

## Extraction Equilibria of Lithium with Tributyl Phosphate in Kerosene and FeCl<sub>3</sub>

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**ABSTRACT:** To explore the feasibility of extracting lithium metal from brine sources, three salts, MgCl<sub>2</sub>, CaCl<sub>2</sub>, and NH<sub>4</sub>Cl, were selected as chloride sources, and the extraction equilibrium of lithium was studied with tributyl phosphate (TBP) in kerosene and FeCl<sub>3</sub> as a coextracting agent at different values of Fe/Li. The extraction mechanism for lithium with TBP in kerosene and FeCl<sub>3</sub> as a coextracting agent was investigated too. The results showed that the extraction of the lithium ion is a cation-exchange reaction, and the extraction of iron ion is the precondition of the extraction of lithium ion. All of the extractability of the iron ion increased with the chloride concentration with MgCl<sub>2</sub>, CaCl<sub>2</sub>, and NH<sub>4</sub>Cl as chloride sources, and the extraction capacity of lithium ion followed the sequence: MgCl<sub>2</sub> > CaCl<sub>2</sub> > NH<sub>4</sub>Cl, with recoveries from MgCl<sub>2</sub> as chloride sources being much higher than that for CaCl<sub>2</sub> and NH<sub>4</sub>Cl as chloride sources at all values of Fe/Li. There exists competitiveness between Li<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> when combined to TBP and FeCl<sub>3</sub> and a salting-out effect of three salts. MgCl<sub>2</sub> benefits from weaker competitiveness and a stronger salting-out effect than the other two. Choosing MgCl<sub>2</sub> as chloride sources at Fe/Li = 1.9 obtains the highest partition coefficient with TBP/kerosene as an extractant and FeCl<sub>3</sub> as a coextracting agent.

### INTRODUCTION

Lithium is an important rare element and is known as the promoting world process metal. As its lightest weight and chemical activity, lithium and some lithium metal compounds are greatly used in the fields of batteries, refrigerants, lubricants, controlled nuclear fusion reactions, and so forth.<sup>1,2</sup> The application of lithium and lithium compounds in nuclear energy and lithium ion batteries seems to be very important under the energy shortage conditions. Currently most lithium production comes from mining. Recent research has emphasized recovery from brine sources, such as adsorption by acid and sodium Amberlite,<sup>3</sup> extraction using supported liquid membranes,<sup>4</sup> the nanofiltration method,<sup>5</sup> adsorption on novel nanocrystal MnO<sub>2</sub>,<sup>6,7</sup> and so forth.

Liquid–liquid extraction is an economical, efficient, and environmentally friendly method for the separation of dilute solutions, including carboxylic acids, amino acids, amines, phenols, metal ions, and so forth. The extractive recovery of solutes from dilute aqueous solutions is receiving increasing attention.<sup>8–14</sup>

Liquid–liquid extraction has been widely studied as an attractive technology for recovering lithium from brine sources, which uses the specific affinity to achieve the purpose of extraction of lithium.<sup>15</sup> The most typical extraction system is tributyl phosphate (TBP)/kerosene–FeCl<sub>3</sub>,<sup>16,17</sup> which is very suitable for the brine sources of a high Mg/Li ratio. TBP is one of the most popular neutral organophosphorus extractants, and kerosene is a typical diluent. In this system FeCl<sub>3</sub> solution plays the role of a coextracting agent, which makes a great contribution for extracting lithium.

In this study, three salt solutions of MgCl<sub>2</sub>, CaCl<sub>2</sub>, and NH<sub>4</sub>Cl were selected as the agents which provide chloride sources. MgCl<sub>2</sub> and CaCl<sub>2</sub> are the most important components of brine sources. NH<sub>4</sub>Cl is the typical monovalent inorganic nonmetallic salt, and it is also regarded as a potential stripping agent. Meanwhile, the competitive effect of cations with the lithium

ion and salting-out effect of salts may affect the extraction effect of the lithium ion. The extraction equilibria of the lithium ions extracted by TBP in kerosene and FeCl<sub>3</sub> at different values of Fe/Li and the extraction mechanism were investigated.

