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Solvent Extraction of Lithium Ions using Benzoyltrifluoroacetone in New Solvents

Abderrazak Masmoudi^{a*}, Guillaume Zante^{a,b}, Dominique Trébouet^a, Rémi Barillon^a, Maria Boltoeva^a

^a Université de Strasbourg, CNRS, Institut Pluridisciplinaire Hubert Curien (IPHC), UMR7178, F-67000 Strasbourg, France

^b ADEME, 20 Avenue du Grésillé, 49004 Angers Cédex 01, France

Corresponding author: abderrazak.masmoudi@iphc.cnrs.fr

Abstract

The chelating agent benzoyltrifluoroacetone (HBTA) was used for the extraction of lithium ions from alkaline solutions. Aiming to develop an eco-friendly extraction system, hydrophobic room-temperature ionic liquids (RTILs) were investigated as diluents. The influence of several experimental parameters on the extraction efficiency was investigated, including, aqueous pH, the nature of counter-ion, and the synergistic agent effect. It was found that contrary to the classical systems using molecular organic solvents, HBTA alone dissolved in 1-ethyl-3-Alkylimidazolium *bis*(trifluoromethylsulfonyl)imide ([C₂mim][Tf₂N]) ionic liquid can highly extract lithium without the need of a synergistic agent such as tri(*n*-octyl)phosphine oxide (TOPO). The extraction mechanism was studied using the electro-neutrality principle based on concentration measurements of the IL constituent ions and deprotonated HBTA (BTA⁻). It was found that a neutral lithium-extractant complex is extracted to the IL phase. The system combining HBTA and [C₆mim][Tf₂N] ionic liquid has high selectivity for lithium over sodium but poor selectivity over calcium. We have shown also that a high stripping ratio can be obtained using relatively concentrated hydrochloric acid. Finally, it was found that the use of deep eutectic solvents (DESs) as diluents is much less efficient compared with ILs.

Keywords: Lithium (I), Benzoyltrifluoroacetone, Ionic liquids, Deep Eutectic Solvents, Solvent extraction

Highlights:

- High extraction of lithium from alkaline solutions using HBTA in ionic liquids
- No need for neutral ligands for synergism to the extraction of lithium using HBTA in ionic liquids
- A neutral lithium-organic ligand complex is extracted to the IL phase
- High stripping ratio is obtained using relatively concentrated hydrochloric acid
- High selectivity for Li(I) over Na(I) but poor selectivity over Ca(II)

1 Introduction

The numerous applications of lithium like lithium-ion batteries and ceramics will make of it one of the important strategic elements in the next years. Its demand is expected to increase by 8% to 11% every year from 2017 [1].

This rapidly growing demand is increasing pressure on lithium producers to ensure supply security and ensure the balance of lithium consumption-production without increasing considerably its price. Lithium is found in suitably large concentrations in only two types of materials; mineral deposits and brines [2]. Considering the limited resources of lithium, researchers are asked to find new processes leading to recycling lithium from spent lithium-ion batteries or recover it from aqueous resources such as brines, geothermal waters, or even seawater [3-5].

Liquid-liquid extraction (solvent extraction) is a highly effective and economical technique for the extraction and separation of metal salts from dilute solutions [6]. It offers many advantages over other techniques such as the ability to selectively separate similar metals even from lowly concentrated solutions. Several studies on the extraction of lithium with liquid-liquid extraction have been reported [7-9].

Synergistic systems composed of a β -diketone as a chelate extractant and a neutral solvating extractant have been intensively studied. In fact, it is known that the presence of neutral ligands, such as organophosphorus compounds such as trioctylphosphine oxide (TOPO) and tributylphosphate (TBP) has a synergistic effect on the extraction of metals by β -diketones. This phenomenon has been widely investigated from multiple aspects and in many metal- β -diketone-neutral ligand systems [10-13]. For the extraction of lithium ions a combination of some extractants such as dibenzoylmethane (DBM) with certain organophosphorus compounds, the synergistic enhancement in D_{Li} of 10^4 can be attained, compared with the extraction of lithium by either of the extractants alone [14].

Healy *et al.* reported for the first time the extraction of lithium with thenoyltrifluoroacetone (HTTA) and unidentate neutral ligands such as TBP and TOPO [15,14]). Other authors have focused on the use of several synergists in the extraction of Li^+ with HTTA [16-19], and with benzoyltrifluoroacetone (HBTA) [20] in various inert organic solvents. Most of the synergistic extraction systems reported with β -diketone and neutral ligands studied until now can be found in a recent review [21]. Associated with neutral extracting molecules, β -diketones have shown excellent performances for lithium extraction. The major drawbacks that can be considered as obstacles to its application at an industrial scale are the use of toxic organic solvents, the high costs of extractants and synergists and also the lack of a good understanding of the extraction mechanisms [21].

A concern to treat spent lithium-ion batteries is the development of technologies to recover metals efficiently, selectively and ecofriendly. ILs and more recently DESs were proposed as alternatives for the conventional organic solvents. ILs are organic salts composed of an organic cation and an organic or inorganic anion with a melting temperature lower than 100

°C [22]. DESs are constituted of two or more solid compounds associated with each other via hydrogen bonds and van der Waals interactions giving rise to a liquid at ambient temperature [23]. The main advantages of these new solvents are their low vapor pressure and low flammability. The DESs are advantageous as compared to ILs due to their straightforward preparation.

In the present work, the HBTA-TOPO/[C₂mim][Tf₂N] extraction system was studied in detail with regard to different extraction parameters such as the pH, initial concentration of lithium and molar ratio of HBTA. Furthermore, a detailed extraction mechanism had been proposed based on the electroneutrality principle. [C₂mim][Tf₂N] was chosen because of its low viscosity compared to other ILs, and because measuring the aqueous solubility of its constituents using ionic chromatography is relatively easily. After a comparison between seven different ILs for the lithium extraction from ammoniacal solution using 0.1 M HBTA, the HBTA/[C₆mim][Tf₂N] extraction system was used to study the lithium extraction in terms of extraction and selectivity. Lastly, a preliminary study using some DESs was carried out. The extraction of lithium using the β-diketone in ionic liquids and DESs was, to the best of our knowledge, never reported.

