

## Extraction of Cesium and Rubidium with 4 – tert – butyl – 2 – ( $\alpha$ – methylbenzyl) phenol from Salt Lake Brine

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**Abstract:** This work shows the extraction of cesium ( $\text{Cs}^+$ ) and rubidium ( $\text{Rb}^+$ ) from salt lake brine containing potassium ( $\text{K}^+$ ) and magnesium ( $\text{Mg}^{2+}$ ). The results show that 4 – tert – butyl – 2 – ( $\alpha$  – methylbenzyl) phenol ( $t$  – BAMBP) diluted in sulfonated kerosene (SK) has an excellent extraction effect. Infrared spectroscopic studies indicate that polymerize to form the dimer in the  $t$  – BAMBP when  $\text{Cs}^+$  or  $\text{Rb}^+$  were extracted. The effects of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $t$  – BAMBP concentration, the volume ratio of organic phase to aqueous phase (O/A) and the alkalinity (pH) of aqueous phase were investigated. The  $\text{K}^+$  and  $\text{Mg}^{2+}$  should be eliminated through precipitating before the extraction and separation of  $\text{Cs}^+$  and  $\text{Rb}^+$ . The optimum extraction conditions of the experimental brine were as follows: 0.8 mol/L  $t$  – BAMBP diluted in SK,  $\text{pH} \geq 13$ , a phase ratio of 1:1, and an extraction contact time of 2 min at room temperature. The optimal extraction yields of  $\text{Cs}^+$  and  $\text{Rb}^+$  were as high as 100% and 85.8%, in addition, 8.76% of  $\text{K}^+$  was co-extracted. Further work would increase the extraction yield and selectivity of  $\text{Rb}^+$  and realize the efficient separation of  $\text{Cs}^+$  and  $\text{Rb}^+$  from brine.

**Key words:** Salt lake brine; Extraction;  $t$  – BAMBP; Separation; Cesium; Rubidium

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## 1 Introduction

Rare alkali metals such as cesium (Cs) and rubidium (Rb) are widely used in medicine, aeronautics, metal-ion catalysts, fiber optic telecommunication systems, and precision instruments<sup>[1–4]</sup>. Generally, Cs and Rb coexist in salt lake brine and solid

ores, such as lepidolite, pollucite, and others<sup>[5]</sup>. Up to now, the production of Cs and Rb from solid ores cannot meet the increasing demand of the market. Cs and Rb are present as enormous resources reserved in salt lake brine<sup>[6, 7]</sup>. Thus, the reasonable exploitation of Cs and Rb sources from salt lake brine has become a hot research topic. However, it is challenging to effectively extract and separate

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trace Cs and Rb from salt lake brine, where some macroelements are co-extracted on account of their similar physical and chemistry properties<sup>[8, 9]</sup>.

Now, solvent extraction has been widely used in separating Cs and Rb using substituted phenols<sup>[10]</sup>. Horner found that 4-sec-butyl-2-( $\alpha$ -methylbenzyl) phenol (BAMBP, Fig. 1A) used for the extraction of Cs and Rb performed well. 4-tert-butyl-2-( $\alpha$ -methylbenzyl) phenol (*t*-BAMBP, Fig. 1B)<sup>[11, 12]</sup> is one of the isomers of BAMBP that performs similarly to BAMBP in terms of Cs and Rb extraction and has higher synthesis yields. Although a high recovery of Cs and Rb can be achieved, the problem of the potassium (around 10% co-extracted) has not been effectively solved<sup>[13]</sup>. The separation of Cs/Rb and K still needs to be studied further.

