

Solvent extraction of Pu(IV) with TODGA in C₆mimTf₂N

Xiaohong Huang · Qiuyue Zhang · Jinping Liu ·
Hui He · Wenbin Zhu · Xiaorong Wang

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Abstract Studies on the solvent extraction of Plutonium (Pu(IV)) from aqueous nitric acid by *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA) in 1-hexyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (C₆mimTf₂N) room temperature ionic liquid (RTIL) were carried out. It was found that Pu(IV) is extracted into RTIL phase as [Pu(NO₃)(TODGA)]³⁺ through cation exchange mechanism. Extraction reaction equation is obtained by the influence of acidity and extractant concentration, and the parameters of thermodynamic equilibrium constant was calculated.

Keywords Solvent extraction · Plutonium(IV) · TODGA · C₆mimTf₂N

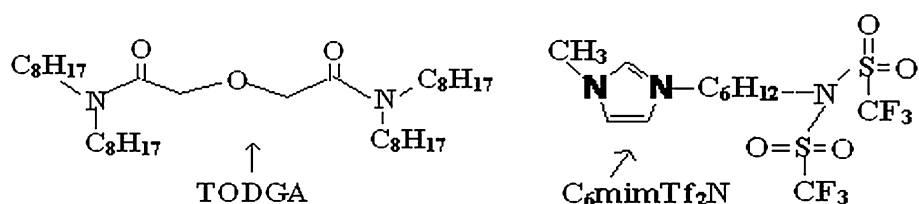
Introduction

Recently, room temperature ionic liquids (RTILs), especially these containing alkylimidazolium cations, such as 1-hexyl-3-methylimidazolium bis(trifluoromethyl)sulphonyl-imide (C₆mimTf₂N) have received increasing attentions as next generation diluents for extractions in nuclear fuel reprocessing. A result of their unique physical and chemical properties [1, 2]. A preliminary assessment showed that the relative viscosity of 1-octyl-3-methylimidazolium bis(trifluoromethyl)sulphonyl-imide C₈mimTf₂N ionic liquid is larger than C₆mimTf₂N ionic liquid [3]. Moreover the extractive ability of C₆mimTf₂N to Pu(IV) is higher

than 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulphonyl-imide (C₄mimTf₂N) ionic liquid [2]. Based on the possible stability towards radiation according to the previous research [4], RTILs are expected to be used in the reprocessing of spent fuel as diluent or extractant [5, 6]. There is big difference between the extraction behavior of metal ions in ionic liquid and that in the molecular organic solvent system. Thus, it is necessary to investigate the solvent extraction of lanthanides and actinides in water/RTIL system. Moreover there are many research reports about the extraction of actinides, lanthanides and strontium (Sr), cesium (Cs) by tri-butyl-phosphate (TBP)/*n*-octyl (phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO)/crown ether, using ionic liquid C_{*n*}mimTf₂N (*n* = 4, 6, 8) as the diluent [1, 7–10]. In comparison, the extraction ratio of one metal ion by TBP is slow, the solubility of CMPO in ionic liquid is low, crown ether is usually used to extract Sr and Cs. TODGA (Fig. 1) as a class of actinides novel extractant, synthesis is simple, low cost, resistance to radiation, not easy hydrolysis, degradation products do not affect the extraction process and overcomes the shortcoming of solubility low compared with CMPO in RTILs [11–19]. Solvent extraction studies on lanthanides and actinides from aqueous solutions suggest that TODGA dissolved in kerosene greatly enhances the extractability of lanthanides and actinides [17–23]. While at the same experimental condition of americium (Am(III)) and europium (Eu(III)), plutonium exists as Pu(IV), which is the reason for the extraction study of Pu(IV) by TODGA because no research is reported in this area. Here, we chose a hydrophobic ionic liquid—C₆mimTf₂N (Fig. 1) as a diluent, using TODGA for the solvent extraction studies of Pu(IV) in the present work for accumulating the basic data for the effective use of this type of RTILs for the solvent extraction of actinides.

