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Extraction of rubidium ion from brine solutions by dicyclohexano-18-crown-6 / ionic liquid system

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Separation among rubidium and potassium ions from salt lake brines remains challenging. In this work, a typical room temperature ionic liquid 1-ethyl-3-metyhlimidazaolium bis(trifluoromethylsulfonyl)imide ($[C_2mim^+][NTf_2^-]$) was used as diluent and synergistic extractant, dicyclohexano-18-crown-6 (DCH18C6) was used as extractant to extract rubidium ions from brine solutions which contain high concentrations of potassium ions was investigated. Under the optimal conditions, the single extraction efficiency of rubidium ions was up 93.63%. The thermodynamic parameters of the rubidium ion extraction were obtained. Based on the slope analysis method, the extracted species in the organic phase were ascertained as 1:1 complex. UV-visible has been performed to investigate the ion concentration of ionic liquid before and after the interaction of metal ions and ligands. Rubidium ions in $[Rb \cdot DCH18C6]^+$ complex were stripped by 2.5 mol $\cdot$ L^{-1} NH_4NO_3. The extraction system offers high efficiency, simplicity and environmentally friendly application prospect to separate rubidium from brine solutions.

Keywords: Rubidium; Ionic liquid; Dicyclohexano-18-crown-6; Solvent extraction.

INTRODUCTION

Rubidium is an important rare alkaline metal and is known as a strategic resource. Rubidium and its compounds are widely used in the fields of electronic devices, catalysts, medicine, special glass, national defense, and new energy[1–3]. Salt lake brines contain a large amount of rubidium ions, which is one of the main sources of rubidium. Compared with ores such as pollucite and lepidolite, salt lake brines has the advantage of being easy to collect and not requiring leaching. Therefore, it is a promising resource for rubidium recovery. However, the extraction and separation of rubidium from salt lake brine remain a great challenge, because of the coexisting elements such as lithium, sodium, potassium, cesium, magnesium, and calcium, especially the high concentrations of potassium[4].

The methods of separating rubidium ions from salt lake brine mainly include solvent extraction, ion exchange, and precipitation[5–7]. Among them, solvent extraction is the most promising method, because of the several advantages such as high selectivity, efficiency, economical, relatively simple equipment, and operating in a continuous mode[8–10]. Phenol-alcohols and crown ethers were found to be the high effective extractants for rubidium recovery. Liu et al.[11] studied the extraction of Rb^+ and Cs^+ from neutral salt lake brines after the removal of K^+ with 4-tert-butyl-2-(α-methylbenzyl)phenol (t-BAMBP) in sulfonated kerosene, after 1mol/L NaOH added into salt lake brines to adjust pH and 5-stage counter current extraction, the final extraction yields of Rb^+ and Cs^+ reached 95.04% and 99.80%, respectively, but the scrubbing yield of rubidium was only about 10.5% when the extraction solvent was washed 3 times with 1×10^{-4} mol $\cdot L^{-1}$ NaOH. The effect of high concentration K^+ on the extraction of Cs^+ and Rb^+ from synthetic brine solution was investigated by Li et al.[12]. Over 97% cesium and 78% rubidium were extracted with 21.5% potassium co-extracted. However, 0.1 mol $\cdot$ L^{-1} NaOH still needed to be added to an aqueous solution. Adding NaOH to the salt lake brine to adjust the pH will consume a large amount of NaOH resulting in the production of a large amount of strongly alkaline wastewater and serious environmental pollution. Moreover, the strong alkaline condition may result in sever corrosion to the equipment. Crown ethers are commonly used to recover cesium ions from high-level waste liquids. Gruner et al.[13] synthesized different types of calixcrown and studied their extraction performance for Cs^+, the results indicated that calixcrown-based extraction systems showed high selectivity for Cs^+, and the maximum distribution coefficient of Cs was 33. Until now, no report has been found on the recovery of rubidium ions from salt lake brines using crown ethers. So it is necessary to establish an efficient and environmentally friendly extraction system to recover rubidium ions from salt lake brines.

Room-temperature ionic liquids (RTILs) are composed of cations and anions, with melting points near room temperature. Due to their unique characteristics, such as low volatility, low melting, and high thermal stability, RTILs are considered to be one of the green solvents that have become a substitute for traditional organic solvents used in the extraction system[14–16]. Simultaneously, RTILs are playing an important role in separation, catalysis, and material sciences[17]. Shi et al.[18] investigated an efficient extraction system for the recovery of lithium ions from salt lake brine by tri-n-butyl phosphate using 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($[C_4mim^+][NTf_2^-]$). The separation of neodymium from cobalt and nickel by using IL-based aqueous two-phase system was reported by Chen et al.[19]. The extraction systems used crown ether as the extractants and ILs as the diluents have aroused great interest among investigators. Vendilo et al.[20] studied the correlation of caesium-18-crown-6 complex formation constants with the extraction capability for hydrophobic ionic liquids. Sengupta et al.[21] investigated the extraction of radio strontium from nuclear waste solution using crown ethers

in room-temperature ionic liquids. Extraction of alkali and alkaline earth cations from acidic nitrate and chloride by a crown ether with different types of ions liquid was reported by Garvey et al.[22], the results indicated that higher IL anion hydrophobicity was a greater tendency toward ion exchange as the predominant mode of extraction. All of these works use IL as a medium to separate metal ions from the aqueous phase and greatly increase the separation factor of the target ions.

