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Extraction of uranyl ion into ionic liquid by *N*,*N*,*N*′,*N*′-tetrabutylsuccinamide and spectroscopic study of uranyl complex

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Abstract Interactions of uranyl with an amide ligand *N*,*N*,*N*′,*N*′-tetrabutylsuccinamide (TBSA) in ionic liquid [Bmim][NTf$_2$] was investigated. $[UO_2(TBSA)_3]^{2+}$ is formed from uranyl and excess TBSA, with two TBSA ligands in bidentate mode and the third in monodentate mode. The efficiency of uranyl extraction by TBSA in [Bmim][NTf$_2$] is dependent on the aqueous nitric acid concentrations. At low HNO_3 concentration as 0.01 mol·L^{-1}, the distribution ratio (*D*) is over 20 times larger than that in common organic solvents, and the extracted complex is $[UO_2(TBSA)_3]^{2+}$. The *D* value decreases drastically with increase of HNO_3 concentration.

Keywords Urany · Amide ligand · TBSA · Extraction · Ionic liquid

Introduction

Ionic liquids (ILs) have attracted significant attention and received a tremendous boost as a class of green solvent. They are actually quoted as "green designer solvents" and they have numerous fascinating properties such as low melting point, good thermal stability [1], high conductivity, and wide electrochemical window [2]. ILs are extensively used in numerous fields including organic synthesis, liquid–liquid extraction, metal ions separation, and electrochemical media [1]. The bis(trifluoromethanesulfonyl)imide anion ($[NTf_2]^-$) based hydrophobic ILs are widely used and have been popular, in particular, for extractions [3, 4] because of their chemical stability [5, 6], radiation stability [7], low viscosity [5, 6], and good solubility for uranium salts [4, 8].

Tri-*n*-butyl phosphate (TBP) is the extractant of choice in the commercial plutonium uranium reduction extraction (PUREX) process for recovering uranium and plutonium from spent nuclear fuel [9]. Moreover, numerous studies involving extraction of uranium also use TBP in combination with ILs as alternatives for volatile and flammable solvents such as kerosene [10]. The extraction involving TBP in IL [11, 12] is different than that in organic solvents [9]. IL phase is rather different from the common organic solvent because of the difference in their fundamental properties; therefore, ILs influences the extraction and structure of the formed complexes.

Amide ligands have attracted significant attention of the scientists since 1960s [13]. Compared to TBP, the amide ligands exhibit superior chemical characteristics such as easy synthesis and complete combustion without any remaining solid residue after treatment [14]. For the uranium extraction process, amide ligands have been extensively investigated as extractant instead of TBP. Shen et al. [15] investigated the extraction of the uranyl ions (UO_2^{2+}) from the aqueous phases into ILs by diglycolamide, such as *N*,*N*,*N*,*N*-tetrabutyl-3-oxapentanediamide and *N*,*N*,*N*,*N*-dimethyldibutyl-3-oxapentanediamide. The study demonstrated that compared to a negligible extraction in traditional organic solvents such as chloroform, diglycolamide in imidazolium type ILs provided an efficient extraction of UO_2^{2+} from aqueous solutions under low acidity conditions.

N,*N*,*N*′,*N*′-tetrabutyl succinamide (TBSA), one of the amide ligands, has two polar C=O bonds, which make it a

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good extraction agent for the extraction of actinides from the aqueous phases. Mowafy et al. [16] investigated the extraction of uranium (VI) and thorium (IV) from nitric acid aqueous phases using TBSA. The results of the extraction studies revealed that uranium (VI) was extracted mainly as $UO_2(NO_3)_2{\cdot}2TBSA$, and the value of distribution ratio (D) of extraction became maximum when toluene was used as diluent. Wang et al. [17, 18] synthesized solid coordination complexes of diamides for uranium (VI) and characterized them. The result of elemental analysis illustrated that the formed complex of UO_2^{2+} with TBSA was $UO_2(NO_3)_2{\cdot}TBSA$ [18]. Extraction of actinides from aqueous to traditional organic solvents using TBSA has been extensively investigated and documented; however, using TBSA in IL as extractant has rarely been studied. This study involved the investigation of the interaction of the UO_2^{2+} and TBSA ligands in Bmim-NTf_2 (IL), with main focus on the extraction and spectroscopic analysis of formed uranyl complex.

