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Metal Extraction with Ionic Liquids-Based Aqueous Two-Phase System

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Abstract

Although ionic liquids (ILs) have excellent properties, their use as extractants in solvent extraction has not completely overcome the problems encountered when organic solvents are used. In conventional solvent extraction, a hydrophobic IL should be used to establish an IL/water biphasic system to replace the conventional organic solvent with ILs. However, the number of water-immiscible ILs is currently limited, and most contain fluorinated anions which are expensive and environmentally nonbenign. Furthermore, the use of an organic solvent as a diluent agent cannot be avoided because of the very high viscosity of ILs. An IL-based aqueous two-phase system (ATPS) can overcome these drawbacks. This chapter summarizes the use of an IL-based ATPS for the separation of metals used in various areas of human life.

Keywords: aqueous two-phase system, metal extraction, solvent extraction, ionic liquid

1. Introduction

Solvent extraction is the most commonly used method to separate metal ions. This technique is performed by mixing the aqueous phase containing metal salt with an organic phase containing an extraction agent (extractant) [1]. The simplicity with which the parameters controlling extraction, such as pH of the aqueous solution, extractants and diluent, can be changed is a major advantage of solvent extraction [2]. However, it is not environmentally friendly as it requires a large volume of organic solvents which are often toxic and/or flammable. Using ILs, with their excellent properties such as near-zero vapor pressure, good chemical and thermal stability and the tunability of their physicochemical properties by altering the substitutive groups, may overcome the problems of organic solvents [3].

In conventional solvent extraction, a hydrophobic IL should be used to create an IL/water biphasic system to replace the conventional organic solvent with ILs. However the number of water-immiscible ILs is currently limited, and most contain fluorinated anions which are expensive and environmentally nonbenign, such as PF_6^- , which can decompose to a dangerous HF gas in the presence of water [4]. Furthermore, the use of organic solvent as a diluent cannot be avoided because of the very high viscosity of ILs [5]. On the other hand, the use of ILs as an extractant in conventional solvent extraction has not completely resolved the drawbacks encountered when organic solvents are used as diluents. An IL-based aqueous two-phase system (ATPS) can overcome these disadvantages. This chapter summarizes the use of an IL-based ATPS for the separation of metals. Metals are widely used in many aspects of human life, and their existence in the environment at high concentrations is a cause for concern. For a better understanding of this topic, we will begin with a brief discussion of ILs and ATPSs.

2. Extraction of metal ions

Metal ion extraction is a hot topic and is important economically and environmentally. Metals are obtained from ores or scraps through metallurgical processes and then manufactured into final products used by humans, either directly or indirectly. The processing of raw materials into final products produces waste containing metal ions. These products are utilized and later discarded as waste. Metal ion extraction is an effort to recover the metal ions both from ores and from waste due to their limited availability in nature. In addition, metal ion extraction from metal-containing waste can reduce the level of environmental pollution. Therefore, an effective, efficient, economic and environmentally friendly method for the recovery of metal ions from ores and waste is an absolute necessity.

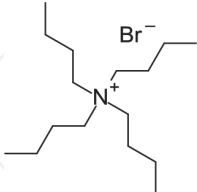
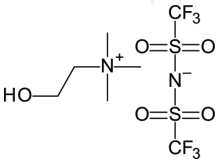
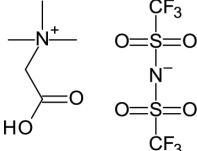
A number of processes have been explored for metal ion recovery, such as precipitation [6], reverse osmosis [7], adsorption [8], ion exchange [9] and solvent extraction using organic solvents [10]. Solvent extraction (liquid-liquid extraction) is the most commonly used method for the separation of metal ions [2]. In this technique, the aqueous solution of metal salt is mixed with an organic solvent containing an extraction agent (extractant). The metal ions form a hydrophobic complex with the extractant and migrate to the organic phase. The migration of complexes from the aqueous to the organic phase is driven by the difference of the complexes' affinity towards the aqueous phase and organic phase, as well as the relative solubility of the complexes in both phases. Solvent extraction can be implemented in a continuous mode and is suitable for the processing of high metal feed concentrations. However, the main disadvantage of this method is that it uses a large amount of organic solvents, such as kerosene, toluene, dichloromethane or diethyl ether, which are often toxic and/or flammable and therefore environmentally unfriendly [2]. Not only are their volatility and flammability an issue, but these organic solvents also have a negative impact on human health if their vapors are emitted into the air. ILs can be used to solve the problem faced when organic solvents are used as extractants in conventional liquid-liquid extraction.

3. Ionic liquid and aqueous two-phase system

Ionic liquids (ILs), according to the widely accepted definition, are molten salts under 100°C. The most investigated ILs are comprised of organic cation such as imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium, and their counterions can be either inorganic (e.g. tetrafluoroborate, hexafluorophosphate, chloride) or organic (e.g. trifluoromethylsulfonate, bis[(trifluoromethyl) sulfonyl]imide) anions [11]. ILs possess many unique physicochemical properties such as low vapor pressure, high thermal stability, high viscosity, good solvation ability, wide electrochemical windows, wide liquid range and tunable polarity [3, 12]. Tuning of these properties by combining the cations and anions makes ILs unique compounds for applications in different areas [13]. With these properties, using ILs instead of organic solvents as extractants in solvent extraction can reduce the negative impact on the environment.

