

Extraction of Lithium from Brine Containing High Concentration of Magnesium by Tri-*n*-Butyl Phosphate Dissolved in Kerosene

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Abstract Tri-*n*-butyl phosphate (TBP) dissolved in kerosene was chosen as extractant for lithium from a model brine having high magnesium-to-lithium ratio and ferric chloride was added to the system. The influences of contact time, concentration of the extractant, concentrations of some salts (Mg^{2+} , Na^+ , K^+) in the solution, acidity of hydrochloric acid and extraction temperature on the extraction of lithium with TBP-kerosene system were studied. The suitable extraction conditions were found to be: contact time not any less than 20 min; at 20—25 °C; $[Fe^{3+}]/[Li^+]$ about 1.5—2.0; TBP concentration 50%—70%; $[MgCl_2]$ exceeding $3 \text{ mol} \cdot L^{-1}$; pH about 2; while most sodium and potassium salts in the aqueous phase should be removed before the extraction.

Keywords lithium, solvent extraction, tri-*n*-butyl phosphate, ferric chloride

1 INTRODUCTION

Lithium is one of the rare elements. During recent years, metallic lithium and various kinds of lithium compounds have become important materials in a wide variety of applications such as ceramics, dry batteries, absorption refrigerants, medicines. It is expected that the future demand for metallic lithium and lithium compounds will expand to a large extent especially in the fields of large-capacity batteries, aluminum-based alloys and fuels for nuclear fusion-type reactors.

Crown ethers that have specific structures can strongly and selectively complex lithium cations^[1-2]; experimental achievements have been discussed, but there is no industrial application reported thus far. It is necessary to develop new industry-applicable extractants at present.

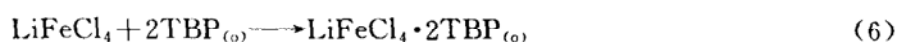
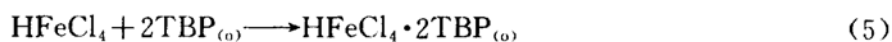
Tri-*n*-butyl phosphate (TBP) has always been an important extractant widely used in many extraction processes. The combination of TBP and β -diketone^[3] has been found to bring about a synergetic effect on the extraction of lithium. For example, lithium can be extracted by TBP-thenoyltrifluoroacetone (TTA) better than by TBP alone^[4]. Lithium can also be synergetically extracted with a mixture of TBP and organophosphorous compounds such as di-2-ethylhexylphosphoric acid (D2EHPA) or 2-ethylhexyl phosphonic acid 2-ethylhexyl ester (MEHPA)^[5]. J. R. Neille, *et al.*^[6] proposed the employment of 20% TBP-80% diisobutyl ketone as the organic solvent to extract lithium from concentrated brine in the presence of $FeCl_3$. The ferric salt reacts with the lithium salt, *e. g.* lithium chloride, present in the liquid to form a compound which then can be extracted from the liquid. The lithium is then separated from the compound in the organic phase and the ferric salt and the organic

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solvent are recycled to the process. This method, however, has some disadvantages. For example, diisobutyl ketone is expensive besides being considerably high in water solubility, and lithium values were recovered in a comparatively low percentage.

TBP-kerosene is a good extraction system to recover lithium from brine with high concentration of MgCl_2 . V. I. Levin, *et al.*^[7] and Sh. Q. Huang^[8] suggested the extraction mechanism of this system be as follows



In this work, TBP-kerosene system was used as the organic solvent in the presence of FeCl_3 and the suitable conditions for the extraction were determined through studies on the influences of certain parameters on the solvent extraction of lithium from a model brine with high magnesium content.

2 EXPERIMENTAL

2.1 Reagents and solutions

TBP, analytical reagent grade, supplied by Tianjin Chemical Reagent No. 1 Factory. Hydrogenated kerosene, provided by Jinzhou Oil Refinery, Liaoning Province, washed twice with 20% (vol) H_2SO_4 to remove aromatics and then with distilled water several times. Other inorganic chemicals, supplied by Xinhua Chemical Plant, Beijing, as analytical reagent grade.

Appropriate amounts of $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in distilled water to form the model initial solution with concentration of LiCl at $0.1 \text{ mol} \cdot \text{L}^{-1}$.

