SEPARATIONS: MATERIALS, DEVICES AND PROCESSES

Ethylammonium nitrate enhances the extraction of transition metal nitrates by tri-*n*-butyl phosphate (TBP)

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Abstract

Several molecular polar solvents have been used as solvents of the more polar phase in the solvent extraction (SX) of metals. However, the use of hydrophilic ionic liquids (ILs) as solvents has seldomly been explored for this application. Here, the hydrophilic IL ethylammonium nitrate (EAN), has been utilized as a polar solvent in SX of transition metal nitrates by tri-*n*-butyl phosphate (TBP). It was found that the extraction from EAN is considerably stronger than that from a range of molecular polar solvents. The main species of Co(II) and Fe(III) in EAN are likely $[Co(NO_3)_4]^{2-}$ and $[Fe(NO_3)_4]^-$, respectively. The extracted species are likely $Fe(TBP)_3(NO_3)_3$ and a mixture of $Co(TBP)_2(NO_3)_2$ and $Co(TBP)_3(NO_3)_2$. The addition of H_2O or LiCl to EAN reduces the extraction because the metal cations coordinate to water molecules and chloride ions stronger than to nitrate ions. This study highlights the potential of using hydrophilic ILs to enhance SX of metals.

KEYWORDS
ethylammonium nitrate, ionic liquids, solvent extraction, transition metals, tri-*n*-butyl phosphate

1 | INTRODUCTION

Solvent extraction (SX) has been widely used in the hydrometallurgical industry for the separation and purification of metals.[1,2] An SX system generally has two immiscible phases, a more polar (MP) phase containing the metals to be separated and a less polar (LP) phase that contains an extractant diluted in an organic diluent.[1,3] Water has been the default solvent for the MP phase, and this is the reason why SX is considered to be a branch of hydrometallurgy. However, only very few studies explored the utilization of polar organic solvents as the solvent in the MP phase for SX of metals. These early studies did not observe superior metal separations compared to traditional SX.[4-8] The use of polar solvents instead of water in the extraction of metals is called *non-aqueous solvent extraction* (NASX).[9] Recently, a series of non-aqueous SX systems have been investigated and several enhanced separations have been obtained.[10-15] The substitution of water by polar organic solvents

changes the solvation of metal cations in the polar solvent, and the relative solubility of the complexes between the two immiscible phases also affects the extraction equilibrium.[15] The extraction of metals from polar organic solvents can be significantly altered by changing polar solvents.

Despite that NASX expands the scope of solvents in the MP phase of SX systems from water to many polar organic solvents, these solvents are all molecular, that is, compounds held together only by covalent bonds. Molten salts are a category of compounds that are composed entirely of ions, and are therefore fundamentally different from molecular solvents. Because of such a distinct difference, the extraction of metals from molten salts can be different from the extraction from molecular solvents. Isaac et al studied the extraction of several metal nitrates (lanthanides, actinides, and transition metals) from the eutectic mixture of $LiNO_3$-KNO_3 (melting point: 120°C) to tri-*n*-butyl phosphate (TBP). It was found that the distribution ratios of metals are 2 to 3 orders of magnitudes higher than those for extraction from aqueous solutions.[16] Similarly, efficient extraction of lanthanide nitrates from the hydrated melt $Ca(NO_3)_2 \cdot 4H_2O$ was

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observed.[17] Besides these molten nitrates, ionic liquids (ILs) are also molten salts, albeit with much lower melting points than traditional molten salts. Although there exist many studies on the use of ILs as extractants in the LP phase of SX systems,[18-21] the number of studies on the use of ILs as solvent of the MP phase is very limited. The extraction of Co(II), Ni(II) and lanthanide chlorides from 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl, melting point: 80°C) by trihexyl(tetradecyl)phosphonium bis (2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) was investigated, but no special extraction performance was observed.[22,23] In addition to ILs, deep-eutectic solvents (DES), which are similar to ILs, have also been used as solvents of the MP phase of SX systems for the extraction of metals.[24,25] These studies mainly described the performance of metal extraction from molten salts, but did not investigate the role of the molten salts in SX of metals, beyond being a solvent for dissolving inorganic salts.

Ethylammonium nitrate (EAN) is an IL with a low melting point (12°C), making it a suitable ionic solvent for the MP phase of SX of metals, without the need for heating. Very recently, extraction of lanthanides from EAN was found to exhibit an opposite sequence across the lanthanide series compared to that from aqueous solutions by a quaternary alkylammonium nitrate extractant, showing the special role of EAN in SX of metals.[26] In this study, we explore the extraction of transition metal nitrates from EAN by TBP and show that the extraction of metals can be significantly enhanced using EAN instead of molecular solvents. Furthermore, the extraction mechanism is discussed based on experimental characterizations.

