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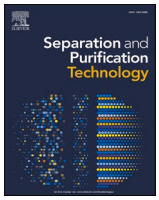

Highly selective extraction of scandium(III) from rare earth elements using quaternary ammonium based ionic liquids: Experimental and DFT studies

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ABSTRACT

Global demand for rare earth elements (REEs) is steadily increasing, emphasizing the necessity of effective extraction and recovery methods. Although REEs recovery from electronic waste using ionic liquid (IL) extractants offers an alternative solution to avoid potential adverse environmental impacts during traditional mining and processing, highly efficient and selective extraction is still essential. Especially, due to similarities with other REEs, recovery of scandium (Sc(III)) is confronting grand challenges. Herein, quaternary ammonium based ILs (QA-ILs), i.e., [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N], have been successfully synthesized for selective Sc(III) extraction from other REEs under various conditions, e.g., initial acidity and IL concentration. Both ILs demonstrate superior selectivity for Sc(III) extraction from other REEs. Specifically, at pH 4.5 and 5, the extraction efficiency of Sc(III) using [N333 MeOAc][Tf_2N] was 73.6 % and 83.4 %, respectively, while it was high up to 90.5 % and 95.9 %, respectively, using [N444 MeOAc][Tf_2N]. Because of stronger hydrophobicity, [N444 MeOAc][Tf_2N] exhibited a higher extraction efficiency. Furthermore, [N444 MeOAc][Tf_2N] demonstrated a higher selectivity for Sc(III) as compared to other REEs, with high separation factor of 17 for Sc(III)/Lu(III) and Sc(III)/Yb(III). Additionally, the ILs can be recycled with a high stripping efficiency up to 86 % using 4 mol·L^{-1} H_2SO_4 solution. Density functional theory calculations further validated neutral exchange of Sc(III) in the neutral IL extraction process. This study presents a feasible solvent extraction system using novel QA-ILs for highly effective and selective Sc(III) extraction from waste streams.

1. Introduction

Rare earth elements (REEs) are a group of 17 chemically analogous elements, including lanthanides, yttrium (Y) and scandium (Sc), that are essential for many high-tech applications, such as smartphones, wind turbines, and electric vehicle motors [1]. The global demand for REEs has been steadily increasing in recent years and continues to grow in future [2,3]. The increasing demand for REEs in various industries has highlighted the importance of developing efficient separation and recovery methods [4,5]. Scandium (Sc) is a particularly valuable REE due to its unique properties, including high melting point, high strength-to-weight ratio, and excellent heat endurance. However, the recovery of Sc from waste streams is complicated due to its chemical similarities with other REEs. Therefore, selective extraction of Sc from other REEs is necessary for efficient recovery [6–8]. Currently, China dominates the global REEs market, producing more than 80 % of the world's REEs [9]. This has raised concerns about supply chain vulnerabilities and geopolitical risks associated with REEs production and export from China. In addition, conventional mining, and processing methods for REEs are often associated with adverse environmental impacts and resource depletion [10].

One potential solution to these challenges is the recovery of REEs from electronic waste (e-waste) that is a growing source of valuable metals and minerals [4,5]. E-waste contains a high concentration of REEs, making it an attractive source for REE recovery. However, selective separation and recovery of REEs from e-waste can be challenging due to the complex composition and variable characteristics of e-waste materials [11]. In recent years, the use of ionic liquids (ILs) for REE extraction has gained attention as a promising alternative to traditional organic solvents [5,12,13]. ILs are liquid salts that are at or close to room temperature and offer special qualities such low volatility, good thermal stability, and variable solubility [14]. ILs can be tailored to selectively extract specific metal ions, including REEs, from complex matrices [15].

Alkylated phosphine oxides (Cyanex 925) that were dispersed in either tricaprylmethylammonium nitrate [A336][NO_3] or 1-octyl-3-methylimidazolium hexafluorophosphate ([C8mim][PF_6]) have been

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applied for the extraction of Sc from aqueous solution [16,17]. Using a combination of 1-butyl-3-methylimidizolium bis(trifluoromethanesulfonyl)imide ([C4mim][Tf_2N]), 2-butyltrifluoroacetone (HTTA), and tri-n-octylphosphine oxide (TOPO), the synergistic extraction of Sc from aqueous solution was investigated. In these procedures, the typical particular extractant was diluted using an organic phase made of ILs [18]. In recent years, researchers have investigated the use of quaternary ammonium or phosphonium based ILs for selective extraction of Sc from REE mixtures. These ILs are a class of hydrophobic ILs that consist of a quaternary ammonium or phosphonium cation and a chloride or other anion. They offer several advantages over traditional ILs, such as lower cost, simpler synthesis, and improved selectivity for Sc extraction [8,17,19–23]. For Sc and lanthanides, these ILs did indeed demonstrate improved extraction efficiency. Onghena and Binnemans et al. employed betainium bis(trifluoromethylsulfonyl)imde [Hbet][Tf_2N] to extract Sc from an aqueous solution [22]. Recently, novel ILs, i.e., [HbetPy][Tf_2N] and [HbetMor][Tf_2N], were synthesized and demonstrated a high selectivity for Sc(III) extraction from a mixture of REEs containing La, Nd, Eu, Ho, and Yb [23]. Thus, selective extraction of Sc from REEs using novel quaternary ammonium based ILs can be a promising approach for its efficient and sustainable recovery. Nevertheless, further research is still essential in terms of extraction conditions optimization and practical application of ILs on a pilot scale towards industrialization.

Therefore, in this study, we have designed and synthesized efficient quaternary ammonium based task specific ILs (QA-TSILs) to extract Sc (III) from REEs aqueous solutions in nitrate medium. Specifically, the extraction and separation performance have been systematically studied under various conditions, e.g., initial acidity and IL concentration. The reusability of spent QA-TSILs have been examined through stripping process to achieve cost-effective IL extraction system. Eventually, density functional theory (DFT) computational calculations have been applied to delve and validate the extraction mechanism using synthesized QA-TSILs towards future practical applications for REEs recovery from waste stream, especially e-waste.

