

INDIUM RECOVERY FROM SULFURIC SOLUTIONS: A COMPARATIVE STUDY INVOLVING ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

P. M. Rosário, P. J. Martins, A. P. Paiva¹

¹Faculdade de Ciências da Universidade de Lisboa, Departamento de Química e Bioquímica,
Rua Ernesto de Vasconcelos, Bloco C8, Campo Grande, 1749-016 Lisboa, Portugal

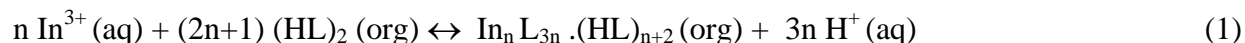
Abstract

The extraction performances exhibited by a phosphoric (D2EHPA), a phosphonic (Ionquest 801), a phosphinic (Cyanex 272) and a dithiophosphinic (Cyanex 301) acid derivative towards indium recovery from a diluted sulfuric solution are evaluated and compared. Equilibrium extraction isotherms were obtained. The chemical reactions involved and the approximate stoichiometry of the In(III) extracted species by the four ligands are presented and discussed. Stripping of In(III) from loaded D2EHPA and Ionquest 801 has been accomplished successfully, but has not been so effective from loaded Cyanex 301. Plots of %E vs. pH were established for D2EHPA, Ionquest 801 and Cyanex 301, denoting their behavior towards the extraction of similar mass concentrations of In(III), Fe(III), Fe(II) and Zn(II). Cyanex 301 is the least selective towards In(III), whereas D2EHPA and Ionquest 801, both for a pH = 0.5, do not extract Zn(II) at all.

Introduction

Indium is a rare metal with some strategic importance due to its actual and potential uses in electronic devices and alloys. It is usually recovered from residues associated with the production of base metal concentrates such as those of copper, lead and specially zinc. Nowadays, this metal is industrially produced using leaching, cementation and electro-refining technologies, and solvent extraction involving acidic organophosphorus compounds is often used to recover it from sulfuric acid leach liquors [1].

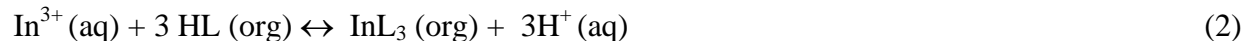
On the 1980 decade a good deal of applied work and some industrial patents were reported on the development of hydrometallurgical routes, often using solvent extraction, for the selective recovery of indium from sulfuric or sulfate leaching solutions [2]. The most chosen extractant has always been bis (2-ethylhexyl) phosphoric acid (D2EHPA), alone or together with a solvating agent such as tri-n-butylphosphate (TBP) [2,3] or with linear and / or branched phosphine oxides [1,4]. Therefore, there is a lot of information concerning In(III) extraction reactions [2,5] or selectivity patterns, specially against Fe(III), Fe(II) and Zn(II) [2,6,7], for an enormous variety of experimental conditions involving this organophosphorus compound. Hence, it is generally accepted that In(III) is extracted from diluted sulfuric acid solutions by D2EHPA, in kerosene, according to the chemical reaction depicted in (1) [5],



for which n is equal or greater than 1 and $(\text{HL})_2$ represents a dimeric D2EHPA. An identical chemical reaction has been found for bis (2-ethylhexyl) phosphonic acid, the active ingredient of Ionquest 801 [5,8]. Regarding the selectivity properties, difficulties in the separation of In(III) from Fe(III) have been exhaustively reported, as both metal ions are frequently co-

extracted [6,7]. In addition, their stripping is not easy as well, as strong acidic aqueous solutions to recover In(III) are necessary. However, as Fe(III) is even more difficult to strip from D2EHPA than In(III), a sequential stripping of In(III) followed by Fe(III) seems possible [6]. However, a better selectivity for In(III) against Fe(III) has been reported for D2EHPA and octylphosphine oxide mixtures, as well as a quite different extraction kinetics for both extraction processes [1,4], suggesting their easiest separation. On the contrary, D2EHPA has shown an acceptable selectivity for In(III) against Zn(II) and Fe(II) [7,9].

Regarding the extraction performances exhibited by Cyanex 272 and Cyanex 301 towards In(III) contained in sulfuric solutions – bis (2,4,4-trimethylpentyl) phosphinic acid and bis (2,4,4-trimethylpentyl) dithiophosphinic acid, respectively -, literature data can be considered scarce [10,11]. In fact, In(III) is not efficiently extracted by Cyanex 272 for sulfuric acid concentrations above 0.3M [10], whereas Cyanex 301 extracts ~100% In(III) for acid concentrations until 5M, but it also shows a very good affinity for Fe(III) and Zn(II) at the same range of sulfuric acid concentrations. Fe(II) is not extracted. These latter results were obtained for acid solutions containing the metal ions separately [10,11]. Considering that Cyanex 301 exists mainly as a monomeric species in the usual organic diluents [10,11], the reaction proposed for In(III) extraction by Cyanex 301 can be written such as in (2),



for which HL denotes the active ingredient of Cyanex 301.

