Research Article

Optimization of Indium Recovery and Separation from LCD Waste by Solvent Extraction with Bis(2-ethylhexyl) Phosphate (D2EHPA)

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Indium tin oxide (ITO) is currently the choice of electrode material in liquid crystal displays (LCDs). D2EHPA is known to be an extractant that can be used to selectively recover indium from 1 M sulfuric acid. In order to optimize the extraction and separation of indium from LCD waste, the effects of pH, temperature, time, and extractant concentration on the distribution ratios of In(III) and the major impurities such as Al(III), Cu(II), Fe(III), and Zn(II) were investigated. Metal concentrations in the aqueous feed were based on the concentrations found in the leach liquor of LCD panel glass at 0.1 g/mL S/L ratio. This study showed that extraction of indium could be increased at <293 K and stripping of indium could be increased at >293 K. Furthermore, by increasing D2EHPA concentration from 0.1 M to 0.25 M, extraction of indium could be increased from 70% to >95%.

1. Introduction

Indium is a rare metal with an average concentration of 0.05 ppm in the Earth's crust [1]. At present, the production of indium tin oxide (ITO) accounts for approximately 70% of global indium consumption [2]. Due to sales of LCDs increasing rapidly over the past decade, an increase in the demand of indium, as well as the amount of LCD waste, is expected in the future. As a result, there has also been a greater interest in the recovery of indium from various secondary sources, such as production waste from ITO etching processes and from discarded LCDs. A previous literature study [3] reviewed many organic molecules and showed that both solvating and acidic organophosphate extractants can separate indium from other metal ions dissolved in various acidic aqueous media. Examples of this type of extractants are bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [4], bis-2,2-ethylhexyl phosphoric acid (D2EHPA) [5], and Cyanex 923 [6]. In more recent studies, Kang et al. [7] investigated the recovery of indium from etching waste by

leaching with NaOH and HCl, followed by solvent extraction with 2-ethylhexyl phosphonic acid mono(2-ethylhexyl) ether (PC88A). Other work [8, 9] studied the recovery of indium from waste ITO by leaching in sulfuric acid, followed by solvent extraction using D2EHPA diluted in kerosene as the organic phase. A follow-up study was also done using LCD waste as the starting material instead of ITO [8, 9]. Solvent extraction equilibriums of metals found in zinc refinery residues (In^{3+}, Ga^{3+}) with D2EHPA and two similar extractants have also been investigated by Nakamura et al. [10].

Experiments performed in the present study were based on an earlier feasibility study [11], where it was shown that extraction from acidic sulfate media with D2EHPA diluted in kerosene, followed by stripping into HCl, was the best alternative with respect to indium recovery and separation. The present work builds on this method by investigating the dependency of metal distribution ratios on factors such as pH, temperature, contact time, and extractant concentration. From experimental results, optimal values of these

TABLE 1: Stability constants of Fe(III) and In(III) in sulfate and chloride media [24].

Sulfate complex	$\log(k_1)$	$\log(k_2)$	Chloride complex	$\log(k_1)$	$\log(k_2)$	$\log(k_3)$
In(III)	1.78	0.75	In(III)	2.36	1.27	0.32
Fe(III)	1.88	0.97	Fe(III)	1.48	0.65	−1.1

TABLE 2: Calculated molar fractions of sulfate and chloride species.

$[SO_4^{2-}]_{tot} = 1\,M$				$[Cl^-]_{tot} = 0.1\,M$			
In^{3+}	0.611	Fe^{3+}	0.547	In^{3+}	0.013	Fe^{3+}	0.186
$InSO_4^+$	0.368	$FeSO_4^+$	0.415	$InCl^{2+}$	0.304	$FeCl^{2+}$	0.561
$In(SO_4)_2^-$	0.021	$Fe(SO_4)_2^-$	0.039	$InCl_2^+$	0.565	$FeCl_2^+$	0.251
				$InCl_3$	0.118	$FeCl_3$	0.002

parameters were chosen for the purpose of indium recovery from LCD waste glass. In addition, a recycling process which recovers indium from waste LCD glass was proposed.

2. Theory

Abbreviations used throughout this paper are shown in Abbreviation section.

Equation (1) is the linear form of Van't Hoff's equation. This equation was used to estimate the ΔH and ΔS of metal extraction as a function of $1/T$:

$$\ln K_{ex} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}. \tag{1}$$

For acidic extractants, the relation between D and K_{ex} can be derived according to

$$\left(ML_a\right)^{\nu+} + \nu\overline{(HA)_2} \longleftrightarrow \overline{(MA_\nu(HA)_\nu)} + \nu H^+ \tag{2}$$
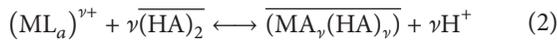
$$D_M = \frac{\overline{[(MA_\nu(HA)_\nu)]}}{[M]_{tot}} \approx m_{ML_a} \cdot \frac{\overline{[(MA_\nu(HA)_\nu)]}}{\left[(ML_a)^{\nu+}\right]} \tag{3}$$

$$K_{ex} = \frac{\overline{[(MA_\nu(HA)_\nu)]}[H^+]^\nu}{\left[(ML_a)^{\nu+}\right]\overline{[(HA)_2]}^\nu} \approx \frac{D_M}{m_{ML_a}} \cdot \frac{[H^+]^\nu}{\overline{[(HA)_2]}^\nu}. \tag{4}$$

Molar fractions of metal complexes were calculated from stability constants given in Table 1, and the results are shown in Table 2. Sulfate and chloride concentrations were assumed to be constant, since these were much greater than the concentrations of the metal ions. Soluble tin complexes in sulfate and chloride media were assumed to be $Sn(SO_4)_2$ and $SnCl_6^{2-}$, respectively [12].

