

Comparison of Diluent Characteristics of Imidazolium Hexafluorophosphate Ionic Liquid with *n*-Dodecane

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Received: July 26, 2004; In Final Form: October 12, 2004

Room temperature ionic liquids (RTILs) are emerging diluents in solvent extraction processes. Unusual extraction behavior was reported for the extraction of fission products and actinides, when ionic liquids were used as diluents in place of customary diluents. In this report, some of the physical properties of the extractant that have to be met for its use in industrial scale liquid-liquid extraction, such as density, solubility, viscosity, and phase disengagement time were measured for TBP diluted in 1-alkyl-3-methylimidazolium hexafluorophosphate and compared with the data on 1.1 M TBP/*n*-dodecane. The results indicate that the RTILs investigated unsuccessfully match *n*-dodecane in many of the characteristics and thus their practical use, as diluent, in reprocessing seems to be questionable.

1. Introduction

Over the past ten years, ionic liquids (ILs) have emerged as possible alternative to volatile organic compounds that are used as solvents in various synthetic and pharmaceutical industries, owing to their environmentally benign nature and potential for use in a variety of areas.¹⁻³ Recently, room temperature ionic liquids (RTILs) are gaining recognition in nuclear reprocessing industry, as well, due to their attractive extraction properties and stability towards radiation.⁴⁻¹¹ Since ionic liquids comprise only of ions, they have negligible volatility, low flammability etc, which are the fundamental requirements for the solvent or diluent in industrial solvent extraction processes. Rogers and co-workers reported⁷⁻⁹ the possible application of ionic liquids as diluents for the separation of fission products and actinides from nuclear wastes.

They have employed crown ether diluted with 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) ionic liquids⁷ for extracting ⁹⁰Sr, ¹³⁷Cs, or actinide specific extractants diluted with bmim triflate imide ionic liquid for extracting *f*-block elements.^{8,9} They observed that, these extractants in conjunction with ILs displayed unusual extraction of target metals from aqueous solution under conditions that gave negligible or meager extraction with customary diluents such as chloroform or dodecane (DD). Chun et al. have studied¹⁰ the structural variation in 1-alkyl-3-methylimidazolium hexafluorophosphate (amimPF₆) ILs for investigating the variation in selectivity of 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 but selectivity increased. Recently^{12,13} we have also studied the extraction of uranium by TBP in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆). It was reported that bmimPF₆ as such extracts uranium and in contrast to the traditional extraction behavior exhibited by TBP/DD, the distribution ratios of uranium in 1.1 M TBP/bmimPF₆ continued to increase even above 5 M nitric acid. In addition, we have also investigated¹⁴ the extraction behavior by substituting octyl (omimPF₆) instead of butyl group in amimPF₆. It was found that the distribution ratios of uranium were similar in both the cases at all nitric acid concentrations. But, the solubility of omimPF₆ in aqueous

nitric acid phase was lowered by a factor of 2–3 as compared to bmimPF₆ and the viscosity of solutions of TBP/omimPF₆ was higher by ~2 fold as compared to TBP/bmimPF₆ solutions.

While the investigation of ionic liquids as diluents for reprocessing has produced encouraging results, the possible chemical and radiolytic degradation,⁶ mechanistic aspects of extraction¹⁵ are yet to be studied in detail. The major factor, which raises concern over the use of IL, is the chemical stability in aqueous medium. Various authors¹⁶⁻¹⁸ have studied the physicochemical and thermodynamic properties of amimPF₆. The solubility of bmimPF₆ in water has been reported to be 1.8 wt%. The solubility was found to decrease by lengthening alkyl chain attached to imidazole or by replacing the anion⁹ with other bulkier anions (e.g. triflate imide). Nevertheless, the physical and chemical properties of ionic liquids need to be investigated from the reprocessing point of view for meeting the qualities of diluent in solvent extraction processes when ILs are put into use.

This communication deals with some physical and chemical properties of the TBP/amimPF₆ that are essential for the qualifying as diluent in reprocessing. The properties such as organic phase density, viscosity, phase disengagement time, and chemical degradation of amimPF₆ and TBP/amimPF₆ were investigated. The results are compared with the data on TBP/DD.

2. Experimental

Materials: All the chemicals and reagents used in this study were of analytical grade. 1-Methylimidazole, 1-chlorobutane and hexafluorophosphoric acid were procured from Lancaster, UK. 1-Chlorooctane and tri-*n*-butylphosphate were obtained from E. Merck. 1-Methylimidazole was distilled before use and other chemicals were used without any purification.

