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Extraction Equilibria of Lithium with Tributyl Phosphate in Three Diluents

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ABSTRACT: To explore the feasibility of extracting lithium metal from brine sources, three salt solutions, $FeCl_3$, $ZnCl_2$, and $CrCl_3$, were selected as coextracting agents, and the extraction equilibrium of lithium was studied with tributyl phosphate (TBP) in kerosene, TBP in methyl isobutyl ketone (MIBK), and TBP in 2-octanol. The results showed that the extraction capacity followed the sequence: TBP/MIBK > TBP/kerosene > TBP/2-octanol, with recoveries from the TBP/MIBK and TBP/kerosene systems being much larger than that for TBP/2-octanol with $FeCl_3$ solution as the coextracting agent. The third phase was found for the TBP/kerosene system with $FeCl_3$ solution as the coextracting agent at a low volume concentration of TBP, which did not appear for other systems at all volume concentrations. Synergistic extraction exists between TBP and MIBK, and the weak hydrogen bond association exists between $-OH$ in 2-octanol and $-P{=}O$ in TBP. The coextracting capacity for $FeCl_3$ was much larger than that for $ZnCl_2$ and $CrCl_3$, and that for TBP/2-octanol with $CrCl_3$ was a little larger than that for others.

INTRODUCTION

Lithium is the lightest alkali metal and is known as the 21st century energy metal. Lithium and lithium metal compounds are widely used in the fields of ceramics, glass, atomic energy, aerospace, military industry, lithium alloy, lithium battery, metallurgy, medicine, and so forth.[1−4] Increasing demand for lithium metal is expected to rise with the development of modern industry. Most lithium production comes currently from mining. Recent research has emphasized recovery from brine sources, such as adsorption by acid and sodium Amberlite,[5] extraction using supported liquid membranes,[6] the nanofiltration method,[7] adsorption on novel nanocrystal MnO_2,[8,9] and so forth.

Liquid−liquid extraction is an economical, efficient, and environmentally friendly benign 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.[10−14] Liquid−liquid extraction has been widely studied as a hot technology for recovering lithium from brine sources, which uses the specific affinity to achieve the purpose of extraction of lithium.[15] The most typical extraction system is TBP/kerosene-$FeCl_3$,[16,17] which is very suitable for the brine sources of high ratio of Mg−Li. Tributyl phosphate (TBP) is one of the most popular neutral organophosphorus extractants, and kerosene is a typical diluent. In this system $FeCl_3$ solution plays the role as a coextracting agent, which makes a great contribution for extracting lithium. But the terrible third phase problem will be appear while the concentration of TBP in the TBP/kerosene system is low.

In this study, three salt solutions, $FeCl_3$, $ZnCl_2$, and $CrCl_3$, were selected as the coextracting agents, and the separation feasibility of the lithium ions extracted by TBP in kerosene, TBP in methyl isobutyl ketone (MIBK), and TBP in 2-octanol were investigated.

Table 1. Physical Properties of Salts

chemical	formula	avg. MW	solubility (g/100 g H_2O, 20 °C)
lithium chloride	LiCl	42.39	78.5
magnesium chloride	$MgCl_2$	95.22	74.0
ferric chloride	$FeCl_3$	162.21	55.1
zinc chloride	$ZnCl_2$	136.30	432.0
chromium(III) chloride	$CrCl_3$	158.38	

Table 2. Physical Properties of Extractants and Diluents

chemical	formula	avg. MW	ρ/g·cm^{-3}
2-octanol	$CH_3(CH_2)_5CH(OH)CH_3$	130.23	0.819
TBP	$OP(O(CH_2)_3CH_3)_3$	266.32	0.980
MIBK	$CH_3COCH_2CH(CH_3)_2$	100.16	0.801
kerosene	$CH_3(CH_2)_{8-16}CH_3$	142.17−254.30	0.800

EXPERIMENTAL SECTION

Materials. The analytical reagents are as follows: LiCl from Beijing Yili Fine Chemical Co., Ltd. with a purity of > 97 %; $MgCl_2$ from Beijing Modern Eastern Finechemical Co., Ltd. with a purity of > 98 %; $FeCl_3$ from Tianjin Yongda Chemical Reagent Co., Ltd. with a purity of > 99 %; $ZnCl_2$ from Beijing Chemical Reagent Plant with a purity of > 98 %, and $CrCl_3$ from Sinopharm Chemical Reagent Co., Ltd. with a purity of > 99 %. The characteristics of the salt are presented in Table 1. 2-Octanol from Sinopharm Chemical Reagent Co., Ltd., TBP from Beijing

