NUCLEAR SCIENCE AND TECHNIQUES **26**, S10306 (2015)

γ-ray induced radiolysis of $[C_2mim][NTf_2]$ and its effects on Dy^{3+} extraction*

YUAN Wei-Jin (袁威津),[1,†] AO Yin-Yong (敖银勇),[2,†] ZHAO Long (赵龙),[1]
WEI Yue-Zhou (韦悦周),[1] ZHAI Mao-Lin (翟茂林),[2,‡] and LI Jiu-Qiang (李久强)[2]

[1]*Nuclear Chemical Engineering Laboratory, School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[2]*Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory for Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

(Received May 19, 2014; accepted in revised form June 23, 2014; published online December 20, 2014)

The water-soluble radiolytic products of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid ($[C_2mim][NTf_2]$) under γ-radiation, such as CF_3SOOH, $CF_3SO_2NH_2$, HF, and H_2SO_3, were identified by using ^{1}H NMR, ^{19}F NMR, and ion chromatography. The extraction behavior of Dy^{3+} using irradiated $[C_2mim][NTf_2]$ in combination with 2,6-di(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine (*iso*butyl-BTP) was studied and the abnormal increase of Dy^{3+} partitioning after irradiation is mainly attributed to the precipitation formed between Dy^{3+} and radiolytic products of $[C_2mim][NTf_2]$ (F^- and SO_3^{2-}). Washing irradiated $[C_2mim][NTf_2]$ with water provides a simple method for ionic liquid recycling.

Keywords: γ-Radiation, $[C_2mim][NTf_2]$, *Iso*butyl-BTP, Radiolytic product, Dy^{3+} extraction

DOI: 10.13538/j.1001-8042/nst.26.S10306

I. INTRODUCTION

Minor actinides-lanthanides (MA-Ln) separation is a huge challenge due to their similar chemical properties [1–3]. Bistriazinylpyridines (BTPs), such as heterocyclic nitrogen donor ligands, presents attractive selectivity for MA, compared to Ln that could make them excellent candidates for separating minor actinides [4–6]. Kolarik *et al.* reported that 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in kerosene/2-etylhexanol extracted Am^{3+} with a distribution ratio of 23 from an aqueous phase [7]. Trumm *et al.* reported that a solution of 50 mmol/L BTPs in kerosene/1-octanol extracted Am^{3+} from 1 mol/L HNO_3 with $SF_{Am/Eu}$ at *ca.* 100 [8]. However, the BTPs in combination with a traditional solvent caused a new problem relating to radiation resistance. For example, a solution of 0.005 mmol/L C5-BTBP in cyclohexanone exhibited about an 80% decrease in the distribution ratio of Am^{3+} at 17 kGy [9]. It was also reported that an absorbed dose of 100 kGy resulted in 80% decomposition of BTPs in n-octanol [10]. It was thought that the reaction between BTPs and the radicals of diluents resulted in subsequent degradation, which was mainly responsible for the decrease in metal ion partitioning.

Due to a number of unique properties, such as non-volatility, good solubility, and chemical stability [11–13], room temperature ionic liquids (RTILs) have been highly studied for their potential application in the reprocessing of spent nuclear fuel [14–17]. Dai *et al.* first reported that the solvation environment offered by RTILs could enhance the extraction efficiency of metal ions from an aqueous solution [18]. Moreover, RTILs have demonstrated a notable radiation resistance under γ-radiation [19–24]. Berthon *et al.* noted that less than 1% underwent radiolysis when RTILs were exposed to a dose of 1200 kGy [25]. The main radiolytic products of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][NTf_2]$) were identified definitely through various spectroscopic methods in our previous work, which greatly improved the radiolysis research on ionic liquids [26, 27]. The overall concentration of non-volatile acidic radiolysis products was less than 1% for $[C_4mim][NTf_2]$, even at 500 kGy. However, $[C_2mim][NTf_2]$ was considered as a better solvent rather than $[C_4mim][NTf_2]$ in the separation of MA-Ln due to its larger dissolving capacity and its liquidity [28, 29]. Accordingly, it is necessary to access the radiation stability of $[C_2mim][NTf_2]$ and extraction ability of extractant in combination with $[C_2mim][NTf_2]$ under γ-radiation.