2 | MATERIALS AND METHODS

2.1 | Chemicals

Ethylamine (70 wt% in water), ethanol (analytical reagent) and dimethyl sulfoxide (analytical reagent) were purchased from Fisher Scientific (Merelbeke, Belgium); nitric acid (65%), tri-n-butyl phosphate (>99%), formamide (99%), Co(NO$_3$)$_2$·6H$_2$O (99%) and gallium standard solution (1,000 ± 10 mg·L^{-1}) were supplied by Chem-lab (Zedelgem, Belgium); n-decane (99%), ethylene glycol (99.5%) and Ni(NO$_3$)$_2$·6H$_2$O (99%) were obtained from Acros Organics (Geel, Belgium); LiNO$_3$ (99%), Mn(NO$_3$)$_2$·4H$_2$O (>97%), Zn(NO$_3$)$_2$·6H$_2$O (99%), Triton™ X-100 (for molecular biology), CDCl$_3$ (99.8%) and acetonitrile-d$_3$ (99.9%) were obtained from Sigma-Aldrich (Diegem, Belgium); Fe(NO$_3$)$_3$·9H$_2$O (99%) was provided by VWR Chemicals (Leuven, Belgium); Cu(NO$_3$)$_2$·6H$_2$O (99.5%) was purchased from BDH Chemicals (Poole, UK). Milli-Q water (18.2 MΩ·cm at 25°C) was used to prepare the aqueous solutions. Ethylammonium nitrate was prepared from ethylamine and nitric acid by a simple acid-base reaction[27] and dried on a Schlenk line to a final water content of <0.5 wt%. Drying of protic ionic liquids with nitrate ions, such as EAN, has to be done very carefully.[28]

2.2 | Solvent extraction

Each extraction experiment was carried out in a 4 mL glass vial with 2.0 mL of the MP phase and 2.0 mL of the LP phase containing 50 vol % TBP in n-decane. Mixtures of the two phases were shaken for 30 min at 300 rpm on a Thermo Scientific 2000 shaker to attain extraction equilibrium. Afterward, the samples were centrifuged for 3 min at 4000 rpm in a Heraeus Megafuge 1.0 centrifuge to accelerate phase separation. Metal concentrations in both phases at equilibrium were measured by total reflection X-ray fluorescence (TXRF). The mutual solubility experiments of EAN and the TBP phase was performed in the same way as extraction experiments. Compositions of the two phases after equilibrium were determined by ^{1}H NMR spectra. All experiments were conducted at room temperature (21 ± 1°C).

The *percentage extraction %E* and the *distribution ratio D* are defined as:

$$\%E = \frac{c_{lp} \cdot V_{lp}}{c_{lp} \cdot V_{lp} + c_{mp} \cdot V_{mp}} \times 100\% \qquad (1)$$

$$D = \frac{c_{lp}}{c_{mp}} \qquad (2)$$

where c_{lp} and c_{mp}, V_{lp} and V_{mp} are concentrations and volumes of the LP phase and the MP phase at extraction equilibrium, respectively.

The *separation factor* α is defined based on the *distribution ratio D*:

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

where M1 and M2 are two metals to be separated and $D_{M1} \geq D_{M2}$.

2.3 | Instrumentation and analytical methods

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz for ^{1}H and 162 MHz for ^{31}P, using acetonitrile-d$_3$ or CDCl$_3$ as the solvent. The metal concentrations in the LP phase and the MP phase were determined by a total reflection X-ray fluorescence (TXRF) spectrometer (Bruker S2 Picofox) after the samples were diluted in mixtures of ethanol and aqueous Triton™ X-100 solution to an appropriate concentration range. A standard gallium solution was added to the samples during dilution as an internal standard. The UV–VIS absorption spectra were recorded by a Varian Cary 5000 spectrophotometer with a matched pair of quartz cuvettes of 10.0 mm path length. The water content was measured by a coulometric Karl Fischer titrator (Mettler-Toledo C30S).

3 | RESULTS AND DISCUSSIONS

3.1 | Extraction of Co(II) from various polar solvents

We first investigated the extraction of Co(II) from LiNO$_3$-saturated water, ethylene glycol (EG), formamide (FM), dimethyl sulfoxide (DMSO), and ethylammonium nitrate (EAN, without LiNO$_3$), by 50 vol

% TBP dissolved in *n*-decane. LiNO$_3$ was added to the polar solvents to enhance the extraction of Co(II), because the extraction was too low without extra added nitrate ions. For example, the extraction of Co(II) from water (without LiNO$_3$) was only 0.02% by 50 vol% TBP in *n*-decane. The LP phase (TBP in *n*-decane) formed clear two-phase systems with all of these LiNO$_3$-saturated polar solvents. The MP phase of all the extraction systems was pink, indicating that Co(II)-complexes with similar geometries were formed in these polar solvents. However, the intensity of the color differed clearly with the same Co(II) concentration, following this order: EAN > DMSO > FM > EG > water. The color of the LP phase at equilibrium agreed well with the extraction efficiency, following the order EAN ≫ water > EG > FM > DMSO (Figure 1). Remarkably, the extraction of Co(II) from EAN was considerably greater than that from any other polar solvent. It is known that transition metals are not in favor of coordinating to nitrates.[29] The presence of polar solvent molecules (e.g., water, formamide, etc.) would compete for the coordination with Co(II), thus reducing the extraction. The efficient extraction of Co(II) from EAN is due to the lack of competing ligands for coordination with Co(II). Nitrate-based ILs provide an environment in which only nitrate ions exist as ligands for the metal ions; in any other polar solvent, the solvent molecules (either neutral molecules or anions) would coordinate to the Co(II) cation to some extent. Most nitrate-based hydrophilic ILs are solids at room temperature. Heating these nitrate-based ILs could cause explosions due to the oxidizing property of nitrates.[28] EAN is a liquid at room temperature, making it a suitable solvent for enhancing the extraction of transition metals by TBP and similar solvating extractants.

