A further understanding of the cation exchange mechanism for the extraction of Sr^{2+} and Cs^{+} by ionic liquid

SUN TaoXiang, SHEN XingHai[*] & CHEN QingDe

Beijing National Laboratory for Molecular Sciences (BNLMS), Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

The cation exchange mechanism was further investigated during the extraction of Sr^{2+} and Cs^{+} using the extractant dicyclohexano-18-crown-6 (DCH18C6) in an ionic liquid (IL) 1-ethyl-3-methyimidazolium bis[(trifluoromethyl)sulfonyl]imide (C$_2$mimNTf$_2$). The concentrations of both the cation C$_2$mim^{+} and the anion NTf$_2^-$ in aqueous phase were detected. The concentration of NTf$_2^-$ in the aqueous phase decreased as Sr^{2+} or Cs^{+} exchanged into the IL phase. Addition of C$_2$mim^{+} or NTf$_2^-$ as well as the variation of the solubility of C$_2$mimNTf$_2$ influenced the extraction efficiency of Sr^{2+} or Cs^{+}.

ionic liquids, extraction, cation exchange, Sr^{2+}, Cs^{+}

1   Introduction

Room-temperature ionic liquids (ILs) have been considered as alternative solvents in the last decade for synthetic, catalytic, electrochemical and separation sciences due to their unique properties such as low melting point, non-flammability, negligible vapor pressure, thermal and radiation stability [1–4]. Hydrophobic ILs such as 1-alkyl-3-methyimidazolium hexafluorophosphate (C$_n$mimPF$_6$) and bis[(trifluoromethyl)sulfonyl]imide (C$_n$mimNTf$_2$) were extensively used in the liquid-liquid extraction of metal ions [5–20]. Because of the ionic compositions and therefore the corresponding physicochemical properties and characteristics of ILs, the ionic species (metal ions and metal-extractant complex) are much more favored thermodynamically solvated in ILs than in conventional solvent and cations/anions of ILs can exchange with metallic complexes into aqueous phase.

The cation or anion exchange mechanism leads to high extraction efficiency in the extraction of metal ions using ILs as solvents [6, 17–22]. The anion exchange mechanism was indicated in the extraction of lanthanides by 2-thenoyltrifluoroacetone (Htta) into the NTf$_2^-$ based ILs (eq. (1)) [20].

$$\text{Ln}^{3+}_{(aq)} + 4\text{Htta}_{(IL)} + \text{NTf}_{2\,(IL)}^- \rightleftharpoons \text{Ln(tta)}^-_{4\,(IL)} +$$
$$4\text{H}^+_{(aq)} + \text{NTf}_{2\,(aq)}^- \tag{1}$$
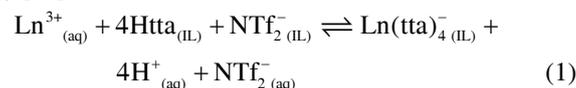
Compared with the anion exchange, the cation exchange mechanism has been extensively suggested for the extraction of metal ions, *e.g.*, Sr^{2+}, Cs^{+}, UO$_2^{2+}$ [6, 17–19, 22]. The imidazolium cation C$_n$mim^{+} is prone to exchange into aqueous phase with metallic complexes during extraction. A typical cation exchange mechanism in the extraction of Sr^{2+} by dicyclohexano-18-crown-6 (DCH18C6) in C$_2$mimNTf$_2$ is shown as eq. (2) [17–19].

$$2\text{C}_2\text{min}^+_{(IL)} + \text{Sr}^{2+} \cdot \text{CE}_{(aq)} \rightleftharpoons 2\text{C}_2\text{min}^+_{(aq)} + \text{Sr}^{2+} \cdot \text{CE}_{(IL)} \tag{2}$$
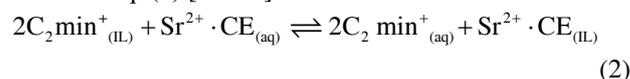
where CE is an abbreviation of DCH18C6.

To detect whether the extraction mechanism is cation exchange, one can measure the concentration of the IL cations in the aqueous phase after the metal ions are extracted into the IL phase or add IL cations into the aqueous phase to detect the variation of the extraction efficiency. According to the cation exchange mechanism, the concentration of

*Corresponding author (email: xshen@pku.edu.cn)

imidazolium cations in aqueous phase was usually calculated as the IL solubility plus the exchanged amount of C_nmim^+ [23]. Several researchers reported a linear relationship between the amount of the IL cations increased in the aqueous phase and that of the extracted metal ions. In the extraction of sodium ions by DCH18C6 in $C_5mimNTf_2$, Dietz *et al.* found a linear dependence of $[C_5mim^+]_{aq}$ upon the concentration of extracted sodium ions with a slope of 0.88 [18]. A slope of approximate 1.8, far from the theoretical value of 3, was found between the amount of C_4mim^+ in the aqueous phase and that of La^{3+} extracted into the IL phase during the extraction by $C_4mimNfO$ in the absence of extractants, where NfO is nonafluorobutanesulfonate [24]. In a recent work, a linear relationship was also reported by Bell *et al.* between the mole number of uranium transferred from the aqueous phase to the IL phase and that of IL cations transferred from the IL phase to the aqueous phase [22]. It is noticed that there is always a deviation between the experimentally obtained slope and the theoretical value. This deviation is usually attributed to the coexistence of another extraction mechanism, e.g., the neutral complex extraction mechanism.

