

The effect of dominant ions on solvent extraction of lithium ion from aqueous solution

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(Received 4 September 2013 • accepted 4 January 2014)

Abstract—Solvent extraction of lithium ion using kerosene as solvent is proposed. The extraction of lithium ion using various mixed extractants of β -diketone and neutral ligand in kerosene was performed to find the optimum extractant combination. Considering the extraction efficiency, the optimum extractant combination was 0.02 M TTA and 0.04 M TOPO. For the development of lithium extraction from seawater, the effects of dominant ions in seawater were examined in various extraction conditions. The extraction efficiencies generally decreased with the concentration of dominant metallic ions and increased with pH of the aqueous solutions, but Cl^- ion showed only minor effect on the efficiency, even up to its concentration in seawater. Except for Mg^{2+} ion, more than 70% of lithium ions could be extracted at pH 10.6 from aqueous solutions with a dominant ion at its concentration in seawater.

Keywords: Lithium, Dominant Ions, Solvent Extraction, TTA, TOPO

INTRODUCTION

Lithium, the lightest alkali metal, is known as the 21st century energy metal. Lithium and lithium compounds are widely used in the fields of ceramics, aerospace, military industry, metallurgy, medicine, cement, and firework. At present, lithium is mainly used as a main raw material of lithium batteries. Their light weight gives a preference over lead batteries: lithium batteries are thus used in electric automobiles, torpedoes, or other battery-powered gadgets or machines. A high energy fuel with the high temperature and fast combustion character is made of lithium compounds [1].

Two important sources of lithium are hard silicate mineral called spodumene, which is found in pegmatite, and brine lake deposits that contain lithium chloride [2]. However, seawater is also a potential source. The average concentration of lithium in seawater is 0.17 mg/L and the full amount of seawater is estimated to be 1.36×10^{21} L; therefore, the total amount of lithium in seawater can reach more than 231.2 billion tons [3].

Seawater can be used directly or after being concentrated, and brine water has a lithium concentration of about 10 ppm [4]. Concentrated water discharged from desalination facilities can be another big resource of lithium. In recent years, a number of desalination facilities have been constructed. Therefore, lithium extraction from concentrated seawater becomes an important challenge to be solved. Various techniques have been proposed for a pre-concentration together with solvent extraction [5].

A combination of β -diketone and neutral ligand is an effective extractant for lithium extraction. There have been many reports on the metal extractions using β -diketone and neutral ligand. β -diketone combined with neutral ligand is known to create a synergistic effect that can increase the extraction efficiencies of metallic ions as form of adduct or ion-pair [6].

Uedee et al. studied mercury (II) extraction by using Tri-n-octyl-

amine (TOA) dissolved in kerosene [7]. Zhu et al. reported experimental results on uranium extraction using 1,3-Diphenyl-1,3-propanedione (dibenzoylmethane, HDBM) and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) [8]. Zhou et al. used tributyl phosphate (TBP) in various solvents for extracting lithium ion [9]. Ma et al. extracted lithium ion with mixed extractant of LIX 54 and tri-n-octylphosphine oxide (TOPO) [10]. Bansal et al. also used the same extractant combination, focusing on the effect of solvents [11]. In another case, Samira et al. compared di-(2-ethylhexyl) phosphoric acid (DEHPA) and 2-thenoyltrifluoroacetone (TTA) as extractant for extraction of Cd (II), Co (II) and Ni (II) [12]. Using TTA for extraction of monovalent cations, such as sodium ion, potassium ion, and lithium-ion, has been reported [13].

In these researches, the effects of extraction conditions on the extraction efficiency, equilibrium constant and stability of adduct have been studied. However, there were no researches on the effect of dominant ions on the solvent extraction of lithium ion. Dominant ions mean the ions present in large amounts in seawater. Some researchers only studied the effect of other ions on the spectrophotometric determination of lithium ion by atomic absorption (AA) [14-15]. In case of Sr^{2+} ion, it is shown that some dominant ions reduce the extraction rate of Sr^{2+} [16]. In this research, Cl^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} were used as dominant ions in the same concentration as their composition in seawater. Generally, seawater contains 19,000 ppm of Cl^- , 10,500 ppm of Na^+ , 380 ppm of K^+ , 1,350 ppm of Mg^{2+} and 400 ppm of Ca^{2+} [3].

