

Extraction of uranium(VI) from nitric acid medium by 1.1M tri-n-butylphosphate in ionic liquid diluent

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A systematic study on the extraction of U(VI) from nitric acid medium by tri-n-butylphosphate (TBP) dissolved in a non-traditional diluent namely 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) ionic liquid (IL) is reported. The results are compared with those obtained using TBP/n-dodecane (DD). The distribution ratio for the extraction of U(VI) from nitric acid by 1.1M TBP/bmimPF₆ increases with increasing nitric acid concentration. The U(VI) distribution ratios are comparable in the nitric acid concentration range of 0.01M to 4M, to the ratios measured using 1.1M TBP/DD. In contrast to the extraction behavior of TBP/DD, the *D* values continued to increase with the increase in the concentration of nitric acid above 4.0M. The stoichiometry of uranyl solvate extracted by 1.1M TBP/IL is similar to that of TBP/DD system, wherein two molecules of TBP are associated with one molecule of uranyl nitrate in the organic phase. Ionic liquid alone also extracts uranium from nitric acid, albeit to a small extent. The exothermic enthalpy accompanying the extraction of U(VI) in TBP/bmimPF₆ decreases with increasing nitric acid and with TBP concentrations.

Introduction

In the past few years, room temperature ionic liquids (RTILs) have emerged as a frontier and novel area of research because of their potential widespread applications in organic synthesis,^{1–4} catalysis^{4–6} and electrochemical techniques.^{7–11} Ionic liquids are regarded as a possible replacement for volatile organic compounds (VOCs) used as solvents in organic industries due to their attractive properties,^{1–3} such as thermal stability, solubility for organic and inorganic materials and insignificant vapor pressure. Chemists have been studying the recovery of organic compounds as well as the separation of precious, chemically toxic or radiotoxic metal ions from aqueous media using ionic liquids. Thus, FADEEV et al.¹² have used RTIL for the separation of butyl alcohol from the fermentation broth. HUDDLESTON et al.¹³ have reported the distribution ratio of various substituted benzene derivatives between water and RTIL, and recommended the replacement of conventional solvents (i.e., VOCs) by butyl-methylimidazolium hexafluorophosphate ionic liquids. VISSER et al.¹⁴ have studied the distribution of various metal ions in hydrophobic RTILs. In all these cases, ionic liquids as such have been employed for separating the target or undesirable contaminants from aqueous media. However, DAI et al.¹⁵ and subsequently VISSER et al.¹⁶ used a metal ion selective crown ether dissolved in ionic liquid as an extractant for improving the selectivity of extraction of group I and II metal ions. CHUN et al.¹⁷ have studied the influence of structural variation in RTILs on the selectivity and efficiency of competitive alkali metal salt extraction by crown ether. They reported that the selectivity of extraction of alkali metal ions by dicyclohexano-18-crown-6 (DC18C6) in

1-alkyl-3-methylimidazolium hexafluorophosphate decreased in the order K⁺>Rb⁺>Cs⁺>Na⁺>Li⁺, similar to the trend exhibited by DC18C6 in conventional VOCs such as chloroform or nitrobenzene at high acidities. It was observed that the solution of DC18C6 in RTILs provided efficient extraction of alkali metal chlorides from aqueous solution under the conditions that gave negligible extraction with customary VOCs used as diluents. Recently, VISSER et al.¹⁸ have also introduced task-specific ionic liquids (TSILs) with metal ion specific extracting functional groups in the cationic part of the ionic liquid leading to enhanced extraction of heavy metal ions. In addition, VISSER et al.¹⁹ have also studied the extraction of f-block elements using a mixture of 0.1M octyl(phenyl)-N,N-diisobutyl-carbamoylmethyl phosphine oxide (CMPO) and 1.0M TBP in ionic liquids and reported higher distribution ratios of actinides when ionic liquids were used.

SEDDON and co-workers^{20,21} have filed a series of patents concerned with the use of ionic liquids in the field of nuclear fuel reprocessing and molten salt waste treatment. Furthermore, they have prepared a novel dimeric dioxouranium(VI) salt containing oxalate and nitrate ligands coordinated to U(VI) in ionic liquid.²² Similarly, ROGERS and co-workers have also published numerous papers^{14,16,18,19} on the separation of metal ions of nuclear interest by various solvents such as crown ethers, TRUEX solvent (mixture of TBP and CMPO), etc., present in ionic liquids and reported the superiority of ILs over customary diluents.