3. Experiments

The aqueous phase was prepared by dissolving chloride or sulfate salts of In(III), Sn(IV), Al(III), Cu(II), Fe(III), and Zn(II) in HCl or H_2SO_4 of different concentrations. Unless otherwise stated, Table 3 lists the metal concentrations in the aqueous phase before extraction. The composition of metal ions was based on the results from previous acid leaching experiments on LCD glass at 0.1 g/mL solid-to-liquid ratio [11].

TABLE 3: Metal composition of the aqueous phase before extraction.

Metal	Concentration/mM
Al	6
Cu	2.5
Fe	3
In	2
Sn	0.2
Zn	2.5

The organic phase was prepared by diluting D2EHPA (97%, Sigma Aldrich) in kerosene (Solvent 70, Statoil). Equal volumes (1.5 mL) of the organic and aqueous phase were mixed mechanically at a rate of 1500 rpm (IKA VIBRAX VXR basic). During the investigation of extraction kinetics the mixing time varied from 5 minutes to 150 minutes. The effects of initial D2EHPA concentrations on metal distribution were studied in the range of 0.001 M to 1 M. Metal concentrations in aqueous phase before and after extraction were sampled and analyzed using inductively coupled plasma with optical emission spectrometer (ICP-OES, Thermo iCAP-6000). External calibration curves made by dilution of 1 mg/mL standard solutions were used to quantify metal contents. The distribution ratios and separation factors were calculated from the mass balance in aqueous phase before and after extraction.

Studies on the effects of pH and temperature on metal extraction were performed using AKUFVE (apparatus for continuous measurement of partition factor in solvent extraction) [13], which was later modified by the addition of pumps [14] and redox control [15]. Distribution ratios of indium and other metals between 1 M (Na, H, and SO_4)-0.1 M D2EHPA/kerosene and 1 M (Na, H, and Cl)-0.1 M D2EHPA/kerosene were investigated. Initially 100 mL of aqueous and organic phase was added to the mixing chamber of AKUFVE. The pH of the aqueous phase was adjusted by addition of small volumes of 3 M or 0.1 M NaOH solutions. An amount of organic phase equal to the volume of added NaOH was added to ensure the same phase ratio. After each addition of NaOH the AKUFVE system was left running for 30 minutes to reequilibrate before sampling. In the temperature dependency study, the temperature of the system

was adjusted by a circulating water bath. The pH of the aqueous phase was measured with a calibrated pH electrode at each data point. Concentration of H^+ in the aqueous phase was determined by calculations using the activity coefficients of $1\,M\ H_2SO_4$ (0.961) and $1\,M$ HCl (0.809) [16].

4. Results and Discussion

4.1. Metal Extraction and Stripping Kinetics. The effect of mixing time was investigated for the extraction of metals from $0.1\,M\ H_2SO_4$ or $1\,M\ H_2SO_4$ as well as the kinetics of metal stripping from loaded organic phase to $1\,M$ HCl. The organic phase was $0.1\,M$ D2EHPA in kerosene. Results are shown in Figures 1, 2, and 3. Data for Al, Cu, and Zn were omitted due to their distribution ratios being lower than 0.1 and stayed relatively constant during experiments.

From Figures 1–3 it could be seen that time required for distribution ratio of indium to reach equilibrium was less than 5 minutes in the $0.1\,M\ H_2SO_4$ system, while for $1\,M$ H_2SO_4 and $1\,M$ HCl 20 minutes was needed. It could also be seen that time required for Fe and Sn extraction to reach equilibrium was slightly longer than for indium in all three cases. Therefore, shorter mixing time has the advantage of improving separation between indium and the coextracted metals (Fe and Sn). This is especially true for the $0.1\,M$ H_2SO_4 system shown in Figure 2, where the separation factor between In and Fe was greater than 100 when mixing time was less than 5 minutes. For stripping, Figure 3 indicates that a mixing time of 20 minutes or longer was preferred. Due to the amount of time required for extraction and stripping to reach equilibrium, if mixer-settlers are to be used as solvent extraction equipment, it will likely require multiple stages or low flow rate in order to quantitatively extract indium.

4.2. Effect of $[H^+]$ on Extraction Equilibrium. Among earlier studies on the extraction equilibrium of D2EHPA, there have been large variations in reported values of both pKa and distribution constant (k_d) of D2EHPA. pKa values between 1.3 [17] and 3 [18] and k_d values between 3.5 [17] and 7.5 [18] were found in the literature. Due to this reason, it was necessary to experimentally determine the effect of $[H^+]$ on metal extraction using D2EHPA as the extractant. Distribution ratios at different equilibrium hydrogen ion concentrations are presented in Figures 4 and 5 for both $1\,M$ sulfate and chloride media, respectively.

