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PAPER

The application of novel hydrophobic ionic liquids to the extraction of uranium(VI) from nitric acid medium and a determination of the uranyl complexes formed

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Novel ammonium based hydrophobic ionic liquids (ILs) have been synthesised and characterised, and their use in the liquid–liquid extraction of uranium(VI) from an aqueous nitric acid solution using tri-*n*-butyl phosphate (TBP), studied. On varying the nitric acid concentration, each IL was found to give markedly different results. Relatively hydrophilic ILs showed high uranium(VI) extractability at 0.01 M nitric acid solution which progressively decreased from 0.01 to 2 M HNO_3 and then increased again as the nitric acid concentration was increased to 6 M. An analysis of the mechanisms involved for one such IL, pointed to cationic-exchange being the predominant route at low nitric acid concentrations whilst at high nitric acid concentrations, anionic-exchange predominated. Strongly hydrophobic ILs showed low extractability for nitric acid concentrations below 0.1 M but increasing extractability from 0.1 M to 6 M nitric acid. The predominant mechanism in this case involved the partitioning of a neutral uranyl complex. The uranyl complexes were found to be $UO_2^{2+}\cdot(TBP)_3$ for the cationic exchange mechanism, $UO_2(NO_3)_2(TBP)_2$ for the neutral mechanism and $UO_2(NO_3)_3^-\cdot(TBP)$ for the anionic exchange mechanism.

Introduction

The current commercial process (PUREX process) for recovering actinides, such as uranium and plutonium, from spent nuclear fuel consists of the dissolution of the spent fuels in an aqueous nitric acid solution and the subsequent selective extraction of U(VI) and Pu(IV) using a 30% solution of tri-*n*-butyl phosphate (TBP) in kerosene.[1] There are, however, a number of drawbacks with this process including the volatility and flammability of kerosene and the risk of the system becoming critical if the concentration of fissile products in the aqueous phase becomes too large. Ionic liquids (ILs) have the potential to act as substitutes for the replacement of kerosene because they have high stability to radiolysis,[2] can help to reduce the risk of criticality occurring,[3] and are non-volatile and non-flammable.

The majority of studies on the extraction of U(VI) using ILs have been performed using imidazolium based ILs.[4–15] For example, Giridhar *et al.* have studied the extraction of U(VI) from a nitric acid medium into 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and into 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($bmimTf_2N$) using TBP as extractant.[4,5] They found that for the $bmimPF_6$ system, the distribution ratio [*D*(U)] of U(VI) varied from 0.05 to 33.2 with an increase in the concentration of nitric acid from 0.01 M to 8 M and determined that the U(VI) complex extracted into the IL was $UO_2(NO_3)_2(TBP)_2$. For the $bmimTf_2N$ system, they observed that the *D*(U) values decreased from 15.3 to 0.7 with an increase in the nitric acid concentration from 0.01 to 0.1 M (M = mol dm^{-3}). Above 0.1 M, the *D*(U) values were found to increase with increasing nitric acid concentration as was observed with $bmimPF_6$. However, they gave no explanation for the decrease in *D*(U) at low nitric acid concentrations or any information on the complexes formed.

Wang *et al.* also studied the extraction of U(VI) from a nitric acid medium into $bmimTf_2N$ using TBP as extractant.[6] They obtained data at 0.1, 1 and 3 M nitric acid, and determined that the complex extracted into the IL was $UO_2(NO_3)_2(TBP)_2$ for all acid concentrations.

Dietz *et al.* studied the extraction of U(VI) from a nitric acid medium into various 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide using TBP as the extractant.[7] They observed that the *D*(U) values varied considerably depending on the alkyl chain length of the IL cation in the range of nitric acid concentration from 0.01 to 8 M. For the ILs with long chain cations (such as C_{10}), it was found that the *D*(U) values increased with increasing nitric acid concentration and that the U(VI) complex extracted into the IL was $UO_2(NO_3)_2(TBP)_2$. For the ILs with short chain cations (such as C_5), it was found that the *D*(U) values decreased as the nitric acid concentration increased from 0.01 M to approximately 1 M and then increased

