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Indium and Gallium Extraction using Ionic liquids: Experimental and Theoretical Study

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Abstract

Due to their remarkable properties, indium and gallium have been used extensively over the last two decades in the production of new electronic devices and semiconductors. Yet natural resources of these critical metals are scarce, and even more so due to increased demand. It is therefore essential to recover them from the waste materials to supply the increasing demand. For this reason, this research studies the extraction of indium and gallium from electric arc furnace (EAF) dust using an ionic liquid solution as solvent. The investigation followed both experimental and theoretical approaches. For this aim, the EAF dust was spiked with In and Ga to simulate a realistic waste matrix. Ionic liquids are emerging solvents, and EAF dust is a valuable industrial waste containing several useful metals. For the experimental part, two ionic liquids [Bmim$^+$HSO$_4^-$] and [Bmim$^+$Cl$^-$] were mixed with three oxidants Fe$_2$(SO$_4$)$_3$, KMnO$_4$, and H$_2$O$_2$ to determine the best ionic liquid and oxidant combination. For the theoretical study, density functional theory (DFT) was applied to calculate the Gibbs free energy (ΔG) and the stability of each possible complex that can form with each of the studied ionic liquid media. To this end, three imidazolium-based ionic liquids ([Bmim$^+$HSO$_4^-$], [Bmim$^+$Cl$^-$],

[Bmim$^+$NO$_3^-$]) which have similar anionic parts as [SO$_4^{2-}$], [Cl$^-$], and [NO$_3^-$] with the most commonly used acids H$_2$SO$_4$, HCl, and HNO$_3$, were selected for DFT calculations.

1 Introduction

In the modern electronic world indium (In) and gallium (Ga) are attracting increasing attention due to their varied and essential applications in different electronic devices, light-emitted diodes (LEDs), liquid crystal display (LCD), photovoltaic panels (PV), and semiconductors. In and Ga have remarkable properties such as being soft, malleable, ductile, having high electric conductivity, transparency and the ability to make a strong bond with glass. This latter property makes them irreplaceable and inseparable parts of new electronic devices with touch screens [1]. Yet there are no single large, high-concentration mineral deposits in nature from which to extract them. In nature In mostly occurs alongside Zn and Pb, within sulfide minerals like sphalerite (ZnS) and galena (PbS) containing only small amounts of In. Low concentrations of Ga on the other hand occur mainly alongside minerals containing Zn, Al, and Ge [2,3]. The scarcity and high demand for In and Ga have led researchers to find efficient ways to recover them from waste materials like electrical and electronic equipment waste broadly known as WEEE or e-waste [4].

Most of the research about In and Ga has focused on their recovery from a leachate solution using different techniques, especially solvent extraction with different extractants. Zhang et al. (2003) studied the extraction and individual separation of In, Ga, and Ti with different carboxylic acids from a hydrochloric acid solution. This research considered the effect of influential parameters on solvent extraction like the initial pH of the solution, extractant concentration, stripping agents, and the existence of foreign ions in the solution [5]. Gupta et al. (2007) investigated the recovery and separation of In and Ga from hydrochloric acid (HCl) solution using the solvent extraction method with bis (2,4,4-trimethylpentyl) phosphinic acid (known as Cyanex 272). They found that solvent extraction of 1 M HCl with Cyanex 272 as the extractant was useful to recover both In and Ga from the HCl solution containing associated metals like Zn, Pb, Al, and Fe [2]. Ma et al. (2011) studied the recovery of Zn^{2+}, In^{3+}, and Ga^{3+} using a system containing sec-octylphenoxy acetic acid (CA12, H2A2) and amine N1923 from an HCl solution [3].

In another study, Lee et al. (2002) examined solvent extraction for separating In and Ga from a sulfuric acid solution using di-2-ethyl-hexylphosphoric acid (D2EHPA) as the extractant [6]. Nusen et al. (2016) investigated a solvent extraction system applying LIX 63 and Versatic 10 extractants which are commercially available, to recover and separate In and Ga from synthetic leach solutions of zinc refinery residues in a sulfuric acid medium. In the system containing 0.2 M Versatic 10 and LIX 63 as the organic phase with the ratio of A/O=1 at 40 °C, 97% In and 99% Ga were successfully recovered. Stripping of the desired metals was done via a single contact in 0.05 M H$_2$SO$_4$, and almost all of the In (100%) and 91% Ga were stripped [7].
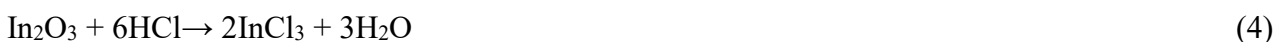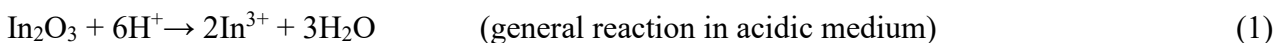
More recent research concentrated on the recovery of scarce and valued metals from waste and secondary resources. For instance, the extraction and recovery of Zn, In, and Ga from spent indium

gallium zinc oxides (IGZO) and gallium zinc oxides (GZO) were investigated by Chen et al. (2017). The spent IGZO, and GZO were leached in 3 M nitric acid solution, with a liquid-solid ratio of 50 ml/g, at 80 ∘C for 2 h. Then solvent extraction was carried out for 5 min to recover indium with 0.02 M D2EHPA as extractant at pH 1, and an A/O ratio of 2. By then adjusting the pH to 3, Ga was recovered within 3 min using 0.015 M D2EHPA and A/O ratio of 3. Ultimately, the target metals were stripped out with 1 M HCl solution with O/A ratio of 1 for 5 min. This process successfully recovered about 99.9% of Zn, In, and Ga with 99.5% purity [8]. Theocharis et al. (2021) examined the extraction and recovery of In, Ga, Cu, Zn, and Mo from end-of-life CIGS ($CuGa_{1-x} In_xSe_2$) photovoltaic panels. The CIGS photovoltaic panels were dismantled and thermally processed at 550 °C for 15 minutes for delamination of ethyl vinyl acetate (EVA), the thin layer of coated glass. Then the prepared sample was leached with 6 M HNO_3, leading to the extraction of In, Ga, Cu, Zn, and Mo. Subsequently, the separation and recovery of the extracted metals from the leachate were attained through solvent extraction using D2EHPA [9]. Similarly, Liu et al, (2022) studied the recovery and separation of Cu, Se, In, and Ga from CIGS-based solar panels. Initially, the crushed solar panels were treated thermally and then leached in 5 M HNO_3 solution with a liquid-solid ratio of 50 ml/g, stirring at 300 rpm at 80 ∘C for 3 h to extract the target metals. The solvent was extracted with di-(2-ethylhexyl) phosphoric acid (D2EHPA), and 90% recovery was achieved for Cu, In, and Ga [10].

