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The extraction of Sr^{2+} with dicyclohexano-18-crown-6 in conventional organic solvent and ionic liquid diluents

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Abstract: ^{90}Sr ($t_{1/2}$ = 28.8 a), one of the most significant fission products in high-level radioactive liquid waste (HLLW), contributes to a large part of the heat load and radiation. Removal of ^{90}Sr from the HLLW is beneficial for the final treatment of nuclear waste. In this paper, the extraction of Sr^{2+} was carried out using dicyclohexano-18-crown-6 (DCH18C6) in a variety of diluents including conventional organic solvents and novel ionic liquid solvents. The effect of several factors, such as nitric acid concentration, crown ether concentration and initial strontium concentration on the extraction of Sr^{2+} have been studied comprehensively. The higher distribution ratio and the stripping efficiency of Sr^{2+} were obtained with the binary diluents consisted of *n*-octanol and acetylene tetrachloride, which were compared with that using pure *n*-octanol as diluent. As for the $C_n$mimNTf$_2$ (n = 2, 4, 6) ionic liquid solvent systems, the distribution ratio of Sr^{2+} was much higher in the nitric acid medium with low concentration than in the traditional solvent systems. The results showed that $D_{C2mimNTf2} > D_{C4mimNTf2} > D_{C6mimNTf2}$, which indicated that shorter carbon chain benefits the extraction of Sr^{2+}.

Keywords: strontium extraction; crown ether; diluent effect; high level liquid waste.

INTRODUCTION

The reprocessing of spent nuclear fuel has aroused more and more attention with the development of nuclear industry in recent years. The high-level radioactive liquid waste (HLLW), produced during the reprocessing of the nuclear fuel, comprises of minor actinides (MAs) such as Am, Cm, and fission product elements (FPs) including lanthanides (Ln(III)), Cs, Sr, Zr, *etc*. Taking into account the viewpoints of minimizing the long-term radioactive risk and facilit-

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ating the management of the HLLW, it is necessary to separate the MAs and FPs from the HLLW.[1] Two long-lived radionuclides ^{90}Sr and ^{137}Cs, whose half-lives are 28.8 and 30.2 years, respectively, have the characteristics of high radioactivity, and their specific activities are 3.2×10^{11} B and 5.1×10^{12} Bq/g, respectively. Therefore, they are also strong heat-release nuclides, which mainly contribute to the temperature elevation of HLLW. On the one hand, the storage time and the management cost of the HLLW will significantly decrease if separating ^{90}Sr and ^{137}Cs from HLLW. On the other hand, the recovered ^{90}Sr and ^{137}Cs can be used in the field of medicine and radiation technology. For example, ^{137}Cs and ^{90}Sr are being used in blood irradiation and radiopharmaceutical applications, respectively.[2] Besides, ^{90}Sr could be used as radioisotope micro-power generator or radiation-source for radiation research.[3] Studies on the separation of ^{90}Sr and ^{137}Cs from the HLLW were reported in quantities.[4–6]

Many separation procedures, such as ion exchange, solvent extraction, precipitation, *etc.*, have been developed for the partitioning of ^{90}Sr from HLLW.[7–13] Solvent extraction has received much more extensive attention and application among them. It is widely accepted because it is a simple operation, which is easily being scaled-up. At the same time, the separation process aimed at ^{90}Sr using solvent extraction is convenient to cooperate with other processes.[14]