On the other hand, although the cation exchange mechanism enhances the extraction efficiency, this extraction procedure induces a further loss of the IL cations besides the dissolution of ILs in aqueous phase, which is considered as a drawback for ILs in the application of extraction or catalysis. To attempt minimizing this drawback, Dai and coworkers adopted sodium tetraphenylborate ($NaBPh_4$) as a sacrificial cation exchanger during the extraction of Cs^+ by calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalixC6) in $C_4mimNTf_2$ and decreased the loss of C_4mim^+ by about 24% [14]. They also utilized ILs with a more hydrophobic anions bis(perfluoroethanesulfonyl)imide ($BETI^-$) in the extraction of Sr^{2+} and Cs^+ [23]. The dissolution of ILs was reduced and the extraction was improved [23]. While the variation of the amount of IL cations in aqueous phase attracted almost all attentions in the research of cation exchange mechanism, the detection of the anion of ILs (e.g., NTf_2^-) was neglected. To evaluate the loss of ILs during extraction, both cations and anions should be quantitatively measured.

In this work, we gave a precise detection of the concentrations of both C_2mim^+ and NTf_2^- in aqueous phase after the extraction of $SrCl_2$ and $CsCl$ by DCH18C6 in $C_2mimNTf_2$. The cation exchange mechanism was further discussed and the loss of both the cation and anion of an IL during the cation exchange was quantitatively evaluated.

2 Experimental

2.1 Materials

$LiNTf_2$ and C_2mimCl were purchased from TCI Chemical Co. and used without further purification. $C_2mimNTf_2$ was

synthesized and purified according to the reported method [25–27], and its purity is over 99% as detected by NMR and element analysis. The extractant bis(2-propyloxy)calix[4] crown-6 (BPC6, > 95%) and DCH18C6 (95%) were obtained from INET, Tsinghua University, China. BPC6 was used as received, while DCH18C6 was purified by recrystallization in *n*-heptane. The structures of DCH18C6, BPC6, the IL cation C_2mim^+ and the IL anion NTf_2^- are showed in Figure 1. $^{134}CsCl$ and $^{85}SrCl_2$ were purchased from Eckert & Ziegler Chemical Co. All other chemicals were of analytical grade and used without further purification.

2.2 Instruments and methods

The extraction experiments were conducted in plastic centrifuge tubes using a radioactive tracer method at 293.2 K controlled by circulating water bath. In detail, for example, in the extraction of Sr^{2+} by DCH18C6 in $C_2mimNTf_2$, 0.5 mL of DCH18C6-$C_2mimNTf_2$ and 0.5 mL aqueous solution of a specific $SrCl_2$ concentration containing ^{85}Sr tracer (ca. 0.005 μCi) were added in a 2 mL plastic centrifuge tube, followed by vortexing 3 min and then in equilibrium at 293.2 ± 0.1 K for 48 h. During the equilibrium, five or six times vortexing (30 s for each time) were needed to reach equilibrium sufficiently. Before the analysis the tube was centrifuged (8000 rad/s, 30 s) to ensure that the two phases were fully separated. 100 μL of each phase was removed into 5 ml cuvette for radiometric analysis. Each experiment was performed three times and the results agreed within an error of 3%. The extraction efficiency (E_{Sr}) was calculated by the ratio of the activity in the IL phase to the total activity in the IL phase and in the aqueous phase. The concentration of Sr^{2+} in the IL phase ($[Sr^{2+}]_{IL}$) was calculated by the initial concentration of Sr^{2+} in aqueous phase ($[Sr^{2+}]_{ini}$) multiplied by the extraction efficiency (E_{Sr}).

$$[Sr^{2+}]_{IL} = [Sr^{2+}]_{ini} \times E_{Sr} \qquad (3)$$
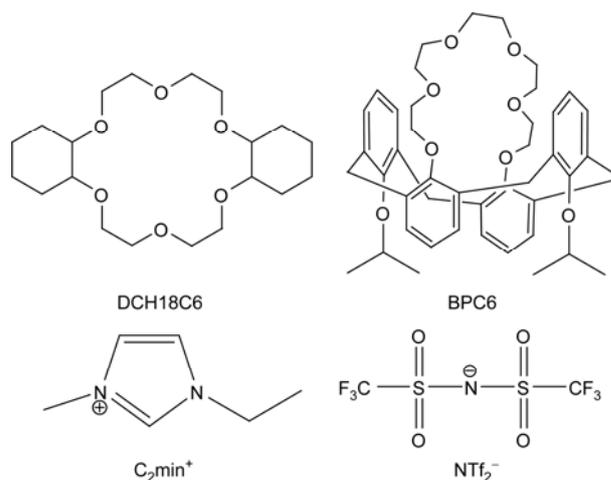
Figure 1 Structures of DCH18C6, BPC6, the IL cation C_2mim^+ and the IL anion NTf_2^-.

