Extraction Relationship of Li⁺ and H⁺ Using Tributyl Phosphate in the Presence of Fe(III)

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During the extraction of lithium from high Mg content salt lake brines by TBP in the presence of Fe(III), H^+ is used to stabilize Fe(III). However, its extraction competes with that of Li^+ which significantly affects lithium extraction. In this study, the competition mechanism between Li^+ and H^+ was investigated by spectral analysis and thermodynamic equilibrium. It is found that the extracted species are $\text{HFeCl}_4 \cdot 2\text{TBP}$ and $\text{LiFeCl}_4 \cdot 2\text{TBP}$ for H^+ and Li^+ , respectively. The apparent equilibrium constants are $K_{\text{H}}=799.8$ and $K_{\text{Li}}=120.6$, respectively, which accuracy is verified because $K_{\text{H}}/K_{\text{Li}}$ is close to the range of 4-6 obtained by $D_{\text{H}}/D_{\text{Li}}$ when they are simultaneously extracted with TBP.

Keywords: lithium; H^+ ; competition mechanism; apparent equilibrium constant; tributyl phosphate

Introduction

Lithium has important applications in lithium-ion batteries (LIBs) due to its very low density and high electrochemical standard potential.^[1] In recent years, the demand for lithium increases due to the rapid development of portable electronic devices and electric vehicles.^[2, 3] Pegmatites and salt lake brines are two main sources for lithium deposits, with the latter accounting for about 80%.^[1, 4] Among lithium deposits in brines, more than 70% is located in

South America (Argentina, Bolivia and Chile), 15% in the Qinghai-Tibet Plateau of China and the rest in the United States, Canada and the Dead Sea region.^[5] Magnesium always accompanies lithium in brines. The brines in South America generally have low Mg/Li ratios (≤ 8), from which lithium can be readily recovered using a traditional process of multi-stage precipitation followed by pre-concentration to produce Li_2CO_3 .^[6, 7] This kind of brines has obvious advantage for the low processing cost due to less reagent consumption and waste generation, although it still suffers from lower recovery efficiency and longer production time period.^[8, 9] However, most brines, particularly in China, have high Mg/Li ratios (> 8 and some even over 1000), resulting in difficulty in the lithium recovery which limits their utilization in a large scale.^[10] Some processes have been developed for lithium recovery from this kind of brines in China. One of typical processes is to converse MgCl_2 to MgO by spray drying at about $800\text{ }^\circ\text{C}$ and followed by the separation of lithium from MgO using multi-stage selective leaching and then precipitation. Apparently, this process is energy and water consuming and also generates a large amount of hazardous HCl gas for treatment.^[11]

Solvent extraction method has its advantages in lithium recovery from high magnesium content brines due to its low chemical consumption, low waste generation, recyclable extractants and simple equipment requirement.^[8, 9, 12] The solvent extraction system containing tributyl phosphate (TBP) and FeCl_3 is the most extensively studied and the most promising system for lithium recovery from Mg-rich brines.^[10, 13, 14] This system has high lithium extraction ($> 70\%$ in a single contact) and high lithium selectivity over magnesium ($\text{SF}_{\text{Li/Mg}} > 300$). During lithium extraction, HCl has to be added to this system to prevent the

hydrolysis of FeCl_3 from the loss of Fe and to achieve the stripping of Li^+ in the stripping process.^[15, 16] However, Li^+ and H^+ have a competitive relationship in the extraction process, the amount of H^+ added will significantly affect the extraction behavior of Li^+ . Zhou et al. compared the competitive extraction sequences for several cations using TBP/ FeCl_3 in MIBK as the extractant.^[10] It clarifies that H^+ is stronger than other ions and is preferentially extracted into the organic phase. However, the quantitative relationship between Li^+ and H^+ has not been reported. Therefore, detailed study on the competition mechanism between the extraction of Li^+ and H^+ is important to optimize the process conditions for Li recovery and develop more efficient solvent systems.

In this study, spectroscopic characterizations and slope analysis were used to study the structure of the complex in the loaded organic phase, apparent equilibrium constants were determined for the extraction of Li^+ and H^+ , and the extraction competition between Li^+ and H^+ with the system of TBP/ FeCl_3 was discussed.