It was observed that the order in which metals were quantitatively extracted with decreasing hydrogen ion concentration was the same for both aqueous phases. Tin and iron were extracted first, followed by indium, aluminum, zinc, and copper. Meaning regardless of which of the two acids is used as the aqueous phase, iron and tin will always be coextracted with indium in the first extraction step. As the results in Figure 5 indicate, at HCl concentration of $1\,M$ or more, it is possible to selectively back-extract or strip indium into the aqueous phase. At higher HCl concentrations it could also be possible to strip Fe as well. Since D2EHPA is an acidic extractant, $[H^+]$ has a direct effect on the aqueous concentration of dissociated extractant, thus the concentration
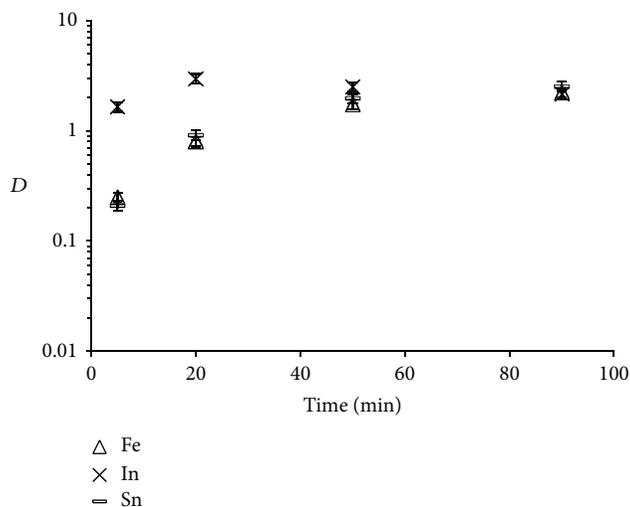
FIGURE 1: Kinetics of metal extraction using $1\,M\ H_2SO_4$ and $0.1\,M$ D2EHPA in kerosene, $\theta = 1$. Mixing time of the mixtures was between 5 minutes and 2.5 hours under mechanical shaking at 1500 rpm and $293 \pm 1\,K$.
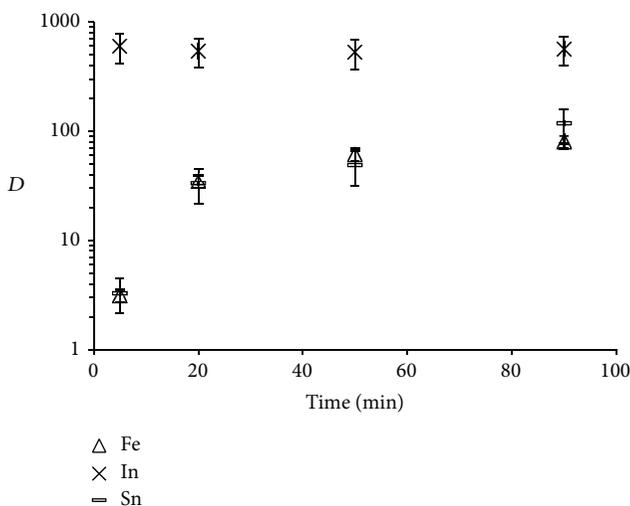
FIGURE 2: Kinetics of metal extraction using $0.1\,M\ H_2SO_4$ and $0.1\,M$ D2EHPA in kerosene, $\theta = 1$. Mixing time of the mixtures was between 5 minutes and 2.5 hours under mechanical shaking at 1500 rpm and $293 \pm 1\,K$.

of metal-extractant complex. As shown in (2), increase in $[H^+]$ shifts the reaction equilibrium towards left-hand side of the reaction, resulting in increased metal concentration in the aqueous phase. Moreover, formation of metal chloride complexes at higher total chloride concentrations can also contribute to decreased metal extraction. Figure 5 also showed that 0.25–$0.3\,M$ HCl or H_2SO_4 could be used as alternatives to $1\,M\ H_2SO_4$ as the first step in the separation of indium from other metals. However, the disadvantage in this case is increased coextraction of aluminum, which could result in an increased number of, for example, mixer-settler stages. Another drawback when using lower acid
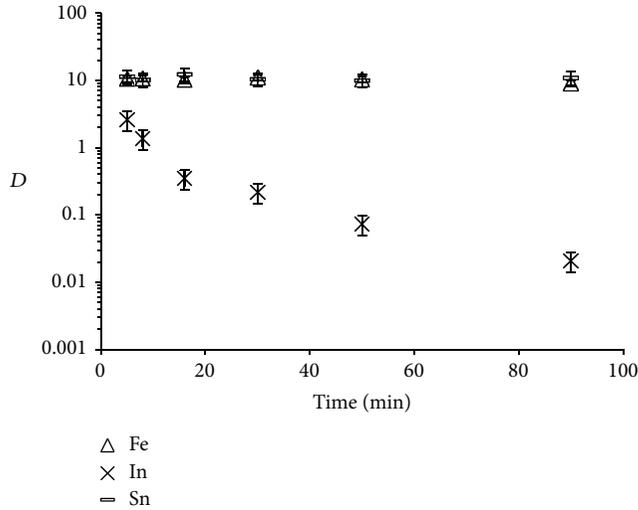
FIGURE 3: Kinetics of metal back-extraction from loaded 0.1 M D2EHPA in kerosene into 1 M HCl at $\theta = 1$. Mixing time of the mixtures was between 5 minutes and 2.5 hours at 1500 rpm and 293 ± 2 K.
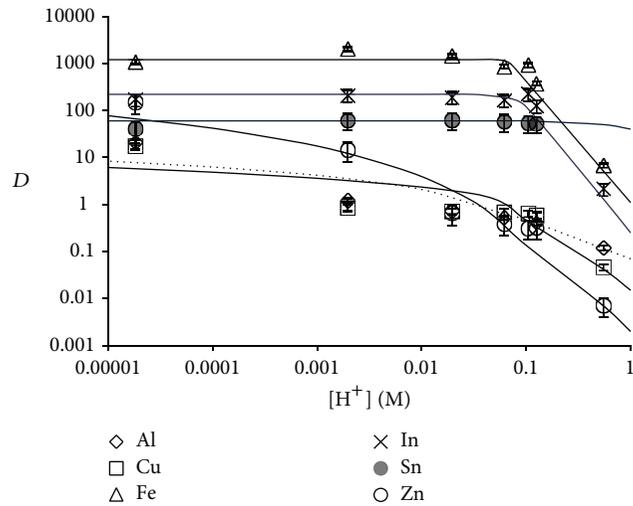
FIGURE 4: Distribution ratios of Al(III), Cu(II), Fe(III), In(III), Sn(IV), and Zn(II) in 1 M sulfate media at 293 K and $\theta = 1$ plotted as a function of the hydrogen ion concentration. The organic phase was 0.1 M D2EHPA diluted in kerosene.