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Table 3. Equilibrium Data for Lithium Solution with $FeCl_3$ as a Coextracting Agent and TBP + Three Diluents as Extractants

	initial C_a of Li^+	equilibrium $C_a{}^a$ of Li^+	equilibrium $C_o{}^b$ of Li^+	
volume fraction of TBP	$mg \cdot L^{-3}$	$mg \cdot L^{-3}$	$mg \cdot L^{-3}$	partition coefficient D^c
TBP + 2-octanol + $FeCl_3$	341.8			
10 % TBP		277.8	37.0	0.1332
20 % TBP		240.2	74.6	0.3106
30 % TBP		201.1	113.7	0.5654
40 % TBP		161.9	152.9	0.9444
50 % TBP		130.9	183.9	1.4049
60 % TBP		104.9	209.9	2.0010
70 % TBP		90.3	224.5	2.4862
80 % TBP		81.3	233.5	2.8721
TBP + MIBK + $FeCl_3$	303.9			
10 % TBP		133.9	169.4	1.2651
20 % TBP		99.2	204.1	2.0575
30 % TBP		80.1	223.2	2.7865
40 % TBP		70.1	233.2	3.3267
50 % TBP		63.7	239.6	3.7614
60 % TBP		62.3	241.0	3.8684
70 % TBP		64.8	238.5	3.6806
80 % TBP		67.6	235.7	3.4867
TBP + kerosene + $FeCl_3$	289.7			
10 % TBP		210.9	78.8	0.3736
20 % TBP		124.6	165.1	1.3250
30 % TBP		91.8	197.9	2.1558
40 % TBP		73.7	216.0	2.9308
50 % TBP		64.6	225.1	3.4845
60 % TBP		62.7	227.0	3.6204
70 % TBP		63.1	226.6	3.5911
80 % TBP		66.6	223.1	3.3498

[a] C_a: equilibrium concentration of Li^+ in aqueous phase, experimentally measured. [b] C_o: equilibrium concentration of Li^+ in organic phase, mass balance calculation. [c] D = (equilibrium C_o of Li^+)/(equilibrium C_a of Li^+).

Chemical Reagent Plant, and MIBK from Beijing Yili Fine Chemical Co., Ltd. are analytical reagents with purity > 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) and 10 mL of the mixed solution of LiCl (0.05 $mol \cdot L^{-1}$), $MgCl_2$ (3.5 $mol \cdot L^{-1}$), and $FeCl_3$ (0.05 $mol \cdot L^{-1}$), $ZnCl_2$ (0.1 $mol \cdot L^{-1}$), or $CrCl_3$ (0.05 $mol \cdot L^{-1}$) 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, it can reach the equilibrium 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.

Analysis. The aqueous samples were analyzed for lithium ion concentration by using a Z-5000-AAS (Hitachi, Japan). The concentration of 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 ± 3 %.

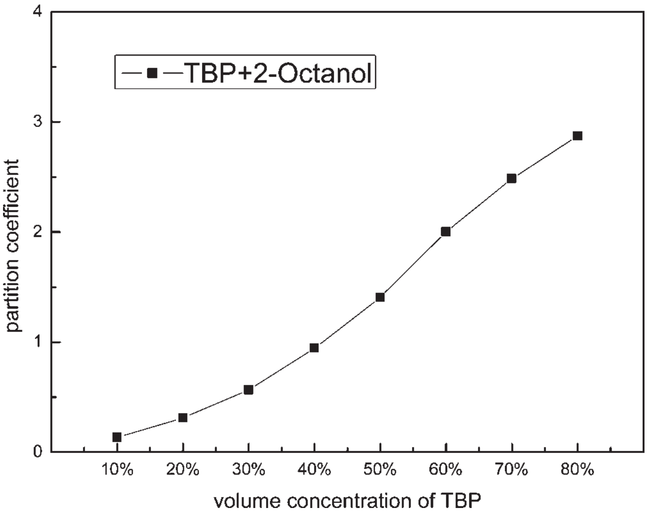

Figure 1. Equilibrium data for lithium solution with $FeCl_3$ as a coextracting agent and TBP + 2-octanol as an extractant.

