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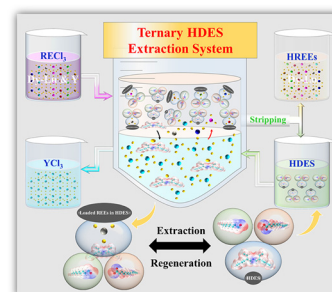
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Tailored ternary hydrophobic deep eutectic solvents for synergistic separation of yttrium from heavy rare earth elements

Shuainan Ni, Yun Gao, Guisu Yu, Sijia Zhang,
Zhiyuan Zeng and Xiaoqi Sun*

Clean, efficient and economical separation of yttrium (Y) from heavy rare earth elements (HREEs) has always attracted attention.

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Tailored ternary hydrophobic deep eutectic solvents for synergistic separation of yttrium from heavy rare earth elements†

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Clean, efficient and economical separation of yttrium (Y) from heavy rare earth elements (HREEs) has always attracted attention. Herein, a strategy for the separation of Y from HREEs based on ternary hydrophobic deep eutectic solvent (HDES) extraction has been first reported. A total of 44 HDESs were prepared with four carboxylic acids as hydrogen bond donors (HBDs), bis(2-ethylhexyl) amine (BEA) as the hydrogen bond acceptor (HBA) and 1-decanol (DL) as the third component. The prepared HDESs have the advantages of simple preparation, no purification requirement, low viscosity, low water solubility and low toxicity. Performances of the HDESs for the separation of Y from HREEs were systematically evaluated. The synergistic effects of each component in the HDESs improve the extraction and separation performances of Y from the HREEs without saponification and organic solvents. Among them, the DL : oleic acid (OA) : BEA-based HDES with OA as the HBD has good extraction ability, higher saturation loading capacity and better phase separation stability. The separation factors of the DL : OA : BEA (9 : 1 : 5) HDES for HREEs (Dy–Lu) and Y in industrial Y-enriched solutions are Dy/Y ≥ 3.05, Ho/Y ≥ 3.37, Er/Y ≥ 4.29, Tm/Y ≥ 6.00, Yb/Y ≥ 10.8, and Lu/Y ≥ 11.2, respectively. The loaded HDES can be easily stripped and remains stable during multiple regeneration cycles. The HDES has shown excellent extraction and separation performance for HREEs (Dy–Lu) and Y, and potential for application in sustainable rare earth separation.

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Introduction

Rare earth elements (REEs, lanthanides plus Sc and Y) have unique physical and chemical properties, are essential and important raw materials in many high-tech fields, and are considered as modern industrial vitamins.^{1,2} In particular, heavy rare earth elements (HREEs, Gd–Lu and Y) are widely used in new energy, new materials, aerospace, electronic information and other fields.^{3–5} Ion-adsorbed rare earth minerals are the world's primary source of HREEs and are mainly distributed in southern China.^{6,7} It is worth noting that Y coexists with lanthanides in ion-adsorbed rare earth minerals due to their

identical cationic charges and remarkable similarities in ionic radii.^{8,9} Although the separation processes of REEs are changed due to the different contents, they all involve the separation of Y from HREEs in ion-adsorbed rare earth minerals. The separation of Y from HREEs is difficult due to their similarities, especially the separation of Y from holmium (Ho) and erbium (Er).^{10,11} Currently, solvent extraction processes are mainly used in industry to separate adjacent REEs.^{12,13} The effective separation, easy automatic control, continuous operation and low cost are the prime advantages of the solvent extraction technique.¹⁴ The industrial process of individual rare earth metal separation from ion-adsorbed rare earth minerals is achieved using the extractants of naphthenic acid (NA, a mixture of carboxylic acids) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507).¹² NA is used for the separation of Y from lanthanides, while P507 is used for the separation of lanthanides.

As for the separation of Y and HREEs, a variety of representative extractants have been reported, such as carboxylic acids,^{15,16} phosphorus acids,¹⁷ neutral phosphorus extractants^{18,19} and amines.²⁰ Among them, carboxylic acid extractants are the most important ones.^{11,21} Particularly, the separation process of Y from HREEs based on naphthenic acid

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1 (NA) extraction systems has been widely used in the rare earth industry of China for decades.^{22,23} However, after long-term production practice, some defects in NA extraction systems have gradually been exposed. For example, NA extraction systems often show severe emulsification and a third phase. In addition, NA is a by-product of the petroleum industry with complex components, unstable properties and high water solubility.^{24,25} In order to overcome the above shortcomings, a series of new carboxylic acid extractants such as sec-octylphenoxyacetic acid (CA12),²⁶ sec-nonylphenoxyacetic acid (CA100),^{27,28} (2,6-dimethylheptyl) propanoic acid (POPA),²⁹ and phosphoryl carboxylic acids³⁰ has been prepared. Furthermore, some attempts at mixed extraction systems based on CA12, including CA12-P507,³¹ CA12-Cyanex 272,³² and CA12-TBP (tributyl phosphate),²⁶ have been made. However, they have excellent performance for the separation of Y and light rare earth elements (LREEs), but still cannot solve the problem of poor separation of Y and HREEs. In addition, carboxylic acid extractants need to be saponified with alkali to effectively extract REEs, which not only consumes alkali, but also produces a large amount of wastewater.^{25,33} It is worth noting that the pollution of the environment by saponification wastewater produced by the rare earth industry has attracted widespread attention.³⁴

In the search for cleaner and better separation strategies for Y and HREEs, recent studies have focused on ionic liquids (ILs).^{35,36} ILs are defined as room-temperature molten salts, also known as ‘designer solvents’, with adjustable structures and properties, low vapor pressures, high thermal stabilities, wide liquid paths and so on.^{37,38} Various ILs with excellent extraction abilities, good stabilities, and good interfacial phenomena have been designed for the separation and purification of Y.^{39–41} For example, bifunctional ILs of [methyltrioctyl ammonium][sec-octylphenoxyacetic] ([A336][CA12]),⁴² [methyltrioctyl ammonium][sec-nonylphenoxyacetic] ([A336][CA100])⁴³ and [methyltrioctyl ammonium][neodecanoate]⁴⁴ were successively used for the extraction and purification of Y-enriched solutions to obtain high-purity Y products. Bifunctional ILs overcome the problems caused by the saponification of carboxylic acid extractants and make the extraction processes more environmentally friendly. However, the higher viscosity of ILs based on methyltrioctyl ammonium as the cation still requires dilution with volatile, flammable and toxic organic solvents. Recently, several novel undiluted functional pyridine carboxylic acid ILs were reported for the separation of Y from Ho and Er with excellent separation performance.⁴⁵ Although the ILs are promising alternatives to conventional organic solvents and have great potential for the separation and purification of Y, the high viscosity and potential toxic manifestations of ILs are important defects.^{46–48}

In recent years, the impacts of volatile, toxic and flammable organic solvents on environmental pollution, production safety and human health have attracted more and more attention.^{49,50} Thus, research on green and sustainable solvents has increased dramatically. An excellent green solvent used in the liquid–liquid extraction process should have the

characteristics of non-volatility, low toxicity, non-flammability, low viscosity, sufficient hydrophobicity and large density differences against water, all of which are beneficial for improving the performance and efficiency of the extraction process.^{51,52}

In 2003, a new and promising class of designer solvents was reported by Abbott *et al.*,⁵³ called deep eutectic solvents (DESSs).⁵⁴ DESSs are eutectic mixtures based on the simple mixing of appropriate proportions of hydrogen bond donor (HBD) components and hydrogen bond acceptor (HBA) components to form liquids at room temperature.⁵⁵ More recently, HDESSs have attracted widespread attention in the field of liquid–liquid extraction since they were first reported in 2015.^{56,57} HDESSs are usually prepared by simply mixing two or more components based on biodegradable, nontoxic, cheap and renewable chemicals.^{58–60} For example, menthol, thymol, long-chain fatty acids, gemfibrozil, ibuprofen, lidocaine and other natural products, drugs and sustainable compounds have been reported for the preparation of HDESSs.^{48,60,61} Compared with traditional molecular solvents and ILs, HDESSs as a new generation of green solvents have a number of important advantages such as easier preparation processes, no need for purification, low cost, potential biodegradability and negligible toxicity, which highly adhere to the 12 principles of green chemistry.^{52,56,62} The unique combination of physical and chemical properties of HDESSs is helpful for diversified and

colourful applications in green chemistry,⁶³ such as the extraction of pharmaceuticals,⁶¹ heavy metal recovery from wastewater,⁶⁴ the separation of carboxylic acids,⁶⁵ the selective extraction of boric acid,^{66,67} liquid–liquid extraction and the separation of metal resources,^{68–72} etc. metals HBDs

