

## 상용화 추출제 및 이온성액체에 의한 염산의 용매추출

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### Solvent Extraction of Hydrochloric Acid Using Commercial Extractants and Synthesized Ionic Liquids

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#### 요 약

염산의 용매추출 및 탈거 거동을 조사하기 위해 상용화추출제인 LIX 63 단독 및 TEHA/ Cyanex 923/ Aliquat 336의 혼합추출제와 ALi-SCN과 ALi-PC 이온성액체를 사용하였다. 상기 추출제중에서 ALi-PC가 가장 높은 추출률(80%)을 보였으나 탈거가 어려웠다. 반면 LIX 63의 경우 추출률은 낮았으나, 탈거율은 81%로 가장 높았다. 옥탄올을 유기상에 첨가하면 염산 추출이 오히려 감소했다. 에탄올을 염산용액에 첨가하면 LIX 63, ALi-PC, ALi-SCN에 의한 염산의 추출과 탈거 거동이 크게 개선되었다.

**주제어** : 염산화수, 용매추출, 탈거, 개질제

#### Abstract

The extraction and stripping of HCl from aqueous solutions by commercial extractants like LIX 63 and its mixture with TEHA/ Cyanex 923/ Aliquat 336 and ionic liquids like ALi-SCN, ALi-PC in kerosene was investigated. Among these extractants, ALi-PC showed the best extraction effectivity (above 80%), but it was difficult to strip HCl from the loaded phase. Although the extraction percentage of HCl by LIX 63 was not high, the stripping performance was above 81%. The addition of octanol to the organic phase led to negative effect on the extraction performance of HCl. The addition of C<sub>2</sub>H<sub>5</sub>OH into aqueous solutions significantly increased the extraction and stripping percentage of HCl by LIX 63, ALi-PC and ALi-SCN.

**Key words** : Hydrochloric acid recovery, Solvent extraction, Stripping, Modifier

#### 1. Introduction

Hydrochloric acid (HCl) is widely employed in hydrometallurgical processes as a metal leaching agent

for ores and secondary resources due to its excellent chemical characteristics such as strong complex formation and fast reaction kinetics<sup>1)</sup>. The chloride system applied in metallurgy can be operated over a wide range of

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oxidizing conditions and acidity<sup>2</sup>). In order to meet the environmental regulation against the treatment of HCl and to improve process economics, it is desirable to recover HCl from the spent leaching solutions<sup>1,2</sup>.

Several methods are available to treat effluents containing inorganic acids, including neutralization, diffusion dialysis, membrane process, precipitation, solvent extraction, and ion exchange<sup>1,3,4</sup>. Among these methods, solvent extraction is considered to be one of the most effective one for extracting inorganic acids from effluents. During solvent extraction, the reaction between the extractants and the protons of the acid might be responsible for the extraction of these acids<sup>5</sup>. In general, most tertiary amines extract hydrogen ions through the protonation mechanism, while neutral extractants can extract through the solvation<sup>6-9</sup>. According to previous works, the commercial extractants such as TEHA (tris 2-ethylhexyl amine), Cyanex 923 (a mixture of four trialkylphosphine oxides), TBP (tributyl phosphate), Alamine 336 (a mixture of tri-octyl/decyl amine) have been employed for the recovery of H<sub>2</sub>SO<sub>4</sub> and HCl<sup>10</sup>. Among them, TEHA has the best performance for extraction but stripping percentage of HCl from the loaded organic phase was low, resulting in low concentration of HCl in the recovered acid<sup>6,10</sup>. The HCl from the loaded TEHA could be completely stripped by 2 M ammonia solution<sup>11</sup>. However, it seems to be an infeasible solution in industry due to the complication of stripping liquor and the difficulty in regeneration of HCl. Although the extraction percentage of H<sub>2</sub>SO<sub>4</sub> and HCl by Alamine 336 is higher than that by Cyanex 923 and TBP, but the stripping of the acids from the loaded Alamine 336 is also very difficult<sup>6,10,12</sup>. It has been reported that some ionic liquids (ILs) can extract hydrogen ions from weak HCl<sup>13,14</sup>. The extraction of hydrogen ion by ILs depends on solution pH. The extraction reaction of hydrogen ions from weak chloride solution by ILs synthesized from Aliquat 336 (N-Methyl-N, N, N-trioctylammonium chloride) and Cyanex 272 (bis(2,2,4 trimethylpentyl)phosphinic acid) can be de-

scribed as solvation mechanism<sup>5</sup>.