Experimental

Materials

TBSA was obtained by the reaction of di-*n*-butylamine with succinyl chloride in methylene chloride [14]:

$$(CH_2)_2(COCl)_2 + 2NH(C_4H_9)_2 \xrightarrow{CH_2Cl_2} (CH_2)_2\left[CON(C_4H_9)_2\right]_2.$$

After alkali, acid and water washing, TBSA was purified by column chromatography with petroleum ether and ethyl acetate as eluents. The final so-obtained TBSA was characterized by electrospray ionization-mass spectroscopy (Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer, Bruker Daltonics, MA, USA) *m*/*z* 341.3 ($M{+}H^+$) and elemental analysis (Vario EL, Selb, Germany): $C = 70.47\ \%$, $H = 11.86\ \%$, $N = 8.19\ \%$; calculated for $C_{20}H_{40}N_2O_2$: $C = 70.54\ \%$, $H = 11.84\ \%$, $N = 8.23\ \%$.

The IL [Bmim][NTf_2] was prepared from 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl) (99 %, Lanzhou Institute of Chemical Physics, CAS, Lanzhou, China) and Li[NTf_2] (99 %, TCI, Japan) following the literature method [5]. Subsequently, it was washed several times with deionized water until Cl^- was not detected in the aqueous phase by $AgNO_3$, when the detection limit of Cl^- was less than 10 ppm. The IL was dried under vacuum at 40 °C for more than 24 h. Amount of water in IL was detected below 100 ppm by Karl Fischer titration [19].

$UO_2(ClO_4)_2{\cdot}xH_2O$ was used as the source of weakly coordinated uranyl in spectroscopic study [20–23] because $[ClO_4]^-$ is a well-known weak coordinating anion [24]. $UO_2(ClO_4)_2{\cdot}xH_2O$ was prepared from UO_3 and perchloric acid according to the method described in the literature [24]. The resulting yellow solid of $UO_2(ClO_4)_2{\cdot}xH_2O$ was dissolved in [Bmim][NTf_2] to prepare stock solutions with $c(UO_2^{2+})$ of approximately 0.2 $mol{\cdot}L^{-1}$. The uranyl stock solution was stored in dark at room temperature [19].

Caution: Heating a mixture of perchloric acid or its salt solution with an organic material to dryness may cause explosion! [19].

$UO_2(NO3)_2{\cdot}TBSA$ was obtained by mixing equivalent $UO_2(NO_3)_2$ and TBSA (mole ratio, 1:1) in [Bmim][NTf_2] [25, 26]. $[UO_2(NO_3)_3]^-$ was obtained by mixing equivalent tetrabutyl-ammonium nitrate ($N(C_4H_9)_4NO_3$) and $UO_2(NO_3)_2$ (mole ratio, 1:1) in [Bmim][NTf_2] [24].

Spectroscopic Study

The ultraviolet–visible (UV–Vis) absorption spectra were recorded in the wavelength range of 340–530 nm with a Shimadzu UV-2450 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The spectra were recorded at room temperature using 1.00 cm quartz cells. $UO_2(ClO_4)_2{\cdot}xH_2O$ (10 $mmol{\cdot}L^{-1}$) samples with varied concentration of TBSA ranging from 20 to 40 $mmol{\cdot}L^{-1}$ in [Bmim][NTf_2] were used. The volume of the samples was 3 mL. The attenuated total reflection-fourier transform infrared (ATR-FTIR) experiments were performed on a Shimadzu IR Affinity-1 ATR-FTIR spectrophotometer (Shimadzu Corporation, Japan) attached with an ATR-crystal fluted body of PIKE 45° Ge-crystal. Samples were 200 $mmol{\cdot}L^{-1}$ TBSA with varied concentration of $UO_2(ClO_4)_2{\cdot}xH_2O$ ranging from 15 to 60 $mmol{\cdot}L^{-1}$ in [Bmim][NTf_2]. The volume of all the samples was 1 mL.

