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Boosting the extraction of rare earth elements from chloride medium by novel carboxylic acid based ionic liquids



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Two novel carboxylic acid based ionic liquids (ILs), benzyltributylammonium myristic acetate ([N444Bn][MA]) and benzyltributylammonium dodecanedioic acetate ([N444Bn]2[DDA]), have been rationally designed and successfully synthesized for the extraction of yttrium (denoted as Y(III)) from a chloride aqueous solution and for the separation of mixed rare earth elements (REEs). Comparison studies of the extraction performances of [N444Bn][MA] and [N444Bn]2[DDA] were carefully investigated under different conditions (e.g., equilibrium time, solution acidity, salting-out agent concentration, and REEs concentration). The results indicated that the extraction efficiency of Y(III) reached 87.18% after 2 min using [N444Bn]2[DDA], whereas it required 10 min to reach an extraction efficiency of 47.37% using [N_{444Bn}][MA], mainly due to the larger electronegativity of the incorporated dicarboxylates in the anions of [N_{444Bn}]₂[DDA], which enhanced its coordination with Y(III) compared to [N_{444Bn}] [MA]. However, [N444Bn][MA] illustrated better selective separation behavior than [N444Bn]2[DDA] in mixed REEs solutions (including La, Nd, Eu, Ho, Yb and Y), and the selective factors of Yb and La were 16.21 and 3.30, respectively. Furthermore, the ion association mechanism, evolved from the slope analysis and FT-IR results, contributed to avoiding the saponification procedures and resultant saponification wastewater during the extraction process. In addition, the back-extraction experiments indicated that ~97% Y(III) can be stripped from [N_{444Bn}]₂ [DDA] and [N_{444Bn}][MA] using 1.0 M and 0.4 M HCl, respectively, demonstrating that these ILs can be further used in large-scale applications for the separation and recovery of REEs.

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1. Introduction

Rare earth elements (REEs) are a group of scandium, yttrium and 15 lanthanides in the periodic table. Due to their unique role in many hightechnology industries and the increasing global demand, the separation and recovery of REEs have attracted tremendous attention [1]. In recent decades, many kinds of techniques have been developed for REEs separation, such as extraction, adsorption, and membrane separation [2–7]. Solvent extraction is still one of the most widely used methods in the rare earth industry owing to its facile operation, large treatment capacity, fast extraction rate and remarkable separation ability [8,9].

REEs are naturally distributed together in geological minerals, including bastnasite, monazite and oil shale residue [10]. The separation of individual REEs is particularly difficult due to their extremely similar electronic structures and physicochemical properties [8]. To date, a series of molecular extractants have been employed for REEs separation, such as ammonium, phosphoric acid, acetic acid, phosphine oxide and phosphate [11–15]. Unfortunately, the extraction performance of organic phosphonic acid and carboxylic acid still suffers from unsatisfactory capacity due to the intermolecular hydrogen bonds between dimers. In addition, the hydrogen ions released from acidic extractants in the ion-exchange mechanism also obviously increase the acidity of the aqueous phase and thereby decrease extraction efficiency [16]. To overcome these disadvantages, saponified acidic extractants developed by neutralizing acidic extractants with aqueous ammonia have exhibited improved extraction capacities. Nevertheless, the resultant ammonium ion in the aqueous phase can cause serious pollution [17]. Therefore, exploring green strategies for rare earth extraction is highly desirable but still presents challenges.

Ionic liquids (ILs), composed of tunable cations and anions, are critical environmentally friendly solvents with low melting points [18]. They have attracted extensive attention due to their unique physicochemical properties, such as negligible vapor pressure, nonflammability and structural flexibility [19–21]. Recently, endowing ILs with carboxylate groups through the anion exchange method has been a promising