The solvent extraction of inorganic acids from spent leaching solutions can be beneficial on the light of environment and process economics but most of the works have been done from weak acidic solutions<sup>12</sup>. In order to overcome some disadvantages of employing single TEHA, the influence of adding neutral extractants such as Cyanex 921 (trioctylphosphine oxide), DOS (din-octyl sulfide), MIBK (methyl isobutyl ketone), TBP (tributyl phosphate), and TOP (tri octyl phosphate) to TEHA has been investigated on the extraction of HCl<sup>11</sup>. LIX 63 (7-Hydroxy-5,8-diethyl-6-dodecanone oxime) is a kind of oxime extractant and many works have been reported on the synergistic effect of the extractant mixture containing LIX 63<sup>15,16</sup>. However, there are few works on the solvent extraction of HCl with the mixture of TEHA and LIX 63.

Some ionic liquids (ILs) which are synthesized by mixing Aliquat 336 and organophosphorus acids can act as bifunctional extractants and thus extract hydrogen ions. Therefore, in this work, solvent extraction of hydrochloric acid from concentrated solution was investigated by employing commercial extractants and ILs. For this purpose, the extraction and stripping behavior of HCl was compared between commercial extractants (LIX 63 and a mixture of LIX 63 and TEHA) and synthesized ILs (ALi-SCN, ALi-PC).

## 2. Experimental

The acidity of the solution was adjusted by adding doubly distilled water or a mixture of doubly distilled water and ethanol (C<sub>2</sub>H<sub>5</sub>OH; Daejung Co., 94.5%) to concentrated HCl (Daejung Co., 35%) and H<sub>2</sub>SO<sub>4</sub> solution (Daejung Co., 95%). The commercial extractants such as TEHA (R<sub>3</sub>N, BASF Co., 99%), LIX 63 (HR, Is Chem. Co., 70%), Cyanex 923 (Cytec Inc., 93%), Aliquat 336 (BASF Co., 93%) were used without any purification. 1-Octanol (Duksan Pure Chemical Co., 99%) was used as a modifier. Ionic liquid (ALi-PC) was

synthesized by mixing an equimolar concentration of Aliquat 336 and PC88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, HA, Cytec Inc., 95%) according to the method reported in the literature<sup>13</sup>. Ali-SCN was synthesized by mixing Aliquat 336 and NH<sub>4</sub>SCN (ammonium thiocyanate, Daejung Co., 99.0%) as reported<sup>17</sup>. Kerosene (Samchun Pure Chemical Co.) was used as a diluent and all the employed chemicals were of analytical grade.

The extraction and stripping experiments were conducted by shaking equal volumes of aqueous and organic phases (20 mL each) in a screwed cap bottle for 30 mins using a Burrell wrist action shaker (model 75, USA) at room temperature (22°C ± 1). The two phases were separated using a separation funnel after holding them for 30 mins. The concentration of hydrogen ions in the aqueous phase before and after extraction was measured by volumetric titration method<sup>18</sup>. The concentration of hydrogen ions in the loaded organic phase was determined by mass balance. The experiments were repeated 3 times with an error of ± 5%.

