

Effect of Alkyl Group in 1-Alkyl-3-methylimidazolium Hexafluorophosphate Ionic Liquids on the Extraction of Uranium by Tri-*n*-butylphosphate Diluted with Ionic Liquids

P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, and P. R. Vasudeva Rao*

Fuel Chemistry Division, Chemical Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Received: August 9, 2004; In Final Form: October 12, 2004

Extraction of uranium by 1.1 M TBP dissolved in 1-octyl-3-methylimidazolium hexafluorophosphate (omimPF₆) ionic liquid (IL) as diluent has been studied as a function of concentration of nitric acid and uranium and that of temperature. The results are compared with those of extraction in 1.1 M TBP in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆). Distribution ratios (*D*) for extraction of uranium in 1.1 M TBP/omimPF₆ were marginally less than those for extraction by 1.1 M TBP/bmimPF₆ at all nitric acid concentrations. The *D* values increased with increase in the concentration of nitric acid but decreased with increase in the concentration of uranium and temperature. In contrast to the behavior of 1.1 M TBP/*n*-dodecane, *D* values for uranium continued to increase even for nitric acid concentrations higher than 5 M, when IL acted as diluent. Solubility of omimPF₆ in nitric acid was 2–3 times less as compared to bmimPF₆. The overall enthalpy change (ΔH_{tot}) for the extraction of uranium in 1.1 M TBP/omimPF₆ was found to be more exothermic than for extraction by 1.1 M TBP/bmimPF₆. This behavior can be attributed to the lower extent of protonation of TBP in omimPF₆ phase. Viscosity of TBP/IL increased when butyl group was substituted with octyl group in IL.

1. Introduction

Room temperature ionic liquids (RTILs) are gaining recognition in various industries including nuclear reprocessing industry owing to their impressive physical, chemical, and environmentally benign properties.^{1–6} Rogers and co-workers have published a number of reports pertaining to the possible application of ionic liquids for separating fission products and actinides from nuclear wastes.^{7–11} The ionic liquids (ILs), as the name implies, consist entirely of ions existing in liquid state and have negligible vapor pressure and low flammability as compared to volatile molecular organic compounds such as chloroform, dodecane (DD) etc., which are used as the diluents in solvent extraction processes. Several workers have employed either crown ether with ILs^{9, 12, 13} as diluents for extracting ⁹⁰Sr and ¹³⁷Cs or actinide specific extractants diluted with ILs for extracting *f*-block elements.¹¹ The main difference observed was that these extractants in conjunction with ILs exhibited substantially higher extraction of target metals from aqueous solutions under the conditions, which gave negligible or meager extraction with customary diluents. Recently, Visser et al. have introduced task-specific ionic liquids (TSILs) incorporating specific extracting moieties^{14, 15} linked to the imidazolium part of the IL. It was reported that these TSILs exhibit very high distribution ratios for Hg²⁺ and Cd²⁺ when functionalized with sulphur containing moieties,¹⁵ and for Pu⁴⁺, Am³⁺ and UO₂²⁺ when functionalized with carbamoylmethylphosphine oxide moieties.¹⁵ In addition, Chun et al.¹³ have studied the structural variation in 1-alkyl-3-methylimidazolium hexafluorophosphate ILs for investigating the variation in selectivity for alkali metal ion extraction. It was found that by increasing the chain length of alkyl group attached to the imidazole, the efficiency of extraction decreased where as the selectivity increased. Recently we have also studied the extraction of uranium by tri-*n*-butylphosphate (TBP) in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆)^{16, 17} and reported that bmimPF₆ also extracts uranium. In contrast to the extrac-

tion behavior exhibited by TBP/*n*-dodecane, the distribution ratios of uranium in 1.1 M TBP/bmimPF₆ continued to increase even above 5 M nitric acid. The extraction equilibrium was similar to that of uranium extraction by TBP/DD.



While the investigation of ILs as diluents for reprocessing has yielded promising results, the possible chemical and radiolytic degradation⁶ and mechanistic aspects of extraction^{9, 12, 16–18} are also being simultaneously investigated owing to the importance of actinide recovery. Swatloski et al. have reported the formation of 1-butyl-3-methylimidazolium fluoride from the decomposition of 1-butyl-3-methylimidazolium hexafluorophosphate.¹⁹ Carda-Broch et al.²⁰ have studied the physico-chemical properties of bmimPF₆ and reported a solubility of 1.8 wt% in water. Alfassi et al.²¹ have investigated the solubility of various ILs in water by electrospray ionization mass spectrometry and reported the solubility of bmimPF₆ as 1.8 wt%. Further, substitution of PF₆⁻ anion with bulkier imide anion was found to decrease the solubility.²¹ Gutowski et al.¹⁵ have studied the extraction of actinides and fission products using imide based ILs to avoid the solubility of PF₆⁻ based ILs in water. Visser et al.⁹ have reported the solubility of bmimPF₆ as 1.2 M when equal volumes of bmimPF₆ or crown ether dissolved in bmimPF₆ was contacted (2–4 min) with 8 M nitric acid. Antony et al.²² have studied the thermodynamic aspects of imidazolium based ILs in water and reported the solubility of bmimPF₆ as 2 wt% in water. It was reported that the solubility decreased to 0.7 wt% when a butyl group was replaced by lengthier octyl groups in 1-alkyl-3-methylimidazolium hexafluorophosphate (amimPF₆). It is, thus, obvious that by changing the cation and anion combination in ILs the solubility of ILs can be altered.