The dimeric character shown by D2EHPA, as well as by the active ingredients of Ionquest 801 and Cyanex 272 when dissolved in the organic diluents at the most usual concentrations, has always been a consensual statement in the recent literature data [12-15]. However, the aggregation number adopted by Cyanex 301 is still a matter of controversy and a recent work clearly explains the state-of-the-art about this subject [16]. The majority of the authors, using different techniques, points out to the predominant monomeric character of the bis (2,4,4-trimethylpentyl) dithiophosphinic acid, at least for concentrations in organic diluents up to 0.1M [12, 14-16]; however, other researchers have considered that purified Cyanex 301, for a concentration range between 0.2 and 1M, is completely dimeric [17,18], and this assumption has probably led to erroneous extraction equilibria, as the real situation for these experimental conditions should be a distribution more or less equal of the monomeric and dimeric forms [16].

The aim of this work is to compare the extraction profiles adopted by some of the most usual acidic organophosphorus extractants, e.g., D2EHPA, Ionquest 801, Cyanex 272 and Cyanex 301 towards In(III) recovery from diluted aqueous sulfuric solutions. In(III) stripping from the loaded solvents has also been evaluated, as well as the selectivity patterns shown by the extractants for the rare metal ion when in presence of other contaminants such as Fe(III), Fe(II) and Zn(II).

Experimental

Organic Solutions

Cyanex 301 – bis (2,4,4-trimethylpentyl) phosphinodithioic acid, 77% purity - and Cyanex 272 – bis (2,4,4-trimethylpentyl) phosphinic acid, 80-87% purity -, were kindly supplied by Cytec

Canada Inc., and used without further purification. Bis (2-ethylhexyl) phosphoric acid (D2EHPA, 93% purity) and Ionquest 801 – bis (2-ethylhexyl) phosphonic acid, 97% purity -, were gently provided by Albright & Wilson Americas Inc., and also used as received.

Generally, 0.1M solutions of those extractants were prepared in kerosene (Fluka, purum, boiling point range of 190-250°C) and used throughout this work, except for the experiments where the influence of using different concentrations of the ligands on In(III) distribution was to be studied.

Aqueous Feed Solutions

Typically, after preparation of 0.3M sulfuric acid solutions (from 95-97% H₂SO₄, p.a.), an adequate amount of anhydrous In₂(SO₄)₃ was dissolved (Fluka, > 98% purity), in order to achieve 0.3M H₂SO₄ solutions with a 0.15 g/L In(III) concentration ($\sim 1.3 \times 10^{-3}$ M). For the plot of the equilibrium extraction isotherms, In(III) concentrations of about 2.0 g/L, 0.5 g/L and 0.15 g/L, in 0.3M H₂SO₄ matrices, were used for Cyanex 301, D2EHPA and Ionquest 801, respectively. Other aqueous solutions containing 5.0 g/L, 2.0 g/L and 0.30 g/L, in 0.3M H₂SO₄, were similarly prepared and used to study the chemical reactions when Cyanex 301, D2EHPA and Ionquest 801, respectively, were involved. The aqueous solution for the Cyanex 272 system contained 0.15 g/L In(III) in 0.3M H₂SO₄. To complete the information about the extraction reactions, other aqueous solutions containing In(III) concentrations of about 0.15 g/L were also prepared but their pH was modified by using different H₂SO₄ concentrations.

Selectivity studies were carried out with sulfuric acid aqueous solutions of different pH containing ~ 0.15 g/L In(III), Fe(III), Fe(II) or Zn(II), each one prepared from the respective metal ion sulfate salts (all with an analytical grade purity). Additional aqueous solutions containing In(III), Fe(III) and Zn(II) simultaneously (0.15 g/L each) were also prepared and used with a similar aim.

Aqueous stripping phases containing different concentrations of sulfuric or hydrochloric acids were used to strip In(III) from Cyanex 301, D2EHPA or Ionquest 801 organic solutions. The aqueous phases used for In(III) extraction had the typical composition.

Extraction and Stripping Procedures

Typically, equal volumes of aqueous and organic phases (A/O=1) were put in contact in a double-wall cell connected to a Julabo F12 refrigerated thermostat in order to control the temperature ($20 \pm 0.1^\circ\text{C}$). Both solutions were shaken at a constant speed - 1000 rpm -; under these conditions, good emulsions were obtained. The shaking period was fixed at 30 minutes for all the extraction systems, this period of time being enough to reach equilibrium conditions, in accordance to some preliminary experiments that confirmed previous reported results [5,7,10].

The method of the variation of A/O ratios was selected for the experiments aimed to collect data for the extraction equilibrium isotherms. All the other experimental conditions were kept constant.