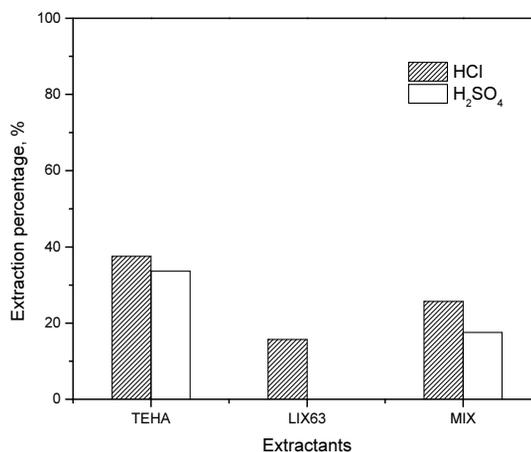
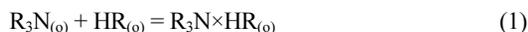
### 3. Results and discussion

#### 3.1. Solvent extraction of HCl by commercial extractants

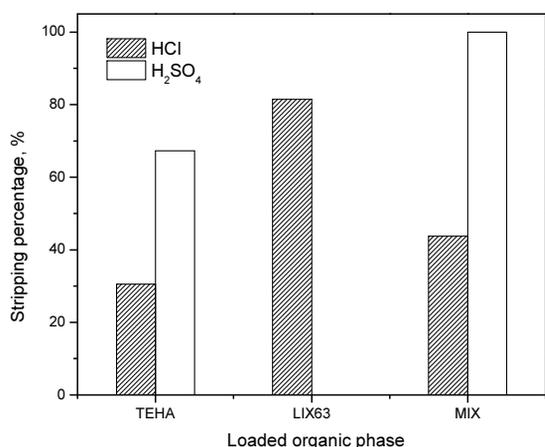
##### 3.1.1. Effect of nature of extractant on solvent extraction of HCl

According to the previous studies, hydrogen ions can be well extracted by amines but the stripping of hydrogen ions from the loaded amines is very difficult<sup>6,10,12</sup>. Among several tertiary amines, TEHA shows the best performance for the extraction of HCl. Addition of neutral extractants such as Cyanex 921, DOS, MIBK, TBP, and TOP to TEHA has negligible effect on the extraction of HCl<sup>11</sup>. Moreover, stripping of HCl from the loaded mixtures of TEHA and neutral extractants is still difficult<sup>6</sup>. Since stripping is the reverse reaction of extraction, it is important to find extraction systems with adequate extraction capability for HCl. It has been

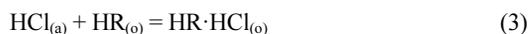
reported that  $\alpha$ -hydroxyoxime like LIX 63 can interact with HCl at high concentration by using characteristic absorption of oxime<sup>19</sup>. Therefore, a mixture of TEHA and LIX 63 was first employed in this work. In order to compare the extraction behavior between HCl and H<sub>2</sub>SO<sub>4</sub>, the concentration of both acids was adjusted to 3 M. Fig. 1 shows the extraction percentage of both acids by TEHA, LIX 63 and a mixture of TEHA and LIX 63. The concentration of single TEHA and LIX 63 was 50 vol% and the total volume percentage of TEHA and LIX 63 in the mixture was 50 vol% (TEHA/LIX 63 ratio = 1) and 20 vol% of octanol was added as a modifier. The extraction performance of single TEHA for both acids was similar, while no sulfuric acid was extracted by single LIX 63. Addition of TEHA to LIX 63 increased the extraction percentage of HCl from 15.7 to 25.7% and H<sub>2</sub>SO<sub>4</sub> from zero to 17.6% compared to single LIX 63. This increase might be ascribed to the interaction between the extractants in binary system, which could lead to synergistic effect. The reactions can be represented as<sup>6,9</sup>



**Fig. 1.** Effect of extractants on hydrogen ion (3 M HCl, 3 M H<sub>2</sub>SO<sub>4</sub>) extraction. Condition: 50% volume of TEHA, LIX 63 and their mixture (MIX) (25:25 vol%) in kerosene and 20% octanol as modifier; O/A = 1; shaking time = 30 mins, 22°C ± 1.