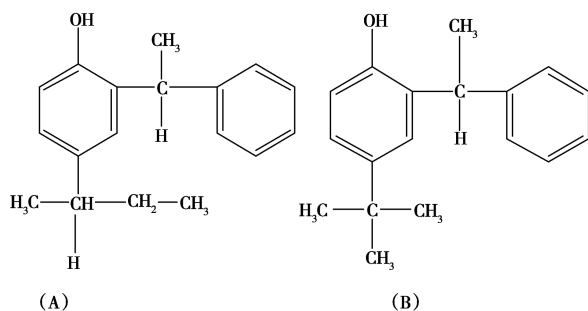


Fig. 1 (A) Molecular structure of BAMBP (B) Molecular structure of *t*-BAMBP

The order of extractability by *t*-BAMBP is  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$  in strong alkaline environments<sup>[14, 15]</sup>. Cs and Rb were effectively separated because of the unique selectivity. Egan<sup>[11]</sup> thought the extraction mechanism could be attributed to the cation exchange between  $\text{Cs}^+$  or  $\text{Rb}^+$  and hydrogen ions in the *t*-BAMBP molecules. It was found that the main *t*-BAMBP exists as a dimer in the organic phase.  $\text{Cs}^+$  or  $\text{Rb}^+$  can be combined with bis-dimer (4 *t*-

BAMBP). The type of bond is shown in Fig. 2 (where  $\text{M}^+$  refers to  $\text{Cs}^+$  or  $\text{Rb}^+$  and ROH refers to *t*-BAMBP).

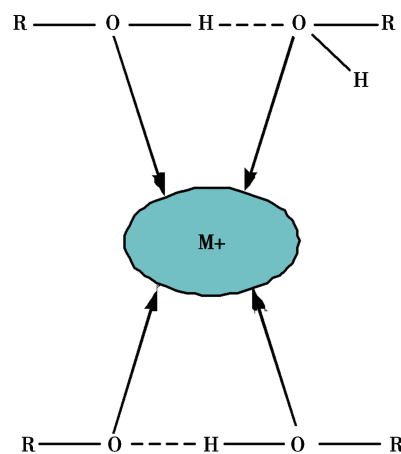


Fig. 2 Binding between *t*-BAMBP and alkali metal ions

The extraction of Cs and Rb from the weak carbonate lake has rarely been reported. In this study, the optimum conditions of Cs and Rb extraction by the dilution of *t*-BAMBP in the sulfonated kerosene (*t*-BAMBP/SK) were studied using orthogonal experiments and single-factor experiments. The results would be helpful for the further study of the extraction and separation of Cs and Rb in practical industry production.

## 2 Experimental

### 2.1 Materials and reagents

The experimental brine was obtained from a salt lake in northern Tibet and was concentrated via evaporation. The pH of the experimental brine was 8.4. The different metal ion concentrations are given in Table 1.

Table 1 The different metal ion concentrations of experimental brine  $\text{g} \cdot \text{L}^{-1}$

| Metal ions | $\text{Cs}^+$ | $\text{Rb}^+$ | $\text{Li}^+$ | $\text{K}^+$ | $\text{Na}^+$ | $\text{Mg}^{2+}$ |
|------------|---------------|---------------|---------------|--------------|---------------|------------------|
| Content    | 0.040 6       | 0.031 7       | 36.94         | 4.630        | 218.30        | 20.12            |

The commercial extractant *t* - BAMBP ( >90% ) was purchased from the Beijing Ruilekang Separation Technology Co. , Ltd. Sulphonated kerosene (SK) was prepared with concentrated H<sub>2</sub>SO<sub>4</sub>. Stripping solutions were prepared by diluting 1 mol/L HCl in deionized water. All other chemical reagents were of analytical reagent (AR) grade without any further process involved unless otherwise stated.

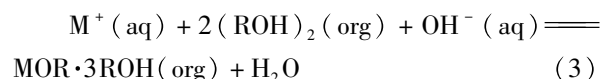
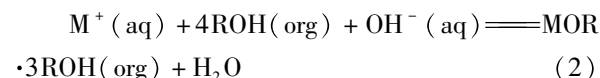
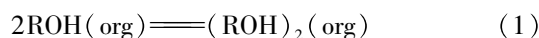
## 2.2 Chemical analysis

An infrared spectrometer and Raman spectrometer were applied to analyze the change of the organic phase. The organic samples were stripped using 1 mol/L HCl to obtain loaded strip liquor. The raffinate and loaded strip liquor containing Cs<sup>+</sup> and Rb<sup>+</sup> were diluted to appropriate concentrations and were analyzed by a Perkinelmer 700/800 atomic absorption spectrometer (AAS). Some samples were also analyzed by using inductively coupled plasma optical emission spectroscopy (ICP - OES, Agilent Model 735) for comparison. K<sup>+</sup> and Mg<sup>2+</sup> were examined by chemical titration<sup>[16]</sup>.