2. Materials and methods

2.1. Chemicals

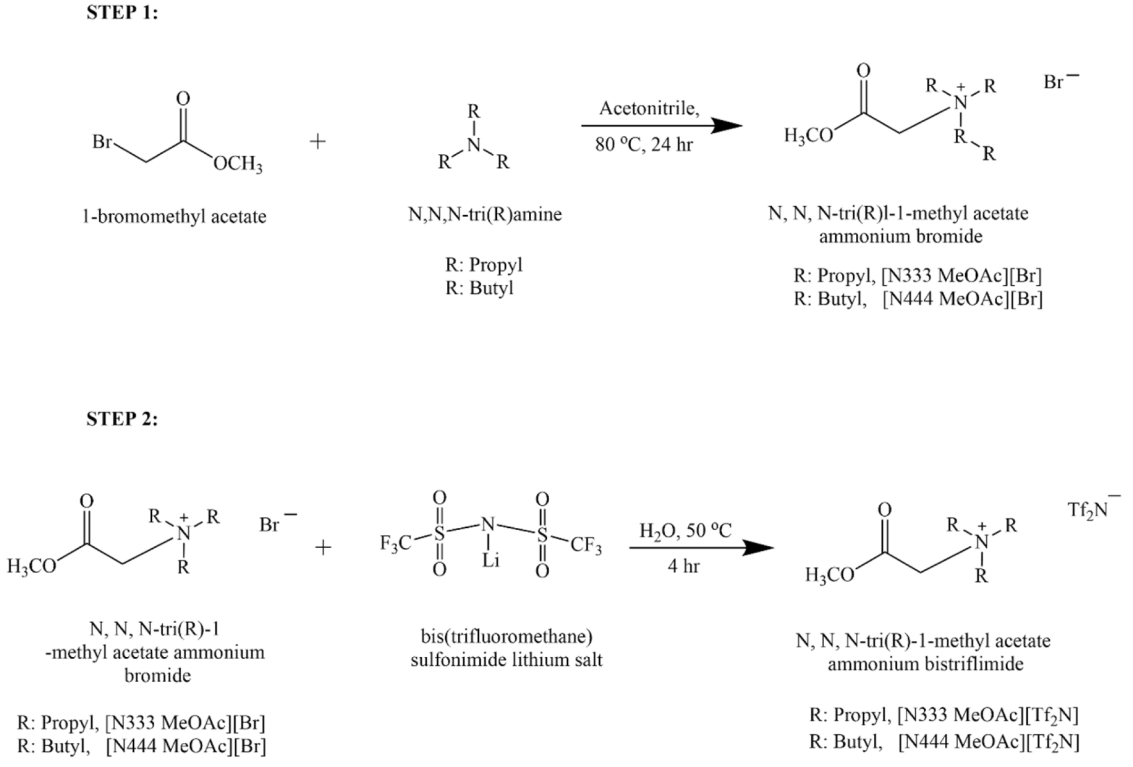
Chemicals, including tripropyl amine, tributyl amine, 1-bromomethyl acetate, lithium bis(trifluoromethanesulfonyl)amide, lanthanide nitrates and solvents (acetonitrile, diethyl ether and hexane), were obtained from Sigma Aldrich Ltd. and used without further purification unless stated otherwise. Nitric acid (67 % purity) was obtained from Sigma Aldrich Ltd. and further diluted with ultrapure (Type 1) Milli-Q water (Milli-Q Direct 8 Water Purification System) for experimental purpose. All REEs in nitrate salts used for this study were acquired from Alfa Aesar (USA). REEs stock solutions were prepared by dissolving their hydrated nitrate salts (>99 % purity) in deionized water. Nitric acid and ammonium hydroxide were used to adjust the pH of resulting solution.

2.2. Synthesis and characterization of QA-TSILs

As illustrated in Scheme 1, two types of QA-TSILs, namely N,N,N-tripropyl-1-methyl acetate ammonium bistriflimide ([N333 MeOAc][Tf_2N]) and N,N,N-tributyl-1-methyl acetate ammonium bistriflimide ([N444 MeOAc][Tf_2N]), were designed and synthesized by employing alkylation, neutralization, and metathesis reactions. The as-synthesized QA-TSILs were subjected to comprehensive characterization using various analytical techniques, including nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), High resolution mass spectrometry (HRMS), thermogravimetric analysis (TGA), and density analysis.

2.2.1. Synthesis of [N333 MeOAc][Tf2N]

Tripropyl amine (0.1 mol, 7.910 g) and 1-bromomethyl acetate (0.1 mol, 13.895 g) in acetonitrile were stirred up under reflux for 48 h. The obtained solution was subjected to vacuum evaporation until being completely dried, resulting in a whitish grey solid. To eliminate any remaining unreacted compounds, the solid was washed using diethyl



Scheme 1. Scheme for synthesis of [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N].

ether. Subsequently, the whitish grey solid precursor was reacted with a 50 mL lithium bis(trifluoromethanesulfonyl)amide ($LiTf_2N$) (0.05 mol, 14.350 g) aqueous solution. Through this reaction, the grey solid precursor underwent transformation into the resulting product [N333 MeOAc][Tf_2N] (yield: ~93 %; ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): δ 4.13 (CH_2, t, J = 15.2 Hz, 2H), 3.85–3.78 (CH_3, m, 3H), 3.42–3.39 (CH_2, m, 6H), 1.75–1.67 (CH_2, m, 6H), 1.05–0.96 (CH_3, m, 9H) (referring to **Fig. S1**); ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 13.42–23.94 (CH3), 53.50–56.63 (CH3), 60.22 (CH2), 76.86–77.37 (6 CH2), 118.28–121.41 (C), 164.69 (CF3) (referring to **Fig. S2**)).

2.2.2. Synthesis of [N444 MeOAc][Tf2N]

In the synthesis process, tributylamine (0.1 mol, 7.910 g) and 1-bromomethyl acetate (0.1 mol, 13.895 g) were combined and stirred under reflux in acetonitrile for 48 h. Subsequently, the resulting solution was subjected to vacuum drying. To remove any unreacted compounds, the dried material was washed with diethyl ether for several times, yielding a whitish grey solid. Afterwards, this whitish grey solid precursor reacted with 50 mL $LiTf_2N$ (0.05 mol, 14.35 g) solution and was then transformed into the final product [N444 MeOAc][Tf_2N] (yield: ~92 %; ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): δ 4.09 (CH_2, t, J = 14.9 Hz, 2H), 3.84–3.77 (CH_3, m, 3H), 3.46–3.36 (CH_2, m, 6H), 1.68–1.58 (CH_2, m, 6H), 1.38 (CH_2, td, J = 14.7, 7.3 Hz, 6H), 1.01–0.92 (CH_3, m, 9H) (referring to **Fig. S3**); ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 13.42–23.94 (CH3), 53.50–56.63 (CH3), 60.22 (CH2), 76.86–77.37 (6 CH2), 118.28–121.41 (C), 164.69 (CF3) (referring to **Fig. S4**)).

2.2.3. Characterization of ILs

High resolution mass spectrometry. HRMS was utilized for structural characterization of ILs. The HRMS spectra revealed the presence of cations for both ILs. For the [N333 MeOAc][Tf_2N], the cationic part was observed at m/z 216.19 in HRMS spectrum. On the other hand, for the IL [N444 MeOAc][Tf_2N], the cationic component appeared at m/z 258.2 in the HRMS spectrum. Based on the HRMS spectra, it was determined that the predominant components of the ILs were tripropyl-methylacetate ammonium (m/z = 216.19) for [N333 MeOAc][Tf_2N] and tributyl-methylacetate ammonium (m/z = 258.24) for [N444 MeOAc][Tf_2N] (**Figs. S5 − S6**).

