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Room temperature ionic liquids (ILs) have been considered as alternative solvents for synthetic, catalytic, electrochemical and separation sciences because of their unique properties such as low vapor pressure, solvating properties, and thermal stability.[1−4] Especially, they have been considered as next generation diluents as the replacements of volatile organic compounds (VOCs) in the reprocessing of spent nuclear fuel.[5−30] For the current commercial

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process (PUREX process) for recovering uranium and plutonium from spent nuclear fuel using a 30% solution of tri- -butyl phosphate (TBP) in kerosene, there are still some drawbacks including the volatility and flammability of kerosene and the risk of the system becoming critical if the concentration of fissile products becomes too large.[20] The utilization of ILs can overcome these drawbacks and help reduce the risk to some extent,[31] and a number of studies have been performed.

The extraction of uranium using ILs as solvents has been performed with TBP as the extractant.[15–21] The extraction of UO_2^{2+} from nitric acid medium by 1.1 mol dm^{-3} of TBP in the ILs 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) and bis(trifluoromethylsulfonyl)imides ($C_4mimNTf_2$) was reported by Rao and coworkers.[15–17] The effect of the concentration of nitric acid on the distribution ratio differs greatly depending upon the nature of the anion of an IL used as diluent. Dietz and Stepinski[18] studied the anion concentration-dependent partitioning mechanism in the extraction of UO_2^{2+} into the ILs C mimNTf$_2$ (=5, 8, 10). The mode of partitioning of UO_2^{2+} between nitrate-containing aqueous phase and the ILs ($C_5mimNTf_2$ and $C_8mimNTf_2$) in the presence of TBP was shown to change from a cation-exchange process to one involving the extraction of a neutral complex $UO_2(TBP)_2(NO_3)_2$ as the concentration of nitrate was increased. In $C_{10}mimNTf_2$ system, the neutral complex extraction was the predominant mode of partitioning, regardless of the nitrate concentration.[18] Billard [19] studied the extraction mechanism in the extraction of UO_2^{2+} by TBP in $C_4mimNTf_2$, where the uranyl extraction is shown to proceed a double cationic exchange at low acidities and an anionic exchange at high acidity, excluding the extraction of the usual $UO_2(NO_3)_2(TBP)_2$ neutral species evidenced in dodecane. Bell and Ikeda[20] used ammonium based hydrophobic ILs in the liquid-liquid extraction of UO_2^{2+} from the aqueous solution of nitric acid by TBP and found that cation-exchange, anion-exchange, and the partitioning of a neutral complex were involved depending on the concentration of nitric acid and the hydrophobicity of the IL used.

The extraction mechanism is more complicated in TBP-IL system than that in TBP-kerosene system. This difference may influence the selectivity of TBP to uranyl ion. For the complicated components of spent nuclear fuel, selective extraction of UO_2^{2+} from aqueous solution containing other fission products must be considered when an IL instead of kerosene acts as diluent. However, there are no reports on the separation of $UO_2{}^{2+}$ from aqueous phase in the presence of other metal ions by TBP in ILs.

Furthermore, although TBP is a very excellent extractant in the present commercial process using kerosene as diluent, it must not be the case in the IL system. Actually, some other extractants, such as octyl-phenyl- , -diisobutylcarbamoylmethylphosphine oxide (CMPO), bis(2-ethylhexyl)phosphate acid (HDEHP), and task specific ILs bearing phosphoryl groups, have been used in the IL system for extracting UO_2^{2+}.[14,32–35] For example, Visser .[32] studied the extraction of UO_2^{2+} by CMPO and TBP in C_4mimPF_6 and $C_8mimNTf_2$, and investigated the coordination environment of uranyl ion in ILs by extended X-ray absorption fine structure (EXAFS) measurements. The utilization of other extractants instead of TBP in ILs also needs the examination of their selectivities to UO_2^{2+} in the presence of other metal ions.

