



Extraction of U(VI) by the ionic liquid hexyltributylphosphonium bis(trifluoromethylsulfonyl)imides: An experimental and theoretical study

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ABSTRACT

In the extraction of U(VI) by tri-*n*-butyl phosphate (TBP) in bis(trifluoromethylsulfonyl)imides (NTf₂⁻) based ionic liquids (ILs), an unexpected high distribution ratio was observed when P_{6,4,4,4}NTf₂ was used as the solvent, where P_{6,4,4,4}⁺ is hexyltributylphosphonium. Further research showed that P_{6,4,4,4}NTf₂ was able to extract U(VI) in the absence of extractants, and the extraction ability of P_{6,4,4,4}NTf₂ was attributed to the combination of the outer-sphere interaction between NTf₂⁻ and U(VI) and the intramolecular interaction between NTf₂⁻ and P_{6,4,4,4}⁺. The outer-sphere interaction of NTf₂⁻ with U(VI) was theoretically explored by DFT calculation. Walden plot were employed to discover the intramolecular interaction in ILs, among which P_{6,4,4,4}NTf₂ showed a much stronger intramolecular interaction than other NTf₂⁻ based ILs. Stripping of U(VI) from P_{6,4,4,4}NTf₂ was also investigated by use of supercritical carbon dioxide (Sc-CO₂). This work shed a light on the role of intramolecular interactions in ILs in the extraction of metal ions.

1. Introduction

Room temperature ionic liquids (ILs) have been considered as promising media for the application in synthesis, catalysis, energy production and separation, due to their unique properties including near-zero vapor pressure, high thermal stability, and good solvating property, etc. [1–4]. Combination of appropriate cations and anions can generate a large amount of ILs with desired properties, and in turn the properties of ILs can be tuned controllably by varying their cations and anions [5]. As alternatives to volatile organic compounds (VOCs), hydrophobic ILs have been widely used as solvents in the extraction of metal ions, among which those containing the anion of bis(trifluoromethylsulfonyl)imide (NTf₂⁻) are most frequently used. Especially, ILs have been regarded as next generation diluents in the reprocessing of spent nuclear fuel [6,7].

In the nuclear fuel cycle, the effective extraction of U(VI) from aqueous solution is of practical importance to the application of ILs in an industrialization separation process. Since Visser et al. reported the first study on the extraction of U(VI) by use of ILs as diluents in combination with the extractants tri-*n*-butyl phosphate (TBP) and octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) [8], there have been a steady increase in the number of studies on U(VI)

extraction by using ILs in the past decade. Multifarious extractants including phosphorus oxide [8–18] and amide compounds [19–25] were employed in conjunction with ILs, and some TSILs were also synthesized and presented excellent extraction ability toward U(VI) [26–33]. In these studies, researchers mainly focused on the extraction performance of different extractants in ILs as well as the extraction mechanism inside such as the coordination structure of U(VI) with extractants. For example, Yuan et al. studied the extraction of U(VI) by *N,N'*-diethyl-*N,N'*-ditolyldipicolinamide (Et₂TDPA) in 1-butyl-3-methylimidazolium based ILs (C₄mimNTf₂ and C₄mimPF₆), and found that in ILs two Et₂TDPA molecules coordinate with one U(VI) through the carbonyl and pyridine nitrogen moieties, while NTf₂⁻ and PF₆⁻ act as counterions [22]. Apart from the investigation on the coordination structure, the extraction mechanism was also widely studied, and it was found that the extraction mechanism is much more complicated in IL systems than that in VOC system. For example, in the extraction of U(VI) by TBP in ILs, cation exchange, anion exchange and the partitioning of a neutral complex were involved, depending on the concentration of nitric acid [10–13]. The study on the coordination structure of U(VI) and the exchange mechanism is of great importance for the understanding of the extraction process and will be useful for the design of new extraction system.

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The specific coordination structures and exchange mechanisms enhanced the extraction efficiency of the IL extraction systems, which originated from the fact that the ionic species (metal ions and metal-extractant complexes) are much more favored thermodynamically solvated in an ionic solvent than in a conventional organic solvent [34]. Furthermore, based on our previous research, the cations and anions of ILs may respectively act as more interesting roles in an extraction process. In an extraction with cation exchange mechanism, for example, the IL anions can interact with the cationic species extracted into the IL phase, facilitating the extraction. Our previous research indicated that NTf_2^- , which was usually regarded as weakly coordinating anions, can coordinate with cesium ions and promote the extraction [35,36]. Besides, the interactions between the cations and anions in ILs may affect the extraction performance, but to the best of our knowledge no report has been found for now. The interactions at molecular level in ILs are very complicated, ranging from the weak, nonspecific, and isotropic forces to strong, specific, and anisotropic forces [37]. An insight from molecular level into the effect of interactions in ILs on the extraction performance will be of scientific and practical importance to the application of ILs in extraction process.

In this work, we selected several NTf_2^- based ILs with different cations as solvents to study the extraction of UO_2^{2+} . The cations include C_4mim^+ , 1-butylpyridinium (C_4Py^+), *N*-butyl-*N*-methylpyrrolidinium ($\text{Py}_{1,4}^+$), *N*-butyl-*N*-methylpiperidinium ($\text{PP}_{1,4}^+$), and hexyltributylphosphonium ($\text{P}_{6,4,4,4}^+$) involving most of the common used IL cations. The structures of the cations and the anion are illustrated in Fig. 1. As the anion of the ILs employed in the present work has been set as NTf_2^- , there are two differences in properties between these ILs. One is the hydrophobicity (or hydrophilicity) of the cations that can influence their exchange ability, and the other is the intramolecular interactions between the cations and anions in ILs. We herein mainly intend to investigate the effect of the interactions between the cations and anions of ILs on the extraction performance toward U(VI).