Extraction Study

In all the extraction experiments, the initial aqueous concentration of $UO_2(NO_3)_2$ was fixed as 1 $mmol{\cdot}L^{-1}$. To investigating the effect of TBSA concentration on extraction efficiency, gradient concentration of TBSA in [Bmim][NTf_2] was set as 10, 15, 20, 30, 40, 50, and 60 $mmol{\cdot}L^{-1}$. The volume of the extraction liquid TBSA/[Bmim][NTf_2] was similar to the volume of the aqueous solution of $UO_2(NO_3)_2/HNO_3$. Moreover, the influence of different concentration of aqueous HNO_3 was investigated. The concentration of TBSA was fixed as 50 $mmol{\cdot}L^{-1}$ in [Bmim][NTf_2]. The concentration of aqueous HNO_3 was changed from 0.01 to 7 $mol{\cdot}L^{-1}$ (0.01, 0.03, 0.1, 0.3, 1, 3, 7 M). In blank control experiment, extraction of HNO_3 without uranyl into 200 $mmol{\cdot}L^{-1}$ TBSA/[Bmim][NTf_2] was studied with concentrations of HNO_3 ranging from 0.01 to 1.5 $mol{\cdot}L^{-1}$ (0.015, 0.03, 0.1, 0.3, 0.5, 1, 1.5 M), and extraction of HNO_3 into neat [Bmim][NTf_2] was studied with that range. It was similar to study the effect of different concentrations of NO_3^- in aqueous solution with 30 mmol·L^{-1} TBSA and varying concentrations of NO_3^- from 0.01 to 1 mol·L^{-1} (0.01, 0.05, 0.1, 0.2, 0.5, 1 M). In all the experiments, uranyl was detected by UV–Vis spectroscopy in aqueous solution with arsenazo(III) as the colorimetric reagent at pH 2. In blank control experiment, the concentration of H^+ was detected by a pH meter (Mettler Toledo FE20, Greifensee, Switzerland).

Results and discussion

Spectroscopic analysis

UV–Vis spectroscopy

Figure 1 displays the UV–Vis spectra of 10 mM $UO_2(ClO_4)_2{\cdot}xH_2O$ with TBSA in [Bmim][NTf_2] and the ratios of ligand-to-uranyl (L/U) are 2.0(a), 2.5(b), 3.0(c), and 4.0(d). It is well known that the characteristic vibronic fine structure represents certain symmetry (and geometry) of the first coordination sphere of the uranyl complexes [24], which enables structure elucidation by UV–Vis spectra [19]. The spectra in Fig. 1 exhibits typical bond splitting in the 380–450 nm region indicating that curves with *L*/*U* values of 2.0, 2.5, and 3.0 are quite different, and all the spectra of samples with TBSA differ from the spectrum of uranyl perchlorate without ligand. The differences among spectra of *L*/*U* from 2.0 to 3.0 indicate that the uranyl complexes in these samples are different, and that uranyl is not completely coordinated by TBSA in complexes with *L*/*U* of 2.0 and 2.5. Further, the curves with *L*/*U* values of 3.0 and 4.0 are almost identical. The similarity of these two curves shown in Fig. 1 indicates that ligands are saturated around the central ion when the *L*/*U* value approaches 3, which suggests that there may be three ligands coordinated to the UO_2^{2+} ion in the complex, and the formula of this complex could be $[UO_2(TBSA)_3]^{2+}$.

