(*Wuli Huaxue Xuebao*)
Acta Phys. -*Chim. Sin.* **2015,** *31* (5),

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Uranium; Ionic liquid; Extraction third phase; Extraction selectivity; Extraction mechanism

. , , . , , .[1–3] (Purex) , . , . , .

, [3,4] CO_2[2] [5] .

.[6–14] , , . .[15–32] Giridhar [15,16] (TBP) $C_4mimNTf_2$ C_4mimPF_6 UO_2^{2+} , $C_4mimNTf_2$, . Dietz [17] $C_nmimNTf_2$ (n= , 8, 10) TBP UO_2^{2+} , , , . Wang [18] TBP $C_4mimNTf_2$ UO_2^{2+}, [2] , CO_2 UO_2^{2+} $UO_2(TBP)_2(NO_3)_2$. Visser [19,20] -N,N- (CMPO) C_4mimPF_6 $C_8mimNTf_2$, X (EXAFS) UO_2^{2+} , $UO_2(NO_3)_2(CMPO)_2$, , $UO_2(NO_3)(CMPO)^+$. Cocalia [21] (2,4,4-) (2-) (HDEHP) $C_{10}mimNTf_2$ UO_2^{2+} Am^{3+} , UO_2^{2+} , Am^{3+} . Shen[22] Rout[23] $C_nmimNTf_2$ C_nmimPF_6 UO_2^{2+} Th^{4+} Pu^{4+} Am^{3+} , .

(TBPO) , , $UO_2(NO_3)_2$. , UO_2^{2+} , .

$C_nmimNTf_2$ 1- -3- (C_nmimBr) ($LiNTf_2$) .[1] C_nmimBr $LiNTf_2$, 99%. TOPO Aldrich , 99%. TBPO , 98%. $UO_2(NO_3)_2\cdot 6H_2O$ Chemapol, 98.5%. .

$Sr(NO_3)_2$, $CsNO_3$, $ZrOCl_2\cdot 8H_2O$, $Cr(NO_3)_3\cdot 9H_2O$, NH_4ReO_4, $Ru(NO)(NO_3)_3$, $Ni(NO_3)_2\cdot 6H_2O$, $Nd(NO_3)_3\cdot 6H_2O$ (1). UO_3 $UO_2(NO_3)_2$, $UO_2(ClO_4)_2$ UO_3 $HClO_4$.

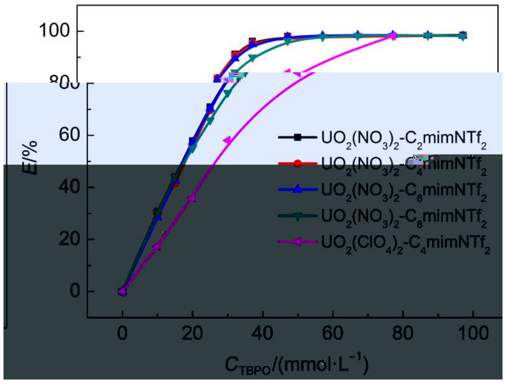
UO_2^{2+} - (ICP-AES, Leeman, USA) . NO_3^- Dionex model ICS-900 (Dionex Corporation, USA) , Chrome-

1 UO_2^{2+} (SLW)[11]

Table 1 Compositions of simulated liquid waste (SLW) used in the selective extraction experiment of UO_2^{2+}[11]

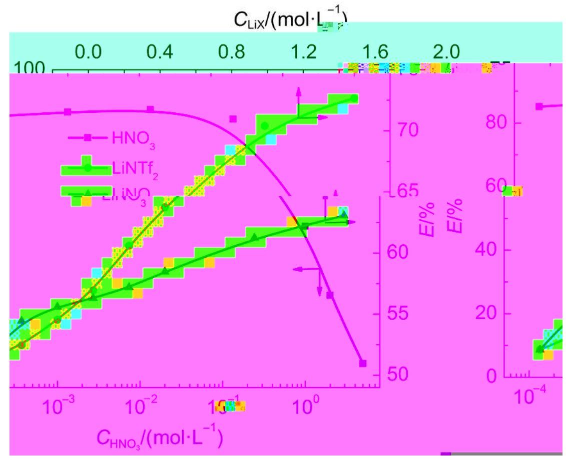
Element	$C/(g\cdot dm^{-3})$	Element	$C/(g\cdot dm^{-3})$
Sr	0.54	Ru	0.38
Cs	0.54	Ni	0.17
Zr	0.68	Nd	1.00
Cr	0.34	U	2.38
Re	0.15		

leon 7.0 . U-3010 (HITA-
CHI, Japan) - .
(CEM, USA)



