

FeCl₃를 함유한 중성추출제의 혼합용매로 약한 염산용액으로부터 리튬(I)의 용매추출

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Solvent Extraction of Li(I) from Weak HCl Solution with the Mixture of Neutral Extractants Containing FeCl₃

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요 약

염산농도가 낮은 용액에서 TBP/MIBK와 다른 중성추출제(Cyanex 923, TOPO, TOP)의 혼합용매에 의한 리튬(I)의 용매추출실험을 수행했다. 0.1 M의 FeCl₃가 추출된 TBP/MIBK는 염산농도를 1에서 9 M로 변화시켜 준비하였다. 약한 염산용액에서 리튬(I)의 추출은 유기상에서 FeCl₃의 안정도와 관계된다. FeCl₃가 추출된 TBP를 진한 염산용액에서 제조하는 경우, 추출시 철의 탈거율이 작아 리튬(I)이 수소이온과의 교환반응에 의해 추출되었다. 혼합용매에서 TBP의 농도도 FeCl₃의 안정에 영향을 미쳤다. TBP에 비해 FeCl₃는 MIBK로부터 쉽게 탈거되어 리튬(I)을 추출하지 못했다. TBP/MIBK와 혼합용매로 첨가된 중성추출제의 종류는 리튬(I)의 추출과 철의 탈거에 영향을 미치지 않았다.

주제어 : 리튬, 추출, 중성추출제, 약 염산, 염화제2철

Abstract

Solvent extraction of Li(I) from weak HCl solution was investigated by the mixture of TBP/MIBK with other neutral extractants such as Cyanex 923, TOPO and TOP. The TBP/MIBK organic phase was loaded with 0.1 M FeCl₃ at different HCl concentrations (1-9 M). Extraction of Li(I) from weak HCl solution is related to the stability of FeCl₃ in the organic mixture. As HCl concentration increased in preparing the loaded TBP phase, the stripping percentage of Fe(III) during the extraction of Li(I) became reduced and thus Li(I) could be extracted by ion exchange reaction with hydrogen ion in the organic. The concentration of TBP in the extractant mixture affected the stability of FeCl₃. Compared to TBP, Fe(III) was easily stripped from the loaded MIBK and thus no Li(I) was extracted by the mixture with MIBK. The nature of neutral extractant with TBP/MIBK showed little difference in the extraction of Li(I) and stripping of Fe(III).

Key words : Lithium, Extraction, Neutral extractants, Weak hydrochloric acid, FeCl₃

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1. Introduction

Application of lithium is increasing in many fields such as ceramics, pharmaceuticals and mostly in electrical and electronic industries and renewable energy storage^{1,2}. The resources of lithium are clays, brines, seawater as well as the waste lithium battery^{3,4}. Much work has been done on the recovery of lithium from brine resources. Several methods have been proposed for the recovery of lithium such as precipitation⁵, ion exchange⁶, solvent extraction^{7,8}, and membrane⁹. Among these methods, solvent extraction is an efficient and environmental-friendly method for the separation and recovery of metals from the aqueous solution.

The extraction efficiency of Li(I) by single extractant from brines is low^{3,10} and thus several synergistic extraction systems have been employed for its separation such as HBTA-TOPO¹¹, LIX 54+TOPO¹² and LIX 54+Cyanex 923². The presence of either TOPO or Cyanex 923 enhances the extraction of Li(I) due to their strong electron donor property^{2,13} and prevents the formation of a third phase. However, Li(I) extraction by these mixtures can be obtained in the solution pH between 10 and 13. The system of TBP/FeCl₃-MIBK plays an efficient role for the extraction of Li(I) when the chloride concentration of strong alkaline solution is high^{14,15}. This might be ascribed to the fact that the hydrogen ion in the loaded TBP containing FeCl₃ can be exchanged with Li(I) in chloride solution. In addition, it has been found that MgCl₂ as a source of chloride ion has better performance for the extraction of Li(I) than CaCl₂ and NH₄Cl¹⁵ and the high concentration ratio of Fe(III) to Li(I) has a positive influence on the extraction of Li(I)¹⁵.