### EXPERIMENTAL SECTION

**Materials.** The analytical reagents are as follows: LiCl from Beijing Yili Fine Chemical Co., Ltd. with a purity of > 97 %; FeCl<sub>3</sub> from Tianjin Yongda Chemical Reagent Co., Ltd. with a purity of > 99 %; MgCl<sub>2</sub> from Beijing Modern Eastern Finechemical Co., Ltd. with a purity of > 98 %; CaCl<sub>2</sub> from Beijing Chemical Reagent Plant with a purity of > 96 %, and NH<sub>4</sub>Cl from Beijing Modern Eastern Finechemical Co., Ltd. with a purity of > 99 %. The characteristics of the salt are presented in Table 1. TBP from the Beijing Chemical Reagent Plant is an analytical reagent with purity of > 99 wt %. The physical properties of the solvent obtained from the manufacturers are listed in Table 2.

**Methods.** All extraction experiments were conducted with 50 mL flasks at 25 ± 2 °C. Solvent (10 mL, 60 % TBP + 40 % kerosene) and 10 mL of the mixed solution of LiCl (0.2 mol·L<sup>-1</sup>), FeCl<sub>3</sub> (Fe/Li = 1.0, 1.3, 1.6, or 1.9), and MgCl<sub>2</sub>, CaCl<sub>2</sub>, or NH<sub>4</sub>Cl were added to each flask. The flask containing the mixture was shaken for about 10 min by hand and then was left to equilibrate and settle for 30 min, followed by separating the two phases. The preliminary experiments were carried out, and it was found that, in 10 min, equilibrium was reached in all experimental solution systems. An aqueous-phase sample was taken from the bottom layer (aqueous phase) using a syringe with a long needle for solute concentration analyses at 25 ± 2 °C.

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Table 1. Physical Properties of Salts

chemical	formula	avg. MW	solubility (g/100 g H <sub>2</sub> O, 20 °C)
lithium chloride	LiCl	42.39	78.5
ferric chloride	FeCl <sub>3</sub>	162.21	55.1
magnesium chloride	MgCl <sub>2</sub>	95.22	74.0
calcium chloride	CaCl <sub>2</sub>	110.98	740.0
ammonium chloride	NH <sub>4</sub> Cl	53.49	37.2

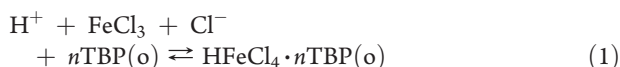
Table 2. Physical Properties of Extractants and Diluents

chemical	formula	avg. MW	$\rho$ / g·cm <sup>-3</sup>
TBP	OP(O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ) <sub>3</sub>	266.32	0.980
kerosene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8-16</sub> CH <sub>3</sub>	142.17–254.30	0.800

**Analysis.** The aqueous samples were analyzed for lithium ion concentration by using an optical atomic absorption spectrometer (Z-5000-AAS, Hitachi, Japan). The concentration of the lithium ion in the organic phase was calculated by the material balance. The preliminary experiment of stripping of the organic phase indicated that the deviation of calculated values of lithium ion concentrations was within  $\pm 3\%$ .

## RESULTS AND DISCUSSION

**Extraction Mechanism for Lithium with TBP in Kerosene and FeCl<sub>3</sub>.** As indicated in the introduction, TBP in kerosene plays a role as a typical extractant for lithium extraction, and FeCl<sub>3</sub> solution plays the role as a coextracting agent, which makes a great contribution for extracting lithium. The extraction mechanism of this typical system for lithium is shown as follows:



where the organic phase is denoted by the "o".

The reaction of eq 1 is an ion association reaction, which only occurs in a high concentration chloride ion environment. So MgCl<sub>2</sub>, CaCl<sub>2</sub>, and NH<sub>4</sub>Cl were selected as chloride sources. Equation 2 shows that the extraction of lithium ion is a cation-exchange reaction, from which we can know that the extraction of the iron ion is very important for lithium ion extraction.

