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A perspective on task-specific ionic liquids for the separation of rare earth elements

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Rare earth elements (REEs) play essential roles in various technological applications. With the demand for these materials increasing globally, numerous efforts have been put into the separation and recovery of REEs. Liquid–liquid extraction is one of the most studied methods for separating and recycling these elements, with ionic liquids (ILs) having been proven as effective extraction solvents. This review looks at recent progress in solvent extraction systems using task-specific ionic liquids (TSILs) as extractants for REE separation.

Sustainability spotlight

Rare earth elements (REEs) are critical materials in consumer products used in daily life due to their unique catalytic, magnetic, and phosphorescent properties. Among their various applications is clean energy technology where they are found in hybrid and electric vehicles, lighting, solar cells, and wind turbines. With rising global demand for REEs, their separation and recovery from primary and secondary sources have become increasingly important. In line with the UN's "Affordable and Clean Energy" goal (SDG 7), this review paper presents an overview of recent advances in systems involving solvent extraction, one of the most promising techniques for separating REEs, and task-specific ionic liquids as extractants.

1. Introduction

Rare earth elements (REEs) are a set of metals that contains the 15 lanthanides, scandium, and yttrium. REEs are used in a variety of green and low-carbon applications in modern science and technology such as magnets, lighting, catalysts, and rechargeable batteries.¹ Due to their prominent role as materials in everyday consumer products, the demand for REEs keeps rising, and therefore, efficient methods are needed to separate and recover these elements.^{2–4}

Among the most frequently studied separation techniques for REEs is liquid–liquid extraction which involves the use of extractants in various solvents.^{5,6} This method utilizes a mixture of REEs, most frequently as nitrates or chlorides, in a low-pH, acidic aqueous solution that is combined with an immiscible organic solvent containing the extractant. In general, REEs are in the cationic form at low pH values while they hydrolyze around pH > 5 and precipitate out of solution as hydroxides.⁷ Accordingly, the common acidity range for extractions is at pH 1–5.

As green alternatives to traditional organic solvents, ionic liquids (ILs) have been increasingly used in solvent extractions to enhance the separation performances of known extractants^{8–11}

due to their beneficial properties such as low vapor pressure, low flammability, the ability to dissolve both organic and inorganic compounds, high thermal stability, high conductivity, and wide electrochemical windows.^{12–16} Generally, the typical IL-based extraction process starts with an aqueous solution of REE ions that comes into contact with an IL layer that includes the extractant. The REE ions are then chelated by a combination of the extractant and cations and/or anions from the IL, followed by traveling from the aqueous phase to the IL phase. After separating the two layers, if needed the IL phase can undergo a stripping procedure in which the REEs are taken away from the extractant and IL to a solution with higher affinity for REEs, usually an acidic aqueous solution containing nitric acid or hydrochloric acid. The remaining IL phase can be reused for additional new extractions.

However, it should be noted that even hydrophobic ILs such as those with the commonly used bis(trifluoromethanesulfonyl) imide ([NTf₂][−]) anion have partial solubilities in water, and therefore, portions of them can be lost to the aqueous phases during extractions. IL process design rarely deals with waste streams containing dissolved [NTf₂][−] in water,¹⁷ which can cause ecotoxicological issues due to the low biodegradability of the anion.^{18,19} To help avoid this loss, the ILs can be made more hydrophobic by using cations with long alkyl chains.²⁰

Besides acting as diluents in extractions, ILs can also contribute to separation processes through solvent interactions²¹ and ion-exchange mechanisms,^{22,23} which allows for tuning the properties of specific extractants.²⁴ Consequently, functionalized ILs known as task-specific ionic liquids (TSILs)²⁵ have attracted increased attention in extraction methods. TSILs

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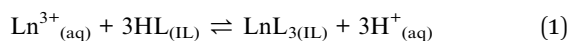
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are made of conventional ILs that include functional groups tailored to provide suitable physicochemical properties to the ILs as extractants or solvents. Due to the ion-exchange mechanisms, these TSILs can avoid the drawback of partial dissolution in the aqueous phase that conventional ILs face.¹⁶

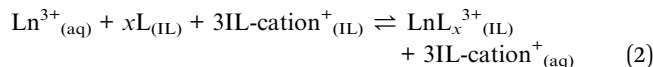
In a typical ion pair extraction involving the target metal ion in an aqueous solution and a neutral ligand as the extractant in a conventional organic solvent, the cations and anions can travel from the aqueous phase to the organic phase to interact with the ligand (Fig. 1a). In contrast, when an ionic liquid is used instead of an organic solvent, there is additional cooperativity coming from the cationic and anionic parts of the IL which can enter the aqueous layer and also interact with the metal ion (Fig. 1b), allowing for stronger solvation.^{8,22}

