

Separation and recovery of gallium(III) ions from aqueous phase by liquid–liquid extraction using a novel extractant, Cyphos IL 101

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Abstract: The present study describes the extraction behavior of gallium(III) using a novel ionic liquid trihexyl(tetradecyl) phosphonium chloride (Cyphos IL 101) diluted with kerosene from acidic chloride medium. The extraction of gallium was found to depend on the hydrochloric acid concentration and quantitative extraction of gallium took place at 2.0 mol/L HCl concentration. The nature of the extracted complex in the organic phase was determined using Job’s method and proposed to be $[R_3R'PGaCl_4]$. The loading capacity of 5.0×10^{-3} mol/L Cyphos IL 101 was determined to be 320.0 mg/L. Two stages of stripping were required for complete removal of gallium from the loaded organic phase using 0.1 mol/L HCl. From the temperature variation study, the extraction process was found to be endothermic. The separation efficiency of gallium from its associated metal ions such as Al(III), Fe(III), Zn(II), Cu(II), and Ni(II) was investigated from binary mixtures and in the presence of all these metal ions, which revealed that the extraction of Zn(II) and Cu(II) were more preferred to Ga(III) while extractions of Al(III) and Ni(II) were nil. The potential of the extractant was assessed to recover gallium from photodiodes.

Key words: Gallium, Cyphos IL 101, extraction, separation

1. Introduction

Gallium, which is one of the energy-critical elements, is considered as the backbone of advanced electronic industries.¹ Diodes like gallium arsenide (GaAs) and gallium nitride (GaN) are employed in electronic chips, microwave transceivers, light-emitting diodes, etc. In solar cells, gallium arsenide and indium phosphide in single crystal form are used as semiconducting materials, whereas gallium chloride is used to detect solar neutrinos. All these applications involve the use of pure gallium and create pressure on the availability of pure gallium. Unfortunately, gallium has no primary source and is mostly associated with aluminum (bauxite), zinc (sphalerite), and, to some extent, copper and germanium. In these sources, the amount of gallium is scanty and hence it has drawn the attention of researchers to extract the metal from leaner sources, namely from electronic wastes. Out of different separation techniques that can be employed for the recovery of metals from complex leaner sources, solvent extraction offers an effective and simple technology to obtain the metal in the purest form. It is also a less time-consuming technique with low operational costs. In this process, the desired metal species could be selectively and efficiently transferred from one phase, namely from the aqueous phase to the water immiscible organic phase, which consists of an extractant and a diluent.² Different types of classical

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extractants like acidic, chelating, basic, and neutral were employed for this purpose, but during the last decade, a new class of extractants called ionic liquids came as the cutting edge of research, replacing the traditional organic solvents. They are considered as green solvents because of good thermal stability, nonflammability, negligible vapor pressure, tunable viscosity, and miscibility with organic solvents.^{3,4} Extraction and separation of various metal ions using different kinds of ionic liquids have been researched and reported.^{5–18} Some ionic liquids contain fluorine anions like PF_6^- or Tf_2N^- , where there is a chance for formation of hydrofluoric acid on hydrolysis.^{19,20} In this context, phosphonium ionic liquids could be considered because they do not contain fluorine and additionally they have good hydrophobicity and thermal stability compared to ammonium-based analogs and faster kinetics in salt formation. Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) has gained much attention from researchers for extraction and separation of many transition metal ions and rare earth ions.^{21–30} Cyphos IL 101 and Cyphos IL 104 were employed for selective extraction of palladium,²¹ where high selectivity of palladium(II) was observed over nickel(II), copper(II), lead(II), iron(III), rhodium(III), and ruthenium(III) for 0.1 mol/L HCl. Using both the ionic liquids with minor coextraction of these metals, 99.0% palladium(III) was effectively extracted. Cyphos IL 101 diluted in Shell Sol A150 was used for extraction of molybdenum and vanadium from sulfate solution.²⁵ Quantitative extraction of molybdenum occurred in the pH range of 0.5–2.0 while for extraction of vanadium, the pH was more than 1.8, which favored the separation of molybdenum and vanadium at around pH 0.5. The kinetics of extractions was very fast and different concentrations of sulfuric acid were employed for complete stripping of the metal ions from the loaded organic phase. A comparative study of extraction capabilities of Aliquat 336 and Cyphos IL 101 diluted with kerosene for cadmium was reported from sulfate medium.²⁶ Cyphos IL 101 was proven to be a promising extractant for cadmium in comparison to Aliquat 336. Extraction of cadmium was pH-independent with Cyphos IL 101, whereas it depends on the aqueous phase pH with Aliquat 336. Five times less dilute solutions of Cyphos IL 101 were required for quantitative extraction of cadmium in comparison with Aliquat 336. Undiluted Cyphos IL 101 and Aliquat 336 were employed for extraction and purification of indium from chloride medium.³⁰ Quantitative extraction of In(III) was achieved in the HCl concentration range of 0.5–12.0 mol/L for both the ionic liquids. Selective extraction of In(III) over commonly associated metal ions was also reported and indium was recovered in the form of $\text{In}(\text{OH})_3$ using the precipitation stripping method. Though a number of papers reported the use of Cyphos IL 101 as an extractant for various metal ions, the extraction of gallium(III) using Cyphos IL 101 is yet to be explored. In the present study, Cyphos IL 101 was assessed for the extraction, separation, and recovery of Ga(III) from chloride medium. The effect of various parameters such as equilibration time, temperature, and concentration of H^+ , Cl^- , metal, and extractant on the extraction of Ga(III) was investigated. In addition to this, separation studies were carried out in the presence of metal ions commonly associated with gallium, tested with leach liquors of waste photodiodes.

