

Study on Solvent Extraction Behavior of Rubidium by t-BAMBP-Sulphonated Kerosene System from Salt Lake Brine

¹Amin Bao and ^{2,3,4}Qian zhiqiang*

¹School of Chemistry and Chemical Engineering, Qinghai Nationalities University, Xining, 810007, Qinghai, P. R. China.

²Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, 810008, Qinghai, P. R. China.

³Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province, Xining, 810008, Qinghai, P. R. China.

⁴University of Chinese Academy of Sciences, Beijing 100049, China.

qzq_isl@163.com*: baoamin606@163.com

(Received on 16th October 2017, accepted in revised form 7th March 2019)

Summary: The system of 4-tert-butyl-2-(α -methyl benzyl) phenol (t-BAMBP) and sulphonated kerosene (SK) solution was used to extract rubidium from Salt Lake Brine which has been removed the Mg^{2+} by precipitation method. Several experimental parameters such as the concentration of t-BAMBP, hydroxide ion and stripping acid, the volume ratio of organic phase to aqueous extraction phase (O/A) and extraction stage were investigated. The obtained results showed that extraction efficiency of Rb^+ can reach 96% after five -stage, and the stripping efficiency of Rb^+ can reach 99% after two-stage. And the extraction equilibrium constant K is calculated to be 25.85, enthalpy change ΔH is -20.79 kJ mol⁻¹ and the separation factor $\beta_{Rb/K}$ of five-stage extraction is 71.77. The system of t-BAMBP and SK could be fully regenerated by water and showed no significant decrease after ten extraction-stripping cycles, indicating that the extractant was stable and reusable. The presence of co-existing ions do not interfere with rubidium extraction, indicating the high selectivity of t-BAMBP and SK for rubidium ion. The method provides an idea for exploitation and utilization rubidium and has the important economically significant for industrialization extraction rubidium.

Keywords: 4-tert-butyl-2-(α - methyl benzyl) phenol, Rubidium, Solvent extraction, Thermodynamics, Kinetics, Salt Lake Brine.

Introduction

The rubidium and its compounds play an important role in electronic devices [1], catalyst [2], glass and ceramics [3], biochemistry [4], MHD power generation [5], laser convert electric power devices [6] and any other fields because of the active chemical properties [7] and excellent performance of the photoelectric effect [8] of rubidium. They keep the great scientific value, commercial value, and broad development prospects.

Rubidium is the abundant metallic elements in the earth crust. It mainly exists in the minerals [9], also occurs in the salt lake brine [10], underground brine [11], oil field water [12], hot springs [13], gas field water and geothermal water [14]. Foundation reserves (calculated with RbCl) of rubidium are amounted to 11,000 tons [15] only in East Taijnar Salt Lake in Qinghai, and which is displayed a huge development value. It has yet to find an industrialized effective method for separating and extracting rubidium from salt lake brine. Rational use of rubidium resources from salt lake brine need to be in conformity with the strategy of sustainable development of our country. It not only meets the need for high-tech field of rubidium, but also has

positive significance for protecting, exploiting and utilizing natural resources of Taijinar Salt Lake and other Salt Lakes. The separation and purification of rubidium from the salt lake brine is very difficult to achieve because of the similar physical and aqueous chemistry properties of alkali metal coexisting with rubidium.

There are three main methods including solvent extraction [16-18], ion exchange [19-21] and precipitation [22] used for enriching and separating rubidium. Ion exchange is currently including organic ion exchange resins [23] and inorganic ion exchange materials [24], then the later is mainly incorporating ferrocyanide and ferricyanide, polyvalent metal acid salt, heteropolyacid salt [25] and zeolite [26]. The representatives are phosphorus ammonium molybdate (AMP) [27] and clinoptilolite [28] is widely studied at present. But the inorganic ion exchange method is poor selectivity, low exchange capacity, and difficult separation. The precipitation method is mainly used heteropolyacid, complexing acid salt, polyhalide [29], and alum compounds as a precipitating agent. However, the precipitation process is usually more complex, repeated

*To whom all correspondence should be addressed.

purification, extremely high loss rate, the low yield and high cost of raw material. Moreover, the solvent extraction and ion exchange methods have been widely used to enrich and separate low-concentration of rubidium. In recent years, the liquid-liquid solvent extraction is considered to be the most ideal method separation technology to separate rubidium from the salt lake brine. It is an economic, efficient, and environmentally friendly method for separating metal ions from their dilute solutions. The solvent extraction including solvent washing, multi-stage extraction and stripping process to make the possibility of increasing the recovery efficiency of rubidium. The solvent extraction methods take the crown ether [30], phenol alcohols reagents [31] and dipicrylamine [32] as a common extractant for extracting rubidium. The 4-Tert-butyl-2-(α -methyl benzyl) phenol (t-BAMBP) belonged to phenol alcohol reagent is the most widely used in the liquid-liquid solvent extraction. The t-BAMBP has good stability, slight water solubility, non-volatility, high selectivity, fast response, easy stripping, low toxicity, cheaper and other advantages. In Qinghai province of China, most of the available rubidium resources are dissolved in the salt lake. Nonetheless the separation and purification of rubidium from the salt lake brine by liquid-liquid solvent extraction used t-BAMBP hardly ever appeared in the studies.

In this work, the solvent extraction of rubidium from the salt lake brine by the extractant of 4-tert-butyl-2-(α -methyl benzyl) phenol (t-BAMBP) were studied. The Mg^{2+} was removed from the salt lake brine by precipitation method due to the extraction process of rubidium was conducted in alkali conditions. The effect of the ions of Li^+ , Na^+ , K^+ and B_2O_3 on the extraction efficiency of rubidium was also discussed. The multi-stage solvent extraction was investigated to efficiently recover the rubidium and simultaneously reduce the potassium in detail. The extraction mechanism was analyzed, and the enthalpy of extraction and the apparent extraction equilibrium constant was calculated. Stability and recycle of t-BAMBP were investigated to save materials and to achieve the economization demand. Results obtained will be useful for future study and process design for recovery of rubidium from other salt lake brines. It also provides strong evidence to achieve industrialization separation and extraction rubidium from liquid ores.

