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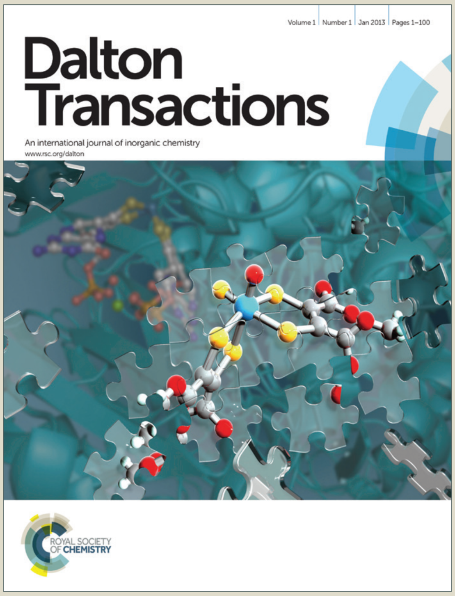

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Solvent extraction of lanthanides and yttrium from aqueous solution with methylimidazole in ionic liquid

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1-methylimidazole (1-MIM) and 2-methylimidazole (2-MIM) are miscible in water and imidazolium based ionic liquids (ILs), and can coordinate with soft metal ions. This paper reports a novel solvent extraction process to trivalent lanthanides and yttrium from aqueous solutions into ILs, which was promoted by a hydrophilic 1-MIM or 2-MIM. Slope analysis confirmed that MIM in ILs formed a 1 : 1 complex with La^{3+}, Y^{3+} and 1 : 4 complex with Eu^{3+}, Lu^{3+}, depending on the atomic number of metal and the metal-ligand interactions that have been characterized by FTIR spectroscopy and ESI-MS. The effect of nitrate concentration on the extraction of lanthanides with 1-MIM in IL was carried out. It indicated that nitrate anions were involved in extraction process. Under the same conditions, the extraction of lanthanides with MIM into *n*-pentanol was carried out. The extractability was by far lower than that obtained in ILs. Both a cationic exchange and neutral solvation mechanism occurred in ILs and only a neutral solvation mechanism occurred in *n*-pentanol, which were demonstrated by the extraction tests and the structure of extracted species determined by ESI-MS. The competitive extraction in ILs showed good selectivity for lanthanides compared to alkali metals and alkaline earth cations. After extraction, lanthanides could be stripped very easily from the ionic liquid phase with dilute

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nitric acid. From the temperature dependence data, the thermodynamic parameters values（ΔH, ΔS and ΔG) were calculated. The results indicated the extraction reactions were spontaneous and went through endothermic process.

Introduction

Over the past decade, ionic liquids (ILs) have attracted considerable attention for metal extraction from aqueous solutions, since they can replace the use of volatile organic solvents that have been widely used for this purpose.[1-7] These solvents exhibit several properties that make them attractive as a potential basis for 'green' separation processes, including negligible vapour pressure, tunable viscosity and miscibility and good thermal and radiation stability for solvent extraction.[8-10] Significant studies have been reported on the extraction with ILs, such as, the extraction of Sr^{2+} from acidic nitrate media by dicyclohexano-18-crown-6,[11] uranyl ion by a CMPO-TBP (tri-n-butyl phosphate) mixture,[12] Ag^+ by calix[4]arenas,[13] Eu^{3+} by 2-thenoyltrifluoroacetone (TTA).[14] Recent several reports deal with the use of diglycolamides and malonamide for the extraction of actinide, lanthanide, and alkali metal, alkaline earth metal with room temperature ionic liquids.[15-23] Binnemans et. al found the solvent extraction process can be carried out using ILs without extra extraction agents for removing transition metals from rare earths.[24, 25] Several reports have been published in the last few years giving summaries of ionic liquid-based separations.[26-28] One of the greatest merits of application of ILs to liquid-liquid extraction lies in the fact that, in comparison with conventional organic solvents, ILs show remarkably high extraction performance for target substances when using certain appropriate ligands. Attempts were also made to understand the mechanism of metal ion transfer and complexation of metal ions in ionic liquids.[29-33]

In liquid-liquid extraction process of metal ions, the extractant has a crucial effect. Selection of an appropriate extractant often determines the success of an extraction process. To date, a large number of acidic, basic, and neutral extractants, such as di-(2-ethylhexyl)phosphoric acid (P204), 2-ethylhexylphosphoric acid mono (2-ethylhexyl) ester (P507), tri-n-butylphosphate (TBP), Cyanex923 (mixture of straight chain alkylated phosphine oxides) and di-(1-methylheptyl)methyl phosphate (P350), amines and carboxylic acids (CA100) have been widely utilized in industry for the solvent extraction separation of rare-earth elements.[34-38] However, these extractants have various shortcomings including poor selectivity, difficult stripping, low extractability and long extraction time.[39] With the increasing demand for rare-earth elements in the international market, the separation and purification of these elements has gained considerable importance. Growing attention is being paid to the development of new extraction systems for the separation of them as a group or from one another.

Imidazole is miscible in ILs or water. It is a five-membered heterocyclic compound and has two potential N coordination sites that enable it to coordinate to some metal ions. Its role as a ligand in various complexes has been demonstrated.[40-42] In the present study, for the first time we found imidazole and relatives extracting lanthanides and yttrium from aqueous solutions into imidazolium based ionic liquids (ILs). The extraction performance and extraction mechanism were studied. The effects of several experimental parameters such as (a) nature of ILs, (b) nature of extractants, (c) contact time, (d) aqueous phase pH, and (e) extractant concentration, on the extraction behavior of metal ions have been investigated. FTIR and ESI-MS have been performed to investigate the interactions between ligand and metal. To compare with the partitioning behavior of lanthanides in the ILs, the extraction of lanthanides (Lu^{3+}, Eu^{3+}, La^{3+}) with methylimidazole was measured in *n*-pentanol system.

Experimental

Reagents

1-methylimidazole (1-MIM), 2-methylimidazole (2-MIM), imidazole and benzimidazole were purchased from Aldrich Chemical Co., *n*-pentanol (analytical grade) was purchased from Kishida Chemical Co. Ltd. and used without further purification. High purity lanthanides and yttrium oxides (>99.95%) were purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Lanthanides and yttrium nitrate were obtained by dissolution corresponding oxide in concentrated nitric acid then drying in the air. Stock solutions were prepared from lanthanides and yttrium nitrate by dissolving them in deionized water without any buffer. All the initial lanthanides and yttrium concentrations were maintained at 0.4 mM. The pH of these metal solutions was about 5.7 by measuring. These solutions were used in all extraction experiments except the effect of pH on extraction. In the variation of pH experiment, pH was adjusted by nitric acid and ammonia water. In the competitive solvent extraction experiment, solutions containing various metal ions ($LiNO_3$, $NaNO_3$, KNO_3, $Mg(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, $La(NO_3)_3$, $Eu(NO_3)_3$, $Lu(NO_3)_3$) were prepared at metal concentrations of 0.1 mM. The ESI-MS data was acquired on Bruker maXis4G or Bruker esquire6000. ESI-MS measurements were made in methanol for the loaded IL phase or the solid isolated from the IL after extraction 10 mM metal solution(pH was about 5.7) by washing the IL with ethyl acetate. ESI-MS spectra were obtained in supporting information. Fourier transform infrared (FTIR) spectra were recorded on a Necolet Nexus spectrometer (NEXUS 670) with KBr pellets in the mid IR range (4000–400 cm^{-1}) for the solid isolated from the IL after extraction metal solution of 10 mM(pH was about 5.7) by washing the IL with ethyl acetate.

IL synthesis

Syntheses of 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ([C_2mim][NTf_2]), 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([C_4mim] [NTf_2]) and 1-octyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ([C_8mim][NTf_2]) were conducted as described in the reference.[43]

Liquid-Liquid extraction of metal ions with ILs or *n*-pentanol

An extract phase was prepared by dissolving 1-MIM or 2-MIM in [$C_n$mim][NTf_2] or *n*-pentanol. The organic phases of 0.5 mL were mixed with 5 mL solution of metal ions (0.4 mM) and shaken on a shaker (at 500 rpm) , at 25 °C for 30 min, to attain equilibrium. These mixtures were then centrifuged for 3 min to promote phase separation. After each phase was separated, the concentration of metal ions in the aqueous phase was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy), which then allowed calculation of the distribution ratio. The distribution ratio (D) was calculated from Eq. (1),

$$D = \frac{C_i - C_f}{C_f} \text{ ¡Á} \frac{\text{volume of aqueous phase}}{\text{volume of organic phase}} \qquad (1)$$

where C_i and C_f represent the initial and final concentrations of metal ions in aqueous phase, respectively.

