Combining selective extraction and easy stripping of lithium using a ternary synergistic solvent extraction system through regulation of Fe³⁺ coordination

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ABSTRACT: Lithium is becoming increasingly important due to its essential role in lithium-ion batteries. Over 70% of the global lithium resources are found in salt lake brines, where lithium is always accompanied by magnesium. The system of TBP (tributyl phosphate)/FeCl₃ has been widely studied for selective lithium extraction from high Mg-containing salt lake brines. However, the system requires a high concentration of HCl for lithium stripping, which causes equipment corrosion, consumes large amounts of reagents and requires careful neutralization of the organic phase for regeneration. In this study, we develop a novel ternary synergistic solvent extraction system of TBP/FeCl₃/P507 (P507 is 2-ethylhexyl phosphonic acid mono 2-ethylhexyl) to significantly enhance the stripping of lithium while largely maintaining lithium extraction capacity. During lithium extraction from Mg-containing solutions, TBP and FeCl₃ coordinate with lithium in the form of Li·2TBP·FeCl₄, while P507 is not involved in the coordination. When the loaded organic phase is contacted with water, P507 and TBP synergistically coordinate with Fe³⁺ in the form of FeCl₂L·(HL)·2TBP (HL denotes P507), leading to efficient stripping of lithium due to the broken of the coordination structure of Li·2TBP·FeCl₄, and Fe³⁺ is maintained in the organic phase for the next extraction cycle. The efficient stripping of lithium using only water, instead of high concentration HCl, is a key step forward towards the sustainable extraction of lithium from brines.

1. INTRODUCTION

Driven by the increasing popularity of electric vehicles, the consumption of lithium has been sharply increasing in the past 10 years, and the trend is expected to continue in the following 2–3 decades.¹⁻⁴ Salt lake brines and pegmatites are the two main sources of lithium with the former accounting for over 70% of the total resources.⁵⁻⁶ Currently, the majority of the global lithium production is obtained from salt lake brines.^{1,7} The Mg/Li ratios of salt lake brines in China are especially high, which makes lithium recovery more difficult.⁸

Solvent extraction (SX) is a promising technique for lithium extraction from Mg-containing brines. In the 1960s, Nelli and Arthur found that FeCl₃ and certain oxygen-containing extractants, particularly diisobutyl ketone (DIBK) and TBP, could selectively extract Li⁺ over Mg²⁺ in chloride media.⁹ Afterward, the synergistic SX system of TBP/FeCl₃ attracted extensive studies for Li⁺ and Mg²⁺ separations due to the good separation factor (SF > 300), low cost and large scale availability of TBP.^{8,10-13} However, this extraction system has the problem of difficult stripping. Zhou *et al.* determined the complex structure of Li⁺ extraction by TBP to be [Li•(TBP)_x(H₂O)_{4-x}]⁺[FeCl₄]⁻ (x = 1, 2).¹⁴ In some other studies, x = 2 is often observed.¹⁵⁻¹⁶ In this extraction, Li⁺ forms a cationic complex with TBP and water, [FeCl₄]⁻ works as the counter anion. The most commonly used stripping agent is HCl, and the mechanism is replacing Li⁺ by the H⁺ in the complex.^{8,17} The extraction and stripping of Li⁺ can be expressed by the following equations:

where the subscripts *aq* and *org* stand for the aqueous and organic phase, respectively, and *x* is assumed to be 2. High concentration of HCl (up to 6 M) is required for stripping, because in addition to exchange with Li⁺, it is also extracted by TBP in a large amount, and TBP is used excessively in lithium extraction.¹⁸ The high HCl concentration not only corrodes equipment, but also requires careful neutralization of the organic phase to regenerate TBP for next recycling. Therefore, the difficult stripping has been the main obstacle, preventing the TBP/FeCl₃ SX system from industrial applications for lithium extraction from brines.

