Solvent extraction of Li+ using organophosphorus ligands in the presence of ammonia

<table>
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<th>Journal:</th>
<th>Separation Science and Technology</th>
</tr>
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<tbody>
<tr>
<td>Manuscript ID:</td>
<td>LSST-2013-6839.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Original Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>n/a</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>EL-ESWED, Bassam; Al-Balqa Applied University, Basic Sciences, Zarqa University College Sunjuk, Mahmoud; Hashemite University, Chemistry Department Al-Degs, Yahya; Hashemite University, Chemistry Department Shtaiwi, Amneh; Hashemite University, Chemistry Department</td>
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<tr>
<td>Keywords:</td>
<td>Li+, organophosphorus ligands, selective extraction, ammonia</td>
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Solvent extraction of Li\(^+\) using organophosphorus ligands in the presence of ammonia

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Abstract

In this work, the selective extraction of Li\(^+\) with the aid of organophosphorus ligands (H-OP) including phenylphosphonic (H-PHO), phenylphosphinic (H-PHI) and bis(2-ethylhexyl) phosphoric (H-BIS) acids in the absence and presence of ammonia was studied. Adding NH\(_3\) to the aqueous phase resulted in significant improvement in the % extraction of Li\(^+\) into the organic phase containing H-OP ligands. The highest % extraction values obtained in the case of H-PHO, H-PHI, and H-BIS were 43.2%, 45.7% and 90.0%, respectively. Two mechanisms were inferred; the first was that the extraction equilibrium reaction of LiCl + H-OP \(\leftrightarrow\) LiTOP + HCl shifted forward due the reaction of the produced HCl with NH\(_3\). The second mechanism was that the Li\(^+\)/NH\(_4\)\(^+\) exchange of NH\(_4\)TOP (produced from the reaction of H-OP with NH\(_3\)) was easier than Li\(^+\)/H\(^+\) exchange of H-OP itself. Competitive extraction experiments indicated that the selectivity factors of Li\(^+\) over Na\(^+\) and K\(^+\) were strongly dependent on the concentration of H-OP ligands which suggested that aggregation of ligand molecules via hydrogen bonding is the limiting factor for selectivity.

Keywords: Li\(^+\); selective extraction; organophosphorus ligands; ammonia

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1. Introduction:

The quantitative and selective extraction of Li\(^+\) ion from aqueous solution is a difficult task due to strong hydration of Li\(^+\) [1]. Much attention has been focused on lithium because of its wide industrial and medical applications [2]. Nowadays, lithium-ion batteries are widely used as electrochemical power sources in mobile telephones, personal computers, and video cameras [3]. In connection with the high demand for supplying lithium, much effort has been paid to extracting Li\(^+\) from hot spring water and sea water [2]. However, little is known about designing an ionophore showing high selectivity for Li\(^+\), not only because Li\(^+\) has strong hydration in water, but also because sodium ion is much more abundant in nature [2]. The recovery of Li\(^+\) from spent lithium-ion batteries is a recent challenge [3,4]. Over the last four decades, several kinds of Li\(^+\) ionophores have been synthesized such as spherands and crown ethers derivatives [1,2,5,6]. The high cost and difficulty of synthesis of these ionophores suppressed their commercial applications for Li\(^+\) extraction and more research is recommended on this subject.

Organophosphorus acids were widely applied for selective separation of actinides, lanthanides and transition metals [7, 8-10]. Only few examples are available for using organophosphorus ligands in extraction of Li\(^+\) [11-14]. Trioctylphosphine oxide–dibenzooyl methan system was used as an extractant for Li\(^+\) from aqueous into p-xylene phase. The % extraction was 99.2% and the selectivity factor with respect to Na\(^+\) was 131 [11]. Alkyl phosphoric acid-crown ether systems were used also as an extractant for Li\(^+\) from aqueous into chloroform phase. The highest % extraction obtained was 37% and the selectivity factor (Li\(^+\)/Na\(^+\)) was 14.7 [12]. Theonyln trifluoroacetone-trioctyl phosphine oxide system was also employed as an extractant for Li\(^+\) from aqueous solutions with 43% extraction efficiency and 630 selectivity factor (Li\(^+\)/Na\(^+\)) [13]. Organophosphorus acids were thought to dissociate on the organic–aqueous interface to release H\(^+\) and then to undergo interfacial chemical reaction with metal ions [14, 15].

