Complexation and extraction investigation of rubidium ion by calixcrown-C_2mimNTf$_2$ system

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ABSTRACT

When the ionic liquid (IL) C_2mimNTf$_2$ was used as solvent, Rb^+ in neutral aqueous solution was successfully extracted by bis(2-propyloxy)calix[4]crown-6 (BPC6) with high efficiency. The crystallographic data and electrospray ionization mass spectra indicated that BPC6 could form the 1:1 complex with Rb^+. Due to a cation exchange mechanism, the addition of NTf_2^- into aqueous phase was able to improve the extraction efficiency of Rb^+, while the extraction was restrained with the addition of C_2mim$^+$. With respect to the mixed solution of RbCl and KCl, the molar ratio of K^+ to Rb^+ decreased remarkably after extraction by using BPC6/C_2mimNTf$_2$. The Rb^+ in ILs could be stripped into aqueous solution with NH_4Cl as back-extractant. Thus, it is believed that Rb^+ can be effectively concentrated from the mixed solution of Rb^+ and K^+ through an extraction-stripping procedure.

1. Introduction

As a scattered alkali metal, rubidium has a broad application in atomic clock, electronic equipment, biomedicine and so on [1–3]. With the rapid development of science and technology, the demand of rubidium increases continuously. For the lack of mineral containing Rb, it is necessary to explore new Rb resources to meet the market demand. There exists a large amount of Rb in salt lake brines. However, the concentration of Rb^+ is too low [4], which coexists with massive alkali metal and alkaline earth metal ions (*e.g.*, Na^+, K^+, Ca^{2+}, and Mg^{2+}). Thus, the extraction of Rb^+ from salt lake brines is much difficult. In traditional technologies, a large amount of Rb resources were wasted. Recently, new technologies to improve the utilization of Rb in saline lakes have attracted much attention in scientific and applied fields.

As ^{137}Cs is one of the key radioactive elements in high level liquid waste, Cs^+ has been focused in the field of extraction and separation, while the investigation on Rb^+ is relatively scarce. Because of their similar physicochemical properties [5] and the resulting co-extraction in most cases [4,6–9], the extraction of Rb^+ was analogized from that of Cs^+. At present, liquid–liquid extraction [10–12] and ion exchange [13,14] are two common separation techniques. Compared with ion exchange, liquid–liquid extraction is performed in industry for easy realization of continuous operation. Meanwhile, substituted phenol (*e.g.*, 4-*tert*-butyl-2-(α-methylbenzyl)-phenol)) [4,8,12,15] and

calixcrown (*e.g.*, bis(2-propyloxy)calix[4]crown-6 (BPC6) [16] and calix[4]arene-bis(tert- octylbenzo-crown-6) (BOBCalixC6)) [17–22] are two kinds of extractants dissolved in organic solvents to extract Rb^+ and Cs^+ from aqueous phase. However, substituted phenol could only be used to extract Rb^+ and Cs^+ in highly basic aqueous solution [4,12,15], while calixcrown was suitable for highly acidic system [23]. Thus, it is necessary to explore new extraction systems which apply under near neutral conditions.

Ionic liquids (ILs) have excellent physical and chemical properties, *e.g.*, wide range of temperature in liquid state, low vapor pressure, thermal stability, non-flammability and so on. Thus, various ILs have been used in the preparation of inorganic materials, electrochemistry, catalysis, gas adsorption, ion extraction [24–30]. In particular, ILs are hopeful to replace volatile organic compounds in the extraction of metal ions, due to the high extraction efficiency and excellent selectivity [31–34]. With respect to the extraction of Cs^+, calixcrown, especially calix[4]arene based compounds, was effective. Luo et al. [35] utilized BOBCalixC6 in 1-alkyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ($C_n$mimNTf$_2$, n = 2, 4, 6, 8) to extract Cs^+ from spent fuel, which was highly selective to Cs^+ in the presence of Sr^{2+} and Na^+. Our research group used BPC6/$C_n$mimNTf$_2$ (n = 2, 4, 6, 8) to extract Cs^+ efficiently from neutral aqueous solution [36]. The distribution ratio of Cs^+ could reach as high as 10^3 under the optimal condition. However, to the best of our knowledge, the effective back extraction of Cs^+ from ILs has not been achieved yet.