In order to investigate the possibility of extracting Li(I) from dilute HCl solution, several neutral extractant mixtures containing FeCl₃ were employed in this work. For this purpose, the mixtures of TBP/MIBK containing FeCl₃ were prepared from different HCl concentrations and these mixtures were employed in the experiments. The effect of TBP concentration on the extraction of Li(I) was also investigated from weak HCl solution.

2. Experimental

The synthetic solution was prepared by dissolving certain amount of FeCl₃ (97%, Duksan pure chemical Co. Ltd. Korea) in HCl solution with different concentration. Lithium solution was prepared by dissolving LiCl (98%, Daejung chemicals & metals Co. Ltd) in HCl solution with certain acidity. The neutral extractants used in this work were TBP (98%), MIBK (98.5%), Cyanex 923 (92%), TOPO (99%) and TOP (99%) which were purchased from Yakuri Pure Chemical Co. Ltd., Daejung Chemical & Metals Co. Ltd. and Samchun Pure Chemical Co. Ltd., respectively. Kerosene was used as diluent.

Extraction experiments were carried out in the 50 ml bottle with screw cap by mixing equal volume of organic and aqueous phases. The mixture was shaken for 30 min using a wrist action shaker (Burrel, USA) at room temperature. Organic phase containing FeCl₃ was prepared by mixing neutral extractants and 0.1 M FeCl₃ solution with different HCl concentration. The mixtures were separated in the separate funnel and the concentration of Li(I) in aqueous phase was measured by ICP-OES (Spectro arcos model). The concentration of Li(I) in the organic phase was calculated by mass balance.

3. Results and Discussion

3.1. Extraction of Li(I) by neutral extractant and its mixture with TBP

In order to investigate the effect of FeCl₃, the extraction of Li(I) by neutral extractants was performed by varying HCl concentration to 0.2 M. When HCl concentration was 0.05 M, 7% of Li(I) was extracted by TOP and about 5% of Li(I) by other extractants (see Fig. 1). The extraction of Li(I) decreased as HCl concentration increased from 0.05 M to 0.2 M. Single neutral extractant could not extract efficiently Li(I) from weak HCl solution.

3.2. Extraction of Li(I) by mixture of neutral extractants and TBP

In this work, Cyanex 923, TOPO and TOP were employed in the solvent extraction experiments. The solvent extraction reaction of FeCl₃ by TBP/MIBK depends on

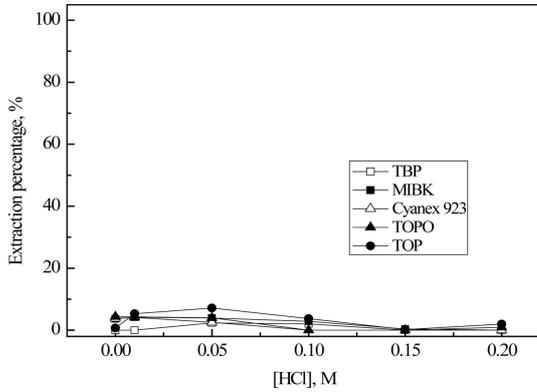


Fig. 1. Effect of HCl on the extraction of Li(I) by single extractant from weak HCl solution. ([HCl] = 0-0.2 M [extractant] = 0.1 M, O/A =1)

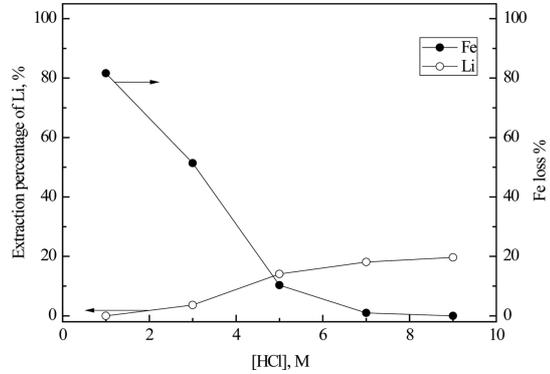
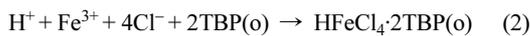
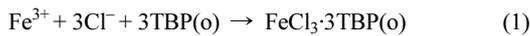