In order to understand Li\(^+\) extraction efficiency and selectivity of organophosphorus acids (H-OP), more extractants should be investigated. The aim of the present work was to test Li\(^+\) extraction efficiency and selectivity using phenylphosphonic (H-PHO),
phenylphosphinic (H-PHI) and bis(2-ethylhexyl) phosphoric (H-BIS) acids in the absence and presence of NH$_3$.

2. Materials and methods

Analytical grade reagents were used in this work. Lithium chloride, phenylphosphonic (H-PHO), phenylphosphinic (H-PHI) and bis(2-ethylhexyl) phosphoric (H-BIS) acids were purchased from Aldrich (Germany). Ammonia was obtained from TEDIA (USA), pentanol was obtained from GPR (UK), sodium chloride and potassium chloride were purchased from GCC (UK).

The concentrations of Li$^+$, Na$^+$, and K$^+$ were determined by AFP-100 Flame photometer (Biotech Engineering Management Corporation, UK). Propane fuel and air were fed into the flame. The signal of instrument was adjusted to zero using deionized water. The signals of standards (5-105 ppm) and samples were then measured. Before measurements, the blank and standards were subjected to the extraction procedure in order to eliminate the effect extraction procedure on the signal (section 2.2). A Julabo GFL 1083 thermostatic water bath shaker at 25$^\circ$C was used in this study. All pH measurements of extraction samples were made using a Russell pH meter (USA) with a
combined glass electrode. Analytical standard SCALTEC SBC32 balance (± 0.0001 g) and CLIFTON BS402-D Centrifuge (company, England) were used in the present study.

2.1. Preparation of organic and aqueous solutions
Stock solutions of 0.30 M concentration of H-OP ligands were prepared by dissolving appropriate amounts of H-PHI, H-PHO, and H-BIS in pentanol. Diluted concentrations of the ligands were prepared from the earlier stock solutions using pentanol. Standard aqueous solutions of of Li⁺, Na⁺, and K⁺ ions were prepared by dissolving appropriate amounts of analytical reagents of LiCl, NaCl, and KCl in 250.0 ml solutions. Different aqueous solutions of ammonia of variable concentrations were prepared to be used for preparing metal ions solutions.

2.2. Procedure of Li⁺ extraction from solution
The general extraction protocol was adopted in this work. Aliquot of 6.0 mL of pentanol containing H-OP ligand was mixed with 6.0 mL of aqueous solution (containing Li⁺ either alone or with Na⁺ or K⁺) and the final mixture was agitated using a thermostated shaker at 25°C for 120 min. Finally, the two phases were centrifuged for 15 min to achieve complete separation. The aqueous phase was taken and analyzed for Li⁺ or other competing ions using flame photometer. Effect of H-OP ligand concentration, NH₃ and other competing ions (Na⁺ and K⁺) on Li⁺ extraction was studied as outlined in the following sections.

2.3. Influence of ligands concentration on Li⁺ extraction
Influence of H-OP ligands concentration on Li⁺ extraction was studied using the following concentrations: 0.15, 0.075, 0.060, 0.045, 0.030, and 0.015 M. The initial concentration of Li⁺ in the aqueous phase was kept at 0.015 M. The earlier extraction procedure (section 2.2) was applied.

2.4. Influence of NH₃ concentration on Li⁺ extraction
Different solutions of Li⁺ (0.015 M) were prepared in the presence of NH₃. The final concentrations of NH₃ in the solutions were 4.00, 2.00, 1.00, 0.50, 0.10, 0.01 and 0.001 M. The outlined extraction procedure (section 2.2) was applied. The pH of the aqueous phase was measured before and after extraction with the organic phase containing H-OP
ligands. The effect of using NaOH instead of NH₃ (to increase the pH of aqueous phase) on the % extraction of Li⁺ ion was also studied in order to make a comparison with the effect of using NH₃.