More specifically, various extraction mechanisms are possible when cations or anions from ILs are transferred to the aqueous phase during extraction. In the neutral exchange mechanism, which is similar to that in extractions using conventional organic solvents, hydrophobic ILs can extract neutral complexes made of the REE cation and anionic ligands. In this case, the IL simply acts as a polar non-aqueous solvent. The extraction for a trivalent REE (Ln^{3+}) with a monobasic Brønsted acid ligand (HL) can be shown in the following equation:

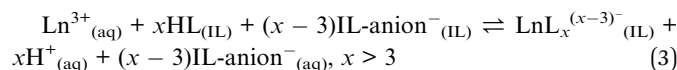


where subscripts (aq) and (IL) represent the aqueous and IL phases, respectively.

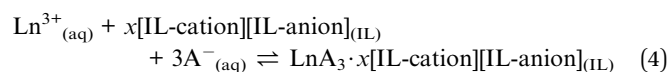
In the cation-exchange mechanism, the IL acts as a liquid ion exchanger with cationic complexes that are formed between the REE cation and a certain number (x) of neutral ligands (L). Cations from the IL are transferred to the aqueous phase while the REE cation moves to the IL phase to form the complex as expressed in the following example:



In the less common anion-exchange mechanism, an over-neutralized anionic complex is formed between the REE cation and a certain number (x) of anionic ligands (L).²⁶ Anions from the IL are transported to the aqueous phase while the REE cation goes to the IL phase for complex formation as seen in this scheme:



Another possible pathway is the ion-association mechanism which can be found in the presence of long alkyl chains on ILs, which help avoid ion exchange, and other anions (A^{-}) in the aqueous phase such as chloride and nitrate coming from salts or their conjugate acids. In this case, both cations and anions from the IL take part in the REE extraction, resulting in a hydrophobic neutral complex¹⁶ as follows:



Additionally, by utilizing TSILs as ligands, the extractants themselves become charged, thereby enabling another way to interact with the metal and influence the extraction process. For example, one strategy to explore is whether a positively charged extractant having an IL cation from a TSIL can change extraction efficiencies and selectivities. Neutral extractants favor the smaller and heavier metals, showing a linear dependence of extraction efficiencies on $1/r$, the inverse radius of the metal ion. With the introduction of a cation into the extractant, the question becomes whether this linear dependence can be attenuated (Fig. 2).

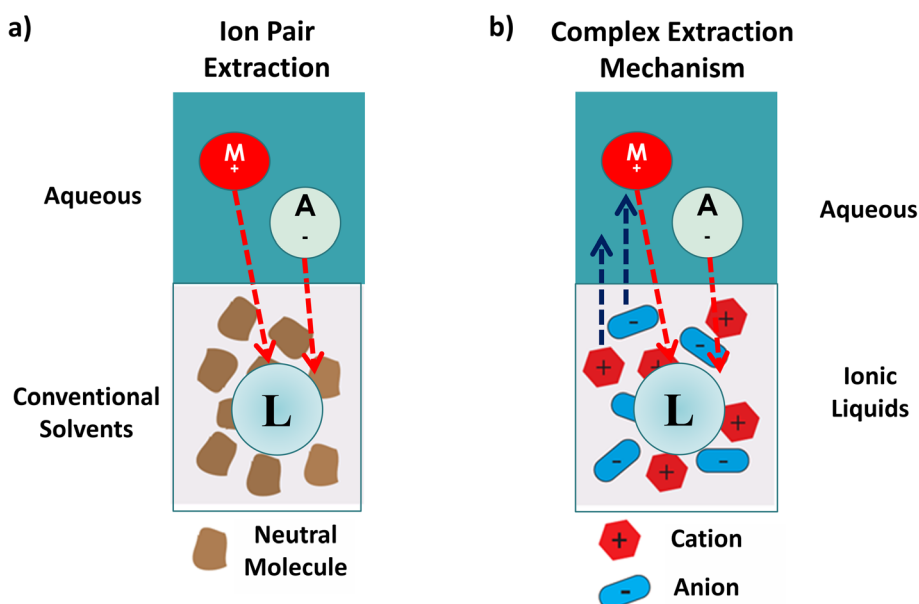


Fig. 1 Liquid-liquid extractions involving (a) conventional organic solvents and (b) ionic liquids.



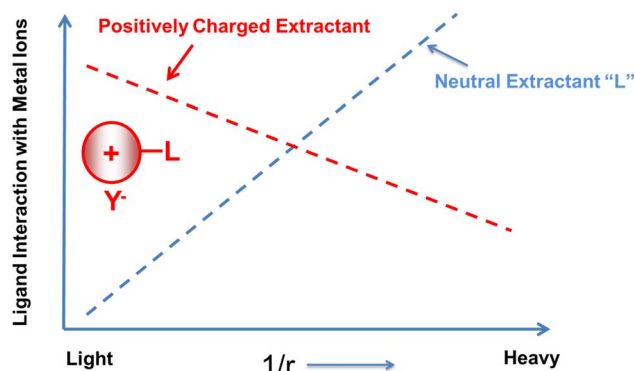


Fig. 2 Possible effect of cationic charges on metal extractions.

