

Study on the 4-ethyl-2(α -methyl benzyl) phenol Extraction-Separation Between Rubidium and Potassium

Zheng-gen Huang^{1,2*}, Lian-ying An^{1,2}, He-yin Yi¹, Tao Wang²

¹National Quality Supervision and Inspection Test Center of Architecture Ceramic, Leshan 614000.

²College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059;

Abstract. More than 92% of rubidium resources on the earth exist in salt lake brine and underground brine. Rubidium in brine coexists with a large amount of potassium with very similar physical and chemical properties, making the extraction technology of rubidium extremely difficult, and a large amount of rubidium resources in brine have not been rationally utilized. Therefore, the development of a new type of high-selectivity rubidium-potassium separation extractant is of great significance to the establishment of efficient separation and extraction technology of rubidium. By modifying the structure of 4-tert-butyl-2-(α -methylbenzyl)phenol, the traditional rubidium extractant, the steric hindrance effect of tert-butyl is reduced and the reaction efficiency of rubidium and extractant is improved. A new extractant 4-ethyl-2-(α -methylbenzyl)phenol was obtained. The thesis carried out the research on the extraction and separation performance of potassium rubidium 4-ethyl-2-(α -methylbenzyl)phenol. The results show that the new extraction agent 4-ethyl-2-(α -methylbenzyl)phenol and potassium rubidium brine are extracted and separated with a ratio of 10:1. The minimum separation coefficient of rubidium potassium can reach 15 or more, showing excellent separation performance; When the organic phase is composed of 0.8mol/L extractant and D60 solvent oil, the alkalinity of the aqueous phase is 0.5mol/L sodium hydroxide, and the extraction time is 3 minutes, the single-stage extraction rate of rubidium can reach more than 76.0%, rubidium potassium The separation coefficient can reach more than 26. After repeated use, the extraction rate of rubidium can be maintained above 73% and the separation coefficient of rubidium potassium can reach 23, without a significant drop. It provides a new way and idea for the extraction and separation technology of rubidium in high potassium brine.

1 Introduction

As a rare alkali metal element, rubidium is widely used in the fields of organic catalysts, photomultiplier tubes, special glasses and anticancer drugs, and has great economic and strategic significance^[1-6]. Rubidium has no independent minerals, and often coexists with other alkali metals in lepidolite, pollucite, hectorite, natural carnallite, salt lake brine and underground brine^[7-8]. Rubidium in brine coexists with a large amount of potassium with very similar physical and chemical properties, making the extraction technology of rubidium extremely difficult, and a large amount of rubidium resources in brine have not been rationally utilized^[9-10]. Traditional methods for the separation of potassium rubidium include ion exchange, precipitation, fractional crystallization, and solvent extraction. Compared with other methods, the solvent extraction method has a large exchange capacity, easy to achieve industrial operation, and good selectivity. It has become an important and promising method for the separation of potassium rubidium. method. There have been many related reports on t-BAMBP as a special

extractant for rubidium, but the extractant is expensive. The extractant must be extracted and separated at high alkalinity (above 1mol/L), and the single-stage extraction rate of rubidium is only 60 %, the separation coefficient β of rubidium and potassium can only reach about 15^[11-12]. Therefore, the development of a new type of rubidium extractant with high selectivity, mild extraction conditions and relatively low price for rubidium has great economic significance and application prospects for the establishment of efficient separation and extraction of rubidium technology.

In order to overcome the above shortcomings and deficiencies of the existing extraction system, based on the study of the relationship between the structure of the extractant and the extraction performance, according to the mechanism that the extraction capacity is controlled by the balance between the cavity and the hydroxyl group, the structure of the traditional special extractant t-BAMBP is reduced. The steric hindrance effect of the extraction process reduces the chemical exchange resistance of the extraction process and improves the extraction exchange efficiency. Our laboratory has prepared 4-methyl-2-(α -methylbenzyl)phenol, which shows good extraction and separation effects. Compared with t-BAMBP (4-tert-

*Corresponding author's e-mail:lszjs2102660@aliyun.com

butyl-2-(α -methylbenzyl) phenol), the extraction performance of 4-methyl-2-(α -methylbenzyl) phenol [13] is improved. Due to the increase in polarity, the loss of the water phase and the oil phase is also increasing. Therefore, by further modifying the t-BAMBP group to prepare 4-ethyl-2-(α -methylbenzyl) phenol, it is planned to further improve the performance of extraction and separation of rubidium potassium while reducing the oil-water phase of the extractant itself in the extraction process. loss.

