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Separation of lithium, cobalt and nickel from spent lithium-ion batteries using TBP and imidazolium-based ionic liquids

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Abstract

Solvent extraction of lithium ions from sulfuric acid solutions was investigated using imidazolium-based ionic liquids as diluents and tri-*n*-butyl phosphate as specific ligand. Aqueous phases used were simulating leach liquors of spent lithium-ion batteries, with lithium, cobalt and nickel ions in acidic solutions. A low acidity and a large amount of extractant can ensure high extraction efficiency. But the better selectivity for the lithium ions over the transition metals is obtained using a low amount of extractant and a low pH (pH<3). The extraction of the lithium ions occurs by cation exchange with the ionic liquid cations. A sacrificial cation was introduced in the organic phase to prevent the losses, but the cation exchange is only reduced by 20 %. The increase of the ionic liquid cation alkyl chain length can presumably suppress the cation exchange mechanism, reducing substantially the losses. But the addition of a lipophilic counter-anion in the organic phase is needed to ensure a mechanism of ion pairing with the lithium ion in the organic phase. Using the 1-decyl 3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid associated to tri-butyl phosphate, a satisfying extraction efficiency is obtained for the lithium ion, together with a sufficient selectivity among the transition metal ions.

Keywords: Ionic liquids; tri-butyl phosphate; solvent extraction; lithium recycling;

1. Introduction

Lithium-ion batteries (LIBs) are commonly used for portable electronic devices (laptops, mobile phones, cameras, etc.). This kind of batteries is also expected to play a key role for the

storage of energy, especially renewable one [1]. These evolutions have outlined the importance of metals for the manufacture of the batteries, and the supply risk associated with most of these metals [2]. Lithium, cobalt and nickel are the main constituents of lithium-ion battery cathodes in the so called “nickel-cobalt-aluminum” (NCA, cathode made of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) batteries [3]. As a result, concern is rising about the future availability of these metals. For instance, cobalt is already considered as a critical material by the European Commission, while lithium is a near critical element [4].

Moreover, lithium-ion batteries are expected to implement future electric vehicles [5-6]. Consequently, an increase in lithium extraction from primary resources is needed [7]. However, knowing the low concentrations found in ores and brines and the environmental implications of mining, the recycling of LIBs could become relevant [8]. Moreover, several valuable metals can be also recovered. A number of authors have reviewed the different ways and options which can be consider to recycle one or several metals from these batteries [9-10].

The recycling of metals from spent lithium-ion batteries could be made using pyrometallurgy [11], but this technique implies the use of very high temperatures and lithium is lost in slag. Hydrometallurgy offers the possibility to recycle several elements at low temperature. After a mechanical pretreatment, batteries are dissolved in acidic media [12]. Several mineral and organic acids have been studied for the leaching of lithium-ion batteries. The use of sulfuric acid is privileged due to its lower corrosivity and in order to avoid the production of noxious gases [13]. After the leaching step, a complex mixture containing the metal ions in aqueous acidic solution is obtained. This solution contains mainly lithium, cobalt and nickel ions at various concentrations [14]. These metals have to be separated and recovered. Solvent extraction (also called liquid-liquid distribution) is a widely used technique for the recovery of metals from aqueous solutions. A solvent phase containing an organic ligand (extractant) and a diluent is contacted with the aqueous phase. Depending on the affinity of the extractant for the target metal, a good efficiency and selectivity could be obtained, even with low concentrations of metals in the aqueous phase and advantageously with a low concentration of extractant in the organic phase. The recovery of lithium from the cathodes of spent lithium-ion batteries using solvent extraction has been the object of a few studies [15-16]. Most of the investigations have focused on the extraction of cobalt, the most critical element in lithium-

ion batteries [17-18]. The extraction of lithium remains challenging, and the common option used is to leave lithium in solution while extracting the other metals [19]. Solvent extraction allows to extract directly a metal from an aqueous solution, thus avoiding to use several steps to isolate each metal independently. However, the current solvent extraction systems are not selective for the lithium-ion and the divalent metals will be extracted prior to the lithium-ion [20-21]. Alternatives to solvent extraction have been designed to extract directly lithium among the multivalent metals based on the use of Donnan dialysis for instance [22]. But solvent extraction is a simple and widely used technique that can be applied with current existing equipment.

However, conventional solvent extraction processes generally employ organic diluents, such as toluene, kerosene or dodecane, *etc.*. The flammability and toxicity of these volatile organic compounds is problematic, particularly when using them in a large scale. Recently, ionic liquids (ILs) have emerged as a possible alternative to these solvents [23].

First observed in 1914 [24], these solvents are low temperature molten salts constituted of a cation and an anion. Part of them is liquid at ambient temperature and called room temperature ionic liquids (RTILs). The use of RTILs instead of molecular diluents could be advantageous due to their physicochemical properties such as a negligible vapor pressure, leading to a low volatility and the non-flammability of most of the ILs [25]. However, the toxicity of some of the RTILs remains an issue [26]. Moreover, several properties of ILs could be tuned by selecting among the various cations and anions available. In solvent extraction, the change in the cations and anions of the ILs and their structure leads to several differences in the behavior of the metals. For example, the extraction efficiency and mechanism of extraction are highly dependent of the IL used in the organic phase [24-25].

This work is focusing on the selective extraction of lithium ions from sulfuric acid media. A well-known solvent extraction system based on imidazolium-based ILs associated to tri-n-butyl phosphate (TBP) has been already applied to lithium extraction [26-27]. However, previous studies have not assessed the possibility to treat leach liquors of lithium-ion batteries. Furthermore, to the best of our knowledge the direct recovery of lithium ions from spent lithium-ion batteries using solvent extraction has never been assessed.

While using imidazolium-based ionic liquids, a cation exchange mechanism between the metal ion in the aqueous phase and the IL cation is observed during the extraction of the metal. This exchange leads to loss of IL in the aqueous phase, which is unfavorable from both an economic and environmental point of view, knowing the high cost and low biodegradability of the imidazolium cation. This is why our work explores different ways to reduce, if not suppress, the cation exchange mechanism during the extraction of the lithium ions, and to limit the loss of ionic liquid.

2. Materials and methods

2.1. Reagents

The hydrophobic ionic liquids, namely 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide (abbreviated as [C₄mim][NTf₂], 99.5% purity, water content below 100 ppm) and 1-decyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([C₁₀mim][NTf₂], 99.5%, water content below 20 ppm) were purchased from Solvionic (France), and used without further purification. The water content of the ionic liquid was checked after extraction using a Mettler Toledo Karl Fischer titrator (V20S model). The organophosphorous extractant, tri-*n*-butyl phosphate (TBP, >99% purity) was purchased from Acros Organics and used as received. The sodium salt of tetrakis(trifluoromethyl)phenylboron (NaTFPB, 97.5% purity) was supplied from Alfa Aesar and used without further purification. The chemical structures of the ionic liquids and the organic reagents used in this work are shown in Fig. 1. The sulfate salts of lithium (Li₂SO₄·H₂O, Fluka), cobalt (CoSO₄·7H₂O, Merk) and nickel (NiSO₄·6H₂O, Merk) were used as received.