The extraction selectivity toward UO_2^{2+} is of great importance for the recycling uranium in the reprocessing of the spent nuclear fuel. Especially, research should be focused on the extraction performance of UO_2^{2+} in the presence of other metal ions and the discovery of the competing ions. The extraction of UO_2^{2+} by TBP and CMPO in ILs have been studied in the literature,[32] but their extraction selectivity toward UO_2^{2+} has not yet been investigated. Thus, in this work, we mainly focused our attention on the selective extraction of UO_2^{2+} from aqueous phase in the presence of other metal ions, using CMPO and TBP as the extractants in the ILs C mimNTf$_2$.

C mimNTf$_2$ (=2, 4, 6, 8) were synthesized metathetical reaction from C mimBr and LiNTf$_2$,[36] and the purity was over 99% as detected by NMR and elemental analysis. Both C mimBr and LiNTf$_2$ (AR) were purchased from Lanzhou Institute of Chemical Physics, China. CMPO (97%) was purchased from Strem Chemicals Inc., USA. TBP (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. $Sr(NO_3)_2$, $CsNO_3$, $ZrOCl_2$ $8H_2O$, $Cr(NO_3)_3$ $9H_2O$, and $Ni(NO_3)_2$ $6H_2O$ were all of analytical grade. NH_4ReO_4 (99%) was purchased from Sigma-Aldrich. $Ru(NO)(NO_3)_3$ (1.5% Ru / (g mL^{-1}

Table 1 Concentrations of metal ions in the simulated liquid waste (SLW) used in this work

Element	Concentration/(g dm^{-3})
Sr	0.54
Cs	0.54
Zr	0.68
Cr	0.34
Re	0.15
Ru	0.38
Ni	0.17
Nd	1.00
U	2.38

The concentration of the adding HNO_3 varies from 0 to 4 mol dm^{-3}.

listed in Table 1.

In each extraction experiment, 0.5 mL of C mimNTf$_2$ containing CMPO or TBP and 0.5 mL of aqueous solution containing metal ions were slowly added by a transfer liquid gun (Eppendorf) into a plastic centrifuge tube, followed by vibrating for 24 h at 298.2 K. Actually, we performed the kinetic experiments and found that the equilibration time was about 1 and 6 h for the extraction of UO_2^{2+} by 1.1 mol dm^{-3} of TBP in C$_4$mimNTf$_2$ and 0.02 mol dm^{-3} of CMPO in C mimNTf$_2$ (=4, 8), respectively. However, we previously found that the equilibration time was about 16 h for the extraction of Cs$^+$ by C$_4$mimNTf$_2$ only. The equilibration time for the extraction of Zr^{4+} and ReO_4^- by IL systems was both less than 1 h. Because Cs$^+$ was one of the metal ions in the SLW, we performed all the extraction experiments with vibrating time of 24 h in this work. After vibrating, the mixture was centrifuged for 2 min at 10000 r min^{-1} and the two phases were separated. The concentrations of metal ions remained in the aqueous phase were analyzed by ICP-AES with the uncertainty within 5%. The distribution ratio ( ) was calculated as

$$=\frac{{}_{i}\quad{}_{f}}{{}_{f}}\tag{1}$$

where $_{i}$ and $_{f}$ designate the initial and final concentrations of metal ions in the aqueous phase, respectively.

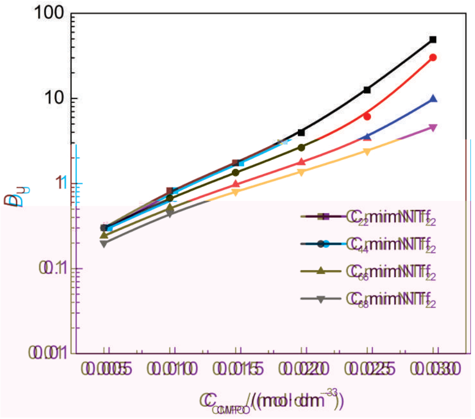

Fig.1 Dependence of the distribution ratio of UO_2^{2+} (D_u) from the aqueous solutions with near zero free acidity on the concentration of CMPO in the ILs C$_n$mimNTf$_2$ (n=2, 4, 6, 8)

The initial concentration of UO_2^{2+} in the aqueous phase is 0.01 mol dm^{-3}.

