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Keywords: ionic liquids, hydrochloric acid, indium, gallium, solvent extraction

## Abstract:

The manufacture of semiconductor materials containing gallium and indium requires the separation of these metals owing to their coexistence in the resources of these materials. In this work, solvent extraction of In(III) and Ga(III) from a hydrochloric acid solution by ionic liquids (ILs) was investigated to separate them. The ILs were synthesized by reacting organophosphorus acids (Cyanex 272, PC88A and D2EHPA) and Aliquat 336 (ALi-CY, ALi-PC, and ALi-D2). In(III) was selectively extracted over Ga(III) by the ILs in the range of initial pH from 0.1 to 2.0. The equilibrium pH was always higher than the initial pH because of the coextraction of hydrogen ions. The highest separation factor between In(III) and Ga(III) was 87, which was obtained by ALi-PC at an initial pH of 1.0. Stripping of the loaded ALi-PC with hydrochloric and sulfuric acid led to selective stripping of In(III) over Ga(III). Scrubbing of the loaded ALi-PC with pure In(III) solution was not effective in removing the small amount of Ga(III) present in the loaded ALi-PC. Batch simulation experiments for the three counter-current extraction stages indicated that the complete separation of both metal ions was possible by extracting In(III) using ALi-PC, with remaining Ga(III) in the raffinate.

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Article

# Separation of Gallium(III) and Indium(III) by Solvent Extraction with Ionic Liquids from Hydrochloric Acid Solution

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**Abstract:** The manufacture of semiconductor materials containing gallium and indium requires the separation of these metals owing to their coexistence in the resources of these materials. In this work, solvent extraction of In(III) and Ga(III) from a hydrochloric acid solution by ionic liquids (ILs) was investigated to separate them. The ILs were synthesized by reacting organophosphorus acids (Cyanex 272, PC88A and D2EHPA) and Aliquat 336 (ALi-CY, ALi-PC, and ALi-D2). In(III) was selectively extracted over Ga(III) by the ILs in the range of initial pH from 0.1 to 2.0. The equilibrium pH was always higher than the initial pH because of the coextraction of hydrogen ions. The highest separation factor between In(III) and Ga(III) was 87, which was obtained by ALi-PC at an initial pH of 1.0. Stripping of the loaded ALi-PC with hydrochloric and sulfuric acid led to selective stripping of In(III) over Ga(III). Scrubbing of the loaded ALi-PC with pure In(III) solution was not effective in removing the small amount of Ga(III) present in the loaded ALi-PC. Batch simulation experiments for the three counter-current extraction stages indicated that the complete separation of both metal ions was possible by extracting In(III) using ALi-PC, with remaining Ga(III) in the raffinate.

**Keywords:** solvent extraction; gallium; indium; hydrochloric acid; ionic liquids

## 1. Introduction

Gallium and indium are raw materials for the production of the semiconductor, solar cell and transparent electrodes of liquid crystal displays (TVs and computer monitors) [1–3]. Gallium and indium are rarely present as a single ore in the earth's crust, and most of them are produced from by-products of either bauxite or zinc ores [3]. In addition, their weight percentage in the earth's crust is extremely low, resulting in their small production and high price. Therefore, lots of studies have been conducted to recover gallium and indium from secondary resources (see Table 1) [4–6].

**Table 1.** References for the separation of In(III) and Ga(III) from waste electronic device.

Secondary Source	Leaching Medium	Extractant	Extraction Percentage, (%)			Ref.
			Ga(III)	In(III)	Zn(II)	
IGZO Targets	9 M HCl HCl (pH = 2)	30% TBP 15% D2EHPA	99.8	99.5	14	[4]
			3.4	98.8	1.2	
GZO and IGZO Targets	3 M HNO <sub>3</sub>	0.02 M E2EHPA at pH = 1 <sup>1</sup> , A/O = 2	0.4	99.9	0.5	[5]
Synthetic solution	H <sub>2</sub> SO <sub>4</sub> (eq. pH = 2)	0.05 M D2EHPA	26	99.9	-	[6]

<sup>1</sup> Solution pH of the leaching solution was adjusted to pH 1 for solvent extraction.

Although several studies have been reported on the separation of the two metals from the solution, most of the process is complicated. Some researchers separated Ga(III) and In(III) from weak acidic solutions using single extractants such as Cyanex 272, PC88A and D2EHPA [5–8]. In solvent extraction with these organophosphorus acids, the hydrogen ions liberated during the extraction can negatively affect the metal extraction efficiency owing to the reduction in equilibrium pH. Therefore, it is necessary to control solution pH in order to maintain a high extraction performance. Some tri-octyl-ammonium-based ionic liquids (ILs) can extract Ga(III) and In(III) [9]. However, it is difficult to commercialize these ILs due to the complicated manufacturing method and high cost. Thus, the synthesis of ILs from commercial extractants can be a good choice for the separation process because of a reduction in the production cost owing to simple synthesis. The ILs synthesized by organophosphorus acids (Cyanex272, PC88A, and D2EHPA) and Aliquat 336 show the selective and effective extraction of metals [10–12].

The extraction of In(III) and Ga(III) in several media such as nitric, sulfuric and hydrochloric acid solutions was carried out [7,13]. In most of the extraction systems, In(III) is selectively extracted over Ga(III) from weak acidic solutions. However, the separation efficiency of In(III) and Ga(III) becomes worse as solution pH increases due to the coextraction of Ga(III), while the extraction percentage of In(III) becomes lower as the acidity of the solution increases. Of the three inorganic acid solutions, HCl solution is widely employed as a leaching solution owing to the chloride ion's strong tendency to form complexes with metal ions. It has been reported that separation of In(III) and Ga(III) is possible from a strong HCl solution, such as a 9 M solution [7,12]. However, few studies have been focussed on the separation of Ga(III) and In(III) from moderate to weak hydrochloric acid solutions.