2.5. Influence of competing ions (Na⁺ and K⁺) on Li⁺ extraction: selectivity study

A mixture of Li⁺, Na⁺ and K⁺ of initial concentration 0.015 M was prepared using 4.0 M ammonia solution. The multi-ions mixture was extracted using different concentration of H-OP ligands (0.15, 0.075, 0.060, 0.045, 0.030, and 0.015 M) by applying the outlined extraction protocol (section 2.2). The concentrations of Li⁺, Na⁺ and K⁺ in the aqueous layer were determined using flame photometer.

2.6. Modeling extraction data

1. Effect of pH: The data obtained from studying the effect of NH₃ on the extraction of Li⁺ was treated in terms of a simple model similar to that used by Zushi et al. [14]. The extraction equilibrium of Li⁺ using H-OP ligands was considered to occur according to equation 1.

\[ \text{Li}^+(aq) + n \text{H-OP}(org.) \leftrightarrow \text{Li-}(\text{OP})_n(\text{org.}) + x\text{H}^+(aq) \] ………………(1)

The corresponding equilibrium constant is defined as:

\[ K = \frac{[\text{Li-}(\text{OP})_n][\text{H}^+]^x}{[\text{Li}^+][\text{H-OP}]^n} \] …………………………(2)

By introducing the distribution ratio:

\[ D = \frac{[\text{Li-}]_{\text{org}}/[\text{Li}^+]_{\text{aq}} = [\text{Li-}(\text{OP})_n]/[\text{Li}^+] \] …………………………(3)

By substitution of equation 3 in 2, the following logarithmic expressions are obtained:

\[ \log D = n \log [\text{H-OP}] + \text{constant (if pH is kept constant)} \] …………..(4)

\[ \log D = x \text{pH} + \text{constant (if [H-OP] is kept constant)} \] …………….…(5)

2. Ammonium organophosphate: In this approach, ammonia was assumed to participate in the Li- OP complex in the organic layer as NH₄-OP (equation 6).

\[ \text{Li}^+(aq) + n \text{H-OP}(org.) + m \text{NH}_3(aq) \leftrightarrow \text{Li-}(\text{OP})_n(\text{NH}_4)_m(\text{org.}) \] …………..(6)

The corresponding equilibrium constant is defined as:

\[ K = \frac{[\text{Li-}(\text{OP})_n(\text{NH}_4)_m(\text{org.})]/[\text{Li}^+][\text{H-OP}]^n[\text{NH}_3]^m}{ \] …………………………(7)

By introducing the distribution ratio:
D = [Li⁺]_{org}/[Li⁺]_{aq} = [Li-(OP)_n(NH₄)_m]/[Li⁺] ..............................(8)

By substitution of equation 8 in 7, the following logarithmic expression is obtained:

\[ \log D = m \log[\text{NH}_3] + \text{constant} \text{ (if } [\text{H-OP}] \text{ is kept constant)} \] ..............................(9)

3. Results and Discussion
3.1. Effect of H-OP concentration on Li⁺ extraction

The values of % extraction of Li⁺ from aqueous solutions into pentanol using different concentrations of H-OP ligands were presented in Figure 1. The % extraction of Li⁺ was defined as the concentration of Li⁺ extracted into the organic layer divided by the initial concentration of Li⁺. As shown in Figure 1, the % extraction of Li⁺ from its aqueous solutions was low, even if relatively large amounts (up to 0.15 M) of OP ligands were employed. Changing the pH of aqueous solution from 7 to 12 using NaOH (Figure 2) did not result in any improvement in the % extraction of Li⁺. However, this may be due to the competition of Na⁺ with Li⁺. This suggested using ammonia instead of using NaOH to increase the pH of aqueous solution.

In the most recent reference, the reported coordination number of Li⁺ ion in aqueous solutions was 4 [16]. So the low extraction efficiency of H-OP ligands may be due to the inability of these ligands to satisfy the coordination sphere of Li⁺, especially because the extraction is carried out under acidic environment. Actually, in the present work, ammonia was introduced because it was supposed to have dual role in increasing the pH of extraction and/or completing the coordination number of Li⁺.

