

Extraction Behavior of Uranyl Ion From Nitric Acid Medium by TBP Extractant in Ionic Liquid

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In this study, extraction of uranium(VI) from an aqueous nitric acid solution was investigated using tri-n-butyl phosphate (TBP) as an extractant in an ionic liquid, 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide ($[C_n\text{mim}][\text{Tf}_2\text{N}]$). The distribution ratio of U(VI) in 1.1 M TBP/ $[C_n\text{mim}][\text{Tf}_2\text{N}]$ was significantly high when the concentration of nitric acid was low. The value of the distribution ratio decreased as the concentration of the nitric acid increased at lower acidities, and then increased with a nitric acid concentration of up to 8 M. This can be attributed to the different extraction mechanisms of U(VI) based on nitric acid concentrations. Thus, a cation exchange at low acidity levels and an ion-pair extraction at high acidity levels were suggested as the extraction mechanism of U(VI) in the TBP/ $[C_n\text{mim}][\text{Tf}_2\text{N}]$ system.

Keywords: Extraction, Uranium, TBP, Ionic liquid

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1. Introduction

Ionic Liquids (ILs) have attracted significant attention in various stages of nuclear fuel cycle. ILs are being evaluated as an alternative to the conventional diluent, n-dodecane (n-DD), in aqueous reprocessing and as a substitute to the traditional high-temperature molten salts in the non-aqueous reprocessing of spent nuclear fuels [1-5]. ILs are compounds composed fully of dissociated ions and melt at temperatures lower than 373 K [6, 7]. The reason why ILs attract attention is that they have several attractive properties suitable for aqueous and non-aqueous reprocessing applications. They have unique properties such as insignificant vapor pressure, a non-flammability, an amazing ability to dissolve organic and inorganic compounds, and a wide electrochemical window suitable for nuclear fuel cycle applications [8-10].

The solvent extraction technique is frequently used in the study of uranium separation, and TBP is the extractant for recovering uranium and plutonium from spent nuclear fuel in the PUREX (Plutonium URanium Reduction EXtraction) process [11]. There have been many reports on the extraction of U(VI) by TBP in combination with ILs as alternatives for conventional organic solvents such as n-DD or kerosene. Studies on the U(VI) extraction with ILs were mostly performed using imidazoiium based ILs. For instance, the extraction of U(VI) from nitric acid medium in a solution of TBP in $[C_4mim][PF_6]$ or $[C_4mim][Tf_2N]$ was reported [12]. A high extraction efficiency has been achieved using hydrophobic alkyl imidazole type ionic liquids as a diluent, such as 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nmim][PF_6]$, $n = 4, 6, 8$), combined with TBP for the extraction of U(VI) from a nitric acid medium [13, 14]. Wang [15] and Dietz [16] also studied the extraction of U(VI) from a nitric acid medium into $[C_4mim][Tf_2N]$ using TBP as the extractant.

The above studies indicate that, while the ILs are attractive alternatives to a conventional organic solvent, and they investigated the extraction mechanism of U(VI) in

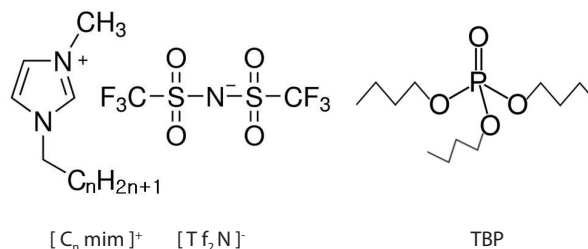


Fig. 1. Molecular structures of ionic liquid and extractant TBP.

TBP and ILs, further work is necessary to understand its extraction behavior. Therefore, the extraction behavior of Uranium(VI) from an aqueous nitric acid solution was investigated using TBP as an extractant in the ILs, $[C_nmim][Tf_2N]$ ($n = 2, 4, 6, 8$). This study was undertaken in order to examine the potential of hydrophobic ILs for uranyl (UO_2^{2+}) extraction from acidic water, and the aim was to establish the best extraction conditions and to obtain the basic data for the effective use of ILs for the solvent extraction of actinides. The effects of various parameters such as the kinetics of extraction, the concentration of nitric acid, and the alkyl chain length of ionic liquid on the distribution ratio of uranium were examined. Based on the experimental results, the extraction mechanism in the ILs system is discussed.