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approach to efficiently extract REEs. In light of these findings, deprotonated sec-octylphenoxy acetic acid (HSOPAA), N,N-dioctyl diglycolamic acid (DODGAA) and oleic acid (OL) can be used as anions [22-24]. To obtain hydrophobic carboxylate-based ILs, tri-noctylmethylammonium ($[N_{1888}]^+$), tetraoctylammonium ($[N_{8888}]^+$), and trihexyl(tetradecyl)phosphonium $([P_{66614}]^+)$ are usually used as cations due to their long alkyl chains and commercial availability [22-24]. In previous studies, better extractability and selectivity for Y(III) have been observed in [P₆₆₆₁₄][SOPAA] than in conventional extractant counterparts, demonstrating the excellent superiority of ILs over organic extractants [25]. After combining $[N_{1888}]^+$ with the phenoxyacetic acid analogs n-octylphenoxyacetic acid (OCTPOA), the generated [N1888][OCTPOA] also exhibits advanced extraction performance towards Y(III), which is attributed to the optimized Y–O bond distances, as confirmed by the extended X-ray absorption fine structure (EXAFS) [26]. In terms of other REEs, different kinds of carboxylic acid-based ILs have emerged as popular and efficient extractants. For example, the newly fabricated tetraoctylammonium di(2-ethylhexyl)oxamate ([N₈₈₈₈][DEHOX]) exhibited better extraction efficiency in all lanthanides than [N₈₈₈₈][DODGA] and can be reused without loss of extraction performance after HNO₃ regeneration [23]. More interestingly, the most common vegetable oils, such as peanut oil, rapeseed oil, sunflower seed oil and flaxseed oil, can be converted into carboxylic acid-based ILs, resulting in the selectivity of mixed lanthanides during extraction that is similar to the selectivity of conventional extractants such as 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (P507) and di(2-ethylhexyl)phosphate (P204) [27]. Nevertheless, the carboxylic acid based ILs still can be improved in their extractability for REEs and the high viscosity for facile use. Therefore, we expect that by integrating anions with dicarboxylate groups and cations with shorter alkyl chains, ILs can be constructed with a hydrophobic nature, lower viscosity and higher extraction efficiency.

Herein, two novel carboxylic acid-based ILs with a hydrophobic nature were successfully synthesized and investigated as extractants for REEs extraction. (seen in Scheme 1) The cationic structures ($[N_{444Bn}]^+$) of the synthesized ILs exhibit larger electronegativity after benzyl is substituted for alkyl chains, resulting in decreased viscosity and better extractability. Encouraged by the advancement of incorporating dicarboxylate-functionalized groups in anions, the electronegativity can be further strengthened, and a higher extraction capacity for Y(III) is observed in $[N_{444Bn}]_2$ [DDA]. However, $[N_{444Bn}]$ [MA] provides better selective separation of mixed REEs (e.g., separation factor is 16.21 vs. 3.30 for La/Yb and 5.13 vs. 1.65 for La/Y). Based on slope analysis and FT-IR characterization, an ion association mechanism has been proposed to elucidate the extraction process. Moreover, the influences of extraction time, pH values, salt concentration, initial REEs concentration and temperature, as well as the regeneration of REEs, have also been investigated, and the results demonstrate the potential of using synthesized ILs for further applications related to industrial-scale REEs separation.

2. Experimental

2.1. Chemicals and reagents

Benzyltributylammonium chloride ([N_{444Bn}][Cl]), myristic acid (MA), dodecanedioic acid (DDA), yttrium and lanthanide chloride hexahydrate (Y, La, Nd, Eu, Ho, Yb, 99.99%), kerosene, ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) and anion-exchange resin (Amberlite-717) were purchased from Aladdin Co., Ltd. N-octanol, methyl red and bromocresol green indicators were obtained from Macklin Co., Ltd. Sodium hydroxide, sodium chloride and xylenol orange indicators were supplied by Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid was obtained from Xilong Scientific Co., Ltd. All chemicals were used without further purification.

2.2. Apparatuses and measurements

The ¹H and ¹³C NMR spectra of the ILs were obtained in CDCl₃ with an AVIII-500 BRUKER spectrometer. The IL structures were further characterized using FT-IR (Nicolet 6700). The concentration of Y(III) in the aqueous phase was determined using EDTA titration with xylenol orange used as the indicator and hexamethylene tetraamine used as the buffer. The concentration of single REEs ions in the REEs mixture was determined by inductively coupled plasma optical emission spectrometry (ICP-AES, Agilent 700). The pH values were determined by a pH-ISE-EC Hanna. The chloride concentrations in [N_{444Bn}][MA] and [N_{444Bn}]₂ [DDA] were measured by the AgNO₃ test.

2.3. Synthesis and characterization of ionic liquids

2.3.1. Preparation of benzyl(tributyl)azanium myristic acetate [N_{444Bn}] [MA]

A solution of $[N_{444Bn}]OH$ in ethanol was converted from $[N_{444Bn}]Cl$ (1.5597 g, 0.005 mol) using amberlite 717-type anion-exchange resin. Then, 1.1419 g MA (0.005 mol) was added to the $[N_{444Bn}]OH$ solution. The mixture was then stirred at room temperature for 12 h until the neutral solution was obtained. Ethanol and water were removed by a rotary evaporator. $[N_{444Bn}][MA]$ was obtained after drying at 70 °C in a vacuum for 12 h with 84.57% yield. The density and viscosity were 0.952 g·cm⁻³ and 343.7 mPa·s, respectively. The structure was