The application of ILs in metal ion extraction is very promising. The main problem is their solubility in the aqueous phase, which can decrease the extraction efficiency. To overcome this issue, a hydrophobic IL can be used. However, hydrophobic ILs are partly soluble in the acidic aqueous solutions from which metal ions are extracted, which results in a costly undesirable loss [14]. In addition, hydrophobic ILs are still limited, and most contain fluorinated anions which can be expensive and environmentally nonbenign [5, 15]. Due to the very high viscosity of ILs, the diffusion of solute from the aqueous to the organic phase probably is slow, thus requiring either a longer stirring time [16] or an organic solvent which can be flammable and toxic as diluent agent. An ATPS can resolve the issues associated with the hydrophobic properties and high viscosity limitations. By using the ATPS, a more hydrophilic IL can be employed as the extractant because this technique needs a water-soluble IL. The ILs used in the ATPS are listed in **Table 1**.

The ATPS was accidentally discovered by Martinus Willem Beijerinck (1896) whilst mixing an aqueous solution of starch and gelatin. However, its real application was developed by Per-Åke

Acronym	Chemical name	Molecule structure	
TBAB	Tetrabutylammonium bromide		(b) (c)
[Chol][NTf ₂]	Choline bis(trifluoromethylsulfonyl) imide		(a) (d)
[Hbet][NTf ₂]	Betainium bis(trifluoromethylsulfonyl) imide		(a) (d)

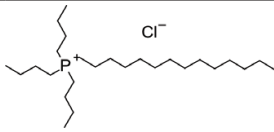
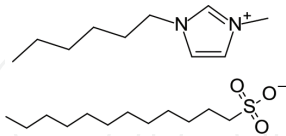
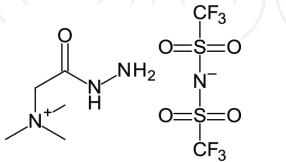
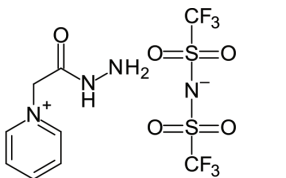
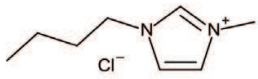
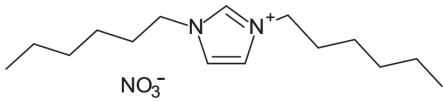
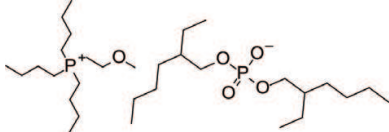
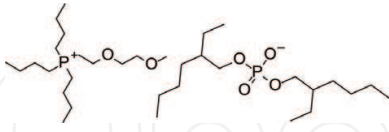
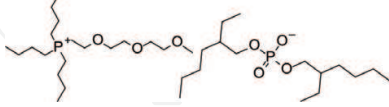
Acronym	Chemical name	Molecule structure	
[P ₄₄₁₄][Cl]	Tributyltetradecyl phosphonium chloride		(b) (d)
[C ₆ C ₁ im][C ₁₂ SO ₃]	1-Hexyl-3-methyl imidazolium dodecyl sulfonate		(b) (c)
[Nxyzhcm][NTf ₂] Girard's T cation	(Hydrazinocarbonylmethyl) trimethylammonium bis(trifluoromethylsulfonyl)imide		(b) (d)
[Phcm] [NTf ₂] Girard's P cation	(Hydrazinocarbonylmethyl)pyridinium bis(trifluoromethylsulfonyl)imide		(b) (d)
[C ₄ C ₁ im]Cl	1-Butyl-3-methylimidazolium chloride		(b) (c)
[C ₆ C ₆ im][NO ₃]	1,3-Dihexylimidazolium nitrate		(b) (d)
[P ₄₄₄ E][DEHP]	Tri-n-butyl-2-methoxyethylphosphonium bis(2-ethylhexyl)phosphate		(b) (d)
	Tri-n-butyl[2-(2-methoxyethoxy)ethyl]phosphonium bis(2-ethylhexyl)phosphate		
	Tri-n-butyl-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]phosphonium bis(2-ethylhexyl)phosphate		

Table 1. Ionic liquids employed in ATPS for separation of metal ions with (a) or without (b) an extra extractant other than IL, with (c) or without (d) a salting-out agent.

Albertsson [17]. Under specific thermodynamic conditions, an ATPS is spontaneously formed by mixing the aqueous solutions of two chemically different hydrophilic polymers or by combining the aqueous solutions of a polymer and an electrolyte, which in turn separate two immiscible aqueous phases in equilibrium—a polymer-enriched top phase and a polymer or an electrolyte-enriched bottom phase [18]. The phase separation of the polymer-polymer

system is derived by the steric exclusion of large aggregates generated by the interaction between the polymer and water. With a polymer-salt ATPS, the salt absorbs a large amount of water, and the similar steric exclusion occurs [19].

Conventional polymer-based ATPSs have been largely exploited since the 1980s and mainly consist of mixtures of two incompatible polymers or a polymer and a salt that induces salting out. However, the use of polymer-based ATPS for separation is restricted by the similarity in the polarities of the two phases. By using ILs instead of polymer, it is easier to adjust the polarity phases by changing the substitutive groups of ILs [15, 20].