ATR-FTIR spectroscopy

Figure 2 exhibits the ATR-FTIR spectra of different concentration of $UO_2(ClO_4)_2$ with 200 mM TBSA in [Bmim][NTf_2]. The absorption spectrum curve e shown in Fig. 2 is attributed to 200 mmol·L^{-1} TBSA ligand without any uranyl in [Bmim][NTf_2]. It demonstrates that the absorption peak corresponding to C=O bond, which is not involved in coordination, shows up at a wave number of 1630 cm^{-1} [25, 26]. However, the coordinated C=O bond appears at 1584 cm^{-1} [25, 26]. Simultaneously, the absorption peak of UO_2^{2+} shifts after being coordinated with TBSA. The uranyl asymmetric stretching band in $[UO_2(TBSA)_3]^{2+}$ shifts to 930 cm^{-1}, from 968 cm^{-1} (not shown in Fig. 2) in $UO_2(ClO_4)_2$ [27], indicating the existence of strong interaction in [Bmim][NTf_2]. Figure 2 clearly exhibits that increase in the concentration of added $UO_2(ClO_4)_2$ leads to the shift in the value of absorption peak corresponding to C=O bond from 1584 cm^{-1} to larger value; however, the value of absorption peak at 1630 cm^{-1} corresponding to C=O bond decreases. Based on the C=O absorption peak at 1630 cm^{-1}, quantitative analysis [28, 29] of the concentration of uncoordinated ligands in samples was performed to evaluate the amount of TBSA involved in coordinating with UO_2^{2+} ions, which further confirms the coordination in $[UO_2(TBSA)_3]^{2+}$. The slope

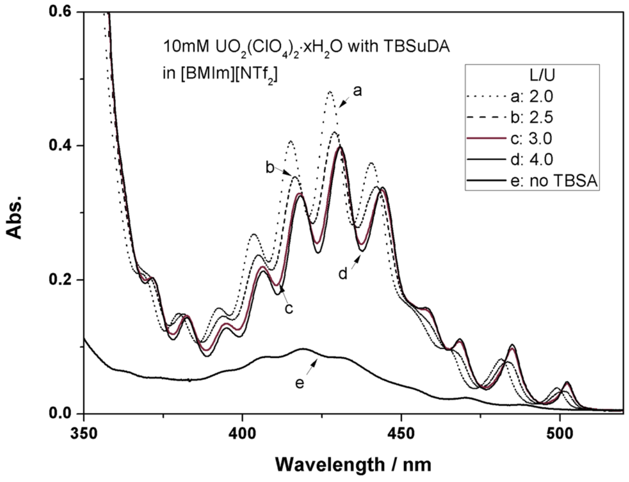

Fig. 1 UV–Vis spectra of different TBSA/UO_2^{2+} ratio in [Bmim][NTf_2]

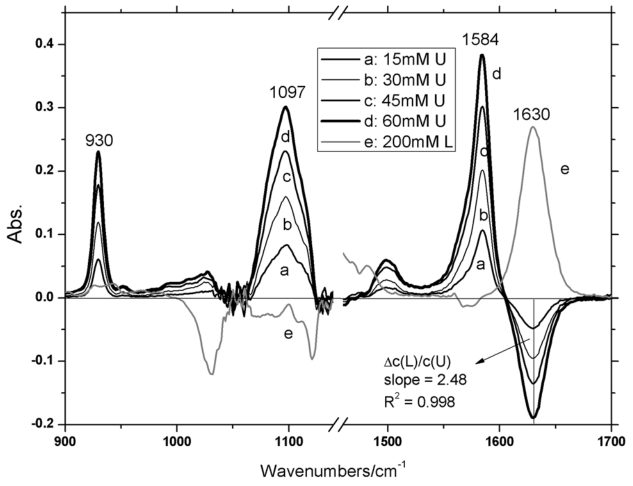

Fig. 2 IR spectra of different concentration of $UO_2(ClO_4)_2$ with fixing 200 mM TBSA in [Bmim][NTf_2] ($c(UO_2^{2+})$: 15, 30, 45, 60 mmol·L^{-1})

of fitting line in quantitative analysis is 2.48 (with $R^2 = 0.998$), which confirms that 2.5 TBSA ligands actually participated in coordination. It illustrates that 5 C=O groups are coordinated to central metal ion in $[UO_2(TBSA)_3]^{2+}$. Therefore, in $[UO_2(TBSA)_3]^{2+}$ the three TBSA ligands exhibit two different ways to coordinate to uranyl: via two bidentate ligands and one monodentate ligand.

Figure 3 shows the structure of $[UO_2(TBSA)_3]^{2+}$ complexes formed in [Bmim][NTf$_2$]. Clearly, $UO_2(NO_3)_2\cdot$TBSA [17, 18] and $UO_2(NO_3)_2\cdot$2TBSA [16] are formed in common organic solvents; however, the structure of $[UO_2(TBSA)_3]^{2+}$ complex in [Bmim][NTf$_2$] is entirely different.