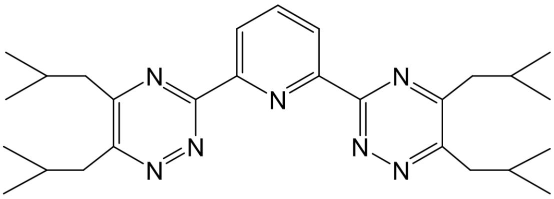

Fig. 1. The chemical structure of *iso*butyl-BTP.

In this paper, an extraction system consisted of *iso*butyl-BTP (Fig. 1) as extractant and $[C_2mim][NTf_2]$ as diluents is designed in our lab. The radiation effect on extraction behavior of the diluent $[C_2mim][NTf_2]$ is mainly investigated. Dy^{3+} is a non-redox-active trivalent ion and has similar properties to the trivalent actinides, thus Dy^{3+} is chosen for assessing the extractability and the radiation stability of the *iso*butyl-BTP/$[C_2mim][NTf_2]$ system.

---

* Supported by the Ph.D. Programs Foundation of Ministry of Education of China (No. 20130073120051), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, and the National Natural Science Foundation of China (No. 11475112)

† These authors contributed equally.

‡ Corresponding authors, ryuuchou@sjtu.edu.cn, mlzhai@pku.edu.cn

II. EXPERIMENTAL SECTION

A. Materials

$[C_2mim][NTf_2]$ (with a purity $> 99\%$) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected by ^1H NMR spectrometry. The *iso*butyl-BTP($> 95\%$) was synthesized according to [30]. All other solvents were analytical-grade reagent and used without further purification.

B. Irradiation

The irradiation of $[C_2mim][NTf_2]$ was carried out in air ((298 ± 4) K) using a ^{60}Co source, with an average dose rate of *ca.* 240 Gy/min (Institute of Applied Chemistry of Peking University). The absorbed dose was traced by a Fricke dosimeter.

C. Extraction of Dy^{3+}

The organic phase (0.5 mL) contained 20 mmol/L of *iso*butyl-BTP dissolved in $[C_2mim][NTf_2]$, and the aqueous phase (0.5 mL) contained 8 mmol/L of Dy^{3+}. The extraction experiments were oscillated in a constant temperature incubator shaker, which maintained a thermo-stated water bath at 25 °C with a rotating speed of 120 rpm, then were centrifuged for 2 min to ensure that the two phases were completely separated. After phase separation, the aqueous solution was diluted with deionized water and the concentration of Dy^{3+} in the diluted aqueous solution was measured by the Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICPS-7510, SHIMADZU, JPN). The distribution ratios ($D_{\rm Dy}$) were calculated by $D_{\rm Dy} = (C_{\rm i} - C_{\rm f})/C_{\rm f}$ and the calculation of extraction efficiencies ($E_{\rm Dy}$) was based on $D_{\rm Dy} = (C_{\rm i} - C_{\rm f})/_{\rm i}$, where $C_{\rm i}$ and $C_{\rm f}$ designate the initial and final concentrations of Dy^{3+} in the diluted aqueous solution, respectively.

D. Characterization

Micro-FTIR. The Micro Fourier transform infrared spectroscopies (Micro-FTIR) were recorded on a Thermo Scientific Micro Fourier transform infrared spectrometry.

^1H and ^{19}F NMR. NMR experiments were carried out with a Bruker AV-500. The chemical shift scale was calibrated with tetramethylsilane at 0 ppm and NTf_2^- at -78.87 ppm for ^1H NMR and ^{19}F NMR, respectively.

Ion chromatography analysis. The water-soluble products from the irradiated samples were analyzed using a MIC ion chromatography (IC) System (Metrohm Swiss). A Metrosep A SUPP 5-250 column (4 mm × 250 mm) was used to provide a quantitative study on the radiolytic products of $[C_2mim][NTf_2]$ ionic liquids. The 819 IC conductivity detector was applied and the injection volume was set at 10 µL. The eluent was 3.2 mmol/L Na_2CO_3/1.0 mmol/L $NaHCO_3$ solution at a constant flow rate of 0.7 mL/min. The operating back pressure was 11.6 MPa.

XPS analysis. The X-ray photoelectron spectra (XPS) of the samples were recorded by an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K_α radiation and low energy electron flooding for charge compensation.