Analyses of the metal ion contents in the aqueous phases before and after equilibration were accomplished by flame atomic absorption spectrophotometry. Metal ion concentrations in organic solutions were found by mass balance. At least two different aliquots from the same solution were carried out for analysis and the majority of the experiments whose results are presented in this work were made in duplicate. The deviation error associated to the extraction

and stripping percentages is assumed to be $\pm 2.5\%$. The pH control, whenever necessary, was made with a WTW InoLab pH meter.

Results and Discussion

Indium Extraction

The efficiencies shown by D2EHPA, Ionquest 801, Cyanex 272 and Cyanex 301, dissolved in kerosene, for the extraction of 0.15 g/L In(III) in 0.3M H₂SO₄ solutions are presented in table I.

Table I. Percentages of In(III) extraction by the four acidic organophosphorus extractants

| <u>Extractants</u> | <u>% In(III) extraction</u> |
|--------------------|-----------------------------|
| D2EHPA | 98 |
| Ionquest 801 | 96 |
| Cyanex 272 | 12 |
| Cyanex 301 | ~100 |

It is well known that all these compounds extract metal ions through a cation exchange reaction; therefore, the nature and number of atoms linked to phosphorus affect intrinsically their acid-base properties. The S-H bond is the most acidic and, for the oxygen derivatives, the ease of proton release will increase with the number of oxygen atoms in the molecules, hence the order of increasing acidity will be phosphinic < phosphonic < phosphoric. The affinity for In(III) extraction shown by these organophosphorus acids is in perfect accordance with their relative acidities.

The In(III) equilibrium extraction isotherms obtained for the three best extraction systems are plotted in Figure 1.

The three extraction isotherms have a similar shape, however the high affinity for In(III) shown by D2EHPA and specially by Cyanex 301, in contrast to the results obtained for Ionquest 801, is clearly evidenced. For the adopted set of experimental conditions, the values found for the In(III) maximal saturation capacities were 4.4 g/L, 1.3 g/L and 0.3 g/L for Cyanex 301, D2EHPA and Ionquest 801, respectively.

Indium Extraction Reactions

The extraction characteristics of Cyanex 301 and D2EHPA for In(III) were further investigated through a series of experiments aimed to study the influence of using different concentrations of extractant on the distribution ratio of the metal ion. Relatively concentrated In(III) solutions were used, e.g. 5 g/L and 2 g/L In(III) in 0.3M H₂SO₄ for Cyanex 301 and D2EHPA, respectively. The results obtained are displayed in Figure 2.

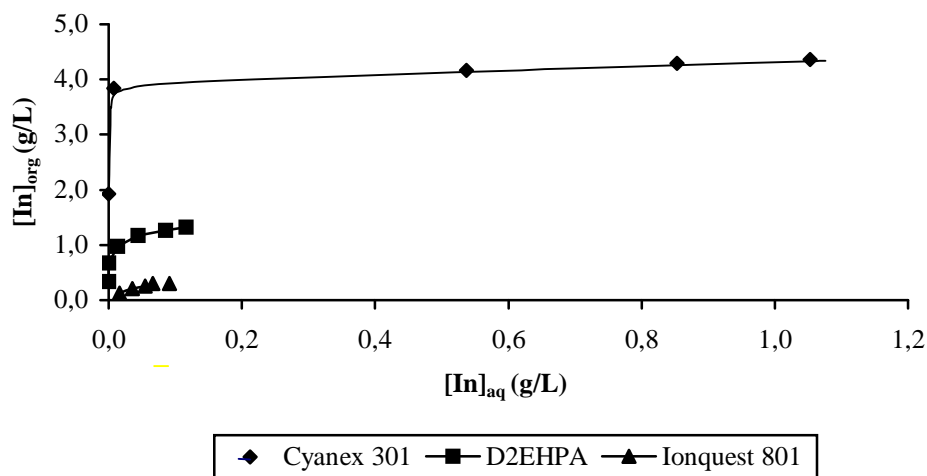


Figure 1: In(III) equilibrium extraction isotherms obtained for D2EHPA, Ionquest 801 and Cyanex 301.

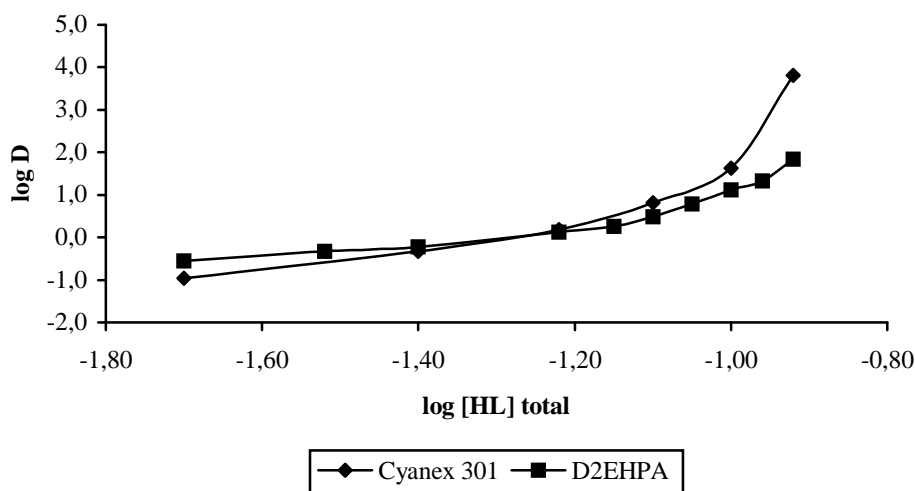


Figure 2: In(III) distribution data expressed by log. D vs. log. [HL] total for Cyanex 301 and D2EHPA.