Extraction

Effect of the concentration of ligands

The ability of extracting UO_2^{2+} from 0.01 M aqueous HNO_3 phase using TBSA/[Bmim][NTf$_2$] has been studied. The result exhibited positive correlation with the concentration of TBSA in low concentration of HNO_3, indicating that the value of *D* increases with the increasing concentration of ligands in [Bmim][NTf$_2$]. Compared to the extractions using TBSA in traditional organic solvents, the value of *D* in [Bmim][NTf$_2$] is significantly greater. Value of *D* becomes over 100 when the concentration of TBSA is 50 mmol·L^{-1} in IL extraction system, which indicates bare existence of UO_2^{2+} in the aqueous solution of HNO_3; however, in traditional organic extraction system, the value of *D* becomes below 5 with 200 mmol·L^{-1} TBSA [16]. Figure 4 shows that the log of *D* value exhibits linear relationship with the log of concentration of the ligands. The slope of fitting line is 2.9 and the extraction reaction is as follows:

$$UO_2^{2+} + 3\ TBSA = \left[UO_2(TBSA)_3\right]^{2+}$$

The combined analysis of the extraction reaction and slope of the fitting line illustrates that three TBSA ligands are coordinated to UO_2^{2+} ions in extraction process resulting in the formation of the complex $[UO_2(TBSA_3)]^{2+}$.

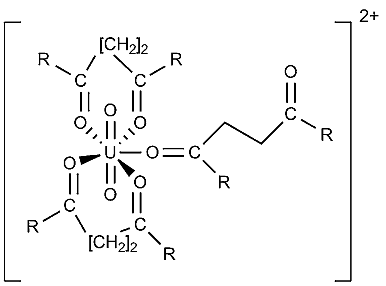

Fig. 3 $[UO_2\cdot(TBSA)_3]^{2+}$ in [Bmim][NTf$_2$] (R = $N(C_4H_9)_2$)

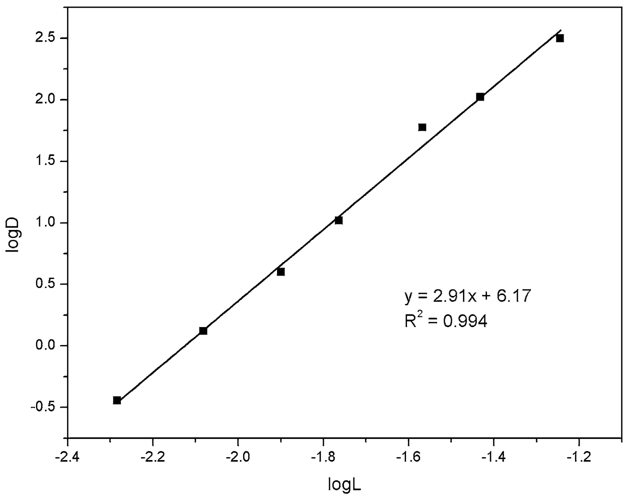

Fig. 4 The fitting line of log*D* and log*L* with different concentration of TBSA (mmol·L^{-1}) in extraction with 0.01 M HNO_3 in aqueous phase

Moreover, the extracted complexes were examined through UV–Vis spectroscopy and the results are shown in Fig. 5. Curve b is the absorption spectrum corresponding to $[UO_2(TBSA)_3]^{2+}$ that composition and structure have been confirmed by spectroscopic studies in the previous section, and curve a is UO_2^{2+} complex extracted from 0.01 M aqueous solution of HNO_3 into ILs using 100 mM TBSA/[Bmim][NTf$_2$]. Apparently, those two curves coincide well. Main peaks in the spectra are identical. It indicates that the extracted complex is $[UO_2(TBSA)_3]^{2+}$. The results again confirm that three TBSA ligands are coordinated to UO_2^{2+} ion in the extraction process. This is also different from the extracted complexes in common organic solvents,

