]; 60.65 [3 CH$_2$(a)]; 62.80 [CH$_2$(α)]; 164.61 [CO(2)]. IR, ν/cm^{-1}: 2957, 2932, 2873 (ν_{C-H}), 1738 ($\nu_{C=O}$).

N,N,N-tri(n-pentyl)[2-ethoxy-2-oxoethyl]ammonium-bis(trifluoromethylsulfonyl)imide [Pn$_3$NC$_2$OC$_2$][Dca]

N,N,N-tri(*n*-pentyl)[2-ethoxy-2-oxoethyl]ammonium bromide (0.1 mol) was dissolved in water (100 mL), and a solution of sodium dicyanamide (19.58 g, 0.22 mol) in water (100 mL) was added. The mixture was stirred for 6 h, and then allowed to settle into two phases. The lower ionic liquid phase was extracted with ethyl acetate (2 × 50 mL) and washed with water (3 × 50 mL). The absence of bromide ions was controlled by an AgNO$_3$ test of the aqueous phase. The organic phase was dried over anhydrous MgSO$_4$, which was filtered, and the solvent was then evaporated under reduced pressure at 50 °C to give a yellowish viscous product that was vacuum dried at 50 °C overnight.

Yield: (91%). Elemental analysis: calculated for $C_{21}H_{40}N_4O_2$ (MW = 380.57 g.mol^{-1}): C 66.28%. H is 10.59%, and N is 14.72%. Found: C 65.82%, H 11.03%, and N 14.34%. %. ^{1}H NMR, δ/ppm (500 MHz, CDCl$_3$): 0.84 [t, 9H, 3 CH$_3$(e)]; 1.27 [m, 15 H, 6 CH$_2$-CH$_2$(d+c) + CH$_3$(β)]; 1.62 [m, 6 H, 3 CH$_2$(b)]; 3.42 [m, 6 H, 3 CH$_2$(a)]; 4.14 [s, 2 H, CH$_2$(1)]; 4.22 [q, 2 H, CH$_2$(α)]. ^{13}C NMR, δ/ppm (125.7 MHz, CDCl$_3$): 13.05 [3 CH$_3$(e)];13.19 [CH$_3$(β)]; 21.10, 21.37 [3 CH$_2$(d+c)]; 27.51 [3 CH$_2^-$(b)]; 56.17 [CH$_2$(1)]; 59.81 [3 CH$_2$(a)]; 62.59 [CH$_2$(α)]; 119.32 [CH$_2$(1)]; 163.49 [CO(2)]. IR, ν/cm^{-1}: 2958, 2933, 2872 (ν_{C-H}), 2226, 2190, 2127 (ν_{Dca}), 1744($\nu_{C=O}$).

N,N,N-tri(n-pentyl)[2-ethoxy-2-oxoethyl]ammonium-bis(trifluoromethylsulfonyl)imide [Pn$_3$NC$_2$OC$_2$][Tf$_2$N]

This product was obtained by the same synthesis method of dicyanamide-based AGB-ILs described above using lithium bis(trifluoromethysulfonyl)imide (31.58 g, 0.11 mol) instead of sodium dicyanamide.

Yield: (94%). Elemental analysis: calculated for $C_{21}H_{42}N_2O_7S_2F_6$ (MW = 612.66 g.mol^{-1}): C 41.17%. H 6.91% N 4.57 and S 10.44%. Found: C 40.84, H 7.22, N 4.66%, and S 10.36%. %. ^{1}H NMR, δ/ppm (500 MHz, CDCl$_3$): 0.84 [t, 9 H, 3 CH$_3$(e)]; 1.24 [m, 15 H, 3 CH$_2$(d+c) + CH$_3$(β)]; 1.58 [m, 6 H, 3CH$_2$(b)]; 3.36 [m, 6 H, 3 CH$_2$(a)]; 3.98 [s, 2 H, CH$_2$(1)]; 4.21 [q, 2 H, CH$_2$(α)].
^{13}C NMR, δ/ppm (125.7 MHz, CDCl$_3$): 13.56 [CH$_3$(β)]; 13.62 [3 CH$_3$(e)]; 21.58, 21.88 (3CH$_2$(d+c)]; 28.00 [3 CH$_2$(b)]; 56.77 [3 CH$_2$(a)], 60.31 [CH$_2$(1)]; 63.07 [CH$_2$(α), 117.68–127.3 [2 CF$_3$], 164.07 [CO(1)]. IR, ν/cm^{-1}: 2962, 2936, 2876 (ν_{C-H}), 1747($\nu_{C=O}$), 1136 (ν_{S-O}).

2.3. Extraction Experiments

Metal aqueous solutions were prepared by dissolving their nitrate salt in deionized water. The extractant phase was prepared by dissolving 2.5 g of AGB-IL in 10 mL of the MBIK solvent, which will be called hereafter the organic phase. Metal ion distribution ratios were determined by mixing 2 mL of organic and aqueous phases. The mixture was shaken for 12 h to reach equilibrium and then centrifuged at 2000 rpm for 5 min. The separated organic and aqueous phases were both clear and transparent. The phases were then separated for analysis. 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 its concentration before and after extraction. The efficiency of the extraction process was evaluated by calculating the extraction percentage (% *E*) using the following equation:

$$E = 100 * \frac{\left(C_{in} - C_{fin}\right)}{C_{in}}$$

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 analysis was performed by UV-vis spectroscopy and by ICP-OES. The metal extraction percentages (% E) were determined at 298 K. The concentration of metal solutions is fixed at 5×10^{-2} 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.

For the liquid-liquid extraction experiments, the distribution coefficient (*D*) is calculated using the following formula:

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

V_w and V_{IL} correspond to the volumes of the 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 ± 10%. Experimental results done in duplicate agree within 5%.

In stripping experiments, the IL phase with metal extracted was contacted with 2 cm^3 of water or Na$_2$SO$_4$ solution (C = 1.5 mol L^{-1}) during 4 h of stirring. The percentage of metal back extracted has been determined from the analysis of the aqueous phase.

2.4. Determination of Organic Cation Concentration in the Aqueous Phase

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 was obtained after saturation of the aqueous phase with the ionic liquid, was added. The mixture is dissolved in 700 µL of deuterated water (D$_2$O). For measurements after metal extraction, we use a D$_2$O solution with 0.1 M 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 that is not overlapping with the different studied ionic liquid 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% [41].

2.5. Determination of Water Concentration in the Organic Phase after Extraction and Stripping

To analyze the concentration of water in the organic phase after stripping steps, 200 µL of organic phase was dissolved in 0.7 mL of CDCl$_3$. A ^{1}H NMR spectrum was performed in standard conditions. The concentration of water in the sample is determined by the integration of the water peaks. The integration includes the peaks of the water and the organic cations, which have a similar chemical shift and are difficult to separate under our conditions. The water content is deduced by subtracting the six protons of the organic cation from the overall integration.