Fig. 2. Effect of HCl concentration on extraction of Li(I) by the mixture of Cyanex 923 and TBP containing 0.1 M FeCl₃. ([Cyanex 923] = 0.1 M, [HCl]_{Li(I) solution} = 0.05 M)

the concentration of chloride ion¹⁴⁻¹⁷) and can be represented as Eqs. (1) and (2). Eq.(1) occurs when HCl concentration is lower than 6 M, while Eq. (2) occurs in the HCl concentration range from 6 to 9 M. In the course of preparing organic phase containing FeCl₃, the solution of 0.1 M FeCl₃ with HCl concentration range of 1 M to 9 M was employed for the experiments. Around 0.1 M FeCl₃ was loaded into the organic phase. The neutral extractant mixtures containing 0.1 M FeCl₃ which was prepared at different HCl concentrations were employed in the experiments.



According to the reported works, Cyanex 923 shows synergistic effect as well as the function of preventing the formation of a third phase^{2,18}). Thus, the mixture of 0.1 M FeCl₃ in TBP with 0.1 M Cyanex 923 was investigated. In preparing the TBP containing FeCl₃, the concentration of HCl was varied from 1 to 9 M. When HCl concentration was 0.05 M, 80% of Fe(III) loaded in the organic phase came into the aqueous solution and no Li(I) was extracted (see Fig. 2). As HCl concentration increased to 9 M, the stripping of Fe(III) into the aqueous phase rapidly decreased to zero at 9 M HCl and about 20% of Li(I) was extracted. When HCl concentration was low, Fe(III) was easily stripped from

the TBP phase but the stability of FeCl₃ in TBP increased with HCl concentration. This stability might be due to the change of the extracted species of FeCl₃ with HCl concentration. Eqs. (1) and (2) indicate that the species of FeCl₃ extracted into TBP changes from FeCl₃·3TBP to HFeCl₄·2TBP as chloride ion concentration increases¹⁹). The species of HFeCl₄·nTBP has a strong tendency to form complex with Li(I). The extraction reaction can be represented as Eq. (3)²⁰. Eq. (3) shows that high concentration of hydrogen ion in aqueous solution could suppress the extraction of Li(I).

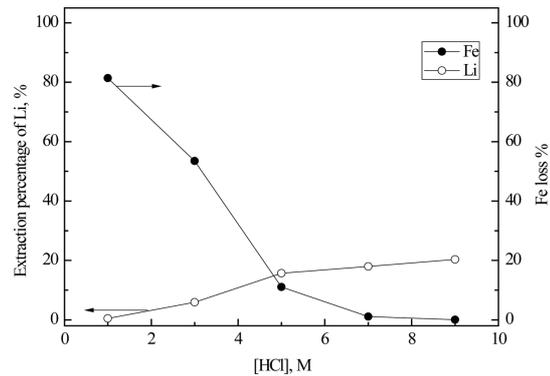
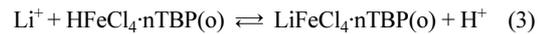


Fig. 3. Effect of HCl concentration on extraction of Li(I) by the mixture of TOPO and TBP containing 0.1 M FeCl₃. ([TOPO] = 0.1 M, [HCl]_{Li(I) solution} = 0.05 M)

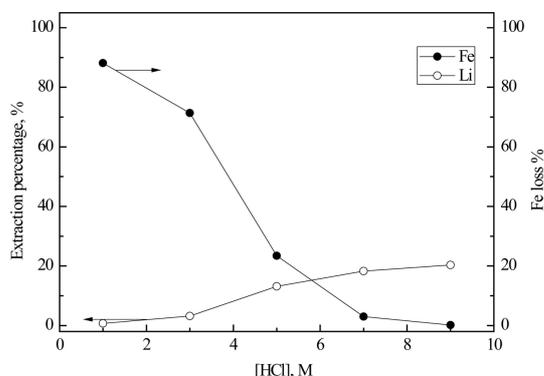


Fig. 4. Effect of HCl concentration on extraction of Li(I) by the mixture of TOP and TBP containing 0.1 M FeCl_3 . ($[\text{TOP}] = 0.1 \text{ M}$, $[\text{HCl}]_{\text{Li(I) solution}} = 0.05 \text{ M}$)