Besides [FeCl₄]⁻, [PF₆]⁻-containing ionic liquids (ILs) with hydrophilic cations also showed potential to extract Li⁺. In such extraction, the cations of the ionic liquids enter into the aqueous solution and the anions are involved in the complex formation with Li⁺.¹⁹⁻²⁰ Following this discovery, many kinds of ionic liquids²¹⁻²² and salts (e.g. NaClO₄ and NaB(Phen)₄) with symmetric anions were found to be similar in extraction capability of lithium with TBP. However, these ionic liquids have considerable limitations: expensive and lose cations (not reusable). Moreover, replacing FeCl₃ with these alternative anions (either as salts or ionic liquids) does not really improve stripping, especially when a high organic to aqueous phase ratio (O/A) is used. These studies show that ionic liquids are now unsuitable for lithium recovery from brines.

In this study, we developed a novel ternary synergistic solvent extraction system of TBP/FeCl₃/P507 to enhance stripping of lithium using only water by controlling the coordination

of Fe^{3+} during extraction and stripping, while largely maintaining the lithium extraction capacity. The mechanism of the lithium extraction and stripping of this system was explained and the structures of extracted complexes were proposed. It is proved to be a sustainable lithium extraction process with large-scale industrial application value.

2. EXPERIMENTAL SECTION

Reagents and Solution Preparation. LiCl (> 97%), MgCl_2 (> 99%), FeCl_3 (> 98%) and HCl (37 wt%) were purchased from Beijing Chemical Works. The synthetic brine solutions were prepared by dissolving certain amounts of chloride salts into de-ionized water, according to the composition of real brine solutions. TBP (> 98.5%) and P507 (> 95%) was provided by Shanghai Rare Earth Chemical Co., Ltd. Sulfonated kerosene (MW=142–254) and cyclohexane (> 99.5%) were purchased from Sinopharm Group Chemical Reagent Co. Organic solutions were prepared by mixing TBP and P507 with kerosene according to the required volume ratio. AgNO_3 (> 99.7%), K_2CrO_4 (> 99.5%) and NaOH (> 98%) used for Cl^- concentration determination were purchased from Beijing reagents company.

Extraction Procedures. The synthetic feed solution containing 0.10 M LiCl , 0.13 M FeCl_3 , 4.0 M MgCl_2 and 0.03 M HCl were used to closely simulate the composition of concentrated brines in West Tajinar Salt Lake (China). The optimum Fe/Li ratio of 1.3/1 was selected based on our previous studies, and 0.03 M HCl was added to the solution to prevent the hydrolysis of Fe^{3+} . The organic phase contained varying concentrations of TBP and P507 diluted in kerosene. The

synthetic feed solution was mixed with the organic phase in hexagonal jars using a mechanic shaker (HD-100B, Jintan Yineng, China) with a O/A ratio of 1:1 (20 mL/20 mL) at 25 ± 2 °C for 30 min. After shaking, the mixtures were settled for 30 min for phase separation. Subsequently, aqueous samples were taken from the bottom phases using a syringe with a long needle for the determinations of metal concentrations and pH. The concentration of Li^+ and Mg^{2+} in the organic phases were determined after stripping with 6 M HCl and Fe^{3+} in the organic phases were calculated by mass balance based on aqueous concentration (because Fe^{3+} cannot be stripped by high HCl concentration solution).

The extraction percentage $E\%$, stripping percentage $S\%$, distribution ratio D and separation factor α are defined as:

$$E\% = \frac{C_{org} \cdot V_{org}}{C_{org} \cdot V_{org} + C_{aq} \cdot V_{aq}} \times 100\% \quad (3)$$

$$S\% = \frac{C_{org} - C_{org,s}}{C_{org}} \times 100\% \quad (4)$$

$$D = \frac{C_{org}}{C_{aq}} \quad (5)$$

$$\alpha = \frac{D_A}{D_B} \quad (6)$$

where C_{org} and C_{aq} , V_{org} and V_{aq} are concentrations and volumes of the organic and the aqueous phase at extraction equilibrium, respectively; $C_{org,s}$ is the concentration of the organic phase after stripping; D_A and D_B are the distribution ratios of metals A and B, respectively.