As far as we know, however, HDESSs have not been used for the separation of Y from HREEs. In this work, a total of 44 HDESSs were prepared based on four carboxylic acids, *i.e.*, decanoic acid (DA), OA, 2-hexyl-decanoic acid (HDA) and gemfibrozil (GE) as hydrogen bond donors, BEA as the HBA and DL as the third component. The key physiochemical properties of the prepared ternary HDESSs were determined, including densities, viscosities and the cross-contamination of the HDESS phase and water phase. Furthermore, to evaluate the application potential of ternary HDESSs in the extraction and separation of Y from HREEs, a multi-criterion optimization was performed, including the composition ratio of each component in ternary HDESSs, the initial pH of the aqueous solution and the concentration of salting-out agents in the extraction performance of Y and HREEs. The stripping and recycling stabilities of the HDESSs were determined, highlighting the trade-offs in the solvent performance from multiple perspectives. Besides, the extraction mechanism of REEs extracted using a ternary HDESS was studied. The performance of ternary HDESSs for the extraction and separation of Y from HREEs in the industrial Y-enriched solutions was evaluated under the optimal experimental conditions. The prepared ternary HDESSs have the advantages of simple preparation, no need for purification, low viscosity, low water solubility, low toxicity and non-volatility. Moreover, Y and HREEs can be extracted and separated using the ternary HDESSs without saponification. The extrac-

“is helpful for diversified and colourful applications” should be revised to be “facilitates diverse applications”

tion and separation performance can be customized and adjusted, and the extraction process is cleaner, safer and more economical.

Experimental

The chemicals (Table S1[†]), instrumentation, sample preparation, experiment details and density functional theory (DFT) computational details are provided in the ESI.[†]

Results and discussion

Selection and characterization of HDES materials

As a novel designable solvent, HDESs have been considered as a greener solvent alternative to conventional organic solvents and ILs. HDESs based on natural products, drugs and low-toxicity components are very attractive. In this work, a bottom-up approach was used to develop novel efficient and sustainable HDESs for Y and HREE (Dy–Lu) separation. The HDESs were prepared from a combination of biocompatible materials, including DA, OA, HDA and GE as **hydrogen bond donors** with BEA as the HBA and DL as the third component. The relevant physiochemical properties of the selected materials are summarized in Table S2.[†] Notably, all of the selected materials were based on common nature products, and pharmaceutical and commercial products. They were all characterized by low-toxicity compounds (median lethal dose, LD50 >1000 mg kg⁻¹) and low solubility in water (<500 mg L⁻¹). The selection of DA, OA, HDA and GE as HBDs in HDESs is important because they may have selectivities in the separation of Y from HREEs (Dy–Lu). This deduction is based on the classical studies of carboxylic acid extractants and carboxylic acid-based ILs, which could achieve the separation of Y from HREEs (Dy–Lu) through a multi-stage counter-current extraction process.^{11,73}

Furthermore, BEA was chosen as the HBA component in the HDES. Previous studies showed that there were acid–base interactions between the BEA and octanoic acid/bis(2-ethylhexyl)phosphoric acid (P204), and the protons were transferred from octanoic acid and P204 to the BEA.^{74–76} Similarly, decanoic acid : lidocaine (2 : 1). **The** HDES was also shown to have proton interaction and transfer, and about 25% of the decanoic acid was ionized.⁷⁷ Therefore, we speculated that the BEA was able to form stable HDESs with the selected HBD. In addition, the electrostatic potential (ESP) of the HBDs, HBA and DL mapped on the van der Waals surface was plotted using Multiwfn 3.8^{78,79} and VMD 1.9.3⁸⁰ programs, as shown in Fig. 1. It can be seen that the H of COOH in the HBDs has the most positive region. The N of NH in the BEA has the most negative region. Interaction of the HBDs towards the BEA is expected to occur along with the minimum and maximum points. As for the tertiary component, the addition of DL into HDESs is based on the fact that long-chain alcohols (such as isooctanol) are often used as phase modifiers in the rare earth industrial extraction and separation process to improve the

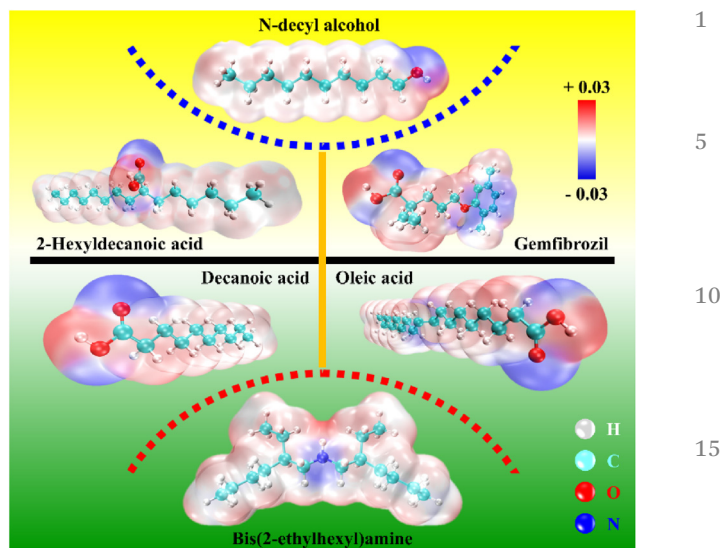


Fig. 1 HBA, HBD and DL electrostatic potential values mapped on the van der Waals surface (the negative regions are indicated in blue and the positive regions are indicated in red).

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extraction, separation and stripping performance and phase separation stability of the extractant.⁸¹

By adjusting the molar ratio of the HBA, HBD and DL components, a total of 44 HDESs were prepared at room temperature (as shown in Table S3[†]). The prepared HDESs remained as clear and transparent liquids after being stored at room temperature for more than 48 hours. The FT-IR **spectral** analysis results are shown in Fig. S1 and S2.[†] In the spectrum of pure HBDs, it can be noted that the C=O stretching vibration peaks appear in the 1691–1705 cm⁻¹ range. Interestingly, a doublet appears at about 1617–1627 cm⁻¹ and 1553–1557 cm⁻¹ in the HDESs, and is absent in pure HBDs, due to the symmetric and antisymmetric stretching vibrations of the COO⁻. The results are similar to previous reports of decanoic acid-lidocaine HDES and octanoic acid-BEA mixtures.^{75,77} In addition, it is worth noting that no stretching vibration absorption due to the free NH group is observable in the pure BEA and HDESs, suggesting that these groups are engaged in strong hydrogen bonds and head to head association. In the FT-IR spectrum of pure DL (Fig. S1[†]), the broad OH stretching vibration peaks appear in the 3600–3000 cm⁻¹ range. However, the marked intensities of both the broad OH and CO stretching vibration peaks of DL in the HDESs decrease (Fig. S1 and S2[†]). These features suggest significant proton transfer from the COOH in HBDs to the NH group in the BEA and the various components in the HDESs have hydrogen bond interactions. Furthermore, the ¹H NMR analysis results (Fig. S3[†]) reveal the absence of new characteristic peaks in the HDES spectra relative to the spectra of the pure compounds, which indicates that there is no other reaction between the HDES components during the preparation process.

The key physiochemical properties of the prepared ternary HDESs were also determined, including the cross-contami-

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nation of the HDES phase and water phase, viscosity and density. As can be seen in Fig. 2, all the HDES phases and water phases have low solubilities in each other, even after the HDES is fully brought into contact with deionized water. The water contents in the HDESs do not exceed 3 wt%. On the other hand, the total nitrogen (TN) and total organic carbon (TOC) dissolved in an aqueous phase are less than 40 mg L⁻¹ and 500 mg L⁻¹, respectively. The lower TN dissolved in the aqueous phase can effectively avoid water pollution by ammonia nitrogen. The above results also prove that the prepared HDESs have good hydrophobic properties. In addition, the lower the viscosity of the extractant, the better the mass transfer effect between the organic phase and aqueous phase. The viscosities of the prepared HDESs are all below 60 mPa s, which are much lower than those of the ionic HDESs and carboxylic acid-based ILs reported.^{44,82,83} Therefore, HDESs do not need to be diluted with toxic and volatile organic solvents during the liquid-liquid extraction processes. Furthermore, the densities of the HDESs are all less than 0.90 g cm⁻³. The greater the density difference between the HDES and water, the better the phase separation effect of the HDES and water. Overall, the key physicochemical properties of the ternary HDESs were in line with the previously introduced criteria for assessing the suitability of the HDESs.^{52,84} The excellent physicochemical properties of the HDESs can help to realize the sustainable, efficient, safe and economical extraction of the target substances in the aqueous phase.

