

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/26316873>

# Radiation Effects on Hydrophobic Ionic Liquid [C(4)mim][NTf2] during Extraction of Strontium Ions

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · AUGUST 2009

Impact Factor: 3.3 · DOI: 10.1021/jp9016079 · Source: PubMed

CITATIONS

42

READS

73

6 AUTHORS, INCLUDING:



Liyong Yuan

Peking University

12 PUBLICATIONS 247 CITATIONS

SEE PROFILE



Jing Peng

Peking University

90 PUBLICATIONS 1,555 CITATIONS

SEE PROFILE



Zhai Maolin

Peking University

127 PUBLICATIONS 2,293 CITATIONS

SEE PROFILE

# Radiation Effects on Hydrophobic Ionic Liquid [C<sub>4</sub>mim][NTf<sub>2</sub>] during Extraction of Strontium Ions

Liyong Yuan, Jing Peng, Ling Xu,<sup>†</sup> Maolin Zhai,\* Jiuqiang Li, and Genshuan Wei

Beijing National Laboratory for Molecular Sciences (BNLMS), Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, 100871, Beijing, P. R. China

Received: February 21, 2009; Revised Manuscript Received: May 4, 2009

The applications of room-temperature ionic liquids (RTILs) in separation of high level radioactive nuclides demand a comprehensive knowledge of the stability and metal ion extraction of RTILs under radiation. Herein, we assessed the influence of  $\gamma$ -irradiation on the [C<sub>4</sub>mim][NTf<sub>2</sub>]-based extraction system, where [C<sub>4</sub>mim]<sup>+</sup> is 1-butyl-3-methylimidazolium and [NTf<sub>2</sub>]<sup>−</sup> is bis(trifluoromethylsulfonyl)imide, by solvent extraction of Sr<sup>2+</sup> using irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] in combination with dicyclohexyl-18-crown-6 (DCH18C6). It was found that the degree of extraction for Sr<sup>2+</sup> from water to irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] decreased compared with that to unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>], and the decrement enhanced obviously with increasing dose. NMR spectroscopic probe analysis revealed the formation of acids during irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>]. The decrease of Sr<sup>2+</sup> partitioning in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] is attributed to the competition between H<sup>+</sup> with Sr<sup>2+</sup> to interact with DCH18C6. Accordingly, washing irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] with water gives a simple way of ionic liquid recycling. Furthermore, the degree of extraction for Sr<sup>2+</sup> from 3 mol·L<sup>−1</sup> nitric acid solution to [C<sub>4</sub>mim][NTf<sub>2</sub>] is independent of the irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>] since the amount of the radiation-generated H<sup>+</sup> is negligible in such a high acidic solution.

## 1. Introduction

Room-temperature ionic liquids (RTILs), especially those containing imidazolium cations, for instance, 1,3-dialkylimidazolium, associated with various inorganic anions such as bis(trifluoromethylsulfonyl)imide (NTf<sub>2</sub><sup>−</sup>) or hexafluorophosphate (PF<sub>6</sub><sup>−</sup>) are receiving an ever-increasing amount of interest due to their wide and diverse potential as environmentally benign alternatives to volatile organic solvents and caustic inorganic acids in a variety of synthetic, catalytic, and electrochemical applications.<sup>1–6</sup> Recent efforts by several investigators have focused on the application of the RTILs in separations, in particular, on the utility of these materials as next generation diluents in traditional liquid–liquid extraction of metal ions.<sup>7–14</sup> A preliminary study by Dai et al. demonstrated that highly efficient extraction ( $D > 10^4$ ) of strontium ions (Sr<sup>2+</sup>) from water can be achieved using RTILs, especially 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>]), in combination with crown ether.<sup>15</sup> The investigation of solvent extraction of cesium ions (Cs<sup>+</sup>) from aqueous solution by calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6) using [C<sub>*n*</sub>mim][NTf<sub>2</sub>] ( $n = 2, 3, 4, 5, 8$ ) showed that the solutions of BOBCalixC6 in these ILs provide efficient extraction of Cs<sup>+</sup> under the conditions that give negligible extraction with conventional organic solvents.<sup>16</sup> The recovery of rare earth and actinide metals from aqueous solution and nitric acid media was studied using [C<sub>4</sub>mim][PF<sub>6</sub>]<sup>12</sup> and [C<sub>4</sub>mim][NTf<sub>2</sub>],<sup>12,14</sup> where octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) was used as extractant. It was shown that the use of ILs greatly enhances the extraction efficiency and selectivity of CMPO for metal ions compared to when *n*-dodecane was

used as the extracting solvent. These works highlight the vast opportunities of RTILs as novel media for the separations of high level radioactive nuclides from wastewater.