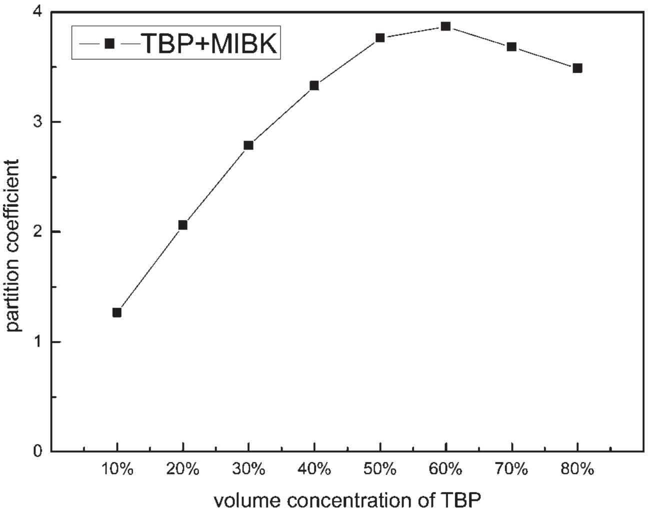

Figure 2. Equilibrium data for lithium solution with $FeCl_3$ as coextracting agent and TBP + MIBK as extractant.

RESULTS AND DISCUSSION

Extraction Behavior with TBP + 2-Octanol. To avoid appearance of the third phase, 2-octanol was used instead of kerosene as a new diluent. The reason for appearance of the third phase is that extraction complex cannot be dissolved in an inert diluent as kerosene. As kerosene is a nonpolar diluent, there is no interaction between the extraction complexes and kerosene. On the contrary, the polar diluent 2-octanol has strong intermolecular forces with the extraction complexes. As the partition coefficient depends on the volume concentration of TBP, the effects of solvent concentrations on the extraction behavior were investigated with 2-octanol as the diluent and $FeCl_3$ as coextracting agent, and the results are shown in Table 3 and Figure 1. It can be seen that the partition coefficient (D = (equilibrium C_o

Table 4. Equilibrium Data for Lithium Solution with $ZnCl_2$ as a Coextracting Agent and TBP + Three Diluents as Extractants

volume fraction of TBP	initial C_a of Li^+ $mg \cdot L^{-3}$	equilibrium C_a of Li^+ $mg \cdot L^{-3}$	equilibrium C_o of Li^+ $mg \cdot L^{-3}$	partition coefficient D
TBP + 2-octanol + $ZnCl_2$	367.7			
10 % TBP		355.2	12.5	0.0352
20 % TBP		354.5	13.2	0.0372
30 % TBP		346.6	21.1	0.0609
40 % TBP		342.1	25.6	0.0748
50 % TBP		338.8	28.9	0.0853
60 % TBP		331.2	36.5	0.1102
70 % TBP		317.7	50.0	0.1574
80 % TBP		305.2	62.5	0.2048
TBP + MIBK + $ZnCl_2$	369.4			
10 % TBP		353.3	16.1	0.0456
20 % TBP		342.6	26.8	0.0782
30 % TBP		335.3	34.1	0.1017
40 % TBP		322.3	47.1	0.1461
50 % TBP		310.1	59.3	0.1912
60 % TBP		302.7	66.7	0.2203
70 % TBP		293.7	75.7	0.2577
80 % TBP		283.5	85.9	0.3030
TBP + kerosene + $ZnCl_2$	330			
10 % TBP		313.7	16.3	0.0520
20 % TBP		321	9.0	0.0280
30 % TBP		316.5	13.5	0.0427
40 % TBP		310.8	19.2	0.0618
50 % TBP		295.8	34.2	0.1156
60 % TBP		280.5	49.5	0.1765
70 % TBP		273.2	56.8	0.2079
80 % TBP		265.7	64.3	0.2420

of Li^+)/(equilibrium C_a of Li^+), C_a: equilibrium concentration of Li^+ in aqueous phase, C_o: equilibrium concentration of Li^+ in organic phase) always increases with the volume concentration of TBP, which indicates that 2-octanol just plays a role as diluent and cannot extract lithium with $FeCl_3$ as a coextracting agent. Besides, there was no appearance of the third phase at all volume concentrations of TBP.

