

## A study of extraction of metals with aqueous two phase system for ionic liquids

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**Abstract-** Ionic liquids (ILs) have desirable properties that make them attractive as extractants in solvent extraction. However, the use of ILs in this application has not completely resolved the issues encountered when organic solvents are used. In traditional solvent extraction, a hydrophobic IL must be employed to establish an IL/water biphasic system that replaces the conventional organic solvent with ILs. However, the number of water-immiscible ILs is presently limited, and most of them contain fluorinated anions that are both costly and environmentally harmful. Additionally, the extremely high viscosity of ILs necessitates the use of an organic solvent as a diluent agent, which cannot be avoided. To address these concerns, an IL-based aqueous two-phase system (ATPS) can be utilized. This chapter provides an overview of the use of an IL-based ATPS for separating metals used in a variety of human applications.

**Keywords:** Ionic Liquids, Fluorinated ions, Viscosity of ILs, ATPs etc

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### I. Introduction

Metal ion separation is commonly accomplished through solvent extraction. This process involves mixing the aqueous phase, which contains metal salt, with an organic phase that contains an extraction agent (extractant). Solvent extraction is advantageous because the parameters that control extraction, such as pH of the aqueous solution, extractants, and diluent, can be easily modified. However, this method is not environmentally friendly due to the large volume of organic solvents required, which are often toxic and/or flammable. Ionic liquids (ILs), which possess excellent properties such as near-zero vapor pressure, good chemical and thermal stability, and the ability to tune their physicochemical properties by altering the substituent groups, may resolve the issues associated with organic solvents. In conventional solvent extraction, a hydrophobic IL is 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 such as PF<sub>6</sub><sup>-</sup>, which are expensive and environmentally hazardous. These anions can also decompose into dangerous HF gas in the presence of water. Additionally, the high viscosity of ILs necessitates the use of an organic solvent as a diluent. Nonetheless, using ILs as an extractant in conventional solvent extraction has not completely resolved the drawbacks encountered when organic solvents are used as diluents. The use of an IL-based aqueous two-phase system (ATPS) can mitigate these disadvantages. This paper provides an overview of the use of an IL-based ATPS for separating metals. Metals are utilized in various aspects of human life, and their presence in the environment at high concentrations is a cause for concern. To better understand this topic, we will briefly discuss ILs and ATPSs.

### Extraction of Metal ions

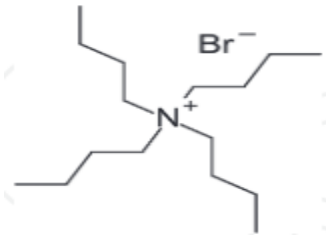
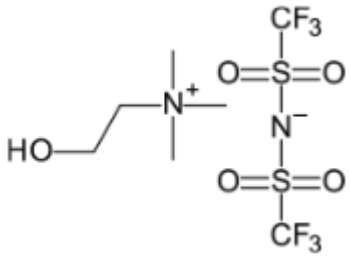
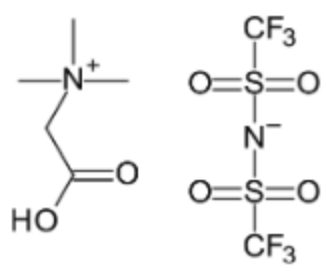
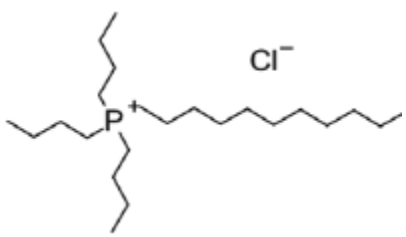
Metal ion extraction is a crucial process that has economic and environmental significance. Metals are obtained from ores or scraps via metallurgical processes, and then turned into final products that are utilized by humans, either directly or indirectly. During the processing of raw materials, waste containing metal ions is produced, which is later discarded. Recovering metal ions from ores and waste is important due to their limited availability in nature and to reduce environmental pollution. Several methods have been explored for metal ion recovery, including precipitation, reverse osmosis, adsorption, ion exchange, and solvent extraction using organic solvents. Solvent extraction, or liquid-liquid extraction, is the most commonly used technique for metal ion separation. In this process, the metal salt solution is mixed with an organic solvent containing an extraction agent, and the metal ions form a hydrophobic complex with the extractant, which migrates to the organic phase. Solvent extraction can be implemented in a continuous mode and is suitable for processing high metal feed concentrations. However, the large amount of organic solvents used in this method is a major drawback, as they are often toxic and flammable, posing a risk to the environment and human health. Ionic liquids (ILs) can be used as a substitute for organic solvents in conventional liquid-liquid extraction to overcome these issues.