Fig.1 shows the results of the extraction by CMPO in C mimNTf$_2$ (=2, 4, 6, 8) from the aqueous solution of uranyl nitrate with near zero free acidity (with near zero free acidity means the aqueous solution without the addition of HNO_3, and the pH of the aqueous solution is about 3.10 at 298.2 K). Increase in the concentration of CMPO leads to high distribution ratio of UO_2^{2+}. Among the selected ILs C mimNTf$_2$ (=2, 4, 6, 8), C$_2$mimNTf$_2$ system has the highest distribution ratio toward UO_2^{2+}. Lengthening the alkyl chain of ILs decreases the distribution ratio.

The effect of nitric acid on the extraction of UO_2^{2+} by 0.02 mol dm^{-3} of CMPO in C mimNTf$_2$ (=2, 4, 6, 8) is shown in Fig.2. The distribution ratio in the CMPO-C$_2$mimNTf$_2$ system shows a very little variation as the concentration of the adding HNO_3 ($_{HNO_3}$) varies from 0 to 4 mol dm^{-3}. For the system using an IL with long alkyl chain on the imidazolium cation, e.g., C$_8$mimNTf$_2$, adding nitric acid induces an obvious increase in the distribution ratio. Lengthening the alkyl chain leads to a decrease in the distribution ratio at $_{HNO_3}$=0 mol dm^{-3} and an increase in the distribution ratio at 4 mol dm^{-3} of HNO_3. The difference of the extraction behavior of CMPO in different ILs is very likely due to the difference in the extraction mechanism, i.e., the different proportions between the cation exchange, the anion exchange, and the neutral complex extraction.[18–20,39]

Previous studies of the extraction of UO_2^{2+} by TBP-C mimNTf$_2$ showed that the distribution ratio varied significantly upon the addition of nitric acid.[16–18] For comparison, we also performed the extraction of UO_2^{2+} by 1.1 mol dm^{-3} of TBP in C$_4$mimNTf$_2$ as $_{HNO_3}$ varied from 0 to 4 mol dm^{-3}, and the result is also shown in Fig.2. TBP-C$_4$mimNTf$_2$ can efficiently extract UO_2^{2+} with a distribution ratio of 4.6 from the aqueous solution with near zero free acidity. The distribution ratio of UO_2^{2+} decreases upon the addition of nitric

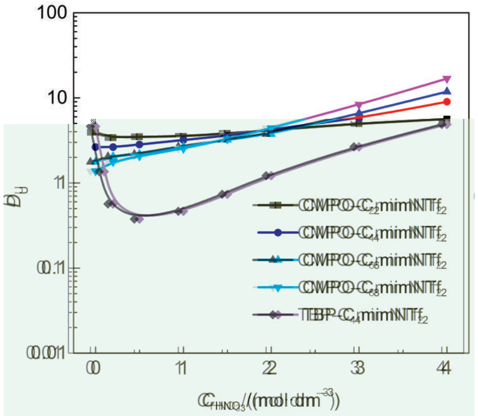

Fig.2 Distribution ratio of UO_2^{2+} by 0.02 mol dm^{-3} of CMPO in C$_n$mimNTf$_2$ (n=2, 4, 6, 8) and 1.1 mol dm^{-3} of TBP in C$_4$mimNTf$_2$ at different concentrations of the adding HNO_3 in the aqueous phase

The initial concentration of UO_2^{2+} in the aqueous phase is 0.01 mol dm^{-3}.

acid and reaches the lowest value of 0.38 at 0.5 mol dm^{-3} of HNO_3, and then increases upon continuous addition of HNO_3, which is consistent with the tendency reported in the literature.[16–18]