This paper deals with the extraction of uranium by TBP/omimPF₆ from nitric acid medium and compares the results with those obtained for TBP/bmimPF₆. The effect of concentration of HNO₃ and uranium and that of temperature on the distribution coefficient of uranium has been studied. Solubility of amimPF₆ and TBP/amimPF₆ in nitric acid medium and the

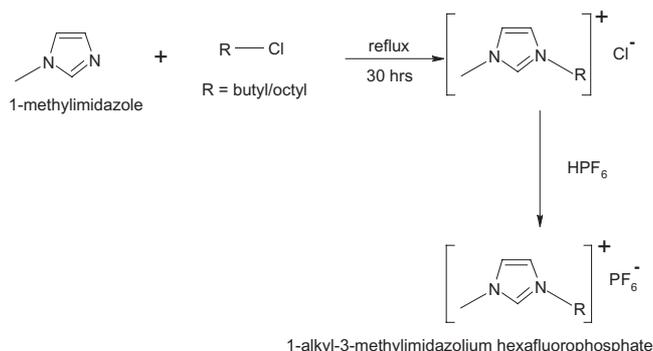
*Corresponding author. E-mail: vasu@igcar.ernet.in. FAX: +91-4114-280065.

influence of temperature on the viscosity of solvents are reported.

2. 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-Chlorooctane was obtained from E. Merck. 1-Methylimidazole was distilled before use and other chemicals were used without any purification. TBP and uranyl nitrate were obtained from E. Merck, Mumbai.

Preparation of ionic liquids. The procedure adopted for preparing the ILs is described elsewhere.⁷ Briefly it involves refluxing a mixture of 1-methylimidazole with chloroalkane in the mole ratio of 1:1.2. The resulting product was washed few times with ethylacetate followed by acetonitrile and evaporated under vacuum. Nearly quantitative yield was obtained. The hexafluorophosphate IL was then prepared by adding a pre-cooled liquid of hexafluorophosphoric acid (1.3 mol) to the mixture containing 1-alkyl-3-methylimidazolium chloride (1 mol) in water kept at -5°C . The entire mixture was stirred for 2 days and the bottom IL layer was separated and washed several times with water until the aqueous solution was no longer acidic. The IL was heated to remove moisture at 70°C using rotary evaporator. An yield of 60% for bmimPF₆ and 82% for omimPF₆ was obtained. Elemental analysis yielded for bmimPF₆: C 33.81 (33.80), H 5.31 (5.32), N 9.85 (9.86) P 10.9 (10.9) and for omimPF₆: C 42.52 (42.35), H 6.79 (6.81), N 8.28 (8.23) P 9.1 (9.1). 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 imidazole ring symmetric stretch, 1425, 1378 (MeC-H asymmetric stretch), 834 cm⁻¹ (P-F stretch).



Scheme 1. Preparation of 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids.

Extraction studies. All the extraction studies were carried out at 298 K with 1:1 organic to aqueous phase ratio, unless otherwise mentioned. 1.1 M TBP in amimPF₆ was prepared and pre-equilibrated with desired nitric acid concentration. Extraction of uranium as a function of nitric acid concentration was studied by equilibrating 2 mL of organic phase i.e. 1.1 M TBP/amimPF₆ with 2 mL of nitric acid solution containing ²³³U tracer. The concentration of nitric acid in the test solution was varied from 0.01 M to 8 M. After three hours of equilibration, the radioactivity of ²³³U distributed between organic and aqueous phases was measured by liquid scintillation counting. The distribution ratio (*D*) of uranium and % extraction (*E*) were calculated using eqs 1 and 2.

$$D = \frac{[^{233}\text{U}]_{\text{org}}}{[^{233}\text{U}]_{\text{aq}}} \quad (1)$$

$$E = \frac{[^{233}\text{U}]_{\text{org}}}{[^{233}\text{U}]_{\text{org}} + [^{233}\text{U}]_{\text{aq}}} \times 100 \quad (2)$$