In this paper, 4-ethyl-2-(α -methylbenzyl) phenol was prepared by F-C reaction, and the separation performance of rubidium and potassium was investigated using this substance as an extractant. The separation process of rubidium and potassium was preliminarily established through extraction test, with the hope of extracting rubidium and potassium. The practical application of separation industry provides a certain theoretical and technical reference, and provides a new method and idea for the separation of high potassium and low rubidium salt brine

2 Materials and methods

2.1 Main reagents and instruments

The analytical alcohol has included that CTAB, NaAlO₂, TEOS, RbCl, KCl, C₈H₈, C₈H₉O, PE, C₆H₁₂, EA, D60, The analytical alcohol has produced by Chengdu Kelon Chemical Reagent Factory.

2.2 Test method

2.2.1 Alkylation method[14-16] Synthetic extractant 4-ethyl-2 (α -methylbenzyl) phenol reaction test method

Using styrene and p-ethylphenol as raw materials, mesoporous molecular sieve Fe-Al-MCM-41^[13] as a catalyst for F-C reaction to synthesize 4-ethyl-2 (α -methylbenzyl) phenol. The specific method is as follows: Add 4mmol of p-ethylphenol, a certain amount of Fe-Al-MCM-41 molecular sieve catalyst and 50mL cyclohexane into a 250mL three-necked flask equipped with a condensing device and a constant pressure funnel, and heat the oil bath to a certain temperature under stirring Start dropping styrene and continue the reaction for a certain period of time, then cool to room temperature to separate the reaction liquid and the solid catalyst to obtain a light yellow transparent liquid product, which is distilled under reduced pressure to remove unreacted raw materials. The product was purified by silica gel column chromatography, separated and purified with a mixed solution of ethyl acetate and petroleum ether as the developing solvent, the effluent was collected and detected by TLC, the effluents with the same composition were combined, and the petroleum ether in the effluent was removed by vacuum distillation With ethyl acetate, a light yellow viscous main product and a light yellow solid by-product are obtained. The reaction equation and synthesis mechanism for the synthesis of 4-ethyl-2 (α -

methylbenzyl) phenol are as follows:

(1) The synthesis reaction equation is shown in Figure 1.

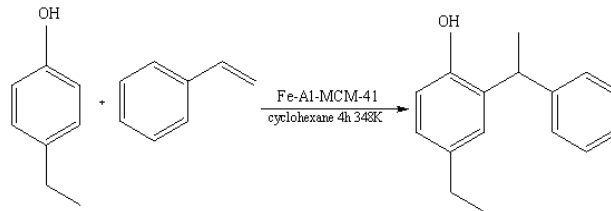


Figure1 Synthesis reaction equation of 4-ethyl-2(α -methylbenzyl)phenol

(2) Analysis of the synthesis mechanism of 4-ethyl-2(α -methylbenzyl)phenol:

The reactants p-ethylphenol and alkylation reagent styrene diffuse into the pores of the molecular sieve, the alkylation reagent styrene and the molecular sieve acid center are activated to form the methylbenzyl carbenium ion, and the methylbenzyl carbenium ion attacks the benzene ring to form a sigma complex After the proton is removed, the alkylation process is completed, and the final target product 4-ethyl-2 (α -methylbenzyl) phenol and the by-product 4-ethyl-2,6 bis (α -methyl benzyl) phenol diffuses out of the pores of the molecular sieve. Due to the different adsorption states of p-cresol and styrene on the molecular sieve, on the other hand, it is restricted by the shape-selective catalysis of the pore structure of the molecular sieve. The reaction mainly produces 4-ethyl-2 (α -methylbenzyl) phenol, 4-ethyl -2,6 (di- α -methylbenzyl) phenol accounts for only a small part.

