Extraction of cesium from aqueous solution through t-BAMBP/C$_2$mimNTf$_2$ and recovery of cesium from waste desalination brine

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ABSTRACT
This research demonstrates an ionic liquid-based extraction system for extracting cesium by using 4-tert-butyl-2-(α-methylbenzyl)phenol (t-BAMBP) as a conventional extractant and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C$_2$mimNTf$_2$) as a diluent. The factors that affected the extraction efficiency such as the concentration of t-BAMBP, contacting time, initial pH value of the aqueous solution, organic phase/aqueous phase ratio (O/A ratio), and reaction temperature were optimized. In this work, the thermodynamics parameters of cesium extraction with t-BAMBP/C$_2$mimNTf$_2$ system were investigated as well. Moreover, the extraction system was extended to study the recovery of cesium from waste desalination brine. The extraction efficiencies of cesium, rubidium, potassium, and sodium were 96%, 64.7%, 5.6%, and 3.3%. However, other impurities such as lithium, calcium, and magnesium could not be extracted through the t-BAMBP/C$_2$mimNTf$_2$ system. After extracting, cesium could then be stripped back to the liquid phase through ammonia. In a nutshell, this study shows the optimal parameters of the t-BAMBP/C$_2$mimNTf$_2$ system for cesium extraction and verifies its feasibility of applying it to desalination brine.

Keywords: Extraction; t-BAMBP; C$_2$mimNTf$_2$; Ionic liquid; Cesium; Waste desalination brine

1. Introduction
According to the U.S. Geological Survey report, the cesium resources are mainly from pollucite, garnet, and lepidolite [1]. Most pollucite contains 5% to 32% cesium oxide, and the reserves of cesium are estimated based on the occurrence of pollucite. The world’s total reserves were 220,000 metric tons in 2020, and the principal reserves are in Australia, Canada, Namibia, Zimbabwe, and some other countries [1]. Because of difficulties in mining and the production of cesium in small quantities, it has become rarer in recent years. However, cesium metal and its compounds are valuable and useful in many industries. For example, the isotope of cesium, $^{137}$Cs, can be used in the atomic clock, and the error is 2 s for 66 million years.

In the optoelectronics industry, cesium is the material of radar, television, and reconnaissance telescope [2]. On the other hand, cesium sulfide (Cs$_2$S), cesium chloride (CsCl), and cesium trifluoroacetate (CF$_3$COOCs) can be used in the density gradient centrifugation method to separate viruses, organelles, and nucleic acids in the biological sample [3]. Cesium nitrate (CsNO$_3$) is the raw material of colorant and oxidizer in pyrotechnics because its optical radiation is in the near-infrared spectrum [1,4]. Also, cesium bromide (CsBr), cesium carbonate (Cs$_2$CO$_3$), cesium hydroxide (CsOH), and cesium iodide (CsI) all have their characteristics to be used in electronics industries [1,2]. Due to the rarity and development of applications of cesium, various methods have been developed to separate and recover cesium from minerals and wastes to date.

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Solvent extraction [5–7] and ion exchange [8,9] are two universal methods to separate cesium now. Chemical precipitation and displacement methods are not common due to the high solubility of cesium compounds in the aqueous solutions and the high activity of cesium. Compared with all methods, solvent extraction is preferred to separate cesium on account of easy operation, high extraction efficiency, and high throughput. 4-tert-butyl-2-(α-methylbenzyl)phenol (t-BAMBP) [5–7], 4-sec-butyl-2-(α-methylbenzyl) phenol (BAMBP) [10–12], bis(2-propoxy)calix[4] crown-6 (BPC6) [13], and calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOB-calixC6) [14–16] are extractants which can be dissolved in organic diluent such as kerosene, cyclohexane, toluene, xylene, and diethylbenzene to extract cesium. Although conventional organic extractants with diluents can separate and purify cesium efficiently, their drawbacks are high volatility, low thermal stability, and difficulty for recycling. To overcome these disadvantages, ionic liquids (ILs) are gradually used in extraction techniques.

ILs are novel materials which are usually made up of organic cations and inorganic or organic anions. Due to their high conductivities, low vapor pressure, low flammability, and tunable characteristics, they can be used in many areas like electrochemistry [17–19], separation technology [20–24], treatment of wastewater [25], capture and storage of carbon [26–30], and synthesis of organic compounds [31]. The recent development of ILs in separation technology is the use as extractant or diluent in metal ion extraction. Most ILs have extraction ability for specific metal ions, so they can be directly used as extractants or combined with conventional organic extractants as diluents to increase extraction efficiency. Nowadays, imidazolium ionic liquids and phosphonium ionic liquids are commonly used to extract metal ions. For example, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (Cn mimNTf2, n = 2,4,6,8) can be used to extract K+, Rb+, and Cs+ as extractants and diluents [32,33]. Ethylene glycol functionalized bis-imidazolium ionic liquid and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid can respectively extract Hg2+ and Cu2+ [34,35]. On the other hand, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphate (Cyphos IL 104) and trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) can extract Pb2+ [36], Cd2+ [37], Ga3+ [38], In3+ [39], Nd3+ [40], and other metals [41,42] under different conditions.

