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-\textit{n}-butyl phosphate (TBP) in bis(trifluoromethylsulfonyl)imides (NT\textsubscript{f}2\textsuperscript{−}) based ionic liquids (ILs), an unexpected high distribution ratio was observed when P\textsubscript{6,4,4,4}\textsuperscript{+} was used as the solvent, where P\textsubscript{6,4,4,4}\textsuperscript{+} is hexyltributylphosphonium. Further research showed that P\textsubscript{6,4,4,4}\textsuperscript{+}NT\textsubscript{f}2\textsuperscript{−} was able to extract U(VI) in the absence of extractants, and the extraction ability of P\textsubscript{6,4,4,4}\textsuperscript{+}NT\textsubscript{f}2\textsuperscript{−} was attributed to the combination of the outer-sphere interaction between NT\textsubscript{f}2\textsuperscript{−} and U(VI) and the intramolecular interaction between NT\textsubscript{f}2\textsuperscript{−} and P\textsubscript{6,4,4,4}\textsuperscript{+}. The outer-sphere interaction of NT\textsubscript{f}2\textsuperscript{−} with U(VI) was theoretically explored by DFT calculation. Walden plot were employed to discover the intramolecular interaction in ILs, among which P\textsubscript{6,4,4,4}\textsuperscript{+}NT\textsubscript{f}2\textsuperscript{−} showed a much stronger intramolecular interaction than other NT\textsubscript{f}2\textsuperscript{−} based ILs. Stripping of U(VI) from P\textsubscript{6,4,4,4}\textsuperscript{+}NT\textsubscript{f}2\textsuperscript{−} was also investigated by use of supercritical carbon dioxide (Sc-CO\textsubscript{2}). 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 (NT\textsubscript{f}2\textsuperscript{−}) 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-\textit{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′-ditolylidipicolinamidene (Et\textsubscript{2}TTPA) in 1-butyl-3-methylimidazolium based ILs (C\textsubscript{4}mimNT\textsubscript{f}2 and C\textsubscript{4}mimPF\textsubscript{6}), and found that in ILs two Et\textsubscript{2}TTPA molecules coordinate with one U(VI) through the carbonyl and pyridine nitrogen moieties, while NT\textsubscript{f}2\textsuperscript{−} 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 extraction mechanism is of great importance for the understanding of the extraction process and will be useful for the design of new extraction system.
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 NTf2−, 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 NTf2−-based ILs with different cations as solvents to study the extraction of UO2(NO3)2·6H2O. The cations include C4mim+, 1-butylpyridinium (C4Py+), N-butyl-N-methylpyrrolidinium (Py1,4+), N-butyl-N-methylpiperidinium (PP1,4+), and hexyltributylphosphonium (P6,4,4,4+) 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 NTf2−, 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 C4mimNTf2, C4PyNTf2, Py1,4NTf2, PP1,4NTf2 and P6,4,4,4NTf2 were purchased from Lanzhou Institute of Chemical Physics, China. UO2(NO3)2·6H2O was obtained from INET, Tsinghua University. Aqueous solution of U(VI) was prepared by directly dissolving UO2(NO3)2·6H2O in water containing appropriate amount of HNO3. Without HNO3 added, no precipitate was observed and the pH for the aqueous solution is about 2.8. TBP (AR) and methanesulfonic acid (MSA) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Trietylphosphine oxide (TOPO, 99%) was purchased from Aldrich. Tetrabutylammonium hydroxide (TBAOH, 40 wt% in H2O) 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 r·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

\[
D = \frac{C_{f} - C_{i}}{C_{i}}
\]

