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RECOVERY OF INDIUM FROM AQUEOUS SOLUTIONS BY SOLVENT EXTRACTION

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ABSTRACT

This review identifies the most significant knowledge acquired on the recovery of indium from aqueous solutions using solvent extraction. Research on the efficient and selective recovery of this valuable element from aqueous solutions is particularly emphasized, as this information is useful for potential hydrometallurgical applications. A good comprehension of the extraction reactions involved can be important for further development; therefore, the data provided are systematically classified according to the different types of chemical reactions that occur during metal ion extraction. Some complexation studies may also be mentioned, particularly if they contribute additional information to a promising solvent extraction system.

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INTRODUCTION

Indium (In) is not mined for itself, as it appears very widely dispersed on the earth's surface. Rather, the metal is produced from several commercial ores, together with zinc (sphalerite), lead (galena), copper (polymetallic ores), and tin (stannite and cassiterite) (1). World production of indium was 173 tons in 1996 (66 from the European Union, 40 from Canada, 25 from China, 20 from Japan, 18 from the Community of Independent States, and 4 from Peru). Metaleurop, in France, has been quoted as the main European company leader for indium production, but other companies such as Falconbridge and Cominco from Canada, Zhuzhou from China, and Dowa Mining and Sumitomo Metal Mining from Japan (1) have also been important producers, just to mention only a few. London prices for 1 kg of indium in February 2000 varied between US \$140 and \$160 (2).

Due to the strategic importance of this element, any efforts made to develop new processes for its recovery are completely justified. Nowadays, commercial grade indium is industrially produced using leaching, cementation, and electrorefining technologies; solvent extraction (SX) is often used to recover indium from leach residues (1).

The aim of a SX treatment applied to the leaching solutions obtained from ores and concentrates—a technique which is currently used in several integrated processes operating in the hydrometallurgical industry (3,4)—is to promote the selective and efficient transfer of the desired metallic species to an organic solvent, after which the metal ions are stripped from the solvent to a new aqueous phase and then further processed.

Although mainly applied to the reprocessing of nuclear fuels and the recovery of base metals such as copper, nickel, and zinc (4,5), SX can also be used to recover minor elements, particularly the most valuable (4,6). The economical value of those minor elements can potentially compensate their relative scarcity in leaching solutions. In addition, the increasing development of selective extractants for specific metals—those with the capacity to leave undesired species or metallic contaminants in the feed aqueous solutions—works as a powerful attraction for the enhancement of SX research.

Within the several alternatives foreseen for metal recovery from aqueous phases, e.g., cementation, ion exchange, and selective precipitation, SX maintains its place as one of the most promising separation operations (3,4).

A suitable hydrometallurgical treatment of copper, zinc, and lead sulfide concentrates obtained from ores such as chalcopyrite, blende, or galena, often provides leaching solutions that contain appreciable amounts of valuable minor elements (7). SX studies have thus been developed in order to recover trace amounts of indium which are frequently present in various kinds of zinc ores, in slags or residues issued from zinc and lead refining (8), and also in flue dust leaching solutions (9).

Phenomena associated with the extraction of In(III) from different types of aqueous solutions have been widely investigated for more than thirty years (10–12). Although some of the published data exhibits mainly analytical interests (13–16), beginning in the 1980s, a good deal of applied work and some patents have appeared on the development of hydrometallurgical routes—including SX—for the metal recovery from sulfuric acid or sulfate leaching solutions (17–21).

The increasing economical value in the metal markets achieved by indium is intrinsically related to its actual and potential uses in electronic devices, such as in indium–phosphorus semiconductors (8) and in tin–indium oxides (9), and has increased the pressure for applied SX investigations for indium recovery during the last twenty years. A recent work points out that indium can sometimes appear as an impurity in some processes, or as a toxic element that needs to be eliminated (22); SX can even be useful in these circumstances.

The main aim of this review is to stress and highlight the most significant knowledge of the SX of indium from aqueous solutions. Information will be presented by joining those extraction systems whose general chemical reactions are of a similar nature; therefore acidic-type, solvating, and basic-type extractions will be considered.

Researchers usually establish the composition of the extracted species after the treatment of several sorts of distribution data; therefore, their proposals of structure only take the stoichiometric coefficients of the involved moieties into account. The comparison of results for similar extraction systems allowed this review to present a critical selection of the most representative works; sometimes, an effort to unify the presentation of data has been necessary. Whenever possible, mention is given when authors base their structural proposals on additional means.

Synergic mixtures are often used to enhance extraction abilities and selectivity factors; therefore, the most relevant synergistic systems employed for indium extraction will also be mentioned. Data on selectivity details, whenever available, will also be included, but this review will not discuss features related to SX diagrams under development or those currently in use in industrial hydrometallurgy.

