

## Extraction Behavior of Sr(II) from Nitric Acid Solution using DtBuCH18C6 Containing Ionic Liquid Extraction System and its medical application

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4',4'(5'')-di-(*tert*-butyl cyclohexano)-18-crown-6 (DtBuCH18C6) as an extractant in combination with three types of ionic liquids, [C<sub>4</sub>mim][X] (X = NfO, NTf<sub>2</sub>, FAP) as solvents to separate Sr(II) effectively from HNO<sub>3</sub> solution. Under the experimental conditions, within the acidity range studied, the  $D_{Sr}$  follows the order of [C<sub>4</sub>mim][NfO] > [C<sub>4</sub>mim][NTf<sub>2</sub>] > [C<sub>4</sub>mim][FAP]. In their extraction systems,  $D_{Sr}$  decreases with increasing concentration of HNO<sub>3</sub> solution. Thermodynamic parameters for the extraction of Sr(II) tested elements were calculated using the Van't Hoff equation, showing that the reaction is spontaneous and exothermic. Existence of inorganic salts such as KNO<sub>3</sub> usually reduces  $E_{Sr}$  for all systems, and the decreasing degree is much larger than that of NaNO<sub>3</sub>. The extraction systems exhibited high extraction efficiency and high selectivity for Sr(II) from simulated HLLW containing 20 typical elements and 2M HNO<sub>3</sub>. From the results, the present system may provide an alternative for extraction of Sr(II) under HLLW conditions.

### 1. Introduction

In order to minimize the long-term radiological risk and reuse of valuable nuclides in the field of spent nuclear fuel reprocessing, the partitioning of <sup>90</sup>Sr and of some specific fission products (FPs) from high-level liquid waste (HLLW) is very desirable [1-3]. The heat-generated elements, <sup>90</sup>Sr, having a half-life of 28 years and contributes about 25% of heat generation in HLLW (~1.1 kg/1 tHU, 45 GWd/t) [4] with its daughter nuclide <sup>90</sup>Y. Furthermore, <sup>90</sup>Y is also expected for the utilization as radioactive material in the medicine field. Therefore the selective separation of <sup>90</sup>Sr from HLLW is necessary. A number of recovery methods have been reported in literature for the separation of Sr(II) from HLLW, such as ion exchange [5-9], solvent extraction [10-14] and extraction chromatography [15-16]. Over the last decade, in the ionic liquids extraction has selective extractability to Sr(II) that has been widely used for extraction process. Ionic liquids are composed of heterocyclic organic cations and inorganic anions and have even more advantageous properties, such as nonvolatility, nonflammability, thermal and electrochemical stabilities and conductivity instead of the traditional diluents, enhancement of extraction efficiency, possibly leading to cost-reduction in extraction processes. This evaluation study was carried out based on a novel extraction process for HLLW treatment which was proposed by our group [17]. In this extraction process, the FPs elements PGMs and Cs(I) have been separated from simulated HLLW firstly by [C<sub>4</sub>min][NfO] and Calix[4]arene-R14 as an extractant and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C<sub>n</sub>mim][NTf<sub>2</sub>]) as solvents

successfully.

In this work, the extraction of Sr(II) from HNO<sub>3</sub> solution has been investigated using DtBuCH18C6 as an extractant in combination with three kinds of ionic liquid [C<sub>4</sub>mim][X] (X = NfO, NTf<sub>2</sub>, FAP) as solvents, where DtBuCH18C6 is 4,4', (5')-di-(*tert*-butyl cyclohexano)-18-crown-6, [C<sub>4</sub>mim]<sup>+</sup> is 1-butyl-3-methylimidazolium and [NfO]<sup>-</sup> is nonafluorobutane-sulfonate, [NTf<sub>2</sub>]<sup>-</sup> is bis(trifluoro-methyl sulfonyl)amide, [FAP]<sup>-</sup> is tris(pentafluoroethyl)trifluorophosphate. The extraction system was studied in detail with regard to different extraction parameters such as the concentration of HNO<sub>3</sub>, concentration of extractant, temperature, concentration of inorganic salts, and under coexistence of various metals, on the extraction of Sr(II).