Experimental

Reagents and solution preparation

LiCl (purity > 97%), MgCl_2 (purity > 99%), FeCl_3 (purity > 98%) and HCl (36–38 wt%) were analytical reagents purchased from Beijing Chemical Works. The simulated feed solutions were prepared by dissolving chloride salts into de-ionized water and adding desired HCl for extraction tests. TBP (purity > 98.5%) as the extractant was provided by Shanghai Rare Earth Chemical Co., Ltd., isotridecanol (purity > 99%) as the phase modifier and Exxsol D110 (>98%

aliphatic hydrocarbon) as the diluent were the products of US ExxonMobil Chemical Company. Organic solutions were prepared by diluting TBP and isotridecanol with a volume ratio of 2:1 using Exxsol D110 in to desired concentrations. $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (purity > 99.5%) , K_2SO_4 (purity > 99%) and NaOH used for acid titration were analytical reagents purchased from Beijing reagents company. AgNO_3 (purity > 99.7%) and K_2CrO_4 (purity > 99.5%) used for Cl^- concentration determination were analytical grade also purchased from Beijing reagents company.

Extraction procedures

The feed solutions containing MgCl_2 , FeCl_3 , HCl and/or LiCl were mixed with the organic solutions consisting of TBP, isotridecanol and Exxsol D110 in hexagonal jars using a mechanic shaker (HD-100B, Jintan Yineng, China) at an A/O ratio of 1:1 and 25 ± 2 °C for 20 min. After reach equilibriums, the mixtures were settled for 30 min for phase separation. Aqueous samples were taken from the bottom phases using a syringe with a long needle extension for the determinations of metal concentrations and metals in the organic phases were calculated by mass balance.

Sample analysis

The concentrations of Li^+ , Mg^{2+} and Fe(III) in the aqueous samples were determined after dilution to a proper concentration range by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300V, Pekin-Elmer, USA). The H^+ concentration was

determined by titration using a standard NaOH solution with a masking solution containing saturated K_2SO_4 and 0.2 mol/L $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Masking solution was used to eliminate the effect of iron(III) hydrolysis by producing extra H^+ .^[17, 18] A composite pH probe (Ross Sure-Flow 8172BN, Orion, US) connected with a pH meter (PHSJ-6L, INESA, Shanghai, China) was used to monitor aqueous pH. The Cl^- concentration was determined by AgNO_3 titration using K_2CrO_4 as the indicator. The spectrum characterization of loaded organic were performed on a UV–visible spectrophotometer (9100b, Labtech, Beijing), a laser Raman spectrometer (LabRAM HR800, Horiba Jobin Yvon, France) and a Fourier transform IR spectrometer (Tensor 2, Bruker, Germany).

Results and Discussion

Spectroscopic characterization of the loaded organic

The loaded TBP organic samples containing various Fe(III), Li^+ and H^+ were prepared by contacting 1.0 mol/L TBP/toluene with the feed solutions containing 0.5 mol/L LiCl , 0.5 mol/L FeCl_3 and 3 mol/L MgCl_2 under various HCl concentrations, and subsequently, toluene being evaporated. UV-visible spectra of the loaded organic samples were measured with results presented in Figure 1. Three main absorption peaks appeared at 532 nm, 619 nm and 688 nm which well matched the characteristic absorption peaks of $[\text{FeCl}_4]^-$,^[19, 20] suggesting that Fe(III) presented in the organic was in the form of $[\text{FeCl}_4]^-$. Raman spectra of these organic samples (Figure 2) showed distinct exhibiting bands at 111, 333 and 384 cm^{-1} which also were attributed to the vibrations of $[\text{FeCl}_4]^-$,^[21-23] again suggesting that Fe(III) presented

in the organic was in the form of $[\text{FeCl}_4]^-$. In addition, the intensity of both UV-Vis spectra and the Raman spectra increased with the increase in HCl concentration, meaning that HCl enhanced the extraction of Fe(III) which increased $[\text{FeCl}_4]^-$ concentration in the organic. As very small amount of Mg^{2+} could be extracted by the organic system, the charge balance of $[\text{FeCl}_4]^-$ was dominantly by H^+ and Li^+ . Therefore, both extraction reactions were happened simultaneously as shown in equations (1) and (2), with 2 mol TBP involved being verified in the following tests.

where the top bar represents the organic phase. These reaction mechanisms were in agreement with that studied by W. Xiang et al.^[24] Clearly, the extractions of H^+ and Li^+ have close relationship. It is important to elucidate this relationship for lithium extraction optimization.