In this work, the ILs synthesized by Cyanex 272, PC88A and D2EHPA with Aliquat 336 were employed to separate Ga(III) and In(III) from HCl solution with moderate to weak acidity. First, the extraction behavior of Ga(III) and In(III) was investigated by varying the initial pH of the aqueous solution. Moreover, the effect of the molar ratio of In(III) to Ga(III) on the separation was investigated. The concentration of sulfuric and hydrochloric acid was varied to investigate the stripping behavior of Ga(III) and In(III) from the loaded IL. Moreover, scrubbing of Ga(III) from the loaded organic was tested by varying the concentration of In(III) in the scrubbing solution. Batch simulation experiments for the three counter-current extraction stages verified the complete separation of In(III) and Ga(III) by employing ALi-PC.

## 2. Materials and Methods

### 2.1. Materials

Synthetic solutions of In(III) and Ga(III) were prepared by dissolving GaCl<sub>3</sub> (99.999%, Alfa Aesar, Ward Hill, MA, USA) and InCl<sub>3</sub> (>99%, Alfa Aesar, Ward Hill, MA, USA) in doubly distilled water. At this time, the acidity of the solution was adjusted with hydrochloric acid (35%, Daejung Chemicals and Metals Co., Ltd., Shiheung, Korea). In all experiments, the concentration of Ga(III) was fixed at 100 mg/L, and the concentration of In(III) was adjusted to 100–1000 mg/L. In addition, NaCl (99%, Tedia Company, Inc., Fairfield, CT, USA) was added to the aqueous phase to suppress the formation of an emulsion during the extraction. ILs were prepared by reacting Aliquat 336 (93%, BASF Co. Ltd., Ludwigshafen, Germany) with equimolar concentrations of Cyanex 272 (85%, Cytec Solvay Industries, Woodland Park, CO, USA), PC88A (95%, Daihachi Chem. Industries, Osaka, Japan), and D2EHPA (95%, Daihachi Chem. Industries, Osaka, Japan), respectively, according to the method reported in the literature [10]. The synthesized ionic liquids were used directly without further purification. The chemical formula and structure of the ionic liquids used in this study are shown in Appendix A (Figure A1). Kerosene (100%, Daejung Chemicals and Metals Co., Ltd., Shiheung, Korea) was used as a diluent without further purification and all reagents used were of analytical grade.

## 2.2. Procedure

Extraction experiments were performed by mixing an equal volume of aqueous and organic phases (20 mL) at ambient temperature using a Burrell wrist action shaker (Model 75, Burrell Scientific, Pittsburgh, PA, USA) for 30 min. The mixed solution was left on a separatory funnel for 30 min to separate the organic phase and the aqueous phase. The separated organic phase was used for stripping and scrubbing experiments. The pH of the aqueous phase before and after extraction was measured using a thermal scientific pH meter (Orion Star A211, Thermo Scientific, Waltham, MA, USA). The concentration of the metal present in the aqueous phase was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos, Cleve, Germany), and the metal concentration extracted into the organic phase was determined by mass balance. The extraction percentage, distribution ratio and separation factor of the metals were defined by the following equations.

$$\text{Extraction percentage (\%E)} = (m_{\text{ini}} - m_{\text{eq}})/m_{\text{ini}} \times 100, \quad (1)$$

$$\text{Distribution ratio (D)} = C_{\text{org}}/C_{\text{aq}}, \quad (2)$$

$$\text{Separation factor (SF)} = D_{\text{In(III)}}/D_{\text{Ga(III)}}, \quad (3)$$

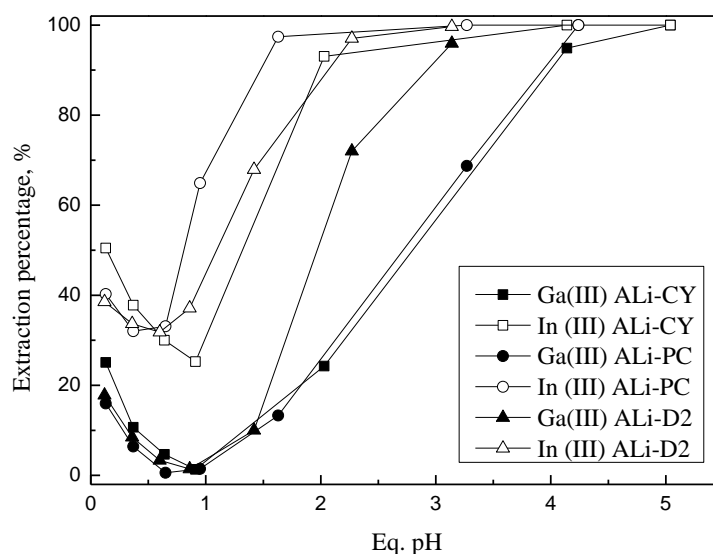
where  $m_{\text{ini}}$  and  $m_{\text{eq}}$  represent the mass of the metal in the aqueous phase before and after extraction, respectively. Moreover,  $C_{\text{org}}$  and  $C_{\text{aq}}$  represent the equilibrium concentration of metal in the organic and aqueous phase, respectively. In the separation factor,  $D_{\text{Ga(III)}}$  and  $D_{\text{In(III)}}$  represent the distribution ratio of Ga(III) and In(III), respectively.

## 3. Results

### 3.1. Effect of pH on the Extraction of Ga(III), In(III) and Hydrogen Ions

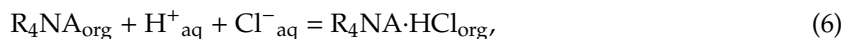
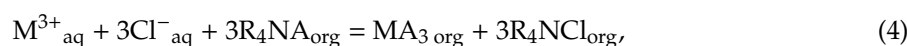
Unlike organophosphorus acidic extractants, some ILs can extract both metal and hydrogen ions [14]. During the extraction with ILs, solution pH strongly affects the extraction of metal as well as hydrogen ions [14]. In order to investigate the extraction behavior of In(III) and Ga(III) together with hydrogen ions, the initial pH of the aqueous mixed solution was adjusted from 0.1 to 2.0. In these experiments, the concentration of the ILs was fixed at 0.1 M. The formation of an emulsion was observed during the extraction when solution pH was above 1.0. This might be ascribed to the interaction of ILs with the aqueous phase [15]. Therefore, in this study, 0.1 M NaCl was added to the aqueous phase to prevent the formation of an emulsion [14]. NaCl is considered as a salting-out agent which can interact with water, leading to phase separation. Owing to the ionic properties of the ILs, some ions may be dissolved in the aqueous phase, and the solubility of the ILs is reduced by adding NaCl to the aqueous phase [15].