However, there is no report in the literature on the extraction behavior of U(VI) by the PUREX solvent, tri-n-butylphosphate, dissolved in ionic liquid. Such data are very much desirable in order to assess the performance of TBP in ionic liquid vis-à-vis TBP

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dissolved in the conventional diluent n-dodecane. Our work attempts to fill this gap. 1.1M TBP dissolved in n-dodecane is being used as extractant in PUREX process for reprocessing of nuclear fuels all over the world.²³ This concentration has been established to be the optimum concentration for the extraction of U(VI) and Pu(IV) from the spent fuel solution. Therefore, studying and comparing the results obtained using 1.1M TBP dissolved in a suitable diluent is of importance from the process point of view. Thus, the extraction behavior of U(VI) by TBP dissolved in the ionic liquid, namely 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), is compared with the results obtained with the conventional TBP/dodecane system. The effect of various parameters such as the concentrations of nitric acid, sodium nitrate and TBP, as well as temperature, on the distribution ratio of U(VI) is reported.

Experimental

Materials

All the chemicals and reagents used were of analytical grade, 1-methylimidazole, 1-chlorobutane and hexafluorophosphoric acid were procured from Lancaster, UK, 1-methylimidazole was distilled before use and other chemicals were used without any purification. Tri-n-butylphosphate and uranyl nitrate were obtained from E. Merck, Mumbai.

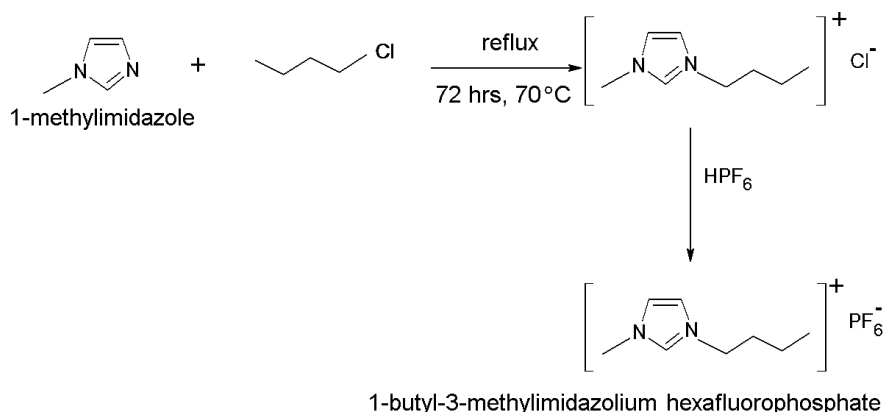
Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆)

The procedure adopted for preparing the ionic liquid has been described in Reference 13. Briefly, it involves refluxing a mixture of 1-methylimidazole with 1-chlorobutane in the mole ratio of 1:1.2. The resulting

product is washed few times with ethylacetate followed by acetonitrile and evaporated under vacuum. Nearly quantitative yield was obtained. The hexafluorophosphate ionic liquid was then prepared by adding pre-cooled hexafluorophosphoric acid (1.3 mol) to a solution of 1-butyl-3-methylimidazolium chloride (1 mol) in water kept at -5 °C. The mixture was stirred for 2 days and the bottom layer of ionic liquid was separated and washed several times with water until the aqueous solution was no longer acidic. The ionic liquid was evaporated to remove moisture at 70 °C using a rotary evaporator. The overall yield was 72%. Elemental analysis of bmimPF₆ yielded (% , calculated value in brackets) C 33.81% (33.80%), H 5.31% (5.32%), N 9.85% (9.86%). IR bands: 3175, 3122 cm⁻¹ (C-H stretch) imidazole ring, 2964, 2932, 2868 cm⁻¹ (C-H stretch) aliphatic, 1564, 1465, 1168 cm⁻¹ (C-C stretch) imidazole ring symmetric stretch, 1425, 1378 (methyl, C-H asymmetric stretch), 834 cm⁻¹ (P-F stretch) (Scheme 1).