Broader aspects of extraction systems with ILs and TSILs have recently been covered in several review articles.^{26,27} In this review, we describe recent progress in liquid-liquid extraction systems using TSILs as novel extractants for the separation of REEs.

2. Task-specific ionic liquids as extractants

2.1 Early extraction work with task-specific ionic liquids

Initial research efforts by Visser *et al.* focused on extracting heavy metal ions Cd^{2+} and Hg^{2+} from water with TSILs made of dialkylimidazolium cations that have been derivatized with thioether, thiourea, and urea functional groups and combined with the PF_6^-

anion (Fig. 3) in order to act as both the extractant and the hydrophobic solvent in liquid-liquid extractions.²⁸ The more hydrophobic environment provided by the extractant aimed to facilitate the transport of the metal ion out of the aqueous phase, and having the metal-binding group tethered to the imidazolium cation would lower the chance of losing the extractant to the aqueous phase. The attached functional groups and alkyl chains influenced the extraction performance, with the thiourea and urea groups together with longer alkyls giving the highest distribution ratios (D values) for each metal ion.

Another study from our group utilized TSILs consisting of aza-crown ethers (Fig. 3) bound to imidazolium cations to extract Cs^+ and Sr^{2+} from aqueous solutions.²⁹ Compared to the neutral extractants dicyclohexano-18-crown-6 and *N*-octyl monoaza-18-crown-6, the TSILs showed lower extraction and recovery efficiencies due to charge repulsion between the imidazolium groups and metal cations. These results indicated that a stronger complexation capability may be needed in the extractant to overcome the repulsion. Among the TSILs, the binding ability of the aza-crown ether group was observed to be affected by the substitution pattern of the alkyl groups on the attached imidazolium ring.

2.2 Recent extraction systems using task-specific ionic liquids

2.2.1 Carbamoylmethylphosphine oxide. Bidentate carbamoylmethylphosphine oxide (CMPO) ligands have previously been used as extractants for processing liquid acidic radioactive

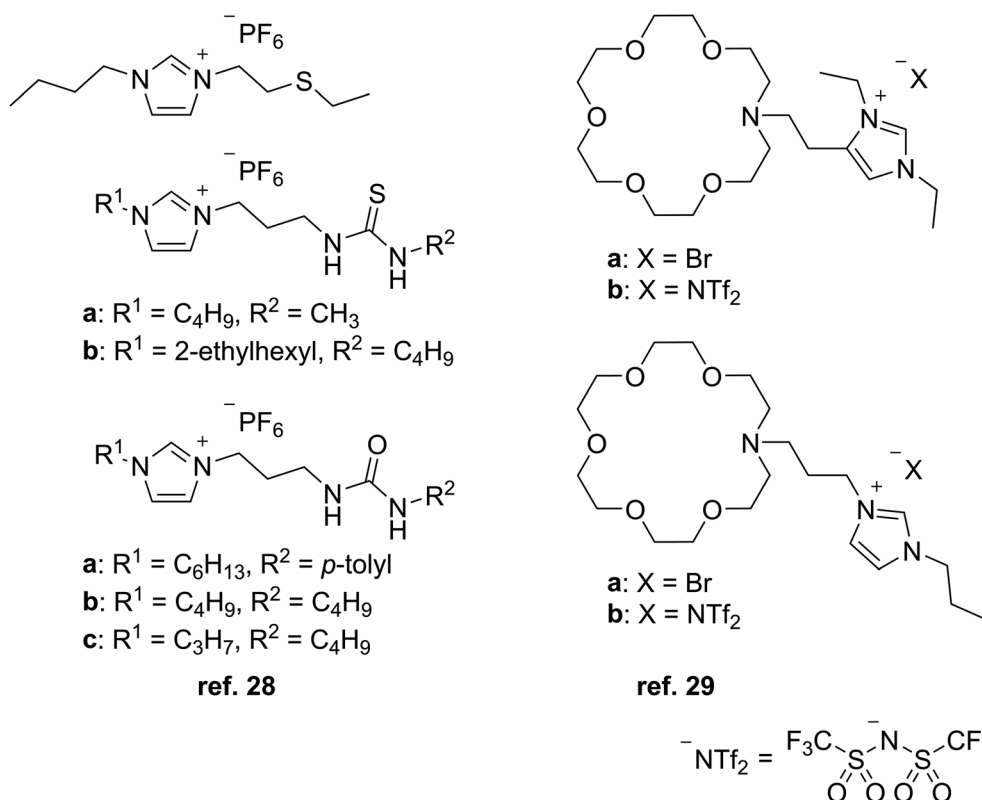


Fig. 3 Structures of TSILs from early extraction work.