< Figure 1 >
< Figure 2 >

3.2. Effect of H-OP concentrations on % extraction of Li⁺ in the presence of NH₃

The results of % extraction of Li⁺ in the presence of 1% NH₃ were presented in Figure 1. The presence of 1% NH₃ (pH = 11.4) in the aqueous phase resulted in significant improvement in the % extraction of Li⁺. The % extraction had increased from 4% to 19.7% in the case of H-PHI by addition of 1% NH₃. A similar behavior was observed in H-PHO and H-BIS cases and the maximum extraction values were 21.3% and 83.0%, respectively. Plots of log concentration of H-OP versus log D (Figure 3, equation 4) indicated that about 0.5 H-PHO, 1 H-PHI and 1 H-BIS ligands are bound to Li⁺ in the
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extraction process. Note that 1% NH$_3$ concentration was chosen only as a first trial and the effect of different concentrations of NH$_3$ will be studied in the next section.

<Figure 3>

3.3. Effect of NH$_3$ concentration on the % extraction of Li$^+$

The results of effect of NH$_3$ concentration on the % extraction of Li$^+$ using H-OP ligands were displayed in Figure 4 which indicated that NH$_3$ plays a significant effect on the % extraction of Li$^+$. The addition of 4M NH$_3$ resulted in an increase of % extraction of Li$^+$ to 43.2%, 45.7% and 90.0% in the case of H-PHO, H-PHI and H-BIS, respectively (compared with 4.0%, 4.7% and 1.9% in the absence of NH$_3$).

Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) and 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester (PC-88A) were reported by Zhao et al. as poor extractants for recovery of Li$^+$ from acidic leaching solution of waste cathodic material of spent lithium batteries containing Co(II), Mn(II) and Li$^+$ [15]. Furthermore, a zirconium phosphate – based material was found to be very poor extractant for Li$^+$ [17]. Since these extractants are effective for many other metal ions, this reflects the difficulty of extracting Li$^+$ using organo and inorgano-phosphorus compounds. However, Zushi et al. showed that 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester was effective in extracting Li$^+$ from aqueous solution if the pH of the aqueous solution is increased (from 5 to 7) using a buffer of potassium dihydrogen phosphate and sodium teteraborate [14]. It is worth to mention that Zushi et al. used 0.005 M Li$^+$ solutions compared with 0.015 M Li$^+$ solutions in the present work and the role of the buffer system employed by them might be similar to that of ammonia.

From Table 1 and Figure 4, it was noted that the difficulty of extracting Li$^+$ was overcome by using a minimum concentration of NH$_3$ that is equivalent to the concentration of H-OP (0.15 M). This suggested that H-OP reacted with NH$_3$ to form NH$_4$-OP.

For NH$_3$ concentrations < 0.5 M (Table 1), and as reflected from a comparison between initial pH$_i$ (before extraction) and equilibrium pH$_{eq}$ (after extraction) values, it was clear from the great drop in pH values upon extraction that all the NH$_3$ was consumed by the
H-BIS. This consumption may be due to formation of either NH₄Cl in the aqueous layer or NH₄-OP in the organic layer.

Plots of log concentration of NH₃ versus log D (Table 1, equation 9) indicated that the number of NH₃ ligands bound to Li⁺ in the organic layer is low (0.2-0.6) and dependant on the concentration range of NH₃ used. So, ammonia is not a probable complexing (or synergistic) ligand for Li⁺. Furthermore, plots of pH versus log D (Table 1, equation 5) indicated that about 0.5 to 1 mole of H⁺ were replaced in the extraction process.