In this work, for the purpose of development of a solvent extraction process of lithium ion from seawater, a series of experimental researches have been performed. An optimum extractant combination of β -diketone and neutral ligand has been obtained. And the effects of dominant ions on the extraction efficiency of lithium ion from aqueous solutions have been found.

EXPERIMENTAL

1. Reagents and Instruments

All reagents used were analytical grade and the distilled water

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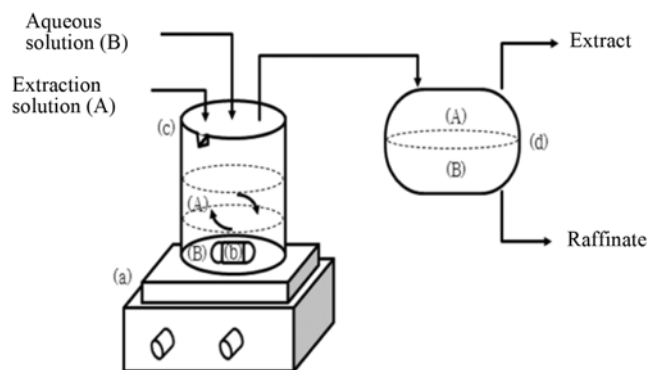


Fig. 1. Schematic diagram of solvent extraction apparatus. (a) Stirrer, (b) Magnetic bar, (c) Extraction chamber, (d) Settler.

was further purified by Millipore Milli-Q water system. A schematic diagram of the solvent extraction apparatus is shown in Fig. 1.

Lithium aqueous solution was prepared by diluting lithium standard solution of 1,000 ppm in 1 wt% HCl (Aldrich Co.). Some metallic ions were obtained from NaCl (Tedia Inc.), KCl (Shinyo Pure Chem.), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and CaCl_2 (Junsei Co.), NH_4OH (Junsei Co.) was used for pH adjustment of the aqueous solutions. For extraction solution, β -diketone and neutral ligand were dissolved in kerosene (Aldrich Co.). 4,4,4 Trifluoro-1-phenyl-1,3-butanedione (TPB), TTA, and HDBM (Aldrich Co.) were selected for β -diketone, TOPO and TBP (Aldrich Co.) were selected for neutral ligand.

Flame atomic absorption spectroscopy (AA-7000, Shimadzu) for measuring the absorbance of metallic ions, was used for determination of the concentration of lithium.

2. Experimental Procedure

For determining the optimum extractant combination, various combinations of β -diketone and neutral ligand were added in kerosene to make extraction solutions. The extraction solutions were used to extract lithium ion in aqueous solutions.

Solvent extraction was performed in a batch type extraction chamber to extract lithium ion from aqueous solution. 50 ml of extraction solution and the same volume of aqueous solution were stirred for 60 minutes. And the two phases were separated in a separatory funnel. 10 ml of aqueous solution (raffinate) was sampled for AA analysis. Extraction efficiency (E.E.) of solvent extraction was calculated by the following equation:

$$\text{E.E. (\%)} = \frac{[\text{Li}(\text{TTA})_2(\text{TOPO})_2]}{[\text{Li}^+]_0} \times 100$$

where, $[\text{Li}^+]_0$ is initial concentration of lithium ion in aqueous solution, and $[\text{Li}(\text{TTA})_2(\text{TOPO})_2]$ is concentration of lithium ion in extraction solution.

To examine the effect of dominant ions in seawater, such as Cl^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , one of the ions was added in lithium aqueous solution in various concentrations. In this experiment, pH of the aqueous solution was adjusted using NH_4OH from 9 to 11.5.

RESULTS AND DISCUSSION

1. Equilibrium Extraction Time

For the establishment of equilibrium extraction time, a kinetic study of the solvent extraction of lithium ion using TTA and TOPO

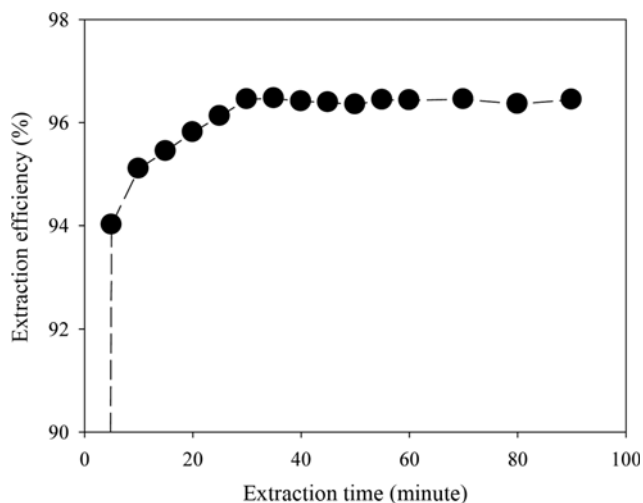


Fig. 2. Time profile of lithium extraction efficiency. $[\text{Li}]_0=1$ ppm, $[\text{TTA}]=0.02$ M, $[\text{TOPO}]=0.04$ M. pH=10.2.