Figure 1. UV-visible spectra of the loaded organic phase.

Figure 2. Raman spectra of the loaded organic phase.

Two different solute solutions were extracted (6mol/L LiCl and 6mol/L HCl), each of which contained different cation but had the same concentration of Cl^- . For the two solutions, 0.5mol/L FeCl_3 was applied as the coextracting agent along with 1 mol/L TBP as the extractant. FTIR spectra of pure TBP and loaded with HFeCl_4 and LiFeCl_4 were measured and their second derivatives were calculated as shown in Figure 3. It was observed that a strong peak appeared at 1284 cm^{-1} with pure TBP which could be attributed to the P=O group. The peak shifted to 1274 cm^{-1} when LiFeCl_4 was loaded and shifted further to 1268 cm^{-1} when loaded with HFeCl_4 . It has been investigated that P=O bond of TBP could be weakened to decrease its vibration frequency when cationic ions were extracted as these ions combined with the negative-charge rich O atom decreased the bonding energy of P=O . As a result, the FTIR absorption will shift towards short wavelength number side.^[25] When Li^+ was extracted with TBP, the molecules of TBP could partially substitute the H_2O molecules in the complex species of $\text{Li}(\text{H}_2\text{O})_4^+$ in aqueous phase by P=O group binding with Li^+ ,^[26] and then a negative

charged group of FeCl_4^- was combined to balance the electronic charge. The remaining H_2O molecules in the extracted species could provide negative charge, reducing the effect of Li^+ extraction on the $\text{P}=\text{O}$ bond.^[20] It is suggested that no H_2O molecule will present in the H^+ extracted species and the effect of H^+ extraction on $\text{P}=\text{O}$ will be stronger than that of Li^+ . Therefore, HFeCl_4 extraction shifted the $\text{P}=\text{O}$ absorption more to the short wavelength number at FTIP spectrum than that of LiFeCl_4 . It also suggested that H^+ extraction will be stronger than that of Li^+ . This conclusion was well proved by the following tests. It is very important to control proper HCl concentration to maximize Li extraction.

Figure 3. Second derivative FTIR spectra of TBP and its loading with LiCl and HCl from aqueous solutions containing 6 mol/L LiCl and 6 mol/L HCl in the presence of 0.7 mol/L FeCl_3 .

The extraction of H^+ with TBP and its mechanism study

The extractions of H^+ using TBP with and without the presence of Fe(III) are very different. Fe(III) as a co-extraction ion could significantly improve the extraction efficiency.^[15, 27, 28]

The extraction of H^+ from a solution containing 0.1 mol/L HCl, 3.3 mol/L $MgCl_2$ and 0.1 mol/L $FeCl_3$ with TBP was studied as shown in Figure 4. The extraction efficiency was 82.29% at 1.0 mol/L TBP, and further reached 91.69% at 3.0 mol/L. The distribution ratio of H^+ increased from 4.9 to 11.5 accordingly. It is obvious that H^+ was strongly extracted with TBP as co-extracted with Fe(III).

Figure 4. H^+ extraction with various TBP concentrations in the presence of Fe(III).

Plotting the logarithm of D_H against the logarithms of Fe(III) and TBP concentrations while maintain other factors approximately constant gives out straight lines with a slop near 1 (Figure 5) and 2 (Figure 6), respectively. These results suggest that one mol H^+ extraction requires one mol Fe(III) and two mol TBP which further proves that the extraction reaction of H^+ follows Equation (1). Thus, the apparent equilibrium constant K_H of H^+ extraction in the presence of Fe(III) can be expressed as Equation (3).

$$K_H = \frac{[HFeCl_4 \cdot 2TBP]}{[H^+][Fe^{3+}][Cl^-]^4[TBP]^2} = \frac{D_H}{[Fe^{3+}][Cl^-]^4[TBP]^2} \quad (3)$$