3. Results and Discussion

3.1. Synthesis

The preparation of different AGB-ILs was carried out by two main steps: the first is the preparation of the cationic ester derivate of glycine-betaine bromide [Pn$_3$NC$_2$OC$_2$][Br], and the second is the anionic metathesis reaction of bromide by dicyanamide (Dca$^-$) or bis(trifluoromethylsulfonyl)imide (Tf$_2$N$^-$) to generate hydrophobic AGB-ILs. The synthetic pathway is given in Figure 2.
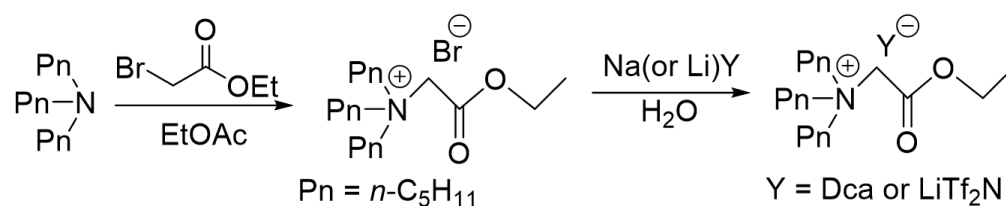
Figure 2. Synthetic route of hydrophobic analogues of glycine-betaine ionic liquids (AGB-ILs).
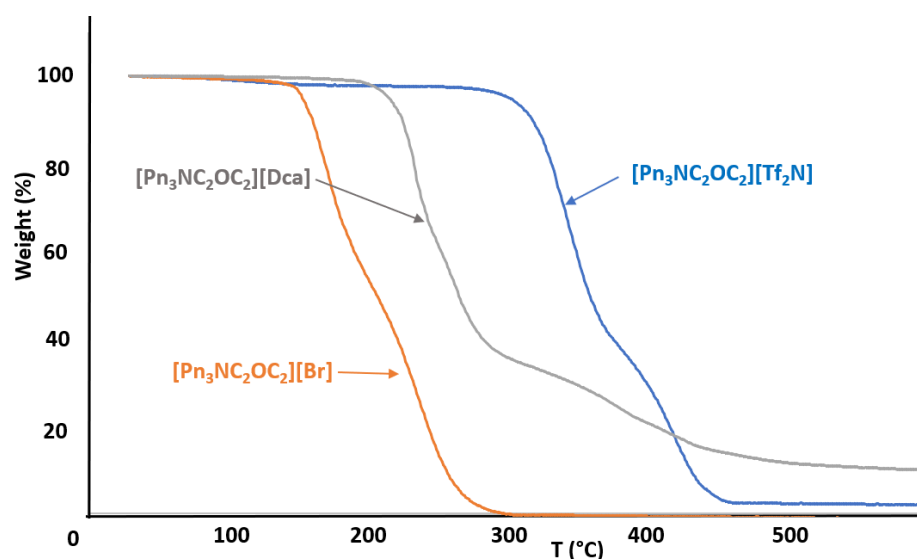
The cationic ester derivative of betaine [Pn$_3$NC$_2$OC$_2$][Br] was successfully synthesized by the reaction of the corresponding amine and ethyl bromoacetate. The kinetics of the reaction were followed by ^{1}H NMR spectroscopy (with DMSO-d$_6$ as solvent), showing the disappearance of the methylene group signals of the reactant. Indeed, the signal of the methylene groups (Br-**CH$_2$**CO$_2$**CH$_2$**CH$_3$) of the ethyl bromoacetate reactant appears at 4.12 ppm (singlet, Br-**CH$_2$**-) and 4.14 ppm (quadruplet, **CH$_2$**CH$_3$), respectively, while the same methylene groups in the product AGB-Br (Pn$_3$N**CH$_2$**CO$_2$**CH$_2$**CH$_3$) appear at 4.40 ppm (singlet, N**CH$_2$**CO$_2$$^-$) and 4.24 ppm (quadruplet, **CH$_2$**CH$_3$), respectively. In all cases, the association of the obtained bromide salt with Dca$^-$ or Tf$_2$N$^-$ anions by anionic metathesis generates hydrophobic AGB-ILs. The aqueous phase pre-equilibrated with ILs allows the control of the absence of Br$^-$ ions in ionic liquids with an AgNO$_3$ test. ^{1}H and ^{13}C NMR spectrometry analyses revealed the absence of organic impurities in the purified ionic liquids. These fluids are isolated in good yield (>90%). Only bromide-based AGB-ILs are solid. At room temperature, all AGB-ILs form two liquid phases when contacted with water. In a biphasic system, water is the top phase and the ionic liquid is the bottom phase.

3.2. Physical Properties

3.2.1. Thermal Properties

The thermal behavior of these hydrophobic AGB-ILs has been studied by differential scanning calorimetry (DSC). The melting point (T$_m$) was identified only for the solid salt [Pn$_3$NC$_2$OC$_2$][Br] (T$_m$ = 65.2 °C), but no corresponding glass transition temperature (Tg) has been detected for all three AGB-ILs. The thermal stability of the AGB-ILs was studied by thermal thermogravimetric analysis (TGA) over the temperature range of 30–500 °C (Figure 3). The thermal degradation temperature (T$_{dec}$) of all the salts lies in the range of 153–330 °C; [Pn$_3$NC$_2$OC$_2$][Br], T$_{dec}$ = 153 °C; [Pn$_3$NC$_2$OC$_2$][Dca], T$_{dec}$ = 221 °C; [Pn$_3$NC$_2$OC$_2$][Tf$_2$N], T$_{dec}$ = 330 °C. The relative anion stabilities can be suggested as [Br]$^-$ < [Dca]$^-$ < [Tf$_2$N]$^-$. Thermal analysis also shows that in the absence of fluorinated anion, the thermal stability of the ionic liquids is significantly reduced. With Tf$_2$N$^-$ anion, the ionic liquids display degradation at 330 °C, whereas, AGB-IL with Br$^-$ and Dca$^-$ anions decompose at 153 °C and 221 °C, respectively. Such a difference is explained by the weaker coordinating properties of Br$^-$ and Tf$_2$N$^-$ compared to those of Dca$^-$, indeed, it is generally observed that the weaker the coordinating anion, the higher the thermal stability of ionic liquids [49].

Figure 3. Thermal decomposition curves of AGB-ILs.

3.2.2. Solubility of Ionic Liquids in Water and Salt Media

Assuming congruent dissolution of the anion and cation of the ionic liquid in water or saline media, the solubility of the ionic liquid can be considered equivalent to the concentration of the organic cation in the aqueous phase (with or without added salt) in equilibrium with the organic phase. The concentration of the organic cation in the aqueous phase was determined by ^{1}H NMR following the methodology described in the experimental section.

The concentration of organic cations in aqueous media is higher when the aqueous phase is contacted with a pure ionic liquid phase than when dissolved in an organic solvent, meaning that the dissolution of ionic liquid in solvent will limit its loss during the extraction and stripping steps. The lowest release has been found with the MIBK solvent. As seen in Table 1, the use of an aqueous Na_2SO_4 solution instead of pure water limits the release of the cation of the ionic liquid due to the "salting-out" effect, thus limiting the loss of AGB-ILs during stripping steps.

Table 1. Concentration of organic cation $[Pn_3NC_2OC_2]^+$ in water and in aqueous saline media in $mmol \cdot L^{-1}$.

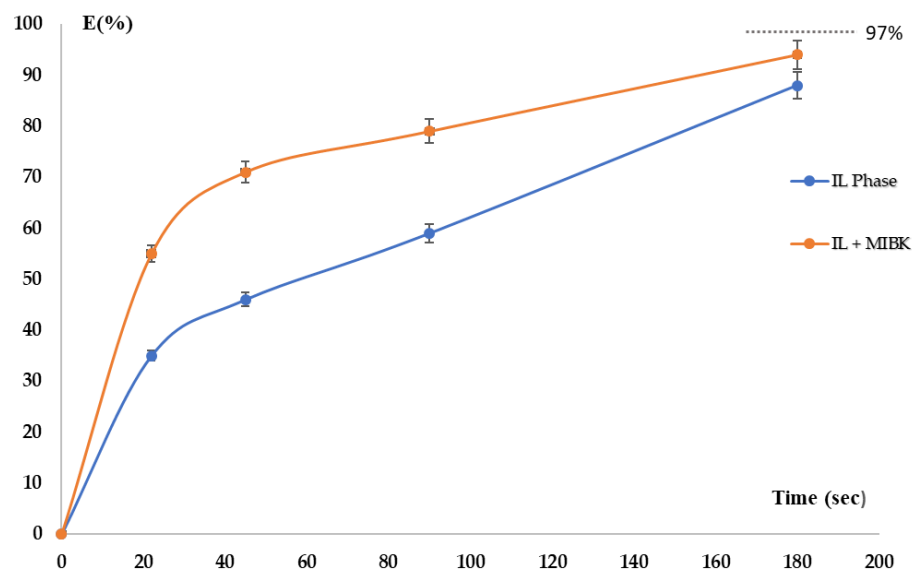| Media	Water	Na_2SO_4 (1.5M)	NaCl 2M	NaCl 4M
IL	19	6.9	5	n.m
Il/MIBK	20	2.8	6	n.m
Il/butyl acetate	13.5	2.4	5	n.m
IL/met-THF	14.75	2.75	5.9	n.m

n.m = not measurable.