Experimental

Reagents

RbCl (Sinopharm Chemical Reagent Co. Ltd., Spectrographic grade pure); NaOH (Sinopharm Chemical Reagent Co. Ltd., Analytical grade pure);

HCl (Tianjin Kemiou chemical reagent Co. Ltd., Analytical grade pure); t-BAMBP (Beijing Ruilekang separation Co. Ltd., purity>98%); sulphonated kerosene (Hubei seven eight nine chemical Co. Ltd.); the simulated salt lake brine sample only containing rubidium; the raw brine (Qinghai Lianyu group co., LTD); distilled water (homemade, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences).

Instruments

The GBC-908 atomic absorption spectrometer (AAS) (Australia the GBC scientific instrument Co., LTD); ELAN DRC-e inductively coupled plasma mass spectrometer (ICP-MS) (American PerkinElmer company); Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES); HL-20 centrifugal extraction machine (Beijing institute of the extraction applied technology); AB204-Selectronic balance (Mettler-Toledo instruments Co., LTD); PSB300-Flatbed centrifuge (Shanghai ChaoLong Welding Electrical Co., Ltd.).

Methods

The system of t-BAMBP and sulphonated kerosene extraction agent was prepared. And the raw brine was prepared after removed the Mg^{2+} by Na_2CO_3 . All extraction and reverse extraction experiments were carried out on the HL-20 centrifugal extraction machine. All experiments (except the temperature) were conducted under optimum conditions at the room temperature. The simulated Salt Lake Brine sample was for finding the best extraction conditions. Potassium(I) ion was detected by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and rubidium(I) ion was detected by the GBC-908 atomic absorption spectrometer (AAS) and ELAN DRC-e inductively coupled plasma mass spectrometer (ICP-MS). The detection of rubidium in Salt Lake Brine is seriously disturbed by other high concentration ions such as lithium, sodium and potassium and these ions can be analyzed by ICP-OES. In order to ensure the accuracy of detection of rubidium, the ICP-MS is employed because of its low detection limit. And the AAS is considered an ideal method for detecting rubidium in simulated brine.

Results and Discussion

The extractant (t-BAMBP) ability of extraction rubidium

The structure of t-BAMBP (extractant) as Fig. 1 shown,

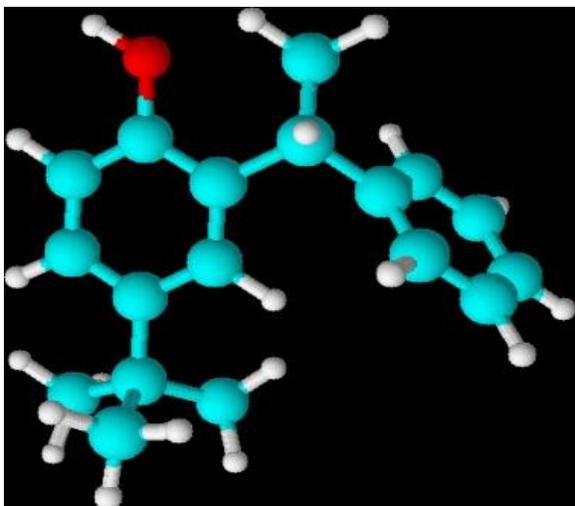


Fig. 1: Structure of t-BAMBP.

The t-BAMBP is a kind of faintly acid substituted phenol extraction agent. It has high selectivity for Rb^+ and Cs^+ compares to other alkali metal ions. In alkaline solution, the phenolic hydroxyl of phenol easily dissociated hydrogen protons, then alkali metal ions (M^+) and hydrogen ions (H^+) conducted cation exchanged, afterwards the phenol salt were formed, and the alkali metal ions (M^+) can be extracted into the organic phase. The chemical reaction equation is expressed as follows,



M^+ and ROH represent Rb^+ and the extractant (t-BAMBP).

Inorganic acid can be readily stripping down the Rb^+ which was extracted into the organic phase. Meanwhile, the extractant is recovered by the inorganic acid. The chemical reaction equation is expressed as follows,



The effect of t-BAMBP concentration

As we know, the system of the extractant t-BAMBP with the diluent sulphonated kerosene has very excellent extraction ability for the rubidium. Kerosene is most alkanes, which also contains a small amount of unsaturated alkenes, alkynes and aromatic hydrocarbon. And the kerosene must be sulphonated to remove the unsaturated hydrocarbon. The concentration of t-BAMBP reflects solvent extraction ability and influences the extraction efficiency. In this work, the extraction conditions

were selected: $c_{(OH^-)} = 1.2 \text{ mol L}^{-1}$; $T = 291 \text{ K}$; O/A = 2:1; $n = 3000 \text{ r min}^{-1}$; and the different concentrations of extractant. Through the experimental investigation, the optimum t-BAMBP concentration was selected according to the effects of extraction solvent concentration on extraction efficiency. The experimental results are as shown in Fig. 2, and the equation is obtained by curve fitting the results as follows,

$$\begin{aligned} E\% &= 97.70 - 130.62 \times 0.005^c \\ R^2 &= 0.9997 \\ SD &= 0.0477 \end{aligned} \quad (3)$$

Form Fig. 2 and the equation can be illustrated that the extraction efficiency increased obviously less than $1.0 \text{ mol} \cdot \text{L}^{-1}$ and then remain unchanged with continuously increased concentration of t-BAMBP. The equation also demonstrated that the extraction efficiency increasing rapidly when the concentration of t-BAMBP less than $1.0 \text{ mol} \cdot \text{L}^{-1}$ and increasing inconspicuous when the concentration of extractant more than $1.0 \text{ mol} \cdot \text{L}^{-1}$. Increasing concentration of t-BAMBP can lead to high viscosity of oil phase, easy emulsification, likely mixed phase and unfavourable separated phase. And $1.0 \text{ mol} \cdot \text{L}^{-1}$ concentration of t-BAMBP would be selected the suitable condition considering the economic aspect to save raw materials.