Extraction studies

The extraction studies were carried out at 298 K in 1:1 organic to aqueous phase ratio, unless mentioned otherwise. 1.1M tri-n-butylphosphate (TBP) in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) and 1.1M TBP in n-dodecane (DD) were prepared. Extraction of U(VI) was studied as a function of nitric acid by equilibrating 2 ml of organic phase with 2 ml of nitric acid solution containing ²³³U tracer. The concentration of nitric acid in the test solution was varied from 0.01M to 8M. After three hours of equilibration, the radioactivity of ²³³U distributed between organic and aqueous phases was measured by liquid scintillation counting.



Scheme 1. Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate¹³

The distribution ratio (D) or the amount of U(VI) extracted into the organic phase was calculated by:

$$D = \frac{[^{233}\text{U}]_{\text{org}}}{[^{233}\text{U}]_{\text{aq}}}$$

$$\text{or } \% \text{Extn} = \frac{[^{233}\text{U}]_{\text{org}}}{[^{233}\text{U}]_{\text{org}} + [^{233}\text{U}]_{\text{aq}}} \times 100 \quad (1)$$

Similar experiments were also performed when 1.1M TBP/DD and also with ionic liquid alone.

The effect of nitrate ion concentration on the U(VI) distribution ratio was studied by equilibrating 2 ml of organic phase containing 1.1M TBP/bmimPF₆ with 2 ml of aqueous phase containing 0.1M nitric acid, varying the concentration of sodium nitrate, and uranium added in the form of ²³³U tracer. The concentration of sodium nitrate was varied from 0.9M to 3.9M, while the total nitrate concentration was varied from 1.0M to 4.0M. The initial and final concentrations of uranium in the aqueous phase were determined as described above and the distribution ratios were calculated.

The extraction of U(VI) as a function of TBP concentration in the ionic liquid phase was studied by equilibrating 2 ml of 0.2M TBP/bmimPF₆ with 2 ml of 2M nitric acid solution spiked with ²³³U for three hours. The concentration of uranium in the organic and aqueous phases after equilibration was determined by measuring the radioactivity of ²³³U in the respective phases as described above. Some experiments were performed when the concentration of TBP present in IL was varied from 0.4M to 1.1M TBP/IL. The entire experiment was repeated with 3M and 4M nitric acid.

The extraction isotherm of nitric acid was obtained by equilibrating equal volumes of 1.1M TBP/bmimPF₆ or 1.1M TBP/DD or bmimPF₆ with nitric acid. The concentration of nitric acid was varied from 0.01M to 8M. The amount of nitric acid present in organic and aqueous phases was determined by titrating a known volume of the phase with sodium hydroxide.

The enthalpy change accompanying the extraction of U(VI) with 1.1M TBP/bmimPF₆ was determined by equilibration experiments performed at various temperatures (298 K to 338 K). The experiments involved the mixing of 2 ml of organic phase and 2 ml of nitric acid solution spiked with ²³³U in a stoppered test tube and equilibrating at constant temperature for three hours. The nitric acid concentration was varied from 2.0M to 4.0M. The radioactivity of ²³³U distributed between organic and aqueous phases was

measured as described above. Similar experiments were performed for 0.2M and 0.8M TBP/bmimPF₆ concentrations.