## 2. Experimental

### 2.1 Materials

4',4'(5'')-di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6, 90 wt%) was purchased from Sigma-Aldrich Chemical Co. and used without purification. The ionic liquid of [C<sub>4</sub>mim][NfO] was synthesized. Its synthesis method was reported in detail by Kozonoi [18]. [C<sub>4</sub>mim][NTf<sub>2</sub>], [C<sub>4</sub>mim][FAP] ionic liquids were purchased from Sigma-Aldrich Chemical Co. The molecular structure of DtBuCH18C6 and [C<sub>4</sub>mim][X] (X = NTf<sub>2</sub>, NfO, FAP) are shown in Figure 1. Chemical reagents, NaNO<sub>3</sub>, KNO<sub>3</sub>, AgNO<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, RE(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (RE = Y, La, Ce, Pr, Nd, Sm, and Gd), ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were of analytical grade and supplied by Kanto Chemical Co.

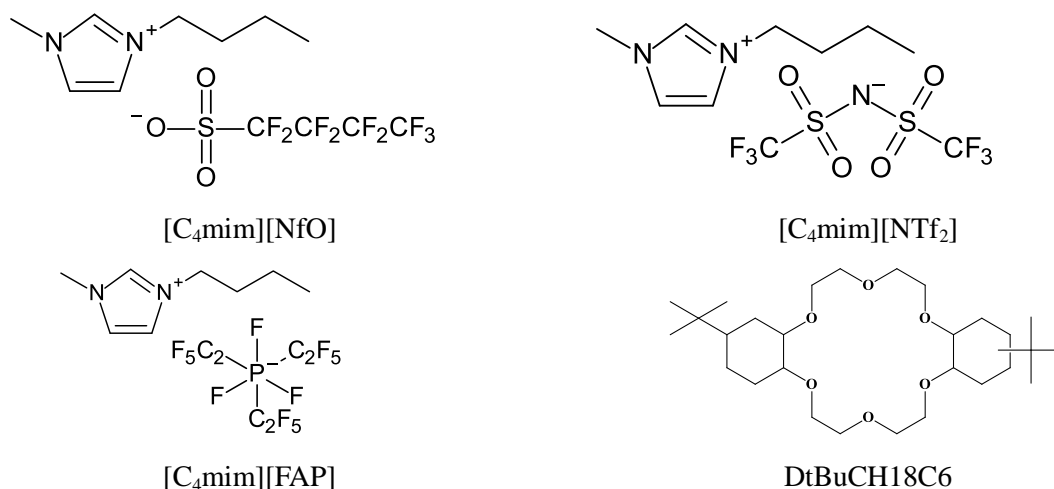


Figure 1. Chemical structure of the cations [C<sub>4</sub>mim]<sup>+</sup> and anions [NfO]<sup>-</sup>, [NTf<sub>2</sub>]<sup>-</sup>, [FAP]<sup>-</sup> and extractant (DtBuCH18C6).

### 2.2 Batch extraction method

The extraction behaviors of metal ions for DtBuCH18C6 containing ionic liquid extraction system were estimated by batch methods. An aqueous solution (2 cm<sup>3</sup>) containing 5 mM Sr(II) ion was contacted with 2 cm<sup>3</sup> of ionic liquid containing DtBuCH18C6 in a thermostatic bath up to 15 min, which was found to be sufficient for attaining equilibrium. The concentrations of metal ions were

measured using an atomic absorption spectrophotometer (AAS) and inductively coupled plasma atomic emission spectrometer (ICP-AES). The distribution ratios ( $D_{Sr}$ ) and extraction efficiencies ( $E_{Sr}$ ) were calculated as follows:

$$D_{Sr} \equiv \frac{C_{IL}}{C_{Aq}} = \frac{C_{0,Aq} \times \frac{V_{0,Aq}}{V_{IL}} - C_{Aq} \times \frac{V_{Aq}}{V_{IL}}}{C_{Aq}} \quad (1)$$

$$E_{Sr} = \frac{100 \times D_{Sr}}{D_{Sr} + \frac{V_{Aq}}{V_{IL}}} \quad (2)$$

where  $C_{0,Aq}$  and  $C_{Aq}$  represent the initial and final concentrations of Sr(II) in an aqueous solution,  $V_{0,Aq}$  and  $V_{Aq}$  ( $\text{cm}^3$ ) indicate the volume of the aqueous phase before and after extraction, respectively, and  $V_{IL}$  ( $\text{cm}^3$ ) is the volume of the ionic liquid phase after extraction.