To be successful in such an application, however, RTILs should be robust to high radiation dose. A preliminary assessment of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -radiation effect on hydrophilic RTILs, such as [C<sub>4</sub>mim]NO<sub>3</sub>, [C<sub>2</sub>mim]Cl, and [C<sub>6</sub>mim]Cl, showed that the tested ILs exhibit radiation-induced darkening and increasing of light absorbance, but less than 1% of the samples undergo radiolysis even after exposed to a dose of 400 kGy, suggesting very high radiation stability of these ILs.<sup>17</sup> Moisy and his co-workers investigated the radiation stability of hydrophobic RTILs [C<sub>4</sub>mim][PF<sub>6</sub>] and [C<sub>4</sub>mim][NTf<sub>2</sub>]<sup>18</sup> and [N<sub>1444</sub>][NTf<sub>2</sub>],<sup>19</sup> where [N<sub>1444</sub>]<sup>+</sup> is the methyltributylammonium cation. They proposed possible degradation schemes of the RTILs based on the NMR and ESI-MS analysis. Wu et al. further investigated in detail  $\gamma$  radiolysis of neat [C<sub>4</sub>mim][PF<sub>6</sub>]<sup>20</sup> and [C<sub>4</sub>mim][BF<sub>4</sub>]<sup>21</sup> by the spectroscopic method and differential scanning calorimetry. Bartels et al. determined the yields of hydrogen gas in irradiated ionic liquids based on imidazolium, pyridinium, and phosphonium cations.<sup>22</sup> Recently, we have studied the radiation stability of [C<sub>4</sub>mim][PF<sub>6</sub>] in the presence of nitric acid<sup>23</sup> and the decoloration of irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>].<sup>24</sup> The results indicated that nitric acid, as an oxidant, slightly accelerates the decomposition of [C<sub>4</sub>mim][PF<sub>6</sub>] at a high dose (550 kGy) but obviously inhibits the radiation-induced darkening of [C<sub>4</sub>mim][PF<sub>6</sub>] and discolors the irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. Besides, the reaction kinetics and the primary effects of radiation in RTILs were studied using pulse radiolysis techniques<sup>25–34</sup> and laser photolysis techniques.<sup>35,36</sup> All of the above-mentioned studies have dealt with the influence of radiation on RTILs themselves. The radiation may have considerable influence on metal ion extraction of RTILs, although very few publications are concerning this topic.

\* Corresponding author. Tel./Fax: 86-10-62753794. E-mail: mlzhai@pku.edu.cn.

<sup>†</sup> Department of Energy and Resources Engineering, College of Engineering, Peking University, 100871, Beijing, P. R. China.

Very recently, we preliminarily studied the solvent extraction of Sr<sup>2+</sup> using irradiated [C<sub>4</sub>mim][PF<sub>6</sub>] in combination with crown ether.<sup>37</sup> Herein, the influence of  $\gamma$ -irradiation on another typical RTIL [C<sub>4</sub>mim][NTf<sub>2</sub>] for extraction of Sr<sup>2+</sup> was investigated with a <sup>60</sup>Co source. [C<sub>4</sub>mim][NTf<sub>2</sub>], as is known, possesses the lower viscosity and melting point, possesses the higher conductivity and stability,<sup>38–41</sup> and also provides more efficient extraction of metal ions<sup>14</sup> than [C<sub>4</sub>mim][PF<sub>6</sub>]. These properties might be particularly important for the applications of RTILs within the separations of high level radioactive nuclides from wastewater.

## 2. Experimental Section

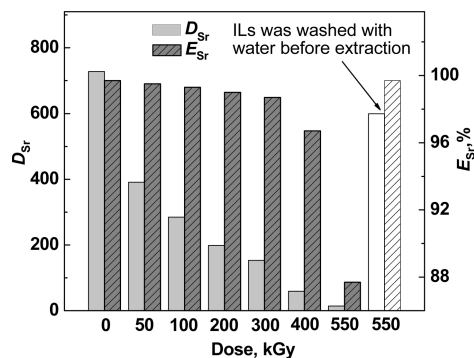
**2.1. Materials.** 1-Butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl, Lanzhou Institute of Chemical Physics, >99%) and lithium bis[(trifluoromethyl)sulfonyl]amide (LiNTf<sub>2</sub>, TCI Chemical Co., >98%) were used as received. Dicyclohexyl-18-crown-6 (DCH18C6, TCI Chemical Co.) was used after recrystallization from *n*-heptane.