Determination of Cl⁻ Concentration. The Cl⁻ concentration was determined by AgNO₃ titration using K₂CrO₄ as the indicator. The aqueous samples were diluted to the Cl⁻ concentration range of 10–500 mg·L⁻¹. NaOH solution was added to the sample to adjust the pH to 6.5–10.5, then 0.02 M AgNO₃ standard solution was used for titration with K₂CrO₄ as the indicator. Cl⁻ concentration was calculated based on the consumption of AgNO₃.

UV-Vis Spectrometry and Raman Spectrometry. UV–Vis spectra was acquired by characterizing the loaded organic samples, which were prepared by 60 vol% TBP-20 vol% P507-20 vol% kerosene with the synthetic feed solution containing 0.1 M LiCl, 0.13 M FeCl₃ and 0.03 M HCl under various MgCl₂ concentrations. Raman spectra was acquired by characterizing the loaded organic samples which were prepared by 60 vol% TBP-20 vol% P507-20 vol% cyclohexane with the above synthetic feed solution and subsequently, cyclohexane being evaporated.

Analysis. The concentrations of Li⁺, Mg²⁺ and Fe³⁺ in the aqueous samples were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300V, Pekin-Elmer, USA) after diluting to a proper concentration range. A composite pH probe (Ross Sure-Flow 8172BN, Orion, US) connected with a pH meter (PHSJ-6L, INESA, Shanghai, China) was used to monitor the pH of aqueous samples. UV–Vis spectra were recorded on a UV–Visible spectrophotometer (9100b, Labtech, Beijing) using a pair of quartz cuvettes with 10.0 mm light path. The absorbance range is 0–3 ABS, resolution is 0.1 nm, sweeping step length is 0.5 nm, and the wavelength range is 50–1000 nm. Raman spectra were recorded by a laser Raman

spectrometer (LabRAM HR800, Horiba Jobin Yvon, France) with a Leica optical microscope to focus the laser light. The excitation light was the 514.5 nm line of an Ar⁺ laser with a real output power of 10–50 mW. The resolution is 0.3 cm⁻¹ and the measurement range is 50–1000 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Stripping of Lithium from the TBP/FeCl₃ System.

Despite the fact that the extraction and stripping of lithium by the TBP/FeCl₃ system has been reported by many researchers, we tested the system again for comparison with the ternary system of TBP/FeCl₃/P507 in the following section. 60 vol% TBP dissolved in kerosene was used for lithium extraction from the synthetic brine solution, because the third phase occurred when TBP concentration was lower than 60 vol%. After extraction, 0.44 g·L⁻¹ Li⁺, 1.9 g·L⁻¹ Mg²⁺ and 5.85 g·L⁻¹ Fe³⁺ was loaded to the organic phase, and the extraction of Li⁺, Mg²⁺ and Fe³⁺ were 72%, 1.9% and 100%, respectively. The loaded organic phase was then stripped by HCl and water with various phase ratios. The effect of HCl concentration for the stripping of metals with a O/A ratio of 1 is shown in Figure 1a. Almost all metal ions were stripped by water, including Fe³⁺. The stripping of Fe³⁺ is due to the lack of chloride anions, which is essential for the formation of [FeCl₄]⁻. Once [FeCl₄]⁻ cannot be maintained, Fe³⁺ is subjected to the aqueous solution and consequently Li⁺ is stripped as well due to the broken of the Li·2TBP·FeCl₄, according to Eq. (1). With the increase of HCl concentration, the stripping percentage of Fe³⁺ decreased rapidly and only 5% Fe³⁺ was stripped at 3.0 M HCl, while stripping of Li⁺ and Mg²⁺ were still almost

complete. Under this condition, Li^+ was stripped by being replaced by H^+ , while Fe^{3+} was kept in the organic phase in the form of $\text{H}\cdot 2\text{TBP}\cdot\text{FeCl}_4$, according to Eq. (2). Despite almost complete stripping of Li^+ , the concentration of Li^+ in the stripping solution was only $0.44\text{ g}\cdot\text{L}^{-1}$ at 3.0 M HCl, which is too low for the further precipitation of Li_2CO_3 .