### 3. Results and Discussion

#### 3.1 Extraction kinetics in ILs

In order to evaluate the equilibrium time of Sr(II) for DtBuCH18C6 containing ILs extraction systems, the effect of mixing time on  $E_{Sr}$  was examined in the presence of 2 M  $\text{HNO}_3$  by the batch method. The  $E_{Sr}$  increases with an increase in mixing time and reaches an equilibrium state within 10 min. Under the experimental conditions, the  $E_{Sr}$  shows an order of  $[\text{C}_4\text{mim}][\text{NfO}] > [\text{C}_4\text{mim}][\text{NTf}_2] > [\text{C}_4\text{mim}][\text{FAP}]$ . The data showed that the extraction capability of Sr(II) decreased with anions under same conditions. This result shows that the extraction capabilities for metal ions have a strong preference for the aqueous phase.

#### 3.2 Effects of $\text{HNO}_3$ solution concentration

To understand the effect of  $\text{HNO}_3$  concentration, the extraction behavior of 5 mM Sr(II) into DtBuCH18C6 (10 mM) containing ILs systems were examined at different concentrations of  $\text{HNO}_3$  from 0.015 M to 4 M by batch method (Figure 2). As for Sr(II), a decrease in the  $D_{Sr}$  for the  $[\text{C}_4\text{mim}][\text{NfO}]$ ,  $[\text{C}_4\text{mim}][\text{NTf}_2]$  systems with increasing concentrations of  $\text{HNO}_3$  is observed. In contrast,  $[\text{C}_4\text{mim}][\text{FAP}]$  was considerably low in the all range of  $\text{HNO}_3$  concentration. Within the acidity range studied, the  $D_{Sr}$  values for Sr(II) maintain the order of  $[\text{C}_4\text{mim}][\text{NfO}] > [\text{C}_4\text{mim}][\text{NTf}_2] > [\text{C}_4\text{mim}][\text{FAP}]$ .

The extraction mechanism with participation of hydrophobic ILs has been continuously studied. Similar results were observed in a study conducted by Luo et al. [19]. Luo has reported that the hydrophobicity of the IL anion has controlling extraction strength. Moreover, several studies have reported that the extraction ratio decreases with an increase in the  $\text{HNO}_3$  concentration. Xu et al. has shown that the competition of  $\text{H}^+$  might be a leading factor that

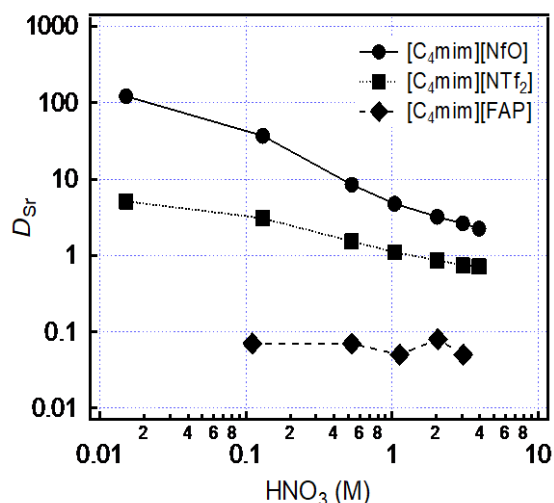


Figure 2. Dependence of  $D_{Sr}$  on  $\text{HNO}_3$  concentration.

causes an overall decrease in the extraction efficiency [20]. In the same manner, it is possible that competition of  $H^+$  accounts for the decrease in  $D_{Sr}$  with an increase in the  $HNO_3$  concentration. These observations suggest that one of the mechanisms for extraction is cation exchange.