[C<sub>4</sub>mim][NTf<sub>2</sub>] was synthesized according to the procedure previously reported.<sup>38,42</sup> [C<sub>4</sub>mim]Cl was dissolved in deionized water in a flask, and then the solution of LiNTf<sub>2</sub> ([C<sub>4</sub>mim]Cl:LiNTf<sub>2</sub> = 1:1.1, molar ratio) was added slowly to the flask. The reaction mixture was stirred for 5 h at room temperature. After decanting the upper aqueous phase, the colorless viscous liquid, [C<sub>4</sub>mim][NTf<sub>2</sub>], was obtained. To ensure that the liquids are free from any impurities, we took special care for purification of the [C<sub>4</sub>mim][NTf<sub>2</sub>] by adopting the steps described elsewhere.<sup>43</sup> Briefly, the [C<sub>4</sub>mim][NTf<sub>2</sub>] salt was washed several times with triply distilled water to remove halide and acid impurities. Then the IL was diluted with acetone (2:1 by volume) and treated with activated charcoal (100:5 by weight) for at least 48 h and eventually filtered a couple of times with double deck quantitative paper. The liquid thus prepared was distilled by circumvolve distillation and then kept in a vacuum (pressure 10<sup>−1</sup>–10<sup>−2</sup> mbar) for 48 h at 65 °C for the removal of any organic impurities and water. After purification, the water content in the [C<sub>4</sub>mim][NTf<sub>2</sub>] sample was less than 150 ppm, measured by Karl Fischer titration, and no impurities were detected by NMR spectrometry analysis. Then the sample was transferred to a clean and dry plastic sample container and stored in a desiccator for further experiments.

All other chemicals were of analytical grade and were used without further purification.

**2.2. Sample Irradiation.** Irradiation of the samples was carried out at room temperature using the <sup>60</sup>Co source in the Department of Applied Chemistry of Peking University. The samples of 5 mL of [C<sub>4</sub>mim][NTf<sub>2</sub>] contained in glass tubes with plugs were deaerated first by bubbling N<sub>2</sub> for at least 20 min, and then the sealed tubes were subjected to  $\gamma$ -irradiation using a dose rate of 55–65 Gy·min<sup>−1</sup>, up to a maximum dose of 550 kGy. The absorbed dose was traced using a conventional ferrous sulfate dosimeter.

**2.3. Liquid/Liquid Extractions.** The aqueous solution containing 0.01 mol·L<sup>−1</sup> Sr<sup>2+</sup> was prepared by dissolving its nitrate salt in deionized water. The extraction phase of [C<sub>4</sub>mim][NTf<sub>2</sub>] containing 0.1 mol·L<sup>−1</sup> DCH18C6 was prepared by dissolving the extractant DCH18C6 in each IL irradiated at different doses with the assistance of ultrasonic agitation. The extraction experiments were conducted by contacting 0.5 mL of extraction phase with a 1 mL aqueous solution of Sr(NO<sub>3</sub>)<sub>2</sub> for about 30 min in a vibrating mixer, followed by centrifuging to ensure that the phases were fully mixed and separated. After phase separation, the aqueous solution was diluted 20 times with



**Figure 1.** Influence of dose on Sr<sup>2+</sup> extraction from aqueous solutions by irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] in combination with DCH18C6.

deionized water, and then the concentration of Sr<sup>2+</sup> in the diluted solution was measured by a Hitachi 180-80 polarize zeeman atomic absorption spectrophotometer. Acetylene was used as fuel in the measurement at a flow rate of 0.25 kg·cm<sup>−2</sup>, while the air was used as oxidant at a flow rate of 1.6 kg·cm<sup>−2</sup>. All values were measured in duplicate with uncertainty within 5%.

**2.4. Analytical Techniques.** The NMR spectra of the samples in deuterated DMSO were measured using a Bruker Avance AV 400 MHz NMR spectrometer. The FTIR spectra were recorded as liquid films between KBr plates using a VECTOR22 FTIR spectrometer.