2 Materials and methods

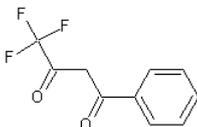
2.1 Reagents

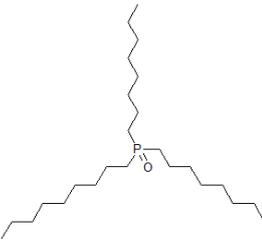
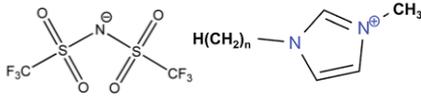
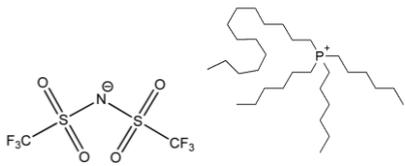
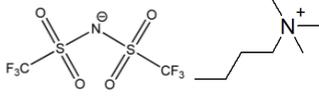
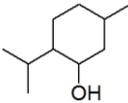
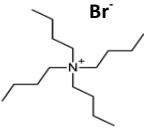
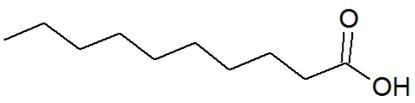
The room-temperature ionic liquids (shown in Table 1) of 99% purity were purchased from Solvionic (France) and used without any further purification. HBTA and TOPO with >98% purity were obtained from VWR.

For the preparation of the DES, acetic acid (Alfa Aesar, 99% purity), DL-menthol (Alfa Aesar, 98+% purity), as well as Tetra-N-butylammonium Bromide (Alfa Aesar, 98+% purity) were used as received. Metal aqueous solutions were prepared using lithium chloride (LiCl from PROLABO) or Lithium bis(trifluoromethanesulfonyl)imide salt (LiTf₂N from Solvionic). For selectivity experiments, CaCl₂ (PROLABO) and NaCl (PROLABO) with > 99 % purity were used. Aqueous solutions were prepared using deionized water (resistivity of 18.2 MΩ.cm). The pH was adjusted by adding appropriate aliquots of ammonium hydroxide (NH₄OH). Anhydrous Na₂CO₃ and NaHCO₃ used for chromatographic analysis are obtained from VWR.

Organic solutions were prepared by dissolving the given weight of HBTA and TOPO in all diluents (ILs and DESs) by heating gently to improve the dissolution of the organic molecules.

Table 1. Room-temperature ionic liquids and compounds used for the preparation of DESs used in this study.

| Reagent | Abbreviation | Chemical structure |
|-----------------------|--------------|--|
| Benoytrifluoroacetone | HBTA |  |

| | | |
|--|--|--|
| Tri(<i>n</i> -octyl)phosphine oxide | TOPO |  |
| 1-Alkyl-3-Alkylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide | [C _n mim][Tf ₂ N] |  |
| Trihexyl(tetradecyl)phosphonium <i>bis</i> (trifluoromethylsulfonyl)imide | [P ₆₆₆₁₄][Tf ₂ N] |  |
| <i>N</i> -trimethyl- <i>N</i> -butylammonium <i>bis</i> (trifluoromethanesulfonyl)imide | [N ₁₁₁₄][Tf ₂ N] |  |
| DL-menthol | |  |
| Tetra- <i>N</i> -butylammonium bromide | TBAB |  |
| Acetic acid | |  |
| Decanoic acid | |  |

2.2 Liquid-liquid extraction procedure

The liquid-liquid experiments were performed in Eppendorf tubes (2 mL), using equal volumes of the organic and aqueous phases. The mixture was shaken mechanically using a Thermo-shaker (BIOSAN-TS100) for a defined time at 1400 rpm. The two phases are then separated carefully after centrifugation at 5000 rpm for 2 min with a VWR Micro Star 12 centrifuge. An aliquot of the aqueous phase was diluted by 1 vol. % hydrochloric acid solution to analyze metal ions concentrations by Inductively Coupled Plasma Optic Emission Spectroscopy (ICP-OES) using a Varian 720-ES apparatus. Five standards solutions were

prepared in the same matrices as samples and used for calibration. These analyses allowed us to determine the metal ions concentration in the initial and equilibrium aqueous phases.

The distribution ratio defines the affinity of the metal for the organic or aqueous phase and is calculated using the following equation:

$$D = \frac{[M]_{IL}}{[M]_{aq}} = \frac{[M]_{init} - [M]_{aq}}{[M]_{aq}} \quad (1)$$

Where $[M]_{init}$, $[M]_{aq}$ and $[M]_{IL}$ denote the aqueous metal concentration initially, after extraction and the metal concentration in ionic liquid after extraction respectively,

All the extraction experiments were conducted at 25 ± 1 °C (except for the experiments on the temperature effect), repeated at least two times, and the standard deviations of the extraction percentages were within an experimental error of $\pm 5\%$.

2.3 Solubility Measurements

The concentrations of the IL constituent ions and chloride anion in the aqueous phase were determined by ion chromatography. The concentration of the deprotonated HBTA (BTA^-) in the aqueous phase was measured also by ion chromatography. All chromatographic analysis was performed using a Metrohm ECo IC with suppressor module in the case of anion concentration measurements. For cation concentration measurement the eluent was a solution of 3 mM HNO_3 in 75% deionized water and 25% acetonitrile and for anion measurement, the eluent was a solution of 1.8 mM sodium carbonate (Na_2CO_3) and 1.7 mM sodium hydrogen carbonate ($NaHCO_3$) in 70% deionized water and 30% acetonitrile. All analysis was done at room temperature. Standards samples were prepared using an aqueous solution with a known concentration of the IL constituent ions, which correspond to the solubility of $[C_2mim][Tf_2N]$ in pure water (42 mM), determined by UV-vis spectroscopy ($\lambda_{max} = 211$ nm, $\epsilon = 4397.7$ $cm^{-1} \cdot mol^{-1} \cdot dm^3$) [24].

2.4 Synthesis of the DES

In this study, three DESs (DES_1, DES_2, and DES_3) were studied (Table 2). The preparation protocol consists of mixing the two or more solids compounds able of forming a eutectic mixture via hydrogen bonds, at an adequate molar ratio, heating up them to around 80 °C in a water bath for a few minutes using a hot plate until a clear liquid is obtained. The resulting liquid is allowed to cool down to room temperature one night prior to use. DL-menthol can play the role of hydrogen bonds donor and also hydrogen bonds acceptor.