2. Results and discussion

2.1. Liquid–liquid extraction of Ga(III) using Cyphos IL 101

Solvent extraction of 1.0×10^{-3} mol/L Ga(III) from the acidic chloride medium was performed using 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene to find out the equilibration period, where the shaking time was varied from 1 min to 30 min. The results illustrated in Figure 1 indicate that the kinetics of extraction was very fast as gallium(III) extraction of 51.0% was achieved within 5 min and further increasing the shaking period had no adverse effect on percentage extraction. In all experiments, 10 min of shaking time was maintained to assure

complete equilibration. Similarly, the acid concentration was also varied from 1.0×10^{-3} mol/L to 5.0 mol/L, keeping the gallium concentration at 1.0×10^{-3} mol/L and Cyphos IL 101 at 5.0×10^{-3} mol/L. From Figure 2, it can be observed that an increase in hydrochloric acid concentration increased the percentage extraction of gallium. For instance, the extraction of Ga(III) at 1.0×10^{-3} mol/L HCl was 22.7% and it increased to 98.5% at 2.0 mol/L HCl.

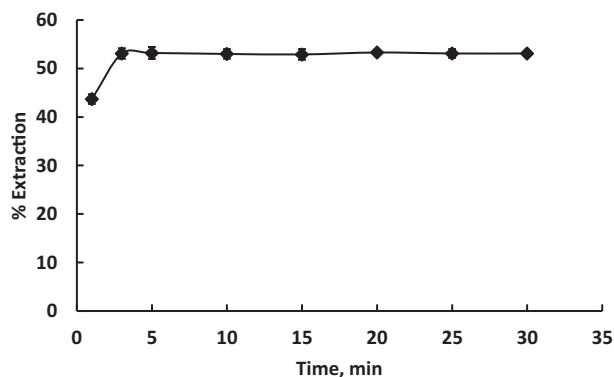


Figure 1. Plot of percentage extraction of gallium versus equilibration time. Aq. phase: 1.0×10^{-3} mol/L Ga(III), 1.0 mol/L HCl; org phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

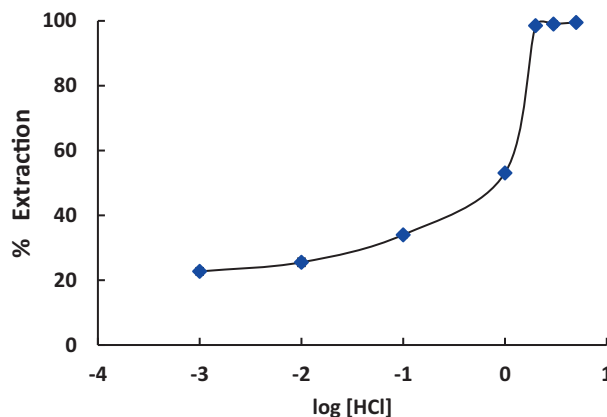


Figure 2. Relationship between percentage extraction of gallium and acid concentration of aqueous phase. Aq. phase: 1.0×10^{-3} mol/L Ga(III); org phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

As Cyphos IL 101 is not explored for gallium extraction, Job's method was followed to determine the stoichiometry of the gallium complex with Cyphos IL 101. For this, experiments were carried out in which the concentrations of gallium and Cyphos IL 101 were varied, keeping the total concentration fixed at 1.0×10^{-2} mol/L and acid molarity at 2.0 mol/L. The plot of gallium extracted into the organic phase in mg/L versus mole fraction of Cyphos IL 101 is illustrated in Figure 3, revealing that gallium forms a 1:1 metal:ionic liquid complex with Cyphos IL 101.³¹ To verify this, two sets of experiments, loading tests and extractant variation tests, were carried out. The loading experiments were performed varying the gallium concentration from 1.0×10^{-3} mol/L to 1.0×10^{-2} mol/L where aqueous acidity was maintained at 2.0 mol/L and organic phase concentration was retained at 5.0×10^{-3} mol/L. The experimental results plotted in Figure 4 as the ratio of initial extractant concentration $[\text{IL}]_i$ and the concentration of gallium extracted to the organic phase $[\text{Ga}]_{org}$ versus initial gallium concentration were found to gradually decrease and reach 1.0 with increase in gallium concentration, which supported the formation of the 1:1 metal:ligand complex. The other set of experiments was carried out by varying the extractant concentration from 1.0×10^{-3} mol/L to 1.0×10^{-2} mol/L and keeping all other parameters constant. The slope value of 1.3 obtained from the log-log plot of the distribution coefficient and Cyphos IL 101 (Figure 5) further supports the involvement of one mole of ionic liquid per one mole of gallium in the extraction process.