3.3. Co(II) and Ni(II) Extraction and Stripping in Saline Media

3.3.1. Co(II) Extraction Kinetic

Our objective is to define systems that can operate in a continuous non-equilibrium environment. For this, it is necessary to ensure that the extraction kinetics will allow high extraction yields to be achieved with short transit times (a few tens of seconds) in the extraction phase. The extraction kinetics of Co(II) were followed over a time range of 0 to 3 min. Figure 4 shows the variation of the extraction yield as a function of time for a pure ionic liquid or an ionic liquid dissolved in MBIK. The experiments were carried out in NaCl 4M. In order to ensure a better comparison of the results and to estimate the impact of the solvent on the extraction kinetics, the amount of ionic liquid used is identical for both

experiments. The time mentioned corresponds to the time during which the two-phase system is maintained under stirring immediately after contact between the aqueous and organic phases.

Figure 4. Kinetics of the extraction of Co(II) by [Pn$_3$NC$_2$OC$_2$][Dca] with pure IL and IL dissolved in MIBK (dotted lines = extraction yield at equilibrium). Extraction with pure IL phase [blue lines, Co(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 2 mL; m$_{IL}$ = 0.5 g. Extraction with IL in MIBK [orange lines, Co(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{MIBK}$ = 0.25 g.mL^{-1}; V$_{org}$ = 1 mL. The dotted line indicates the extraction yield at equilibrium.

Figure 4 shows very high kinetics for the extraction of Co(II), with an extraction rate reaching 42% for the pure AGB-IL phase and 65% in the solvent phase after 20 s of stirring. It is interesting to note that with the solvent phase, the extraction yield is very close to the value found at equilibrium after 3 min. For a pure AGB-IL phase, the time to reach equilibrium is higher than 3 min, which means that the dissolution of the ionic liquid in a solvent reduces the viscosity of the extractant phase, which improves the contact between the metal and the extractant. This allows the shortest contact time to reach a high extraction yield, leading to a positive effect on the extraction rate. This shows the advantage of the development of continuous operation systems.
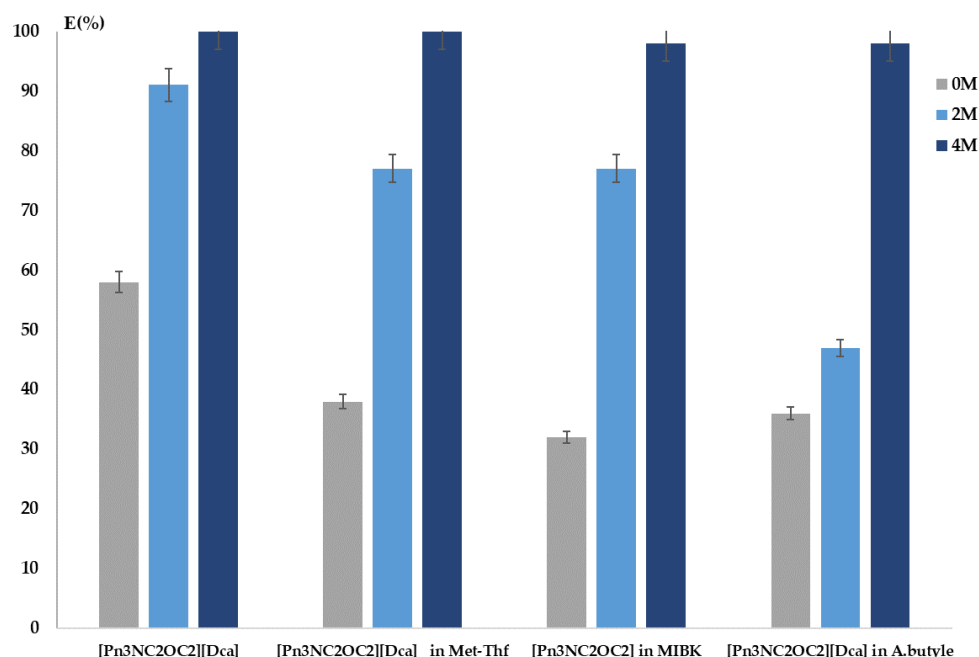
3.3.2. Co(II) Extraction in Saline Media

(a)   Influence of the solvent and salt concentration

Figure 5 depicts the comparison of the extraction yields of a pure AGB-IL phase with those obtained by AGB-IL dissolved in a solvent (Me-THF, MBIK, or BuOAc) for different NaCl concentrations.
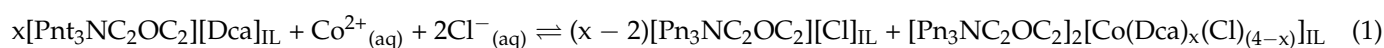
It is also known that the addition of an electrolyte with a chaotropic anion in the aqueous phase increases the extraction yields of metal [23]. Extraction in aqueous salt media is a credible path for the implementation of an extraction process limiting the release of ionic liquid species in aqueous solutions, thus showing a real environmental benefit. This is already experienced with hydrophilic ionic liquids for the selective separation of 3d metals [32] and with hydrophobic ionic liquids for the extraction of Co(II) and the separation of Co(II) and Ni(II) [38].

Figure 5. Extraction yields (%E) of Co(II) by [Pn$_3$NC$_2$OC$_2$][Dca] for different NaCl concentrations in the pure IL phase or dissolved in an organic solvent. Extraction with pure IL phase [Co(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 2 mL; m$_{IL}$ = 0.5 g. Extraction with IL diluted in organic solvent: [Co(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{org}$= 0.25 g mL^{-1}; V$_{org}$ = 1 mL.

The salt effects associated with the extraction mechanism can be described by the following equilibrium:

$$x[Pnt_3NC_2OC_2][Dca]_{IL} + Co^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \rightleftharpoons (x-2)[Pn_3NC_2OC_2][Cl]_{IL} + [Pn_3NC_2OC_2]_2[Co(Dca)_x(Cl)_{(4-x)}]_{IL} \quad (1)$$

$$Log\ D = \log K + 2 \log [Cl^-] + x \log ([Pn_3NC_2OC_2][Dca]_{IL}) - (x-2) \log [Pn_3NC_2OC_2]_2[Cl]_{IL} \quad (2)$$

This equilibrium clearly describes an extraction by ion-pair mechanism with two major contributions: (i) the formation of an anionic complex between the metal and the anion of the ionic liquid, and (ii) the formation of an ion-pair between the cation of the ionic liquid and the anion of the metal salt. It is to be noted that a chaotropic anion that forms a stable ion pair with the organic cation of the ionic liquid shifts the equilibrium to the right towards a higher extraction yield.

The dicyanamide anion forms moderately stable complexes with Co(II) ions in ionic liquids and in the absence of salt; more precisely, this anion is known as a weak complexing agent in water but a strong one in ionic liquid media [50]. Dicyanamide-based AGB-ILs are therefore prime candidates for reversible extraction systems based on the above-mentioned equilibrium. On the one hand, the extraction process will be exalted in the presence of a chaotropic electrolyte, and on the other hand, the equilibrium in the stripping process will be reversed by using an aqueous saline solution with a kosmotrope anion such as Na$_2$SO$_4$. In previous studies, we have shown that the most efficient system for metal extraction is to use NaCl as the chaotropic electrolyte for extraction [38]. Chloride, due to its position in the Hofmeister series, is more of an intermediate than a chaotropic anion, but its coordinating ability can help the dicyanamide anion form an anion complex and help improve the process of extraction.

The role of the AGB cation is essential in that it allows the formation of ion pairs both with the anionic complex and with the chaotropic anion of the electrolyte. It must therefore be sufficiently hydrophobic to form stable ion pairs with a more important affinity for the aqueous phase than for the organic phase to limit the effects of salting out.