concentration is the decreased leaching kinetics. For example, when HCl concentration was decreased from 1 M to 0.1 M, the time needed to reach equilibrium increased from less than 1 day to 4 days [11].

4.3. Extraction Stoichiometry. Metal distribution ratios at different extractant concentrations are shown in Figures 6 and 7. Linear regression analysis was performed for indium extraction with results shown in Figure 6 for 1 M H$_2$SO$_4$ and 7 for 1 M HCl.

The stoichiometric ratio between indium and the extractant in 1 M H$_2$SO$_4$ was calculated to be close to 3, while for
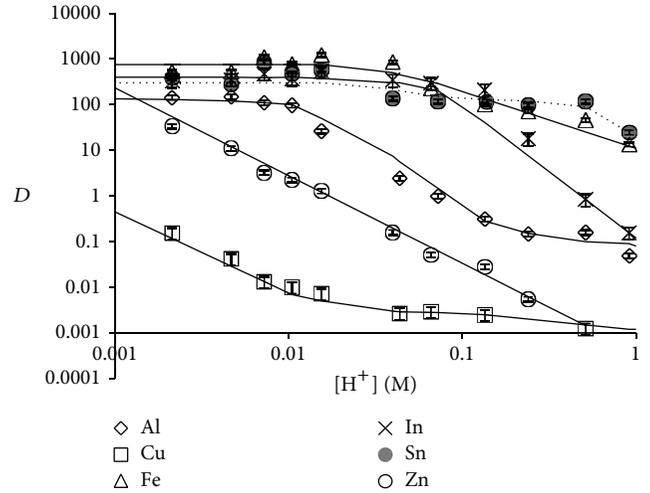
FIGURE 5: Distribution ratios of Al(III), Cu(II), Fe(III), In(III), Sn(IV), and Zn(II) in 1 M chloride media at 293 K and $\theta = 1$ plotted as a function of the hydrogen ion concentration. The organic phase was 0.1 M D2EHPA diluted in kerosene.

indium extraction in 1 M HCl it was close to 1.5. Distribution ratios of Al, Cu, and Zn were not included due to small changes in D. In an earlier work [19], extraction mechanisms for indium extraction from sulfate and chloride media were proposed, according to (5) and (6). The results obtained in this work agree well with the proposed reactions, with $m = 1$ for both HCl and H$_2$SO$_4$:

$$\text{HCl}: m\,\text{In}\,\text{Cl}^{2+} + \overline{(m+1)(\text{HA})_2}$$
$$\longleftrightarrow \overline{\text{In}_m\text{Cl}_m\text{A}_{2(m+1)}} + 2m\text{H}^+ \quad (5)$$

$$\text{H}_2\text{SO}_4: m\,\text{In}^{3+} + \overline{(2m+1)(\text{HA})_2}$$
$$\longleftrightarrow \overline{\text{In}_m\text{A}_{2(2m+1)}\text{H}_{m+2}} + 3m\text{H}^+ \quad (6)$$
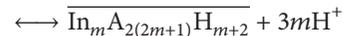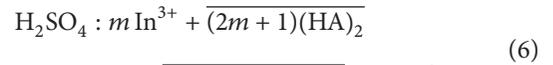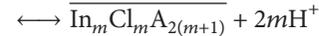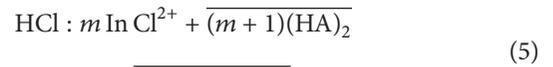
The effect of anionic ligand on indium extraction is shown in Figure 8. An increase in total chloride concentration at 1 M or above led to a decrease in distribution ratio. This was due to the complex formation constants K_1 and K_2 for indium chloride being much greater than 1. Molar fraction of the extractable indium chloride species (InCl^{2-}) in aqueous phase will decrease from 30% to <2% when [Cl$^-$]$_{tot}$ increases from 0.1 M to 1 M. A reversed trend was observed for H$_2$SO$_4$, where distribution ratio of indium increased with total sulfate concentration in the aqueous phase. This indicates the extraction of an indium sulfate complex into the organic phase. However, the increase diminishes when sulfate concentration became higher than 1.5 M. Therefore the effect of total sulfate concentration on indium extraction was not as significant as extractant concentration.