## 3. Results and Discussion

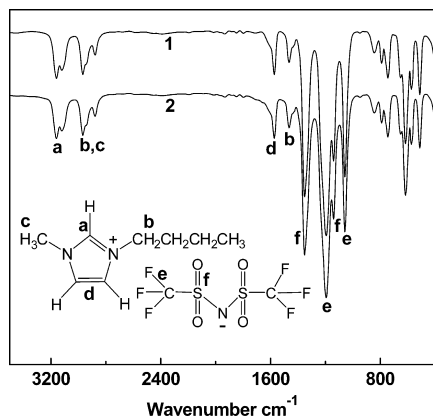
Solvent extractions of Sr<sup>2+</sup> from its aqueous solution into irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] in the presence of DCH18C6 were performed at room temperature. For comparison, identical extraction experiment was also conducted using unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. The distribution ratio ( $D_{Sr}$ ) and the degree of extraction ( $E_{Sr}$ ) for Sr<sup>2+</sup> were defined as follows

$$D_{Sr} = \frac{2(C_i - C_f)}{C_f} \quad (1)$$

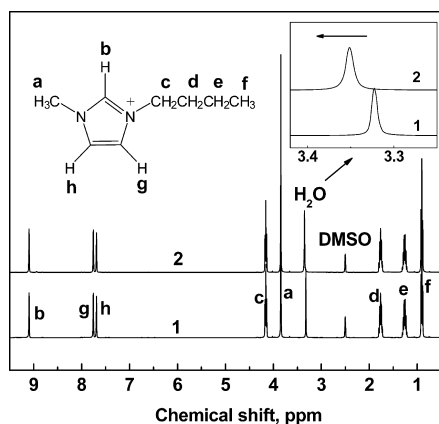
$$E_{Sr} = \frac{(C_i - C_f)}{C_i} \quad (2)$$

where  $C_i$  and  $C_f$  represent the initial and final concentrations of Sr<sup>2+</sup> in the aqueous phase, respectively; and 2 designates the volume ratio of the aqueous phase and the RTIL phase in the extraction experiment. The above equations for calculation of  $D_{Sr}$  and  $E_{Sr}$  made a convenience that only the aqueous phase was measured.

Figure 1 shows extraction results for [C<sub>4</sub>mim][NTf<sub>2</sub>] containing 0.1 mol·L<sup>−1</sup> DCH18C6. As can be seen, a very high  $D_{Sr}$  of 728 for unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>], compared with that of 30 for [C<sub>4</sub>mim][PF<sub>6</sub>]<sup>37</sup> and that of 0.77 for chloroform<sup>15</sup> at the same conditions, was obtained. Accordingly, the removal of Sr<sup>2+</sup> from aqueous solution was almost complete (99.7%), suggesting that a [C<sub>4</sub>mim][NTf<sub>2</sub>]-based extraction system is more effective media for liquid/liquid extraction of metal ions. However, a significant decline of the  $D_{Sr}$  was observed when the [C<sub>4</sub>mim][NTf<sub>2</sub>] solvent was irradiated, and the decline enhanced obviously with increasing dose (Figure 1). After being irradiated at a dose of 550 kGy, for example, the  $D_{Sr}$  of [C<sub>4</sub>mim][NTf<sub>2</sub>] was even less than 15, a value 50 times lower than that of unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>], while the  $E_{Sr}$  decreased from 99.7 to 87.7%.



**Figure 2.** FTIR spectra of [C<sub>4</sub>mim][NTf<sub>2</sub>] before (1) and after  $\gamma$ -irradiation at 550 kGy (2) under a nitrogen atmosphere.



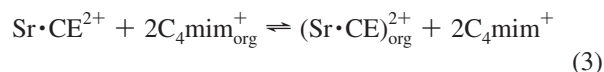
**Figure 3.** NMR spectra of [C<sub>4</sub>mim][NTf<sub>2</sub>] before (1) and after  $\gamma$ -irradiation at 550 kGy (2) under a nitrogen atmosphere. Deuterated DMSO was used as solvent in the measurement.