There is also some research on the extraction of valuable metals using ionic liquid as an emerging solvent. Ionic liquids are new solvents entirely made of ions, typically a large cation with an anion of different sizes. They are liquid at a temperature below 100 °C and have remarkable physicochemical properties [11,12]. Topçu & Rusen (2020) investigated Cu extraction from copper anode slime using 1-butyl-3-methylimidazolium-based ionic liquids with different anions (HSO_4^-, Cl^-, and BF_4^-). The most effective ionic liquid was 1-butyl-3-methylimidazolium hydrogen sulphate (BmimHSO4) under the conditions of 50% v/v ionic liquid/water concentration, 1/20 g/ml solid to liquid ratio at 50 °C, and 8 hours leaching time, yielding 27.7% Cu extraction [13].

Generally, In can be extracted in acidic solutions of H_2SO_4, HNO_3 and, HCl in the form of $In_2(SO_4)_3$, $In(NO_3)_3$, $InCl_3$ or In_2Cl_6 (dimer complex), based on reactions 1 to 4 [14]. The most stable oxidation state of both In and Ga is +3, and since they both are in the same group (13) in the periodic table one can extrapolate these same/similar reactions for Ga in the acidic solutions.

$$In_2O_3 + 6H^+ \rightarrow 2In^{3+} + 3H_2O \qquad \text{(general reaction in acidic medium)} \qquad (1)$$

$$In_2O_3 + 3H_2SO_4 \rightarrow In_2(SO_4)_3 + 3H_2O \qquad (2)$$

$$In_2O_3 + 6HNO_3 \rightarrow 2In(NO_3)_3 + 3H_2O \qquad (3)$$

$$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O \qquad (4)$$

Therefore, three imidazolium-based ionic liquids [$Bmim^+HSO_4^-$], [$Bmim^+NO_3^-$], and [$Bmim^+Cl^-$] which have a similar anionic part to the commonly used acids, were selected for this research. Figure 1 demonstrates the chemical structure of the cationic part (1-butyl-3-methylimidazolium– known as $Bmim^+$) and the different anions (Cl^-, HSO_4^-, NO_3^-) that create the three chosen ionic liquids. However, the commercial production of [$Bmim^+NO_3^-$] has been discontinued, making experiments with

this ionic liquid non-viable. The theoretical calculations with density functional theory (DFT) of [Bmim$^+$NO$_3^-$] therefore only serve to gain a better understanding of the stability and possibility of a complex formed with the [NO$_3^-$] ligand.
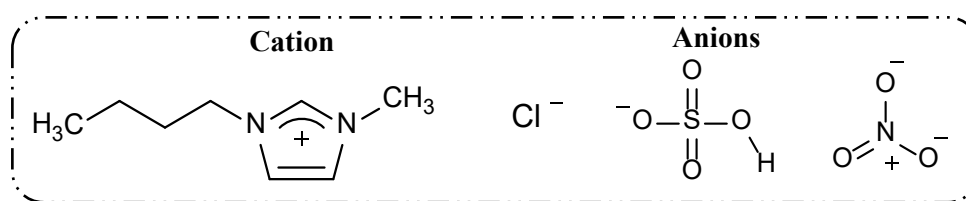

Figure 1: Chemical structure of the three ionic liquids having same cation and different anions (Cl$^-$, HSO$_4^-$, and NO$_3^-$).

In this research, the feasibility of extracting In and Ga mixed with EAF dust as a realistic industrial waste containing other metals (like Zn and Fe), which can be dissolved by ionic liquids was examined. Imidazolium-based ionic liquids were employed in this experimental and theoretical approach. The effect of the type of ionic liquid which compromises the same cation (Bmim$^+$), but different anionic parts (HSO$_4^-$ and Cl$^-$), and also the oxidant mixed with the ionic liquid solution were evaluated. For this aim, two ionic liquids [Bmim$^+$HSO$_4^-$] and, [Bmim$^+$Cl$^-$] were mixed with three oxidants Fe$_2$(SO$_4$)$_3$, KMnO$_4$, and H$_2$O$_2$, respectively, to determine which combination of the ionic liquid and oxidant are the best to extract the target metals. Subsequently, the influential experimental parameters such as concentration of the ionic liquid, oxidant concentration, solid-to-liquid ratio, time and temperature were optimized to achieve the maximum In and Ga extraction.

A theoretical study with density functional theory (DFT) was conducted to calculate the Gibbs free energy (ΔG) of the possible complexes which can form with the available ligands i.e. chloride (Cl$^-$), sulfate (SO$_4^{2-}$), and nitrate (NO$_3^-$) in the ionic liquid media with In and Ga. Furthermore, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the possible complexes was also calculated. A low Gibbs free energy (ΔG) represents a high possibility of a complex forming and a large gap between HOMO and LUMO indicates the stability of the formed complex. All calculations in DFT were performed using Gaussian 16, the B3LYP functional method in the gas phase and the PBEPBE Def2TZVP basis set. Ultimately the experimental results and the theoretical calculations were compared to draw a comprehensive conclusion.

The purpose of the study was to first investigate the effect of the co-extraction of metals like Zn which often occur in natural ores in conjunction with In and Ga on their leaching efficiency. Secondly to determine how well and to what extent In and Ga can be extracted by ionic liquids, and lastly to assess the feasibility of employing ionic liquids as more environmentally benign solvents than mineral acids to use in extraction processes.