Extraction Behavior with TBP + MIBK. MIBK is a good middle-boiling solvent which is colorless and transparent. It is usually used as a dressing agent, adhesives, and an inorganic salt separating agent and also used in industrial organic synthesis. In this paper MIBK was selected as the other diluent because of its low density and low viscosity. As shown in Table 3 and Figure 2, the partition coefficient first increased and then decreased with the volume concentration of TBP. It can be seen that this is a typically synergistic extraction system for TBP + MIBK. When comparing the value of the partition coefficient at low volume concentrations of TBP to that at high volume concentration of TBP, it can be found that each of TBP and MIBK can extract lithium ion from aqueous phase to organic phase alone, and the extraction capacity of TBP is much stronger than that of MIBK. Meanwhile, similar to TBP + 2-octanol system, there was no appearance of the third phase at all volume concentration of TBP.

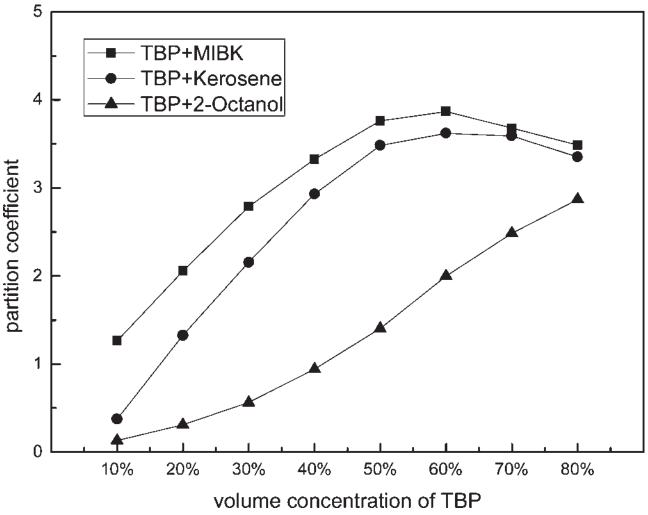

Figure 3. Equilibrium data for lithium solution with $FeCl_3$ as a coextracting agent and TBP + three diluents as extractants.

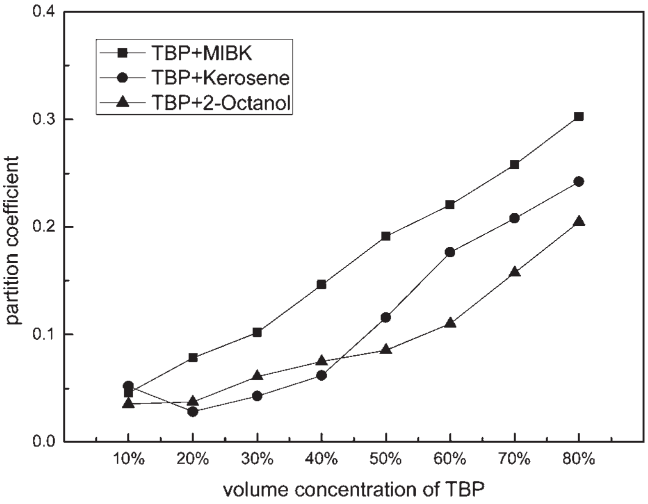

Figure 4. Equilibrium data for lithium solution with $ZnCl_2$ as a coextracting agent and TBP + three diluents as extractants.

Comparison of Extraction Behavior with TBP + Three Diluents. A comparison of the effects of solvent concentrations on the extraction behavior with MIBK, kerosene, and 2-octanol as diluents and $FeCl_3$ as coextracting agents is shown in Table 3 and Figure 3. The results showed that the extraction capacity followed the sequence: TBP/MIBK > TBP/kerosene > TBP/2-octanol, with recoveries from the TBP/MIBK and TBP/kerosene systems being much larger than that for TBP/2-octanol with $FeCl_3$ solution as the coextracting agent.

Obviously, synergistic extraction exists between TBP and MIBK, and the reason for that should be that there is an effective functional group in each extractant, as $-P{=}O$ in TBP and $-C{=}O$ in MIBK; both can extract lithium from brine sources alone. As the extraction capacity of $-C{=}O$ is much weaker than that of $-P{=}O$, the partition coefficient of high volume concentration of TBP is much larger than that of low volume concentration of TBP.