Figure 1 shows the variation in the extraction percentage of Ga(III) and In(III) with equilibrium pH using ALi-CY, ALi-PC, and ALi-D2. The extraction behavior of the two metal ions by the three ILs was similar. When equilibrium pH was less than 4.2, the extraction percentage of In(III) was higher than that of Ga(III) and both metal ions were almost completely extracted after this equilibrium pH. At the same initial pH, the extraction percentage of both metal ions by ALi-D2 was lower than that by the other two ILs. Both metal ions were completely extracted by ALi-CY and ALi-PC when equilibrium pH was 5.0 and 4.2, respectively. Most of Ga(III) and In(III) were extracted by ALi-D2 at equilibrium pH of 3.1. The difference in the equilibrium pH at which most of the metal ions were extracted is related to the extraction of hydrogen ions.



**Figure 1.** Effect of equilibrium pH on the extraction of Ga(III) and In(III) by ionic liquids (ILs) from hydrochloric acid solution. ( $[Ga^{3+}] = [In^{3+}] = 100 \text{ mg/L}$ ,  $[ILs] = 0.1 \text{ M}$ ).

The extraction of metal ( $M^{3+}$ ) and hydrogen ions by the ILs ( $R_4NA$ ) employed in this work can be represented as Equations (4)–(6).



where R and A denote the alkyl group of Aliquat 336 and the anion group of organophosphorus acids, respectively.

Equation (5) refers to the extraction of hydrogen ions by the anion of the ILs, while Equation (6) shows the adduct formation reaction between HCl and the ILs. Especially, Equation (5) can be simply represented as



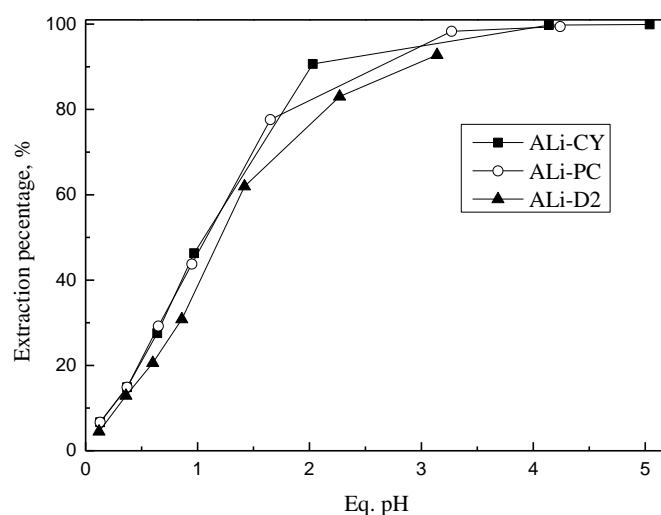
Equation (7) is related to the basicity of the weak acids. Since the product of acidity and basicity constants of a weak acid is equal to the water dissociation constant, the basicity constant of the weakest acid is the largest. Table 2 summarizes the pH change of the aqueous phase after extraction with the three ILs. Equilibrium pH was higher than initial pH, indicating that some of hydrogen ions was extracted by the ILs. Compared to ALi-D2, there is a larger increase in the equilibrium pH during the extraction with ALi-CY and ALi-PC. Among the three organophosphorus acidic extractants (D2EHPA, PC88A, and Cyanex 272), the acidity of Cyanex 272 is the weakest. Therefore, the basicity constant of the anion of Cyanex 272 is the largest among the three extractants. This is in good agreement with the increase order in the equilibrium pH (ALi-CY > ALi-PC > ALi-D2) observed in our data. This order is consistent with the pKa value of the organophosphorus acids (Cyanex 272 (6.37), PC 88A (4.51), and D2EHPA (3.42)). It can be said that the acidity constant of the three extractants affects the extraction of metal as well as hydrogen ions in our experimental conditions.

In order to calculate the extraction percentage of hydrogen ions from Table 2, the activity coefficient of hydrogen ions was assumed to be unity. Figure 2 shows the variation in the extraction percentage of hydrogen ions with equilibrium pH. With the increase in equilibrium pH, the extraction percentage of hydrogen ions increased linearly in the range of equilibrium pH from 0.1 to 3.3. The complete extraction of hydrogen ions was obtained when equilibrium pH was higher than 4.5.

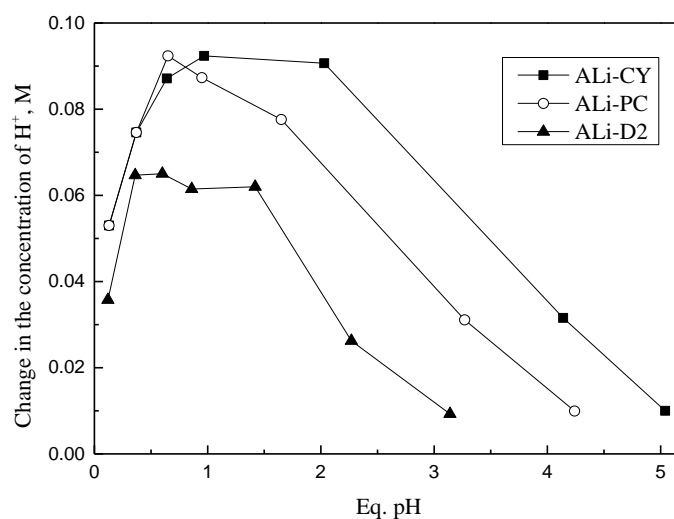
**Table 2.** Data on the variation in the equilibrium pH with initial pH during the extraction of In(III) and Ga(III) by the ILs.

Initial pH	0.10	0.30	0.50	0.70	1.00	1.50	2.00
Equilibrium pH <sub>ALi-CY</sub>	0.13	0.37	0.64	0.97	2.03	4.14	5.04
Equilibrium pH <sub>ALi-PC</sub>	0.13	0.37	0.65	0.95	1.65	3.27	4.24
Equilibrium pH <sub>ALi-D2</sub>	0.12	0.36	0.60	0.86	1.42	2.27	3.14

[Extractant] = 0.1 M; [NaCl] = 0.1 M.