2 Experimental

2.1 Materials

The raw material used in this study along with indium and gallium oxide (In_2O_3 & Ga_2O_3) was electric arc furnace (EAF) dust as industrial waste obtained from Ovako Imatra Oy steel plant in Finland. The chemical composition of the EAF dust was determined by X-ray fluorescence (XRF). Table 1 listed the main component of the EAF dust which existed in large amounts as Zn, Fe, and lower amounts of Ca, Mn, and Pb. The mineralogy of the material was also analysed with X-ray diffraction (XRD) as the pattern displayed in Figure 2. The XRD phase analysis evaluation identified the main phases in EAF dust as zincite (ZnO), zinc ferrite ($ZnFe_2O_4$), and magnetite (Fe_3O_4), with some minor phases of $Ca(OH)_2$, PbO, MnO_2, MgO. The mineral phase evaluation in XRD was corresponding with XRF analysis.

Table 1: Chemical composition of the EAF dust as valuable industrial waste examined by XRF

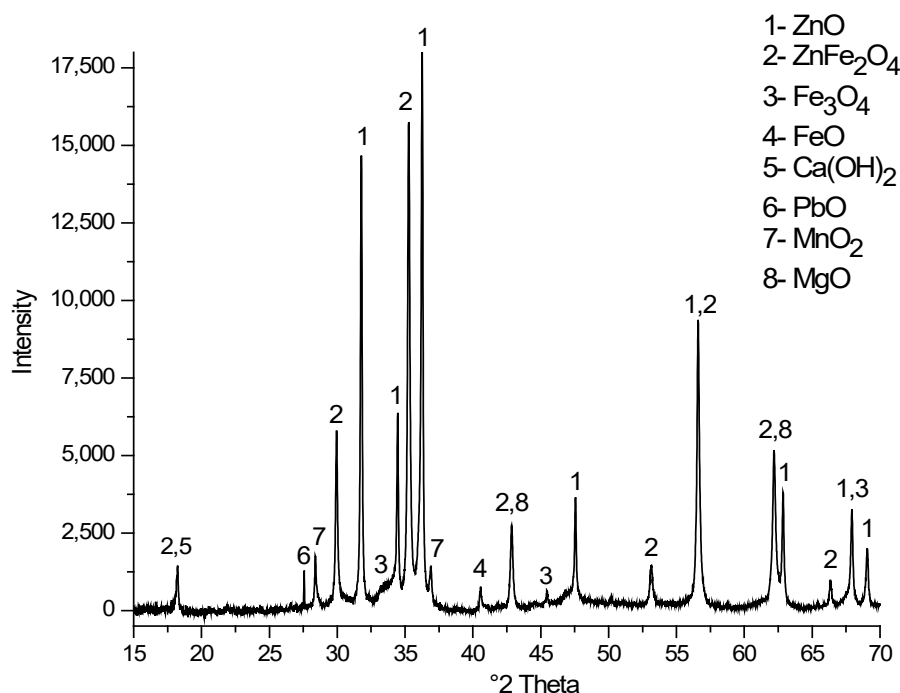| Element	Content [Wt%]
ZnO	34.7
Fe_2O_3	18.1
CaO	3.8
MnO	2.7
K_2O	2.6
PbO	1.7
S	1.2
SiO_2	1.02
MgO	0.82
Al_2O_3	0.53
Cr_2O_3	0.36
CuO	0.32
NiO	0.17
P_2O_5	0.14
Co_3O_4	0.10

Figure 2: The XRD pattern of the EAF dust as the industrial waste

2.2 Apparatuses and Chemicals

The leached solution was analysed by AAS (atomic absorption spectroscopy, Varian AA240, USA). The EAF dust chemical composition was examined with XRF (X-ray fluorescence-PANalytical Axios max) and XRD (X-ray diffraction, Malvern PANalytical-X'Pert PRO Powder, Almelo, Netherlands) with CuKα radiation source, applying a 40 mA current, and 45 kV acceleration voltage. The pH and redox potential in the ionic liquid leaching solutions were measured by a Digital pH electrode (HI 11,310, Hanna Instruments) and InLab Ag/AgCl 3M KCl (Mettler Toledo), respectively. The chemicals used in the experimental study were Indium and Gallium oxide (In_2O_3 and Ga_2O_3), two ionic liquids, 1-Butyl-3 methylimidazolium hydrogen sulfate [$Bmim^+HSO_4^-$], and 1-Butyl-3 methylimidazolium chloride [$Bmim^+Cl^-$] along with three oxidants ferric sulfate ($Fe_2(SO_4)_3$), hydrogen peroxide (H_2O_2), and potassium permanganate ($KMnO_4$). The chemicals used in this research were all acquired from Merck.

2.3 Experimental Procedure

The leaching experiment in ionic liquid medium as leaching solution was carried out in a 250 ml three-neck round bottom vessel (the reactor) immersed in a water bath on a hot plate magnetic stirrer under atmospheric pressure. The leaching reactor was connected to a condenser, the other neck holding the thermometer inside the leaching solution and the other one for taking sample at intervals. The mixing was done by a stirring bar inside the reactor to provide a uniform pulp. The leaching experiment was conducted as follows: the ionic liquid solution with a specific concentration was preheated to the desired temperature, and then a certain amount of EAF dust with 5% In_2O_3 and Ga_2O_3 with the

known amount of the oxidant was added to the heated leaching solution. The experimental conditions for the first part of the research to determine the best combination of ionic liquid and the oxidant were as follows: 50% (v/v) ionic liquid concentration ([Bmim$^+$HSO$_4^-$], and [Bmim$^+$Cl$^-$]), with Fe$_2$(SO$_4$)$_3$ (0.5 g), or, KMnO$_4$ (0.5 g), or, H$_2$O$_2$ (50%) 1 ml oxidant, at 65 °C, 1/20 solid to liquid ratio, and 8 h leaching time. After finding the best combination of the ionic liquid and oxidant, the influential factors such as concentration of the ionic liquid (30- 40- 50- 60% v/v), the concentration of the oxidant [Fe$_2$(SO$_4$)$_3$ or KMnO$_4$ (0.25-0.5-0.75-1 g)] and H$_2$O$_2$ (%50) [(1-1.5-2-2.5 ml)], S/L ratio (1/10- 1/15- 1/20- 1/25 g/ml) and temperature (55, 65, 75, and 85 °C) were studied to discover the optimum condition to attain the highest extraction of In and Ga from the ionic liquid solution mixed with spiked EAF dust. The leachate was filtered and then analysed with AAS to measure the amount of extracted In and Ga along with Zn.