Preparation of ionic liquid. Ionic liquid, 1-alkyl-3-methylimidazolium hexafluorophosphate (alkyl = butyl or octyl) was prepared by the procedure described elsewhere.¹⁹ Briefly, it involves refluxing 1-methylimidazole with 1-chloroalkane followed by reacting the product with hexafluorophosphoric acid.

Density and viscosity measurements. All the equilibration experiments were carried out at 298 K, in 1:1 phase ratio, unless otherwise mentioned. Ten milliliters of 1.1 M TBP/amimPF₆ was equilibrated with equal volume of aqueous phase of desired nitric acid concentration ranging from 0.1 to 8 M. After 10 minutes of vigorous shaking, the equilibration tube

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containing the phases was centrifuged. The organic/aqueous density was determined by transferring the organic/aqueous phase into 5 mL specific density bottle and measuring its weight using an electronic balance. The amount of water dissolved in ionic liquid phase was measured by Karl-Fischer titration. The viscosity of organic phase was measured using Brookfield viscometer (model D-II +) with a small sample adapter.

Phase disengagement. Phase disengagement time (PDT) was taken as the time taken for the disappearance of all the dispersed primary globules at the interface formed after a vigorous shaking of organic and aqueous phases. Typically, 5 mL of 1.1 M TBP/amimPF₆ was shaken vigorously with 5 mL of aqueous phase containing desired concentration of nitric acid ranging from 0.1 M to 8 M, in a 10 mm inner diameter, 20 mL stoppered test tube. The two phases were allowed to disengage and the time was measured using a stop-watch of 0.01 sec resolution.

Solubility of ionic liquids. The solubility of amimPF₆ in nitric acid phase was determined when neat amimPF₆ as well as 1.1 M TBP solutions in amimPF₆ were contacted with nitric acid solution of desired concentration ranging from 0.01 M to 8 M. The experiment involved vigorous shaking 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 ionic liquid in nitric acid phase was determined by measuring the absorbance of imidazolium cation present in the aqueous phase after appropriate dilution at the λ_{\max} of 289 nm using diluted nitric acid as reference. Base-line correction was performed with appropriately diluted nitric acid. The concentration of amim⁺ cation in the aqueous phase was calculated with the use of calibration plot obtained by measuring the absorbance of bmimCl (0.01–0.6 M prepared in water) and omimCl (0.01–0.2 M prepared in water) at the λ_{\max} of 289 nm using water as reference. The molar absorptivity of 2.2 L mol⁻¹ cm⁻¹ for bmimCl obtained by us is in good agreement with the value (2.2 L mol⁻¹ cm⁻¹) reported by Visser et al.⁷ and the molar absorptivity for omimCl was found to be 7.8 L mol⁻¹ cm⁻¹. Using this, the concentration of amimPF₆ dissolved into the aqueous phase was calculated. The concentration of phosphorous in the aqueous phase was determined by amidol method²⁰ after digesting an aqueous aliquot with perchloric acid.

3. Results and Discussion

Figure 1 represents the variation of organic phase density of 1.1 M TBP/amimPF₆ with initial concentration of nitric acid. It can be seen that the density of 1.1 M TBP/omimPF₆ decreased from 1.15 g/mL to 1.12 g/mL when the concentration of nitric acid was varied from 0.1 to 1 M and the decrease was not significant above 1M. Similarly the density of 1.1 M TBP/bmimPF₆ decreased from 1.25 g/mL to 1.20 g/mL when the concentra-

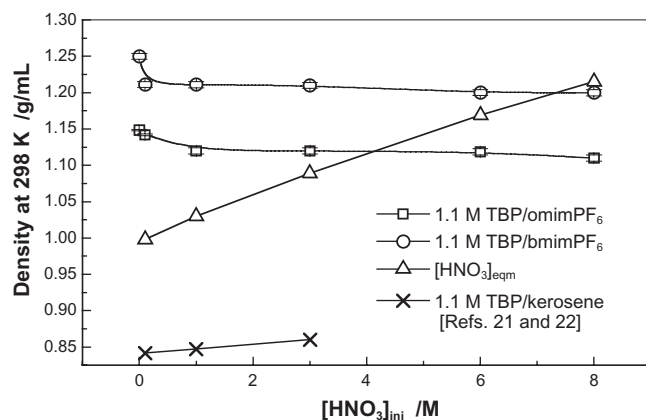


Figure 1. Variation in the density of organic and aqueous phases with initial concentration of nitric acid.