X. Huang · Q. Zhang · J. Liu · H. He (✉) · W. Zhu · X. Wang
Department of Radiochemistry, China Institute of Atomic
Energy, Beijing 102413, People's Republic of China
e-mail: hehui@ciae.ac.cn

Fig. 1 Structure of TODGA and $C_6\text{mimTf}_2\text{N}$

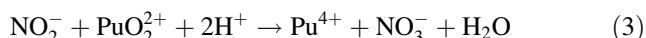
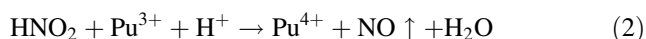


Experimental

Reagents and instruments

All chemicals were reagent grade or higher. The TODGA was synthesized in our laboratory with a purity over 98 %. $C_6\text{mimTf}_2\text{N}$ was synthesized and purified according to the method described in paper [24] and its purity was >99 % checked with [1] H and [13] C NMR spectral data, TLC, and mass spectrometry.

Stock solution of [9, 23] Pu was purified with 256×4 pyridine-type resin (the length of the column is 350 mm, with the diameter 6 mm) through adsorption in 8 M HNO_3 solution and eluate in 0.5 M HNO_3 , and purity was measured by alpha spectrometry. Pu in 0.5–1 M HNO_3 was adjusted to Pu(IV) by using liquid N_2O_4 . Required amount of Pu (about 10 $\mu\text{g}/\text{mL}$) was transferred into the equilibration tube containing aqueous phase and its valency was adjusted to Pu(IV) by N_2O_4 liquid. Because in nitric acid solution, the main valence state of plutonium includes III, IV and VI. N_2O_4 oxidizes Pu(III) to Pu(IV) and reduces Pu(VI) to Pu(IV), so it can be used for the valence adjustment of plutonium as Pu(IV), which can be proved by the extraction of TTA/xylene and then measured by the α spectrometry. Reaction equations as follows:



TODGA in RTILs, were equilibrated with the given concentration of HNO_3 three times before the extraction of Pu(IV) in the same concentration of HNO_3 .

An LS-600LL liquid scintillation counter. (Shichema, Japan) was used to measure the concentration of Pu(IV).

Procedure

Equal volumes of ionic liquids containing TODGA and aqueous nitric acid solution containing Pu(IV) were vortexed for a certain time and equilibrated in a shaker bath at required temperature. The mixed solutions were then centrifuged for phase separation, aliquots from both phases were withdrawn for liquid scintillation counting. At 293.15 K, the density of $C_6\text{mimTf}_2\text{N}$ ionic liquid is 1.3

times larger than that of water. The viscosity and the density of TODGA are larger than those of water also [3]. Thus the aqueous phase is at upper position of the solution. From activities of Pu(IV) in initial solution and that of in raffinate, the distribution ratio (D) is calculated as follows:

$$D = \frac{M_{\text{total}} - M_{\text{remainder/aq}}}{M_{\text{remainder/aq}}}$$

where M_{total} stands for the total concentration of M , namely the metal added and $M_{\text{remainder/aq}}$ means the concentration of M remained in aqueous phase.

The distribution ratio was measured repeatedly over a period of time until it reaches equilibrium. All the measurements were done in duplicate and D values obtained were within $\pm 5\%$ with good material balance (≥ 95).

Results and discussion

The effect of extraction time

0.1 mol/L TODGA/ $C_6\text{mimTf}_2\text{N}$ were selected to extract HNO_3 and tracer amount of Pu(IV) in the aqueous phase in which the HNO_3 concentration was 0.988 and 3.93 mol/L respectively. The effect of extraction time on the extraction at different conditions were shown in the Fig. 2. The equilibrium was established after 1 min of contact. For the sake of reaching efficient equilibrium, the distribution ratio were all measured after 10 min of vortexing.

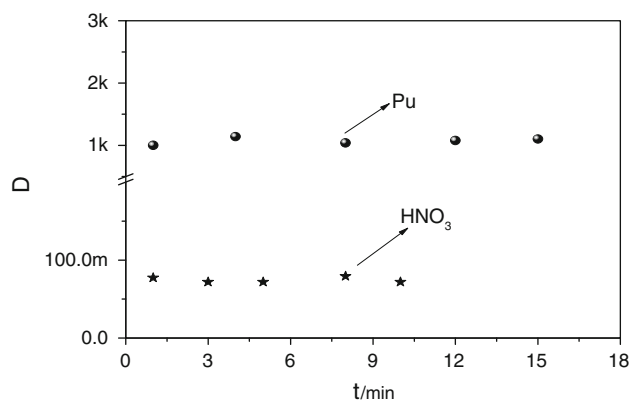


Fig. 2 Equilibrium time of HNO_3 and Pu(IV). Organic phase 0.1 M TODGA/ $C_6\text{mimTf}_2\text{N}$, Aqueous phase 0.988 M HNO_3 (HNO_3) and Trace amount Pu(IV) 3.93 M HNO_3 respectively