UV-vis measurement was performed on a Hitachi 3010 UV-vis Spectrometry to obtain the spectrum of C_2mim^+ in the aqueous phase and the absorbance at 211 nm was used to calculate the concentration of C_2mim^+. Figure 2 shows a linear relationship between the absorbance at 211 nm and the equilibrium concentration of C_2mim^+ in the aqueous phase ($[C_2mim^+]_{aq}$).

^{19}F-NMR spectra were recorded on a Bruker AV400 MHz NMR spectrometer and the concentration of NTf_2^- in the aqueous phase were obtained by the area ratio of ^{19}F NMR signal of NTf_2^- to the $-CF_3$ peak of benzotrifluoride ($C_6H_5CF_3$). In detail, approximate 300 μL samples were added to an NMR tube within a stem coaxial capillary tube containing benzotrifluoride dissolved in *d*-acetone as external reference. Area integral of each peak near -80.70 ppm, which referred to the assigned value 1.00 of -63.90 ppm, was proportional to the NTf_2^- concentration (Figure 3).

Water content in the IL phase after extraction was detected using the Mettler-Toledo DL31/38 Karl-Fischer titrator. The water content in the IL phase is about 1.6×10^4 ppm in all samples. The detection by UV absorption showed that $C_2mimNTf_2$ has a solubility of about 0.0479 mol dm^{-3} in water. The dissolution of water in the IL phase induces a 1.6% decrease of the volume of the aqueous phase. The dissolution of $C_2mimNTf_2$ in the aqueous phase induces a 1.2% decrease of the volume of the IL phase. The water dissolution in the IL phase and the IL dissolution in the aqueous phase induced the volume of the IL phase increment and decrement, respectively. These two effects on the volume change of the IL phase were both very slight and could be compensated, so that the volume of the IL phase was considered constant. Similarly, the volume of the aqueous phase was also considered constant.
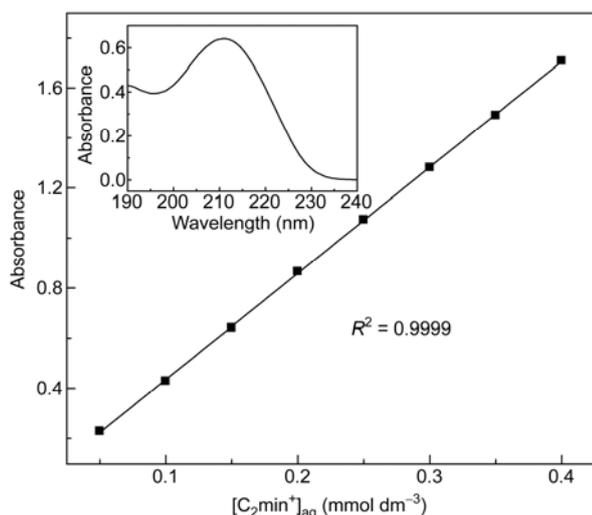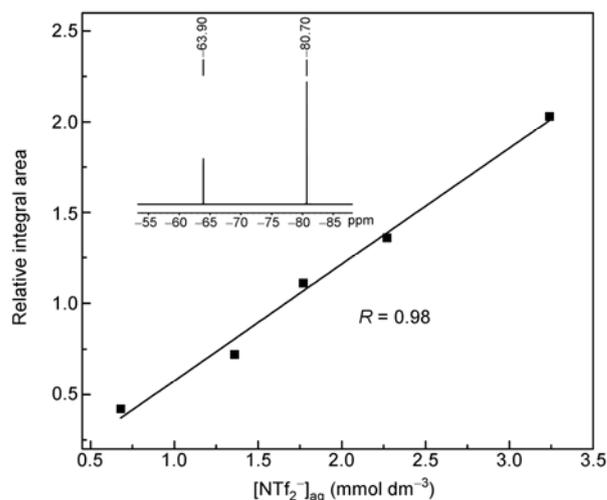
Figure 3 Relative integral area of the peak near -80.70 ppm of ^{19}F NMR signal depending on the concentration of NTf_2^- in the aqueous solution ($[NTf_2^-]_{aq}$). Inset: A typical ^{19}F NMR spectrum of $C_2mimNTf_2$ in aqueous solution using benzotrifluoride dissolved in *d*-acetone as external reference.