HDESs

Effect of HDES composition on the extraction and separation performance of REEs

The separation ability and extraction efficiency of the HDES for REEs depend on the specific composition of the HDES. Therefore, the influence of HDES composition on the extraction and separation behaviour of REEs was first evaluated. The extraction experiments were carried out under the same experimental conditions by adjusting the molar ratio of the HBD and HBA components in the HDESs.

As seen from Fig. 3, all of the HDESs can effectively extract REEs without solvents and saponification. With the increase in the BEA proportion in the HDESs, the extraction abilities of HDESs to REEs, especially HREEs (Dy-Lu), are gradually increased and then decreased slightly. At the same composition ratio, the order of extraction percentages (*E* %) of REEs by different hydrogen bond donor-based HDESs is as follows: DL : DA : BEA > DL : OA : BEA > DL : GE : BEA > DL : HDA : BEA. Except for the four DL : DA : BEA-based HDESs (molar ratios of 5 : 3 : 1 to 5 : 1 : 2) (Fig. 3(a)), they show the third phase after REE extraction. The upper and lower phases are all clear and transparent after the phase separation of the other HDESs and aqueous solution.

When the HBD component is used as a single extractant (Fig. 4), the *E* % of REEs is negligible. After the four HBDs were saponified by 10%, the *E* % values of REEs were greatly

E %

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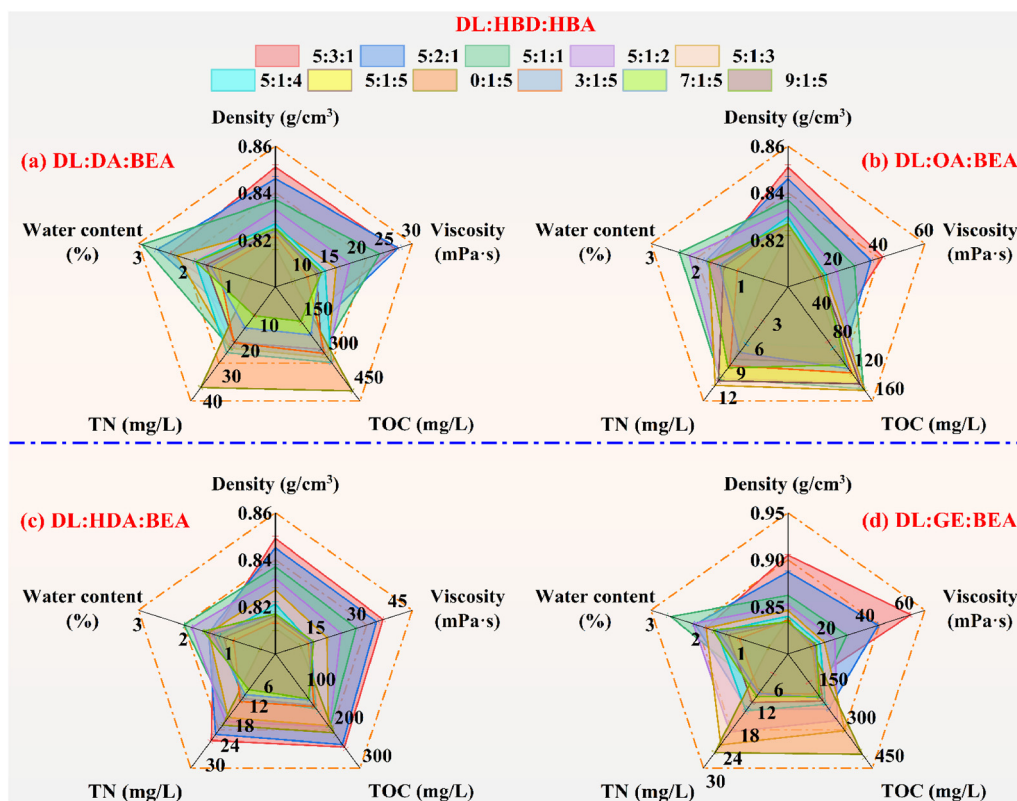


Fig. 2 The physical and chemical properties of 44 HDESs (density, viscosity and HDES/water solubility, at 25 °C). (a) DL : DA : BEA-based HDESs, (b) DL : OA : BEA-based HDESs, (c) DL : HDA : BEA-based HDESs and (d) DL : GE : BEA-based HDESs.

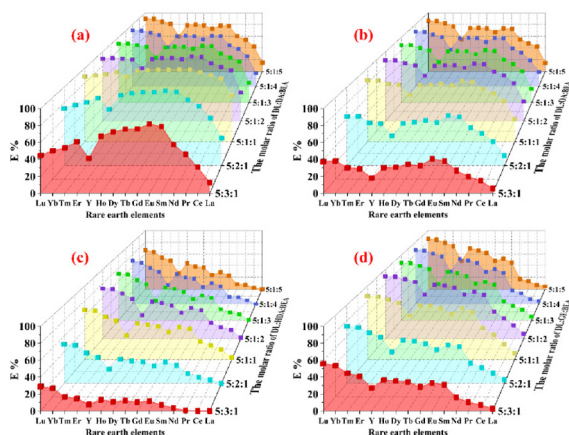


Fig. 3 Extraction performance of REEs by different HDESs. (a) DL : DA : BEA HDESs, (b) DL : OA : BEA HDESs, (c) DL : HDA : BEA HDESs and (d) DL : GE : BEA HDESs. The molar ratios of DL : HBD : HBA ranged from 5 : 3 : 1 to 5 : 1 : 5.

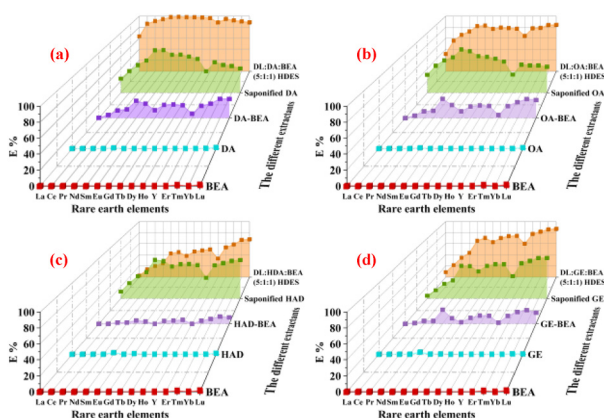


Fig. 4 Extraction of REEs by different extractants in conventional solvent extraction and HDES systems. (a) BEA, DA, saponified DA, DA-BEA and DL : DA : BEA (5 : 1 : 1) HDES, (b) OA, saponified OA, OA-BEA and DL : OA : BEA (5 : 1 : 1) HDES, (c) HDA, saponified HDA, HDA-BEA and DL : HDA : BEA (5 : 1 : 1) HDES and (d) GE, saponified GE, GE-BEA and DL : GE : BEA (5 : 1 : 1) HDES. Except for HDESs, all other extractants in the single and synergistic solvent extractions were diluted in sulfonated kerosene (0.5 mol L^{-1} , 10% DL as phase modifier).

improved. This phenomenon is in agreement with the previous reports that the carboxylic acid-based extractants were not efficient for the extraction of REEs without saponification.¹¹ When the BEA is used as an extractant, its extraction abilities for REEs are also almost zero. Diluting DA : BEA (1 : 1), OA : BEA (1 : 1), HDA : BEA (1 : 1) or GE : BEA (1 : 1) with sulfonated kerosene can improve the extraction efficiencies of REEs. However, it is obvious that the *E* % value of REEs in the synergistic solvent extraction system is much lower than those of the ternary HDES extraction systems. The results show that the interaction of HBDs and HBA components synergistically enhances the extraction of REEs by HDESs. As an extractant, the ternary synergetic HDES does not need to be diluted. The

are values

concentrations of active ingredients are much higher, so that the extraction abilities are stronger.