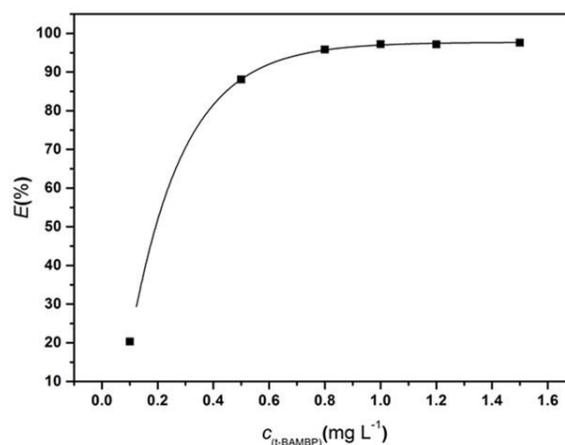


Fig. 2: The effect of the concentration of t-BAMBP on extraction efficiency.

The effect of $c_{(OH^-)}$

The alkali environment is conducive to the dissociation of H^+ on phenolic hydroxyl. The effect of basicity on extraction efficiency through the

experiment has been studied. Other extraction conditions were selected: $c_{(t-BAMBP)} = 1.0 \text{ mol L}^{-1}$; $T = 291 \text{ K}$; $O/A = 2:1$; $n = 3000 \text{ r} \cdot \text{min}^{-1}$; and the different concentrations of hydroxyl ion. Through the experimental investigation, the optimum concentration was chose according to the effects of hydroxyl ion concentration on extraction efficiency in the simulated brine sample. The extraction results are as showed in Fig. 3, and the equation obtained as follows,

$$\begin{aligned} E\% &= 83.49 + 22.92c - 9.704c^2 \\ R^2 &= 0.9959 \\ SD &= 0.1194 \end{aligned} \quad (4)$$

Results were shown that the extraction efficiency was not significantly resistant to the increased $c_{(\text{OH}^-)}$ of simulated brine sample since the concentration was up to $1.2 \text{ mol} \cdot \text{L}^{-1}$. And then the curve of extraction efficiency leveled off when the $c_{(\text{OH}^-)}$ above $1.2 \text{ mol} \cdot \text{L}^{-1}$. It is obvious that alkalinity of salt lake brine influence seriously the extraction efficiency of rubidium. However, high basicity of the system can lead to miscible oil and aqueous phase and separating difficultly. Also it can result in the extractant converting to sodium phenolate and going into the water phase. So considering avoid loss of extractant, $1.2 \text{ mol} \cdot \text{L}^{-1} c_{(\text{OH}^-)}$ of the system would be selected the best condition.

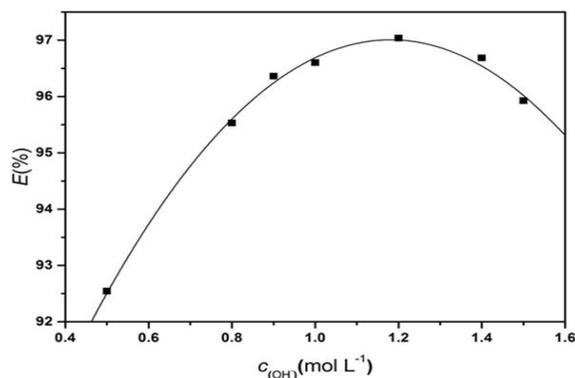


Fig. 3: The effect of $c_{(\text{OH}^-)}$ on extraction efficiency.

The effect of O/A

The volume of the aqueous phase has remained the same, and changed the different volume of extractant to obtain different ratio of organic phase to the aqueous phase. The influence of the ratio of organic phase to the aqueous phase on extraction efficiency was studied. Other selected extraction conditions as follows: $c_{(t-BAMBP)} = 1.0 \text{ mol L}^{-1}$; $c_{(\text{OH}^-)} = 1.2 \text{ mol} \cdot \text{L}^{-1}$; $T = 291 \text{ K}$; $n = 3000 \text{ r} \cdot \text{min}^{-1}$; and the difference the volume ratio of organic phase to the

aqueous phase (O/A). The extraction results are as showed in Fig. 4, the equations as follows,

$$\begin{aligned} E\% &= 94.14 + 2.16r - 0.214r^2 \\ R^2 &= 0.9994 \\ SD &= 0.05 \end{aligned} \quad (5)$$

It indicated that the extraction efficiency is relatively rising with the O/A enlargement. The rubidium concentration in the salt lake brine used in this experiment is very low, although the rubidium at low concentration, the extraction efficiency can still maintain at a high level. It is not necessary to blindly increase the O/A in order to increase the extraction efficiency. Otherwise, it will cause the waste of extractant. Therefore, the O/A=1:1 would be selected.

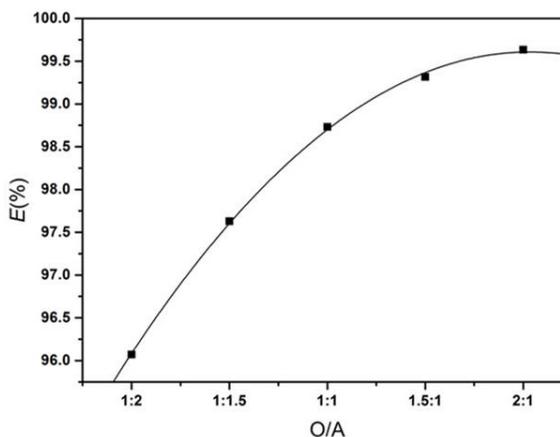


Fig. 4: The effect of O/A on extraction efficiency.