In Equation (3), $[\text{Fe(III)}]$ can be replaced by $\frac{[\text{Fe}]_{\text{tot}}}{\sum_{i=0}^4 K_i [\text{Cl}^-]^i}$, $[\text{Fe}]_{\text{tot}}$ represents the total concentration of Fe(III), which can form four different types of complexes of FeCl^{2+} , FeCl_2^+ , FeCl_3 and FeCl_4^- and their forming constants are $K_1 = \frac{[\text{FeCl}^{2+}]_a}{[\text{Fe}^{3+}]_a [\text{Cl}^-]_a}$, $K_2 = \frac{[\text{FeCl}_2^+]_a}{[\text{Fe}^{3+}]_a [\text{Cl}^-]_a^2}$, $K_3 = \frac{[\text{FeCl}_3]_a}{[\text{Fe}^{3+}]_a [\text{Cl}^-]_a^3}$, and $K_4 = \frac{[\text{FeCl}_4^-]_a}{[\text{Fe}^{3+}]_a [\text{Cl}^-]_a^4}$, respectively.^[29] Therefore, Equation (3) can also be written as Equation (4).

$$K_H = \frac{D_H \left(\sum_{i=0}^4 K_i [\text{Cl}^-]^i \right)}{[\text{Fe}]_{\text{tot}} [\text{Cl}^-]^4 [\text{TBP}]^2} \quad (4)$$

K_H was calculated to be about 799.8 based on Equation (4). It is indicated that the extraction ability of H^+ is very strong for the large apparent equilibrium constant and almost all H^+ extracted with TBP system was in the form of HFeCl_4 . This is in very good agreement with the conclusion reached by spectrum characterization.

Figure 5. Plot of $\log D_H$ against total concentration of Fe in solution

Figure 6. Plot of $\log D_H$ against TBP concentration in the presence of Fe(III)

([HCl]=0.1mol/L, [Cl⁻]=7mol/L and

[TBP]=0.5mol/L).

([HCl]=0.1mol/L, [Cl⁻]=7mol/L and

[Fe³⁺]=0.1mol/L).

The extraction of Li⁺ with TBP and its mechanism study

Significant Li⁺ extraction with TBP only occurs in the presence of Fe(III). In order to inhibit Fe(III) hydrolysis, HCl has to be added in the system. Therefore, Li⁺ extraction with TBP through the co-extraction of Fe(III) requires some HCl to maintain Fe(III) stable in the system. To reduce HCl effect on the Li⁺ extraction, possibly small amount of HCl was used to study the Li⁺ extraction. Figure 7 shows the Li⁺ extraction at various TBP concentrations from a solution containing 0.1 mol/L LiCl, 0.1 mol/L FeCl₃, 3.3 mol/L MgCl₂ and 0.01 mol/L HCl. The extraction of Li⁺ increased rapidly from 12% to 53% with TBP concentration increased from 0.5 mol/L to 2.0 mol/L, and further slightly increased to 54% at 3.0 mol/L TBP. The distribution ratio were 1.08 and 1.17 at TBP concentration of 2.0 mol/L and 3.0 mol/L, respectively. Compared to H⁺ extraction obtained in Figure 4, it is obvious that Li⁺ extraction is much weaker than H⁺ extraction in the presence of Fe(III), meaning that extraction reaction (1) is much stronger than extraction reaction (2). The extraction of H⁺ strongly competes with that of Li⁺.

Figure 7. Li⁺ extraction with various TBP concentrations in the presence of Fe(III).

Maintaining other factors approximately unchanged, plotting the logarithm of D_{Li} against the logarithm of Fe(III) and TBP concentrations also gives out straight lines with slopes near 1 and 2, respectively (Figures 8 and 9), indicating that one mol of Li⁺ extraction requires one mol Fe(III) and two mol TBP. These results further verified the Li⁺ extraction mechanism through reaction Equation (2) with K_{Li} expressed in Equation (5).

$$K_{Li} = \frac{[\overline{LiFeCl_4 \cdot 2TBP}]}{[Li^+][Fe^{3+}][Cl^-]^4[TBP]^2} = \frac{D_{Li}}{[Fe^{3+}][Cl^-]^4[TBP]^2} \quad (5)$$

where K_{Li} is apparent equilibrium constant of Li⁺ extraction in the presence of Fe(III).