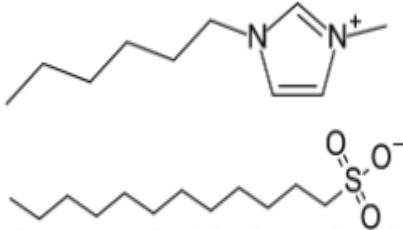
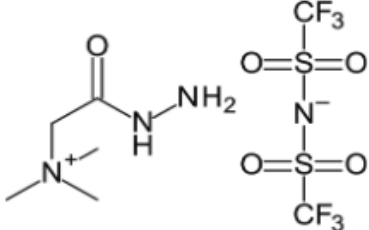
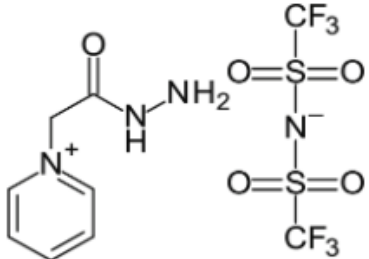
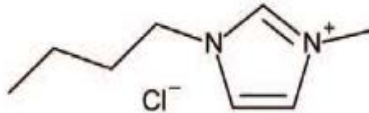
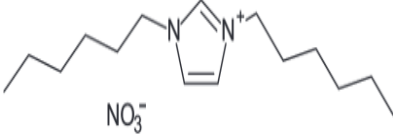
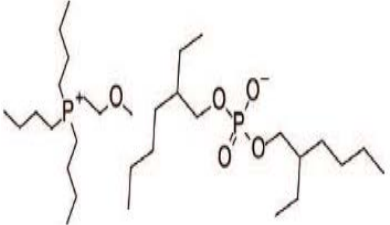
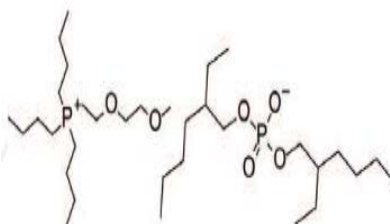
### Ionic liquid and aqueous two-phase system

Ionic liquids (ILs) are molten salts that are liquid at temperatures below 100°C. They are composed of organic cations, 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. ILs exhibit several unique physicochemical properties, including low vapor pressure, high thermal stability, high viscosity, good solvation ability, wide electrochemical windows, wide liquid range, and tunable polarity. By tuning the properties of ILs through the combination of cations and anions, they can be used in a variety of applications. The use of ILs as extractants in solvent extraction can reduce the negative impact on the environment that is associated with the use of organic solvents.

The use of ionic liquids (ILs) in metal ion extraction shows great potential. However, a significant challenge is their limited solubility in the aqueous phase, which can reduce extraction efficiency. To address this issue, hydrophobic ILs have been employed, but they are only partially soluble in the acidic aqueous solutions used for metal ion extraction, resulting in unwanted losses and increased costs. Additionally, hydrophobic ILs are often limited and may contain expensive and environmentally harmful fluorinated anions. Moreover, due to their high viscosity, the diffusion of solutes from the aqueous to the organic phase is slow, requiring a longer stirring time or the use of flammable and toxic organic solvents as diluents. To overcome these limitations, aqueous two-phase systems (ATPS) have been developed. ATPS allows for the use of more hydrophilic ILs as extractants, which require water-soluble ILs. The ILs used in 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. Its real application was developed by Per-Åke Albertsson in the 1980s.

Acronym	Chemical name	Molecule structure
<b>TBAB</b>	Tetrabutylammonium bromide	 <p>(b) (c)</p>
<b>[Chol][NTf<sub>2</sub>]</b>	Choline imide bis(trifluoromethylsulfonyl)	 <p>(a) (d)</p>
<b>[Hbet][NTf<sub>2</sub>]</b>	Betainiumbis(trifluoromethylsulfonyl) imide	 <p>(a) (d)</p>
<b>[P<sub>44414</sub>][Cl]</b>	Tributyltetradecylphosphonium chloride	 <p>(b) (d)</p>

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

Tri-n-butyl-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphoniumbis(2-ethylhexyl) phosphate