Stripping test

The loaded organic phase after extraction metal solution was mixed with 5 mL different concentrations of nitric acid. The mixtures were shaken at 298 ± 1 K for 30 min. The aqueous solution was separated from the organic phase and the metal concentrations were quantified to evaluate the stripping ratio, $St = (W_{a,e}/W_{o,i}) \times 100\%$, where $W_{a,e}$ and $W_{o,i}$ represented the mass of metal ions in stripping acid and the initial mass of metal ions in the organic phase, respectively.

Results and discussion

The room temperature ionic liquids used in the present study did not extract lanthanides and yttrium in the absence of extractants. Similar behaviour was reported by Shimojo et al.[15] in their studies on lanthanide extraction using a identical set of ionic liquids. In the presence of MIM, however, a sharp increase in the D values was observed. The extraction ability of Lu^{3+} with 1-MIM is different in different ionic liquids varying in the order $[C_2mim][NTf_2]$ > $[C_4mim][NTf_2]$ > $[C_8mim][NTf_2]$ as shown in Fig. 1.

Extraction kinetics

In order to get information on the attainment of the extraction equilibrium, the extraction kinetics was investigated. The extraction kinetics of Lu^{3+} was studied by extracting a 0.4 mM Lu^{3+} solution with 0.088 M 1-MIM in $[C_4mim][NTf_2]$ and the results are presented in Fig. 2. The D value increases gradually with the increase of time up to 10 min, followed by a plateau with a D value of ~ 57. The studies show that 10 min is sufficient for achieving extraction equilibrium (Fig. 2), suggesting that the kinetics of extraction is relatively fast in the ILs medium. In order to ensure the complete extraction, all the studies have been carried out with an equilibration time of 30 minutes.

Metal extraction with MIM into ILs

To assess the partitioning behavior of lanthanides and yttrium in the IL ([C_4mim][NTf_2]) system, extraction equilibria of metal ions (La^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+},Tm^{3+}, Yb^{3+}, Lu^{3+}, Y^{3+}) at 0.4 mM metal concentration were measured as a function of the 1-MIM concentration. The results are shown in Fig. 3, where it can be seen that the extractability of lanthanides and yttrium increases with increasing 1-MIM concentration. This indicates that 1-MIM is participating in the extraction process by being part of the extracted species. Furthermore, the distribution ratios vary considerably for the heavy and light lanthanide ions under the same extraction condition (Fig. 3). The light lanthanide ions are poorly extracted, whereas the heavier lanthanide ions are much better extracted with low concentration of 1-MIM. The heavier lanthanide ions show a rapid increase in distribution ratios as 1-MIM concentration increases and the light lanthanides and yttrium give a slow growth in distribution ratios. This type of extraction behavior allows splitting of the rare earths into two groups. The extraction behavior of yttrium resembles that of the light lanthanides. In addition, when 1-MIM concentration increases continuously up to a certain extent, all metals will be completely extracted.

When using 2-MIM in place of 1-MIM, the partitioning behavior of lanthanides (La^{3+}, Eu^{3+}, Lu^{3+}) in the IL [C_4mim][NTf_2] system was carried out as a function of the extractant concentration (shown as in Fig. 4). It was found that the distribution ratios of Lu^{3+}, Eu^{3+}, La^{3+} increase dramatically with increasing 2-MIM concentration from Fig. 4. Comparing with 1-MIM, to achieve the same degree of extraction, less 2-MIM is required. 2-MIM provides by far superior extraction ability than 1-MIM in same solvent ([C_4mim][NTf_2]. The extraction trend is similar to 1-MIM. 2-MIM and 1-MIM are isomers, the difference is there is an N-H bond in the imidazole ring of 2-MIM. There are several reports [44-47] demonstrating ligand–ligand interactions, particularly hydrogen bonds, between ligands in the outer coordination spheres of metal complexes having a major effect on their stabilities which contribute to the strength and selectivity of metal extraction. The N-H bond in the imidazole ring of 2-MIM could be responsible for the higher extractability of lanthanides.

Slope analysis was conducted as a function of the equilibrium concentrations of 1-MIM and 2-MIM in the extracting phases to determine the stoichiometry of metal-MIM complex. As shown in Fig. 5, the linear regression analysis of the extraction data results in a slope of 4 for Lu^{3+}, Eu^{3+} (Fig. 5a）and 1 for La^{3+}, Nd^{3+}, and Y^{3+}（Fig. 5b）in both ionic liquids, suggesting that four molecules of MIM are involved during the extraction process for Lu^{3+} and Eu^{3+} and one molecule of MIM is involved for La^{3+}, Nd^{3+}, and Y^{3+}.

In order to obtain a detailed insight into the involvement of the nitrate ion in the extraction process, the effect of the nitrate ion on the distribution ratio of La^{3+} and Lu^{3+} was carried out by varying the nitrate ion concentration using different concentrations of sodium nitrate in the aqueous phase keeping metal concentration in aqueous phase and extractant concentration in ILs constant (shown as in Fig. 6). It is observed that the distribution ratios increase with an increase in nitrate ion concentration for both metal ions. The increase of extraction of lutetium is more pronounced than the extraction of lanthanum. The results demonstrate that nitrate anions participate in the extraction reaction and form complexes with lanthanides.

Besides, when the metal concentration is increased to a certain extent, a solid can be seen clearly in the IL phase (The photo of the solid in IL is shown in supporting information). The extracted species were isolated from the IL after extraction 10 mM metal solution by washing the IL with ethyl acetate, then the white insoluble solid was obtained in ethyl acetate and was determined by ESI-MS. The representative extracted species are $Lu(MIM)_4(NO_3)_3$ (MS (ESI), m/z = calcd. 689.3533, found 689.3253) and $La(MIM)(NO_3)_3$ (MS (ESI), m/z = calcd.

407.0054, found 408.3094), which implies that the neutral solvation mechanism is contained in the extraction of lanthanides. The extraction reactions are illustrated as represented by eq. (2) and (3).

$$Lu^{3+}_{aq} + 4MIM_{or} + 3NO_3^-{}_{aq} \longrightarrow [Lu(MIM)_4\,(NO_3)_3]_{or} \tag{2}$$

$$La^{3+}_{aq} + MIM_{or} + 3NO_3^-{}_{aq} \longrightarrow [La(MIM)(NO_3)_3]_{or} \tag{3}$$

However, the extractability of Lu^{3+} with 1-MIM in ILs is $[C_2mim][NTf_2] > [C_4mim][NTf_2] > [C_8mim][NTf_2]$ (shown as in Fig. 1). If the extraction mechanism is pure neutral solvation mechanism, the extractability should be $[C_8mim][NTf_2] > [C_4mim][NTf_2] > [C_2mim][NTf_2]$, because an increase of carbon chain length of the alkyl group leads to an increase of hydrophobicity of the IL, which favors the transfer of neutral complex. It is well known that an ion exchange mechanism often occurs during solvent extraction using imidazolium based ionic liquid as diluents. In order to confirm the existence of ion-exchange mechanism, the effect of the concentration of C_nmim^+ cations on the extractability of Lu^{3+} and La^{3+} was studied. If the lanthanides transfer involves C_nmim^+, the extractability of lanthanides would decrease with increasing the C_nmim^+ concentration in the aqueous phase based on the equilibrium shift. The extraction of Lu^{3+} and La^{3+} using 1-MIM in $[C_4mim][NTf_2]$ was conducted as a case. Water soluble IL $[C_4mim][Br]$ was employed to adjust the C_4mim^+ concentration in the aqueous phase. As shown in Fig. 7a, the degree of Lu^{3+} and La^{3+} extraction in the IL system is gradually reduced with increasing C_4mim^+ concentration. The slopes of plots of log*D* *versus* $\log[C_4mim^+]$ are about -1.5 for the extraction of Lu^{3+} and La^{3+} (Fig. 7b). These data suggest that the transfer of lanthanides with MIM into IL proceeds simultaneously through a cation-exchange mechanism.