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So far, most of studies on the separation of Rb^+ under the interference of coexisting metal ions were focused on using t-BAMBP [4,12,15] or 18-crown-6 ether [37]. t-BAMBP is an excellent extractant to selectively separate Rb^+ and Cs^+ from K^+, nevertheless, it is useful under the condition of strong basic solution. 18-crown-6 ether exhibits preferred best size-fit match with K^+ and Rb^+ rather than other alkali metal ions, which means no selectivity to Rb^+ from K^+. It is necessary to choose macrocyclic extractant with larger cavity to selective match with Rb^+. Calixcrown/ILs is a common system that was used for the extraction of K^+, Cs^+ and Sr^{2+} [35,36], but the extraction of Rb^+ by calixcrown/ILs has not been studied yet. As expected, the interference from K^+ is more serious in the extraction of Rb^+ than that of Cs^+ [15,38]. It is necessary to investigate the selectivity of Rb^+ by calixcrown/ILs in the presence of K^+. Moreover, the back extraction of Rb^+ from ILs is the other key problem, which directly affects the application of calixcrown/ILs.

Herein, we report the extraction and separation of Rb^+ by using $BPC6/C_2mimNTf_2$. We aim to ascertain the mechanism of the extraction process and the structure of the extracted complex. Furthermore, the results concerning the stripping of Rb^+ will be presented.

2. Experimental

2.1. Materials

$C_nmimNTf_2$ ($n = 2, 4, 6, 8$) used in this work was synthesized and purified according to the method previously reported [39]. C_nmimCl ($n = 2, 4, 6, 8$) and $LiNTf_2$ were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The extractant BPC6 ($> 95\%$) was obtained from Institute of Nuclear and New Energy Technology (INET), Tsinghua University, P. R. China. All other reagents were of analytical grade and used without further purification. Distilled deionized water was obtained from a Hitech-Sciencetool ultrapure water system (resistivity 18.2 MΩ·cm) and was used to prepare all aqueous solutions.

2.2. Instruments

The concentration of metal ions in aqueous solution was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Leeman, USA) with relative standard deviation (RSD) below 5%. The pH value of aqueous solution was measured by pH meter (Delta 320, Mettler-Toledo, Switzerland) with relative standard deviation (RSD) below 1%. The electrospray ionization mass spectrometry (ESI-MS) of the IL phase after extraction was acquired by a Bruker Apex IV FTMS (German). The mass fraction of C, H, N of the single crystal was quantified by Element Analyzer (Elementar Analysensysteme GmbH, German). The crystallographic data for the single crystal were analyzed on a single crystal X-ray diffractometer (SXRD, Rigaku, Japan) with a 2.0 kW sealed anode source using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

2.3. Liquid-liquid extraction

In the extraction experiments, 0.5 mL IL with BPC6 was contacted with 0.5 mL aqueous solution containing MCl (M = K, Rb), In order to fully extraction, the mixed system was vibrated for 2 h in room temperature and standed for phase separation. The concentration of metal ions in aqueous solution was analyzed by ICP-AES. The extraction efficiency (E), the distribution ratio (D) and the separation factor (β) were calculated by Eqs. (1)–(3), respectively.

$$E = \left(1 - \frac{C_i}{C_0}\right) \times 100\% \tag{1}$$

Table 1
Crystallographic data for the complex.

	$[(BPC6 \cdot Rb^+)_2 NTf_2^-][NTf_2^-]$
Chemical formula	$C_{46}H_{54}F_6NO_{12}RbS_2$
Formula weight	1076.49
T (K)	100
Crystal system	Monoclinic
Space group	P 21/C
a (Å)	10.5402(3)
b (Å)	17.2288(4)
c (Å)	52.6751(15)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9565.5(4)
Z	8
ρ (g·cm^{-3})	1.495
λ (Mo Kα)(mm^{-1})	0.71073
Crystal size (mm)	0.15 × 0.1 × 0.04
T_{min}, T_{max}	0.609, 1.000
$\theta_{min}, \theta_{max}$ (°)	2.2730, 27.4190
Reflections collected	30,445
Independent reflections (R_{int})	9702(0.0435)
Data/restraints/parameters	13373/828/1112
R_1,wR_2 ($I \geq 2\sigma(I)$)	0.1159, 0.2790
R_1,wR_2 (all data)	0.1485, 0.2924
Goodness-of-fit (GOF)	1.883
Maximum and mean Δ/σ	0.015, 0.002

$$D = \frac{C_0 - C_i}{C_i} \tag{2}$$

$$\beta = \frac{D_1}{D_2} \tag{3}$$

where C_0 and C_i are the concentrations of metal ions in aqueous solution before and after extraction, separately.

The procedure of back extraction is similar to that of extraction.