3 Results and discussion

3.1 Variation of $[C_2mim^+]$ and $[NTf_2^-]$ in the aqueous phase

DCH18C6 in $C_2mimNTf_2$ can efficiently extract both Sr^{2+} and Cs^+. The concentrations of both C_2mim^+ and NTf_2^- in the aqueous phase were detected after extraction. According to the cation exchange mechanism, the concentration of C_2mim^+ in aqueous phase ($[C_2mim^+]_{aq}$) would increase as metal ions extracted into the IL phase. Figure 4(a) shows the dependence of $[C_2mim^+]_{aq}$ on the concentration of Sr^{2+} in IL phase ($[Sr^{2+}]_{IL}$) after extraction. One can see that the value of $[C_2mim^+]_{aq}$ increases as Sr^{2+} extracted. However, linear fitting of $[C_2mim^+]_{aq}$ vs $[Sr^{2+}]_{IL}$ found a slope of about 1.4, which is far from the theoretical value of 2 according to Eq. 2. The dependence of $[C_2mim^+]_{aq}$ on $[Cs^+]_{IL}$ is also detected in the extraction of CsCl by DCH18C6 in $C_2mimNTf_2$ (Figure 4(b)) and the slope of $[C_2mim^+]_{aq}$ vs. $[Cs^+]_{IL}$ is 0.7, different from the theoretical value of 1.

The discrepancy does not originate from Cl^- transfering into IL phase accompanied with the cation exchange process, according to the literature [23]. There are four kinds of ions in the aqueous phase in the extraction system, i.e., Sr^{2+} (Cs^+), Cl^-, C_2mim^+ and NTf_2^-. The concentration of NTf_2^- in the aqueous phase ($[NTf_2^-]_{aq}$) depending on the extraction of Sr^{2+} or Cs^+ is also shown in Figure 4. One can see that $[NTf_2^-]_{aq}$ decreases from 47.9 to 26.5 mmol dm^{-3} as $[Sr^{2+}]_{IL}$ increases from 0 to 34.1 mmol dm^{-3} and decreases from 39.5 to 32.6 mmol dm^{-3} as $[Cs^+]_{aq}$ increases from 15.4 to 35.6 mmol dm^{-3}.

Le Chatelier's principle is applied to interpret this phe-

Figure 2 Dependence of the absorbance at 211 nm on the equilibrium concentration of C_2mim^+ in the aqueous solution ($[C_2mim^+]_{aq}$). Inset: a typical absorbance curve of $C_2mimNTf_2$ (0.15 mmol dm^{-3}) in aqueous phase.

$$a \,/\, (10^{-10}\,\mathrm{m}) = \frac{216}{\lambda^\circ /(\mathrm{S\ cm^2\ mol^{-1}})} \tag{8}$$

The λ° values for C_2mim^+ and NTf_2^- are 31.3 and 32.2 S cm^2 mol^{-1}, respectively, according to the literature [31, 32]. The values of a for the organic ions are usually between 5 and 8 [30], and they are calculated to be 6.9, 6.7 for C_2mim^+ and NTf_2^-, respectively. Using the extended Debye-Hückel equation, Kielland calculated the individual activity coefficients of 130 inorganic and organic ions in water at concentrations up to $I = 0.2$ mol dm^{-3}, and the calculated results are in sufficient accordance with experimental values [30]. For the corresponding sample in the extraction of Sr^{2+} (Figure 4(a)), the ionic strength varies from 0.216 to 0.208 mol dm^{-3}, and the values of γ_+, γ_- vary from 0.768 to 0.770 and from 0.765 to 0.767, respectively. For the Cs^+ system (Figure 4(b)) the ionic strength varies from 0.160 to 0.146 mol dm^{-3}, and the values of γ_+, γ_- vary from 0.783 to 0.787 and from 0.776 to 0.781, respectively. The activity coefficients can be considered invariable during the extraction, so that Eq. 6 is transformed to

$$K' = \frac{K}{\gamma_+ \cdot \gamma_-} = [C_2mim^+]_{aq} \cdot [NTf_2^-]_{aq} \tag{9}$$

The application of Le Chatelier's principle on the extraction system indicates that as C_2mim^+ exchanges into aqueous phase the dissolution of $C_2mimNTf_2$ will be opposed, thus leading to the decrement of $[NTf_2^-]_{aq}$ and less C_2mim^+ loss into the aqueous phase (Figure 4). However, Le Chatelier's principle only provides a qualitative explanation of the variations of the concentrations of C_2mim^+ and NTf_2^- in aqueous phase and we attempt to give a quantitative interpretation. The mass-action and electric conservation are subsequently performed to calculate the theoretical value of the concentrations of C_2mim^+ and NTf_2^- in aqueous phase after the extraction of Sr^{2+} by DCH18C6 in $C_2mimNTf_2$, and the results are shown in eqs. (10) and (11).