It is worth noting that the selective separation of Y from HREEs (Dy–Lu) can be successfully achieved by adjusting the types and contents of HBDs. As shown in Fig. 5 and Fig. S4,[†] the separation factors (β) of lanthanides/Y by HDESs with different HBD and HBA molar ratios are given. The separation factors of HREEs (Tm–Lu)/Y (Fig. 5(a)) vary greatly with the molar ratio of the DL : DA : BEA-based HDESs and change from 5 : 3 : 1 to 5 : 1 : 2, which may be due to the formation of the third phase after extraction. Subsequently, the separation factors of the HREEs (Dy–Lu) and Y are increased with the increasing proportion of BEA. As shown in Fig. 5(b) and (d), the higher the BEA content in the HDES, the greater the separation factors of HREEs (Dy–Lu)/Y, which is more favourable for the separation of the HREEs (Dy–Lu) and Y. As for the DL : HDA : BEA-based HDESs (Fig. 5(c)), the separation factors

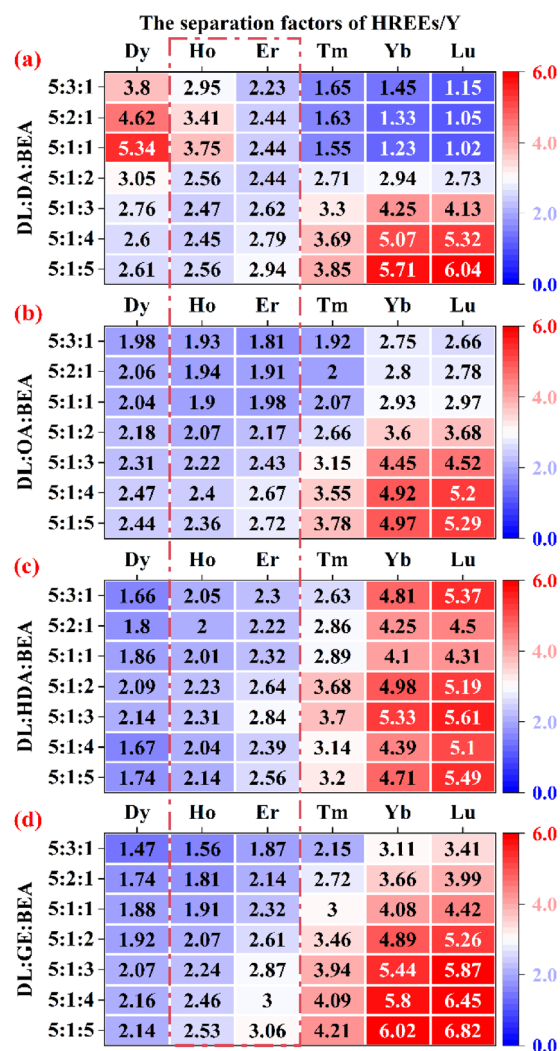


Fig. 5 Separation performance of Y from HREEs by different HDESs. (a) DL : DA : BEA HDESs, (b) DL : OA : BEA HDESs, (c) DL : HDA : BEA HDESs and (d) DL : GE : BEA HDESs. The molar ratios of DL : HBD : HBA ranged from 5 : 3 : 1 to 5 : 1 : 5.

of the HREEs (Dy–Lu)/Y in the DL : HDA : BEA (5 : 1 : 3) HDES are the largest. As the proportion of BEA continues to increase, the separation factors of the HREEs and Y are decreased slightly. In particular, the separation factors of Ho/Y and Er/Y in the HDESs (DL : HBD : HBA ranging from 5 : 1 : 3 to 5 : 1 : 5) are greater than 2.2. The synergistic HDESs exhibit excellent extraction and separation performance for the HREEs (Dy–Lu)/Y without diluents and saponification. The designable and customizable extraction and separation performances of the HDES are of great significance for realizing the separation of REEs in practical feed liquids.

The task specificity of DL as a tertiary component in HDESs

In the process of rare earth extraction and separation, isoctanol, 1-octanol, *etc.* are often used as phase modifiers.⁸¹ For example, after NA is saponified with NH_4OH , it will polymerize due to hydrogen bonding after dissolving in a non-polar solvent. In particular, ammonium naphthenate dissolved in kerosene with a volume concentration of more than 20% appears jelly-like and has poor fluidity. Emulsification may occur during the extraction of REEs, making it difficult to separate the organic phase and the aqueous phase. After adding phase modifiers such as isoctanol, the fluidity of the organic phase will be greatly improved. The two phases can also be quickly separated after the extraction of REEs, thereby reducing the risk of emulsification.⁸⁵

In this work, the natural product DL was first used as a tertiary component in HDESs. Compared with isoctanol and 1-octanol, DL has lower water solubility, which reduces the hydrophilicity of HDES. In order to further investigate the specific tasks or roles played by DL in HDESs, extraction experiments were conducted by changing the proportion of DL in HDESs. The results are shown in Fig. 6 and 7. Compared with the ternary HDESs of DL : HBD : HBA, the binary HDESs of HBD : HBA (1 : 5) without DL show stronger extraction abil-

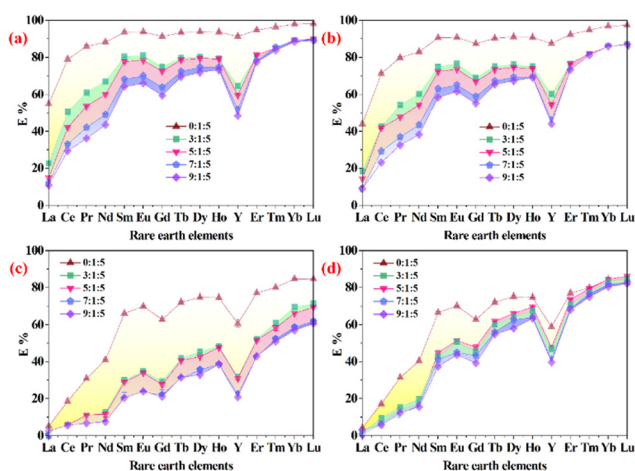


Fig. 6 Extraction performance of REEs by different proportions of DL in HDESs. (a) DL : DA : BEA-based HDESs, (b) DL : OA : BEA-based HDESs, (c) DL : HDA : BEA-based HDESs and (d) DL : GE : BEA-based HDESs. The molar ratios of DL : HBD : HBA ranged from 0 : 1 : 5 to 9 : 1 : 5.

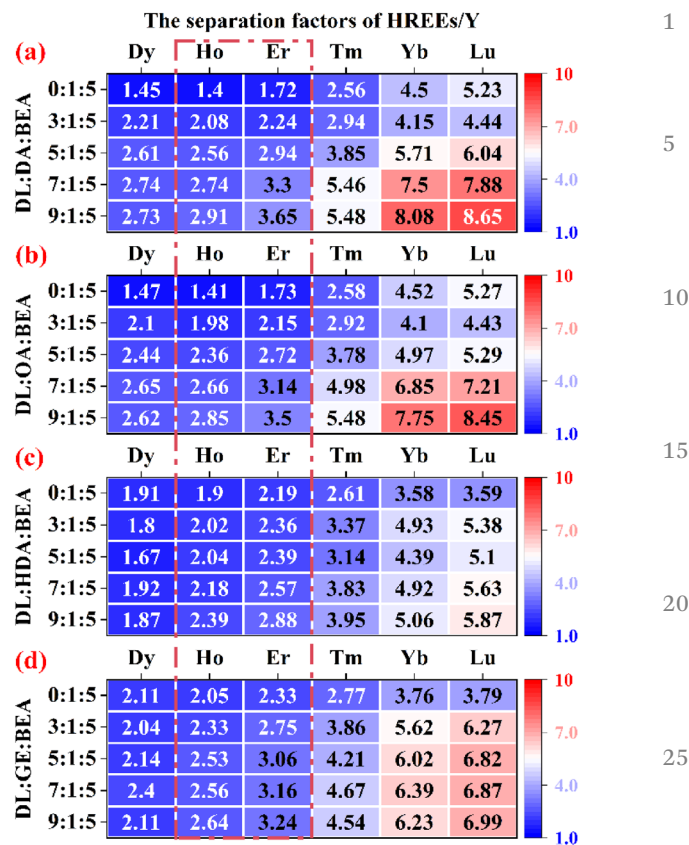


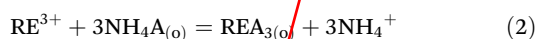
Fig. 7 Separation performance of Y from HREEs (Dy–Lu) by different proportions of DL in HDESs. (a) DL : DA : BEA HDESs, (b) DL : OA : BEA HDESs, (c) DL : HDA : BEA HDESs and (d) DL : GE : BEA HDESs. The molar ratio of DL : HBD : HBA ranged from 0 : 1 : 5 to 9 : 1 : 5.