## 3.2 | Co(II) and Fe(III) in EAN

Co(II) and Fe(III) were chosen as representatives of transition metals with oxidation states of +2 and +3, respectively, for the study of the extraction mechanism. First, the speciation of Co(II) and Fe(III) in EAN should be discussed. The UV–Vis absorption spectra of Co(II) in water, EAN, and their mixtures are presented in Figure 2. The Co(II) species in water is known to be [Co(H$_2$O$_6$)]$^{2+}$.[30-32] In EAN, the spectrum of Co(II) has a similar shape as that of [Co(H$_2$O$_6$)]$^{2+}$, but it is red-shifted for 31 nm and the intensity is much higher. The peak wavelength of 543 nm is comparable to that of Co(II) in [HO(CH$_2$)$_2$mim][NO$_3$] (1-[2-hydroxyethyl]-3-methylimidazolium nitrate)[33] and [As(C$_6$H$_5$)$_4$]$_2$[Co(NO$_3$)$_4$][34] in nitromethane that were found at 544 nm and 540 nm, respectively. The molar extinction coefficient (ε) of [As(C$_6$H$_5$)$_4$]$_2$[Co(NO$_3$)$_4$] in nitromethane and Co(II) in [HO(CH$_2$)$_2$mim][NO$_3$] was about 107 L·mol^{-1}·cm^{-1} and 102 L·mol^{-1}·cm^{-1}, respectively, both of which are close to the value in this study, which is 103 L·mol^{-1}·cm^{-1}. The species in these cited studies are both [Co(NO$_3$)$_4$]$^{2-}$, so is the species in EAN. Unfortunately, these studies did not determine the exact geometry of [Co(NO$_3$)$_4$]$^{2-}$. Some other studies have reported tetranitratocobaltate(II) salts with various cations, and the crystal structures of these salts exhibited coordination numbers of 6,[35] 7,[36-38] and 8.[36,37,39,40] The difference in the coordination number of [Co(NO$_3$)$_4$]$^{2-}$ is affected by the size and shape of the cations.[35]

Several studies described salts with the [Fe(NO$_3$)$_4$]$^-$ anion.[41-43] The crystal structures of [Fe(NO$_3$)$_4$]$^-$ reported by Fedorova et al[42] and Logan et al[43] both suggest eight-fold coordination of Fe(III) with four symmetric bidentate nitrates, exhibiting a dodecahedral structure with D_{2d} symmetry. Therefore, the species of Co(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ in EAN are proposed to be [NH$_3$C$_2$H$_5$]$_2$[Co(NO$_3$)$_4$] and [NH$_3$C$_2$H$_5$][Fe(NO$_3$)$_4$], respectively. The exact geometry of [Co(NO$_3$)$_4$]$^{2-}$ is not conclusive since coordination numbers of 6, 7, and 8 have been reported. [Fe(NO$_3$)$_4$]$^-$ is likely a dodecahedral structure with Fe(III) eight-fold coordinated.
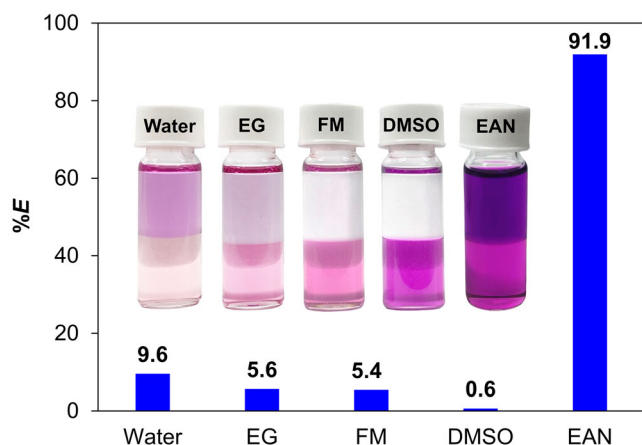
FIGURE 1 Extraction of Co(NO$_3$)$_2$ from various polar solvents by TBP. The LP phase was 50 vol% TBP in *n*-decane, the MP phase was 0.05 mol·L^{-1} Co(NO$_3$)$_2$ in LiNO$_3$-saturated polar solvents and EAN (without LiNO$_3$) [Color figure can be viewed at wileyonlinelibrary.com]
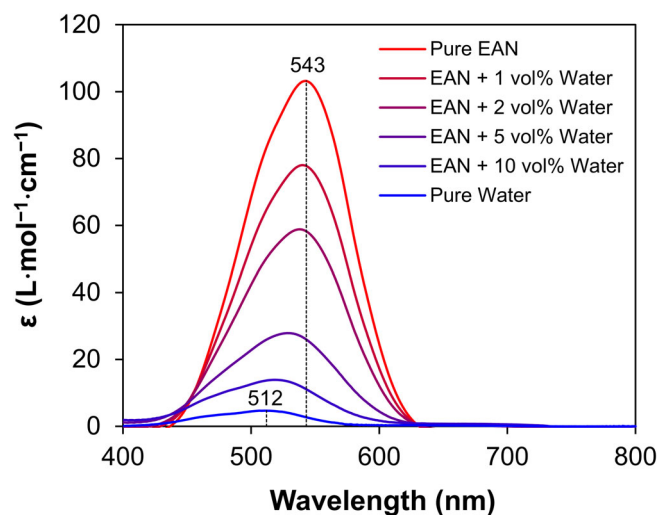
FIGURE 2 UV–vis absorption spectra of 0.01 mol·L^{-1} Co(NO$_3$)$_2$ in water, EAN, and their mixtures [Color figure can be viewed at wileyonlinelibrary.com]
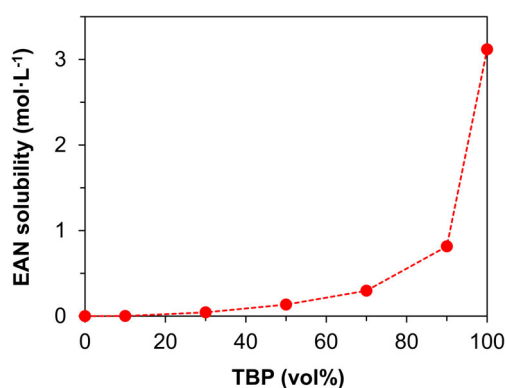
3.3 | Mutual solubility of EAN and TBP