2.4. Synthesis and crystallography of crystalline complex

1 mL *n*-octanol solution containing BPC6 (15 mmol/L) and $C_2mimNTf_2$ (15 mmol/L) was contacted with 1 mL RbCl aqueous solution (58.5 mmol/L). After standing in room temperature for 2 days, some colorless sheet-like crystals appeared at the interface. Elemental analysis of the complex (C, 51.42; N, 1.37; H, 5.00) is close to the calculated result according to the chemical formula $C_{46}H_{54}F_6NO_{12}RbS_2$ (C, 51.23; N, 1.30; H, 5.23). The crystallographic data of crystalline complex are shown in Table 1.

3. Results and discussion

3.1. Influence of the BPC6 concentration

As shown in Fig. 1, the extraction efficiency of Rb^+ by $BPC6/C_2mimNTf_2$ increases with an increase in the concentration of BPC6. When the concentration of BPC6 exceeds 12 mmol/L, E_{Rb} is close to 100% and D_{Rb} is more than 10^3. The pure $C_2mimNTf_2$ without BPC6 can extract Rb^+ to some extent, while the addition of BPC6 in ionic liquids can enhance greatly extraction efficiency of Rb^+ (from 30.4% to 99.3%), which may be ascribed to the complex interaction between BPC6 and Rb^+.

In addition, the length of the alkyl chain on the imidazolium cation has an effect on the extraction of Rb^+. E_{Rb} decreases from 30.4% to approximately about 10% with the increasing of alkyl chain length when using pure ionic liquid to extract Rb^+. This phenomenon seems to suggests that the extraction follows a cation exchange mechanism, where the imidazolium with a shorter alkyl chain exchanges with Rb^+ more easily.
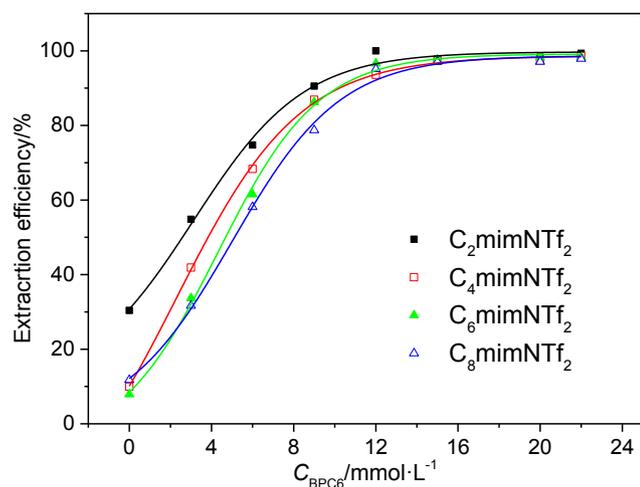
Fig. 1. Relationship between extraction efficiency of Rb$^+$ and the concentration of BPC6 in C$_n$mimNTf$_2$ (n = 2, 4, 6, 8), C_0(Rb$^+$) = 9 mmol/L.

3.2. Influences of C$_2$mim$^+$ and NTf$_2^-$ in the aqueous phase

To investigate the salt effect, LiNTf$_2$ and C$_2$mimBr were added to the RbCl solution, respectively. Fig. 2 shows that the cation (C$_2$mim$^+$) and anion (NTf$_2^-$) of ionic liquid in the aqueous phase have different influences on the extraction efficiency of Rb$^+$. With an increase in the concentration of C$_2$mim$^+$ from 0 to 1 mol/L in water, E_{Rb} decreases from 43.6% to 21.2%. On the contrary, the addition of NTf$_2^-$ in the aqueous phase is beneficial to the extraction of Rb$^+$, where the efficiency increases from 43.6% to 82.8%. These results further demonstrate that the extraction follows a cation exchange mechanism. If complexation between Rb$^+$ and BPC6 were the first step during the extraction process, the Cl$^-$ (counter ion) would enter IL phase simultaneously. Thus, the increasing of Cl$^-$ in aqueous solution would improve the extraction efficiency of Rb$^+$. However, the result shown in Fig. 2 illustrates that Cl$^-$ has little effect on the extraction efficiency of Rb$^+$. In a word, it is a simultaneous process of complex Rb with BPC6 and exchange to IL phase.