**Extraction Behavior with MgCl<sub>2</sub> as Chloride Sources at Different Value of Fe/Li.** MgCl<sub>2</sub> is a typical salt and is very rich in brine sources. The effects of chloride ion concentrations and value of Fe/Li on the extraction behavior were investigated with TBP/kerosene as an extractant, FeCl<sub>3</sub> as a coextracting agent, and MgCl<sub>2</sub> as chloride sources, and the results are shown in Table 3 and Figure 1. It can be seen that the extractability ( $E = (C_o/C_0)$ ,  $C_o$ : equilibrium concentration of Fe in the organic phase,  $C_0$ : initial concentration of Fe in the aqueous phase) of the iron ion increased with the concentration of the chloride ion, and it reached 100% when the chloride ion concentration was 6 mol·L<sup>-1</sup> at all values of Fe/Li. Meanwhile, the partition coefficient ( $D = (C_o/C_a)$ ,  $C_o$ : equilibrium concentration of Li in the organic phase,  $C_a$ : equilibrium concentration of Li in aqueous phase) of lithium ion increased with the extractability of the iron

Table 3. Equilibrium Data for Lithium Solution with MgCl<sub>2</sub> as Chloride Sources at Different Values of Fe/Li

concentration of MgCl <sub>2</sub> mol·L <sup>-1</sup>	$E^a$ of Fe <sup>3+</sup> %	$E$ of Li <sup>+</sup> %	$D^b$ of Li <sup>+</sup>
Fe/Li = 1.0			
1	39.50	14.23	0.1659
2	93.36	44.55	0.8034
3	100.00	71.24	2.4771
4	100.00	78.44	3.6382
Fe/Li = 1.3			
1	30.70	18.05	0.2203
2	88.11	55.16	1.2303
3	100.00	80.65	4.1680
4	100.00	89.17	8.2336
Fe/Li = 1.6			
1	28.86	16.88	0.2031
2	83.62	56.68	1.3084
3	99.85	83.03	4.8928
4	100.00	90.27	9.2775
Fe/Li = 1.9			
1	24.93	25.95	0.3504
2	82.50	63.30	1.7248
3	99.34	83.59	5.0938
4	100.00	91.92	11.3762

<sup>a</sup>  $E = (C_o/C_0)$ , where  $C_o$  is the equilibrium concentration in the organic phase and  $C_0$  is the initial concentration in the aqueous phase. <sup>b</sup>  $D = (C_o/C_a)$ , where  $C_o$  is the equilibrium concentration in the organic phase and  $C_a$  is the equilibrium concentration in the aqueous phase.

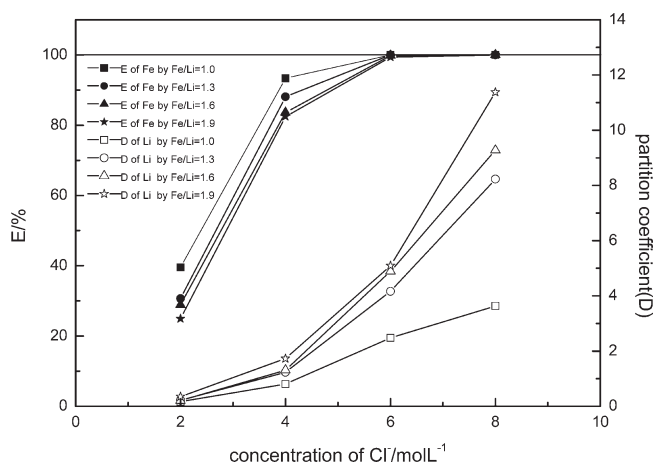


Figure 1. Equilibrium data for lithium solution with MgCl<sub>2</sub> as chloride sources at different values of Fe/Li.

ion and the concentration of the chloride ion, which indicates that the extraction of iron ion is the precondition of the extraction of lithium ion. Besides, Fe/Li = 1.9 can obtain the highest partition coefficient of the lithium ion with MgCl<sub>2</sub> as chloride sources.