In order to concentrate Li^+ in the stripping solution, the effect of O/A ratios on lithium stripping was investigated with 3.0 M HCl (Figure 1b). In all phase ratios, Fe^{3+} was largely maintained in the organic phase. When O/A ratio was less than 10, more than 95% Li^+ was stripped. The concentration of Li^+ in the aqueous phase was 4.37 g/L at the O/A ratio of 10. When O/A ratio was further increased, the stripping of Li^+ decreased rapidly and it became 63%, 30% and 4% at the O/A ratio of 20, 30 and 50, respectively.

The effect of O/A ratios on the stripping using water was also studied, with results shown in Figure 1c. With the increase of the O/A ratio, the stripping of Li^+ and Fe^{3+} decreased rapidly and they could hardly be stripped at the O/A ratio of 30. The stripping of Li^+ and Fe^{3+} has the same trend, meaning that either both Li^+ and Fe^{3+} are kept in the organic phase with very low stripping, or Li^+ is stripped but Fe^{3+} is lost to the aqueous solution as well. Neither of the two cases is wanted. Therefore, water cannot strip Li^+ from the TBP/ FeCl_3 system.

Figure 1. Stripping of lithium from the loaded organic phase of the TBP/FeCl₃ system: (a). effect of HCl concentration with a O/A ratio of 1, (b). effect of O/A ratio using 3.0 M HCl as the stripping agent, (c). effect of O/A ratio using water as the stripping agent.

3.2 Stripping of Lithium from the New TBP/FeCl₃/P507 System.

Following the performance of the well-known TBP/FeCl₃ system, we tested the new TBP/FeCl₃/P507 system for Li⁺ extraction and stripping. Firstly, various volumes of P507 was added to the TBP/FeCl₃ system to test the extraction of metals. It was found that P507 slightly suppresses the extraction of Li⁺, as the extraction of Li⁺ slightly decreases with increasing P507 concentration (Figure 2). 20 vol% P507 was chosen because under this condition Li⁺ extracting capacity is largely maintained while P507 is high enough to play a role in the stripping. Therefore the new TBP/FeCl₃/P507 system has 60 vol% TBP, 20 vol% P507 in kerosene and 0.13 M FeCl₃ (loaded from the aqueous solution). Then, the organic phase was contacted with the synthetic brine solution to load metals. It was found that 5.84 g·L⁻¹ Fe³⁺ (100%), 0.35 g·L⁻¹ Li⁺ (57%) and 2.68 g·L⁻¹ Mg²⁺ (2.7%) was extracted.

Figure 2. Effect of P507 concentration on metals extraction.

The loaded organic phase was stripped with water at different O/A ratios with the results

shown in Figure 3a. By contrast to the TBP/ FeCl_3 system where the stripping of Li^+ and Fe^{3+} have the same trend (Figure 1c), the stripping lines of Li^+ and Fe^{3+} are separated in the new TBP/ FeCl_3 /P507 system when the O/A ratio was less than 20, meaning that Li^+ can be stripped while maintaining Fe^{3+} in the organic phase, which is a preferred result. However, with the further increase of O/A ratio, stripping of lithium decreased rapidly. The reduction of Li^+ stripping was due to the increase of Cl^- concentration that is mainly caused by the increase of MgCl_2 concentration in the aqueous phase. Although the percentage extraction of MgCl_2 is low (about 2%), the amount is large because MgCl_2 in the feed solution is high. In order to obtain high Li^+ stripping and concentrate Li^+ in the stripping solution at a large O/A ratio, MgCl_2 should be scrubbed before lithium stripping. According to Figure 3a, at the O/A ratio of 20, Li^+ and Fe^{3+} were hardly scrubbed (or stripped) (5.2% and $< 0.01\%$, respectively), while about 75% Mg^{2+} was scrubbed. The Mg^{2+} and Li^+ concentration in the aqueous phase after scrubbing was $> 70 \text{ g}\cdot\text{L}^{-1}$ and $< 0.7 \text{ g}\cdot\text{L}^{-1}$. This aqueous solution can be sent back to the feed solution for further recovery of the scrubbed Li^+ without changing the composition of the feed solution much. The scrubbed organic phase can be further stripped by water.