3.3. Influence of acid concentration

Influences of acid concentration on E_{Rb} and logD were shown in Fig. 3. With the increasing of pH, the extraction efficiency of Rb$^+$ by C$_2$mimNTf$_2$ rises from 10.7% to 35.3%. When pH > 3, the E_{Rb} and
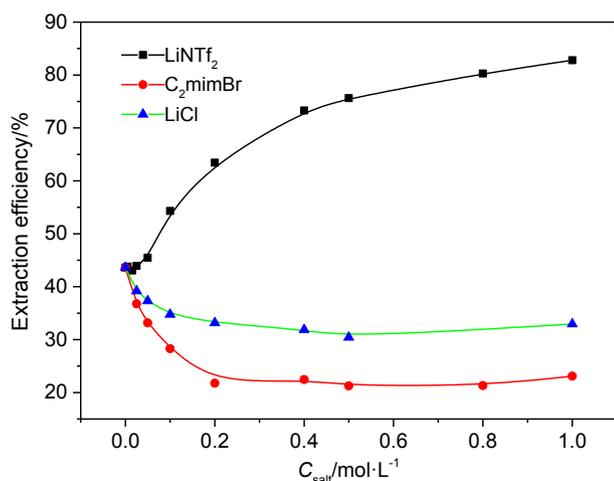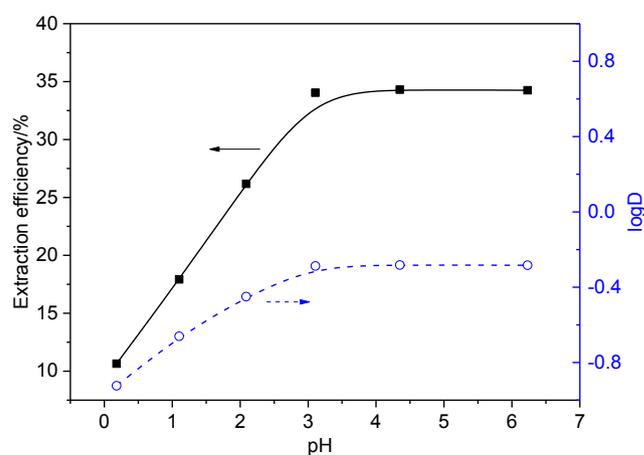

Fig. 3. Extraction efficiency and distribution ratio of Rb$^+$ at different pH values, C_0(Rb$^+$) = 5.85 mmol/L.

logD remain relatively constant. The pH values at extraction equilibrium are 0.18, 1.10, 2.09, 3.11, 4.35, 6.23. The corresponding pH values of initial solution before extraction are 0.06, 1.01, 2.06, 3.05, 4.31, 6.21, respectively. In condition of high acid concentration, pH increases slightly after extraction. The difference of pH gradually decreases with the increasing of pH. The H$^+$ would compete with Rb$^+$ to exchange with C$_2$mim$^+$ in acidic solution. As well as results in Section 3.2, these results also confirm the cation exchange mechanism.

3.4. The structure of complex during extraction

In the ESI-MS spectrum (Fig. 4) of the IL phase after extraction, a peak in positive mode appears at m/z = 795.3, which is attributed to [BPC6·Rb$^+$], indicating the formation of the 1:1 complex.

Although the crystallization in-situ is difficult, the crystalline complex formed at the interface between n-octanol and aqueous phase helps understand the structure of the extracted complex. The structure is shown in Fig. 5A. There are eight complexes in each unit (Fig. 5B). Unlike triclinic crystal system of [BPC6·Cs$^+$][NTf$_2^-$] reported previously, [40] it is a crystal belonging to orthorhombic system with $\alpha = \beta = \gamma = 90°$. In the complex, a Rb$^+$ ion is coordinated with six oxygen atoms in the crown ether moiety with a Rb-O distance in the range of 2.843–3.123 Å (Table 2). There are two relative positions between [BPC6·Rb$^+$] and NTf$_2^-$. A NTf$_2^-$ only serves as a counter-ion to compensate the positive charge of [BPC6·Rb$^+$], however, an oxygen

Fig. 2. Influence of the concentration of additional salts on the extraction efficiency of Rb$^+$, C_0(Rb$^+$) = 23 mmol/L, C_{BPC6} = 6 mmol/L.
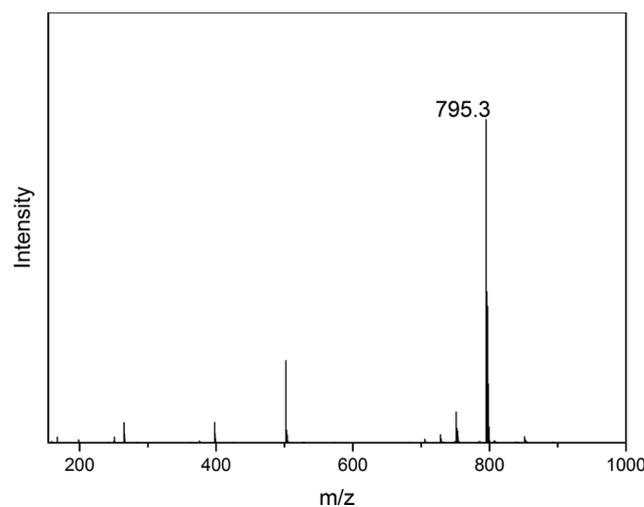