Thermal analysis. The thermal stabilities of the QA-TSILs ([N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N]) were assessed using a thermogravimetric analyzer (TA Instruments Shimadzu DTG-60H). The samples were heated at a rate of 10 K·min^{-1} under a nitrogen gas atmosphere, with temperatures ranging from 313 to 1073 K. Both ILs had one-step breakdown behaviour according to TGA data. The onset decomposition temperatures for [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] were approximately 213 °C and 218 °C, respectively (as shown in Fig. S7). Notably, for [N444 MeOAc][Tf_2N], two distinct transitions were observed during the analysis, likely indicating the disintegration of diverse parts of the IL at different temperatures. TGA curves further indicated that the breakdown of [N333 MeOAc][Tf_2N] occurred at a slightly faster rate compared to [N444 MeOAc][Tf_2N]. The results also suggested that [N333 MeOAc][Tf_2N] underwent complete disintegration at around 330 °C, while the total decomposition of [N444 MeOAc][Tf_2N] took place at approximately 356 °C (**Figs. S7 and S8**). Melting points (Stuart melting point apparatus SMP10) for [N333 MeOAc][Tf2N] was 79 °C and for [N444 MeOAc][Tf2N] was 75 °C, respectively.

Density measurement. The densities of the QA-TSILs ([N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N]) were assessed using a typical 2 mL specific gravity bottle at ambient temperature. The density of [N333 MeOAc][Tf_2N] was found to be 0.62 g/mL, indicating that it has a slightly lower density compared to [N444 MeOAc][Tf_2N], with a density of ca. 0.69 g/mL.

Fig. 1 presents the chemical structures of the specific QA-TSILs that were synthesized and utilized during this study. The structures of ILs were characterized using ^{1}H NMR (500 MHz) proton in $CDCl_3$, with tetramethyl silane as a standard using JEOL ECZR 500 instrument. The chemical changes in relation to tetramethylsilane (TMS) were recorded. High-resolution mass spectrometry (Waters ESI-TOF MS spectrometer) and FTIR was also utilized to analyze the IL structures. The thermal stability of ILs was assessed via TGA in nitrogen (N_2) atmosphere (N_2 flow rate: 60 mL·min^{-1}, heating rate: 10 K·min^{-1}, temperature range: 313 to 1073 K). Density measurements were conducted using a 50 mL pycnometer, while pH values were measured using Metronohm 780 pH meter. All spectra and graphs pertaining to the characterization of the ILs are described in the supplementary data.

2.3. Extraction and stripping experiments

Extraction experiments were performed in metal-free vials using a temperature-controlled thermoshaker with a shaking speed of 250 rpm for 90 min at 40 °C. To conduct extraction tests, equivalent amounts of REEs aqueous solutions were combined with ILs that had been diluted in chloroform. Biphasic separation was carried out using a benchtop centrifuge (Nüve NF400) at 4500 rpm for 5 min. The concentration of REEs in aqueous phase was further diluted if necessary for analysis using inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific iCAPTM RQ). The spike recovery rate was reported to be 99.8 % when standard samples, duplicate samples, and spike samples were used for method validation.

Stripping experiments were carried out by loading and agitating the mixture of 2 mL organic phase with 2 mL H_2SO_4 solution at various concentrations until equilibrium for 90 min. The extraction performance can be evaluated by determining the extraction efficiency (E, %), distribution ratio (D), stripping efficiency (S), and separation factor (β) using following equations.

$$E = \frac{M_i - M_f}{M_i} \times 100\% \quad (1)$$

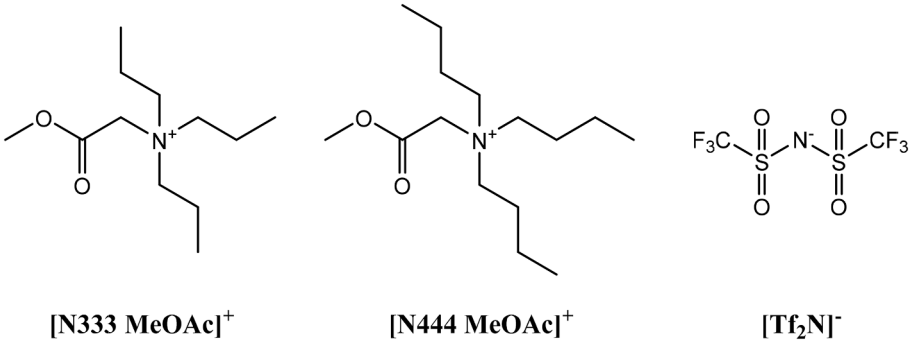


Fig. 1. Structures of the synthesized ILs in this study.

$$D = \frac{M_i - M_f}{M_f} \quad (2)$$

$$S = \frac{M_{aq}}{M_{ILs}} \times 100\% \quad (3)$$

$$\beta = \frac{D_a}{D_b} \quad (4)$$

In **Eqs. (1) - (4)**, the primary and final concentration of REEs in the aqueous phase is denoted as M_i and M_f, respectively. The equilibrium concentration of REE ions in the stripping acid is represented as M_{aq}, while the initial concentration of loaded REE ions in the extracting phase is denoted as M_{ILs}. The distribution ratios of two different REE ions are referred as D_a and D_b. As mentioned earlier, the concentrations of REE ions in the aqueous phase were determined using ICP-MS. The limit of detection was 11 ng/l for Sc ion, 1 ng/l for Y, La, Ce, Nd ions, and 0.1 1 ng/l for other REE ions. To ensure accuracy and reproducibility, all experiments were performed at least in duplicate. Mean values were reported with measurement data being statistically analyzed at a 95 % confidence level.

2.4. Thermodynamic analysis for Sc(III) extraction

To evaluate the Sc(III) extraction from aqueous solution, [N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N] and chloroform were utilized as extractant and diluent, respectively. **Eq. (5)** describes the thermodynamic equation for the solvent extraction process of Sc(III) from aqueous solution using [N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N] and chloroform as extractant and diluent, respectively.

$Sc(III)_{(aq)} + 3HL_{(org)} \rightleftharpoons ScL_{3(org)} + 3H^+$ (5).

Where Sc(III) represents the Sc ion in aqueous solution, L represents the extractant ([N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N]), and ScL_3 represents the Sc complex formed in the organic phase. The equilibrium constant (K) can be expressed using **Eq. (6)**.

$$K = \frac{[ScL_{3(org)}][H^+]^3}{[Sc(III)_{(aq)}][HL_{(org)}]^3} \quad (6)$$

The extraction efficiency of Sc(III) can be evaluated based on the equilibrium constant (K) and other thermodynamic variables, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°).