Effect of HNO₃ concentration on $D_{(\text{HNO}_3)}$ and $D_{\text{Pu(IV)}}$

Figure 3 gives distribution ratios of HNO₃ as a function of [HNO₃] at 0.1 M TODGA/C₆mimTf₂N. $D_{(\text{HNO}_3)}$ remains almost <0.15 with 0.34 M up to 7.5 M HNO₃. At nitric acid concentration higher than 1.8 M, the $D_{(\text{HNO}_3)}$ values increased with increase of nitric acid concentration.

Figure 4 gives the plot of distribution ratios of Pu(IV) as a function of [HNO₃] at 0.1 M TODGA/C₆mimTf₂N and 0.1 M TODGA/*n*-dodecane. The results indicate that the distribution ratio of Pu(IV) in ionic liquid is much higher than that of in the system of *n*-dodecane.

Figure 5 displays log–log plot of distribution ratios of Pu(IV) as a function of [HNO₃] at 0.1 M TODGA–C₆mimTf₂N. From the slope of the plot in Fig. 5, it can be seen that in the acidity range studied, the slope of 0.85 close to 1, which suggests that the molar ratio of NO₃[−] and Pu(IV) in the complex is 1:1, the stoichiometry of the

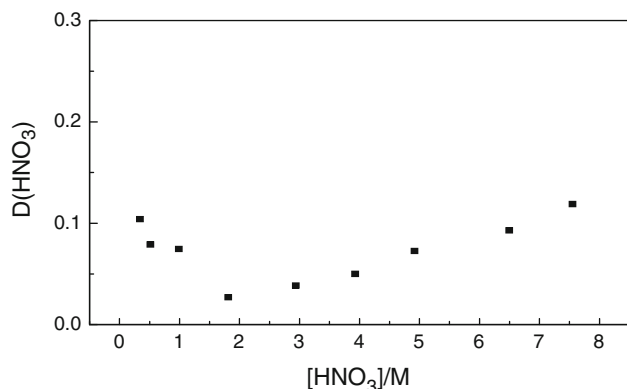


Fig. 3 Dependence of distribution ratios of HNO₃ versus HNO₃ concentration. *Organic phase* 0.1 M TODGA/C₆mimTf₂N, *Aqueous phase* HNO₃

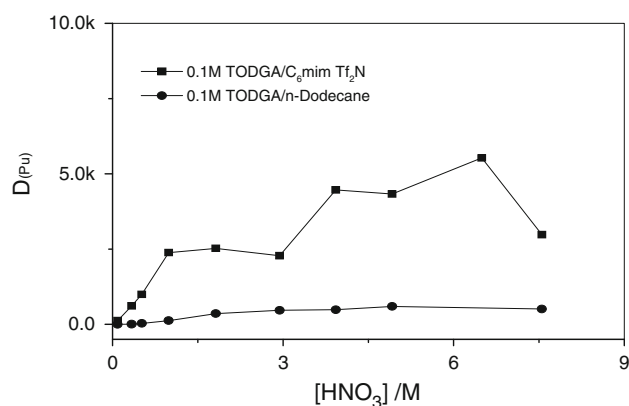


Fig. 4 Dependence of distribution ratios of Pu versus HNO₃ concentration. *Organic phase* 0.1 M TODGA/C₆mimTf₂N, 0.1 M TODGA/*n*-dodecane respectively. *Aqueous phase* trace amount Pu(IV) + HNO₃