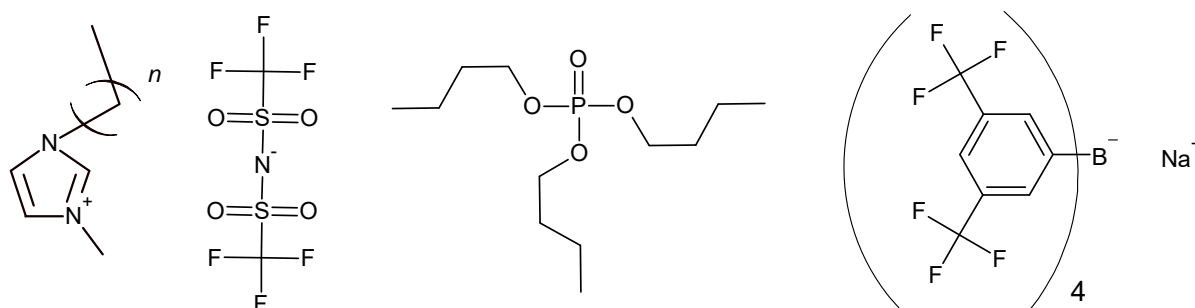


Fig. 1. From left to right, chemical structures of the [C_nmim⁺] cation, the [NTf₂⁻] anion, TBP extractant and NaTFPB salt.

2.2. Solvent extraction

The aqueous phases were prepared by dissolving gravimetrically the metal salts into de-ionized water. De-ionized water was obtained after percolation through activated carbon and ion-exchange resins (type ORC and type R3 resin from Thermo-Fischer Scientific). The aqueous concentrations of metal ions were fixed at 50 mg.L⁻¹ (0.4 mmol.L⁻¹ of lithium, 0.3 mmol.L⁻¹ of nickel and 0.2 mmol.L⁻¹ of cobalt) for all extraction experiments, to ensure a sufficient extraction efficiency. The pH of the aqueous solutions was adjusted by adding small aliquots of sulfuric acid (Fischer Scientific, 95% purity). The pH was measured using a WTW pH 196 pH meter. The organic phases were prepared by mixing the compounds (TBP, NaTFPB and ionic liquid) at the desired proportion. The organic solutions were then mixed and heated up to 50°C for a few minutes to favor the dissolution of the NaTFPB salt and to ensure the homogeneity of the mixture. Aliquot of the aqueous solution (0.6 mL) was then placed in contact with the organic phase (0.6 mL) of the desired composition (volume phase ratio is close to 1).

The phases were shaken at 1500 rpm for 30 minutes at 25±2°C using a Biosan TS-100 Thermoshaker apparatus to ensure the equilibrium was reached. The phases were then centrifugated at 9500 rpm for 4 minutes to favor phase disengagement using a VWR microstar 12 apparatus. The metal content in the aqueous phases before and after extraction was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 720 ES apparatus). The metal distribution ratio (D_M) was calculated using the following equation:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} = \frac{[M]_{ini,aq} - [M]_{aq}}{[M]_{aq}} \quad (1)$$

where $[M]_{ini,aq}$ and $[M]_{aq}$ denote the aqueous metal concentration before and after extraction respectively. The separation factor (SF) between a metal 1 and a metal 2 was calculated as follows:

$$SF = \frac{D_{M1}}{D_{M2}} \quad (2)$$

where D_{M1} and D_{M2} are the distribution ratios for metal 1 and metal 2, accordingly.

All of the results shown in this study are the average of three experiments and are reproducible within a 10 % error.

2.3. Determination of the aqueous imidazolium cation concentration

The imidazolium cation content in the aqueous phase was determined using UV-visible spectrophotometry, with a Shimadzu UV-PC 2401 apparatus. The aqueous samples were analyzed with quartz cells (optical path way of 1 cm). The absorption band of the imidazolium cations is located at a wavelength of 211 nm [31]. The concentration of the ionic liquid cation dissolved in the aqueous phase was calculated using the Beer-Lambert law. A molar extinction coefficient of $4407 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ [32] was retained for the $[\text{C}_4\text{mim}^+]$ cation.

3. Results and discussion

3.1. Solvent extraction of lithium using $[\text{C}_4\text{mim}][\text{NTf}_2]$ ionic liquid associated to TBP

3.1.1. Effect of pH

Tri-*n*-butyl phosphate is known to have a good ability to extract lithium ions from aqueous solutions when associated with imidazolium-based ILs [29]. Moreover, it was shown that only small proportion of $[\text{C}_4\text{mim}][\text{NTf}_2]$ diluted in TBP is beneficial to increase the distribution ratio values for lithium [33]. For the current study, we decided to use hydrophobic $[\text{C}_4\text{mim}][\text{NTf}_2]$ ionic liquid as cosolvent also due to its relatively low solubility in water ($\approx 12 \text{ mmol}\cdot\text{L}^{-1}$, [34,35]). Thus, the competitive extraction of lithium(I), cobalt(II) and nickel(II) ions from sulfuric acid solutions into the organic phase composed of 90% v/v TBP and 10% v/v $[\text{C}_4\text{mim}][\text{NTf}_2]$ was studied in this work. The distribution ratio values for these metals as a function of pH in the aqueous initial phase is shown in Fig. 2.