In the past few years, research on biphasic systems with ILs has received crucial attention for the development of novel and more efficient separation processes [21]. The phase separation of systems composed of ILs and water can be induced by temperature. These systems are characterized by either an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST). At a temperature higher than the UCST, the organic phase (ILs) is completely miscible with water, and a homogeneous solution is obtained. Application of this method for metal ion separation allows the reaction between the metal complex and ILs to occur at the entire volume of the solution and does not depend on the metal complex' diffusion from the aqueous to the organic phase, which is slower due to the high viscosity of ILs. Therefore, mixture stirring and organic solvents are unnecessary. In other words, the reaction rate is only determined by the kinetics of the chemical reactions [22]. Upon cooling, the phases separate, and the metal complex is extracted to the organic phase. In a system with an LCST, a homogeneous mixture is formed at temperatures below the LCST, and it returns to a two-phase system when its temperature is higher than the LCST. These temperature-dependent phase transitions, known as homogeneous liquid-liquid extraction (HLLE), coalescence extraction or phase-transition extraction, have proven to be highly advantageous in the selective separation of metals [23]. Because HLLE is composed mainly of water and no organic solvent is needed, which is a feature of the classical ATPS, we believe that HLLE can be categorized as a more recent ATPS. In HLLE, a salting-out agent is not needed because phase separation is induced by temperature (temperature-dependent separation). In the next section, we will discuss several articles reporting the extraction of metals using an ATPS composed of ILs with and without a salting-out agent.

4. IL-based ATPS for metal separation

4.1. ATPS with salting-out agent

As with ATPSs in general, an ATPS composed of ILs and a salting-out agent has a unique phase diagram under a particular set of conditions, such as pH and temperature (**Figure 1**). This phase diagram, known as a binodal curve, is like a fingerprint identifying the potential working area of the ATPS. In this example (**Figure 1**), the total composition of the mixture, the composition of each phase and the critical point are defined as M, D, B and C, respectively. The total mixture compositions above the binodal curve fall into the biphasic regime, whereas mixture compositions below the solubility curve are homogeneous [15]. The salting-out agent

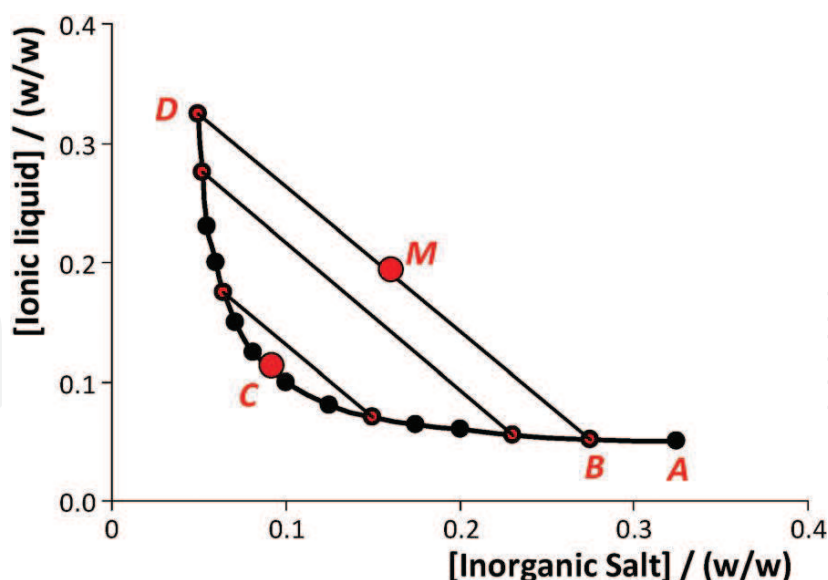


Figure 1. Phase diagram for a hypothetical system composed of polymer + inorganic salt + water (weight fraction units).

in ATPS is employed to separate the more hydrophobic agents from the more hydrophilic one. The general salting-out agents used in combination with ILs include inorganic salt [24], carbohydrates [25] and polymer [26]. However, to the best of our knowledge, carbohydrates have not been used as salting-out agents for metal ion extraction in combination with ILs.

Ammonium sulphate was used as a salting-out agent incorporated with tetrabutylammonium bromide (TBAB) for Cr (VI) separation. The results showed that the extraction of Cr (VI) was influenced by pH due to the existence of HCrO_4^- as the predominant species at pH 5.5. Therefore, Cr (VI) was satisfactorily extracted into the upper phase at pH 5, where its extraction percentage was found to be 93–98% with the following extraction mechanism:



On the other hand, the extraction percentage of Cr (III) was below 1.0% in all cases, indicating that this system was very selective when used for separating Cr (VI) from Cr (III). The $(\text{NH}_4)_2\text{SO}_4$ increase resulted in an increase in the extraction of Cr (VI) attributed to the progressive increase in the hydrophobicity of upper phase [27]. This system was also used to separate cadmium from cobalt, copper, iron (III) and zinc. The upper phase permitted the complete extraction of Cd^{2+} over the widest possible ranges of pH (1–10) with recovery in the range of 91–99%. Almost complete extraction of Cd^{2+} was obtained even though the concentration of Cd^{2+} in the mixture was far lower (20 μg) than the concentration of Co^{2+} , Cu^{2+} , Fe^{3+} and Zn^{2+} (2 mg for each) which coexisted with Cd^{2+} . The proposed method also successfully detected trace Cd in zinc nitrate [28]. In collaboration with tributyl(tetradecyl)phosphonium chloride $[\text{P}_{44414}][\text{Cl}]$, a certain concentration of sodium chloride also underwent temperature-induced phase separation (TIPS); thus it can be considered a thermomorphic mixture applicable to HLLE (IL-ABS-HLLE).