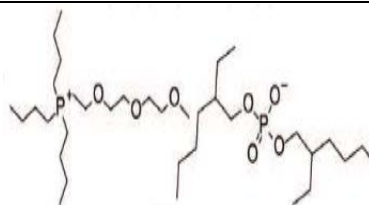


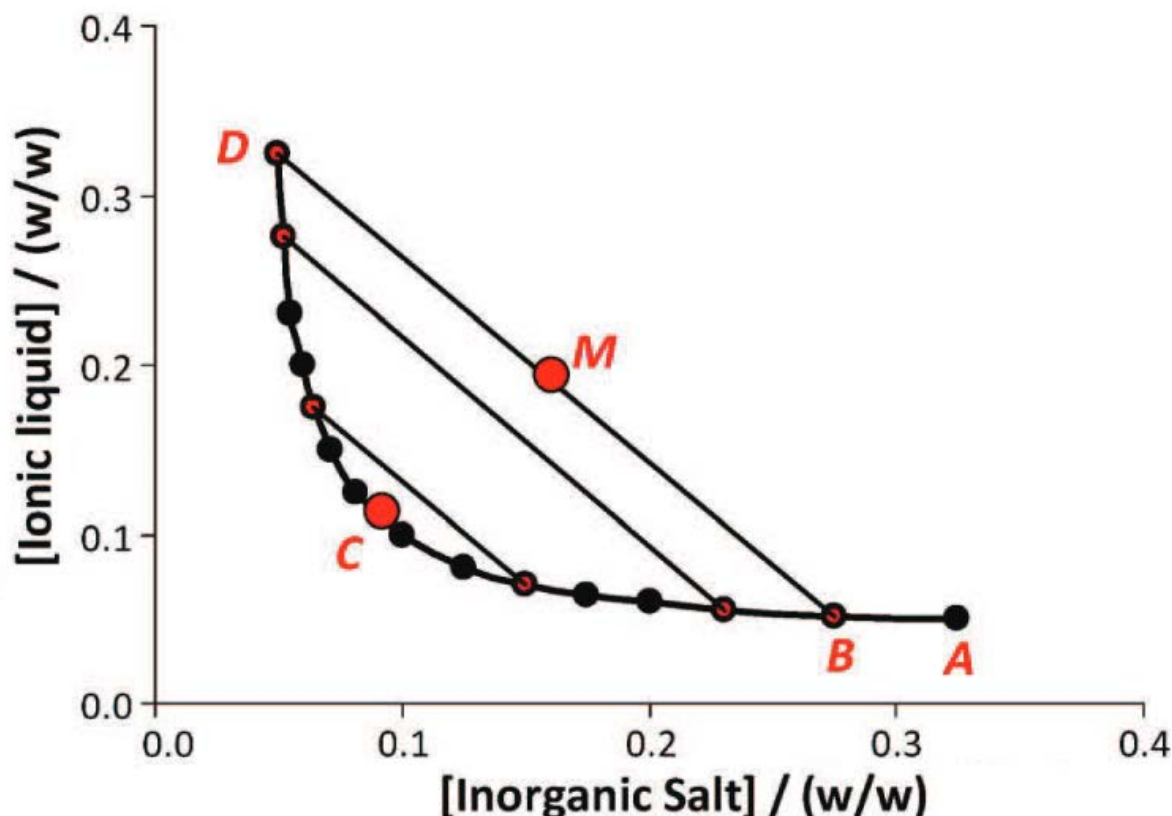
Table 1. Ionic liquids employed in ATPS for separation of metal ions with (a) or without (b) an extra extractant other than IL, with (c) or without (d) a salting-out agent.

Albertsson developed the real application of ATPS, where two chemically different hydrophilic polymers or a polymer and an electrolyte are mixed to spontaneously form two immiscible aqueous phases. The phase separation is derived from steric exclusion of large aggregates generated by the interaction between polymer and water, while a salt absorbs water leading to similar steric exclusion.

Conventional ATPSs consist of incompatible polymers or a polymer and a salt, but their use for separation is limited due to similar polarities of the phases. IL-based ATPSs allow for easier adjustment of phase polarity. Recent research has focused on IL-water systems with phase separation induced by temperature, known as HLL. This method does not require a salting-out agent and does not depend on metal complex diffusion from aqueous to organic phase, allowing for more efficient metal ion separation. Several studies have reported successful extraction of metals using IL-based ATPSs with and without salting-out agents.