2.2.2 Extraction performance inspection test

Three simulated brines with different concentrations of potassium rubidium ratio of 10:1 are configured, and the newly synthesized extractant is used for the extraction and separation test of rubidium and potassium. Place the material liquid and the extractant in a separatory funnel according to a certain ratio, shake and mix for a certain period of time, and then stand to separate. Analyze and determine the concentration of rubidium and potassium in the raffinate aqueous phase, calculate the extraction rate and separation coefficient of rubidium and potassium, and evaluate the separation ability of the new extractant rubidium and potassium.

2.2.3 Process test of rubidium potassium separation

Extraction test: configure a feed solution containing potassium rubidium, in which the K⁺ concentration is 1.5446mol/L (60g/L) and the Rb⁺ concentration is 0.0712mol/L (6g/L). The organic phase is composed of 4-ethyl-2-(α -methylbenzyl)phenol as the extractant. Except for the discussion of the influence of the diluent, D60 is used as the diluent. Accurately measure 5ml of the aqueous phase to be extracted into a 125ml separatory funnel, and then use a pipette to measure a certain volume of organic phase into the same separatory funnel. Shake and mix for a certain period of time and then stand for phase separation.

3 Results and discussion

3.1 The extraction and separation principle of rubidium potassium 4-ethyl-2-(α -methylbenzyl)phenol

4-ethyl-2-(α -methylbenzyl)phenol is a weakly acidic phenol derivative like t-BAMBP. It has a selective extraction effect on alkali metals. After diluting with mineral spirits, in an alkaline environment, phenol The H^+ on the hydroxyl group dissociates, and the H^+ exchanges with metal ions to form hydrophobic phenolate into the organic phase. Since the atomic radius of Rb^+ is larger than that of K^+ , the probability of generating hydrophobic phenolate is greater. Therefore, the order of extraction capacity is $Rb^+ > K^+$. The phenolate that forms rubidium

ion during extraction is more likely to enter the organic phase, and the formed phenol The acid salt is also more stable. On the contrary, K^+ enters the water phase more easily during washing and stripping, so as to realize the separation of rubidium and potassium.

3.2 Investigation results of extraction and separation performance of 4-ethyl-2-(α -methylbenzyl) phenol rubidium potassium

A simulated brine with a mass concentration ratio of rubidium and potassium = 10/1 and 4-ethyl-2-(α -methylbenzyl)phenol as the extractant was used for the extraction and separation test of rubidium and potassium. The results are shown in Table 1.

Table 1 4-Ethyl-2-(α -methylbenzyl)phenol extraction rubidium potassium separation performance experiment

Group	NaOH concentration (mol/L)	Rubidium extraction rate (%)	Potassium extraction rate (%)	Rubidium and potassium separation coefficient
1	0.20	82.07	9.28	41.40
2	0.20	79.60	9.61	36.70
3	0.80	78.78	13.50	23.78
4	0.80	66.52	14.81	11.42

Note: 1. Extraction conditions: $C_{Rb^+}=0.1g/L$, $C_{K^+}=1g/L$ in the feed liquid, and the organic phase composition is 0.4mol/L 4-ethyl-2-(α -methylbenzyl)phenol + D60 solvent oil, Compared with O/A=3, two minutes extraction;
 2. Extraction conditions: $C_{Rb^+}=1g/L$, $C_{K^+}=10g/L$ in the feed liquid, and the organic phase composition is 0.5mol/L 4-ethyl-2-(α -formaldehyde) Benzyl)phenol + D60 solvent oil, compared to O/A=3, two minutes extraction;
 3. Extraction conditions: $C_{Rb^+}=6g/L$, $C_{K^+}=60g/L$ in the feed liquid, and the organic phase composition is 0.8mol/L 4 -Ethyl-2-(α -methylbenzyl)phenol+D60 solvent oil, compared to O/A=3, two minutes extraction;
 4. Extraction conditions: $C_{Rb^+}=6g/L$, $C_{K^+}=60g/L$ in the feed liquid , The organic phase composition is 1.0mol/L t-BAMBP+D60 solvent oil, compared with O/A=3, two minutes extraction