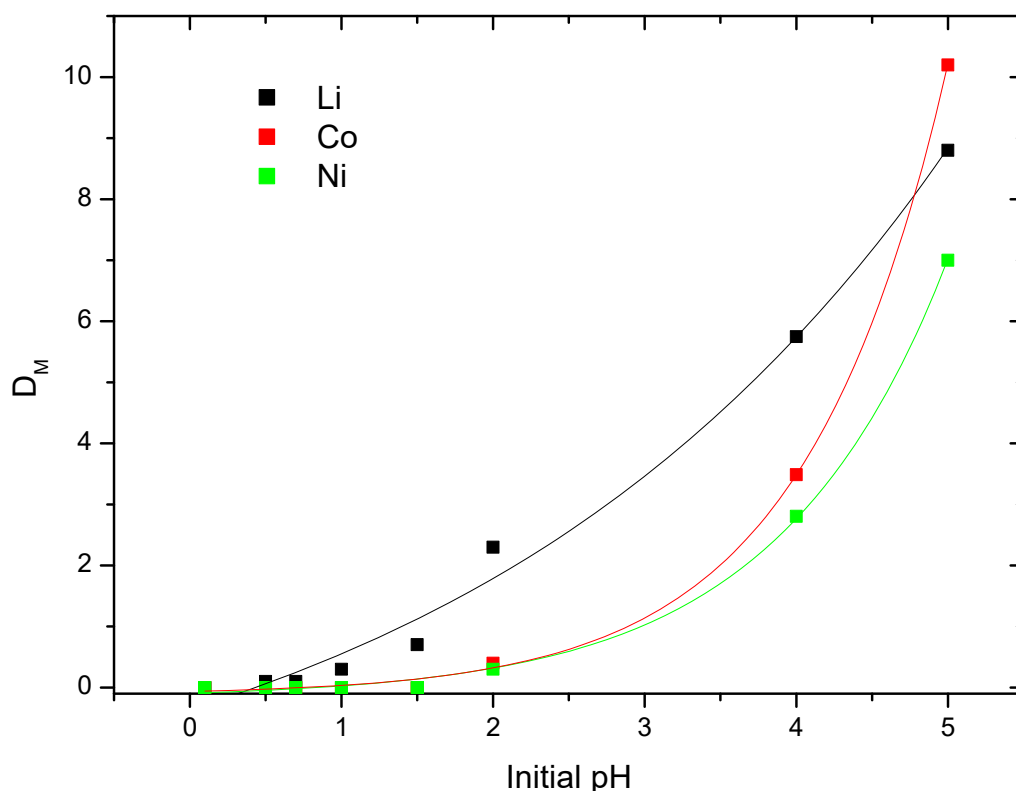


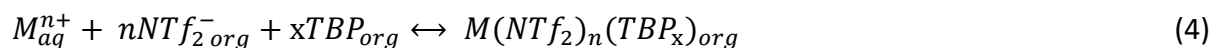
Fig. 2. Distribution ratio values for lithium, cobalt and nickel ions as a function of initial pH in the aqueous phase. Solvent phase: $[C_4mim][NTf_2]$ (10% v/v) dissolved in TBP (90% v/v). Lines are drawn for clarification purpose.

As can be seen, the distribution ratio values for lithium, cobalt and nickel are dependent on the aqueous phase acidity. A higher content of acid protons in the aqueous phase leads to decline of metal distribution ratios at higher acidity. However, the aqueous acidity is the factor governing the selectivity for the lithium ions. It can be seen that at pH close to 2 the distribution ratio value for lithium is higher than 2, while cobalt and nickel ions are only few extracted. This outcome could be explained by the small size of the lithium ion, which is co-extracted by TBP molecules with acid protons while the other metals are left in solution. However, at an initial pH of 5, this system appears to be cobalt selective with distribution ratios in the order $Co > Li > Ni$. The particular ability of cobalt to form lipophilic complexes could explain its higher extraction at $pH=5$.

Since the extraction of lithium is very low using pure TBP [36], the extraction of the metals is mainly related to the presence of ionic liquid in the organic phase. However, the extraction of metals into imidazolium ionic liquids often occurs *via* cation exchange mechanism, in which the ionic liquid cation is exchanged with the metal at the interface [26 ; 32]. This extraction mechanism can be written as follows:



This mechanism leads to non-negligible losses of ionic liquid in the aqueous phase. The extraction can also occur by formation of ion pairs in the organic phase with the ionic liquid anion ($[NTf_2^-]$) as written below:



Even if no clear proof of interactions between the ionic liquid anion and the metal can be found using infrared spectra of the organic phase after extraction [30], this mechanism can't be excluded. The use of more precise techniques that give access to the coordination sphere of the metal and/or to the spectra of the NTf_2^- anion after extraction should give more information about the role of the ionic liquid anion in the extraction efficiency. The ionic liquid can act as a source of hydrophobic anion for the extraction of metal ions [38].

The lowering of the distribution ratios for metals with an increase of the acidity is frequently observed when using imidazolium ionic liquids as extraction solvents [28]. This effect has been attributed to a competition between the extraction of protons and the extraction of the metals [30]. But this explanation is not satisfying, knowing the large amount of extractant available in the organic phase as compared to the amount of protons in the aqueous phase. More likely, the acidity has an effect on both mechanisms described (Eq. (3) and Eq. (4)). The formation of the bis-trifluoromethanesulfonic acid ($HNTf_2$) could decrease the probability of forming ion pairs with the metals. Concerning the cation exchange, the acidity is known to increase the solubility of the ionic liquid in water [39]. The reduction of the extraction of metals in acidic media could be explained as an effect of Le Chatelier's principle. An increase of the ionic liquid cation content in the acidic aqueous phase could shift the equilibrium described in Eq. 3 in a way that disfavor the extraction of the metal.

3.1.2. Effect of sacrificial cation

In order to prevent the loss of ionic liquid in the aqueous phase without reducing the metal ion extraction efficiency, one solution is to introduce a sacrificial cation in the organic phase, as evidenced by Luo et al. [40]. While introducing this sacrificial cation (under the form of a sodium tetraphenylboron salt), sodium will be exchanged instead of the ionic liquid cation,

thus reducing the loss of ionic liquid. But sodium tetraphenylboron is unstable under acidic conditions, which limits its application. This is why the sacrificial cation is introduced under the form of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]boron (NaTFPB). This salt has shown a lower solubility in water and a good stability under highly acidic conditions [41]. The reduction of the ionic liquid loss can be seen in Table 1 and Fig. 4, where the UV-vis spectra of the aqueous phase is reported after extraction, with (0.005 M) and without sodium TFPB in the organic phase.

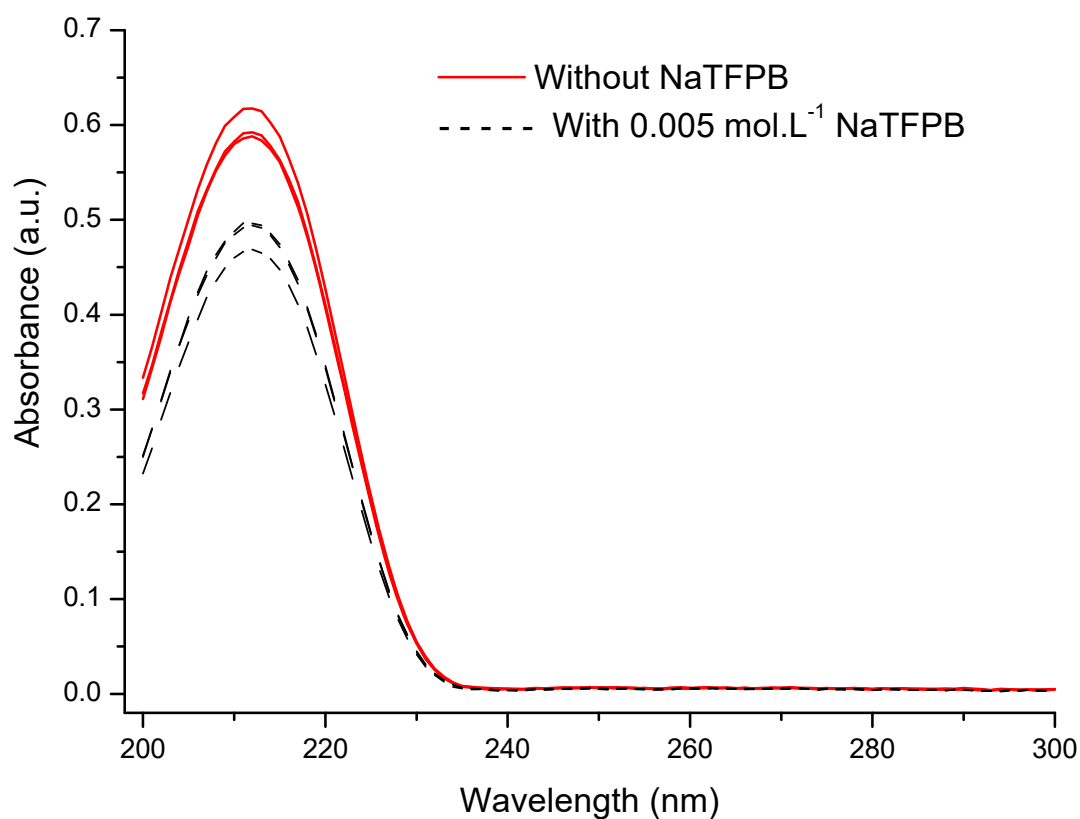
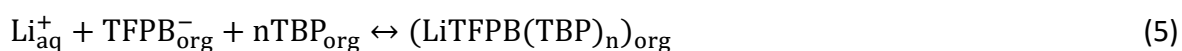