### IL-based ATPS for metal separation

In general, an ATPS consisting of ILs and a salting-out agent has a specific phase diagram under particular conditions, such as temperature and pH (Figure 1). This binodal curve or phase diagram is unique to the ATPS and defines the potential working area. (Figure 1), M, D, B, and C represent the total composition, phase compositions, and critical point, respectively. The biphasic regime is defined by total mixture compositions above the binodal curve, whereas homogeneous compositions are below the solubility curve.



The salting-out agent is added to ATPS to facilitate the separation of more hydrophobic agents from the more hydrophilic one. Inorganic salts, carbohydrates, and polymers are the commonly used salting-out agents with ILs. However, it is worth noting that carbohydrates have not been utilized as salting-out agents for metal ion extraction in combination with ILs, according to the available literature.

A salting-out agent, namely ammonium sulphate, was combined with tetrabutylammonium bromide (TBAB) to extract Cr (VI). The pH was found to have a significant impact on the extraction, as the predominant species was present at pH 5.5. The extraction of Cr (VI) was optimized at pH 5, with a high extraction percentage of 93-98%. The extraction mechanism is as follows:



ATPS employs salting-out agents to separate hydrophobic agents from hydrophilic ones. Inorganic salts, carbohydrates, and polymers have been used as general salting-out agents in combination with ILs. However, carbohydrates have not been used as salting-out agents for metal ion extraction in combination with ILs, to the best of our knowledge.

Ammonium sulphate was used as a salting-out agent incorporated with tetrabutylammonium bromide (TBAB) for Cr (VI) separation. The extraction of Cr (VI) was influenced by pH as the predominant species at pH 5.5. Therefore, Cr (VI) was extracted into the upper phase at pH 5, where its extraction percentage was found to be 93-98%. However, the extraction percentage of Cr (III) was below 1.0% in all cases, indicating that this system was highly selective when used for separating Cr (VI) from Cr (III).

Increasing the  $(\text{NH}_4)_2\text{SO}_4$  concentration resulted in an increase in the extraction of Cr (VI) due to the progressive increase in the hydrophobicity of the upper phase. This system was also used to separate cadmium from cobalt, copper, iron (III), and zinc. The upper phase permitted the complete extraction of  $\text{Cd}^{2+}$  over the widest possible ranges of pH (1-10) with recovery in the range of 91-99%. Almost complete extraction of  $\text{Cd}^{2+}$  was obtained even though the concentration of  $\text{Cd}^{2+}$  in the mixture was far lower than the concentration of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Zn}^{2+}$  which coexisted with  $\text{Cd}^{2+}$ . The proposed method also successfully detected trace Cd in zinc nitrate.

In collaboration with tributyl(tetradecyl)phosphonium chloride [ $\text{P}_{44414}$ ][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% [ $\text{P}_{44414}$ ][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, while Ni (II) does not, even at high chloride concentrations.

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 ([C6C1im][C12SO3]) 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.

To date, there are limited studies on the use of ATPS with a salting-out agent for metal ion separation. However, the studies mentioned above demonstrate the effectiveness and selectivity of using ILs in combination with a salting-out agent for metal ion separation. Therefore, it can be concluded that the use of an ATPS comprising of ILs and a salting-out agent is a promising approach for efficient and selective metal ion separation.

#### **ATPS without salting-out agent (HLLE)**

Chemical separation methods have been developed to simplify and miniaturize sample preparation procedures in order to reduce the consumption of solvents and reagents and to minimize laboratory waste [27]. Unconventional liquid-liquid extractions, such as HLLE, have been developed with this intention [28]. Because HLLE does not require a salting-out agent, it is often used more frequently in metal ion separation than an ATPS with a salting-out agent. In this technique, 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 to increase the extraction percentage, in which case the IL only acts as a separator agent. Choline hexafluoroacetylacetonate and betaine have been widely applied as extractants for metal ion separation using the HLLE technique. The structures of these compounds are shown in Figure 2. Choline bis(trifluoromethylsulfonyl)imide [Chol][Tf2N], in combination with choline hexa-fluoroacetylacetonate

[Chol][hfac], has been employed as specific chelating agents mixed with water that displays thermomorphic behavior with a UCST of 72°C for neodymium (III) extraction.