In the present study, an efficient extraction system using imidazolium-based IL, 1-ethyl-3-metyhlimidazaolium bis(trifluoromethylsulfonyl)imide ($[C_2mim^+][NTf_2^-]$) as part of extraction solvent and DCH18C6 as extractant for the separation of rubidium ions from brine solutions. The environmental pollution and equipment corrosion have been avoided in new extraction system. Several variables such as the aqueous phase initial pH, composition of the diluent, alkyl carbon chain length of the ionic liquid, the concentration of DCH18C6 and phase ratio which effecting the extraction efficiency and separation factor of the extraction process were systematically investigated. Thermodynamic parameters of the rubidium ion extraction were obtained through thermodynamic analysis. The stripping of rubidium from the loaded organic phase was also investigated. Based on the slope analysis, a cation exchange mechanism between $[C_2mim^+]$ and rubidium was proposed.

EXPERIMENTAL

Materials and apparatus

Dicyclohexano-18-crown-6 (DCH18C6) (AR, >97%) was purchased from Alfa Aesar Co., Ltd. (Shanghai, China). Room temperature ionic liquid, viz. 1-(ethyl, butyl, hexyl, octyl, decyl)-3-metyhlimidazaolium bis(trifluoromethylsulfonyl)imide ($[C_{2,\,4,\,6,\,8,\,10}\,mim^+]$ $[NTf_2^-]$) with purities >99% were purchased from Lanzhou Institute of Chemical Physics, CAS (Lanzhou, China). 1,2-dichloroethane (AR, >99%) was purchased from Tianjin Kermel Reagent Co., Ltd. (Tianjin, China). All other reagents were of analytical grade. The brine solution used in the experiment was obtained by diluting 10 times the brine in solar pond in northern Tibet. The concentration of main ions in the brine solution used in the experiment is shown in Table 1. The following instruments were used: pH meter (pHS-3C), Shanghai LeiCi Scientific Instrument Co., Ltd; thermostatic water bath oscillators (SHA-B, The Jintan city, Jiangsu province Youlian Instrument Research Institute.); atomic absorption spectrometer, AAS (GBC 908, GBC Scientific Equipment Pty., Ltd.); inductively coupled plasma mass spectrometry, ICP-MS (ELAN DRC-e, Perkin Elmer Company, USA); UV-visible spectroscopic studies were carried out using a Shimadzu (Kyoto, Japan) UV-2600 single beam spectrophotometer using quartz cells and suitable reference solutions.

Solvent extraction experiments

Extraction organic phase was prepared by dissolving a certain amount of DCH18C6 in a mixed organic phase, which contained a proportion of 1, 2-dichloroethane and ionic liquid. The organic phase and the aqueous phase were added to a split funnel. The volume of the aqueous phase is fixed at 5.0 mL, and the volume of the organic phase is adjusted according to the comparison. Extractions were performed by shaking of the split funnel on thermostatic water bath oscillators at a certain temperature for 15 min to ensure equilibrium. The organic phases and aqueous phases were separated assisted by centrifugation. Afterwards, the aqueous phase was properly diluted after phase disengagement. Then, the concentration of Rb^+ was measured using an AAS and K^+ was measured by ICP-MS. For stripping experiments, the loaded organic phase was scrubbed by ammonium nitrate solution, which was performed under shaking in split funnel for 10 min. The concentration of metal ions in the organic phase was calculated as the difference between the initial and final concentration of ions in the aqueous phase.

The extraction efficiency (E), distribution ratio (D) and separation factor (β) were calculated according to the following equations:

$$E(\%) = \frac{(C_i - C_f) \times V_{aq}}{C_i \times V_{aq}} \times 100 \tag{1}$$

$$D_{Rb} = \frac{C_{Rb^+,org}}{C_{Rb^+_{aq}}} = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{org}} \tag{2}$$

$$\beta_{RbK} = \frac{D_{Rb}}{D_K} \tag{3}$$

where C_i and C_f (mg · L^{-1}) are the initial and final equilibrated concentrations of metal ions in the aqueous phase, respectively. V_{aq} (mL) and V_{org} (mL) represent the volume of the aqueous phase and organic phase, respectively. D_{Rb} and D_K are the distribution ratio of Rb and K, respectively. The more $\beta_{Rb/K}$ value differs from 1, the better the effect of separation Rb and K.