2. Experimental section

2.1. Materials

The ILs $\text{C}_4\text{mimNTf}_2$, C_4PyNTf_2 , $\text{Py}_{1,4}\text{NTf}_2$, $\text{PP}_{1,4}\text{NTf}_2$ and $\text{P}_{6,4,4,4}\text{NTf}_2$ were purchased from Lanzhou Institute of Chemical Physics, China. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from INET, Tsinghua University. Aqueous solution of U(VI) was prepared by directly dissolving

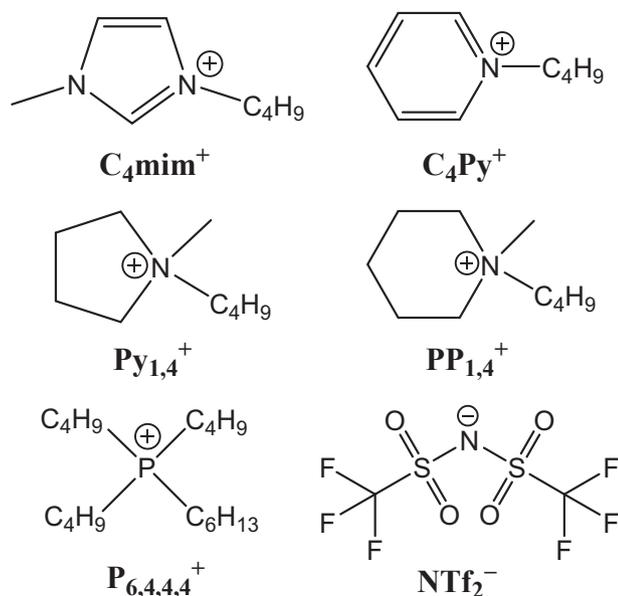


Fig. 1. Chemical structures of the IL cations and anion used in the present work.

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water containing appropriate amount of HNO_3 . Without HNO_3 added, no precipitate was observed and the pH of the aqueous solution is about 2.8. TBP (AR) and methanesulfonic acid (MSA) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Trioctylphosphine oxide (TOPO, 99%) was purchased from Aldrich. Tetrabutylammonium hydroxide (TBAOH, 40 wt% in H_2O) was purchased from J & K Scientific Ltd., China. All other chemicals were of analytical grade.

2.2. Extraction experiments

In each extraction experiment, 0.5 mL of IL solution and 0.5 mL of aqueous solution containing uranyl ions were added into a plastic centrifuge tube, followed by vibrating for 8 h. The temperature was controlled at 298.2 K. Then the mixture was centrifuged for 2 min at $10,000 \text{ r} \cdot \text{min}^{-1}$ and the two phases were separated. The concentration of uranyl ion in aqueous solution was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Leeman, USA). The distribution ratio (D) were calculated as

$$D = \frac{C_i - C_f}{C_f} \quad (1)$$

where C_i and C_f designate the initial and final concentrations of metal ions in the aqueous phase, respectively. All the extraction experiments were carried out three times, and the results agreed within an error of 5%.

2.3. Ion chromatography

The determination of the concentrations of C_4mim^+ , NTf_2^- and NO_3^- in aqueous solutions was performed on a Dionex model ICS-900 ion chromatograph (IC) with Chromeleon 7.0 software (Dionex Corporation, USA). For the analysis of C_4mim^+ by ion chromatograph, an IonPacCS12A analytical column ($250 \times 4 \text{ mm}$) and an IonPacCG12A guard column ($50 \times 4 \text{ mm}$) were used. The analytes were eluted by isocratic elution with an aqueous solution of $33 \text{ mmol} \cdot \text{dm}^{-3}$ of MSA and 10% (v/v) acetonitrile at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The suppressor CSRS 300 was installed for chemical suppression with $100 \text{ mmol} \cdot \text{dm}^{-3}$ of TBAOH. For the simultaneous analysis of NTf_2^- and NO_3^- , an IonPacAS16 analytical column ($250 \times 4 \text{ mm}$) and an IonPacAG16 guard column ($50 \times 4 \text{ mm}$) were used. The analytes were eluted by isocratic elution with an aqueous solution of $30 \text{ mmol} \cdot \text{dm}^{-3}$ of KOH and 30% (v/v) acetonitrile at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The suppressor AMMS 300 was installed for chemical suppression with $67 \text{ mmol} \cdot \text{dm}^{-3}$ of H_2SO_4 . The peak of C_4mim^+ emerged at about 12 min and the peaks of NO_3^- and NTf_2^- emerged at about 3 and 8 min, respectively, as shown in Fig. S1. The peak area of C_4mim^+ , NTf_2^- and NO_3^- in the chromatogram linearly depends on their concentrations (Fig. S1). The uncertainty in the determination of the concentration of the ions by IC is less than 5%.

2.4. Determination of Walden plot

Before the experiment of conductivity, density and viscosity, all the NTf_2^- based ILs were vacuum dried at 80°C for over 5 days and equilibrated in glove box for over one week to eliminate water (The water content for each IL at last was too low to be detected by Karl-Fisher titration method). Conductivity was determined using a Mettler Toledo FE30 conductivity meter, and the cell constant was calibrated by $0.01 \text{ mol} \cdot \text{dm}^{-3}$ of KCl aqueous solution. Density measurements were carried out using a Mettler Toledo DE45 density meter. Viscosity measurements were performed using a BrookField rotational viscometer. All the experiments for the measurements of conductivity, density and viscosity operated in a glove box (Mikrouna) were performed three times with the uncertainty within 3%.