ities for REEs, but are less selective. At the same composition ratio, the order of extraction capacities of different HBD-based HDESs is as follows: DL : DA : BEA > DL : OA : BEA > DL : GE : BEA > DL : HDA : BEA. With the gradual increase in DL proportion in the ternary HDESs, the $E\%$ values of LREEs and Y are significantly decreased. Although the extraction abilities of HREEs (Dy–Lu) are also decreased with the increase in DL proportion, the $E\%$ values of HREEs are still maintained at a good level ($E\% > 35\%$). At the same time, the separation performances of Y and the HREEs have been greatly improved. For example, the separation factors of the DL : DA : BEA-based HDESs for Dy/Y, Ho/Y, Er/Y, Tm/Y, Yb/Y and Lu/Y were increased from 1.45, 1.4, 1.72, 2.56, 4.5 and 5.23 to 2.73, 2.91, 3.65, 5.48, 8.08 and 8.65, respectively (Fig. 7(a)). According to the separation factors of the HDESs (Dy–Lu)/Y, the order of separation capacities of different HDESs is as follows: DL : DA : BEA (9 : 1 : 5) > DL : OA : BEA (9 : 1 : 5) > DL : GE : BEA (9 : 1 : 5) > DL : HDA : BEA (9 : 1 : 5). The hydrogen bond interactions of the DL, HBA and HBD in the HDESs may be the main reason for the improved separation effects of the HREEs and Y. However, on the other hand, the saturation loading capacities of the HDESs are decreased as the proportion of DL is increased (Fig. S5†); this is because the concentrations of

the HBA and HBD components that play synergistic extraction roles in HDESs are decreased. Compared with other HDESs, the DL : OA : BEA-based HDESs have higher saturation loading capacities and show better phase separation performance at the same DL : HBD : HBA composition ratio. The concentration of Ho^{3+} loaded in the DL : OA : BEA (9 : 1 : 5) HDES is greater than 0.1 mol L^{-1} (Fig. S5(b)†). Although increasing the proportion of DL as the third component in the HDESs weakens the extraction and loading capacities of the HDESs to some extent, it greatly improves the separation factors of the HDESs (Dy Lu)/Y. The higher separation factors of the HREEs (Dy–Lu)/Y are beneficial for effectively reducing the number of extraction stages, improving the production efficiency, and reducing the use of equipment and the consumption of chemical reagents. Taking into account the various criteria of HDESs including extraction capacity, separation performance, saturation loading capacity and phase separation stability, the DL : OA : BEA (9 : 1 : 5) HDES was used in the subsequent experiments.

The extraction mechanism of the HDES for REEs

Organic carboxylic acid extractants always exist as dimers in non-polar organic solvents and have lower acidity. In order to increase the extraction capacity of carboxylic acid extractants, alkaline solutions such as NH_4OH can be used for the saponification of the extractant. The extraction mechanism is ion exchange; the NH_4^+ in the organic phase is ion-exchanged by a trivalent rare earth ion (RE^{3+}) and enters the aqueous phase, thereby producing saponification wastewater.²⁹ The reaction equations are as follows:

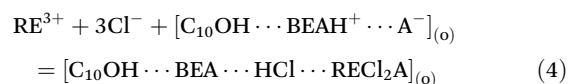
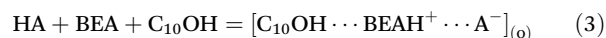


where $(\text{HA})_{2(o)}$ is a carboxylic acid that exists in the form of dimers in organic solvents.

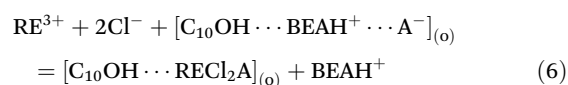
Recently, the decanoic acid : lidocaine HDES was used for the removal of transition metal ions in water.⁶⁴ The extraction mechanism of transition metal ions with the HDES is that the metal ions form complexes with deprotonated acid groups. The low distribution ratio of chloride ions was presumed that the formed lidocaine hydrochloride was dissolved in water. Similarly, the ternary HDES shows a high $E\%$ value of REEs without saponification in this study. It is speculated that the main reason is also that the deprotonated COOH from HBD in HDES participates in the coordination of REEs. The generation of COO^- in the HDES avoids the saponification process of the acidic extractant, thereby eliminating the generation of saponification wastewater, reducing alkali consumption and saving costs.

Taking DL : OA : BEA (9 : 1 : 5) HDES extraction of Dy^{3+} and Ho^{3+} as examples, the mechanism of HDES extraction for REEs was investigated by slope analysis and FT-IR analysis (Fig. 8). Different from the decanoic acid : lidocaine HDES, the ternary HDES extracts both the chloride ion and RE^{3+} in the extraction process (Fig. 8(a)). If the stoichiometric ratio of the chloride ion to RE^{3+} in the HDES is 3, the extraction mechanism of REEs by the HDES is ion association similar to pre-

vious investigations.^{43,82} The reaction equations for the HDES extraction of RE^{3+} are shown in eqn (3) and (4):



where HA represents the HBD component, C_{10}OH represents the DL, $[\text{C}_{10}\text{OH} \cdots \text{BEAH}^+ \cdots \text{A}^-]_{(o)}$ represents the HDES and $[\text{C}_{10}\text{OH} \cdots \text{BEA} \cdots \text{HCl} \cdots \text{RECl}_2\text{A}]_{(o)}$ represents the HDES loaded with RE^{3+} . If the stoichiometric ratio of the chloride ion to RE^{3+} is 2, according to the principle of electrical neutrality, the COO^- in the HBD should participate in coordination. The same stoichiometric ratio of the BEA protonated by H in COOH should be ion-exchanged into the aqueous phase, so as to ensure that the HDES phase and the aqueous phase remain electrically neutral after the extraction of RE^{3+} by the HDES. The reaction equations for the HDES extraction of RE^{3+} are shown in eqn (5) and (6):



where HA represents the HBD component, C_{10}OH represents the DL, $[\text{C}_{10}\text{OH} \cdots \text{BEAH}^+ \cdots \text{A}^-]_{(o)}$ represents the HDES, $[\text{C}_{10}\text{OH} \cdots \text{RECl}_2\text{A}]_{(o)}$ represents the HDES after loading RE^{3+} and BEAH^+ represents the protonated BEA.

It is worth noting that the results of the slope analyses in Fig. 8(a) show that the stoichiometric ratios of chloride ions to Dy^{3+} and Ho^{3+} are 2.1 and 2.6, respectively, which are less than 3. Therefore, it is speculated that ion association and partial cation exchange reactions occur simultaneously after the extraction of RE^{3+} by the HDES. On the other hand, the increase in TN in raffinate with the increase in RE^{3+} concentration loaded in the HDES also confirms the existence of the cation exchange reaction when HDESs are used to extract REEs. In addition, the FT-IR spectrum results (Fig. 8(b)) show that, compared with the stretching vibration peak of $\text{C}=\text{O}$ of pure OA at 1693 cm^{-1} , the symmetric and antisymmetric stretching vibration peaks of COO^- appear (at 1624 and 1556 cm^{-1}) before and after the DL : OA : BEA (9 : 1 : 5) HDES extraction of Dy and Ho. The results further prove that the HBD deprotonated by the HBA in the HDES was mainly involved in complexation with REEs. Interestingly, the broad OH stretching vibration peak of DL in the HDES shifts from 3311 cm^{-1} to 3333 cm^{-1} after extraction. This feature indicates the existence of hydrogen bonding interactions between the DL components and the rare earth complexes in the loaded HDES. As for some of the HDESs that are not directly involved in the reaction, they act as a solvent and have weak interaction with the final complex. The schematic diagram of the REE complexation mechanism with HDESs is shown in Fig. 8(c). In addition, the thermograms for the DL : OA : BEA (9 : 1 : 5) HDES before and after extraction are shown in Fig. S6;† it can

“was presumed that the formed” should be revised to be “may be caused by the formation of”