TOPO has a synergistic effect due to its powerful electron donor properties¹³. Therefore, the effect of TOPO on the extraction of Li(I) with the mixture of TBP with 0.1 M FeCl_3 was investigated. Fig. 3 shows that the extraction behavior of Li(I) and the stripping of Fe(III) by the mixture with TOPO was similar to that of Cyanex 923. The same experiments were done with the mixture of 0.1 M TOP with the TBP containing 0.1 M FeCl_3 . Fig. 4 shows that the extraction and stripping behavior of Li(I) and Fe(III) by the mixture with TOP was similar to that of Cyanex 923 and TOPO.

3.3. Extraction of Li(I) by neutral extractant and its mixture with MIBK

In order to compare the extraction behavior of Li(I) between TBP and MIBK, 0.1 M FeCl_3 was extracted into MIBK and this organic was mixed with Cyanex 923, TOPO and TOP. In these experiments, HCl concentration was varied from 1 to 9 M. According to Fig. 5, Fe(III) was easily stripped from the MIBK during the extraction of Li(I) from the experimental ranges. Therefore, the organic mixture with MIBK was not effective in extracting Li(I) and thus no Li(I) was extracted.

3.4. Effect of TBP concentration

Based on the reports¹⁴, TBP concentration has an important influence on the extraction of Li(I) in the salt lake brine with high concentration ratio of Mg(II) to Li(I). In order to investigate the effect of TBP concentration

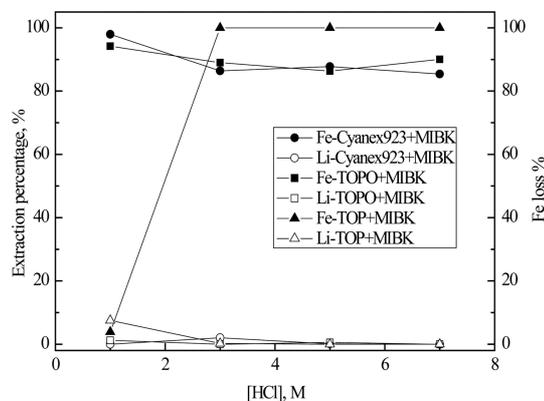


Fig. 5. Effect of HCl concentration on extraction of Li(I) by the mixture of MIBK containing 0.1 M FeCl_3 . ($[\text{Cyanex 923}] = [\text{TOPO}] = [\text{TOP}] = 0.1 \text{ M}$, $[\text{HCl}]_{\text{Li(I) solution}} = 0.05 \text{ M}$)

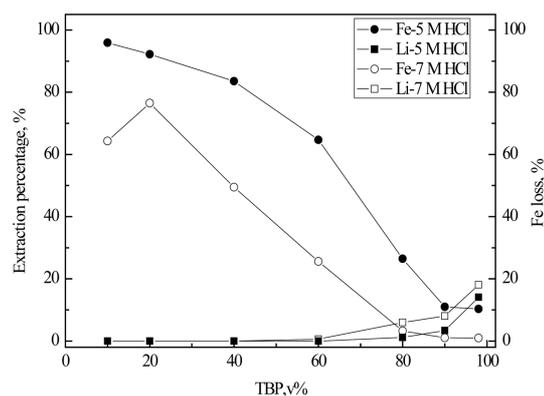


Fig. 6. Effect of TBP concentration on extraction of Li(I) by the mixture of Cyanex 923 and TBP containing 0.1 M FeCl_3 . ($[\text{Cyanex 923}] = 0.1 \text{ M}$, $[\text{HCl}]_{\text{FeCl}_3 \text{ solution}} = 5 \text{ M}$ and 7 M , $[\text{HCl}]_{\text{Li(I) solution}} = 0.05 \text{ M}$)

on the extraction of Li(I) from the weak HCl solution, the concentration of TBP was varied from 10 to 98%. The organic mixture of TBP containing 0.1 M FeCl_3 with neutral extractants was prepared at 5 M and 7 M HCl. Fig. 6 shows that the stripping percentage of Fe(III) decreased rapidly with TBP concentration in the mixture with Cyanex 923. In addition, when the TBP concentration was fixed, stripping percentage of Fe(III) decreased as HCl concentration increased. Compared to 5 M HCl, a little more Li(I) was extracted into organic phase prepared at 7 M HCl. Fig. 7 shows the effect of TBP concentration in the mixture of TOPO.