In order to understand the stoichiometry of the extracted complex in the organic phase, the effects of chloride and hydrogen ion concentrations were investigated. For the chloride variation study, the concentration of sodium chloride was varied in the range of 0.1–2.0 mol/L with a constant concentration of H^+ ion (1.0 mol/L) and keeping the gallium concentration at 1.0×10^{-3} mol/L and Cyphos IL 101 at 5.0×10^{-3} mol/L. The percentage extraction of gallium increased with the increase in chloride ion concentration. The percentage

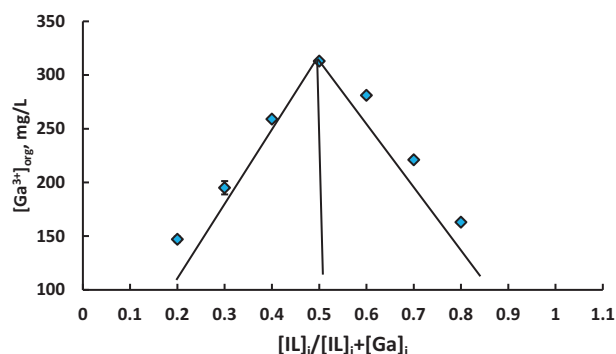


Figure 3. Job's plot for gallium(III) ions: [Cyphos IL 101] + [Ga(III)] = 1.0×10^{-2} mol/L.

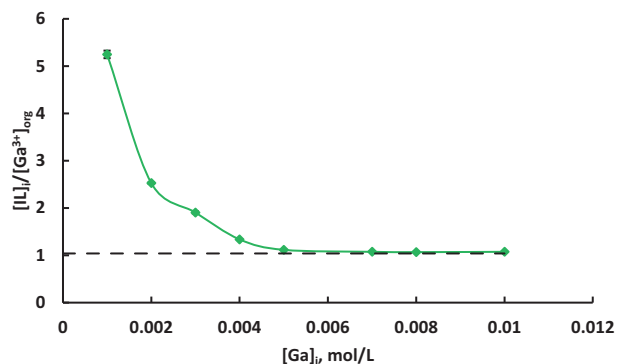


Figure 4. Loading test for Ga(III) on the ionic liquid Cyphos IL 101.

extraction was 74.3% when 0.1 mol/L NaCl was present and it increased to 94.6% when NaCl concentration was increased to 1.0 mol/L. The linear plot of $\log D$ versus $\log Cl^-$ yields a slope of ~ 4.0 (Figure 6), indicating the involvement of four chloride ions in the extracted species. Similarly, the H^+ ion concentration was varied in the range 1.0×10^{-3} mol/L to 2.0 mol/L, keeping the chloride ion concentration fixed at 2.0 mol/L by adding a calculated amount of NaCl. The slope value from Figure 7 indicates no involvement of the H^+ ion in the extraction process. Based on the observations and the slope values, the following extraction mechanism was proposed for gallium from acidic chloride medium using Cyphos IL 101 ($R_3R'PCl$):^{22,32}

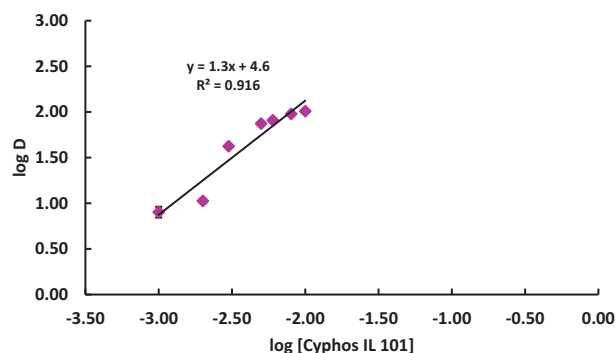


Figure 5. Log-log relationships between distribution ratio and Cyphos IL 101 concentration.