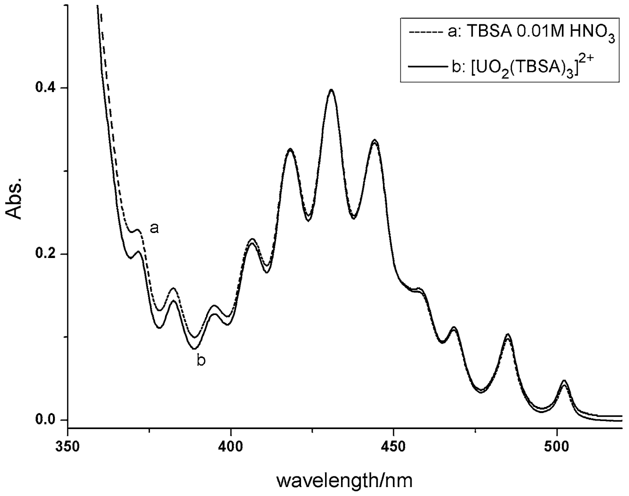

Fig. 5 UV–Vis spectrum of $[UO_2(TBSA)_3]^{2+}$ and UO_2^{2+} complexes extracted using TBSA/[Bmim][NTf$_2$] from 0.01 M $UO_2(NO_3)_2$ aqueous phase with 0.01 M HNO_3

where only one or two ligands are coordinated to the UO_2^{2+}.

Effect of concentration of HNO_3

The pH of aqueous solution is one of the most important factors influencing the extraction process. In this experiment, the influence of concentration of HNO_3 on the extraction of UO_2^{2+} was investigated. Figure 6 shows that changing concentration of HNO_3 significantly affects the extraction. Value of *D* rapidly declines with increasing concentration of HNO_3 below 1 M, and it reaches the minimum value in 1 M HNO_3 solution. With the concentration increasing continuously, the value of *D* increases gradually and slightly. However, in organic solvents, the *D* value increases at first, reaches the maximum value at about 5 M HNO_3 solution, and then it decreases slightly till the concentration of HNO_3 solution is 7 M [16]. The differences are attributed to different extraction mechanisms in organic solvents and in ILs. In organic solvents, neutral compounds extraction is the main mechanism [16, 17],

$$UO_2^{2+} + 2(NO_3)^{-} + 2TBSA \rightarrow UO_2(NO_3)_2{\cdot}2TBSA$$

$$UO_2^{2+} + 2(NO_3)^{-} + TBSA \rightarrow UO_2(NO_3)_2{\cdot}TBSA$$

However, the extraction mechanisms are complicated in [Bmim][NTf_2].

The above mentioned results demonstrate that the concentration of HNO_3 in aqueous solution could affect the extraction process, and there might be different extraction mechanisms in low and high concentration of HNO_3. The relation between the value of *D* and concentration of HNO_3 below 1 M (Fig. 6) suggests that under lower concentration of HNO_3, the mechanism involves the exchange of cations [11, 30]. Otherwise, the effect of different concentrations of NO_3^- is studied separately by adding potassium nitrate to the 0.01 M aqueous solution of HNO_3. The results in Fig. 6 did not reveal any significant influence, which indicated that NO_3^- ions did not participate in extraction in low concentration of HNO_3.

Figure 7 clearly shows the extracted acid from aqueous solution of HNO_3 into [Bmim][NTf_2] with 200 mM TBSA ligands (black cube) and without TBSA (white cube). Amount of acid extracted into the IL increases with the increase in the concentration of HNO_3. From Fig. 7, it is confirmed that TBSA in [Bmim][NTf_2] extracts acid strongly from aqueous solution whereas neat [Bmim][NTf_2] only slightly extracts acid. The acid extracted by TBSA forms protonated TBSA ligand, which is proved by the ATR-FTIR spectra in Fig. 8. With increasing amount of acid extracted, the band at ~1630 cm^{-1} of free C=O group shrinks gradually, and the band at ~1520 cm^{-1} of protonated C=O group appears. For sample extracted from 1.5 M HNO_3, ~0.4 M of acid is extracted by 0.2 M TBSA, indicating that the 2 C=O groups in TBSA are both protonated. The full protonation of TBSA ligands in this sample is confirmed by the disappearance of the ~1630 cm^{-1} band in its ATR-FTIR spectrum. It is obviously that the uranyl extraction ability of protonated TBSA ligand is much lower than which of the free ligand, thus the *D* value decreases drastically with increase of aqueous HNO_3 concentration.