was performed. Fig. 2 shows the time profile of lithium extraction efficiency at the same volume of aqueous solution with extraction solution. The extraction efficiency increases with extraction time and reaches an equilibrium value after about 30 minutes. Because the equilibrium extraction time might be changed with extraction conditions, our experiments were performed at the equilibrium extraction time of 60 minutes.

2. Effect of Extractant Combinations

To determine the optimum extractant combination for lithium ion extraction, some combinations of β -diketone and neutral ligand in kerosene were tested with lithium aqueous solution at different pH. pH was adjusted in the range 9–11.5, considering the pH of natural seawater is 8. The initial concentration of lithium in the aqueous solution was 1 ppm. TTA, HDBM, and TPB were used as β -diketone. And TBP and TOPO were used as neutral ligand, because these ligands have higher extraction efficiency in combination with

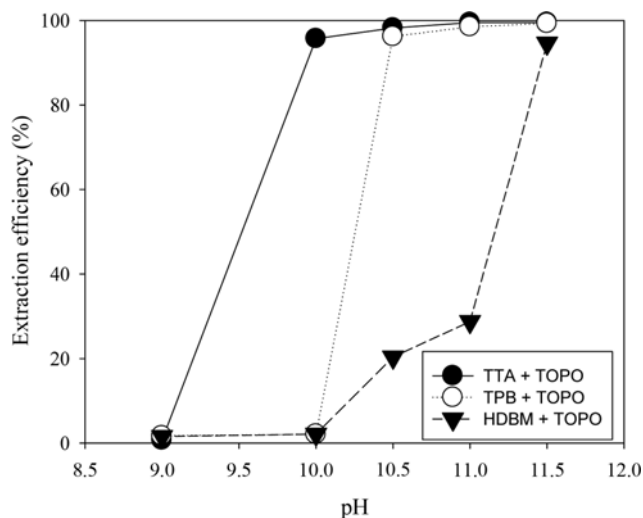


Fig. 3. Effect of β -diketones combined with TOPO on the lithium extraction from aqueous solution. $[\text{Li}^+]_0=1.0$ ppm, $[\beta\text{-diketone}]=0.02$ M, $[\text{TOPO}]=0.04$ M.

β -diketone [6,9,11].

To examine the effect of β -diketones on the extraction efficiency of lithium ion in aqueous solutions, 0.04 M TOPO was combined with 0.02 M β -diketones for the extraction solution. These concentrations were selected on the basis of previous researches [6], and Lee et al. concluded the extraction efficiency can reach more than 95% by using 0.02 M TTA and 0.04 M TOPO [17].

As shown in Fig. 3, the extraction efficiencies generally increase with pH. The efficiency of TTA combination with TOPO reaches above 90% at lower pH (10.0) than any other combinations. However, that of HDBM combination reached similar value at pH 11.5.

To examine the effect of neutral ligands on the extraction efficiency, 0.02 M β -diketones were combined with 0.25 M TBP for the extraction solution. The mole ratio was chosen from experimental results shown in Fig. 4. Fig. 4 shows the extraction efficiency

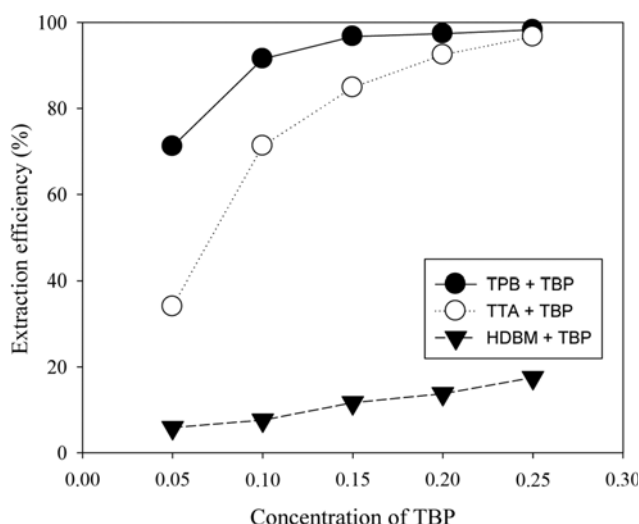


Fig. 4. Effect of concentration of TBP on the lithium extraction from aqueous solution. $[Li^+]_0=1.0$ ppm, $[\beta\text{-diketone}]=0.02$ M, pH=11.0.