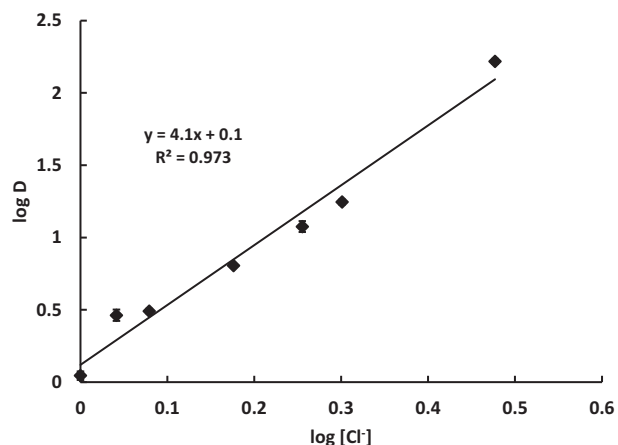
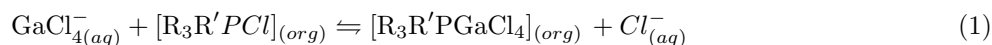


Figure 6. Relationship between gallium extraction efficiency ($D = [M]_{org}/[M]_{aq}$) and chloride ion. Aq. phase: 1.0×10^{-3} mol/L Ga(III), 1.0 mol/L HCl; org. phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.



Temperature sometimes has a remarkable effect on extraction kinetics and it was examined with the extraction of Ga(III) in 1.0 mol/L HCl using 5.0×10^{-3} mol/L Cyphos IL 101 in the temperature range of 300–333 K. It was observed that the distribution ratio increased with rise in temperature, indicating the process to be endothermic (Figure 8).

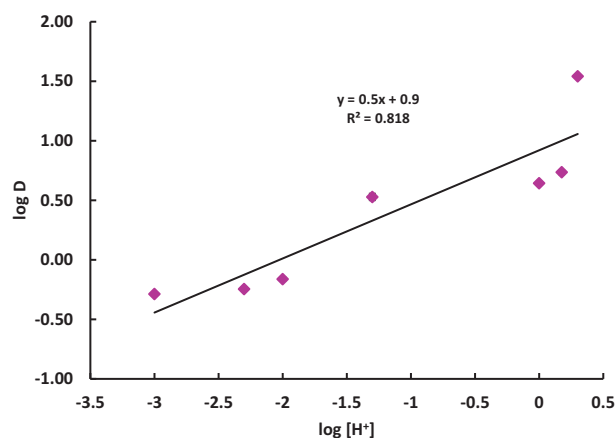


Figure 7. Relationship between gallium extraction efficiency ($D = [M]_{org}/[M]_{aq}$) and hydrogen ion. Aq. phase: 1.0×10^{-3} mol/L Ga(III); org. phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

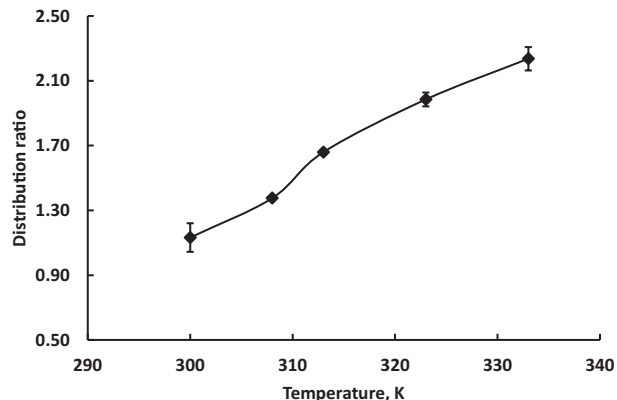


Figure 8. Effect of temperature on extraction of gallium using Cyphos IL 101. Aq. phase: 1.0×10^{-3} mol/L Ga(III), 1.0 mol/L HCl; org. phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

2.2. Stripping

The kind and concentration of a stripping phase have an effect on the efficiency of the process. Hence, four different stripping solutions, ammonia, hydrochloric acid, sulfuric acid, and nitric acid, each having a concentration of 0.1 mol/L, were investigated for stripping study. Equal volumes of the stripping agents and the loaded organic phase containing 320.0 mg/L gallium were equilibrated for 10 min in a separating funnel. The results reported in Table 1 reveal that the highest percentage of stripping (92.0%) was observed with 0.1 mol/L HCl. A two-stage stripping experiment was carried out with 0.1 mol/L HCl and it was found that gallium was completely stripped from the loaded organic phase.

Table 1. Effect of various stripping agents on the stripping of gallium from loaded 5.0×10^{-3} mol/L Cyphos IL 101 containing 320.0 mg/L gallium.