**Figure 2.** Effect of equilibrium pH on the extraction of hydrogen ions by ILs from hydrochloric acid solution. ( $[Ga^{3+}] = [In^{3+}] = 100 \text{ mg/L}$ , [ILs] = 0.1 M).

In Figure 1, the abnormal extraction behavior of both metal ions can be observed. Namely, the extraction percentage of In(III) and Ga(III) increased as equilibrium pH decreased from around 1.0 to 0.12. Figure 3 represents the change in the concentration of hydrogen ions during the extraction with the ILs. It is observed that there is an equilibrium pH at which the maximum change in the concentration of hydrogen ions occurs. This is related to the basicity of the anions of the three ILs. Therefore, it can be concluded that the extraction of metal ions was enhanced by suppressing the extraction of hydrogen ions.

**Figure 3.** Effect of equilibrium pH on the change in the concentration of hydrogen ions in the aqueous phase owing to its extraction into ILs from hydrochloric acid solution. ( $[Ga^{3+}] = [In^{3+}] = 100 \text{ mg/L}$ , [ILs] = 0.1 M).

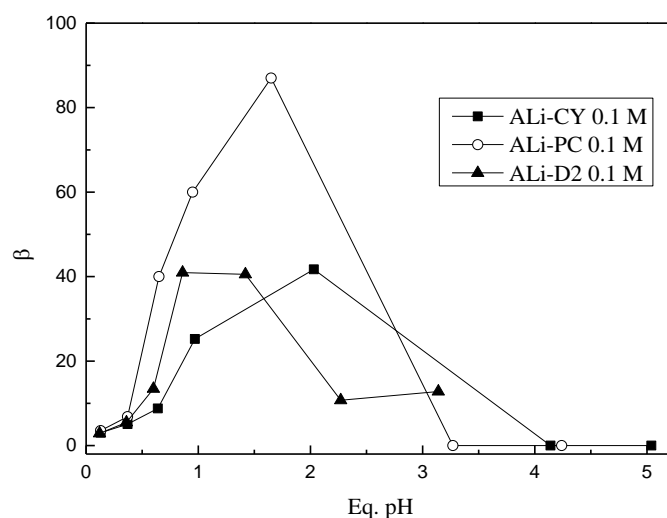
According to Janssen et al. [15], when an ion exchange reaction is responsible for the extraction of metal ions by an ionic liquid, the interaction force between the anions and the cations of the ionic liquid is reduced and thus the ionic liquid is partially dissolved in the aqueous phase. Therefore, it can be inferred that in our experimental conditions metal ions are extracted by ion exchange at a pH of 1 or higher in which the formation of emulsion occurred, and metal ions are extracted by a solvation reaction when pH was less than 1.

The precipitation pH of 0.1 M In(III) and Ga(III) in water at 25 °C is around 2.6 [16]. Table 3 lists the complex formation constants of In(III) and Ga(III) at 25 °C, indicating that In(III) has a stronger tendency to form complexes with chloride ions than Ga(III). The formation of complexes reduced the concentration of free metal ions and thus the precipitation pH would be increased compared to the metal–water system. However, an equilibrium pH higher than 4 in our experiments indicates that most of Ga(III) and In(III) had been extracted by the ILs. The kinetic measurement of solution pH at certain time intervals would give some data on the selective extraction of metal and hydrogen ions. Although In(III) can form several kinds of complexes with chloride ions, the higher extraction percentage of In(III) than Ga(III) indicates that the ILs have a selectivity for In(III) over Ga(III) in our experimental ranges.

**Table 3.** Comparison of the complex formation constants with chloride ions between Ga(III) and In(III). Adapted from Reference [17]. Copyright 1976, Springer US.

Equilibrium	Log K	
	Ga(III)	In(III)
$M^{3+} + Cl^{-} = MCl^{2+}$	0.01	$2.32 \pm 0.05$
$M^{3+} + 2Cl^{-} = MCl_2^{+}$	-	$3.62 \pm 0.05$
$M^{3+} + 3Cl^{-} = MCl_3$	-	$4.0 \pm 0.2$

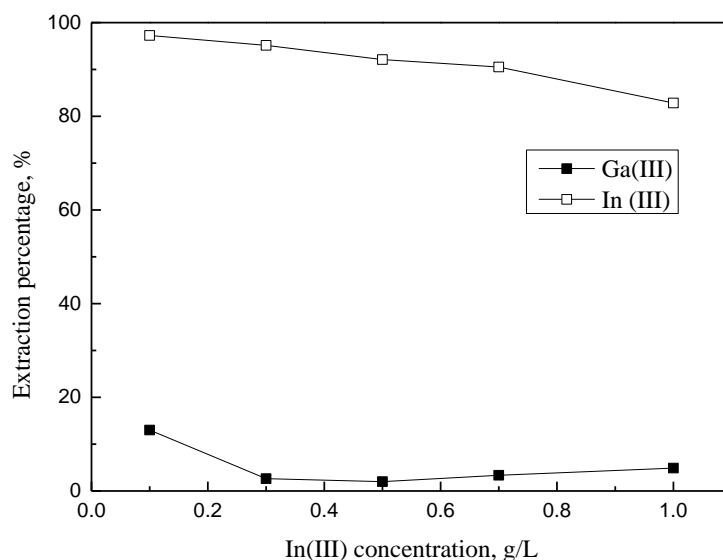
Figure 4 shows the variation in the separation factors between In(III) and Ga(III) by the three ILs. All three ILs show the highest separation factor values between equilibrium pH 1.5 and 2. Among them, ALi-PC had the highest separation factor compared to the other two ILs when the equilibrium pH was about 1.6. However, when the equilibrium pH was higher than 4, both metals were completely extracted and thus it was impossible to separate them. Therefore, in this study, ALi-PC was selected as an optimal extractant for separating Ga(III) and In(III) from hydrochloric acid solution with an initial pH of 1. At this condition, the extraction percentage of In(III) and Ga(III) was 97% and 13%, respectively. Subsequent experiments will be performed at this optimum condition.