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Table 1 Ionic liquids synthesised and characterised

R	R′	R″	Yield/Purity (Cl⁻)	ID
CH_3	CH_3	CH_2CH_2OMe	80%[a]/<10 ppm	IL1
CH_3	CH_3	$CH_2CH_2CH_3$	88%[a]/<10 ppm	IL2
CH_3	CH_3	CH_2CH_2Cl	74%/<10 ppm	IL3
CH_3	CH_3	$CH_2C_6H_5$	64%[a]/<10 ppm	IL4
CH_3	CH_3	$CH_2C_6H_4NO_2$	86%/<10 ppm	IL5
CH_3	$CH_2(CH_2)_{14}CH_3$	$CH_2C_6H_5$	89%/<10 ppm	IL6
CH_3	$(CH_2)_2O(CH_2)_2OC_6H_4$-$C(CH_3)_2CH_2C(CH_3)_3$	$CH_2C_6H_5$	84%/<30 ppm	IL7

[a] ILs reported previously in the literature.[18,19]

with nitric acid concentration up to 8 M. They determined that the complex extracted into the IL phase from a solution of low nitric acid concentration was $UO_2(TBP)_2^{2+}$ and deduced that in nitric acid solutions of high concentrations the neutral complex $UO_2(NO_3)_2(TBP)_2$ was the principal species. Furthermore, they considered that the differences in *D*(U) values observed for the different chain length cations was due to the relative hydrophobicity of the respective ILs.

We are aware of only two studies in the literature that have been performed with ammonium based ILs.[16,17] Ouadi *et al.* studied the extraction of U(VI) using ammonium based ILs bearing phosphoryl groups.[16] They obtained an impressive *D*(U) of 170 by extracting U(VI) using a 30% v/v mixture of their IL $[(BuO)_2OPNH(CH_2)_3N(CH_3)_3][Tf_2N]$ and trimethylbutylammonium bis(trifluoromethanesulfonyl)imide $[Me_3NBu][Tf_2N]$ in order to lower its viscosity. Srncik *et al.* examined the extraction of U(VI) using long chain quaternary ammonium ILs with selected aliphatic and aromatic anions[17] and found that U(VI) species were successfully extracted from nitric acid of 2 M concentration. In both studies however, no work was undertaken to determine the extraction mechanisms and the chemical form of extracted species.

In this paper, we report the results of investigations to determine the key factors for optimising the separation of U(VI) from nitric acid medium using novel hydrophobic ammonium based ILs, and a detailed examination of the extraction mechanisms and the extracted U(VI) species.

Experimental

Synthesis of ionic liquids

The ionic liquids (ILs) used in the present study (see Fig. 1 and Table 1) were synthesised *via* a standard metathesis reaction from their chloride salt, which was either commercially available or synthesised as below. As a typical example, $[(CH_3)_3NCH_2CH_2OMe][Tf_2N]$ was synthesised as follows: 2-chloroethyl methyl ether (16.1 mL, 176.7 mmol) and trimethylamine (45 wt% aqueous solution, 16.5 mL, 126.2 mmol) were dissolved in acetonitrile (10 mL) in a sealed metal container. The flask was heated with stirring at 140 °C for 5.5 h. The flask was then cooled to room temperature overnight and the volatiles were removed *in vacuo* to give methoxyethyl trimethylammonium chloride (19.3 g, 100% yield). This product (3.43 g, 0.02 mol) was then dissolved in the minimum amount of distilled water and lithium bis(trifluoromethylsulfonyl)imide (6.40 g, 0.02 mol) added. The mixture was stirred for 2 h at room temperature. The ionic liquid phase (bottom) was then separated from the aqueous phase and washed twice with copious amounts of distilled water to remove any LiCl impurity. $[(CH_3)_3NCH_2CH_2OMe][Tf_2N]$ (7.1 g, 80% yield) was obtained as a clear liquid at room temperature.

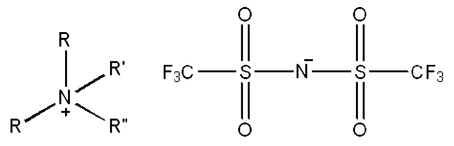

Fig. 1 Generic structure of ionic liquids synthesised.