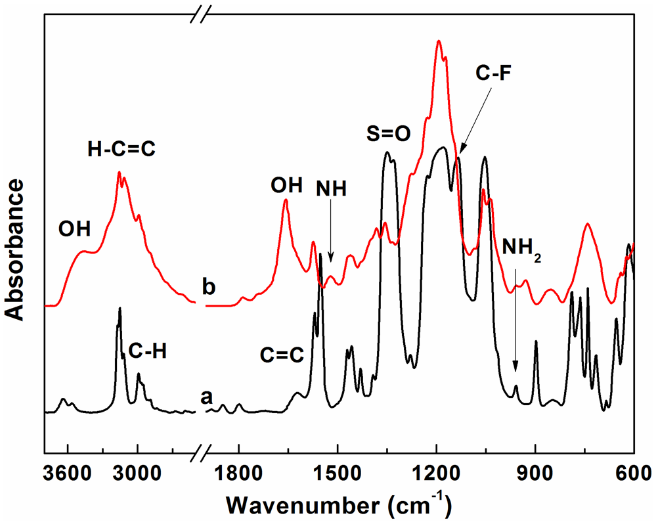

Fig. 2. (Color online) Micro-FTIR spectra of $[C_2mim][NTf_2]$ in D_2O before (a) and after irradiation at 500 kGy (b).

III. RESULTS AND DISCUSSION

A. Identification of water-soluble radiolytic products of $[C_2mim][NTf_2]$ under γ-radiation

The water-washed sample of irradiated $[C_2mim][NTf_2]$ was analyzed by Micro-FTIR based on previous work [26]. As illustrated in Fig. 2, the Micro-FTIR spectrum of irradiated sample changes obviously in comparison with that of unirradiated sample. The absorption is band at 1136 cm^{-1} (1350 cm^{-1}), corresponding to the vibration of the C−F bonds (S=O) of NTf_2^-, dropping obviously after γ-radiation. This indicated that C−F and S=O bonds were broken during irradiation. In addition, OH groups (NH_2 groups) are observed at 1655 cm^{-1} and 3450 cm^{-1} (960 cm^{-1}) in Fig. 2b. These results indicate that the radiolytic products containing OH and NH_2 groups were formed after irradiation. These results are similar to that of $[C_4mim][NTf_2]$ during irradiation [26] because $[C_2mim][NTf_2]$ has analogous anion ions (NTf_2^-) with $[C_4mim][NTf_2]$. Hence, the observed results in Micro-FTIR are mainly attributed to the radiolysis of $[NTf_2]$ anions.

^1H NMR and ^{19}F NMR were employed to identify the radiolytic products of $[C_2mim][NTf_2]$ after irradiation. As shown in Fig. 3, no discernible changes was observed in ^1H NMR at

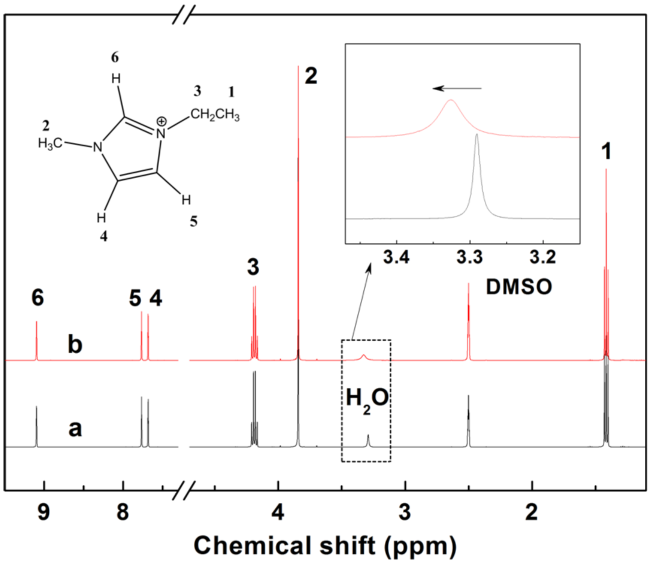

Fig. 3. (Color online) ^{1}H NMR spectra of $[C_2mim][NTf_2]$ before (a) and after irradiation at 500 kGy (b).