**Figure 4.** The fluctuation in the separation factor between In(III) and Ga(III) with equilibrium pH.

### 3.2. Effect of In(III) Concentration

The effect of In(III) concentration on the extraction of the two metals by 0.1 M ALi-PC was investigated (see Figure 5). In these experiments, the concentration of In(III) varied from 100 to 1000 mg/L, while that of Ga(III) was fixed at 100 mg/L. Moreover, the initial pH of the solution was fixed at 1.0. In these experimental ranges, the extraction percentage of In(III) slightly decreased from 97% to 83% as In(III) concentration increased to 1000 mg/L. The extraction percentage of Ga(III) was less than 5% regardless of In(III) concentration, except when the In(III) concentration was 100 mg/L.



**Figure 5.** Effect of In(III) concentration on the extraction of Ga(III) and In(III) by ALi-PC from HCl solution. (Aqueous:  $[Ga^{3+}] = 100$  mg/L,  $[In^{3+}] = 100\text{--}1000$  mg/L;  $[ALi-PC] = 0.1$  M).

### 3.3. Stripping

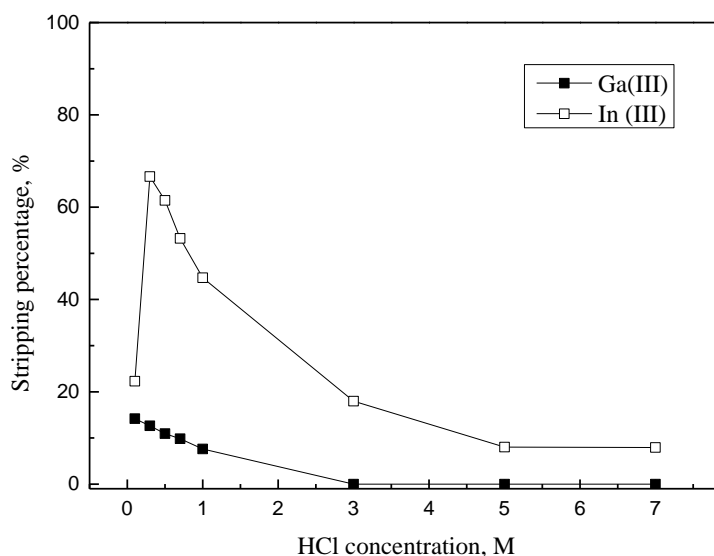
At the optimum extraction conditions, a small amount of Ga(III) was coextracted into ALi-PC. Therefore, it is necessary to separate the metal ions from the loaded IL. Since stripping is the reverse reaction of the extraction, it might be possible that Ga(III) can be selectively stripped from the loaded IL. In order to investigate the possibility of separating both metal ions from the loaded IL by stripping, hydrochloric and sulfuric acid solutions were employed. The loaded ILs were prepared by contacting 0.1 M ALi-PC with the solution containing the two metals at initial pH of 1.0. The effect of acid concentration on the stripping percentage of Ga(III) and In(III) was investigated by varying the acid concentration from 0.1 to 7 M. The concentration of In(III) and Ga(III) in the loaded ALi-PC was 99 and 13 mg/L, respectively. The stripping percentages of the two metals with acid concentrations are shown in Figures 6 and 7. Contrary to our expectation, In(III) was selectively stripped over Ga(III) by both acid solutions in the whole acid range. This might be ascribed to the fact that In(III) has a greater tendency to form complexes with chloride and sulfate ions than Ga(III) [14,18,19]. The stripping reaction can be written as Equation (8). It is estimated that the stripping percentage of In(III) by hydrochloric acid is lower than that by sulfuric acid solution. This might be ascribed to the re-extraction of the stripped metal ions by the IL.



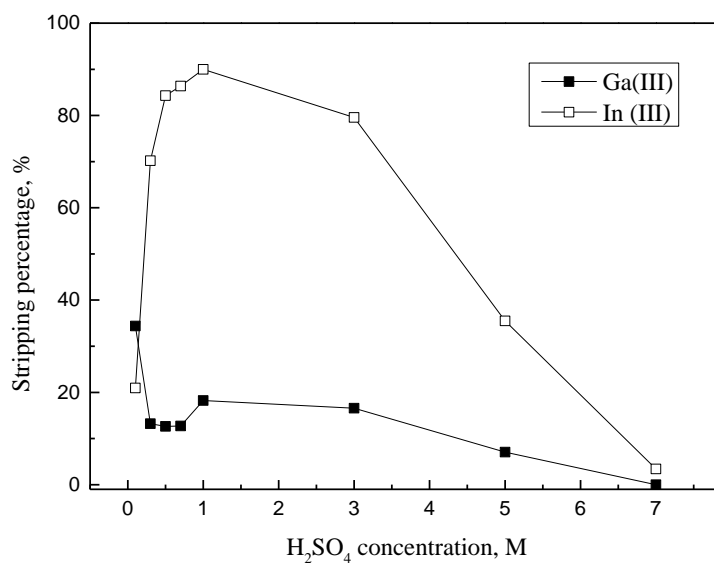
When hydrochloric acid was used as the stripping solution, the highest stripping percentage of In(III) and Ga(III) was 67% and 13%, respectively. As the acid concentration increased to above 0.3 M, the stripping percentage of both metal ions decreased. As shown in Figure 6, the stripping percentage of In(III) and Ga(III) by HCl solution is lower than that reported in the previous work [6]. This can be attributed to the difference in the concentration of the stripping solution and the metals in the loaded organic phase. Comparing between Figures 6 and 7, the stripping percentage of In(III) by sulfuric acid



solution was higher than that by the hydrochloric acid solution. About 90% of In(III) was stripped by 0.7 M H<sub>2</sub>SO<sub>4</sub> solution, while the stripping percentage of Ga(III) was 18%. The stripping percentage of both metals decreased as the sulfuric acid concentration increased above 0.7 M.