RESULTS AND DISCUSSION

Effect of the alkyl carbon chain length of the ionic liquid

The length of the ionic liquid alkyl chain affects the hydrophobicity of the ionic liquid and may have a significant effect on the extraction performance of the extraction system. Therefore, the effect of ionic liquids with different alkyl chains on the extraction of Rb^+ in the DCH18C6 system was studied. As shown in Fig. 1, the extraction rate of Rb^+ decreased with increasing number of carbon atoms in the alkyl chain of imidazolium-based ILs. The carbon chain length from 2 to 4 decreases the extraction rate very little, but the extraction rate from 4 to 10 is obvious. Firstly, the viscosity and steric hindrance of ionic liquids increase

Table 1. The concentration of main ions in the brine solution used in the experiment

Ion type	Rb^+	Cs^+	Na^+	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2-}
Concentration (mg · L^{-1})	186.8	1.4	92542	22322	130	3480	105937	6384

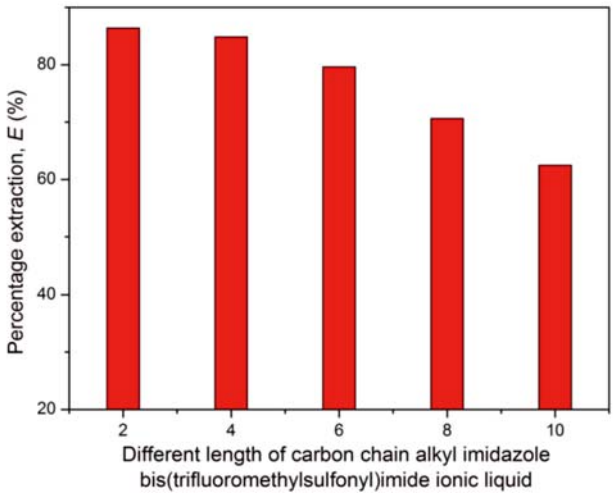


Figure 1. The effect of [C_n mim^+] [NTf_2^-] (n = 2, 4, 6, 8, 10) on the extraction of Rb^+ in the DCH18C6 system. (CDCH18C6 = 0.2 mol · L^{-1}, the volume of IL in diluent is 10%, pH = 9.47, Vo/Va = 1:1)

with the alkyl carbon chain increases, which results in a decline in the mass transfer efficiency of the chemical exchange reaction. Secondly, the increase in the length of the carbon chain of the substituted alkyl group in [$C_n$mim$^+$] simultaneously increases the hydrophobicity of the IL cation, and the exchange between the cation and the cationic rubidium-crown crown ether complex becomes difficult. Similar results appeared in previous reports[16, 23]. Based on the above analysis, the [C_2mim$^+$] [NTf_2^-] was selected as a part of the organic phase to obtain a relatively higher extraction efficiency of rubidium ion in the following experiments.

Effect of composition of the diluent

As an important component of the organic phase, the ionic liquid will directly affect the extraction rate of rubidium ions. Therefore, the volume of ionic liquid in diluent used for extraction of Rb^+ was investigated. The [C_2mim$^+$][NTf_2^-] volume percentage in diluent was varied in the range of 0–50% and the results were presented in Fig. 2. When the ionic liquid content is 0–10%, the extraction rate of Rb^+ and K^+ increased rapidly with the increase of ionic liquid content. When the ionic liquid content exceeds 10%, the extraction rate of Rb^+ tends to be balanced, but the extraction rate of

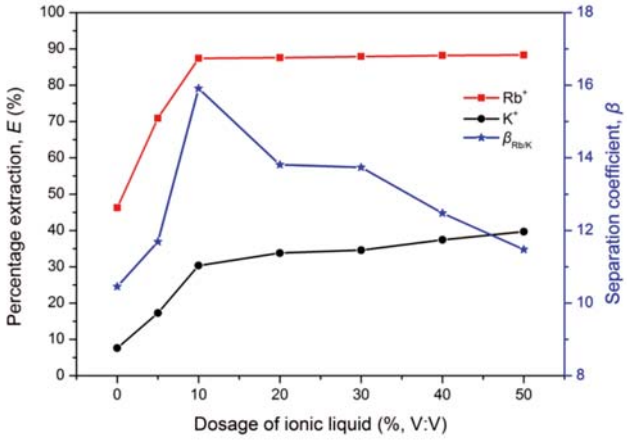


Figure 2. Effect of IL volume in diluent on the extraction efficiency of metal ions in the DCH18C6 system. (CDCH18C6 = 0.2 mol · L^{-1}, pH = 9.47, Vo/Va = 1:1

K^+ continues to increase. The separation factor of $\beta_{Rb/K}$ increased first and then decreased with the increase of ionic liquid content, and the maximum value appeared at 10%. The reason may be that the content of K^+ in aqueous phase is much higher than Rb^+. When the Rb^+ reaches the equilibrium of extraction, the K^+ has not yet reached. Therefore, when the ionic liquid content is greater than 10%, the extraction rate of K^+ is still increasing. To obtain higher Rb^+ extraction rate and better separation of Rb^+ and K^+. Therefore, in the following experiments, the ionic liquid content in the diluent was selected to be 10%.