tion of nitric acid was varied from 0.1 M to 8 M. Contrary to this, in 1.1TBP/kerosene system,^{21,22} the density of organic phase was reported to increase from 0.8418 g/mL to 0.8601 g/mL, when the concentration of nitric acid was increased from 0.1 M to 3.0 M. It should be noted from Figure 1 that the densities of 1.1 M TBP/omimPF₆ and aqueous phase intersect at the initial nitric acid concentration of 4.1 M and thus the phase reversal is observed above 4.1 M. Similarly for 1.1 M TBP/bmimPF₆ phase, the phase reversal occurs at the later stage, i.e. at 7.1 M, since the initial density of organic phase is higher than 1.1 M TBP/omimPF₆. The occurrence of phase reversal is the major limiting factor for the application of ionic liquid in counter-current liquid-liquid extraction process. Mixer settler and pulse columns are designed with the assumption that the organic phase remains either on top or bottom phase all the time depending upon the density of aqueous phase. The decrease of density of organic phase with increase in the nitric acid concentration could be attributed to the extraction of water by the organic phase. Karl Fischer titration of organic phase indicated that nearly ~2 wt% and ~3.5 wt% of water was respectively extracted by 1.1 M TBP/omimPF₆ and 1.1 M TBP/bmimPF₆ phases at all nitric acid concentrations.

The viscosity of organic phase as a function of initial concentration of nitric acid is shown in Figure 2. It is apparent that viscosity decreases remarkably from 76 cP to 35 cP in the case of 1.1 M TBP/omimPF₆ when equilibrium aqueous nitric acid concentration is varied from 0.1 M to 8.0 M. But in 1.1 M TBP/bmimPF₆ (85 cP at 298 K) is lower compared to 1.1 M TBP/omimPF₆ (115 cP at 298 K), the variation is not much and it remains at ~36 cP at all concentrations of nitric acid. The presence of water in the organic phase seems to hydrate the ions and reduces the tendency of the ionic liquid species from aggregation, which results in lowering the viscosity of organic phase.²³ In 1.1 M TBP/DD the viscosity was reported^{21,22} to decrease marginally from 3.95 cP to 2.51 cP when the nitric acid concentration was varied from 0.1 M to 3.0 M.

Figure 3 shows PDT as a function of concentration of nitric acid. PDT is the time taken for the disappearance of all the dispersed primary globules at the interface formed during vigorous shaking. Rogoz and Kulawik²⁴ have reported for TBP-CCl₄ system, that PDT increased with increasing aqueous phase nitric acid concentration, but it decreased for paraffin and aromatic diluents. PDT was reported to vary from 30–70 s for TBP-HNO₃ system depending upon the concentration of nitric acid and choice of various diluents. From Figure 3 it can be observed that PDT for 1.1 M TBP/bmimPF₆ increases with increase in the equilibrium concentration of nitric acid. However, for TBP/omimPF₆, PDT increases gradually and reaches a maximum at the nitric acid concentration of 5.8 M followed by a decrease. When PDT was plotted against the difference in the densities of organic and aqueous phases, as

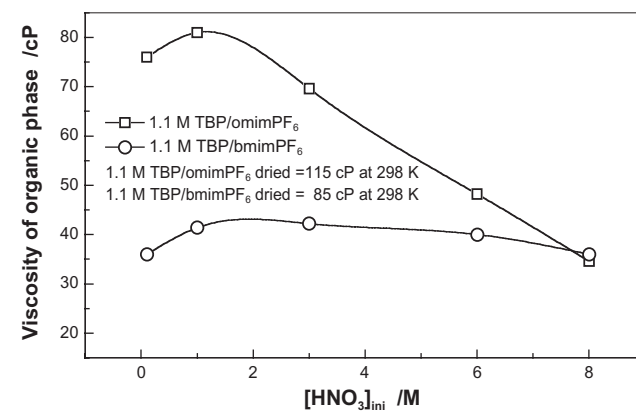


Figure 2. Variation of viscosity of organic phase with initial concentration of nitric acid at 298 K.

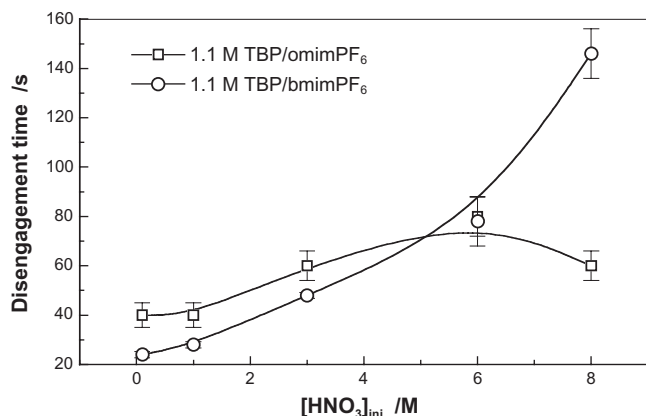


Figure 3. Variation of phase disengagement time with initial concentration of nitric acid.