The formation of an anionic complex has been evidenced by the UV-vis spectra of the extraction phase recorded after Co(II) extraction (Figure 6). The spectrum shows a single band and a shoulder in the visible region, with a maximum absorption located at 605 nm and a molar absorption coefficient ranging between 600 and 800 mol^{-1} L cm^{-1}. These spectral features are characteristic of a Co(II) in a tetrahedral environment and indicate a change of the coordination sphere of the metal from octahedral [Co(OH$_2$)$_6$$^{2+}$] to tetrahedral [Co(Dca)$_x$Cl$_{(4-x)}$] after extraction, which is in agreement with the coordination of anionic ligands (Cl$^-$ or/and Dca$^-$).
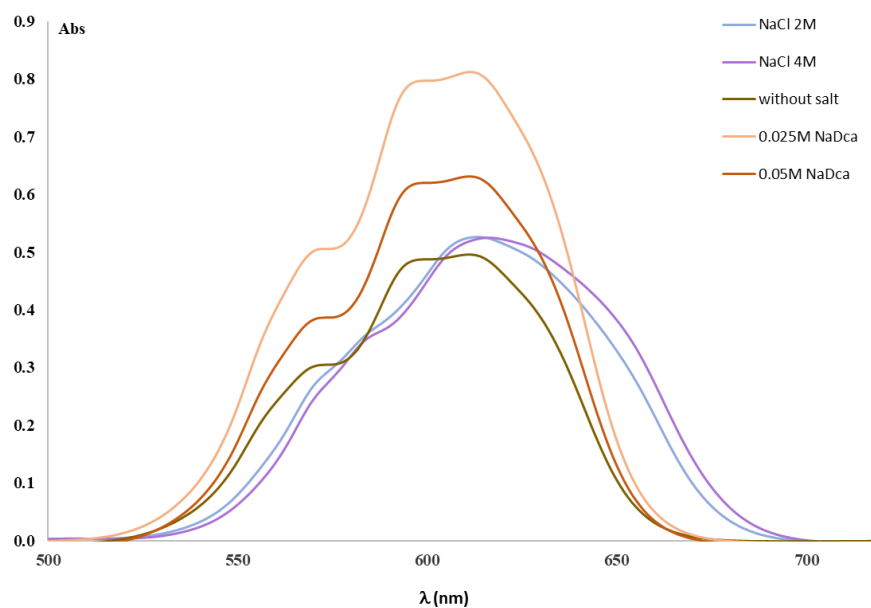
Figure 6. UV-vis spectra of the organic phase after extraction of Co(II) dissolved in an aqueous NaCl or NaDca solution.

Since the salt effect has been demonstrated with pure ionic liquid phases [38], it would be interesting to see if this effect can be applied to an ionic liquid diluted in an organic solvent.

As seen in Figure 5, the influence of NaCl is still relevant in the solvent medium. The effect of salt seems to be only slightly dependent on the nature of the solvent since the extraction rates have similar values regardless of the nature of the solvent and the concentration of the salt used. The average extraction rate is 35–40% obtained in the absence of electrolyte, whatever the solvent used. The extraction yield is slightly lower than that using an undiluted ionic liquid phase. The addition of NaCl increases the extraction rate, and at 4 mol L^{-1}, it is almost quantitative (above 98%). At this concentration of the salt, the extraction efficiency of the solvent medium towards Co(II) compares well with those with a pure ionic liquid phase. The gain in extraction rate obtained by the addition of salt constitutes the fraction of metal recoverable during the stripping phase. The three solvents (Me-THF, MBIK, or BuOAc) used show similar performance towards the extraction of Co(II), especially in NaCl 4M. From a practical point of view, we have chosen to continue the experiments with MIBK solvent, which presents an interesting price/availability ratio.

(b)   *Influence of the coordinating anion of the ionic liquid*

To check whether the effects of salts can be no longer applied, whatever the ionic liquid used as extractant, we determined the extraction of aqueous Co(II) ions in NaCl 4M medium with bromide and bis(trifluorosulfonyl)imide-based AGB-ILs. Both bromide and bis(trifluorosulfonyl)imide have weaker coordinating abilities compared to dicyanamide; the bis(trifluorosulfonyl)imide anion can even be considered a non-coordinating anion.

Figure 7 shows the strong influence of the coordinating ability of the anion of the ionic liquid on the Co(II) extraction. Although the extraction of Co(II) is quantitative with

[Pn$_3$NC$_2$OC$_2$][Dca], [Pn$_3$NC$_2$OC$_2$][Tf$_2$N] does not extract Co(II) even in aqueous NaCl 4M. The salt effect is moderate with [Pn$_3$NC$_2$OC$_2$][Br] with an extraction yield equal to 45%. In agreement with equilibrium 1, the use of saline media to improve the extractive capacities of ionic liquid phases is only beneficial to coordinating anion-based AGB-ILs. With bromide-based AGB-ILs, the weak coordinating ability of the bromide anion cannot counterbalance the alkaline salt effect, as is the case with dicyanamide-based AGB-ILs, which have demonstrated their efficiency to extract Cu(II) and Co(II) [38]. The contribution of a saline medium with bromide- and Tf$_2$N$^-$-based AGB-ILs is limited and nonexistent, respectively. The formation of stable complexes in ionic liquid medium is a driving force that allows overcoming the metal dehydration process, which acts as a brake on the transfer of metal from the aqueous phase to the ionic liquid phase. Further investigation of the effects of salts on the extraction of 3d metals with predictive data would require (i) the precise definition of the stoichiometry of the complexes, [Co(Dca)$_x$(Cl)$_{(4-x)}$]$_{IL}$ (ii) the determination of their formation constant in the IL phase in the absence of competition with water, (iii) as well as the association constant between the ammonium cation and the chloride ions. The determination of the stoichiometry of the extracted complex will be investigated in the next section. The determination of the formation constant is beyond the scope of this paper.
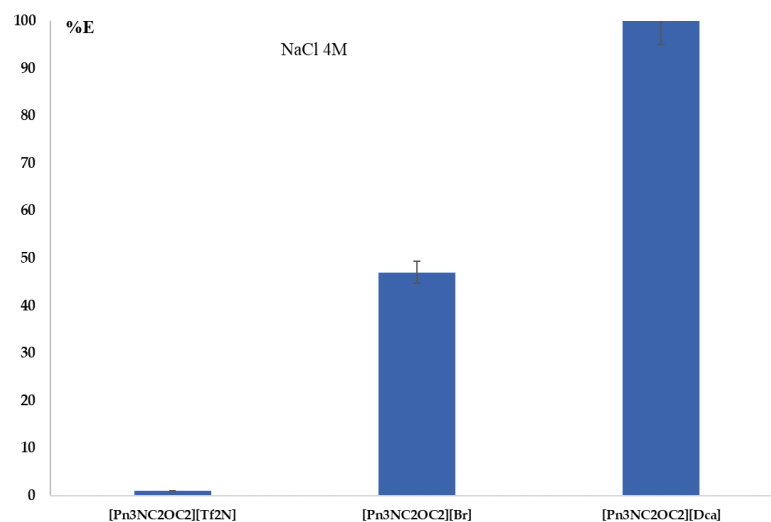

Figure 7. Extraction yields (%E) of Co(II) in NaCl 4M by [Pn$_3$NC$_2$OC$_2$][Dca], [Pn$_3$NC$_2$OC$_2$][Tf$_2$N], [Pn$_3$NC$_2$OC$_2$][Br]; [Co(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{org}$= 0.25 g.mL^{-1}; V$_{org}$ = 1 mL.

(c)   Extraction mechanism of Co(II) by [Pn$_3$NC$_2$OC$_2$][Dca]

The logD-logC representations will be used to define the equilibrium involved in the exteraction mechanism and also to determine the stoichiometry of the complex extracted in the organic phase. According to Equation (2), we will investigate the influence of the ionic liquid, the sodium chloride, and the dicynamide concentration on the stocheometry of the extracted complex.