The above findings led to two mechanisms of extraction. The extraction equilibrium reaction (equation 8) between H-OP and LiCl has very low equilibrium constant. The produced HCl is consumed by NH₃ (equation 9) and so forcing the equilibrium forward.

\[
\text{LiCl + H-OP} \leftrightarrow \text{Li-OP + HCl} \tag{8}
\]

\[
\text{HCl + NH}_3 \rightarrow \text{NH}_4\text{Cl} \tag{9}
\]

Another possible mechanism is that H-OP reacts with equimolar amount of NH₃ (equation 10) and the resultant NH₄-OP undergoes equilibrium ion exchange reaction with LiCl (equation 11). The exchange of NH₄⁺ with Li⁺ is more favored than the exchange of H⁺ with Li⁺ because the difference in charge to size ratio between the NH₄⁺ and Li⁺ is greater than that between H⁺ and Li⁺.

\[
\text{NH}_3 + \text{H-OP} \rightarrow \text{NH}_4\text{-OP} \tag{10}
\]

\[
\text{LiCl + NH}_4\text{-OP} \leftrightarrow \text{Li-OP + NH}_4\text{Cl} \tag{11}
\]

Thus, both mechanisms lead to similar species (Li-OP and NH₄Cl).

< Figure 4 >

3.4. Selective extraction of Li⁺

The selective extraction of Li⁺ in the presence of Na⁺ and K⁺ ions was tested to evaluate the practical application of the proposed method. The selective extraction of Li⁺ was studied in 4M NH₃ solutions. The results of competitive extraction of Li⁺, Na⁺, K⁺ were given in Figures 5. The presence of Na⁺ and K⁺ with Li⁺ resulted in a decrease in the % extraction of Li⁺ by H-PHO from 43.2% in the case of single ion to 29.2 in the case of
multi-ion extraction. Similarly, for H-PHI, the value dropped from 45.7% to 29.6 in the case of multi-ion extraction. This reflects a negative competitive process. However, for H-BIS, the % extraction of Li$^+$ slightly decreased from 90.0% in the case of single ion to 81.1% in the case of multi-ion extraction. Actually, Li$^+$ is less polar and less basic than Na$^+$ and K$^+$. So H-BIS has more preference for Li$^+$ than H-PHO and H-PHI.

Figure 5 indicated that the order of preference of competitive ions was dependent on the concentration of H-OP ligands. For example, the order was Li$^+$ > Na$^+$ > K$^+$ at low concentrations of H-OP ligands. However, the order was reversed at high concentrations of H-OP ligands. This suggested that the selectivity toward Li$^+$ is dependent on the degree of aggregation of ligand molecules. The aggregation of H-PHO and H-BIS was reported previously in the literature [14, 15, 16].

3.5. Separation factors
Separation factor (SF) was calculated by dividing distribution ratio of different metals:

$$ SF_{Li/Na} = \frac{D_{Li}}{D_{Na}} \quad or \quad SF_{Li/K} = \frac{D_{Li}}{D_{K}} $$

(12)

Where D is the distribution coefficient defined in equation 3. Although the water solubility of LiCl (0.26 mmol/L) is much higher than the solubility of NaCl (0.08 mmol/L) and KCl (0.05 mmol/L) [20], separation factors $SF_{Li/Na}$ and $SF_{Li/K}$ greater than unity were achieved in the case of PHO (Figure 6) as 1.82 and 2.85, respectively. Furthermore, the highest separation factors $SF_{Li/Na}$ and $SF_{Li/K}$ achieved in the case of H-PHI (Figure 6) were 2.47 and 2.13, respectively. On the other hand, the highest separation factors $SF_{Li/Na}$ and $SF_{Li/K}$ achieved in the case of H-BIS were 1.42 and 4.76, respectively. The earlier separation factors indicated that the proposed extraction method would have practical application for removing Li$^+$ from solution even in the presence of Na$^+$ and K$^+$ ions.

Figure 6 revealed that the separation factor $SF_{Li/Na}$ increases with increasing concentration of PHO and PHI. On the other hand, the separation factor $SF_{Li/K}$ was found to decrease with increasing concentration of PHO and PHI extractant. This reflected the effect of ligands aggregation (hydrogen bonded framework) on the
selectivity of these ligands toward Li\(^+\). It seems that the hydrogen bonding frameworks of organophosphorus acids or their ammonium derivatives creates different environments that are suitable for specific metal ion size.