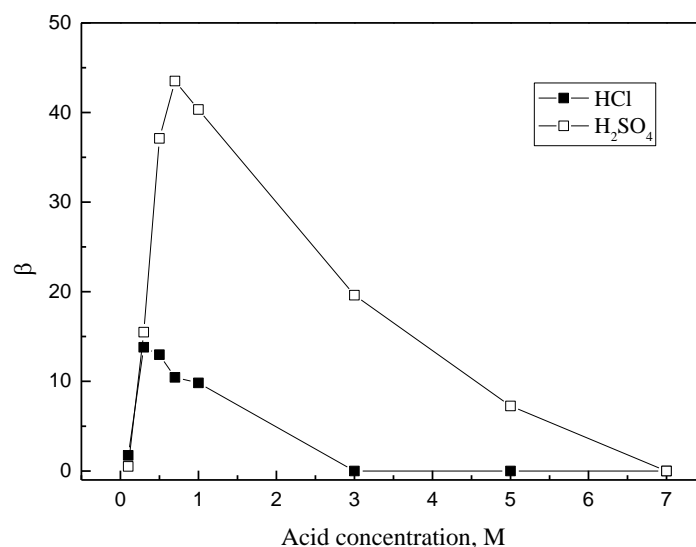
**Figure 6.** Effect of hydrochloric acid concentration on the stripping of Ga(III) and In(III) from the loaded ALi-PC phase. (Loaded ALi-PC: [Ga<sup>3+</sup>] = 13 mg/L, [In<sup>3+</sup>] = 99 mg/L; [HCl] = 0.1–7 M).



**Figure 7.** Effect of sulfuric acid concentration on the stripping of Ga(III) and In(III) from the loaded ALi-PC phase. (Loaded ALi-PC: [Ga<sup>3+</sup>] = 13 mg/L, [In<sup>3+</sup>] = 99 mg/L; [H<sub>2</sub>SO<sub>4</sub>] = 0.1–7 M).

Figure 8 shows the comparison of the separation factor between sulfuric and hydrochloric acid solutions. In most of the conditions, sulfuric acid solution results in a much higher separation factor than hydrochloric acid solution. Moreover, the separation factor increased sharply as the concentration of both acid solutions decreased to a certain value and then reduced. In the case of hydrochloric acid, the stripping percentage of both metal ions was nearly the same when the concentration of hydrochloric acid was higher than 3.0 M. Meanwhile, the separation factor by sulfuric acid decreased rapidly to unity when the sulfuric acid concentration increased from 1.0 to 7.0 M. In particular, a separation factor of 44 was obtained by 0.7 M sulfuric acid solution as a stripping solution. At this condition, the purity

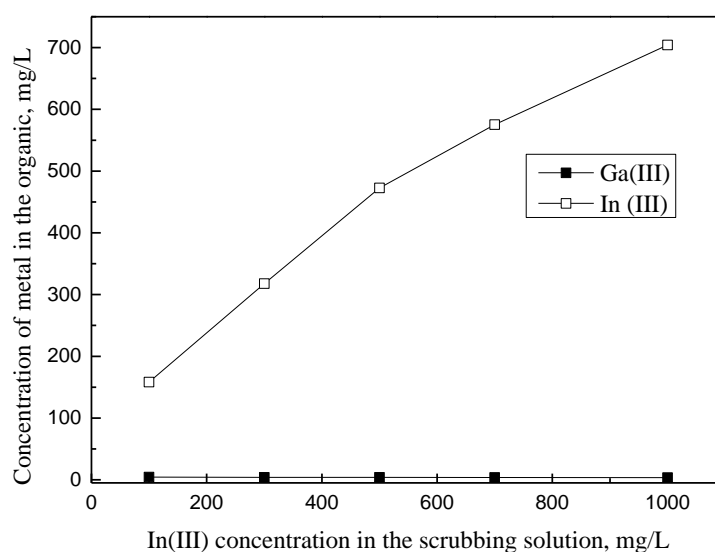
of In(III) in the stripping solution was 98.1%. After stripping step, the stripped organic phase should be treated with  $\text{NaHCO}_3$  in order to regenerate the ILs.



**Figure 8.** Variation in the separation factor between In(III) and Ga(III) during the stripping from the loaded ALi-PC with the acid concentration.

### 3.4. Scrubbing

Stripping results indicated that it was impossible to selectively strip Ga(III) over In(III) from the loaded ALi-PC. Therefore, scrubbing experiments were conducted to remove Ga(III) from the loaded IL. For this purpose, the concentration of In(III) in the scrubbing solution varied from 100 to 1000 mg/L. The experimental results are shown in Figure 9. Prior to scrubbing, the concentration of Ga(III) and In(III) in the loaded 0.1 M ALi-PC was 13 and 99 mg/L, respectively. At this time, the purity of In(III) was 90.7%. As In(III) concentration in the scrubbing solution increased to 1000 mg/L, the concentration of In(III) in the loaded ILs increased steadily, indicating that the loading capacity of 0.1 M ALi-PC was not reached.



**Figure 9.** Variation in the concentration of Ga(III) and In(III) in the loaded ALi-PC with the concentration of In(III) in the scrubbing solution. (Loaded organic:  $[\text{Ga}^{3+}] = 13 \text{ mg/L}$ ,  $[\text{In}^{3+}] = 99 \text{ mg/L}$ ; Aqueous:  $[\text{In}^{3+}] = 100\text{--}1000 \text{ mg/L}$ ;  $[\text{ALi-PC}] = 0.1 \text{ M}$ ).

Table 4 shows the variation in the scrubbing percentage of Ga(III) with the concentration of In(III) in the scrubbing feed solution. As In(III) concentration increased from 100 to 1000 mg/L, the scrubbing percentage of Ga(III) increased a little from 52% to 58%. The scrubbing percentage of Ga(III) obtained in our experiments was not satisfactory for the separation of In(III) and Ga(III). As a result, a small amount of Ga(III) (5.4 mg/L) still remained in the organic phase after scrubbing. In(III) was further extracted by ILs and the purity of In(III) increased as Ga(III) was scrubbed from the organic phase. When the concentration of In(III) in the scrubbing solution was 1000 mg/L, the purity of In(III) in the scrubbed IL was 99.5%. It can be said that scrubbing increased the purity of indium in the IL from 90.7% to 99.5%.