2.2 Procedure

Appropriate volumes of the aqueous and organic phases with known concentrations were introduced into 60ml stoppered flasks, immersed in a thermostatic water bath (Model HZS-D) and mechanically shaken for 20 minutes under isothermal conditions. Once the two phases were separated, samples were taken and the concentrations of lithium were determined. The lithium concentration in the aqueous phase was analyzed with a polarized Zeeman atomic absorption spectrophotometer (Model 180-80) at a wavelength of 670.8nm. The content of lithium in the loaded organic phase was also measured after it was stripped with $6 \text{ mol} \cdot \text{L}^{-1}$ HCl . The mass balance for the metal was proved within $\pm 5\%$ in the extraction-stripping procedure. The distribution ratio of lithium is defined as follows

$$D(\text{Li}) = [\text{Li}^+]_{(o)} / [\text{Li}^+]_{(a)} \quad (7)$$

3 RESULTS AND DISCUSSIONS

3.1 Determination of contact time

In this experiment, a 50%TBP-50%kerosene extractant was employed as the organic

phase. In the aqueous phase, the concentrations of LiCl and FeCl₃ were 0.1 mol·L⁻¹ and 0.2 mol·L⁻¹, respectively, and MgCl₂ was saturated. From Fig. 1, it can be found that the equilibrium time is very short. The distribution ratio of lithium becomes approximately constant after about 8 minutes. According to the change of color in the aqueous phase from saffron to transparent, it also can be seen that Fe³⁺ has been extracted completely after 15 minutes. 20 minutes was adopted as the contact time in the subsequent experiments.

3.2 Effect of temperature

From Fig. 2, it can be observed that temperature influences the extraction of lithium quite significantly, and the distribution ratio of lithium decreases almost linearly with rises in temperature. The result shows that the extraction process of lithium is an exothermic reaction. The lower the temperature is, the more readily lithium would be extracted. In practice, most extraction processes are carried out at 20—25°C.

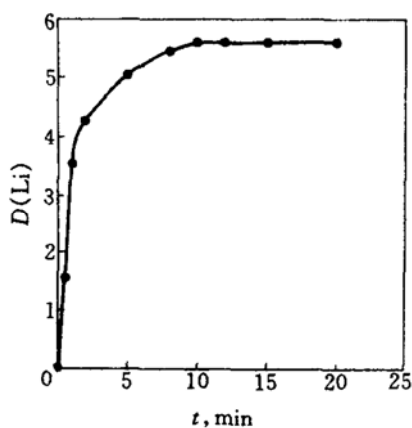


Figure 1 Effect of extraction time on the distribution ratio of lithium

Organic Phase: 50% TBP-50% kerosene;
 Aqueous Phase: [LiCl]=0.1 mol·L⁻¹,
 [FeCl₃]=0.2 mol·L⁻¹,
 [MgCl₂] is saturated, pH=2—3,
 Color is saffron;
 O/A=1:1; Temperature is 20°C

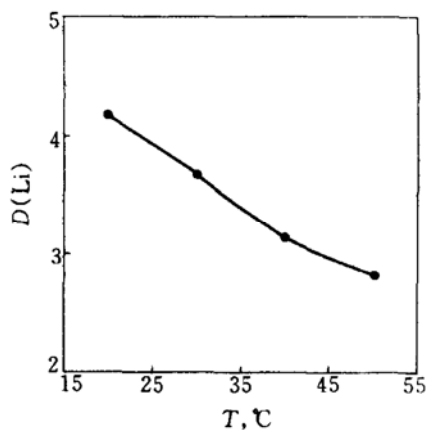


Figure 2 Effect of temperature on the distribution ratio of lithium

Organic Phase: 50% TBP-50% kerosene;
 Aqueous Phase: [LiCl]=0.1 mol·L⁻¹,
 [FeCl₃]=0.15 mol·L⁻¹,
 [MgCl₂]=4.0 mol·L⁻¹,
 pH=2;
 O/A=1:1

3.3 Effect of [Fe³⁺]/[Li⁺]

Fig. 3 shows the effect of [Fe³⁺]/[Li⁺] on the distribution ratio of lithium. *D*(Li) increases gradually as [Fe³⁺]/[Li⁺] increases and approaches constant when [Fe³⁺]/[Li⁺] reaches 1.5. However, the formation of a third phase is found when [Fe³⁺]/[Li⁺] exceeds 2.0. [Fe³⁺]/[Li⁺] had better be limited in the range from 1.5 to 2.0 to avoid the formation of the third phase due to high concentration of Fe³⁺ in the organic phase.