The structures of the ILs synthesised were determined using ^1H and ^{19}F NMR (JEOL JNM-L400WB) and the purity was confirmed by ion chromatography (Toso IC-2001).

NMR data for novel ILs (IL3, IL5, IL6 and IL7). All chemical shift values in ppm:

IL3: ^1H (400 MHz, d^6-DMSO) $\delta = 3.13$ (s, 9 H, $N(CH_3)_3$), 3.70 (t, 2H, NCH_2), 4.03 (t, 2H, CH_2Cl). ^{19}F (376 MHz, d^6-DMSO) $\delta = -77.87$ ($2 \times CF_3$). IL5: ^1H (400 MHz, d^6-DMSO) $\delta = 3.03$ (s, 9 H, $N(CH_3)_3$), 4.61 (s, 2H, NCH_2), 7.86 (dd, 2H, C_6H_4), 8.12 (dd, 2H, C_6H_4). ^{19}F (376 MHz, d^6-DMSO) $\delta = -78.55$ ($2 \times CF_3$). IL6: ^1H (400 MHz, d^6-DMSO) $\delta = 0.84$ (t, 3 H, CH_3), 1.22 (app s, 26H, $(CH_2)_{13}$), 1.75 (qu, 2H, $CH_2\underline{CH_2}(CH_2)_{13}$), 2.91 (s, 6H, $N(CH_3)_2$), 3.22 (t, 2H, $\underline{CH_2}CH_2(CH_2)_{13}$), 4.46 (s, 2H, $C_6H_5CH_2$), 7.49 (app s, 5H, C_6H_5). ^{19}F (376 MHz, d^6-DMSO) $\delta = -78.64$ ($2 \times CF_3$). IL7: ^1H (400 MHz, d^6-DMSO): 0.68 (s, 9H, $(CH_3)_3$), 1.26 (s, 6H, $(CH_3)_2$), 1.65 (s, 2H, CH_2), 2.99 (s, 6H, $N(CH_3)_2$), 3.20 (app s, 2H, $OCH_2\underline{CH_2}N(CH_3)_2$), 3.51 (t, 2H, $OCH_2\underline{CH_2}O$), 3.80 (t, 2H, $O\underline{CH_2}CH_2O$), 4.10 (t, 2H, $OCH_2CH_2N(CH_3)_3$), 4.58 (s, 2H, $N(CH_3)_2\underline{CH_2}C_6H_5$), 6.81 (dd, 2H, C_6H_4), 7.22 (dd, 2H, C_6H_4), 7.45 (m, 5H, C_6H_5). ^{19}F (376 MHz, d^6-DMSO) $\delta = -78.52$ ($2 \times CF_3$).

Extraction experiments

All extraction studies were carried out with a 1 : 1 organic to aqueous phase volume ratio at 298 K for room temperature ILs and 348 K for non-room temperature ILs (IL3 and IL4).

The experiments for the extraction of U(VI) were performed as follows: initially, a 1.2 M (30 wt%) solution of TBP in IL was prepared and phase equilibrated with an aqueous solution of nitric acid (0.01 M to 8 M) by shaking the two layers together at 2500 rpm for 60 min. The TBP/IL layer was then separated. Uranium nitrate (0.02 M) in an aqueous nitric acid solution (0.01 M to 8 M) was added to the TBP/IL layer. After shaking the aqueous solution (3 mL) and the IL (3 mL) together at 2500 rpm for 60 min followed by phase separation, the top layer contained the aqueous solution and the bottom layer contained the IL. An aliquot from the aqueous phase was taken together with an aliquot from the starting uranium nitrate solution. Both were diluted 100 fold and ICP-AES (PerkinElmer Optima 3000) analysis performed. The distribution ratio (*D*) and the extractability (*E*, %) into the IL phase were calculated by the standard method.[4] An additional experiment was also carried out using the same conditions as above but with a 1 min extraction time at a concentration of 3 M nitric acid.