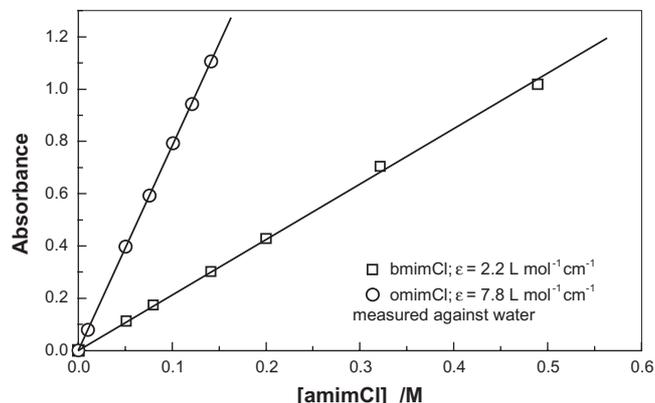


Figure 1. Variation of absorbance with concentration of 1-alkyl-3-methylimidazolium chloride in water.

Extraction of nitric acid was also studied by equilibrating equal volumes of 1.1M TBP/amimPF₆ with nitric acid for three hours. The concentration of nitric acid was varied from 0.01 M to 8 M. The amount of nitric acid present in organic/aqueous phases was determined by titrating a known volume of the organic/aqueous phase with sodium hydroxide. Similar experiment was performed when bmimPF₆ or omimPF₆ acted as organic phase.

Enthalpy change accompanied by the extraction of uranium in 1.1 M TBP/amimPF₆ was determined by measuring the *D* of uranium as a function of temperature ranging from 298 K to 338 K. In this study 2 mL of organic phase was equilibrated with 2 mL of nitric acid spiked with ²³³U and the concentration of nitric acid was varied from 2.0 M to 4.0 M.

The solubility of amimPF₆ in nitric acid phase was determined by contacting neat amimPF₆ as well as 1.1 M TBP solutions in amimPF₆ with nitric acid of desired concentration ranging from 0.01 M to 8 M. The experiment involved vigorous equilibration of 1 g of organic phase with 1 mL of desired aqueous phase. At various intervals of time, the shaking was stopped. The concentration of IL in aqueous phase was determined by measuring independently the concentrations of imidazolium cation (by spectrophotometry) and PF₆⁻ anion (by phosphorous analysis). The absorbance of imidazolium cation in the aqueous phase was measured at the λ_{max} of 289 nm. The concentration of amim⁺ cation in the aqueous phase was calculated with the use of calibration plot, shown in Figure 1. The molar absorptivity for bmimCl and omimCl was found to be 2.2 L mol⁻¹ cm⁻¹ and 7.8 L mol⁻¹ cm⁻¹ respectively. The concentration of phosphorous in the aqueous phase was determined by amidol method²³ after digesting an aqueous aliquot with perchloric acid.

The effect of aqueous uranium concentration on the extraction of uranium was studied by equilibrating the 1.1 M TBP/amimPF₆ phase with aqueous phase spiked with ²³³U tracer containing uranium in the concentration range of 4.3×10^{-5} M to 8.6×10^{-3} M (added in the form of uranyl nitrate) in 3 M nitric acid.

3. Results and Discussion

A comparison of distribution ratios of uranium in amimPF₆ and 1.1 M TBP/amimPF₆ as a function of nitric acid concentration is shown in Figure 2. Modest *D* values were obtained when amimPF₆ alone acted as extractant and the *D* values varied from 0.004 (~0.3% extraction) to 0.41 (~30% extraction) when the concentration of nitric acid was varied from 0.01 to 8 M. This behavior could be attributed to the solubility of uranyl nitrate species in ILs, which are known for dissolving and stabilizing a wide variety of ionic salts.^{7, 8, 24, 25} The increase in the solubility with increase in [HNO₃] could be due to the increased formation of species such as, [UO₂(NO₃)₂], [UO₂(NO₃)₃]⁻ which can be extracted by the solvation/ion

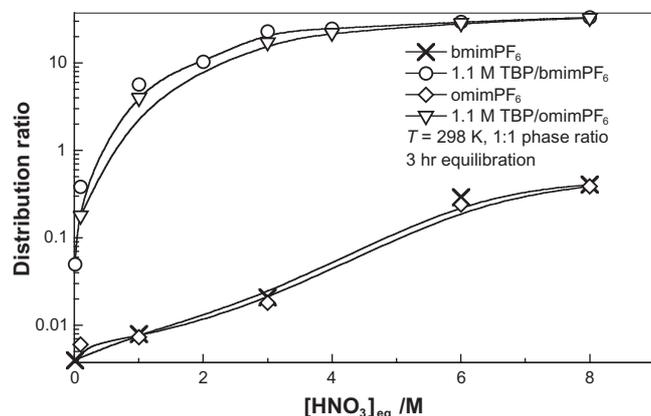


Figure 2. Comparison of distribution ratio for extraction of uranium by ionic liquids and 1.1 M TBP/ionic liquids from HNO_3 medium.