2. Experimental

2.1 Reagents and apparatus

All chemicals and reagents used in this study were of analytical grade and used without further purification. The molecular structure of the used ILs and extractant TBP is shown in Fig. 1. Ionic liquids, $[C_nmim][Tf_2N]$ ($n = 2, 4, 6, 8$) were procured from C-TRI, Korea. To remove the water and volatile impurities, the ILs were kept for more than 3 hours under a reduced pressure at 373 K, and the residual water concentrations measured using a Karl Fisher moisture content meter (Metrohm 831 KF Coulometer) were below 100 ppm. The uranyl nitrate was procured from Merck,

Table 1. Experimental parameters and conditions

Parameters	Conditions
Initial concentrations of uranyl ion in HNO ₃	5 g·L ⁻¹
Organic to aqueous phase ratio	1 : 1 (2 mL : 2 mL)
Equilibration time	1 hr
TBP concentration in ILs	0.2 ~ 1.1 M
HNO ₃ concentration	0.01 ~ 8 M

and TBP was obtained from Aldrich Chemical Company. Aqueous acid solutions were prepared using Milli-Q2 water and nitric acid. A stock solution of 100 g·L⁻¹ U(VI) was prepared by dissolving an appropriate amount of UO₂(NO₃)₂ in deionized water. The uranium solution used in the extraction experiment was diluted from a stock solution.

2.2 Extraction procedure

All extraction studies were carried out at room temperature (298 K) in duplicate. The experimental parameters and conditions of solvent extraction are shown in Table 1. The organic phase was equilibrated with the desired concentration of nitric acid. The initial concentration of uranium in an aqueous phase was fixed at 5 g·L⁻¹. A significant amount of nitric acid was also extracted by the organic phase, and the extraction of acid increases with the increase in nitric acid concentration in the aqueous phase. Therefore, the ionic liquid phase was pre-equilibrated with the desired concentration of nitric acid to fix the equilibrium acidity. The extraction of Uranium(VI) as a function of nitric acid concentration was performed by equilibrating the ionic liquid phase (2 mL) with the aqueous phase (2 mL) containing the uranium solution. The concentration of nitric acid was varied from 0.01 M to 8 M. After 1 hour of equilibration, the concentration of uranium in an aqueous phase was determined by a spectrophotometric method using arsenazo III as a coloring agent [17]. The concentration of uranium in the organic phase was calculated from the difference be-

tween the uranium ion concentration in the aqueous phase before and after extraction. The distribution ratio (D_U) and extraction efficiency were calculated using Eq. (1) and (2).

$$D_u = \frac{[U]_{aq,i} - [U]_{aq,f}}{[U]_{aq,f}} \quad (1)$$

$$\text{Extraction efficiency (\%)} = 100 D_U / (1 + D_U) \quad (2)$$

where $[U]_{aq,i}$ and $[U]_{aq,f}$ are the initial and final concentrations of uranium ions in the aqueous phases respectively.

3. Results and Discussion

3.1 Kinetics of extraction

The extraction kinetics is one of the important parameters in studies involving ionic liquids. This is evident from the fact that the viscosity of ionic liquid is usually high and hence the mass transfer is expected to be slower than that expected in commonly employed organic diluents such as n-DD and kerosene. To obtain information on the attainment of the extraction equilibrium of U(VI) in ILs, the extraction kinetics was investigated. The kinetics of U(VI) extraction was examined from a 2 M HNO₃ feed solution using 1.1 M TBP in ILs with an organic to aqueous volume ratio of 1. Fig. 2 shows the results in which the distribution coefficient of uranium ions is plotted as a function of shaking time between the two phases. Although there were some differences in the time required to attain equilibrium extraction, all ILs showed a relatively fast extraction equilibrium. The extraction of U(VI) could be completed within 20 min as shown in the figure. Hence, in subsequent extraction experiments, 1 h was selected as the shaking time, which was sufficient to attain the extraction equilibrium.

When ILs are used as diluents for the extraction of uranyl from nitric acid solutions, some amounts of nitric acid are also extracted by the organic phase [18]. Thus, the extraction of nitric acid by TBP and ILs was investigated in

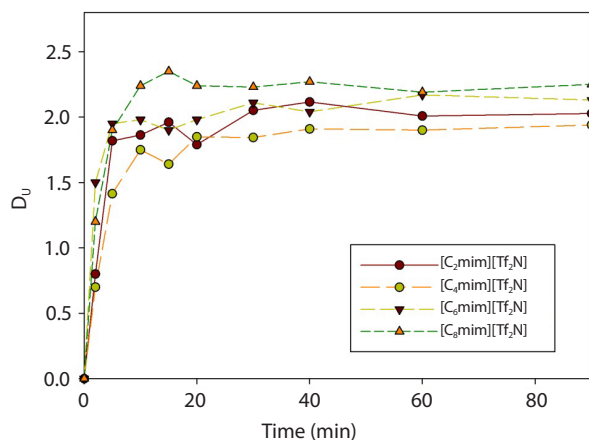


Fig. 2. Extraction kinetics of uranium from 1 M HNO₃ feed into 1.1 M TBP in ionic liquids.