At higher HNO_3 concentrations, the *D* value grows slightly with the increase of HNO_3 concentration, suggesting the change of extraction mechanism. Similar trends for extraction of uranium by amide ligands in ILs were reported by literatures [11, 30, 31]. Different from the cation-exchange mechanism for extraction at low HNO_3

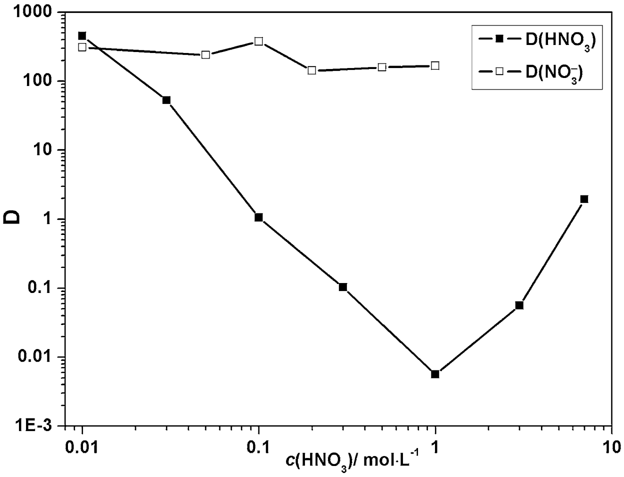

Fig. 6 The *D* values in extraction with different concentrations of HNO_3 and KNO_3 in aqueous phase ($c(HNO_3)$: 0.01, 0.03, 0.1, 0.3, 1, 3, 7 M; $c(KNO_3)$: 0.01, 0.05, 0.1, 0.3, 1 M)

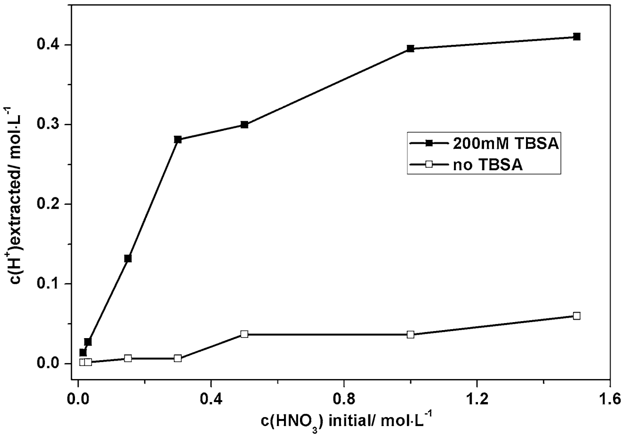

Fig. 7 The $c(H^+)$ in [Bmim][NTf_2] after extraction in HNO_3 by 200 mM TBSA/[Bmim][NTf2] (*black cube*) and without TBSA (*white cube*) ($c(HNO_3)$: 0.015, 0.03, 0.1, 0.3, 0.5, 1, 1.5 M)

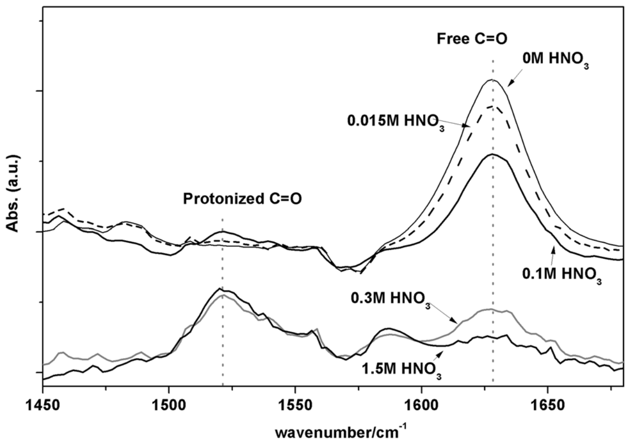

Fig. 8 IR spectra of 200 mM TBSA in [Bmim][NTf$_2$] extracted H$^+$ from different concentration of HNO$_3$ aqueous solution (c(HNO$_3$): 0, 0.015, 0.1, 0.3, 1.5 M)