2.5. Stripping

U(VI) extracted into $P_{6,4,4,4}NTf_2$ was stripped by using supercritical carbon dioxide (Sc-CO₂), performed with a lab-scale supercritical fluid extraction apparatus (100 mL, SEPAREX, France). The apparatus includes a liquid-CO₂ tank, a high-pressure piston pump (P200), a modifier syringe pump, a high-pressure extraction vessel, an automatic back pressure regulator, and a collection vessel [38]. In a typical stripping experiments, 0.5 mL of $P_{6,4,4,4}NTf_2$ containing 10 mmol·dm⁻³ of U(VI) in a 10 mL glass-basket was placed in the high-pressure extraction vessel. Dynamic mode was used during the stripping process, in which the Sc-CO₂ fluid containing stripping agent passed through the extraction chamber continuously. The pressure was controlled at 20 MPa and the temperature was controlled at 313 K in the high-pressure extraction vessel. The flow rate of Sc-CO₂ was fixed at 0.2 mL·min⁻¹, and 0.05 mol·dm⁻³ of TOPO dissolved in acetonitrile was used as stripping agent. The stripping efficiency (SE) was calculated on the basis of the content of U(VI) in the initial IL phase and in the residue IL phase, which was analyzed by ICP-AES after microwave digestion. The relative error in the stripping experiments was less than 5%. For more details in the stripping experiments, see [38,39].

2.6. Computation methods

All theoretical calculations were performed using the Gaussian 09 software package [40]. The structures of the complexes were fully optimized by DFT using the hybrid B3LYP exchange correlation functional [41,42] in conjunction with the Stuttgart-Dresden relativistic effective core potential (RECP) basis set for uranium and 6-31G(d,p) for other atoms. All the optimized structures were confirmed to be local minima structures on the potential energy hypersurface by vibrational frequency analysis at the same level of theory.

3. Results and discussion

3.1. Extraction performance of ILs toward U(VI)

As a successful extractant in the extraction of U(VI), TBP has shown an excellent extraction ability (including efficiency and selectivity) in combination with the traditional organic solvents kerosene. However, the extraction performance of TBP cannot meet the same case in combination with the ILs such as $C_4mimNTf_2$ [11,14]. After examining the extraction of U(VI) by TBP in the five aforementioned NTf_2^- based ILs, an unexpected high distribution ratio was observed only when $P_{6,4,4,4}NTf_2$ was used as the solvent. As shown in Fig. 2, the distribution ratio of U(VI) by TBP in $C_4mimNTf_2$, C_4PyNTf_2 , $Py_{1,4}NTf_2$ and $PP_{1,4}NTf_2$ are all very low (0.4–0.7) whilst in the system using $P_{6,4,4,4}NTf_2$ as solvent the distribution ratio of U(VI) achieves nearly 15. A further study showed that $P_{6,4,4,4}NTf_2$ itself was able to extract U(VI) with a substantial distribution ratio. Fig. 3 illustrates that the distribution ratio of U(VI) increases first and then decreases upon the addition of HNO₃ in the aqueous phase in the extraction of U(VI) by pure $P_{6,4,4,4}NTf_2$. These results suggest that $P_{6,4,4,4}NTf_2$ can act as both solvent and extractant in the extraction of U(VI). Notably, the distribution ratio of U(VI) in the extraction by pure $P_{6,4,4,4}NTf_2$ at $C(HNO_3) = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ is 22.8, whilst that in the extraction by 30% TBP in $P_{6,4,4,4}NTf_2$ at the same HNO₃ concentration is only 14.2. This result suggests that the extraction ability of $P_{6,4,4,4}NTf_2$ toward U(VI) is higher than that of TBP at $C(HNO_3) = 1.0 \text{ mol}\cdot\text{dm}^{-3}$.

To understand why $P_{6,4,4,4}NTf_2$ can extract U(VI), we first attempted to examine the variation of the concentration of cations and anions including U(VI), NO₃⁻, $P_{6,4,4,4}^+$ and NTf_2^- in IL phase or in aqueous phase involved in the extraction of U(VI) by pure $P_{6,4,4,4}NTf_2$, but unfortunately $P_{6,4,4,4}^+$ cannot be detected by ion chromatography. We subsequently dissolved $P_{6,4,4,4}NTf_2$ in $C_4mimNTf_2$ and used the mixture as the IL phase to extract U(VI), and found that the distribution ratio

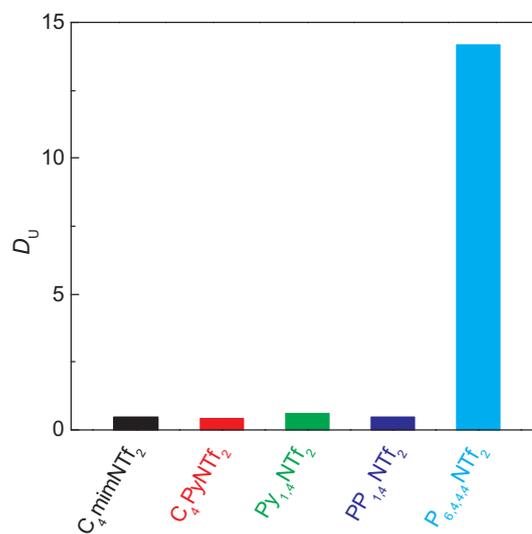


Fig. 2. Distribution ratio of U(VI) in the extraction by using 30% TBP in different ILs. The initial concentration of U(VI) and HNO₃ in the aqueous phase was 0.01 and 1 mol·dm⁻³, respectively.