With respect to indium recovery, increasing D2EHPA concentration can result in higher D-values for indium without significantly affecting the separation of indium from Fe and Sn during stripping. 1 M H$_2$SO$_4$ could be a better choice of aqueous phase than 0.1 M H$_2$SO$_4$, since the latter will coextract Zn and Al at higher extractant concentrations.
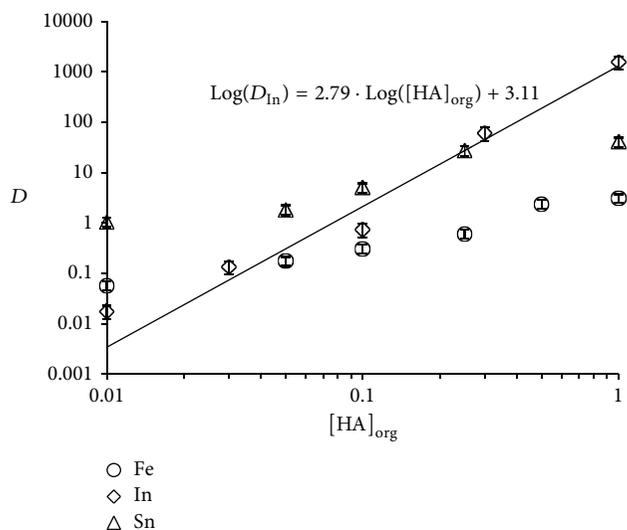
FIGURE 6: Effect of free D2EHPA concentration on the extraction of metals from $1\,M\,H_2SO_4$ at $293 \pm 2\,K$ and $\theta = 1$.
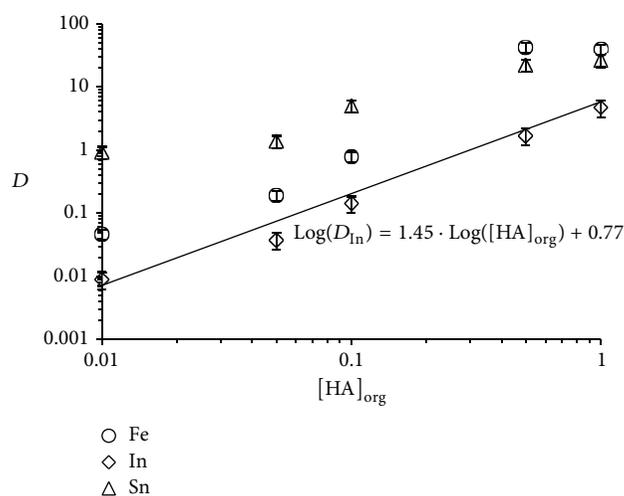
FIGURE 7: Effect of free D2EHPA concentration on the extraction of metals from $1\,M\,HCl$ at $293 \pm 2\,K$ and $\theta = 1$.
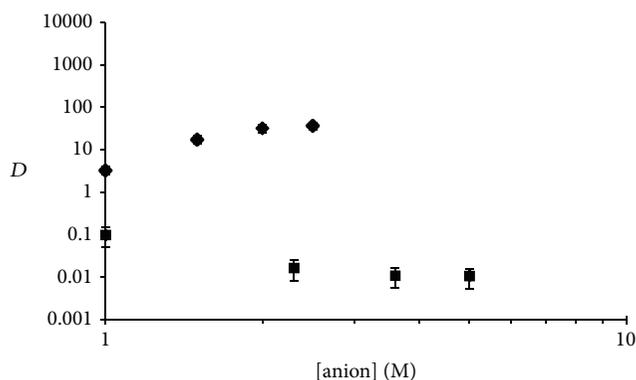
FIGURE 8: Effect of inorganic anion concentration on the distribution ratio of indium, (◆) $[SO_4^{2-}]_{tot}$, (■) $[Cl^-]_{tot}$. Organic phase was $0.1\,M$ D2EHPA/kerosene, $[H^+] = 1\,M$.

However, higher extractant concentrations will also hinder stripping with $1\,M\,HCl$. Therefore, for the extraction of indium from $1\,M\,H_2SO_4$ and stripping using $1\,M\,HCl$, the recommended D2EHPA concentration is $0.25\,M$.

4.4. Temperature Effect on Extraction Equilibrium. In Figures 9 and 10, the effect of temperature on extraction constant, K_{ex}, was calculated for In, Fe, and Sn according to (4). K_{ex} for indium was calculated from the extraction reaction proposed in (5) and (6). Based on results shown in Figures 6 and 7, (7) to (10) were proposed for the extraction reactions for iron and tin, and these equations were used to calculate K_{ex} values for these two metals:

$$FeCl^{2+} + \overline{2(HA)_2} \longleftrightarrow \overline{FeClH_2A_4} + 2H^+ \qquad (7)$$

$$SnCl_6{}^{2-} + \overline{(HA)_2} \longleftrightarrow \overline{SnCl_4H_2A_2} + 2Cl^- \qquad (8)$$

$$Fe(SO_4)^+ + \overline{(HA)_2} \longleftrightarrow \overline{Fe(SO_4)HA_2} + H^+ \qquad (9)$$

$$Sn(SO_4)_2 + \overline{(HA)_2} \longleftrightarrow \overline{Sn(SO_4)_2H_2A_2} \qquad (10)$$
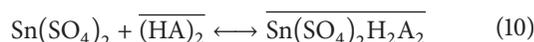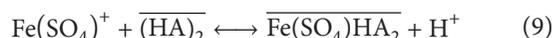
Acid concentrations of the aqueous phases were chosen where the D-values of indium were greater than 1 at 293 K. Since K_{ex} of indium is inversely proportional to temperature and distribution ratio is proportional to K_{ex} according to (3), extraction of indium decreases with increasing temperature in the temperature range studied. This agreed well with the results from T. Sato and K. Sato [19], where an inverse proportionality between D-value of indium and temperature was also observed.