A system composed of 40% $[\text{P}_{44414}][\text{Cl}]$ and lower than 11% NaCl showed the LCST and therefore has been used to separate Co (II) and Ni (II). Ni (II) was only poorly extracted to the IL-rich phase (distribution ratio, $D = 0.1$), and extraction did not improve with increased NaCl

content in the mixture up to 11 wt%. On the other hand, Co (II) extraction improved, with D values up to 100 at 11 wt% NaCl. This is because Co (II) easily forms extractable anionic chloride complexes, whilst Ni (II) does not, even at high chloride concentrations [29].

In the case of polymer salting out, Zheng et al. reported the use of polyethylene glycol (PEG) incorporated with 1-hexyl-3-methyl imidazolium dodecyl sulfonate ($[\text{C}_6\text{C}_1\text{im}][\text{C}_{12}\text{SO}_3]$) IL for the extraction of gold (III) from an aqueous solution. Gold (III) was quantitatively extracted to the IL phase in the range of pH 1.13–1.90 with extraction percentages of 97.56% (PEG 6000), 76.60% (PEG 4000) and 71.83% (PEG 2000) in 5 min, and thereafter the extraction was not related to vibration time. It was also confirmed that the extractability of gold (III) was derived by the reaction between the cation of IL with the gold chloro complex anion [30].

An IL-based ATPS with a salting-out agent was also successfully applied to the separation of radioactive elements. An ATPS composed of 1-butyl-3-methylimidazolium chloride, $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and K_2HPO_4 separated no-carrier-added (NCA) ^{109}Cd which was produced by irradiation of the $^{\text{nat}}\text{Ag}$ target with a α -particle from bulk Ag. The salt-rich phase was predominantly alkaline as a result of the hydrolysis of K_2HPO_4 to produce KOH and H_3PO_4 . Therefore, both Ag^+ and Cd^{2+} were in anionic form, i.e., $\text{Ag}(\text{OH})_2^-$ and $\text{Cd}(\text{OH})_4^{2-}$ which then reacted with the cation of IL. However, the affinity of $\text{Ag}(\text{OH})_2^-$ to the IL cation is greater than $\text{Cd}(\text{OH})_4^{2-}$; thus, the extractability of bulk Ag was higher. Under optimum conditions, the extraction percentage of both the bulk Ag and NCA ^{109}Cd in the IL phase reached 87% for bulk Ag and 4% for NCA ^{109}Cd , respectively, and an overall separation of 91% NCA ^{109}Cd free from bulk Ag was finally achieved by re-extraction twice with 0.1 mL IL to free from the bulk Ag of the salt-rich phase [31].

Thus far in our search, an ATPS with a salting-out agent for metal ion separation is still limited. However, the application of ILs in collaboration with a salting-out agent reported in the above studies confirms that an ATPS consisting of ILs and a salting-out agent is a highly efficient and selective means of separating metal ions.

4.2. ATPS without salting-out agent (HLLC)

Chemical separation methods aim to simplify and miniaturize sample preparation procedures to consume fewer solvents and reagents and drastically reduce laboratory waste [32]. Unconventional liquid-liquid extractions such as HLLC have been developed with this intent [33]. Probably because HLLC does not require a salting-out agent, this method is more often used in metal ion separation than an ATPS with a salting-out agent. IL is mixed with an aqueous solution of metal ions and heated to a temperature higher than the UCST (for mixtures with a UCST) or cooled to lower than the LCST (for mixtures with an LCST) to obtain a homogeneous solution. The temperature of the solution is then returned to its original temperature allowing for phase separation. This technique sometimes requires an extra extractant in addition to the ILs in order to increase the extraction percentage. In this case, the IL only acts as a separator agent. Choline hexafluoroacetylacetonate and betaine, whose structures are shown in **Figure 2**, have been widely applied as extractants for metal ion separation using the HLLC technique.

Choline bis(trifluoromethylsulfonyl)imide $[\text{Chol}][\text{Tf}_2\text{N}]$, in combination with choline hexafluoroacetylacetonate $[\text{Chol}][\text{hfac}]$ as specific chelating agents mixed with water that displays thermomorphic behaviour with a UCST of 72°C, has been employed for neodymium (III)

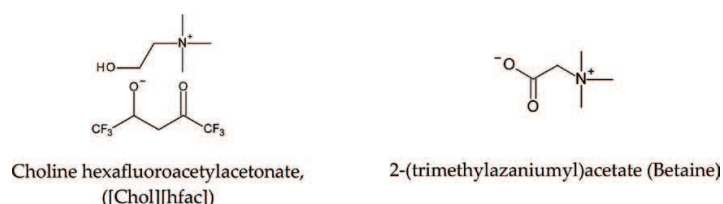


Figure 2. Molecule structures of the extractants applied in HLLE for metal ion extraction.

extraction. The results demonstrate that the heating temperature of mixture greatly influences the extraction percentage. Under heating temperature lower than 45°C , almost no Nd (III) was extracted. The extraction of Nd (III) was less than 50% at 60°C due to decreasing viscosity, and by heating the mixture to 80°C (higher than the UCST), almost 100% of Nd (III) was extracted after shaking for 5 s when 60 mmol kg^{-1} $[\text{Chol}][\text{hfac}]$ was contained in the organic phase. Nd (III) was extracted at pH 5.5 and sharply decreased to pH 3–5 because of the protonation of $[\text{hfac}]^{-}$ anion. Extraction stoichiometry was confirmed by slope analysis, revealing that Nd (III) was extracted by $[\text{Chol}][\text{hfac}]$ in a 1:4 ratio [34].