At present, tons of the extractants have been studied for the partitioning of ^{90}Sr, of which crown ether has attracted much attention due to its similar cavity size to the ion diameter of Sr^{2+}. Pedersen *et al.*[15] first synthesized crown ether with macrocycles like 18-crown-6 (18C6) which was an excellent extractant for Sr^{2+}. To improve the hydrophobicity of 18C6, dicyclohexano-18-crown-6 (DCH18C6) was synthesized after two cyclohexyls were planted on the cyclic polyether. The efficient separation of Sr^{2+} using DCH18C6 in different diluents as the extractant has been reported extensively. Horwitz *et al.*[16] studied the effect of various diluents, including esters (*n*-butyl acetate, 3-methylbutyl acetate, *n*-hexyl acetate), ketones (2-hexanone, 4-methyl-2-pentanone, 2-octanone, *etc.*), alcohols (*n*-amyl, *n*-hexyl, *n*-heptyl, *etc.*) and carboxylic acids (pentanoic, hexanoic, heptanoic, octanoic, *etc.*) on the extraction efficiency of Sr^{2+}, with DCH18C6 and its di-tert-butyl derivative (DTBCH18C6) serving as extractants. It was found that *n*-octanol seemed to be the best choice as a potential process-scale solvent from the point of view of physical properties (*e.g.*, flash point). However, the unfavourable extraction behaviour was also observed when the crown ether concentration and the nitric acid concentration were not quite high. Amar Kumar[17] reported the extraction of strontium from nitric acid medium employing DCH18C6 in the mixture of 80/20 vol. % butanol/*n*-octanol, and it was found that higher distribution ratio (D_{Sr}) values were obtained in this mixture diluent as compared to various pure alcohol diluents. Compared with the SREX (strontium extraction) solvent (pure *n*-octanol), it was indicated that the favourable extraction and stripping efficiency was obtained with 80/20 volume ratio toluene/*n*-octanol used as the diluent for DTBCH18C6, which principally contributes to the lower uptake of acid in the mixture diluents than that in pure *n*-octanol.[18] In the following study, another mixture diluent consisted of *n*-octanol and chloroform was put forward. It was found that 1:1 mixture diluent resulted in the highest D_{Sr} value when DTBCH18C6 was used as extractant of Sr^{2+}. The synergistic solvent extraction of *n*-octanol and chloroform was used to explain these experimental results.[19]

Apart from applying the binary diluents composed of *n*-octanol and another organic reagent to upgrade the extraction performance, some other outstanding diluents aimed at strontium extraction were also put forward. Fan *et al.*[20] investigated the extraction performance of Sr^{2+} employing DCH18C6 as extractant in tetrachloride acetylene (TCA), and it was found that the extraction efficiency of Sr^{2+} could reach up to 92 % when HNO_3 concentration was 1 $mol \cdot L^{-1}$. Better stripping performance was also obtained when deionised water was used as stripping agent. However, the diluent TCA is a kind of unstable halohydrocarbon which easily breaks down, so it is unadvisable to use alone in a large scale. Considering the great extraction ability and shortcoming of TCA, it is worthy to investigate the extraction performance of the binary diluent of TCA and *n*-octanol.

In the recent 10 years, a novel type of diluent, room-temperature ionic liquids (ILs), have been studied for the reprocessing of the spent nuclear fuel.[21,22] Compared with traditional organic solvent, room-temperature ILs have the features of non-toxic, physical and chemical stability which can be used for the separation of metal cation, and extraction of actinides, lanthanides, and fission products by use of ionic liquids have been conducted.[23] Dai *et al.*[24] obtained "unprecedented large D_{Sr}" by DCH18C6 dissolved in various imidazolium-based ILs (with either PF_6^- or NTf_2^-), which had risen up to 10^4, while in toluene or chloroform, D_{Sr} the only reached values of the order of 10^{-1}. In the following study, the extraction mechanism of cation exchange was proposed by Dietz through investigating the ILs extraction systems aimed at the separation of Sr^{2+}.[25] Monoaza-substituted crown ethers in ILs were investigated for the separation of Sr^{2+} and Cs^+ from the aqueous phase.[26] Visser *et al.* studied the extraction of Sr^{2+}, Cs^+ and Na^+ using DCH18C6 and Dtb18C6 dissolved in the room temperature ILs $C_n mimPF_6$ (n = 4, 6, 8).[27,28] Considering the small number of studies about the different kinds of the ILs on the extraction and stripping performance for Sr^{2+}, the bis(trifluoromethylsulfonyl)imide-based ILs for the partitioning of Sr^{2+} deserves to be further investigated.

In the present work, a solution of DCH18C6 in a variety of diluents including mixture of *n*-octanol and TCA, ILs of $C_n mimNTf_2$ (n = 2, 4, 6) were studied for more efficient extraction behaviour of Sr^{2+}, and the effect of nitric acid concentration, crown ether concentration, Sr^{2+} concentration and temperature on the extraction of Sr^{2+} were investigated. In addition, stripping Sr^{2+} from traditional diluents and ionic liquid systems were investigated, respectively.

EXPERIMENTAL

Reagents

DCH18C6 (>98 %), whose chemical structure formula was shown in Fig. 1, was obtained from Tokyo Chemical Industry and was used as received. A.R. grade *n*-octanol and TCA, ionic liquids $C_n$mimNTf$_2$ (n = 2, 4, 6; >99 %) obtained from the Sinopharm Chemical Reagent Co., were used as received. All other reagents including various nitrate salts were of A.R. grade without further purification.