### 3.3 Influence of the DtBuCH18C6 concentration

To understand the extractant effect, the extraction behavior of Sr(II) into DtBuCH18C6 containing ILs systems in a 2 M  $HNO_3$  solution was investigated at different concentrations. Figure 3 shows the relation between  $E_{Sr}$  and DtBuCH18C6 concentration in combination with  $[C_4mim][X]$ . As shown in Figure 3,  $E_{Sr}$  increases with increasing DtBuCH18C6 concentration. The  $[C_4mim][NTf_2]$  and  $[C_4mim][FAP]$  showed no extraction of Sr(II) in the absence of DtBuCH18C6, *i.e.*, ILs themselves cannot extract Sr(II) in the absence of proper extractants. On the other hand,  $[C_4mim][NfO]$  has extraction ability for Sr(II). Kozonoi et al. has shown that  $[C_4mim][NfO]$  extract various metal ionic species from the aqueous solution. This observation suggests that  $[NfO]$  anion is extractant for Sr(II) in  $[C_4mim][NfO]$ . The results in Figure 3 also indicate that the extraction capability of the three selected  $[C_4mim][X]$  systems follows the general order of  $[C_4mim][NfO] > [C_4mim][NTf_2] > [C_4mim][FAP]$  under given conditions. The  $[C_4mim][NfO]$  matches best with DtBuCH18C6 to extract Sr(II).

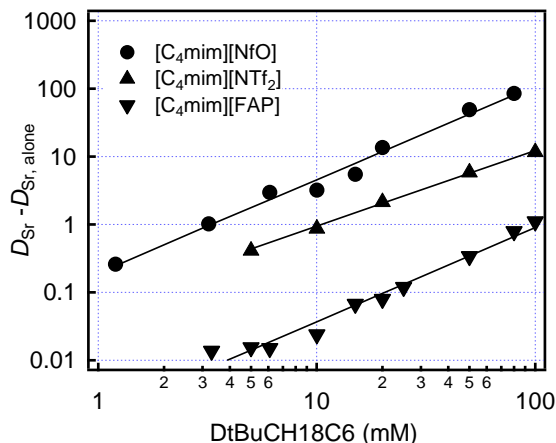
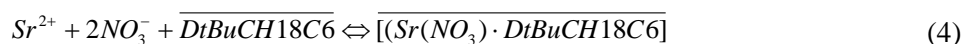
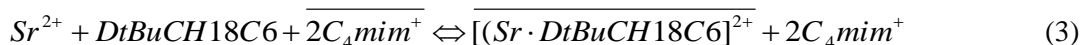


Figure 3. Dependence of  $D_{Sr}$  on DtBuCH18C6 concentration.

A linear regression analysis of the  $D_{Sr}$  resulted in a straight line with a slope of 1.1, suggesting the involvement of 1 molecule of DtBuCH18C6 during the extraction processes as shown in Eq(3) and (4).

Such a phenomenon has been observed by Dietz and Stepinski while studying the extraction of sodium by crown ether (dicyclohexano-18-crown-6) under low acid conditions [21].



### 3.4 Extraction thermodynamics

To understand the temperature effect, the extraction behavior of Sr(II) onto DtBuCH18C6 containing ILs systems in 2 M  $HNO_3$  solution was investigated at different temperatures. In order to gain insight into the thermodynamic nature of the extraction process, several thermodynamic parameters for the present system were calculated. The Gibbs free energy,  $\Delta G^\circ$ , is the fundamental

criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^\circ$  is a negative quantity. The Gibbs free energy of the extraction process is given by the equation as follows

$$\Delta G^\circ = -RT \times \ln D \quad (5)$$

Otherwise, the values of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) for Sr(II) in the extraction processes can be calculated from the slope and intercept of the plots of  $\ln D$  vs.  $1/T$  by the van't Hoff equation as follows

$$\ln D = \frac{-\Delta H^\circ}{R \cdot T} + \frac{\Delta S^\circ}{R} \quad (6)$$

where  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature in Kelvin, is the distribution ratios ( $D_{\text{Sr}}$ ) on equilibrium state defined as Eq. (1).

The experimental temperature was controlled in the range of 288 to 323 K and the corresponding plots of  $\ln D$  vs.  $1/T$  are depicted in Figure 4. From the plots in Figure 4, all the calculated parameters of the extraction reactions for DtBuCH18C6 containing ILs systems,  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are summarized in Table 1. The negative value of  $\Delta G^\circ$  means the extraction processes occur spontaneously at a given temperature. The change in  $\Delta H^\circ$  for Sr(II) is observed to be negative, confirming the exothermic nature of the extraction processes.