concentrations, the dominating extraction mechanism at high HNO$_3$ concentrations is proposed either anion exchange [11] or neutral extraction [30, 31]. In case of extracting uranyl by TBSA from aqueous solutions with high HNO$_3$ concentration, the extracted anionic uranyl complex would be $[UO_2(NO_3)_3]^-$ and the neutral complex be $UO_2(NO_3)_2 \cdot TBSA$. UV–Vis spectra can be used to identify the extracted uranyl complex, for their distinct spectra. Figure 9 shows the UV–Vis spectra of $UO_2(NO_3)_2 \cdot TBSA$, $[UO_2(NO_3)_3]^-$, and the extracted complex from 6 M HNO$_3$. The spectra of $UO_2(NO_3)_2 \cdot$ TBSA [25, 26] and $[UO_2(NO_3)_3]^-$ [24] are same as which in literatures, but they are different from each other. The spectrum of the extracted complex (c) resembles neither that of $UO_2(NO_3)_2 \cdot TBSA$ nor $[UO_2(NO_3)_3]^-$. However, it is similar with the simulated spectrum (d) by mixing the spectra of a and b with 1:1 ratio, suggesting that the extracted complexes consists of both neutral $UO_2(NO_3)_2 \cdot$ TBSA and anionic $[UO_2(NO_3)_3]^-$. From Fig. 9, it is proposed that TBSA extracts uranyl from high concentration of HNO$_3$ with a combined mechanism of anion exchange and neutral extraction.

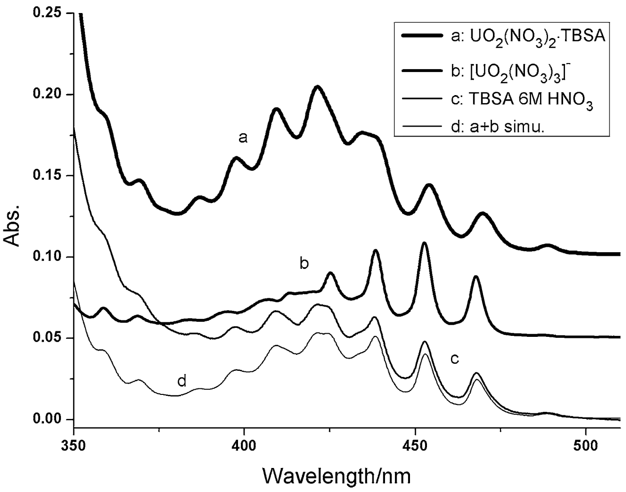

Fig. 9 UV–Vis spectra of different species of UO_2^{2+} in [Bmim][NTf$_2$] **a** $UO_2(NO_3)_2 \cdot TBSA$; **b** $[UO_2(NO_3)_3]^-$; **c** extracted species in 6 M HNO$_3$; **d** equal mixture of (**a**) and (**b**)

Conclusion

The interaction of UO_2^{2+} ions and TBSA in [Bmim][NTf$_2$] was studied through spectroscopic analysis and liquid–liquid extraction. The results reveal that the coordinated complexes are $[UO_2(TBSA)_3]^{2+}$ in [Bmim][NTf$_2$], and the three TBSA molecules are coordinated to uranyl via two different modes: two bidentate ligands and one monodentate ligand. The extraction efficiency of UO_2^{2+} ions from aqueous HNO$_3$ (0.01 M) into TBSA/[Bmim][NTf$_2$] is in positive correlation with the concentration of ligands in low concentration of nitric acid. Moreover, the extraction efficiency is significantly higher than that of the traditional organic solution as the value of D in [Bmim][NTf$_2$] could be 20 times larger in low concentration of HNO$_3$. The concentration of HNO$_3$ exhibits significant effect on the extraction process. The results indicate that extraction mechanism is dependent on the concentration of nitric acid and two distinct mechanistic approaches may be: cation-exchange mechanism in low concentration; however, combination of anion and neutral complexes-exchange mechanisms in higher concentration.

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