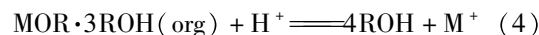
## 2.3 Experimental design

Phenols are excellent extractants for alkali metals and have high selectivities for Cs<sup>+</sup> and Rb<sup>+</sup> over other elements in the same group. Cs<sup>+</sup> and Rb<sup>+</sup> were effectively extracted by *t* - BAMBP only in the

strong alkaline solution<sup>[17]</sup>. It is proposed to form phenolic salt that participates in cation exchange between Cs<sup>+</sup> or Rb<sup>+</sup> and the H atom of phenolic hydroxyl group in the *t* - BAMBP molecules. Then, the resulting phenolic salt is dissoluble in organic phase and aqueous phase and can be easily stripped by the inorganic acid. The extraction reaction can be described as follows (where ROH refers to phenols and M<sup>+</sup> refers to Cs<sup>+</sup> or Rb<sup>+</sup>)<sup>[18]</sup>.



The Cs<sup>+</sup> and Rb<sup>+</sup> extracted into the organic phase can be easily stripped by inorganic acid in the following reaction<sup>[19]</sup>. Meanwhile, the extractant was readily recovered.



## 2.4 Orthogonal experiment design

Many factors influenced the extracting efficiency, and this work will study the concentrations of *t* - BAMBP, pH, phase ratio, and contact time. Salt lake brine concentrated by evaporation was used in orthogonal test. The orthogonal table of L<sub>16</sub>(4<sup>4</sup>) was chosen, shown in Table 2.

Table 2 The different conditions of orthogonal experiment

| Concentrations of <i>t</i> - BAMBP<br>/(mol·L <sup>-1</sup> ) | pH | Phase ratio<br>(O/A) | Extraction time<br>/min |
|---|----|----------------------|-------------------------|
| 0.4   | 10 | 1                    | 1                       |
| 0.8   | 11 | 2                    | 2                       |
| 1.2   | 12 | 3                    | 3                       |
| 1.6   | 13 | 4                    | 4                       |

## 2.5 Technological experimental process

In the experimental brine, K<sup>+</sup> was firstly removed with H<sub>2</sub>SO<sub>4</sub> and tartaric acid (H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) to decrease the influence on purification. Na<sub>2</sub>CO<sub>3</sub> and

NaOH was used to remove Mg<sup>2+</sup>. Mg(OH)<sub>2</sub> precipitation can be used for fire retardant generation or rubber stuffing after separation. Then, the alkalinity was adjusted, and the metal ions were extracted with *t* - BAMBP/SK solution. Almost all Cs<sup>+</sup> and Rb<sup>+</sup> in

the brine were extracted into the organic phase through multistage continuous countercurrent extraction.  $\text{Cs}^+$  and  $\text{Rb}^+$  were readily obtained by washing the organic phase with deionized water and the multistage stripping with HCl. The stripping liquid was

successively evaporated and crystallized, and the  $\text{Cs}^+$  and  $\text{Rb}^+$  were separated after recrystallization and alkalization, obtaining the pure  $\text{CsCl}$  and  $\text{RbCl}$ , respectively. The technological process is described in Fig. 3.