where Ci and Cf 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 C4mim+, NTf2− and NO3− in aqueous solutions was performed on a Dionex ICS-900 ion chromatograph (IC) with Chromeleon 7.0 software (Dionex Corporation, USA). For the analysis of C4mim+ by ion chromatograph, an IonPacCS12A analytical column (250 × 4 mm) and an IonPacCG12A guard column (50 × 4 mm) were used. The analytes were eluted by isocratic elution with an aqueous solution of 33 mmol·dm−3 of MSA and 10% (v/v) acetonitrile at a flow rate of 1 mL·min−1. The suppressor CSRS 300 was installed for chemical suppression with 100 mmol·dm−3 of TBAOH. For the simultaneous analysis of NTf2− and NO3−, an IonPacAS16 analytical column (250 × 4 mm) and an IonPacAG16 guard column (50 × 4 mm) were used. The analytes were eluted by isocratic elution with an aqueous solution of 30 mmol·dm−3 of KOH and 30% (v/v) acetonitrile at a flow rate of 1 mL·min−1. The suppressor AMMS 300 was installed for chemical suppression with 67 mmol·dm−3 of H2SO4. The peak of C4mim+ emerged at about 12 min and the peaks of NO3− and NTf2− emerged at about 3 and 8 min, respectively, as shown in Fig. S1. The peak area of C4mim+, NTf2− and NO3− 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 NTf2−-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 mol·dm−3 of KCl aqueous solution. Density measurements were carried out using a Mettler Toledo DE4S 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 P6,4,4,4NTf2 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 (P2000), a modifier syringe pump, a high-pressure extraction vessel, and an automatic back pressure regulator, and a collection vessel [38]. In a typical stripping experiments, 0.5 mL of P6,4,4,4NTf2 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 C4mimNTf2 [11,14]. After examining the extraction of U(VI) by TBP in the five aforementioned NTf2− based ILs, an unexpected high distribution ratio was observed only when P6,4,4,4NTf2 was used as the solvent. As shown in Fig. 2, the distribution ratio of U(VI) by TBP in C4mimNTf2, C4PyNTf2, Py1,4NTf2 and PP1,4NTf2 are all very low (0.4–0.7) whilst in the system using P6,4,4,4NTf2 as solvent the distribution ratio of U(VI) achieves nearly 15. A further study showed that P6,4,4,4NTf2 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 P6,4,4,4NTf2. These results suggest that P6,4,4,4NTf2 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 P6,4,4,4NTf2 at C(HNO3) = 1.0 mol dm−3 is 22.8, whilst that in the extraction by 30% TBP in P6,4,4,4NTf2 at the same HNO3 concentration is only 14.2. This result suggests that the extraction ability of P6,4,4,4NTf2 toward U(VI) is higher than that of TBP at C(HNO3) = 1.0 mol dm−3.

To understand why P6,4,4,4NTf2 can extract U(VI), we first attempted to examine the variation of the concentration of cations and anions including U(VI), NO3−, P6,4,4,4− and NTf2− in IL phase or in aqueous phase involved in the extraction of U(VI) by pure P6,4,4,4NTf2, but unfortunately P6,4,4,4− cannot be detected by ion chromatography. We subsequently dissolved P6,4,4,4NTf2 in C4mimNTf2 and used the mixture as the IL phase to extract U(VI), and found that the distribution ratio increased gradually with the increase of the concentration of P6,4,4,4NTf2 in the IL phase (Fig. 4A). Without P6,4,4,4− in the IL phase, no U(VI) was extracted. As shown in Fig. 4B, the concentration of C4mim+ in the aqueous phase increases gradually as U(VI) extracted into the IL phase. Meanwhile, the concentration of NTf2− in the aqueous phase decreases, to keep the solubility product of C4mimNTf2 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−, C4mim+ and NTf2−, one can obtained that the concentration of P6,4,4,4− cation in the extraction based on the matter and charge conservation. It was found that the amount of the exchanged C4mim+ and P6,4,4,4− 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 UO2(NO3)2−. This result is also in good agreement with the nitric acid effect on the
Because C4mim+ is more hydrophilic. If no C4mimNTf2 is added in the aqueous phase was 0.01 mol·dm$^{-3}$, and no HNO$_3$ was added. The IL phase mixture of C4mimNTf2 and P6,4,4,4NTf2, one should keep in mind that C4mimNTf2 itself cannot extract U(VI). Presence of P6,4,4,4NTf2 in the IL phase is the key factor inducing the extraction of U(VI). The higher exchanged amount of C4mim$^+$ cation is more hydrophilic. If no C4mimNTf2 is added in the extraction, C4mimNTf2 was added with the purpose to examine the existence of cation exchange mode in the extraction of U(VI) by P6,4,4,4NTf2. Although the exchanged amount of C4mim$^+$ cation is higher than that of the P6,4,4,4$^+$ cation in the extraction of U(VI) by the mixture of C4mimNTf2 and P6,4,4,4NTf2, one should keep in mind that C4mimNTf2 itself cannot extract U(VI). Presence of P6,4,4,4NTf2 in the IL phase is the key factor inducing the extraction of U(VI). The higher exchanged amount of C4mim$^+$ as compared with that of P6,4,4,4$^+$ is because C4mim$^+$ is more hydrophilic. If no C4mimNTf2 is added in the extraction system, that is, in the extraction of U(VI) by P6,4,4,4NTf2 itself, a rational speculation is that there should be more P6,4,4,4$^+$ 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 P6,4,4,4NTf2.