Effect of the aqueous phase initial pH

The initial pH of the aqueous phase has an important influence on many extraction systems and cannot be ignored. So it was necessary to evaluate the pH value in the aqueous phase influence on the extraction of Rb^+ using DCH18C6 in [C_2mim$^+$][NTf_2^-]. As the results are shown in Fig. 3, the extraction rate of Rb^+ has no obvious difference when pH is 5 to 13. But the extraction efficiency was lower in strong acid environment, of which pH was 1 to 3. The probable reason was the associated reaction competition between hydrogen ions and other metal ions were not very strong. Besides that, Fig. 3 shows that the extraction efficiency of Rb^+ was much greater than K^+, which indicated high selectivity to Rb^+ in this system. Since pH of the brine solutions is 9.47, brine solutions can be used for extracting directly without adjusting pH in this extraction system. So, compared with the traditional phenol alcohol extraction system, it simplifies the extraction process and is more conducive to environmental protection.

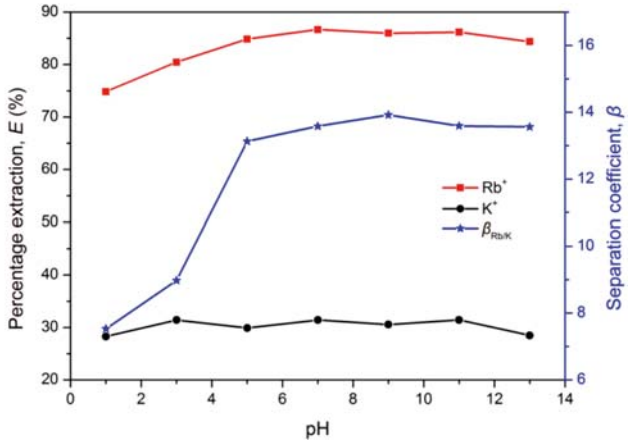


Figure 3. Effects of aqueous phase pH on extraction efficiencies of metal ions. (The volume of IL in diluent is 10%, CDCH18C6 = 0.2 mol · L^{-1}, Vo/Va = 1:1

Effect of the concentration of DCH18C6 in the organic phase

The concentration of the extractant has an important effect on the extraction rate of target metal ions when the composition of the aqueous phase is constant. So extraction behaviors of metal ions by the DCH18C6/ [C_2mim$^+$][NTf_2^-] system with various concentrations of DCH18C6 in the organic phase were studied. It can be seen from Fig. 4 that with the increase of extractant concentration, the extraction rate of Rb^+ and K^+ is increasing. When the concentration of the extractant is 0.2 mol · L^{-1}, the single-stage extraction rate of rubidium

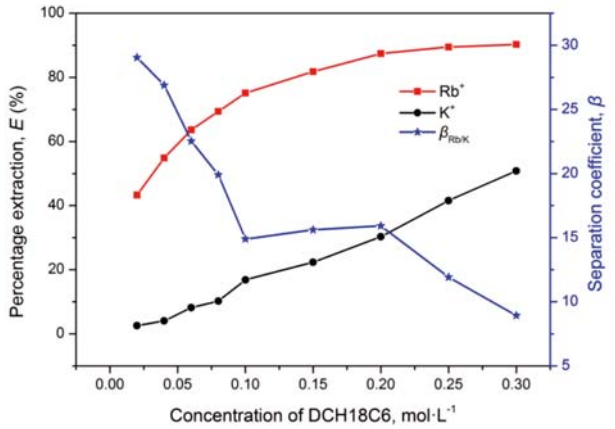


Figure 4. Effect of DCH18C6's concentration on the extraction efficiency of metal ions. (The volume of IL in diluent is 10%, pH = 9.47, Vo/Va = 1:1)

ion reaches 87.39%, and when the concentration of the extractant continues to increase, the extraction rate of Rb^+ tends to balance, but the extraction of K^+ continues to increase rapidly. Therefore, the curve of separation factor of Rb and K shows a trend of rapid decrease. The reason may be that when the concentration of the extractant less than 0.2 mol · L^{-1}, the extractant will give priority to the formation of complex with Rb^+. When the concentration of the extractant is up to or greater than 0.2 mol · L^{-1}, most of the Rb^+ in the aqueous phase have been extracted, and a large amount of K^+ is extracted when the extractant overdoses. In order to obtain a higher Rb^+ extraction rate and $\beta_{Rb/K}$, the extractant concentration was selected as 0.2 mol · L^{-1} for subsequent studies.

Effect of Vo/Va phase ratio

The effect of phase ratio on the rubidium and potassium ions extraction was investigated covering different volume ratios of the organic phase (Vo) to the aqueous phase (Va) from 0.5 to 3. As the results were shown in Fig. 5, the extraction efficiency of Rb^+ and K^+ increased with the increasing of the Vo/Va phase ratio, simultaneous, the separation factor of $\beta_{Rb/K}$ is also increasing rapidly. When the phase ratios is 1.5, the extraction yield of Rb^+ reached 93.63%, 33.5% of K^+ have been co-extracted, and the value of $\beta_{Rb/K}$ is up to the maximum. But with a further increase of Vo/Va phase ratio, the extraction efficiency of K^+ increased faster than Rb^+, and the separation factor of $\beta_{Rb/K}$ tend to be decreased. The reason may be that the probability of collision between the organic molecule and alkali ions has increased with the increase in the O/A phase ratio. However, when the ratio is greater than 1.5, Rb^+ extraction can reach equilibrium. With the continuous extraction of K^+, the separation coefficient of rubidium and potassium will unavoidably decrease. Based on the above analysis, the value of the phase ratio was selected as 1.5 in the next study.