ESI-MS measurements were made in methanol for the loaded IL phase after extraction of Lu^{3+} and La^{3+}, respectively. The peaks at m/z 82.8659, 139.7869, 166.9894, 282.2807, 628.6253 and 688.7801 can be found and they correspond to 1-MIM, C_4mim^+ and the complex $Lu(C_4H_6N_2)_4{}^{3+}$, $Lu(C_4H_6N_2)_4(NO_3)^{2+}$, $Lu(C_4H_6N_2)_4(NO_3)_2{}^+$ and $Lu(C_4H_6N_2)_4(NO_3)_3$, respectively; the peaks at m/z 139.2538, 140.1227, 346.3347and 408.3125 can be found and they correspond to C_4mim^+ and the complex $La(C_4H_6N_2)(NO_3)^{2+}$, $La(C_4H_6N_2)(NO_3)_2{}^+$ and $La(C_4H_6N_2)(NO_3)_3$, respectively. These species are extracted species of ion-exchange and neutral solvation transfer. That is a strong evidence to prove both of ion-exchange and neutral solvation mechanism are co-existed in the extraction process. The extraction reactions are illustrated as represented by eq. (4) and eq. (5).

$$Lu^{3+}{}_{aq} + 4MIM_{or} + nNO_3^-{}_{aq} + (3-n)[C_4mim]^+{}_{or} \longrightarrow [Lu(MIM)_4\,(NO_3)_n]^{3-n}{}_{or} + (3-n)[C_4mim]^+{}_{aq} \quad (4)$$

$$La^{3+}{}_{aq} + MIM_{or} + nNO_3^-{}_{aq} + (3-n)[C_4mim]^+{}_{or} \longrightarrow [La(MIM)(NO_3)_n]^{3-n}{}_{or} + (3-n)[C_4mim]^+{}_{aq} \quad (5)$$

where n= 0-3.

Other metal shows a similar trend in IL, it is reasonable to assume that heavy and middle lanthanides may follow a lutetium extraction mechanism; light lanthanides and yttrium follow a lanthanum extraction mechanism.

Effect of a substituent on the ring of imidazole

The effect of a substituent in the imidazole ring on extractability of Lu^{3+} was also investigated using $[C_4mim][NTf_2]$ as the diluent. The chemical structures of the studied compounds are listed in table 1. The results (listed in table 2) show that the extractability of Lu^{3+} with imidazole and benzimidazole is lower than that with 1-MIM and 2-MIM, which clearly indicates that the various substituents in the imidazole ring should affect the basicity of its 'pyridine like' nitrogen and this in turn should be reflected in the stability of the complexes. The 1-MIM and 2-MIM are far more effective for Lu^{3+} ion extraction with electron-donating methyl that enhances the basicity of nitrogen. Benzimidazole with electron-donating phenyl is less soluble in both water and ionic liquid, which causes lower extraction of Lu^{3+}. It is worth noting that 2-MIM offers higher extraction for Lu^{3+} compared with 1-MIM used in ILs due to the hydrogen-bond formed between 2-MIM and nitrate coordinated with metal, which was demonstrated by IR spectra (shown as in Fig. 8). The observations suggest that hydrogen-bond buttressing is dominant in determining the performance of these extractants and indicate that interaction in the outer coordination spheres of complexed metals can greatly influence complex stability. The role of the hydrogen-bond was also demonstrated by another case of extraction lanthanides with 2-MIM in *n*-pentanol.

Fig. 8 shows the IR spectra of 2-MIM and the extracted complex of Lu^{3+} by 2-MIM extraction. It is observed that the new peaks at 1354 cm^{-1} and 835 cm^{-1} appear in the IR-spectra of the extracted complex that are assigned to the signature peaks of stretching vibration of N=O and N-O bonds of nitrate in comparison with the IR-spectra of 2-MIM. The peak at 3180 cm^{-1} in the IR-spectra of 2-MIM is assigned to the stretching vibrations of N–H in imidazole ring, which suffered a shift towards a lower wavenumber 3155 cm^{-1} in the IR-spectra of the extracted complex, suggesting the hydrogen bond is involved in the complex formation. Furthermore, there are some change for the absorption peaks at 1845, 1675 and 1596 cm^{-1} in the IR-spectra of 2-MIM which can be attributed to the skeleton vibration of imidazole ring, and all these peaks suffered a weakened and shifted to lower wavenumbers 1801, 1629 and 1567 cm^{-1} change in the

IR of the extracted complex, respectively. This information implies that the interaction among Lu^{3+} ion, nitrate ion and 2-MIM during the complex formation exists.

Table 1 Chemical structure of the studied compounds

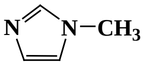
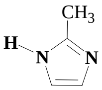
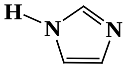
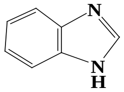
Compound	1-MIM	2-MIM	Imidazole	Benzimidazole
Chemical structure				

Table 2 Dependence of extractability of lutetium from the aqueous phase to the IL phase ($[C_4mim][NTf_2]$) on the concentration of different extractant in the IL

Concentration (M)	Distribution ratio of different extractant			
	1-Methylimidazole	2-Methylimidazole	Imidazole	Benzimidazole
0.0126	11.10	77.68	4.030	0.967
0.0252	20.03	108.8	4.493	2.099
0.0378	28.81	132.9	6.499	2.851
0.0504	39.11	293.1	7.354	3.066
0.0630	46.62	485.2	8.303	3.415

Metal extraction with MIM in *n*-pentanol

To compare with the partitioning behaviors of lanthanides in the ILs, the extraction equilibria of lanthanides (Lu^{3+}, Eu^{3+}, La^{3+}) were measured as a function of 1-MIM and 2-MIM concentration in *n*-pentanol (Fig. 9a). From Fig. 9a, an increase in extraction ability of metal ions with increasing 2-MIM concentration in *n*-pentanol is observed. While no extraction of lanthanides occurs with same concentration of 1-MIM in the n-pentanol. In addition, the extraction ability of 2-MIM in *n*-pentanol is lower compared to that in ILs. It is observed that achieving same degree extraction of lanthanides more 2-MIM is needed in *n*-pentanol than in ILs. The extraction trend is similar to that obtained in ILs, wherein light lanthanides are poorly extracted; the heavier lanthanides are much better extracted. This indicates 2-MIM provides a good selectivity for heavier lanthanides. The log$D$ *vs.* log[2-MIM] was plotted shown as in Fig. 9b, it produced straight lines with a slope of 4 for Lu^{3+}, and 1 for La^{3+} and Eu^{3+} (the concentration of 2-MIM increasing from 0.013M to 0.139M). We also found at higher ligand concentration (from 0.127 to 0.761M), the slope value is 4 for La^{3+} and Eu^{3+} (Fig. 9b), which indicates the slope increases as the ligand concentration increases. As shown in Fig. 6 the distribution ratio of Lu^{3+} extraction with 2-MIM in *n*-pentanol increases with an increase in nitrate ion concentration which indicates nitrate ion participating in extraction process. Besides, ESI-MS measurements were made for loaded *n*-pentanol phase after extraction of Lu^{3+} and La^{3+}. The peaks at m/z 689.0136 and 408.1126 can be found and they correspond to the complex $Lu(C_4H_6N_2)_4(NO_3)_3$ (m/z calcd. 689.3533) and $La(C_4H_6N_2)(NO_3)_3$ (m/z calcd. 407.0054). These species are products of neutral solvation transfer. These experiments reveal the extraction process following a neutral solvation mechanism. Extraction reactions in *n*-pentanol are illustrated as eq. 2 and eq. 3

Determination of thermodynamic parameters

The effect of temperature on the extraction of Lu^{3+} from aqueous solution by 50 mM 1-MIM in $[C_4mim][NTf_2]$ was studied (Fig. 11). The D value for Lu^{3+} extraction is found to increase with increasing temperature, indicating that the extraction is an endothermic process. The change in enthalpy (ΔH) during the extraction can be calculated from the Van't Hoff eq. (6),

$$\text{¦¤}H\ \text{£½£-}\ 2.303\ R\ \text{¦¤}\log D\ /\text{¦¤}(1/T) \qquad (6)$$

A plot of log*D* *vs*. 1000/T yields a straight line with a slope of -Δ*H*/2.303 R, from which Δ*H* value is calculated. The change in Gibb's free energy (ΔG) is calculated by eq. (7),

$$\text{¦¤}G\ \text{£½£-}\ 2.303\ RT \log K\ \text{¡ä} \qquad (7)$$

where *K′* is the conditional extraction constant. The extraction of Lu^{3+} with MIM in IL can be represented as follows:

$$Lu^{3+}{}_{aq} + mMIM_{or} + nNO_3^-{}_{aq} + (3\text{-}n)[C_n mim^+]_{or} \longrightarrow [Lu(MIM)_m\,(NO_3)_n]^{3\text{-}n}{}_{or} + (3\text{-}n)[C_n mim^+]_{aq} \qquad (8)$$

$$K = \frac{[[Lu(MIM)_m(NO_3)_n]^{3\text{-}n}]_{or}\,[C_n mim^+]_{aq}{}^{3\text{-}n}}{[Lu^{3+}]_{aq}\,[MIM]_{or}{}^{m}\,[NO_3^-]_{aq}{}^{n}\,[C_n mim^+]_{or}{}^{3\text{-}n}} \qquad (9)$$

$$D = \frac{[[Lu\,(MIM)_m(NO_3)_n]^{3\text{-}n}]_{or}}{[Lu^{3+}]_{aq}}$$

$$K = \frac{D\,[C_n mim^+]_{aq}{}^{3\text{-}n}}{[MIM]_{or}{}^{m}\,[NO_3^-]_{aq}{}^{n}\,[C_n mim^+]_{or}{}^{3\text{-}n}} \qquad (10)$$