$$[C_2mim^+]_{aq} = \sqrt{[Sr^{2+}]_{IL}^2 + K'} + [Sr^{2+}]_{IL} \tag{10}$$

$$[NTf_2^-]_{aq} = \sqrt{[Sr^{2+}]_{IL}^2 + K'} - [Sr^{2+}]_{IL} \tag{11}$$

Notably, the volume ratio of the IL phase to the aqueous phase is 1:1 in our experiments and it is omitted in the above two equations. The data in Figure 4(a) are fitted based on Eqs. (10) and (11) (see Figure 4(a)), and the calculated value of K' is 0.00245 (mol dm^{-3})^2. The calculated solubility of $C_2mimNTf_2$ is 0.0494 mol dm^{-3} according to Eq. (9), which is very close to the experimental value of 0.0479 mol dm^{-3}. On the other hand, one can see that the concentration of C_2mim^+ cannot be simply calculated as reported in the literature [23]. The concentration of C_2mim^+ and NTf_2^- increases and decreases, respectively, not linearly along with Sr^{2+} extracted, although it appears a linear relationship within a certain range of concentration. For the decrease in the concentration of the IL anion in the aqueous phase during the cation exchange procedure, the deviation

Figure 4 Dependence of the concentration of C_2mim^+ ($[C_2mim^+]_{aq}$) and NTf_2^- ($[NTf_2^-]_{aq}$) in the aqueous phase on the concentration of (a) Sr^{2+} ($[Sr^{2+}]_{IL}$) and (b) Cs^+ ($[Cs^+]_{IL}$) in the IL phase after extraction using DCH18C6 in $C_2mimNTf_2$. Symbol: experimental data, line: fitting result.

nomenon. The hydrophobic IL $C_2mimNTf_2$ can be dissolved in water and the equilibrium is depicted as

$$C_2minNTf_{2(IL)} \rightleftharpoons C_2minNTf_{2(aq)} \tag{4}$$

$$C_2minNTf_{2(aq)} \rightleftharpoons C_2min^+_{(aq)} + NTf_2^-_{(aq)} \tag{5}$$
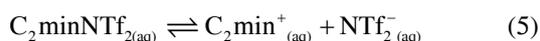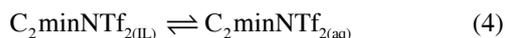
in which the equilibrium constant is depicted as K_1 and K_2, respectively. Thus

$$K = K_1 \cdot K_2 = [C_2mim^+]_{aq} \cdot \gamma_+ \cdot [NTf_2^-]_{aq} \cdot \gamma_- \tag{6}$$

where γ_+ and γ_- are the activity coefficients of C_2mim^+ and NTf_2^- in the aqueous phase. The γ_+ and γ_- values in each sample can be calculated by the extended Debye-Hückel equation

$$\log \gamma = \frac{-A\sqrt{I}}{1 + aB\sqrt{I}} \tag{7}$$

where a and I are the ion size parameter and the ionic strength, respectively, while the constants A, B at 293.2 K are 0.5070 (mol kg^{-1})$^{-0.5}$ and 0.3282×10^{10} (mol kg^{-1})$^{-0.5}$ m^{-1}, respectively [28]. The a value for univalent ions was evaluated from the limiting ionic molar conductivity (λ°) at 298.2 K according to the empirical equation by Brüll [29, 30].

reported previously between the experimentally obtained slope and the theoretical value is now explained reasonably. Same treatment is also performed in the case of the extraction of Cs^+ by DCH18C6 in $C_2mimNTf_2$ (Figure 4(b)), and the fitting result of K' is 0.00224 $(mol\ dm^{-3})^2$.

3.2 Effect of adding IL cation or anion on the extraction

The cation exchange procedure opposes the dissolution of anions of ILs in aqueous phase and induces relative small loss of cations, indicating a relative low loss of ILs during extraction. Moreover, adding cations/anions of ILs into aqueous phase can also affect the cation exchange of metal ions. Thus, we have tried to add C_2mimCl and $LiNTf_2$ into the aqueous phase during the extraction of Sr^{2+} by DCH18C6 in $C_2mimNTf_2$ to examine their effects on the extraction, and LiCl was used to subtract the influence of Li^+ (Figure 5(a)). The addition of C_2mimCl leads to a reduction in the extraction efficiency, implying that C_2mim^+ indeed decreases the extraction of Sr^{2+}. This phenomenon can be easily understood, for the addition of C_2mim^+ op-

poses the cation exchange. On the contrary, the extraction efficiency increases upon the addition of $LiNTf_2$. For example, adding 1 mol dm^{-3} $LiNTf_2$ induces the extraction efficiency an increase from 49.6% to 53.0%. The addition of NTf_2^- makes the dissolution of C_2mim^+ in the aqueous phase decrease, which facilitates C_2mim^+ exchanged into the aqueous phase from the ILs phase, leading to an increase of E_{Sr}. One can see that the addition of LiCl induces a decrease of the extraction efficiency of Sr^{2+}, due to the competition of Li^+ with Sr^{2+} in complexing with DCH18C6.