In addition, the same procedure was adopted for Ionquest 801 and Cyanex 272. The aqueous feed phase used for Ionquest 801 contained 0.3 g/L In(III) in 0.3M H₂SO₄, whereas for Cyanex 272 a 0.15 g/L In(III) concentration in a similar H₂SO₄ matrix was used instead. The distribution results obtained are presented in Figures 3 and 4.

For D2EHPA and Cyanex 301, the metal ion loadings for all the extractant concentrations in the organic phase is high; therefore, the free extractant concentrations cannot be considered similar to the initial ones in the organic phase, the determination of the dependency of log D on the logarithm of the extractant concentrations being not possible. However, if one considers the proportion between the molar concentration of the extractant and that of In(III) that was effectively extracted, for each experimental point, it can be found that, for D2EHPA, those

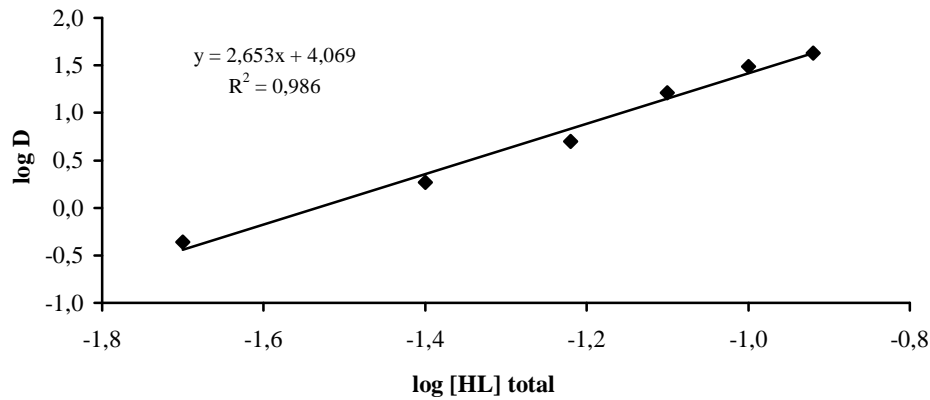


Figure 3: In(III) distribution data expressed by log. D vs. log. [HL] total for Ionquest 801.

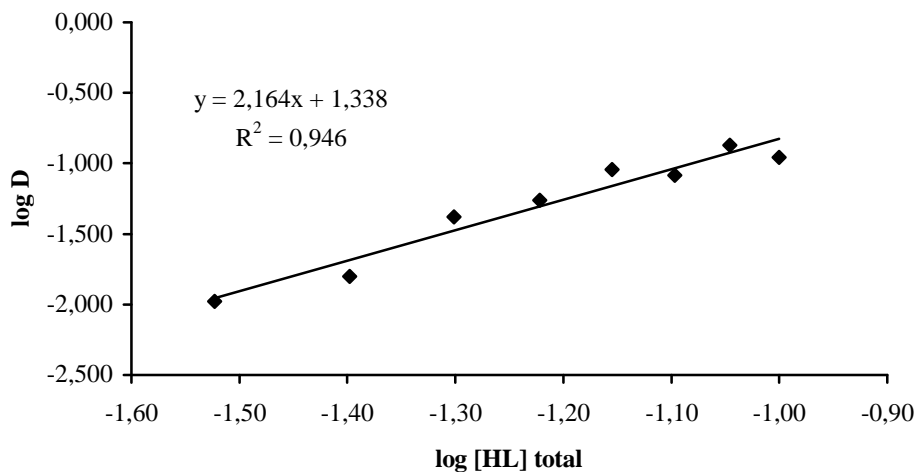


Figure 4: In(III) distribution data expressed by log. D vs. log. [HL] total for Cyanex 272.

ratios vary between 6.0 and 8.5 for the total range of extractant concentrations studied, whereas for Cyanex 301 the same proportion changes from 2.5 to 3. Due to the high affinity of D2EHPA and Cyanex 301 for In(III), it can be considered that both extractants are almost completely saturated with metal ion using these experimental conditions; thus, the minimal proportion of [L] / [In(III)] for D2EHPA is 6 and for Cyanex 301 is approximately 3.

For Ionquest 801 and Cyanex 272, the usual slope approach is valid, therefore the slope values found were 2.7 for Ionquest 801 and 2.2 for Cyanex 272, denoting that [HL] total / [In(III)] is approximately 3 for the former extractant and for Cyanex 272 is of about 2. This latter result can be probably explained by the fact that, at this pH, the affinity of Cyanex 272 for In(III) is really quite low.