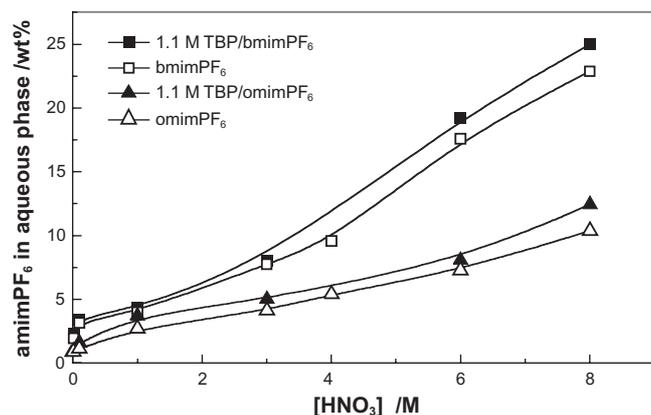


Figure 3. Comparison of ionic liquid solubility in aqueous phase at various nitric acid concentrations.

exchange by IL. A similar observation was reported by Visser et al.¹⁴ for the extraction of various complexing metal ions from aqueous phase into IL and it was indicated that ILs prefer to extract hydrophobic and larger complex species than hydrated and smaller complexes.

The extraction of uranium by both 1.1 M TBP/amimPF₆ was similar at all nitric acid concentrations and *D* gradually increased from 0.05 to 33 when the concentration of nitric acid was increased from 0.01 M to 8 M. In contrast to TBP/DD,¹⁷ the distribution ratios continued to increase even when the concentration of nitric acid was >5 M. This indicates that ILs play a significant role in extracting uranium from aqueous phase to organic phase at high nitric acid concentrations.

Table 1 shows the aqueous solubility of IL as a function of the concentration of nitric acid. The solubility values were obtained both from phosphorous analysis using amidol method²¹ and by the measurement of absorbance of imidazolium cation dissolved in nitric acid. It can be seen that both the values are

TABLE 1: Solubility of amimPF₆ in Nitric Acid Medium

[HNO ₃] _{ini} M	Solubility of bmimPF ₆		Solubility of omimPF ₆	
	P found, M	bmim ⁺ found, M	P found, M	omim ⁺ found, M
0.01	0.069	0.063	0.026	0.025
0.10	0.116	0.113	0.033	0.030
1.00	0.140	0.146	0.080	0.076
3.00	0.351	0.345	0.121	0.116
6.00	0.619	0.636	0.214	0.201
8.00	0.810	0.816	0.310	0.309

Contact time: 3 hours. The values are based on phosphorous analysis and spectrophotometric measurement of alkylimidazolium cation.

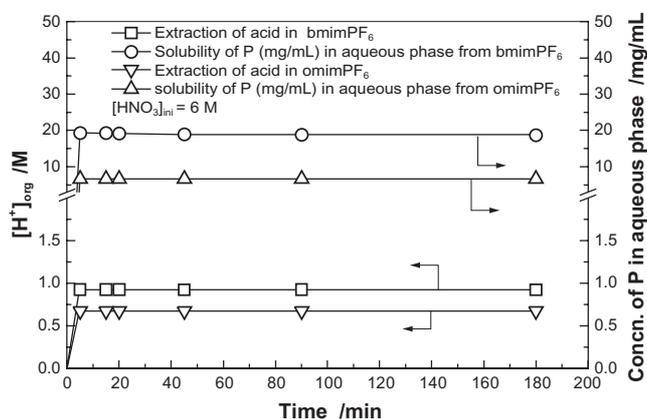


Figure 4. Rate of acid extraction into organic phase and solubility of PF_6^- in aqueous phase.

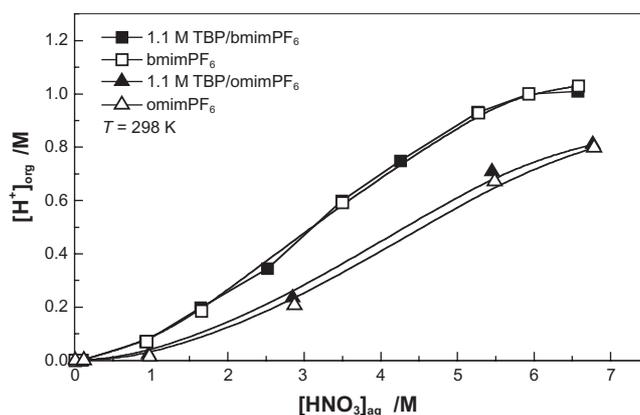


Figure 5. Comparison of acid extraction behavior of various ionic liquids and 1.1 M TBP/IL.