Fig. 4. ESI-MS of the IL phase in positive mode after extraction, C_0(Rb$^+$) = 9 mmol/L, C_{BPC6} = 12 mmol/L.
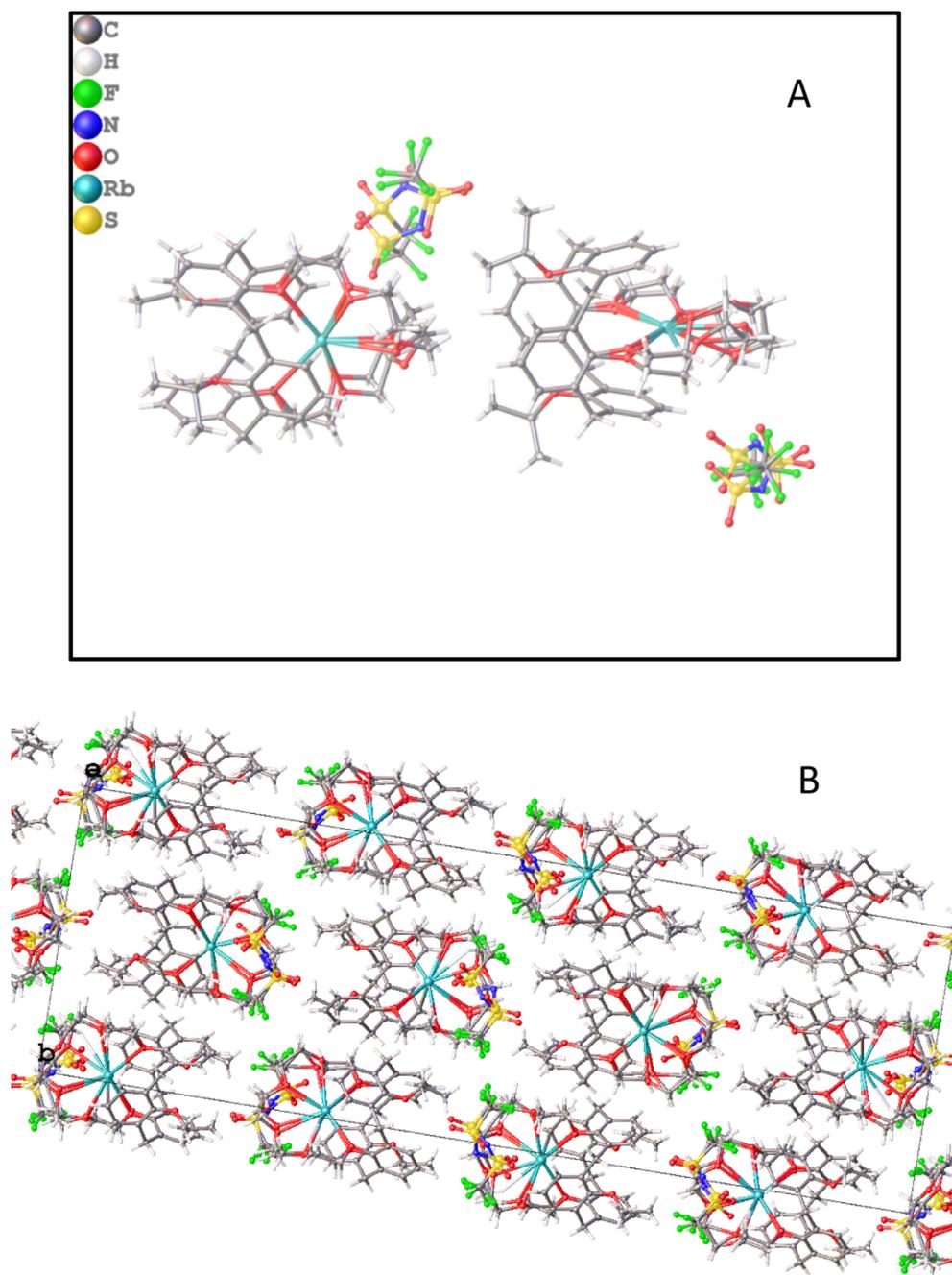
Fig. 5. (A) Structure of $[(BPC6 \cdot Rb^+)_2NTf_2^-][NTf_2^-]$; (B) Packing of $[(BPC6 \cdot Rb^+)_2NTf_2^-][NTf_2^-]$ molecules.