Stripping agent	% Stripping
0.1 mol/L H_2SO_4	42.6 ± 0.3
0.1 mol/L HNO_3	40.0 ± 2.3
0.1 mol/L NH_3	46.3 ± 0.3
0.1 mol/L HCl	92.0 ± 0.3

2.3. Selectivity and recovery of gallium from photodiodes

Gallium(III) is associated mainly with Al(III), Zn(II), Cu(II), and Fe(III) in Bayer's liquor, leach liquor of sphalerite, diodes, and red mud. The extraction behavior of gallium in the presence of these metal ions was studied using the novel ionic liquid Cyphos IL 101 from synthetic solutions. First binary separations were investigated and then extractions in the presence of all these metal ions were also examined. The experimental part was carried out such that binary mixtures containing equimolar concentrations of the metal ions (Ga(III)/Al(III), Ga(III)/Zn(II), Ga(III)/Fe(III), Ga(III)/Cu(II), Ga(III)/Ni(II)) were investigated from different hydrochloric acid molarities using 5.0×10^{-3} mol/L Cyphos IL 101 diluted with kerosene. Similarly, a solution containing equimolar concentrations of all these metal ions was also extracted with 5.0×10^{-3} mol/L Cyphos IL 101 at different acid concentrations. The partition data obtained for the metal ions are presented

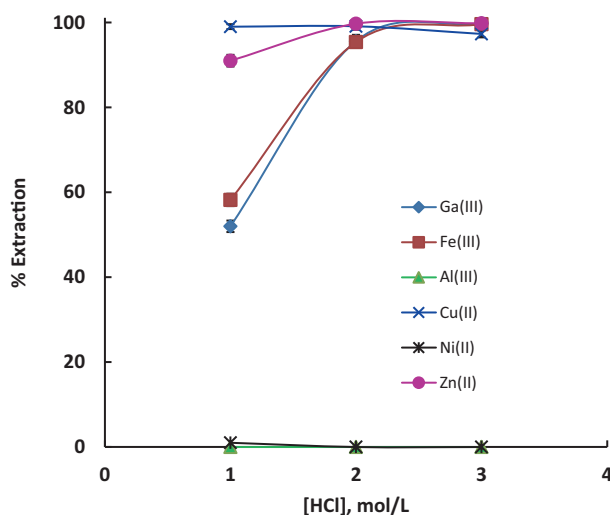


Figure 9. Plot of percentage extraction of metal ions versus hydrochloric acid concentration. Aq. phase: 1.0×10^{-3} mol/L each of Ga(III), Al(III), Cu(II), Zn(II), Fe(III), and Ni(II); org. phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

in Table 2 and Figure 9, from which it can be observed that effective separation of gallium could be achieved in the presence of Al(III) and Ni(II) using Cyphos IL 101. At the same time, there is a possibility of gallium separation from Cu(II) and Zn(II) at 1.0 mol/L HCl. For example, the separation factor (β) of Cu(II) over Ga(III) was 556.2 at 1.0 mol/L HCl and it decreased to 4.9 when the HCl concentration was increased to 2.0 mol/L. Similarly, the separation factor of Zn(II) over Ga(III) was 3324.8 and 2.3 with HCl concentrations of 1.0 mol/L and 2.0 mol/L, respectively. The β values of Fe(III) over Ga(III) were much lower (Table 2) in the acid concentrations used for this investigation because similar amounts of both metal ions were extracted by the ionic liquid. This study was extended to photodiodes, which were collected from obsolete printed circuit boards. The collected material was ground in a mortar and pestle to make a fine powder and from that 2.0 g of the powdered photodiode was leached with 50.0 mL of 4.0 mol/L HCl at 60 °C for 3 h. The sample was cooled and filtered and the filtrate with the washings was collected and diluted to 100.0 mL. Analysis of leach liquor is reported in Table 3; the major amount of metal ions present in the solution were gallium and copper. Minor quantities of other metals such as As, Pb, Al, Ag, and Ni were also present. This leach liquor was equilibrated with 5.0×10^{-3} mol/L Cyphos IL 101 at equal phase ratio and analysis of the raffinate (Table 3) revealed that 99.4% gallium was extracted with 2.3% coextraction of copper. Other metal ions present in leach liquor were not extracted with Cyphos IL 101. From the loaded organic phase 99.5% gallium ions were stripped using 0.1 mol/L HCl with a negligible amount of copper contamination (Table 3).

2.4. Comparative study

The present extraction system involving gallium(III) with Cyphos IL 101 and some of the previously studied extraction systems of gallium(III) with other extractants are summarized in Table 4. It was observed that most of the studies were carried out in chloride medium, but the extractant concentration required for extraction and separation of gallium is high, and selectivity and separation were achieved in some cases. In our proposed method, the extractant concentration is lower at 5.0×10^{-3} mol/L for 1.0×10^{-3} mol/L of gallium(III). High loading capacity of 320.0 mg/L was reported for 5.0×10^{-3} mol/L Cyphos IL 101. Gallium was selectively

Table 2. Effect of hydrochloric acid concentration on separation efficiency of gallium from binary mixtures. Aq. phase: 1.0×10^{-3} mol/L Ga (III), 1.0×10^{-3} mol/L (Al (III)/Cu (II)/Zn (II)/Fe (III)/Ni (II)); org. phase: 5.0×10^{-3} mol/L Cyphos IL 101 in kerosene.