Unlike indium, extraction of tin was an endothermic process. Extraction of Fe from sulfate media was exothermic; however in chloride media it was shown to be endothermic. In previous work, a similar change in the extraction enthalpy of Bi extraction from $HClO_4$ was observed [20]. When dinonyl naphthalene sulfonic acid (HDNNS) was used as the extractant, the extraction process was slightly endothermic, but when 2-ethylhexyl phenylphosphonic acid (HEHΦP) was used, extraction of Bi was exothermic. It could be concluded that due to different metal complex being formed and broken, the enthalpy change of an extraction process was affected by factors such as the choice of aqueous media and organic extractant. Changes in enthalpy and entropy during the extraction of In, Fe, and Sn were obtained by linear regression and listed in Table 4 for $1\,M\,H_2SO_4$ and Table 5 for $1\,M\,HCl$. Values for Al, Zn, and Cu were not calculated due to low D-values. Between 293 K and 333 K, extraction of iron and extraction of indium in the sulfate system were driven by changes in enthalpy, since both $\Delta^\circ H$ and $\Delta^\circ S$ are negative, and $\Delta H > T\Delta S$ in the temperature interval studied. On the other hand, extraction of iron and extraction of tin in the chloride system were driven by changes in entropy, due to both $\Delta^\circ H$ and $\Delta^\circ S$ being positive in these cases and $\Delta H < T\Delta S$.

By comparing the two systems, it can be seen that both $\Delta^\circ H$ and $\Delta^\circ S$ are lower in the chloride system compared to the sulfate system. The difference can be explained by (5) and (6). In sulfate media, for each extracted In^{3+} ion, three H^+ ions were released to the aqueous phase, while for chloride
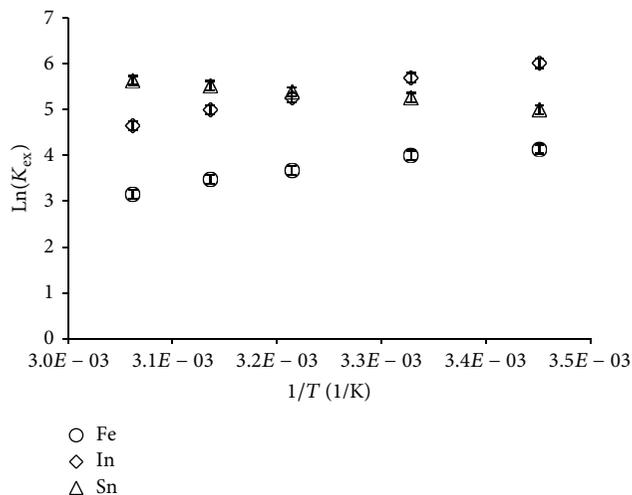
FIGURE 9: The effect of temperature on the extraction equilibrium of Fe(III), In(III), and Sn(IV). The aqueous phase was $1\,M\,H_2SO_4$ and the organic phase was $0.1\,M\,D2EHPA/kerosene$, $\theta = 1$.
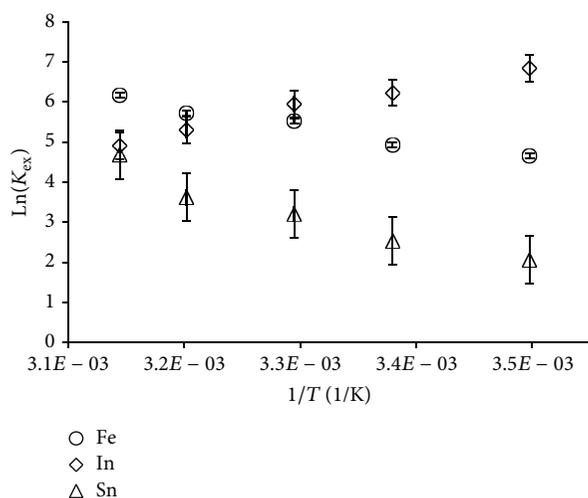
FIGURE 10: The effect of temperature on the extraction equilibrium of Fe(III), In(III), and Sn(IV). The aqueous phase was $0.1\,M\,HCl$ and the organic phase was $0.1\,M\,D2EHPA/kerosene$, $\theta = 1$.

TABLE 4: $\Delta°H$ and $\Delta°S$ for extraction from $1\,M\,H_2SO_4$. Values are obtained by linear fitting of (1).

Metal	Fe	In	Sn
$\Delta°H/\text{kJ/mol}$	-20.9 ± 1.2	-29.1 ± 3.8	13.3 ± 0.6
$\Delta°S/\text{J/mol/K}$	-36.1 ± 1.0	-48.6 ± 6.6	123 ± 5.4

media the ratio was $1:2$. Therefore there was a greater increase in configurational entropy when indium was extracted from H_2SO_4. The differences for Fe and Sn could be attributed to the difference in extraction stoichiometry. Figures 7 and 8 showed the ratio between D_{Fe} and extractant concentration was $1:1$ in $1\,M\,H_2SO_4$, but in chloride systems it was $1:2$. This trend is the same for Sn. Thus compared to sulphate media, in

TABLE 5: $\Delta°H$ and $\Delta°S$ for extraction from $0.1\,M\,HCl$. Values are obtained by linear fitting of (1).