Where $[NO_3^-]$ is constant, the values of $[C_4mim^+]_{aq}$ and $[C_4mim^+]_{or}$ can be regarded as constant ones. Thus, log *D* can be given by Eq. (10):

$$\log D = \log K' + m\log\,[MIM] \qquad (11)$$

The *K′*-value is calculated from the intercept of a plot of log *D* vs. log[MIM] at a same pH. The change in entropy (Δ*S*) at a particular temperature can be calculated by Eq. (11):

$$\text{¦¤}G\ \text{£½¦¤}H\ \text{£-}\ T\ \text{¦¤}S \qquad (12)$$

The thermodynamic values over the temperature range 293-328K were obtained using eq. (6), (7), (12) and are shown in Table 3. Δ*H* is positive, so the reaction is endothermic. All values of **Δ***G* are negative, so the reaction of lutetium extraction is spontaneous and favorable for complexation and extraction. The positive value of **Δ***S* shows that more disorder is introduced in the system upon Lu^{3+} extraction.

Table 3 Thermodynamic parameters (ΔG, ΔH and ΔS) for Lu^{4+} extractions from a aqueous solution using 1-MIM as an extractant in [C_4mim][NTf_2] at 298.15 K.

Metal ion	K'	log K'	ΔH(kJmol^{-1})	ΔG(kJmol^{-1})	ΔS(JK^{-1}mol^{-1})
Lu^{3+}	650279.4	5.8131	46.763	-33.185	268.15

Stripping studies

Stripping is an important feature for evaluating an extraction system. The efficiency of lanthanides extraction by MIM in IL reduces with increasing nitric acid concentration. The stripping test for Lu^{3+} extracted by 1-MIM in [C_4mim][NTf_2] was performed using 5 mL different concentrations of dilute nitric acid. The percentage stripping of lutetium increase with increasing acidity and reached nearly 95% when the initial concentration of stripping nitric acid solution is 0.05 M(shown as in Fig.12), which indicates that Lu^{3+} is easily stripped from the loaded IL. The IL phase after stripping can be easily regenerated by washing it with water until the washings are neutral. The reason of efficient transfer of Lu^{3+} into the receiving phase at acidity conditions was protonation of 1-MIM under acidic conditions.

Competitive extraction of lanthanides

A competitive extraction of three lanthanides, representing light, middle, and heavy respectively, with alkali metals and alkaline earth cations by 1-MIM in IL of [C_4mim][NTf_2] was carried out to assess the selectivity of the present system. The distribution ratios are plotted in Fig. 13. The lanthanides are effectively extracted under the extraction conditions, whereas alkali metals and alkaline earth cations are barely extracted at all. Two possible reasons for this selectivity could be that the lower stability and superior affinity to water of the complexes formed from 1-MIM with alkali metals and alkaline earth metal.

Conclusions

A solvent extraction system based on combining ILs and 1-methylimidazole or 2-methylimidazole was investigated. Methylimidazole dissolved in $[C_n\text{mim}][\text{NTf}_2]$ is able to extract lanthanides and yttrium. These compounds transfer lanthanides and yttrium into ILs phases via a cation-exchange mechanism and neutral solvation mechanism and form a stable 1:4 complex with middle and heavy lanthanides and 1:1 complex with light lanthanides and yttrium. In addition, when using *n*-pentanol as diluents, lanthanides can be extracted only by 2-MIM. The extraction ability of 2-MIM in *n*-pentanol is lower compared to that in ILs. High selectivity for lanthanides from alkali metals and alkaline earth cations was demonstrated. Furthermore, recovery of metal ions from ILs into a receiving phase can be achieved while using MIM as the extractant. These results highlight the potential of methylimidazole as the extractants in ILs systems.

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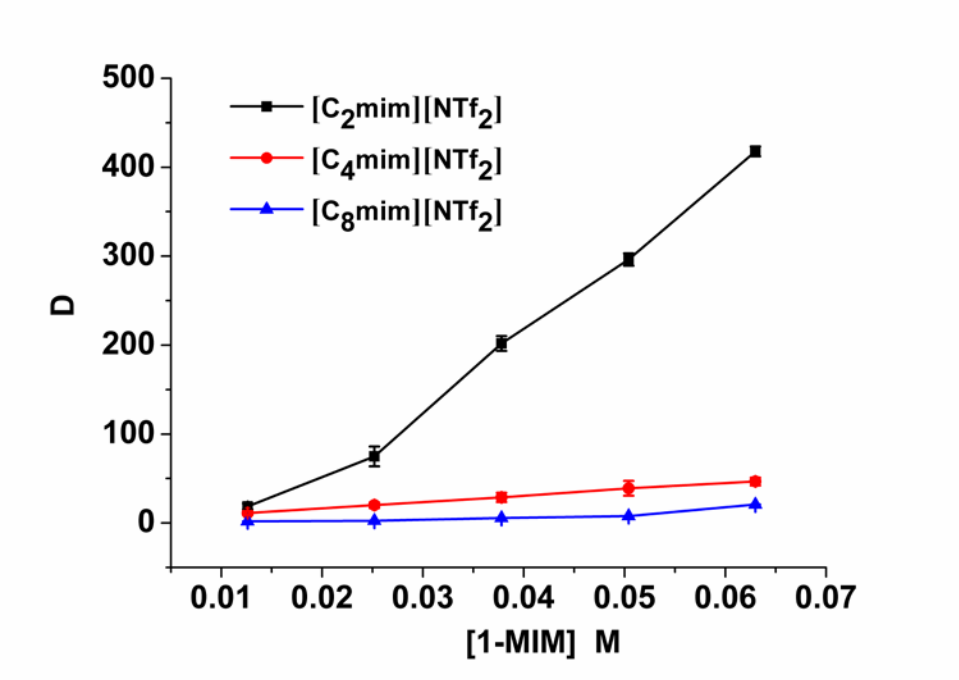


Fig. 1 The distribution ratios of lutetium from the aqueous phase to the IL phase ($[C_nmim][NTf_2]$) as a function of the 1-MIM concentration in the IL.

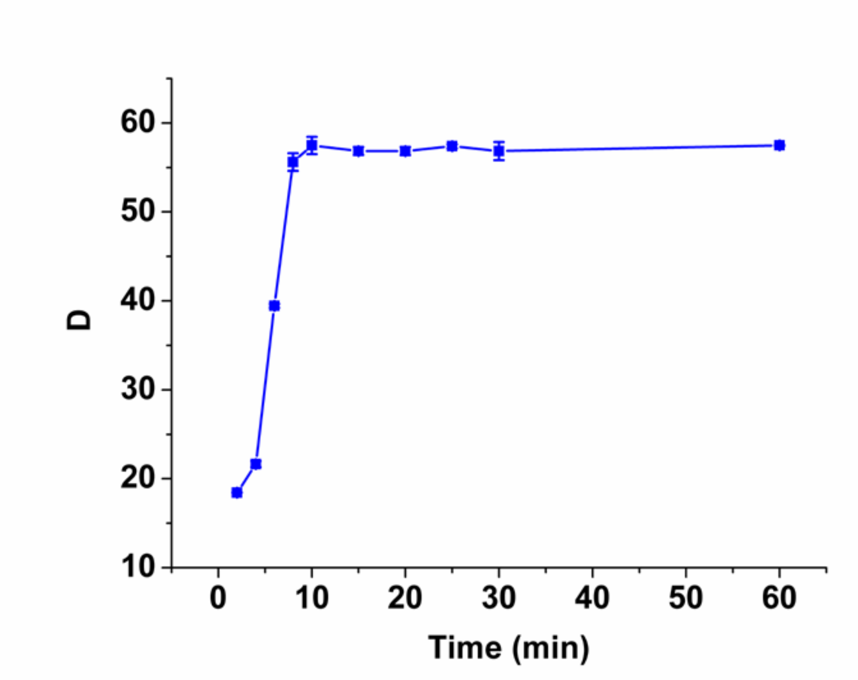


Fig. 2 Extraction kinetics of lutetium from 0.4mM aqueous solution with 0.088 M 1-MIM in $[C_4mim][NTf_2]$.