Analysis of chemical species in IL1

The concentrations of $[cat]^+$ (cat = cationic component of ILs) and $[Tf_2N]^-$ distributed into the aqueous phases were measured by using ^{1}H and ^{19}F NMR (JEOL JNM-L400WB) as follows. For ^{1}H NMR measurements, a solution of sodium acetate in D_2O (0.05 wt%, 500 µl) was prepared and mixed with an aliquot (100 µl) of the separated aqueous phase. The concentrations of $[cat]^+$ were evaluated from the area ratios of ^{1}H NMR signals of the cationic component of IL1 to the $-CH_3$ signal of acetate. The sample solutions for measuring concentrations of $[Tf_2N]^-$ were prepared by mixing the aqueous phase (100 µl) with a solution of trifluoroacetic acid in D_2O (0.03% v/v, 500 µl). The concentrations of $[Tf_2N]^-$ were obtained from the area ratio of ^{19}F NMR signal of $[Tf_2N]^-$ to the $-CF_3$ peak of trifluoroacetate.

Nitric acid and water determination in IL1

The amount of nitric acid present in IL1 was determined by titration. The aqueous nitric acid solution (0.01 M) before (2 mL) and after the phase equilibrium stage (2 mL) were titrated against a 0.01 M aqueous sodium hydroxide solution using bromothymol blue as indicator. The difference in volume of sodium hydroxide required to neutralise the nitric acid (indicator colour change from yellow to blue) was recorded. The procedure was repeated in triplicate and an average reading obtained.

The amount of water present in IL1 was determined by Karl Fischer titration (Metrohm 831 KF Coulometer) prior to and following the pre-equilibrium stage at 0.1 M, 3 M and 6 M nitric acid concentrations. Duplicate readings were obtained and an average result calculated.

UV-visible analysis of complexes

UV-visible spectrophotometry of the suspected cationic and anionic complexes in the IL1 phase after extraction, at 0.01 and 6 M nitric acid concentration respectively, was performed using a SHIMADZU UV-2400 PC spectrophotometer. A spectrum of the neutral complex in the dodecane phase after extraction was also obtained.

Results and discussion

Hydrophobic ammonium based ionic liquids

A range of hydrophobic ammonium based ILs of the form $[R_2NR'R''][Tf_2N]$, ($Tf_2N = (CF_3SO_2)_2N^-$) were produced (see Fig. 1 and Table 1). A number of these were designed with cations containing either an aromatic ring or a chloride ion. An aromatic ring absorbs radiation energy and subsequently relaxes non-dissociatively thereby bestowing extra stability on ILs exposed to radiation. A chloride ion is known to be an efficient neutron absorber and can therefore provide an extra measure of safety in nuclear waste extraction systems. Several long-chain cationic based ILs were also synthesised. Although determination of an ILs hydrophobicity is known to be primarily controlled by the anionic component, increasing the chain length of the cation can also help to increase the relative hydrophobicity.[20] Bis(trifluoromethylsulfonyl)imide was chosen as the anion because it is known to be very effective in producing hydrophobic ILs with low viscosity[2] (Fig. 1). All ILs were liquid at room temperature, except IL3 and IL4 (melting points: approximately 40 °C), and synthesised in good yield with high purity.

Effect of nitric acid concentration and hydrophobicity of ILs on the extraction of U(VI)

In order to examine the effect of nitric acid concentration on the extraction of U(VI) in ILs, we performed extractions using an aqueous phase containing uranyl(VI) nitrate (0.02 M) and an IL phase containing TBP (1.2 M) at various nitric acid concentrations (for IL1, 2, 6 and 7: 0.01 M to 8 M; for IL 3, 4 and 5: 0.01 M to 3 M) with a 60 min extraction time. The *D*(U) values calculated were plotted as a function of nitric acid concentration as shown in Fig. 2. Data for 1.2 M TBP/dodecane was also generated so that the results in IL systems could be compared to those obtained in the PUREX process (in line with the work of others in this field, dodecane was used as a proxy for kerosene[4,16]). For two of the ILs, IL6, and IL7, the extractability of U(VI) appeared to resemble that observed with dodecane in that the extractability increased steadily with nitric acid concentration to 6 M (*D*(U) values: IL6 = 19, IL7 = 20 and dodecane = 24) after which it began to decrease. This phenomenon contrasted with that for both IL1 and IL2 which showed high extractability of U(VI) at 0.01 M nitric acid (*D*(U) values = 216 and 40 respectively), followed by a gradual reduction as the nitric acid concentration was increased to approximately 2 M. Above this concentration, the extractability increased gradually up to 6 M nitric acid.