Unlike the variation of the temperature below the UCST, the application of different temperatures around and above the UCST had no influence on the extraction equilibrium and the percentage extraction of Nd (III) by a HLLE system composed of betainium bis(trifluoromethylsulfonyl) imide $[\text{Hbet}][\text{NTf}_2]$ as the organic phase and betaine as the extractant with a UCST of 55°C . As with the heating temperature, settling temperature tested at $6\text{--}50^{\circ}\text{C}$ had no effect on the extractability. The complex formed during extraction can be described as $[\text{Nd}_2(\text{bet})_3(\text{H}_2\text{O})_y]^{3+}$.

Electrical neutrality can be achieved by bis(trifluoromethylsulfonyl)imide (or chloride or nitrate) counterions [5]. This similar system was also applied to metal ion separation including La^{3+} , Pr^{3+} , Nd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Y^{3+} , Sc^{3+} , Ga^{3+} , In^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Ag^{+} . Sc^{3+} , Ga^{3+} and In^{3+} were almost completely extracted to the organic phase, and the distribution ratios of Mn^{2+} , Ni^{2+} , Zn^{2+} and Ag^{+} are very low (almost no extraction). Cu^{2+} was reasonably well extracted to the IL phase, indicating the possibility of separating Cu^{2+} from Ni^{2+} , Zn^{2+} and Mn^{2+} . The distribution ratios for lanthanide ions were about 10 with no significant differences between the different lanthanide ions [16].

Another study of this system specifically focused on scandium (III) extraction from red mud leachates. Individual study on Sc (III) extraction indicates that the distribution of the Sc (III)– $[\text{Hbet}][\text{NTf}_2]$ complex is solely controlled by the difference in solubility in the aqueous phase and the IL phase. Red mud consists of the major elements iron, aluminum, titanium, calcium, sodium and silicon and some minor constituents including scandium and other rare-earth elements. Therefore, the tested metal ions include the rare-earth elements Y (III), La (III), Ce (III), Nd (III), and Dy (III) and the major elements Al (III), Fe (III), Ca (II), Ti (IV) and Na (I) and were compared to the extraction of Sc (III). A high affinity for Sc (III) (extraction percentage, $\%E > 90\%$) as compared to the other rare-earth metal ions ($\%E$ between 4% and 12% at an initial pH of 3, depending on the rare-earth element) was shown by $[\text{Hbet}][\text{NTf}_2]$, as well as a very low affinity for almost all the major elements present in red mud, except for Fe(III), which is very similar to the $\%E$ of Sc (III). The higher $\%E$ for Fe (III) and Sc (III) was derived by the smaller ionic radius, and thus there are higher charge densities than the trivalent lanthanide

ions and Y (III). Furthermore, the ATR-FTIR spectra of the IL phase of the extraction mixture, loaded with varying amounts of scandium, showed that coordination of the IL to the scandium ion occurs via the carboxylic acid function of the cation. Sc(III) was extracted in a ligand-to-metal ratio of 3:1, as suggested from the calculations based on the maximum loading [35].

Another mixture having thermomorphic properties with the UCST is demonstrated by the IL analogues of Girard's reagents ($[N_{xyz}hcm][NTf_2]$), in which hcm is hydrazinocarbonylmethyl. $[N_{222}hcm][NTf_2]$ was selected as the extractant for extraction of four common metal ions, viz., $[Ni(OH_2)_6]^{2+}$, $[Co(OH_2)_6]^{2+}$, $[Cu(OH_2)_6]^{2+}$ and $[Cr(OH_2)_6]^{3+}$. To create a homogeneous solution, the mixture of IL and aqueous solution of metal ions was heated at 60°C for 20 min. The order of distribution coefficients was Cu (II) (28586) >> Ni (II) (767) > Co (II) (36) > Cr (5.4), which reflects the well-known Irving-Williams series [36]. Nitrate IL (1,3-dihexylimidazolium nitrate, $[C_6C_6im][NO_3]$) was used in metal ion separation for the first time. Most extraction experiments were performed with an aqueous phase containing 6 M $NaNO_3$, wherein the solubility of IL was much lower (<0.5 wt%). IL presaturated with a 6 M $NaNO_3$ solution had a slightly higher viscosity than a water-saturated sample, but the viscosity was still lower than 50 mPa·s at room temperature, which is far lower than water-saturated trihexyltetradecylphosphonium nitrate (265 mPa·s). First-row transition metals were far less efficiently extracted than the rare earths. Among the tested transition metals, no clear trend could be observed; all percentage extractions were around 30%. For the rare earths, as the charge density increased ($La^{3+} < Nd^{3+} < Sm^{3+} < Sc^{3+}$), the %E decreased.

This system was also applied to Sm (III)/Co (II) separation to mimic a $SmCo_5$ magnet. The higher the molar concentration of $NaNO_3$, the more Sm (III) was extracted, facilitated by the inner salting-out effect. At 6 M $NaNO_3$, nearly 100% of the Sm (III) was extracted. However, there was also a significant co-extraction of Co (II), of about 30%. The extraction was not affected by the shaking time or the pH of the aqueous solution. La (III)/Ni (II) pairs were investigated to mimic nickel metal hydride batteries. A synthetic solution of 9.6 g L⁻¹ La (III) and 35.4 g L⁻¹ Ni (II) was prepared. La (III) was fully extracted, and only 15% of Ni(II) was co-extracted into the IL phase [37].