Results and discussion

Figure 1 shows the distribution ratios of U(VI) in 1.1M TBP/bmimPF₆ phase as a function of nitric acid concentration. The data are compared with 1.1M TBP/DD and also with ionic liquid alone. The D values of U(VI) in ionic liquid varied from 0.004 (=0.4% extraction) to 0.41 (=30% extraction) when the concentration of nitric acid was varied from 0.01M to 8M. Ionic liquids are known to dissolve and stabilize ionic salts.^{7,8,13,14} Thus, U(VI) can be expected to dissolve in ionic liquid phase at all nitric acid concentrations. The extraction of U(VI) by IL appears to be the result from the solubility of uranyl nitrate in ionic liquid phase. A similar observation was reported by VISSER et al.¹⁴ for the extraction of various metal ions from aqueous phase into ionic liquid. They reported that ionic liquids easily dissolve hydrophobic and big ions as compared to hydrophilic and hydrated ions. In the case of uranium nitrate system, as the concentration of nitric acid is increased, the uranyl ion forms a series of complex species: $[\text{UO}_2\text{NO}_3]^+$, $[\text{UO}_2(\text{NO}_3)_2]$, $[\text{UO}_2(\text{NO}_3)_3]^-$. Among these species, the neutral $[\text{UO}_2(\text{NO}_3)_2]$ can be regarded as having more hydrophobicity. Among the charged species, the complex ion with bigger size may be more hydrophobic than the smaller complex. The initial increase in the extraction of U(VI) by ionic liquid alone with increasing HNO₃ concentration can be attributed to the extraction of the hydrophobic neutral uranium complex, which is in agreement with the observation of VISSER et al.¹⁴ When the concentration of nitric acid is >6M, a significant part of uranyl cation is converted to the anionic nitrate complex, $[\text{UO}_2(\text{NO}_3)_3]^-$. Since these species are charged, they may be expected to be less hydrophobic than the neutral uranyl nitrate complex and should have resulted in lower distribution ratios. However, the continued increase in D value of U(VI) with nitric acid is indicative of the involvement of other possible mechanisms such as ion-exchange in which PF₆⁻ of the ionic liquid is exchanged for anionic species. It is to be noted that at 8M nitric acid, where the majority of U(VI) would exist as a large anionic complex, nearly 30% U(VI) was extracted. We expect our continuing studies to bring more clarity in the understanding of the system.

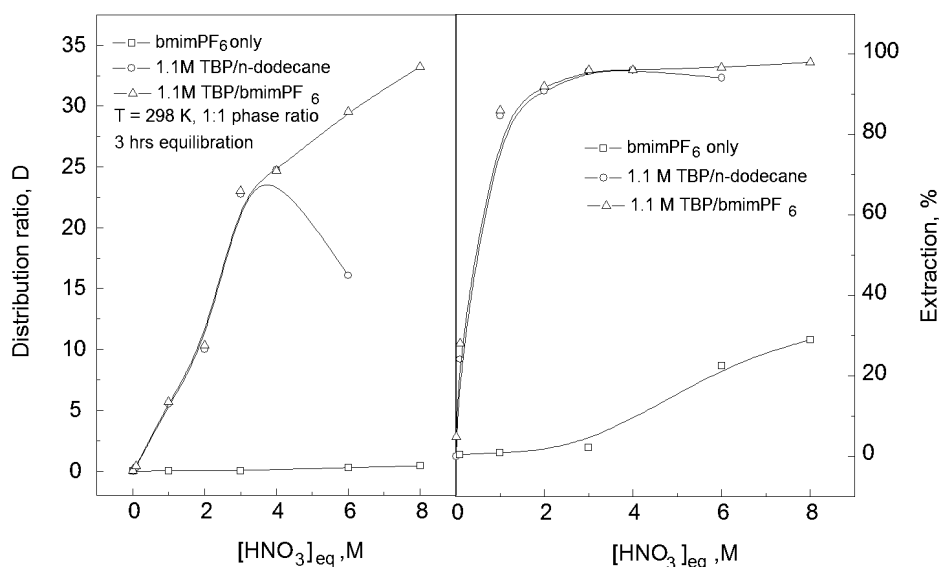


Fig. 1. Distribution ratio with equilibrium concentration of nitric acid for the extraction of U(VI) in various 1.1M TBP/diluent