1 TBPO $C_n$mimNTf$_2$ (n=2, 4, 6, 8) 10 mmol·L^{-1} $UO_2(NO_3)_2$ C_4mimNTf$_2$ 10 mmol·L^{-1} $UO_2(ClO_4)_2$ (E)

Fig.1 Dependence of the extraction efficiency (E) of 10 mmol·L^{-1} $UO_2(NO_3)_2$ in $C_n$mimNTf$_2$ (n=2, 4, 6, 8) and 10 mmol·L^{-1} $UO_2(ClO_4)_2$ in C_4mimNTf$_2$ on the concentration of TBPO



2 TBPO C_4mimNTf$_2$ 10 mmol·L^{-1} $UO_2(NO_3)_2$

Fig.2 Dependence of the extraction efficiency of 10 mmol·L^{-1} $UO_2(NO_3)_2$ by TBPO-C_4mimNTf$_2$ on the concentration of HNO$_3$ and salts in the aqueous phase

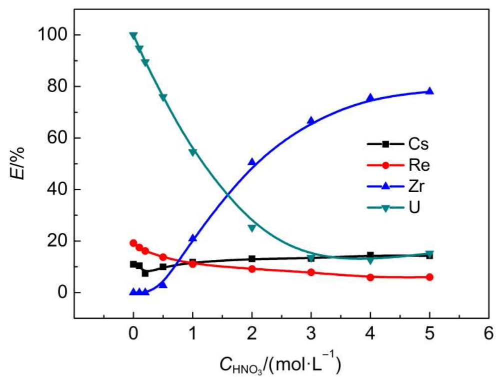
, .
TBPO ($C_n$mimNTf$_2$)
$UO_2(NO_3)_2$,
. TBPO $C_n$mimNTf$_2$,
$UO_2(NO_3)_2$.
$C_n$mimNTf$_2$, ,
. , NO_3^-
,
. TBPO
$C_n$mimNTf$_2$ $UO_2(NO_3)_2$
. TOPO $C_n$mimNTf$_2$ $UO_2(NO_3)_2$
, $C_n$mimNTf$_2$
( ).

2 TBPO C_4mimNTf$_2$ $UO_2(NO_3)_2$
. 2 ,
HNO$_3$ 0.1 mol·L^{-1} ,
85% , HNO$_3$ 0.1 mol·L^{-1} ,
. HNO$_3$
$UO_2(NO_3)_2$.
, HNO$_3$
.[33] , HNO$_3$
.
TBPO ,
. 2 ,
LiNTf$_2$.
TBPO C_4mimNTf$_2$ $UO_2(NO_3)_2$

( ).

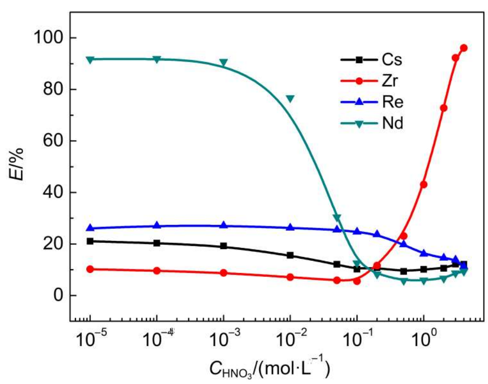
UO_2^{2+} . TBPO-C_4mimNTf$_2$
,
. U Cs Re Zr Nd
Sr Cr Ru Ni 9 . , Sr Cs
, Re Tc , Nd
. TBPO-C_4mimNTf$_2$
, U Cs Re Zr
, 0–5 mol·L^{-1}
. 3 ,
1 mol·L^{-1} U, ,
Re Cs , Zr
, U .
TBPO-C_4mimNTf$_2$ U
HNO$_3$ 1 mol·L^{-1} . U
, TBPO-C_4mimNTf$_2$
,
Nd (4), . U
, Zr Nd
.
U ,
,
.