Table 2
Select bond lengths (Å) for $[(BPC6 \cdot Rb^+)_2NTf_2^-][NTf_2^-]$.

Bond	Length/ Å	Bond	Length/ Å
Rb1-O1A	3.017	Rb2-O9A	2.993
Rb1-O1B	3.071	Rb2-O9B	2.961
Rb1-O2A	3.076	Rb2-O10A	2.893
Rb1-O2B	2.981	Rb2-O10B	3.178
Rb1-O3A	2.845	Rb2-O11A	3.11
Rb1-O3B	3.084	Rb2-O11B	3.217
Rb1-O4A	3.123	Rb2-O12A	3.021
Rb1-O4B	3.183	Rb2-O12B	3.484
Rb1-O5A	3.05	Rb2-O13A	3.024
Rb1-O5B	3.098	Rb2-O13B	3.021
Rb1-O6A	3.021	Rb2-O14A	3.014
Rb1-O6B	3.052	Rb2-O14B	3.014
		Rb2-O20B	3.372

atom of another NTf_2^- further coordinates with Rb^+ with a Rb-O distance of 3.372 Å. The molecular formula is $C_{92}H_{108}F_{12}N_2O_{24}Rb_2S_4$, which means $[(BPC6 \cdot Rb^+)_2NTf_2^-][NTf_2^-]$. In addition, there exists Rb^+-π interaction between Rb^+ and two phenyl rings because the distances between Rb^+ and the two ring centroids are 3.367 Å and 3.469 Å, respectively. In the structure, the anion and crown ether moiety show disorder to some extent, with the oxygen atoms of crown ether in two orientations (the occupancy of each atom site is 0.5). It is the formation of the 1:1 complex between BPC6 and Rb^+ that results in the extraction of Rb^+ by BPC6 in ILs with high efficiency.

Combining the discussion as mentioned above, we deduce the mechanism of extraction as Eqs. (4) and (5).
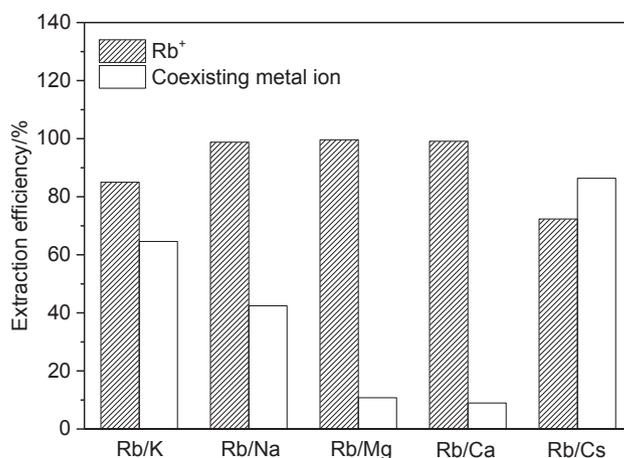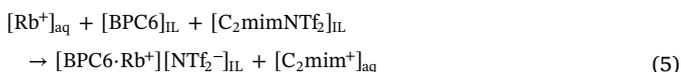
$$[Rb^+]_{aq} + [C_2mimNTf_2]_{IL} \rightarrow [RbNTf_2]_{IL} + [C_2mim^+]_{aq} \tag{4}$$

Fig. 6. The interference effect of coexisting metal ion to the extraction of Rb^+, $C_{BPC6} = 9$ mmol/L, $C_0(Rb^+) = C_0(K^+) = C_0(Na^+) = C_0(Mg^{2+}) = C_0(Ca^{2+}) = C_0(Cs^+) = 5.85$ mmol/L.

$$[Rb^+]_{aq} + [BPC6]_{IL} + [C_2mimNTf_2]_{IL}$$

$$\rightarrow [BPC6 \cdot Rb^+][NTf_2^-]_{IL} + [C_2mim^+]_{aq} \quad (5)$$

On the one hand, $C_2mimNTf_2$ itself participates in the extraction process by the exchange of C_2mim^+ with Rb^+ (Eq. (4)), leading to the extraction of Rb^+ by pure ILs with a certain efficiency (Fig. 1). On the other hand, BPC6 coordinates with Rb^+ to form the 1:1 complex and changes with C_2mim^+ in the IL phase simultaneously (Eq. (5)), which is analogized by extraction of Cs^+ in our previous work [36]. It is a complex and rapid process of interfacial extraction that now we could not decide which step should be taken first. During the extraction, ILs can be regarded as a bifunctional media here.