### 3.2. Interactions of NTf$_2^-$ with U(VI)

It is very interesting that the ILs P6,4,4,4NTf2 can extract U(VI). The above inspection illustrates that U(VI) is extracted into the IL phase in the form of UO$_2$(NTf$_2$)$_2$ and UO$_2$(NO$_3$)$_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 C4mimNTf2 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 P6,4,4,4NTf2. To illustrate this speculation, we first designed an extraction experiment of U(VI) by a mixture of P6,4,4,4PF$_6$, C4mimNTf2 and C4mimPF$_6$, in which the concentration of the cation P6,4,4,4$^+$ was fixed at 0.1 mol·dm$^{-3}$, that of NTf$_2^-$ was varied, and C4mimPF$_6$ 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 P6,4,4,4NTf2, that is, NTf$_2^-$ should interact with U(VI) in the IL phase in the extraction by P6,4,4,4NTf2.

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$_2$)$_2$·xH$_2$O or UO$_2$(ClO$_4$)$_2$·xH$_2$O 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 requires 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 [46,47]. The other is that NTf$_2^-$ acts as a bidentate ligand directly coordinating with U(VI). Therefore, UO$_2$(H$_2$O)$_2$(NO$_3$)$^-$ and UO$_2$(H$_2$O)$_3$(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$_2$O)$_2$$^+$ and UO$_2$(H$_2$O)$_3$(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$_2^-$, that 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$_2$O)$_2$(NTf$_2$)$^+$...
and UO2(H2O)(NO3)(NTf2), two oxygen atoms from two sulfonyl group of NTf2− contact to U(VI) and the two −CF3 fragments of NTf2− are trans to each other. The U−O(NTf2−) distances are 2.34 Å and 2.36 Å in UO2(H2O)3(NTf2)+, and these values increase to 2.39 Å and 2.43 Å respectively in UO2(H2O)(NO3)(NTf2). In the outer-sphere complexations UO2(H2O)5(NTf2)+ and UO2(H2O)3(NO3)(NTf2), the two −CF3 fragments of NTf2− are cis to each other allowing three oxygen atoms of NTf2− 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 UO2(H2O)5(NTf2)+, the distances between the oxygen atoms of NTf2− and the hydrogen atoms of H2O 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 NTf2− are listed in Table 1. As compared with the formation of inner-sphere complexes, the formation of outer-sphere complexes (Reaction 2 and 4) is associated with more exothermic enthalpies and negative entropies (positive −TΔS). This is in line with the thermodynamic process that the formation of outer-sphere complexations requires no the exclusion of water molecules from the primary coordinating sphere of U(VI). The Gibbs free energies are −625 kJ mol−1 and −347 kJ mol−1 for the formation of UO2(H2O)3(NTf2)+ and UO2(H2O)3(NO3)(NTf2), respectively, which are both more negative than those for the formation of inner-sphere complexations. These results indicate that U(VI) and NTf2− 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 NTf2−. However, it is still unclear why only P6,4,4,4NTf2 is able to extract U(VI) whilst other NTf2− 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., C4mimNTf2, but C4mimNTf2 in fact is unable to extract U(VI). Some specific interactions in P6,4,4,4NTf2 should be responsible for its extraction ability. The extracted species of U(VI) in the IL phase first interact with the IL anion NTf2−, and a reasonable speculation is that the interactions between the anion (NTf2−) and the cation (P6,4,4,4−) in P6,4,4,4NTf2 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 temperatures.
temperatures as a function of viscosity based on the Walden rule [58]:

\[ \Lambda_m \eta = k \]  \hspace{1cm} (2)

\[ \log \Lambda_m = \log \eta^{-1} + \log \]  \hspace{1cm} (3)