< Figure 6 >

4. Conclusions

The % extraction of Li\(^+\) using H-OP ligands was very low. However, the addition of NH\(_3\) resulted in a significant increase in the % extraction of Li\(^+\) to reach 43.2%, 45.7% and 90.0% in the case of H-PHO, H-PHI and H-BIS, respectively. The results indicated that NH\(_3\) could increase the % extraction of Li\(^+\) through two mechanisms. The first was by forcing the equilibrium reaction of LiCl with H-OP forward by consuming the produced HCl. In the second mechanism, NH\(_4\)-OP undergo more effective ion exchange with Li\(^+\) than H-OP itself. The selectivity toward Li\(^+\) was found to be dependent on the degree of aggregation of H-OP ligand molecules. The aggregation of H-OP or their ammonium derivatives through hydrogen bonding creates different environments which may be more suitable for one metal than another. The proposed extraction protocol could be applied for Li\(^+\) extraction from real matrices.

Acknowledgments

This work was financially supported from the deanship of graduate studies and academic research/The Hashemite University (Zarqa, Jordan) in 2011. We would like to thank Shwekar Bostangi Nedal Abo-Farah for their technical help.
References


Figures Captions

Figure 1. Effect of the concentrations of H-PHO, H-PHI and H-BIS on the % extraction of Li$^+$ ions in the absence and presence of 1% NH$_3$.

Figure 2. Effect of pH, adjusted using NaOH solution, on the % extraction of Li$^+$ using H-BIS.

Figure 3. Plots of log concentration of H-PHO, H-PHI and H-BIS ligands versus log D in the presence of 1% NH$_3$.

Figure 4. Effect of concentration of NH$_3$ on the % extraction of Li$^+$ ions using H-PHO, H-PHI and H-BIS Ligands.

Figure 5. Effect of concentration of H-PHO, H-PHI and H-BIS ligands on the competitive extraction of Li$^+$, Na$^+$ and K$^+$ in the presence of 4M NH$_3$.

Figure 6. Effect of concentration H-PHO and H-PHI ligands on the separation factors Li$^+$/Na$^+$ and Li$^+$/K$^+$ in the competitive extraction of Li$^+$, Na$^+$ and K$^+$ in the presence of 4M NH$_3$. 

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Table 1. Effect of NH$_3$ concentration on the initial (pH$_i$) and equilibrium pH (pH$_{eq}$) and the estimated stoichiometries (m) of the assumed reaction of NH$_3$ with lithium and the number of H$^+$ replaced (x).

<table>
<thead>
<tr>
<th>Concentration of NH$_3$ (M)</th>
<th>pH$_i$</th>
<th>pH$_{eq}$</th>
<th>% Extraction of Li$^+$</th>
<th>H-PHO</th>
<th>H-PHI</th>
<th>H-BIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>12.5</td>
<td>12.1</td>
<td>90.0</td>
<td>m=0.4(0.96)* x=0.9(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
</tr>
<tr>
<td>2</td>
<td>12.2</td>
<td>11.8</td>
<td>86.5</td>
<td>m=0.4(0.96) x=0.9(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
</tr>
<tr>
<td>1</td>
<td>12.0</td>
<td>11.4</td>
<td>84.1</td>
<td>m=0.4(0.96) x=0.9(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
</tr>
<tr>
<td>0.5</td>
<td>11.9</td>
<td>11.1</td>
<td>83.5</td>
<td>m=0.4(0.96) x=0.9(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
<td>m=0.4(0.97) x=0.8(0.97)</td>
</tr>
<tr>
<td>0.1</td>
<td>11.5</td>
<td>6.1</td>
<td>68.4</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.6(0.98) x=1(0.98)</td>
</tr>
<tr>
<td>0.01</td>
<td>11.0</td>
<td>4.4</td>
<td>25.2</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.6(0.98) x=1(0.98)</td>
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<tr>
<td>0.001</td>
<td>10.3</td>
<td>3.9</td>
<td>12.0</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.2(0.95) x=0.4(0.95)</td>
<td>m=0.6(0.98) x=1(0.98)</td>
</tr>
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</table>