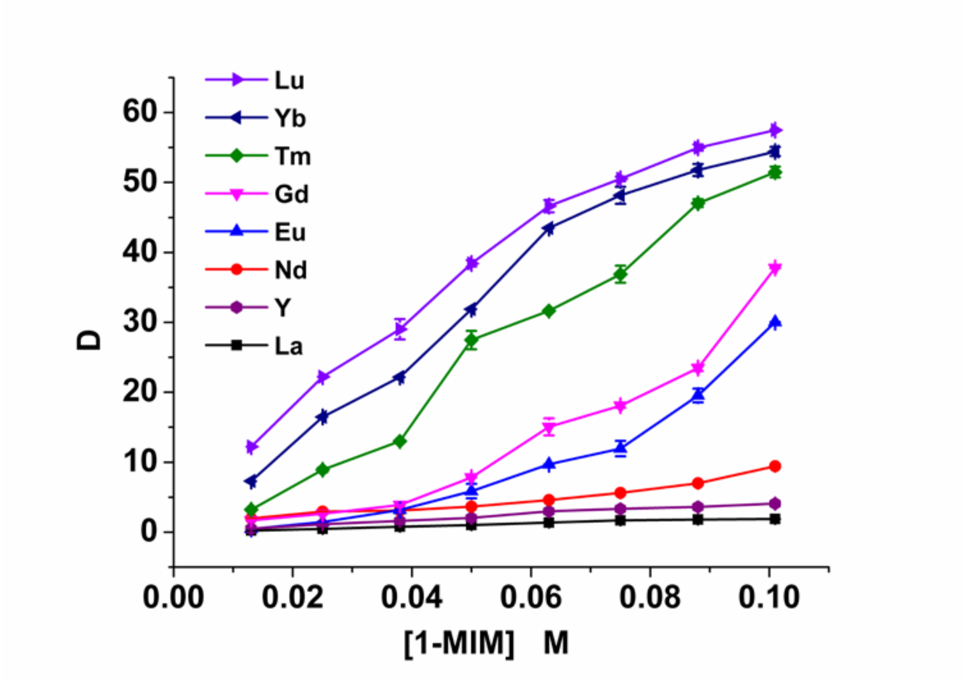


Fig. 3 Dependence of distribution ratios of metal ions from aqueous phase to IL phase ($[C_4mim][NTf_2]$) on the concentration of 1-MIM in the IL.

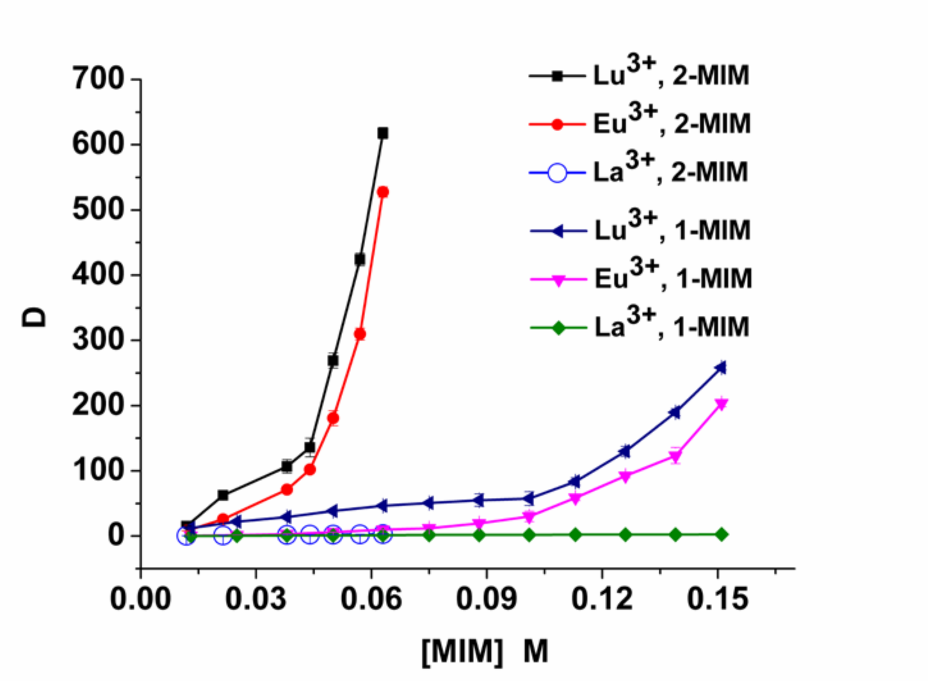


Fig. 4 Dependence of distribution ratios of Lu^{3+}, Eu^{3+}, La^{3+} from the aqueous phase to IL ($[C_4mim][NTf_2]$ phase on the MIM concentration in the ILs.

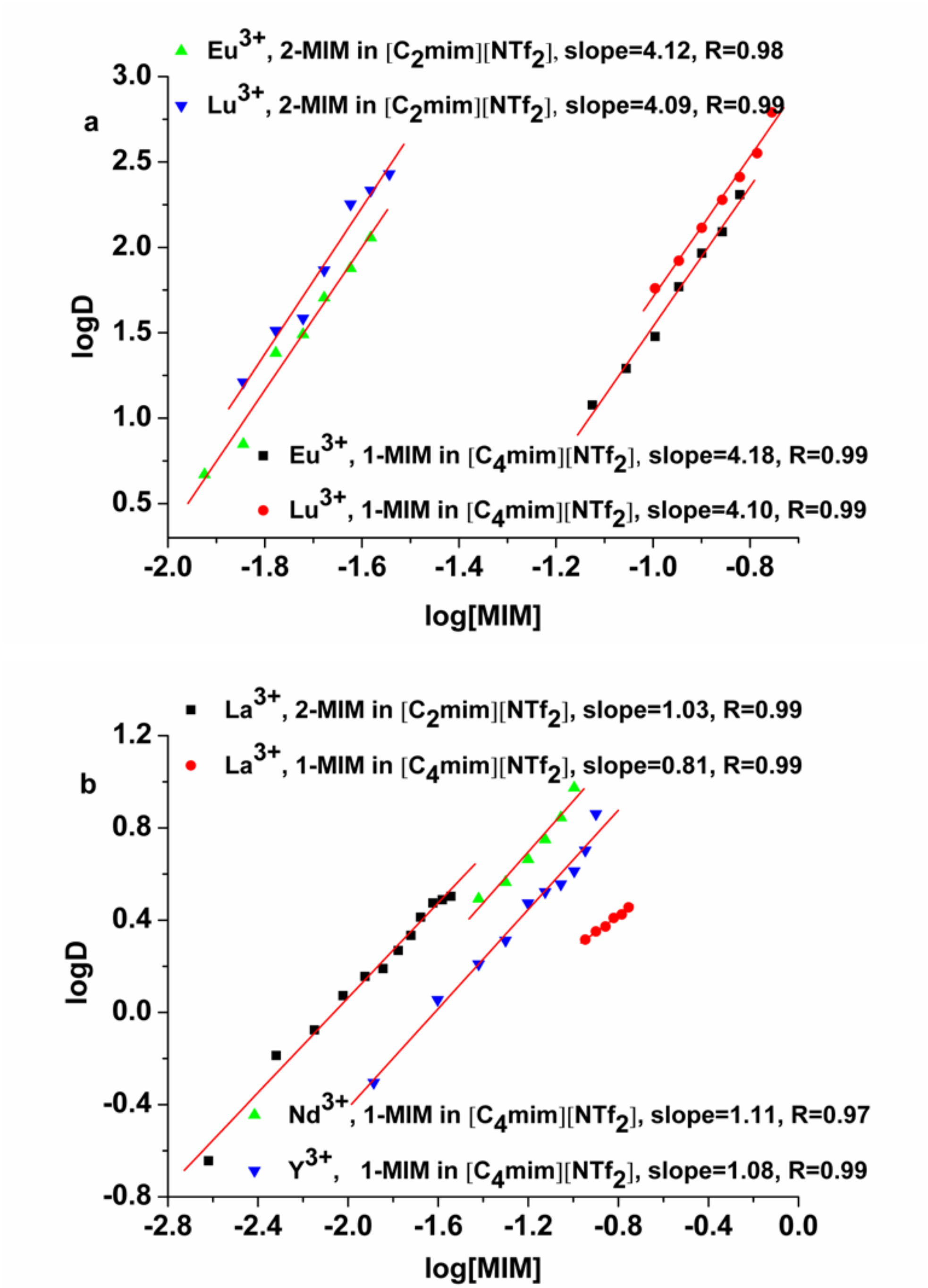


Fig. 5 Plots of log *D* *vs*. log[MIM], $[M^{3+}]$ = 0.4 mM, (a) for Eu^{3+}, Lu^{3+} ;(b) for La^{3+}, Nd^{3+}, Y^{3+}.