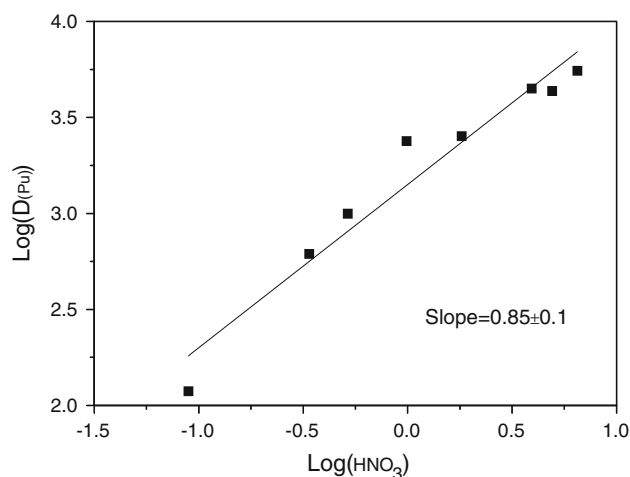
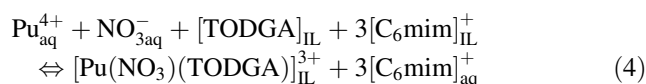


Fig. 5 Dependence of distribution ratios of Pu(IV) on HNO₃ concentration. *Organic phase* 0.1 M TODGA/C₆mimTf₂N, *Aqueous phase* trace amount Pu(IV) + HNO₃

cationic complex transferred into the IL phase is [Pu(NO₃)(TODGA)_x]³⁺.

Extraction mechanism

Figures 6, 7, 8 and 9 show plots of distribution ratios of Pu(IV) in C₆mimTf₂N as a function of TODGA concentration at different concentration of HNO₃. The results show that the slopes of log($D_{\text{Pu(IV)}}$) vs log([TODGA]) change from 0.8 to 1.09, which can be considered as 1 approximately. Therefore, in the aqueous acidity studied, the extraction reaction equation can be written as follows:



The equilibrium constant can be expressed as [25, 26]:

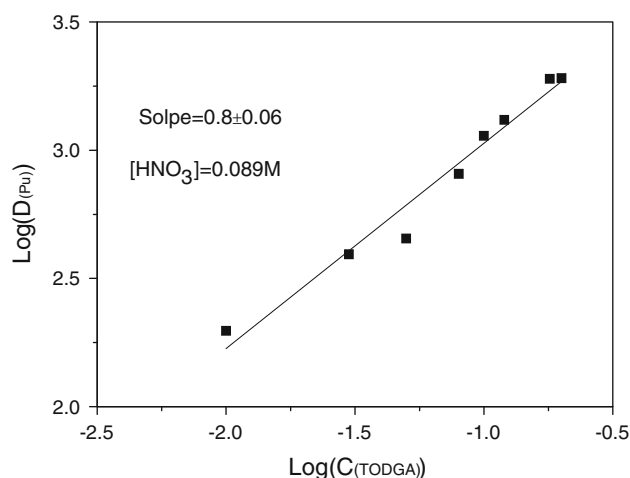


Fig. 6 TODGA dependency of distribution ratios of Pu(IV) in C₆mimTf₂N. *Organic phase* 0.1 M TODGA/C₆mimTf₂N, *Aqueous phase* trace amount Pu(IV) + 0.089 M HNO₃

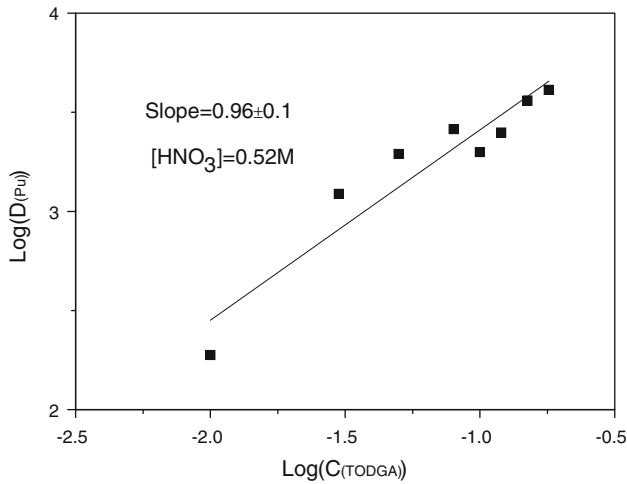


Fig. 7 TODGA dependency of distribution ratios of Pu(IV) in $C_6\text{mimTf}_2\text{N}$. Organic phase 0.1 M TODGA/ $C_6\text{mimTf}_2\text{N}$, Aqueous phase trace amount Pu(IV) + 0.52 M HNO_3