HLLE with a UCST has been also applied to U (VI) extraction, which has a strong radioactive nature from the aqueous HNO_3 solution. In this system, betainium bis(trifluoromethylsulfonyl) imide ionic liquid $[Hbet][Tf_2N]$ does not only act as a solvent but also as an extractant with an extraction percentage of 60%. The *D* value in both HLLE and conventional liquid-liquid extraction decreased with an increase in the initial $[HNO_3]$ and were almost consistent with each other. That the carboxyl group of $[Hbet]^+$ takes part in the extraction of U (VI) has been confirmed by the fact that the *D* value clearly decreases with an increase in $[H^+]$; the plot seems to follow a linear relationship with a slope of 1.2; it is independent of $[NO_3^-]$. The decrease in *D* value was derived by decreasing the deprotonated carboxyl group due to the increase in $[H^+]$. This mechanism was also confirmed by the fact that the *D* values were almost zero using an unfunctionalized IL ($[TMPA][Tf_2N]$) [38].

Previous applications of an IL-based HLLE have been a mixture of ILs with water with a UCST. Some ILs that form a homogeneous phase below the critical solution temperature were also applied in metal ion separation. Gras et al. [39] reported the formation of a two-phase system by mixing concentrated hydrochloric acid with tributyl(tetradecyl) phosphonium

chloride ($[P_{44414}][Cl]$), which is water miscible below the critical solution temperature. The use of concentrated hydrochloric acid allows for the simultaneous leaching and extraction of metal ions. This system was used to separate Fe (III), Pt (IV), Ni (II) and Co (II). After stirring in a rotator for 2 hours until complete dissolution, the mixture was then placed in a heating bath for 6 hours until phase separation. Fe (III) and Pt (IV) were close to quantitatively extracted towards the IL-rich phase for all experimental mixtures for temperatures of all system. Co (II) was also efficiently extracted from 75 to 97% in mixtures composed of 10.2% IL, 19% HCl and 70.8% water and 18.6% IL and 15.7% HCl and 65.7% water, respectively, at 50°C, whilst the majority of Ni (II) remained in the HCl-rich phase. The extraction mechanism was derived by the anion exchange between a metalchlorocomplex with Cl^- of IL. The selectivity of this system was evaluated towards Co (II) and Mn (II), which is relevant for the recycling of NiMH batteries. Mixtures containing 17.8% IL, 25.9% HCl, 56.3% H_2O and 18.1% IL, 20.8% HCl and 61.1% H_2O at 50°C yielded a nearly pure Co(II) in the IL-rich phase, with a separation factor of 400 and 376, respectively. These promising results demonstrate that an acidic aqueous biphasic system can be used simply and efficiently for the critical separation of Co (II) and Ni (II) directly from the HCl leachates of NiMH batteries [39].

Another system, composed of IL-water with a dependent temperature homogeneous below the critical solution temperature, was obtained by mixing ether-functionalized ILs with bis(2-ethylhexyl)phosphate (DEHP), which is well known as a metal extractant anion with water. The cations investigated were tri-*n*-butyl-2-methoxyethylphosphonium ($[P_{444}E_1]$), tri-*n*-butyl[2-(2-methoxyethoxy) ethyl]phosphonium ($[P_{444}E_2]$) and tri-*n*-butyl-{2-[2-(2-methoxyethoxy)ethoxy]ethyl} phosphonium ($[P_{444}E_3]$). All synthesized chloride ILs ($[P_{444}E]Cl$) were fully miscible with water, whilst all synthesized DEHP ILs $[P_{444}E][DEHP]$ displayed LCST-phase behaviour. To determine the distribution ratios, four different aqueous solutions of approximately 5000 ppm of the metal ($CoCl_2$, $CuCl_2$, $NiCl_2$ and $ZnCl_2$) at a pH of around 3.5 were mixed with the IL $[P_{444}E_3][DEHP]$ in the homogeneous phase. The distribution ratio of Co (II), Ni (II), Cu (II) and Zn (II) were 4.4, 19, 34 and 25, respectively, which meets the Irving-Williams series. Indium and some rare earths formed the precipitation with the IL probably due to the strong complexation with the anion of IL [40].

5. Conclusion

This chapter reviewed several articles discussing the use of an IL-based ATPS for metal ion extraction. In general, an ATPS composed of ILs and a salting-out agent is excellent for metal ion separation because of its efficiency, selectivity and environmental friendliness. Due to the temperature dependence of a mixture comprised of ILs with water, it has been manipulated for metal ion extraction known as homogeneous liquid-liquid extraction (HLL). With this technique, a salting-out agent is not necessary. In some cases, ILs in HLL act as both an extractant and separator agent simultaneously. In other cases, the IL acts only as a separator agent. Therefore, an extractant should be added to the system in order to increase the extraction percentage of metal ions. HLL also showed high efficiency and selectivity in the metal ion extraction. Metal ions can be extracted by both an ATPS and HLL, including transition metals, rare-earth elements and radioactive substances.

Conflict of interest

No conflict of interest.