In the reprocessing of the spent nuclear waste, the composition of the liquid waste is very complicated. There are many kinds of metal ions in the liquid waste. The selective extraction of UO_2^{2+} from the SLW by the IL systems was detected in the present work. Among the metal ions in the SLW, Cs^+ and Sr^{2+} are the major radioactive fission products in the spent nuclear waste, contributes a large part of the heat load and radiation. ReO_4^- is used as the surrogate for TcO_4^-, which is one of the main fission products of uranium. Nd^{3+} is a representative of the lanthanides and minor actinides.

Detection of the extraction of the SLW by 1.1 mol dm^{-3} of TBP, 0.02 mol dm^{-3} of CMPO in $C_4mimNTf_2$, and 0.02 mol dm^{-3} of CMPO in $C_8mimNTf_2$ shows that only UO_2^{2+}, Zr^{4+}, ReO_4^-, and Cs^+ in the SLW are extracted while other metal ions are not extracted. Fig.3 shows the distribution ratios of UO_2^{2+}, Zr^{4+}, ReO_4^-, and Cs^+ depending on $_{HNO_3}$. For clarity, the distribution ratios of the metal ions which are not extracted are not presented in the figures. It was noticed that the distribution ratio of UO_2^{2+} by TBP in $C_4mimNTf_2$ at $_{HNO_3}$=0.5 mol dm^{-3} in Fig.3(a) is higher than that in Fig.2. This is because the concentration of NO_3^- is about 0.1 mol dm^{-3} in the SLW without the addition of HNO_3, which influences the extraction of UO_2^{2+}. Zr^{4+} is extracted at $_{HNO_3}$ over 2 mol dm^{-3} and its distribution ratio increases with the increase in the concentration of HNO_3. Cs^+ and ReO_4^- are extracted at all HNO_3 concentrations. In general, CMPO-$C_4mimNTf_2$ system behaves better than CMPO-$C_8mimNTf_2$ system in the selective extraction of UO_2^{2+} from the SLW, and CMPO in $C_4mimNTf_2$ shows a relatively good selectivity towards UO_2^{2+}, as compared with TBP in $C_4mimNTf_2$.

We also studied the extraction of the SLW by 0.04 mol dm^{-3} of CMPO in $C_4mimNTf_2$ and the result is shown in Fig.4. The distribution ratio of UO_2^{2+} is enhanced dramatically and almost all the UO_2^{2+} ions in the SLW are extracted into the IL phase. Simultaneously, the distribution ratio of Zr^{4+} is increased and Nd^{3+} is extracted. Different from the extraction of the SLW by 0.02 mol dm^{-3} of CMPO in ILs, Zr^{4+} is extracted at low $_{HNO_3}$. The distribution ratio of Nd^{3+} decreases as HNO_3 is added. This result suggests that the concentration of the extractant in ILs should be fixed carefully if CMPO is utilized in the practical application.

We detected the extraction of the SLW by $C_4mimNTf_2$ and $C_8mimNTf_2$, and the results are shown in Fig.5. One can see that ReO_4^- and Cs^+ are extracted by the IL in the absence of extractants. The distribution ratio of Cs^+ is close to that in the systems with extractants. Our group[25] previously reported that C mimNTf$_2$ can extract Cs^+ from aqueous solution cation exchange. A further study suggested that the coordination of the anion NTf_2^- to Cs^+ accounts for the extraction.[40] The extraction ability of C mimNTf$_2$ to Cs^+ induces high distribution ratio during the extraction of Cs^+ from aqueous solution, but it leads to an undesirable problem in the selective extraction of UO_2^{2+}. Especially, the competing extraction of Cs^+ is hard to be reduced by varying the concentration of HNO_3.