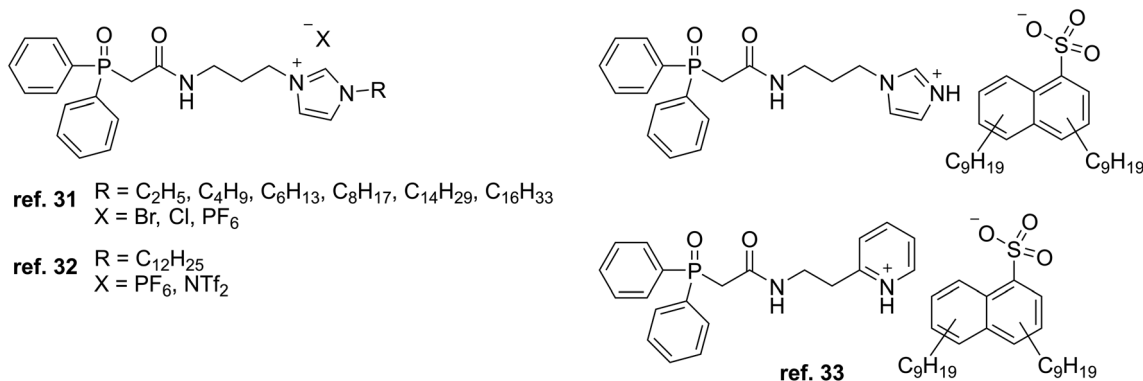


Fig. 4 CMPO-based TSILs.

waste and were shown to extract lanthanide nitrates from water while dissolved in an imidazolium IL.³⁰ Odinet *et al.* developed the first series of TSILs containing CMPO moieties linked to imidazolium groups with various alkyl chains (Fig. 4) for the solid phase extraction of REE Eu³⁺ and actinides Pu⁴⁺ and Am³⁺ from nitric acid solutions.³¹ The solid phase extractants were generated by treating polyacrylonitrile (PAN) fibers, acrylate resins, hypercrosslinked styrenes, and multi-walled carbon nanotubes with solutions of the TSILs.

Mohapatra *et al.* used a similar CMPO-based TSIL with different alkyl chain lengths and anions (Fig. 4) for the solvent extraction of Eu³⁺ and actinide ions Pu⁴⁺, Am³⁺, and UO₂²⁺ from acidic solutions mixed with various imidazolium ILs and *n*-dodecane as solvents.³² For Eu³⁺, the extraction efficiencies with the TSIL were lower than those with the neutral CMPO ligand (*N,N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide, while the systems using the IL solvent with the shortest alkyl chain, [C₄mim][NTf₂], gave the highest distribution ratios compared to the other solvents, likely due to ILs being less able to go through ion exchange with having longer alkyl chains and being more hydrophobic.

More recently, Turanov *et al.* prepared TSILs made of CMPO and protonated imidazolium and pyridinium cations alongside the dinonylnaphthalenesulfonate anion (Fig. 4) for extracting lanthanide ions from nitric acid solutions with 1,2-dichloroethane as the organic solvent.³³ The cations were designed for coordination solvation of the lanthanide ions, while the anion contributes to the hydrophobicity to help the target ions transfer into the organic phase. The extraction efficiency of the

TSILs decreased across the lanthanide series as the atomic number increased. In contrast, the corresponding neutral CMPO analogues showed increasing efficiencies with increasing atomic number while overall being lower than those for the TSILs. The neutral conjugate acid of the anion also had lower distribution ratios, indicating the presence of the “inner synergistic effect”³⁴ for the TSILs.

2.2.2 Diglycolamides. Two diglycolamide (DGA)-based TSILs containing imidazolium cations (Fig. 5) were analyzed by Mohapatra *et al.* for extracting actinides and lanthanides from acidic feed solutions (typically containing 1 M nitric acid) as a pure IL phase without additional solvents.³⁵ The distribution coefficient values of all tested ions were around two orders of magnitude higher than those for the analogous neutral *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA) extractant in ILs and *n*-dodecane, but the extraction kinetics were much slower due to the higher viscosity of the TSILs. *D* values decreased with increasing acidity for both systems, indicating a nitric acid uptake. Slope analysis of the TSIL system showed a 1 : 2 metal-ion : extractant stoichiometry with an additional nitrate ion present. Efficient stripping of the extracted ions was possible *via* a modified solvent system using dilution and buffered complexing agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), and the radiolytic stability of the TSILs was superior to that of other DGA-based or IL-based solvent systems.