**Extraction Behavior with CaCl<sub>2</sub> as Chloride Sources at Different Values of Fe/Li.** CaCl<sub>2</sub> is another typical salt which is one of the components of brine sources. As shown in Table 4 and

**Table 4.** Equilibrium Data for Lithium Solution with CaCl<sub>2</sub> as Chloride Sources at Different Values of Fe/Li

concentration of CaCl <sub>2</sub> mol·L <sup>-1</sup>	E of Fe <sup>3+</sup>		D of Li <sup>+</sup>
	%		
Fe/Li = 1.0			
1	0.88	16.00	0.1905
2	86.51	38.00	0.6129
3	98.34	41.98	0.7235
4	99.68	34.56	0.5281
Fe/Li = 1.3			
1	24.77	19.13	0.2366
2	87.44	37.22	0.5929
3	98.93	43.58	0.7724
4	99.52	41.83	0.7191
Fe/Li = 1.6			
1	33.64	30.12	0.4329
2	83.53	48.81	0.9535
3	99.22	53.88	1.1683
4	98.93	51.86	1.0773
Fe/Li = 1.9			
1	23.49	17.11	0.2064
2	83.13	41.21	0.7010
3	99.00	47.34	0.8990
4	98.83	46.62	0.8734

**Table 5.** Equilibrium Data for Lithium Solution with NH<sub>4</sub>Cl as Chloride Sources at Different Values of Fe/Li

concentration of NH <sub>4</sub> Cl mol·L <sup>-1</sup>	E of Fe <sup>3+</sup>		D of Li <sup>+</sup>
	%		
Fe/Li = 1.0			
2	3.93	13.4	0.1547
3	20.02	17.13	0.2067
4	33.46	18.84	0.2291
5	73.31	24.67	0.3275
Fe/Li = 1.3			
2	35.83	20.95	0.2650
3	51.26	23.81	0.3125
4	71.12	27.19	0.3734
5	83.94	30.67	0.4424
Fe/Li = 1.6			
2	27.95	18.78	0.2312
3	41.70	22.92	0.2974
4	58.44	27.53	0.3799
5	74.31	29.69	0.4222
Fe/Li = 1.9			
2	26.10	18.34	0.2249
3	35.46	22.05	0.2829
4	56.32	28.15	0.3918
5	67.38	32.02	0.4710

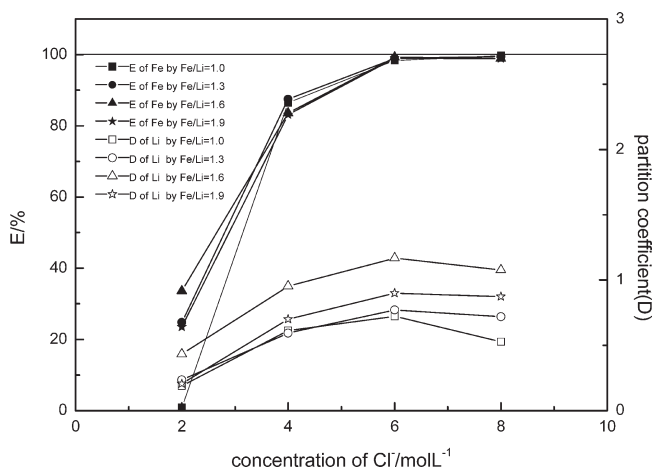
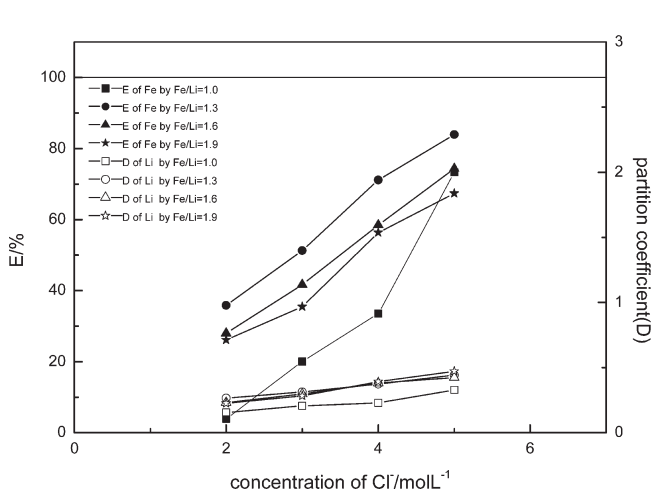
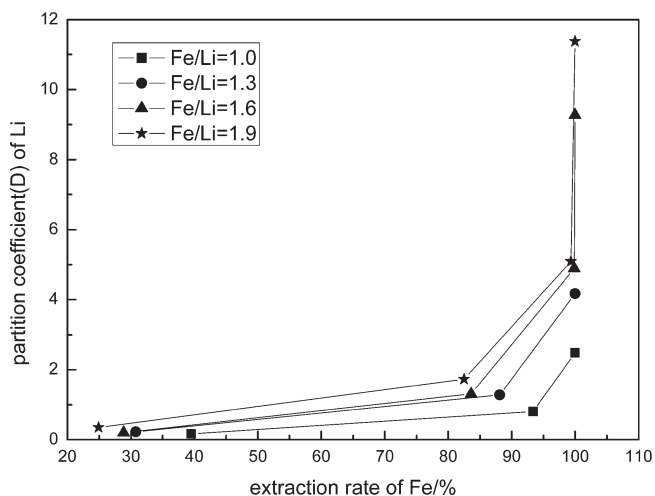
**Figure 2.** Equilibrium data for lithium solution with CaCl<sub>2</sub> as chloride sources at different values of Fe/Li.