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References

- [1] Kislik V. Solvent Extraction, Classical and Novel Approaches. Amsterdam: Elsevier; 2011
- [2] Hoogerstraete TV, Wellens S, Verachttert K, Binnemans K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: Separations relevant to rare-earth magnet recycling. *Green Chemistry*. 2013;**15**:919-927. DOI: 10.1039/c3gc40198g
- [3] Matsumoto M. Ionic liquid-based supported liquid membranes. In: Mohanty K, Purkait MK, editors. *Membrane Technology and Applications*. Boca Raton, USA: CRC Press; 2012. pp. 305-316
- [4] Swatloski RP, Holbrey JD, Rogers RD. Ionic liquids are not always green: Hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chemistry*. 2003;**5**:361-363. DOI: 10.1039/b304400a
- [5] Hoogerstraete TV, Onghena B, Binnemans K. Homogeneous liquid-liquid extraction of rare earths with the betaine—Betainium bis(trifluoromethylsulfonyl)imide ionic liquid system. *International Journal of Molecular Sciences*. 2013;**14**:21353-21377. DOI: 10.3390/ijms141121353
- [6] Fu F, Xie L, Tang B, Wang Q, Jiang S. Application of a novel strategy-advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater. *Chemical Engineering Journal*. 2012;**189-190**:283-287. DOI: 10.1016/j.cej.2012.02.073
- [7] Lee KP, Arnot TC, Mattia D. A review of reverse osmosis membrane materials for desalination: Development to date and future potential. *Journal of Membrane Science*. 2011;**370**:1-22. DOI: 10.1016/j.memsci.2010.12.036
- [8] Lakherwar D. Adsorption of heavy metals: A review. *International Journal of Environmental Research and Development*. 2014;**4**:41-48

- [9] Nikoloski AN, Ang K. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Mineral Processing and Extractive Metallurgy Review*. 2014;**35**:369-389. DOI: 10.1080/08827508.2013.764875
- [10] Xie F, Zhang TA, Dresinger D, Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering*. 2014;**56**:10-28. DOI: 10.1016/j.mineng.2013.10.021
- [11] Liu J, Jonsson JÅ, Jiang G. Application of ionic liquids in analytical chemistry. *Trends in Analytical Chemistry*. 2005;**24**:20-27. DOI: 10.1016/j.trac.2004.09.005
- [12] Anderson JL, Armstrong DW. High-stability ionic liquids. A new class of stationary phases for gas chromatography. *Analytical Chemistry*. 2003;**75**:4851-4858. DOI: 10.1021/ac0345749
- [13] Joshi MD, Anderson JL. Recent advances of ionic liquids in separation science and mass spectrometry. *RSC Advances*. 2012;**2**:5470-5484. DOI: 10.1039/c2ra20142a
- [14] Ternova D, Boltoeva M, Cointeaux L, Gaillard C, Kalchenko V, Mazan V, Miroshnichenko S, Mohapatra PK, Ouadi A, Papaiconomou N, Petrova M, Billard I. Dramatic changes in the solubilities of ions induced by ligand addition in biphasic system $D_2O/DNO_3/[C_1C_4im][Tf_2N]$: A phenomenological study. *The Journal of Physical Chemistry. B*. 2016;**120**:7502-7510. DOI: 10.1021/acs.jpcc.6b05424
- [15] Freire MG, Cláudio AFM, Araújo JMM, Coutinho JAP, Marrucho IM, Lopes JNC, Rebelo LPN. Aqueous biphasic systems: A boost brought about by using ionic liquids. *Chemical Society Reviews*. 2012;**41**:4966-4995. DOI: 10.1039/c2cs35151j
- [16] Hoogerstraete TV, Onghena B, Binnemans K. Homogeneous liquid-liquid extraction of metal ions with a functionalized ionic liquid. *Journal of Physical Chemistry Letters*. 2013;**4**:1659-1663. DOI: 10.1021/jz4005366
- [17] Iqbal M, Tao Y, Xie S, Zhu Y, Chen D, Wang X, Huang L, Peng D, Sattar A, Shabbir MAB, Hussain HI, Ahmed S, Yuan Z. Aqueous two-phase system (ATPS): An overview and advances in its applications. *Biological Procedures Online*. 2016;**18**:18. DOI: 10.1186/s12575-016-0048-8
- [18] de Lemos LR, Santos IJB, Rodrigues GD, da Silva LHM, da Silva MCH. Copper recovery from ore by liquid-liquid extraction using aqueous two-phase system. *Journal of Hazardous Materials*. 2012;**237-238**:209-214. DOI: 10.1016/j.jhazmat.2012.08.028
- [19] Asenjo JA, Andrews BA. Aqueous two-phase systems for protein separation: A perspective. *Journal of Chromatography. A*. 2011;**1218**:8826-8835. DOI: 10.1016/j.chroma.2011.06.051
- [20] Pereira JFB, Rebelo LPN, Rogers RD, Coutinho JAP, Freire MG. Combining ionic liquids and polyethylene glycols to boost the hydrophobic-hydrophilic range of aqueous biphasic systems. *Physical Chemistry Chemical Physics*. 2013;**15**:19580. DOI: 10.1039/c3cp53701c