The Figure 8 show a linear dependence of logD on log[Pn$_3$NC$_2$OC$_2$][Dca] with a correlation coefficient for these two lines greater than 0.99 and a slope close to 1.93 in NaCl 2M and 1.45 in water. This means that in NaCl 2M, the cobalt ions are mainly extracted in the organic phase as a mixed complex of stoichiometry [Co(Dca)$_2$(Cl)$_2$] corresponding to equilibrium:

$$2\ [Pn_3NC_2OC_2][Dca]_{IL} + Co^{2+}_{(aq)} + 2\ Cl^-_{(aq)} \rightleftharpoons [Pn_3NC_2OC_2]_2[Co(Dca)_2(Cl)_{(2)}]_{IL} \quad (3)$$
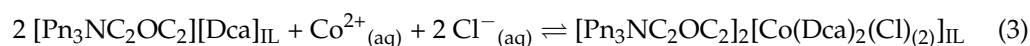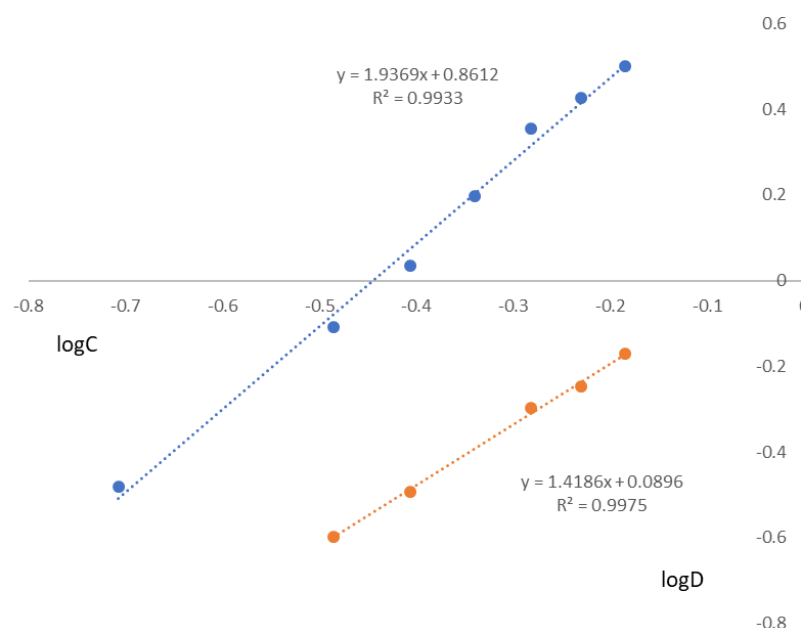
Figure 8. LogD = f(logC$_{IL}$) representation for the extraction of Co(II) by [(Pn$_3$NC$_2$OC$_2$][Dca] dissolved in MIBK; [Co(II)]$_{aq}$ = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{org}$= 0.25 g.mL^{-1}; V$_{org}$ = 1 mL.

In water, in addition to the formation of the [Pn$_3$NC$_2$OC$_2$][Dca]$_{IL}$ species, the ion-pair [Pn$_3$NC$_2$OC$_2$][Co(Dca)$_2$(Cl)$_2$]$_{IL}$ can also be formed to some extent. The log-log representation was also used to study the influence of the concentration of NaCl and NaDCa in aqueous solution on the stoichiometry of the complex extracted (Figure 9). However, there is no linear dependence of logD on log[NaCl (or Dca)]. The slope of the log-log representation increases regularly with the concentration of salt, meaning that the coordination sphere of the cobalt extracted changes with the concentration of NaCl (or NaDca), due to a progressive integration of both chloride and dicynamide anions in the coordination sphere of the complex with the increase of the aqueous concentration of both these alkaline salts. The slope of logD versus logC (C = concentration of NaCl or NaDca) was determined for each experiment by calculating the value of the derived curves. As shown in Figure 9, the value of the slopes increases with the salt concentration.
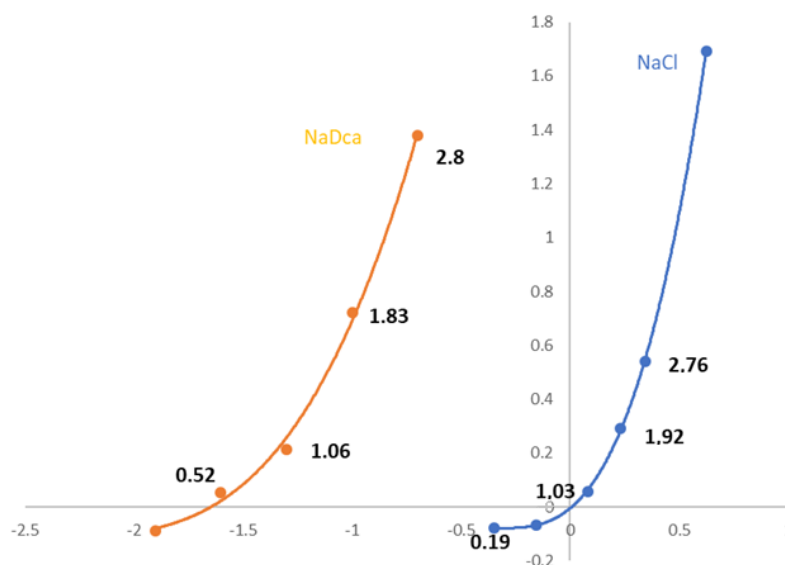

Figure 9. Curves logD versus logC$_{NaCl (and Dca)}$ for the extraction of Co(II) by [Pn$_3$NC$_2$OC$_2$][Dca] dissolved in MIBK. The bold numbers indicate the values of the slopes at the experimental point. [Co(II)]$_{aq}$ = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{org}$ = 0.25 g.mL^{-1}; V$_{org}$ = 1 mL.

The UV-vis spectrum of Co(II) extracted in the absence of salt evidenced the formation of an extracted anionic complex (see Figure 6). The extraction of Co(II) from an aqueous Co(II) in NaDca solution is enhanced, but this does not bring about a significant change in the spectral features of the organic phase, whereas in an aqueous NaCl solution, the spectrum is slightly modified compared to those observed in NaDCa. Nevertheless, we observe a shift towards lower energy for the main transition, which is centered at 612 nm and 618 nm in NaCl 2M and NaCl 4M, respectively. As before, the spectra exhibit a shoulder, but it is less marked than that observed in an aqueous NaDca solution or in the absence of salt. The change in spectral features as well as the slight red shift are characteristic of the coordination of chloride ions subsituting the dicyanamide ligand; chloride ions have a weaker crystal field effect than the dicyanamide anion.
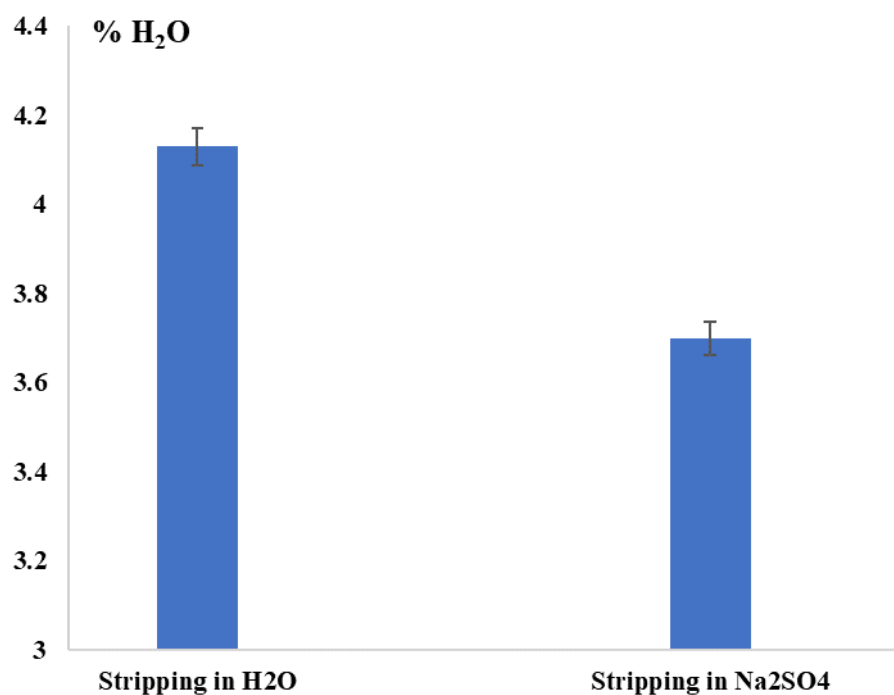
(d)   Co(II) stripping