SOLVENT EXTRACTION OF INDIUM

Acidic Organic Reagents: Formation of Neutral Complex Species

Simple Acidic-Type Extractants

In order to clarify the presentation of indium extraction data, the simple acidic-type extractants, e.g., carboxylic and phosphorous acids, will be reviewed first. The majority of the work that has been carried out uses phosphorous acid derivatives, and some of these extractants profit from the synergistic effect than can sometimes occur when the acidic compound is mixed with a solvating agent. The main achievements accomplished for indium extraction by this sort of organic ligand are summarized in Table 1, in which features such as the general composition of the aqueous solution, stripping phases, and selectivity data, whenever determined, are also referred to.

The use of several leach solutions, usually from zinc processing, and the efforts to find suitable stripping media, are an indication that there has been a deep commitment to the development of technological SX applications of acidic-type compounds for indium recovery. This is why the majority of the published data involve sulfuric acid solutions, either as feed or as stripping agents.

The analysis of distribution data and application of IR and ^{1}H NMR spectroscopies to organic extracts of purified di(2-ethylhexyl)phosphoric acid (D2HEPA) in kerosene, after extraction of In(III) from sulfuric (29,38) and nitric (29) acid solutions, allowed the proposal of Eq. (1) as a general scheme for the metal ion extraction,

$$n\mathrm{In}^{3+}_{(aq)} + (2n+1)(\mathrm{HL})_{2(org)} \leftrightarrow \mathrm{In}_n\mathrm{L}_{2(2n+1)}\mathrm{H}_{(n+2)(org)} + 3n\mathrm{H}^{+}_{(aq)} \tag{1}$$

for which n is greater than or equal to 1 and $(\mathrm{HL})_2$ represents a dimeric D2HEPA species in the organic diluent. On the other hand, Eq. (2) best describes the experimental data achieved when In(III) extraction is carried out from hydrochloric acid medium of low acidity (29). As in Eq. (1), it considers the possibility of the formation of polymeric species at high loading ratios.

$$n\mathrm{InCl}^{2+}_{(aq)} + (n+1)(\mathrm{HL})_{2(org)} \leftrightarrow \mathrm{In}_n\mathrm{Cl}_n\mathrm{L}_{2(n+1)}\mathrm{H}_{2(org)} + 2n\mathrm{H}^{+}_{(aq)} \tag{2}$$

In addition, for higher HCl concentrations, the extraction equilibrium seems to proceed through a solvation reaction involving $\mathrm{InCl_3}$ species (29), as shown in Eq. (3).

$$\mathrm{InCl}_{3(aq)} + (\mathrm{HL})_{2(org)} \leftrightarrow \mathrm{InCl_3{\cdot}2HL}_{(org)} \tag{3}$$

The effect of the kind of acidic aqueous solution used on the efficiency of In(III) extraction by D2HEPA follows the order $\mathrm{HNO_3} > \mathrm{H_2SO_4} > \mathrm{HCl}$ at low aqueous acidity, but this order is reversed for higher acidities (29). This behavior may be intrinsically related to the fact that a competition can occur between In(III) cationic species and protons, for extraction by D2HEPA, when high concentrations of nitric and sulfuric acids are present (In(III) nitrate species are not detected in organic extracts). Therefore, $\mathrm{InCl_3}$ species may actually be responsible for an increase in In(III) extraction when HCl concentrations up to 5 M are used.

It is worthwhile to mention that no systematic studies have been performed in order to establish the chemical equilibria that occurs when In(III) is extracted by a synergistic mixture of D2HEPA and a solvating extractant (17,19,27,35).

Equations (1) to (3) are also suitable for expressing In(III) extraction by 2-ethylhexyl-2-ethylhexylphosphonic acid (29) using similar experimental condi-

Table 1. Acidic-Type Extractants Used for Indium Extraction

Extractant	Aqueous Phase(s)	Stripping Phase(s)	References	Additional Comments
Fatty acids (C_{11}–$C_{15}CO_2H$)	Aq. H_2SO_4	—	23	Extracted complex $[In_2(OH)L_5 \cdot 5HL]_x$
Saturated fatty acids	Diluted solutions from Zn or Pb refinery residues	H_2SO_4 or HCl, pH 3–5	24	Fe(III), Ga, Sn co-extracted; kerosene used as diluent
Versatic 10 (carboxylic acid)	Zn residue treatment, aq. H_2SO_4	—	21	In, Ga selectively recovered
Versatic 10, 2-bromodecanoic, naphtenic, 3, 5-diisopropyl salicylic acids	Aq. HNO_3 + $NaNO_3$ or aq. HCl + NaCl	—	25	Several data on metal ion interferences in In extraction (Cu, Zn, Cd, Hg, Pd, Fe(III), Al, Ga, Tl)
2-bromodeccanoic acid	Aq. H_2SO_4	Aq. H_2SO_4	26	In, Ga selectively recovered against Zn and Al; supported liquid membrane
Di(2-ethylhexyl) phosphoric acid (D2HEPA)	Aq. H_2SO_4	Aq. HCl or H_2SO_4	17–19, 27–29	Separation factors: In/Zn, Cd, Cu, Fe, Ni > 97; In/As > 32, In/Bi < 19 (19); synergistic mixture with TBP (17,19,27)
D2HEPA	Acidic sulfate solutions	Aq. HCl	30	Fe(III), Sn, Pb, Zn, Sb co-extracted; Cu, Cd, and As not extracted; stripping phase purified with TBP
D2HEPA	Sulfuric liquor from Zn processing, aq. H_2SO_4	Aq. H_2SO_4	31–34	Fe(III) co-extracted, but good In/Fe(III) concentration factor (33)
D2HEPA	Zn leach residues	—	35	Some Fe(III) co-extracted; synergic mixture with YW100