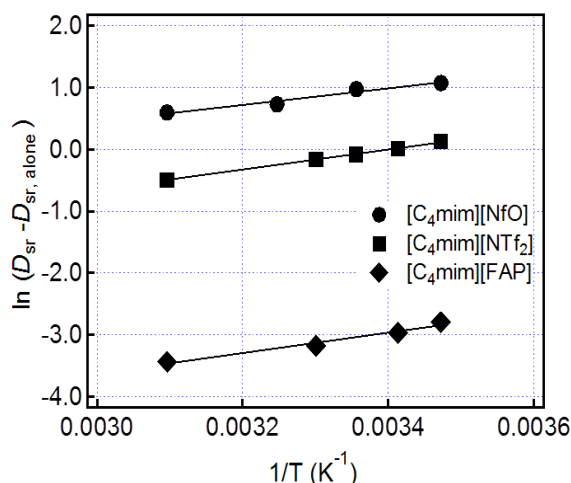


Figure 4. Van't Hoff plots for the extraction of Sr(II) on DtBuCH18C6/ ILs.  $[\text{HNO}_3] = 2.0 \text{ M}$ ,  $[\text{DtBuCH18C6}] = 10 \text{ mM}$ ,  $[\text{Sr}] = 5 \text{ mM}$

Table 1. Values of the thermodynamic parameters for extraction of Sr(II) on DtBuCH18C6/ILs

Tem (K)	$\Delta G^\circ (\text{kJ mol}^{-1})$			$\Delta H^\circ (\text{kJ mol}^{-1})$			$\Delta S^\circ (\text{kJ mol}^{-1} \text{ K}^{-1})$		
	[NfO]	[NTf <sub>2</sub> ]	[FAP]	[NfO]	[NTf <sub>2</sub> ]	[FAP]	[NfO]	[NTf <sub>2</sub> ]	[FAP]
288	-2.59	-0.27	6.81						
293	-	-0.04	7.17						
298	-2.30	0.19	-	-11.15	-13.46	-13.77	-0.030	-0.046	-0.071
303	-	0.42	7.89						
308	-2.00	-	-						
323	-1.55	1.33	9.32						

### 3.5 Effect of inorganic salts

HLLW containing a large quantity of inorganic salts derived from alkaline liquid waste has an especially large amount of Na(I). To examine the applicability of separation process for HLLW, it is necessary to study the effects of  $\text{NaNO}_3$  and  $\text{KNO}_3$  on the extraction of Sr(II) using DtBuCH18C6 containing ILs systems.

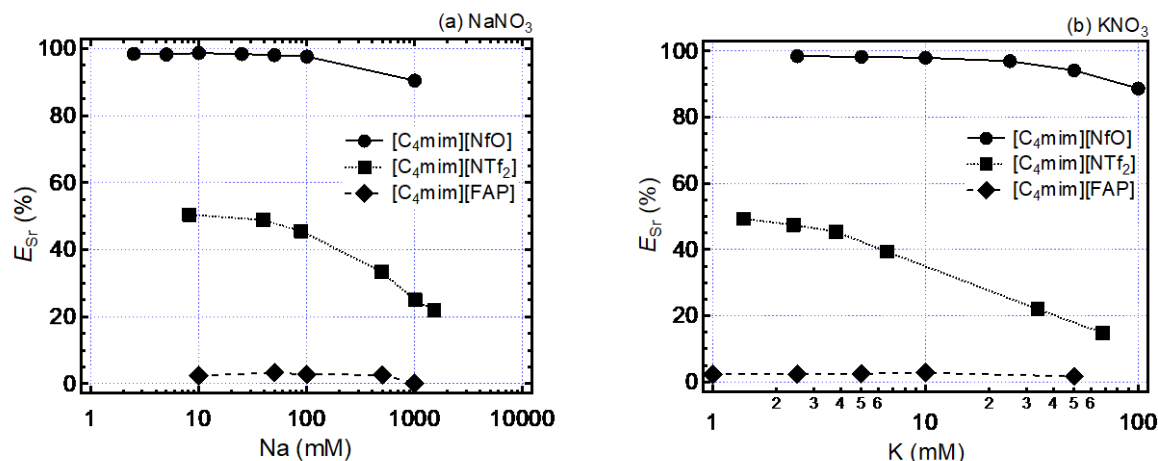


Figure 5. Dependence of the extraction efficiency of Sr(II) in DtBuCH18C6/ILs on the concentration of inorganic salts. ( $[\text{HNO}_3] = 2.0 \text{ M}$ ,  $[\text{DtBuCH18C6}] = 10 \text{ mM}$ ,  $[\text{Sr}] = 5 \text{ mM}$ ,  $T = 295 \text{ K}$ )