- [21] Kohno Y, Ohno H. Ionic liquid/water mixtures: From hostility to conciliation. *Chemical Communications*. 2012;**48**:7119-7130. DOI: 10.1039/c2cc31638b
- [22] Onghena B, Jacobs J, Meervelt LV, Binnemans K. Homogeneous liquid-liquid extraction of neodymium(III) by choline hexafluoroacetylacetonate in the ionic liquid choline bis(trifluoromethylsulfonyl)imide. *Dalton Transactions*. 2014;**43**:11566. DOI: 10.1039/c4dt01340a
- [23] Nockemann P, Thijs B, Pittois S, Thoen J, Glorieux C, Hecke KV, Meervelt LV, Kirchner B, Binnemans K. Task-specific ionic liquid for solubilizing metal oxides. *The Journal of Physical Chemistry. B*. 2006;**110**:20978-20992. DOI: 10.1021/jp0642995
- [24] JNC L. ABS composed of ionic liquids and inorganic salts. In: Freire MG, editor. *Ionic-Liquid-Based Aqueous Biphasic Systems*. Berlin Heidelberg: Springer-Verlag; 2016. pp. 27-35. DOI: 10.1007/978-3-662-52875-4_2
- [25] da Costa Lopes AM, Bogel-Lukasik R. ABS constituted by ionic liquids and carbohydrates. In: Freire MG, editor. *Ionic-Liquid-Based Aqueous Biphasic Systems*. Berlin Heidelberg: Springer-Verlag; 2016. pp. 37-60. DOI: 10.1007/978-3-662-52875-4_3
- [26] Sadeghi R. ABS composed of ionic liquids and polymers. In: Freire MG, editor. *Ionic-Liquid-Based Aqueous Biphasic Systems*. Berlin Heidelberg: Springer-Verlag; 2016. pp. 61-88. DOI: 10.1007/978-3-662-52875-4_4
- [27] Akama Y, Sali A. Extraction mechanism of Cr(VI) on the aqueous two-phase system of tetrabutylammonium bromide and $(\text{NH}_4)_2\text{SO}_4$ mixture. *Talanta*. 2002;**57**:681-686. DOI: 10.1016/S0039-9140(02)00076-0
- [28] Akama Y, Ito M, Tanaka S. Selective separation of cadmium from cobalt, copper, iron (III) and zinc by water-based two-phase system of tetrabutylammonium bromide. *Talanta*. 2000;**53**:645-650. DOI: 10.1016/S0039-9140(00)00555-5
- [29] Onghena B, Opsomer T, Binnemans K. Separation of cobalt and nickel using athermomorphic ionic-liquid-based aqueous biphasic system. *Chemical Communications*. 2015;**51**:15932-15935. DOI: 10.1039/c5cc06595j
- [30] Zheng Y, Tong Y, Wang S, Zhang H, Yang Y. Mechanism of gold (III) extraction using a novel ionic liquid-based aqueous two phase system without additional extractants. *Separation and Purification Technology*. 2015;**154**:123-127. DOI: 10.1016/j.seppur.2015.09.014
- [31] Ghosh K, Maiti M, Lahiri S, Hussain VA. Ionic liquid-salt based aqueous biphasic system for separation of ^{109}Cd from silver target. *Journal of Radioanalytical and Nuclear Chemistry*. 2014;**302**:925-930. DOI: 10.1007/s10967-014-3412-7
- [32] Anthemidis AN, Adam ISI. Development of on-line single-drop micro-extraction sequential injection system for electrothermal atomic absorption spectrometric determination of trace metals. *Analytica Chimica Acta*. 2009;**632**:216. DOI: 10.1016/j.aca.2008.10.078
- [33] Anthemidis AN, Ioannou K-IG. Recent developments in homogeneous and dispersive liquid-liquid extraction for inorganic elements determination. A review. *Talanta*. 2009;**80**:413-421. DOI: 10.1016/j.talanta.2009.09.005

- [34] Onghena B, Jacobs J, Meervelt LV, Binnemans K. Homogeneous liquid-liquid extraction of neodymium(III) by choline hexafluoroacetylacetonate in the ionic liquid choline bis(trifluoromethylsulfonyl)imide. *Dalton Transactions*. 2014;**43**:11566-11578. DOI: 10.1039/c4dt01340a
- [35] Onghena B, Binnemans K. Recovery of scandium(III) from aqueous solutions by solvent extraction with the functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide. *Industrial and Engineering Chemistry Research*. 2015;**54**:1887-1898. DOI: 10.1021/ie504765v
- [36] Blesic M, Gunaratne HQN, Jacquemin J, Nockemann P, Olejarz S, Seddon KR, Strauss CR. Tunable thermomorphism and applications of ionic liquid analogues of Girard's reagents. *Green Chemistry*. 2014;**16**:4115-4121. DOI: 10.1039/c4gc01159g
- [37] Depuydt D, den Bossche AV, Dehaen W, Binnemans K. Metal extraction with a short-chain imidazolium nitrate ionic liquid. *Chemical Communications*. 2017;**53**:5271. DOI: 10.1039/c7cc01685a
- [38] Mori T, Takao K, Sasaki K, Suzuki T, Arai T, Ikeda Y. Homogeneous liquid-liquid extraction of U(VI) from HNO₃ aqueous solution to betainium bis(trifluoromethylsulfonyl)imide ionic liquid and recovery of extracted U(VI). *Separation and Purification Technology*. 2015;**155**:133-138. DOI: 10.1016/j.seppur.2015.01.045
- [39] Gras M, Papaiconomou N, Schaeffer N, Chainet E, Tedjar F, Coutinho JAP, Billard I. Ionic-liquid-based acidic aqueous biphasic systems for simultaneous leaching and extraction of metallic ions. *Angewandte Chemie, International Edition*. 2018;**57**:1563-1566. DOI: 10.1002/anie.201711068
- [40] Depuydt D, Liu L, Glorieux C, Dehaena W, Binnemans K. Homogeneous liquid-liquid extraction of metal ions with non-fluorinated bis(2-ethylhexyl)phosphate ionic liquids having a lower critical solution temperature in combination with water. *Chemical Communications*. 2015;**51**:14183. DOI: 10.1039/c5cc05649g

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