2.5. Computational calculations

Full geometry optimization as well as frequency and thermochemical analysis were performed by using DFT calculations at the (U)B3LYP level for complex. The LANL2DZ basis set with effective core potential was used for all elements. All the calculations were run with the Gaussian 16 program package [24]. Computations were performed on ILs solvated with $CHCl_3$ using the integral equation formalism variant of PCM, with the default parameters for $CHCl_3$ [23]. All calculated structures were visualized by using ChemCraft [25].

3. Results and discussion

3.1. Effect of pH value of aqueous phase

To investigate the influence of aqueous phase pH on the extraction behaviour of QA-TSILs, the recovery of Sc(III) from other REEs was performed using [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] at different pH values (i.e., 0.5, 1, 2, 3, 4, 4.5 and 5). Despite the fact that the actual pH at which $Sc(OH)_3$ begins to precipitate varies depending on Sc intensity, pH was not increased beyond 5 to avoid $Sc(OH)_3$ precipitation [22].

As shown in Fig. 2, extraction efficiency of Sc(III) decreased with an enhancement in aqueous phase acidity. The extraction efficiency was ca. 14 % and 15 % at pH 0.5 for [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N], respectively, which was increased to about 73.6 % and 90.5 % at pH 4.5, respectively. This observation indicates that higher acidity negatively impacted the extraction efficiency of QA-TSILs. The pH dependence on the extraction process can be attributed to the competitiveness between H^+ and Sc(III) ion to bond with the ligand. The H^+ ions extraction, or protonation, decreases the extraction effectiveness by lowering the effective ligand concentration in the organic phase. By identifying the dominion of uncomplexed and hydrolytic species of metal ions, the Eh-pH diagram used in extractive metallurgy aids in understanding the nature and stability of each species. Monitoring revealed that the hydrolysis of Sc(III) was not substantial until the pH value exceeded 5. The production and precipitation of $Sc(OH)_3$ was the main influence altering the solubility of Sc ions under both mildly acidic and alkaline environments. In particular, adjusting the concentration, temperature, pH, and taking the presence of other ions into account when determining the solution's composition can adjust the domains and shapes of various species. Fig. 2**a and 2b** demonstrate that raising the pH value increased extraction efficiency, and Sc(III) exhibited the highest extraction efficiency at pH 4.5. There was a significant improvement in extraction efficiency as pH was varied from 0.5 to 4.5. At pH 4.5, it is distinctly proven that Sc(III) was selectively extracted from Y and other lanthanides present in the nitrate aqueous solution (Fig. 2**c and 2d**).

3.2. Effect of alkyl chain length of QA-TSIL extractants

At pH 4.5 and 5, the extraction efficiency of Sc(III) using [N333 MeOAc][Tf_2N] was 73.6 % and 83.4 %, respectively, which was high up to 90.5 % and 95.9 %, respectively, using [N444 MeOAc][Tf_2N] (Fig. 3). It is clearly visible that the alkyl chain length of the ILs had a substantial effect on the extraction efficiency of Sc(III) with the order being [N444 MeOAc][Tf_2N] > [N333 MeOAc][Tf_2N]. The observed order of higher extraction efficiency for [N444 MeOAc][Tf_2N] compared to [N333 MeOAc][Tf_2N] indicates that the stronger hydrophobicity of the IL extractants could be the underlying factor contributing to this difference. It is hypothesized that during the REE extraction process, the metal ion and extractant work together to create a hydrophobic metal complex, which is subsequently transferred to the organic phase. The metal ions extraction significantly depends on the relative solubility of the complex in both aqueous and organic phases. It is easier for a more hydrophobic complex to migrate from the aqueous phase to the organic phase. Consequently, higher Sc(III) extraction efficiency by [N444 MeOAc][Tf_2N] can be ascribed to its higher hydrophobicity as compared to [N333 MeOAc][Tf_2N], making it more efficient in transferring the metal complex from the aqueous phase to the organic phase. Hence, [N444 MeOAc][Tf_2N] demonstrates higher extraction efficiency than [N333 MeOAc][Tf_2N].

3.3. Effect of QA-TSIL concentration

The extraction of 0.01 $mmol{\cdot}L^{-1}$ Sc(III) using different concentrations of QA-TSILs (ranging from $0.1 - 1.0$ $mmol{\cdot}L^{-1}$) in chloroform from nitrate solution was studied to determine the optimum concentration required for efficient extraction. Fig. 4 depicts the extraction percentage versus the concentration of QA-TSILs, indicating that the E (%) surged at first, and then decreased with an increase in the concentration of QA-TSILs. Interestingly, [N444 MeOAc][Tf_2N] required only 0.5 $mmol{\cdot}L^{-1}$ to recover just about 96 % of Sc(III) ion, whereas the highest recovery obtained with 0.2 $mmol{\cdot}L^{-1}$ of [N333 MeOAc][Tf_2N] was 83 %. This observation is in agreement with the outcomes of studies related to the influence of Sc(III) concentration. This implies that a lower loading capacity of [N444 MeOAc][Tf_2N] was required for the extraction. Furthermore, it suggests that [N444 MeOAc][Tf_2N] is a more efficient