A set of dicationic DGA-based TSILs consisting of two imidazolium groups (Fig. 5) was also synthesized and evaluated by Y. Wu *et al.* for extracting lanthanides in an imidazolium IL

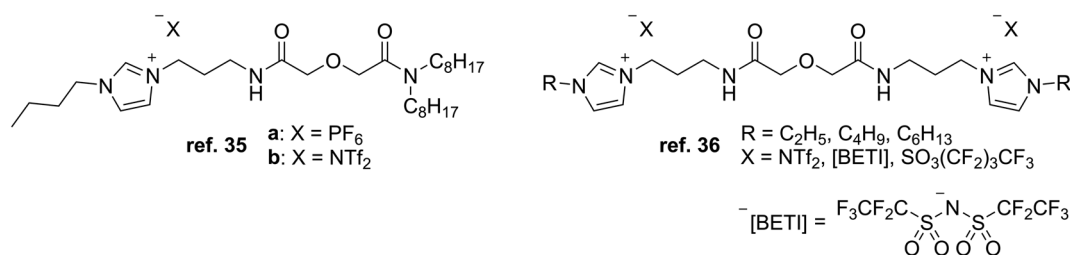


Fig. 5 Diglycolamide-based TSILs (DGAILs).



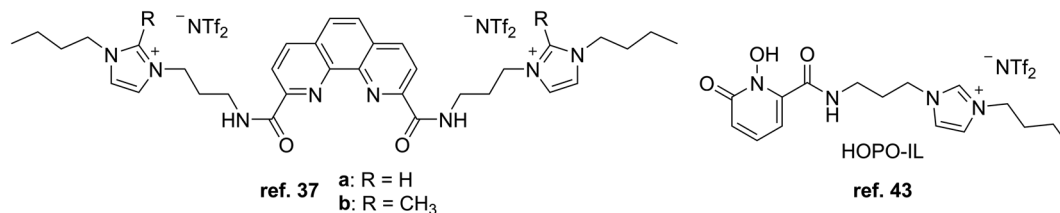


Fig. 6 Phenanthroline-dicarboxamide and hydroxypyridinone-based TSILs.

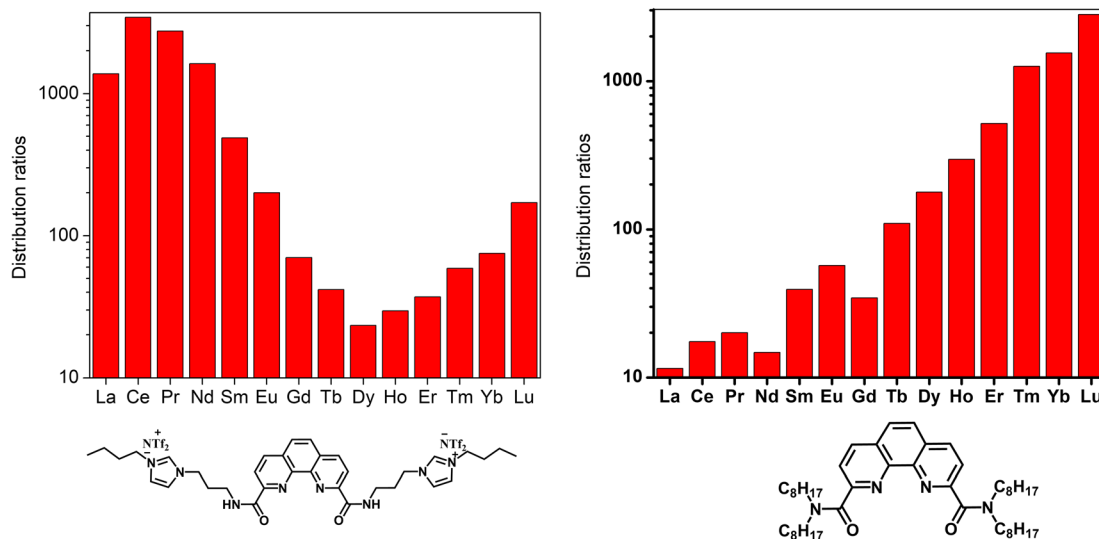


Fig. 7 Extraction selectivities of the phenanthroline-dicarboxamide TSIL and neutral extractant.

solvent.³⁶ Unfortunately, no lanthanide extraction from the aqueous phase into the IL solvent was possible at any acidity, indicating that the TSILs suppressed extraction by forming water-soluble complexes.