Kinds of the literature demonstrated that ILs have unlimited development to extract metal ions efficiently as extractants or diluents. Our group has studied the t-BAMBP/kerosene system for cesium extraction before [7], and the high volatility of kerosene made the experiment unstable. Besides, kerosene could only be diluent without extraction ability. To improve the stability and efficiency of the extraction system, C2 mimNTf2 was then chosen in this study to be diluent. The characteristics of low vapor pressure, high thermal stability, and the extraction ability of C2 mimNTf2 could overcome the drawbacks of conventional diluents. Moreover, the simulated solution in this study is basic, and the t-BAMBP/C2 mimNTf2 system could be used in the alkaline situation, whereas the other system such as BPC6/C2 mimNTf2 system, was suitable for the weak acid and neutral situation [33]. Due to the above reasons, the t-BAMBP/C2 mimNTf2 system in this study is expected to be a novel extraction method. Therefore, the parameters such as the concentration of t-BAMBP, contacting time, initial pH value of the aqueous medium, organic phase/aqueous phase ratio (O/A ratio), reaction temperature, and thermodynamic parameters were all investigated. Among them, initial pH value and reaction temperature were the most critical parameters in this research. Furthermore, this extraction process is applied to separate cesium from waste desalination brine, and the results are compared with previous works to make distinctions. After the extracting process, the cesium was stripped back to the liquid phase through ammonia, and the cesium resources could then be reused.

2. Experimental

2.1. Reagents and chemicals

Cesium carbonate (99.9%) was obtained from Sigma-Aldrich (St. Louis, MO, USA) and dissolved in deionized water to be a cesium simulated solution in this research. The organic extractant t-BAMBP (≥90%) was acquired from Realkan Corporation (Beijing, China) for the extraction process, and its structure is shown in Fig. 1 [5]. C2 mimNTf2 was a low melting point (≥–15°C) and hydrophobic ionic liquid (≥97%, water < 0.5%). It was purchased from Sigma-Aldrich (St. Louis, MO, USA) to be used as a diluent, and its structure is shown in Fig. 1. Lithium hydroxide (99.995%) and sulfuric acid (≥98%) were both acquired from Sigma-Aldrich (St. Louis, MO, USA). They were used to adjust the pH value in the extraction process. In the stripping process, nitric acid (≥65%), sulfuric acid (≥98%), and ammonia (30%–33%) were all obtained from Sigma-Aldrich (St. Louis, MO, USA) to strip cesium back to the liquid phase. During the analysis procedure, ICP cesium standard solution, ICP rubidium standard solution, and ICP multi-element standard solution were acquired from High-Purity Standards, Inc. (North Charleston, SC, USA). The nitric acid (≥65%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and dissolved in deionized water to be a cesium simulated solution in this research. Besides, all chemicals and aqueous solutions were dissolved and diluted by deionized water (resistivity 18.0 MΩ-cm) to avoid impurities affecting the results.

2.2. Apparatus

The concentration of cesium ion and rubidium ion was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) with a Perkin Elmer ICP-OES 3000. The instrument was used with an autosampler (Perkin Elmer autosampler). The cesium ion and rubidium ion concentration was determined by ICP-OES. The calibration curves were established by standard solutions prepared from cesium carbonate and rubidium carbonate standards. The detection limits were calculated to be 0.01 mg/L for cesium ion and 0.05 mg/L for rubidium ion. The repeatability was better than 5%, and the trueness was better than 10%.

Fig. 1. The structure of t-BAMBP.
3. Results and discussion

3.1. Effect of t-BAMBP concentration

In this process, the various concentrations of the t-BAMBP/C$_2$mimNTf$_2$ system were prepared to extract cesium from the 10 mmol/L cesium carbonate solution. The initial pH value of the solution was 10.8, and other fixed parameters were Cs concentration of 2,640 mg/L, contacting time of 15 min, O/A ratio of 1, and temperature at 298 K. Fig. 3 shows that $E_{Cs}$ was above 60% without t-BAMBP. It means that the extraction ability of C$_2$mimNTf$_2$ itself reached a fairly high level. $E_{Cs}$ then rose along with increased t-BAMBP concentration. The $E_{Cs}$ were 66.5%, 99.8% and 99.9% with 1, 15, and 20 mmol/L t-BAMBP, respectively. Although it was effective from the concentration of 5, 15 mmol/L was chosen as an optimal parameter to ensure the complete extraction of cesium ion.