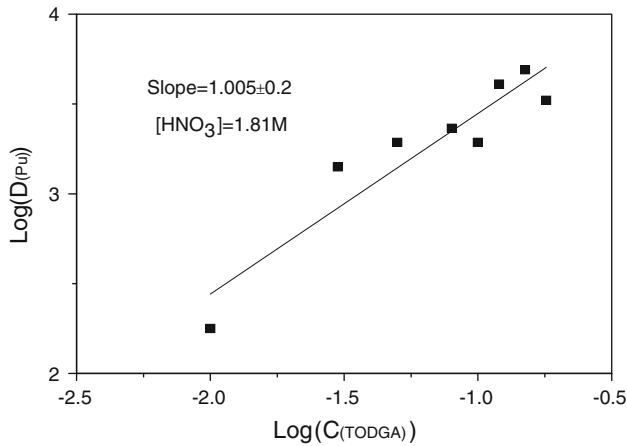


Fig. 8 TODGA dependency of distribution ratios of Pu(IV) in $C_6\text{mimTf}_2\text{N}$. Organic phase 0.1 M TODGA/ $C_6\text{mimTf}_2\text{N}$, Aqueous phase trace amount Pu(IV) + 1.81 M HNO_3

$$\beta = \frac{\{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}\}}{[\text{Pu}^{4+}][\text{NO}_3^-][\text{TODGA}]} \cdot \frac{f_{\{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}\}}}{f_{[\text{Pu}^{4+}]}\cdot f_{[\text{NO}_3^-]}\cdot f_{[\text{TODGA}]}} \quad (5)$$

here, $[M]$ represents molar concentration (mol/L), and $f_{[M]}$ means the activity coefficient. According to the theory of Debye–Hückel [27], as a first approximation, the activity coefficient of dilute solution is correlative with ionic strength only. When the concentration of individual ion is moderate, Davies equation can be used for the calculation of activity coefficients, which can be written as follows:

$$-\log f_{z\pm} = AZ^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right] \quad (6)$$

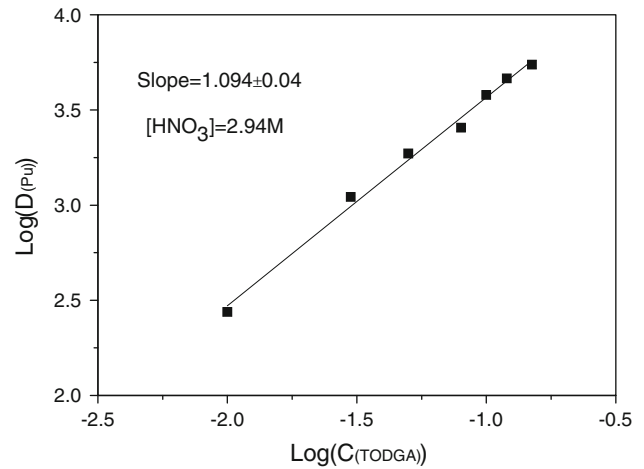


Fig. 9 TODGA dependency of distribution ratios of Pu(IV) in $C_6\text{mimTf}_2\text{N}$. Organic phase 0.1 M TODGA/ $C_6\text{mimTf}_2\text{N}$, Aqueous phase trace amount Pu(IV) + 2.94 M HNO_3

$$I = 0.5 \times (C_1Z_1^2 + C_2Z_2^2 + C_3Z_3^2 + \dots) = 0.5 \times \sum C_iZ_i^2 \quad (7)$$

here I is the ionic strength in molality, C is the molar concentration of ion in mol/L and Z is the charge of it. As for aqueous solution, the constant A is 0.509 at room temperature and about 0.52 at the temperature of $(28 \pm 0.5)^\circ\text{C}$. Nitric acid solution of 0.988 M, with the Pu(IV) concentration 5.8×10^{-8} M, I is calculated as follows:

$$I = 0.5 \times (0.988 \times 1^2 + 0.988 \times 1^2 + 5.8 \times 10^{-8} \times 4^2) = 0.988$$

so we get

$$-\log f_{z\pm} = 0.52 \times Z^2 \times (0.4985 - 0.1976) = 0.156Z^2$$

$$f_{[\text{NO}_3^-]} = 10^{-0.156}, f_{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}} = 10^{-0.156 \times 9}, f_{[\text{TODGA}]} = 1, f_{[\text{Pu}^{4+}]} = 10^{-0.156 \times 16}$$

$$\text{And the activity coefficient } f = \frac{f_{\{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}\}}}{f_{[\text{Pu}^{4+}]}\cdot f_{[\text{NO}_3^-]}\cdot f_{[\text{TODGA}]}} = 17.701.$$