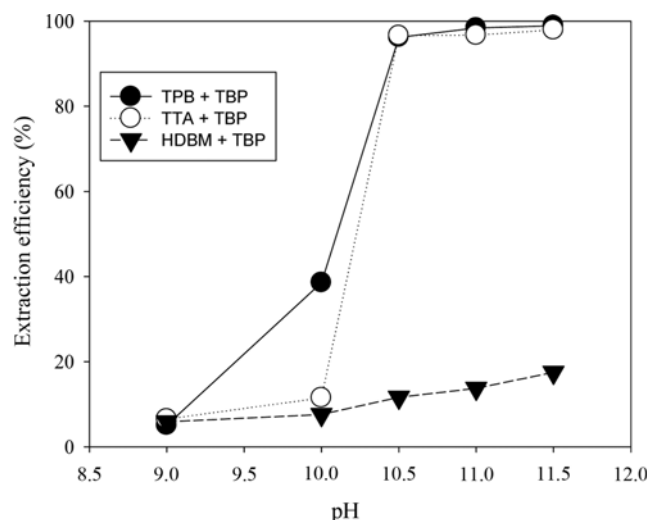


Fig. 5. Effect of β -diketones combined with TBP on the lithium extraction from aqueous solution. $[Li^+]_0=1.0$ ppm, $[\beta\text{-diketone}]=0.02$ M, $[TBP]=0.25$ M.

increases with the concentration of TBP for all β -diketones, and get to more than 95% at 0.25 M except HDBM. However, the increasing tendency significantly decreases with the concentration of TBP. Fig. 5 shows the effect of neutral ligands.

As shown in Fig. 5, the extraction efficiencies also generally increase with pH. The efficiencies of TPB and TTA combinations with TBP were higher than that of HDBM combination, and reach higher than 90% at pH 10.5. However, this pH value is higher than that of TTA combination with TOPO.

From these results, it could be concluded that the combination of TTA and TOPO is the optimum extraction solution, showing higher extraction efficiency at lower pH than any other combinations.

3. Effect of Concentrations of β -Diketone

To determine the optimum concentrations of extractants, extraction efficiencies were also measured at various β -diketone concentrations at pH 10.2. The concentration of TOPO was 0.04 M and the volume ratio of extraction solution to lithium aqueous solution was 1 : 1. The initial concentration of lithium in aqueous solution was 1 ppm.

Fig. 6 shows extraction efficiencies increase with concentration of β -diketones until the concentration reaches 0.02 M for all extractant combinations. As expected, the extraction efficiency of TTA combination with TOPO is higher than any other combinations.

From these results, 0.02 M TTA and 0.04 M TOPO has been chosen as optimum concentration of extractants for lithium extraction at the volume ratio of extraction solution to aqueous solution 1 : 1.

4. Effect of Dominant Ions

For the purpose of development of solvent extraction process of lithium ion from sea water, the effect of dominant ions in sea water on the solvent extraction of lithium ion have been studied. For more detailed study, each dominant ion with different concentrations was added to lithium aqueous solution, considering their concentrations in seawater. pH of the solutions was changed in the range of 9.4-11.0. The optimum extractant combination in kerosene was used for extraction solution, and the initial concentration of lithium aqueous solution was 1 ppm.