The added salts, C_2mimCl and $LiNTf_2$, induce the extraction efficiency of Sr^{2+} decrease and increase, respectively, but Li^+ competes with Sr^{2+} in complexing with DCH18C6. The extraction of Cs^+ by BPC6 in $C_2mimNTf_2$ was subsequently employed due to the extraordinary high selectivity of Cs^+ by BPC6 so that the influence of Li^+ on the extraction would be reduced [6]. Figure 5(b) shows the effects of the addition of LiCl, C_2mimCl and $LiNTf_2$ on the extraction of Cs^+ by BPC6 in $C_2mimNTf_2$. Apparent decrease and increase are found in the variation of extraction efficiency upon the addition of C_2mimCl and $LiNTf_2$, respectively. For example, the extraction efficiency is 91.1% at the $LiNTf_2$ concentration of 1 mol dm^{-3}, while it is 28.0% upon the addition of 1 mol dm^{-3} of C_2mimCl, which are both far from the value of 54.1% in the absence of salts. The addition of LiCl shows little influence on the extraction, suggesting the high selectivity of Cs^+ by BPC6.

3.3 Effect of the variation of the IL solubility on the extraction

The variation of the IL solubility, in which the concentrations of C_2mim^+ and NTf_2^- in the aqueous phase vary simultaneously, also affects the cation exchange of metal ions. The solubility of hydrophobic ILs $C_nmimNTf_2$ in water or in aqueous solution has been studied [33–35], and it is influenced by several facts such as temperature and salt concentration. For instance, the solubility of imidazolium based ILs in water increased and achieved a highest value upon the addition of 0.1 mol dm^{-3} of alkaline earth metal ions, *e.g.*, $MgCl_2$, $CaCl_2$ and $SrCl_2$, and then decreased as salts further added [33]. We tried to add different salts into the aqueous phase during extraction of Sr^{2+} or Cs^+ to examine the effect of the variation of the solubility of $C_2mimNTf_2$ on the extraction efficiency. However, the added salts would complex more or less with the extractants. In the absence of extractants, it was found that $C_2mimNTf_2$ can extract Cs^+ to some extent whereas no Sr^{2+} was extracted [5, 6, 15]. It was found that the mechanism in the extraction of Cs^+ by $C_2mimNTf_2$ is cation exchange, which is the same as that in the extraction of Cs^+ by BPC6 in $C_2mimNTf_2$ [6]. Therefore we added $SrCl_2$ in the extraction of Cs^+ by $C_2mimNTf_2$ in the absence of extractants. Figure 6 shows the variation of the extraction efficiency as salt added. The extraction efficiency of $C_2mimNTf_2$ extracting 10 mmol dm^{-3} Cs^+ is
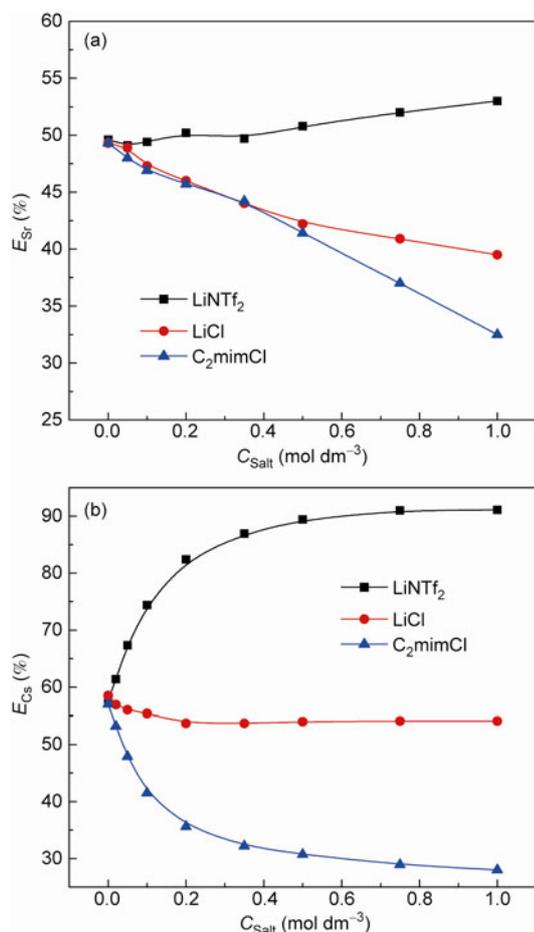
Figure 5 Influence of $LiNTf_2$, LiCl and C_2mimCl on the extraction of (a) Sr^{2+} (5 mmol dm^{-3}) by DCH18C6 (3 mmol dm^{-3}) and (b) Cs^+ (10 mmol dm^{-3}) by BPC6 (3 mmol dm^{-3}) in $C_2mimNTf_2$.
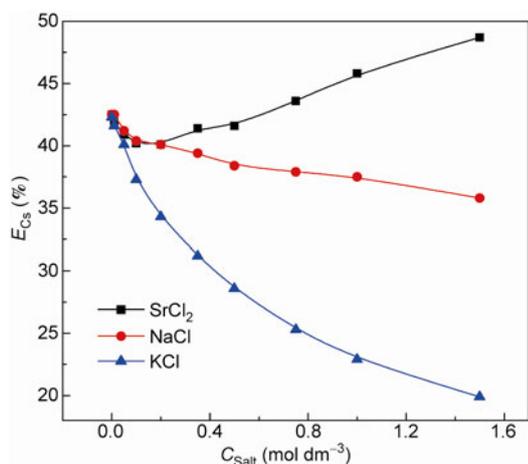
Figure 6 Influence of SrCl₂, NaCl and KCl on the extraction of Cs⁺ (10 mmol dm⁻³) by C₂mimNTf₂ in the absence of extractants.