In general, K can be represented as

$$K = \frac{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}}{[\text{Pu}^{4+}][\text{NO}_3^-][\text{TODGA}]} \quad (8)$$

here K is the equilibrium constant. Pu(IV) in aqueous solution exists as $\text{Pu}(\text{NO}_3)^{3+}$, $\text{Pu}(\text{NO}_3)_2^{2+}$ etc. If C_{Pu} is the total concentration of plutonium in the aqueous phase and β_1 is the stepwise formation constant between Pu(IV) and NO_3^- , C_{Pu} can be expressed as

$$C_{\text{Pu}} = [\text{Pu}^{4+}] \left(1 + \sum \beta_1 [\text{NO}_3^-]^1 \right)$$

Table 1 TODGA dependency of equilibrium constant and thermodynamic equilibrium constant

[TODGA] M	$D - D_0$	$\log K$	K	β
0.01	6.49×10^2	5.24	1.74×10^5	3.09×10^6
0.05	1.18×10^3	4.80	6.34×10^4	1.12×10^6
0.08	1.87×10^3	4.80	6.29×10^4	1.11×10^6
0.1	3.70×10^3	5.00	9.95×10^4	1.76×10^6
0.12	4.20×10^3	4.97	9.41×10^4	1.67×10^6

So the Eq. (8) can be written

$$K = \frac{\{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}\} (1 + \sum \beta_1 [\text{NO}_3^-]^1)}{C_{\text{Pu}} [\text{NO}_3^-] [\text{TODGA}]} \quad (9)$$

The distribution ratio:

$$D = \frac{\{[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}\}}{C_{\text{Pu}}} \quad (10)$$

Inserting (10) into (9) gives

$$K = \frac{(D - D_0)(1 + \sum \beta_1 [\text{NO}_3^-]^1)}{[\text{NO}_3^-] [\text{TODGA}]} \quad (11)$$

where D and D_0 denote the distribution ratios of Pu(IV) in organic phase of TODGA–RTIL and RTIL, respectively.

$(1 + \sum \beta_1 [\text{NO}_3^-]^1)$ is 2.69 ± 0.14 in 1 M $[\text{HNO}_3]$, which was taken from the literature [20]. So, we obtain

$$K = \frac{2.69 \times (D - D_0)}{[\text{NO}_3^-] [\text{TODGA}]}$$

and

$$\log K = 0.43 + \log(D - D_0) - \log[\text{NO}_3^-] - \log[\text{TODGA}]$$

According to the D values obtained at $(28 \pm 0.5)^\circ\text{C}$ and 1 M $[\text{HNO}_3]$, the $\log K$ and β values are determined as described in Table 1

In general, the solubility of the neutral complex in aqueous solution is far less than that of in organic solvents due to the polarity. Thus, the neutral complex is easy to be extracted into the organic solvents, while the charged complex is difficult to be transferred into organic phase. For example, the uranium and plutonium are extracted into TBP/OK in the Purex process. However, ionic liquid is a very strong polar organic solvent, which means that the charged complex extracted should be larger for ionic compounds than the neutral complex. The above results are accordable completely with this basis theory [28].

Conclusion

In the range of experimental conditions, the extraction percentage of Pu(IV) is more than 99 % in 0.1 M TODGA/

$\text{C}_6\text{mimTf}_2\text{N}$. Through cation exchange mechanism, Pu(IV) is extracted into RTIL phase, as $[\text{Pu}(\text{NO}_3)(\text{TODGA})]^{3+}$. Extraction reaction equation is obtained by the influence of acidity and extractant concentration, and the parameters of thermodynamic equilibrium constant is calculated.

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