Substituting $[Fe^{3+}] = [Fe]_{tot} / \sum_{i=0}^4 K_i [Cl^-]^i$ into Equation (5), Equation (6) was obtained.

$$K_{Li} = \frac{D_{Li} \left(\sum_{i=0}^4 K_i [Cl^-]^i \right)}{[Fe]_{tot} [Cl^-]^4 [TBP]^2} \quad (6)$$

K_{Li} was calculated to be about 120.6 based on Equation (6). Compared with K_H of 799.8 which is almost 6 times larger than K_{Li} , H⁺ extraction is much stronger than that of Li⁺. It

suggests that HCl can significantly affect Li^+ extraction with TBP and well control HCl concentration for lithium recovery is necessary.

Figure 8. Plot of $\log D_{\text{Li}}$ against total

concentration of Fe in solution

($[\text{LiCl}] = 0.1 \text{ mol/L}$, $[\text{Cl}^-] = 7 \text{ mol/L}$,

$[\text{HCl}] = 0.01 \text{ mol/L}$ and $[\text{TBP}] = 0.5 \text{ mol/L}$).

Figure 9. Plot of $\log D_{\text{Li}}$ against TBP

concentration in the presence of Fe(III)

($[\text{LiCl}] = 0.1 \text{ mol/L}$, $[\text{Cl}^-] = 7 \text{ mol/L}$,

$[\text{HCl}] = 0.01 \text{ mol/L}$ and $[\text{Fe}^{3+}] = 0.1 \text{ mol/L}$).

Competitive extraction of Li^+ and H^+ with TBP

Li^+ and H^+ were simultaneously extracted by TBP in the presence of Fe(III). Simultaneous extraction of H^+ and Li^+ from solutions containing various HCl concentrations (Figure 10) and various LiCl concentrations (Figure 11) in the presence of 0.1 mol/L FeCl_3 and 3.3 mol/L MgCl_2 with 1.5 mol/L TBP was studied. The results also showed significantly stronger extraction of H^+ than that of Li^+ . Both Li^+ and H^+ extractions decreased with the increase in HCl and LiCl concentrations. This is due to the decreased organic loading capacity with the increase in their concentrations. The extraction of Li^+ decreased rapidly from 68.03% to 15.88%

when HCl concentration increased from 0.05 mol/L to 0.3 mol/L (Figure 10), indicating that HCl concentration has significantly effect on the lithium extraction. However, with the increase in LiCl concentration, the extraction of H^+ decreased relatively slowly from 87.18% to 66.34% (Figure 11). Under various HCl and LiCl concentrations, although the extraction of Li^+ and H^+ changed much, D_H/D_{Li} was slightly changed in a range of 4-6 as shown in Figures 10 and 11. This indicates that H^+ extraction is approximately 4-6 times stronger than that of Li^+ when they were simultaneously extracted. Based on Equations (6) and (8), D_H/D_{Li} should equal K_H/K_{Li} , being about 6.6, which is close to the above range, thus the accuracy of apparent equilibrium constant was verified.

Figure 10. Effect of HCl concentration on the extraction of Li^+ and H^+ (0.1 mol/L LiCl).

Figure 11. Effect of LiCl concentration on the extraction of Li^+ and H^+ (0.1 mol/L HCl).

Conclusions

The extraction of H^+ and Li^+ with TBP in the presence of Fe(III) in the form of $H[FeCl_4]$ and $Li[FeCl_4]$, respectively. Their extractions compete with each other to combine with $[FeCl_4]^-$ to balance charge in the organic phase. Their extracted complex species are $HFeCl_4 \cdot 2TBP$ and

LiFeCl₄·2TBP for the extraction of H⁺ and Li⁺, respectively. H⁺ extraction with TBP is much stronger than that of Li⁺ with apparent equilibrium constants $K_H=799.8$ and $K_{Li}=120.6$. D_H/D_{Li} in the range of 4-6 were obtained under various HCl and LiCl concentrations when they were simultaneously extracted showing that H⁺ extraction is 4-6 times stronger than that of Li⁺. Since the ratio of K_H/K_{Li} is close to the above range, the accuracy of the apparent equilibrium constant is verified. It is suggested that lithium recovery can be maximized if HCl concentration is controlled possibly smaller and the loaded lithium can be stripped at increased HCl concentration using H⁺ extraction to replace Li⁺ extraction.

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