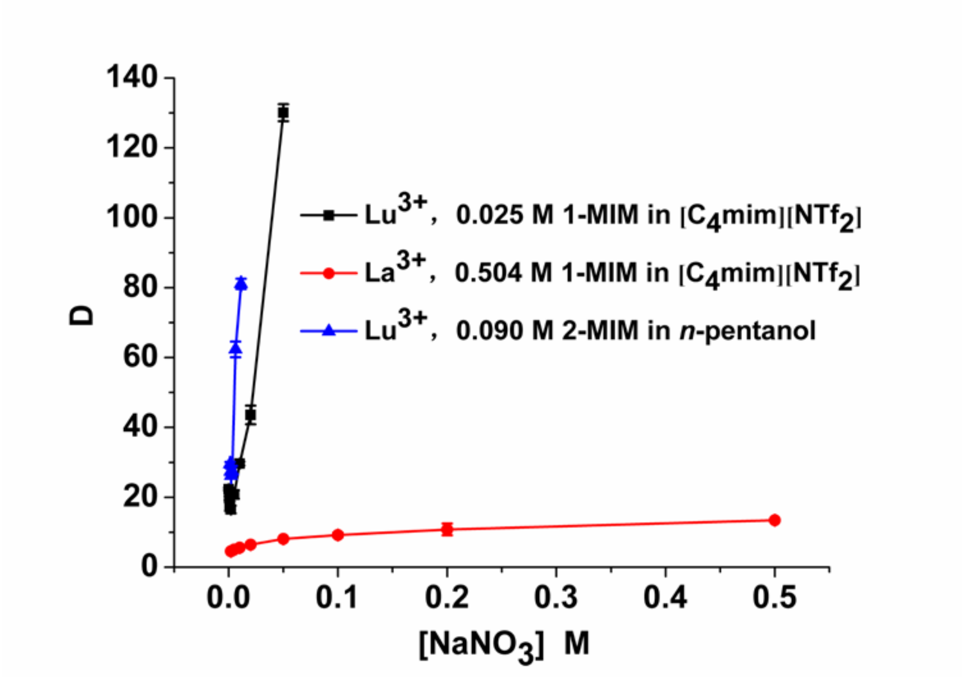


Fig. 6 Effect of nitrate concentration on distribution ratios of lanthanides with 1-MIM in [C_4mim][TNf_2] and 2-MIM in *n*-pentanol.

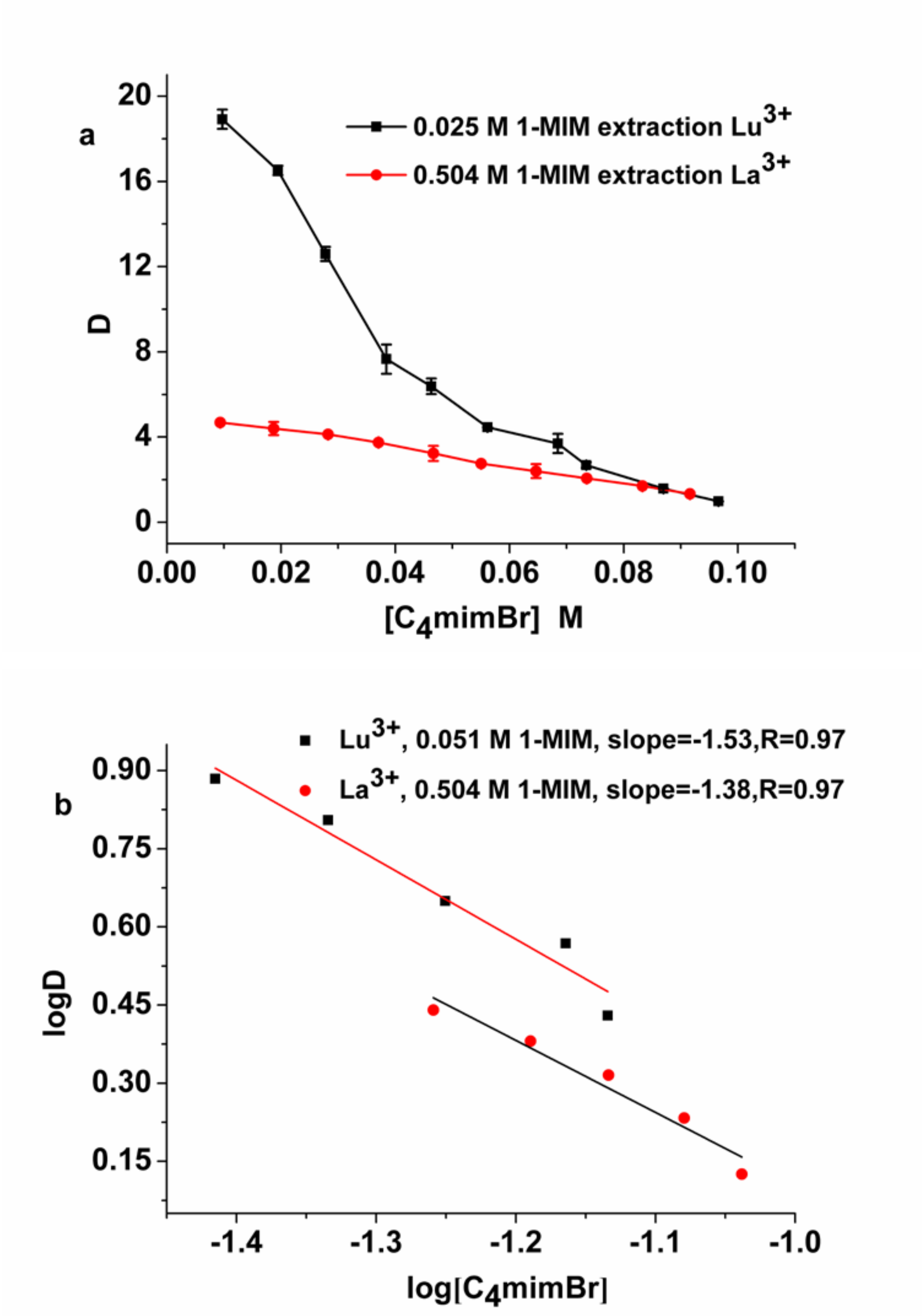


Fig.7 (a) Effect of aqueous-phase C_4mimBr concentration on distribution ratios of lanthanides using 1-MIM in [C_4mim][NTf_2]; (b) Plots of log *D vs.* log[C_4mimBr].

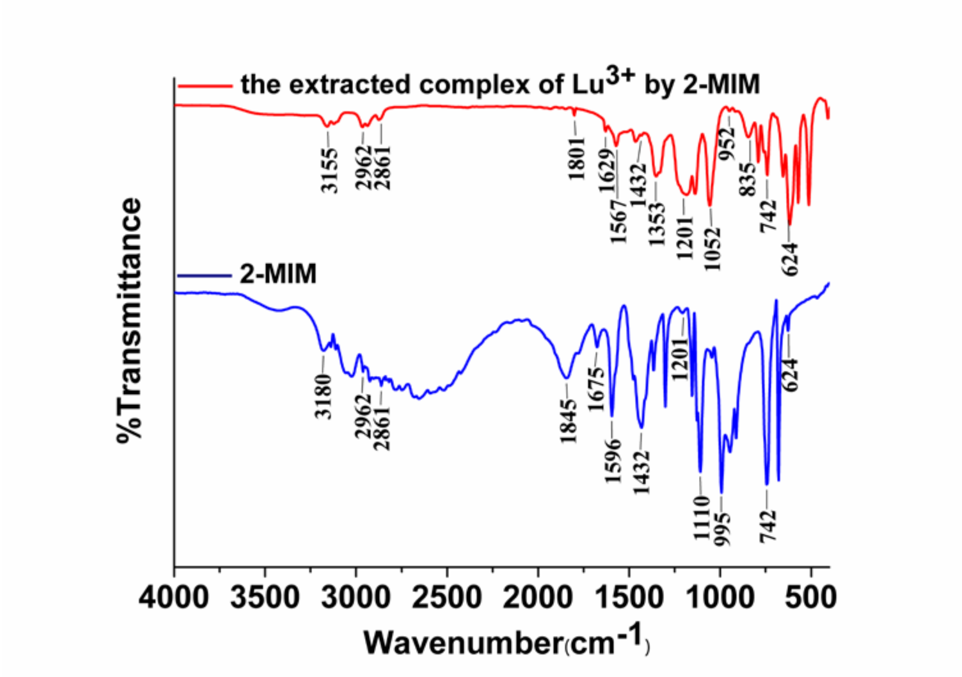


Fig. 8 FT-IR spectra of 2-MIM and the extracted complex of Lu^{3+} by 2-MIM.