The effect of Li^+ , Na^+ , K^+ and B_2O_3

The extraction system of t-BAMBP and sulphonated kerosene solution hardly extract B_2O_3 , Li^+ and Na^+ , which the extraction efficiency is quite low due to the smaller ionic radii than Rb^+ and Cs^+ . The alkalinity extraction environment is the essential and optimum condition. However, the metal ions such as Mg^{2+} and Ca^{2+} can be precipitated in the presence of OH^- , and formed $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ precipitates, which lead to the extraction can't be continued. As a consequence, the Mg^{2+} , Ca^{2+} must be removed before extracting the Rb^+ . The Na_2CO_3 was used to precipitate Mg^{2+} significantly instead of NaOH , on account of extremely sticky and difficult to filter with the precipitate by NaOH . And second fractional precipitation can precipitate Mg^{2+} effectively. The K^+ also absolutely affects the Rb^+ extraction efficiency. As regards K^+ , the multi-stage

solvent extraction will be applied to separate K^+ and Rb^+ according to the separation coefficient.

The extraction ability of t-BAMBP and sulphonated kerosene system towards rubidium ion affects by the competition influence of coexistence ion species and concentrations. Therefore, different coexistence metal ion species which are abundant in salt lake brine were mainly considered as interference metal ions. The influence of interference ions on extraction efficiency of rubidium ion was studied. The extraction experiments were conducted in simulated brine which contains rubidium and each different metal ions. The extraction efficiency of rubidium ion as a function of coexistence ion species was shown in Fig. 5. As is shown in Fig. 5, compared with other typical cations of Li^+ and Na^+ , K^+ showed a certain degree of influence on the extraction efficiency of rubidium by t-BAMBP and sulphonated kerosene because of the similar ionic radius with Rb^+ . However, the extractant for rubidium ion can be used efficiently even in the presence of relatively high concentrations of sodium ions. In addition, there is little interference by Li^+ and B_2O_3 on the extraction efficiency of rubidium.

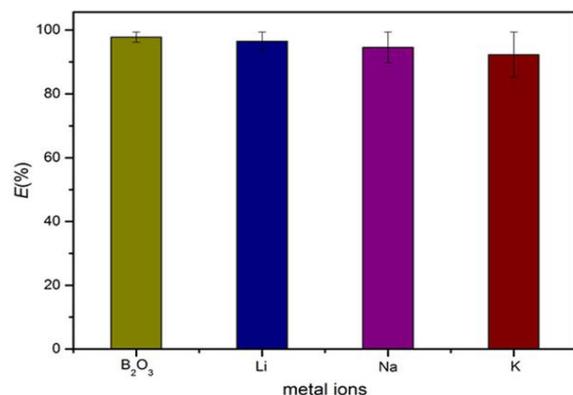


Fig. 5: The effect of coexistence ion species on extraction efficiency.

The effect of concentration of stripping solution of HCl

The extracted Rb^+ in the oil phase can be stripped efficiently with acid. The organic phase was stripped with different concentration HCl after enriched Rb^+ with the system of t-BAMBP and sulphonated kerosene (1:1). The effect of $c_{(HCl)}$ on stripping condition through the experiment to be studied and other conditions were selected: the organic phase had been enriched Rb^+ ; $T = 291\text{ K}$; $O/A = 1:1$; $n = 3500\text{ r}\cdot\text{min}^{-1}$; and different

concentrations of HCl. The extraction results are as showed in Fig. 6, $0.1\text{ mol}\cdot\text{L}^{-1}$ HCl were the best condition according to the stripping efficiency. Thus, $0.1\text{ mol}\cdot\text{L}^{-1}$ was served the optimum concentration for stripping Rb^+ .

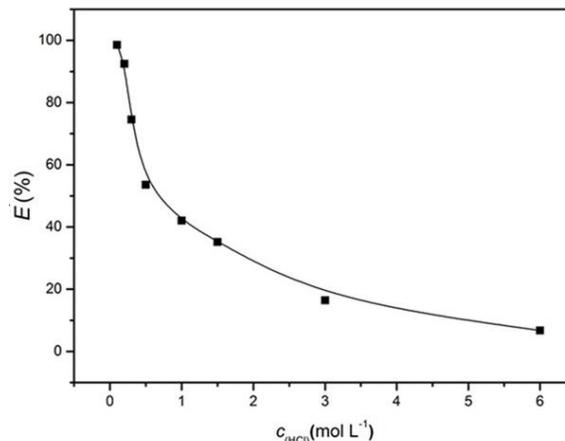


Fig. 6: The effect of $c_{(HCl)}$ on stripping efficiency.