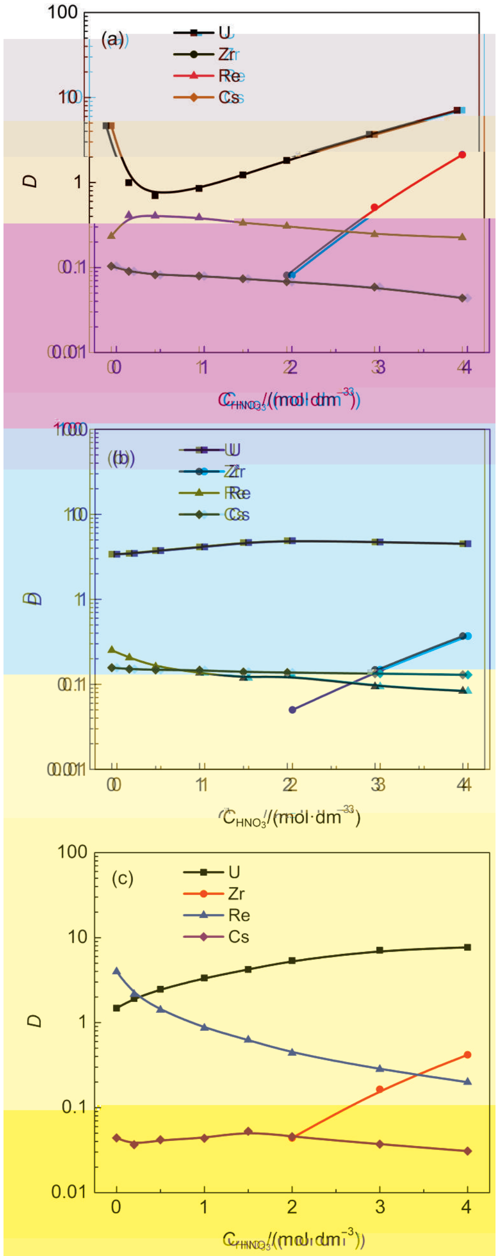

Fig.3 Distribution ratio of metal ions depending on the concentration of the adding HNO_3 in the extraction of SLW by (a) 1.1 mol dm^{-3} of TBP in $C_4mimNTf_2$, (b) 0.02 mol dm^{-3} of CMPO in $C_4mimNTf_2$, and (c) 0.02 mol dm^{-3} of CMPO in $C_8mimNTf_2$

Other metal ions in the SLW are not extracted.

The extraction of ReO_4^- by $C_4mimNTf_2$ and $C_8mimNTf_2$ results from the anion exchange, according to the literature.[24] However, one can see that the distribution ratios of ReO_4^- in Fig.5 is much lower than those in Fig.3 and Fig.4. It was reported that TcO_4^- acts as the counterion in the extraction of UO_2^{2+}.[41] On the other hand, Chaumont [42] studied the complexation of ReO_4^- and UO_2^{2+} in

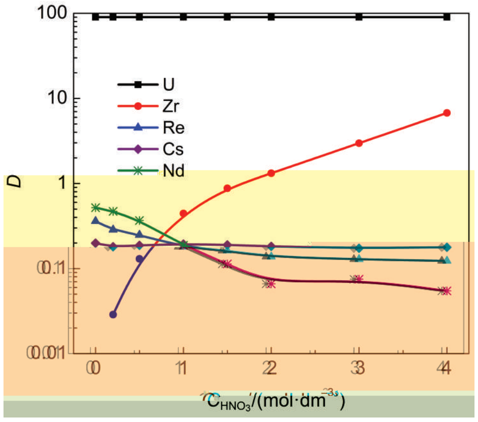

Fig.4 Distribution ratio of metal ions depending on the concentration of the adding HNO$_3$ in the extraction of SLW by 0.04 mol dm^{-3} of CMPO in C$_4$mimNTf$_2$

Other metal ions in the SLW are not extracted.