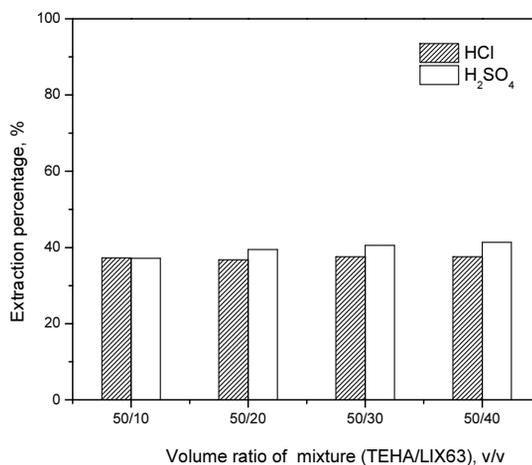
**Fig. 2.** Stripping of hydrogen ion from the loaded phase with H<sub>2</sub>O at 60°C in 30 mins. Condition: organic phase: 50% volume of TEHA, LIX 63 and their mixture (MIX) (25:25 vol%) in kerosene and 20% octanol as modifier; O/A = 1.



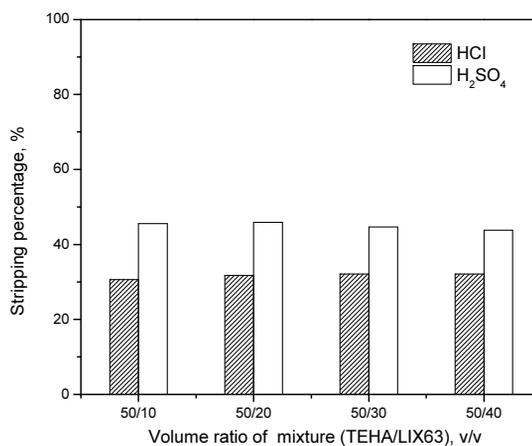
where R<sub>3</sub>N denotes TEHA, HR denotes LIX 63, subscript a and o represent the aqueous and organic phase, respectively.

It has been reported that temperature has a great influence on the stripping efficiency of hydrogen ions from the loaded phase by distilled water<sup>10</sup>. Therefore, the stripping of HCl and H<sub>2</sub>SO<sub>4</sub> from the loaded organic phases was carried out at 60°C. The results indicate that highest stripping percentage of both acids was obtained from the loaded mixture. Especially, H<sub>2</sub>SO<sub>4</sub> was completely stripped with water under from the loaded mixture of TEHA and LIX 63. Besides, HCl was also easily stripped from the organic loaded phase of LIX 63 (% stripping (%S) > 81%, A/O = 1, only one stage) (see Fig. 2).

In order to investigate the effect of the composition of the mixture, the volume percentage of LIX 63 in the mixture was varied from 10 to 40%, while that of TEHA was fixed at 50% v/v. A slight increase in extraction



**Fig. 3.** Effect of concentration of mixture of TEHA and LIX 63 on hydrogen ion (HCl, H<sub>2</sub>SO<sub>4</sub>) extraction. Condition: extractants in kerosene and 20% octanol as modifier; O/A = 1; shaking time = 30 mins.



**Fig. 4.** Stripping of hydrogen ion from the loaded mixture TEHA and LIX 63 with H<sub>2</sub>O at 60°C in 30 mins (O/A = 1).

percentage of both acids was observed when the volume percentage of LIX 63 increased from 10 to 40% (see Fig. 3). Namely, the extraction percentage increased from 36.8 to 37.6% and 37.1 to 41.3% for HCl and H<sub>2</sub>SO<sub>4</sub>, respectively. However, there was little difference in the stripping percentage of both acids in the experimental ranges (see Fig. 4). The stripping percentage of H<sub>2</sub>SO<sub>4</sub> was a little higher than that of HCl with H<sub>2</sub>O at 60°C. Fig. 4 shows that the stripping performance were less

than 50%. Compared to single extractants TEHA/ LIX 63, using their mixture slightly enhance extraction performance (Figs. 1 & 3). However, stripping of HCl from the loaded phase of mixture TEHA and LIX 63 was easier than that of single TEHA (Figs. 2 & 4). Thus, the employment of LIX 63 is more efficient for extraction of HCl on the light of the stripping step.