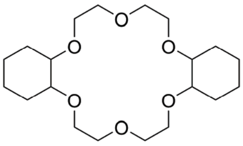

Fig. 1. Structure of dicyclohexano-18-crown-6.

Solvent extraction experiments

The extraction experiments were conducted by equilibrating 10^{-3} L (or 0.5×10^{-3} L) organic phase with 10^{-3} L aqueous phase in a constant temperature vibrator at 25±0.3 °C for half an hour. The oscillation equilibrium time experiment has been carried out in advance, which proved that 30 min is enough to achieve the two-phase equilibrium. The DCH18C6 concentration in organic phase was 0.01 mol·L^{-1}, the initial HNO_3 concentration was 1.0 mol·L^{-1}, and the Sr^{2+} concentration in aqueous phase was 1.14×10^{-3} mol·L^{-1}, except for the experiments of the effect of the concentration of DCH18C6, HNO_3 and Sr^{2+}, respectively. After centrifugation, an aliquot of the raffinate was separated and its concentration was assayed by inductively coupled plasma mass spectroscopy (ICP/MS). The concentration of Sr^{2+} in the organic phase was determined by the subtraction of the Sr^{2+} concentration in the raffinate from the initial aqueous Sr^{2+} concentration. The distribution ratio, D_{Sr}, presented as Eq. (1), was defined as the ratio of the Sr^{2+} concentration in the organic phase to that in the aqueous phase. The extraction efficiency, E_{Sr}, presented as Eq. (2), was defined as the ratio of the Sr^{2+} concentration in organic phase to the initial Sr^{2+} concentration in the aqueous phase. As for the stripping experiments, an aliquot of the organic phase was taken and mixed with the strippant solution in a constant temperature vibrator at 25±0.3 °C or half an hour, which is enough to achieve the two-phase equilibrium. After centrifugation, an aliquot of the aqueous was separated and the Sr^{2+} concentration in it was assayed by ICP/MS. The stripping efficiency, E_{Sr}', presented as Eq. (3), was defined as the ratio of the Sr^{2+} concentration in aqueous phase to the initial Sr^{2+} concentration in the organic phase:

$$D_{Sr}=\frac{C_{org}}{C_{aq}}=\frac{V_{aq}(C_{int}-C_{aq})}{V_{org}C_{aq}} \tag{1}$$

$$E_{Sr}=\frac{V_{org}C_{org}}{V_{int}C_{int}} \tag{2}$$

$$E_{Sr}'=\frac{V_{aq}'C_{aq}'}{V_{org}C_{org}} \tag{3}$$

where C_{int} denotes the initial Sr^{2+}concentration in aqueous phase, C_{aq}, C_{org} and C_{aq}' refer to the Sr^{2+} concentration in aqueous phase, organic phase and the stripping aqueous phase when the extraction reaction or the back-extraction reaction reach the equilibrium, respectively. The experiments were carried out in duplicate and experimental errors in the distribution measurements were within ±5 %.

RESULTS AND DISCUSSION

Extraction of Sr^{2+} with traditional diluents

Solvent extraction studies were carried out in the mixture diluents composed of *n*-octanol and TCA and the results are given in Table I. As is seen, D_{Sr} values increased along with the increase of TCA in the mixture diluents. It should be noted that higher distribution ratio was obtained when small volume of TCA was mixed with *n*-octanol. Besides, the viscosity of the obtained mixture is lowered and DCH18C6 became easier to dissolve in the mixture diluents, and it was usually accepted that the decreasing fraction of *n*-octanol in mixture diluents reduced the amount of nitric acid extracted into the organic phase.[29] Considering the irradiation instability of TCA, which easily decomposes and generates corrosive hydrochloric acid under irradiation conditions, mixture diluents should be mainly constituted of n-octanol. Thus, we made a detailed investigation on the effect of mixture diluents with 30 and 50 % TCA on Sr^{2+} extraction.