The new extractant 4-ethyl-2-(α -methylbenzyl)phenol is used as the extractant, the single-stage extraction rate of rubidium can reach more than 80%, the separation coefficient can reach more than 40, the extraction conditions are mild, and the phase separation speed is fast , No emulsification, small dissolution loss in the oil phase and water phase, and reduced alkalinity requirements, showing that its extraction and separation performance is superior, and it has the conditions to become a new efficient rubidium extractant. Compared with the original rubidium special extractant t-BAMBP, the newly synthesized extractant 4-ethyl-2-(α -methylbenzyl)phenol can be seen from the single-stage extraction rate of rubidium or the separation coefficient of rubidium and

potassium. Have a big improvement

3.3 Extraction test

A material solution containing potassium rubidium is configured, in which the K^+ concentration is 1.5446mol/L (60g/L) and the Rb^+ concentration is 0.0712mol/L (6g/L). Using 4-ethyl-2-(α -methylbenzyl)phenol as the extractant, D60 as the solvent oil, and the extraction time of 3min, investigate the different phase ratio (O/A), extractant concentration, and water basicity to rubidium The effect of potassium extraction and separation performance, the results are shown in Table 2 to Table 4

Table 2 The influence of different comparisons on the extraction rate and separation coefficient of rubidium potassium

O/A	$Rb^+(g/L)$	$K^+(g/L)$	Rb Extraction rate%	K Extraction rate%	Rb/K
2	2.043	55.98	65.95	6.70	26.97
2.5	1.448	54.23	75.87	9.62	29.52

3	1.395	52.95	76.75	11.75	24.79
3.5	1.361	52.75	77.32	12.08	24.79
4	1.458	50.85	77.37	15.25	19.00

Note: The extraction conditions are time: 3min, material liquid alkalinity 0.5M NaOH, extractant concentration 0.8M

Table 3 The influence of different extractant concentration on the extraction rate and separation factor of potassium rubidium

Concentration	Rb ⁺ (g/L)	K ⁺ (g/L)	Rb Extraction rate%	K Extraction rate%	Rb/K
0.4M	3.000	56.80	50.00	5.33	17.76
0.6M	2.310	54.49	61.50	9.18	15.80
0.8M	1.392	53.05	76.80	11.58	25.27
1.0M	1.297	51.00	78.38	15.01	20.54
1.2M	1.158	47.89	80.70	20.18	16.54

Note: The extraction conditions are time: 3min, material liquid alkalinity 0.5M NaOH、O/A=2.5

Table 4 Effect of different sodium hydroxide concentration on the extraction rate and separation coefficient of rubidium potassium

Alkalinity	Rb ⁺ (g/L)	K ⁺ (g/L)	Rb Extraction rate%	K Extraction rate%	Rb/K
0.1M	3.557	58.62	40.72	2.30	29.17
0.3M	2.838	57.38	52.70	4.37	24.38
0.5M	1.398	53.28	76.70	11.20	26.10
0.8M	1.3	50.86	78.33	15.23	20.11
1M	1.18	47.92	80.33	20.13	16.20

Note: The extraction conditions are time: 3min, extractant concentration 0.8M, O/A=2.5

It can be seen from the above table that with the comparison, the extractant concentration, the alkalinity of the feed liquid and the extraction rate of rubidium and potassium show a positive correlation. The increase in the concentration of the extractant increases the mass transfer of the extraction. Power, the alkalinity of the feed liquid increases the ability of the extractant to dissociate H⁺, which is more conducive to the ability of Rb⁺ and K⁺ to form hydrophobic phenolate into the organic phase. But when it exceeds a certain limit, rubidium increases the extraction rate and the extraction rate of potassium also increases significantly, and the trend of potassium growth is greater than that of rubidium. In the extraction of 3min, compared with O/A=2.5, the extractant concentration is 0.8M, When the alkalinity of the material liquid is 0.5M, the extraction rate of rubidium can reach more than 76%,

and the separation coefficient of rubidium and potassium can reach more than 26, showing an excellent separation effect of rubidium and potassium