Further experiments were conducted in order to check the release of $3H^+$ for these extraction systems. In fact, the experimental points displayed in the plots of log D on equilibrium pH for D2EHPA, Ionquest 801 and Cyanex 272 – Figure 5 – lay over straight lines whose slopes are approximately 3. Cyanex 301 has not been considered for this study because the pH values where the significant In(III) distribution variations occur are too low to be measured.

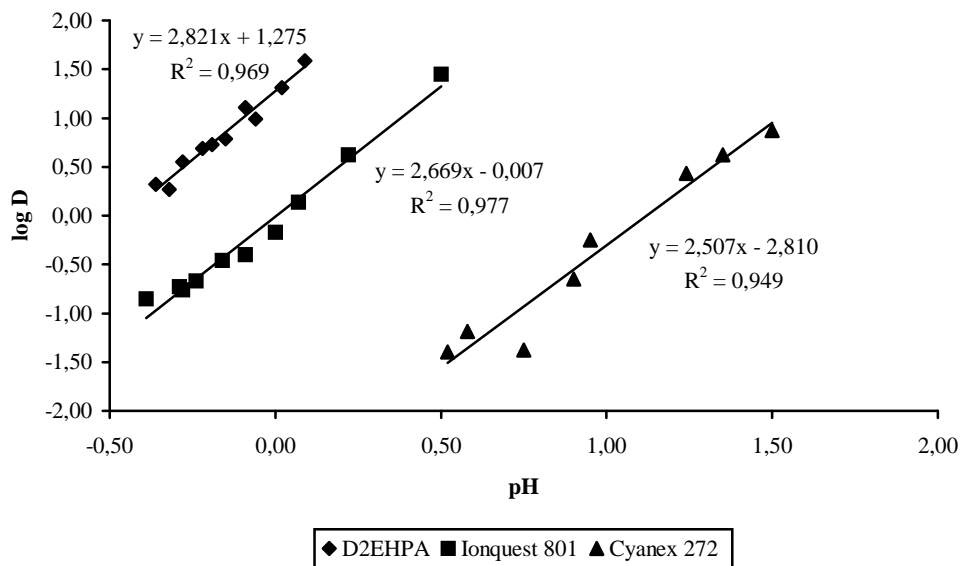
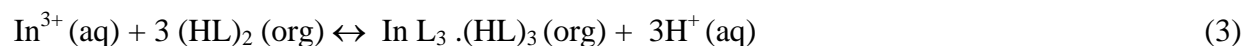
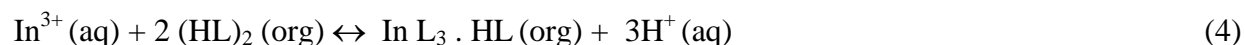


Figure 5: In(III) distribution data expressed by log. D vs. equilibrium pH for D2EHPA, Ionquest 801 and Cyanex 272.

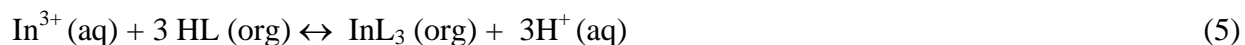
The results of the treatment of the experimental data that were collected are in accordance with the general ones described in literature for similar extraction systems, therefore the chemical reaction (3) can be proposed to express the In(III) extraction pathways adopted by D2EHPA and Ionquest 801 [2,5,8],



for which $(\text{HL})_2$ is the acidic extractant in the dimeric form. Regarding Cyanex 272, the results obtained point out to a lower number of extractant molecules per each In(III); therefore, at least for these experimental conditions leading to low In(III) extraction profiles, the chemical reaction involved should be as in (4).



For Cyanex 301, the data collected in this work and in literature [12,14,16] justify the proposal of equation (5).



Acidic organophosphorus extractants with high metal ion loadings sometimes form chain polymers with gel characteristics, e.g., D2EHPA with Y^{3+} and with several other metal ions including lanthanides [19]. The data reported suggests that the general structure of those gels should be $(\text{ML}_3)_n$, for which M is a trivalent metal ion and L is the conjugate base of D2EHPA [19]. For the experimental conditions used in this work, those metal ion aggregates have not been detected when D2EHPA was used, but a solid gel appeared for Cyanex 301 when its most diluted solutions were saturated with In(III), therefore a polymer with an alike structure should have formed in those cases.

Indium Stripping

Larger volumes of organic phases containing either D2EHPA, Cyanex 301 or Ionquest 801 were equilibrated with In(III) aqueous 0.3M H₂SO₄ feeds and then divided in smaller volumes to systematically study their stripping by sulfuric or hydrochloric acids. Therefore, kerosene solutions of D2EHPA or Cyanex 301 containing 0.15 g/L In(III), and loaded Ionquest 801 phases with 0.14 g/L of the rare metal ion, were used in stripping experiments. The results obtained for In(III) stripping are displayed in Table II.