[HCl], mol/L	Metal ions	Concentration ratio	% E (Ga)	% E (Al / Cu / Zn / Ni / Fe)	Separation factor (β)
1.0	Ga (III): Al (III)	1:1	50.2 ± 1.1	0.0	-
2.0			98.2 ± 2.3	0.0	-
3.0			99.8 ± 0.4	0.0	-
1.0	Ga (III): Cu (II)	1:1	26.8 ± 0.5	99.5 ± 0.3	556.2 ± 7.5
2.0			95.9 ± 0.4	99.5 ± 0.4	$4.9 \pm 4.7 \times 10^{-2}$
3.0			99.8 ± 0.3	98.0 ± 0.4	$0.9 \pm 3.0 \times 10^{-3}$
1.0	Ga (III): Zn (II)	1:1	22.3 ± 0.4	99.9 ± 0.5	3324.8 ± 7.6
2.0			98.5 ± 0.3	99.3 ± 0.1	2.8 ± 0.2
3.0			99.9 ± 0.3	99.1 ± 0.2	$0.2 \pm 2.2 \times 10^{-2}$
1.0	Ga (III): Ni (II)	1:1	51.3 ± 0.3	$1.2 \pm 1.0 \times 10^{-2}$	71.2 ± 1.1
2.0			97.7 ± 0.3	0.0	-
3.0			99.8 ± 0.4	0.0	-
1.0	Ga (III): Fe (III)	1:1	51.0 ± 0.3	58.2 ± 0.3	$1.4 \pm 9.0 \times 10^{-2}$
2.0			98.7 ± 0.2	95.4 ± 0.5	$0.3 \pm 4.0 \times 10^{-2}$
3.0			99.7 ± 0.3	99.6 ± 0.3	$0.7 \pm 4.0 \times 10^{-2}$

Table 3. Reports on leaching, extraction, and recovery of gallium from photodiodes.

Metal	Composition of leach solution (mg/L)	Composition of solution after extraction with 5.0×10^{-3} mol/L Cyphos IL 101 (mg/L)	Composition of solution after stripping with 0.1 mol/L HCl (mg/L)
Ga	16.0 ± 0.4	$1.0 \times 10^{-1} \pm 3.5 \times 10^{-2}$	15.9 ± 0.3
As	1.3 ± 0.2	1.2 ± 0.1	$3.0 \times 10^{-1} \pm 2.5 \times 10^{-2}$
Pb	$2.0 \times 10^{-2} \pm 4.0 \times 10^{-3}$	$0.2 \pm 3.0 \times 10^{-2}$	$3.0 \times 10^{-2} \pm 3.0 \times 10^{-3}$
Al	1.1 ± 0.2	$1.0 \times 10^{-2} \pm 9.0 \times 10^{-3}$	0.0
Ag	1.7 ± 0.2	$140.0 \times 10^{-1} \pm 3.0 \times 10^{-2}$	$1.0 \times 10^{-2} \pm 6.0 \times 10^{-3}$
Cu	1272.0 ± 9.7	1242.0 ± 18.7	27.0 ± 2.1
Ni	2.4 ± 0.2	2.4 ± 0.2	0.0
In	0.0	0.0	0.0

removed in the presence of aluminum and nickel. In short, the ionic liquid Cyphos IL 101 is a better extractant in terms of quick attainment of equilibrium, high loading capacity, and selectivity.

2.5. Conclusions

The present study established that Cyphos IL 101 is a potential extractant for gallium(III) from chloride medium. The Ga(III) ions were quantitatively extracted to the organic phase at and above 2.0 mol/L HCl concentration. The mechanism for the extraction of Ga(III) with Cyphos IL 101 has been evaluated by Job's method, extractant, and metal variation studies. From the slope values, the formation of $[R_3R'PGaCl_4]$ species in the organic phase

Table 4. Comparison of various extraction systems of Ga(III).