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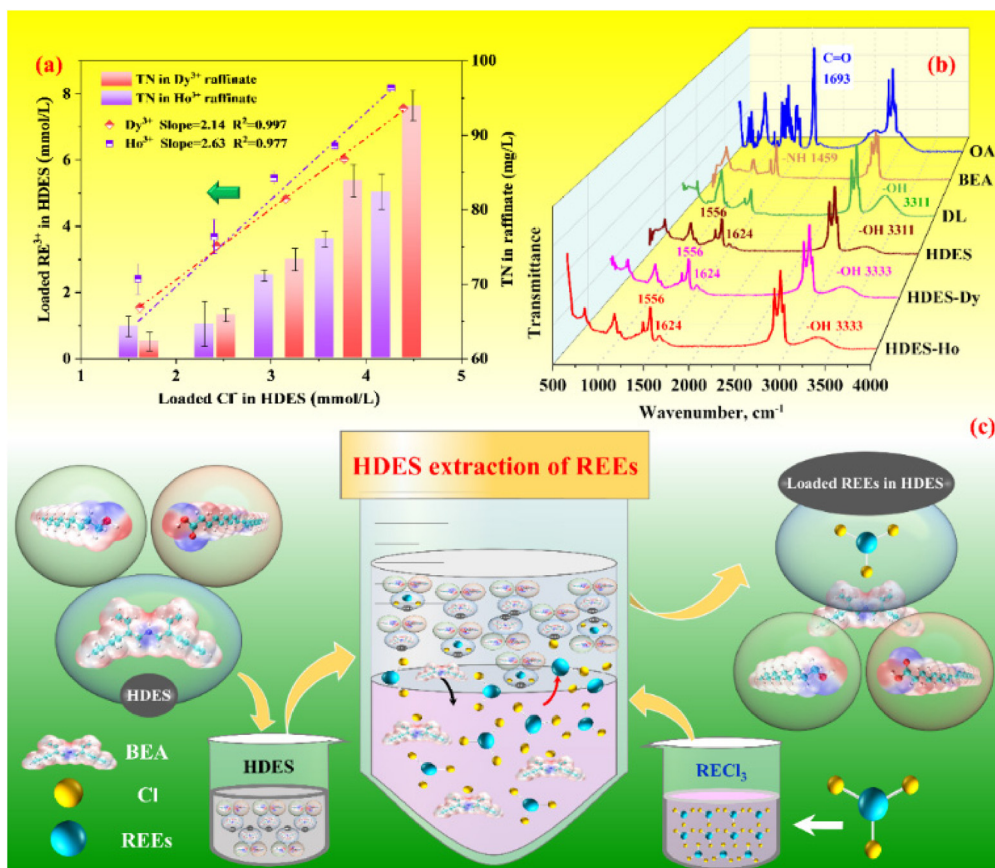


Fig. 8 The extraction mechanism of REEs with HDES. (a) Slope analyses of the relationship between the chloride ion and RE³⁺, (b) FT-IR analyses of the HDES before and after REE extraction and (c) schematic diagram of the REE extraction mechanism with HDES.

be deduced that the decomposition of the DL:OA:BEA (9:1:5) HDES generally occurs around 160 °C, which proves that the DL:OA:BEA (9:1:5) HDES has good thermal stability.

Based on the analysis of the extraction mechanism of the HDES for REEs, the differences in the extraction abilities of different HBD-based HDESSs may be mainly due to the steric hindrance effect of the HBD itself. Obviously, GE and HDA are more sterically hindered than DA and OA, which may lead to a lower degree of proton transfer from the COOH in the GE and HDA to the NH group in the BEA. Therefore, the *E* % values of REEs by the DL:HDA:BEA HDESSs and DL:GE:BEA HDESSs are lower. In addition, the rigidities of the HBD components and the properties of the donating atoms can also affect the extraction and separation performance of the HDES. With the proportion increase of the DL component in the HDES, the separation performance of the HDES for the HREEs (Dy–Lu) and Y can be improved. This may be attributed to the hydrogen bond interactions between the DL and the RE complexes.

Effects of initial aqueous pH and salting-out agent concentration on the extraction performance of the DL:OA:BEA (9:1:5) HDES

The pH value and salting-out agent concentration of the feed solution are important factors for the extraction and separ-

ation of REEs. The **abovementioned** extraction mechanism confirms that H⁺ and Cl⁻ are involved in the reaction processes of the HDES and REEs. Therefore, two operational parameters of the aqueous initial pH and the salting-out agent concentration in the extraction performance of the DL:OA:BEA (9:1:5) HDES were investigated. As shown in Fig. 9(a), the *E* % values of the HREEs by the DL:OA:BEA (9:1:5) HDES gradually increase over the pH range from 1.0 to 3.0, followed by stabilization above pH = 3. The extraction sequence of the HREEs (Dy–Lu) and Y by the DL:OA:BEA (9:1:5) HDES is Lu ≥ Yb > Tm > Er > Ho ≥ Dy ≫ Y. Moreover, the separation factors of the HREEs (Dy–Lu)/Y are all greater than 2.8 above pH = 2 (Fig. 9(b)). The low extraction performance of the HDES at a lower pH is due to the presence of excess H⁺ ions in the solution, which compete with REEs and prevent the extraction reaction. On the other hand, the increase in NaCl concentration in the feed solution promotes the forward progress of the DL:OA:BEA (9:1:5) HDES extraction of HREEs (Fig. 9(c)). This result is consistent with the extraction mechanism of the DL:OA:BEA (9:1:5) HDES, that is, the chloride ion participates in the reaction of extracting REEs from the HDES. Increasing the concentration of the chloride ion is conducive to the forward progress of the extraction reaction. Moreover, the addition of a salting-out agent can effectively

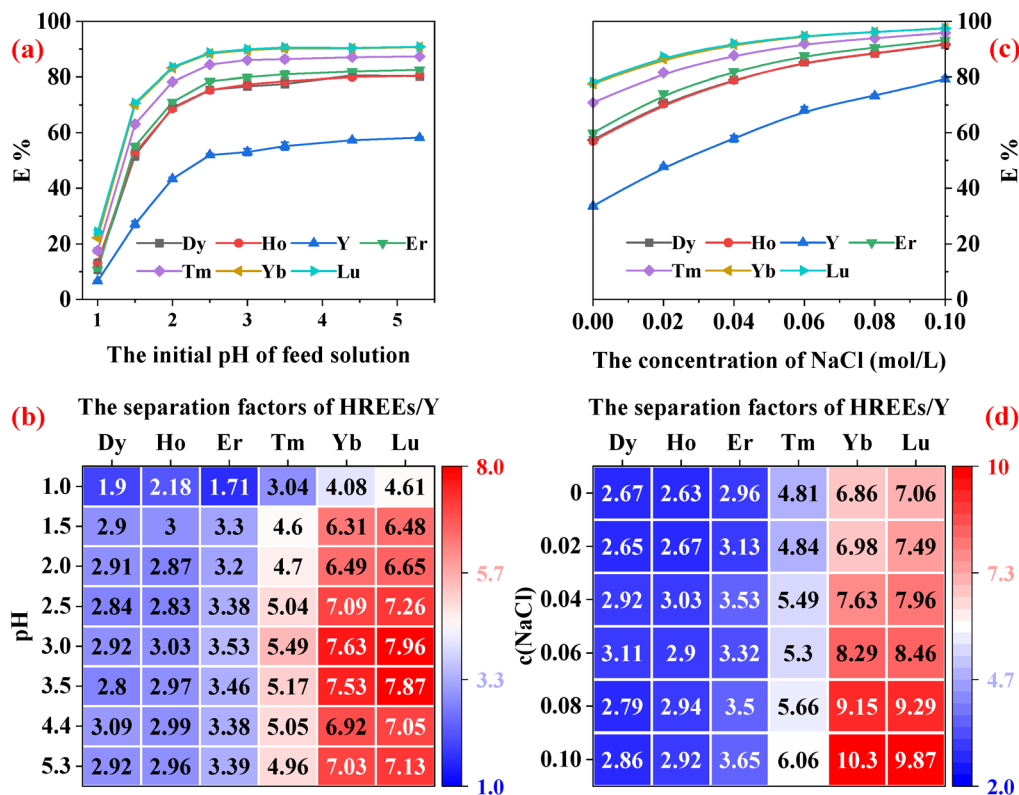


Fig. 9 Influence of aqueous initial pH and the salting-out agent on DL: OA: BEA (9:1:5) HDES extraction. Influence of aqueous initial pH on the DL: OA: BEA (9:1:5) HDES: (a) extraction of HREEs, (b) separation of HREEs (Dy–Lu) and Y, pH = 1.0–5.3. Influence of the salting-out agent on the DL: OA: BEA (9:1:5) HDES: (c) extraction of HREEs (Dy–Lu)/Y and (d) separation of HREEs (Dy–Lu) and Y, $c(\text{NaCl}) = 0\text{--}0.10\text{ mol L}^{-1}$.

improve the separation factors of the HREEs (Dy–Lu)/Y, especially of Er/Y, Tm/Y, Yb/Y and Lu/Y. When the salting-out agent concentration is 0.10 mol l^{-1} , the separation factors of the HREEs (Dy–Lu)/Y reach 2.86, 2.92, 3.65, 6.06, 10.30 and 9.87, respectively (Fig. 9(d)). As can be seen in Fig. S7,† the extraction equilibria of the HDES for the HREEs and Y are achieved quickly, within 10 min.