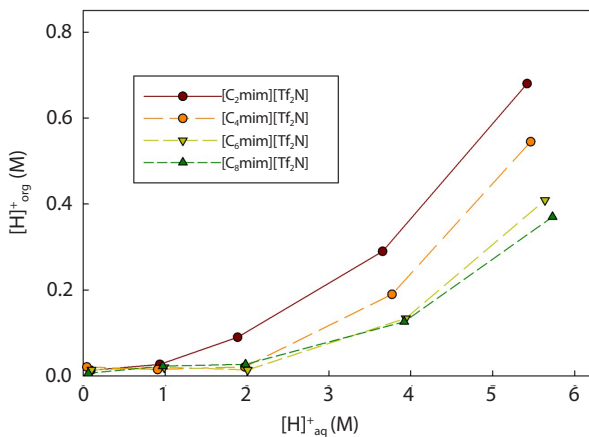


Fig. 3. HNO₃ acid extraction behavior in ionic liquids.

this study. The concentration of TBP was fixed at 1.1 M and the nitric acid concentration in the aqueous phase was varied from 0.01 to 6 M. After 1 h of equilibration between the two phases, the concentrations of nitric acid in the organic and aqueous phase were determined using acid-base titration with phenolphthalein as an indicator. The results of the extraction behavior of nitric acid in 1.1 M TBP/ILs are shown in Fig. 3. It can be seen that the extraction of nitric acid by the organic phase increases with an increase in the nitric acid concentration in the aqueous phase. In addition, the extraction of nitric acid increases with the decrease in the alkyl chain length of the cationic part of the ILs, which

is attributed to the hydrophobicity of the ILs. Hydrophobicity of an ionic liquid increases with an increase in the alkyl chain length [19], and the increase in distribution ratios with a decrease in the alkyl chain length in the cationic part of the ILs has been well reported [20].

3.2 Effect of aqueous phase acidity

The extraction behavior of U(VI) in the 1.1 M TBP/[C_nmim][Tf₂N] phase was studied under different nitric acid concentrations. Fig. 4 shows the distribution ratios of U(VI) as a function of nitric acid concentration. Similar observations have been reported for the extraction of U(VI) by TBP in various [C_nmim][Tf₂N] (n=4, 5, 8, 10) [16]. The D values are relatively high in 0.01 M nitric acid, followed by a gradual decline as the nitric acid concentration increases, and then increases gradually up to 8 M nitric acid. For the conventional organic solvents, n-alkanes, the extraction of uranium into each solvent rises with an increase in acid concentration, and variations in the hydrocarbon chain length of the alkane have little effect on the extraction of uranium at the given acidity. In contrast, as shown in Fig. 4, the acid dependency of uranium extraction into [C_nmim][Tf₂N] varies considerably as the nitric acid concentration is changed. Further, the alkyl chain length of the imidazolium cation also has an influence on the extraction of uranium. The distribution ratio increases with a decrease in the alkyl chain length from octyl to butyl cation, indicating that a shorter alkyl chain of [C_nmim]⁺ shows a higher distribution ratio. The dependencies for [C_nmim][Tf₂N] comprise two distinct regions; one, a lower acidity region below 1 M of HNO₃ in which increasing the acidity is accompanied by reducing the uranium extraction; and second, a higher acidity region above 1 M of HNO₃ in which uranium extraction increases with the nitric acid concentration. In the latter higher nitric acid concentration region, D values in four ILs which have a different hydrocarbon chain length of the cation are closely the same. The close correspondence of the uranium distribution ratios obtained in the four ILs

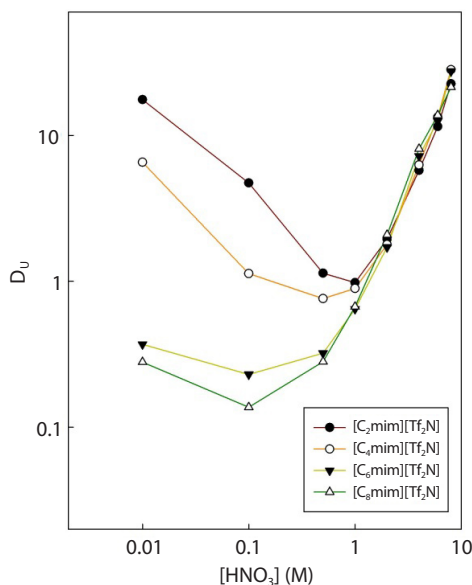


Fig. 4. Dependency of the uranium distribution ratio on HNO_3 concentration in 1.1 M TBP/[Cnmim][Tf_2N] ionic liquids.

