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Investigation on the extraction of strontium ions from aqueous phase using crown ether-ionic liquid systems

XU Chao, SHEN XingHai†, CHEN QingDe & GAO HongCheng

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

The extraction of strontium ions using DCH18C6 as the extractant and various ionic liquids (ILs) as solvents has been investigated. The distribution ratio of Sr^{2+} can reach as high as 10^3 under certain conditions, much larger than that in DCH18C6/ -octanol system. The extraction capacity depends greatly on the structure of ionic liquids. In Ils-based extraction systems, the extraction efficiency of strontium ions is reduced by increasing the concentration of nitric acid and can also be influenced directly by the presence of Na^+ and K^+ in the aqueous phase. It is confirmed that the extraction proceeds mainly via a cation-exchange mechanism.

strontium ions, ionic liquid, extraction, crown ether

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^{90}Sr, [illegible] lifetime, [illegible] tion in high [illegible] se [illegible] subst [illegible] transpo [illegible] treatment. [illegible] low melting point usu-

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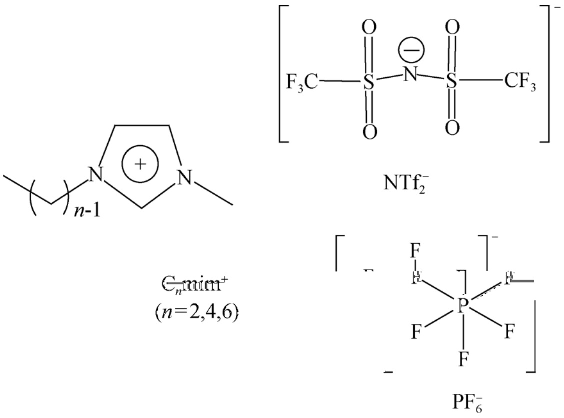

Figure 1 Structures of the cations C mim$^+$ and anions NTf$_2^-$, PF$_6^-$ of RTILs.

(DCH18C6) as extractant. Much higher extraction capability has been reached as compared with that using toluene as diluent. Visser et al.[9] further studied the extraction ability of Sr^{2+} by different crown ethers in 1-butyl-3-methylimidazolium hexaflurousphosphate (C_4-mimPF$_6$, Figure 1) and the result indicated that crown ether with higher rigidity structure shows higher extraction efficiency. However, C_4mimPF$_6$ is unstable under [illegible] of high acidity. Dietz has also studied the [illegible]

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RTILs bearing different structures.

2 Experimental

2.1 Reagents

C_4mimPF$_6$ and C mimNTf$_2$ (= 2,4,6) were synthesized and purified according to reported methods[13 15]. The purity is above 99% as determined by ^{1}H NMR and Elemental Analysis.

Dicyclohexano-18-crown-6 (DCH18C6) was received as a racemate from INET, Tsinghua University and purified by recrystallization in -heptane. The purity of final product was above 98%.

$Sr(NO_3)_2$, $SrCl_2$, $NaNO_3$, KNO_3, H_2SO_4, K_2SO_4, HNO_3, -octanol and other reagents were of analytical grade.

2.2 Instruments

HZQ-C Thermostatic Vibrator, LZD4-0.8 Centrifuge, Hitachi 180-80 Atomic Absorption Spectrometry (AAS), Hitachi U-3010 UV-Vis spectrometry, and IKA Genius 3 Vortex Agitator.

2.3 Methods

The extraction experiments were conducted as follows: [illegible] DCH18C6 with different [illegible] before measurement.

3 Results and discussion

3.1 Extraction capability of different RTILs

The extraction results of Sr^{2+} by DCH18C6 in -octanol and four RTILs under same conditions are shown in Table 1.

Table 1 Results of extracting Sr^{2+} by DCH18C6 in various solvents under neutral conditions

	-Octanol	C_4mimPF_6	$C_2mimNTf_2$	$C_4mimNTf_2$	$C_6mimNTf_2$
(%)	0	95.5	100	>99.5	90.0
	0	21.2	>1000	>400	18

[DCH18C6] = 0.1 mol·L^{-1}, [Sr^{2+}] = 0.01 mol·L^{-1}.

As shown in Table 1, the extraction efficiencies with RTILs as solvents are much higher than that with -octanol. In the case of $C_2mimNTf_2$, the distribution ratio of Sr^{2+} can be more than 10^3, which exceeds all reported results of extraction systems with conventional organic solvent as diluents. This large value may be attributed to the easy dissolution of the Sr^{2+}/crown ether complex by the total ionic environment of RTILs.

In addition, the extraction efficiency differs largely when different RTILs are used. Generally, $_{Sr}$ for RTILs with NTf_2^- anion is higher than that with PF_6^-. And with the same anion NTf_2^-, RTILs bearing shorter substituted alkyl chain on the imidazolium ion give higher $_{Sr}$.