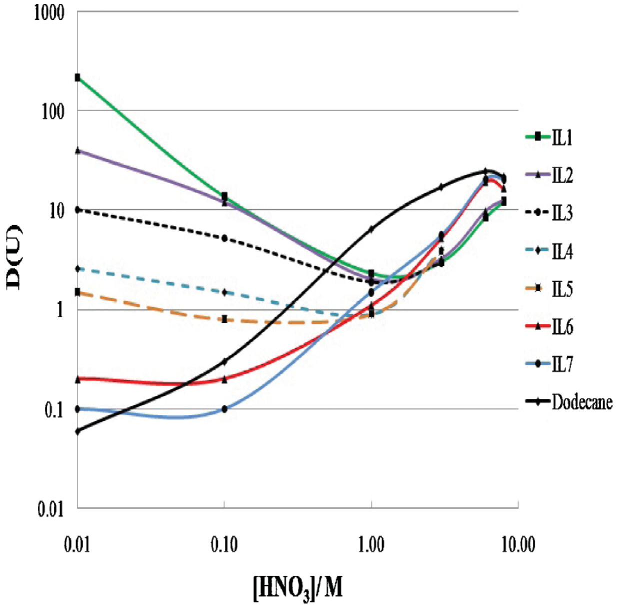

Fig. 2 Dependency of *D*(U), on $[HNO_3]$ at constant TBP (1.2 M) concentration in ionic liquids and dodecane.

Given these findings, it is suggested that the extraction of U(VI) from the aqueous phase to the IL phase in our system could proceed through either a cationic exchange, neutral partitioning or anionic exchange mechanism depending on the nitric acid concentration. In order to investigate these possible mechanisms, IL1 and IL6 were selected for a more detailed study.

The cationic exchange mechanism would be expected to be favoured at low nitric acid concentrations, given the lower concentration of NO_3^- ions present. This suggests that at 0.01 M nitric acid IL1 predominantly extracts *via* such a mechanism. This is in contrast to IL6 which shows very little or no extraction ability at low nitric acid concentrations, suggesting that it is unable to participate in this type of exchange. This may be explained by the greater hydrophobicity of IL6 compared to IL1. The latter consisting of much shorter chain cations.

As the nitric acid concentration increases, the neutral mechanism or the anionic mechanism would be expected to predominate.

For the dodecane system, U(VI) extraction has been extensively studied and is known to occur through the neutral mechanism:[21,22]

$$UO_2{}^{2+}{}_{(aq)} + 2NO_3{}^{-}{}_{(aq)} + 2TBP_{(org)} \rightleftharpoons UO_2(NO_3)_2(TBP)_{2(org)}$$

The small decrease in *D*(U) values observed above 6 M nitric acid concentration can be explained by competing extractions of nitric acid and uranyl species by TBP.[7] As IL6 shows a similar trend to dodecane with varying nitric acid concentration, it is reasonable to assume that it may follow a similar mechanism. To examine this further, a ^{19}F NMR spectrum (in D_2O) was obtained of the aqueous phase after extraction at 6 M [HNO_3] in order to determine if any IL anion (Tf_2N^-) was present, as would be expected for the anionic exchange mechanism. No Tf_2N^- was detected and therefore it is probable that IL6 is extracting U(VI) through the neutral mechanism. For IL1, a measurement of the ^{19}F NMR spectrum was also performed and on this occasion, Tf_2N^- was detected. However, although this could arise as a result of an anionic exchange mechanism, it could also be explained by small amounts of IL dissolving in the water layer during extraction as has been observed for imidazolium based ILs.[23,24] Therefore, further studies on both the possible cationic and anionic mechanisms for IL1 were undertaken, the results from which are presented in the following sections of this paper.