Table 2. DESs used in this study and their compositions.

| DES | Hydrogen bonds acceptor | Hydrogen bonds donor | Molar ratio | Reference |
|-----|-------------------------|----------------------|-------------|-----------|
| | | | | |

| | | | | |
|-------|--|--------------------|-----|-----------|
| DES_1 | <i>DL</i> -menthol | Acetic acid | 1:1 | [25] |
| DES_2 | Tetra- <i>N</i> -butylammonium bromide | Decanoic acid | 1:1 | This work |
| DES_3 | Tetra- <i>N</i> -butylammonium bromide | <i>DL</i> -menthol | 1:5 | This work |

3 Results and discussions

3.1 Extraction of Lithium with HBTA and TOPO dissolved in [C₂mim][Tf₂N]

The extraction of Li⁺ was carried out using 0.1 M HBTA and 0.025 M TOPO dissolved in [C₂mim][Tf₂N]. Experiments were performed using lithium salt with two various counter anions, namely Cl⁻ or Tf₂N⁻ dissolved in ammoniacal solutions. The initial aqueous pH values were varied from about 7 to 12. As shown in [Figure 1](#), whatever the pH, the extraction of lithium was less favored when Tf₂N⁻ was used as counter-ion. We suggest that the presence of Tf₂N⁻ in the aqueous phase leads to an increase of Tf₂N⁻ present in the coordination sphere of Li⁺, therefore decreasing interactions between HBTA and Li⁺.

The extraction of Li⁺ was negligible when the pH of aqueous solutions was lower than 10.4 whatever the counter-ion used. A sharp increase in the D_{Li} values was seen with increasing pH of the aqueous feed up to a pH value of 11.24. The D_{Li} values obtained in this work are more important than the most molecular solvents used as diluents for β -diketone-neutral ligand to extract lithium under similar experimental conditions [20,18].

The need for a sufficiently alkaline solution to obtain high extraction can be explained by the necessity to deprotonate HBTA. It is known that it is the dissociated form of HBTA (BTA⁻) that coordinates to Li⁺ [20]. Beyond a pH value of 11.3, a decrease of D_{Li} values was seen up to pH 11.9. This could be probably related to the increase of ammonia concentration and therefore the decrease of HBTA and Li⁺ interactions which seems to reduce lithium extraction as it was seen when increasing Tf₂N⁻ concentration. In view of the higher metal ion extraction obtained at pH of 11.3, the subsequent studies were carried out using an aqueous solution with a pH of around 11.3.

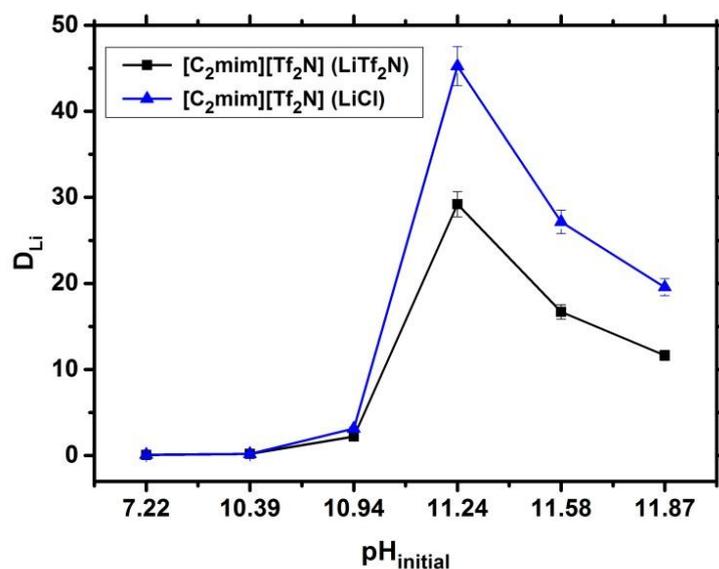


Figure 1. Variation of the distribution ratio for lithium ions as a function of aqueous pH. Organic phase: 0.1 M HBTA and 0.025 M TOPO in [C₂mim][Tf₂N]. Aqueous phase: LiCl or LiTf₂N in ammoniacal solution. [Li⁺]_{aq, init} = 20 mM.

The effect of initial lithium concentration in the alkaline feed solution was investigated by using 0.1 M HBTA and 0.025 M TOPO dissolved in [C₂mim][Tf₂N] (Figure 2). The initial lithium concentration was varied from 7.2 to 288.2 mmol.L⁻¹. By increasing initial Li⁺ concentration in the aqueous phase, the distribution ratio is decreasing gradually until it reaches a value close to zero. However, the absolute amount of lithium extracted to the ionic liquid phase increases sharply until it reaches a plateau from 56 mmol.L⁻¹. The absolute amount of lithium extracted stabilizes to a constant value because the maximum loading of the extractant (HBTA) is reached. So, 0.1 M HBTA and 0.025M TOPO could load about 56 mM of lithium ions.

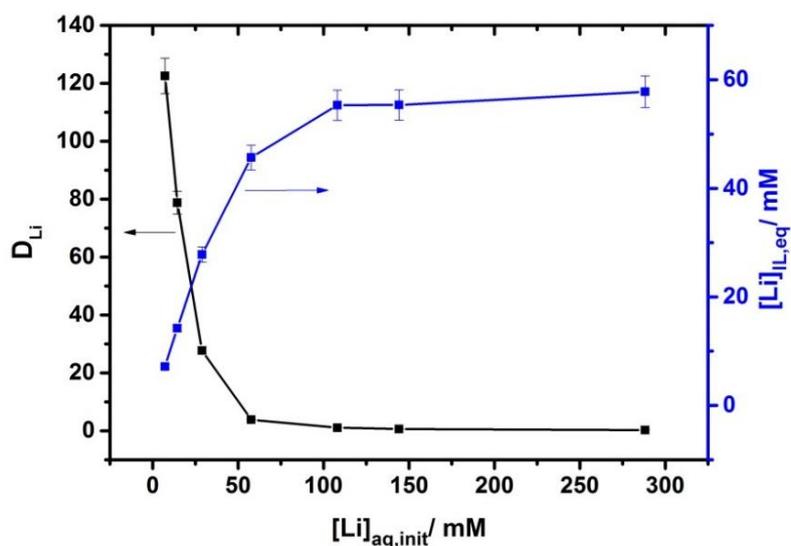


Figure 2. Lithium distribution ratio (Black curve) and lithium concentration extracted to the organic phase (Blue curve) as a function of the initial lithium concentration in the aqueous phase. Organic phase: 0.1 M HBTA and 0.025 M TOPO in [C₂mim][Tf₂N].

As it was mentioned previously, β -diketones with neutral extractants in molecular diluents have shown excellent performances for lithium extraction. Licheng Zhang *et al.* [26] studied lithium extraction from the alkaline brine solution. They found that when using HBTA alone in kerosene the lithium extraction was unsatisfactory. Therefore, they investigated different kinds of neutral donors on the synergistic extraction of lithium. Their results indicated that TOPO produces the greatest synergistic effect, in line with its powerful donor properties.