3.2 Influence of the DCH18C6 concentration

The concentrations of DCH18C6 in RTILs exhibit obvious influence on the extraction of Sr^{2+}. As shown in Figure 2, $_{Sr}$ increases with increasing the DCH18C6 concentration. RTILs show no extraction of Sr^{2+} in the absence of DCH18C6, i.e., RTILs themselves cannot extract Sr^{2+} in the absence of proper extractants.

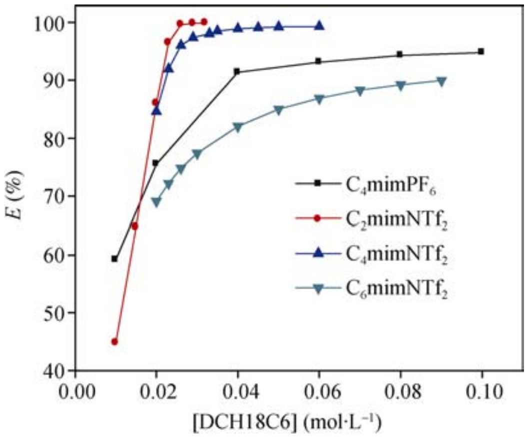

Figure 2 Relation between the extraction efficiency of Sr^{2+} and the concentration of DCH18C6 in various RTILs. [Sr^{2+}] = 0.01 mol·L^{-1}, $_{IL}$/ $_{Aq}$ = 1/2.

The results in Figure 2 also indicate that the extraction capability of the four selected RTILs systems fol-The creasing the acidity of aqueous phase to more than 5 mol·L^{-1} leads to a rapid decrease of $_{\mathrm{Sr}}$, which can be attributed to the decompose of C_4mimPF_6, i.e., PF_6^- is transferred to PO_4^{3-}, caused by the strong oxidation capability of high concentration of HNO_3. The interface between C_4mimPF_6 and the aqueous phase will disappear after contacting with 8 10 mol·L^{-1} HNO_3 for a short time.

The trend of the influence of HNO_3 in RTILs-based extraction systems differs distinctly from that with -octanol as the diluent. In the later case[2], $_{\mathrm{Sr}}$ increases with the increase of the concentration of HNO_3 and an obvious extraction is achieved only under high HNO_3 concentrations (> 1 mol·L^{-1}). The difference between the two extraction systems may indicate a different extraction mechanism involved with RTILs as solvents.

3.4 Effects of inorganic salts

adopted to precipitate Sr^{2+} from RTIL phase. It is demonstrated that more than 99% of Sr^{2+} can be efficiently stripped by K_2SO_4 solution. The RTIL phase after stripping has been reused to extract Sr^{2+} and the extraction capability is not obviously decreased.

3.6 Exploration of extraction mechanism

As shown above, the extraction behaviors in RTILs based extraction system differ clearly from that of conventional solvent extraction systems. These differences should be related to the different extraction mechanism. In conventional solvent extraction system, the extraction of metal ions mostly proceeds through a neutral complex mechanism, i.e., the metal ions and extractant form neutral complexes with counter anions and then transfer to the organic phase. For the extraction of Sr^{2+} by DCH18C6/octanol, the extraction mechanism can be expressed as follows[16]:

$$\mathrm{Sr}_{\mathrm{aq}}^{2+} + \mathrm{CE}_{\mathrm{org}} + 2\mathrm{NO}_{3\ \mathrm{aq}}^{-} \rightleftharpoons \mathrm{Sr}\cdot\mathrm{CE}\cdot\left(\mathrm{NO}_3\right)_{2\ \mathrm{org}} \qquad (1)$$

where CE represents the crown ether DCH18C6.

As reported[10,17], the extraction mechanism also differs in different RTILs-based extraction systems but usually involves cation exchange. By measuring the UV absorption at 211 nm for imidazolium ions, the concentration of C_2mim^+ in the aqueous phase before and after extraction can be determined. We have performed a study to explore the mechanism of extracting Sr^{2+} by DCH18C6/$C_2mimNTf_2$ and the results are shown in Table 2 and Figure 5. Considering that nitrate ions have intense interference on the UV absorption of imidazolium ions, $Sr(NO_3)_2$ is replaced by $SrCl_2$ in following experiments.

From Table 2, it is found that the decrease of the concentration of Sr^{2+} correlates closely with the increase of the concentration of C_2mim^+ in the aqueous phase. It can be thus deduced that the extraction of Sr^{2+} mainly proceeds via a cation exchange mechanism, which agrees well with that reported by Dietz et al.[10].