3 Results and Discussion

Optimisation of the experimental variables indicates that the optimum conditions for the extraction of the different metals of interest from the EAF dust spiked with In and Ga using the studied ionic liquids ([Bmim$^+$HSO$_4^-$] and [Bmim$^+$Cl$^-$]). Table 2 listed the optimum conditions *refer to published paper here).
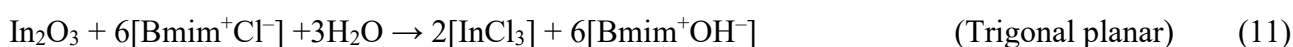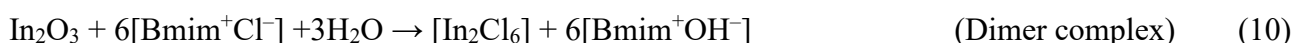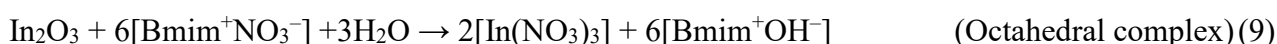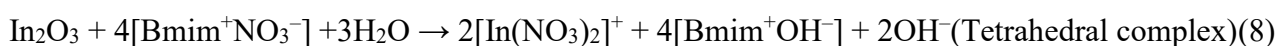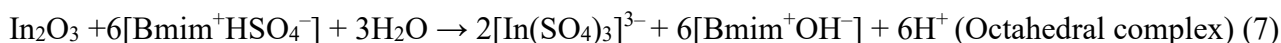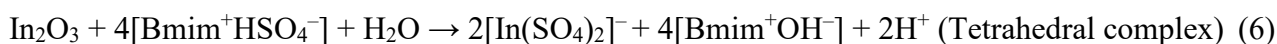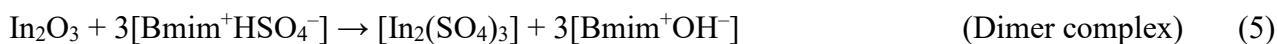
Table 2: The optimum conditions for the extraction of the metals of interest from the EAF dust

Factors	Optimum point		
Ionic liquids/Oxidants	[Bmim$^+$HSO$_4^-$]/Fe$_2$(SO$_4$)$_3$		
Ionic liquid concentration (v/v%)	30%		
Oxidant concentration (g)	1 g Fe$_2$(SO$_4$)$_3$		
Solid/Liquid (g/l)	1/20		
Temperature (ºC)	85		
Yield (%E)	%E In	%E Ga	%E Zn
	97.4	17.3	92.7
Kinetic model	Diffusion-controlled		
Activation energy (kJ/mol)	In: 33.6	Ga: 30.3	Zn: 8.2

3.1 Theoretical part: Density Functional Theory (DFT)

In this research, density functional theory (DFT) calculations based on the Kohn-Sham equation were applied to get a better understanding of the ligand-metal complexation, the shape of the formed complexes and their stability [15]. The studied ionic liquids have the same cationic part (Bmim$^+$) but different anionic parts as [SO$_4^{2-}$], [NO$_3^-$], and [Cl$^-$], respectively, which act as a ligand to make complex with In and Ga. All DFT calculations were performed using Gaussian 16, the B3LYP functional method in the gas phase and the PBEPBE Def2TZVP basis set.

The possible reactions (5-13) resulting in a different complex format (i.e. dimer, tetrahedral, octahedral), which can occur for In in the form of (In_2O_3) in each ionic liquid are written as follows, with similar reactions extrapolated for (Ga_2O_3):

$In_2O_3 + 3[Bmim^+HSO_4^-] \rightarrow [In_2(SO_4)_3] + 3[Bmim^+OH^-]$ (Dimer complex)   (5)
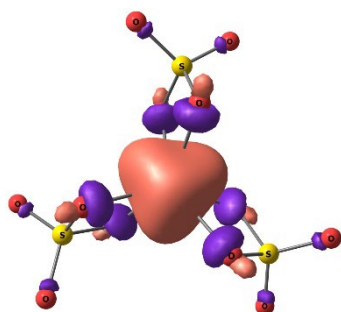
$In_2O_3 + 4[Bmim^+HSO_4^-] + H_2O \rightarrow 2[In(SO_4)_2]^- + 4[Bmim^+OH^-] + 2H^+$ (Tetrahedral complex) (6)

$In_2O_3 + 6[Bmim^+HSO_4^-] + 3H_2O \rightarrow 2[In(SO_4)_3]^{3-} + 6[Bmim^+OH^-] + 6H^+$ (Octahedral complex) (7)

$In_2O_3 + 4[Bmim^+NO_3^-] + 3H_2O \rightarrow 2[In(NO_3)_2]^+ + 4[Bmim^+OH^-] + 2OH^-$ (Tetrahedral complex)(8)

$In_2O_3 + 6[Bmim^+NO_3^-] + 3H_2O \rightarrow 2[In(NO_3)_3] + 6[Bmim^+OH^-]$ (Octahedral complex)(9)

$In_2O_3 + 6[Bmim^+Cl^-] + 3H_2O \rightarrow [In_2Cl_6] + 6[Bmim^+OH^-]$ (Dimer complex)   (10)

$In_2O_3 + 6[Bmim^+Cl^-] + 3H_2O \rightarrow 2[InCl_3] + 6[Bmim^+OH^-]$ (Trigonal planar)   (11)