The scrubbed organic phase was then further stripped with water at different O/A ratios (Figure 3b). Compared with Figure 1c, the TBP/ FeCl_3 /P507 system exhibited dramatically different trends for Li^+ and Fe^{3+} stripping. The stripping of Li^+ was close to 100%, and that of Fe^{3+} was only about 16% at O/A ratio of 1. With the increasing O/A ratio, the loss of Fe^{3+} to the aqueous solution minimized rapidly, and the stripping of Li^+ decreased from the O/A ratio of 20

onwards. The detail results for O/A ratio of 20 and 30 are listed in Table 1. At the O/A ratio of 20, Li^+ was completely stripped, the resultant stripping solution had 6.70 g/L of Li^+ , 0.90 g·L⁻¹ Fe^{3+} (0.68% stripping) and 7.14 g·L⁻¹ Mg^{2+} (91% stripping). At the O/A ratio of 30, the stripping of Li^+ was about 85%, and the concentration of Li^+ in the stripping solution reached a maximum of 8.25 g/L. Only 0.41 g·L⁻¹ Fe^{3+} was stripped to the aqueous solution, which is largely negligible. However, the concentration of Mg^{2+} in the stripping solution reached 9.16 g·L⁻¹. Mg^{2+} can be minimized by optimizing the scrubbing stages, which will be discussed in our next study. In summary, in the new TBP/ FeCl_3 /P507 system, Mg^{2+} can be largely scrubbed by water at the O/A ratio of 20 with only 5% scrubbing of Li^+ and no loss of Fe^{3+} ; then Li^+ in the scrubbed organic phase can be efficiently stripped by water at the O/A ratio of 20 with little loss of Fe^{3+} . The stripped organic phase is readily reusable in the next extraction cycle without regeneration.

Figure 3. Stripping (scrubbing) of Li^+ from the loaded organic phase by water in the TBP/ FeCl_3 /P507 system:

(a) scrubbing of Mg^{2+} by water; (b) stripping of Li^+ by water.

Table 1. Metals stripping and concentrations in stripping solution at the O/A ratios of 20 and 30 in

TBP/FeCl₃/P507 system

	O/A ratio	Li ⁺	Fe ³⁺	Mg ²⁺
Stripping/%	20	100	0.68	91
	30	85	0.21	95
Concentration in stripping solution/(g·L ⁻¹)	20	6.70	0.90	7.14
	30	8.25	0.41	9.16

3.3 Lithium Extraction and Stripping Mechanism from the TBP/FeCl₃/P507 System.

3.3.1 Extraction of Fe³⁺ by P507 alone system.

To investigate the extraction of metals by the ternary system of TBP/FeCl₃/P507, the extraction of metals by P507 alone system was firstly studied. The aqueous solutions containing lower concentrations 0.10 M LiCl, 0.10 M FeCl₃ and 0.10 M MgCl₂ were mixed with P507 diluted in kerosene to avoid the effect of solution ionic strength. The effect of P507 concentration on metals extraction has been investigated with the results shown in Figure 4. Fe³⁺ was efficiently extracted with the increase of P507 concentration, while Li⁺ was slightly extracted, and the extraction of Mg²⁺ was also low, although higher than Li⁺.

Figure 4. Effect of P507 concentration on metals extraction in P507 alone system.

The extraction of Fe^{3+} from the chloride solution with P507 alone can be described as Eq.

(8). P507 is shown to be a dimer $(HL)_2$ in non-polar solvents like kerosene.²³

where m and n are the stoichiometry of Cl^{-} and $(HL)_2$ in the reaction, respectively. The equilibrium constant (K_{ex}) of the extraction reaction is shown in Eq. (9):

$$K_{ex} = \frac{[FeCl_m L_{3-m} \cdot (HL)_{2n-3+m}]_{(org)} [H^{+}]_{(aq)}^{3-m}}{[Fe^{3+}]_{(aq)} [Cl^{-}]_{(aq)}^m [(HL)_2]_{(org)}^n} \quad (9)$$

The distribution ratio of Fe^{3+} (D) is calculated as:

$$D = \frac{[FeCl_m L_{3-m} \cdot (HL)_{2n-3+m}]_{(org)}}{[Fe^{3+}]_{(aq)}} \quad (10)$$