*Values between brackets are for correlations coefficients of linear plots (R$^2$).
Figure 1. Effect of the concentrations of H-PHO, H-PHI and H-BIS on the % extraction of Li+ ions in the absence and presence of 1% NH3.
Figure 2. Effect of pH, adjusted using NaOH solution, on the % extraction of Li+ using H-BIS.
Figure 3. Plots of log concentration of H-PHO, H-PHI and H-BIS ligands versus log D in the presence of 1% NH3.
Figure 4. Effect of concentration of NH3 on the % extraction of Li+ ions using H-PHO, H-PHI and H-BIS Ligands.
Figure 5. Effect of concentration of H-PHO, H-PHI and H-BIS ligands on the competitive extraction of Li+, Na+ and K+ in the presence of 4M NH3.
Figure 6. Effect of concentration H-PHO and H-PHI ligands on the separation factors Li+/Na+ and Li+/K+ in the competitive extraction of Li+, Na+ and K+ in the presence of 4M NH3.
Reviewer 1

1. In the revised version of the article, the idea of synergistic ammonia was excluded and replaced by new treatment which involves the ammonium salt of organophosphorus acid.

2. Table 1: The initial and equilibrium pH values are given and discussed in the text.

3. The effect of using different concentrations of NH$_3$ are given in section 3.3 and the study was not restricted to 1% NH$_3$. Concentrations of 0.5, 1, 2, 4M NH$_3$ were sufficient to convert the organophosphorus acids into the ammonium salt.

4. A new Figure 2 was added to show the effect of raising the pH using NaOH. This experiment was not included in the first version of the article because of the competing effect of Na$^+$ on extraction of Li$^+$. However, this experiment showed that there is no positive effect of raising the pH using NaOH on the % extraction.

5. Two related mechanism were proposed in the revised version of the article:

   a) The extraction equilibrium reaction (equation 8) between H-OP and LiCl has very low equilibrium constant. The produced HCl is consumed by NH$_3$ (equation 9) and so forcing the equilibrium forward.

   \[
   \text{LiCl} + \text{H-OP} \leftrightarrow \text{Li-OP} + \text{HCl} \quad \text{........................................................... (8)}
   \]

   \[
   \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl} \quad \text{........................................................... (9)}
   \]

   b) Another possible mechanism is that H-OP reacts with equimolar amount of NH$_3$ (equation 10) and the resultant NH$_4$-OP undergoes equilibrium ion exchange reaction with LiCl (equation 11). The exchange of NH$_4^+$ with Li$^+$ is more favored than the exchange of H$^+$ with Li$^+$ because the difference in charge to size ratio between the NH$_4^+$ and Li$^+$ is greater than that between H$^+$ and Li$^+$.

   \[
   \text{NH}_3 + \text{H-OP} \rightarrow \text{NH}_4\text{-OP} \quad \text{........................................................... (10)}
   \]

   \[
   \text{LiCl} + \text{NH}_4\text{-OP} \leftrightarrow \text{Li-OP} + \text{NH}_4\text{Cl} \quad \text{........................................................... (11)}
   \]

6. The Written English was revised.
Reviewer 2

1. The abbreviations suggested by the reviewer were thankfully included through all the text.

2. The references suggested by the reviewer were included in the article and the results of their works were compared with those in the present article.

3. Li\(^+\) was used through all the article.

4. The first sentence in the abstract was removed.

Reviewer 3

a) The written English was revised.

b) Details for analysis of alkali metals were added in section 2. Actually we did not analyze NH\(_3\) or NH\(_4\)\(^+\) in the organic phase. We have tried to analyze the residual solid after evaporation of the organic layer by FTIR. The results indicated that ammonium salt may be formed, but the bands were overlap with those of the organophosphorus acid.

c) The extraction mechanism introduced in the revised version of the article takes into account the formation of ammonium salt of the organophosphorus acid (see section 3.3).

d) Thanks for the reviewer for the explanation. It was included in sections 3.4.