3.2. Effect of contacting time

Equilibrium periods were set up from 1 to 15 min with fixed parameters of Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, pH 10.8, O/A ratio of 1, and reaction temperature at 298 K in this study. Fig. 4 shows the $E_{Cs}$ from 1 to 5 min were all below 75% and were about 99% for 10 and 15 min. This study's equilibrium period of the t-BAMBP/C$_2$mimNTf$_2$ system was more extended than the normal extraction process [7]. The reasonable explanation is that the dynamic viscosity of C$_2$mimNTf$_2$ was higher than common diluents such as kerosene, cyclohexane, and xylene. (Dynamic viscosities of different diluents and dynamic viscosities of C$_2$mimNTf$_2$ at different temperatures are shown in Tables 1 and 2.) The higher viscosity of C$_2$mimNTf$_2$ made the extraction system challenging to mix with the aqueous phase thoroughly. To ensure higher $E_{Cs}$ in every process, contacting time of 15 min was selected in this study.

3.3. Effect of initial pH value

Because t-BAMBP is an extractant suitable for alkaline conditions, the initial pH values were set up from 8 to 14 with lithium hydroxide and sulfuric acid in this study. Owing to the property of t-BAMBP, C$_2$mimNTf$_2$, and the experiment we conducted, it was found that lithium was hardly extracted in this system which could be neglected. Other fixed parameters were Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, O/A ratio of 1, and temperature at 298 K. Fig. 5 shows that the $E_{Cs}$ was 1.5% at pH 8 and gradually increased to above 98% from pH 11 to 14. Due to the results and the lower usage of chemicals, pH 11 was chosen as a suitable parameter. Compared with the previous articles which used the systems of t-BAMBP/kerosene [7] and BPC6/C$_2$mimNTf$_2$ [33], there were some unique characteristics of the t-BAMBP/C$_2$mimNTf$_2$ system. This system could be used in the alkali condition, whereas the BPC6/C$_2$mimNTf$_2$ system was suitable for the weak acid and neutral situation. Although cesium ion could be extracted by t-BAMBP/kerosene in alkali solution, emulsification occurred when pH value was 13 and 14, reducing the extraction efficiency. However, this phenomenon did not occur when pH value was 11.
appear with t-BAMBP/C₂mimNTf₂. Therefore, it demonstrated that this system could be applied at a higher pH value than the t-BAMBP/kerosene system.

3.4. Effect of O/A ratio

Fig. 6 shows the O/A ratios were set from 0.1 to 10 with the fixed parameters of Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, pH 10.8, O/A ratio of 1 at 298 K. The results reveal that $E_{Cs}$ was below 70% when O/A ratios were from 0.1 to 0.5. When O/A ratios were above 0.5, the $E_{Cs}$ were then above 99% and became stable. The reason was that cesium ion could not be extracted efficiently due to insufficient t-BAMBP availability. In this research, the concentration ratio and multistage extraction were not considered, so O/A ratio of 1 was the optimal parameter.

3.5. Effect of reaction temperature and thermodynamic parameters

The effect of reaction temperatures was set up from 278 to 318 K with fixed parameters of Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, O/A ratio of 1 at 298 K. Fig. 7 demonstrates that the $E_{Cs}$ increased with an increase in temperature. For example, the extraction efficiency of cesium at 278 K was 81.7% which was increased to 99% and 99.2% when the temperature was 308 and 318 K. Because of the lower thermal energy usage, 308 K was chosen as the optimal parameter in this research.
study. To get more details of thermodynamic parameters, Fig. 8 illustrates the plot of \( \log D \) vs. \( \frac{1}{1000/T} \). The thermodynamic parameters such as \( \Delta H \), \( \Delta G \), and \( \Delta S \) were calculated with Eqs. (4)–(6). The slope of the line was \( -\Delta H/2.303R \), so \( \Delta H = 67.36 \text{ kJ/mol} \), which indicated the extraction of cesium with t-BAMBP/C\(_2\)mimNTf\(_2\) was endothermic. \( \Delta G \) can be calculated with the intercept of the line, so the Gibbs free energy was \( -6.61 \text{ kJ/mol at 308 K} \). Therefore, the Gibbs free energy was negative, indicating the extraction behavior of cesium with t-BAMBP/C\(_2\)mimNTf\(_2\) was spontaneous. By substituting \( \Delta H \) and \( \Delta G \), \( \Delta S \) could then be calculated. \( \Delta S = 240.16 \text{ J/K mol at 308 K} \), which indicated the reaction was spontaneous at a higher temperature.

\[
\frac{\partial \log D_{\text{Cs}}}{\partial (1/T)} = -\frac{\Delta H}{2.303R}
\]  