To study this potential synergistic effect in the extraction system under study, the Continuous Variation Method (Job's plot) was employed. It consists of fixing the total concentration of HBTA and TOPO at 0.1 M and varying their individual concentration. Then, the distribution ratio for lithium was measured at various molar ratios of HBTA to the total concentration. The results were summarized in Figure 3. This Figure shows that the extraction of lithium using TOPO alone is negligible, while when using HBTA alone, high lithium extraction efficiency is obtained. When mixing both extractants, no synergistic enhancement was observed as compared with the extraction of lithium by HBTA alone.

Therefore, it is very interesting to conclude that HBTA alone dissolved in $[C_2mim][Tf_2N]$ can effectively extract lithium without the help of TOPO or any other synergistic agent, contrary to the case where it is dissolved in a classical molecular solvent [20,26]. For further experiments, HBTA will be used alone as an extracting agent. In the case of synergistic systems, HL (like HBTA), thanks to its deprotonation, forms a neutral chelating compound with the metallic ion, while the neutral ligand, S (like TOPO), expels the remaining water molecules in order to enhance solubility in the organic phase [27]. In our case, the hydrophobic Tf_2N^- anions play probably this role, thus making the use of a neutral solvating molecule redundant and unnecessary.

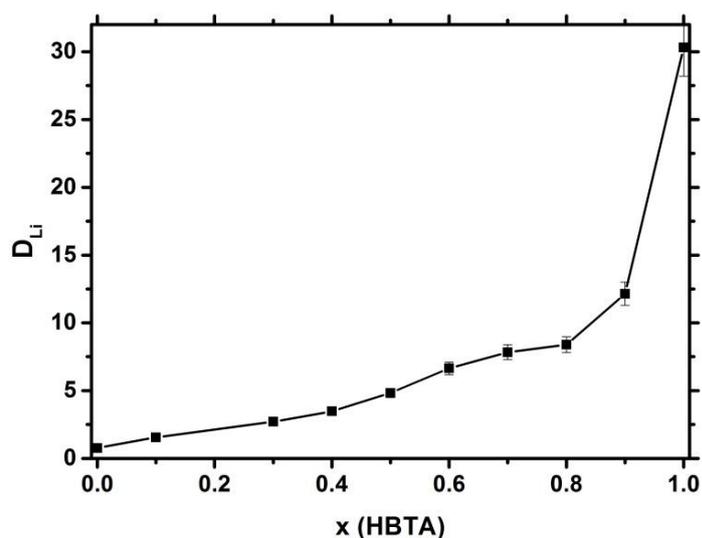
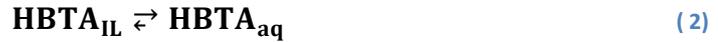


Figure 3. Effect of HBTA and TOPO concentrations on lithium extraction. $[HBTA] + [TOPO] = 0.1$ M diluted in $[C_2mim][Tf_2N]$. Initial aqueous pH = 11.3 and $[Li^+]_{aq,init} = 28.8$ mM. $x_{HBTA} = \frac{[HBTA]_{IL}}{[HBTA]_{IL} + [TOPO]_{IL}}$

3.2 Extraction mechanism

According to the results of the above section, the extraction equilibrium of lithium by HBTA and TOPO in [C₂mim][Tf₂N] can be described by the following steps:

(1) Solubility and deprotonation (dissociation) of HBTA :



The HBTA partition ratio of HBTA between IL and aqueous phases, and the acidity constant can be written as follow:

$$D_{\text{HBTA}} = \frac{[\text{HBTA}]_{\text{aq}}}{[\text{HBTA}]_{\text{IL}}} \quad (4)$$

$$K_{\text{a}} = \frac{[\text{BTA}^{-}]_{\text{aq}}[\text{H}^{+}]_{\text{aq}}}{[\text{HBTA}]_{\text{aq}}} \quad (5)$$

We must take into consideration all forms of A (*i.e.*, A⁻ and HA), the distribution ratio becomes:

$$D_{\text{HBTA}} = \frac{[\text{HBTA}]_{\text{aq}} + [\text{BTA}^{-}]_{\text{aq}}}{[\text{HBTA}]_{\text{IL}}} \quad (6)$$

These two phenomena are extremely related, for this reason, they are presented together. In fact, the partition ratio of HBTA (solubility) increases at high pH, because of the dissociated form of the acid A⁻, increases [28].

(2) Coordination of lithium ions by BTA⁻:

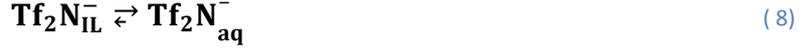


Where, (aq) and (IL) represent aqueous phase and organic phase, respectively. While (n) represents the number of deprotonated HBTA molecules involved in the extracted complexes.

There are two possibilities, either n=1, the complex extracted will be neutral or n>1, in this case, a third step called charge balancing is necessary.

(3) Charge balancing :

The ligand-lithium complex extracted to the IL is [Li.nBTA]_{IL}⁽ⁿ⁻¹⁾⁻. So, if n>1, this complex will be negatively charged. It creates a charge imbalance between the aqueous and the IL phases. To maintain the charge neutrality in both phases, the negative charge of the complex anion in the IL phase must be balanced either by displacing an anion from the IL phase to the aqueous phase or/and transferring a cation from the aqueous phase:



Or/and:



In the anion exchange mechanism, the compound moving from the IL to the aqueous phase can be Tf_2N^- of $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$. This mechanism was reported in some studies especially for the extraction of lanthanide(III) (Ln) by thenoyltrifluoroacetone (HTTA) [29].

For the cation exchange mechanism, the cation moving from the aqueous phase to the IL phase can be C_2mim^+ initially solubilized in the aqueous phase. This mechanism is reported very commonly with ionic liquid-based extraction systems [30].

Therefore, to determine the coordination number (n), we based our reasoning on the principle of electro-neutrality conservation between the two phases (aqueous phase and IL phase).