Fig. 3. UV-vis spectra of the aqueous phase (initial pH=5) after its contact with organic phase composed of TBP and ionic liquid with and without NaTFPB (0.005 M).

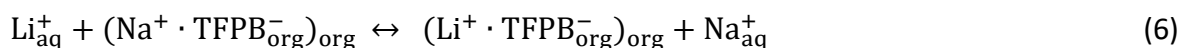
It can be seen that the imidazolium cation content in the aqueous phase is considerably lower when sodium TFPB is placed in the organic phase. However, the cation exchange is not suppressed entirely, the absorbance in the aqueous phase is 18 % lower with the sacrificial cation rather than without it. This result is in accordance with the results of Luo et al., who found that a higher concentration of sodium tetraphenylborate (0.12 mol.L⁻¹) in the organic phase decreases the loss of ionic liquid by 24 %.

Furthermore, the tetraphenylboron anion is known to have a good ability to form water-insoluble compounds with large cations [42]. The use of sodium tetraphenylboron for the extraction of cesium or lithium has been emphasized previously [38, 39]. Table (1) shows that despite the reduction of the ionic liquid content in the aqueous phase, the distribution ratio of all of the metals is increased when NaTFPB is introduced in the organic phase.

The extraction of lithium occurs via different mechanisms. The former is described in Eqs. (3) and (4). The latter is the formation of ion pairs with the lipophilic TFPB anion in the organic phase, that can be written as follows:



Another mechanism that could be involved in the lithium extraction is exchange between sodium and lithium, thus forming a LiTFPB salt in the organic phase:



This exchange is responsible for the diminution of the imidazolium cation content found in the aqueous phase after extraction. The ion pairs formed have a low solubility in water as compared with the ion pairs possibly formed with the NTf_2^{-} anion [45]. As reported in Table (1), the extraction efficiency of the metals is higher, due to the occurrence of these concomitant mechanisms. Another effect of the highly hydrophobic anion TFPB has been detailed by Naganawa et al. [46]. The non-coordinating anion favors the transfer of dehydrated metallic ion pairs. The absence of hydrating water molecules in the coordination sphere of the metal increases the coordination ability of the extracting molecule. The use of precise spectroscopic techniques would offer access to the exact form of the complex form in the organic phase.

Table 1.

Amount of ionic liquid found in the aqueous phase after extraction at pH=5 and distribution ratios of the metals

Organic phase	D_{Li}	D_{Co}	D_{Ni}	$[C_4mim^+]_{aq}$ after extraction (mmol.L ⁻¹)
TBP + [C ₄ mim][NTf ₂] (10% (v/v))	8.79	10.2	7.58	8.14
TBP + [C ₄ mim][NTf ₂] (10% (v/v)) + NaTFPB (0.005 mol.L ⁻¹)	10.7	13.8	10.2	6.60

The effect of the aqueous phase acidity has been studied with sodium TFPB in the organic phase. The results of the competitive extraction are reported in Fig. 4.

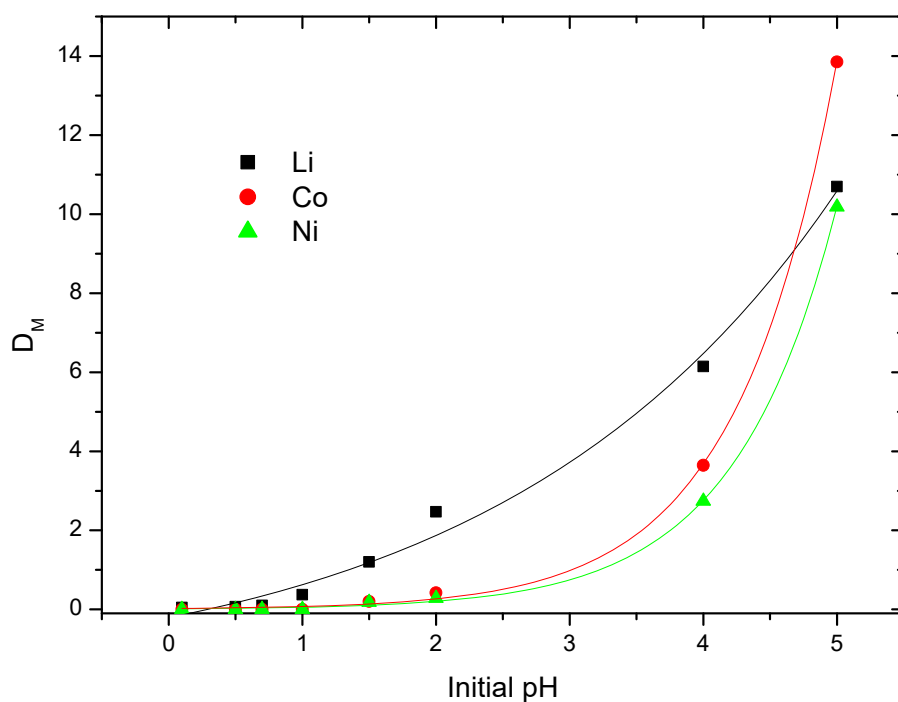
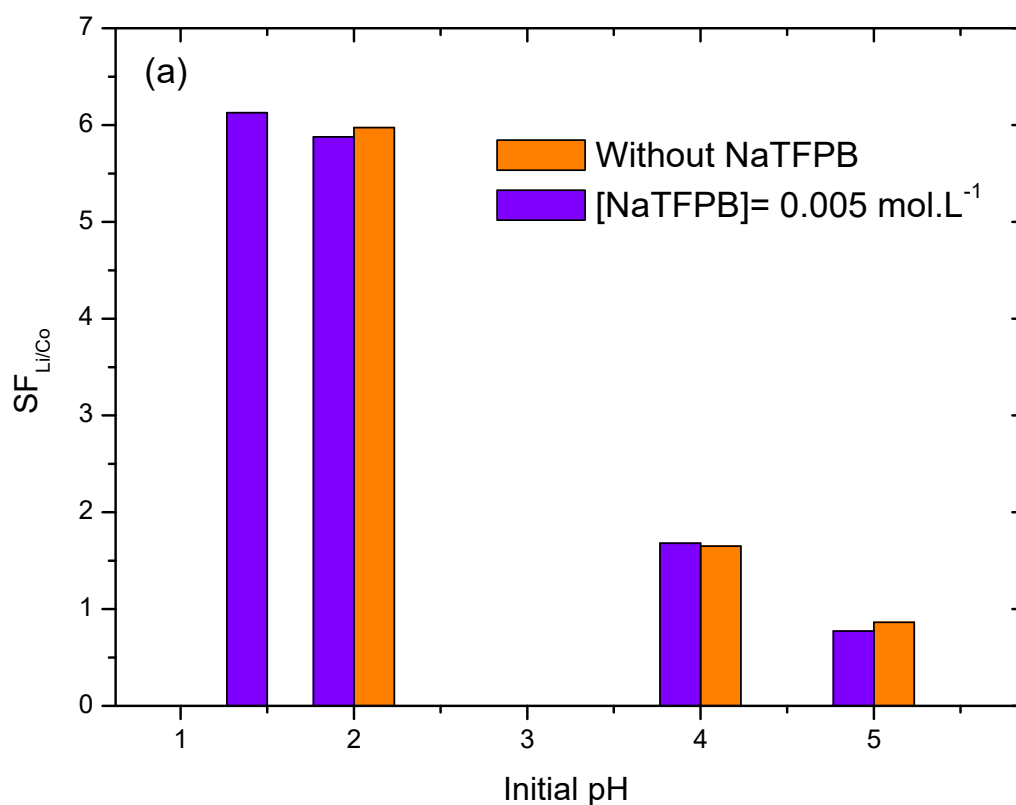