Scheme 1. Structures of ionic liquids (a) [N_{444Bn}][MA] an [N_{444Bn}]₂[DDA] used in this study

identified by FT-IR, ¹H and ¹³C NMR (see Supplementary Information, **Figs. S1, S2** and **S5**). FT-IR (cm⁻¹): 2956–2869 (CH in CH₂), 1638 (CO in COOH), 1379 (C–N in N⁺_{444Bn}). ¹H NMR (300 MHz, CDCl₃, δ /ppm): 0.85–0.88 (CH₃, t, 3H), 0.97–1.01 (3CH₃, t, 9H), 1.21–1.23 (8CH₂, m, 16H), 1.36–1.45 (4CH₂, m, 8H), 1.51–1.55 (1CH₂, t, 2H), 1.73–1.81 (4CH₂, m, 8H), 2.07–2.11 (1CH₂, t, 2H), 3.20–3.24, (3CH₂, t, 6H), 4.79 (1CH₂, s, 2H), 7.42–7.49 (5Ar–H, m, 5H). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 13.50 (3CH₃), 18.26 (1CH₃), 19.50 (3CH₂), 20.60 (1CH₂), 24.01 (3CH₂), 26.72 (1CH₂), 29.53 (4CH₂), 29.81 (4CH₂), 34.18 (1CH₂), 38.39 (1CH₂), 57.02 (1CH₂), 5 s8.08 (4CH₂), 62.45 (1CH₂), 65.84 (1CH₂), 127.36 (1Ar-CH), 127.90 (1Ar-CH), 128.37 (1Ar-CH), 129.22 (1Ar-CH), 130.58 (1Ar-CH), 132.26 (1Ar-CH), 179.34 (C).

2.3.2. Preparation of benzyl(tributyl)azanium dodecanedioic acetate $[N_{444Bn}]_2[DDA]$

A solution of [N_{444Bn}]OH in ethanol was prepared from [N_{444Bn}]Cl (1.5597 g, 0.005 mol) using amberlite 717-type anion-exchange resin. Then, 0.5758 g DDA (0.0025 mol) was added to the [N_{444Bn}]OH solution. The mixture was then stirred at room temperature for 12 h until the solution became neutral. After the ethanol and water were distilled in a rotary evaporator, the product was dried in a vacuum at 70 °C to yield a slightly yellowish viscous liquid (90.55% yield). The density and viscosity were 0.967 $g \cdot cm^{-3}$ and 1445 mPa \cdot s, respectively. The structure was identified by FT-IR ¹H and ¹³C NMR (see Supplementary Informa-tion, **Figs. S3-S5**). FT-IR (cm⁻¹): 2950–2848 (CH in CH₂), 1637 (CO in COOH), 1389 (C–N in N_{444Bn}^+). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.98-1.02 (6CH₃, m, 18H), 1.20-1.25 (6CH₂, m, 12H), 1.37-1.46(6CH₂, m, 12H), 1.53-1.60 (2CH₂, m, 4H), 1.73-1.81 (6CH₂, m, 12H), 2.14-2.18 (2CH₂, t, 4H), 3.23-3.27 (6CH₂, t, 12H), 4.85 (2CH₂, s, 4H), 7.33-7.36 (2Ar-H, m, 2H), 7.45-7.49 (8Ar-H, m, 8H). ¹³C NMR (75 MHz, CDCl₃, δ/ppm): 13.44 (6CH₃), 19.45 (6CH₂), 22.46 (2CH₂), 24.00 (4CH₂), 26.90 (2CH₂), 29.13 (2CH₂), 29.53 (2CH₂), 29.88 (2CH₂), 38.86 (2CH₂), 56.91 (2CH₂), 58.10 (4CH₂), 62.44 (2CH₂), 127.37 (4Ar-CH), 129.15 (2Ar-CH), 130.50 (2Ar-CH), 132.26 (4Ar-CH), 179.34 (2C).

2.4. Extraction experiments

All extraction experiments were performed by mixing equal volumes of organic phase (the as-prepared ILs dissolved in a mixture of sulfonated kerosene and n-octanol with a volume ratio of 7:3) and aqueous phase containing REEs ions. The extractions were performed in vials and shaken at 1700 rpm for 30 min at 303 K in a temperaturecontrollable turbo thermoshaker (HUXI, HX-20). Sodium chloride was used to maintain constant ionic strength during the extraction. After the extraction, two-phase separation was achieved by a benchtop centrifuge (CENCE, TGL-16 M) operating at 8000 rpm for 5 min. The Y(III) ions were back-extracted from the loaded organic phase with dilute hydrochloric acid. The stripping efficiency was calculated by measuring the concentration of Y(III) ions in the stripping acid. The extraction efficiency (E), distribution ratio (D), stripping efficiency (S) and separation factors (β) were obtained using the following equations:

$$E = \frac{[M]_i - [M]_t}{[M]_i} \times 100\%$$
 (1)

$$D = \frac{[M]_i - [M]_t}{[M]_t}$$
(2)

$$S = \frac{[M]_{aq}}{[M]_{ILS}} \times 100\%$$
⁽³⁾

$$\beta = \frac{D_1}{D_2} \tag{4}$$

where $[M]_i$ and $[M]_t$ represent the initial and final concentrations of REEs in the aqueous phase, D_1 and D_2 are the distribution ratios of REE