First, the equilibrium concentration of BTA^- in the aqueous phase was measured as a function of the initial lithium concentration in the aqueous phase (Table 3). The equilibrium aqueous concentration of BTA^- decreases by increasing the initial lithium concentration. This is because it forms a complex with lithium ions, which is transferred to the IL phase ($[\text{Li} \cdot n\text{BTA}]_{\text{IL}}^{(n-1)-}$). To determine therefore the coordination number (n), we must calculate the equilibrium IL concentration of BTA^- ($[\text{BTA}^-]_{\text{IL,eq}}$) corresponding to the amount of BTA^- that was extracted with lithium ions. It is calculated using the following equation:

$$[\text{BTA}^-]_{\text{IL,eq}} = [\text{BTA}^-]_{\text{aq,eq}}^0 - [\text{BTA}^-]_{\text{aq,eq}} \quad (10)$$

Where, $[\text{BTA}^-]_{\text{aq,eq}}^0$ is the equilibrium aqueous concentration of BTA^- without lithium ions in the aqueous phase (Table 3).

The plot of $[\text{BTA}^-]_{\text{IL,eq}}$ versus $[\text{Li}^+]_{\text{IL,eq}}$ presented in Figure 4(a), results in a slope of 1.07, suggesting that one BTA^- formed a complex with a lithium cation during the extraction process ($n = 1$).

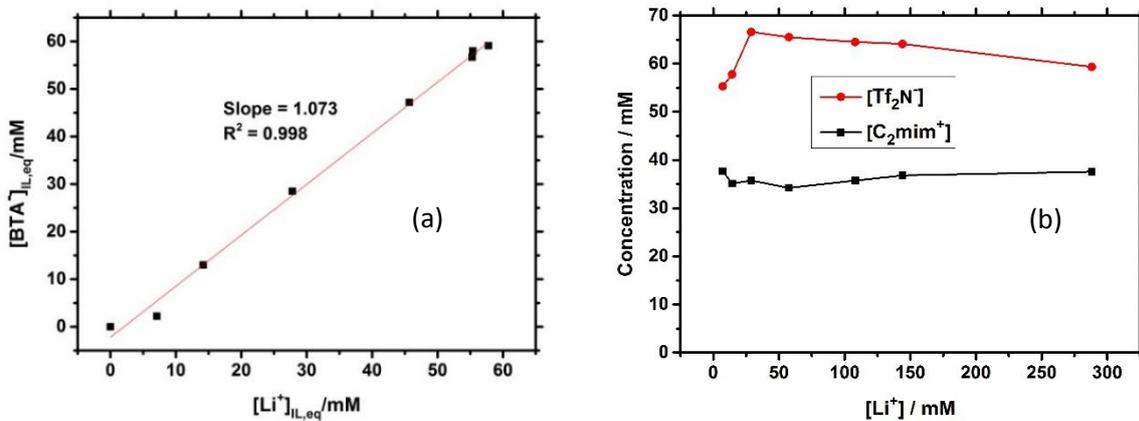


Figure 4. (a) The plot of $[\text{BTA}^-]_{\text{IL,eq}}$ versus $[\text{Li}^+]_{\text{IL,eq}}$. (b) Equilibrium aqueous concentrations of the IL constituents as a function of the initial lithium concentration in the aqueous phase.

The equilibrium aqueous concentrations of the IL constituents were also measured as a function of the initial lithium concentration in the aqueous phase (Figure 4(b)). It shows that by increasing the initial lithium concentration, the equilibrium aqueous concentration of C_2mim^+ remains constant, and that of Tf_2N^- increases a little bit in the beginning and then remains approximately stable. These findings suggest that there is no considerable transferring neither of the IL cation nor the IL anion to maintain the charge neutrality which confirms that the lithium-BTA⁻ complex extracted is neutral.

We can also notice that the IL anion has a higher solubility than the cation. In this context, the equilibrium aqueous concentrations of IL constituent ions were measured as a function of HBTA molar fraction to understand the higher solubility of IL anion in the aqueous phase. The results are presented in Figure 5.

Table 3. Equilibrium aqueous concentrations BTA⁻ as a function of the initial lithium concentration in the aqueous phase. Equilibrium IL concentrations of Li⁺ and BTA⁻ were calculated and presented. [HBTA] = 0.1 M and [TOPO] = 0.025 M in [C₂mim][Tf₂N]. Initial aqueous pH = 11.3.

| [Li ⁺] _{aq,init} /mM | [Li ⁺] _{IL} /mM | [BTA ⁻] _{aq,eq} /mM | [BTA ⁻] _{IL,eq} /mM |
|--|---|---|---|
| 0.0 | 0.0 | 63.4±3.2 | 0 |
| 7.2±0.35 | 7.1±0.7 | 60.6±3.0 | 2.2±6.2 |
| 14.4±0.7 | 14.2±1.1 | 50.4±2.5 | 13.0±5.7 |
| 28.8±1.4 | 27.8±1.4 | 34.9±1.7 | 28.5±4.9 |
| 57.6±2.9 | 45.7±2.3 | 16.2±0.8 | 47.2±4.0 |
| 108.1±5.4 | 55.3±2.8 | 6.7±0.3 | 56.7±3.5 |
| 144.1±7.2 | 55.4±2.8 | 5.4±0.3 | 58.0±3.4 |
| 288.2±14.4 | 57.8±2.9 | 4.3±0.2 | 59.1±3.4 |

Figure 5 shows that by increasing the molar fraction of HBTA and decreasing the molar fraction of TOPO, the equilibrium aqueous concentration of C_2mim^+ decreases, and that of Tf_2N^- increases. Tf_2N^- aqueous solubility in aqueous phase increases, probably due to its exchange with BTA⁻, and C_2mim^+ solubility decreases, probably because it forms with BTA⁻ a new hydrophobic IL ([C₂mim][BTA]) that goes back to the IL phase. Therefore, these

variations of the IL constituent ions solubility are explained by the increasing of BTA^- concentration in the aqueous phase and not by the extraction of lithium.

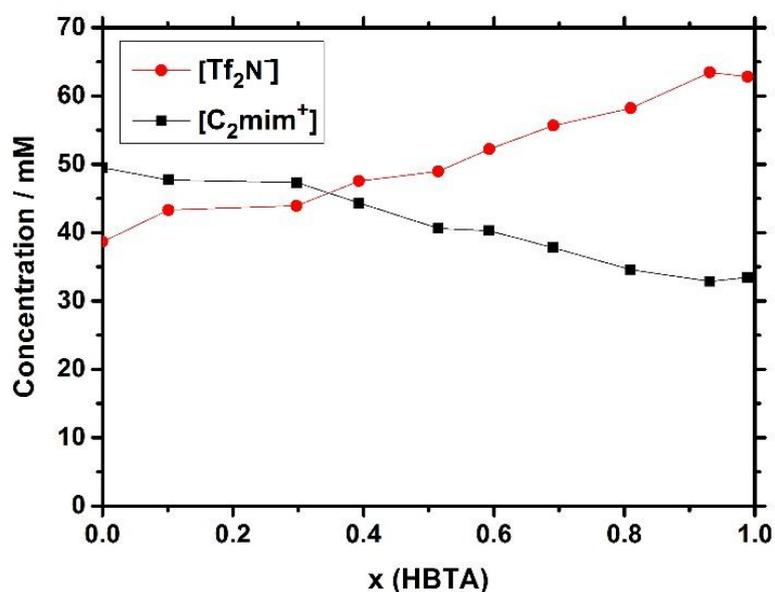


Figure 5. Equilibrium aqueous concentration of the IL constituents as a function of HBTA mole fraction.