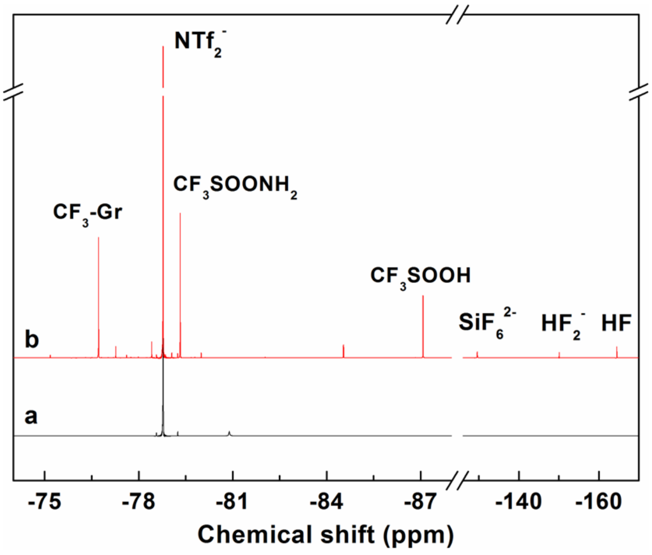

Fig. 4. (Color online) ^{19}F NMR spectra of $[C_2mim][NTf_2]$ in D_2O before (a) and after irradiation at 500 kGy (b).

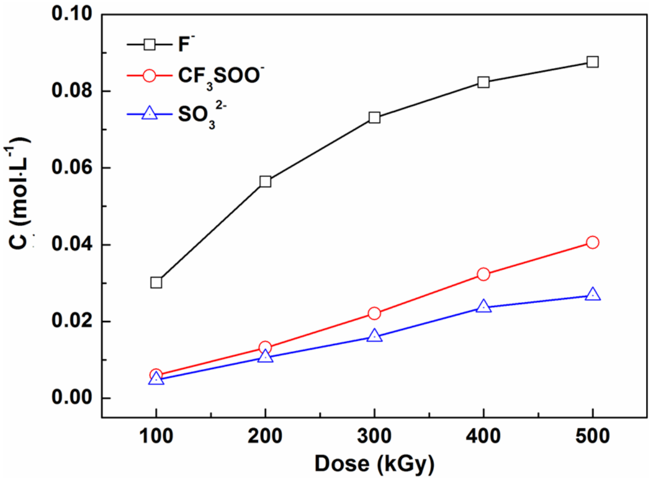

Fig. 5. (Color online) The relationship between the concentration of main radiolytic products and doses.

500 kGy, suggesting that the nonvolatile radiolysis products of $[C_2mim][NTf_2]$ do not exceed 1%. However, the peak of water broadened and shifted toward the low field after irradiation. This is consistent with information reported by Yuan *et al.*, who found that the change of water peak shape was attributed to the acidic radiolytic products [28]. Therefore, acidic radiolytic products were formed during the irradiation of $[C_2mim][NTf_2]$.

The ^{19}F NMR spectra of $[C_2mim][NTf_2]$ before and after irradiation are shown in Fig. 4. A single peak at -78.78 ppm, which is assigned to NTf_2^- was observed. Similar to the radiolysis of $[C_4mim][NTf_2]$ [26], several fluorine-containing compounds in irradiated $[C_2mim][NTf_2]$ have been identified as CF_3SOONH_2 (-79.33 ppm), CF_3SOOH (-87.08 ppm), HF (-164.55 ppm), and SiF_6^{2-} (-129.56 ppm) [26]. However, a new radiolytic product, which was not observed in irradiated $[C_4mim][NTf_2]$, is shown at -76.75 ppm. The difference in alkyl chain between C_2mim^+ and C_4mim^+ leads to the formation of different radiolytic products.

B. A quantitative analysis of trace water-soluble radiolytic products of $[C_2mim][NTf_2]$ under γ-irradiation

Ion chromatography was employed to provide a quantitative analysis of these water-soluble radiolytic products (HF, CF_3SOOH, and H_2SO_3) and the experimental details are given in a previous paper [26]. As indicated in Fig. 5, the amounts of radiolytic products increased obviously with the increase of each dose. For instance, the concentration of F^- increased from 0.030 mol/L at 100 kGy to 0.087 mol/L at 500 kGy. The G value of HF, CF_3SOOH, and H_2SO_3 was calculated at 0.22 μmol/L, 0.035 μmol/L, and 0.029 μmol/L, respectively. Compared with the G value of acidic radiolytic products of $[C_4mim][NTf_2]$ (Table 1), the radiolysis of $[C_2mim][NTf_2]$ is close to that of $[C_4mim][NTf_2]$. The quantitative study using ion chromatography indicated that the overall concentration of nonvolatile acidic radiolysis products was less than 1% for $[C_2mim][NTf_2]$ even at 500 kGy, in which the results show that $[C_2mim][NTf_2]$ still has excellent radiation stability under γ-irradiation.