3.5. Influences of coexisting metal ions in salt lake brines on the extraction of Rb^+

In order to compare the influences of several coexisting metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Cs^+) on the extraction of Rb^+ by BPC6/$C_2mimNTf_2$, equal concentration of metal ions in mixed solution were prepared in extraction process. As shown in Fig. 6, Na^+, Mg^{2+} and Ca^{2+} have almost no interference on the extraction of Rb^+. Interferences of K^+ and Cs^+ are serious under the equal concentration due to their similar properties with Rb^+. The corresponding separation factor of Rb to M (M = K^+, Na^+, Mg^{2+}, Ca^{2+}, Cs^+) reach 3.106, 110.6, 2062, 1091 and 0.4126, respectively. On the one hand, Rb^+ and Cs^+ are simultaneously extracted in most studies due to their similar properties [4,6–9]. On the other hand, the concentration of Cs^+ is lower than that of Rb^+ in salt brines [41], while the concentration of K^+ is far more than that of Rb^+ [8]. It is necessary for us to study the influence of K^+ concentration on the extraction of Rb^+ during the extraction of BPC6/$C_2mimNTf_2$. We chose K^+ as interference metal ion to study the extraction of Rb^+ in the following context.

3.6. Study of Rb^+ separation from RbCl and KCl mixed solution

According to other studies [15,38] and our discussion in Section 3.5, the interference from K^+ was serious during the extraction of Rb^+. In order to study the extraction ability of BPC6/$C_2mimNTf_2$ and pure $C_2mimNTf_2$ in the present of K^+, the effect of initial K^+ concentration was investigated in a single stage extraction. By comparing distribution ratio (solid line) and separation factor (dash line) in Fig. 7, it is obvious that separation effect of Rb^+ by BPC6/$C_2mimNTf_2$ is better than that by pure $C_2mimNTf_2$ owing to the interaction between BPC6 and Rb^+. As the concentration of K^+ increases in initial solution, the distribution
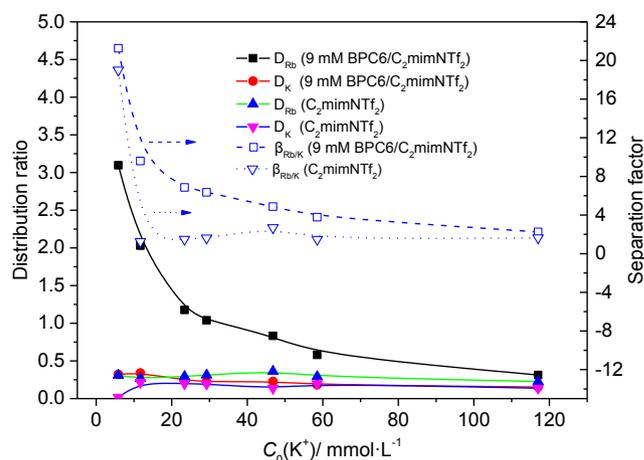

Fig. 7. Effect of $C_0(K^+)$ on distribution ratio and separation factor of Rb^+ in 9 mM BPC6/$C_2mimNTf_2$ and pure $C_2mimNTf_2$, $C_0(Rb^+) = 5.85$ mmol/L.
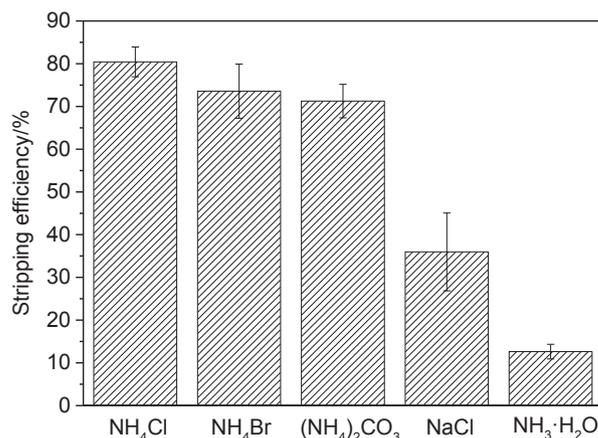
Fig. 8. Stripping efficiency by different back extractants, $C_0(Rb^+) = 5.85$ mmol/L, $C_{BPC6} = 9$ mmol/L, $C(NH_4Cl) = C(NH_4Br) = C(NaCl) = C(NH_3 \cdot H_2O) = 2$ mol/L, $C((NH_4)_2CO_3) = 1$ mol/L.
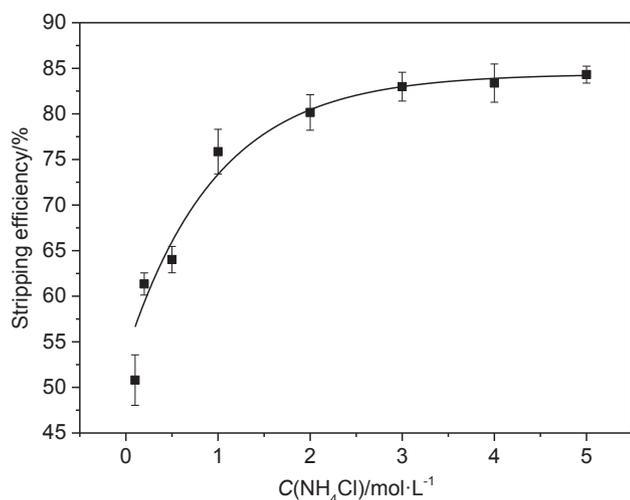
Fig. 9. Dependence of Rb^+ stripping efficiency on the NH_4Cl concentration, $C_0(Rb^+) = 5.85$ mmol/L, $C_{BPC6} = 9$ mmol/L.