Moreover, it can be seen from Figure 5 that there is a linear relationship between variations of $[Sr^{2+}]$ and $[C_2mim^+]$ in the aqueous phase before and after extraction of Sr^{2+}. Therefore, the degree of ion exchange is independent on the initial concentration and the extracted concentration of Sr^{2+}, i.e., more Sr^{2+} is extracted, more C_2mim^+ is exchanged. Meanwhile, it is noticed that the C_2mim^+ exchanged can not afford charge equilibrium of the two phases, so there must have a part of Cl^- entering the RTILs phase. In

Table 2 Variations of $[Sr^{2+}]$ and $[C_2mim^+]$ in the aqueous phase before and after extraction of Sr^{2+} by DCH18C6/$C_2mimNTf_2$ (DCH18C6 = 0.1 $mol\cdot L^{-1}$)

$[Sr^{2+}]_{initial}$ (10^{-3} $mol\cdot L^{-1}$)	0	5.00	10.0	15.0	20.0
$[Sr^{2+}]_{aq}$ (10^{-3} $mol\cdot L^{-1}$)	0	–5.00	–10.0	–15.0	–19.4
$[C_2mim^+]_{aq}$ (10^{-3} $mol\cdot L^{-1}$)	0	5.94	12.6	19.6	26.3

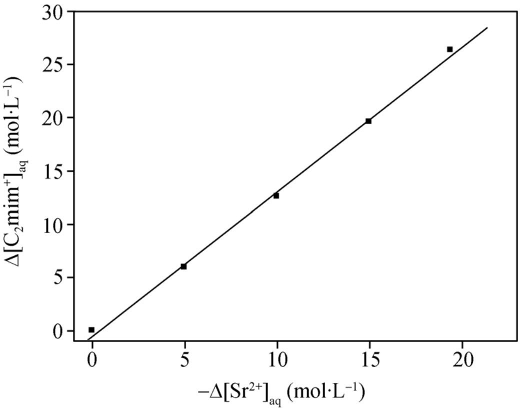

Figure 5 Relation between variations of $[Sr^{2+}]$ and $[C_2mim^+]$ in the aqueous phase before and after extraction of Sr^{2+} by DCH18C6/$C_2mimNTf_2$.

Table 3 Comparison of the effects of HNO_3 on the extraction of Sr^{2+} by octanol and RTILs systems

	-Octanol	RTILs
Equilibria existing in the systems	$\mathrm{Sr \cdot CE^{2+} + 2NO_3^- \rightleftharpoons Sr \cdot CE^{2+} \cdot 2NO^-_{3org}}$ $\mathrm{H \cdot CE^{+} + NO_3^- \rightleftharpoons H \cdot CE^{+} \cdot NO^-_{3org}}$	$\mathrm{Sr \cdot CE^{2+} + 2C\ \ min^+_{org} \rightleftharpoons Sr \cdot CE^{2+}_{org} + 2C\ \ mim^+}$ $\mathrm{Sr \cdot CE^{2+} + 2NO_3^- \rightleftharpoons Sr \cdot CE^{2+} \cdot 2NO^-_{3org}}$ $\mathrm{H \cdot CE^{+} + NO_3^- \rightleftharpoons H \cdot CE^{+} \cdot NO^-_{3org}}$
Key factor	salt out effect of NO_3^-	competition effect of H^+
Second factor	competition effect of H^+	salt-out effect of NO_3
The overall effect	increase of $_{\mathrm{Sr}}$	decrease of $_{\mathrm{Sr}}$

the aqueous phase and thus pushes the above equilibrium to the right direction, facilitating the extraction of Sr^{2+}[3]. Notice that in this case H^+ can also be complexed competitively with DCH18C6, however, the dominant effects are caused by NO_3^-. For RTILs-based extraction system where cation exchange is dominated, NO_3^- participates in the extraction to a relatively limited extent and the competition of H^+ might be the leading factor which causes an overall decrease in the extraction efficiency of Sr^{2+}. The effects of HNO_3 on the extraction are summarized in Table 3.

From the mechanism proposed, we can have a deeper understanding of the role of RTILs in the extraction sys- [illegible] as diluents for the extractant [illegible]

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KNO_3 usually reduces $_{\mathrm{Sr}}$, with the detailed trends related to the structure of RTILs selected. Sr^{2+} can be stripped from the RTILs phase by competition or precipitation methods. A cation exchange mechanism has been demonstrated by detecting the variation of C_2mim^+ concentrations in the aqueous phase before and after extraction.

According to the investigation results shown above and the specialty of RTILs, it can be deduced that RTILs have provided several advantages for the extraction of Sr^{2+} when compared with conventional solvent extraction systems.

(1) Reduce the amount of extractant and RTILs in practical processes as a result of the high extraction effi[illegible]. Therefore, the cost can be saved to some extent. [illegible]

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