The Composition of extracted complex and the extraction equilibrium of rubidium

According to the equation (1), the composition of the extracted complex and the extraction equilibrium of rubidium may be affected by $c_{(OH^-)}$ and $c_{(t-BAMBP)}$. The equation (1) shows the extracted complex $(MOR)\cdot(n-1)(ROH)$ can be formed rapidly into the organic phase after extracted the rubidium. The extraction equilibrium constant of extracted for Rb, K, can be defined as,

$$K = \frac{[(MOR)\cdot(n-1)(ROH)]}{[M^+][ROH]^n[OH^-]} \quad (6)$$

The distribution coefficient is defined as,

$$D = \frac{c_{o,eq}}{c_{a,eq}} \quad (7)$$

The $c_{o,eq}$ and $c_{a,eq}$ represent rubidium ion concentrations in the organic and aqueous phases. From the equation (6), the distribution coefficient also can be expressed as,

$$D = \frac{[(MOR)\cdot(n-1)(ROH)]}{[M^+]} \quad (8)$$

From the equation (6) and (8), the equation can be obtained,

$$D = K \times [ROH]^n \times [OH^-] \quad (9)$$

The logarithmic equation can be expressed as,

$$\lg D = \lg K + n \lg [ROH] + \lg [OH^-] \quad (10)$$

From the equation (10) can be released that the distribution coefficient (D) and extraction equilibrium constant of extracted rubidium (K) are related to the concentration of t-BAMBP and the alkali solution. Therefore, the concentration of alkali solution $c_{(OH^-)}$ was fixed a constant, and then changing the concentration of extractant $c_{(ROH)}$ to investigate $c_{(ROH)}$ effect on the distribution coefficient D . the results of $\lg D$ plot to $\lg [ROH]$ were illustrated in Fig. 7, and the equation as follow,

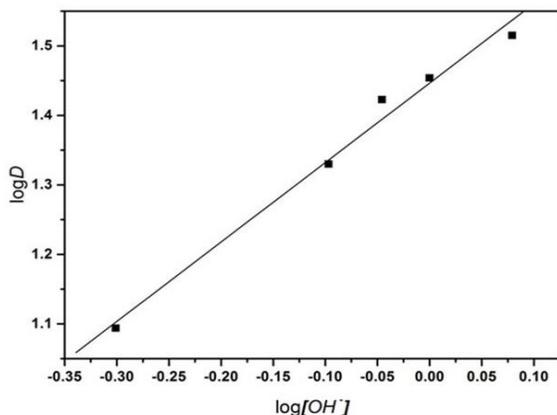
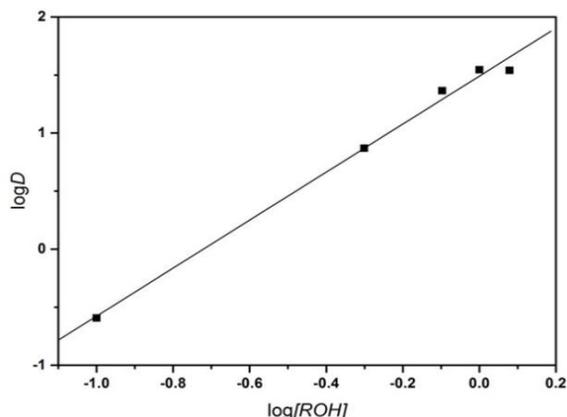


Fig. 7: The relationship of $\log D$ and $\log c_{(ROH)}$ and $\log D$ and $\log c_{(OH^-)}$.

$$\begin{aligned} \lg D &= 1.49 + 2.07 \lg c_{(ROH)} \\ R^2 &= 0.9911 \\ SD &= 0.0218 \end{aligned} \quad (11)$$

In our experiment, K is a constant at a given temperature ($T=291$ K) because of it only related to temperature. The concentration of Rb^+ is very low in

the solution before and after the extraction. Therefore, $c_{(OH^-)}$ can be regarded as unchanged and considered as constant of $1.2 \text{ mol} \cdot \text{L}^{-1}$. Fig. 7 shows that the slope of the linear regression equation is 2.07 and regarded as 2. Thus the extracted complex can be speculated: $RbOR \cdot ROH$. The extraction equilibrium constant K is calculated to be 25.85.

And extractant concentration $c_{(ROH)}$ was fixed a constant, and then changing the concentration of alkali solution $c_{(OH^-)}$ to investigate $c_{(OH^-)}$ effect on the distribution coefficient D . the results of $\lg D$ plot to $\lg [OH^-]$ were illustrated in Fig. 7, and the equation as follow,

$$\begin{aligned} \lg D &= 1.45 + 1.14 \lg c_{(OH^-)} \\ R^2 &= 0.9821 \\ SD &= 0.0015 \end{aligned} \quad (12)$$

The equation (12) demonstrated that the slope of a linear fitting curve is 1.14, approximating calculation 1. It indicated that the distribution coefficient D changes with the one party changes of $c_{(OH^-)}$, that is to say, Rb^+ exchanges with the H^+ on a phenolic hydroxyl group of t-BAMBP solution, H^+ reacts with OH^- generate to H_2O . And it is demonstrating that the reaction is a cation exchange reaction.

The effect of temperature on extraction efficiency

The influence of temperature on extraction was studied, and the selected extraction conditions as follows: $c_{(t-BAMBP)} = 1.0 \text{ mol L}^{-1}$; $c_{(OH^-)} = 1.2 \text{ mol L}^{-1}$; $O/A = 2:1$; $n = 3000 \text{ r} \cdot \text{min}^{-1}$; and the different temperature. The extraction results are as showed in Fig. 8, the equations as follows,

$$\lg D = \frac{-\Delta H}{2.303RT} + c \quad (13)$$

$$\frac{d \lg D}{dT} = \frac{-\Delta H}{2.303R} \quad (14)$$

$$\begin{aligned} \lg D &= 1.086 \times \frac{1000}{T} - 2.195 \\ R^2 &= 0.9942 \\ SD &= 0.0065 \end{aligned} \quad (15)$$

From the equation (14) and (15), the enthalpy of extraction can be calculated that the value is $\Delta H = -20.79 \text{ KJ mol}^{-1}$. It can be concluded that the extraction reaction is an exothermic reaction which reducing the temperature is conducive to the extraction reaction.