To study the effect of the aqueous pH on the IL constituent ions solubility and HBTA deprotonation, their individual concentrations were measured as a function of the initial aqueous pH without lithium salt (Figure 6). It can be seen from this figure that with an increase of the pH, the equilibrium concentrations of Tf_2N^- and C_2mim^+ remain stable until $\text{pH}=10.5$. After that the equilibrium concentration of Tf_2N^- increases and that of C_2mim^+ decreases. This variation is associated with an increase of BTA^- concentration in the aqueous phase due to the deprotonation of HBTA at high pH as it can be seen in the same figure. In others words, increasing of BTA^- concentration in the aqueous phase is accompanied by an increase of Tf_2N^- aqueous solubility due to an anion exchange, and a decreasing C_2mim^+ solubility due to the formation of a new hydrophobic IL ($[\text{C}_2\text{mim}][\text{BTA}]$) that goes back to the IL phase.

Surprisingly, the deprotonation of HBTA starts at a pH value very high compared to its acid dissociation constant (pK_a) which was found to be equal to 6.4 [31]. In fact, HBTA can exist in solutions in two forms, keto and enol. The chemical equilibrium between the two forms is called keto-enol tautomerism. Before HBTA deprotonation, it must be in enol form [18]. According to literature, it is known that the keto-enol tautomerism to obtain the enol form is influenced by the temperature, and solvent [32]. In our conditions, the keto-enol tautomerism of HBTA is probably taking place at a high pH value, thus, the deprotonation of HBTA starts at a high pH value. We can ascribe these results to another phenomenon which is the tuning of pK_a due to IL influences. Atanassova et al. have developed an analytical method aiming at determining the pK_a values of some acidic ligands dissolved in water-

saturated IL phases and they have obtained evidence for a strong effect of the IL cation's chemical structure on the pK_a values [33].

Beyond a pH value of about 11.4, even if BTA^- concentration continues to increase, the equilibrium concentration of Tf_2N^- decreases and that of C_2mim^+ increases again. This is in concordance with the decrease of lithium extraction that was observed beyond that pH.

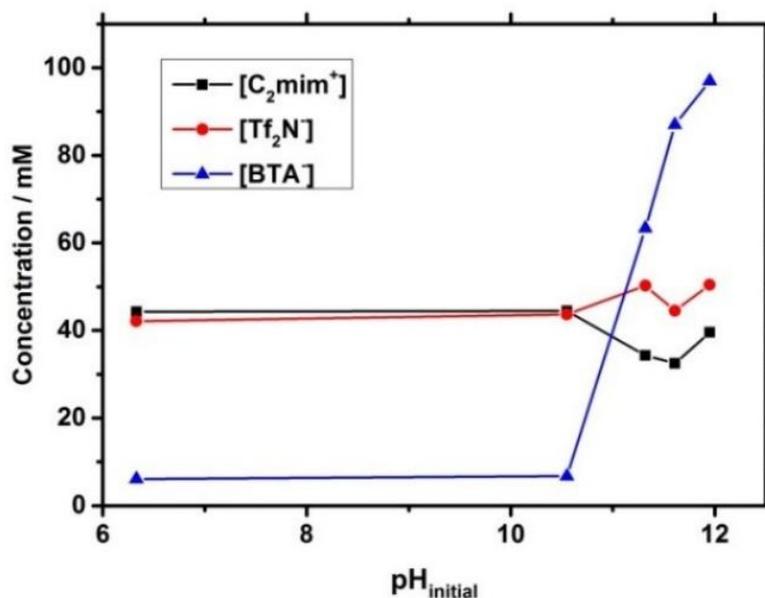


Figure 6. The equilibrium concentration of the IL constituents and BTA- in the aqueous phase as a function of the initial aqueous pH (without lithium salt). $[HBTA] = 0.1$ M and $[TOPO] = 0.025$ M in $[C_2mim][Tf_2N]$.

3.3 Effect of the IL composition

Seven different ILs were evaluated with respect to their extraction efficiency for lithium from an ammoniacal solution using 0.1 M HBTA. Six ILs are studied, with fixed anion (Tf_2N^-) and three different cations. Four of them are imidazolium-based ionic liquids with various alkyl chain lengths ($[C_nmim]$, where, $n = 2, 4, 6$ and 8), one is phosphonium-based IL and finally an ammonium-based IL. The seventh IL is an imidazolium-based IL with FSI^- as an anion.

The measured distribution ratios of lithium (D) are presented in Figure 7. As can be seen, as the alkyl chain length of C_nmim^+ is increased, D increases. The imidazolium-based ionic liquids give higher distribution ratios than phosphonium and ammonium-based ILs. In addition, when using the same IL cation (C_2mim^+), the IL with Tf_2N^- as anion shows a higher distribution ratio than that with FSI^- .

Increasing the length of the alkyl chain of the IL cation affect three parameters of the IL: the density decreases, the viscosity increases and the hydrophobicity increases [34]. The hydrophilic/hydrophobic behavior is the most significant for the recovery of products by solvent extraction using ILs [35]. Generally, when the IL cation hydrophobicity is increased, a downward shift in the extraction is usually observed. This is because usually the extraction is conducted by a cation exchange mechanism. Indeed, the IL cation exchange into the

aqueous phase becomes progressively more difficult as its alkyl chain length (i.e., hydrophobicity) increases [36].

The trend of lithium ion extraction in all ILs used in this study was: $[C_8mim][Tf_2N] > [C_6mim][Tf_2N] > [C_4mim][Tf_2N] > [C_2mim][Tf_2N] > [N_{1114}][Tf_2N] > [C_2mim][FSI] > [P_{66614}][Tf_2N]$.