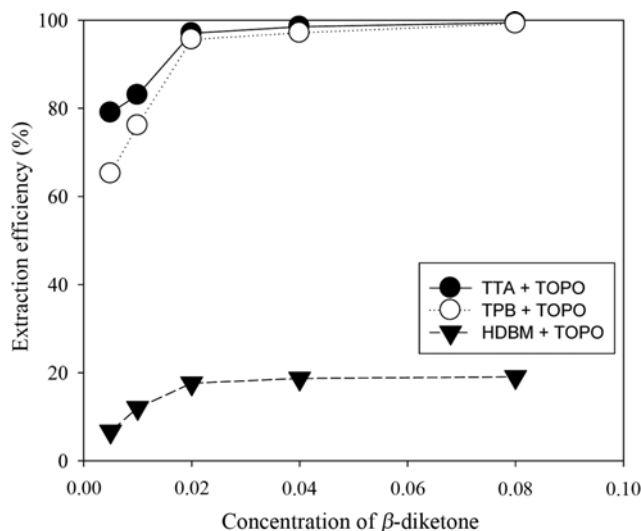


Fig. 6. Effect of concentration of β -diketones on lithium extraction from aqueous solution. pH 10.20, $[Li^+]_0=1.0$ ppm, $[TOPO]=2 \times [\beta\text{-diketone}]$.

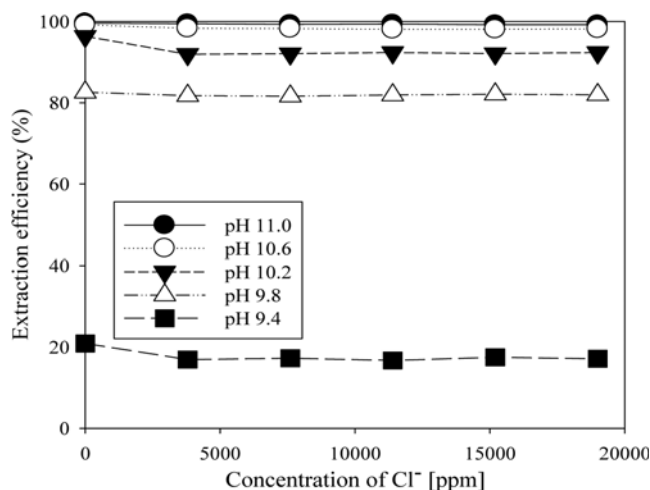


Fig. 7. Effect of chloride ion on the extraction of lithium ion from aqueous solution. $[Li^+]_0=1.0$ ppm, $[TTA]=0.02$ M, $[TOPO]=0.04$ M.

Chloride is the most abundant element in seawater whose concentration is 19,000 ppm. The effect of chloride ion on the extraction was experimentally examined in the range of 0-19,000 ppm and shown in Fig. 7.

As shown in Fig. 7, chloride ion has only minor effect on the extraction efficiency of lithium ion. However, the efficiencies increase with pH of the aqueous solutions, and reach higher than 90% when pH is above 10.2. This phenomenon could be explained by the bonding mechanism of extractants with metallic ions [6], which means lithium ion does not compete with chloride ion for bonding with TTA and TOPO combination.

To examine the effects of metallic dominant ions in sea water, metallic salts were added to lithium aqueous solutions. Since chloride ion in aqueous solution has minor effect on the lithium extraction, NaCl, KCl, $CaCl_2$, and $MgCl_2$ were selected as metallic salts.

The effect of Na^+ ion on the extraction efficiency of lithium ion from aqueous solution is shown in Fig. 8. Extraction efficiencies generally decrease with concentration of Na^+ ion up to its concen-

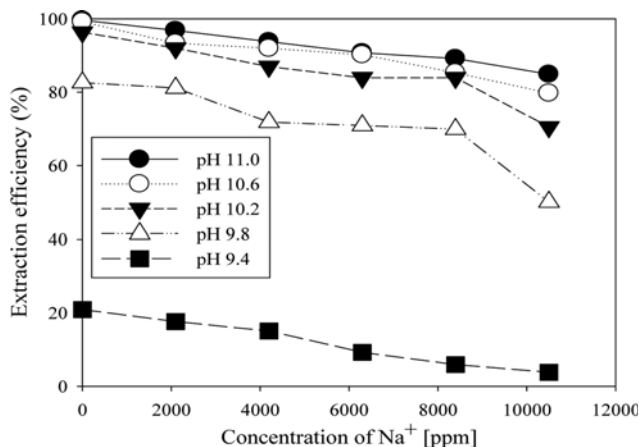


Fig. 8. Effect of sodium ion on the extraction of lithium ion from aqueous solution. $[Li^+]_0=1.0$ ppm, $[TTA]=0.02$ M, $[TOPO]=0.04$ M.