Table II. Percentages of In(III) stripping from loaded solvents containing D2EHPA, Ionquest 801 and Cyanex 301, by H₂SO₄ or HCl solutions.

| Extractants | H ₂ SO ₄ stripping solutions (M) | | | | | HCl stripping solutions (M) | | | | |
|--------------|--|----|----|----|----|-----------------------------|----|----|----|----|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| D2EHPA | 3 | 18 | 36 | 63 | 74 | 60 | 86 | 70 | 65 | 61 |
| Ionquest 801 | 44 | 85 | 90 | 87 | 91 | 98 | 90 | 73 | 70 | 64 |
| Cyanex 301 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 11 |

It can be seen from the table that good In(III) stripping efficiencies from D2EHPA and Ionquest 801 were achieved either with H₂SO₄ or HCl solutions. Hence, the increase in sulfuric acid concentration facilitates In(III) release from D2EHPA, but a 2M HCl solution seems the most appropriate when hydrochloric acid is used. On the other hand, In(III) from Ionquest 801 is almost totally recovered by a 3M H₂SO₄ aqueous phase, and stripping is even better if a 1M HCl solution is used instead. As already expected, In(III) from Cyanex 301 is very difficult to strip, and only a very concentrated HCl aqueous phase (typically 7M or higher, [10]) can probably afford reasonable In(III) stripping results.

Selectivity for Indium

In order to collect information on the selectivity patterns adopted by D2EHPA, Ionquest 801 and Cyanex 301 towards In(III) extraction from H₂SO₄ solutions when other contaminating metal ions are present in the aqueous feed phases, systematic experiments were carried out. Hence, aqueous solutions containing 0.15 g/L of each metal ion – In(III), Fe(III), Fe(II) or Zn(II) – for different H₂SO₄ proportions, were contacted with 0.1M organic phases of each extractant. The chosen interfering ions were those which mainly exist in the leaching solutions containing In(III) [1]. The plots of the extraction percentages of each metal ion vs. equilibrium pH for the D2EHPA, Ionquest 801 and Cyanex 301 systems can be found in Figures 6, 7 and 8.

From these Figures it can be concluded that Fe(III) will always interfere with In(III) extraction by D2EHPA, Ionquest 801 or Cyanex 301. Regarding Fe(II), its interference seems to be more significant for D2EHPA and Ionquest 801 than for Cyanex 301, as %E obtained for the two former extraction systems at equilibrium pH = 0.5 should probably be higher than that achieved for Cyanex 301 at the same pH value.

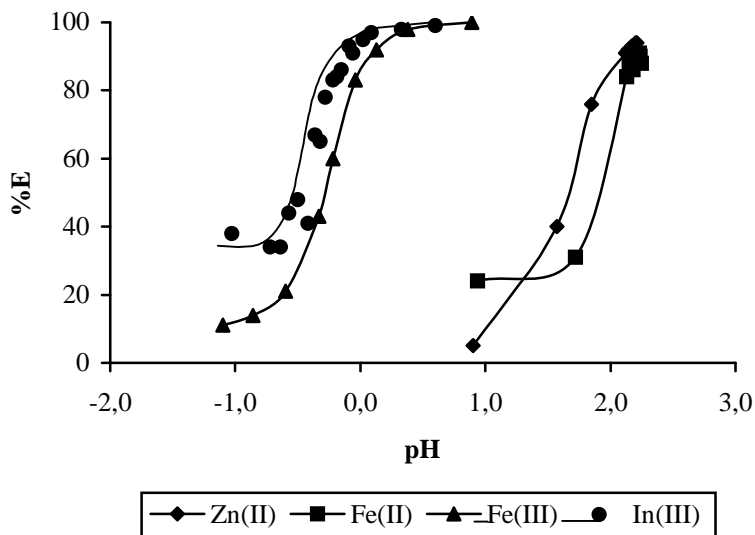


Figure 6: %E for In(III), Fe(III), Fe(II) and Zn(II), vs. equilibrium pH, by D2EHPA.

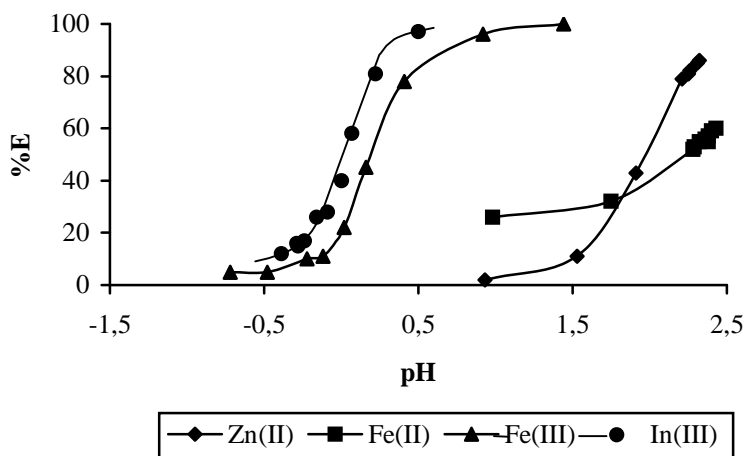


Figure 7: %E for In(III), Fe(III), Fe(II) and Zn(II), vs. equilibrium pH, by Ionquest 801.