Let's try to define which parameter could be responsible for this trend: (1) Hydrophobicity: In analogous systems employing thenyltrifluoroacetone (HTTA) as extractant to extract metals (M) in ILs, the authors found that the extraction is favored using more hydrophobic ILs [37]. This is not true in our case, because $[C_2mim][Tf_2N]$ is less hydrophobic than ammonium and phosphonium ILs. (2) The water solubility in ILs: M. Atanassova and co-workers suggest that an increase in water solubility leads to a decrease in extraction efficiency. This is also not true in our case, because $[C_2mim][Tf_2N]$ accept more water than ammonium and phosphonium ILs, and knowing that by increasing the length of alkyl chain of the IL cation the water solubility decreases [38]. (3) The viscosity: Increasing the IL viscosity leads to a decrease of the mass transfer and therefore may lead to a decrease in the extraction efficiency. This cannot explain the trend observed, because $[C_2mim][Tf_2N]$ is the less viscous of all the ILs used. (4) HBTA aqueous solubility: We may think that this trend is probably due to the fact that the lithium extraction depends on HBTA aqueous solubility, which in turn depends on the type of IL where it is initially dissolved. For this reason, we measured the aqueous solubility of HBTA in an ammoniacal solution at pH 11.1 without lithium ions. 0.1M HBTA was dissolved in the different ILs used. We found that the aqueous solubility of HBTA depends on the IL anion. In fact, for all ILs with Tf_2N^- as anion the aqueous concentration of BTA^- was around 30 mM while it was 22.8 mM for $[C_2mim][FSI]$. Therefore, HBTA aqueous solubility cannot explain the trend of lithium extraction observed, but, it should be remembered that a small variation of the initial experimental conditions of extraction can cause of BTA^- aqueous concentration. Indeed, probably there is not only one phenomenon that leads to obtain the observed trend but several phenomenons that play an active role. In addition to those mentioned above, others must be taken in account such as, for example, the activation energy and the solvation of the complex in the IL.

In view of the results, the subsequent studies were carried out using $[C_6mim][Tf_2N]$ which is less viscous than $[C_8mim][Tf_2N]$ and allows to get very high lithium extraction.

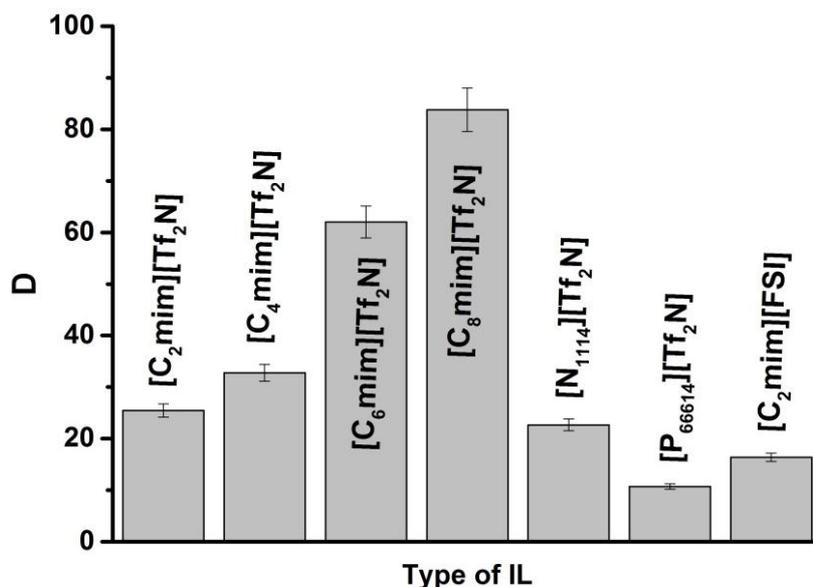


Figure 7. Effect of the type of IL on lithium extraction. Organic phase: 0.1M HBTA in [C_nmim][Tf₂N] (n= 2, 4, 6 or 8), [P₆₆₆₁₄][Tf₂N], [N₁₁₁₄][Tf₂N] or [C₂mim][FSI]. Initial aqueous pH = 11.1 and [Li⁺]_{aq, init} = 28.8 mM.

3.4 Selectivity and stripping studies

To assess the selectivity of HBTA in [C₆mim][Tf₂N] for lithium over other metals such as sodium (Na⁺) and calcium (Ca²⁺) (an alkaline ion (Na⁺) and an alkaline earth metal ion (Ca²⁺)), distribution ratios for the three metals were calculated as a function of the initial [Mⁿ⁺]/[Li⁺] (Mⁿ⁺: Na⁺ or Ca²⁺) ratio and as a function of a slight variations of aqueous pH. The results are presented in Table 5. At equal concentrations of all metals, the selectivity pattern was Ca²⁺ > Li⁺ > Na⁺.

A slight increase in the aqueous phase pH increases the lithium distribution ratio, while that of sodium remains negligible. This is consistent with the observations reported by Seely et al. [39], who studied lithium separation from alkaline metal ions and alkaline earth metal ions. It was found that the systems studied based on fluorinated b-diketone HFDMOD in organic solvents showed strong selectivity for lithium over alkaline ions while poor selectivity over alkaline earth metal ions.

An increase of [Mⁿ⁺] / [Li⁺] ratio greatly diminishes the lithium distribution ratio, while the sodium distribution ratio increases and that of calcium diminishes also but is still superior to the two alkali metal ions. It is possible to conclude that the high selectivity for lithium over sodium is not due to the synergistic effect and it depends on the initial concentrations.

Table 5. Distribution ratios of lithium, sodium and calcium according to pH and metal-lithium ratio ([M] / [Li], with M = Na or Ca). [HBTA] = 0.1 M in [C₆mim][Tf₂N], and [Li⁺]_{aq, init} = 28.8 mM. All metals were used as metal chloride in the same ammoniacal aqueous solution.

| pH = 11.10 ± 0.02 | pH = 11.30 ± 0.02 | pH = 11.50 ± 0.02 |
|-------------------|-------------------|-------------------|
| | | |

| [M]/[Li] | D_{Li} | D_{Ca} | D_{Na} | D_{Li} | D_{Ca} | D_{Na} | D_{Li} | D_{Ca} | D_{Na} |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1.0 | 1.1 | 50 | 0.0 | 13.4 | 50 | 0.1 | 35.2 | 50 | 0.1 |
| 5.0 | 0.1 | 3.2 | 0.7 | 0.5 | 50 | 0.7 | 0.5 | 50 | 0.7 |
| 10.0 | 0.1 | 1.7 | 1.4 | 0.1 | 2.9 | 1.4 | 0.1 | 3.9 | 1.4 |

The IL phase consisting of 0.1 M HTTA in $[C_6mim][Tf_2N]$ was first loaded with 28.8 mM Li^+/NH_4OH at pH=11.3. Stripping study was conducted by mixing the loaded organic phase and hydrochloric acid with different concentrations at different phase ratios (Figure 8). This was done in order to determine the effect of two parameters on the stripping efficiency: the acidity and the aqueous-IL phase ratio. From the results, it can be concluded that the stripping ratio increases by increasing the HCl concentration from 0.01M to 1M. And it decreases by increasing the aqueous-IL phase ratio from 1 to 10. The same trends were observed previously using the synergistic system HBTA-TOPO in organic solvents [26,20].