3.4 Effect of MgCl₂ concentration

In our earlier experiments, it has been found that high concentration of MgCl₂ can pose significant effects on the extraction of lithium, as shown in Fig. 4, with the salting-out effect indicated. In the aqueous phase, large quantities of Cl⁻ present tend to promote the reaction of lithium chloride with the ferric salt to form a compound extractable by the TBP-kerosene

system. To acquire a high extraction efficiency of lithium, $[\text{MgCl}_2]$ should be kept above $3.0 \text{ mol}\cdot\text{L}^{-1}$.

There are many kinds of brines in China that contain high content of magnesium. The employment of a TBP-kerosene system as extractant may possibly be a good approach to recover lithium from such brines.

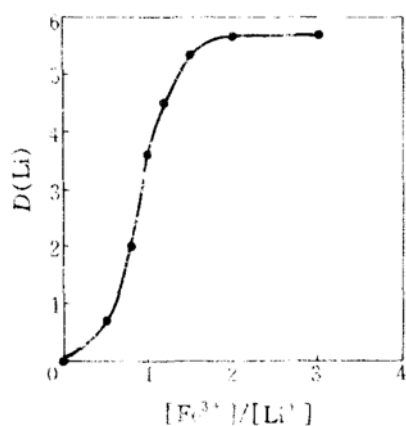


Figure 3 Effect of $[\text{Fe}^{3+}]$ on the distribution ratio of lithium

Organic Phase: 50%TBP-50%kerosene;
Aqueous Phase: $[\text{LiCl}]=0.1 \text{ mol}\cdot\text{L}^{-1}$,
 MgCl_2 is saturated, $\text{pH}=2$;
 $O/A=1:1$; Temperature is 20°C

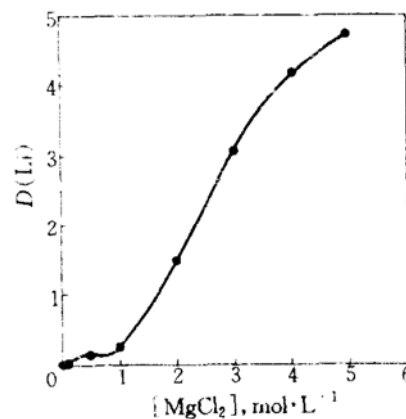


Figure 4 Effect of $[\text{MgCl}_2]$ on the distribution ratio of lithium

Organic Phase: 50%TBP-50%kerosene;
Aqueous Phase: $[\text{LiCl}]=0.1 \text{ mol}\cdot\text{L}^{-1}$,
 $[\text{FeCl}_3]=0.15 \text{ mol}\cdot\text{L}^{-1}$, $\text{pH}=2$;
 $O/A=1:1$; Temperature is 20°C

3.5 Effect of TBP concentration

To acquire a suitable extraction condition, it is necessary to add an appropriate diluent to regulate the physical properties of the organic phase, which have great influence on the mixing and separation process in the extraction system. Since the viscosity of TBP ($3.32 \times 10^{-3} \text{ Pa}\cdot\text{s}$) is rather high and its density is very close to that of water, kerosene has to be added. Such that the extraction system may reach equilibrium more quickly and readily. Fig. 5 shows 50%—70%TBP/50%—30%kerosene is a suitable ratio.

3.6 Effect of $[\text{Na}^+]$ and $[\text{K}^+]$

Na^+ and K^+ , monovalent cations, are competitive extractives with lithium. As shown in Fig. 6, the competitive extractability of Na^+ is stronger than that of K^+ . These findings suggest that most sodium and potassium salts should be removed before extraction operations.