As shown in Figure 5, the addition of the two salts will generally reduce the extraction efficiency of Sr(II); however, the  $E_{\text{Sr}}$  of solutions containing Na(I) was much larger than that of K(I). This can be explained by the similar ionic radius between K(I) and Sr(II), which causes much more competition with the crown ether complex.

### 3.6 Separation of Sr(II) for simulated HLLW

The components in HLLW after removing actinides are very complicated. Apart from the  $^{90}\text{Sr}$  radioactive nuclide, there are many other coexisting elements such as Cs, Ba, PGMs, rare earths and minor actinide. To understand the separation behavior of Sr(II) as well as other fission products, a group partitioning experiment for a simulated HLLW containing 20 elements and 2 M  $\text{HNO}_3$  was performed using the DtBuCH18C6 containing ILs systems at 298 K. The relevant extraction of Sr(II) is illustrated in Figure 6. All extraction systems exhibited a high distribution ratio and high selectivity for separation of Sr(II) and Ba(II) from sHLLW. The separation factor (SF) of Sr from most other elements such as Cs and PGMs is much higher. In addition, the SF of Y(III) is more than  $10^3$ . The results indicate that DtBuCH18C6 containing ILs systems show stronger extraction ability and selectivity for Sr(II) in the HLLW medium.

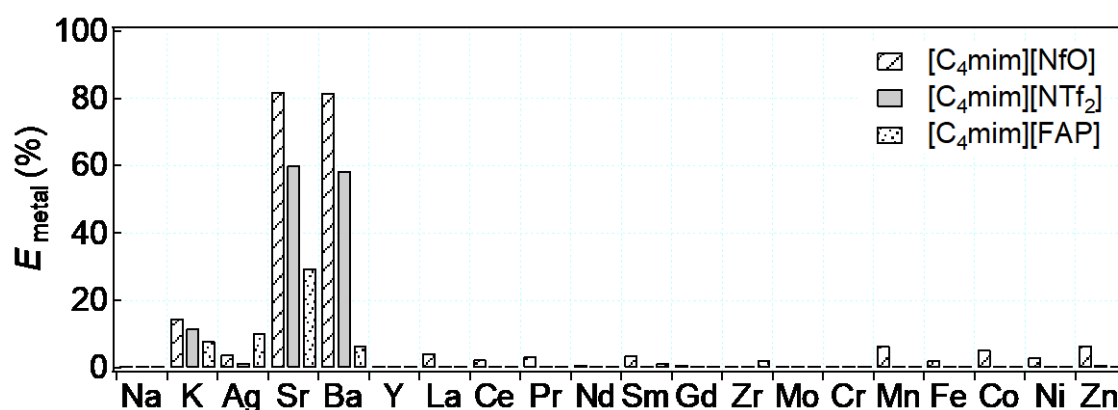


Figure 6. Extraction of Sr(II), Ba(II) from a sHLLW using DtBuCH18C6/ ILs. ( $[\text{H}^+] = 2.0 \text{ M}$ ,  $[\text{DtBuCH18C6}] = 100 \text{ mM}$ ,  $T = 298 \text{ K}$ )



#### 4. Conclusion

Extraction of Sr(II) ions using DtBuCH18C6 and three ILs as solvents has been investigated. All extraction systems are rapid reactions that reach extraction equilibrium in approximately 10 min. The extractions exhibit a decrease in  $D_{Sr}$  with increasing concentration of  $HNO_3$ . Within the  $HNO_3$  concentration range studied, the  $D_{Sr}$  maintains the order of  $[C_4mim][NfO] > [C_4mim][NTf_2] > [C_4mim][FAP]$ . The calculated thermodynamic parameters of the extraction of Sr(II) based on Van't Hoff equation indicate that the reaction is spontaneous and exothermic. The existence of inorganic salts such as  $KNO_3$  reduces the  $E_{Sr}$  for the three systems, and the degree of decrease is much larger than that of  $NaNO_3$ ; however, the  $E_{Sr}$  of solution containing Na(I) was much larger than that of K(I). In the present system, a medium acidity extraction behavior has been revealed, which may provide an alternative method for extraction of Sr(II). This method was observed to effectively separate Sr(II) from the simulated HLLW, avoiding the use of high concentration of  $HNO_3$  when using conventional solvents.