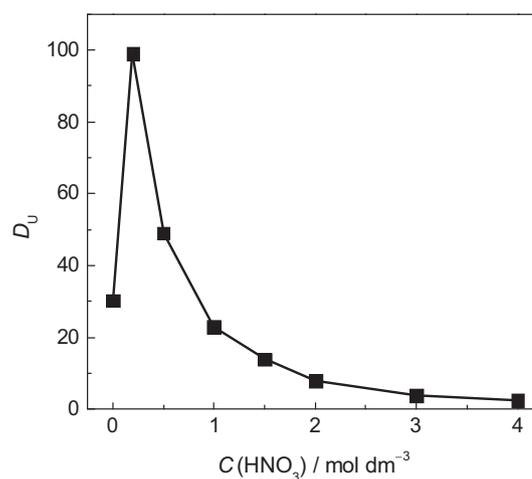


Fig. 3. Effect of HNO₃ on the extraction of U(VI) by $P_{6,4,4,4}NTf_2$. The initial concentration of U(VI) in the aqueous phase was 0.01 mol·dm⁻³.

increased gradually with the increase of the concentration of $P_{6,4,4,4}NTf_2$ in the IL phase (Fig. 4A). Without $P_{6,4,4,4}^+$ in the IL phase, no U(VI) was extracted. As shown in Fig. 4B, the concentration of C_4mim^+ in the aqueous phase increases gradually as U(VI) extracted into the IL phase. Meanwhile, the concentration of NTf_2^- in the aqueous phase decreases, to keep the solubility product of $C_4mimNTf_2$ constant in the aqueous solution according to the results in our previous study [43]. This is a typical phenomenon of cation exchange mechanism. Besides, the concentration of NO₃⁻ in IL phase obtained by the reduction of the concentration of NO₃⁻ in the aqueous phase from its initial value indicates that NO₃⁻ was partitioning into the IL phase along with U(VI) extraction. This is a typical phenomenon of neutral complex extraction mechanism (solvation mechanism). After monitoring the variation of the concentration of U(VI), NO₃⁻, C_4mim^+ and NTf_2^- , one can obtain that of the concentration of $P_{6,4,4,4}^+$ cation in the extraction based on the matter and charge conservation. It was found that the amount of the exchanged C_4mim^+ and $P_{6,4,4,4}^+$ were about 45 mol% and 15 mol% of the extracted U(VI) while the amount of NO₃⁻ in the IL phase was about 40 mol% of the extracted U(VI). According to the above results, it can be concluded that U(VI) is extracted into the IL phase in the form of UO_2^{2+} and $UO_2(NO_3)^+$. This result is also in good agreement with the nitric acid effect on the

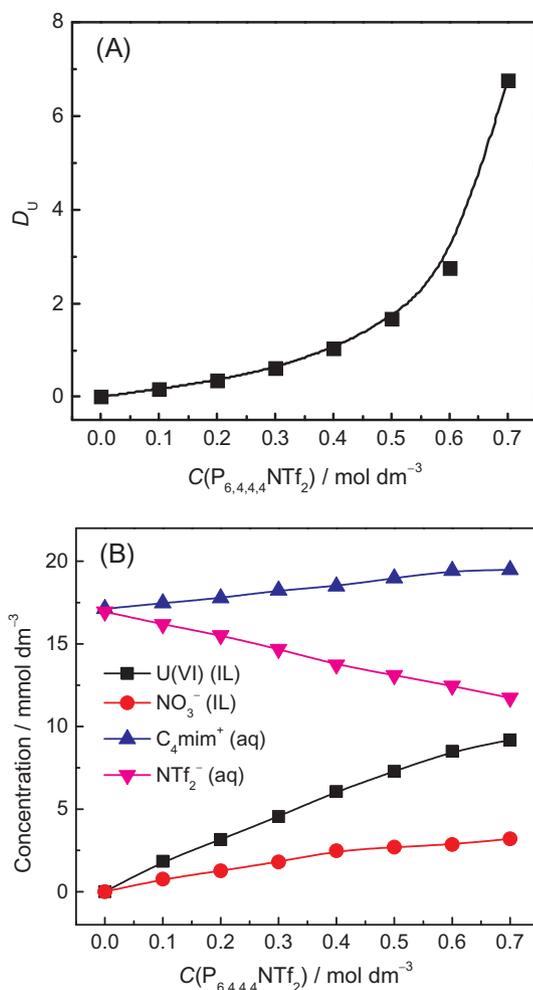


Fig. 4. (A) Distribution ratio of U(VI) and (B) variation of the concentration of U(VI) and nitrate in IL phase and that of C_4mim^+ and NTf_2^- in aqueous phase depending on the concentration of $P_{6,4,4,4}NTf_2$ in $C_4mimNTf_2$. The initial concentration of U(VI) in the aqueous phase was $0.01 \text{ mol}\cdot\text{dm}^{-3}$, and no HNO_3 was added.

extraction of U(VI) by $P_{6,4,4,4}NTf_2$ (Fig. 3). It must be noted that, in the above extraction, $C_4mimNTf_2$ was added with the purpose to examine the existence of cation exchange mode in the extraction of U(VI) by $P_{6,4,4,4}NTf_2$. Although the exchanged amount of C_4mim^+ cation is higher than that of the $P_{6,4,4,4}^+$ cation in the extraction of U(VI) by the mixture of $C_4mimNTf_2$ and $P_{6,4,4,4}NTf_2$, one should keep in mind that $C_4mimNTf_2$ itself cannot extract U(VI). Presence of $P_{6,4,4,4}NTf_2$ in the IL phase is the key factor inducing the extraction of U(VI). The higher exchanged amount of C_4mim^+ as compared with that of $P_{6,4,4,4}^+$ is because C_4mim^+ is more hydrophilic. If no $C_4mimNTf_2$ is added in the extraction system, that is, in the extraction of U(VI) by $P_{6,4,4,4}NTf_2$ itself, a rational speculation is that there should be more $P_{6,4,4,4}^+$ cation exchanged into aqueous phase. Nevertheless, one definite conclusion from the results in Fig. 4 is that both cation exchange mode and neutral complex extraction mode present in the extraction of U(VI) by $P_{6,4,4,4}NTf_2$.