Metal	Fe	In	Sn
$\Delta°H/\text{kJ/mol}$	35.3 ± 11	-44.9 ± 1.3	57.9 ± 6.1
$\Delta°S/\text{J/mol/K}$	161 ± 45	-99.7 ± 3.1	218 ± 25

chloride media a greater number of hydrated water molecules were replaced by extractant molecules for each extracted metal ion. The dehydration process often causes both an increase in the randomness of the system and an increase in enthalpy, due to the disruption of bonds in hydrated species [21]. Moreover, since the aqueous phase is acidic and $[Cl^-]$ is much higher than $[Fe^{3+}]$, different Fe(III) chloride complexes exist in the aqueous phase [22]. Therefore Fe(III) could be partially extracted through a mechanism similar to (11) which in turn contribute to the much higher $\Delta°H$ and $\Delta°S$ values observed for Fe(III) extraction in chloride media compared to sulfate media:

$$\overline{FeCl_2^+ + \overline{2(HA)_2}} \longleftrightarrow \overline{FeClH_2A_4} + Cl^- + 2H^+ \qquad (11)$$

Experimental results showed that low temperatures favor the extraction of indium from sulfate media and that stripping with HCl at greater than 293 K will increase both the amount of indium recovered and its separation from Fe and Sn. However, considering other factors, such as the need to install cooling and heating systems, 293 K to 298 K is still likely to be the optimal extraction temperature.

4.5. Recovery Process. Based on the results obtained in this work, a possible process for the recovery of indium from waste LCD glass was outlined, as seen in Figure 11. The acidic leachate containing In, Sn, and other metal impurities was extracted by $0.25\,M\,D2EHPA$ in kerosene to separate In from Cu, Al, and Zn. An optional scrub step following the extraction can remove most of the remaining Cu, Al, and Zn, as well as a portion of the Fe and Sn from the organic extract. $1\,M\,HCl$ could be used to selectively strip indium from the organic phase. Aqueous raffinate from the scrub step can be fed back to the acid leaching step, since metal concentrations in the solution were less than 10% of metal concentrations in the leachate.

Batch experiments using an extraction system consisting of single extraction, scrub, and strip stage were performed. Metal concentrations in the initial feed were as shown in Table 3. The results obtained after batch experiments are presented in Tables 6 and 7.

The extraction of indium was quantitative using $0.25\,M\,D2EHPA$ diluted in kerosene. Stripping by $1\,M\,HCl$ could selectively recover indium into the aqueous phase. In Table 7, it could be seen that the inclusion of a scrubbing stage removed most of the coextracted Zn from the organic phase. However, most of the extracted Al was not removed in the scrubbing stage and was thus stripped together with indium into $1\,M\,HCl$. In the extraction systems studied, Fe and Sn would accumulate in the organic phase. By using a higher concentration of HCl ($>3\,M$) in the stripping stage, Fe can

TABLE 6: Single stage batch test of extraction, washing, and stripping. Aqueous phases were 1 M H_2SO_4 (extraction and scrubbing) and 1 M HCl (stripping). The organic phase was 0.25 M D2EHPA diluted in kerosene with 2% 1-decanol.

Metal ion	Wt % in aq. phase after extraction (1 M H_2SO_4)	Wt % in aq. phase after scrubbing (1 M H_2SO_4)	Wt % stripped into aq. phase (1 M HCl)	Wt % remains in the organic phase
Al(III)	98.4 ± 1.0%	1.0 ± 0.4%	0.4 ± 0.1%	<1.7%
Cu(II)	98.8 ± 0.8%	0.2 ± 0.1%	0.1 ± 0.1%	<1.8%
Fe(III)	19.8 ± 2.5%	1.9 ± 0.1%	1.0 ± 0.1%	73.3 ± 2.7%
In(III)	0.8 ± 0.2%	0.7 ± 0.1%	95.7 ± 0.2%	2.8 ± 0.5%
Sn(IV)	2.9 ± 1.3%	0.3 ± 0.2%	0.1 ± 0.1%	96.7 ± 1.7%
Zn(II)	99.4 ± 0.1%	0.2 ± 0.1%	0.1 ± 0.1%	<0.6%

TABLE 7: Single stage batch test of extraction, washing, and stripping. Aqueous phases were 0.1 M H_2SO_4 (extraction and scrubbing) and 1 M HCl (stripping). The organic phase was 0.25 M D2EHPA diluted in kerosene with 2% 1-decanol.