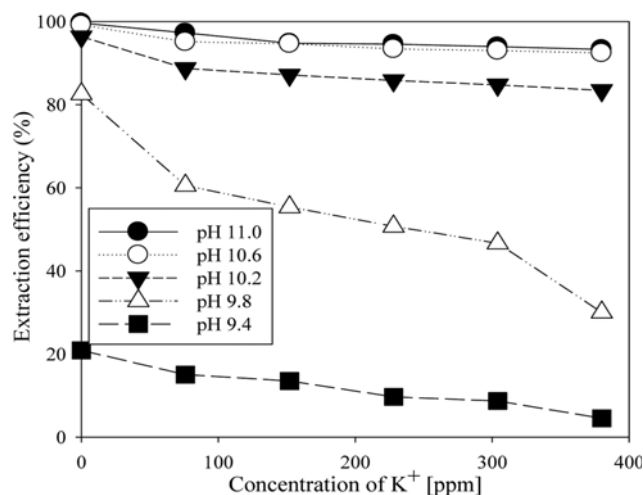


Fig. 9. Effect of potassium ion on the extraction of lithium ion from aqueous solution. $[Li^+]_0=1.0$ ppm, $[TTA]=0.02$ M, $[TOPO]=0.04$ M.

tration in seawater, and increase with pH of aqueous solution. However, the increasing tendency significantly diminishes with pH. Nevertheless, the extraction efficiency still maintained more than 70% at its concentration in the seawater when pH is above 10.2.

Fig. 9 shows the effect of K^+ ion on extraction of lithium ion from aqueous solutions. The extraction efficiencies significantly decrease with concentration of K^+ ion in the pH range of 9.4-9.8, but slightly decrease in the pH range of 10.6-11.0. Overall effect of K^+ ion on the efficiency is similar to that of Fig. 8 for Na^+ ion. Decrease in extraction efficiencies for Na^+ ion and K^+ ion might have occurred because these monovalent ions compete with lithium ion for the complex formation with extractants.

The effect of Ca^{2+} ion on the extraction of lithium ion is shown in Fig. 10. Fig. 10 represents that the extraction efficiencies significantly decrease with concentration of Ca^{2+} ion in the pH range of 9.4-10.2, and slightly decrease in the pH range of 10.6-11.0. When pH of the aqueous solution is higher than 10.6, the efficiency remains

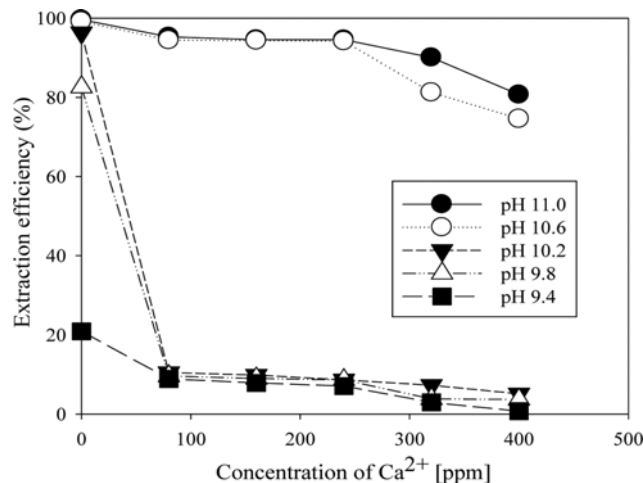


Fig. 10. Effect of calcium ion on the extraction of lithium ion from aqueous solution. $[Li^+]_0=1.0$ ppm, $[TTA]=0.02$ M, $[TOPO]=0.04$ M.

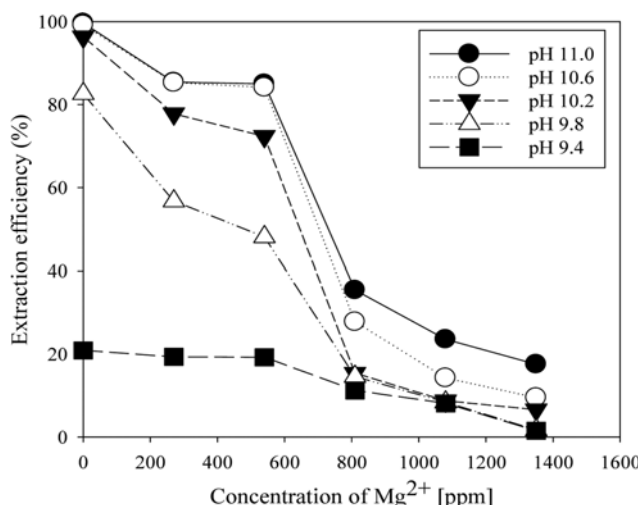


Fig. 11. Effect of magnesium ion on the extraction of lithium ion from aqueous solution. $[\text{Li}^+]_0 = 1.0$ ppm, $[\text{TTA}] = 0.02$ M, $[\text{TOPO}] = 0.04$ M.

above 80% even at its concentration in seawater.