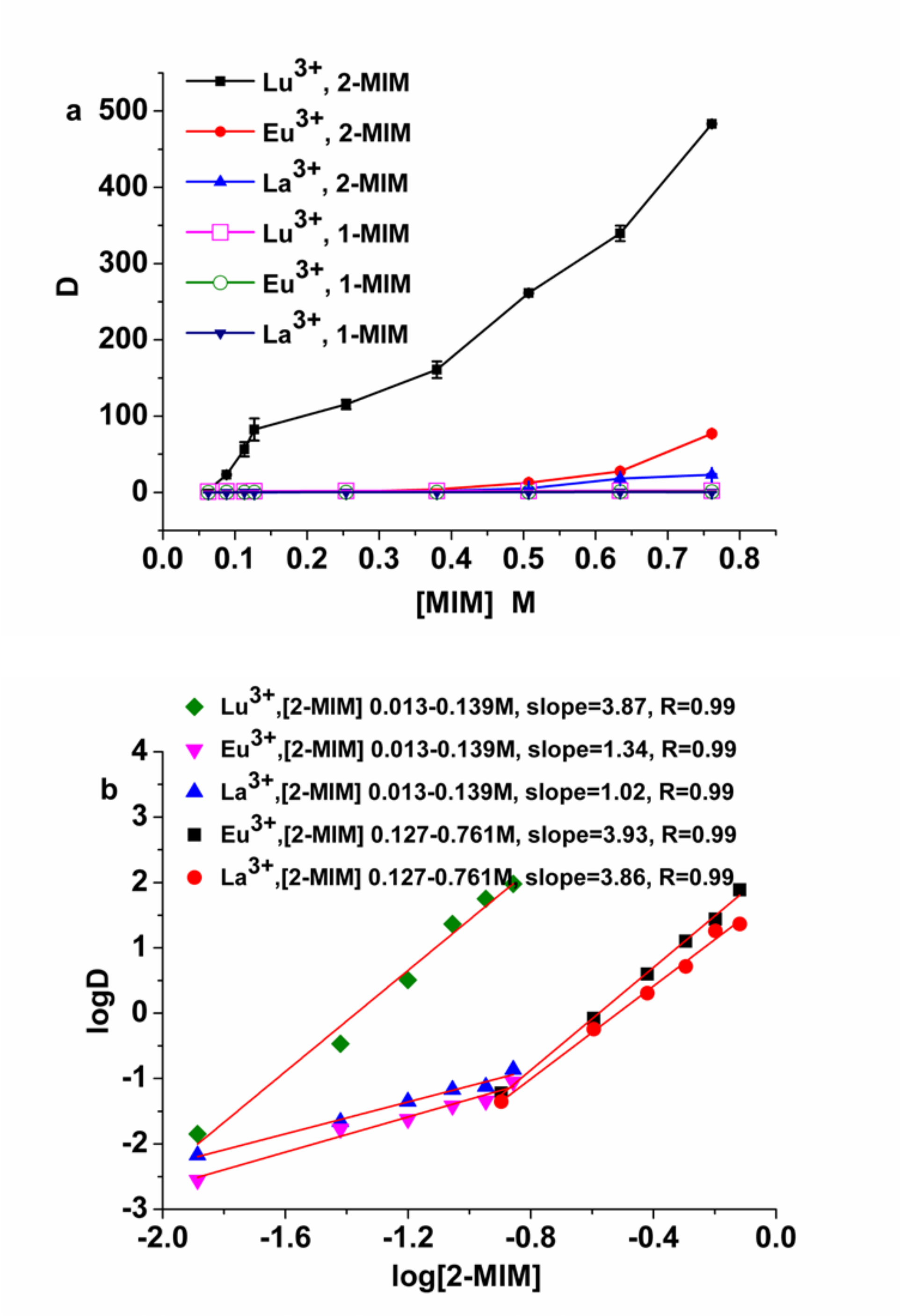


Fig. 9 (a) Dependence of distribution ratios of Lu^{3+}, Eu^{3+} and La^{3+} from aqueous phase to *n*-pentanol on the concentration of different extractant in *n*-pentanol; (b) Plots of log*D* *vs.* log[2-MIM].

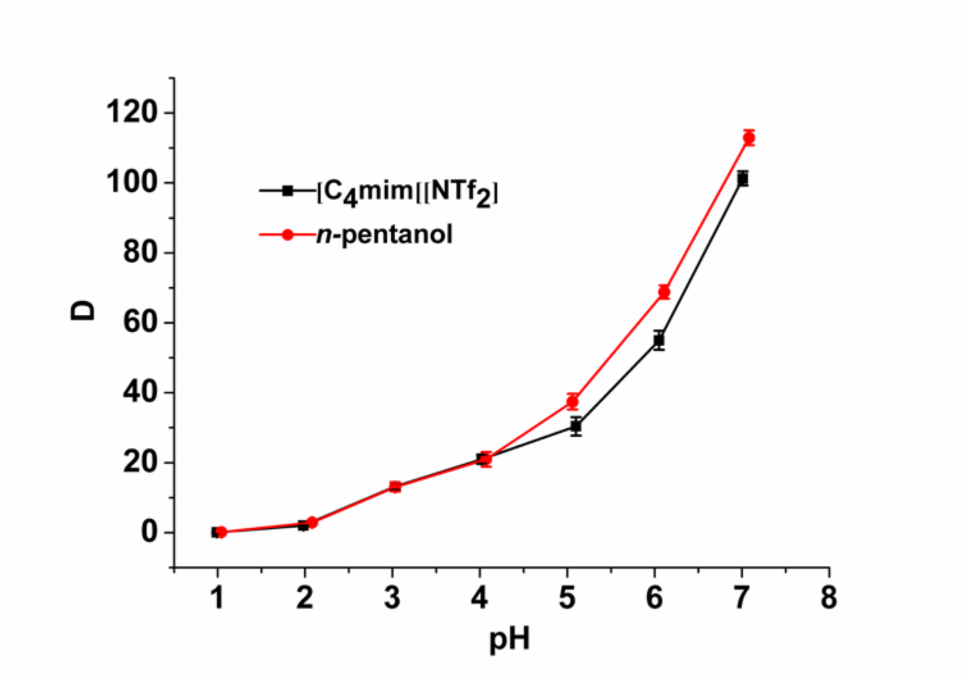


Fig. 10 The effect of pH on distribution ratios of lutetium with [C_4mim][NTf_2] and *n*-pentanol, organic phase: 0.051 M 1-MIM in [C_4mim][NTf_2], 0.090 M 2-MIM in *n*-pentanol.