**Choline hexafluoroacetate**

**2-(trimethylazaniumyl)acetate(Betaine)**

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

The study investigated the effect of heating and settling temperature on the extraction percentage of Nd (III) using a heterogeneous liquid-liquid extraction (HLLE) system. The results revealed that heating temperature greatly influenced the extraction percentage, with almost no extraction observed below 45°C, while at 80°C, almost 100% of Nd (III) was extracted after 5 s of shaking when 60 mmol kg<sup>-1</sup> [Chol][hfac] was present in the organic phase. The settling temperature, however, had no effect on the extractability. The stoichiometry of extraction was confirmed, and the complex formed during extraction was [Nd<sub>2</sub>(bet)<sub>3</sub>(H<sub>2</sub>O)<sub>y</sub>]<sup>3+</sup>. The HLLE system was also applied to metal ion separation, and the distribution ratios of Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Ag<sup>+</sup> were very low, while Sc<sup>3+</sup> and Ga<sup>3+</sup> were almost completely extracted to the organic phase. Sc (III) extraction was further studied from red mud leachates, and [Hbet][NTf<sub>2</sub>] was shown to have a high affinity for Sc (III) extraction with a percentage extraction of over 90% compared to other rare-earth metal ions. The ATR-FTIR spectra of the IL phase of the extraction mixture showed coordination of the IL to the scandium ion via the carboxylic acid function of the cation. Sc(III) was extracted in a ligand-to-metal ratio of 3:1.

Another mixture describes the application of a thermomorphic ionic liquid (IL) with an upper critical solution temperature (UCST) for the extraction of various metal ions. Specifically, [N<sub>222</sub>hcm][NTf<sub>2</sub>] and [C<sub>6</sub>C<sub>6</sub>im][NO<sub>3</sub>] were used for the extraction of common metal ions and rare earth metals, respectively. The UCST-ILs were found to be efficient extractants, with distribution coefficients reflecting the well-known Irving-Williams series. The extraction efficiency was affected by factors such as the concentration of the metal ions, the initial acidity, and the presence of co-extracted metal ions. The authors also demonstrated the extraction of U (VI) using betainumbis(trifluoromethylsulfonyl) imide ionic liquid [Hbet][Tf<sub>2</sub>N], which acted as both a solvent and an extractant. The article provides a comprehensive insight into the application of thermomorphic ILs for metal ion extraction, which can potentially have significant implications in various industries.

In previous studies, IL-based homogeneous liquid-liquid extraction (HLLE) has been applied using ILs mixed with water with a UCST (upper critical solution temperature). Metal ion separation has been achieved using some ILs that form a homogeneous phase below the critical solution temperature. For instance, Gras et al. reported the use of a two-phase system formed by mixing concentrated hydrochloric acid with tributyl(tetradecyl) phosphonium chloride ([P<sub>44414</sub>][Cl]), which is water-miscible below the critical solution temperature. The system was used to simultaneously leach and extract metal ions, including Fe (III), Pt (IV), Ni (II), and Co (II), and showed promising results. The extraction mechanism was derived by the anion exchange between a metalchlorocomplex with Cl<sup>-</sup> of IL. The selectivity of this system was evaluated towards Co (II) and Mn (II), which is relevant for the recycling of NiMH batteries, and yielded a nearly pure Co(II) in the IL-rich phase with a high separation factor. Another system using 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 a well-known metal extractant anion with water. The synthesized chloride ILs were fully miscible with water, while the synthesized DEHP ILs displayed LCST (lower critical solution temperature) phase behavior. The distribution ratio of various metal ions, including Co (II), Ni (II), Cu (II), and Zn (II), was determined, which showed good results according to the Irving-Williams series. Some rare earths formed the precipitation with the IL, possibly due to the strong complexation with the anion of IL. These studies suggest that IL-based HLLE can be a promising method for metal ion separation and recovery.

## II. Discussion & Conclusions

This section provides an overview of various studies investigating the use of IL-based ATPS for metal ion extraction. The combination of ILs and a salting-out agent in ATPS has been found to be highly effective for metal ion separation due to its efficiency, selectivity, and environmentally friendly properties. One of the methods used for metal ion extraction is the homogeneous liquid-liquid extraction (HLLE), which takes

advantage of the temperature-dependent behavior of ILs in water. This technique eliminates the need for a salting-out agent. In some cases, ILs in HLLLE can serve as both an extractant and a separator agent simultaneously. However, in other cases, an additional extractant is necessary to enhance the extraction percentage of metal ions. HLLLE has shown high efficiency and selectivity in extracting various types of metal ions, including transition metals, rare-earth elements, and radioactive substances. Overall, both ATPS and HLLLE have demonstrated their potential as effective methods for metal ion extraction.

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