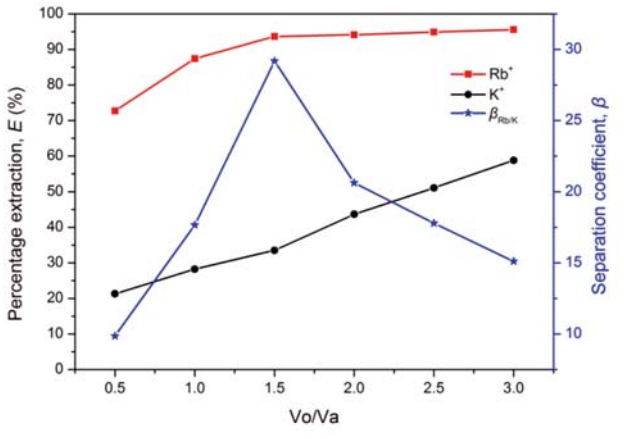


Figure 5. Effect of phase rate on the extraction efficiency of metal ions. CDCH18C6 = 0.2 mol · L^{-1}, the volume of IL in diluent is 10%, pH = 9.47

EXTRACTION MECHANISM

The extraction rate of rubidium ion has been greatly improved after adding [C_2mim$^+$][NTf_2^-] to the DCH18C6 system, which was shown in Fig. 2. Therefore, compared with the traditional dilute extraction system, the mass transfer process of metal ions from aqueous phase to organic phase changed after adding ionic liquids. In crown ether extraction system, when using a traditional organic solvent as a diluent, the extraction mechanism is mostly neutral composite mechanism. That is, metal ions, extractant and some other ions to form a neutral complex into the organic phase. Take DCH18C6 in the n-octanol system extraction of Sr^{2+} as an example[24], the mechanism is shown below:

$$Sr^{2+}{}_{aq} + \mathrm{DCH18C6}_{org} + 2NO_3^-{}_{aq} \rightarrow \rightarrow Sr \cdot \mathrm{DCH18C6} \cdot (NO_3)_{2org} \quad (4)$$

So in this work, the mechanism of the ionic liquid/crown ether extraction system needs to be studied.

To analyze the extraction process of the ionic liquid system, the absorbance of [C_2mim]$^+$ in the aqueous phase had been determined by UV-vis spectra before and after the extraction equilibrium of Rb^+ into the organic phase. As results were shown in Fig. 6, there is a strong ultraviolet absorption peak at λ_{max} = 211nm, which is the ultraviolet absorption peak of [C_2mim$^+$]. Moreover, the absorbance of the aqueous phase has been greatly improved after extraction, which indicated that part of [C_2mim$^+$] in the extraction process has entered the aqueous phase due to exchange. Dai et al.[25] pointed out that in terms of thermodynamic, ionic compounds are easier to dissolve in ionic liquids than organic so-

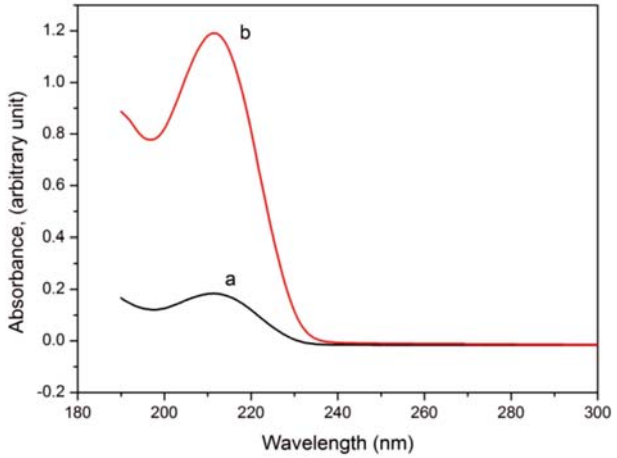


Figure 6. UV-vis spectra of the aqueous phase before and after extraction. (a: before extraction; b: after extraction)

lvents. Therefore, the cation exchange mechanism is more universal for the extraction of metal ions in an ionic liquid system.