where \( \Lambda_m \) is the molar conductivity, \( \eta \) 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 \( \Delta W \) 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 \( \Delta W \) 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 conductivity of all ILs increases while the viscosity decreases obviously, and the density slightly decreases. Among the five ILs, \( \text{P}_{6,4,4,4}\text{NTf}_2 \) has the lowest conductivity and density and the highest viscosity. The Walden plot is illustrated in Fig. 8, and the values of \( \Delta W \) are listed in Table 2. One can see that the values of \( \Delta W \) for each IL increase in the following order: \( \text{C}_{4}\text{mimNTf}_2 < \text{P}_{4}\text{PyNTf}_2 < \text{P}_{1,4}\text{NTf}_2 < \text{C}_{4}\text{PyNTf}_2 \ll \text{P}_{6,4,4,4}\text{NTf}_2 \). \( \text{P}_{6,4,4,4}\text{NTf}_2 \) shows a far higher \( \Delta W \) value as compared with other ILs, meaning the much stronger interactions between the cation \( \text{P}_{6,4,4,4}^{+} \) and anion \( \text{NTf}_2^{-} \) in \( \text{P}_{6,4,4,4}\text{NTf}_2 \). Part of the results are in

\[ \text{Fig. 7. Conductivity, density and viscosity of the IL } \text{C}_{4}\text{mimNTf}_2 \text{ (square), } \text{C}_{4}\text{PyNTf}_2 \text{ (circle), } \text{P}_{4,1}\text{NTf}_2 \text{ (uptriangle), } \text{PP}_{1,4}\text{NTf}_2 \text{ (downtriangle) and } \text{P}_{6,4,4,4}\text{NTf}_2 \text{ (diamond) along with the variation of temperatures.} \]

\[ \text{Fig. 8. Walden plot for the ILs over temperature range from 10 to 60 °C.} \]

\[ \text{Table 2} \]

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<tr>
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<tr>
<td>( \text{P}_{6,4,4,4}\text{NTf}_2 )</td>
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</table>

\[ \text{Fig. 9. Optimized structure of } [\text{P}_{6,4,4,4}\text{NTf}^{+}]^{1+}[[\text{UO}_2\text{H}_2\text{O}_3\text{NO}_3]^{2-}] \text{ and the reduced density gradient isosurface map with an isovalue of 0.75.} \]

\[ \text{Table 3} \]

<table>
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line with the results in the literature. Luska et al. compared the ionticy of five NTf2−-based ILs with cations containing C2mim+1, 1-butyl-2,3-methylimidazolium, P4,4,4,4−, P4,4,4,8− and P6,4,4,4+ 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 P4,4,4,4+NTf2 toward U(VI), that is, the cationic species of U(VI) (U(VI) or the complex of U(VI) with NO3−) extracted into the IL phase first interact with the IL anion NTf2− via outer-sphere complexing mode, and the interaction of P6,4,4,4+ with NTf2− then stabilizes U(VI) in the IL phase. To describe the interactions more picturesquely, to describe the interaction between P6,4,4,4+, NTf2− and UO2(H2O)3(NO3)+ in one complex was further investigated by DFT calculation. The optimized structure is presented in Fig. 9. After interacting with UO2(H2O)3(NO3)+, NTf2− can interact with P6,4,4,4+ 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 NTf2− and UO2(H2O)3(NO3)+ and between NTf2− and P6,4,4,4+. NTf2− forms hydrogen bonding via three oxygen atoms with two water molecules in UO2(H2O)3(NO3)+, insignificantly varied from the structure in Fig. 6. Simultaneously, NTf2− 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 electronegative areas around phosphorus atom in P6,4,4,4+. Besides, Fig. S2 also shows the penetration of the ESP of NTf2− with those of P6,4,4,4+ and UO2(H2O)3(NO3)+ in the complex, suggesting the mutual interactions. Thus the NTf2− 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 P6,4,4,4+NTf2

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 Sc2CO3 can strip metal species from IL phase without the loss and cross contamination of ILs during stripping process [38,39]. We also employed Sc2CO3 in this work to examine the stripping of U(VI) from P6,4,4,4+NTf2 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 P6,4,4,4+NTf2 by TOPO in Sc2CO3.

4. Conclusions

The IL P6,4,4,4+NTf2 shows an excellent extraction ability toward U(VI), which is attributed to the specific interactions including the outer-sphere complexation between NTf2− and U(VI) and the intramolecular interaction between NTf2− and P6,4,4,4+. At molecular level, the anion NTf2− 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 P6,4,4,4+. 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 P6,4,4,4+NTf2 can be stripped by Sc2CO3 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

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References