We have recently investigated the influence of  $\gamma$ -radiation on [C<sub>4</sub>mim][PF<sub>6</sub>] for extraction of Sr<sup>2+</sup>. The result showed that the Sr<sup>2+</sup> partitioning in [C<sub>4</sub>mim][PF<sub>6</sub>]/DCH18C6 decreased as the absorbed dose of [C<sub>4</sub>mim][PF<sub>6</sub>] increased, and the decrease of Sr<sup>2+</sup> partitioning is related to radiation-generated H<sup>+</sup>.<sup>37</sup> It was thought that the radiation-generated H<sup>+</sup> was also the main factor that influences the extraction of Sr<sup>2+</sup> in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. Herein, FTIR and <sup>1</sup>H and <sup>19</sup>F NMR spectra of [C<sub>4</sub>mim][NTf<sub>2</sub>] before and after irradiation were compared. All main peaks in FTIR spectra are assigned to appropriate groups (Figure 2), and all the chemical shifts in <sup>1</sup>H NMR spectra were assigned to appropriate H atoms (Figure 3). The comparison showed no discernible changes in both FTIR and NMR spectra even at the dose of 550 kGy, suggesting that the amount of nonvolatile radiolysis products does not exceed 0.5% in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. This is consistent with that reported by Berthon et al.,<sup>18</sup> who found by electrospray ionization mass spectrometry and NMR analysis that less than 0.5% of [C<sub>4</sub>mim][NTf<sub>2</sub>] underwent radiolysis after irradiation at 450 kGy. However, as seen from Figure 3, the peak of water broadened and shifted toward the low field direction in the irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] compared with that in unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. Such an observation reveals the formation of acidic radiolysis products since the addition of acids such as nitric acid in unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] results in the similar broadening and shifting of the water signal. In fact, that washing irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] with deionized water yielded an aqueous phase at pH  $\approx$  2–3 seems to be a more direct evidence that the acids were formed during irradiation. It is expected that

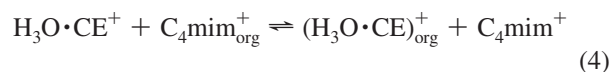
the initial steps of C<sub>4</sub>mim<sup>+</sup> cation radiolysis are ionization, forming a thermalized electron and the remaining radical C<sub>4</sub>mim<sup>•2+</sup>,<sup>25,33,34</sup> and loss of the H atom from both alkyl groups and the imidazolium ring.<sup>17,18,20,25</sup> The heterolytic dissociation of the H–C2 bond of the imidazolium ring in excited C<sub>4</sub>mim<sup>•2+</sup>, and/or further ionization of the H atom, lead to the formation of H<sup>+</sup>.

The studies of solvent extraction of Sr<sup>2+</sup> from nitric acid media by crown ethers using RTILs demonstrated that the partitioning of Sr<sup>2+</sup> in ILs decreased as the acidity of aqueous solution increased.<sup>44,45</sup> Similarly, acidic products were generated during irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>] as mentioned above and were cumulated with increasing dose, leading to the increase of the acidity of aqueous solution when the extraction was conducted. As a result, the partitioning of Sr<sup>2+</sup> in ILs decreased. To prove that, we have adopted a strategy that the irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] at 550 kGy was washed several times with deionized water before extraction, and the removal of H<sup>+</sup> was confirmed by making sure that a neutral upper aqueous phase was obtained. Expectably, the Sr<sup>2+</sup> partitioning in [C<sub>4</sub>mim][NTf<sub>2</sub>] recovered after washing irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. The high *D*<sub>Sr</sub> of 599 and the complete removal of Sr<sup>2+</sup> (99.7%) from the aqueous solution were regained (Figure 1). Hence, we unambiguously establish that H<sup>+</sup> is responsible for the decline of partitioning of Sr<sup>2+</sup> in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] with DCH18C6 as extractant.

We now attempt to rationalize why the radiation-generated H<sup>+</sup> decreases the Sr<sup>2+</sup> partitioning in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. As is well-known, Sr<sup>2+</sup> partitioning from aqueous solution into RTILs involves a cation-exchange mode, which is very different from conventional solvents such as *n*-alcohol.<sup>44</sup> Here the cationic constituent of RTILs is C<sub>4</sub>mim<sup>+</sup>, and the related cation-exchange mode of the Sr•CE<sup>2+</sup> complex can be depicted as follows