in close agreement. Thus, it would appear that both the imidazolium and hexafluorophosphate ions distribute to the aqueous phase and there is no preferential stripping/ion exchange of cation or anion, when IL is contacted with nitric acid. The solubility of bmimPF₆ and omimPF₆ in 0.01 M nitric acid was found to be 1.9 wt% and 0.9 wt% respectively, which is in close agreement with the values reported^{19–21} for these ILs in water. Solubility of IL in nitric acid is one of the important parameters from the PUREX process point of view. Visser et al.⁹ have reported the solubility of bmimPF₆ as 1.2 M when equal volumes of bmimPF₆ or crown ether dissolved in bmimPF₆ was contacted (2–4 min) with 8 M nitric acid. Figure 3 compares the aqueous phase solubility of amimPF₆ and 1.1 M TBP/amimPF₆ as a function of nitric acid concentration. The solubilities of both the ILs increase with increase in the concentration of nitric acid and the presence of TBP in IL enhances the solubility. However, the solubility of omimPF₆ IL is 2–3 times lower depending upon [HNO₃], as compared to bmimPF₆. The rate of distribution of IL to the aqueous phase and acid extraction by organic phase are shown in Figure 4. It can be seen that rapid extraction of acid takes place and the equilibrium is established in five minutes. Similarly, the solubility of IL reaches the saturation value in less than 10 minutes of equilibration. The acid extraction isotherm of ILs and 1.1 M TBP/ILs are shown in Figure 5. The concentration of acid extracted by the organic phase increased with increase in the concentration of nitric acid present in the aqueous phase in both the cases. But the amount of acid extracted by omimPF₆ was 2–3 times lower than the corresponding value for bmimPF₆.

Figures 6a, 6b, and 6c show the IR spectra of 1.1 M TBP/diluents (diluent is *n*-dodecane, bmimPF₆, or omimPF₆) equilibrated with various nitric acid concentrations. A doublet at 1281 cm⁻¹ and 1269 cm⁻¹ can be assigned to the P=O stretching of 1.1 M TBP/DD and it gets broadened and shifts to 1234 cm⁻¹ and 1210 cm⁻¹ respectively when 1.1 M TBP/DD is equilibrated

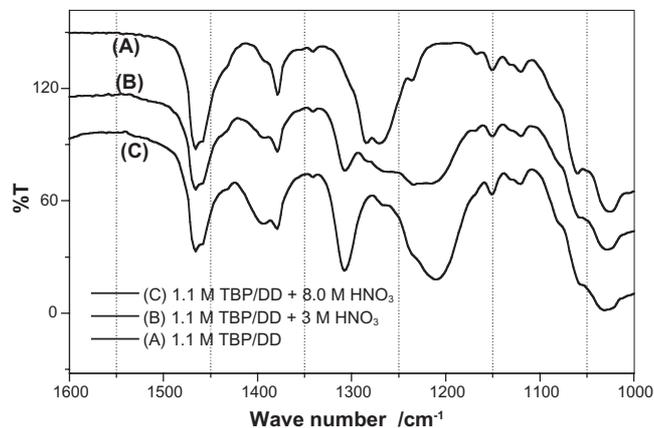


Figure 6a. IR spectra of 1.1 M TBP/DD equilibrated with nitric acid of different concentrations.

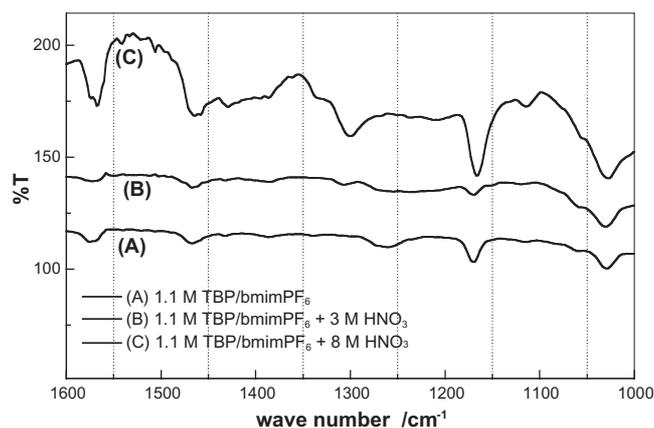


Figure 6b. IR spectra of 1.1 M TBP/bmimPF₆ equilibrated with different concentrations of nitric acid.

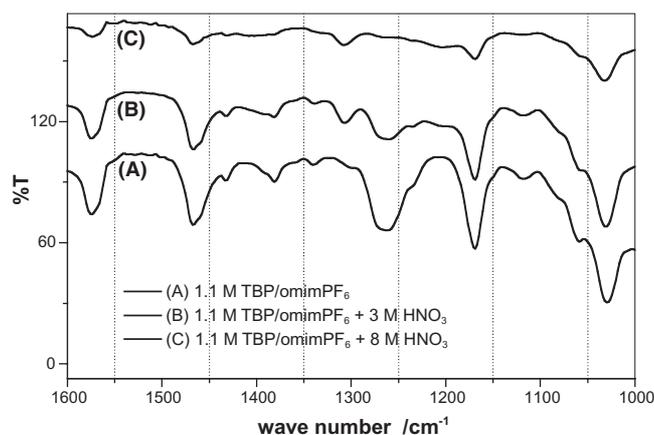


Figure 6c. IR spectra of 1.1 M TBP/omimPF₆ equilibrated with nitric acid of various concentrations.