Fig. 4. Distribution ratio values for lithium, cobalt and nickel as a function of initial pH in the aqueous phase . Organic phase: [C₄mim][NTf₂] (10% (v/v)) and 0.005 M TFPB dissolved in TBP (90% (v/v)). Lines are drawn for clarification purpose.

As already observed without sodium TFPB, a higher aqueous acidity favors the selectivity for lithium. In this case, the distribution ratio values are higher for all the metals due to the presence of sodium TFPB in the organic phase. This effect leads to similar or slightly lower separation factors for lithium over cobalt and nickel, as shown in Fig. 5 (a) and 5 (b), with and without NaTFPB in the organic phase. At an initial pH of 1.5 without NaTFPB, the separation factors can't be given because the distribution ratios of nickel and cobalt are too low.



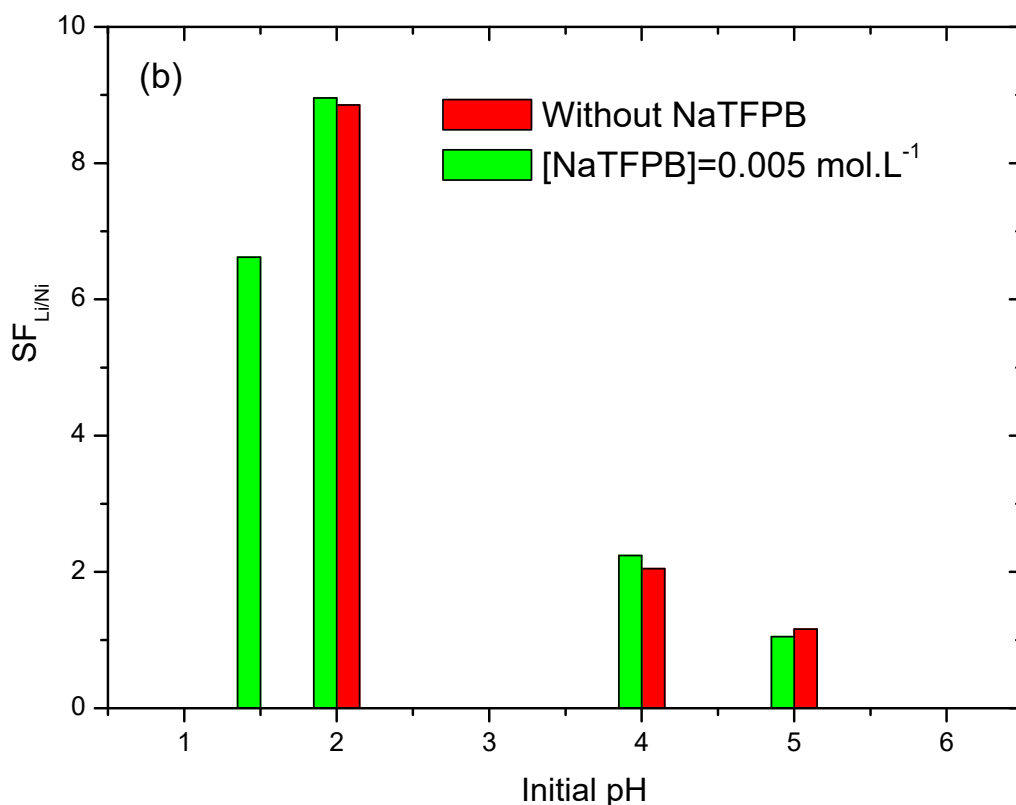


Fig. 5. Separation factor for Li/Co (6. (a)) and Li/Ni (6. (b)) as a function of the aqueous phase initial pH, with and without NaTFPB in the organic phase. Separation factor were not calculated at pH=1.5 because D_{Co} and D_{Ni} are negligible.

3.1.3. Effect of TBP proportion in the organic phase

The TBP proportion in the organic phase is also relevant to favor the selectivity for lithium over cobalt and nickel. Metal distribution ratios at pH=5 as a function of the TBP proportion in the organic phase are shown in Fig. 6.