### 3.1.2. Effect of some additives on HCl extraction

In order to investigate the effect of dielectric constant of aqueous phase, C<sub>2</sub>H<sub>5</sub>OH was added to the aqueous phase to reduce the interaction between hydrogen ions and water molecules, which might enhance the extraction of hydrogen ions as well as hinder the extraction of water<sup>20</sup>). The use of polar and protic solutes shows a favorable effect on the extraction of hydrogen ions through ion pair formation. For this purpose, HCl extraction was compared between H<sub>2</sub>O and a mixture of H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH. In these experiments, the volume ratio of water and C<sub>2</sub>H<sub>5</sub>OH was equal. Table 1 shows the extraction percentage of HCl by LIX 63 from the mixture was 2 times higher than that from water. Although the extraction percentage of HCl was less than 10%, this result indicates that addition of C<sub>2</sub>H<sub>5</sub>OH to water can enhance the extraction of HCl. However, addition of too much C<sub>2</sub>H<sub>5</sub>OH to water can lead to the loss of extractant owing to the increase in its solubility in water mixture. Therefore, the volume ratio of H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH in the mixture was fixed at unity in further experiments.

Moreover, the results showed that HCl was efficiently stripped from loaded organic phases containing LIX 63. Therefore, in order to investigate the extraction and stripping behavior of HCl from the aqueous phase containing C<sub>2</sub>H<sub>5</sub>OH, three kinds of organic phases, namely, single LIX 63 (50%), a mixture of 50% LIX 63 and 20% Cyanex 923 and a mixture 50% LIX 63 and 20% Aliquat 336 were also employed. Among them, the mixture of LIX 63 and Aliquat 336 displays the best extraction capacity (see Table 2).

**Table 1.** Effect of C<sub>2</sub>H<sub>5</sub>OH on HCl extraction by LIX 63 50 vol% in kerosene

Aqueous phase	Extraction percentage, %
HCl in H <sub>2</sub> O	4.0
HCl in H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub> OH	8.5

\*Note: aqueous phases include 1 M HCl in H<sub>2</sub>O and 1 M HCl in the mixture of 50% H<sub>2</sub>O and 50% C<sub>2</sub>H<sub>5</sub>OH (v/v), O/A = 1.

**Table 2.** Effect of extractant on the extraction of 1 M HCl in the mixture 50% H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH

Organic phase	Ratio of components, v/v	Extraction percentage, %
LIX63: kerosene	50:50	8.5
LIX63:Cyanex 923:kerosene	50:20:30	6.5
LIX63:Aliquat 336:kerosene	50:20:30	11.3

**Table 3.** Effect of diluent on HCl extraction by LIX 63, Aliquat 336 and their mixture

Organic phase	Ratio of components, v/v	Extraction percentage, %
LIX 63:octanol:kerosene	50:20:30	6.2
Aliquat 336:octanol:kerosene	50:20:30	0.0
LIX 63:Aliquat 336:octanol:kerosene	50:20:10:20	8.1
LIX 63:Aliquat 336:octanol:kerosene	50:20:20:10	6.2
LIX 63:Aliquat 336:octanol	50:20:30	7.1
LIX 63:Aliquat 336:kerosene	50:20:30	11.3

\*Note: aqueous phases were 1 M HCl in the mixture of 50% H<sub>2</sub>O and 50% C<sub>2</sub>H<sub>5</sub>OH (v/v), O/A = 1.

Modifier can affect the extraction<sup>4,7,21</sup>) and thus the addition of modifier like octanol to the extractants was tested. In these experiments, the aqueous was prepared by adding C<sub>2</sub>H<sub>5</sub>OH to water. Table 3 shows that polar modifier like octanol affects little the HCl extraction and the extraction efficiency was very low. This effect can be explained by the interaction between modifier and extractants. The interaction between extractant and modifier is proportional to the polarity of the modifier, leading to a decrease in the effective concentration of extractants<sup>22</sup>). Therefore, it can be said that addition of poplar modifier to organic phase has negative effect on HCl extraction.