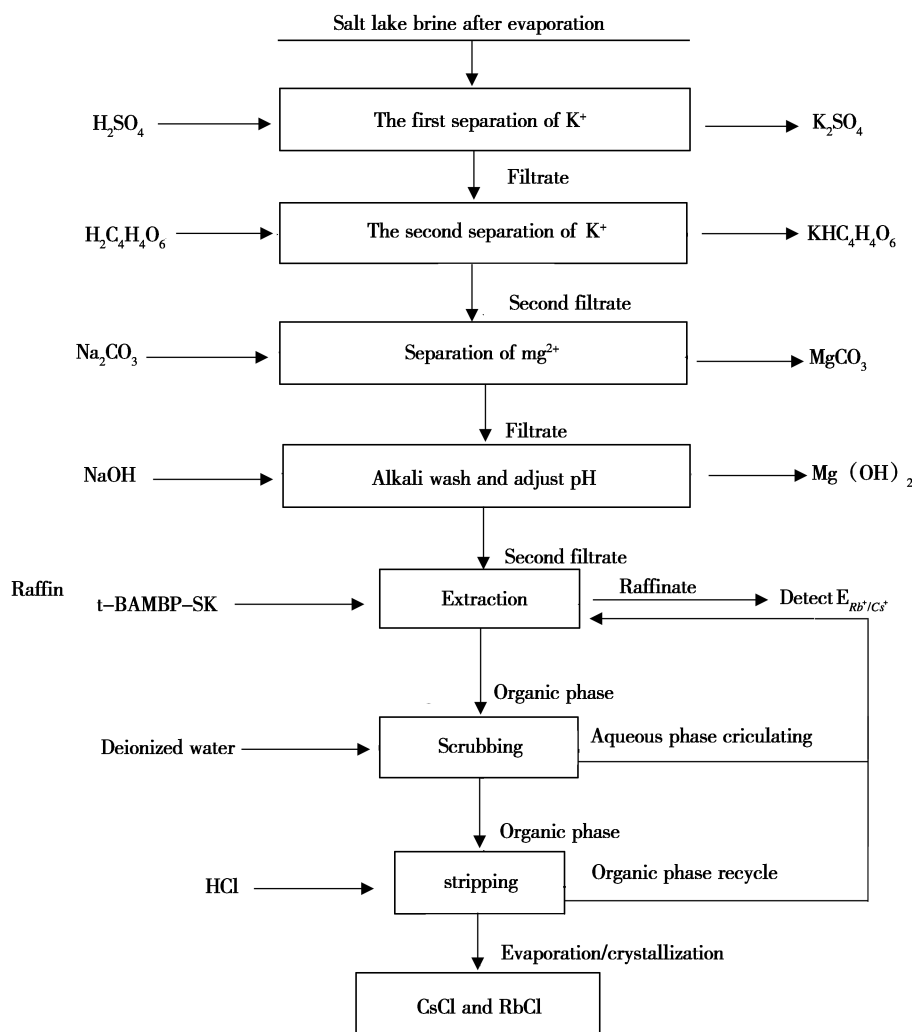


Fig. 3 Technological process of separation and extraction

## 2.6 The removing of $\text{K}^+$ and $\text{Mg}^{2+}$

A certain amount of  $\text{H}_2\text{SO}_4$  was added into the experimental brine in a Bunsen beaker for static settlement for 1 h at room temperature. The residue was filtered by a vacuum suction machine. The above procedures were repeated twice before the  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  was added into filtrate liquor. The residue and the filtrate liquor of  $\text{K}^+$  were analyzed by chemical titration.

To remove the impact of  $\text{Mg}^{2+}$  on the extraction, the second filtrate was treated by adding a certain dosage of  $\text{Na}_2\text{CO}_3$  and then boiling it<sup>[20]</sup>. The cooled down solution was filtered, and NaOH was added to the filtrate liquor to alkali wash and adjust the pH to change the alkalinity. Chemical titration was used to analyze the collected samples from the residue and the filtrate. The final filtrate liquors were used for the solvent extraction.

## 2.7 Solvent extraction and reverse extraction experiment

The *t*-BAMBP was diluted in sulfonated kerosene. Solvent extraction was carried out with a tap funnel and solution to maintain an alkaline environment. An oscillator was controlled at a constant temperature and vibration strength in the extraction and reverse extraction experiments.

The extraction coefficient (*E*) is defined as follows<sup>[11]</sup>:

$$E = \frac{M_1}{M_1 + M_2} \times 100 \quad (4)$$

Where  $M_1$  is the number of extracted ions in organic phase;  $M_2$  is the amount of the residue ions in the aqueous phase.

## 3 Results and discussions

### 3.1 Effect of $Mg^{2+}$ and $K^+$

Since  $K^+$  and  $Mg^{2+}$  have similar physicochemi-

cal properties to those of  $Cs^+$  and  $Rb^+$ , the extraction and purification would be influenced. Thus, pretreatment of the experimental brine is vital<sup>[17]</sup>. The practical approach is to use  $H_2SO_4$  to decrease  $K^+$  while adjusting the experimental brine pH to around five. Too high or too low of a pH would result in lower recovery rates. Excess  $H_2C_4H_4O_6$  is needed to decrease  $K^+$  by half, and the remaining  $K^+$  in the experimental brine can be effectively decreased. A comparison of the above results indicated that 84.38% of  $K^+$  was eliminated through the two precipitations (without  $Mg^{2+}$  precipitation).