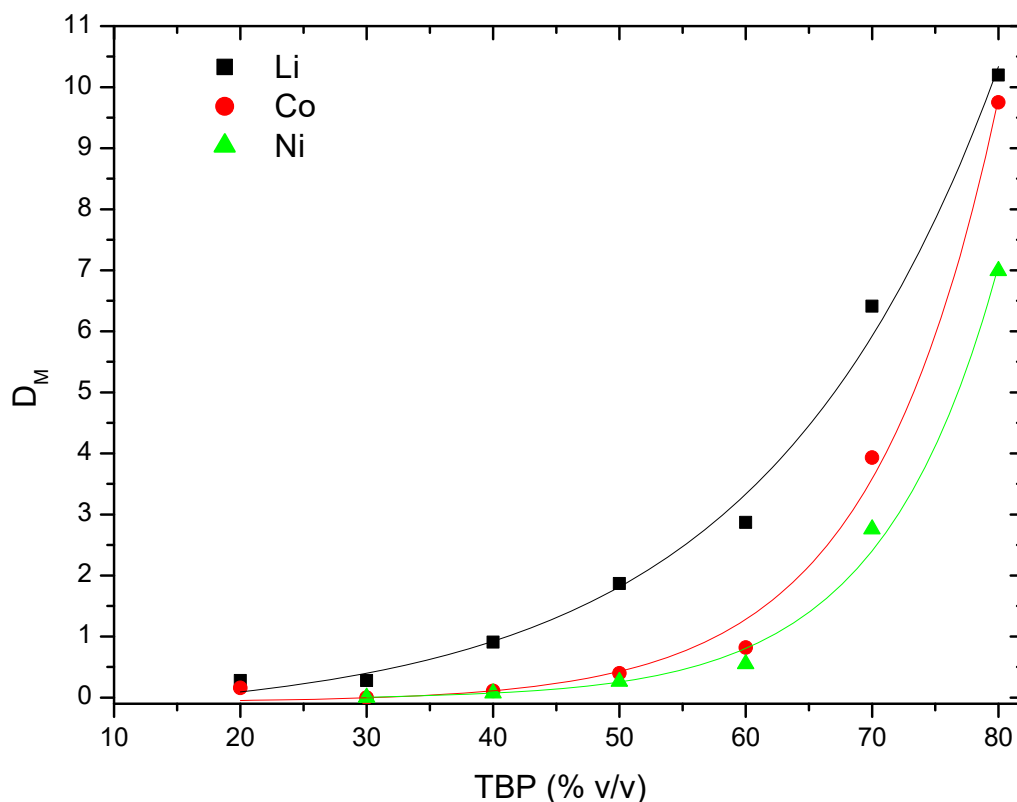


Fig. 6. Distribution ratios of lithium, cobalt and nickel as a function of the TBP proportion in the organic phase (TFPB=0.005 M, pH=5). Lines are drawn for clarification purpose.

As already mentioned, the distribution ratio of lithium is higher with a small proportion of ionic liquid dissolved in TBP. However, the selectivity for lithium is better with a lower content of TBP in the organic phase (TBP < 60% (v/v)). By increasing the amount of ionic liquid in the organic phase, the interaction between the extracting molecule and the ionic liquid cation reduces the extraction efficiency by reducing the amount of available TBP in the organic phase [38]. The separation factor for lithium over cobalt and nickel is reported in fig. 7, as a function of the TBP proportion in the organic phase.

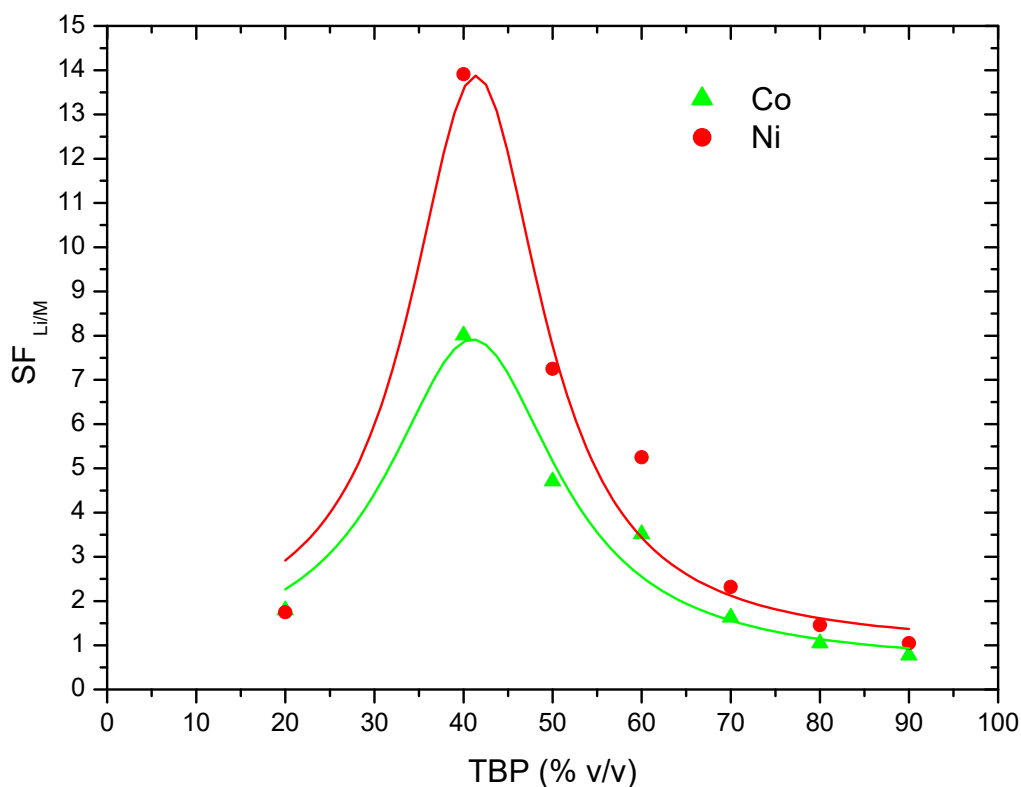


Fig. 7. Separation factor of lithium over cobalt and nickel as a function of the TBP proportion in the organic phase (TFPB=0.005 M, pH=5). Lines are drawn for clarification purpose.

The separation factor can reach values up to 14 for lithium over nickel and up to 8 for lithium over cobalt at a TBP proportion of 40% (v/v) in the organic phase. But the separation factors are decreasing for a higher content in TBP in the organic phase. This could be related to a higher content of TBP available in the organic phase to extract the divalent metals. The selective extraction of lithium over cobalt and nickel can be made with TBP associated to imidazolium ionic liquids. A low pH and a low content of TBP in the organic phase will favor lithium extraction upon cobalt and nickel extraction. The selectivity for the lithium ion can be tuned using these two factors but both will result on a decrease of the extraction efficiency. Despite this negative trend on the extraction efficiency, the lithium distribution ratio remains elevated ($D > 1$) while the other metals are only poorly extracted from the aqueous phase.

3.2. Solvent extraction of lithium using $[C_{10}mim][NTf_2]$ ionic liquid associated to TBP

3.2.1. Effect of NaTFPB concentration

As it has been concluded previously, the addition of the cation exchanger can be a way to reduce the cation exchange, but not to suppress it entirely. In order to avoid the cation exchange, another solution is to increase the length of the ionic liquid alkyl chain. It will result

on an increase in the ionic liquid hydrophobicity, which could prevent the IL cation to undergo the exchange [29]. However, when using $[C_{10}mim][NTf_2]$, the distribution ratios of the metals is negligible. No exchange occurs between the lithium and the ionic liquid cation, but it results on a suppression of the extraction.

In order to increase the distribution ratio for the metals, a lipophilic counter anion can be added to the organic phase. The distribution ratio of lithium at pH=5 can be seen in fig. 8, as a function of the sodium TFPB concentration dissolved in $[C_{10}mim][NTf_2]$.