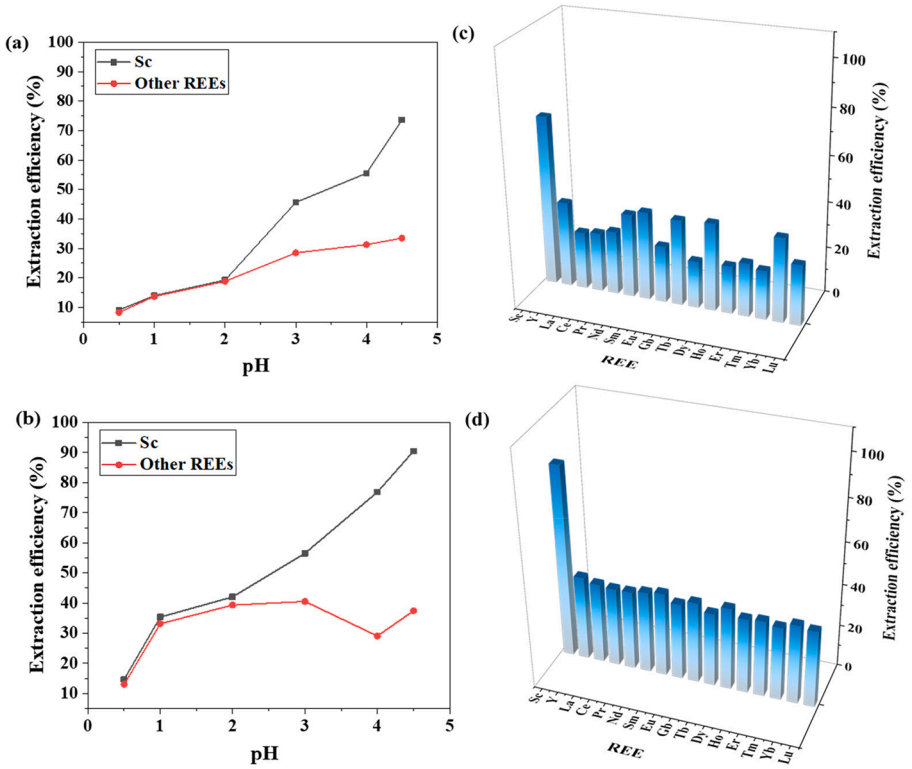


Fig. 2. Extraction efficiency (*E*, %) for Sc and other REEs using **(a)** [N333 MeOAc][Tf_2N] and **(b)** [N444 MeOAc][Tf_2N] in chloroform under various REEs nitrate solution pH values, and extraction efficiency (*E*, %) for all REEs using **(c)** [N333 MeOAc][Tf_2N] and **(d)** [N444 MeOAc][Tf_2N] in chloroform with optimal REEs nitrate solution pH of 4.5. REEs concentration: 50 μg/L, IL concentration: 0.1 mmol·L^{-1}, temperature: 40 °C, time: 90 min.

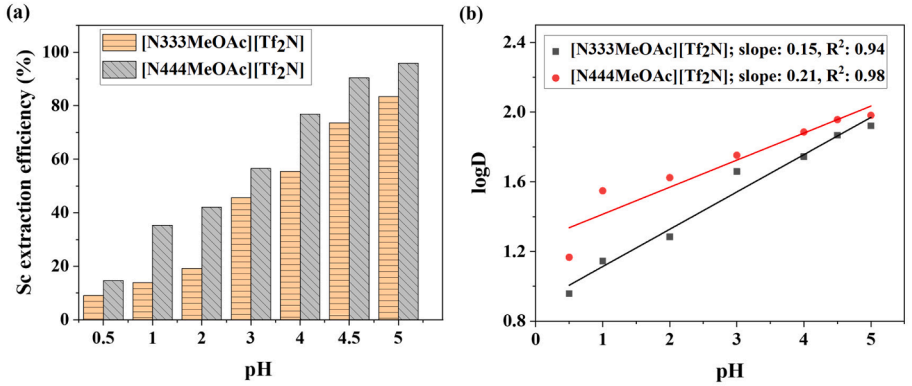


Fig. 3. (a) Correlation of feed Sc nitrate aqueous solution (50 μg/L) at pH 4.5 to extraction efficiency (*E*, %) using [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] (0.1 mmol·L^{-1}) in chloroform. (b) The correlation between logD and pH for Sc(III) extraction using [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] (0.1 mmol·L^{-1}) in chloroform.

extractant for the Sc(III) ion recovery from nitrate solution than [N333 MeOAc][Tf_2N]. The ideal concentration of QA-TSILs for extraction depends on the specific application and extractant used. More investigations are essential to investigate the beneficial conditions for efficient extraction of Sc(III) ion using QA-TSILs.

3.4. *The role of QA-TSILs in Sc(III) extraction process*

The role of [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] for Sc (III) extraction from aqueous phase in solvent extraction differs according to their intrinsic properties. [N333 MeOAc][Tf_2N] can act as a chelating agent that in the aqueous phase, it can form a stable complex with Sc(III) ion, which increases the concentration of chelating agent in the organic phase and facilitates the extraction efficiency and selectivity for Sc(III). In addition, [N333 MeOAc][Tf_2N] can promote the solvation of Sc(III) ion, leading to an increased mass transfer of Sc(III) ion from aqueous to organic phase. On the other hand, [N444 MeOAc][Tf_2N] acts as a solvating agent that enhances the solubility of Sc(III) ion in the organic phase, resulting in an increased mass transfer of Sc(III) ion from aqueous to organic phase and thus more efficient extraction of Sc(III) from the aqueous phase. [N444 MeOAc][Tf_2N] can also improve the stability of the organic phase and increase its resistance to degradation, contributing to a more efficient and stable extraction process. Both [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] exhibited promising results in Sc(III) extraction with enhanced extraction efficiency and selectivity based on their active roles.

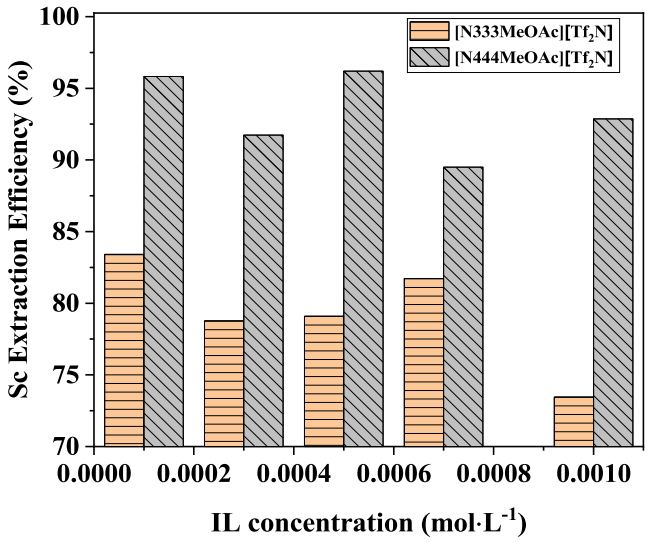


Fig. 4. Extraction of 50 μg/L Sc(III) from nitrate solution employing different concentrations of QA-TSILs (0.1–1.0 mmol·L^{-1}) in chloroform at pH 4.5.

3.5. Performance evaluation of selective extraction and separation for REEs

Trivalent REE have comparable physicochemical features, which makes it difficult to separate them from one another, and they have low separation factors. [26,27]. In this study, the potential of several REEs to be separated was investigated using as-synthesized [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N], with the aqueous phase containing all REE nitrate solutions at a concentration of ca. 50 mg/L, and the equilibrium pH as the variables. The Sc(III) extraction curves showed a significant deviation from those of the other tested REE ions in Fig. 2**a and 2b**. The extraction efficiency started to increase at pH 3 for Sc(III), and reached the highest value of ca. 96 % at pH 5. In contrast, the efficiency of other REEs to be extracted remained less than 35 % at identical pH, resulting in substantially outstanding separation factors between Sc(III) and the other REEs. For instance, the separation factor (β) of Sc(III)/Tb(III), Sc(III)/Ho(III) and Sc(III)/Tm(III) was 10 for [N333 MeOAc][Tf_2N], while that of Sc(III)/Lu(III) and Sc(III)/Yb(III) was 17 for [N444 MeOAc][Tf_2N]. Sc(III) has a higher charge density and a lower ionic radius than those of trivalent lanthanides, which makes it easier to coordinate with the ILs and form stable complex towards its higher selectivity in extraction. Furthermore, the extractability of the REEs was closely reliant on the pH value for [N444 MeOAc][Tf_2N], with a trend of Sc(III) < Y(III) < La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Eu(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III) < Tm(III) < Yb (III) < Lu(III). This pattern demonstrated a shift in extractability away from heavy lanthanides towards the light ones as the pH was increased, which aligned with similar results from previous research where neutral extractants were used [27–29]. Following a thorough comparison with the most recently reported ILs for the selective separation of REEs, it is clear that [N444 MeOAc][Tf_2N] still demonstrates the exceptional separation performance towards the mixed REEs (Fig. 5).