TABLE I. D_{Sr} using 0.01 mol·L^{-1} DCH18C6 in the mixture diluents of n-octanol and TCA from 1 mol·L^{-1} HNO_3

n-Octanol/TCA ratio	D_{Sr}
100	0.18
90	0.56
80	0.84
70	1.60
50	3.81
30	6.65
20	8.62
10	10.24
0	11.06

Effect of the HNO_3 concentration

The effect of the HNO_3 concentration on the extraction of Sr^{2+} was carried out using 0.01 mol·L^{-1} DCH18C6 in 70/30 volume ratio *n*-octanol/TCA and 50/50 volume ratio *n*-octanol/TCA, respectively. The results are shown in Fig. 2. The D_{Sr} values firstly increased and then decreased with the increase in HNO_3 concentration, and the nitric acid concentration corresponding to the maximum D_{Sr} value in the volume ratios 50/50 *n*-octanol/TCA and 70/30 *n*-octanol/TCA solvents systems were about 1.0 and 2.0 mol·L^{-1}, respectively. Generally, the salting-out effect of NO_3^- could facilitate the extraction of Sr^{2+} and dominated the extraction at lower nitric acid feed. Conversely, the competition effect of H^+ decreased the extraction of Sr^{2+} because of the decrease of the free DCH18C6 concentration in the organic phase, and this competition effect dominated especially at higher nitric acid feed.

The higher TCA solvent system were actually more sensitive to the change of concentration of HNO_3. As is seen in Fig. 2, the D_{Sr} values of 50/50 v/v% n-octanol/TCA solvent system were higher than that of 70/30 v/v% n-octanol/TCA solvent system at ⩽3 mol·L^{-1} HNO_3. However, the D_{Sr} values of 50/50 v/v% n-octanol/TCA solvent system were lower than that of 70/30 v/v% n-octanol/TCA solvent system at ⩾4 mol·L^{-1} HNO_3. The results showed that using DCH18C6 in lower proportion of TCA in the binary diluents as extractant was more convenient for the extraction of Sr^{2+} at high acid feed, whereas relatively higher proportion of TCA was more favourable at high acid feed.

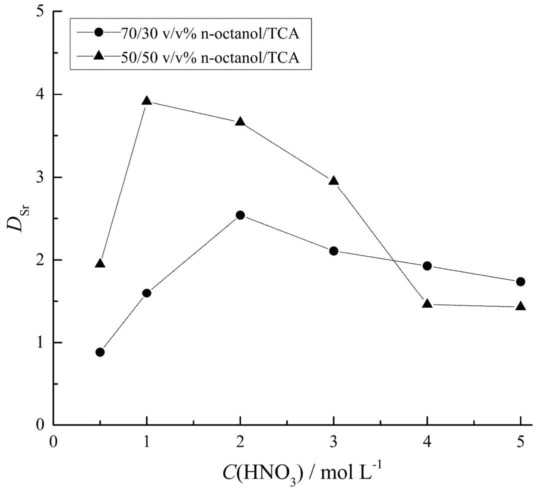

Fig. 2. The effect of the initial HNO_3 concentration in aqueous phase on the D_{Sr}. Organic phase: 0.01 mol·L^{-1} DCH18C6.

Effect of the DCH18C6 and initial Sr²⁺ concentration

The effect of the crown ether concentration and the initial Sr^{2+} concentration on the extraction of Sr^{2+} in these different extraction systems were studied. Fig. 3 shows a correlation between the D_{Sr} values and the initial Sr^{2+} concentration. The initial Sr^{2+} concentration was investigated in the range of 0.4-2 mol·L^{-1}, considering the average concentration of $^{90}Sr^{2+}$ in HLLW[5,14]. As indicated, D_{Sr} values were barely affected by the initial Sr^{2+} concentration in the aqueous medium within a certain range. Fig. 4 shows the dependence of D_{Sr} values on the extractant concentration. As indicated, the D_{Sr} values increased with the increasing crown ether concentration and an excellent linear correlation between log D_{Sr} and log C(DCH18C6) was observed.

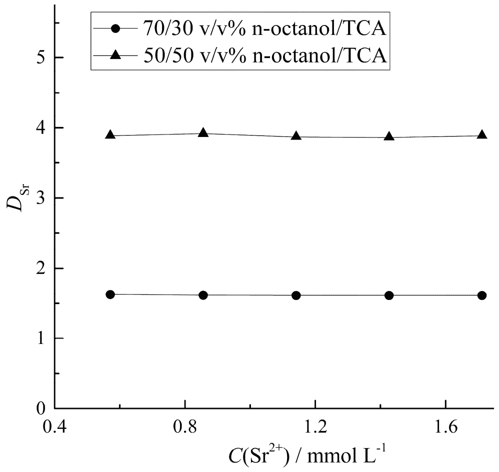

Fig 3. The effect of the initial Sr^{2+} concentration in aqueous phase on the D_{Sr}. Organic phase: 0.01 mol·L^{-1} DCH18C6.