Figure 2, similar to that of MgCl<sub>2</sub>, the extractability of iron ion increased with the concentration of chloride ion, and it reached 100 % when the chloride ion concentration was 6 mol·L<sup>-1</sup> at all values of Fe/Li. But the partition coefficient of lithium ion first increased and then decreased a little with the extractability of the iron ion and the concentration of the chloride ion. When comparing the value of the partition coefficient of lithium ion with CaCl<sub>2</sub> as chloride sources to that with MgCl<sub>2</sub> as chloride sources, it can be found that the combined influence of the competitive effect between Ca and Li when in combination with TBP and FeCl<sub>3</sub> and the salting-out effect of CaCl<sub>2</sub> on the

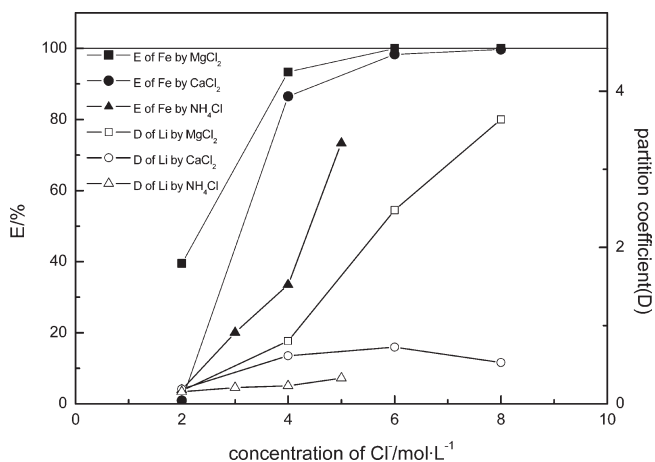
**Figure 3.** Equilibrium data for lithium solution with NH<sub>4</sub>Cl as chloride sources at different values of Fe/Li.

partition coefficient of Li is much weaker than that of MgCl<sub>2</sub>, which makes the extraction of lithium ion weaker.

**Extraction Behavior with NH<sub>4</sub>Cl as Chloride Sources at Different Values of Fe/Li.** NH<sub>4</sub>Cl is a typical monovalent inorganic nonmetallic salt. As shown in Table 5 and Figure 3, the extractability of iron ion increased with the concentration of chloride ion. Meanwhile the results showed that the partition coefficient of lithium ion with NH<sub>4</sub>Cl as chloride sources was a little lower than that of CaCl<sub>2</sub> as chloride sources, which was due to the weaker combined influence of the competitive and the



**Figure 4.** Relationship between partition coefficient ( $D$ ) of Li and extractability of Fe at different values of Fe/Li.

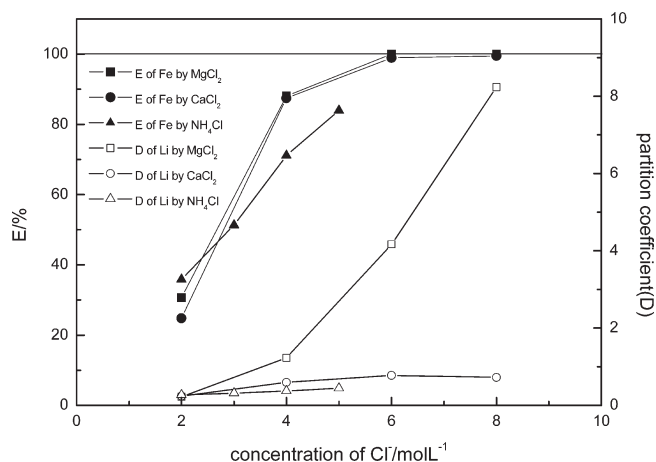


**Figure 5.** Equilibrium data for lithium solution with three salts as chloride sources at Fe/Li = 1.0.

salting-out effect of  $\text{NH}_4\text{Cl}$ . Different values of Fe/Li had not had a big effect on the partition coefficient of the lithium ion.