Taking logarithm on both sides of the resulting equation by inserting Eq. (10) into Eq. (9)

leads to:

$$\log D = \log K_{ex} - (3 - m) \log [H^+]_{(aq)} + m \log [Cl^-]_{(aq)} + n \log [(HL)_2]_{(org)} \quad (11)$$

Since LiCl is not extracted by P507, it was chosen as a chloride source added to the FeCl₃ solution to adjust the concentration of Cl⁻. Plotting the (logD + log[H⁺]) against the log[Cl⁻], while maintaining the concentration of P507 constant, gives a straight line with a slope close to 2 (Figure 5a). This slope mean that $m = 2$ in Eq (8), indicating that extraction of one mole Fe³⁺ requires two moles of Cl⁻, and one mole of H⁺ is released. Biswas *et al.* studied the solvent extraction of Fe³⁺ from the chloride solution by di-(2-ethylhexyl) phosphoric acid (P204 HA) in kerosene, and also found that FeCl₂⁺ was extracted into the organic phase and one mole of H⁺ was released. The extracted species was proposed to be [FeCl₂A·(HA)₃] at 1.0 M aqueous Cl⁻ concentration.²⁴ Since both P204 and P507 are phosphorous-based acidic extractants and their structures and properties are very similar, the species of Fe³⁺ extraction by P204 and P507 are expected to be similar.²⁵⁻²⁶

Plotting the (logD + log[H⁺]) against the log[P507], while maintaining the concentration of Cl⁻ constant gives out a straight line with a slope close to 2 (Figure 5b). This slope means that $n = 2$ in Eq. (8), indicating that extraction of one mole Fe³⁺ requires two moles of dimer P507 ((HL)₂).

Figure 5. Effect of Cl⁻ and P507 concentration on the extraction of Fe³⁺. FeCl₃ concentration was 0.1 M in all cases. (a) 0.40 M P507; (b) 0.30 M [Cl⁻].

On the basis of the above slope analysis and the principle of charge neutrality, the species of Fe³⁺ in the loaded organic phase is proposed to be FeCl₂L·(HL)₃, as expressed by Eq. (12). The structure of the complex is proposed as shown in Figure 6a, in which Fe³⁺ has a coordination number of six. The negatively charged P-O⁻ group and the two Cl⁻ anions should directly bind to Fe³⁺ for charge neutrality, and the three neutral P507 molecules bind to Fe³⁺ via the polar P=O group. The coordination mechanism of this structure is the same as the extraction of Fe³⁺ by P204, as proposed by Jin *et al.*²⁵

Figure 6. The possible structure of the complex (a) $\text{FeCl}_2\text{L} \cdot (\text{HL})_3$ and (b) $\text{FeCl}_2\text{L} \cdot (\text{HL}) \cdot 2\text{TBP}$. $\text{R} = -\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; $\text{R}_1 = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

3.3.2 Extraction of Fe^{3+} by the TBP/ FeCl_3 /P507 System.

When Fe^{3+} was extracted by the TBP/P507 solvent mixture in chloride solution, the reaction can be described as Eq. (13).

where s , p and q are the stoichiometry of Cl^{-} , $(\text{HL})_2$ and TBP in the reaction, respectively. The equilibrium constant (K_{ex}') of the extraction reaction shown in Eq. (14) is:

$$K_{\text{ex}}' = \frac{[\text{FeCl}_s\text{L}_{3-s} \cdot (\text{HL})_{2p-3+s} \cdot q\text{TBP}]_{(org)} [\text{H}^{+}]_{(aq)}^{3-s}}{[\text{Fe}^{3+}]_{(aq)} [\text{Cl}^{-}]_{(aq)}^s [(\text{HL})_2]_{(org)}^p [\text{TBP}]_{(org)}^q} \quad (14)$$

The distribution ratio of Fe^{3+} (D') is calculated as:

$$D' = \frac{[\text{FeCl}_s\text{L}_{3-s} \cdot (\text{HL})_{2p-3+s} \cdot q\text{TBP}]_{(org)}}{[\text{Fe}^{3+}]_{(aq)}} \quad (15)$$