Metal ions	Medium	Extractant and diluent	Loading capacity	Extraction mechanism	Separation	Ref.
Ga(III) and In(III)	Chloride	Cyanex 272 (0.5 mol/L) in toluene	In(III) - 3.3×10^{-2} mol/L Ga(III) - 2.5×10^{-2} mol/L	$\text{In(OH)}_{\text{aq}}^{3+} + \text{H}_2\text{R}_{\text{org}} \rightleftharpoons \text{In(OH)R}_{2\text{org}} + 2\text{H}_{\text{aq}}^+$ (at low acidity) $\text{Ga(OH)}_{\text{aq}}^{3+} + \text{H}_2\text{R}_{\text{org}} \rightleftharpoons \text{Ga(OH)R}_{2\text{org}} + 2\text{H}_{\text{aq}}^+$ (at low acidity) $\text{GaCl}_{4\text{aq}}^- + \text{H}_2\text{R}_{\text{org}} \rightleftharpoons \text{H}^+ \text{GaCl}_4^- \cdot 2\text{HR}_{\text{org}}$ (at high acidity)	Binary and ternary separation, Ga(III) separation from LED and bottom ash using 0.5 mol/L Cyanex 272 In(III) separation from sphalerite and galena	[33]
Ga(III) and In(III)	Sulfuric acid	D2EHPA (5.0×10^{-2} mol/L) in kerosene		$\text{M}^{3+}_{\text{(aq)}} + 3/2(\text{HA})_{2\text{(aq)}} \rightleftharpoons \text{MA}_{3\text{(org)}} + 3\text{H}^+_{\text{(aq)}}$	Binary separation consisting of 0.5 g/L Ga(III) and 1.0 g/L In(III) using 2.5×10^{-2} mol/L D2EHPA	[34]
Ga(III)	Hydrochloric acid	Cyanex 923 (0.5 mol/L) in toluene	0.5 mol/L Cyanex 923 - 3.5×10^{-2} mol/L Ga(III)	$\text{GaCl}_3 \cdot 3\text{RH}$ indicating solvation mechanism	Ga(III) separation from LED and bottom ash using 0.5 mol/L Cyanex 923	[35]
Ga(III)	2.0 mol/L NaOH	Kelex 100 in kerosene			Separation of Al(III) (1100.0 mg/L) and Ga(III) (150.0 mg/L) at high pH of ≥ 13.5 ; average recovery of gallium is 95.0% using 14.0%–20.0% Kelex 100 in pure kerosene without addition of modifier	[36]
Ga(III), In(III), and Zn(II)	Chloride	sec-octyl-Phenoxyacetic acid and primary amine N1923 in n-heptane		$\text{ZnCl}_{2\text{(aq)}} + x\text{H}_2\text{A}_{2\text{(org)}} + y\text{B}_{\text{(org)}} \rightleftharpoons \text{ZnCl}_{2-x} \cdot \text{H}_{2x} \cdot \text{A}_{2x} \cdot \text{B}_y_{\text{(org)}} + x\text{H}^+_{\text{(aq)}} + y\text{Cl}^-_{\text{(aq)}}$	The mixtures can enhance the selectivity between Ga(III)/In(III) and Zn(II) at a proper concentration ratio of CA12 and N1923	[37]
Ga(III), In(III), and Zn(II)	Sulfuric acid	5.5×10^{-2} mol/L antioxime from LIX 63 and 1.2×10^{-1} mol/L Versatic 10 in ShellSol D70	7.2×10^{-1} g/L Ga(III) and 7.7×10^{-1} g/L In(III)		Separation of gallium(III) and indium(III) from zinc refinery residue	[38]

Table 4. Continued.

Metal ions	Medium	Extractant and diluent	Loading capacity	Extraction mechanism	Separation	Ref.
Ga(III)	Hydrochloric acid	Cyanex 923 and Cyanex 925 in kerosene	1.6 × 10 ⁻³ mol/L of Ga(III) for Cyanex 923 and 2.2 × 10 ⁻³ mol/L of Ga(III) for Cyanex 925	$\text{Ga}^{3+}_{(aq)} + 3\text{Cl}^{-}_{(aq)} + 2\text{L}_{(org)} \rightleftharpoons \text{GaCl}_3 \cdot 2\text{L}_{(org)}$	Separation of Ga(III) from Cu(II) and Zn(II)	[39]
Ga(III)	Hydrochloric acid	2-octyl-Aminopyridine (2-OAP) (3.3 × 10 ⁻² mol/L) in chloroform	2.0 mg	$\begin{aligned} &[\text{RR}'\text{NH}](\text{org}) + \text{HCl}_{(aq)} \rightleftharpoons [\text{RR}'\text{NH}_2^+\text{Cl}^{-}]_{(org)} \\ &\text{GaCl}_3(\text{aq}) + \text{Cl}^{-}_{(aq)} \rightleftharpoons [\text{GaCl}_4^{-}]_{(aq)} \\ &[\text{RR}'\text{NH}_2^+\text{Cl}^{-}]_{(org)} + [\text{GaCl}_4^{-}]_{(aq)} \rightleftharpoons [\text{RR}'\text{NH}_2^+\text{GaCl}_4^{-}]_{(org)} + \text{Cl}^{-}_{(aq)} \end{aligned}$ where R = -C ₅ H ₄ N and R' = -CH ₂ (CH ₂) ₆ CH ₃ .	Separation of Ga(III) from binary mixtures of Zn(II), Pb(II), Cd(II), Hg(II), Al(III), Se(IV), Sb(III), Sn(IV), In(III), and Tl(I) using 7.0 mol/L HCl, 3.3 × 10 ⁻² mol/L 2-OAP in chloroform	[40]
Ga(III) and In(III)	Nitrate	p-tert-Butylcalix[4]arene tetrahydroxamic acid Adogen-464 in toluene		$\text{M}^{3+}_{(aq)} + \text{H}_4\text{R}_{(org)} \rightleftharpoons \text{MHR}_{(org)} + 3\text{H}^{+}_{(aq)}$	Ga(III) > In(III) > Fe(III) > Cu(II) >> Zn(II), Ni(II)	[41]
Ga(III)	Hydrochloric acid	Cyphos IL 101 in kerosene (5.0 × 10 ⁻³ mol/L)	320.0 mg/L	$\text{GaCl}_4^{-}_{(aq)} + [\text{R}_3\text{R}'\text{P}]\text{Cl}_{(org)} \rightleftharpoons [\text{R}_3\text{R}'\text{PGaCl}_4]_{(org)} + \text{Cl}^{-}_{(aq)}$	Binary separation involving Ga(III) with Al(III), Zn(II), Fe(III), Cu(II), and Ni(II) with 5.0 × 10 ⁻³ mol/L Cyphos IL 101 and extended to study the separation of gallium from photodiodes	Present study