1 and 2 ions, $[M]_{\rm aq}$ is the equilibrium concentration of REEs ions in stripping acid, and $[M]_{\rm ILs}$ is the initial concentration of loaded REEs ions in the extracting phase, respectively.

3. Results and discussion

3.1. The effect of extraction time and aqueous pH

In solvent extraction investigations, accelerating kinetics is important for improving extraction performance [28,29]. To study the extraction kinetics, a feed solution of 0.007 M YCl₃ with pH value of 4 was contacted with 0.018 M organic phase at an organic/aqueous phase volume ratio (O/A) of 1. As shown in Fig. 1a, the extraction efficiencies reached 45.15% and 87.18% after shaking for 2 min for [N_{444Bn}][MA] and [N_{444Bn}]₂[DDA], respectively. Then, the extraction efficiencies slightly increased within 10 min and were maintained at 89.01% and 47.45% after 20 min, indicating that 20 min was enough to achieve extraction equilibrium between the two phases. Notably, to ensure that the extraction equilibrium is reached and keep the experimental conditions consistent, the shaking time is prolonged. Therefore, all further extraction experiments were performed within 30 min.

To investigate the effect of solution acidity on extraction behavior, the extraction efficiency of Y(III) was measured at different pH values using [N_{444Bn}][MA] and [N_{444Bn}]₂[DDA]. The initial aqueous phase contained 0.007 M YCl₃ and 0.1 M NaCl. By adding a certain amount of 1 M HCl or 1 M NaOH solution, the pH values of the aqueous phase were adjusted and varied between 1.5 and 5.0. As presented in Fig. 1b, all the extraction efficiencies of Y(III) increased with increasing aqueous pH value. For example, the extraction efficiencies were 1.12% and 1.11% at pH = 1.8 for $[N_{444Bn}][MA]$ and $[N_{444Bn}]_2[DDA]$, respectively, and then increased to 48.27% and 94.14% at pH = 5.0. The negative effect of high acidity could be attributed to the competitive extraction between Y(III) and H⁺ [30]. More specifically, the amount of ILs combined with protons obviously increased with increasing H⁺ concentration in the aqueous phase, resulting in a reduced probability of coordination between the ILs and Y(III), accordingly leading to a decay in the extraction efficiency of Y(III) [31]. More importantly, the comparison of the extractability also revealed that $[N_{444Bn}]_2$ [DDA] was much better than [N_{444Bn}][MA] at pH values ranging from 2.5 to 5.0, showing that [DDA]⁻ was dominant in improving the REEs extraction capacity over [MA]⁻.

3.2. The effect of salting-out agent and extractant concentration

The salting-out agent is essential to the extraction process due to the elimination of emulsification and improved extractability with the addition of NaCl [32]. Therefore, the effect of the salting-out agent on extraction behaviors was investigated in 0.007 M YCl₃ solution with different amounts of NaCl (Fig. 2a). As expected, the extraction efficiencies of Y (III) for both [N_{444Bn}][MA] and [N_{444Bn}]₂[DDA] significantly increased with increasing concentrations of NaCl, which efficiently facilitated the generation of chloro-complexes containing REEs ions and thereby enhanced extractability. The main reason is assumed to be that NaCl with a high water-binding capacity can reduce the hydration of Y(III) and cause free water to continue to be lost in aqueous solution [33]. Salt anions also act as bridges to connect with the IL and REEs ions and undergo strong complexation at the liquid-liquid interface [34]. Furthermore, the effect of the extractant concentration was also studied in 0.007 M YCl₃ aqueous solution associated with the addition of 0.1 M NaCl. As depicted in Fig. 2b, the extractabilities of Y(III) exhibited an increasing trend with increasing IL concentration for both fabricated ILs. For [N_{444Bn}][MA], the extraction efficiency of Y(III) reached approximately 95% when the extractant concentration reached 0.035 M. In the case of [N_{444Bn}]₂[DDA], a higher extraction efficiency (i.e., 98%) was realized with a much lower IL concentration (i.e., 0.018 M),



Fig. 1. The effects of (a) time and aqueous (b) pH on the extraction efficiency of Y(III). Organic phase: 0.018 M [N_{444Bn}]₂[DDA] or [N_{444Bn}][MA]; aqueous phase: 0.007 M YCl₃, 0.1 M NaCl; O/A = 1, T = 303 K; (a) time = 1 - 20 min, pH = 4; (b) pH = 1.5 - 5, time = 30 min.

demonstrating the superior extraction performance of Y(III) with $[N_{444Bn}]_2[DDA]$ compared with $[N_{444Bn}][MA]$ at the same extractant concentrations.