$In_2O_3 + 8[Bmim^+Cl^-] + 5H_2O \rightarrow 2[InCl_4]^- + 8[Bmim^+OH^-] + 2H^+$ (Square complex)   (12)

$In_2O_3 + 12[Bmim^+Cl^-] + 9H_2O \rightarrow 2[InCl_6]^{3-} + 12[Bmim^+OH^-] + 6H^+$ (Octahedral complex)(13)

To theoretically determine which of these ligands [SO_4^{2-}], [NO_3^-] or [Cl^-] provided by each ionic liquid produce the most possible and stable complex with In and Ga as the critical metals in the leaching solution, DFT calculations were conducted using High-Performance Computing (HPC). For this aim, the reaction Gibbs free energy (ΔG) which indicates the possibility of the formation of each complex was calculated using the mentioned reactions, and also the gap between HOMO and LUMO which states the stability of a complex [16], among the proposed complexes. The following Figures (3-5) depicted the HOMO and LUMO structure of In complexes with each studied ionic liquid. The HOMO and LUMO structure for Ga complexes with the studied ionic liquids were excluded due to limited space since they have similar structure.
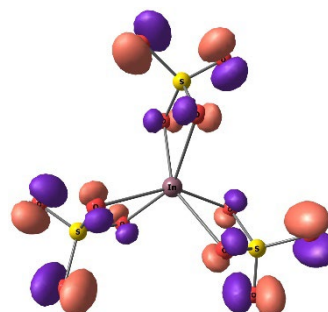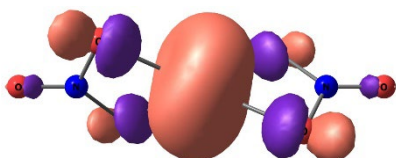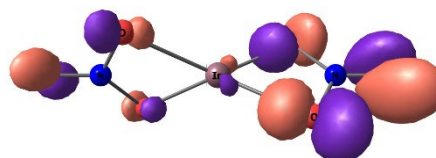
[$In_2(SO_4)_3$] Dimer complex

Alpha MO 94 – LUMO   Alpha MO 93 – HOMO

[$In(SO_4)_2^-$] Tetrahedral complex

Alpha MO 60 – LUMO   Alpha MO 59 – HOMO
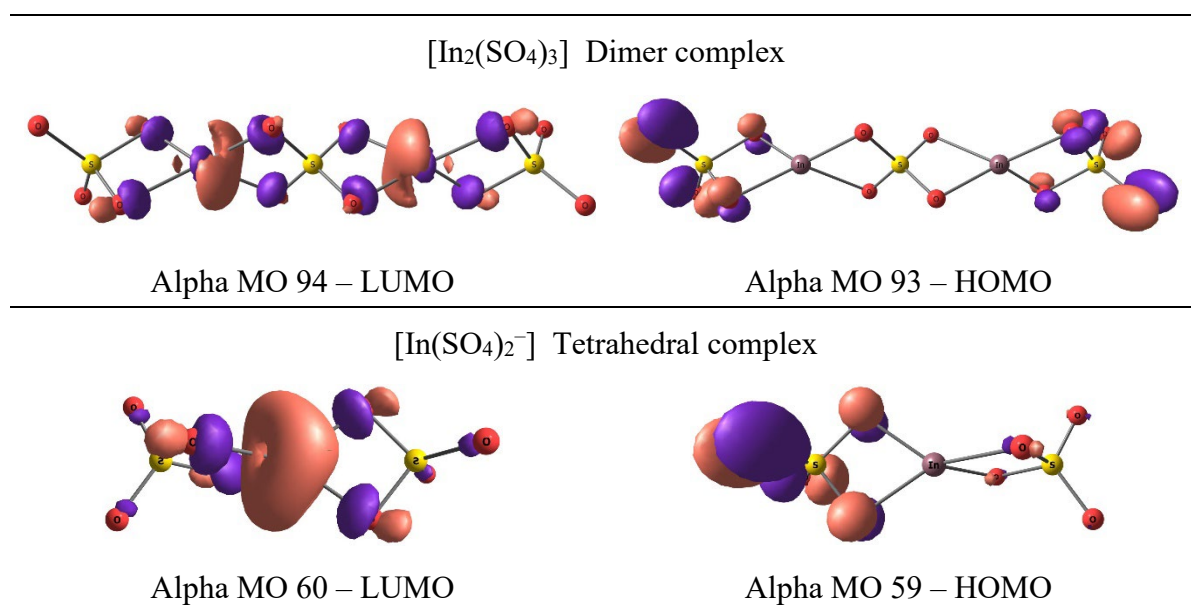
[In(SO$_4$)$_3^{-3}$] Octahedral complex

Alpha MO 85 – LUMO

Alpha MO 85 – HOMO

Figure 3: The LUMO & HOMO of the possible complexes of In with [SO$_4^{2-}$] ligand provided by [Bmim$^+$HSO$_4^-$].

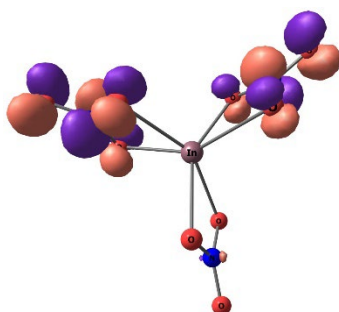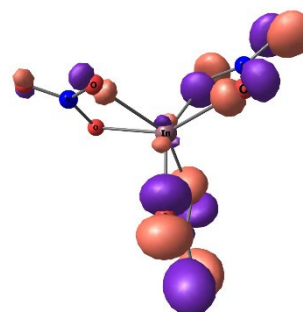[In(NO$_3$)$_2^+$] Tetrahedral complex

Alpha MO 42 – LUMO

Alpha MO 41 – HOMO

[In(NO$_3$)$_3$] Octahedral complex

Alpha MO 58 – LUMO

Alpha MO 57 – HOMO

Figure 4: The LUMO & HOMO of the possible complexes of In with [NO$_3^-$] ligand provided by [Bmim$^+$NO$_3^-$].