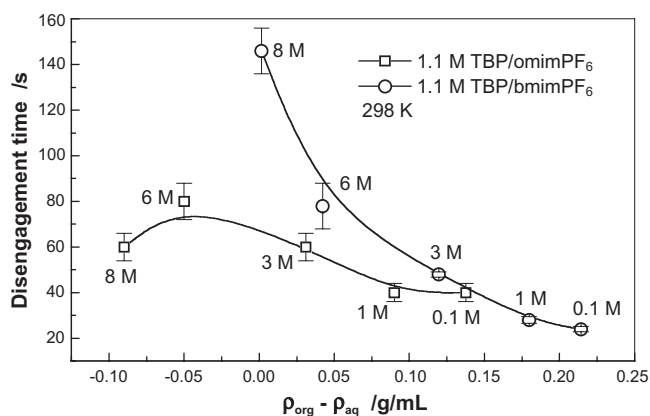


Figure 4. Variation in the difference of density of phases with disengagement time.

shown in Figure 4, it is evident that PDT approaches the maximum value when the $|\rho_{\text{org}} - \rho_{\text{aq}}| \rightarrow \text{zero}$. Thus, when the densities of organic and aqueous phases are similar, the time required for the disengagement is found to be longer as expected. However, apart from density, other factors such as interfacial surface tension of organic phase need to be taken into account for obtaining a good understanding of PDT.

Figure 5 shows the solubility of ionic liquid as a function of concentration of nitric acid. Measurement of solubility either by phosphorous analysis or absorbance of imidazolium cation gave identical result. The solubility of bmimPF₆ and omimPF₆ in 0.01 M nitric acid were found to be 1.9 wt% and 0.9 wt% respectively, which are in close agreement with the reported¹⁶⁻¹⁸ solubilities in water (2 wt% for bmimPF₆ and 0.7 wt% for omimPF₆). Solubility of both amimPF₆ ionic liquids increases with increase in the concentration of nitric acid and the presence of TBP in amimPF₆ enhanced the solubility of ionic liquid. It is noted that the solubility of omimPF₆ is lower by 2-3 times depending upon [HNO₃] as compared to bmimPF₆. Solubility of amimPF₆ in nitric acid media is a critical limiting factor for its application in reprocessing since the dissolved PF₆⁻ ion would react with nitric acid leading ultimately to the formation of phosphoric acid.⁸ Actinides form stable complex with phosphoric acid in aqueous phase and this would significantly affect the extraction and stripping behavior of actinides.

4. Conclusions

Physical properties of 1.1 M TBP diluted with non-traditional diluent 1-alkyl-3-methylimidazolium hexafluorophosphate, namely density, viscosity, PDT, and solubility in aqueous phase, have been reported in this communication. PDT of 1.1 M TBP/amimPF₆ is the only property which was found to be comparable with that of 1.1 M TBP/DD. Significant solubility

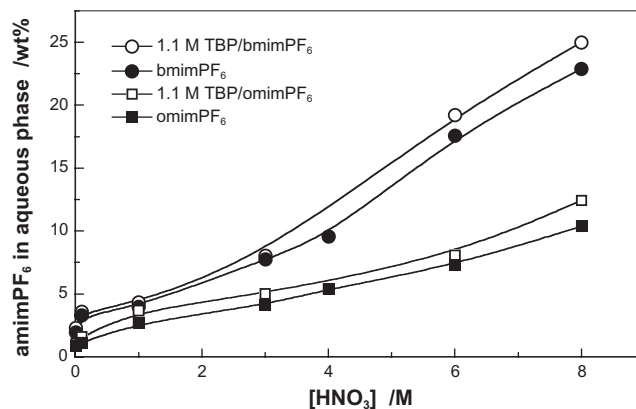


Figure 5. Comparison of ionic liquid solubility in aqueous phase at various nitric acid concentrations at 298 K.

of imidazolium hexafluorophosphate ILs in aqueous phase and phase reversal are very crucial limiting factors for their applicability in reprocessing. Increase in the length of the alkyl group attached to the imidazolium cation of IL decreases the solubility. However, in this case, there is still the limitation of early phase reversal and increased viscosity of organic phase. The studies carried out so far seem to indicate that the imidazolium hexafluorophosphate based RTILs poorly match *n*-dodecane as diluent from the reprocessing point of view and thus their applicability seems to be very limited.

However, ionic liquids have inscribed a beginning in reprocessing. Since the tunability, low volatility and incredible extraction characteristics of RTILs are very promising and going by the extensive research being carried out all over the world in recent years, it might yet be possible to discover other kind of ionic liquids that can have matching or even better properties than the conventional diluents.

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