The mutual solubility of EAN and the TBP phase as a function of TBP vol% after drying the solvents (water content ~0.5 wt%) was determined (Figure 3). When pure TBP was mixed with pure EAN, about 3.1 mol·L^{-1} EAN was dissolved in TBP at equilibrium, and 0.32 mol·L^{-1} TBP was found in EAN. With the addition of 10 vol% and 50 vol% n-decane, the solubility of EAN in the TBP phase decreased rapidly to 0.82 mol·L^{-1} and 0.13 mol·L^{-1}, respectively, and further decreased to negligible concentrations with increasing n-decane.

The solvent extraction experiments were conducted using 50 vol% TBP with an overall water content of about 1.0 wt% (unless otherwise specified). Under this condition, the solubility of EAN in the TBP phase was about 0.23 mol·L^{-1}, and 0.12 mol·L^{-1} TBP was found in EAN. The volume change of the two phases before and after equilibrium due to the mutual solubility was <2%, and hence was negligible. The solubility of EAN in the TBP phase was found sensitive to the water content because EAN is freely miscible with water and TBP is hygroscopic. The reduction of water content reduces the EAN solubility in the TBP phase.

3.4 | Role of EAN and TBP in the loaded phase

EAN is slightly soluble in the LP phase (Figure 3). Whether EAN is involved in the extraction of metals and the role of TBP in the extraction was investigated. The ^{1}H or ^{31}P NMR spectra of the LP phase with Co(II)-complex cannot be recorded because of the paramagnetism of the Co(II)-complex. As a substitute of the Co(II)-complex, the Zn(II)-complex was used for recording NMR spectra, assuming that the extraction of Zn(II) proceeds via the same mechanism as Co(II), since [Zn(NO$_3$)$_4$]$^{2-}$ can be formed similarly as [Co(NO$_3$)$_4$]$^{2-}$.[44,45]

The ^{31}P NMR spectra and their shifts as a function of Zn(II) loading in the LP phase are shown in Figure 4. With the increase of Zn(II) concentration in the LP phase, the resonances in the ^{31}P NMR spectra shifted downfield, indicating the involvement of TBP in

the coordination with Zn(II). Interestingly, the shift is more or less proportional to the amount of Zn(II) loaded in the LP phase. The concentration of EAN in the LP phase decreased with increasing Zn(II) loading (Figure 4B). The decrease indicates that EAN is not involved in the extraction of Zn(II), otherwise, it should increase with increasing Zn(II) loading. The decrease of EAN might be due to two reasons: (1) more loading of Zn(II) occupies TBP molecules, making the LP phase less capable to dissolve EAN; (2) more Zn(II) loading was achieved by using higher Zn(II) concentration in the feed solution, which reduces the activity of EAN, leading to the lower solubility of EAN in the LP phase. In summary, TBP is directly involved in coordination with Zn(II), but EAN is not.