As an additional experiment to confirm that the uranium distribution equilibrium between the IL/dodecane phase and the aqueous phase had been reached by the 60 min extraction time, experiments were performed at shorter extraction times. These results showed that a very short extraction time of 1 min produced *D*(U) values equivalent to that for 60 min, and therefore equilibrium had been fully reached in the experiments for both the ILs and dodecane.

Distribution behaviour of cations and anions between IL1 and aqueous phase

In order to determine whether the proposed cationic exchange mechanism was reasonable, we carried out extraction experiments at 0.01 M nitric acid concentration by mixing the aqueous solutions of uranium nitrate ((1.50 to 3.00) × 10^{-2} M) with IL1, and then measuring the mole numbers of uranium transferred from the aqueous to the IL phase, and those of $[cat]^+$ transferred from IL1 to the aqueous phase. These were plotted against each other as shown in Fig. 3 (upper). A straight line with a slope of 1 was obtained. These results indicate that a cationic exchange mechanism is occurring with one cation from the IL involved.

Additionally, it has been reported that with some metal extraction processes with imidazolium ILs, movement of H^+ between the aqueous and IL layers may also play a part in the cationic exchange process.[25] This is considered to be due to large amounts of nitric acid dissolving in the IL during the phase equilibrium stage. Therefore, we examined by titration whether this was happening in our system. As a result, we found that approximately 7.9 × 10^{-3} M of nitric acid, which equates to 79% of the total amount present, had transferred to the IL phase. This indicates that there are likely to be sufficient H^+ ions available in the IL phase to play a significant role in our system too.

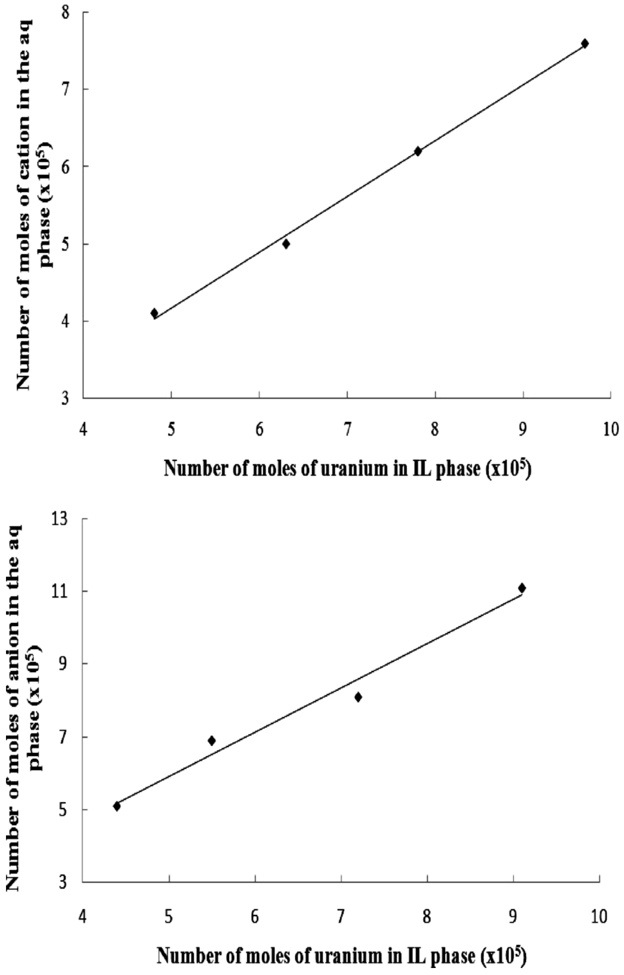

Fig. 3 (upper) A plot of $[cat]^+$ *vs.* U(VI) for the extraction of U(VI) species from the aqueous phase to the ionic liquid (IL1) phase at 0.01 M nitric acid concentration. (lower) A plot of $[Tf_2N]^-$ *vs.* U(VI) for the extraction of U(VI) species from the aqueous phase to the ionic liquid phase (IL1) at 6 M nitric acid concentration.