3.5.1



3 HNO_3 TBPO (40 mmol·L^{-1})-$C_4mimNTf_2$

Fig.3 Dependence of the extraction efficiency of SLW by TBPO (40 mmol·L^{-1})-$C_4mimNTf_2$ on the concentration of HNO_3



4 HNO_3 TBPO (150 mmol·L^{-1})-$C_4mimNTf_2$ UO_2^{2+} (U)

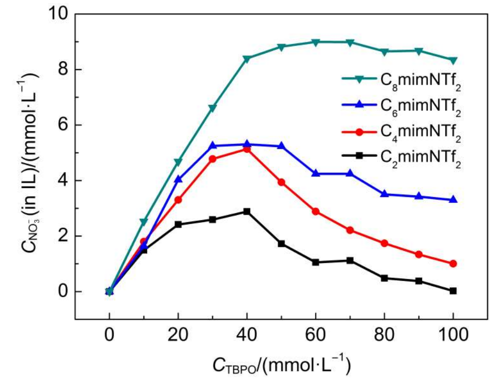
Fig.4 Dependence of the extraction efficiency of SLW (without U) by TBPO (150 mmol·L^{-1})-$C_4mimNTf_2$ on the concentration of HNO_3

NO_3 TBPO $C_4mimNTf_2$ $UO_2(NO_3)_2$. NO_3^- ,

$C_n$mimNTf$_2$ (n=2, 4, 6, 8) NO_3^-

. 5 $UO_2(NO_3)_2$ (pH=3.3), , NO_3^- .

, TBPO 0 100 mmol·L^{-1} , NO_3^- . $C_2mimNTf_2$, NO_3^- 2−3 mmol·L^{-1}, . TBPO $C_2mimNTf_2$ $UO_2(NO_3)_2$ NO_3^- ; , NO_3^- , , NO_3^- ,

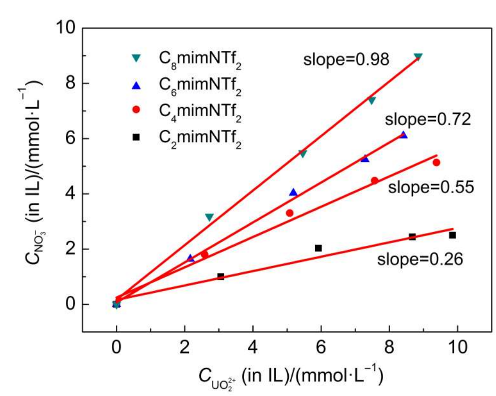


5 TBPO $C_n$mimNTf$_2$ (n=2, 4, 6, 8) 10 mmol·L^{-1} $UO_2(NO_3)_2$ NO_3^-

Fig.5 Relationship between the concentrations of NO_3^- and TBPO in $C_n$mimNTf$_2$ (n=2, 4, 6, 8) phase after TBPO extracting 10 mmol·L^{-1} $UO_2(NO_3)_2$

. $C_2mimNTf_2$, TBPO $C_8mimNTf_2$ $UO_2(NO_3)_2$, NO_3^- $C_2mimNTf_2$. TBPO 50 mmol·L^{-1} , $C_8mimNTf_2$ NO_3^- . $C_4mimNTf_2$ $C_6mimNTf_2$, NO_3^- $C_2mimNTf_2$ $C_8mimNTf_2$, .