3.5 | Co(II) and Fe(III) complexes in TBP

Slope analysis was performed to determine the stoichiometric ratio of TBP and Co(II) in the extracted species. A slope of 2.63 was obtained (Figure 5). This slope is higher than that obtained by the extraction of Co(II) by TBP from molten LiNO$_3$-KNO$_3$ mixtures, which was 2.1.[16] This slope of 2.63 indicates that either two or three TBP molecules are involved in the extraction of one Co(II) cation, that is, the possible structures are Co(TBP)$_3$(NO$_3$)$_2$ and Co(TBP)$_2$(NO$_3$)$_2$. For comparison,
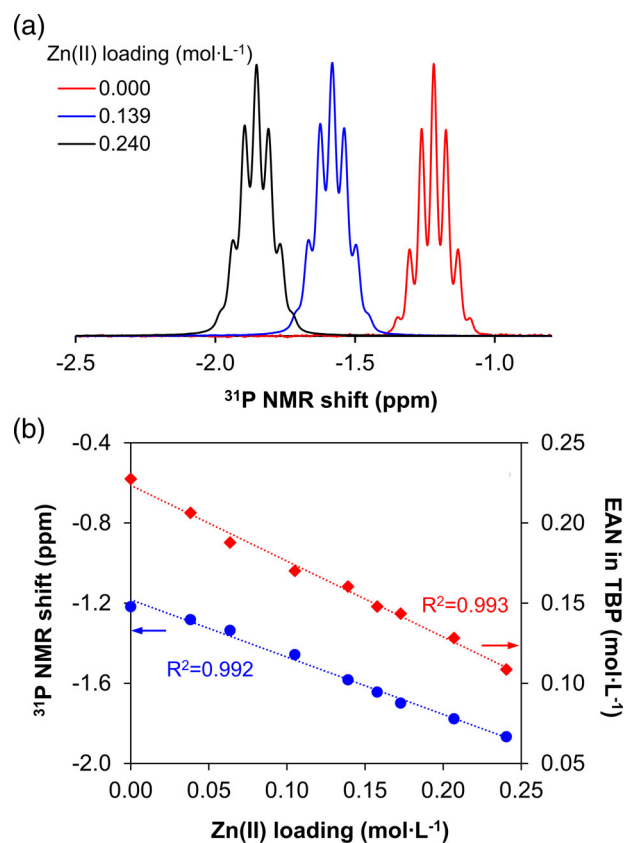
FIGURE 3 The solubility of EAN in the TBP phase as a function of TBP vol% in n-decane [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 A, ^{31}P NMR spectra of the TBP phase loaded with varying Zn(II) concentrations; B, ^{31}P NMR shift of the TBP phase and the concentration of EAN in the TBP phase as a function of Zn(II) loading [Color figure can be viewed at wileyonlinelibrary.com]
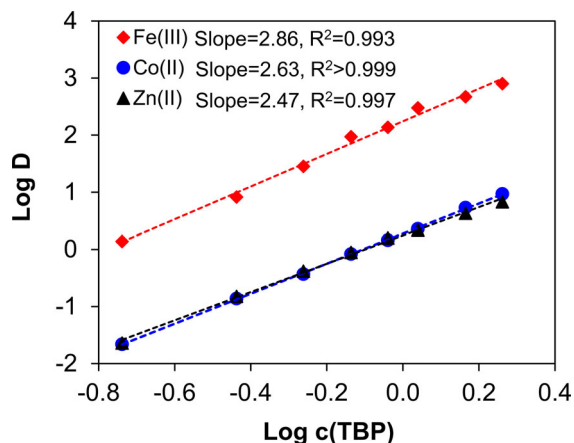
FIGURE 5 Slope analysis of Fe(III), Co(II), and Zn(II) extraction by TBP. MP phase was 0.05 mol·L^{-1} Fe(NO$_3$)$_3$, Co(NO$_3$)$_2$, or Zn(NO$_3$)$_2$ in EAN, LP phase was various concentrations of TBP in n-decane [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 6 UV–vis absorption spectrum of 0.01 mol·L^{-1} Co(II) in the TBP phase and the EAN solution [Color figure can be viewed at wileyonlinelibrary.com]

slope analysis was also performed for Zn(II) extraction, and a slope of 2.47 was obtained, which is similar to the slope of Co(II) extraction. The similar slopes of Co(II) and Zn(II) extraction indicate that the two metal ions are extracted via similar mechanisms, and justify the rationality of using the Zn(II)-complex to substitute Co(II)-complex for NMR study.

The LP phase loaded with 0.01 mol·L^{-1} Co(II) was recorded for the absorption spectrum (Figure 6). Both the shape and the characteristic band of the spectrum is very similar to the spectrum of [Co(NO$_3$)$_4$]$^-$ (Co(II) in EAN), except that the molar absorptivity is lower. The different molar absorptivities of species in the EAN and the LP phase might be due to two differences of the structures: (1) [Co(NO$_3$)$_4$]$^-$ has a possible coordination number of 6, 7, or 8 due to the very special environment, whereas both Co(TBP)$_3$(NO$_3$)$_2$ and Co(TBP)$_2$(NO$_3$)$_2$ are likely to have the usual coordination number of 6 (assumed to be octahedral); (2) the average bond length of Co(TBP)$_3$(NO$_3$)$_2$ and Co(TBP)$_2$(NO$_3$)$_2$ might be shorter than that of [Co(NO$_3$)$_4$]$^-$ considering the strong extraction of Co(II) to the TBP phase.