In order to confirm whether the proposed anionic exchange mechanism was reasonable, we carried out extraction experiments at 6 M nitric acid concentration by mixing the aqueous solutions of uranium nitrate ((1.50 to 3.00) × 10^{-2} M) with IL1. The mole numbers of uranium transferred from the aqueous to the IL phase and those of $[Tf_2N]^-$ transferred from IL1 to the aqueous phase were measured and plotted against each other as shown in Fig. 3 (lower). As with the cationic exchange mechanism, a straight line with a slope of 1 was obtained. These results indicate that an anionic exchange mechanism is occurring with one anion from the IL involved. For both the mechanism studies shown in Fig. 3, it is possible to deduce that even when no moles of uranium are present in the IL phase, some IL is present in the aqueous phase. This indicates that IL1 is slightly soluble in the aqueous phase. To quantify this, the extraction was repeated with no U(VI) present and the amount of IL present in the aqueous phase determined by NMR as above. From these measurements, it was found that approximately 0.3% of IL was dissolved in the aqueous phase.

The transfer of water from the aqueous phase to the IL phase (containing TBP) during the pre-equilibrium stage at various nitric acid concentrations (0.1 M, 3 M and 6 M) was also examined by Karl Fischer titration. Large amounts of water dissolving in the IL phase are known to modify the density and viscosity of the IL phase so these findings might be of industrial interest.[25] Additionally, experimental data on the transfer of water are very scarce at present and only available for a few imidazolium based IL extraction systems. The results showed that around 3 to 5% of the available water was transferred according to the proportion of nitric acid present (0.1 M [HNO_3]: 25 992 ppm, 3 M [HNO_3]: 36 857 ppm and 6 M [HNO_3]: 45 208 ppm).

Stoichiometry determination for complexes in IL1

The TBP stoichiometry of the resulting complexes was determined. A log–log plot of the *D*(U) values *versus* [TBP] provides an indication of the stoichiometry of the predominant species present in the IL phase in the form of the slope of the resulting linear relationship.[25]

A slope of approximately 3 was obtained at a nitric acid concentration of 0.01 M (Fig. 4) indicating the presence of 3 TBP groups involved in the cationic exchange mechanism for IL1. A slope of close to 1 was obtained at nitric acid concentration of 6 M (Fig. 4) indicating the presence of 1 TBP group involved in the anion exchange mechanism for IL1.

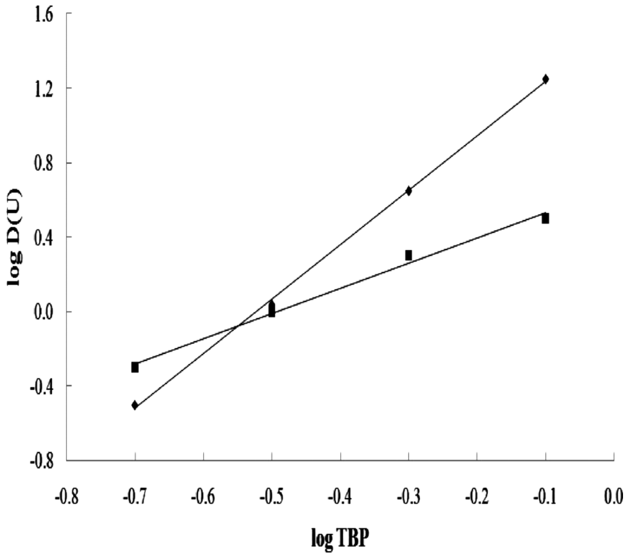

Fig. 4 Log–log plot of *D*(U) as a function of [TBP] for IL1 (◆ = 0.01 M, ■ = 6 M [HNO_3]).

Based on the distribution behaviour and stoichiometry determination studies, it is possible to suggest that the following complexes are extracted through the cationic exchange and anionic exchange mechanisms.