TABLE 1. Radiation chemical yields of acidic radiolytic products of $[C_2mim][NTf_2]$ and $[C_4mim][NTf_2]$

RTILs	$G(F^-)$ (μmol/J)	$G(CF_3SOO^-)$ (μmol/J)	$G(SO_3^{2-})$ (μmol/J)
$[C_2mim][NTf_2]$	0.22	0.035	0.029
$[C_4mim][NTf_2]$[a]	0.20	0.010	0.031

[a] Data was obtained from Ref. [26].

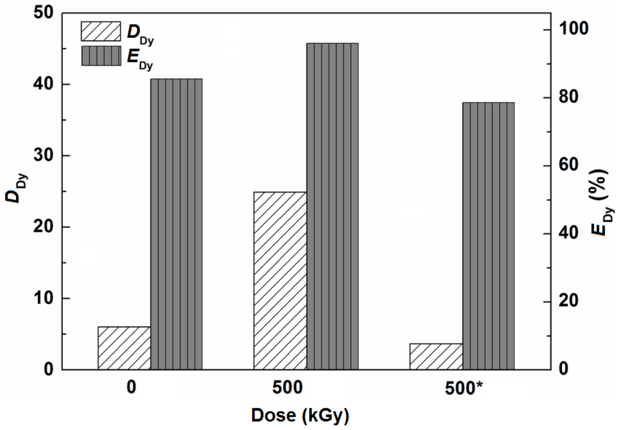

Fig. 6. Influence of dose on Dy^{3+} extraction from aqueous solution by irradiated [C_2mim][NTf_2] in combination with *iso*butyl-BTP. *The irradiated sample was washed by water for 3 times before extraction experiment.

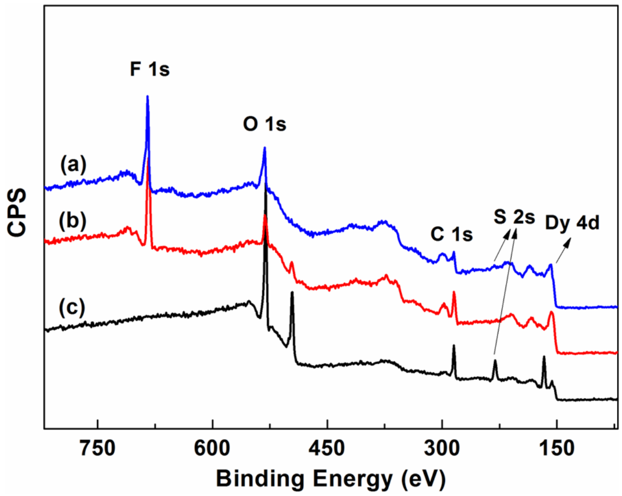

Fig. 7. (Color online) XPS spectra of the precipitate (a), DyF_3 (b), and $Dy_2(SO_3)_3$ (c).

C. The influence of acidic radiolytic products of [C_2mim][NTf_2] on the extraction of Dy^{3+}

The influence of dose on Dy^{3+} extraction was shown in Fig. 6. An abnormal increase of Dy^{3+} partitioning is obtained when irradiated [C_2mim][NTf_2] is used as extracting solvent. Some water-insoluble compounds were observed at the interface between irradiated [C_2mim][NTf_2] and the aqueous solution. After the irradiated [C_2mim][NTf_2] was washed by deionized water 3 times, Dy^{3+} partitioning recovered to the unirradiated level. These results suggest that the abnormal increase of D_{Dy} in irradiated [C_2mim][NTf_2] is ascribed to the influence of water-soluble radiolytic products. Based on our previous work [27], Dy^{3+} is precipitated with the radiolytic products generated from ionic liquid (F, SO_3^{2-}), resulting in the increase of Dy^{3+} partitioning in irradiated [C_2mim][NTf_2].