3.2. Interactions of NTf_2^- with U(VI)

It is very interesting that the ILs $P_{6,4,4,4}NTf_2$ can extract U(VI). The above inspection illustrates that U(VI) is extracted into the IL phase in the form of UO_2^{2+} and $UO_2(NO_3)^+$. Note that the hydration of U(VI) should be considered in the extraction process and it is not showed in the two forms. These two cationic species should first interact with the IL anion NTf_2^- in the IL phase. In a previous study, we found that the IL

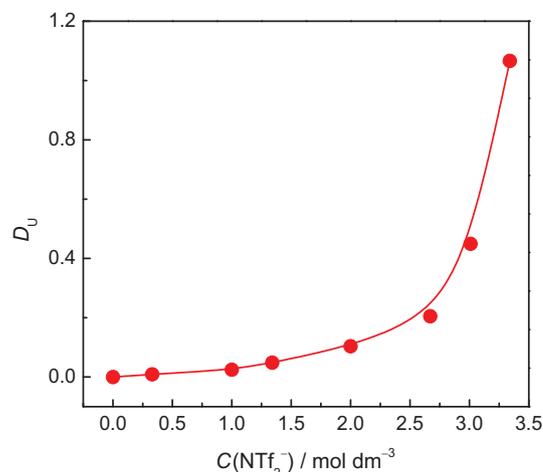


Fig. 5. Dependence of the distribution ratio of U(VI) on the concentration of NTf_2^- in the IL phase. The initial concentration of U(VI) in the aqueous phase was $0.002 \text{ mol}\cdot\text{dm}^{-3}$, and no HNO_3 was added. The IL phase was a mixture of $P_{6,4,4,4}PF_6$, $C_4mimNTf_2$ and C_4mimPF_6 . The concentration of $P_{6,4,4,4}^+$ was set as a constant ($0.1 \text{ mol}\cdot\text{dm}^{-3}$) by adding a specific amount of $P_{6,4,4,4}PF_6$, the concentration of NTf_2^- was adjusted by the addition of $C_4mimNTf_2$, and C_4mimPF_6 was employed as diluent.

$C_4mimNTf_2$ could extract Cs^+ with a substantial extraction efficiency via cation exchange, due to the coordination ability of the anion NTf_2^- to Cs^+ [35,43]. There probably exists an interaction between NTf_2^- and U(VI) responsible for the extraction of U(VI) by $P_{6,4,4,4}NTf_2$. To illustrate this speculation, we first designed an extraction experiment of U(VI) by a mixture of $P_{6,4,4,4}PF_6$, $C_4mimNTf_2$ and C_4mimPF_6 , in which the concentration of the cation $P_{6,4,4,4}^+$ was fixed at $0.1 \text{ mol}\cdot\text{dm}^{-3}$, that of NTf_2^- was varied, and C_4mimPF_6 acted as diluent. It can be seen from Fig. 5 that the distribution ratio of U(VI) increases with the adding of NTf_2^- in the IL phase. In the absence of NTf_2^- , U(VI) is not extracted. This result suggests that the anion NTf_2^- is crucial in the extraction of U(VI) by $P_{6,4,4,4}NTf_2$, that is, NTf_2^- should interact with U(VI) in the IL phase in the extraction by $P_{6,4,4,4}NTf_2$.

The interaction between NTf_2^- and U(VI) has been experimentally investigated by some authors [44,45]. In conclusion, NTf_2^- does not directly coordinate with U(VI) in the IL solutions and U(VI) is pentahydrated as dissolved $UO_2(NTf_2)_2\cdot xH_2O$ or $UO_2(ClO_4)_2\cdot xH_2O$ into NTf_2^- based ILs [46]. This was further demonstrated by Maerzke and coworkers via molecular dynamics (MD) simulations [47]. However, specific interactions between NTf_2^- and the hydrated U(VI) species are not very clear yet, and the interactions between U(VI) and NTf_2^- still needs further examination by other methods. We herein employed DFT calculations to gain insights into the interactions between NTf_2^- and U(VI).

Both experimental studies and theoretical calculations demonstrated that the average number of water molecules coordinated to U(VI) in the equatorial plane is close to 5 [46–50]. Besides, there have been a lot of crystal structures regarding the interactions of NO_3^- with U(VI), in which NO_3^- acts as a bidentate ligand directly coordinating with U(VI). Therefore, $UO_2(H_2O)_5^{2+}$ and $UO_2(H_2O)_3(NO_3)^+$ were used as the initial structure for the following calculation, and their optimized structures are shown in Fig. 6.

Based on the results in the literature [46,47], the interaction of NTf_2^- with U(VI) was considered via two modes. One is that NTf_2^- replaces two water molecules in $UO_2(H_2O)_5^{2+}$ and $UO_2(H_2O)_3(NO_3)^+$ directly coordinating with U(VI), as the so-called “inner-sphere” interaction [51]. The other is that NTf_2^- and U(VI) form as ion pairs, in which the water molecules in the primary solvation sphere of U(VI) are not replaced by NTf_2^- . This is the so-called “outer-sphere” interaction [52]. Both the structures of the inner- and outer-sphere interaction of NTf_2^- with U(VI) were optimized in the DFT calculation. It can be seen from Fig. 6 that, in the inner-sphere complexations $UO_2(H_2O)_3(NTf_2)^+$