**Relationship Between the Extractability of the Iron Ion and the Partition Coefficient of the Lithium Ion.** The relationship between the extractability of the iron ion and the partition coefficient of the lithium ion with  $\text{MgCl}_2$  [(1 to 4)  $\text{mol}\cdot\text{L}^{-1}$ ] as chloride sources is shown in Figure 4. It can be seen that the partition coefficient of lithium ion increased with the extractability of the iron ion, which indicates that the extraction mechanism presented in the first section of Results and Discussion is correct and the extraction of the iron ion is the precondition of extraction of the lithium ion.

**Extraction Behavior with Three Salts as Chloride Sources at Different Values of Fe/Li.** The effects of chloride ion concentration on the extraction behavior with  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NH}_4\text{Cl}$  as chloride sources at Fe/Li = 1.0 and 1.3 are respectively shown in Figures 5 and 6. It can be perceived that all of the extractability of the iron ion increased with the chloride concentration with  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NH}_4\text{Cl}$  as chloride sources, and the extractability of iron ion with  $\text{MgCl}_2$  and  $\text{CaCl}_2$  was a little higher than that with  $\text{NH}_4\text{Cl}$  as chloride sources.



**Figure 6.** Equilibrium data for lithium solution with three salts as chloride sources at Fe/Li = 1.3.

Meanwhile, the extraction capacity of lithium ion followed the sequence:  $\text{MgCl}_2 > \text{CaCl}_2 > \text{NH}_4\text{Cl}$ , with recoveries from  $\text{MgCl}_2$  as chloride sources being much higher than that for  $\text{CaCl}_2$  and  $\text{NH}_4\text{Cl}$  as chloride sources, which indicates that the combined influence of the competitive and salting-out effect followed the sequence:  $\text{MgCl}_2 > \text{CaCl}_2 > \text{NH}_4\text{Cl}$ .

Generally speaking, the most typical extraction system, TBP/kerosene with  $\text{FeCl}_3$  as a coextracting agent, can extract lithium ion from brine sources, and  $\text{MgCl}_2$  as chloride sources at Fe/Li = 1.9 obtains the highest partition coefficient in this paper.

## CONCLUSION

In this work, the equilibrium data for lithium ion extracted by TBP in kerosene with  $\text{FeCl}_3$  as a coextracting agent and  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NH}_4\text{Cl}$  as chloride sources at different values of Fe/Li were shown. All of the extractability of the iron ion increased with the chloride concentration with  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NH}_4\text{Cl}$  as chloride sources, and the extractability of iron ion with  $\text{MgCl}_2$  and  $\text{CaCl}_2$  was a little higher than that with  $\text{NH}_4\text{Cl}$  as chloride sources at all values of Fe/Li. The extraction capacity of lithium ion followed the sequence:  $\text{MgCl}_2 > \text{CaCl}_2 > \text{NH}_4\text{Cl}$ , with recoveries from  $\text{MgCl}_2$  as chloride sources being much higher than that for  $\text{CaCl}_2$  and  $\text{NH}_4\text{Cl}$  as chloride sources at all values of Fe/Li. The combined influence of the competitive and salting-out effect followed by the sequence:  $\text{MgCl}_2 > \text{CaCl}_2 > \text{NH}_4\text{Cl}$ . The partition coefficient of the lithium ion increased with the extractability of the iron ion. The extraction of the iron ion is a precondition of the extraction of the lithium ion. The most typical extraction system, TBP/kerosene with  $\text{FeCl}_3$  as a coextracting agent, can extract lithium ion from brine sources, and  $\text{MgCl}_2$  as chloride sources at Fe/Li = 1.9 can obtain the highest partition coefficient.

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