In case of Mg^{2+} ion, a somewhat different phenomenon was observed. As shown in Fig. 11, extraction efficiencies significantly decrease with the concentration of Mg^{2+} ion in the whole pH range. Even in case of pH 11.0, the efficiency reaches about 20% at 1,350 ppm. This means Mg^{2+} ion in seawater might be a major hindrance to lithium extraction from seawater.

From these results, it could be concluded that dominant metallic ions in seawater, such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , reduce the extraction efficiency of lithium ion and the reduction is serious in lower pH range.

For further discussion, previous experimental results were rearranged into Fig. 12. Fig. 12 shows the effects of pH on the lithium extraction from aqueous solutions with a dominant ion at its concentration in seawater. The extraction efficiencies of lithium ion decrease with dominant ions in order of Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+} .

While monovalent metallic ions reduce the efficiencies by the

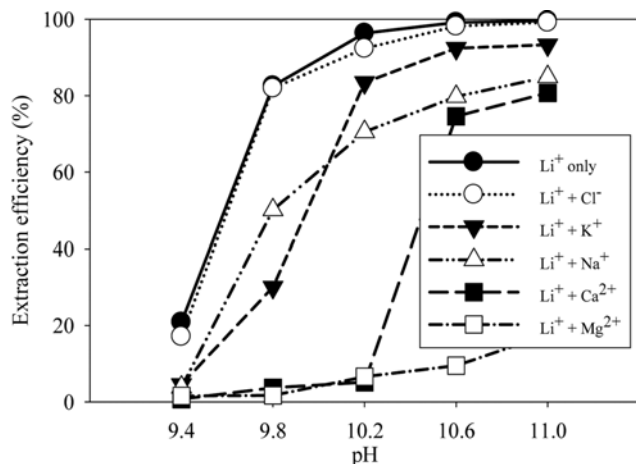


Fig. 12. Effect of pH on the lithium extraction from aqueous solutions with a dominant ion at its concentrations in seawater. $[\text{Li}^+]_0 = 1.0$ ppm, $[\text{TTA}] = 0.02$ M, $[\text{TOPO}] = 0.04$ M.

competition with lithium ion for the complex formation with extractants, divalent ions reduce by some other reasons.

Mg^{2+} ion could significantly reduce the extraction efficiency of lithium ion, because extractant TTA forms a magnesium chelate insoluble in solvent [18].

Ca^{2+} also significantly reduces the efficiency because equilibrium constant of Ca^{2+} for extraction reaction is much higher than those of K^+ and Na^+ , lower than that of lithium ion [18,19].

Even though the extraction of lithium ion is hindered by metallic dominant ions, the extraction efficiencies were higher than 70% when pH was above 10.6, except for Mg^{2+} ion.

The fact that extraction efficiency of lithium ion from aqueous solution with Mg^{2+} ion is very low will not make a serious problem for extraction of lithium ion from seawater, because Mg^{2+} ion can be easily removed by electrodialysis [20], natural and alkaline modified pumice stone systems [21], layer-layer chemical deposition technique [22], etc.

CONCLUSIONS

From the experimental research on the solvent extraction of lithium ion from aqueous solutions using β -diketones and neutral ligands in kerosene, the following results could be obtained.

0.02 M TTA and 0.04 M TOPO in kerosene was an optimum combination of extractants for the extraction of lithium ion from aqueous solutions at the volume ratio of extraction solution to aqueous solution 1 : 1.

The extraction efficiencies of lithium ion from aqueous solutions increased with pH of the aqueous solutions. The efficiencies decreased with the concentration of dominant metallic ions in lithium aqueous solutions, while Cl^- ion showed almost no effect on the efficiency up to its concentration in seawater.

Except for Mg^{2+} ion, more than 70% of lithium ion could be extracted at pH 10.6 from aqueous solutions with a dominant ion at its concentration in seawater.

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