3.6. Application to waste desalination brine and stripping process

After investigating the optimal parameters of cesium extraction, the t-BAMBP/C\(_2\)mimNTf\(_2\) system was then applied to waste desalination brine. Waste brine now causes considerable harm to the environment. For example, waste brine will change the composition of seawater and affect the ecosystem. To reuse waste brine, cesium was extracted from brine through the t-BAMBP/C\(_2\)mimNTf\(_2\) system. The simulated waste desalination brine was prepared as the previous work, and the main elements are shown in Table 3 [7]. The experiment was set up with fixed parameters of 15 mmol/L t-BAMBP, contacting time of 15 min, pH 11, and O/A ratio of 1.

![Fig. 6. Extraction efficiencies of cesium ion at different O/A ratios. Fixed parameters: Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, pH 11 at 298 K.](image)

![Fig. 7. Extraction efficiencies of cesium ion at different reaction temperatures. Fixed parameters: Cs concentration of 2,640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, pH 11, and O/A ratio of 1.](image)

![Fig. 8. Relationship between \( \log D_{\text{Cs}} \) and \( 1000/T \). Fixed parameters: Cs concentration of 2640 mg/L, 15 mmol/L t-BAMBP, contacting time of 15 min, pH 11, and O/A ratio of 1.](image)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>The main elements and compositions of brine</th>
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<tbody>
<tr>
<td>Element</td>
<td>Concentration (mg/L)</td>
</tr>
<tr>
<td>Li</td>
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<tr>
<td>Na</td>
<td>49,180</td>
</tr>
<tr>
<td>K</td>
<td>91</td>
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<tr>
<td>Cs</td>
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\[
\Delta G = -2.303RT \log K
\]  

\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]  

3.6. Application to waste desalination brine and stripping process

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extracted metals in the order of Cs > Rb > K > Na > Li and alkaline earth metals and was in accordance with the previous works [7,32]. Comparing the optimal parameters of contacting time, initial pH value, and O/A ratio with previous work in Table 4, it was found that the contacting time was 3 min, and the initial pH value of the aqueous phase was 8.0 in the t-BAMBP/kerosene system. However, the contacting time was 15 min, and the initial pH value of the aqueous phase was 11.0 in the t-BAMBP/C2mimNTf2 system. The reason was that the higher viscosity and characteristics of C2mimNTf2 made the system require a longer time and higher pH value. Besides, the cesium extraction efficiency of the t-BAMBP/C2mimNTf2 system was lower than the t-BAMBP/kerosene system. The surmise was t-BAMBP/C2mimNTf2 would extract sodium ion, but t-BAMBP/kerosene would not. The solution to this situation is multistage extraction. The sodium concentration would gradually decrease through multistage extraction, and cesium concentration could keep at a level. The comparison in this article reveals that both systems have their features and can be chosen depending on different situations.

After extracting cesium from desalination brine through the t-BAMBP/C2mimNTf2 system, nitric acid, sulfuric acid, and ammonia were used to strip cesium back to the liquid phase. It was found that ammonia could strip cesium efficiently than nitric acid and sulfuric acid. The stripping efficiency of 5M NH4OH was 77.8%, and the nitric acid and sulfuric acid were all below 5%. To get a higher stripping efficiency, this research conducted a three-stage stripping process to obtain more than 90% of cesium.

4. Conclusion

This research illustrated that t-BAMBP/C2mimNTf2 could efficiently extract 99% of cesium ion from 10 mmol/L cesium carbonate solution under 15 mmol/L t-BAMBP, contacting time of 15 min, pH 11, O/A ratio of 1, and reaction temperature at 308 K. The most influencing parameters were the initial pH values and reaction temperature. By adjusting them at optimal situations, the extraction percentage would increase to above 99%. The characteristics of this system were high extraction efficiency under the higher alkaline condition at average temperature but at a higher O/A ratio and longer contacting time than other systems due to the features of t-BAMBP and C2mimNTf2. This system could also be applied to recover cesium from waste brine desalination, and the recovery efficiency was 96%. The comparison with other ions such as rubidium, potassium, sodium, and alkaline earth metals in this study demonstrated that t-BAMBP/C2mimNTf2 had a higher extraction selectivity of cesium ion than impurities. After extracting process, more than 90% of cesium could then be stripped back to the liquid phase through 5 M NH4OH with a three-stage stripping process. To sum up, this research revealed a unique system to extract cesium ion effectively and verify its feasibility. However, there are still some improvements needed in this method. For example, the viscosity of C2mimNTf2 should be controlled, and the extraction efficiency of rubidium must be reduced to avoid side effects. In the future, this system will be completed and be improved to increase its applied value.

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References