### 3.2. Solvent extraction of HCl by synthesized ionic liquids

When metal ions are extracted by some kinds of ILs from weak acidic solutions, hydrogen ions are also extracted by the anion of the ILs and thus equilibrium pH of the aqueous phase increases<sup>13,14,23</sup>. Moreover, binary mixtures consisting of Aliquat 336 and Cyanex 272 can affect the extraction of hydrogen ions from inorganic acid solutions<sup>13,24</sup>. ILs which can be synthesized from Aliquat 336 and Cyanex 272 showed the excellent performance for the extraction of hydrogen ions when the initial pH range was from 0.05 to 5. These ILs can be easily prepared in the laboratory by reacting Aliquat 336 and organophosphorus acids or anion of inorganic salts through anion exchange mechanism<sup>5,25</sup>.

In this work, ILs derived from Aliquat 336 like ALi-SCN and ALi-PC were employed for the extraction of HCl. Firstly, the concentration of HCl was adjusted to 1 M in aqueous phase. For comparison, water and a mixture of water and C<sub>2</sub>H<sub>5</sub>OH were employed. The volume percentage of H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH was 50% in the mixture. In these experiments, distilled water was employed as a stripping agent. As ILs, 0.5 M ALi-SCN and 0.5 M ALi-PC in kerosene were employed. Although there was little difference in the extraction percentage of HCl from water between the two ILs, the stripping percentage of HCl by ALi-SCN was much higher than that by ALi-PC (see Table 4). This may be attributed to the strong interaction of hydrogen ions with PC88A anions in the organic phase, which hindered the liberation of hydrogen ions into the aqueous phase. The addition of C<sub>2</sub>H<sub>5</sub>OH into water led to an increase in the extraction percentage of HCl by ALi-PC from 11.0 to 42.2%, whereas there was only a light raise from 10.2 to 12.8% in the case of ALi-SCN. However, it was noticed that stripping percentage of hydrogen ions from the loaded ALi-SCN was 90.8%. Meanwhile, hydrogen ions were not stripped from the loaded ALi-PC (see Table 5). These results can be ascribed to the change in the dielectric constant of aqueous phase by adding C<sub>2</sub>H<sub>5</sub>OH.

**Table 4.** Comparison on extraction and stripping of 1 M HCl in distilled water by ionic liquids

Extractants	Extraction percentage, %	Stripping percentage, %
ALi-SCN	10.2	22.8
ALi-PC	11.0	6.3

\*Note: Organic phase: 0.5 M extractant in kerosene, O/A = 1, shaking time = 30 mins, room temperature (22°C ± 1), stripping agent: H<sub>2</sub>O.

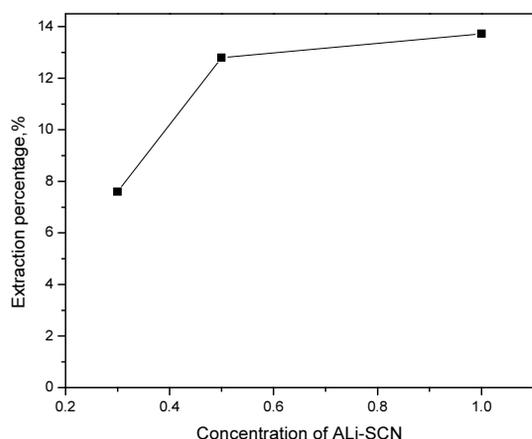
**Table 5.** Extraction and stripping of 1 M HCl in the mixture of 50% H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH (v/v) by ionic liquids

Extractants	Extraction percentage, %	Stripping percentage, %
ALi-SCN	12.8	90.8
ALi-PC	42.2	0.9

\*Note: Organic phase: 0.5 M extractant in kerosene, O/A = 1, shaking time = 30 mins, room temperature (22°C ± 1), stripping agent: H<sub>2</sub>O.

Besides, the hydrophobic anions of ALi-PC may stabilize the hydrogen ions in the organic phase. This means that the hydrophobic anions of ALi-PC has stronger basicity (pK<sub>a</sub> = 4.51) than that of SCN<sup>-</sup> (pK<sub>a</sub> = 0.926) and thus these anions have stronger affinity for the hydrogen ions of HCl.