3.7 Effect of the acidity of the aqueous phase

Fig. 7 indicates that $D(\text{Li})$ tends to decrease with higher initial $[\text{H}^+]$ of the aqueous phase. Lower initial $[\text{H}^+]$ appears to be favorable to the extraction of lithium. On the contrary, high concentration hydrochloric acid can be used to back-extract lithium from the organic phase in which lithium is enriched. Fig. 8 also indicates the effect of H^+ on the extraction of lithium. The peak of the extraction curve of H^+ appears at $0.1116 \text{ mol}\cdot\text{L}^{-1}$ while

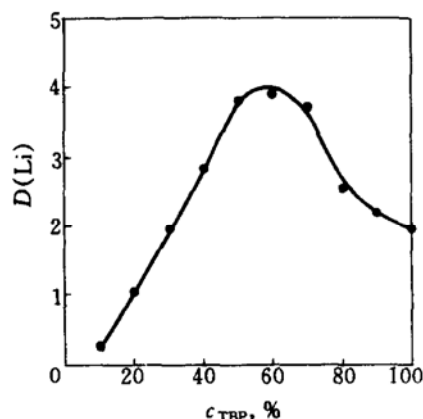


Figure 5 Effect of TBP concentration on the distribution ratio of lithium

Organic Phase: TBP-kerosene;
 Aqueous Phase: $[\text{LiCl}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$,
 $[\text{FeCl}_3] = 0.15 \text{ mol} \cdot \text{L}^{-1}$,
 $[\text{MgCl}_2] = 4 \text{ mol} \cdot \text{L}^{-1}$, $\text{pH} = 2-3$,
 $O/A = 1:1$; Temperature is 25°C

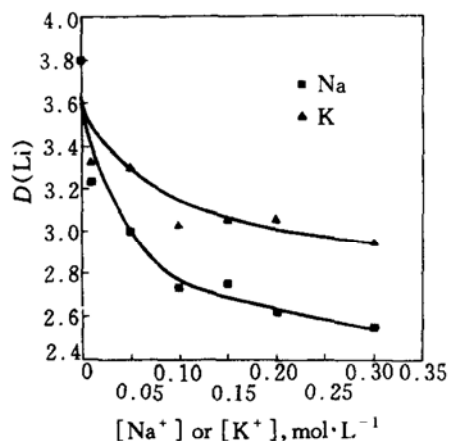
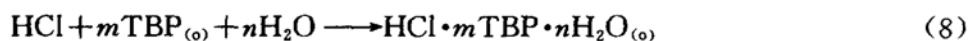


Figure 6 Effect of $[\text{Na}^+]$ and $[\text{K}^+]$ on the distribution ratio of lithium

Organic Phase: 50% TBP-50% kerosene;
 Aqueous Phase: $[\text{LiCl}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$,
 $[\text{FeCl}_3] = 0.15 \text{ mol} \cdot \text{L}^{-1}$,
 $[\text{MgCl}_2] = 4 \text{ mol} \cdot \text{L}^{-1}$, $\text{pH} = 2$,
 $O/A = 1:1$; Temperature is 25°C

the extraction of Li^+ falls sharply at that acidity. As shown by Eqs.(5) and (6), the extraction efficiency of Fe^{3+} is the sum of H^+ and Li^+ extracted. The experimental data show that $[\text{H}^+] + [\text{Li}^+] = 0.1429 \text{ mol} \cdot \text{L}^{-1}$ which equates approximately to the total concentration of Fe^{3+} ($0.15 \text{ mol} \cdot \text{L}^{-1}$) at the peak of $E(\text{H}^+)$. This means that Fe^{3+} has been readily extracted. The color change of the aqueous phase from saffron to transparent also suggests that most Fe^{3+} should be transferred to the organic phase.

When Fe^{3+} has been extracted to a great extent, the reactions in the extraction system will not be described with Eqs.(5) or (6). Instead, the following equation will be applicable



At this time, $[\text{H}^+]_{(o)}$ is still increasing with the initial $[\text{H}^+]_{(a)}$ due to the extraction of HCl by TBP.

Considering that the hydrolysis of the ferric salt must be inhibited, the pH of the model solution should be kept at about 2.