After centrifuging and washing and drying, the white sediment was obtained and analyzed by XPS. The binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV. The composition of sediment was determined to consist of F, O, S and Dy elements according to the XPS record (Fig. 7), indicating the main components of the sediment are DyF_3 and $Dy_2(SO_3)_3$. Similar results have been reported in the α-radiolysis of [C_4mim][NTf_2] ionic liquid irradiated with the helium ion beam [27]. Consequently, the increase of Dy^{3+} partitioning in irradiated [C_2mim][NTf_2] is due to the precipitation between the water-soluble radiolytic products of [C_2mim][NTf_2] with Dy^{3+}.

IV. CONCLUSION

The main water-soluble radiolytic products of [C_2mim][NTf_2] (CF_3SOOH, $CF_3SO_2NH_2$, HF and H_2SO_3) under γ-irradiation were systematically investigated by using micro-FTIR, ^{1}H NMR, ^{19}F NMR, and ion chromatography. The radiolytic products of [C_2mim][NTf_2] are similar to that of [C_4mim][NTf_2], because the two ionic liquids have a similar chemical structure and the same anion ions. The radiolytic behavior of [C_2mim][NTf_2] changes slightly compared to [C_4mim][NTf_2] as the difference of the alkyl chain length. The extracting behavior of Dy^{3+} using irradiated [C_2mim][NTf_2] in combination with *iso*butyl-BTP showed an abnormal increase of Dy^{3+} partitioning due to the precipitation between the acidic radiolytic products of the anion with Dy^{3+}. The water-washing is a very effective and easy method to avoid the influence of radiolytic products of [C_2mim][NTf_2]. This work provides an assessment about the feasibility of [C_2mim][NTf_2] as alternative medium for the separations of MA-Ln from spent nuclear fuel.

---

[1] Alexander V. Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides. Chem Rev, 1995, **95**: 273–342. DOI: 10.1021/cr00034a002

[2] Nash K L. A review of the basic chemistry and recent developments in trivalent f-elements separations. Solvent Extr Ion Exc, 1993, **11**: 729–768. DOI: 10.1080/07366299308918184

[3] Mathur J, Murali M, Nash K. Actinide partitioning—a review. Solvent Extr Ion Exc, 2001, **19**: 357–390. DOI: 10.1081/SEI-100103276

[4] Panak P J and Geist A. Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine n-donor ligands. Chem Rev, 2013, **113**: 1199–1236. DOI: 10.1021/cr3003399

[5] Dam H H, Reinhoudt D N, Verboom W. Multicoordinate ligands for actinide/lanthanide separations. Chem Soc Rev, 2007, **36**: 367–377. DOI: 10.1039/B603847F

[6] Cocalia V A, Gutowski K E, Rogers R D. The coordination chemistry of actinides in ionic liquids: A review of experiment and simulation. Coordin Chem Rev, 2006, **250**: 755–764. DOI: 10.1016/j.ccr.2005.09.019

[7] Kolarik Z, Mullich U, Gassner F. SELECTIVE EXTRACTION OF Am (III) OVER Eu (III) BY 2, 6-DITRIAZOLYL-AND 2, 6-DITRIAZINYLPYRIDINES 1. Solvent Extr Ion Exc, 1999, **17**: 1155–1170. DOI: 10.1080/07360299908934598

[8] Trumm S, Geist A, Panak P J, *et al.* An improved hydrolytically-stable bis-triazinyl-pyridine (BTP) for selective actinide extraction. Solvent Extr Ion Exc, 2011, **29**: 213–229. DOI: 10.1080/07366299.2011.539129

[9] Nilsson M, Andersson S, Drouet F, *et al.* Extraction Properties of 6, 6'¯Bis¯(5, 6¯dipentyl¯[1, 2, 4] triazin¯3¯yl)¯[2, 2'] bipyridinyl (C5¯BTBP). Solvent Extr Ion Exc, 2006, **24**: 299–318. DOI: 10.1080/07366290600646947

[10] Hudson M J, Boucher C E, Braekers D, *et al.* New bis (triazinyl) pyridines for selective extraction of americium (III). New J Chem, 2006, **30**: 1171–1183. DOI: 10.1039/B514108G

[11] Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev, 1999, **99**: 2071–2084. DOI: 10.1021/cr980032t

[12] Endres F and El Abedin S Z. Air and water stable ionic liquids in physical chemistry. Phys Chem Chem Phys, 2006, **8**: 2101–2116. DOI: 10.1039/B600519P