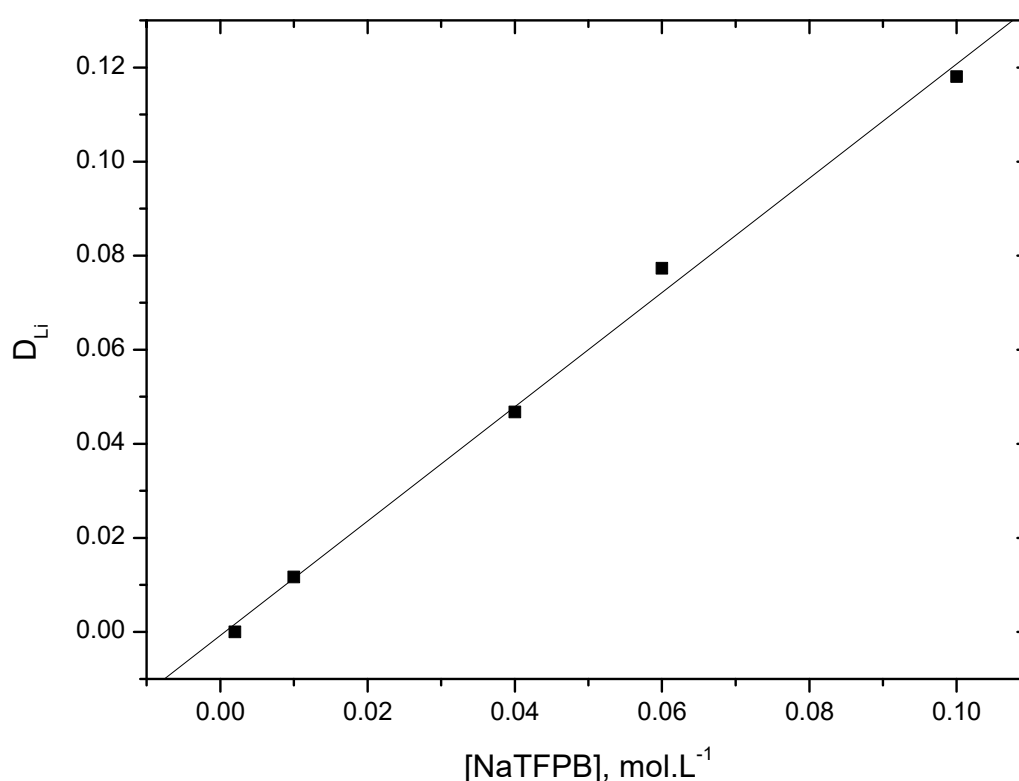
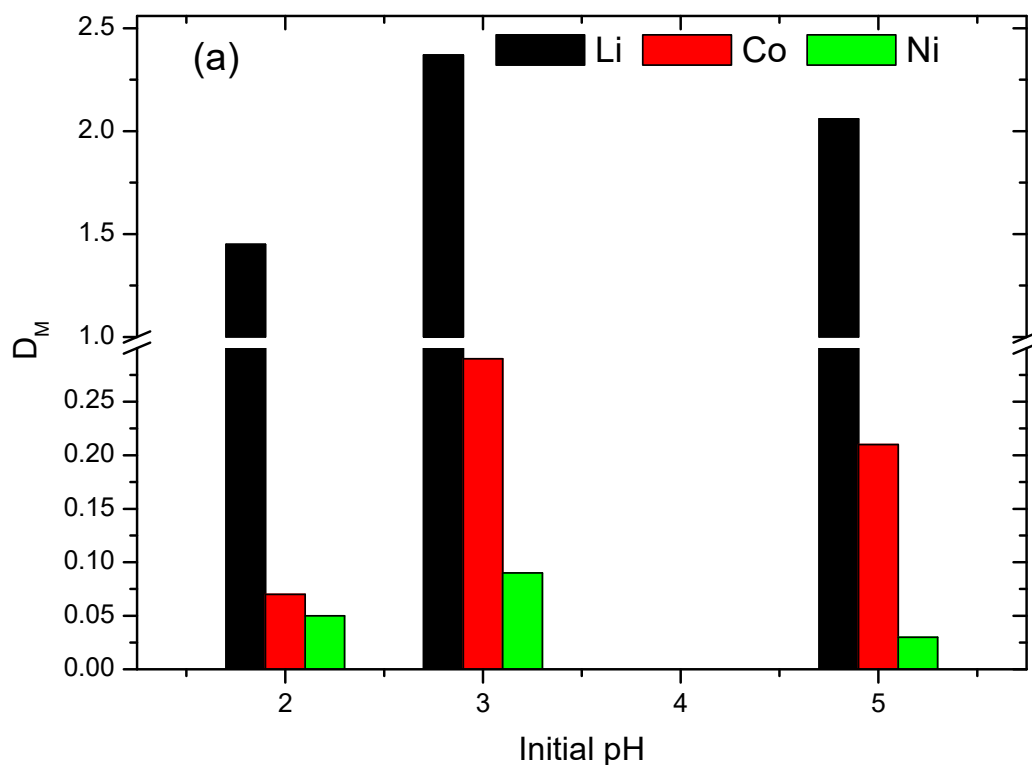


Fig. 8. Lithium distribution ratio values as a function of TFPB concentration in $[C_{10}mim][NTf_2]$ ($Li_2SO_4=0.4\text{ mmol.L}^{-1}$, pH=5). Line is drawn for clarification purpose.

The lithium distribution ratio is increasing with an increasing content of TFPB in the organic phase. The formation of ion pairs between lithium cation and the lipophilic counter anion TFPB allows an increase of the distribution ratio, even with an ionic liquid of longer alkyl chain length. But this distribution ratio is still very low. The formation of ion pairs in the organic phase is not sufficient to obtain a satisfying extraction of the lithium ion.

3.2.2. Effect of TBP proportion in $[C_{10}mim][NTf_2]$ and acidity of the aqueous phase

To increase the extraction efficiency of lithium, a solvating agent can be introduced in the organic phase [47]. According to the results obtained with the $[C_4mim][NTf_2]$ ionic liquid, a proportion of TBP lower than 50% (v/v) is advantageous for the selective extraction of lithium, together with a low pH. A concentration of TFPB of 0.1 M is used in the organic phase to favor the formation of ion pairs. The distribution ratios of the metals at various pH are reported in fig. 9 for a TBP content of 30% (v/v) and 70% (v/v) in the organic phase.