However, the affinity of Cyanex 301 for Zn(II) is much higher than those exhibited by D2EHPA and Ionquest 801: for instance, at a pH = 0.5, In(III) is almost completely extracted by Ionquest 801 and specially by D2EHPA and Zn(II) is not extracted at all. The same situation does not occur with Cyanex 301: at a pH = 0, Zn(II) is already very efficiently extracted, therefore it is not possible to separate In(III) from Zn(II) using this extractant.

Aqueous phases containing similar concentrations of In(III), Fe(III) and Zn(II) simultaneously, in 0.3M H₂SO₄, were contacted with 0.1M solutions of D2EHPA and Ionquest 801 in kerosene, in order to compare the results with the %E values obtained for all the metal ions when isolate. The aqueous feed equilibrated with Cyanex 301 contained the three metal ions in 3.2M H₂SO₄. The results obtained are displayed in table III.

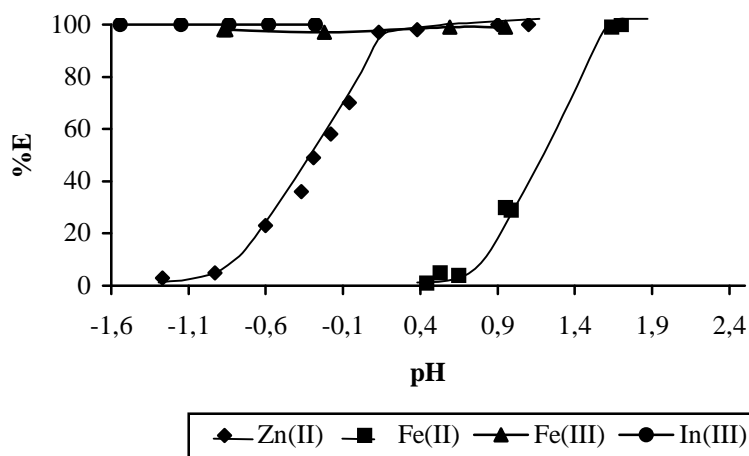


Figure 8: %E for In(III), Fe(III), Fe(II) and Zn(II), vs. equilibrium pH, by Cyanex 301.

Table III. Percentages of In(III), Fe(III) and Zn(II) extraction by D2EHPA, Ionquest 801 and Cyanex 301.

| Extractants | % In(III) extraction | % Fe(III) extraction | % Zn(II) extraction |
|--------------|----------------------|----------------------|---------------------|
| D2EHPA | 99 | 94 | 7 |
| Ionquest 801 | 96 | 92 | 8 |
| Cyanex 301 | 99 | 99 | 99 |

As can be seen from table III, the extraction efficiencies found for each metal ion are comparable to the ones already achieved and presented in the plots displayed in Figures 6, 7 and 8, only the Zn(II) extraction values verified for the three systems are a bit higher than expected.

Conclusions

Cyanex 301 is a very efficient extractant for In(III) recovery from strong acidic H₂SO₄ aqueous phases; however, In(III) stripping is quite difficult, even by use of very concentrated sulfuric or hydrochloric acid solutions. This extractant is selective for In(III) when Fe(II) is present, but it is not when Fe(III) or Zn(II) co-exist. The In(III) extracted species should be of the type InL₃, L being the conjugate base of the acidic extractant HL.

D2EHPA and Ionquest 801 extract In(III) very efficiently at a pH = 0, but D2EHPA presents a higher loading capacity. In(III) from Ionquest 801 is easier to strip than from D2EHPA, but both stripping processes are feasible. Regarding selectivity patterns, both extractants are very similar: In(III) is not selectively extracted when Fe(III) is present, but Fe(II) causes little interference. For a pH = 0.5, Zn(II) is practically not extracted. These two organophosphorus compounds seem to extract In(III) through the formation of organo-metallic species of the type ML₃ · (HL)₃.

Cyanex 272 only presents a good In(III) extraction performance for pH values higher than 1.5. A stoichiometry such as ML₃ · HL has been found for the In(III) species formed with this extractant, and their occurrence can be justified by the low affinity towards In(III) verified at the acidic pH range used for these experiments.