42.5% and decreases as SrCl₂ added, achieving a lowest value of 40.2% as the concentration of SrCl₂ is 0.1 mol dm⁻³. One can see that the concentration of SrCl₂ at the lowest value of the extraction efficiency of Cs⁺ is in good agreement with that at the highest value of the solubility of ILs in aqueous phase. The extraction efficiency is further enhanced by the addition of more SrCl₂, and achieved a value of 48.7% at 1.5 mol dm⁻³ of SrCl₂. The dependence of the extraction efficiency of Cs⁺ by C₂mimNTf₂ on the concentration of SrCl₂ just reflects that the variation of the solubility of C₂mimNTf₂ does affect the cation exchange in the extraction of metal ions by IL systems. For comparison, the addition of KCl and NaCl induces a decrease of the extraction efficiency due to the competing extraction of K⁺ and Na⁺ by C₂mimNTf₂.

4 Conclusion

The concentration of the anions of C₂mimNTf₂ in aqueous phase decreases as metal ions (Sr²⁺ and Cs⁺) extracted *via* a cation exchange mechanism. The equilibria of the dissolution and dissociation of C₂mimNTf₂ in the aqueous phase coexist with the cation exchange. After knowing the extracted amount of metal ions, one can calculate the loss of both the cation and anion of an IL induced by the cation exchange. The addition of C₂mim⁺ decreases whereas addition of NTf₂⁻ increases the extraction efficiency of Sr²⁺ or Cs⁺. Variation of the solubility of C₂mimNTf₂ also alters the extraction efficiency of metal ions. Our results help cognize the cation exchange mechanism more deeply and also suggest a method to promote the extraction of metal ions using ILs as solvents.

1 Hallett JP, Welton T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem Rev*, 2011, 111(5): 3508–3576

2 Armand M, Endres F, MacFarlane DR, Ohno H, Scrosati B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat Mater*, 2009, 8(8): 621–629

3 Han XX, Armstrong DW. Ionic liquids in separations. *Accounts Chem Res*, 2007, 40(11): 1079–1086

4 Sun XQ, Luo HM, Dai S. Ionic liquids-based extraction: A promising strategy for the advanced nuclear fuel cycle. *Chem Rev*, 2012, 112(4): 2100–2128

5 Xu C, Shen XH, Chen QD, Gao HC. Investigation on the extraction of strontium ions from aqueous phase using crown ether-ionic liquid systems. *Sci China Ser B-Chem*, 2009, 52(11): 1858–1864

6 Xu C, Yuan LY, Shen XH, Zhai ML. Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: Mechanism and radiation effect. *Dalton Trans*, 2010, 39(16): 3897–3902

7 Sun TX, Wang ZM, Shen XH. Crystallization of cesium complex containing bis(2-propyloxy)calix-4-crown-6 and bis (trifluoromethyl) sulfonyl imide. *Inorg Chim Acta*, 2012, 390: 8–11

8 Sun XQ, Bell JR, Luo HM, Dai S. Extraction separation of rare-earth ions via competitive ligand complexations between aqueous and ionic-liquid phases. *Dalton Trans*, 2011, 40(31): 8019–8023

9 Marin TW, Shkrob IA, Dietz ML. Hydrogen-bonding interactions and protic equilibria in room-temperature ionic liquids containing crown ethers. *J Phys Chem B*, 2011, 115(14): 3912–3918

10 Wang JS, Sheaff CN, Yoon B, Addleman RS, Wai CM. Extraction of uranium from aqueous solutions by using ionic liquid and supercritical carbon dioxide in conjunction. *Chem-Eur J*, 2009, 15(17): 4458–4463

11 Shimojo K, Kurahashi K, Naganawa H. Extraction behavior of lanthanides using a diglycolamide derivative TODGA in ionic liquids. *Dalton Trans*, 2008, 37(37): 5083–5088

12 Dietz ML, Jakab S, Yamato K, Bartsch RA. Stereochemical effects on the mode of facilitated ion transfer into room-temperature ionic liquids. *Green Chem*, 2008, 10(2): 174–176