3.6. Reusability of QA-TSILs

Metal ions recovery from IL phase is crucial for IL-based extraction system. Since the acidity of the aqueous phase has a significant impact on the efficacy of Sc(III) extraction, the pH of the stripping solution could dramatically affect the recovery of metal ions from the IL phase. Therefore, a series of stripping experiments were carried out for Sc(III) separation from [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] phase using 2 mL of aqueous H_2SO_4 at various concentrations. As depicted in Fig. 6, the Sc(III) stripping efficiency was steadily improved as the acidity of aqueous solution increased along with the higher concentration of H_2SO_4. In particular, by utilizing a 4 mol·L^{-1} H_2SO_4 solution, the stripping efficiency was high up to 86 % in a single step, indicating that Sc(III) could be readily stripped from the loaded IL phase. It is important to note that, [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] can be recovered by the formation of the restored [N333 MeOAc]$^+$ and [N444 MeOAc]$^+$ cation and [Tf_2N]$^-$ anion. Therefore, metal ion stripping and restoration of [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] could be achieved at the same time. Additionally, once Sc(III) was stripped, [Tf_2N] would be generated in the IL. However, increased solubility of

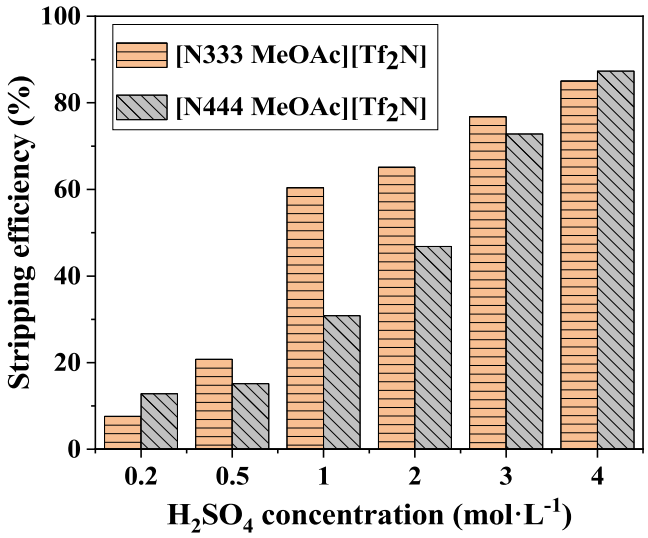


Fig. 6. Stripping of the loaded [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] with various concentrations of nitric acid (temperature = 25 °C; time = 90 min).

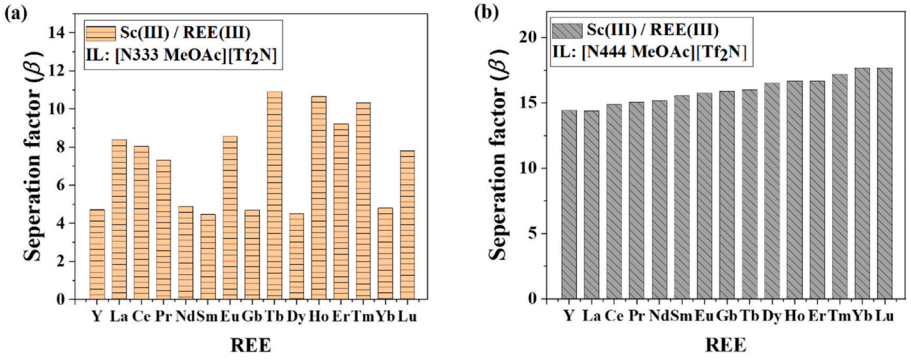


Fig. 5. Separation factor values for the extracted REEs using [N444 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] at pH 4.5.

[Tf_2N] in water could make it partially soluble in the aqueous phase. Nevertheless, it is possible to recover and utilize the IL that was lost during the extraction and stripping steps to extract metal ions again.

3.7. Extraction mechanism

Using the DFT approach at the (U)B3LYP level, full geometry optimizations (Fig. 7) as well as frequency and thermochemical analyses were performed for the ILs (i.e., [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N]) as well as for the three plausible illustrative mechanisms, including neutral, cationic, and anionic exchange, using chloroform as a solvent. A 6-31G** basis set was assigned to each element. It was achieved using the LANL2DZ basis set with an efficient core potential.

DFT calculations results in Table 1 revealed that the neutral exchange mechanism exhibited the lowest energy, indicating that the interaction between Sc(III) and the neutral IL is more favourable than other mechanisms, such as anionic or cationic exchange. The extraction mechanism of Sc(III) using [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] as extractant can be explained as neutral exchange in Fig. 8. This dominant neutral exchange further confirms the high extraction efficiency of Sc(III) using [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N] in experimental results.

In the neutral exchange mechanism (Fig. 8), the metal ion Sc(III) interacts favourably with the IL (**Eqs. (7)** and **(8)**). The solvent extraction process leads to the bonding of Sc with the neutral [N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N], with the release of nitrate ion in the aqueous phase. The overall extraction mechanism can be represented as follows.

a) **Initial state:**

$ScNO_3$ (aq) + [N333 MeOAc]Tf_2N (org) ⇌ Sc(III) (org) + [N333 MeOAc]Tf_2N (org) + NO^{3-}(aq) (7)

or

$ScNO_3$ (aq) + [N444 MeOAc]Tf_2N (org) ⇌ Sc(III) (org) + [N444 MeOAc]Tf_2N (org) + NO^{3-}(aq) (8)

b) **Neutral exchange process:**

Sc(III) (org) + [N333 MeOAc]Tf_2N (org) ⇌ Sc[Tf_2N]$_3$ (org) + [N333 MeOAc]Tf_2N (org) (9)

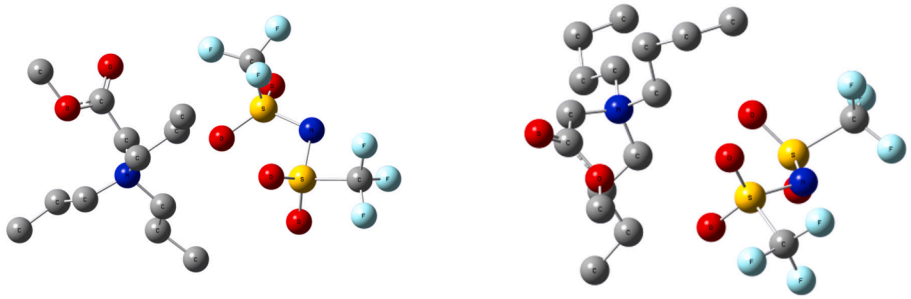
or

Sc(III) (org) + [N444 MeOAc]Tf_2N (org) ⇌ Sc[Tf_2N]$_3$ (org) + [N333 MeOAc]Tf_2N (org) (10)

Table 1
Theoretically calculated parameters for different IL extraction mechanisms.