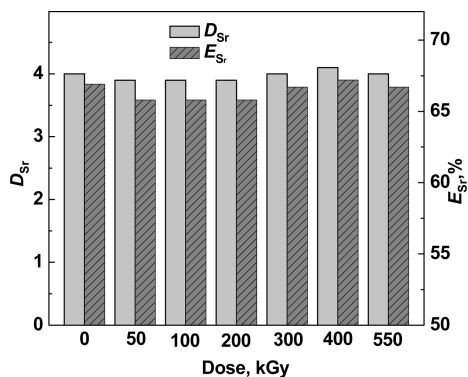


where CE represents crown ether, i.e., DCH18C6, and the subscript designates the organic phase. When H<sup>+</sup> coexists in the extraction system, its hydrate may influence the extraction of Sr<sup>2+</sup> by interacting with crown ether and then moving into the organic phase by similar cation exchange (eq 4). In fact, the formation of the H<sub>3</sub>O•CE<sup>+</sup> adduct in ionic liquid has been identified IR-spectrometrically during acid extraction by crown ether.<sup>46</sup>



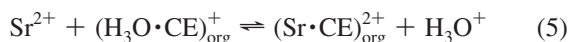
The amount of H<sup>+</sup> in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] was simply quantified by a pH measurement. After being irradiated at 400 kGy, for example, washing [C<sub>4</sub>mim][NTf<sub>2</sub>] with deionized water yielded an aqueous phase at pH  $\approx$  2.5, revealing the presence of H<sup>+</sup> in irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] at concentrations below 0.01 mol•L<sup>-1</sup>. The H<sup>+</sup> with such amount, as shown in Figure 1, dramatically decreased the *D*<sub>Sr</sub> of [C<sub>4</sub>mim][NTf<sub>2</sub>]. However, if the extraction of Sr<sup>2+</sup> is performed not from water but from nitric acid media that is common in practical applications, the case may be very different. With this view in mind, a further study was carried out, in which Sr<sup>2+</sup> was extracted from nitric acid solution (3 mol•L<sup>-1</sup>) into [C<sub>4</sub>mim][NTf<sub>2</sub>] containing 0.1 mol•L<sup>-1</sup> DCH18C6. The experimental results are shown in Figure 4. It is clear that the *D*<sub>Sr</sub> of [C<sub>4</sub>mim][NTf<sub>2</sub>] for extraction





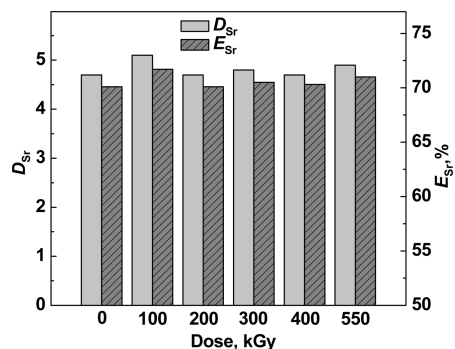
**Figure 4.** Influence of dose on Sr<sup>2+</sup> extraction from 3 mol·L<sup>-1</sup> nitric acid solution by irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] in combination with DCH18C6.

of Sr<sup>2+</sup> from nitric acid media is much lower than that from aqueous solution, suggesting that nitric acid in the aqueous phase dramatically decreases the Sr<sup>2+</sup> partitioning in the IL phase. This is consistent with that reported by Visser et al.<sup>45</sup> and Dietz et al.,<sup>44</sup> who demonstrated that the  $D_{Sr}$  of RTILs decreases with increasing concentration of nitric acid in the aqueous phase. However, the  $D_{Sr}$  of 4 is greater than that of a conventional organic solvent such as toluene<sup>15</sup> under the same conditions, which indicated that even at high acidity Sr<sup>2+</sup> partitioning into [C<sub>4</sub>mim][NTf<sub>2</sub>] can also be achieved by another cation exchange as follows by similarity with well-known sodium partitioning<sup>46</sup>