Consequently, we considered that the extraction of Rb^+ with DCH18C6 in $[C_2mim^+][NTf_2^-]$ involves a cation-exchange mode. So the expression for the Rb^+ participation into the organic phase can be presented as:

$$Rb^+_{aq} + [C_2mim^+]_{org} + nDCH18C6_{org} \rightarrow \\ \rightarrow [Rb \cdot nDCH18C6]^+_{org} + [C_2mim^+]_{aq} \quad (5)$$

According to Eq (5), the extraction equilibrium constant (K_e) can be expressed as:

$$K_e = \frac{[Rb \cdot nDCH18C6]^+_{org}[C_2mim^+]_{aq}}{Rb^+_{aq}[c_2mim^+]_{org}[DCH18C6]^n_{org}} \quad (6)$$

The distribution ratio of rubidium (D_{Rb}) is equal to the ratio of the total concentration of rubidium ion in the organic phase to its total concentration in the aqueous phase. Therefore, K_e can be simplified to:

$$K_e = D_{Rb}\frac{[C_2mim^+]_{aq}}{[C_2mim^+]_{org}[DCH18C6]^n_{org}} \quad (7)$$

The logarithm of the two sides of the Eq (7) can be obtained:

$$\log D_{Rb} + \log[C_2mim^+]_{aq} - \log[C_2mim^+]_{org} = \\ = n\log[DCH18C6]_{org} + \log K_e \quad (8)$$

where the value of K_e is only related to the temperature for an extraction reaction. According to the equilibrium concentration of DCH18C6 in the extraction stage, slope analysis was carried out to determine the stoichiometry of the Rb·DCH18C6 complex.

At constant temperature, the distribution ratio of rubidium at different concentrations can be obtained when the concentration of DCH18C6 is changed from 0.02 mol · L^{-1} to 1.5 mol · L^{-1}. As shown in Fig. 7, the plots of ($\log D_{Rb}$ + $\log[C_2mim^+]_{aq}$ – $\log[C_2mim^+]_{org}$) versus $\log[DCH18C6]_{org}$ showed a straight line with a slope of 1.06, which indicated that only one molecule of DCH18C6 was involved during the extraction process for rubidium ions. Hence, the extraction reaction of rubidium ions by DCH18C6 in $[C_2mim^+][NTf_2^-]$ can be represented as follows:

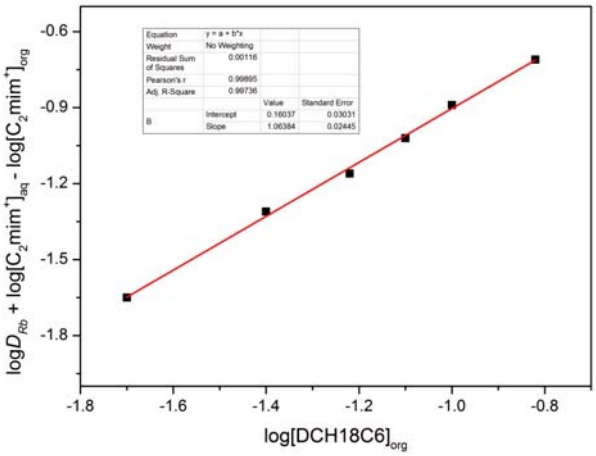


Figure 7. Linear relationship between ($\log[D_{Rb}] + \log[C_2mim^+]_{aq} - \log[C_2mim^+]_{org}$) and $\log[DCH18C6]_{org}$ in Rb^+ extraction equilibrium. (The volume of IL in diluent is 10%, pH = 9.47, Vo/Va = 1:1)

$$Rb^+_{aq} + [C_2mim^+]_{org} + DCH18C6_{org} \rightarrow \\ Rb^+_{aq} + [C_2mim^+]_{org} + DCH18C6_{org} \rightarrow \quad (9)$$

Through the above analysis, the mechanism of extracting rubidium ions from salt lake brine with DCH18C6 as extractant and ionic liquid as co extractant can be shown in Figure 8.

THERMODYNAMIC RESEARCH

In order to study the effect of temperature on the extraction of rubidium ions from the brine solutions by DCH18C6 in $[C_2mim^+][NTf_2^-]$, experiments were carried out in a constant temperature water bath oscillator, and the temperature varies from 274 K to 313 K. As shown in Fig. 9, when the temperature rises from 294 K to 313 K, the extraction rate of Rb^+ was reduced from 91.85% to 71.09%. The reason may be that the increase of temperature reduces the stability of the rubidium containing extractive compound in the organic phase, which leads to a decrease in the extraction rate of rubidium ion.

According to the Van't Hoff equation, it is known that the change in enthalpy (ΔH^0), the extraction temperature and the distribution ratio of rubidium ions have the following relations.