[In$_2$Cl$_6$] Dimer complex

Alpha MO 73 – LUMO

Alpha MO 72 – HOMO

[InCl₃] Trigonal complex

Alpha MO 37 – LUMO   Alpha MO 36 – HOMO

[InCl₄⁻] Square complex

Alpha MO 46 – LUMO   Alpha MO 45 – HOMO
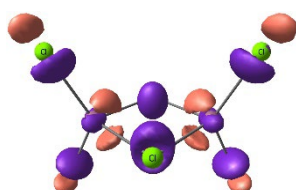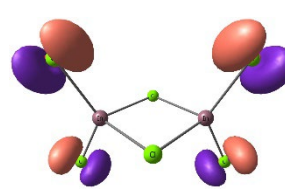
[InCl₆³⁻] Octahedral complex

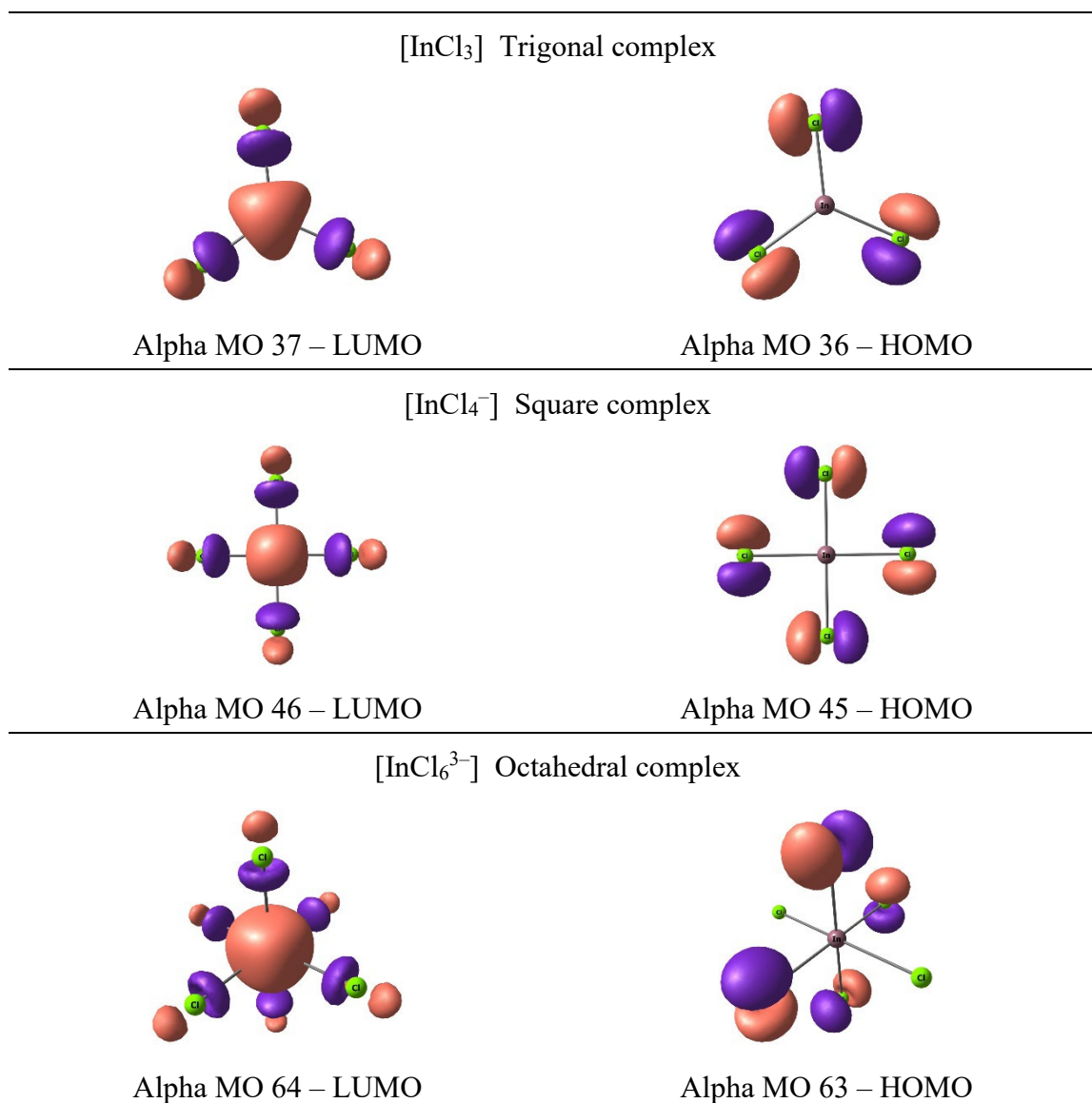Alpha MO 64 – LUMO   Alpha MO 63 – HOMO

Figure 5: The LUMO & HOMO of the possible complexes of In with [Cl⁻] ligand provided by [Bmim⁺Cl⁻].

There were 18 possible complexes for both In and Ga for the theoretical evaluation. After DFT calculation the obtained results for ΔG, and the HOMO-LUMO gap for all of the different possible complexes of the three ligands with In and Ga are summarised in Tables 3 and 4. Typically, the low Gibbs free energy (ΔG) represents a high possibility of a complex to form and a large gap between HOMO and LUMO indicates high stability of the formed complex [16]. Thus, amongst all of these possible complexes, the dimer complex of $[In_2(SO_4)_3]$ and $[Ga_2(SO_4)_3]$ had the lowest ΔG, and the largest HOMO-LUMO gap indicating the most possible and stable complex to form. Therefore, the ionic liquid [Bmim⁺HSO₄⁻] which provides $[SO_4^{2-}]$ –O-donor chelating ligand in the leaching solution performs best. It should be mentioned that the dimer complex of the [Cl⁻] ligand provided by [Bmim⁺Cl⁻] with In and Ga producing $[In_2Cl_6]$ and $[Ga_2Cl_6]$ also can be possible due to a small ΔG, and large HOMO-LUMO gap, however in lower amount compared to complexes with $[SO_4^{2-}]$ ligand.