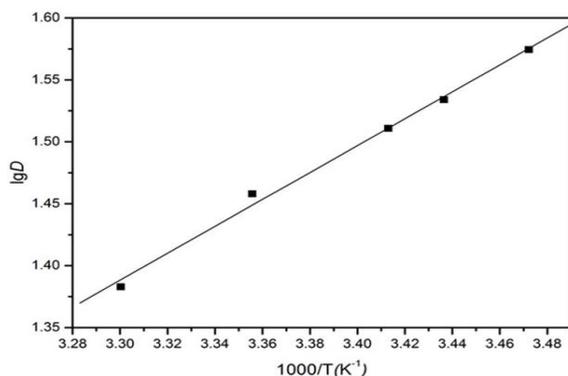


Fig. 8: The relationship of $\log D$ and $(1000/T)$.

The effect of extraction stage on extraction efficiency

The influence of extraction stage on extraction was studied, and the selected extraction conditions as follows: the raw brine; $c_{(t-BAMB P)} = 1.0 \text{ mol L}^{-1}$; $c_{(\text{OH}^-)} = 1.2 \text{ mol}\cdot\text{L}^{-1}$; $\text{O/A} = 2:1$; $T = 291 \text{ K}$; $n = 3000 \text{ r min}^{-1}$; and different extraction stages. The extraction results are as showed in Fig. 9, the equations as follows,

$$\begin{aligned} E\% &= 97.04 - 62.41 \times 0.44^s \\ R^2 &= 0.9989 \\ SD &= 0.2664 \end{aligned} \quad (16)$$

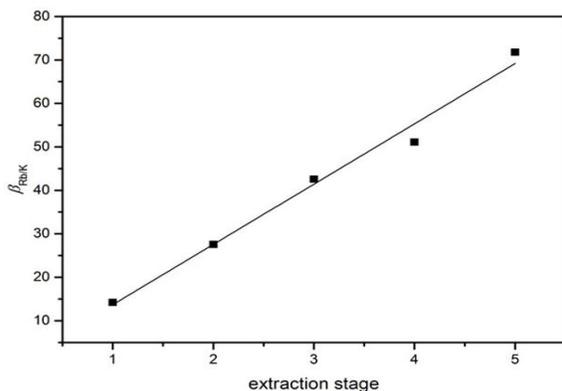
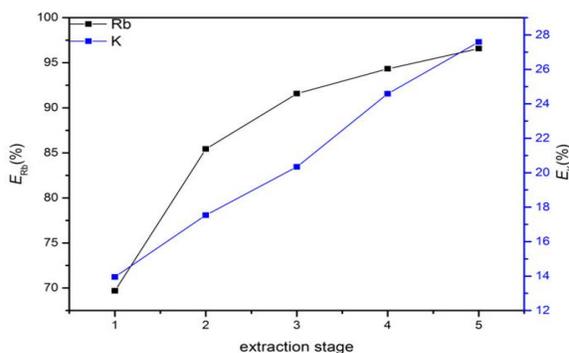


Fig. 9: The effect of extraction stage on extraction efficiency and separation factor

Also the effect of the extraction stage on the separation factor was discussed. And the separation factor can be defined as:

$$\beta_{\text{Rb/K}} = \frac{D_{\text{Rb}}}{D_{\text{K}}} \quad (17)$$

The D_{Rb} and D_{K} were calculated for the separation factor. The relationship of separation factor with the extraction stage as Fig. 9, the equation as follows,

$$\begin{aligned} \beta_{\text{Rb/K}} &= -0.17 + 13.87s \\ R^2 &= 0.9933 \\ SD &= 2.9 \end{aligned} \quad (18)$$

From the Fig. 9, it can be shown that the separating factor increases linearly with the extraction stage increasing. It indicated that increased extraction stage would improve the extraction efficiency of rubidium and conducive to the separation of rubidium and potassium. But the extraction stage was continued to increase, the extraction efficiency of potassium increased fast and the extraction efficiency of rubidium has reached the maximum value. In addition, it can cause the raw material consumption and the mixed phase then goes against the separation phase. It can be predicted that rubidium and potassium ions can be separated if the extraction stage reaches to a certain value.

From the equation, it can be concluded that the K^+ removed by multi-stage extraction and the separation factor of 5-stage extraction is 71.77.

The conditions were remaining the same. And the extraction and stripping process were repeated more than 5 times. The extraction efficiency of Rb^+ was maintain above 96%, meanwhile removed K^+ simultaneously. It is achieved that the Rb^+ and K^+ can be separated absolutely by this method.

The recycle of the extractant (*t*-BAMB P) and its stability

It is worth to prove the extractant can be recycled because of high price of extractant. It is on keeping with economization, pollution-free requirements for industrialized extraction rubidium. The oil phase was washed at least 3 times used the

distilled water after the stripping step (reverse extraction). The conditions of extraction and stripping steps consist with the above, and the conditions of washing step as follows: O/A=1:2 (5:10); $T = 291$ K; $n = 3500$ r min⁻¹ and the distilled water. The Rb⁺ and K⁺ were detected by ICP-MS and ICP-OES, respectively, after diluted aqueous phase 100 times, the data as follows,

Table-1: The concentration and extraction efficiency of K⁺ and Rb⁺ in different phases were extracted by t-BAMBP and sulfonated kerosene from salt lake brine.

phase	C_{Rb} $\mu\text{g L}^{-1}$	E %	C_K $\mu\text{g L}^{-1}$	E %
Raffinate phase	21.5	83.0	82.06	34.1
Stripping phase	36.0	69.9	5.383	25.3
First washing	6.85	42.2	1.043	5.0
Second washing	1.59	16.9	0.60	3.0
Three washing	0.73	9.4	0.1831	0.96

The oil phase after washing with distilled water was continued to extract rubidium from the raw brine. To validate its extraction ability, the extraction data as follows,

Table-2: The concentration and extraction efficiency of K⁺ and Rb⁺ in different phases were extracted by t-BAMBP washed with distilled water from salt lake brine.

phase	C_{Rb} $\mu\text{g L}^{-1}$	E %	C_K $\mu\text{g L}^{-1}$	E %
Raffinate phase	22.8	81.9	85.8	31.1
Stripping phase	38.8	75.2	5.204	13.4
First washing	6.98	54.5	1.029	6.1
Second washing	2.52	43.3	0.3710	2.4
Three washing	0.85	25.8	0.1087	0.7

From the above data, it can be predicted that the t-BAMBP has good stability, which could be used recycled. Its extraction ability after washing with distilled water to remove a large number of ions is still strong.