Slope analysis was also applied to the extraction of Fe(III) from EAN by TBP, which yielded a slope of 2.93, meaning that three TBP molecules are involved in the extraction of one Fe(III) cation. Taking into account that three nitrates are needed to keep charge neutrality, the extracted species is possibly Fe(TBP)$_3$(NO$_3$)$_3$.

3.6 | Effect of water on the extraction

Co(II) can be efficiently extracted from EAN solution by TBP, but could hardly be extracted from water (Figure 1). The effect of water on the extraction of transition metals is worth investigating. Extraction of some first-row transition metal nitrates (Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II)) by TBP was investigated for the effect of water content (Figure 7A). These metals were chosen because they often occur together in ores (e.g., laterite[46,47]) and secondary resources (e.g., waste batteries[48,49]). All the metals studied were extracted
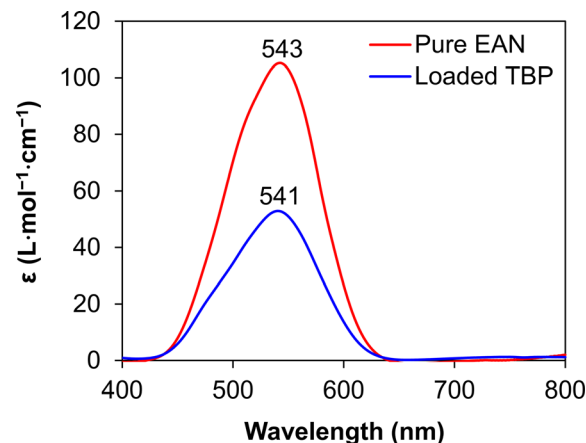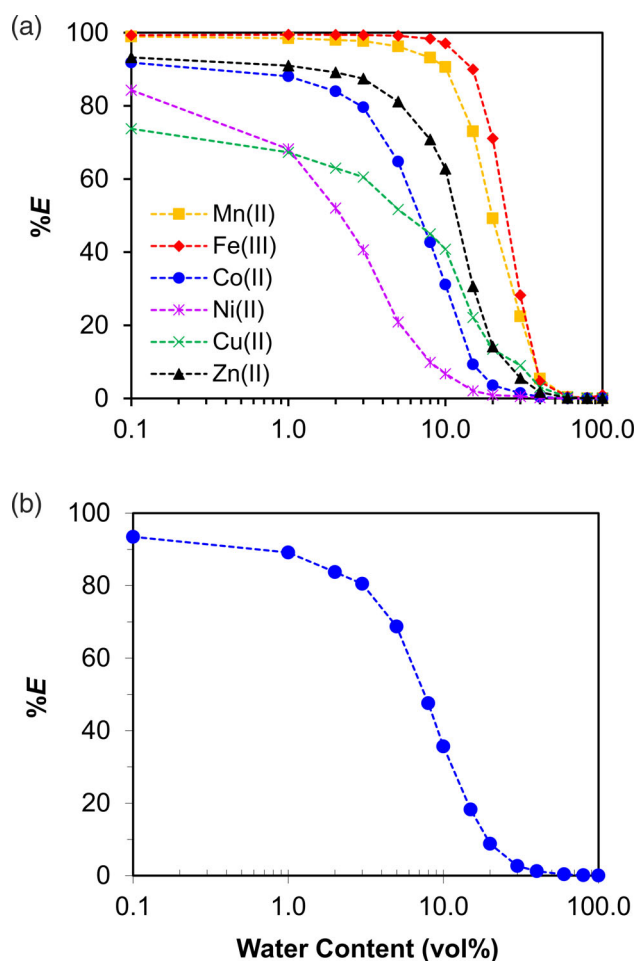
efficiently from the EAN solution with Fe(III) and Mn(II) extracted completely. The different extraction efficiencies of the metals were due to the different coordination strength of the metal cations to TBP in the LP phase. With the addition of water, extraction of all the metals decreased, however, Fe(III) was the least affected by water, followed by Mn(II), while Ni(II) was the most sensitive to water. The extraction of the metals was reduced because of the hydration of metal cations in the EAN solution. With addition of 5 vol% water, 99% Fe(III), 96% Mn(II), 81% Zn(II), 65% Co(II), 52% Cu(II), and 21% Ni(II) were extracted. The separation factors of each metal pair under this condition are given in Table 1. Fe(III) can be efficiently separated from Ni(II) and Cu(II) with separation factors >100. The separation factors of Fe(III)/Co(II) and Mn(II)/Ni(II) are also impressive. When the water content was above 60%, the extraction of all the metals was below 0.5%.