aqueous solution, acetonitrile, C$_4$mimNTf$_2$ and other two ILs. They found that ReO$_4^-$ behaves as a weak ligand in aqueous solution and as a strong ligand in acetonitrile and in the ILs.[42] Thus the higher distribution ratio of ReO$_4^-$ as UO$_2^{2+}$ was extracted could be attributed to the counterion effect, i.e., the interaction of ReO$_4^-$ with UO$_2^{2+}$. Furthermore, if we relook the distribution ratio of ReO$_4^-$ in Fig.6, we can infer that the extractant also influences the interaction between ReO$_4^-$ and UO$_2^{2+}$ in ILs, thus the distribution ratios of ReO$_4^-$ are different in the extraction of the SLW by TBP-C$_4$mimNTf$_2$ and CMPO-C$_4$mimNTf$_2$ systems.

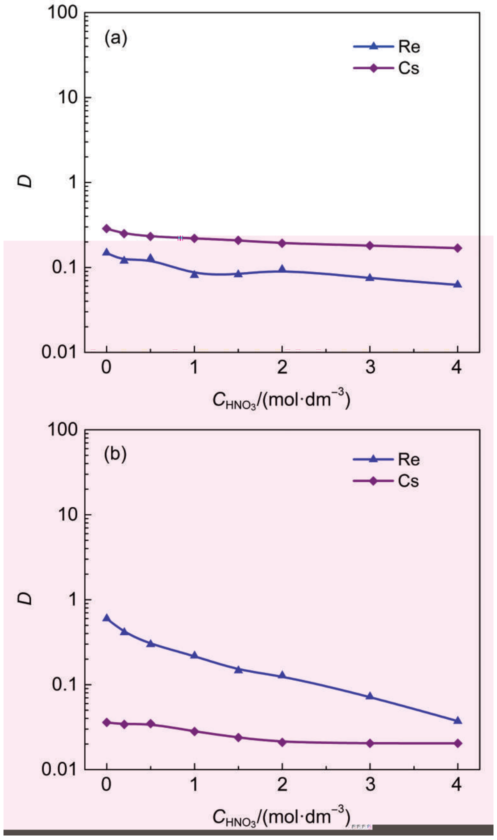

Fig.5 Distribution ratio of metal ions depending on the concentration of the adding HNO$_3$ in the extraction of SLW by (a) C$_4$mimNTf$_2$ only and (b) C$_8$mimNTf$_2$ only

Other metal ions in the SLW are not extracted.

The above results indicate that Zr^{4+}, ReO$_4^-$, and Cs$^+$ are the main competing ions in the separation of UO$_2^{2+}$ from the SLW by the C mimNTf$_2$ systems, and Nd^{3+} is extracted at high CMPO concentration. Compared the results in Fig.3 and Fig.4, one can see that Nd^{3+} is only extracted at high CMPO concentration. This is because CMPO in C$_4$mimNTf$_2$ can extract the lanthanide ions with a high distribution ratio according to the literature,[43] and the extraction of Nd^{3+} is restrained in the presence of UO$_2^{2+}$.

The results in Fig.5 indicate that no Zr^{4+} is extracted by C mimNTf$_2$. Actually, the extraction of Zr^{4+} is attributed to the presence of CMPO or TBP. As shown in Fig.6, CMPO in ILs can extract Zr^{4+}, and the distribution ratio increases with the increase in $_{\mathrm{HNO_3}}$. The distribution ratio of Zr^{4+} in C$_4$mimNTf$_2$ system is lower than that in C$_8$mimNTf$_2$ system at high $_{\mathrm{HNO_3}}$, consisting with the result in the extraction of the SLW. Different from CMPO, TBP does not extract Zr^{4+} in C$_4$mimNTf$_2$ at $_{\mathrm{HNO_3}}$ lower than 2 mol dm^{-3}.