3.3. Determination of loading capacity

The loading capacities of $[N_{444Bn}][MA]$ and $[N_{444Bn}]_2[DDA]$ were tested with different initial concentrations of Y(III) in feed solutions ranging from 0.004 to 0.02 M. The concentration of the extractants and the aqueous phase pH were 0.018 M and 4.0, respectively. As illustrated in Fig. 3a, the extraction efficiencies of Y(III) gradually decreased when the initial concentrations of Y (III) in the feed solution were increased. At an initial Y(III) concentration of 0.0046 M in the aqueous phase, approximately 51.15% of the Y(III) was extracted by $[N_{444Bn}]_2$ [DDA]. Because the IL extractant was excessive, all the Y(III) in the aqueous phase could be extracted from the organic phase with a low Y(III) concentration (0.0046–0.0067 M). In the high Y(III) concentration region, the IL quantities were insufficient to coordinate with the Y(III) ions, leading to a sharp decreasing trend. In addition, Fig. 3b showed that the loading capacities of Y(III) in $[N_{444Bn}][MA]$ and $[N_{444Bn}]_2[DDA]$ gradually increased with increasing Y(III) concentration. The saturation loading capacities of Y(III) for $[N_{444Bn}]_2[DDA]$ were much higher than that those for $[N_{444Bn}][MA]$ (0.433 vs. 0.172 mol \cdot mol $^{-1}$, the mole ratio of Y(III) to ILs), which could be attributed to the fact that there were dicarboxylic acid groups in DDA and accordingly more carboxylates in $[DDA]^-$ compared with $[MA]^-$. More importantly, the large electronegativity derived from the carboxylate group obviously promotes the coordination of the C=O bond with Y(III), ultimately giving rise to the higher loading capacity towards Y(III) [35]. Benzyl groups could usually act as weak electron donors due to the inductive effect. Therefore, the electronegativity of $[N_{444Bn}]^+$ in our as-prepared ILs became stronger after the alkyl chains of the quaternary ammonium cation were replaced by benzyl groups, also contributing to proton dissociation and enabling cations to extract REEs.

3.4. Extraction mechanism

Understanding the extraction mechanism of IL is beneficial for developing more efficient IL extractants for the extraction and separation of REEs. Two possible mechanisms for REEs extraction with ILs are termed the ion exchange mechanism and the neutral mechanism



Fig. 2. The effects of (a) NaCl concentration and (b) extractant concentration on the extraction efficiency of Y(III). Organic phase: (a) 0.018 M [N_{444Bn}]₂[DDA] and [N_{444Bn}][MA], (b) 0.005-0.025 M [N_{444Bn}]₂[DDA] and 0.005-0.045 M [N_{444Bn}][MA]; aqueous phase: 0.007 M YCl₃, 0.1 M NaCl, pH = 4, 0/A = 1; T = 303 K, time = 30 min.



Fig. 3. The effects of initial Y(III) concentration on the (a) extraction efficiency and (b) loading capacity of $[N_{444Bn}]_2[DDA]$ and $[N_{444Bn}][MA]$. Organic phase: 0.018 M $[N_{444Bn}]_2[DDA]$ or $[N_{444Bn}][MA]$; aqueous phase: 0.004 – 0.021 M YCl₃, 0.1 M NaCl, pH = 4, 0/A = 1; T = 303 K, time = 30 min.