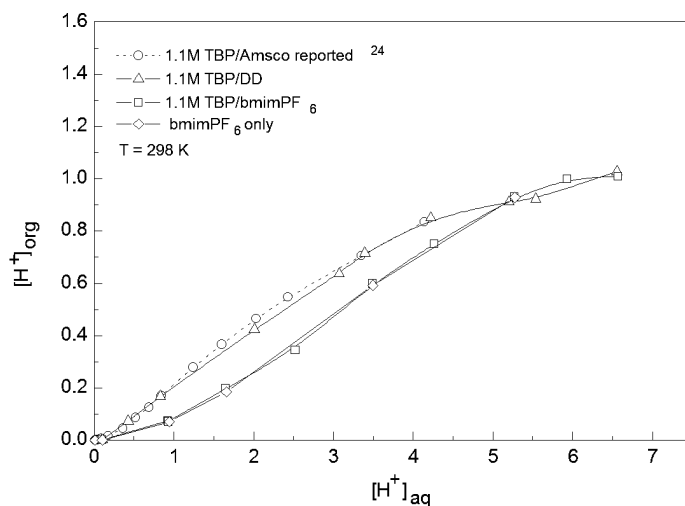


Fig. 2. Comparison of acid extraction in various 1.1M TBP/diluent systems

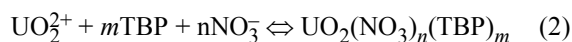
The distribution ratio of U(VI) in 1.1M TBP/ $bmimPF_6$ gradually increased from 0.05 to 33.2 when the concentration of nitric acid was increased from 0.01M to 8M. At nitric acid concentrations lower than 4M, the distribution ratios obtained for the extraction of U(VI) by 1.1M TBP/ $bmimPF_6$ are comparable with the distribution values observed for the extraction of U(VI) by 1.1M TBP/DD. However, above 4M, the distribution values of U(VI) in 1.1M TBP/ $bmimPF_6$ continue to increase, in contrast to the behavior seen in the case of 1.1M TBP/DD. This indicates the significant influence

of the ionic liquid vis-à-vis the hydrocarbon diluent usually used. When the initial nitric acid concentration was 8M, phase reversal was found to occur since the density of 8M nitric acid (1.22 g/ml) was higher than the equilibrated 1.1M TBP/ $bmimPF_6$ phase (1.19 g/ml). With all other nitric acid concentrations, the density of organic phase was higher and, therefore, it settled in the bottom after equilibration.

In traditional solvents, the decrease in D value of U(VI) above 4M nitric acid is normally attributed to the non-availability of free TBP, due to significant

extraction of nitric acid and also to the conversion of uranyl ion to the less extractable anionic uranyl nitrate species at high nitric acid concentrations.^{24–26} CHAIKO et al.²⁶ have modeled organic phase speciation of 1.1M TBP as a function of nitric acid and reported that the concentration of free TBP, $[TBP]_f$, was lowered to 0.01M at 6M nitric acid. Acid extraction isotherm for 1.1M TBP/bmimPF₆ is shown in Fig. 2 and the data are compared with that for 1.1M TBP/DD. It is seen that the extraction of acid increases with the increase of nitric acid concentration in the aqueous phase. It should be noted that extraction of nitric acid by TBP is somewhat less favored when bmimPF₆ acts as diluent at nitric acid concentrations less than 5M. Above this concentration, the acid extraction by 1.1M TBP/bmimPF₆ is comparable with that by 1.1M TBP/DD. Thus, the reason for the increase in the D value for the extraction of U(VI) by 1.1M TBP/bmimPF₆ from nitric acid concentration more than 5M is not clear at present. Nevertheless, the present data provide the information that U(VI) extraction is feasible using TBP dissolved in ionic liquid. The data presented henceforth focus on the extraction behavior of U(VI) from 2–4M nitrate concentrations, which is of importance since the PUREX process²³ streams have the acidity in this range (~3M).

Figure 3 shows the variation of distribution ratio of U(VI) as a function of nitrate ion concentration, which was added as sodium nitrate. D values for U(VI) were significantly higher in this case than those observed for the extraction of U(VI) from nitric acid at equal nitrate ion concentration. A similar trend has also been observed for the extraction of U(VI) by TBP/DD.²⁶ This effect is attributed to the salting out of uranyl nitrate by the addition of sodium nitrate and also to the reduced extraction of nitric acid into the organic phase. If the extraction of U(VI) by TBP/IL involves the following simplified equilibrium:



Then, the equilibrium constant (K) of the reaction can be represented by:

$$K = \frac{[UO_2(NO_3)_n(TBP)_m]_{org}}{[UO_2^{2+}]_{aq} [TBP]^m [NO_3^-]_{aq}^n} \quad (3)$$

$$K = \frac{D}{[TBP]^m [NO_3^-]_{aq}^n} \quad (4)$$

At constant concentration of TBP and assuming that K varies marginally in the concentration range studied, Eq. (4) can be rewritten as:

$$\log D = \log K_1 + n \log [NO_3^-]_{aq} \quad (5)$$

where K_1 is constant. Thus, a plot of $\log D$ against $\log [NO_3^-]$ should yield a slope of n . For the extraction of U(VI) by TBP/DD such a plot was shown to result in a slope of 2.²³ The log-log plot for the extraction of U(VI) by TBP/IL is shown in Fig. 3. A slope of 1.73 obtained from the plot can be taken to indicate that two molecules of nitrate ions are involved in the extraction of U(VI) by 1.1M TBP/bmimPF₆ also.