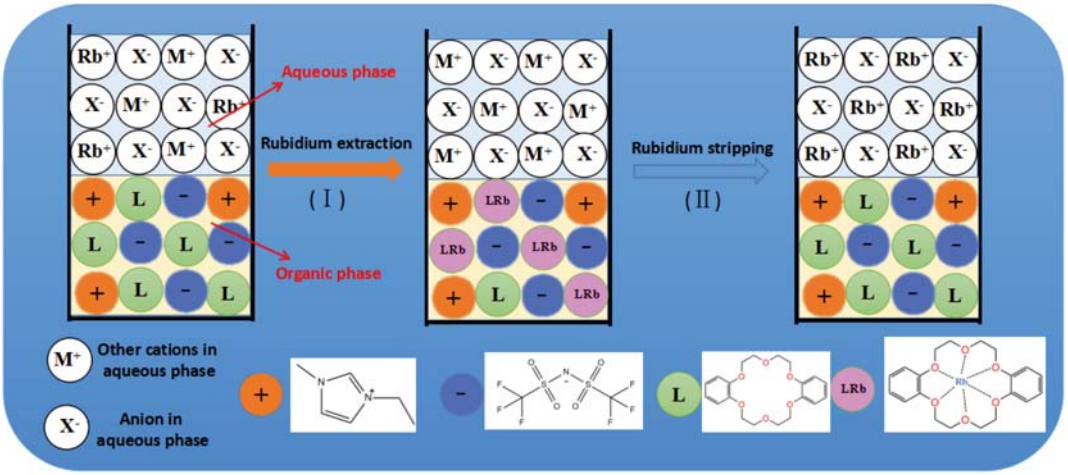


Figure 8. Schematic diagram of mechanism of extracting rubidium ions from salt lake brine with DCH18C6 as extractant and ionic liquid as co extractant

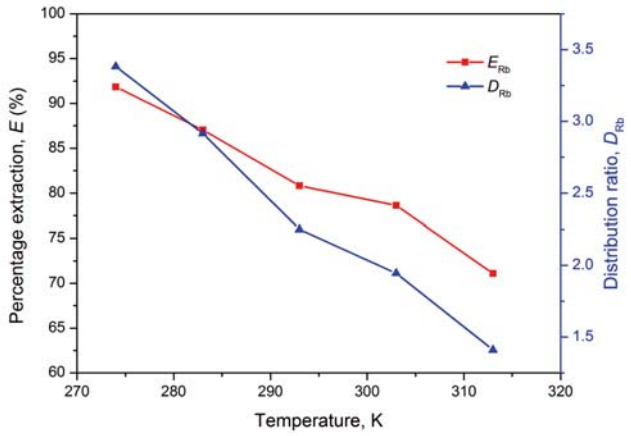


Figure 9. Effect of temperature on the extraction of Rb^+. (The volume of IL in diluent is 10%, pH = 9.47, CDCH18C6 = 0.2 mol · L^{-1}, Vo/Va = 1:1)

$$\log D_{Rb} = -\frac{\Delta H^0}{2.303R} \cdot \frac{1}{T} + C \tag{10}$$

where R is the universal gas constant, and the C is the integral constant. According to eq (10), there is a linear relationship between the logarithm of rubidium ion distribution ratio and the reciprocal of temperature, and its slope is $-{}_{\Delta}H^0/2.303R$. From the slope of Fig. 10, the ${}_{\Delta}H^0$ was obtained equal to –15.46 kJ · mol^{-1}. So, the extraction process is exothermic. Because of the adverse effect of temperature on the extraction rate, the extraction of Rb^+ by DCH18C6/[C_2mim$^+$][NTf_2^-] system is carried out at room temperature.

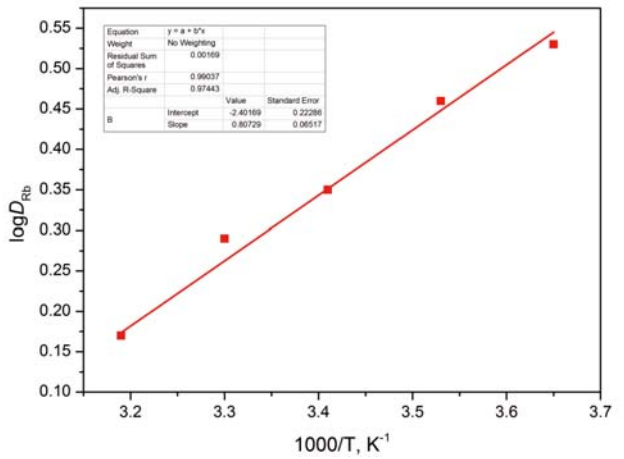


Figure 10. Polt of logD_{Rb} versus 1000/T for Rb^+ extraction. (The volume of IL in diluent is 10%, pH = 9.47, CDCH18C6 = 0.2 mol · L^{-1}, Vo/Va = 1:1)

The relationship between the change in Gibbs free energy (${}_{\Delta}G^0$) and the temperature of the extraction reaction can be expressed as follows:

$$\Delta G^o = -RT \ln K_e = -2.303RT \log K_e \tag{11}$$

where K_e *is* the extraction equilibrium constant. According to eq (8), the value of log K_e is the intercept of the logarithmic graph of Fig. 7. At 293 K temperature, the log K_e value was substituted by eq (11), and the ${}_{\Delta}G^0$ of the extraction reaction was obtained as –899.69 J · mol^{-1}. The ${}_{\Delta}G^0$ of the reaction is negative, which indicates that the reaction of extracting Rb^+ by DCH18C6/[C_2mim$^+$][NTf_2^-] system is spontaneous.