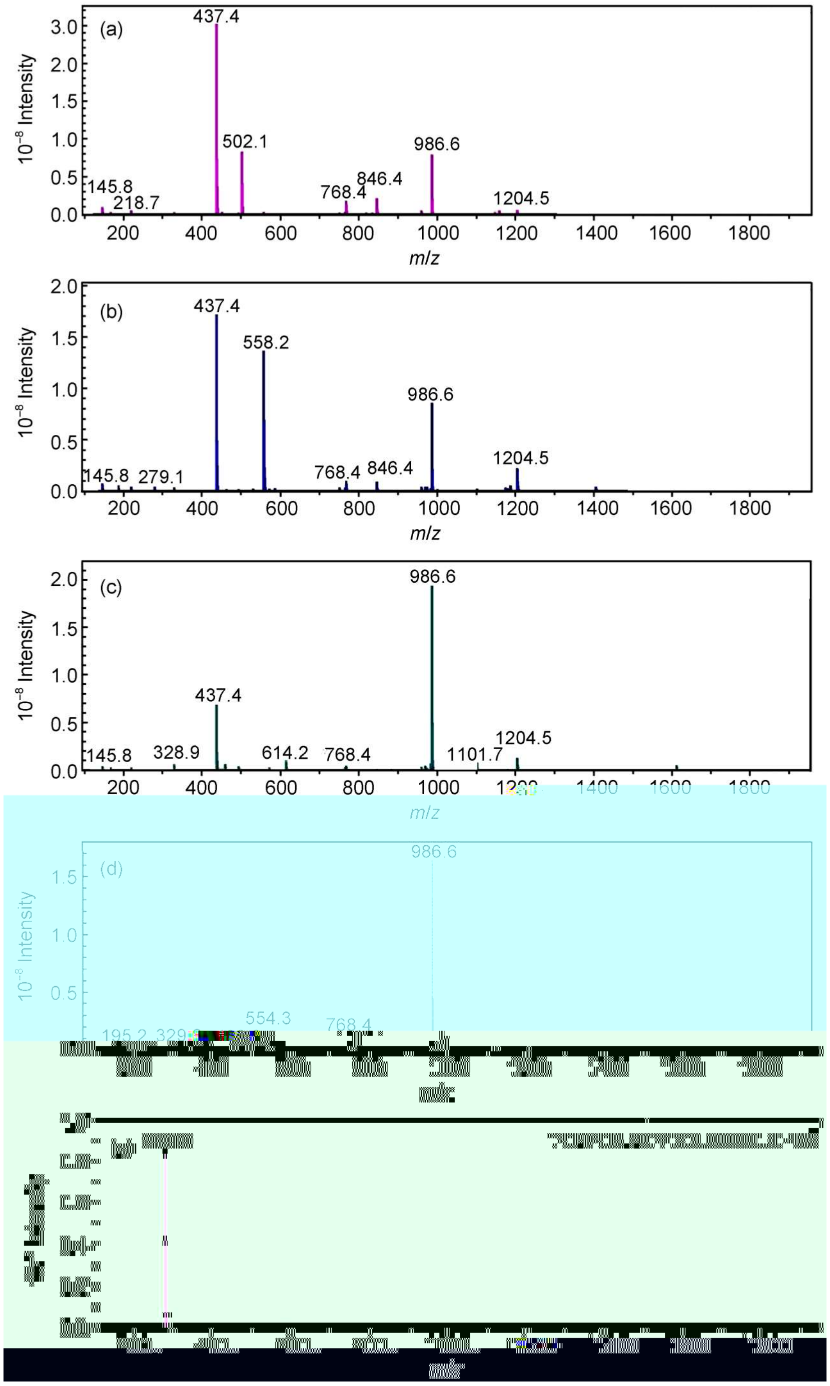
, TBPO $UO_2(NO_3)_2$ NO_3^- UO_2^{2+} , 6 . $C_8mimNTf_2$, 1, UO_2^{2+} NO_3^- 1:1 ,



6 TBPO $C_n$mimNTf$_2$ (n=2, 4, 6, 8) 10 mmol·L^{-1} $UO_2(NO_3)_2$ NO_3^- UO_2^{2+}

Fig.6 Linear relationship between the concentrations of NO_3^- and UO_2^{2+} in $C_n$mimNTf$_2$ (n=2, 4, 6, 8) phase after TBPO extracting 10 mmol·L^{-1} $UO_2(NO_3)_2$

$UO_2(TBPO)_n(NO_3)^+$. $C_2mimNTf_2$, $C_2mimNTf_2$. $C_4mimNTf_2$ $C_6mimNTf_2$, 1/4, NO_3^- 1 1/4 , 0.55 0.72, $C_8mimNTf_2$, NO_3^- $C_nmimNTf_2$ $UO_2(TBPO)_n(NO_3)^+$ $UO_2(TBPO)_n^{2+}$, .