**Table 4.** Effect of the concentration of In(III) in the scrubbing solution on the scrubbing of Ga(III) and the purity of In(III) in the scrubbed organic.

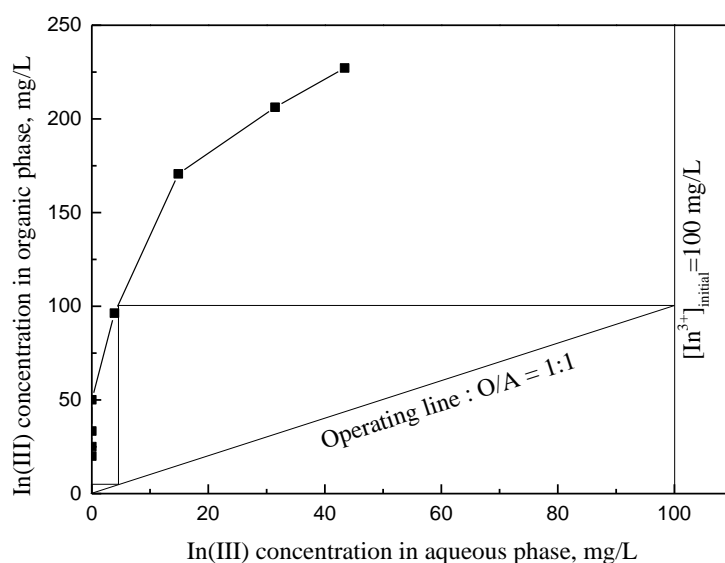
In(III) Conc. in Scrubbing Feed, (mg/L)	Eq. Concentration of Ga(III) in Scrubbing Soln., (mg/L)	Eq. Concentration of In(III) in Organic, (mg/L)	Ga(III) Scrubbing, (%)	Purity of In(III) in Organic, (%)
100	6.8	158	52	97.3
300	7.1	318	55	98.8
500	7.3	478	56	99.2
700	7.4	575	57	99.4
1000	7.6	704	58	99.5

### 3.5. Batch Simulation Experiments for the Counter-Current Extraction

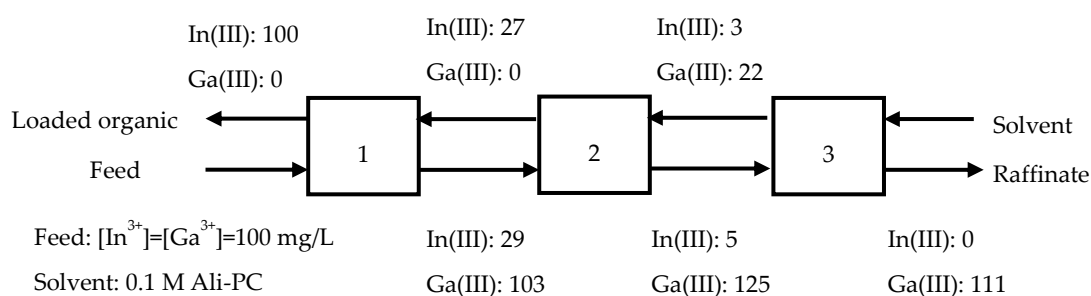
Our experimental data indicate that the small amount of Ga(III) loaded in the IL cannot be separated from In(III) by either scrubbing or stripping. However, there is much difference in the extraction percentage between In(III) and Ga(III) by the IL employed in this work. In this condition, the employment of a multistage counter-current extraction would result in the complete separation of both metal ions by selectively extracting In(III). During the extraction of In(III), some amount of hydrogen ions are extracted by the IL, leading to an increase in equilibrium pH. When most of Ga(III) remains in the raffinate, the increase in solution pH would lead to the precipitation of Ga(III). In this condition, crud can be formed and the multistage counter-current extraction cannot be operated. Therefore, it is very important to select an optimum condition of the IL for the separation of both metal ions and to control the solution pH within the precipitation limit of Ga(III).

In order to verify the complete separation of the two metal ions by multistage counter-current extraction, the necessary number of stages was determined from the McCabe–Thiele diagram for the extraction of In(III). The mixed solution containing 100 mg/L Ga(III) and 100 mg/L In(III) was extracted with 0.1 M ALi-PC by varying the volume ratio of the two phases from 1:5 to 5:1. In these experiments, the initial pH of the aqueous phase was fixed at 1.0 and the equilibrium pH was controlled to 1.0 by adding HCl solution during the extraction.

Figure 10 shows the McCabe–Thiele diagram for the extraction of In(III) from the mixed solution. When the volume ratio of the two phases is unity, two stages of counter-current extraction with ALi-PC would completely extract In(III). Considering the stage efficiency of counter-current extraction, batch simulation experiments for the three-stage counter-current extraction were conducted in this work. Figure 11 shows the composition of the raffinate in each stage. The composition of the two metal ions in the loaded organic phase was calculated by mass balance. Our results clearly verified that In(III) and Ga(III) were completely separated by three-stage counter-current extraction with ALi-PC. In the batch simulation experiment, there was a slight difference in the concentration of Ga(III) between the feed and the aqueous outlet. It might be thought that the concentrations of Ga(III) in the outlet were within the experimental error range.



**Figure 10.** McCabe–Thiele diagram for the extraction of In(III) by 0.1 M ALi-PC from HCl solution with initial pH of 1. (Aqueous:  $[Ga^{3+}] = 100$  mg/L,  $[In^{3+}] = 100$  mg/L;  $[ALi-PC] = 0.1$  M;  $O/A = 5:1-1:5$ ).



**Figure 11.** The composition of the raffinate and loaded ALi-PC during batch simulation experiment for a three-stage counter-current extraction. (Aqueous:  $[Ga^{3+}] = 100$  mg/L,  $[In^{3+}] = 100$  mg/L;  $[ALi-PC] = 0.1$  M;  $O/A = 1$ ; Initial pH = 1; Equilibrium pH was fixed at 1.0).