Taking logarithm on both sides of the resulting equation after inserting Eq. (15) into Eq. (14) leads to:

$$\log D' = \log K_{ex}' - (3-s)\log[H^+]_{(aq)} + s\log[Cl^-]_{(aq)} + p\log[(HL)_2]_{(org)} + q\log[TBP]_{(org)} \quad (16)$$

The concentration of Cl^- in the solution was varied by adding LiCl. Plotting the $(\log D' + \log[H^+])$ against the $\log[Cl^-]$, while maintaining the concentration of TBP and P507 constant, gives out a straight line with a slope close to 2 (Figure 7a). The slope means that $s = 2$ indicating that extraction of one mole Fe^{3+} requires two moles of Cl^- anions and one mole of H^+ is released. Following the same procedure, slope analysis for P507 and TBP yields two slopes close to 1 and 2, respectively (Figures 7b, 7c). These slopes mean that $p = 1$ and $q = 2$. In other words, one P507 dimer and two TBP molecules are involved in the extraction of one moles of Fe^{3+} . Now Eq. (16) can be expressed as Eq. (17). The extracted species is therefore proposed to be $FeCl_2L \cdot (HL) \cdot 2TBP$. The structure of the complex is shown in Figure 6b, by analogy to Figure 6a. In the TBP/P507 extraction system, two TBP molecules replaces one P507 dimer in the extracted complex, compared to the P507 alone system.

Figure 7. Effect of Cl^- , P507 and TBP concentration on the extraction of Fe^{3+} . FeCl_3 concentration was 0.1 M in all cases. The organic phase was: (a) 0.15 M TBP and 0.15 M P507, (b) 0.15 M TBP and varying P507 concentrations, (c) 0.09 M P507 and varying TBP concentrations.

3.3.3 Effect of Chloride Concentration on Fe^{3+} Extraction by the TBP/ FeCl_3 /P507 System.

During the extraction of Li^+ from concentrated brine solutions, Cl^- concentration is high up to 8 M. However, the Cl^- concentration is low when stripping using water. Therefore, it is helpful to understand the role of Cl^- concentration on the extraction and stripping of Li^+ . The loaded organic samples mixed with the synthetic feed solution under various MgCl_2 concentrations have been characterized by UV-visible spectra and Raman spectra with results shown in Figure 8. When there was no MgCl_2 in the aqueous solution, the UV-Vis spectrum (Figure 8a) does not shown characteristic bands. With the addition of MgCl_2 three main absorption peaks appeared at 531 nm, 619 nm and 683 nm which well match the characteristic absorption peaks of FeCl_4^- ,^{14,27-29} suggesting that Fe^{3+} presented in the organic was in the form of FeCl_4^- . Raman spectra (Figure 8b) of these organic samples showed distinct exhibiting bands at 111, 333 and 384 cm^{-1} at the concentration of MgCl_2 greater than 0 M, which are also attributed to the vibrations of FeCl_4^- ,³⁰⁻³³ again suggesting existence of FeCl_4^- . In addition, the intensity of both the UV-visible spectra and the Raman spectra increase with the increasing MgCl_2 concentration, meaning that Cl^- enhance the formation of FeCl_4^- .

The metals extraction at different concentrations of MgCl_2 is shown in Table 2. Without MgCl_2 , the extraction of Li^+ is negligible and the extraction of Fe^{3+} is about 78%, which is assumed to be extracted by TBP and P507 in the form of $\text{FeCl}_2\text{L}\cdot(\text{HL})\cdot 2\text{TBP}$. With the addition of MgCl_2 , the extraction of both Li^+ and Fe^{3+} increased. On the one hand, Fe^{3+} is still partially extracted as $\text{FeCl}_2\text{L}\cdot(\text{HL})\cdot 2\text{TBP}$; on the other hand, more and more Fe^{3+} is extracted in the form of $\text{Li}\cdot 2\text{TBP}\cdot\text{FeCl}_4$, which is supported by the increasing intensity of the UV-Vis and Raman spectra of FeCl_4^- and the increasing extraction of Li^+ . At the highest MgCl_2 concentration (4.0 $\text{mol}\cdot\text{L}^{-1}$), the $\text{Li}\cdot 2\text{TBP}\cdot\text{FeCl}_4$ species should be dominating because of too high Cl^- concentration, and P507 is hardly involved in Fe^{3+} extraction although it is presented in the organic phase. This condition is the same as the Li^+ extraction from the brine solution.