The variation of distribution ratio for the extraction of U(VI) as a function of TBP concentration in ionic liquid is shown in Fig. 4. It is seen that D value increases with increasing TBP concentration. From Eq. (4) for constant nitrate ion concentration, we get:

$$\log D = \log K_2 + m \log [TBP]_{org} \quad (6)$$

where K_2 is constant. The $\log D$ – $\log ([TBP])$ plot is shown in Fig. 4. A slope of ~2 obtained for the extraction of U(VI) from 2–4M nitric acid concentrations confirms that 2 molecules are involved in the extraction of U(VI). Thus, the stoichiometry of U(VI) extraction by 1.1M TBP/IL resembles that of TBP/DD system, wherein two molecules of nitrate and TBP are complexed with U(VI) in organic phase.

The enthalpy of extraction ($-\Delta H_{tot}$) of U(VI) by TBP/bmimPF₆ can be calculated from the Van't Hoff's equation of the form given by:

$$\frac{\partial \ln D}{\partial (1/T)} = \frac{-\Delta H_{tot}}{R} \quad (7)$$

where R is the gas constant. The U(VI) distribution ratio obtained at various concentrations of nitric acid and TBP are plotted as $\ln(D)$ against $(1/T)$ in Fig. 5. The enthalpy of the extraction can be calculated from the slope obtained by linear regression of the data given in Table 1. It can be seen that with the increase in the concentration of nitric acid the extraction of U(VI) becomes less exothermic, as in the case of extraction by TBP/DD.²⁷ The enthalpy is in close agreement with those of TBP/DD system. However, in contrast to TBP/DD, the U(VI) extraction was found to be more exothermic with increasing $[TBP]$ concentration in bmimPF₆.

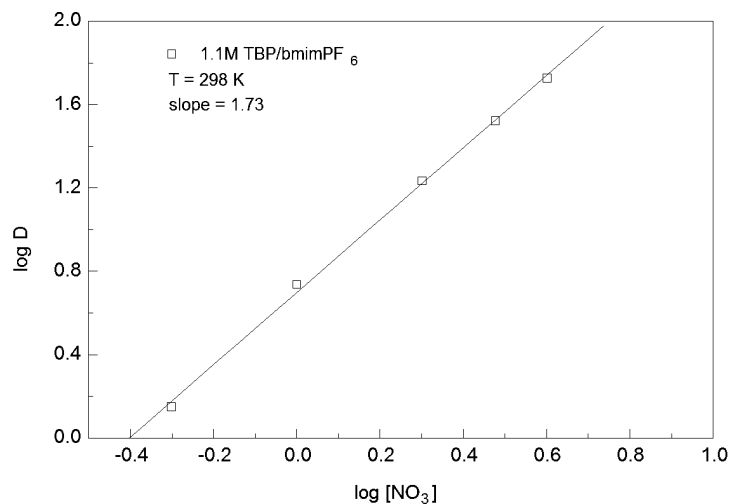


Fig. 3. Variation of log *D* with log [NO₃] for the extraction of U(VI) by 1.1M TBP/bmimPF₆ at 298 K