2.2.3 Phenanthroline-dicarboxamides. Our group synthesized and investigated dicationic TSILs comprising a 1,10-phenanthroline-2,9-dicarboxamide core and two imidazolium units (Fig. 6) for the extraction of trivalent f-ions from aqueous solutions into imidazolium IL solvents.³⁷ The TSILs had higher distribution ratios and separation factors than the analogous neutral extractant, with all values decreasing steeply with increased acidity. *D* values also decreased with longer alkyl chains in the imidazolium IL solvent, indicating that the extraction proceeds *via* a cation-exchange mechanism.^{38,39} Interestingly, the neutral extractant selectively extracted the heavy lanthanides (having smaller ionic radii) over the light lanthanides (larger ionic radii), while one of the TSILs showed higher extraction performance for the light lanthanides over the heavy ones (Fig. 7).

Phenanthroline ligands are known in the literature^{40,41} to form 1:2 metal:ligand complexes that can also include a nitrate anion ligand, similar to the aforementioned DGA-TSIL system. Computational modeling for the complexes with the TSILs revealed strong hydrogen bonding between the amide hydrogen and a sulfur group from the NTf₂⁻ anions that are

paired with the imidazolium cations, allowing these anions to fit between the phenanthroline core and imidazolium groups, which can compensate for the positive charge of the lanthanide ion in the center of the complex and still leave enough space for the nitrate ligand. Energy calculations suggested that nitrate addition is energetically unfavorable for the heavy lanthanides. In comparison, the complexes with neutral ligands did not show a reaction energy barrier due to the lack of cations that would electrostatically interact with nitrate in the outer second coordination sphere. These results implied that metal–ligand coordination can be tuned *via* coulombic interactions in the outer coordination sphere, allowing the cationic charges from the TSIL to control the separation properties of the extractant.

2.2.4 Hydroxypyridinone. Another known ligand with high affinity for lanthanides is 1,2-hydroxypyridinone (HOPO).⁴² Very recently, our group synthesized a novel TSIL incorporating HOPO and imidazolium moieties (Fig. 6) for the extraction of lanthanides from aqueous solutions with various ILs and 1-octanol as solvents.⁴³ The extraction performance of this HOPO-IL was significantly higher in all ILs than in the organic solvent. As seen in some of the previous examples mentioned above, the *D* values were the highest when using the IL solvents with a shorter alkyl chain length, supporting the cation-exchange extraction mechanism.



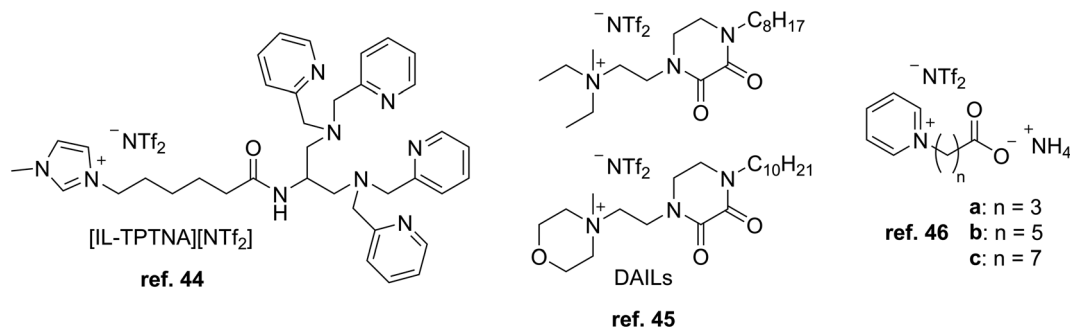


Fig. 8 Amide-based TSILs and ammonium salt form of pyridinium-carboxylic acid TSILs.

The effect of acidity in the aqueous phase on extraction was also analyzed with varying concentrations of nitric acid. Extraction efficiencies dropped sharply after increasing the acid concentration to around 0.01 M, making it possible to develop stripping strategies for recovering the lanthanide ions under strongly acidic conditions.

2.2.5 Other amide ligands. H. Wu *et al.* prepared a new TSIL containing an N,N,N',N' -tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amido (TPTNA) ligand connected to an imidazolium cation (Fig. 8) and studied the extraction of Eu^{3+} from nitric acid solution using $[\text{C}_6\text{mim}][\text{NTf}_2]$ as the IL solvent.⁴⁴ Extraction kinetics for Eu^{3+} were fairly fast with reaching equilibrium within 1 h, and performance decreased with higher acidity. Nearly complete stripping of Eu^{3+} was achieved when increasing the nitric acid concentration to 1.0 M. When evaluating the extraction of other lanthanides, the TSIL system selectively extracted the heavy lanthanides over the light ones.