7 TBPO (200 mmol·L^{-1})-$C_n$mimNTf$_2$ (n=2 (a), n=4 (b), n=6 (c), n=8 (d)) 40 mmol·L^{-1} $UO_2(NO_3)_2$ (ESI-MS) TBPO (200 mmol·L^{-1})-C_2mimNTf$_2$ 40 mmol·L^{-1} $UO_2(NO_3)_2$ ESI-MS (e)

Fig.7 Positive ion spectra of electrospray ionization mass spectra (ESI-MS) of IL phases after extracting 40 mmol·L^{-1} $UO_2(NO_3)_2$ by TBPO (200 mmol·L^{-1})-$C_n$mimNTf$_2$ (n=2 (a), n=4 (b), n=6 (c), n=8 (d)) and negative ion spectrum of ESI-MS in the case of C_2mimNTf$_2$ (e)

3.5.2

TBPO

$UO_2(NO_3)_2$,

(ESI-MS) . 7 TBPO

$UO_2(NO_3)_2$ ESI-MS .

7(a) , $C_2mimNTf_2$ $UO_2(TBPO)_3(NO_3)^+$

$[UO_2(TBPO)_3^{2+}+NTf_2^-]^+$, (m/z)

986.6 1204.5, TBPO-$C_2mimNTf_2$ $UO_2(NO_3)_2$

. (m/z=437.4) [2TBPO+H]$^+$. TBPO-$C_4mimNTf_2$ TBPO-$C_6mimNTf_2$

$UO_2(NO_3)_2$ (7(b, c)) ,

$UO_2(TBPO)_3(NO_3)^+$ (m/z=986.6) $[UO_2(TBPO)_3^{2+}+NTf_2^-]^+$ (m/z=1204.5) , TBPO-$C_8mimNTf_2$ $UO_2(TBPO)_3(NO_3)^+$ (m/z=986.6) . TBPO-$C_8mimNTf_2$

$UO_2(TBPO)_3(NO_3)^+$.

$C_nmimNTf_2$ (n=2, 4, 6, 8) $UO_2(TBPO)_3(NO_3)^+$ (m/z=986.6) ,

, $C_8mimNTf_2$ (7(d))

, .

$UO_2(TBPO)_3(NO_3)^+$

. $C_nmimNTf_2$ (n=2, 4, 6, 8)

m/z=279.9 ,

NTf_2^- (7(e) $C_2mimNTf_2$

). 3 .

3.5.3 -

-

(8) ,

, 422 nm ($C_2mimNTf_2$)

425 nm ($C_8mimNTf_2$).

TBPO $UO_2(NO_3)_2$

. NO_3^- ,

NO_3^-

.

,

.

$$C_nmimNTf_{2\,IL} \quad C_nmim^+_{aq} + NTf^-_{2\,aq} \tag{2}$$

$$UO^{2+}_{2\,aq} + NO^-_{3\,aq} + 3TBPO_{IL} + C_nmim^+_{IL} \quad UO_2(TBPO)_3(NO_3)^+_{IL} + C_nmim^+_{IL} \tag{3}$$

$$UO^{2+}_{2\,aq} + 3TBPO_{IL} + 2C_nmim^+_{IL} \quad UO_2(TBPO)^{2+}_{3\,IL} + 2C_nmim^+_{aq} \tag{4}$$

3 200 mmol·L^{-1} TBPO-$C_nmimNTf_2$ (n=2, 4, 6, 8) 40 mmol·L^{-1} $UO_2(NO_3)_2$ ESI-MS

Table 3 Peak positions associated in the ESI-MS of IL phase after extracting 40 mmol·L^{-1} $UO_2(NO_3)_2$ by 200 mmol·L^{-1} TBPO-$C_nmimNTf_2$ (n=2, 4, 6, 8)