Effect of ALi-SCN concentration on the extraction of 1 M HCl from aqueous phase was also investigated. Fig. 5 shows that as ALi-SCN concentration increased from 0.3 to 1.0 M, the extraction percentage of HCl rose from 7.6 to 13.7%. Table 6 compares the effect of stripping temperature from the loaded ALi-SCN between water and the mixture of water and C<sub>2</sub>H<sub>5</sub>OH. Compared to the nature of the stripping agent, stripping temperature shows negligible effect. Addition of C<sub>2</sub>H<sub>5</sub>OH to water greatly improves the stripping percentage of HCl from the loaded ALi-SCN. Table 7 shows the same experiments from the loaded ALi-PC. Not only stripping temperature but also the nature of stripping agents did not show any effect on the stripping of HCl. The strong affinity between hydrogen ions of HCl and anion of ALi-PC might be the cause of the difficulty in stripping. Although using mixture of C<sub>2</sub>H<sub>5</sub>OH and water as



**Fig. 5.** Effect of ALi-SCN concentration on extraction of 1 M HCl in the mixture of 50% H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH. Condition: O/A = 1, shaking time = 30 mins, room temperature (22°C ± 1).

**Table 6.** Comparison of stripping of HCl from the loaded 1 M ALi-SCN phase

Extraction percentage, %	Stripping percentage, %		
	Stripping agent	22°C	60°C
13.7	H <sub>2</sub> O	60.2	60.2
	H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub> OH(*)	91	95.5

\*Note: O/A = 1, shaking time = 30 mins; aqueous phase for extraction was 1M HCl in distilled water; (\*): 50 vol% C<sub>2</sub>H<sub>5</sub>OH was added to water for stripping.

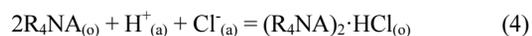
**Table 7.** Comparison of extraction and stripping of HCl by ALi-PC phase

Concentration of ALi-PC	Extraction percentage, %	Stripping percentage, %		
		Stripping agent	22°C	60°C
0.5 M	42.2	H <sub>2</sub> O	0.8	0.8
1.0 M	80.4	H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub> OH (*)	3.8	3.8

\*Note: O/A = 1, shaking time = 30 mins; aqueous phase was 1 M HCl in the mixture of 50% H<sub>2</sub>O and 50% C<sub>2</sub>H<sub>5</sub>OH (v/v) for extraction; (\*): 50 vol% C<sub>2</sub>H<sub>5</sub>OH was added to water for stripping.

stripping agent did not improve stripping efficiency from the loaded phase of ALi-PC, addition of C<sub>2</sub>H<sub>5</sub>OH into aqueous phase was essential for enhancement of the extraction. When ALi-PC concentration increased from 0.5 to 1.0 M, the extraction percentage increased from

42.2 to 80.4% respectively (see Table 7). The solvent extraction reactions of HCl by ILs can be represented as<sup>5,20,26</sup>



where R<sub>4</sub>NA = ALi-PC/ ALi-SCN

#### 4. Conclusions

In order to investigate the recovery of HCl from aqueous solutions, solvent extraction experiments were performed by employing commercial extractants such as LIX 63 and its mixture with TEHA, Aliquat 336, and Cyanex 923 and synthesized ILs such as ALi-PC and ALi-SCN. Among these, ALi-PC showed higher extraction percentage than the others, but the stripping was negligible. In contrary, stripping of HCl from the loaded LIX 63 was effective (>81%). In the case of ILs, extraction performance of HCl by ALi-PC was higher than that by ALi-SCN. However, the stripping of HCl from the loaded ALi-PC was more difficult than from ALi-SCN. The extraction and stripping efficiency of HCl was enhanced by adding C<sub>2</sub>H<sub>5</sub>OH to the aqueous phase owing to polar modifier effect. However, addition of modifier like octanol to organic phase lowered extraction performance. Also, the effect of temperature on stripping HCl from the loaded ILs was insignificant. The difficulty in stripping of HCl from the loaded organic phase can be attributed to the excessive chemical interaction between HCl with extractant like ALi-PC, resulting in chemical conversion and formation of sustainable products in the organic phase. Further studies on the kinetics and interaction of HCl with extractants should be conducted to verify the interaction.

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