[13] Plechkova N V and Seddon K R. Applications of ionic liquids in the chemical industry. Chem Soc Rev, 2008, **37**: 123–150. DOI: 10.1039/B006677J

[14] Dietz M L. Ionic liquids as extraction solvents: Where do we stand? Separ Sci Technol, 2006, **41**: 2047–2063. DOI: 10.1080/01496390600743144

[15] Binnemans K. Lanthanides and actinides in ionic liquids. Chem Rev, 2007, **107**: 2592–2614. DOI: 10.1021/cr050979c

[16] Tokuda H, Tsuzuki S, Susan M, *et al.* How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. J Phys Chem B, 2006, **110**: 19593–19600. DOI: 10.1021/jp064159v

[17] Dietz ML, Jakab S, Yamato K, *et al.* Stereochemical effects on the mode of facilitated ion transfer into room-temperature ionic liquids. Green Chem, 2008, **10**: 174–176. DOI: 10.1039/B713750H

[18] Dai S, Ju Y, Barnes C. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. J Chem Soc Dalton, 1999, 1201–1202. DOI: 10.1039/A809672D

[19] Allen D, Baston G, Bradley A E, *et al.* An investigation of the radiochemical stability of ionic liquids. Green Chem, 2002, **4**: 152–158. DOI: 10.1039/B111042J

[20] Qi M Y, Wu G Z, Chen S M, *et al.* Gamma radiolysis of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Radiat Res, 2007, **167**: 508–514. DOI: 0033-7587/07

[21] Howett S E, Joseph J M, Noel J J, *et al.* Effect of gamma irradiation on gas-ionic liquid and water-ionic liquid interfacial stability. J Colloid Interf Sci, 2011, **361**: 338–350. DOI: 10.1016/j.jcis.2011.05.034

[22] Yuan L Y, Xu C, Peng J, *et al.* Identification of the radiolytic product of hydrophobic ionic liquid [C4mim][NTf2] during removal of Sr2+ from aqueous solution. Dalton T, 2009, 7873–7875. DOI: 10.1039/B911026G

[23] Yuan L Y, Peng J, Xu L, *et al.* Radiation effects on hydrophobic ionic liquid [C4mim][NTf2] during extraction of strontium ions. J Phys Chem B, 2009, **113**: 8948–8952. DOI: 10.1021/jp9016079

[24] Yuan L Y, Peng J, Xu L, *et al.* Influence of γ-radiation on the ionic liquid [C 4 mim][PF 6] during extraction of strontium ions. Dalton T, 2008, 6358–6360. DOI: 10.1039/B811413G

[25] Berthon L, Nikitenko S, Bisel I, *et al.* Influence of gamma irradiation on hydrophobic room-temperature ionic liquids [BuMeIm] PF 6 and [BuMeIm](CF 3 SO 2) 2 N. Dalton T, 2006, 2526–2534. DOI: 10.1039/B601111J

[26] Ao Y Y, Peng J, Yuan L Y, *et al.* Identification of radiolytic products of [C 4 mim][NTf 2] and their effects on the Sr 2+ extraction. Dalton T, 2013, **42**: 4299–4305. DOI: 10.1039/c2dt32418k

[27] Ao Y Y, Zhou H Y, Yuan W J, *et al.* α-Radiolysis of ionic liquid irradiated with helium ion beam and the influence of radiolytic products on Dy 3+ extraction. Dalton T, 2014, **43**: 5580–5585. DOI: 10.1039/c3dt53297f

[28] Yuan L Y, Peng J, Xu L, *et al.* Radiation effects on hydrophobic ionic liquid [C4mim][NTf2] during extraction of strontium ions. J Phys Chem B, 2009, **113**: 8948–8952. DOI: 10.1021/jp9016079

[29] Billard I, Ouadi A, Gaillard C. Is a universal model to describe liquid–liquid extraction of cations by use of ionic liquids in reach? Dalton T, 2013, **42**: 6203–6212. DOI: 10.1039/C3DT32159B

[30] Bhattacharyya A, Mohapatra P, Roy A, *et al.* Ethyl-bis-triazinylpyridine (Et-BTP) for the separation of americium (III) from trivalent lanthanides using solvent extraction and supported liquid membrane methods. Hydrometallurgy, 2009, **99**: 18–24. DOI: 10.1016/j.hydromet.2009.05.020