After extraction, if the organic phase is contacted with water or with an electrolyte solution with a kosmotropic anion, such as Na_2SO_4, the weaker affinity of the kosmotropic anion, like sulphate for the organic ammonium cation of the AGB-IL, will shift the equilibrium to the left, restoring the situation before the extraction. The advantage of using a saline solution is that it limits the loss of ionic liquid by dissolution in the aqueous phase during the stripping steps. Indeed, ionic liquids are less soluble in a saline solution than in pure water. Stripping was performed in pure water and in an aqueous Na_2SO_4 solution. Figure 8 shows the fraction of Co(II) recovered from the organic phase after extraction steps. The comparison of the results obtained using water or an aqueous solution of Na_2SO_4 (1.5M) shows in all cases a higher efficiency of sodium sulphate solution, with a stripping yield 5–10% higher than those obtained with H_2O (Figure 10).
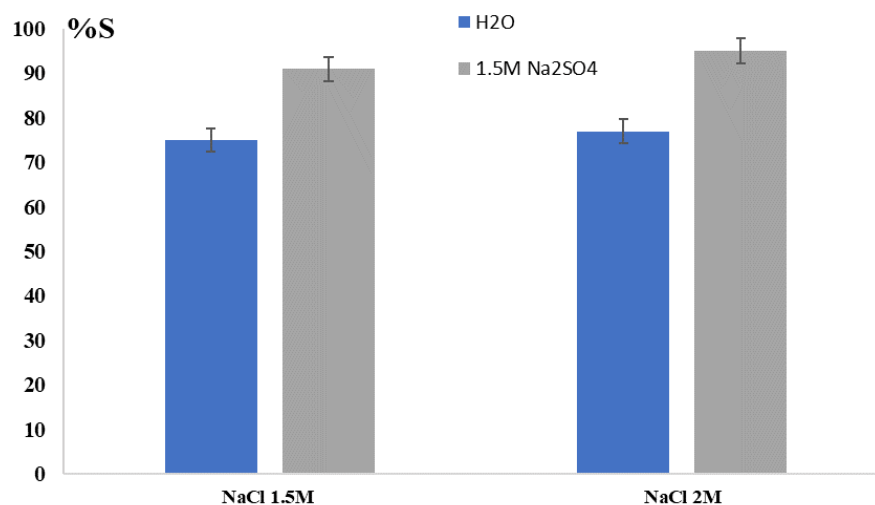
Figure 10. Stripping yields (%E) of Co(II) in H_2O and Na_2SO_4 1.5 M. Previous extractions were performed from Co(II) solutions in 1.5M or NaCl 2M by [Pn$_3$NC$_2$OC$_2$][Dca] in MIBK. Exp cond: [Co(II)] = 0.05 mol L^{-1}; V_{aq} = 1 mL; [IL]$_{org}$ = 0.25 g.mL^{-1}; V_{org} = 1 mL.

To understand the greater efficiency of an aqueous Na_2SO_4 solution in the stripping of Co(II), we have determined the concentration of water solubilized in the organic phase after the stripping step by ^1H NMR and Karl Fisher titrations. To allow a better comparison, the measurements were carried out on solutions with the same extraction conditions. In all cases, the concentration of water in the organic phase after stripping is higher when the stripping step is performed with H_2O than with a Na_2SO_4 solution. SO_4^{2-} is a kosmotropic anion, as indicated by its position in the Hofmeister series; consequently, it has a strong affinity for water molecules and can easily surround itself with water molecules in its first and second solvation spheres, which results in a decrease of the free solvent volume at high concentrations of Na_2SO_4. This phenomenon limits the transfer of water molecules from the aqueous phase to the organic phase. Indeed, for the extraction in 2M NaCl, the

content of H_2O dissolved in the organic phase and determined with Karl Fisher titrations is 4.1% and 3.7% with a stripping agent H_2O and an aqueous Na_2SO_4 1.5M solution, respectively. ^{1}H NMR results also confirm this tendency (Figure 11). Previous work [47,51] has shown the importance of the role of water solubilized in the organic phase for the extraction of metal cations. Water can form stable nanodomains in the ionic liquid phase. These hydrophilic nanodomains create a favorable solvation environment for metals, which induces their transfer from the aqueous phase to the ionic liquid phase [47,51]. At this stage of our investigations, it is relevant to state that the structuring of the organic phase in the presence of ionic liquids may show similarities to those of a pure ionic liquid phase. Therefore, the lower concentration of water in the organic phase when it is contacted with a Na_2SO_4 solution contributes to creating a solvation environment that is less favorable to the solvation of cobalt in the organic phase. This also favors the phenomenon of the transfer of this ion to the aqueous phase, which increases the percentage of stripping. Further research on the structuring of the organic phase in contact with the water or the electrolyte solution will be useful to have a better knowledge of the environment of the metal in the organic phase and to better understand the transfer phenomena between the aqueous and organic phases. However, such work is beyond the scope of this article.


Figure 11. Comparison between the percentage of water in the organic phase after the stripping in H_2O and aqueous Na_2SO_4 1.5 M.

3.3.3. Ni(II) Extraction in Saline Media

Figure 12 depicts the extraction of Ni(II) and Co(II) with [Pn$_3$NC$_2$OC$_2$][Dca] under the influence of increasing concentrations of sodium chloride. The extraction yield increases slightly with the concentration of salt and does not exceed 20% even in NaCl 4 M. It is well known that the affinity of the dicyanamide anion for Ni(II) is lower than that for Co(II) but with this system, the salt effect is less efficient with Ni(II) than with Co(II). This result can be used to perform efficient Ni/Co separation. Indeed, if we refer to the extraction rates obtained on monometallic solutions of Ni(II) and Co(II), the Co/Ni separation factor would be equal to 108 and 160 in NaCl 2M and 4M medium, respectively. In this case, [Pn$_3$NC$_2$OC$_2$][Dca] in MIBK as the organic phase and NaCl 4M as the aqueous phase could be an excellent medium to efficiently separate both metals. The efficiency of this system should be tested on a mixture of Co/Ni.
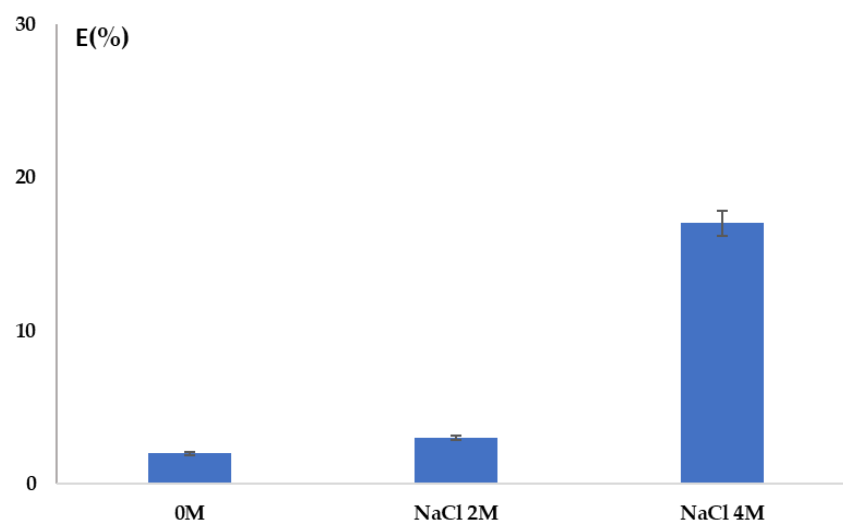
Figure 12. Extraction yields (%E) of Ni(II) by [Pn$_3$NC$_2$OC$_2$][Dca] diluted in MIBK for different NaCl concentrations: [Ni(II)] = 0.05 mol L^{-1}; V$_{aq}$ = 1 mL; [IL]$_{org}$ = 0.25 g.mL^{-1}; V$_{org}$ = 1 mL.