with 3 M and 8 M nitric acid. It is interesting to observe from Figures 6b and 6c that the P=O stretching band of TBP appears at 1263 cm⁻¹ instead of 1281 cm⁻¹ – 1269cm⁻¹, when TBP is diluted with IL. Equilibration of 1.1 M TBP/bmimPF₆ with 3 M nitric acid significantly broadens the P=O band and shifts the peak to 1250 cm⁻¹ (Figure 6b). This band disappears when TBP/bmimPF₆ is equilibrated with 8 M nitric acid, probably merging with the bands of bmimPF₆ at 1200 cm⁻¹. However, the features in IR spectrum of 3 M acid equilibrated 1.1 M TBP/omimPF₆ are different from 1.1 M TBP/bmimPF₆. Due to lower extraction of nitric acid by 1.1 M TBP/omimPF₆, the peak position at 1263 cm⁻¹ is not affected and the band is only broadened. However, this band merges with other peaks of omimPF₆ when equilibrated with 8 M nitric acid.

The effect of temperature on the distribution ratio for extraction of uranium and enthalpy of extraction (ΔH_{tot}) of uranium

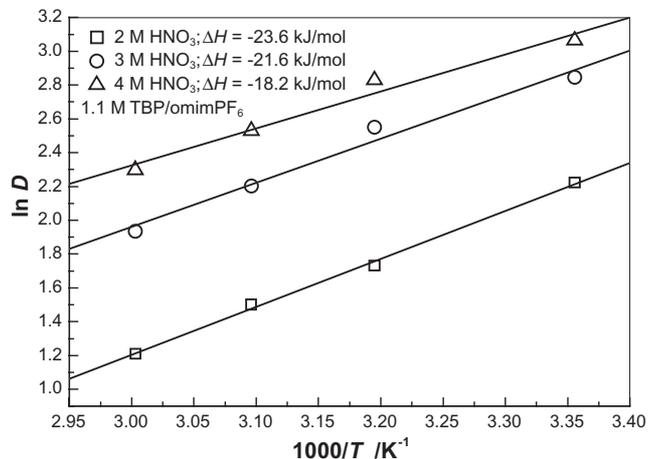


Figure 7. Variation of $\ln D$ with $1/T$ for the extraction of uranium by 1.1 M TBP/omimPF₆.

by 1.1 M TBP/omimPF₆ can be given by the van't Hoff's relation shown in eq 3

$$\frac{\partial \ln D}{\partial (1/T)} = \frac{-\Delta H_{\text{tot}}}{R} \quad (3)$$

where R is gas constant. The plot of $\ln D$ against $1/T$ is shown in Figure 7. From the linear regression of the experimental data, ΔH_{tot} for the extraction of uranium by 1.1 M TBP/omimPF₆ was calculated and these values are tabulated in Table 2 along with the values obtained¹⁷ for the extraction of uranium by 1.1 M TBP/bmimPF₆. It can be observed from the table that the exothermicity decreases with increase in nitric acid concentration in both the cases, which could be due to the combination of a number of factors as indicated by Burger.²⁶ However, it is interesting to note that the exothermicity observed for the extraction of uranium by 1.1 M TBP/omimPF₆ is higher than that for 1.1 M TBP/bmimPF₆. This could be attributed to a lower extent of protonation of TBP in 1.1 M TBP/omimPF₆ phase, which results in increase in the availability of free TBP for complexing the uranium transported to the organic phase, resulting in higher exothermicity.

The distribution ratios of uranium extraction by 1.1 M TBP/amimPF₆ at various initial concentrations of uranium in the aqueous phase are shown in Table 3. It is seen that D values

TABLE 2: Enthalpy Change Observed for the Extraction of Uranium by 1.1 M TBP/ILs at Various Nitric Acid Concentrations

[HNO ₃], M	- ΔH_{tot} , kJ/mol	
	1.1 M TBP/bmimPF ₆	1.1 M TBP/omimPF ₆
2	17.0	23.6
3	15.2	21.6
4	14.4	18.2

TABLE 3: Variation in the Distribution Ratio of Uranium (at 298 K) with Initial Concentration of Uranium in the 3 M Nitric Acid

[U] × 10 ⁴ , M	Distribution ratio of U	
	1.1 M TBP/bmimPF ₆	1.1 M TBP/omimPF ₆
0.43	23.0	17.2
4.3	21.4	16.6
21.5	20.0	14.3
43.0	17.1	13.1
86.0	16.6	11.8

decrease with increase in uranium concentration. It is difficult to explain this observed behavior, since the concentration of TBP in organic phase is much higher than the concentration of uranium in aqueous phase.