The extractant was usually subjected to several bath operations of extraction - stripping-washing in order to identify the stability and reusability. Therefore, it is important to determine the extraction ability of t-BAMBP for rubidium from water resources for a variety of reasons: allow the extractant to be disposed in safer ways, provide opportunity to recover metals that can be valuable commodities, and reduce the cost involved in the reagent of extractant as they are regenerated in more than one cycle. The extraction efficiency and stripping efficiency were calculated according to the extraction-stripping cycles by the above experimental conditions. And the experimental results were showed in Fig. 10, the adsorption and desorption efficiency both maintain high value. Therefore, it can be concluded that the extractant of t-BAMBP(SK) showed good performance of stability and reusability

towards Rb(I) ions. It can be speculated that the breakthrough is provided economic thought for industrialized extraction of rubidium from salt lake brine and other salt lakes.

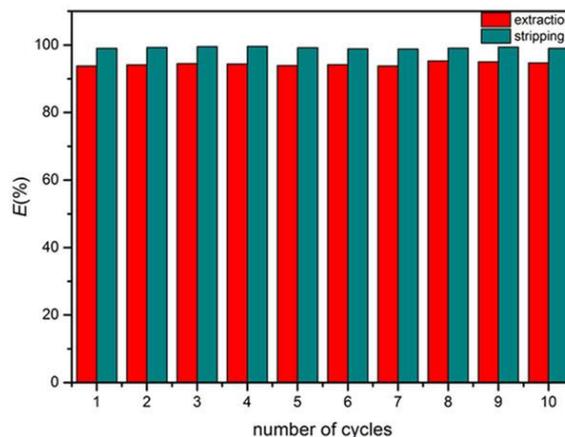


Fig. 10: The reproductivity of t-BAMBP-SK system.

Conclusions

The system of 4-tert-butyl-2-(α -methyl benzyl) phenol (t-BAMBP) and sulphonated kerosene (SK) solution was used to extract and separate rubidium from Salt Lake Brine. From the obtained experimental results, the 1.0 mol L⁻¹ of t-BAMBP and raw brine with 1.2 mol L⁻¹ of hydroxide ion in a volume ratio of 2:1 at five-stage extraction under 291 K allows the extraction efficiency of rubidium to reach above 96%. And 0.1 mol L⁻¹ of HCl and organic phase which is loaded rubidium ion in a volume ratio of 1:1 at two-stage stripping under 291 K allows the stripping efficiency of rubidium to reach above 99%. And the extraction equilibrium constant K is calculated to be 25.85, enthalpy change ΔH is -20.79 kJ mol⁻¹ and the separation factor $\beta_{Rb/K}$ of five-stage extraction is 71.77. The presence of co-existing ions Li⁺, Na⁺ and most of K⁺ could not be extracted by t-BAMBP, and do not interfere with rubidium extraction, indicating the high selectivity of t-BAMBP and SK for rubidium ion. Furthermore, K⁺ can be removed and separated with Rb⁺ by multi-stage extraction. The system of t-BAMBP and SK could be fully regenerated by water and recycled with strong extraction ability, indicating that the extractant was stable and reusable. The method provides an idea for exploitation and utilization rubidium and has the important economically significant for industrialization extraction rubidium.

Acknowledgements

This work was financially supported by Natural Science Foundation in Qinghai Province (Project No: 2019-ZJ-956Q), The "Light of West China" Program, The Thousand Talent Plan in Qinghai Province(2019), and The Science and Technology Natural Science Project of Qinghai University for Nationalities(Project No: 2019XJG03).