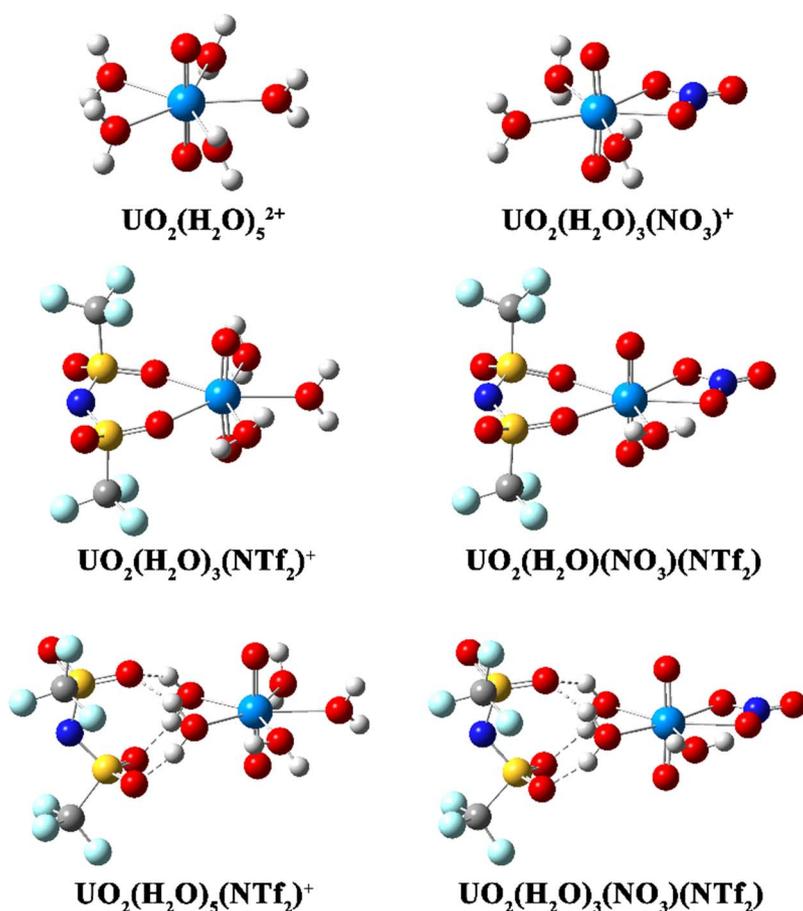


Fig. 6. Optimized structures of the inner- and outer-sphere coordination of NTf_2^- with $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$.

and $\text{UO}_2(\text{H}_2\text{O})(\text{NO}_3)(\text{NTf}_2)$, two oxygen atoms from two sulfonyl group of NTf_2^- contact to U(VI) and the two $-\text{CF}_3$ fragments of NTf_2^- are trans to each other. The U–O(NTf_2^-) distances are 2.34 Å and 2.36 Å in $\text{UO}_2(\text{H}_2\text{O})_3(\text{NTf}_2)^+$, and these values increase to 2.39 Å and 2.43 Å respectively in $\text{UO}_2(\text{H}_2\text{O})(\text{NO}_3)(\text{NTf}_2)$. In the outer-sphere complexations $\text{UO}_2(\text{H}_2\text{O})_5(\text{NTf}_2)^+$ and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)(\text{NTf}_2)$, the two $-\text{CF}_3$ fragments of NTf_2^- are cis to each other allowing three oxygen atoms of NTf_2^- interacting with the water molecules in the primary sphere of U(VI). The O–H distances and the O–H–O angles indicate the formation of hydrogen bonds. For example, in $\text{UO}_2(\text{H}_2\text{O})_5(\text{NTf}_2)^+$, the distances between the oxygen atoms of NTf_2^- and the hydrogen atoms of H_2O vary from 1.71 Å to 1.94 Å, and the angles of O–H–O vary from 139° to 161°.

The calculated energies for the formation of inner- and outer-sphere complexations of U(VI) with NTf_2^- are listed in Table 1. As compared with the formation of inner-sphere complexations, the formation of outer-sphere complexations (Reaction 2 and 4) is associated with more exothermic enthalpies and negative entropies (positive $-T\Delta S$). This is in line with the thermodynamic process that the formation of outer-sphere complexations requires no the exclusion of water molecules

Table 1

Calculated thermodynamic parameters ($\text{kJ}\cdot\text{mol}^{-1}$) for the inner- and outer-sphere complexation of NTf_2^- with U(VI) at 298.15 K.

Number	Reaction	ΔH	$-T\Delta S$	ΔG
1	$\text{UO}_2(\text{H}_2\text{O})_5^{2+} + \text{NTf}_2^- \rightarrow \text{UO}_2(\text{H}_2\text{O})_3\text{NTf}_2^+ + 2\text{H}_2\text{O}$	-585	-18	-603
2	$\text{UO}_2(\text{H}_2\text{O})_5^{2+} + \text{NTf}_2^- \rightarrow \text{UO}_2(\text{H}_2\text{O})_5(\text{NTf}_2)^+$	-697	72	-625
3	$\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+ + \text{NTf}_2^- \rightarrow \text{UO}_2(\text{H}_2\text{O})(\text{NO}_3)(\text{NTf}_2) + 2\text{H}_2\text{O}$	-286	-25	-311
4	$\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+ + \text{NTf}_2^- \rightarrow \text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)(\text{NTf}_2)$	-410	63	-347

from the primary coordinating sphere of U(VI). The Gibbs free energies are $-625 \text{ kJ}\cdot\text{mol}^{-1}$ and $-347 \text{ kJ}\cdot\text{mol}^{-1}$ for the formation of $\text{UO}_2(\text{H}_2\text{O})_5(\text{NTf}_2)^+$ and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)(\text{NTf}_2)$, respectively, which are both more negative than those for the formation of inner-sphere complexations. These results indicate that U(VI) and NTf_2^- prefer to form outer-sphere complexations, in line with the results from experiments and MD simulations in the literature [46,47].

3.3. Intramolecular interactions in ILs

The above investigation illustrates the mechanism of the partitioning of U(VI) into the IL phase and the interactions of U(VI) with NTf_2^- . However, it is still unclear why only $\text{P}_{6,4,4,4}\text{NTf}_2$ is able to extract U(VI) whilst other NTf_2^- based ILs cannot. According to the cation exchange mechanism [53,54], U(VI) should be more preferable to be extracted by the ILs with relatively more hydrophilic IL cation, e.g., $\text{C}_4\text{mimNTf}_2$, but $\text{C}_4\text{mimNTf}_2$ in fact is unable to extract U(VI). Some specific interactions in $\text{P}_{6,4,4,4}\text{NTf}_2$ should be responsible for its extraction ability. The extracted species of U(VI) in the IL phase first interact with the IL anion NTf_2^- , and a reasonable speculation is that the interactions between the anion (NTf_2^-) and the cation ($\text{P}_{6,4,4,4}^+$) in $\text{P}_{6,4,4,4}\text{NTf}_2$ should be different from the intramolecular interactions in other ILs.