Cationic exchange:

$$UO_2{}^{2+}{}_{(aq)} + 3TBP_{(IL)} + ILcat^{+}{}_{(IL)} + H^{+}{}_{(IL)} \rightleftharpoons UO_2{}^{2+}\cdot(TBP)_{3(IL)} + ILcat^{+}{}_{(aq)} + H^{+}{}_{(aq)}$$

Anionic exchange:

$$UO_2{}^{2+}{}_{(aq)} + 3NO_3{}^{-}{}_{(aq)} + TBP_{(IL)} + Tf_2N^{-}{}_{(IL)} \rightleftharpoons UO_2(NO_3)_3{}^{-}\cdot(TBP)_{(IL)} + Tf_2N^{-}{}_{(aq)}$$

To further analyse the complexes present in IL1 at 0.01 M and 6 M nitric acid concentration, UV-visible spectrophotometry was performed (Fig. 5). A spectrum of the known neutral complex in dodecane ($UO_2(NO_3)_2(TBP)_2$) was also obtained, which was found to be the same as that reported elsewhere[26] (Fig. 5). As can be seen, the spectrum of the complex present at 0.01 M nitric acid concentration was well resolved but differed significantly from that of the neutral complex. This finding is consistent with it being the cationic complex as previously determined. The spectrum of IL1 at 6 M nitric acid concentration was not however well resolved suggesting that the IL solution in this case consists of a mixture of complexes. We have already demonstrated in Fig. 3 lower that the anionic complex is likely to be present at this acidity and, after taking account of the 0.3% of IL which dissolved in the aqueous phase, it is possible to estimate from this graph that the majority of the uranium present is probably being extracted through such a mechanism. On comparing the spectrum to that of the assigned neutral and cationic species, it is also feasible that either, or both, of these might also be present in the IL solution. However, others who have carried out similar studies to ours with imidazolium based ILs have reported that the U(VI) extraction mechanism changes from cationic exchange at low acidities to either extraction of the neutral species or to anionic exchange at high acidities.[7,25] It is therefore likely that the IL1 solution at 6 M nitric acid concentration consists of a mixture of the anionic and neutral complexes with the former being in the majority.

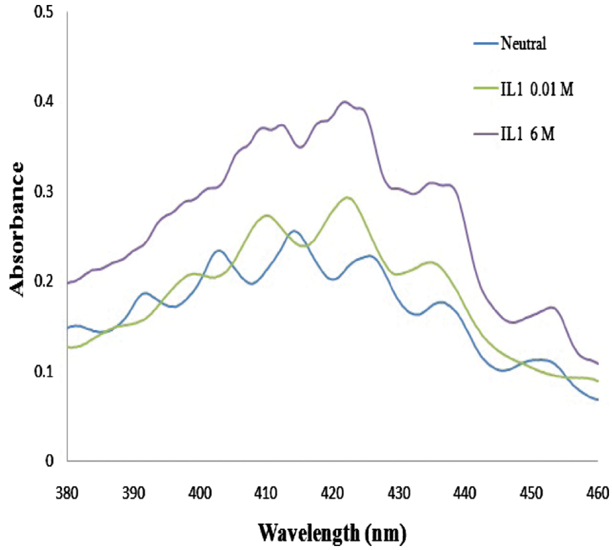

Fig. 5 UV-visible spectra of the complexes present in IL1 at 0.01 M and 6 M [HNO_3] and the neutral complex.

Conclusions

A variety of novel ammonium based hydrophobic ILs have been synthesised and examined as solvents for uranium extraction from nitric acid solutions. Distribution ratios, comparable to, or better than dodecane were obtained in a number of cases. The mechanism of extraction and the subsequent complexes formed have been shown to depend on the IL concerned. For a relatively hydrophilic IL, both cationic and anionic exchange mechanisms occur depending on the concentration of the nitric acid, whilst for a strongly hydrophobic IL the mechanism, which is independent of the nitric acid concentration, involves the partitioning of a neutral complex. Strongly hydrophobic ILs of the type reported here therefore could have considerable potential for use as replacements for dodecane as they do not suffer from the drawback of the loss of IL to the aqueous layer which has been observed with other ILs.

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