For comparison, the extraction of the SLW by 1.1 mol dm^{-3} of TBP in dodecane has been performed and the result is shown in Fig.7. In the dodecane system, the distribution ratio of UO$_2^{2+}$ increases with the increase in $_{\mathrm{HNO_3}}$. Zr^{4+} is not extracted at $_{\mathrm{HNO_3}}$ lower than 2 mol dm^{-3}, similar to that in the TBP-C$_4$mimNTf$_2$ system. Compared with the TBP-dodecane system, one can see that one of the advantages to use ILs as solvents is that Ru(III) is not extracted by the IL systems. Because of the complicated complexes of nitrosylruthenium,[44] more research is required in the future to figure out why the dodecane system can but the IL systems cannot extract Ru(III). On the other hand, a disadvantage in the IL systems is that the IL itself is able to extract Cs$^+$ despite the variation of HNO$_3$ concentration, although the distribution ratio of Cs$^+$ can be decreased with the increase in the alkyl length of the IL cations.

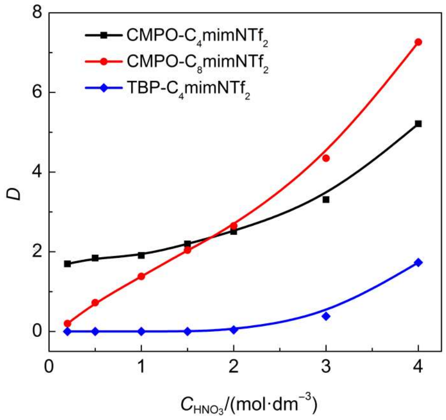

Fig.6 Distribution ratio of Zr^{4+} depending on the concentration of the adding HNO$_3$ by 0.02 mol dm^{-3} of CMPO in C$_n$mimNTf$_2$ (n=4, 8) and by 1.1 mol dm^{-3} of TBP in C$_4$mimNTf$_2$

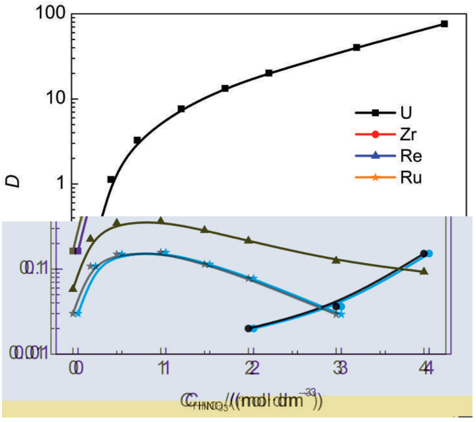

Fig.7 Distribution ratio of metal ions depending on the concentration of the adding HNO_3 in the extraction of SLW by 1.1 mol dm^{-3} of TBP in dodecane

Other metal ions in the SLW are not extracted.

The above results suggest that TBP and CMPO in ILs can selectively extract UO_2^{2+} from the SLW, and Zr^{4+}, ReO_4^-, Cs^+ are the main competing ions. Compared with TBP, CMPO may be a better candidate for the application of ILs in the separation of UO_2^{2+} in the reprocessing of spent nuclear fuel. However, this work is a very preliminary study, for the composition of the spent nuclear waste is much more complicated than that of the SLW employed in this work. To evaluate the IL-based extraction system as a promising strategy in the reprocessing of spent nuclear waste, a great deal of work will be required in the future.

UO_2^{2+} can be selectively extracted by TBP or CMPO in imidazolium based ILs from aqueous solution in the presence of other metal ions. Among the selected metal ions, Zr^{4+}, ReO_4^-, and Cs^+ are the main competing ions. CMPO performs a better selectivity to UO_2^{2+} than TBP does. Both the extraction capacity and selectivity of CMPO in ILs vary as the alkyl chain of C mimNTf$_2$ lengthens. CMPO-C$_4$mimNTf$_2$ may be a candidate for the application of ILs in the separation of UO_2^{2+} in the reprocessing of spent nuclear fuel. This work will be helpful for the practical application of IL-based extraction system in the reprocessing of spent nuclear fuel.

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