As the experiments with [Bmim$^+$Cl$^-$] as the leaching solution resulted in low extraction of In and Ga compared to [Bmim$^+$H$_2$SO$_4$$^-$], which was consistent with theoretical evaluation and indicates that practical experimental conditions also play a part in the extraction efficiency.

Table 3: The In complex shape, charge, Gibbs free energy of the formation reaction (ΔG), and HOMO-LUMO gap

Complex	Complex shape	Complex charge	ΔG (eV)	HOMO-LUMO gap (eV)
[In$_2$(SO$_4$)$_3$]	Dimer	0	7.47	4.14
[In(SO$_4$)$_2$$^-$]	Tetrahedral	−1	33.74	3.05
[In(SO$_4$)$_3$$^{3-}$]	Octahedral	−3	109.24	3.81
[In(NO$_3$)$_2$$^+$]	Tetrahedral	+1	28.30	3.47
[In(NO$_3$)$_3$]	Octahedral	0	13.45	3.89
[In$_2$Cl$_6$]	Dimer	0	10.73	4.06
[InCl$_3$]	Trigonal	0	11.23	3.99
[InCl$_4$$^-$]	Square	−1	43.09	3.14
[InCl$_6$$^{3-}$]	Octahedral	−3	127.44	3.42

Table 4: The Ga complex shape, charge, Gibbs free energy of the formation reaction (ΔG), and HOMO-LUMO gap

Complex	Complex shape	Complex charge	ΔG (eV)	HOMO-LUMO gap (eV)
[Ga$_2$(SO$_4$)$_3$]	Dimer	0	7.79	5.07
[Ga(SO$_4$)$_2$$^-$]	Tetrahedral	−1	33.52	4.59
[Ga(SO$_4$)$_3$$^{3-}$]	Octahedral	−3	110.04	2.95
[Ga(NO$_3$)$_2$$^+$]	Tetrahedral	+1	28.60	4.49
[Ga(NO$_3$)$_3$]	Octahedral	0	13.38	4.04
[Ga$_2$Cl$_6$]	Dimer	0	11.33	4.95
[GaCl$_3$]	Trigonal	0	11.64	4.93
[GaCl$_4$$^-$]	Square	−1	44.57	3.38
[GaCl$_6$$^{3-}$]	Octahedral	−3	130.73	3.50

However, it should be considered that the DFT calculation for ΔG was conducted in a gas phase hence the ΔG values for even the most possible complex i.e. [In$_2$(SO$_4$)$_3$] was a small positive number (7.47 eV), not a negative value which indicating a reaction occurs spontaneously. The calculations presented here are to get an idea of the relative possibility of a reaction to occur. The experiments were conducted in a liquid phase (the ionic liquid/water media with other ions/molecules from the EAF dust also present), at which the solvent etc. have a driving force to assist the reaction to happen. For example, when calculating reaction 5 and 10 (producing the dimer complex of [In$_2$(SO$_4$)$_3$] and [In$_2$Cl$_6$] individually) in water as implicit solvent, the free energies reduced to 4.67 and 6.78 eV respectively. However, in water as implicit solvent, a lower energy product for [Bmim$^+$OH$^-$], where a H was transferred to the OH$^-$ ion was identified, lowering the calculated ΔG further to 1.53 and 0.50

eV, respectively. Further calculations taking the real solvent environment into account, that is outside the scope of the present work, should lead to spontaneous (negative) reaction energies.

It was also interesting to observe that the more the charge was for a particular complex, the less chance existed for it to form. For instance, the octahedral complexes of $[In(SO_4)_3{}^{3-}]$ and $[Ga(SO_4)_3{}^{3-}]$ with the -3 charge which formed with the same $[SO_4{}^{2-}]$ ligand, have large ΔG values of 109.24 and 110.04, respectively, indicating a low probability to form. The dimer complex of sulfate ligand leading to $[In_2(SO_4)_3]$ with no charge was the most stable.