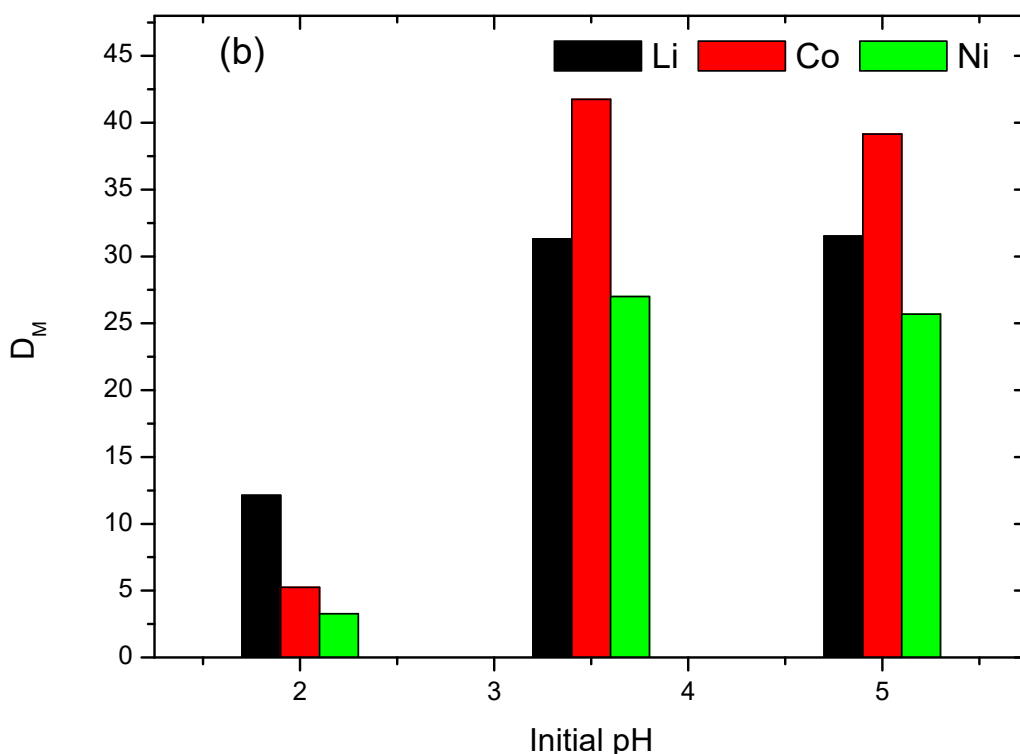


Fig. 9. D_{Li} , D_{Co} and D_{Ni} as a function of the aqueous phase initial pH, with TBP=30% (v/v) in [C₁₀mim][NTf₂] (9. (a)) and TBP=70% (v/v) mixed with [C₁₀mim][NTf₂] (9. (b)), in the presence of NaTFPB (0.1 M) in the organic phase. Fig. 10. (a): break on the Y axis between 0.3 and 1.

As already mentioned, the distribution ratios are much higher when the pH is higher than 2 in the aqueous phase, and with a higher TBP content in the organic phase. Distribution ratios higher than 20 can be reached with 70% of TBP in the organic phase at a pH higher than 3 for all three metals. Concerning the selectivity, as observed with the [C₄mim][NTf₂] ionic liquid, the higher separation factors for lithium can be reached with a higher acidity in the aqueous phase and a lower content of TBP in the organic phase. With 30% of TBP in the organic phase and a pH = 2, a good selectivity is obtained for lithium over cobalt ($SF_{Li/Co}=20$), while no or negligible extraction of nickel occurs. Furthermore, the distribution ratio of lithium remains elevated ($D_{Li}=1.5$).

The direct extraction of lithium from leach liquors of lithium-ion batteries could be considered using this composition of the organic phase. Considering the lowering of the distribution ratio in acidic media, the stripping of the metals can be done by contacting the loaded organic phase with acidic solutions. The high hydrophobicity of the [C₁₀mim][NTf₂] will limit the losses of organic phase and prevent the ionic liquid cation to be exchanged at the interface. Moreover, the extraction of metals is still possible using the protonated form of the TFPB salt [48]. Thus,

it seems that the organic phase can be recycled and re-used several times after the stripping stage. No extraction occurs without using NaTFPB in the organic phase, indicating that the ion pairing in the organic phases is mandatory to provide extraction of the lithium ion. The extraction of the lithium ion can be described by Eqs. (4) and (5). The cation exchange with the ionic liquid cation is presumably suppressed. But it has already been evidenced with a different system that an increase of the alkyl chain length is not sufficient to suppress the exchange of the ionic liquid cation [49]. The exact mechanism of extraction cannot be confirmed until more precise techniques are used to define it.

The use of molecular diluents instead of ionic liquids could be envisaged to ensure the ion pair extraction of metals [48], the addition of a diluent being mandatory to favor the selectivity for the lithium ion. But the solubility of NaTFPB appears to be limited in molecular diluents [48], while it is sufficient in ionic liquid media. From an environmental point of view, the presence of fluorine and sulfur atoms in the ionic liquid anion as well as the use of an imidazolium cation affects the “greenness” of the organic phase used. In this case, the use of an ionic liquid is beneficial in terms of efficiency and selectivity for the lithium ion in acidic media, which is difficult to achieve with the current solvent extraction processes.

The use of ionic liquids based on hydrophobic anions has shown promising results for the extraction of metal ions. The ionic liquid acts as a source of hydrophobic anions, allowing to form neutral ion pairs that are readily extracted to the organic phase using an extracting molecule. However, the large-scale synthesis of these anions remains challenging and will be related to the developments of future lithium-ion batteries, these kinds of anions being used as electrolytes. The type of cation associated to this anion to form the ionic liquid also needs further developments. Imidazolium cations are well known and gives interesting ionic liquids (higher extraction efficiency than other cations associated to the NTf_2 anion [50], low viscosity hydrophobic ionic liquids...). However, the mechanism of extraction leads to an exchange of the ionic liquid cation, which is unfavorable knowing the low biodegradability of this cation. The method proposed herein allows to extract the metal using only one mechanism of extraction which makes the system easier to model and to scale-up. However, an increase of the alkyl chain length of the imidazolium cation increase the toxicity of the cation. Both the environmental and economic aspects as well as the efficiency of the system and the

mechanism of extraction involved have to be considered while selecting the cation of the ionic liquid.

Conclusion

In this study, we investigated the solvent extraction of lithium, cobalt and nickel from synthetic leach liquors of spent lithium-ion batteries. We have demonstrated that the recovery of lithium in the leach liquor is feasible using an organic phase composed of TBP extractant and imidazolium-based ILs. Two options can be considered to provide a good selectivity for the lithium ions among cobalt and nickel in sulfuric acid media: the first is to use a larger amount of TBP (> 50 % v./v.) in the organic phase and a higher acidity ($\text{pH} < 3$) of the aqueous phase. The second option is to use a smaller amount of TBP with a higher pH ($\text{pH} > 3$) of the aqueous phase. However, the extraction of lithium occurs via a cation exchange with the ionic liquid cations, which leads to substantial loss of ionic liquid in the aqueous phase. The use of a sacrificial cation in the form of a sodium tetraphenylboron salt was investigated to prevent this loss. The cation exchange was reduced, but not suppressed entirely. However, the distribution ratios are considerably enhanced when the lipophilic counter anion was added to the organic phase. On the other hand, the cation exchange can be reduced using a more hydrophobic imidazolium-based ionic liquid. In this case, the use of a lipophilic counter anion such as TFPB in the organic phase is needed to favor the formation of ion pairs with lithium ions and to obtain better extraction efficiency. The principles of selectivity remain the same as those obtained with an ionic liquid with shorter alkyl chain length: low acidity and lower amounts of ionic liquid in the organic phase favor the extraction efficiency but decrease the selectivity for the lithium ions. A satisfying selectivity for lithium over cobalt and nickel was obtained at $\text{pH} = 2$. The loss of ionic liquid to the aqueous phase is low and the equilibrium is reached in a few minutes, accrediting the application of this system to treat leach liquors of spent lithium-ion batteries. However, the real leach liquors are much more complex than those studied here, with metals more concentrated and the presence of several other metal (Al, Fe, Cu...) and further study is currently ongoing in the laboratory.

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