	Lowest energy (Hartrees)	Enthalpy (H°) / kcal mol^{-1}	Gibbs free energy (G°) / kcal mol^{-1}
[N333 MeOAc][Tf_2N]	−1728.25	21.64	−43.10
[N444 MeOAc][Tf_2N]	−1846.60	26.98	−52.83
Neutral exchange ([N333 MeOAc][Tf_2N])	−4927.35	62.75	−100.40
Cationic exchange ([N333 MeOAc][Tf_2N])	−3876.53	50.20	−75.30
Anionic exchange ([N333 MeOAc][Tf_2N])	−4249.28	47.18	−85.59
Neutral exchange ([N444 MeOAc][Tf_2N])	−5045.26	64.34	−106.36
Cationic exchange ([N444 MeOAc][Tf_2N])	−3995.04	51.51	−86.09
Anionic exchange ([N444 MeOAc][Tf_2N])	−4249.28	47.18	−85.59

In this mechanism, after the bonding of metal ion Sc(III) with the neutral [N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N] in aqueous phase, the Sc(III)-IL complex migrates into the organic phase. As a consequence of energetically favourable reaction, a neutral metal complex Sc[Tf_2N]$_3$ is consequentially formed. This translocation is driven by an energetically favourable reaction facilitated by the specific chemical interactions between the metal ion and IL. Generally, this process can be described by **Eqs. (9)** and **(10)** to explain the underlying chemical transformations. Thus, the stable and neutral Sc[Tf_2N]$_3$ complex can be formed due to the harmonious interplay between Sc(III) ion and [N333 MeOAc][Tf_2N] or [N444 MeOAc][Tf_2N]. These reactions and subsequent complex formation constitute pivotal stages in the overall solvent extraction mechanism, contributing to the selective extraction of Sc(III) ion from aqueous solution to organic phase.



[N333 MeOAc][Tf_2N] [N444 MeOAc][Tf_2N]

Fig. 7. Optimized geometrical structures for ILs. Hydrogens attached to carbon have been omitted for clarity.

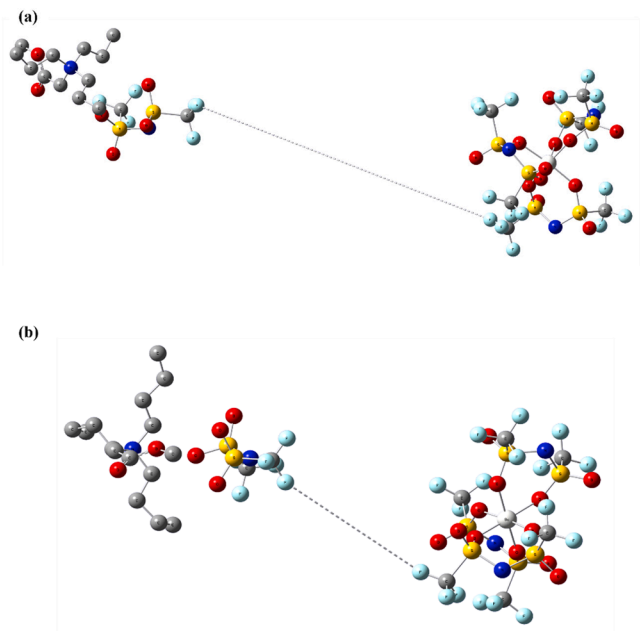


Fig. 8. Neutral exchange process for Sc(III) with (a) [N333 MeOAc][Tf_2N] and (b) [N444 MeOAc][Tf_2N]. Hydrogens attached to carbon have been omitted for clarity.

4. Conclusions

Two types of QA-TSILs, namely [N333 MeOAc][Tf_2N] and [N444 MeOAc][Tf_2N], have been newly designed and successfully synthesized for selective extraction and separation of Sc(III) from other REEs. The extraction efficiency of Sc was found to be dependent on the pH of the aqueous phase and the alkyl chain length of the ILs. At low pH value, the extraction efficiency of Sc(III) was low due to the competition between H^+ and Sc(III) ions for the ligand. However, at pH 4.5 and 5, the extraction efficiency of Sc(III) using [N333 MeOAc][Tf_2N] was 73.6 % and 83.4 %, respectively, while it was high up to 90.5 % and 95.9 %, respectively, using [N444 MeOAc][Tf_2N]. Moreover, stronger hydrophobicity of [N444 MeOAc][Tf_2N] favoured a higher extraction efficiency. Importantly, these QA-TSILs demonstrated a higher selectivity for Sc(III) as compared to other REEs, with high separation factor β of 10 for Sc(III)/Tb(III), Sc(III)/Ho(III), and Sc(III)/Tm(III) using [N333 MeOAc][Tf_2N], and β *of* 17 for Sc(III)/Lu(III) and Sc(III)/Yb(III) using [N444 MeOAc][Tf_2N]. In addition, the ILs could be reused with a high stripping efficiency up to 86 % when 4 mol·L^{-1} H_2SO_4 solution was used. DFT calculations validated that the neutral exchange dominated the IL extraction process for Sc(III). Hence, these new neutral extractants could be a promising substitute to conventional solvent for selective extraction of Sc(III) from REEs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.126038.