4 CONCLUSIONS

Lithium chloride can be selectively extracted from a model brine that has high magnesium content with a TBP-kerosene system in the presence of FeCl_3 . The suitable extraction conditions are as follows: contact time, $> 20 \text{ min}$; temperature, around $20-25^\circ\text{C}$; $[\text{Fe}^{3+}]/[\text{Li}^+]$, 1.5-2.0; TBP concentration, 50%-70%; $[\text{MgCl}_2]$, $> 3 \text{ mol} \cdot \text{L}^{-1}$; pH, about 2; whereas most sodium and potassium salts in the model brine must be removed before the extraction.

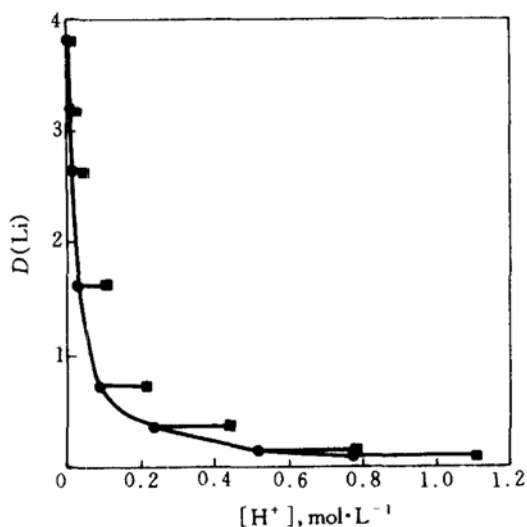


Figure 7 Effect of aqueous phase acidity on the distribution ratio of lithium

Organic Phase: 50% TBP-50% kerosene;
 Aqueous Phase: $[\text{LiCl}] = 0.1 \text{ mol}\cdot\text{L}^{-1}$,
 $[\text{FeCl}_3] = 0.15 \text{ mol}\cdot\text{L}^{-1}$,
 $[\text{MgCl}_2] = 4 \text{ mol}\cdot\text{L}^{-1}$;
 $O/A = 1:1$; Temperature is 25°C ;
 ■ initial aqueous phase $[\text{H}^+]$;
 ● equilibrium aqueous phase $[\text{H}^+]$

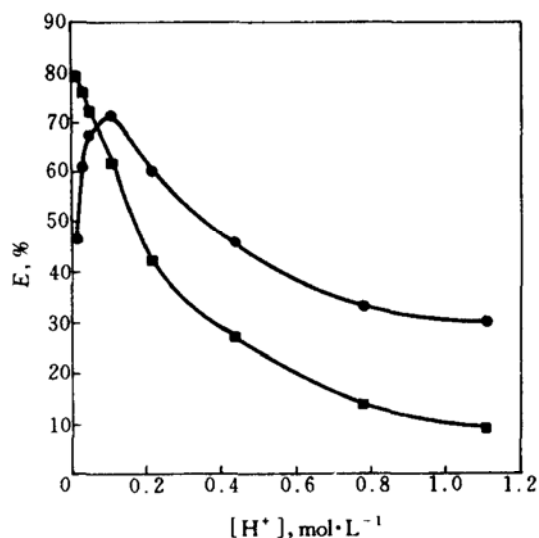


Figure 8 Effect of initial acidity of aqueous phase on the extraction efficiency of H^+ and Li^+

Organic Phase: 50% TBP-50% kerosene;
 Aqueous Phase: $[\text{LiCl}] = 0.1 \text{ mol}\cdot\text{L}^{-1}$,
 $[\text{FeCl}_3] = 0.15 \text{ mol}\cdot\text{L}^{-1}$,
 $[\text{MgCl}_2] = 4 \text{ mol}\cdot\text{L}^{-1}$;
 $O/A = 1:1$; Temperature is 25°C ;
 ● extraction efficiency of H^+ ;
 ■ extraction efficiency of Li^+

NOMENCLATURE

A volume of aqueous phase
 c_{TBP} TBP concentration
 $D(\text{Li})$ distribution ratio of lithium
 E extraction efficiency, %
 m, n unknown parameter
 O volume of organic phase
 T temperature, $^\circ\text{C}$
 t time, min

Subscript

o organic phase
 a aqueous phase

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