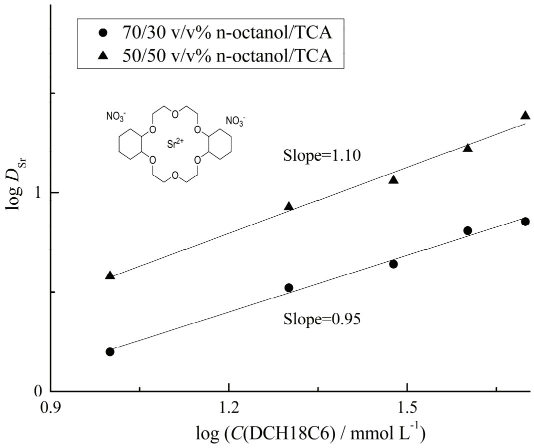

Fig 4. The dependence of log D_{Sr} on the log C(DCH18C6).

In order to confirm the stoichiometry of the extracted complex, an equilibrium equation of Sr^{2+} is listed as follows:

$$m\mathrm{Sr_{aq}}^{2+} + 2m\mathrm{NO_{3aq}}^{-} + n\mathrm{DCH18C6} \rightarrow [\mathrm{Sr(NO_3)_2}]_m n(\mathrm{DCH18C6}) \qquad (3)$$

Eq. (4) is derived based on the definition of strontium distribution:

$$\log D = \log K_{ex} + 2m\log C(\mathrm{NO_3^-}) + (m-1)\log C(\mathrm{Sr^{2+}}) + \\ + n\log C(\mathrm{DCH18C6}) \qquad (4)$$

where K_{ex} is defined as the equilibrium constant of the extracted reactions.

The plots of log D_{Sr} *vs*. log C(DCH18C6) give straight line with the slope of 0.95 and 1.10, and it implies that n equal 0.95 and 1.10 in these extraction systems. In addition, the result that D_{Sr} kept almost constant with the change of the initial Sr^{2+} concentration indicates all the m values are close to 1 in these extraction systems. Therefore, the extracted complex can be described as

$Sr(NO_3)_2 \cdot DCH18C6$. The schematic depiction of the Sr^{2+} complex is inserted in Fig. 4. Good agreement between the results by this work and the former conclusions is obtained. Fan *et al.*[20] investigated the extraction mechanism of Sr^{2+} using DCH18C6 as extractant in TCA by the slope analysis method. It was found that the extracted species corresponded to $Sr(NO_3)_2 \cdot DCH18C6$, as well as the element analysis and ^1H-NMR data for DCH18C6 and the complex well supported the conclusion by the slope analysis method. There was other more detailed summing-up of the Sr^{2+} extraction with DCH18C6 from HNO_3 medium. Yang *et al.*[30] studied the stoichiometric ratio of Sr^{2+} to DCH18C6 in the extracted complexes by plotting the logarithm of D_{Sr} against the logarithm of the concentration of DCH18C6 in organic phase. From the slopes of the obtained curve it can be deduced that the stoichiometric ratio were 2:1 when $C_o(DCH18C6) < 8\ mmol \cdot L^{-1}$, and 1:1 when $C(DCH18C6) \geq 8\ mmol \cdot L^{-1}$, which was in agreement with our conclusion that 1:1 when $C(DCH18C6) = 10\ mmol \cdot L^{-1}$.

Stripping

The diluent nitric acid, H_2CO_3, DTPA, *etc.*, were the commonly used strippants. In this work, the different strippants were employed to study the stripping performance for Sr^{2+}, including diluent nitric acid, deionised water, KNO_3 (in view of their similar ionic radius to Sr^{2+}), and the results were shown in Table II. It was found that the deionised water had great stripping performance for the solvent extraction systems.

TABLE II. Multi-stage stripping efficiency of Sr^{2+} (%) from 70/30 *n*-octanol/TCA using different strippants

No. of stripping stage	Strippant			
	Deionized water	$0.01\ mol \cdot L^{-1}\ HNO_3$	$0.1\ mol \cdot L^{-1}\ HNO_3$	$2\ mol \cdot L^{-1}\ KNO_3$
I	81.9	76.1	74.8	76.6
II	93.2	87.9	82.8	84.9
III	96.9	95.6	89.0	87.9
IV	99.9	99.9	94.2	91.7

Table III gives the stripping data when deionised water was used as strippant. It was found that the stripping efficiency was higher from the mixture diluents than that from pure n-octanol, and the stripping efficiency increased with the rising proportion of TCA. Besides, about 4 stripping stages were needed to separate the Sr^{2+} from the mixture diluents, while 5 or more stripping stages were necessary when pure *n*-octanol was the diluent of DCH18C6. The results further illustrated that the binary diluent, mixture of *n*-octanol and TCA, had a better extraction and stripping performance than what we used before (pure *n*-octanol).