ILs have been regarded as supramolecular networks in which the introduction of other molecules or ions occurs with the formation of inclusion-type compounds. This model is based on the fact that ILs display a pronounced self-organization in the solid, liquid and even in the gas phase [55]. The interactions at molecular level in ILs are very complicated, and properties of ILs are substantially affected by these interactions. The intensity of the interaction between cations and anions of ILs can be qualitatively characterized by Walden plot [56,57], which emphasizes the differences in conductivity at different

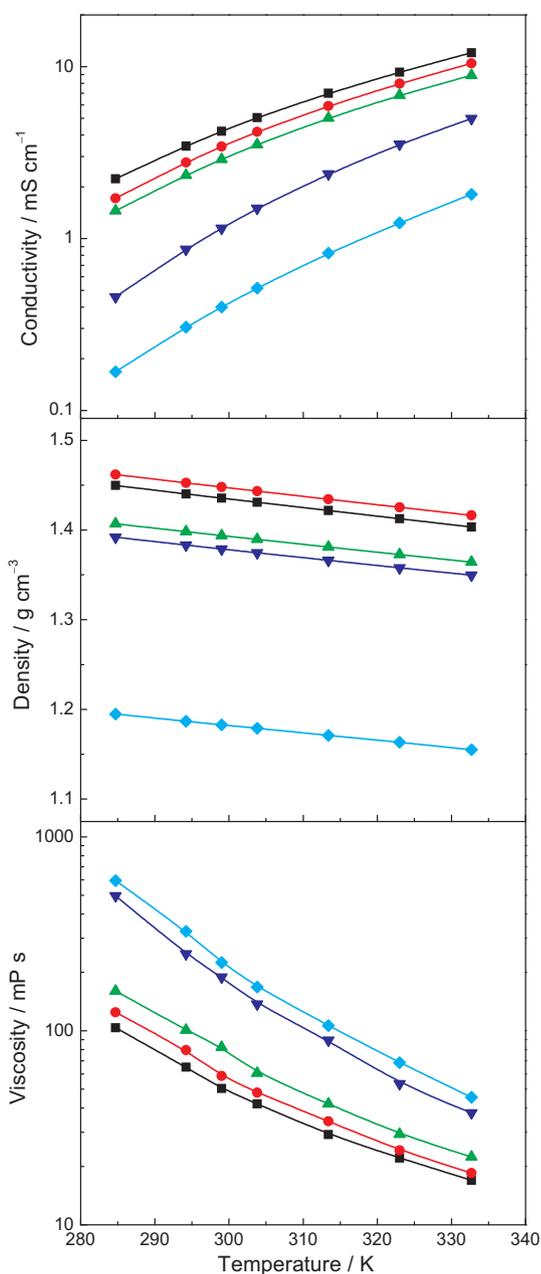


Fig. 7. Conductivity, density and viscosity of the IL $C_4mimNTf_2$ (square), C_4PyNTf_2 (circle), $Py_{1,4}NTf_2$ (uptriangle), $PP_{1,4}NTf_2$ (downtriangle) and $P_{6,4,4,4}NTf_2$ (diamond) along with the variation of temperatures.

temperatures as a function of viscosity based on the Walden rule [58]:

$$\Lambda_m \cdot \eta = k \quad (2)$$

$$\log \Lambda_m = \log \eta^{-1} + \log k \quad (3)$$

where Λ_m is the molar conductivity, η is the dynamic viscosity and k is a temperature-dependent constant. Angell and coworkers denoted the vertical deviation from the ideal line (dilute KCl solution) as ΔW for the identification of the ionicity of an IL, i.e., the intensity of the interactions between the cation and anion of an IL [56]. An IL lying far from the ideal line with a large ΔW value has a low degree of ionicity, which signifies a high intensity of the interaction between the cation and anion of the IL. Walden plot has been extensively applied to characterize the ionicity of various ILs [59–67].

To obtain a Walden plot of an IL, the conductivity, density and viscosity of the IL in a certain range of temperature should be determined (Fig. 7). Along with the increase of temperature, the

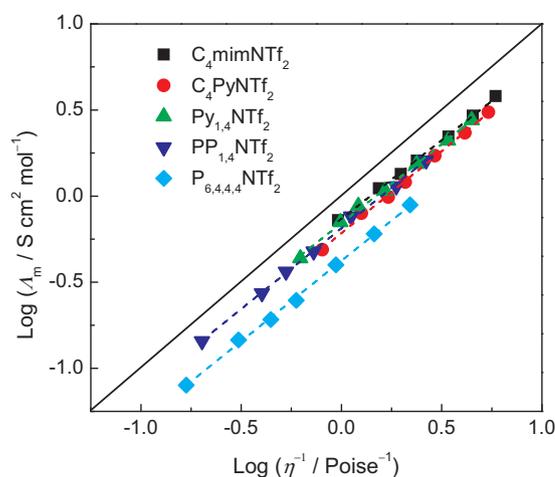


Fig. 8. Walden plot for the ILs over temperature range from 10 to 60 °C.

Table 2

Deviation of ILs from the ideal line in the Walden plot.

IL	ΔW
$C_4mimNTf_2$	0.13
C_4PyNTf_2	0.21
$Py_{1,4}NTf_2$	0.16
$PP_{1,4}NTf_2$	0.19
$P_{6,4,4,4}NTf_2$	0.38

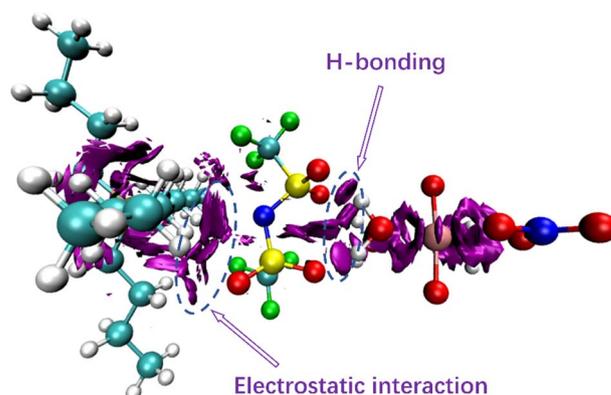


Fig. 9. Optimized structure of $[P_{6,4,4,4}^+][NTf_2^-][UO_2(H_2O)_3(NO_3)^+]$ and the reduced density gradient isosurface map with an isovalue of 0.75.