 $\label{eq:FIR-analysis of the organic phase. (a) $$ [N_{444Bn}][MA]; (b) $$ [N_{444Bn}][MA]$ loaded with Y (III), (c) $$ [N_{444Bn}]_2[DDA]; (d) $$ [N_{444Bn}]_2[DDA]$ loaded with Y (III). $$ \label{eq:FIR-analysis}$

[24,36]. In this work, the extraction mechanism for this kind of IL was determined by FT-IR characterization and slope analysis. The FT-IR spectra of [N_{444Bn}][MA], [N_{444Bn}][MA] loaded with Y(III), [N_{444Bn}]₂[DDA] and [N_{444Bn}]₂[DDA] loaded with Y(III) were displayed in Fig. 4. The comparison showed that the peak of the C=O stretching vibration at 1638 cm⁻¹ obviously increased to 1664 cm⁻¹ when $[N_{444Bn}]$ [MA] was loaded with Y(III), demonstrating the interactions between the Y(III) and C=O groups of [N_{444Bn}][MA] [32,37]. Similar results could also be obtained with [N_{444Bn}]₂[DDA] because the C==0 stretching vibration at 1637 cm⁻¹ in [N_{444Bn}]₂[DDA] increased to 1650 cm⁻¹ in loaded [N_{444Bn}]₂[DDA] [38]. Furthermore, the C–N stretching vibration at 1389 cm⁻¹ in pristine [N_{444Bn}]₂[DDA] downshifted to 1373 cm⁻¹ after loading with Y(III), indicating that more electronegative $[N_{444Bn}]^+$ participates in this extraction [39]. Therefore, the ion association mechanism could be used to elucidate the extraction process of Y(III) with these carboxylate-functionalized ILs.

To further investigate the extraction mechanism, the complex stoichiometries were determined using the slope analysis method [25,38]. The extraction equilibrium between Y(III), chloride ions, and ILs may be represented by Eq. (5).

$$Y_{(aq)}^{3+} + x[ILs]_{(org)} + yCl_{(aq)}^{-} \stackrel{K_{ex}}{\iff} [ILs]_{x}YCl_{y}$$
(5)

The subscripts (org) and (aq) indicate the organic and aqueous phases, respectively. The distribution ratio (D) and equilibrium constant (K_{ex}) are defined as Eqs. (6) and (7).

$$D = \frac{[ILs]_x YCl_y}{Y^{3+}_{(aq)}}$$
(6)

$$K_{ex} = \frac{[ILs]_{x}YCl_{y}}{Y_{(aq)}^{3+}[ILs]_{(org)}^{x}[Cl^{-}]_{(aq)}^{y}}$$
(7)

Applying Eq. (6) to Eq. (7) yields Eq. (8)

$$K_{ex} = \frac{D}{\left[ILs\right]_{(org)}^{x}\left[CI^{-}\right]_{(aq)}^{y}}$$
(8)

Then, logD can be concluded by Eq. (9)

$$\log D = \log K_{ex} + x \log [ILs]_{(org)} + y \log Cl_{(aq)}^{-}$$
(9)

As shown in Fig. 5a, the linear relationship between logD and log $[N_{444Bn}]$ [MA] could be obtained with a slope of 1.6 in the extractant concentration region ranging from 0.008 to 0.021 M, indicating that the stoichiometry of $[N_{444Bn}]$ [MA] with Y(III) was assumed to be approximately 1.5:1. For $[N_{444Bn}]_2$ [DDA] (Fig. 5b), the plot of logD as a function of log $[N_{444Bn}]_2$ [DDA] resulted in a straight line with a slope of 2.02 when the extractant concentrations were changed from 0.005 to 0.013 M, also confirming that the stoichiometry of $[N_{444Bn}]_2$ [DDA] with Y(III) is 2:1 during the extraction process. In addition, three weakly coordinating rare-earth chloride ions were involved in the rare-earth-containing complex according to the electroneutrality principle. Therefore, the extraction mechanism of Y(III) by ILs could be represented by the following equations:

$$Y^{3+}_{(aq)} + 1.5[N_{444Bn}][MA]_{(org)} + 3Cl^{-}_{(aq)} = [N_{444Bn}]_{1.5}Y[MA]_{1.5}Cl_{3(org)}$$
(10)

$$Y_{(aq)}^{3+} + 2[N_{444Bn}]_2[DDA]_{(org)} + 3Cl_{(aq)}^- = [N_{444Bn}]_4 Y[DDA]_2 Cl_{3(org)}$$
(11)

3.5. Determination of thermodynamic parameters

The effects of temperature on the extraction efficiencies of $[N_{444Bn}]$ [MA] and $[N_{444Bn}]_2$ [DDA] for Y(III) from the aqueous phase were evaluated in the range of 303–343 K. As shown in Fig. 6a, the results revealed



Fig. 5. Plot of logD as a function of $log[N_{444Bn}][MA]$ (a) and $log[N_{444Bn}]_2[DDA]$ (b). Organic phase: (a) 0.005 - 0.013 M $[N_{444Bn}]_2[DDA]$, (b) 0.008 - 0.021 M $[N_{444Bn}][MA]$; aqueous phase: 0.007 M YCl₃, 0.1 M NaCl, pH = 4, O/A = 1; T = 303 K, time = 30 min.

that both the extraction efficiencies of Y(III) for $[N_{444Bn}]_2[DDA]$ and $[N_{444Bn}][MA]$ decreased with increasing temperature, mainly because high temperatures increased the motion of molecules and thereby decreased the stability of the formed complex involved in Y(III) and ILs [31].