When the [C<sub>4</sub>mim][NTf<sub>2</sub>] solvent was irradiated, it was found that the Sr<sup>2+</sup> partitioning from nitric acid solution into irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>], regardless of the doses, had no marked changes compared with those into unirradiated [C<sub>4</sub>mim][NTf<sub>2</sub>]. In other words,  $\gamma$ -irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>] seems to have no influence on the extraction of Sr<sup>2+</sup> from nitric acid solution, which is very different from the extraction of Sr<sup>2+</sup> from aqueous solution. It is thought that the high acidity of the aqueous phase made the difference in the amount of H<sup>+</sup> formed during the irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>] at different doses insignificant, thereby diminishing the influence of  $\gamma$ -irradiation on [C<sub>4</sub>mim][NTf<sub>2</sub>] for extraction of Sr<sup>2+</sup>. When the acidity of the aqueous phase is sufficiently high (e.g., 3 mol·L<sup>-1</sup> nitric acid solution), the influence of irradiation on Sr<sup>2+</sup> extraction is even negligible as shown in Figure 4. Such an observation is actually another support for the conclusion that H<sup>+</sup> formed during irradiation of [C<sub>4</sub>mim][NTf<sub>2</sub>] is responsible for the decrease of Sr<sup>2+</sup> partitioning in [C<sub>4</sub>mim][NTf<sub>2</sub>]/DCH18C6.

For comparison, identical extraction of Sr<sup>2+</sup> from 3 mol·L<sup>-1</sup> nitric acid solution was also performed using irradiated [C<sub>4</sub>mim][PF<sub>6</sub>] in combination with DCH18C6. The results are shown in Figure 5. It is clear that the Sr<sup>2+</sup> partitioning from nitric acid solution into [C<sub>4</sub>mim][PF<sub>6</sub>]/DCH18C6 showed no marked changes with increasing absorbed dose of [C<sub>4</sub>mim][PF<sub>6</sub>], which is very similar with the [C<sub>4</sub>mim][NTf<sub>2</sub>]-based extraction system. This demonstrates that identical extraction mode and identical radiation effect are involved in [C<sub>4</sub>mim][NTf<sub>2</sub>] and the [C<sub>4</sub>mim][PF<sub>6</sub>]-based extraction system and also probably in other imidazolium ionic liquid based extraction systems. Further research on this topic is required.



**Figure 5.** Influence of dose on Sr<sup>2+</sup> extraction from 3 mol·L<sup>-1</sup> nitric acid solution by irradiated [C<sub>4</sub>mim][PF<sub>6</sub>] in combination with DCH18C6.

#### 4. Conclusions

Solvent extraction of Sr<sup>2+</sup> by irradiated [C<sub>4</sub>mim][NTf<sub>2</sub>] with crown ether as extractant was investigated. The present results and those reported recently for the [C<sub>4</sub>mim][PF<sub>6</sub>]-based extraction system clearly suggest that  $\gamma$ -irradiation of the imidazolium ionic liquids markedly decreases Sr<sup>2+</sup> partitioning in RTILs/crown ether extraction phase due to the competition between radiation-generated H<sup>+</sup> and Sr<sup>2+</sup> to interact with the crown ether. However, the radiation effect on the extraction systems can be easily eliminated by washing irradiated RTILs with water. Furthermore,  $\gamma$ -irradiation of the RTILs shows no discernible influence on Sr<sup>2+</sup> extraction from nitric acid solution with high acidity. This work promises to provide new data for assessing the feasibility of RTILs as alternative media for the separations of high level radioactive nuclides from wastewater.