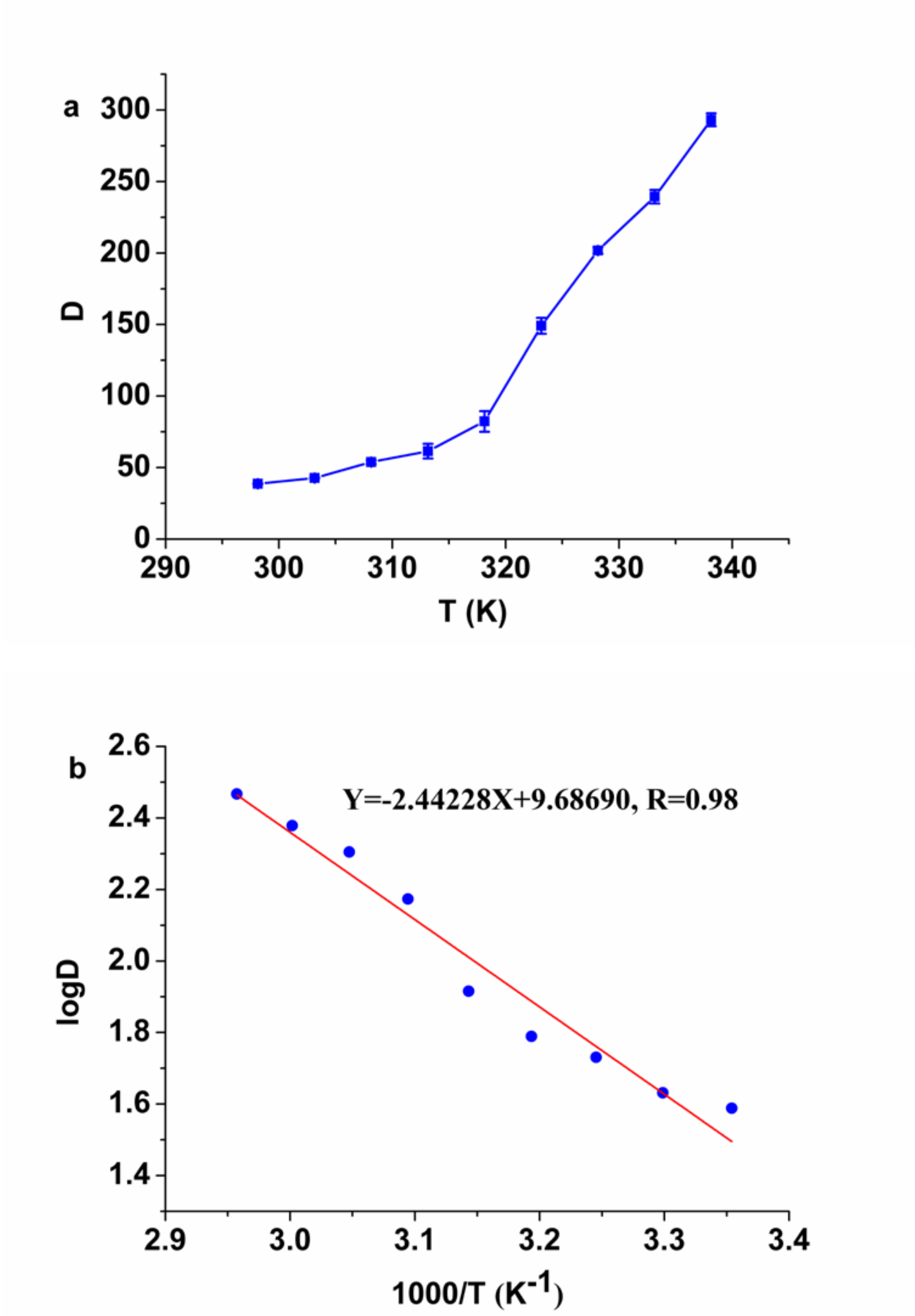


Fig. 11 **(a)** Distribution ratios of lutetium as a function of temperatures, using 1-MIM as the extractant in [C$_4$mim][NTf$_2$], [1-MIM] = 0.05 M; **(b)** Plots of log*D* *versus* 1000/*T* for Lu^{3+} extraction with 1-MIM in [C$_4$mim][NTf$_2$].

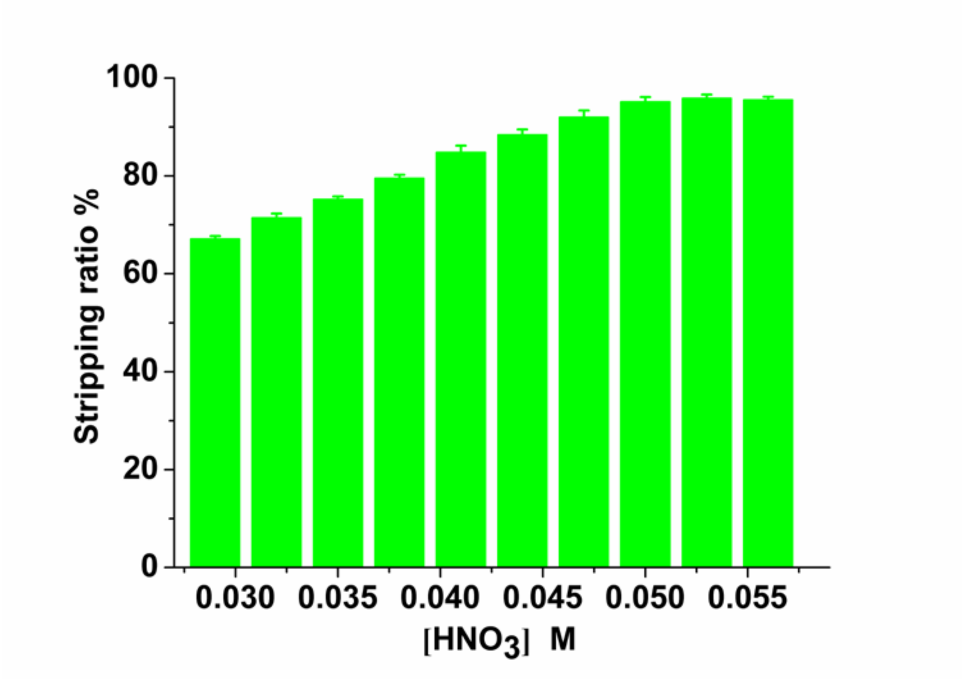


Fig. 12 Stripping ratios of lutetium with different concentrations of HNO_3 from [C_4mim][NTf_2].

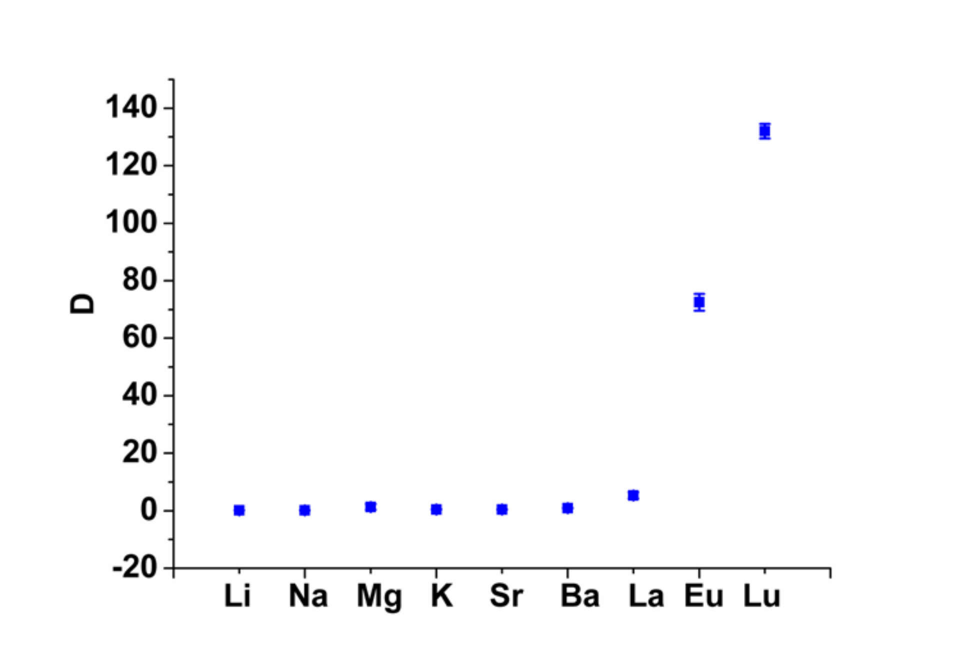
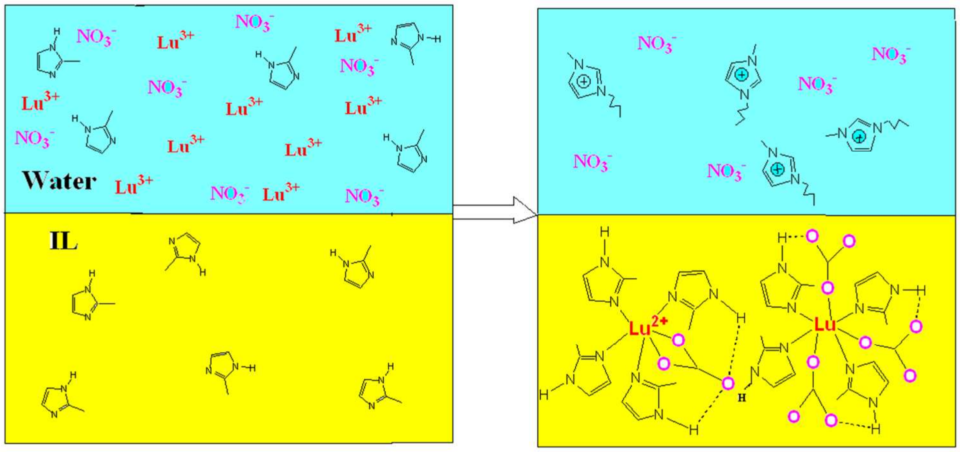


Fig. 13 Distribution ratios of metal ions in [C_4mim][NTf_2], [1-MIM] =10 mM, [M^{n+}] = 0.1 mM for each metal ion.

Methylimidazole combining ILs transfer lanthanides and yttrium from aqueous solution into ILs via a cation-exchange mechanism and neutral solvation mechanism.



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