In addition, a large number of  $Mg^{2+}$  in the experimental brine will lead to emulsification during extraction, reducing the  $Cs^+$  and  $Rb^+$  extraction yield.  $Mg^{2+}$  can be efficiently precipitated by employing  $Na_2CO_3$  and NaOH. It was found that 97.34% of  $Mg^{2+}$  can be removed, and emulsification was also eliminated at the time of extraction. Furthermore, the use of NaOH increases the pH value of the brine before  $Cs^+$  and  $Rb^+$  extraction.

**Table 3** The composition of experimental brine after precipitated  $g \cdot L^{-1}$

| Metal ion | $Cs^+$  | $Rb^+$  | $Li^+$ | $K^+$   | $Na^+$ | $Mg^{2+}$ |
|-----------|---------|---------|--------|---------|--------|-----------|
| Content   | 0.041 4 | 0.030 6 | 36.85  | 0.723 0 | 219.1  | 0.536 5   |

The composition of experimental brine after pretreatment is given in Table 3. Compared with Table 1, 84.38%  $K^+$  and 97.34%  $Mg^{2+}$  were eliminated, and the other metal ions were nearly unchanged. Therefore, preprocessing is beneficial for the efficient extraction and separation of  $Cs^+$  and  $Rb^+$ .

### 3.2 Infrared studies of *t*-BAMBP

Typical characteristics of phenol hydroxyl can be found in the infrared spectrum of *t*-BAMBP. The *t*-BAMBP diluted in cyclohexane ( $C_6H_{12}$ ) leads to the spectrum change, which can be clearly observed. The experimental conditions were 1 mol/L

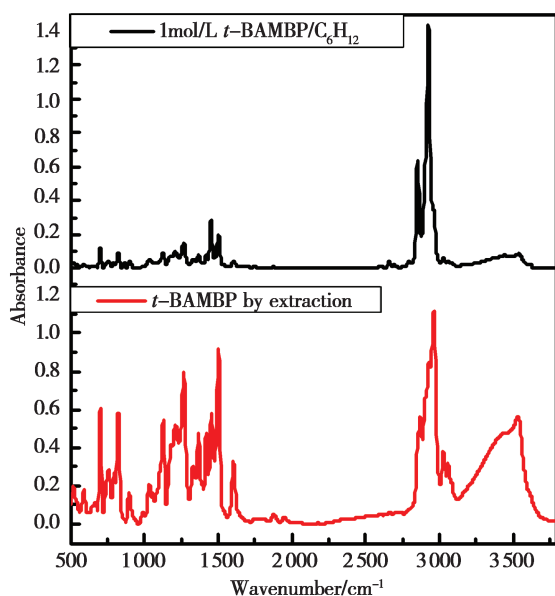
*t*-BAMBP/ $C_6H_{12}$ , PH = 13, phase ratio (O/A) 1:1, and 2 min contact time.

As shown in Fig. 4, when the wavenumber reaches  $3\,500\,cm^{-1}$ , a markable change can be observed in the infrared spectrum. The hydrogen-bonded dimer was formed when the *t*-BAMBP extracts  $Cs^+$ <sup>[11]</sup>. A broader, stronger absorption typically characteristic of the hydrogen-bonded O-H in the dimer was observed at  $3534\,cm^{-1}$ . When  $Cs^+$  was extracted, the fundamental O-H vibrations were attributed to the diminution of hydrogen-bonds in dimers. Thus, the absorption of the bonded O-H in the polymers increases.