To have a deeper understanding of how water content affects the extraction of transition metals, the extraction of Co(II) alone was conducted (Figure 7B). The extraction of Co(II) decreased with the increasing water content, as has been shown in Figure 7A. The decrease of Co(II) extraction can be compared with Figure 2 where the absorption spectra of Co(II) in the mixture of EAN and water are shown. In pure EAN, the species is [Co(NO$_3$)$_4$]$^{2-}$, as discussed in Section 3.2. In water, the species is known to be [Co(H$_2$O)$_6$]$^+$.[30-32] As the water content increased, the spectra gradually shifted and the intensity decreased. This indicates that the water molecules gradually replace nitrate ions and the species gradually converts from [Co(NO$_3$)$_4$]$^{2-}$ to [Co(H$_2$O)$_6$]$^+$. Transition metals generally coordinate to water molecules stronger than to nitrate ions,[29] hence extracting Co(II) as nitrates is difficult in the presence of water. The low extraction of Co(II) from other molecular polar solvents as shown in Figure 1 can be explained by the same principle. The exceptionally high extraction of Co(II) from EAN is because EAN provides an environment where no other ligands exist except for nitrate ions, hence nitrate ions can coordinate to Co(II) to enable the extraction.
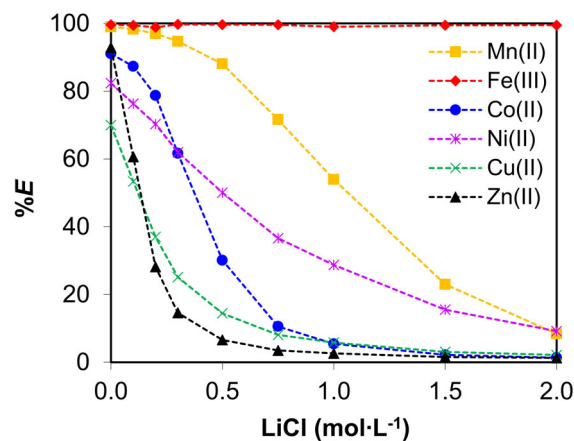
3.7 | Effect of LiCl on the extraction

Transition metals coordinate to chloride ions stronger than to nitrate ions.[29] The effect of Cl^- on the extraction of transition metals from EAN was also investigated (Figure 8). With the addition of LiCl to EAN, the extraction of transition metals decreased rapidly, except for Fe(III), which maintained a high extraction percentage (>99%) over the whole LiCl concentration range. On the contrary, extraction of Zn(II) was the most sensitive to the LiCl concentration, and decreased from 93% without LiCl, to only 6.6% and 2.6% with 0.5 mol·L^{-1} and 1.0 mol·L^{-1} LiCl, respectively. The extraction of the metals was reduced because of the coordination of metal cations to the chloride ions in the EAN solution. The separation factors of each metal pair under the condition of 0.5 mol·L^{-1} LiCl in EAN are given in Table 2.

FIGURE 7 Extraction from transition metal nitrate mixtures, A, and Co(NO$_3$)$_2$, B, by TBP with varying water content. LP phase was 50 vol% TBP in *n*-decane. EAN phase was 0.01 mol·L^{-1} of each metal nitrate for (a) and 0.05 mol·L^{-1} Co(NO$_3$)$_2$ in EAN for, B, with varying water content. 0.1 vol% water is indicative of the dry EAN solution without added water [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Extraction of transition metal nitrates by TBP from EAN with LiCl. The MP phase was 0.01 mol·L^{-1} of each nitrate in EAN with varying LiCl concentrations; the LP phase was 50 vol% TBP in *n*-decane [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Separation factors of six transition metals with 5 vol% water in EAN

		M1					
	$\alpha_{M1/M2}$	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
M2	Mn(II)	1.0	4.8	—	—	—	—
	Fe(III)	—	1.0	—	—	—	—
	Co(II)	14.0	67.1	1.0	—	—	2.3
	Ni(II)	97.6	466.4	7.0	1.0	4.0	16.3
	Cu(II)	24.1	115.2	1.7	—	1.0	4.0
	Zn(II)	6.0	28.6	—	—	—	1.0

TABLE 2 Separation factors of six transition metals with 0.5 mol·L^{-1} LiCl in EAN

		M1					
	$\alpha_{M1/M2}$	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
M2	Mn(II)	1.0	38.5	—	—	—	—
	Fe(III)	—	1.0	—	—	—	—
	Co(II)	17.1	659.0	1.0	2.3	—	—
	Ni(II)	7.4	283.2	—	1.0	—	—
	Cu(II)	43.6	1680.7	2.6	5.9	1.0	—
	Zn(II)	104.2	4012.2	6.1	14.2	2.4	1.0

Fe(III) can be highly efficiently separated from Cu(II) and Zn(II) with separation factors > 1000. The separations of Fe(III)/Co(II), Fe(III)/Ni(II), and Mn(II)/Zn(II) are also efficient with separation factors > 100. In principle, one can take advantage of the drastically different sensitivities of these metals to the LiCl concentration to separate them. However, this system would result in a mixture of nitrates and chlorides, making the recycling of the system difficult.