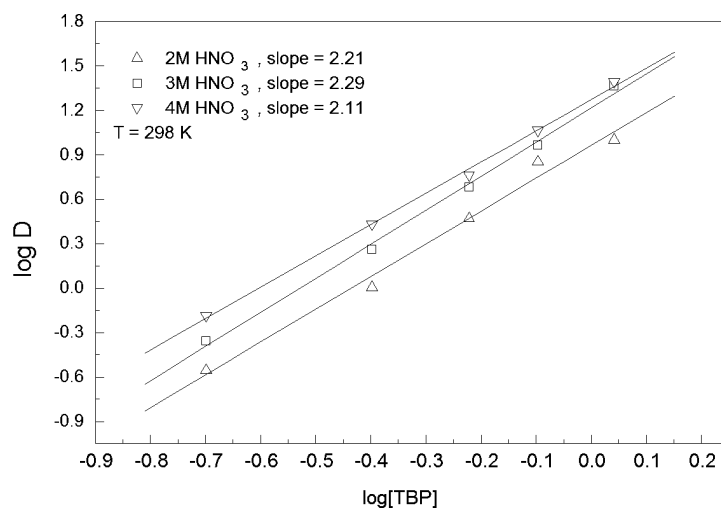


Fig. 4. Variation of log *D* with log [TBP] for the extraction of U(VI) by various concentration of TBP/bmimPF₆

Table 1. Variation in the enthalpy accompanying the extraction of U(VI) by TBP/bmimPF₆ at various nitric acid and TBP concentrations

[HNO ₃], M	[TBP], M	-Δ <i>H</i> , kJ/mol	-Δ <i>H</i> , kJ/mol for TBP/DD (reported) ²⁷
2	1.1	17.0	
3	1.1	15.2	
4	1.1	14.4	13.3
2	0.4	11.2	
2	0.8	14.2	

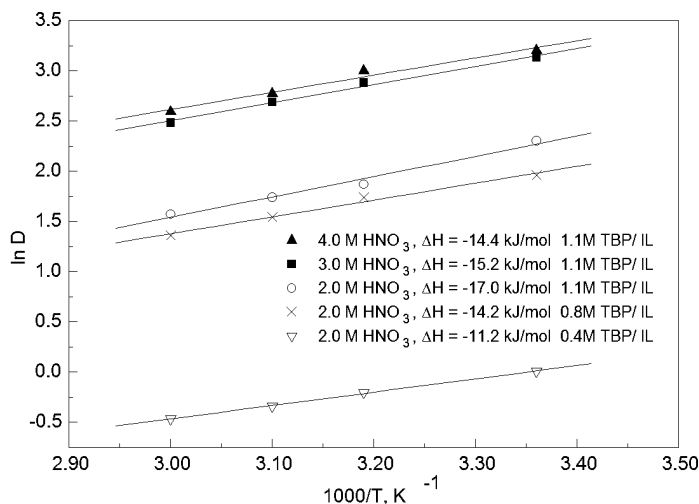
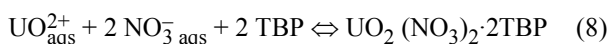


Fig. 5. Variation of distribution coefficient with temperature for the extraction of U(VI) by TBP/bmimPF₆ at different concentrations of HNO₃ and TBP

Conclusions

The extraction of U(VI) by 1.1M TBP dissolved in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, has been studied and the results compared with those obtained with 1.1M TBP/DD. Distribution coefficient of U(VI) in 1.1M TBP/bmimPF₆ was found to vary from 0.05 to 33.2 when the concentration of nitric acid was increased from 0.01M to 8M. The magnitudes of distribution coefficients were comparable with those of TBP/DD for nitric acid concentrations less than 4M. Increased U(VI) extraction was observed from high nitric acid (>4M) concentrations with the TBP solution in ionic liquid. U(VI) was found to be extracted from nitric acid medium by the ionic liquid itself, even though the extraction was moderate $D=0.004$ (0.4% extraction) from 0.01M nitric acid and 0.4 (30% extraction) from 8.0M acid. The apparent stoichiometry of U(VI) extraction resembles that of TBP dissolved in n-dodecane, as given by:



The enthalpy change accompanying U(VI) extraction was found to vary from -17.0 to -14.4 kJ/mol when the concentration of nitric acid was increased from 2.0M to 4.0M. Increase in the concentration of TBP increased the exothermicity.

In summary, the extraction of U(VI) by 1.1M TBP/bmimPF₆ is similar to the traditional behavior exhibited by TBP/DD when the concentration of nitric acid is less than 4.0M. It is difficult to explain from the available data, the increased extraction of U(VI) from nitric acid concentration higher than 4M. Ion exchange

of PF₆⁻ with the anionic uranyl nitrate complexes cannot be ruled out along with the extraction by solvation.

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