3.4 Reusable performance test of extractant

The organic phase is composed of 0.8mol/L extractant and D60 solvent oil, the alkalinity is 0.5mol/L sodium hydroxide in the water phase, and the extraction time is 3 minutes, compared with O/A=2.5/1 for extraction; water washing phase The ratio O/A=4/1, the washing time is 2 minutes for water washing; the back extraction agent is 2mol/L HCl, the back extraction ratio O/A=5/1, the back extraction time is 2 minutes for back extraction, after the above extraction, Water washing and back extraction are

a cycle, and the extraction performance of the extractant after multiple cycles is investigated. The results are shown

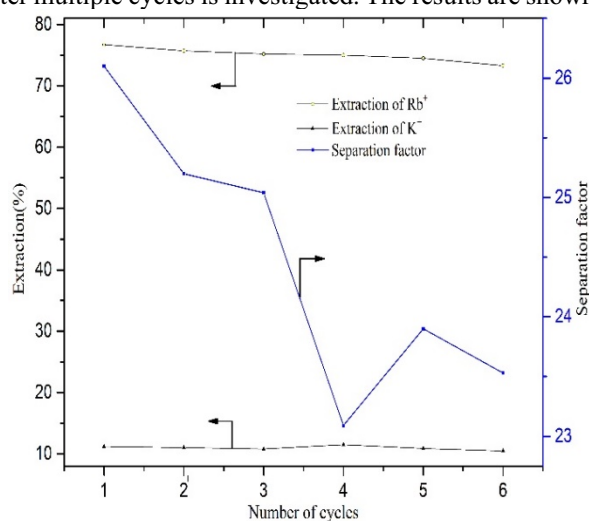


Figure.2 The effect of number of cycles on extraction and separation factor

From the above figure, it can be seen that the extraction rate of rubidium can still be maintained above 73.0% after repeated use, the extraction rate of rubidium only drops by 4.43%, the separation coefficient of rubidium potassium remains above 23, and the increase in the number of cycles shows a slower trend in performance degradation. 4-Ethyl-2-(α -methylbenzyl)phenol has good repetitive performance as a separation and extraction agent for potassium rubidium.

4 Conclusion

The performance of extraction and separation of potassium rubidium in simulated brine with 4-ethyl-2-(α -methylbenzyl)phenol as extractant was studied. 4-Ethyl-2-(α -methylbenzyl)phenol was prepared by alkylation method. Using high potassium and low rubidium simulated brine as the research object, the separation effect of rubidium potassium was investigated. Compared with the traditional rubidium extractant t-BAMBP, both the extraction rate and the separation ability have been greatly improved. Finally, the effect of the extraction oil-water ratio, the concentration of the extractant, the alkalinity of the material and the reusability of the extractant on the separation performance was investigated, and the results showed that 4-ethyl-2-(α -methylbenzyl)phenol has the application prospect of being a highly effective extractant for rubidium.

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in Figure 2. and Figure 3.

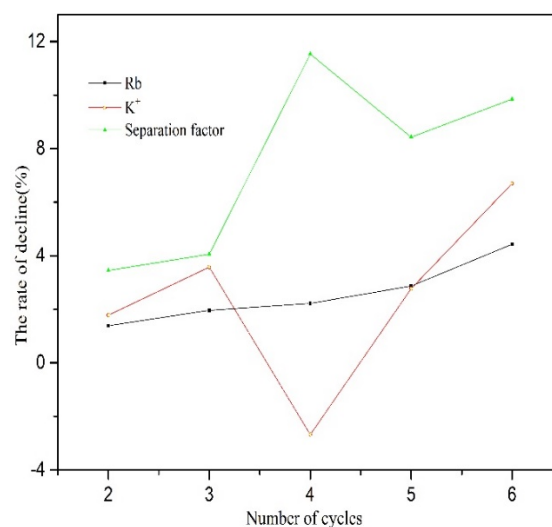


Figure.3 The rate decline of number of cycles on extraction and separation factor

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