in the latter region indicates that TBP extracts U(VI) into ILs through an ion-pair extraction [16, 21], i.e., a similar extraction mechanism as a conventional organic solvent system. For such type of mechanism, the concentration of nitrate ions plays a significant role, and thus the extraction increases with an increase in nitric acid concentration. On the other hand, in the lower nitric acid concentration region, the extraction of uranium ion does not seem to be influenced by the anionic species in the feed solution. D decreases with the nitric acid concentration, and decreases with the alkyl chain length of the cation of ionic liquids. The longer the alkyl chain lengths of the IL cations are, the more hydrophobic the IL cations [22] and the more difficult they are to be transported into aqueous phases through an ion exchange. D decreases as a function of $[\text{H}]^+$ upon the use of HNO_3 . This shows that no anions are involved in the extraction mechanism. The cation-exchange transfer was considered the most convincing extraction mechanism for this system. Thus, a cation-exchange extraction equilibrium equation was suggested for the lower acidity below 1 M of HNO_3 , and will be discussed further later.

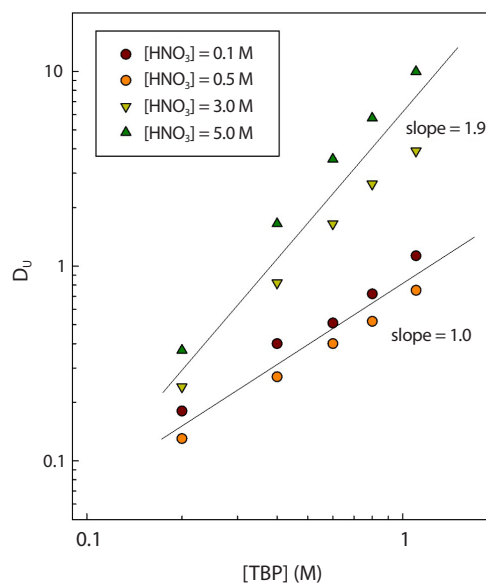


Fig. 5. Dependency of the uranium distribution ratio on TBP concentration in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ at several HNO_3 concentrations.

3.3 Mechanism of extraction

A slope analysis [16, 23] was used to derive the stoichiometry of the extracted species. A log-log plot of the D values versus $[\text{TBP}]$ provides an indication of the stoichiometry of the predominant species present in the form of the slope of the resulting linear relationship. The distribution ratios of U(VI) as a function of TBP concentration in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ phase are shown in Fig. 5. It can be seen that the D value increases with increasing TBP concentration. A slope of about 2 was obtained for the extraction of U(VI) from above 1 M concentrations of nitric acid, and a slope of 1 was obtained from below 1 M concentrations of nitric acid. This indicates that, for the nitric acid concentrations above 1 M, 2 molecules of TBP are involved in the uranium extraction and the extracted species is $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{TBP})_2$. On the other hand, for a nitric acid concentration below 1 M, 1 molecule is involved in the extraction of uranium and the extracted species is $\text{UO}_2 \cdot (\text{TBP})^{2+}$.

The acidities of the aqueous phases after extraction of U(VI) from nitric acid solutions were also measured by ac-

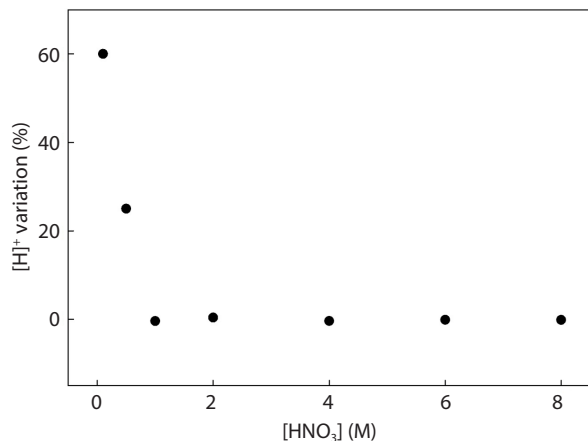


Fig. 6. [H]⁺ variation before and after extraction.