Table 5. Equilibrium Data for Lithium Solution with $CrCl_3$ as a Coextracting Agent and TBP + Three Diluents as Extractants

volume fraction of TBP	initial C_a of Li^+ $mg \cdot L^{-3}$	equilibrium C_a of Li^+ $mg \cdot L^{-3}$	equilibrium C_o of Li^+ $mg \cdot L^{-3}$	partition coefficient D
TBP + 2-octanol + $CrCl_3$	290.2			
10 % TBP		289.6	0.6	0.0021
20 % TBP		285.6	4.6	0.0161
30 % TBP		270.5	19.7	0.0728
40 % TBP		271.6	18.6	0.0685
50 % TBP		266.3	23.9	0.0897
60 % TBP		266.0	24.2	0.0910
70 % TBP		265.0	25.2	0.0951
80 % TBP		254.9	35.3	0.1385
TBP + MIBK + $CrCl_3$	332.9			
10 % TBP		325.4	7.5	0.0230
20 % TBP		330.3	2.6	0.0079
30 % TBP		328.8	4.1	0.0125
40 % TBP		321.8	11.1	0.0345
50 % TBP		318.3	14.6	0.0459
60 % TBP		319.0	13.9	0.0436
70 % TBP		320.4	12.5	0.0390
80 % TBP		326.2	6.7	0.0205
TBP + kerosene + $CrCl_3$	336			
10 % TBP		332.0	4.0	0.0120
20 % TBP		330.8	5.2	0.0157
30 % TBP		333.5	2.5	0.0075
40 % TBP		327.1	8.9	0.0272
50 % TBP		325.5	10.5	0.0323
60 % TBP		328.0	8.0	0.0244
70 % TBP		327.6	8.4	0.0256
80 % TBP		329.8	6.2	0.0188

As there is no functional group for lithium extraction in kerosene and 2-octanol, no synergistic extraction occurs between kerosene + TBP and 2-octanol + TBP. Kerosene is a typically inert diluent, which has no functional effect with TBP. As the weak hydrogen bond association exists between −OH in 2-octanol and −P═O in TBP, a fierce competition between TBP with 2-octanol and TBP with lithium exists in this system. That is the reason why the partition coefficient of TBP + 2-octanol system is much smaller than that of the other two.

Comparison of Extraction Behavior with TBP + Three Salt Solutions. The effects of solvent concentrations on the extraction behavior with MIBK, kerosene, and 2-octanol as diluents and $ZnCl_2$ as a coextracting agent are shown in Table 4 and Figure 4. The results showed that recoveries from the TBP/MIBK system are larger than that for TBP/kerosene and TBP/2-octanol with $ZnCl_2$ solution as the coextracting agent. As shown in Table 5 and Figure 5, the coextracting capacity for TBP/2-octanol is a little larger than that for the other two solvents with $CrCl_3$ as a coextracting agent. When comparing these three coextracting agents, it can be found that $FeCl_3$ shows the strongest coextracting capacity with all three selected diluents, which is much larger than that for the other two.

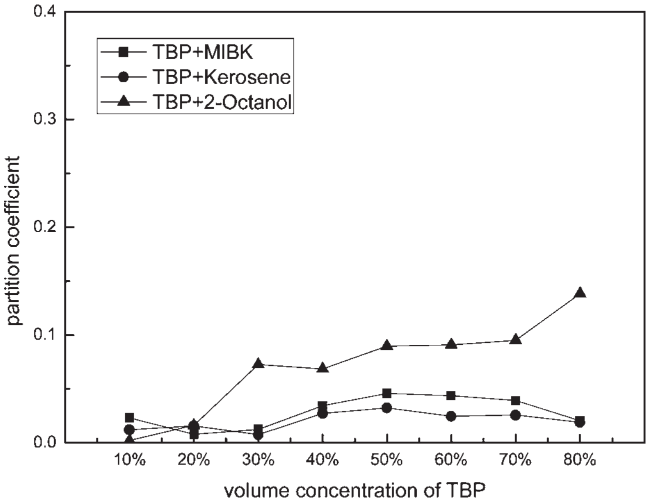

Figure 5. Equilibrium data for lithium solution with $CrCl_3$ as a coextracting agent and TBP + three diluents as extractants.

Generally speaking, TBP/MIBK with $FeCl_3$ as a coextracting agent can obtain the largest partition coefficient in this paper. Meanwhile, this system can completely avoid appearing in the third phase problem.