3.3.4. Co(II)/Ni(II) Extraction in Saline Media

The efficiency of [Pn$_3$NC$_2$OC$_2$][Dca] diluted in MIBK has been tested for extraction in an equimolar aqueous solution of Co/Ni and in aqueous NaCl 4M with a total metal concentration equal to 0.05 mol. L^{-1}. The extraction yields were 97 and 17% for Co(II) and Ni(II), respectively. These results are very close to those found in individual solutions and confirm the efficiency of this system to separate Co from Ni. Further work will concern the implementation of a continuous flow system based on these results that is reliable at the semi-pilot scale.

4. Conclusions

In this work, we reported the synthesis of three new hydrophobic analogues of glycine-betaine (AGB)-based ionic liquids (ILs) associated with bromide, bis(trifluoromethyl sulfonyl)imide, and dicyanamide anions. Their thermal properties, such as decomposition temperature and glass transition temperature, have been determined and discussed in terms of the component ion structure. We observed the dependence of the thermal stability of these AGB-ILs on the nature of the anion.

We have demonstrated that the addition of a supporting electrolyte improves the extraction capacities of coordinating anions-based AGB-ILs. The most effective systems for working with saline media are dicyanamide-based AGB-ILs, which present a moderate complexing power anion and allow the efficient separation of Cu(II) from Ni(II) and Co(II) in aqueous effluents. Extraction experiments were made with pure ILs phase as well as with ionic liquids diluted in organic solvent provided by the biorefinery. In diluted media under experimental conditions similar to those used in pure ionic liquid phases, the ionic liquids retain similar extractant and separation properties.

An in-depth study was carried out to explore the extraction mechanism of Co(II) by analyzing the slopes of log-log diagrams. This method does not allow the identification of a definite stoichiometry for the extracted complex, the latter being strongly dependent on the experimental conditions. It was nevertheless possible to identify the formation of a mixed Co(Dca)$_x$Cl$_{(4-x)}$ complex in the ionic liquid phase. Cobalt could be back-extracted from the ionic liquid phase with water or with an aqueous solution of Na$_2$SO$_4$, the latter limiting the release of ionic liquid cations in aqueous media. The rapid extraction equilibria demonstrated in a solvent medium make it possible to envisage an easy transposition of this methodology into continuous processes working out of equilibrium.

References

1. Di Lecce, D.; Marangon, V.; Jung, H.-G.; Tominaga, Y.; Greenbaum, S.; Hassoun, J. Glyme-based electrolytes: Suitable solutions for next-generation lithium batteries. *Green Chem.* **2022**, *24*, 1021–1048. [CrossRef]
2. Cheng, Q.; Marchetti, B.; Chen, X.; Xu, S.; Zhou, X.-D. Separation, purification, regeneration and utilization of graphite recovered from spent lithium-ion batteries—A review. *J. Environ. Chem. Eng.* **2022**, *10*, 10. [CrossRef]
3. Larsson, K.; Binnemans, K. Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling. *Green Chem.* **2014**, *16*, 4595–4603. [CrossRef]
4. European Commission. *Study on the Review of the List of Critical Raw Materials*; Publications Office of the European Union: Luxembourg, 2017.
5. Goodenough, J.B.; Park, K.-S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176. [CrossRef] [PubMed]
6. Ku, H.; Jung, Y.; Jo, M.; Park, S.; Kim, S.; Yang, D.; Rhee, K.; An, E.-M.; Sohn, J.; Kwon, K. Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching. *J. Hazard. Mater.* **2016**, *313*, 138–146. [CrossRef] [PubMed]
7. Mishra, G.; Jha, R.; Meshram, A.; Singh, K.K. A review on recycling of lithium-ion batteries to recover critical metals. *J. Environ. Chem. Eng.* **2022**, *10*, 108534. [CrossRef]
8. Kursunoglu, S.; Ichlas, Z.T.; Kaya, M. Solvent extraction process for the recovery of nickel and cobalt from Caldag laterite leach solution: The first bench scale study. *Hydrometallurgy* **2017**, *169*, 135–141. [CrossRef]
9. Cheng, C.Y. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. *Hydrometallurgy* **2000**, *56*, 369–386. [CrossRef]
10. Park, K.H.; Reddy, B.R.; Jung, S.H.; Mohapatra, D. Transfer of cobalt and nickel from sulphate solutions to spent electrolyte through solvent extraction and stripping. *Sep. Purif. Technol.* **2006**, *51*, 265–271. [CrossRef]
11. Sayar, N.A.; Filiz, M.; Sayar, A.A. Extraction of Co(II) and Ni(II) from concentrated HCl solutions using Alamine 336. *Hydrometallurgy* **2009**, *96*, 148–153. [CrossRef]
12. Liu, Y.; Lee, M. Separation of Co and Ni from a chloride leach solutions of laterite ore by solvent extraction with extractant mixtures. *J. Ind. Eng. Chem.* **2015**, *28*, 322–327. [CrossRef]
13. Huddleston, J.G.; Rogers, R.D. Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction. *Chem. Commun.* **1998**, *16*, 1765–1766. [CrossRef]
14. Zhao, H.; Xia, S.; Ma, P. Use of ionic liquids as 'green' solvents for extractions. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1089–1096. [CrossRef]
15. Visser, E.; Swatloski, R.P.; Reichert, W.M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J.H., Jr.; Rogers, R.D. Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. *Chem. Commun.* **2001**, 135–136. [CrossRef]
16. Zhang, L.; Hessel, V.; Peng, J. Liquid-liquid extraction for the separation of Co(II) from Ni(II) with Cyanex 272 using a pilot scale Re-entrance flow microreactor. *Chem. Eng. J.* **2018**, *332*, 131–139. [CrossRef]
17. Coll, M.T.; Fortuny, A.; Kedari, C.S.; Sastre, A.M. Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. *Hydrometallurgy* **2012**, *125–126*, 24–28. [CrossRef]
18. Cholico-Gonzalez, D.; Chagnes, A.; Cote, G.; Avila-Rodriguez, M. 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.* **2015**, *209*, 203–208. [CrossRef]
19. de Lemos, L.R.; Santos, I.J.B.; Rodrigues, G.D.; da Silva, L.H.M.; da Silva, M.C.H. Copper recovery from ore by liquid–liquid extraction using aqueous two-phase, system. *J. Hazard. Mat.* **2012**, *237–238*, 209–214. [CrossRef] [PubMed]
20. Papaiconomou, N.; Lee, J.M.; Salminen, J.; Von Stosch, M.; Prausnitz, J.M.; John, M. Selective extraction of copper, mercury, silver, and palladium ions from water using hydrophobic ionic liquids. *Ind. Eng. Chem. Res.* **2008**, *47*, 5080–5086. [CrossRef]
21. De los Rios, A.P.; Hernandez-Fernandez, F.J.; Lozano, L.J.; Sanchez, S.; Moreno, J.I.; Godinez, C. Removal of metal ions from aqueous solutions by extraction with ionic liquids. *J. Chem. Eng. Data* **2010**, *55*, 605–608. [CrossRef]