Table 3

Stripping efficiency depending on stripping time.

Number	Stripping time (min)	SE (%)
1	15	37
2	30	96
3	45	94
4	60	99

conductivity of all ILs increases while the viscosity decreases obviously, and the density slightly decreases. Among the five ILs, $P_{6,4,4,4}NTf_2$ has the lowest conductivity and density and the highest viscosity. The Walden plot is illustrated in Fig. 8, and the values of ΔW are listed in Table 2. One can see that the values of ΔW for each IL increase in the following order: $C_4mimNTf_2 < Py_{1,4}NTf_2 < PP_{1,4}NTf_2 < C_4PyNTf_2 \ll P_{6,4,4,4}NTf_2$. $P_{6,4,4,4}NTf_2$ shows a far higher ΔW value as compared with other ILs, meaning the much stronger interactions between the cation $P_{6,4,4,4}^+$ and anion NTf_2^- in $P_{6,4,4,4}NTf_2$. Part of the results are in

line with the results in the literature. Luska et al. compared the ionicity of five NTf_2^- based ILs with cations including C_4mim^+ , 1-butyl-2,3-methylimidazolium, $\text{P}_{4,4,4,1}^+$, $\text{P}_{4,4,4,8}^+$ and $\text{P}_{4,4,4,14}^+$, and also found that the ionicity of the ILs with phosphonium cations is lower than that of the ILs with imidazolium cations [62]. The Walden plot provides an explanation for the extraction ability of $\text{P}_{6,4,4,4}\text{NTf}_2$ toward U(VI), that is, the cationic species of U(VI) (U(VI) or the complex of U(VI) with NO_3^-) extracted into the IL phase first interact with the IL anion NTf_2^- via outer-sphere complexing mode, and the interaction of $\text{P}_{6,4,4,4}^+$ with NTf_2^- then stabilizes U(VI) in the IL phase.

To describe the interactions more picturesquely, the interaction between $\text{P}_{6,4,4,4}^+$, NTf_2^- and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$ in one complex was further investigated by DFT calculation. The optimized structure is presented in Fig. 9. After interacting with $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$, NTf_2^- can interact with $\text{P}_{6,4,4,4}^+$ with a P–N distance of 4.32 Å and a P–O distance of 4.22 Å. The isosurface of reduced density gradient (RDG) is a valuable tool for revealing weak interaction regions [68,69]. The isosurface map as shown in Fig. 9 clearly depicts where the interactions occur between NTf_2^- and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$ and between NTf_2^- and $\text{P}_{6,4,4,4}^+$. NTf_2^- forms hydrogen bonding via three oxygen atoms with two water molecules in $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$, insignificantly varied from the structure in Fig. 6. Simultaneously, NTf_2^- in cis conformation provides the rest oxygen atom and the nitrogen atom, which are both electronegative (see the electrostatic surface potential in Fig. S2), to interact with the electropositive areas around phosphorus atom in $\text{P}_{6,4,4,4}^+$. Besides, Fig. S2 also shows the penetration of the ESP of NTf_2^- with those of $\text{P}_{6,4,4,4}^+$ and $\text{UO}_2(\text{H}_2\text{O})_3(\text{NO}_3)^+$ in the complex, suggesting the mutual interactions. Thus the NTf_2^- anion can be regarded as a bridge connecting the phosphonium cation and the U(VI) moiety and stabilizing the structure.

3.4. Stripping of U(VI) from $\text{P}_{6,4,4,4}\text{NTf}_2$

From the view point of the application, the stripping process is as vital as the extraction process. Our group previously investigated the stripping of metal ions such as Th(IV) and U(VI) from IL phase, and found that Sc-CO_2 can strip metal species from IL phase without the loss and cross contamination of ILs during stripping process [38,39]. We also employed Sc-CO_2 in this work to examine the stripping of U(VI) from $\text{P}_{6,4,4,4}\text{NTf}_2$, and TOPO was used as stripping agent. Table 3 lists the stripping efficiency of U(VI) depending on the stripping time. At 15 min of stripping time, the stripping efficiency is only 37%. After stripping for over 30 min, the stripping efficiency of U(VI) achieved over 90%. This result suggests that U(VI) can be stripped from $\text{P}_{6,4,4,4}\text{NTf}_2$ by TOPO in Sc-CO_2 .

4. Conclusions

The IL $\text{P}_{6,4,4,4}\text{NTf}_2$ shows an excellent extraction ability toward U(VI), which is attributed to the specific interactions including the outer-sphere complexation between NTf_2^- and U(VI) and the intramolecular interaction between NTf_2^- and $\text{P}_{6,4,4,4}^+$. At molecular level, the anion NTf_2^- provides electronegative oxygen and nitrogen atoms simultaneously forming hydrogen bonds with the water molecules in the cationic U(VI) complexes and interacting electrostatically with the IL cation $\text{P}_{6,4,4,4}^+$. The later one plays a more interesting role, but none of them are dispensable. In other words, these two kinds of interactions present a synergistic effect in the extraction of U(VI). Besides, U(VI) extracted into $\text{P}_{6,4,4,4}\text{NTf}_2$ can be stripped by Sc-CO_2 containing TOPO. This work provides not only interesting phenomena in the extraction of metal ions by use of ionic liquids but also progressive revelation concerning the nanostructure and the related properties of ionic liquids.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2017.07.055>.

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