■ CONCLUSION

In this work, the equilibrium data for lithium ion extracted by TBP in kerosene, TBP in MIBK, and TBP in 2-octanol with $FeCl_3$, $ZnCl_2$, and $CrCl_3$ as coextracting agents were shown. The degree of extraction for $FeCl_3$ is obviously higher than the other two as coextracting agent with three kinds of solvent. The extraction capacity followed the sequence: TBP/MIBK > TBP/kerosene > TBP/2-octanol with $FeCl_3$ as a coextracting agent. Because the weak hydrogen bond association between −OH in 2-octanol and −P═O in TBP exist, recoveries from the TBP/MIBK and TBP/kerosene systems are much larger than that for TBP/2-octanol with $FeCl_3$ as the coextracting agent, as there is a typically synergistic extraction for TBP + MIBK, which can obtain the largest partition coefficient with $FeCl_3$ as a coextracting agent. The coextracting capacity for TBP/2-octanol is a little larger than that for the other two solvents with $CrCl_3$ as a coextracting agent. For the TBP/MIBK and TBP/2-octanol systems, there is no appearance of the third phase at all volume concentrations of TBP.

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■ REFERENCES

(1) Jiang, M. The Application of Lithium and Lithium Compounds. *Inorg. Chem. Ind.* **1983**, *9*, 32–36.

(2) You, Q. Z. The Application of Lithium and Lithium Compounds in Medicine Field. *World J. Nonferrous Metals* **1997**, *12*, 41–43.

(3) Johonson, F. N. The Early History of Lithium Therapy. *Lithium: Curr. Appl. Sci., Med. Technol.* **1985**, *1*, 337–338.

(4) Li, H. Y.; Zhai, X. J.; Fu, Y. Microwave Processing and Constructive Character of $LiCoO_2$ Cathode Materials for Lithium Ion Batteries. *J. Mol. Sci.* **2002**, *18* (4), 199–203.

(5) Navarrete-Guijosa, A.; Navarrete-Casas, R.; Valenzuela-Calahorro, C.; López-González, J. D.; García-Rodríguez, A. Lithium Adsorption by Acid and Sodium Amberlite. *J. Colloid Interface Sci.* **2003**, *264*, 60–66.

(6) Ma, P.; Chen, X. D.; Hossain, M. M. Lithium Extraction from a Multicomponent Mixture using Supported Liquid Membranes. *Sep. Sci. Technol.* **2000**, *35* (15), 2513–2533.

(7) Ma, P. H.; Deng, X. C.; Wen, X. M. Nano-filtration Method, for Separating Magnesium and Enriching Lithium from Salt Lake Brine. China Patent 1542147, 2004.

(8) Zhang, Q. H.; Sun, S. Y.; Li, S. P.; Jiang, H.; Yu, J. G. Adsorption of Lithium Ions on Novel Nanocrystal MnO_2. *Chem. Eng. Sci.* **2007**, *62*, 4869–4874.

(9) Feng, Q.; Miyai, Y.; Kanoh, H.; Ooi, K. Li^+ and Mg^{2+} Extraction and Li^+ Insertion Reactions with $LiMg_{0.5}Mn_{1.5}O_4$ Spinel in The Aqueous Phase. *Chem. Mater.* **1993**, *5*, 311–316.

(10) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269–282.

(11) King, C. J. Amine-based Systems for Carboxylic Acid Recovery: Tertiary Amines and The Proper Choice of Diluent Allow Extraction and Recovery from Water. *Chem. Tech.* **1992**, *5*, 285–291.

(12) Hartl, J.; Marr, R. Extraction Processes for Bioproduct Separation. *Sep. Sci. Technol.* **1993**, *28*, 805–819.

(13) Juang, R. S.; Huang, R. H. Comparison of Extraction Equilibria of Succinic and Tartaric Acids from Aqueous Solutions with Tri-n-octylamine. *Ind. Eng. Chem. Res.* **1996**, *35*, 1944–1950.

(14) Chen, Y. H.; Yan, J. Y.; Li, Y. K.; Feng, H. Z.; Yao, B. L.; Sheng, H. Y. Studies on The Extraction Chemistry of Atkati Metals—II. The Mechanism of The Extraction of Lithium by The Neutral Synergistic System of Sudan I. *Chin. J. Org. Chem.* **1982**, *4*, 257–262.

(15) Zhang, J. C.; Wang, M.; Dai, J. Summarization of The Lithium Extraction System. *J. Salt Lake Res.* **2005**, *13* (1), 42–48.

(16) Sun, X. L.; Chen, B. Z.; Xu, H.; Shi, X. C. Extraction of Lithium from Bittern. *J. Cent. South Univ. (Sci. Technol.)* **2007**, *38* (2), 262–266.

(17) Zhu, S. L; Piao, X. L.; Gou, Z. M. Extraction of Lithium from Brine with Neutral Organophosphorous Solvents. *J. Tsinghua Univ. (Sci. Technol.)* **2000**, *40* (10), 47–50.