Viscosity measurements. Viscosity of the solvent is an important process parameter determining the hydrodynamic nature of the solvent in solvent extraction process. It is essential that the viscosity of the organic phase (~2 cP) is sufficiently low to permit, ready flow of solutions, low power agitators for phase dispersion and efficient phase separation. ILs generally have high viscosity due to strong ionic interaction.²⁷ However, the viscosity of IL can be lowered by operating the extraction process at higher temperature in order to increase the hydrodynamic properties. Figure 8 shows the effect of temperature on the viscosities (η , in cP) of various ILs and 1.1 M TBP/ILs. It can be seen that the viscosity of octyl based ILs are much higher than that for bmimPF₆, which could be due to higher interaction of bigger octyl groups with the adjacent layers of IL. Since the viscous flow is the rate phenomenon,²⁸ it can be represented by eq 4, which relates the activation energy, E_a , and viscosity.

$$\eta = \eta_0 e^{E_a/RT} \quad (4)$$

where η_0 and R are pre-exponential factor and gas constant respectively. The plot of $\ln \eta$ against $1/T$ is shown in Figure 9. From the slope of the straight line the activation energy (E_a) was found to be 42.2 kJ/mol and 33.6 kJ/mol respectively for omimPF₆ and bmimPF₆. For 1.1 M TBP/omimPF₆ and 1.1 M TBP/bmimPF₆, E_a was found to be 33.0 kJ/mol and 27.9 kJ/mol respectively and these values were much higher than the E_a reported (18.2 kJ/mol) for 1.1 M TBP/Shell Spray Base.²⁹

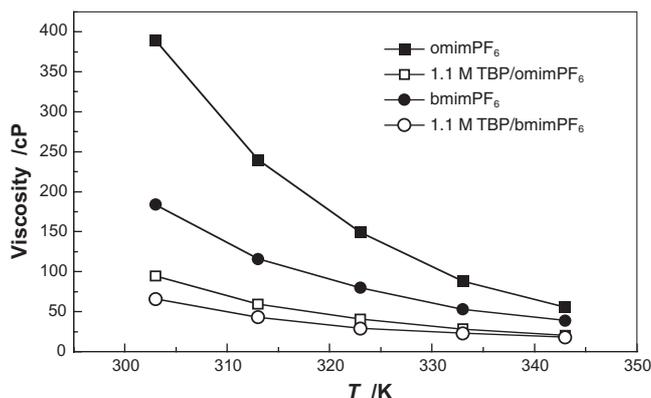


Figure 8. Variation in the viscosity of ionic liquids as a function of temperature.

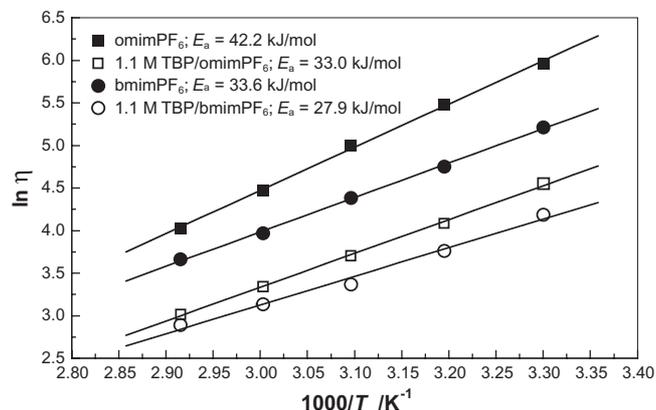


Figure 9. Arrhenius plot for the variation of viscosity with temperature for various ionic liquids and 1.1 M TBP/IL.

4. Conclusions

The extraction of uranium by 1.1 M TBP present in a neoteric diluent namely IL, 1-alkyl-3-methylimidazolium hexafluorophosphate, has been studied and the results are compared with butyl and octyl substituents in ILs. The distribution ratio (D) for extraction of uranium by 1.1 M TBP/omimPF₆ was marginally lower than that observed in 1.1 M TBP/bmimPF₆ and the D values were found to increase with increase in nitric acid concentration. In contrast to the extraction behavior exhibited by 1.1 M TBP/DD system, D values for the extraction of uranium by 1.1 M TBP/amimPF₆ continued to increase when the concentrations of nitric acid was above 5 M HNO₃. The solubility of IL in nitric acid medium increased with increase in the concentration of nitric acid in both the cases, but, the solubility of omimPF₆ was 2–3 times lower depending upon HNO₃ concentrations. The overall extraction of uranium by TBP/omimPF₆ is more exothermic as compared to extraction by TBP/bmimPF₆ perhaps due to lower extent of protonation of TBP in omimPF₆ phase. Substitution of butyl group in amimPF₆ by octyl group increases the viscosity of IL two fold. Similarly, the viscosity, at 303 K, increases from 66 cP to 94 cP when 1.1 M TBP is diluted with omimPF₆ instead of bmimPF₆.