TABLE III. Multi-stage stripping of Sr^{2+} (stripping efficiency, %) from different diluents using deionized water as stripping agent

No. of stripping stage	Diluent		
	Pure *n*-octanol	70/30 *n*-octanol/TCA	50/50 *n*-octanol/TCA
I	73.9	81.9	83.1
II	80.6	93.2	95.6
III	89.3	96.9	98.7
IV	94.8	99.9	99.9

Furthermore, the solvent extraction using DCH18C6 in the binary diluent as the extractant showed greater advantage compared to other methods aimed for the removal of Sr^{2+} from HLLW. For example, Zhang *et al.*[8] studied the co-precipitation method using zirconyl molybdopyrophosphate for the removal of ^{90}Sr, and the result showed that E_{Sr} only reached 92.96 %.

Extraction of Sr^{2+} *with novel diluents*

Extraction studies in the different ILs. The extraction experiments of Sr^{2+} from nitric acid and deionised water medium were carried out. Table IV gives the D_{Sr} data with different diluents from the 1.0 mol·L^{-1} HNO_3 and the deionised water medium. As seen in the top row, the DCH18C6–$C_n$mimNTf$_2$ systems shown unsatisfactory results. The difference of the D_{Sr} values between the traditional and novel diluents in 1.0 mol·L^{-1} HNO_3 medium is small, and the distribution ratios even are lower in C_4mimNTf$_2$ and C_6mimNTf$_2$ solvents than in volume ratio 70/30 *n*-octanol/TCA solvent. It couldn't meet the expectations in these ionic liquids in view of the current reports.[26,31] However, it was found that much higher extraction efficiency of Sr^{2+} could be obtained at the DCH18C6–$C_n$mimNTf$_2$ systems, when there was no HNO_3 in the aqueous phase, and the DCH18C6–70/30 volume ratio *n*-octanol/TCA system scarcely extracted Sr^{2+} from the aqueous phase without HNO_3, as shown in the bottom row of Table IV.

TABLE IV. Distribution ratio (D_{Sr}) values with DCH18C6 in different diluents; conditions: *C*(DCH18C6) = 0.01 mol·L^{-1}, the aqueous medium is 1.0 mol·L^{-1} HNO_3 and water when A/O=1 and 2, respectively

A/O	Diluent			
	70/30 *n*-octanol/TCA	C_2mimNTf$_2$	C_4mimNTf$_2$	C_6mimNTf$_2$
1	1.61	3.19	0.90	0.39
2	0	>750	199	3.79

Accordingly, it was concluded that the better D_{Sr} with the DCH18C6–$C_n$mimNTf$_2$ systems could be obtained as compared to that with the DCH18C6–70/30 volume ratio *n*-octanol/TCA system when HNO_3 concentration in aqueous phase approached to zero. In addition, the extraction efficiency differs largely when different ILs are used. Generally, D_{Sr} with NTf_2^- was higher than that with PF_6^- (Xu *et al.*[32]), and with the same anion NTf_2^-, ILs carrying shorter substituted alkyl chain on the imidazolium ion generated higher D_{Sr}.

Effect of the HNO_3 concentration. To prove the insight into the influence of acidity on the extraction efficiency of Sr^{2+}, the dependence of D_{Sr} on the HNO_3 concentration was investigated, and the results are shown in Fig. 5. It indicates a maximum D_{Sr} value at pure water, followed by a sharp decrease at higher HNO_3 concentration in all the DCH18C6–$C_n$mimNTf$_2$ solvent extraction systems. As for the DCH18C6–70/30 volume ratio *n*-octanol/TCA system, the increasing HNO_3 concentration (above 2.0 mol·L^{-1}) in aqueous phase resulted in higher D_{Sr}, and the explanation was that NO_3^- benefited facilitating the extraction of Sr^{2+}, while H^+ decreased the extraction of Sr^{2+} *via* competing with Sr^{2+}.