**Table 4** The orthogonal experiment extraction coefficient

| Concentrations of<br>$t$ -BAMBP (mol/L) | PH | Phase ratio<br>(O/A) | Extraction time<br>/min | Extraction coefficient/% |                 |                |
|---|----|----------------------|-------------------------|--------------------------|-----------------|----------------|
|   |    |                      |                         | Cs <sup>+</sup>          | Rb <sup>+</sup> | K <sup>+</sup> |
| 0.4                                     | 10 | 1                    | 1                       | 68.10                    | 8.43            | 5.75           |
| 0.4                                     | 11 | 2                    | 2                       | 82.81                    | 10.31           | 6.81           |
| 0.4                                     | 12 | 3                    | 3                       | 78.61                    | 16.00           | 3.66           |
| 0.4                                     | 13 | 4                    | 4                       | 90.13                    | 35.14           | 6.85           |
| 0.8                                     | 10 | 2                    | 3                       | 92.64                    | 33.13           | 13.95          |
| 0.8                                     | 11 | 1                    | 4                       | 95.70                    | 15.93           | 3.28           |
| 0.8                                     | 12 | 4                    | 1                       | 88.86                    | 13.43           | 1.64           |
| 0.8                                     | 13 | 3                    | 2                       | 74.34                    | 59.66           | 11.99          |
| 1.2                                     | 10 | 3                    | 4                       | 87.22                    | 24.04           | 9.98           |
| 1.2                                     | 11 | 4                    | 3                       | 85.85                    | 34.40           | 13.61          |
| 1.2                                     | 12 | 1                    | 2                       | 59.81                    | 5.33            | 10.05          |
| 1.2                                     | 13 | 2                    | 1                       | 68.16                    | 57.22           | 8.39           |
| 1.6                                     | 10 | 4                    | 2                       | 96.61                    | 25.97           | 8.53           |
| 1.6                                     | 11 | 3                    | 1                       | 77.03                    | 27.50           | 10.81          |
| 1.6                                     | 12 | 2                    | 4                       | 81.28                    | 17.60           | 19.68          |
| 1.6                                     | 13 | 1                    | 3                       | 64.91                    | 56.85           | 6.97           |

\* Oscillation at 25°C.

**Fig. 4** Infrared studies of  $t$ -BAMBP

### 3.3 Effect of diluent

It was reported that the diluent would impact on the extraction efficiency and phase disengage-

ment<sup>[21]</sup>. Therefore, the extraction of Cs<sup>+</sup> and Rb<sup>+</sup> from aqueous solution was carried out employing 1 mol/L  $t$ -BAMBP at a phase ratio (O/A) of 1:1 and a contact time of 2 min. Sulfonated kerosene, cyclohexane, and mineral oil were used as diluent to dilute  $t$ -BAMBP. The extraction rate of Cs<sup>+</sup> and Rb<sup>+</sup> is given in Fig. 5. When using cyclohexane as the diluent, the extraction efficiency of Cs<sup>+</sup> and Rb<sup>+</sup> is the highest. However, the extraction efficiency of sulfonated kerosene used as diluent is close to cyclohexane and is cheaper. Accordingly, sulfonated kerosene should be the optimum diluent.

### 3.4 Orthogonal experiment

Table 4 shows the extraction coefficient of various alkali metals from the salt lake brine with  $t$ -BAMBP/SK. The maximum  $E$  of 96.61% for Cs<sup>+</sup> and 59.66% for Rb<sup>+</sup> were recovered after the single-stage extraction. The higher the content of K<sup>+</sup>, the greater the effect on the extraction rate of Cs<sup>+</sup> and Rb<sup>+</sup>. The minimum  $E$  was 1.64% for K<sup>+</sup>.

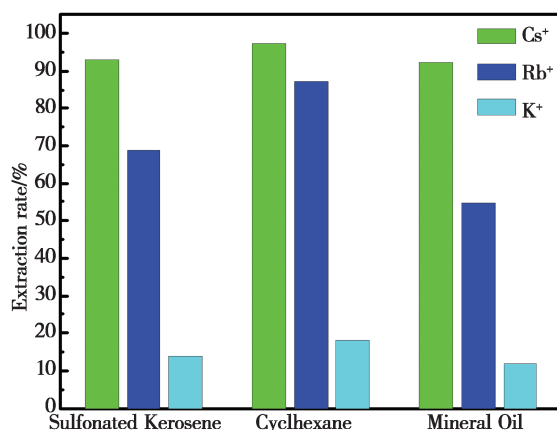


Fig. 5 Effect of diluent on the extraction

It can be found from the orthogonal experimental results of  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$  that the order of different influencing factors from greatest to least was pH, extraction time, concentrations of  $t$ -BAMBP, and phase ratio. The optimal experimental conditions include a pH of 13, a concentration of  $t$ -BAMBP of 0.8 mol/L, a phase ratio (O/A) of 1:1, and a contact time of 2 min.