Boyd *et al.* developed new preorganized 1,2-diamide-functionalized bidentate ligand-embedded hydrophobic ILs (DAILs) consisting of morpholinium or ammonium head groups, a rigid 2,3-diketopiperazine middle unit with the 1,2-diamide moiety for binding REEs, and a hydrophobic decyl tail (Fig. 8).⁴⁵ These highly viscous DAILs were mixed with the phosphonium IL $[\text{P}_{6,6,6,14}][\text{NTf}_2]$ to extract lanthanides from an aqueous feed. Higher D values were observed for the heavy

lanthanides while dilute HCl at pH 0.5 was enough for stripping off all complexed ions. An NMR titration was carried out to analyze complexation with Lu^{3+} , showing a 1 : 3 metal : DAIL complex. The hydrolytic stability of the DAILs was also monitored by NMR spectroscopy in an 80 : 20 v/v $\text{CD}_3\text{OD} : \text{D}_2\text{O}$ solvent mixture saturated with HCl, and no decomposition was found after one week.

2.2.6 Pyridinium carboxylic acids. A set of TSILs made of pyridinium cations tethered to carboxylic acid groups (Fig. 8) was designed by Hu *et al.* for the extraction and separation of yttrium from holmium and erbium from an aqueous phase using $[\text{C}_4\text{mim}][\text{NTf}_2]$ as the IL solvent.⁴⁶ These TSILs needed to be treated with aqueous ammonia before extraction procedures, and an initial aqueous solution pH of 2.5 was set for optimal performance. The extraction efficiency order was $\text{Ho} > \text{Er} > \text{Y}$, and the separation coefficients for Ho/Y and Er/Y were higher than those of other ILs used in the literature. Up to 98.5% of Y^{3+} could be stripped in a single step from the IL phase using 0.04 M HCl, and the TSILs maintained over 98% extraction efficiency of Y^{3+} after 8 regeneration cycles. Slope analysis and FTIR studies suggested a cation-exchange mechanism for extraction.

2.2.7 Anionic ligands. While the majority of TSIL-based extraction systems incorporate a neutral ligand into the cationic portion of an IL, there have also been some anionic TSILs with the anions generally obtained from deprotonating

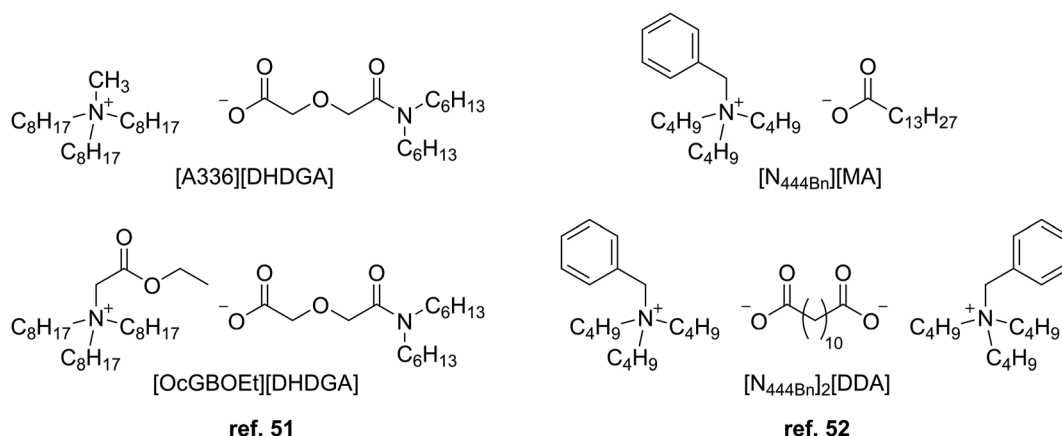


Fig. 9 Ammonium-based TSILs.