References

[1] W.L. Leal Filho, R. Kotter, P.G. Özuyar, I.R. Abubakar, J.H.P.P. Eustachio, N. R. Matandirotya, Understanding Rare Earth Elements as Critical Raw Materials, Sustainability. 15 (2023) 1919, https://doi.org/10.3390/su15031919.
[2] C. Li, J.M. Mogollón, A. Tukker, J. Dong, D. von Terzi, C. Zhang, B. Steubing, Future material requirements for global sustainable offshore wind energy development, Renew. Sustain. Energy Rev. 164 (2022), 112603, https://doi.org/10.1016/j.rser.2022.112603.
[3] S. Zhang, Y. Ding, B. Liu, C. Chang, Supply and demand of some critical metals and present status of their recycling in WEEE, Waste Manag. 65 (2017) 113–127, https://doi.org/10.1016/j.wasman.2017.04.003.
[4] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review, J. Clean. Prod. 51 (2013) 1–22, https://doi.org/10.1016/j.jclepro.2012.12.037.
[5] V. Kaim, J. Rintala, C. He, Selective recovery of rare earth elements from e-waste via ionic liquid extraction: A review, Sep. Purif. Technol. 306 (2023), 122699, https://doi.org/10.1016/j.seppur.2022.122699.
[6] A.D. Salman, T. Juzsakova, S. Mohsen, T.A. Abdullah, P.-C. Le, V. Sebestyen, B. Sluser, I. Cretescu, Scandium Recovery Methods from Mining, Metallurgical Extractive Industries, and Industrial Wastes, Materials. 15 (2022) 2376, https://doi.org/10.3390/ma15072376.
[7] W. Wang, C.Y. Cheng, Separation and purification of scandium by solvent extraction and related technologies: a review, J. Chem. Technol. Biotechnol. 86 (2011) 1237–1246, https://doi.org/10.1002/jctb.2655.
[8] D. Zou, Y. Deng, J. Chen, D. Li, A review on solvent extraction of scandium, J. Rare Earths. 40 (2022) 1499–1508, https://doi.org/10.1016/j.jre.2021.12.009.
[9] Mineral Commodity Summaries (2021), https://doi.org/10.3133/mcs2021.
[10] A. Schreiber, J. Marx, P. Zapp, J.-F. Hake, D. Voßenkaul, B. Friedrich, Environmental Impacts of Rare Earth Mining and Separation Based on Eudialyte: A New European Way, Resources. 5 (2016) 32, https://doi.org/10.3390/resources5040032.
[11] A.R.K. Gollakota, S. Gautam, C.-M. Shu, Inconsistencies of e-waste management in developing nations – Facts and plausible solutions, J. Environ. Manage. 261 (2020), 110234, https://doi.org/10.1016/j.jenvman.2020.110234.
[12] E. Quijada-Maldonado, J. Romero, Solvent extraction of rare-earth elements with ionic liquids: Toward a selective and sustainable extraction of these valuable elements, Curr. Opin. Green Sustain. Chem. 27 (2021), 100428, https://doi.org/10.1016/j.cogsc.2020.100428.
[13] N. Schaeffer, H. Passos, I. Billard, N. Papaiconomou, J.A.P. Coutinho, Recovery of metals from waste electrical and electronic equipment (WEEE) using unconventional solvents based on ionic liquids, Crit. Rev. Environ. Sci. Technol. 48 (2018) 859–922, https://doi.org/10.1080/10643389.2018.1477417.
[14] J.D. Holbrey, K.R. Seddon, Ionic Liquids, Clean Technol. Environ, Policy. 1 (1999) 223–236, https://doi.org/10.1007/s100980050036.
[15] G. Arrachart, J. Couturier, S. Dourdain, C. Levard, S. Pellet-Rostaing, Recovery of Rare Earth Elements (REEs) Using Ionic Solvents, Processes. 9 (2021) 1202, https://doi.org/10.3390/pr9071202.
[16] X. Sun, D. Wu, J. Chen, D. Li, Separation of scandium(III) from lanthanides(III) with room temperature ionic liquid based extraction containing Cyanex 925, J. Chem. Technol. Biotechnol. 82 (2007) 267–272, https://doi.org/10.1002/jctb.1664.
[17] X. Sun, Y. Ji, L. Guo, J. Chen, D. Li, A novel ammonium ionic liquid based extraction strategy for separating scandium from yttrium and lanthanides, Sep. Purif. Technol. 81 (2011) 25–30, https://doi.org/10.1016/j.seppur.2011.06.034.
[18] Z. Zhao, Y. Baba, F. Kubota, N. Kamiya, M. Goto, Synergistic Extraction of Rare-Earth Metals and Separation of Scandium Using 2-Thenoyltrifluoroacetone and Tri-*n*-octylphosphine Oxide in an Ionic Liquid System, J. Chem. Eng. Jpn. 47 (2014) 656–662, https://doi.org/10.1252/jcej.14we360.
[19] Y. Chen, H. Wang, Y. Pei, J. Wang, Selective separation of scandium (III) from rare earth metals by carboxyl-functionalized ionic liquids, Sep. Purif. Technol. 178 (2017) 261–268, https://doi.org/10.1016/j.seppur.2017.01.058.
[20] D. Depuydt, W. Dehaen, K. Binnemans, Solvent Extraction of Scandium(III) by an Aqueous Biphasic System with a Nonfluorinated Functionalized Ionic Liquid, Ind. Eng. Chem. Res. 54 (2015) 8988–8996, https://doi.org/10.1021/acs.iecr.5b01910.
[21] B. Onghena, C.R. Borra, T. Van Gerven, K. Binnemans, Recovery of scandium from sulfation-roasted leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, Sep. Purif. Technol. 176 (2017) 208–219, https://doi.org/10.1016/j.seppur.2016.12.009.
[22] B. Onghena, K. Binnemans, Recovery of Scandium(III) from Aqueous Solutions by Solvent Extraction with the Functionalized Ionic Liquid Betainium Bis (trifluoromethylsulfonyl)imide, Ind. Eng. Chem. Res. 54 (2015) 1887–1898, https://doi.org/10.1021/ie504765v.
[23] Y. Zhang, Y. Deng, W. Guo, D. Liu, Y. Ding, Enhanced Homogeneous Liquid-Liquid Extraction for the Selective Recovery of Sc(III) by Novel UCST-Type Ionic Liquids, ACS Sustain. Chem. Eng. 9 (2021) 9932–9940, https://doi.org/10.1021/acssuschemeng.1c03162.
[24] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H.

Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016., (n.d.).

[25] Chemcraft - graphical software for visualization of quantum chemistry computations. Version 1.8, build 648. https://www.chemcraftprog.com, n.d.

[26] S. Wu, L. Wang, L. Zhao, P. Zhang, H. El-Shall, B. Moudgil, X. Huang, L. Zhang, Recovery of rare earth elements from phosphate rock by hydrometallurgical processes – A critical review, Chem. Eng. J. 335 (2018) 774–800, https://doi.org/10.1016/j.cej.2017.10.143.

[27] M. Van De Voorde, K. Van Hecke, K. Binnemans, T. Cardinaels, Separation of samarium and europium by solvent extraction with an undiluted quaternary ammonium ionic liquid: towards high-purity medical samarium-153, RSC Adv. 8 (2018) 20077–20086, https://doi.org/10.1039/C8RA03279C.

[28] D. Li, Development course of separating rare earths with acid phosphorus extractants: A critical review, J. Rare Earths. 37 (2019) 468–486, https://doi.org/10.1016/j.jre.2018.07.016.

[29] M.K. Jha, A. Kumari, R. Panda, J. Rajesh Kumar, K. Yoo, J.Y. Lee, Review on hydrometallurgical recovery of rare earth metals, Hydrometallurgy. 165 (2016) 2–26, https://doi.org/10.1016/j.hydromet.2016.01.035.