Figure 6, illustrates the dimer complex of $[In_2(SO_4)_3]$ and $[Ga_2(SO_4)_3]$ in the geometry-optimised form, with labelled angles, the length of each bond, and the Van-Der-Waal sphere interactions around.
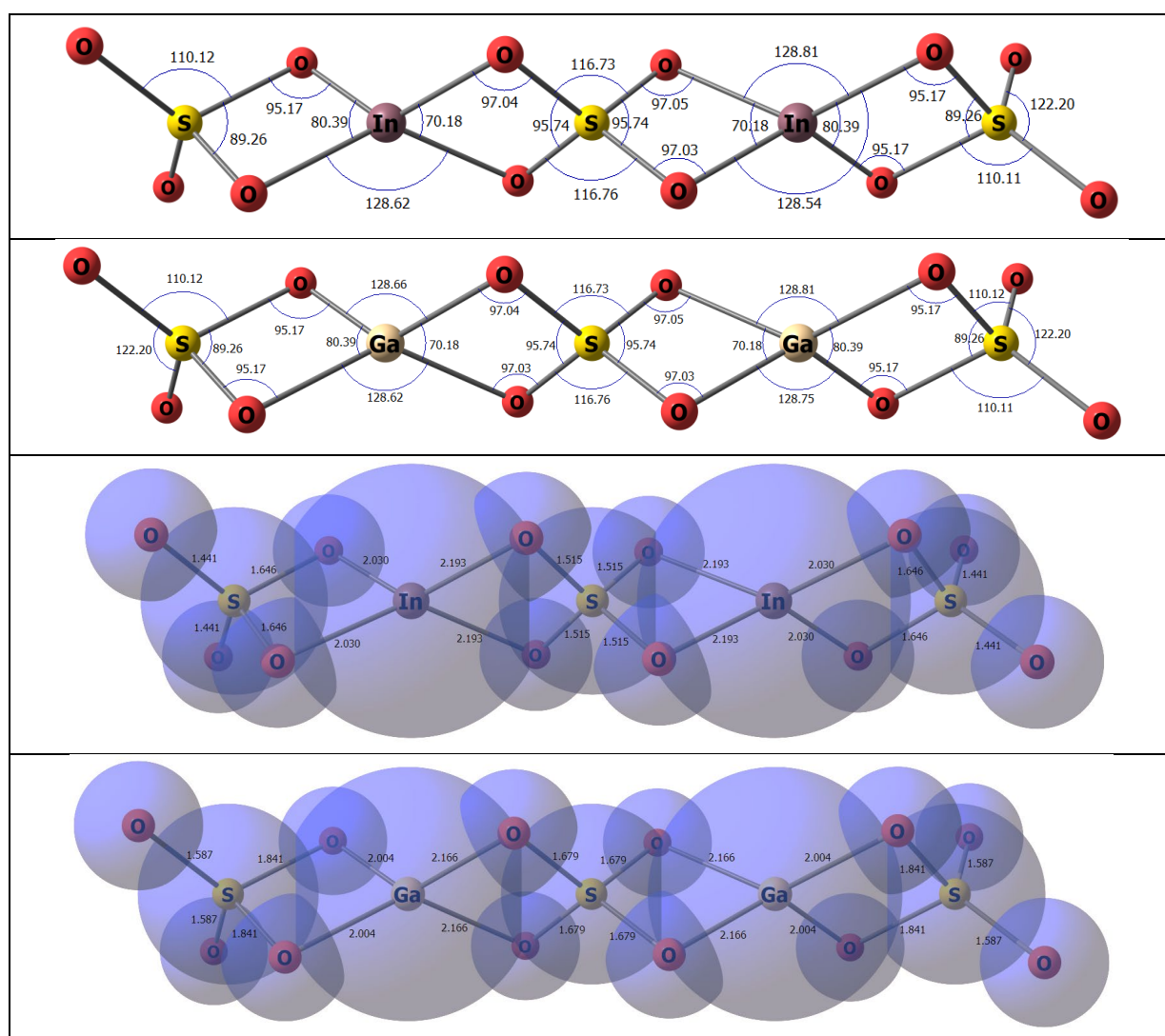

Figure 6: The most stable dimer complex of $[In_2(SO_4)_3]$ and $[Ga_2(SO_4)_3]$ in geometry-optimised form, with labelled angles, the length of each bond, and the Van-Der-Waal sphere.

Ultimately, the HPC-calculated DFT values were compared with the experimental results on extracting In and Ga using the studied ionic liquids. In the experimental part two ionic liquids [Bmim$^+$HSO$_4{}^-$

], and [Bmim⁺Cl⁻] were tested to extract In and Ga. The experimental results indicate that [Bmim⁺HSO₄⁻] leads to higher extraction of the desired metals. According to the DFT calculations, the dimer complex of [In₂(SO₄)₃] and [Ga₂(SO₄)₃] was the most probable and stable complex which could be formed by sulfate [SO₄²⁻] ligand. Therefore, the ionic liquid [Bmim⁺HSO₄⁻] not only was experimentally the most effective ionic liquid for metal extraction, but also theoretically confirmed as the best for forming the most possible and stable complexes with In and Ga. Hence, the experimental work and the theoretical calculation with DFT correlate to confirm that the [Bmim⁺HSO₄⁻] is the most effective ionic liquid.

4 Conclusion

The feasibility of a new hydrometallurgical approach using imidazolium-based ionic liquids for In and Ga extraction was examined experimentally and theoretically with DFT calculations. In this case, two ionic liquids [Bmim⁺HSO₄⁻], and [Bmim⁺Cl⁻] were mixed with three oxidants to find the best combination for In and Ga extraction. The experimental results indicate the mixture of [Bmim⁺HSO₄⁻] and Fe₂(SO₄)₃ oxidant was the optimum combination. Then the influential factors were examined to determine the optimum condition for the extraction of In and Ga.

The experimental achievements were as follows:

- The attained optimal conditions were as 30% v/v [Bmim⁺HSO₄⁻] mixed with 1 gr [Fe₂(SO₄)₃], S/L ratio of 1/20, and 240 min extraction time at 85 °C.

- The extraction efficiency for In, Ga, and Zn under the optimal conditions was 97.4% and 17.03%, 92.7%, respectively.

- The dissolution kinetics of the target metals in 30% v/v [Bmim⁺HSO₄⁻] solution from EAF dust evaluated at temperature 55-85 °C was administrated by the diffusion model, and it was faster in the first hour of leaching before becoming moderate.

- The obtained activation energy for In, Ga, and Zn was 33.6, 30.3, and 8.2 kJ/mol respectively, which all were in the range of the diffusion-controlled model.

The theoretical study by applying DFT calculations on the possible complexes of In and Ga with three studied ionic liquids ([Bmim⁺HSO₄⁻], [Bmim⁺NO₃⁻], and [Bmim⁺Cl⁻]) also confirms that the ionic liquid [Bmim⁺HSO₄⁻] owing [SO₄²⁻] O- donor ligand resulted in the lowest Δ*G,* and the largest HOMO-LUMO gap indicating the most possible and stable complex. Thus, the dimer complex of [In₂(SO₄)₃] and [Ga₂(SO₄)₃] with the lowest Δ*G* of the formation reaction calculated in the gas phase*,* and the largest HOMO-LUMO gap were the most possible and stable complex to form among other possible complexes. Although, the values for Δ*G* for the dimer complex of In and Ga were small and close together representing the high possibility of their formation theoretically, the experiment results for Ga extraction were low.

Therefore, the ionic liquid [Bmim$^+$HSO$_4^-$] not only was approved experimentally as the best ionic liquid for In and Ga extraction but also theoretically confirmed as the best ligand to form the most possible and stable complex. The benefits of using the ionic liquid, like [Bmim$^+$HSO$_4^-$] for metal extraction instead of the common mineral acids could be, that the ionic liquid is recyclable and can be reused in the extraction process which justifies the higher operating cost in the long term. Besides being biodegradable and more environmentally friendly.

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