IL	Species	m/z
$C_2mimNTf_2$	$[UO_2(TBPO)_3^{2+}+NTf_2^-]^+$	1204.5
	$UO_2(TBPO)_3(NO_3)^+$	986.6
	$UO_2(TBPO)_2(NO_3)^+$	768.4
	$[2C_2mim^++NTf_2^-]^+$	502.1
	$[2TBPO+H]^+$	437.4
	NTf_2^-	279.9
$C_4mimNTf_2$	$[UO_2(TBPO)_3^{2+}+NTf_2^-]^+$	1204.5
	$UO_2(TBPO)_3(NO_3)^+$	986.6
	$UO_2(TBPO)_2(NO_3)^+$	768.4
	$[2C_4mim^++NTf_2^-]^+$	558.2
	$[2TBPO+H]^+$	437.4
	NTf_2^-	279.9
$C_6mimNTf_2$	$[UO_2(TBPO)_3^{2+}+NTf_2^-]^+$	1204.5
	$UO_2(TBPO)_3(NO_3)^+$	986.6
	$UO_2(TBPO)_2(NO_3)^+$	768.4
	$[2C_6mim^++NTf_2^-]^+$	614.2
	$[2TBPO+H]^+$	437.4
	NTf_2^-	279.9
$C_8mimNTf_2$*	$UO_2(TBPO)_3(NO_3)^+$	986.6
	$UO_2(TBPO)_2(NO_3)^+$	768.4
	NTf_2^-	279.9

The peak intensity of $UO_2(TBPO)_3(NO_3)^+$ in $C_8mimNTf_2$ extraction system is very high, which results in the disappear of peak of $[2C_8mim^++NTf_2^-]^+$.

2 $LiNTf_2$

, $C_4mimNTf_2$

((2)), NTf_2^- ,

$C_4mimNTf_2$,

C_4mim^+ , ((3) (4))

, .[12] HNO_3

, $LiNO_3$

, NO_3^- ,

.

,

C_nmim^+

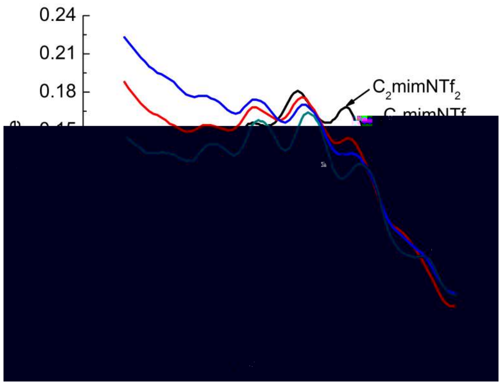
.

,

, . $C_8mimNTf_2$

(3) ,

$UO_2(TBPO)_3(NO_3)^+$ $C_8mimNTf_2$



8 TBPO (40 mmol·L^{-1})-C$_n$mimNTf$_2$ (n=2, 4, 6, 8) 10 mmol·L^{-1} UO$_2$(NO$_3$)$_2$ -

Fig.8 UV-Vis absorption spectra of IL phase after extracting 10 mmol·L^{-1} UO$_2$(NO$_3$)$_2$ by TBPO (40 mmol·L^{-1})-C$_n$mimNTf$_2$ (n=2, 4, 6, 8)

. ,
C$_2$mimNTf$_2$
2 UO$_2$(TBPO)$_3^{2+}$. (4) C$_n$mim$^+$
(3) ,
C$_2$mimNTf$_2$. NO_3^- UO_2^{2+}
, C$_2$mimNTf$_2$
(3) (4) ,
(UO$_2$(TBPO)$_3$(NO$_3$)$^+$ UO$_2$(TBPO)$_3^{2+}$) ,
C$_8$mimNTf$_2$ (3) , UO$_2$(TBPO)$_3$(NO$_3$)$^+$.

TBPO C$_n$mimNTf$_2$ (n=2, 4, 6, 8)
UO$_2$(NO$_3$)$_2$. TBPO C$_n$mimNTf$_2$ (n=2, 4, 6, 8)
. HNO$_3$
, TBPO-C$_n$mimNTf$_2$
UO$_2$(NO$_3$)$_2$. TBPO-C$_4$mimNTf$_2$
U Nd, Zr
.
, NO_3^-
. , NO_3^-
. NO_3^-
C$_8$mimNTf$_2$
UO$_2$(TBPO)$_3$(NO$_3$)$^+$, C$_n$mimNTf$_2$ (n=2, 4, 6) UO$_2$(TBPO)$_3$(NO$_3$)$^+$ UO$_2$(TBPO)$_3^{2+}$
,
.

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