Figure 8. Spectral analysis of the loaded organic phase. (a) UV–Visible spectra; (b) Raman spectra.

Table 2. Metals extraction by 60 vol% TBP-20 vol% P507 at different concentrations of MgCl_2 .

MgCl_2 concentration/ (M)	Metals extraction/%		
	Li^+	Fe^{3+}	Mg^{2+}
0.0	0.27	78.61	0
1.0	1.30	90.96	0.04

2.0	10.31	95.45	0.09
3.0	37.46	96.34	0.49
4.0	57.34	98.96	1.87

In summary of the above studies and discussions, the extraction and stripping of Li^+ and Fe^{3+} by the new TBP/ FeCl_3 /P507 system is as follows: (1) during the lithium extraction, Li^+ and Fe^{3+} are co-extracted in the form of $\text{Li}\cdot 2\text{TBP}\cdot \text{FeCl}_4$ at high Cl^- concentration; (2) P507 dose not or only slightly involved in the extraction; (3) in the stripping by water, Fe^{3+} is re-extracted in the form of $\text{FeCl}_2\text{L}\cdot (\text{HL})\cdot 2\text{TBP}$ due to the the lack of Cl^- , and Fe^{3+} is maintained in the organic phase with negligible loss into the strip liquor. As a results, after stripping, the organic is readily reusable for next extraction cycle without regeneration because non acid was used for stripping. The extraction and stripping is an equilibrium between the two species of $\text{Li}\cdot 2\text{TBP}\cdot \text{FeCl}_4$ and $\text{FeCl}_2\text{L}\cdot (\text{HL})\cdot 2\text{TBP}$, which is controlled by the concentration of MgCl_2 . The reaction equilibrium is expressed in Eq. (18) and demonstrated in Figure 9 respectively.

Figure 9. The mechanism of lithium extraction and stripping by the TBP/FeCl₃/P507 system.

4. CONCLUSIONS

A novel ternary synergistic solvent extraction system of TBP/FeCl₃/P507 that combines selectively lithium extraction and easy stripping by regulation of Fe³⁺ coordination was developed and investigated. 60 vol% TBP and 20 vol% P507 diluted in kerosene was used for lithium extraction from a synthetic brine solution of 0.1 M LiCl, 4.0 M MgCl₂ and 0.13 M FeCl₃ (FeCl₃ is one of the synergistic extraction agents). The loaded organic phase was scrubbed with water at the O/A ratio of 20 to largely remove MgCl₂, and then stripped with water at the O/A ratio of 30, where 85% Li⁺ was stripped and the loss of Fe³⁺ was negligible. The efficient stripping of Li⁺ using water is a significant improvement compared to the existing TBP/FeCl₃ system which requires high HCl concentration for Li⁺ stripping. Slope analysis and spectroscopic studies show that: Li⁺ and Fe³⁺ is extracted from the brine solution in the form of Li·2TBP·FeCl₄; Fe³⁺ is extracted in the form of FeCl₂L·(HL)·2TBP (HL donates P507) when the loaded organic phase is stripped by water. The conversion of the two extracted complexes is controlled by the concentration of MgCl₂. This novel ternary solvent extraction system of TBP/FeCl₃/P507 considerably enhances Li⁺ stripping while largely maintains Li⁺ extraction efficiency and does not require regeneration of extractants, therefore it is a more sustainable system for Li⁺ extraction from Mg-containing brines and has potential for industrialization.

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Notes

The authors declare no competing financial interest.

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TOC/ABSTRACT GRAPHIC

SYNOPSIS

The ternary solvent extraction system TBP/FeCl₃/P507 enables efficient and sustainable lithium stripping using water while maintaining selective lithium extraction capacity.