To further investigate the effect of LiCl on the extraction of transition metals, extraction of Co(II) was compared with the absorption spectrum of Co(II) solutions (Figure 9). The extraction of Co(II) decreased rapidly with the addition of LiCl, which is similar to the results of Figure 8. Without added LiCl, the species in EAN was $[Co(NO_3)_4]^{2-}$. With the addition of 1.5 mol·L^{-1} or 2.0 mol·L^{-1} LiCl, the spectra intensity was much higher and the spectra showed characteristic peaks of the tetrahedral complex $[CoCl_4]^{2-}$. The addition of LiCl to EAN gradually converted $[Co(NO_3)_4]^{2-}$ to $[CoCl_4]^{2-}$, which is more stable. The inability of Co(II) to coordinate to nitrate ions in the presence of chloride ions prevents the extraction of Co(II) by TBP.
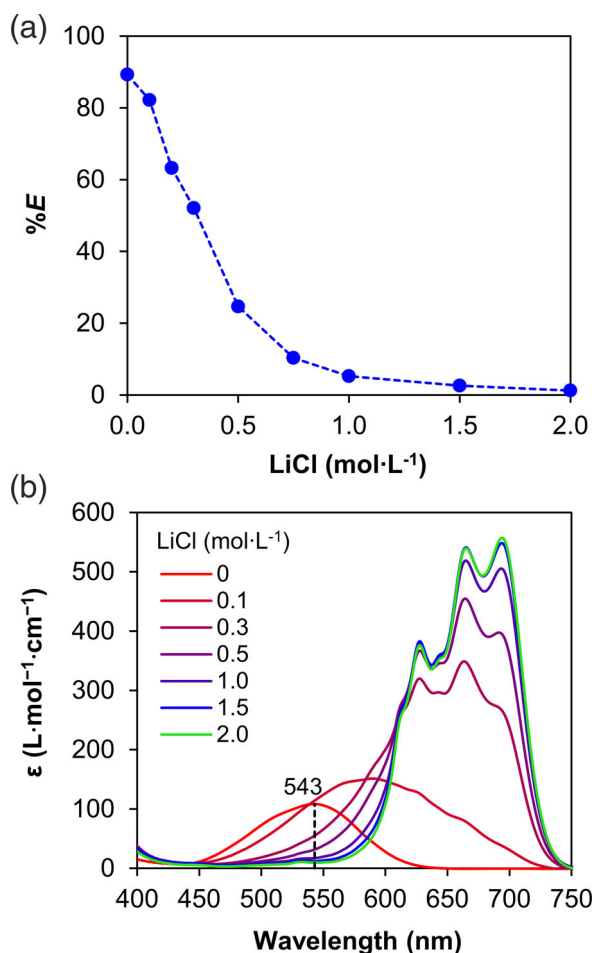
FIGURE 9 A, Effect of LiCl on the extraction of Co(NO$_3$)$_2$. The LP phase was 50 vol% TBP in *n*-decane; the MP phase was 0.05 mol·L^{-1} Co(NO$_3$)$_2$ in EAN with various concentrations of LiCl. B, Absorption spectra of 0.002 mol·L^{-1} Co(NO$_3$)$_2$ in EAN with varying concentrations of LiCl [Color figure can be viewed at wileyonlinelibrary.com]

4 | CONCLUSIONS

The extraction of transition metal nitrates from ethylammonium nitrate (EAN), a hydrophilic ionic liquid, by TBP was found to be considerably more efficient than the extraction from a variety of molecular polar solvents. Co(II) and Fe(III) are in the form of $[Co(NO_3)_4]^{2-}$ and $[Fe(NO_3)_4]^{-}$, respectively, in the EAN solution. Fe(III) is extracted as Fe(TBP)$_3$(NO$_3$)$_3$, and Co(II) is likely extracted as a mixture of Co(TBP)$_2$(NO$_3$)$_2$ and Co(TBP)$_3$(NO$_3$)$_2$. The extraction of transition metal nitrates by TBP is sensitive to both water and chloride ions, because these metal cations coordinate to water molecules and chloride ions stronger than to nitrate ions. EAN provides an environment that is free of other ligands besides nitrate ions, therefore enables efficient extraction of transition metal nitrates by TBP. The use of pure hydrophilic ionic liquids as polar solvents for solvent extraction applications enables extraction performances that could not be achieved using other types of solvents.

AUTHOR CONTRIBUTIONS

Zheng Li: Conceptualization; funding acquisition; investigation; writing-original draft; writing-review and editing. **Zidan Zhang:** Investigation; writing-review and editing. **Bieke Onghena:** Investigation; writing-review and editing. **Xiaohua Li:** Investigation; writing-review and editing. **Koen Binnemans:** Conceptualization; funding acquisition; supervision; writing-review and editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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