References

1. C. Wang, D. Liu and J. Zhang. "Solvent Extraction of Indium(III) and Iron(III) from Sulphuric Acid Media by Mixtures of D₂EHPA and Cyanex 923", *Proceedings of the International Solvent Extraction Conference ISEC'2002*, ed. K. C. Sole, P. M. Cole, J. S. Preston and D. J. Robinson (The South African Institute of Mining and Metallurgy, 2002), 430-435.
2. A. P. Paiva, "Recovery of Indium from Aqueous Solutions by Solvent Extraction", *Separation Science and Technology*, 36 (7) (2001), 1395-1419.
3. K. Yamaguchi and K. Tomii, "Production of Indium by Solvent Extraction", *Nippon Kogyo Kaishi*, 96 (1106) (1980), 257-258.
4. W. A. Rickelton, "Phosphine Oxide Phase Modifiers in the Recovery of Indium", *Proceedings of the International Solvent Extraction Conference ISEC'1993*, ed. D. H. Logsdail and M. J. Slater (Elsevier Science Publishers Ltd., England, 1993), 533-540.
5. T. Sato and K. Sato, "Liquid-liquid Extraction of Indium (III) from Aqueous Acid Solutions by Acid Organophosphorus Compounds", *Hydrometallurgy*, 30 (1992), 367-383.
6. B. Nikov, P. Stojanov and T. Stojadinovic, "Production of Indium from Imperial Smelting Process Residues", *Proceedings of Hydrometallurgy' 94* (Chapman and Hall, London, UK, 1994), 1153-1164.
7. J. S. Benedetto, E. B. Tambourgi and R. M. Mingote, "Indium Recovery from Industrial Zinc Residues", *Proceedings of the International Solvent Extraction Conference ISEC'1999*, ed. M. Cox, M. Hidalgo and M. Valiente (Society of Chemical Industry, London, England, 2001), 711-716.
8. C. Bao, "Extraction Mechanism of Indium with 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester from Sulfuric Acid Solution", *Huaxue Xuebao*, 42 (11) (1984), 1210-1213.
9. P. Fossi and E. Sambarino, "Recovery of Indium from Aqueous Solutions of Other Metals", *European Patent*, Application 8,992 (1980), 26 pp.
10. M. A. Rodriguez, G. Cote and D. Bauer, "Recovery of Indium (III) from Mixed Hydrochloric Acid – Sulphuric Acid media by Solvent Extraction with Cyanex 301®", *Solvent Extraction and Ion Exchange*, 10 (5) (1992), 811-827.
11. S. Facon, M. A. Rodriguez, G. Cote and D. Bauer, "General Properties of Bis (2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301®) in Acidic Liquid – liquid Extraction Systems", *Proceedings of the International Solvent Extraction Conference ISEC'1993*, ed. D. H. Logsdail and M. J. Slater (Elsevier Science Publishers Ltd., England, 1993), 557-564.
12. M. P. Jensen, R. Chiarizia and V. Urban, "Investigation of the Aggregation of the Neodymium Complexes of Dialkylphosphoric-, Oxothiophosphinic- and

- Dithiophosphinic acids in Toluene”, *Solvent Extraction and Ion Exchange* 19 (5) (2001), 865-884.
13. S. Nishihama, T. Hirai and I. Komasaawa, “A Separation and Recovery Process of Gallium and Indium from Zinc Refinery Residue”, *Proceedings of the International Solvent Extraction Conference ISEC'1999*, ed. M. Cox, M. Hidalgo and M. Valiente (Society of Chemical Industry, London, England, 2001), 723-728.
 14. M. P. Jensen and A. H. Bond, “Influence of Aggregation on the Extraction of Trivalent Lanthanide and Actinide Cations by Purified Cyanex 272, Cyanex 301 and Cyanex 302”, *Radiochimica Acta*, 90 (4) (2002), 205-209.
 15. M. P. Jensen and A. H. Bond, “Comparison of Covalency in the Complexes of Trivalent Actinide and Lanthanide Cations”, *Journal of the American Chemical Society*, 124 (33) (2002), 9870-9877.
 16. G. Cote, J.-V. Martin, D. Bauer and Y. Mottot, “Physico-chemical properties of Cyanex® 301”, *Proceedings of the International Solvent Extraction Conference ISEC'2002*, ed. K. C. Sole, P. M. Cole, J. S. Preston and D. J. Robinson (The South African Institute of Mining and Metallurgy, 2002), 291-298
 17. Y. Zhu, J. Chen and R. Jiao, “Extraction of Am(III) and Eu(III) from Nitrate Solution with Purified Cyanex 301”, *Solvent Extraction and Ion Exchange*, 14 (1) (1996), 61-68.
 18. M. L. P. Reddy, J. R. B. Bharati, S. Peter and T. R. Ramamohan, “Synergistic Extraction of Rare Earths with Bis (2,4,4-trimethylpentyl) dithiophosphinic Acid and Trialkylphosphine Oxide”, *Talanta*, 50 (1) (1999), 79-85.
 19. E. Anticó, A. Masana, M. Hidalgo, V. Salvadó, M. Iglesias and M. Valiente, “Solvent Extraction of Yttrium from Chloride Media by Di (2-ethylhexyl) phosphoric Acid in Kerosene. Speciation Studies and Gel Formation”, *Analytica Chimica Acta*, 327 (1996), 267-276.