#### References and Notes

- (1) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221.
- (2) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
- (3) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (4) Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18*, 275.
- (5) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2002**, *37*, 3772.
- (6) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.
- (7) Cocalia, V. A.; Gutowski, K. E.; Rogers, R. D. *Coord. Chem. Rev.* **2006**, *250*, 755.
- (8) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391.
- (9) Dietz, M. L. *Sep. Sci. Technol.* **2006**, *41*, 2047.
- (10) Jensen, M. P.; Neufeind, J.; Beitz, J. V.; Skanthakumar, S.; Soderholm, L. *J. Am. Chem. Soc.* **2003**, *125*, 15466.
- (11) Nikitenko, S. I.; Cannes, C.; Le Naour, C.; Moisy, P.; Trubert, D. *Inorg. Chem.* **2005**, *44*, 9497.
- (12) Visser, A. E.; Rogers, R. D. *J. Solid State Chem.* **2003**, *171*, 109.
- (13) Nakashima, K.; Kubota, F.; Maruyama, T.; Goto, M. *Anal. Sci.* **2003**, *19*, 1097.
- (14) Nakashima, K.; Kubota, F.; Maruyama, T.; Goto, M. *Ind. Eng. Chem. Res.* **2005**, *44*, 4368.
- (15) Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1201.
- (16) Luo, H. M.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C.; Holbrey, J. D.; Bridges, N. J.; Rogers, R. D. *Anal. Chem.* **2004**, *76*, 3078.
- (17) Allen, D.; Baston, G.; Bradley, A. E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J. E.; Healey, M. J. F.; Hodgson, B.; Lewin, R.; Lovell, K. V.; Newton, B.; Pitner, W. R.; Rooney, D. W.; Sanders, D.; Seddon, K. R.; Sims, H. E.; Thied, R. C. *Green Chem.* **2002**, *4*, 152.
- (18) Berthon, L.; Nikitenko, S. I.; Bisel, I.; Berthon, C.; Faucon, M.; Saucrotte, B.; Zor, N.; Moisy, P. *Dalton Trans.* **2006**, 2526.
- (19) Bosse, E.; Berthon, L.; Zor, N.; Monget, J.; Berthon, C.; Bisel, I.; Legend, S.; Moisy, P. *Dalton Trans.* **2008**, 924.
- (20) Qi, M. Y.; Wu, G. Z.; Chen, S. M.; Liu, Y. D. *Radiat. Res.* **2007**, *167*, 508.
- (21) Qi, M. Y.; Wu, G. Z.; Li, Q. M.; Luo, Y. S. *Radiat. Phys. Chem.* **2008**, *77*, 877.
- (22) Tarabek, P.; Liu, S.; Haygarth, K.; Bartels, D. M. *Radiat. Phys. Chem.* **2009**, doi:10.1016/j.radphyschem.2008.11.006.

- (23) Yuan, L.; Peng, J.; Zhai, M.; Li, J.; Wei, G. *Radiat. Phys. Chem.* **2009**, doi.org/10.1016/j.radphyschem.2009.03.064.
- (24) Yuan, L.; Peng, J.; Zhai, M.; Li, J.; Wei, G. *Radiat. Phys. Chem.* **2008**, accepted.
- (25) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607.
- (26) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139.
- (27) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468.
- (28) Grodkowski, J.; Neta, P.; Wishart, J. F. *J. Phys. Chem. A* **2003**, *107*, 9794.
- (29) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 9030.
- (30) Yang, J. F.; Kondoh, T.; Norizawa, K.; Nagaishi, R.; Taguchi, M.; Takahashi, K.; Katoh, R.; Anishchik, S. V.; Yoshida, Y.; Tagawa, S. *Radiat. Phys. Chem.* **2008**, *77*, 1233.
- (31) Wishart, J. F.; Neta, P. *J. Phys. Chem. B* **2003**, *107*, 7261.
- (32) Wishart, J. F.; Lall-Ramnarine, S. I.; Raju, R.; Scumpia, A.; Bellevue, S.; Ragbir, R.; Engel, R. *Radiat. Phys. Chem.* **2005**, *72*, 99.
- (33) Marcinek, A.; Zielonka, J.; Gebicki, J.; Gordon, C. M.; Dunkin, I. R. *J. Phys. Chem. A* **2001**, *105*, 9305.
- (34) Shkrob, I. A.; Chemerisov, S. D.; Wishart, J. F. *J. Phys. Chem. B* **2007**, *111*, 11786.
- (35) Stepnowski, P.; Zaleska, A. *J. Photochem. Photobiol. A, Chem.* **2005**, *170*, 45.
- (36) Zhu, G. L.; Xu, J. J.; Wu, G. Z.; Zhu, H. P.; Long, D. W.; Chen, S.; Yao, S. D. *Int. J. Mol. Sci.* **2006**, *7*, 590.
- (37) Yuan, L.; Peng, J.; Xu, L.; Zhai, M.; Li, J.; Wei, G. *J. Chem. Soc., Dalton Trans.* **2008**, 6358.
- (38) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
- (39) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
- (40) Tokuda, H.; Hayamizu, K.; Ishii, K.; Abu Bin Hasan Susan, M.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.
- (41) Oldham, W. J.; Costa, D. A.; Smith, W. H. *Ionic Liquids* **2002**, *818*, 188.
- (42) Dzyuba, S. V.; Bartsch, R. A. *Chemphyschem* **2002**, *3*, 161.
- (43) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, *402*, 375.
- (44) Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.* **2001**, 2124.
- (45) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596.
- (46) Dietz, M. L.; Stepinski, D. C. *Green Chem.* **2005**, *7*, 747.

JP9016079