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#### References

- 1) M. Kubota, K. Okata, I. Yamaguchi, Y. Morita, *Radioact. Waste Manag. Nucl. Fuel Cycle*, **7**, 303–316 (1986).
- 2) IAEA, *IAEA Technical Report Series*, No. 356, (1993).
- 3) Atomic Energy Society of Japan (AESJ), *J. At. Energy Soc. Jpn.*, **48**, 327–332 (2006). [in Japanese].
- 4) Y. Ando, H. Takano, *JAERI-Research 99-004*, (1999). [in Japanese].
- 5) H. Mimura, T. Kanno, *J. Nucl. Sci. Technol.*, **22**, 284–291 (1985).
- 6) R. Mori, I. Yamagishi, M. Kubota, *JAERI-M 86-013*, (1986) [in Japanese].
- 7) H. Mimura, M. Shibata, K. Akiba, *J. Nucl. Sci. Technol.*, **27**, 835–843 (1990).
- 8) Y. Morita, I. Yamaguchi, T. Fujiwara, H. Koizumi, M. Kubota, *JAERI-Conf 99-004*, 491–497 (1999) [in Japanese].
- 9) T.M. Nenoff, S.G. Thoma, J.E. Miller, D.E. Trudell, *MRS Proc.*, **412**, 659 (1995).
- 10) E.P. Horwitz, M.L. Dietz, D.E. Fisher, *Solv. Extr. Ion Exch.*, **8**, 557–572 (1990).
- 11) J. Chuang, J. Lo, *J. Radioanal. Nucl. Chem.*, **189**, **2**, 307–317 (1995).
- 12) M.L. Dietz, A.H. Bond, M. Clapper, J.W. Finch, *Radiochim. Acta*, **85**, 119–129 (1999).
- 13) N. Takagi, Y. Izumi, K. Ema, T. Yamamoto, K. Nishizawa, *Solv. Extr. Ion Exch.*, **17**, 1461–1471 (1999).
- 14) D.R. Raut, P.K. Mohapatra, V.K. Manchanda, *Radiochim. Acta*, **97**, 565–570 (2009).
- 15) Y. Wu, S.-Y. Kim, D. Tozawa, T. Ito, T. Tada, K. Hitomi, E. Kuraoka, H. Yamazaki and K. Ishii, *J. Nucl. Sci. Technol.*, **49**, 320–327 (2012).
- 16) S.-Y. Kim, Y. Xu, T. Ito, Y. Wu, T. Tada, K. Hitomi, H. Yamazaki and K. Ishii, *J. Radioanal. Nucl. Chem.*, **295**, 1043–1050 (2013).

- 17) T. Takahashi, T. Ito, S.-Y. Kim, Asian Nuclear Prospects 2016, Nuclear Fuel Cycle for Sustainable Energy Supply and Human Prosperity, P-21, 1-2 (2016).
- 18) N.Kozonoi, Y. Ikeda, *Monatshefte für Chemie*, **138**, 1145–1151 (2007).
- 19) H. Luo, S. Dai, P. V. Bonnesen, T. J. Haverlock, B. A. Moyer, A. C. Buchanan III, *Solv. Extr. Ion Exch.*, **24**, 19–31 (2006).
- 20) C. Xu, X. Shen, Q.D. Chen, H.C. Gao, *Sci. China Ser B-Chem.*, **52**, 1858-1864 (2009).
- 21) M.L. Dietz, D.C. Stepinski, *Green Chem.*, **7**, 747-750 (2005).
- 22) L.H. Baetsle, D. Huys, *J. Inorg. Nucl. Chem.*, **30**, 639–649 (1965).