### 3.5 Effect of alkalinity

On the basis of the orthogonal experiment results, the alkalinity is the main variable of influence. Previous research has shown that increased solution alkalinity is beneficial for the extraction of  $\text{Cs}^+$  and  $\text{Rb}^+$  from salt lake brine<sup>[22]</sup>. Fig. 6 shows the effect of various alkali metals under different pH values. The experimental brine alkalinity was adjusted using 1 mol/L NaOH while keeping the other conditions constant (the concentration of 0.8 mol/L  $t$ -BAMBP/SK, phase ratio (O/A) 1:1, and 2 min contact time).

When the pH was increased to 13,  $\text{Cs}^+$  was almost completely extracted, and the extraction yield of  $\text{Rb}^+$  increased from 2% to 58%. Alkalinity had little effect on the  $\text{K}^+$  extraction efficiency, with a maximum of 5%  $\text{K}^+$  being co-extracted. Alkalinity is essential for the extraction system, with the effect of  $t$ -BAMBP/SK in alkaline conditions being much higher than in neutral or acidic conditions. Extra  $\text{Na}^+$  would be introduced into the brine, but it rarely

affects the  $\text{Cs}^+$  and  $\text{Rb}^+$  extraction. In view of this, NaOH is an appropriate choice to precipitate  $\text{Mg}^{2+}$  and to adjust the pH of the aqueous phase. Hence, substances with a pH greater than 13 were more efficient for  $\text{Cs}^+$  and  $\text{Rb}^+$  extraction from salt lake brine.

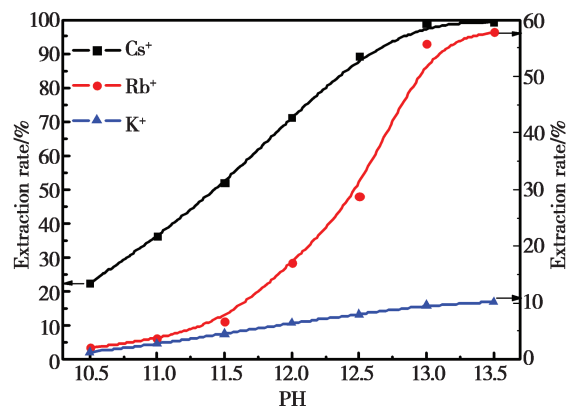
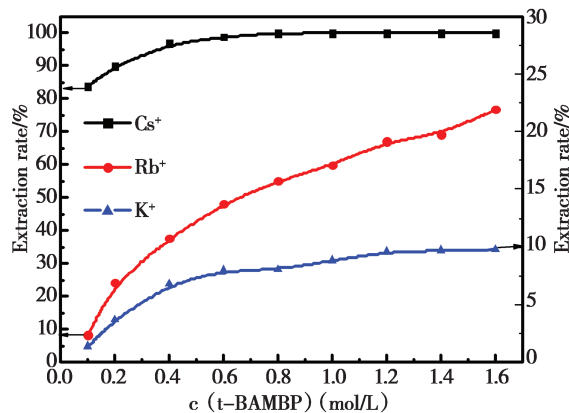


Fig. 6 Effect of pH on extraction efficiency

### 3.6 Effect of $t$ -BAMBP

The effect of  $t$ -BAMBP concentrations on the extraction efficiency was also investigated at a phase ratio (O/A) of 1:1 and pH over 13 at 25 °C for a contact time of 2 min. The concentration of  $t$ -BAMBP has an appreciable influence over the range of 0.1–1.6 mol/L. As shown in Fig. 7, the extraction efficiencies of both  $\text{Cs}^+$  and  $\text{Rb}^+$  clearly increased upon increasing  $t$ -BAMBP concentration. As can be seen, 8.76% of  $\text{K}^+$  was co-extracted, and the highest extraction rates of 100%  $\text{Cs}^+$  and 79.8%  $\text{Rb}^+$  were obtained with  $t$ -BAMBP concentrations of 0.8 mol/L and 1.6 mol/L, respectively.