22.	Messadi, A.; Mohamadou, A.; Boudesocque, S.; Dupont, L.; Guillon, E. Task-specific ionic liquid with coordinating anion for heavy metal ion extraction: Cation ex-change versus ion-pair extraction. *Sep. Purif. Technol.* **2013**, *107*, 172–178. [CrossRef]
23.	Boudesocque, S.; Mohamadou, A.; Martinez, A.; Dechamps, I.; Dupont, L. Use of dicyanamide ionic liquids for metal ions extraction. *RSC Adv.* **2016**, *6*, 107894–107904. [CrossRef]
24.	Diabate, P.D.; Dupont, L.; Boudesocque, S.; Mohamadou, A. Novel task specific ionic liquids to remove heavy and noble metals from aqueous solutions. *Metals* **2018**, *8*, 412. [CrossRef]
25.	Wieszczycka, K.; Filipowiak, K.; Wojciechowska, I.; Aksamitowski, P. Novel ionic liquid-modified polymers for highly effective adsorption of heavy metals ions. *Sep. Purif. Technol.* **2020**, *236*, 116313. [CrossRef]
26.	Whitehead, J.A.; Lawrence, G.A.; Mc Clusquet, A. 'Green' leaching: Recyclable and selective leaching of gold-bearing ore in an ionic liquid. *Green Chem.* **2004**, *6*, 313–315. [CrossRef]
27.	Whitehead, J.A.; Zhang, J.; Pereira, N.; Mc Cluskey, A.; Lawrance, G.A. Application of 1-alkyl-3-methyl-imidazolium ionic liquids in the oxidative leaching of sulphidic copper, gold and silver ores. *Hydrometallurgy* **2007**, *88*, 109–120. [CrossRef]
28.	Lee, J.M. Extraction of noble metal ions from aqueous solution by ionic liquids. *Fluid Phase Equilib.* **2012**, *319*, 30–36. [CrossRef]
29.	Tong, Y.; Yang, H.; Li, J.; Yang, Y. Extraction of Au(III) by ionic liquid from hydrochloric acid medium. *Sep. Purif. Technol.* **2013**, *120*, 367–372. [CrossRef]
30.	Papaiconomou, N.; Génand-Pinaz, S.; Leveque, J.M.; Guittoneau, S. Selective extraction of gold and platinum in water using ionic liquids a simple two-step extraction process. *Dalton. Trans.* **2013**, *42*, 979–1982. [CrossRef]
31.	Papaiconomou, N.; Vite, G.; Leveque, J.M.; Billard, I. Efficient removal of gold complexes from water by precipitation or liquid–liquid extraction using ionic liquids. *Green Chem.* **2012**, *14*, 2050–2056. [CrossRef]
32.	Génand-Pinaz, S.; Papaiconomou, N.; Leveque, J.M. Removal of platinum from water by precipitation or liquid–liquid extraction and separation from gold using ionic liquids. *Green Chem.* **2013**, *15*, 2493–2501. [CrossRef]
33.	Boudesocque, S.; Mohamadou, A.; Dupont, L. Efficient extraction of gold from water by liquid–liquid extraction or precipitation using hydrophobic ionic liquids. *New J. Chem.* **2014**, *38*, 5573–5581. [CrossRef]
34.	Boudesocque, S.; Mohamadou, A.; Conreux, A.; Marin, B.; Dupont, L. The recovery and selective extraction of gold and platinum by novel ionic liquids. *Sep. Purif. Technol.* **2019**, *210*, 824–834. [CrossRef]
35.	Nguyen, V.T.; Lee, J.; Jeong, J.; Kim, B.; Cote, G.; Chagnes, A. Extraction of Gold(III) from Acidic Chloride Media Using Phosphonium-based Ionic Liquid as an Anion Exchanger. *Ind. Eng. Chem. Res.* **2015**, *54*, 1350–1358. [CrossRef]
36.	Jensen, M.P.; Dzielawa, J.A.; Rickert, P.; Dietz, M.L. EXAFS Investigations of the mechanism of facilitated ion transfer into a room temperature ionic liquid. *J. Am. Chem. Soc.* **2002**, *124*, 10664–10665. [CrossRef]
37.	Dietz, M.L.; Dzielawa, J.A. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for the 'greenness' of ionic liquids as diluents in liquid–liquid extraction. *Chem. Commun.* **2001**, *20*, 2124–2125. [CrossRef]
38.	Dietz, M.L.; Dzielawa, J.A.; Laszak, I.; Young, B.A.; Jensen, M.P. Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. *Green Chem.* **2003**, *6*, 682–685. [CrossRef]
39.	Dietz, M.L.; Stepinski, D.C. A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): Implications for the "greenness" of RTILs as extraction solvent. *Green Chem.* **2005**, *7*, 747–750. [CrossRef]
40.	Parmentier, D.; Hoogerstraete, T.V.; Metz, S.J.; Binnemans, K.; Kroon, M.C. Selective extraction of metals from chloride solutions with the tetraoctylphosphonium oleate ionic liquid. *Ind. Eng Chem. Res.* **2015**, *54*, 5149–5158. [CrossRef]
41.	Parmentier, D.; Hoogerstraete, T.V.; Banerjee, D.; Valia, Y.A.; Metz, S.J.; Binnemans, K.; Kroon, M.C. A mechanism for solvent extraction of first row transition metals from chloride media with the ionic liquid tetraoctylammonium oleate. *Dalton. Trans.* **2016**, *45*, 9661–9668. [CrossRef]
42.	Gras, M.; Papaiconomou, N.; Schaeffer, N.; Chainet, E.; Tedjar, F.; Coutinho, J.A.P.; Billard, I. Ionic-Liquid-Based Acidic Aqueous Biphasic Systems for Simultaneous Leaching and Extraction of Metallic Ions. *Angew. Chem. Int. Ed.* **2018**, *57*, 1563–1566. [CrossRef] [PubMed]
43.	Flieger, J.; Tatarczak-Michalewska, M.; Blicharskaa, E.; Madejskaa, A.; Fliegerc, W.; Adamczukc, A. Extraction of cobalt (II) using ionic liquid-based bi-phase and three-phase systems without adding any chelating agents with new recycling procedure. *Sep. Purif. Technol.* **2019**, *209*, 984–989. [CrossRef]
44.	Schaeffer, N.; Gras, M.; Passos, H.; Mojilireddy, V.; Mendoça, C.M.N.; Pereira, E.; Chainet, E.; Tedjar, F.; Coutinho, J.A.P.; Billard, I.; et al. Synergistic Aqueous Biphasic Systems: A New Paradigm for the "One-Pot" Hydrometallurgical Recovery of Critical Metals. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1769–1777. [CrossRef]
45.	Depuydt, D.; Van den Bossche, A.; Dehaen, W.; Binnemans, K. Metal extraction with a short-chain imidazolium nitrate ionic liquid. *Chem. Commun.* **2017**, *38*, 5271–5274. [CrossRef]
46.	Foltova, S.S.; Hoogerstraete, T.V.; Banerjee, D.; Binnemans, K. Samarium/cobalt separation by solvent extraction with undiluted quaternary ammonium ionic liquids. *Sep. Purif. Technol.* **2019**, *210*, 209–218. [CrossRef]
47.	Janssen, C.H.C.; Macias-Ruvalcaba, N.A.; Aguilar-Martinez, M.; Kobrak, M.N. Copper extraction using protic ionic liquids: Evidence of the Hofmeister effect. *Sep. Purif. Technol.* **2016**, *168*, 275–283. [CrossRef]
48.	Diabate, P.D.; Boudesocque, S.; Mohamadou, A.; Dupont, L. Efficient separation of Cobalt, Nickel and Copper using analogues of glycine-betaine based ionic liquids. *Sep. Purif. Technol.* **2020**, *244*, 116782. [CrossRef]

49. Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178. [CrossRef]

50. Gras, M.; Papaiconomou, N.; Chainet, E.; Billard, I. Dicyanamide ions as complexing agents of Co(II): From weak ligands in water to strong ones in an ionic liquid. *Solv. Extr. Ion Exch.* **2018**, *36*, 583–601. [CrossRef]

51. Kobrak, M.; Yager, K. X-ray scattering and physicochemical studies of trialkylamine/carboxylic acid mixtures: Nanoscale structure in pseudoprotic ionic liquids and related solutions. *Phys. Chem. Chem. Phys.* **2018**, *20*, 18639–18646. [CrossRef]