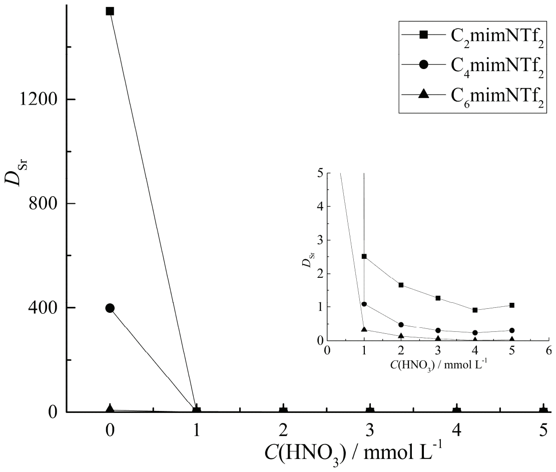

Fig 5. The effect of the nitric acid concentration. Organic phase: 0.01 mol·L^{-1} DCH18C6. Feed: 0.1 g·L^{-1} Sr^{2+}. A/O = 2.

However, HNO_3 had a different effect on the extraction of Sr^{2+} when $C_n$mimNTf$_2$ were used as the diluents. For one thing, the increasing HNO_3 concentration in aqueous phase promoted the degradation of NTf_2^-, which resulted in the decreasing values of D_{Sr} with ionic liquid solvent extraction systems.[27] For another, like the traditional solvent extraction system, the increasing concentration of HNO_3 impeded the extraction of Sr^{2+}. A couple of studies have reported that the distribution ratio decreased with the increase in the HNO_3 concentration. Xu *et al.*[32] showed that the competition of H^+ might be a dominating factor that led to an decrease in the extraction efficiency. Based on this result, the lower pH of solution medium would lead to the extraction of Sr^{2+}, so that the aqueous phase without HNO_3 was selected for further study for high D_{Sr} and the stability of solvent extraction systems. Interestingly, the D_{Sr} values increased modestly when the HNO_3 concentration was more than 4 mol·L^{-1}. The same phenomenon has been found before. Visser[27] studied the dependence of D_{Sr} on HNO_3 concentration using 0.1 mol·L^{-1} Dtb18C6 in C_4mimPF$_6$ and noticed that the D_{Sr} value increased with the rise of HNO_3 concentration at the high HNO_3 feed. This change has been thought to be due to much more water being extracted into the organic phase which resulted in the higher D_{Sr}.

However, taking into account the reality of HLLW that the feed contained 3–4 mol·L^{-1} HNO_3, the ILs solvent extraction systems showed a less-than-ideal result compared to the binary diluent systems.

Effect of the DCH18C6 concentration. Fig. 6 shows the effect of the crown ether concentration on the Sr^{2+} extraction. As presented, the D_{Sr} values in these systems increased along with the increase of DCH18C6 concentration and reached a plateau thereafter where the DCH18C6 concentration was 15, 10 and 20 mmol·L^{-1}, respectively. Moreover, with C_2mimNTf$_2$ and C_4mimNTf$_2$ used as the diluents, much improved Sr^{2+} extraction efficiency was observed, compared with C_6mimNTf$_2$ as the diluent.

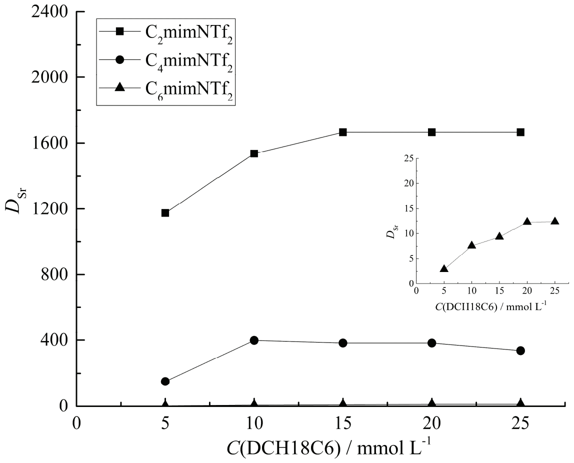

Fig 6. The effect of the DCH18C6 concentration. Organic phase: 0.01 mol·L^{-1} DCH18C6. Feed: 0.1 g·L^{-1} Sr^{2+}. A/O = 2.