Metal ion	Wt % in aq. phase after extraction (0.1 M H_2SO_4)	Wt % in aq. phase after scrubbing (0.1 M H_2SO_4)	Wt % stripped into aq. phase (1 M HCl)	Wt % remains in the organic phase
Al(III)	77.3 ± 1.1%	3.1 ± 0.1%	9.1 ± 2.1%	10.5 ± 3.3%
Cu(II)	97.9 ± 1.0%	0.3 ± 0.1%	0.1 ± 0.1%	1.7 ± 1.2%
Fe(III)	0.8 ± 0.1%	0.6 ± 0.1%	1.9 ± 0.6%	96.7 ± 0.8%
In(III)	0.2 ± 0.1%	0.2 ± 0.1%	91.9 ± 4.9%	7.7 ± 5.1%
Sn(IV)	0.6 ± 0.1%	0.2 ± 0.1%	0.3 ± 0.2%	98.9 ± 0.4%
Zn(II)	93.5 ± 1.9%	6.6 ± 0.1%	0.5 ± 0.1%	<1.6%
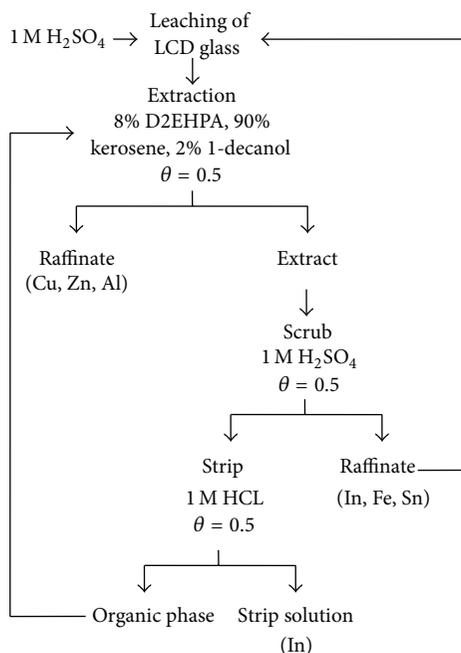
FIGURE 11: Schematic diagram of a potential process for the recycling of indium from LCD glass, showing an extraction, scrubbing, and stripping step. The aqueous phase was 1 M H_2SO_4 (extraction and scrubbing) and 1 M HCl (stripping); organic phase is 0.25 M D2EHPA diluted in kerosene with 2% 1-decanol.

be removed from the organic phase. With more concentrated HCl solutions (>8 M), Sn can be stripped from the organic phase but the stripping efficiency was only 25% in a single stage at 1 : 1 A/O ratio. In a recently published paper [23], it was observed that the stripping efficiency of In(III) was very low in 1 M HCl. Those results differed from results obtained in this work and another earlier paper [8, 9]. The difference in the stripping efficiency of indium could be caused by insufficient mixing time or low extractant concentration (0.1 M) relative to the concentrations of metal ions in the aqueous phase.

5. Conclusion

In the present work, metal extraction from sulfate and chloride media into an organic phase consisting of D2EHPA diluted in kerosene was studied under different conditions: mixing time, temperature, and extractant concentration. In the kinetics study, it was shown that indium extraction reached equilibrium after 5 minutes of mixing in H_2SO_4 media and coextraction of Fe and Sn could be minimized by keeping the mixing time between 5 and 10 minutes. For back-extraction of indium into 1 M HCl, 30 minutes of mixing was required for the quantitative recovery of indium.

Good separation between indium and metals such as Al, Cu, and Zn could be maintained at pH < 1. Quantitative stripping of indium was achieved in HCl at acid concentration of 1 M or higher. Increasing acidity will lead to increased levels of iron impurity in the strip solution.

The extraction stoichiometry of D2EHPA was also investigated by changing extractant concentration. From calculations based on empirical data, it was determined that the stoichiometric ratio between In^{3+} and D2EHPA is 1 : 2 and 1 : 3 in 1 M HCl and 1 M H_2SO_4, respectively. Additionally, it

was concluded that 0.25 M was the optimal extractant concentration, since this would result in quantitative extraction and stripping of indium, while keeping the concentrations of Sn, Fe, and Al in the strip raffinate relatively low.

Results of the temperature study showed the distribution ratio for indium was inversely proportional to temperature between 283 K and 333 K, in both HCl and H_2SO_4 media. This indicates that indium extraction is an exothermic process and should be performed at 293 K or below. Indium recovery could also be improved by performing the stripping process at higher temperatures. In addition, higher values of extraction enthalpy and entropy were observed for iron and tin in chloride media than in sulfate media. This was attributed to greater disturbance of hydrated water molecules and a higher increase in the randomness of the system when metal extraction took place in chloride media.

A batch test was performed, where the metal extraction from 1 M H_2SO_4 and 0.1 M H_2SO_4 was compared at a D2EHPA concentration of 0.25 M in kerosene. The amount of indium recovered after the stripping stage was similar but coextraction of the other metals in 1 M H_2SO_4 was less. It was seen that over 98% of the indium in the aqueous feed was recovered in the stripping raffinate in a single stage extraction, scrubbing, and stripping process while only up to 1% of the other metals were extracted from the feed and stripped into 1 M HCl. It can be concluded that at a D2EHPA concentration of 0.25 M and 1 M H_2SO_4 is more suitable than 0.1 M H_2SO_4 as the aqueous phase. Furthermore, due to the small amounts of metals removed, scrubbing stages can be omitted when 1 M H_2SO_4 is used as the aqueous phase. The experimental conditions used in this work can form a starting point for more detailed lab-scale mixer-settler studies.

Abbreviation

K_{ex}:   Extraction equilibrium constant
ΔH: Change in enthalpy
ΔS: Change in entropy
D: Distribution ratio
D_M: Distribution ratio of metal M
$[M]$:   Concentration in aqueous phase
$\overline{[M]}$:   Concentration in organic phase
$(ML_a)^{y+}$:   Complex between metal ion (M) and
              inorganic ligand (L)
m_{ML_a}:   Molar fraction of species $(ML_a)^{y+}$
HA: Undissociated acidic extractant
θ: Phase volume ratio (V_{org}/V_{aq}).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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