id-base titration under different nitric acid concentrations. The TBP concentration in [C₄mim][Tf₂N] was 1.1 M, and the nitric acid concentration varied from 0.1 to 8 M. Fig. 6 represents the variations of the acidity in the aqueous phase as a function of initial nitric acid concentration. As shown in the figure, the acidities of aqueous phases do not change when the initial nitric acid concentration is higher than 1 M. On the other hand, the acidities increase significantly when the initial nitric acid concentration is lower than 1 M. This result indicates that [H]⁺ in the organic phase is transferred into the aqueous phase when the initial nitric acid concentration of the aqueous phase is below 1 M. Nitric acid dissolves easily in [C₄mim][Tf₂N] [24] and large amounts of acid are readily transferred to the IL phase during the pre-equilibration stage of the extraction experiments. Nitric acid extracted by the IL phase provides large quantities of [H]⁺, and are likely to be backward extracted to counterbalance the U(VI) extraction.

Based on the distribution behavior and stoichiometry determination analyses, the mechanism for the uranium extraction was suggested as follows. The mode of uranium ion distribution in the TBP/[C₄mim][Tf₂N] phase changes from cation-exchange to the ion-pair extraction with the increase in nitric acid concentration in the aqueous phase. For a nitric acid concentration higher than 1 M, an ion-pair extraction mechanism is proposed. Thus, two molecules of

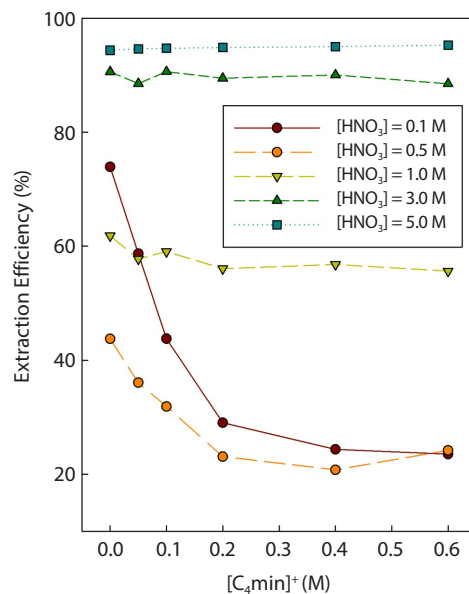


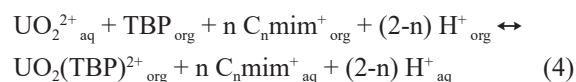
Fig. 7. Influence of [C₄mim]⁺ on the extraction efficiency.

nitrate and TBP form a complex with uranyl ion in an organic phase, and this resembles that of the TBP/n-DD system. In addition, for a nitric acid concentration lower than 1 M, the cation-exchange mechanism involving both [H]⁺ and [C₄mim]⁺ is proposed.

- Ion-pair extraction mechanism, for [HNO₃] > 1 M:



- Cation-exchange mechanism, for [HNO₃] < 1 M:



For the cation-exchange mechanism to be valid, the D values should decrease with an increase in the concentration of [C_nmim]⁺ ions in the aqueous phase based on the equilibrium shift. To ascertain the proposed mechanism, distribution studies of uranium were carried out by adding [C₄mim][Cl] to an aqueous phase as a source of [C₄mim]⁺, and the results are shown in Fig. 7. As shown in this figure, the transfer of uranium into [C₄mim][Tf₂N] at a nitric acid concentration higher than 1 M was independent of the

$[C_4mim]^+$ concentration, whereas the extraction of uranium at a nitric acid concentration lower than 1 M was gradually reduced with an increase in the $[C_4mim]^+$ concentration. These data suggest that the transfer of uranium with TBP into ILs at lower acidities proceeds through a cation-exchange mechanism, as represented through Eq. (4).

4. Conclusion

The extraction behavior of U(VI) by TBP dissolved in $[C_nmim][Tf_2N]$ was studied. The distribution ratio of U(VI) was measured as a function of various parameters such as the concentrations of nitric acid and TBP. In contrast with the extraction behavior observed for a conventional system, the distribution ratio of U(VI) was fairly high when the concentration of nitric acid was low. D values decreased as the nitric acid concentration increased at lower acidities, and then increased with the nitric acid concentration. These can be attributed to different extraction mechanisms of U(VI) depending on the nitric acid concentrations, and the results suggest that the U(VI) extraction mechanism in 1.1 M TBP/ $[C_nmim][Tf_2N]$ changes from a cationic exchange at low acidities to extraction of the neutral species (ion-pair extraction) at high acidities.

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