Separation of Y from HREEs (Dy–Lu) in industrial Y-enriched solution

In order to further verify the industrial application potential of ternary HDESSs, the separation performance of the HREEs (Dy–Lu) and Y by the DL: OA: BEA (9:1:5) HDES in industrial Y-enriched solution was evaluated. The composition of the industrial Y-enriched solution is shown in Table S4.† As shown in Fig. 10(a), the $E\%$ values of the HREEs (Dy–Lu) and Y are increased gradually by increasing the volume ratio of the DL: OA: BEA (9:1:5) HDES to the feed solution (ranging from 1/1 to 5/1). When the phase ratio of O/A is 5/1, the $E\%$ values of Dy, Ho, Er, Tm, Yb, Lu and Y reach 94.1%, 94.8%, 96.0%, 97.2%, 98.4%, 98.5% and 84.0%, respectively. When the ratio of O/A is 1/1, a small amount of the third phase appears after extraction (Fig. S8†). After increasing the phase ratio of O/A, the third phase disappears. The two phases are both clear and transparent solutions after phase separation. After extraction, there may be a smaller amount of the BEA dissolved in the

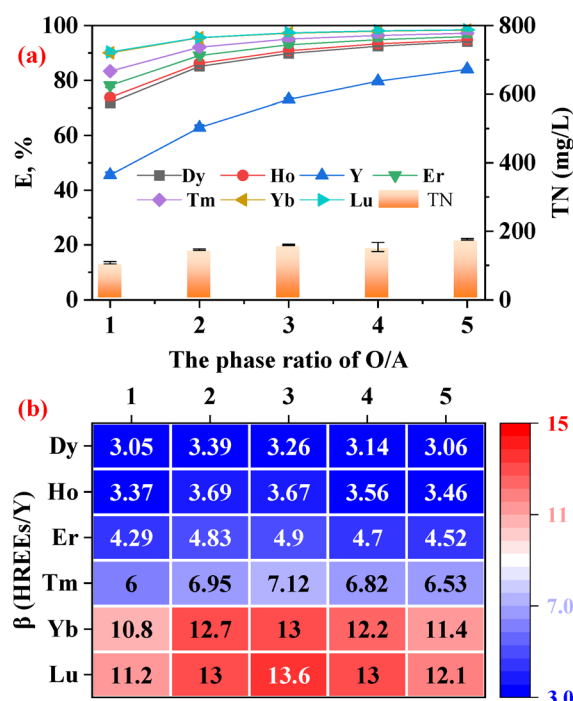


Fig. 10 (a) Extraction and (b) separation performance of the DL: OA: BEA (9:1:5) HDES for the HREEs and Y in industrial yttrium-enriched solution at different volume ratios of O/A (O/A ranging from 1/1 to 5/1).

raffinate due to the cation exchange of the REEs extracted by the HDES. Therefore, the TN values in the raffinate were also measured (Fig. 10(a)). The results showed that the TN is less than 180 mg L^{-1} , while the solubility of the BEA protonated by 3 mol L^{-1} HCl in water is 223.9 mg L^{-1} . It has been reported that China's rare earth industry produces more than 20 million tons of wastewater every year, of which the ammonia nitrogen level is between 300 and 5000 mg L^{-1} .³⁴ The lower TN values in the raffinate after HDES extraction can effectively reduce the level of ammonia nitrogen pollution in water. In addition, the TN of BEA dissolution in water is only 5.8 mg L^{-1} . Therefore, the follow-up work can develop a method for the deprotonation and recovery of the protonated BEA, which can reduce the loss of the BEA and reduce the risk of water pollution by ammonia nitrogen.

Notably, the efficient separation of Y from HREEs (Dy–Lu), especially the separation of Y from Ho and Er, is a challenge due to the cation radius of Y (0.89 \AA), which is fairly close to those of Ho (0.90 \AA) and Er (0.89 \AA).¹⁰ The separation of Ho, Er and Y is usually achieved by combining P507 and NA in industry.⁸⁵ However, it is difficult to obtain high-purity Y due to the low separation factors of Ho/Y and Er/Y. Table 1 indicates the separation factors of some of the currently reported extractants for Ho/Y, Er/Y and Lu/Y, and it can be found that the separation factors of Ho/Y and Er/Y are generally low. In contrast, better separation factors of the HREEs (Dy–Lu)/Y are achieved by the DL:OA:BEA (9:1:5) HDES (Fig. 10(b)). The separation factors of the HREEs (Dy–Lu)/Y are $\text{Dy/Y} \geq 3.05$, $\text{Ho/Y} \geq 3.37$, $\text{Er/Y} \geq 4.29$, $\text{Tm/Y} \geq 6$, $\text{Yb/Y} \geq 10.8$, and $\text{Lu/Y} \geq 11.2$, respectively. The higher separation factors of the HDES to HREEs (Dy–Lu)/Y are beneficial for shortening the separation process of Y from HREEs.^{11,83} Therefore, based on the above results, it can be predicted that using the DL:OA:BEA (9:1:5) HDES as the extractant, separation of the HREEs and Y can be effectively achieved. The excellent extraction and separation performances of the HDES for the HREEs (Dy–Lu)/Y indicate the sustainable separation of Y from the HREEs.

Table 1 The separation factors of Ho/Y, Er/Y and Lu/Y extracted by different extractants

Extraction system	Ho/Y	Er/Y	Lu/Y	Ref.
NA	2.01	2.16	3.14	29
CA12	1.90	1.58	1.08	30
CA100	2.29	1.74	1.51	28
POPA	2.04	2.00	2.46	29
CA12-TBP	2.54	2.08	1.66	26
CA12-isooctanol	2.36	1.86	1.49	26
CA12-cyanex 272	—	1.58	9.21	32
Phosphorylcarboxylic acid	2.07	2.01	1.82	30
[A336][CA12] IL	1.23	1.30	1.94	42
[A336][CA100] IL	2.5	0.84	0.65	43
[A336][neodecanoate] IL	2.64	4.32	16.27	44
Pyridine carboxylic acid IL	2.14	2.03	—	45
DL:OA:BEA (9:1:5) HDES	≥ 3.37	≥ 4.29	≥ 11.20	This work

Stripping and regeneration of the DL:OA:BEA (9:1:5) HDES

The stripping and reusability of the extractant are important considerations in the overall design of liquid–liquid extraction systems for industrial-scale applications. For an effective regeneration of the DL:OA:BEA (9:1:5) HDES, the stripping performances of the HREEs from the loaded DL:OA:BEA (9:1:5) HDES using $\text{Na}_2\text{C}_2\text{O}_4$, H_2O , and HCl were compared (Fig. 11(a), (b) and (c)). As shown in Fig. 11(a) and (c), both $\text{Na}_2\text{C}_2\text{O}_4$ (0.2 mol L^{-1}) and HCl (1.5 mol L^{-1}) can effectively strip the HREEs from the DL:OA:BEA (9:1:5) HDES. The stripping percentages are 96.7% and 94.9%, respectively. However, the ability to extract HREEs with the DL:OA:BEA (9:1:5) HDES stripped and regenerated by HCl (1.5 mol L^{-1}) is almost zero. Compared with $\text{Na}_2\text{C}_2\text{O}_4$ and HCl as the stripping agents, using deionized water as the stripping agent can effectively avoid the consumption of chemical reagents, which is attractive. Using deionized water to strip the loaded DL:OA:BEA (9:1:5) HDES (Fig. 11(b)), the results show that the *S* % value of HREEs is 49.2% when the A/O ratio is 1. When the volume ratio of deionized water to the HDES is increased to 5, the *S* % value of HREEs is only increased to 67.1%.

According to the above results, deionized water and $\text{Na}_2\text{C}_2\text{O}_4$ (0.15 mol L^{-1}) were finally used for two-step stripping. First, deionized water (A/O = 1/1) was used for the single-stage stripping of the loaded DL:OA:BEA (9:1:5) HDES, and then $\text{Na}_2\text{C}_2\text{O}_4$ (A/O = 1/1) was used for single-stage stripping, and finally the regenerated HDES was obtained. The reusability of the DL:OA:BEA (9:1:5) HDES was tested by repeating the extraction-stripping experiments over five cycles. Excitingly, the DL:OA:BEA (9:1:5) HDES exhibited remarkably high stability over the five cycles without significant changes in extraction capacities (Fig. 12(a)) and separation performances (Fig. 12(b)). In addition, the FT-IR characteristic peaks of the DL:OA:BEA (9:1:5) HDES do not change after 5 cycles (Fig. 12(c)).