was proposed. The increase in chloride concentration in the aqueous phase increased the percentage extraction of gallium(III) due to the formation of extractable anionic species. The extraction process was found to be endothermic as the percentage extraction of gallium was increased with the increase in temperature. Gallium was stripped from the loaded organic phase in two stages using 0.1 mol/L HCl. Separation of gallium over aluminum and nickel could be achieved from the HCl concentrations used (1.0–3.0 mol/L) for investigation. On the other hand, separation factors of 3324.8 ($\beta_{Zn/Ga}$) and 556.2 ($\beta_{Cu/Ga}$) were achieved at 1.0 mol/L HCl. Gallium was effectively extracted and separated from the photodiode with little coextraction of copper. A comparative study proved that Cyphos IL 101 is a better extractant compared to classical extractants.

3. Experimental

The stock solution of gallium(III) chloride (0.1 mol/L) was prepared by accurately weighing a calculated amount of gallium chloride in double-distilled water and poured into a volumetric flask of desired volume. A small amount of concentrated HCl was added to prevent hydrolysis of the metal ions. From this, the working solutions were prepared as required for the experiment. The organic phase extractant used for the investigations was Cyphos IL 101 (trihexyl(tetradecyl)phosphonium chloride) ($R_3R'PCL$) obtained from Cytec Inc. (Canada). It was used without further purification. Commercial-grade kerosene supplied by SD Fine Chemicals Limited (India) was used as the diluent. All other chemicals used were of analytical grade.

In all experiments, equal volumes of the aliquot of the organic and aqueous solutions were taken in a 60.0-mL separating funnel and shaken for 10 min, except for the time variation study. After phase separation, the aqueous phase was collected and stored for analysis. The amount of gallium present after and before extraction was measured using inductively coupled plasma mass spectroscopy (ICP-MS) with a PerkinElmer NexIon 300X with proper dilution. Gallium concentration in the organic phase was calculated using mass balance. The distribution ratio (D) and the extraction efficiency (% E) were calculated using the formulae given below:

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad (2)$$

$$\%E = \frac{100 D}{D + \frac{V_{aq}}{V_{org}}} \quad (3)$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively. All the experiments were carried out at 27 ± 2 °C. The selectivity coefficient (β) for two metals was estimated as follows:

$$\beta = \frac{[D]_1}{[D]_2} \quad (4)$$

For stripping studies, 100.0 mL of 5.0×10^{-3} mol/L Cyphos IL 101 was equilibrated for 10 min with an equal volume of aqueous solution, having gallium concentration of 7.0×10^{-3} mol/L at aqueous acidity of 2.0 mol/L. After phase separation, the organic phase was collected filtering through 1PS phase separation paper. Different stripping solutions were contacted with an equal volume of the above prepared loaded organic phase for 10 min and the corresponding aqueous phase was collected. The metal concentration in the aqueous phase was determined by ICP-MS in order to calculate the % stripping (% S) using Eq. (5):

$$\%S = \frac{[M]_{aq,s}}{[M]_{aq,i} - [M]_{aq,r}} \quad (5)$$

where $[M]_{aq,s}$ is the concentration of metal ions in the aqueous phase after stripping and $[M]_{aq,i}$ and $[M]_{aq,r}$ are the concentrations of metal ions in the aqueous phase before and after extraction.

Triplicate experiments were performed and the standard deviations were incorporated in the figures and standard errors in the tables.

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