The relationship between the change in entropy (${}_{\Delta}S^0$) of the extraction reaction and the temperature is as follows:

$$\Delta S^{\circ} = \frac{\Delta H^o - \Delta G^o}{T} \tag{12}$$

The value of $\Delta H°$ and $\Delta G°$ were substituted into eq (12). The reaction $\Delta S°$ of the extraction system at 293 K temperature was calculated to be –49.69 J · K^{-1} · mol^{-1}. This indicates that the order of the organic phase increases after the extraction reaction of Rb^+.

STRIPING STUDIES

Stripping is the recovery of the target metal ions from the loaded organic phase, which is an important part of the extraction system to enrich the target metal ions[26–27]. The optimal extraction conditions of this system were obtained by a series of conditional experiments which included the volume of IL in diluent is 10%, the concentration of DCH18C6 is 0.2 mol · L^{-1}, Vo/Va of 3:2 and unadjusted pH. Under the optimal experimental conditions, the concentration of Rb^+ and K^+ in the loaded organic phase was 174.9 mg · L^{-1} and 1165.8 mg · L^{-1} respectively by unipolar extraction experiments. Strong acids and ammonium salts are often used as stripping agents in extraction systems. As can be seen from Fig. 3, the effect of acidity on the extraction rate of rubidium ions is not obvious in the new extraction system, so acid as an extractant is not a good choice. Moreover, in order to be beneficial to the environment, the use of high concentration of acid is avoided. Therefore, ammonium nitrate is chosen as a stripping agent. Because the concentration of the stripping agent has a significant effect on the stripping, the effect of different concentrations of ammonium nitrate on metal ions stripping was investigated. As the results were shown in Fig. 11, the stripping rate of Rb^+ and K^+ increased with the increase of ammonium nitrate concentration. However, when the concentration of ammonium nitrate is 1.0 mol · L^{-1} and 2.5 mol · L^{-1}, K^+ and Rb^+ reach the stripping balance respectively. In order to better realize the separation of Rb^+ and K^+, the concentration of ammonium nitrate was selected as 2.5 mol · L^{-1}, simultaneously, the stripping rate of Rb^+ and K^+ is 82.94% and 19.71%, respectively. The concentration of Rb^+ and K^+ in the aqueous phase

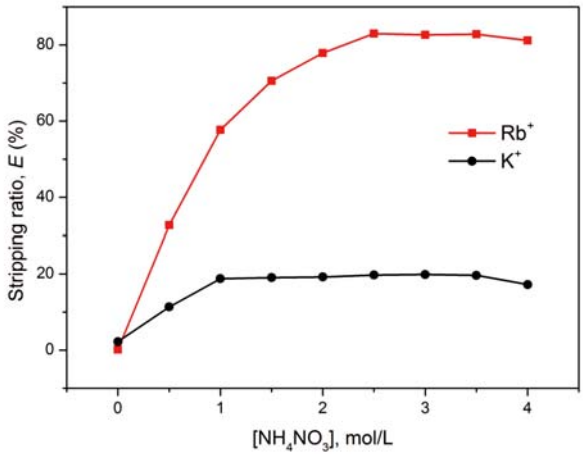


Figure 11. Effect of different concentrations of ammonium nitrate on the stripping of metal ions. (Vo/Va = 1:1, T = 291 K)

after stripped is 145.06 mg · L^{-1}, and 229.78 mg · L^{-1}, respectively. The K/Rb ratio is 1.58 in the aqueous phase after striping, which has dropped 91.52% compared with the initial value. The result is of great significance in enrichment and separation of rubidium and potassium.

CONCLUSIONS

In present study, an efficient liquid-liquid extraction system was successfully developed, which was applied to recovery of rubidium ions from brine solutions containing high concentration of potassium ions, using dicyclohexano-18-crown-6 as extractant and ionic liquid, [C_2mim^+][NTf_2^-], as part of extraction solvent and synergistic extractant. The single extraction efficiency of Rb^+ was up to 93.63%, which was obtained under optimal conditions. The data of thermodynamic parameters indicated that the extraction of rubidium was spontaneous in nature and the process was exothermic with the formation of highly ordered complexes in the organic phase. The extraction mechanism was deduced based on the slope analysis and the UV-visible spectroscopic study. It was shown that the rubidium ion was extracted by formation of [Rb · DCH18C6]$^+$ with a cation exchange extraction mechanism in new ionic liquid system. 2.5 mol · L^{-1} ammonium nitrate on the DCH18C6/[C_2mim^+][NTf_2^-] system has a good stripping effect. Compared with the traditional phenol alcohol/sulfonated kerosene extraction system, the crown ether/ionic liquid system avoids the use of strong acids and bases in the extraction and washing process, reduces the discharge of acid and alkali waste liquid, and is more beneficial to the environment. At the same time, the crown ether/ionic liquid system does not need to pretreat the aqueous phase to remove Mg^{2+} and Ca^{2+}. Therefore, the operation process of the extraction system is more simple. The present findings suggest that it could be potentially used as a promising method for the recovery of valuable metals from salt lake brine.

DECLARATIONS

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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