### 3.6. Comparison of the Extraction and Separation Performance of Metals between D2EHPA and ILs

The previous work was carried out to separate Ga(III) and In(III) from sulfate solution using D2EHPA [6], while the present study investigated the separation of two metals from chloride media by employing ILs. The difference in their metal extraction and separation performance lies in the metal compositions, extractant, and the medium of aqueous solution. Previously reported data [6] indicate that the extraction of metals with D2EHPA followed a cationic mechanism. Hydrogen ions released from D2EHPA during the extraction decreased the equilibrium pH, which depressed the extraction of Ga(III) and In(III). In this case, saponification of D2EHPA is necessary to maintain the solution pH for a favorable extraction of metals but there is no report about this saponification in the previous work [6]. On the other hand, ILs were synthesized in this work by Aliquat336 and some organophosphorus acids. These ILs can act as either anionic or cationic extractants due to their dual function. ILs has not only a selectivity for In(III) over Ga(III) but also the ability to extract hydrogen ions. In the case of extraction with ILs employed in this work, it may be necessary to add a small amount of hydrochloric acid to maintain the pH within the precipitation limit of In(III) and Ga(III).

In the extraction stage, the change of solution pH has a significant effect on the separation of In(III) and Ga(III). The release of hydrogen ions to the aqueous phase after extraction has not been solved in previous work [6]. Meanwhile, the effect of pH on the extraction of Ga(III), In(III) and hydrogen ions by ILs has been investigated in the present work. In the stripping stage, the previous work showed that hydrochloric acid is more efficient than sulfuric acid as a stripping agent of metals. In contrast, sulfuric

acid solution is most suitable for the stripping of metal in this work. The similarity between both works is that the complete separation of In(III) and Ga(III) by a stripping step still remains difficult. Therefore, the multistage counter-current stripping was not employed to obtain an aqueous solution with concentrated In(III) or Ga(III).

In terms of separation factor, the previous work [6] seems to be more efficient than this work; complete separation of In(III) and Ga(III) has been achieved in both works. In general, ILs have many advantages as extractants for metal ions compared to molecular extractants. Therefore, the data on the separation of metal ions by employing ILs which can be synthesized by commercial extractants are of importance in developing a process for separating metal ions.

#### 4. Conclusions

Solvent extraction experiments were investigated to separate Ga(III) and In(III) from hydrochloric acid solution using ILs. The ILs were synthesized by reacting Aliquat 336 with organophosphorus acids (Cyanex 272, D2EHPA, and PC88A). In the initial pH range from 0.1 to 2.0, the extraction behavior of both metal and hydrogen ions was investigated. Equilibrium pH was always higher than initial pH and the extraction percentage of hydrogen ions increased with equilibrium pH. In most of the conditions, In(III) was selectively extracted over Ga(III). However, there were equilibrium pH values at which the extraction percentage of both metal ions was the minimum. The extraction of hydrogen ions was related to the basicity of the anions of the ILs. In terms of the separation factor between In(III) and Ga(III), an initial pH of 1 was the optimum condition for the separation of both metal ions by ALi-PC. Stripping and scrubbing were attempted to remove small amount of coextracted Ga(III) from the loaded ALi-PC. Stripping of the loaded ALi-PC by hydrochloric and sulfuric acid solutions indicated that In(III) was selectively stripped over Ga(III). Only half of the Ga(III) in the loaded ALi-PC was scrubbed by pure In(III) solution. Therefore, scrubbing and stripping were not effective in removing the small amount of Ga(III) in the loaded ALi-PC. Batch simulation experiments of the three-stage counter-current extraction verified that only In(III) was extracted into ALi-PC and Ga(III) remained in the raffinate, which enabled the complete separation of both metal ions by extraction with ALi-PC.

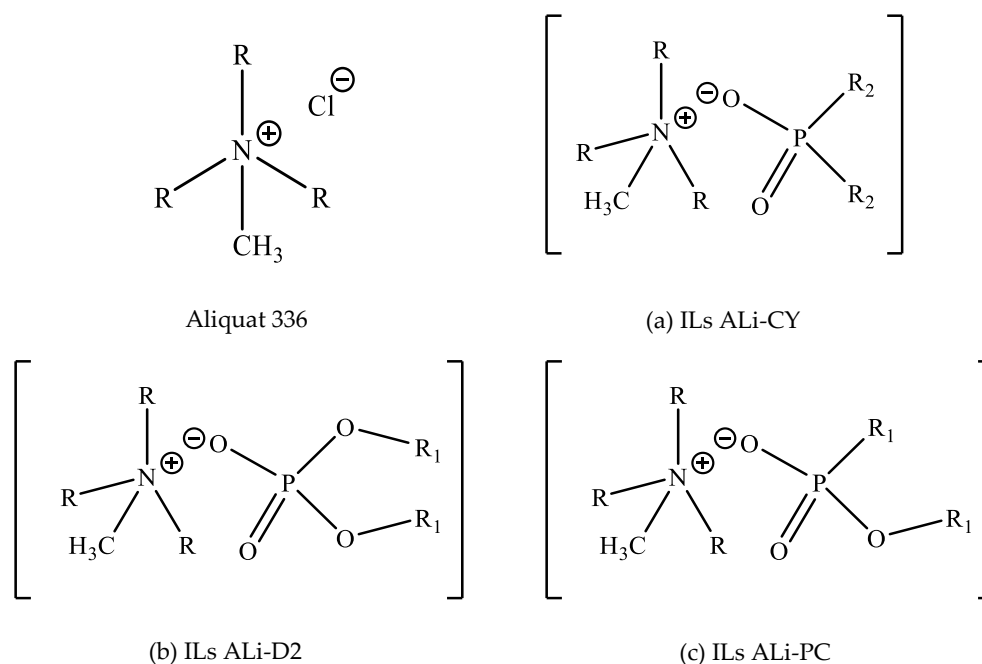
**Author Contributions:** M.S.L. designed the research and helped to analyze the data. S.J.S. performed the experiments and wrote the paper. M.N.L. helped with writing, reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## Appendix A



**Figure A1.** Chemical formula of the ionic liquids (a) ALi-CY, (b) ALi-D2, (c) ALi-PC used in the present study. R, R<sub>1</sub>, R<sub>2</sub> denote n-octyl-, 2-ethylhexyl-, 2,4,4-trimethylpentyl- groups, respectively.

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