13 Dietz ML. Ionic liquids as extraction solvents: Where do we stand? *Sep Sci Technol*, 2006, 41(10): 2047–2063

14 Luo HM, Dai S, Bonnesen PV, Buchanan AC, Holbrey JD, Bridges NJ, Rogers RD. Extraction of cesium ions from aqueous solutions using calix-4-arene-bis(tert-octylbenzo-crown-6) in ionic liquids. *Anal Chem*, 2004, 76(11): 3078–3083

15 Luo HM, Dai S, Bonnesen PV. Solvent extraction of Sr2+ and Cs+ based on room-temperature ionic liquids containing monoaza-substituted crown ethers. *Anal Chem*, 2004, 76(10): 2773–2779

16 Dai S, Ju YH, Barnes CE. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J Chem Soc-Dalton Trans*, 1999, 28(8): 1201–1202

17 Dietz ML, Dzielawa JA. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for the 'greenness' of ionic liquids as diluents in liquid-liquid extraction. *Chem Commun*, 2001, 37(20): 2124–2125

18 Dietz ML, Stepinski DC. A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): Implications for the "greenness" of RTILs as extraction solvents. *Green Chem*, 2005, 7(10): 747–750

19 Jensen MP, Dzielawa JA, Rickert P, Dietz ML. EXAFS investigations of the mechanism of facilitated ion transfer into a room-temperature ionic liquid. *J Am Chem Soc*, 2002, 124(36): 10664

20 Jensen MP, Neuefeind J, Beitz JV, Skanthakumar S, Soderholm L. Mechanisms of metal ion transfer into room-temperature ionic liquids: The role of anion exchange. *J Am Chem Soc*, 2003, 125(50): 15466–15473

21 Dietz ML, Dzielawa JA, Laszak I, Young BA, Jensen MP. Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. *Green Chem*, 2003, 5(6):

682–685

22 Bell TJ, Ikeda Y. The application of novel hydrophobic ionic liquids to the extraction of uranium(vi) from nitric acid medium and a determination of the uranyl complexes formed. *Dalton Trans*, 2011, 40(39): 10125–10130

23 Luo H, Dai S, Bonnesen PV, Haverlock TJ, Moyer BA, Buchanan AC. A striking effect of ionic-liquid anions in the extraction of Sr2+ and Cs+ by dicyclohexano-18-crown-6. *Solvent Extr Ion Exch*, 2006, 24(1): 19–31

24 Kozonoi N, Ikeda Y. Extraction mechanism of metal ion from aqueous solution to the hydrophobic ionic liquid, 1-butyl-3-methyli-midazolium nonafluorobutanesulfonate. *Mon Chem*, 2007, 138(11): 1145–1151

25 Bonhote P, Dias AP, Papageorgiou N, Kalyanasundaram K, Gratzel M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg Chem*, 1996, 35(5): 1168–1178

26 Dzyuba SV, Bartsch RA. Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluorormethyl-sulfonyl)imides on physical properties of the ionic liquids. *ChemPhysChem*, 2002, 3(2): 161–166

27 Paul A, Mandal PK, Samanta A. How transparent are the imidazolium ionic liquids? A case study with 1-methyl-3-butyli-midazolium hexafluorophosphate, [Bmim][PF6]. *Chem Phys Lett*, 2005, 402(4-6): 375–379

28 Dean JA. Lange's handbook of chemistry(13th), 1985, McGraw-Hill Book Company

29 Katsuta S, Ogawa R, Yamaguchi N, Ishitani T, Takeda Y. Ion pair formation of 1-alkyl-3-methylimidazolium salts in water. *J Chem Eng Data*, 2007, 52(1): 248–251

30 Kielland J. Individual activity coefficients of ions in aqueous solutions. *J Am Chem Soc*, 1937, 59: 1675–1678

31 Zhang JJ, Shen XH. Multiple equilibria interaction pattern between the ionic liquids C(n)mimPF(6) and beta-cyclodextrin in aqueous solutions. *J Phys Chem B*, 2011, 115(41): 11852–11861

32 Salomon M. Conductance of solutions of lithium bis(trifluorome-thanesulfone)imide in water, propylene carbonate, acetonitrile and methyl formate at 25-degrees-c. *J Solut Chem*, 1993, 22(8): 715–725

33 Freire MG, Carvalho PJ, Silva AMS, Santos L, Rebelo LPN, Marrucho IM, Coutinho JAP. Ion specific effects on the mutual solubilities of water and hydrophobic ionic liquids. *J Phys Chem B*, 2009, 113(1): 202–211

34 Freire MG, Carvalho PJ, Gardas RL, Marrucho IM, Santos L, Coutinho JAP. Mutual solubilities of water and the C(n)mimTf2N hydrophobic ionic liquids. *J Phys Chem B*, 2008, 112(6): 1604–1610

35 Freire MG, Neves C, Carvalho PJ, Gardas RL, Fernandes AM, Marrucho IM, Santos L, Coutinho JAP. Mutual solubilities of water and hydrophobic ionic liquids. *J Phys Chem B*, 2007, 111(45): 13082–13089