These extraction behaviours should be ascribed to the different extraction mechanisms. Sr^{2+} formed the neutral complex with NO_3^{-}, followed by the solvating complex with DCH18C6 in traditional diluents, so DCH18C6 scarcely extracted Sr^{2+} from the pure water medium. Nevertheless, Sr^{2+} was extracted into the organic phase by the ion exchange with [C$_n$mim]$^+$, and the lower carbon chain lead to the better hydrophilic, so that $D_{\mathrm{C2minNTf2}} > D_{\mathrm{C4minNTf2}} > D_{\mathrm{C6minNTf2}}$.[31]

CONCLUSIONS

In this paper, the extraction behaviours and the mechanisms of Sr^{2+} using DCH18C6 as extractant and the ionic liquids along with the mixture of *n*-octanol and TCA as diluents were investigated. Compared to the frequently-used pure *n*-octanol solvent, lower acidity of $D_{\mathrm{Sr(max)}}$, higher extraction and stripping efficiency of Sr^{2+} could be obtained using 0.01 mol·L^{-1} DCH18C6 in the binary diluents, 70/30 *n*-octanol/TCA or 50/50 *n*-octanol/TCA volume ratio. Furthermore, compared to the investigated traditional solvent extraction systems, higher extraction efficiency of Sr^{2+} could be gained using 0.01 mol·L^{-1} in DCH18C6–$C_n$mimNTf$_2$ (n = 2, 4, 6) from low concentration HNO_3 medium, and a conclusion of $D_{\mathrm{C2mimNTf2}} > D_{\mathrm{C4mimNTf2}} > D_{\mathrm{C6mimNTf2}}$ could be drawn based on these experiments. It was explained that shorter carbon chain of the ILs cation benefited increasing Sr^{2+} extraction efficiency. Adding certain amount of TCA to the *n*-octanol could create a significant increase in extraction and stripping which has the great potential of industrial application, when compared to the much more expensive ILs of the limited economic value and industrial value.

In fact, the real HLLW formed during the reprocessing of the spent nuclear fuel would be at high temperatures due to the radiation energy. The temperature has significant impact on distribution coefficients.[10,20] Thermodynamic data are necessary in order to predict the ^{90}Sr extraction behaviour at high temperatures. Besides, during the extraction stage, the solvent system suffers radiation and chemical degradation, resulting in the formation of a series of degradation products, which would affect the extraction behavior of Sr^{2+}. Yuan *et al.*[33] studied the extraction of Sr^{2+} using irradiated C_4mim PF_6 in the presence of DCH18C6 and found that Sr^{2+} partitioning in irradiated C_4mimPF_6 decreases as the absorption dose increases. And because of the complicated components of HLLW, other ions may affect separation of ^{90}Sr by competitive extraction. Luo *et al.*[26] found that the extraction selectivity order for DCH18C6 in C_4mimNTf$_2$ was $K^+ > Sr^{2+} > Cs^+ > Na^+$. Further research will be made on the effect of the temperature, irradiation and the separation performance from the simulated HLLW. Some different phenomena are expected to be uncovered.

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ИЗВОД

ЕКСТРАКЦИЈА Sr^{2+} СА ДИЦИКЛОХЕКСАНО-18-КРАУН-6 ЕТРОМ ПРИМЕНОМ КОНВЕНЦИОНАЛНОГ ОРГАНСКОГ РАСТВАРАЧА И ЈОНСКИХ ТЕЧНОСТИ

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^{90}Sr ($t_{1/2}$ = 28,8 a), један од најзначајних фисионих производа у течном отпаду високог нивоа радиоактивности (HLLW), у великој мери доприноси нивоу топлоте и зрачења. Уклањање ^{90}Sr из HLLW је важно за коначну температуру радиоактивног отпада. У овом раду, екстракција Sr^{2+} је вршена коришћењем дициклохексано-18-краун-6 етра (DCH18C6) у већем броју растварача укључујући конвенционалне органске раствараче и нове раствараче – јонске течности. Утицај неколико фактора на екстракцију Sr^{2+}, као што су концентрација азотне киселине, концентрација краун етра, почетна концентрација стронцијума, су свеобухватно проучавани. Већи дистрибутивни однос и ефикасније уклањање Sr^{2+} су добијени за бинарне раствараче који су чинили *n*-октанол и ацетилен-тетрахлорид у поређењу са применом чистог *n*-октанола као растварача. У случају $C_n\mathrm{mimNTf}_2$ (n = 2, 4, 6) система јонских течности, дистрибутивни однос Sr^{2+} је био много већи од средине са малом концентрацијом азотне киселине и традиционално коришћених система растварача. Резултати показују да $D_{\mathrm{C2mimNTf2}} > D_{\mathrm{C4mimNTf2}} > D_{\mathrm{C6mimNTf2}}$, што указује да краћи ланац угљеника доприноси екстракцији Sr^{2+}.

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