The enthalpy change (Δ H) during the extraction could be determined based on the slope of the plot of logD versus 1000/T using the van't Hoff Eq. (12):

$$\log D = -\frac{\Delta H}{2.303 \text{RT}} + C \tag{12}$$

where R is the universal gas constant, and C is the constant. As shown in Fig. 6b, plotting logD versus 1000/T resulted in a straight line with a slope of 0.2993 for $[N_{444Bn}]_2[DDA]$ and of 0.1485 for $[N_{444Bn}][MA]$. As presented in Table 1, the enthalpy changes were $-5.73 \text{ kJ} \cdot \text{mol}^{-1}$ and $-2.84 \text{ kJ} \cdot \text{mol}^{-1}$ for $[N_{444Bn}]_2[DDA]$ and $[N_{444Bn}][MA]$, respectively, showing that the extraction process of Y(III) involved an exothermic reaction. The change in Gibbs free energy (ΔG) was calculated using Eq. (13) as follows:

$$\Delta G = -RTlnK_{ex} \tag{13}$$

Table 1 Thermodynamic parameters of Y(III) extractions in chloride medium (T = 303 K, time = 30 min, pH = 4).

ILs	$\Delta H (kJ \cdot mol^{-1})$	$\Delta G (kJ \cdot mol^{-1})$	$\Delta S (J \cdot mol^{-1} \cdot K^{-1})$
[N _{444Bn}] ₂ [DDA]	-5.73	-55.37	163.83
[N _{444Bn}][MA]	-2.84	-45.67	141.35

 K_{ex} is the extraction equilibrium constant and is calculated by plotting logD versus log[ILs] (Fig. 5). The change in Gibbs free energy was $-55.37~kJ\cdot mol^{-1}$ and $-45.67~kJ\cdot mol^{-1}$ for [N_{444Bn}]₂[DDA] and [N_{444Bn}] [MA], respectively. The negative values of Gibbs free energy confirmed the feasibility and favorable nature of the extraction reactions. The change in entropy (ΔS) at a particular temperature was calculated using Eq. (14) as follows:

$$\Delta G = \Delta H - \Delta ST \tag{14}$$

The values of ΔS were determined to be 163.83 J·mol⁻¹·K⁻¹ and 141.35 J·mol⁻¹·K⁻¹, indicating that the extraction system was disordered in nature [31,40].



Fig. 6. (a) Effect of temperature on the extraction of Y(III) and (b) Van't Hoff plot correlating the distribution ratio with the extraction temperature. Organic phase: 0.018 M [N_{444Bn}]₂[DDA] and [N_{444Bn}][MA]; aqueous phase: 0.007 M YCl₃, 0.1 M NaCl, pH = 4, O/A = 1; *T* = 303 K, time = 30 min.



Fig. 7. Stripping of the loaded $[N_{444Bn}]_2[DDA]$ and $[N_{444Bn}][MA]$ with different concentrations of hydrochloric acid. [HCl] = 0– 1.0 M; T = 303 K, time = 30 min.

3.6. Stripping properties

The stripping performance is a significant indicator for assessing the recovery of REEs ions from the organic phase in industrial-scale applications [28]. The stripping properties of Y(III) were studied using hydrochloric acid at 0-1.0 M as the regenerant because the extraction efficiency was highly pH dependent, as indicated in the aforementioned discussions. Before the stripping test, 0.018 M [N_{444Bn}][MA] and [N_{444Bn}] ₂[DDA] were applied to extract 0.0031 and 0.007 M Y(III) from solution, respectively. As shown in Fig. 7, the Y(III) ions were obviously stripped from the loaded $[N_{444Bn}][MA]$ because of the increase in acidity and were almost completely stripped off through the point where the HCl concentration reached 0.04 M. However, the stripping percentage of Y (III) for $[N_{444Bn}]_2[DDA]$ was still lower than that for $[N_{444Bn}][MA]$, mainly because more H⁺ was expended to satisfy the large number of carboxylate-functionalized groups in the IL anions. Fortunately, approximately 83.82%, 93.75% and 96.56% of Y(III) could be back-extracted from the loaded $[N_{444Bn}]_2$ [DDA] with HCl concentrations of 0.1, 0.6 and 1.0 M, respectively, exhibiting excellent regeneration performance.