ratio and separation factor of Rb^+ gradually decline, which means the selective separation effect of Rb^+ is weakened due to the interference from K^+. Nevertheless, the value of K/Rb molar ratio could still decrease from 20 to 10 after a single stage extraction by BPC6/$C_2mimNTf_2$.

3.7. Back extraction of Rb^+ from ionic liquid

Back extraction is the other key problem, which directly determines the practical application of extraction by IL system. In order to realize the effective back extraction of Rb^+ from BPC6/$C_2mimNTf_2$, several back extractants were used. As shown in Fig. 8, the aqueous solution of ammonium halide, especially NH_4Cl, can strip Rb^+ from $C_2mimNTf_2$ phase into aqueous phase efficiently. Compared with Na^+ (0.95 Å) and K^+ (1.33 Å), the ionic radius of NH_4^+ (1.46 Å) is close to that of Rb^+ (1.48 Å) [42,43], which leads to a high efficiency of back extraction by ammonium halide rather than NaCl. Anions could affect back extraction process on some extent. For example, CO_3^{2-} is hydrolyzed in aqueous solution, which would accelerate the hydrolysis of NH_4^+. Decreasing of NH_4^+ concentration leads that back extraction efficiency of $(NH_4)_2CO_3$ is inferior to that of NH_4Cl. It is noteworthy that the back extraction efficiency of $NH_3 \cdot H_2O$ is remarkably lower than those of ammonium salts, due to the weak ionization of $NH_3 \cdot H_2O$. The mechanism of back extraction may be an ion exchange between NH_4^+ in the aqueous phase and Rb^+ in the IL phase.

The effect of NH_4Cl concentration on the back extraction efficiency is shown in Fig. 9. With the increase of NH_4Cl concentration, the back extraction efficiency of Rb^+ rises obviously. When NH_4Cl concentration exceeds 2 mol/L, the back extraction efficiency is more than 80%. When 5 mol/L NH_4Cl is used, the efficiency can reach 84.3 ± 0.9%.

As mentioned above, Rb^+ could be extracted and back extracted by BPC6/$C_2mimNTf_2$ and NH_4Cl solution, respectively. Consequently, we studied the enrichment of Rb^+ from the mixed solution of RbCl and KCl. After an extraction-stripping procedure $(C_0(Rb^+) = C_0(K^+) = 5.85$ mmol/L, $C_{BPC6} = 9$ mmol/L, $C(NH_4Cl) = 2$ mol/L), the molar ratio of Rb^+ to K^+ rised from 1 to 3.

Nevertheless, reusability of the IL system need to be further studied. The extraction efficiency of Rb^+ decreases to 70% of the maximum value after an extraction-striping procedure due to wastage of IL.

4. Conclusions

This work demonstrated that the BPC6/$C_2mimNTf_2$ system could extract Rb^+ efficiently with an extraction efficiency close to 100% at optimum condition. The possible mechanism of extraction was suggested, that is, C_2mim^+ exchanges Rb^+ from aqueous solution to IL phase. The crystal structure was an indication of the 1:1 complex of BPC6 and Rb^+ during the extraction process. In the presence of K^+, Rb^+ could be selectively extracted by BPC6/$C_2mimNTf_2$ to the extent. In the stripping process, NH_4Cl acted as an excellent back extractant to strip Rb^+ from $C_2mimNTf_2$ phase to aqueous phase with an efficiency of 84.3%. This IL system is hopeful to separate Rb^+ from salt lake brines.

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