References

1. P. K. Vudiyasetu, R. M. Camacho and J. C. Howell, Storage and retrieval of multimode transverse images in hot atomic Rubidium vapor, *Phys. Rev. Lett.*, **100**, 3436(2008).
2. A. V. Zaitsev, M. V. Tsapkina, M. M. Savel'Ev, V. Y. Borovkov, A. L. Lapidus and V. B. Kazanskii, Effect of the nature of the alkaline promoter on the properties of iron carbonyl catalysts, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **35**, 1343(1986).
3. M. Kodama, Anomalous Behavior of Ultrasonic Velocity in Rubidium Borate Glasses, *J. Am. Ceram. Soc.*, **74**, 2603(1991).
4. S. M. Meding, R. J. Zasoski, Hyphal-mediated transfer of nitrate, arsenic, cesium, rubidium, and strontium between arbuscular mycorrhizal forbs and grasses from a California oak woodland, *Soil Biol. Biochem.*, **40**, 126(2008).
5. K. Onda, K. Takano and K. Kato, The Spectra of the Pulverized Coal Mixed MHD Combustion Gas, *Trans. Jpn Soc. Mech. Eng. B.*, **50**, 859(1984).
6. L. O. Quarrie, The effects of atomic rubidium vapor on the performance of optical windows in Diode Pumped Alkali Lasers (DPALs), *Opt. Mater.*, **35**, 843(2013).
7. D. K. Belashchenko, Molecular-dynamics simulation of the high-pressure properties of rubidium, *High Temp.*, **48**, 646(2010).
8. A. Miniewicz, S. Bartkiewicz, On the electro-optic properties of single crystals of sodium, potassium and rubidium acid phthalates, *Adv. Mater. Opt. Electron.*, **2**, 157(1993).
9. J. Jandová, P. Dvořák, J. Formánek and N. V Hong, Recovery of rubidium and potassium alums from lithium-bearing minerals, *Hydrometall.*, **119-120**, 73(2012).
10. N. Zhang, D. L. Gao, M. M. Liu and T. Deng, Rubidium and Cesium Recovery from Brine Resources, *Adv. Mater. Res.*, **1015**, 417(2014).
11. D. B. Jiang, Z. Ying and X. D. Yu, Metastable phase equilibria for the quaternary system containing potassium, magnesium, rubidium and chloride at 323.15K, *Fluid Phase Equilib.*, **349**, 67(2013).
12. A. G. Collins, Flame Spectrophotometric Determination of Cesium and Rubidium in Oil Field Waters, *Anal. Chem.*, **35**, 1258(1963).
13. A. N. Chowdhury, B. K. Handa and A. K. Das, High lithium, rubidium, and cesium contents of thermal spring water, spring sediments, and borax deposits in Puga valley, Kashmir, India, *Geochem. J.*, **8**, 61(1974).
14. A. Stettle, C. J. Allègre, ⁸⁷Rb-⁸⁷Sr studies of waters in a geothermal area: The Cantal, France, *Earth Planet. Sci. Lett.*, **38**, 364(1978).
15. S. Chaudhuri, N. Clauer, Strontium isotopic compositions and potassium and rubidium contents of formation waters in sedimentary basins: Clues to the origin of the solutes, *Geochim. Cosmochim. Acta.*, **57**, 429(1993).
16. X. M. Tan, L. Z. Zhang and X. F. Zhang, Research on Separating Rubidium from Deep Potassium-Rich Old Brine by Solvent Extraction, *Appl. Mech. Mater.*, **700**, 572(2014).
17. J. W. Wang, D. H. Che and W. Qin, Extraction of rubidium by t-BAMBP in cyclohexane, *Chin. J. Chem. Eng.*, **23**, 1110(2015).
18. B. S. Mohite, S. M. Khopkar, Solvent extraction separation of rubidium with dicyclohexano-18-crown-6, *Talanta*, **32**, 565(1985).
19. W. J. Yang, S. M. Liu, Y. J. Li, Y. Huang and X. Luo, Process Analysis of Rb⁺ and Cs⁺ Adsorption from Salt Lake Brine by Ammonium Molybdophosphate Composite Material, *Adv. Mater. Res.*, **785**, 812(2013).
20. T. Guo, S. D. Wang, X. S. Ye, H. N. Liu, X. L. Gao, Q. Li, M. Guo and Z. Y. Wu, Competitive adsorption of Li, K, Rb, and Cs ions onto three ion-exchange resins, *Desalin. Water Treat.*, **51**, 3954(2013).
21. B. C. Li, H. N. Liu, X. S. Ye, S. Y. Li and Z. J. Wu, Rubidium and Cesium Ion Adsorption by a Potassium Titanium Silicate-Calcium Alginate Composite Adsorbent, *Sep. Sci. Technol.*, **49**, 1076(2014).
22. Y. J. Zhu, L. P. Wu and H. Z. Yuan, Precipitation of Sodium Tetracyanoborate-Atomic Emission Spectrometric Determination of Rubidium and Cesium in Brine, *J. Salt Lake Res.*, **21**, 26(2013).
23. V. I. Gorshkov, V. A. Ivanov and I. V. Staina, Selectivity of phenol-formaldehyde resins and separation of rare alkali metals, *React. Funct. Polym.*, **38**, 157(1998).
24. C. B. Amphlett, L. A. McDonald and J. S. Burgess Synthetic inorganic ion-exchange materials—III The separation of rubidium and

- caesium on zirconium phosphate, *J. Inorg. Nucl. Chem.*, **10**, 69 (1959).
25. J. Krtil, Exchange properties of ammonium salts of 12-heteropolyacids—II: Separation of rubidium and caesium on ammonium phosphotungstate, *J. Inorg. Nucl. Chem.*, **19**, 298(1961).
26. R. L. Firor, K. Seff, Zero-coordinate rubidium (1+) ion, the dehydrated and hydrated crystal structures of eleven-twelfths rubidium-exchanged zeolite A, *J. Am. Chem. Soc.*, **99**, 1112(2002).
27. X. S. Ye, Z. J. Wu, W. Li, H. N. Liu, Q. Li, B. J. Qing, M. Guo, and F. Ge, Rubidium and cesium ion adsorption by an ammonium molybdophosphate–calcium alginate composite adsorbent, *Colloids Surf., A.*, **342**, 76(2009).
28. I. Smičiklas, S. Dimović and I. Plečaš, Removal of Cs¹⁺, Sr²⁺ and Co²⁺ from aqueous solutions by adsorption on natural clinoptilolite, *Appl. Clay Sci.*, **35**, 139(2007).
29. I. Pantenburg, K. F. Tebbe, Studies on Polyhalides. Part 42. The Pentaiodide-Ion I₅⁻; an Overview: Preparation and Crystal Structure of [Rb(C₁₆H₂₄O₆)](I₅)×H₂O, *J. Cheminf.*, **32**, 115(2001).
30. K. Nishizawa, Isotope separations of potassium and rubidium in chemical exchange system with dicyclohexano-18-crown-6, *J. Radioanal. Nucl. Chem.*, **249**, 569(2001).
31. W. J. Ross, J. C. White, Determination of Cesium and Rubidium after Extraction with 4-sec-Butyl-2(-methylbenzyl) phenol, *Anal. Chem.*, **36**, 59(1964).
32. M. Kyrš, J. Rais, and P. Selucký, Novel applications of dipicrylamine as an extractant in the determination of alkali metals, *Talanta*, **16**, 1169(1969).