3.7. Separation of mixed REEs

To investigate the separation ability of $[N_{444Bn}][MA]$ and $[N_{444Bn}]_2$ [DDA] in mixed REEs solutions, the extraction efficiencies and distribution coefficients of La(III), Nd(III), Eu(III), Ho(III), Yb(III), and Y (III) were obtained. The initial concentration in the aqueous phase was approximately 0.001 M for each metal ion, and the aqueous pH value was fixed at 3. Considering that the loading capacity of $[N_{444Bn}]_2$ [DDA] was approximately twice that of [N_{444Bn}][MA], the concentrations of [N_{444Bn}][MA] and [N_{444Bn}]₂[DDA] were 0.037 M and 0.018 M, respectively, to discern and compare their extractability more easily. As shown in Fig. 8a, the order of the extraction efficiency and distribution coefficient was La(III) < Y(III) < Nd(III) < Ho(III) < Eu(III) < Yb(III)for [N_{444Bn}][MA], which is the inverse order of the ionic radius of lanthanides because lanthanides with decreasing radius coordinate more strongly with [N_{444Bn}][MA] [27,41]. In the case of [N_{444Bn}]₂[DDA], a similar order of mixed REEs extractions could be obtained, except for Eu (III). In addition, selectivity is another important factor for evaluating the extraction performance and can be described as the separation factor (β). From Fig. 8b, the calculated β values of the REEs pairs in [N_{444Bn}] [MA] were almost always higher than those in [N_{444Bn}]₂[DDA]. For example, the β values of La/Y were 5.13 and 1.65 after separation by [N444Bn][MA] and [N444Bn]2[DDA], respectively. Similar results could also be obtained from the β values of La/Eu (14.67 for [N_{444Bn}][MA] vs. 4.12 for [N_{444Bn}]₂[DDA]) and La/Yb (16.21 for [N_{444Bn}][MA] vs. 3.30 for [N_{444Bn}]₂[DDA]), indicating that [N_{444Bn}][MA] exhibited better selectivity for REEs separation than [N_{444Bn}]₂[DDA] and thereby could be used in further recycling rare-earth metals from spent magnets.

4. Conclusions

In summary, new kinds of carboxylic acid based ILs with tailored electronegativity were synthesized and tested as high-performance extractants for REEs from a chloride medium. The results indicated that [N_{444Bn}]₂[DDA] and [N_{444Bn}][MA] both efficiently extract Y(III) at the low acidity associated with salting-out agent NaCl, avoiding the environmental issues produced by conventional acidic and neutral extractants. A linear regression analysis of the plot of logD as a function of log[ILs] revealed the formation of the ~1:1.5 or 1:2 metal:ligand complexes of REEs and ILs. In addition, the ion association extraction mechanism was proposed to describe the extraction behavior according to the slope analysis method and FT-IR characterizations. The enthalpy change value, ΔH , over the temperature range 303–343 K for [N_{444Bn}]₂[DDA] and [N_{444Bn}] [MA] were calculated to be -5.73 and -2.84 kJ·mol⁻¹, respectively, demonstrating that the extraction of Y(III) with the as-prepared ILs was an exothermic reaction. Furthermore, the back-extraction experiments indicated that [N_{444Bn}][MA] exhibited better stripping properties than [N_{444Bn}]₂[DDA], and Y(III) extracted with [N_{444Bn}][MA] can be almost



Fig. 8. (a) Distribution ratio, extraction efficiency and (b) separation factor of REEs extracted by $[N_{444Bn}][MA] [N_{444Bn}]_2[DDA]$ at pH 3. Organic phase: 0.018 M $[N_{444Bn}][MA]$ or 0.037 M $[N_{444Bn}]_2[DDA]$; aqueous phase: mixed REEs solution of 0.0012 M LaCl₃, 0.0015 M NdCl₃, 0.0014 M HoCl₃, 0.0012 M EuCl₃, 0.0012 M YbCl₃ and 0.0014 M YCl₃, 0.1 M NaCl, pH = 3, O/A = 1; T = 303 K, time = 30 min.

totally stripped with 0.2 M acidity. The competitive extraction of mixed REEs illustrated that the extractability of $[N_{444Bn}]_2$ [DDA] was higher than that of $[N_{444Bn}]$ [MA] due to the larger electronegativity, whereas $[N_{444Bn}]$ [MA] exhibited better selectivity and could be employed for further applications related to industrial-scale REEs separations.

Author contribution statement

Yu Deng: Investigation, Data curation, Formal analysis, Writing - Original Draft.

Yigang Ding:Conceptualization, Supervision.

Zhong Huang: Methodology.

Ying Yu: Investigation.

Jun He: Project administration.

Yi Zhang:Conceptualization, Writing - Review & Editing, Funding acquisition.

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

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