The back-extraction of lithium ions proceeds via a cation exchange with protons, which explains the need for a relatively high acidic stripping solution. The free hydrogen acid retained in the IL phase should get rid of it in order to avoid a decrease in the extraction efficiency in the next use of the IL phase. This decrease will be caused by a decrease of the aqueous pH which plays an important role in the extraction as reported previously. Regeneration of the stripped IL phase could be done with NaOH solution.

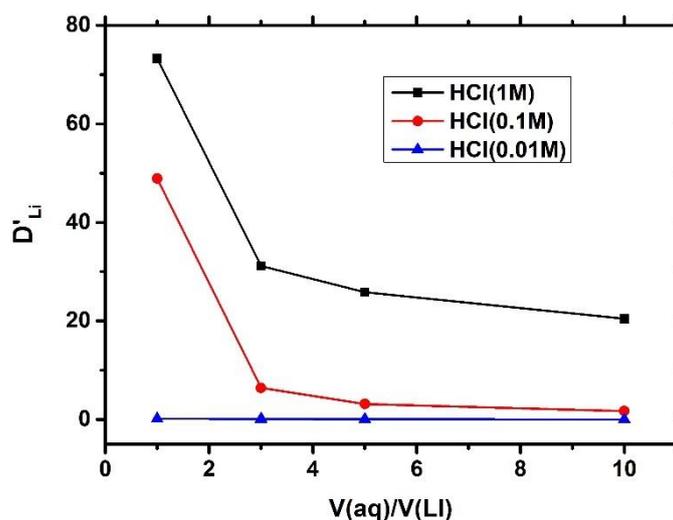


Figure 8. Stripping of lithium from loaded organic solutions: effect of HCl concentration at different aqueous to organic phase ratios. Organic phase: [HBTA] = 0.1 M in $[C_6mim][Tf_2N]$.

3.5 Extraction of Lithium with HBTA and TOPO dissolved in DESs

The extraction of Li^+ was carried out using 0.1 M HBTA and 0.025 M TOPO in three different DESs *viz.* DES_1: DL-menthol:acetic acid 1:1, DES_2: TBAB:decanoic acid 1:1, and finally DES_3: TBAB : DL-menthol 1:5. Aqueous feed solutions were used with varying pH values.

As mentioned previously, these DESs were tested because of their advantages compared to ILs, especially their straightforward preparation.

As shown in Figure 9, the extraction of Li^+ was very low for all DESs compared to ILs, especially at high pH values. The high solubility of acidic DESs acids (DES_1, DES_2) in aqueous solutions leads to a decrease of the aqueous pH as seen in which inhibits the lithium extraction. With regard to the DES_3 which is not acidic, the low extraction of lithium is due probably to the high viscosity and the presence of hydrogen bonds which decrease the solubility of the complex formed in the organic phase

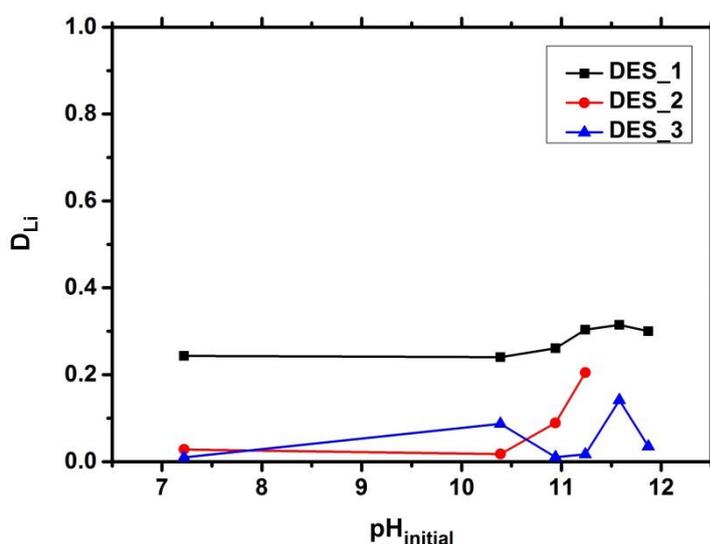


Figure 9. Effect of initial aqueous pH solution on lithium extraction using DESs as diluents. Organic phase: 0.1 M [HBTA] and 0.025 M [TOPO] in DES_1, DES_2 or DES_3. Aqueous phase: LiCl in ammoniacal solution. $[\text{Li}^+]_{\text{aq, init}} = 20 \text{ mM}$.

4 Conclusions

This study of the extraction of lithium ion by the Beta-diketone extractant benzoyltrifluoroacetone (HBTA) in IL demonstrates that this system could be considered as an alternative separation technique for lithium ions especially from brines. This new system is environmentally and economically favorable due to the use of harmless solvents and the absence of a synergistic agent. The extraction mechanism was studied using the electro-neutrality principle. It was found that the IL constituent ions don't participate in the lithium extraction, and a neutral lithium-extractant complex is extracted to the IL phase. This means that there is neither cation exchange nor anion exchange mechanisms that usually intervene in the extraction of metals using ILs. This can be considered as a positive point since it allows us to avoid the loss of the IL. In parallel, results revealed that there is some loss of the IL anion due to its exchange with deprotonated thenoyltrifluoroacetone (BTA^-). The extraction

system based on imidazolium ionic liquids ($C_n\text{mim}^+$) gave the highest ex-tractability of Li^+ . The distribution ratio of lithium was found to be increased as the alkyl chain length of $C_n\text{mim}^+$ is increased. The present findings suggest also that the selectivity for Li^+ over Na^+ is high while it is low over Ca^{2+} and a high stripping ratio can be obtained using relatively high concentrated hydrochloric acid. Primary results for the use of some DESs to replace ILs as diluents show that the extraction is very low. Further tests are needed to find DESs able to be used as good diluents for HBTA to extract lithium

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