Fig. 7 Effect of  $t$ -BAMBP concentrations

The enhancement of extraction rate can be ascribed to the improved extraction capacity of the organic phase. Actually, when the concentration of *t*-BAMBP is over 1.0 mol/L, the organic phase viscosity is so high that phase disengagement becomes a challenge. Considering the higher extraction efficiency of  $\text{Rb}^+$  and phase disengagement, the 0.8 mol/L concentration of *t*-BAMBP was determined to be optimal.

### 3.7 Effect of phase ratio

The effect of the phase ratio *O/A* on the extraction of  $\text{Cs}^+$  and  $\text{Rb}^+$  was researched with 0.8 mol/L *t*-BAMBP and pH exceeding 13 at 25 °C for a contact time of 2 min. As shown in Fig. 8, the metal extraction is improved in the *O/A*, promoted by the *t*-BAMBP. The extraction yield of  $\text{Rb}^+$  is clearly increased with the increase of the volume ratio of *O/A*, while  $\text{Cs}^+$  has a high extraction rate at a low phase ratio. When *O/A* = 1:1, the extraction rates of  $\text{Cs}^+$  and  $\text{Rb}^+$  were 100% and 58.22%, and 8.2%  $\text{K}^+$  was co-extracted. Beyond the phase ratio 1:1, the extraction rate of  $\text{Cs}^+$  remains unchanged. In order to acquire high extraction efficiencies of  $\text{Cs}^+$  and  $\text{Rb}^+$  and take *t*-BAMBP recycling into account, the optimum phase ratio (*O/A*) for extraction was chosen as 1:1.

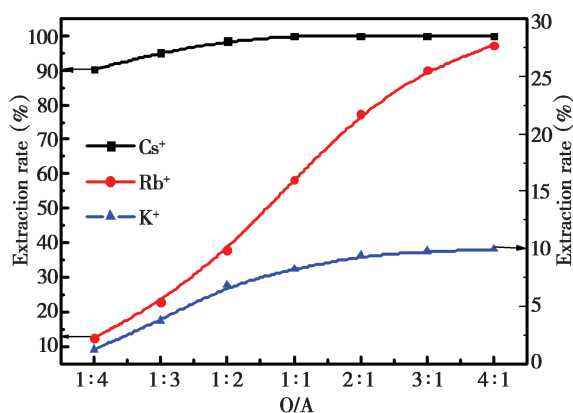


Fig. 8 Effect of phase ratios

## 4 Conclusions

In this work, the solvent extraction of  $\text{Cs}^+$  and  $\text{Rb}^+$  with *t*-BAMBP was investigated. The following conclusions were obtained:

(1) It is crucial to preprocess the experimental brine before extraction. 84.38% of  $\text{K}^+$  and 97.34% of  $\text{Mg}^{2+}$  were eliminated through the double precipitation method. The crystals of  $\text{K}_2\text{SO}_4$  and the sediments of  $\text{Mg}(\text{OH})_2$  are industrial products that were also obtained. Taking into account the cost of the operation, sulfonated kerosene was selected to dilute the *t*-BAMBP. The experiment was carried out at room temperature.

(2) The infrared spectroscopy studies found that polymerize to form the dimer in the *t*-BAMBP after the  $\text{Cs}^+$  or  $\text{Rb}^+$  were extracted. According to the consistent results of orthogonal experiments and single-factor experiments, the optimal conditions for the extraction of  $\text{Cs}^+$  and  $\text{Rb}^+$  were a *t*-BAMBP concentration of 0.8 mol/L, adjusting the feed solution pH to over 13 using 1 mol/L NaOH, a volumetric phase ratio (*O/A*) of 1:1, and a contact time of 2 min. It turned out that nearly 100% of  $\text{Cs}^+$  and 85.8% of  $\text{Rb}^+$  were extracted and 8.76%  $\text{K}^+$  was co-extracted.

(3) The trace  $\text{Cs}^+$  and  $\text{Rb}^+$  of salt lake brine can economically and efficiently be extracted by the technological process proposed in this study. As a result, the methodology is worth researching thoroughly. Further study is needed to increase the extraction yield and the selectivity of  $\text{Rb}^+$  and achieve the efficient separation of  $\text{Cs}^+$  and  $\text{Rb}^+$  products. Therefore, future work can be focused on optimizing the procedures of extraction and separation to reduce the acid and alkali consumption.

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