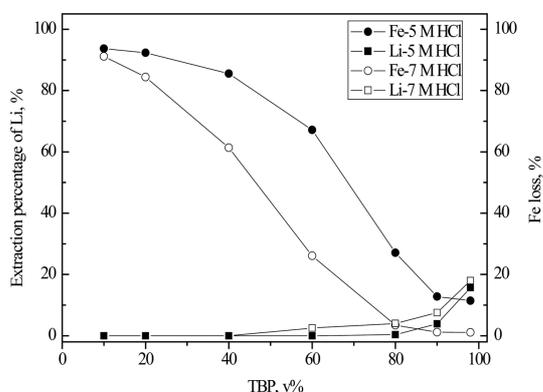


Fig. 7. Effect of TBP concentration on extraction of Li(I) by the mixture of TOPO and TBP containing 0.1 M FeCl₃. ([TOPO] = 0.1 M, [HCl]_{FeCl₃ solution} = 5 M and 7 M, [HCl]_{Li(I) solution} = 0.05 M)

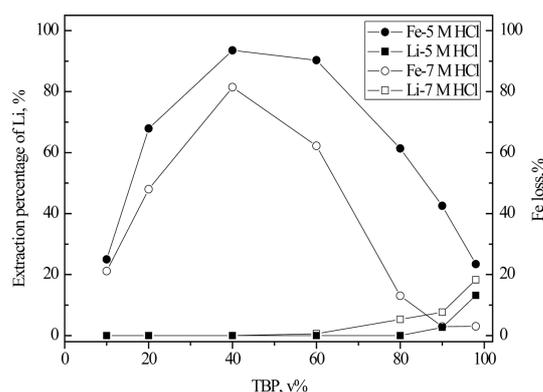


Fig. 8. Effect of TBP concentration on extraction of Li(I) by the mixture of TOP and TBP containing 0.1 M FeCl₃. ([TOP] = 0.1 M, [HCl]_{FeCl₃ solution} = 5 M and 7 M, [HCl]_{Li(I) solution} = 0.05 M)

The extraction and stripping behavior of Li(I) and Fe(III) by the mixture with TOPO was similar to that by the mixture with Cyanex 923.

Fig. 8 shows the extraction and stripping behavior of Li(I) and Fe(III) by the mixture with TOP. The stripping percentage of Fe(III) increased rapidly as TBP concentration increased from 10 to 40% and then quickly decreased to 3% at 98% TBP concentration. This data indicates that the FeCl₃ in the organic composed of TOP and TBP prepared at high HCl solution is more stable than that from low HCl concentration. Therefore, it can be concluded that Li(I) can be extracted by the mixture

with TBP containing FeCl₃ in strong HCl solution with other neutral extractants. In these, the stability of the organic mixture is important to extract Li(I).

4. Conclusions

In current work, the feasibility of extracting Li(I) from weak HCl solution was investigated by neutral extractants like TBP/MIBK mixed with Cyanex 923, TOPO and TOP containing FeCl₃. In the course of Li(I) extraction by the mixtures of neutral extractants and TBP containing FeCl₃, the stability of FeCl₃ in the loaded organic is related to the extraction of Li(I). When the TBP phase containing FeCl₃ was prepared at high HCl concentration, the stripping percentage of Fe(III) from the organic mixture was reduced, which resulted in some extraction of Li(I) from 0.05 M HCl solution. The nature of the neutral extractants in the mixture with TBP did not show difference in the extraction behavior of Li(I). TBP concentration in the mixture had a great effect on the stability of FeCl₃ in the organic and thus the extraction of Li(I). About 20% of Li(I) was extracted from the 0.05 M HCl solution when the mixture with 98% of TBP containing 0.1 M FeCl₃ was prepared from 7 M HCl solution. However, the stability of FeCl₃ in MIBK was low and thus Li(I) was hardly extracted by the mixtures containing MIBK.

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