Table 1 Summary of TSIL-based extraction systems for REEs

| REE ions | Extractants, cation, anion | Extraction solvents | Metal : ligand stoichiometry | Selectivity | Extraction mechanism | Ref. |
|------------------|---|---|------------------------------|-----------------------------------|----------------------|------|
| Eu ³⁺ | CMPO, imidazolium, PF ₆ , NTf ₂ | [C _n mim][NTf ₂] (n = 4, 6, 8) | 1 : 3 | | Cation-exchange | 32 |
| Ln ³⁺ | CMPO, imidazolium, pyridinium, DNNS | 1,2-Dichloroethane | 1 : 2 | Light Ln ³⁺ | | 33 |
| Eu ³⁺ | DGA, imidazolium, PF ₆ , NTf ₂ | None | 1 : 2 | | Cation-exchange | 35 |
| Ln ³⁺ | Phenanthroline, amide, imidazolium, NTf ₂ | [C _n mim][NTf ₂] (n = 4, 6, 8) | 1 : 2 | Light Ln ³⁺ | | 37 |
| Ln ³⁺ | HOPO, imidazolium, NTf ₂ | [C _n mim][NTf ₂] (n = 4, 6, 8, 10), [C ₄ mim][BETI], [BMPip][NTf ₂], [B4Pic][NTf ₂] | 1 : 3 or 1 : 4 | Middle and heavy Ln ³⁺ | Cation-exchange | 43 |
| Ln ³⁺ | TPTNA, imidazolium, NTf ₂ | [C ₆ mim][NTf ₂] | 1 : 3 | Heavy Ln ³⁺ | Cation-exchange | 44 |
| Ln ³⁺ | 1,2-Diamide, ammonium, morpholinium, NTf ₂ | [P _{6,6,6,14}][NTf ₂] | 1 : 3 | Heavy Ln ³⁺ | | 45 |
| Y ³⁺ | Pyridinium, carboxylate, ammonium, NTf ₂ | [C ₄ mim][NTf ₂] | 1 : 3 | | Cation-exchange | 46 |
| Ln ³⁺ | Ammonium, DHDGA | Hexane | 1 : 1 and 1 : 2 | Middle and heavy Ln ³⁺ | Ion-association | 51 |
| Ln ³⁺ | Ammonium, carboxylate | Sulfonated kerosene, <i>n</i> -octanol | 1 : 1.5 or 1 : 2 | Heavy Ln ³⁺ | Ion-association | 52 |

a neutral extractant. Earlier studies prominently featured the di(2-ethylhexyl)phosphate (DEHP) anion coupled with ammonium, imidazolium, phosphonium, and pyrrolidinium cations.^{47–49} Notably, the molecular structure beyond the inner coordination sphere in an extraction system with [P_{6,6,6,14}][DEHP] as the TSIL in imidazolium IL solvents has been investigated using a combination of small-angle neutron scattering (SANS) and X-ray absorption fine structure (XAFS) spectroscopy.⁵⁰

More recently, Khodakarami and Alagha synthesized ammonium-based TSILs with dihexyldiglycolamate (DHDGA) anions (Fig. 9) for extracting REEs from aqueous solutions with hexane as a suitable diluent.⁵¹ The extraction efficiencies of the TSILs for Eu³⁺ were higher than those of their precursors, supporting the inner synergistic effect of both cationic and anionic parts. FTIR spectroscopy suggested an ion-association mechanism for extraction, and slope analysis showed stoichiometric metal : ligand ratios of 1 : 1 and 1 : 2, with the latter for the [OcGBOEt][DHDGA] TSIL variant that has additional oxygen atoms in the cation structure. Both TSILs exhibited higher affinities towards the middle and heavy REEs and were reusable for extraction after stripping with around 0.3 M nitric acid.

Another set of ammonium-based TSILs was prepared by Yu *et al.* with carboxylate anions containing long alkyl chains for the extraction of REEs from a chloride aqueous solution.⁵² One of these TSILs utilized a dicarboxylate dianion to pair with two ammonium cations (Fig. 9). Again, an ion-association extraction mechanism was proposed from FTIR characterization from complexing Y³⁺, and slope analysis indicated the formation of 1 : 1.5 or 1 : 2 metal : ligand complexes. *D* values were higher for the heavy lanthanides with the monocationic [N_{444Bn}][MA] TSIL having better selectivity overall while most extracted ions were stripped off at 0.04 M HCl (Table 1).

3. Conclusion and outlook

An overview of recent advances in TSIL-based extraction systems for the separation of REEs has been presented. While still a fairly new approach to extraction systems, TSILs have already offered vast improvements in extraction over conventional neutral ligands in some cases due to their variety and flexibility of being used as ligands and a pure IL phase, and being soluble in other ILs. With an expanded library of cations and anions available to fine-tune IL properties such as hydrophobicity, viscosity, and radiolytic stability, there still are plenty of structures that have untapped potential to be used as extractants. And even though many IL-based extraction systems have been studied and characterized to date, certain aspects such as investigating the molecular structure of ILs or tuning the electrostatic interactions in the second coordination sphere remain largely underexplored.

Furthermore, computational modeling⁵³ and machine learning⁵⁴ can help accelerate the discovery of new extractants and optimize the separation and selectivities for REEs while another separation application involves the electrodeposition of REEs from ILs.⁵⁵ Other ongoing challenges include selectivity for a specific ion among adjacent elements, high viscosity, slow extraction kinetics, and economic viability. Besides reusing the IL phase after stripping procedures, other recovery and purification methods of ILs⁵⁶ may be necessary to make these systems more cost-effective. It remains challenging to come up with a more environmentally friendly extraction method to replace the traditional liquid–liquid extraction involving conventional solvents on a commercial scale⁵⁷ due to high viscosities, high costs for synthesis and purification, and waste disposal concerns because of the degradation and toxicity of ILs.⁵⁸ Most of these issues will need to be expanded upon and improved in order for these extraction systems to find applications in industrial separation and purification settings.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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