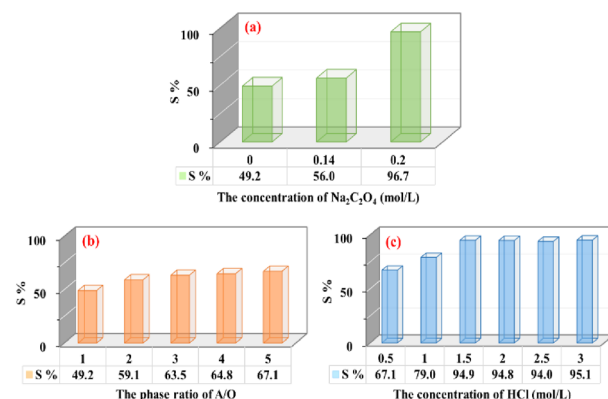


Fig. 11 Stripping of REEs loaded in the DL:OA:BEA (9:1:5) HDES with different chemicals. (a) $\text{Na}_2\text{C}_2\text{O}_4$ stripping at different concentrations, (b) H_2O stripping at different A/O phase ratios and (c) HCl stripping at different concentrations. The phase ratio of O/A = 2/1 for extraction, and the feed is industrial Y-enriched solution.

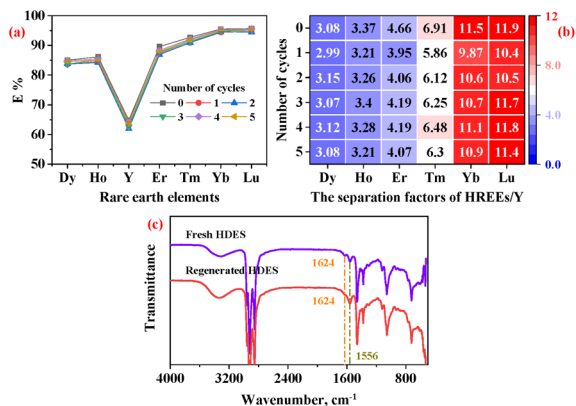


Fig. 12 The reusability of the DL : OA : BEA (9 : 1 : 5) HDES. (a) Stabilities of extraction ability over 5 cycles, (b) stabilities of separation performance over 5 cycles and (c) FT-IR spectra of the HDES before and after 5 cycles.

Sustainability

Cleaner, efficient and economical separation of adjacent REEs has always attracted attention. In this work, the first few examples from a family of new ternary HDESs based on low-toxicity compounds were developed for the synergistic separation of Y from HREEs. The LD₅₀ (oral, rat) for BEA is greater than 1008 mg kg⁻¹ (Table S2⁺), which is four times greater (less toxic) than that of methyltrioctylammonium chloride (LD₅₀ (oral, rat) 223 mg kg⁻¹), previously used to form the HDES and ILs. Compared with bifunctional ILs based on methyltrioctyl ammonium, the HDESs have lower viscosities, allowing them to be used as an extraction phase for aqueous liquid-liquid extraction without volatile, flammable and toxic diluents. In addition, raw materials for the HDES are commercially available and economically feasible. In comparison with the use of conventional saponified naphthenic acid for the extraction and separation of Y from the HREEs, the HDESs have shown significant advantages such as higher extraction and separation performance for HREEs and Y, which can not only shorten the separation process and improve the production efficiency, but also save equipment investment. Saponification was absent in the HDES extraction process, avoiding the consumption of alkali and the generation of saponification wastewater, thereby saving the cost of consuming alkali and wastewater treatment. In general, the developed ternary HDES has shown its application potential in terms of cleanliness, safety, efficiency and economy.

Conclusions

In this article, a novel sustainable strategy for the synergistic extraction and separation of Y from HREEs based on ternary HDESs was developed. A total of 44 HDESs were prepared based on four carboxylic acids, DA, OA, HDA and GE, as HBDs, BEA as the HBA and DL as a tertiary component. All the HDESs are clear liquids at ambient temperature. The prepared

HDESs have the advantages of simple preparation, no need for purification, low viscosity (<60 mP s), low density (0.90 g cm⁻³), low water content (<3%), low solubility in water (TOC <500 mg L⁻¹ and TN <40 mg L⁻¹), low toxicity and non-volatility. Furthermore, the proportion effect of each component in the ternary HDES on the extraction and separation performances of HREEs and Y was studied. The synergistic effect from each component in the HDESs could enhance the extraction and separation performance of HREEs and Y without saponification and organic solvents. The increased proportion of the BEA and DL in HDES improves the separation performance of HDESs to a certain extent. However, the increase in the proportion of DL in HDESs reduces the extraction and saturation loading capacities of HDESs. Besides, it is speculated that ion association and partial cation exchange reactions occur simultaneously in the extraction processes of RE³⁺ by the HDESs. The performance of the HDESs was verified with the sustained HREE extraction efficiency over a wide range of pH (3–5). Increasing the salting-out agent concentration promoted the HREE extraction and the separation of the HREEs and Y. The DL : OA : BEA-based HDESs have good extraction ability, higher saturation loading capacity and better phase separation stability. The separation factors of the DL : OA : BEA (9 : 1 : 5) HDES for the HREEs (Dy–Lu) and Y in industrial Y-enriched solution are Dy/Y ≥ 3.05, Ho/Y ≥ 3.37, Er/Y ≥ 4.29, Tm/Y ≥ 6.00, Yb/Y ≥ 10.8, and Lu/Y ≥ 11.2, respectively. The loaded HDES can be easily stripped and show sustained stability over multiple regeneration cycles. The extraction process of the HDES omits the process of saponification required by traditional carboxylic acid extractants, avoiding the consumption of alkali and the production of saponification wastewater. In addition, the extraction and separation performance can be customized and adjusted. In conclusion, the extraction and separation processes of HREEs and Y based on the HDES have shown the characteristics of cleanliness, safety, high efficiency and economy. The excellent separation performance of the HDES has indicated its application potential in the separation of Y from HREEs.

Abbreviations

DES	Deep eutectic solvents
HDES	Hydrophobic deep eutectic solvent
HBD	Hydrogen bond donor
HBA	Hydrogen bond acceptor
RE	Rare earth
REEs	Rare earth elements
HREEs	Heavy rare earth elements
LREEs	Light rare earth elements
RECl ₃	Rare earth chloride
RE ³⁺	Rare earth ions
DA	Decanoic acid
OA	Oleic acid
HDA	2-Hexyldecanoic acid
GE	Gemfibrozil

1	BEA	Bis(2-ethylhexyl)amine	
	DL	1-Decyl alcohol	
	NA	Naphthenic acid	
	CA12	Sec-octylphenoxy acetic acid	
5	CA100	Sec-nonylphenoxy acetic acid	
	POPA	(2,6-Dimethylheptyl) propanoic acid	
	TBP	Tributyl phosphate	
	P507	2-Ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester	
10	P204	Bis(2-ethylhexyl)phosphoric acid	
	IL	Ionic liquid	
	A336	Methyltrioctyl ammonium	
	[A336][CA12]	[Methyltrioctyl ammonium][sec-octylphenoxy acetic]	
15	[A336][CA100]	[Methyltrioctyl ammonium][sec-nonylphenoxy acetic]	
	[A336][neodecanoate]	[Methyltrioctyl ammonium][neodecanoate]	
20	LD ₅₀	Median lethal dose	
	DFT	Density functional theory	
	ESP	Electrostatic potential	
	E %	Extraction percentage	
	D	Distribution ratio	
25	S %	Stripping percentage	
	β	Separation factors	factor
	TOC	Total organic carbon	
	TN	Total nitrogen	
	FT-IR	Fourier transform infrared spectra	
30	¹ H NMR	Proton nuclear magnetic resonance	

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Author contributions

Shuainan Ni: Conceptualization, methodology, formal analysis, investigation, visualization, and writing – original draft. Yun Gao: Investigation, data curation, formal analysis, and writing – review & editing. Guisu Yu: Investigation, validation, data curation, visualization, and formal analysis. Sijia Zhang: Validation, investigation, visualization, and descriptions. Zhiyuan Zeng: Validation, investigation, and visualization. Xiaoqi Sun: Resources, software, supervision, writing – review & editing, and project administration.

Conflicts of interest

There are no conflicts to declare.

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