In summary, the substitution of butyl groups in amimPF₆ by octyl group does not alter the extraction behavior of uranium in 1.1 M TBP/ILs significantly. The solubility of IL in aqueous nitric acid phase reduces by a factor of 2–3, when omimPF₆ is used as diluent, but, the viscosity of the solvent increases ~2 fold.

References

- (1) T. Welton, Chem. Rev. **99**, 2071 (1999).
- (2) J. D. Holbrey and K.R. Seddon, Clean Products and Processes **1**, 223 (1999).
- (3) J. F. Brennecke and E. J. Maginn, AIChE J. **47**, 2384 (2001).
- (4) A. J. Jeapeas, R. C. Thied, K. R. Seddon, W. R. Pitner, E. W. Rooney, J. E. Hattor, and T. Welton, World patent, WO115175, March 1, 2001.
- (5) A. E. Bradley, J. E. Hatter, M. Nieuwenhuyzen, W. R. Pitner, K. R. Seddon, and R. C. Thied, Inorg. Chem. **41**, 1692 (2002).
- (6) D. Allen, G. Boston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healy, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims, and R. C. Thied, Green Chem. **4**, 154 (2002).
- (7) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, and R. D. Rogers, Chem. Commun. 1765 (1998).
- (8) A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman, and R. D. Rogers, Separation Science and Technology **34**, 785 (2001).
- (9) A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, and R. D. Rogers, Ind. Eng. Chem. Res. **39**, 3596 (2000).
- (10) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Jr., and R. D. Rogers, Chem. Commun. 135 (2001).
- (11) A. E. Visser and R. D. Rogers, J. Solid State Chem. **171**, 109 (2003).
- (12) S. Dai, Y. H. Ju, and C. E. Barnes, J. Chem. Soc. Dalton Trans. 1201 (1999).
- (13) S. Chun, S. V. Dzyuba, and R. A. Bartsch, Anal. Chem. **73**, 3737 (2001).
- (14) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davir Jr., and R. D. Rogers, Environ. Sci. Technol. **36**, 2523 (2002).
- (15) K. E. Gutowski, N. J. Bridges, V. A. Cocalia, S. K. Spear,

- J. D. Holbrey, R. P. Swatloski, J. H. Davis, Jr., and R. D. Rogers, *Proceedings of Global 2003. Atoms for Prosperity: Updating Eisenhower's Global Vision for Nuclear Energy*, New Orleans, LA, Nov 16 – 20, 2003, p1604.
- (16) P. Giridhar, K. A. Venkatesan, M. P. Antony, and P. R. Vasudeva Rao, *14th Annual Conference of Indian Nuclear Society and 1st BRNS Conference on Nuclear Fuel Cycle: Nuclear Fuel Cycle Technologies: Closing the Fuel Cycle*, Indira Gandhi Centre for Atomic Research, Kalpakkam, December 17 – 19, 2003, E13P.
- (17) P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.* (in press).
- (18) K. Nakashima, F. Kubota, T. Maruyama, and M. Goto, *Anal. Sci.* **19**, 1097 (2003).
- (19) R. P. Swatloski, J. D. Holsbrey, and R. D. Rogers, *Green Chem.* **5**, 361 (2003).
- (20) S. Carda-Broch, A. Berthod, and D. W. Armstrong, *Anal. Bioanal. Chem.* **375**, 191 (2003).
- (21) Z. B. Alfassi, R. E. Huie, B. L. Milman, and P. Neta, *Anal. Bioanal. Chem.* **377**, 159 (2003).
- (22) J. L. Antony, E. J. Maginn, and J. F. Brennecke, *J. Phys. Chem. B* **105**, 10942 (2001).
- (23) S. D. Alexandratos, M. A. Strand, D. R. Quillen, and A. J. Walder, *Macromolecules* **18**, 829 (1985).
- (24) F. Endres, *Chem. Phys. Phys. Chem.* **3**, 144 (2002).
- (25) C. L. Hussey, L. A. King, and R. A. Carpio, *J. Electrochem. Soc.* **126**, 1029 (1979).
- (26) L. L. Burger, *Nucl. Sci. Eng.* **16**, 428 (1963).
- (27) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, and R. D. Rogers, *Green Chem.* **3**, 156 (2001).
- (28) S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, (McGraw-Hill, New York, 1941). Chapter IX, Viscosity and Diffusion, p477.
- (29) L. L. Burger, *Science and Technology of Tributylphosphate, Vol. I, Synthesis, Properties, Reactions and Analysis*, ed. W. W. Schultz, J. D. Navratil, and A. E. Talbot, CRC Press, Inc, Boca Raton, Florida, 1984, p25.