(continued)

Table 1. Continued

Extractant	Aqueous Phase(s)	Stripping Phase(s)	References	Additional Comments
D2HEPA	Industrial Cu dross leach solutions	Acidic chloride solution	36	In/Cu:10^4–10^6; concentration factor for In:400; supported liquid membrane
D2HEPA	Aq. H_2SO_4, HCl, H_3PO_4	HCl, H_3PO_4	37–38	In from H_2SO_4: good separation factors against Fe(III), Zn, and Al; In separated efficiently from As and Ge (37)
D2HEPA	Aq. HNO_3 and HCl	—	8, 29, 39	IR and NMR studies (29)
D2HEPA (loaded with In)	—	HCl 4–6 M, addition of Cl^-	40	Aq. H_2SO_4 or H_3PO_4 did not strip In, equilibrium slow
Di-p-octylphenyl phosphoric acid (OPPA)	Aq. H_2SO_4	—	41	Co-extraction of Ga; benzene as diluent
Diisostearyl phosphoric acid (DISPA)	—	—	42	In selectively separated from Ga; supported liquid membrane
Mono(iso-octadecyl) phosphoric acid	Aq. HCl	—	43, 44	Ga, Fe(III) co-extracted
2-ethylhexyl-2-ethylhexyl phosphonic acid	Aq. H_2SO_4	Aq. HCl or H_2SO_4	29, 31, 45, 46	IR and NMR studies (29,46)
2-ethylhexyl-2-ethylhexyl phosphonic acid	Aq. HCl and HNO_3	—	8, 29, 39	IR and NMR studies (29)
Diphosphonate ligands	Aq. H_2SO_4	Aq. HCl	47	Ion exchange resin; co-extraction of Ga
Bis(2-ethylhexyl) phosphinic acid	Aq. H_2SO_4	Aq. H_2SO_4, other acids	31, 34	Fe(III) co-extracted (34)

(*continued*)

Table 1. Continued

Extractant	Aqueous Phase(s)	Stripping Phase(s)	References	Additional Comments
Bis(2-ethylhexyl) phosphinic acid	Aq. HNO_3	—	48	In kinetically separated from Fe(III)
Bis(2,4,4-trimethyl pentyl) phosphinic acid	Aq. HNO_3, HCl–H_2SO_4 mixed	—	8, 9	—
Bis(2,4,4-trimethyl pentyl) phosphino dithioic acid	Aq. HCl, H_2SO_4, or mixed	Aq. HCl	9, 49, 50	Separation from Cd by stripping with HCl (50)

tions as for D2HEPA. However, InL_3 species have been detected for the extraction of the metal ion by the phosphonic acid derivative from H_2SO_4 solutions (46).

Organometallic species such as $(InL_3)_n$ have been proposed as responsible for In(III) extraction from HNO_3 solutions at high loading ratios, using D2HEPA, 2-ethylhexyl-2-ethylhexylphosphonic acid, or bis(2,4,4-trimethylpentyl)phosphinic acid (8) dissolved in toluene. Similarly, $InL_3{\cdot}3HL$ species have been detected after extraction of the metal ion by bis(2-ethylhexyl)phosphinic acid, also dissolved in toluene (34).

The general chemical reaction found for In(III) extraction from a mixed sulfuric–hydrochloric acid media by bis(2,4,4-trimethylpentyl)phosphinodithioic acid [9] in kerosene can be generally expressed by Eq. (4),

$$In^{3+}_{(aq)} + 3HL_{(org)} \leftrightarrow InL_{3(org)} + 3H^{+}_{(aq)} \tag{4}$$

for which the extractant can be considered as a monomeric species in the chosen organic diluent. Of course, that individualized or only hydrated In^{3+} species do not exist in a chloride medium, an In(III)-chlorocomplex equilibria may be considered instead. This equation is also valid when only HCl or only H_2SO_4 are used in the feed solution (9,49,50). An evaluation of the interference caused by different metal ions in the developed SX schemes has also been carried out [As(III), Cd(II), Cu(II), Fe(III), Zn(II) (9), these and others (49), and Cd(II) (50)], and have contributed relevant data to an adequate scheme aimed at the hydrometallurgical In(III) recovery. From a kinetic point of view, the equilibrium extraction of In(III) from H_2SO_4 is slow ($t_{1/2} = 60$ minutes), but it is rapid from a HCl medium ($t_{1/2} =$

1 minute). The kinetics of the system increase markedly even when HCl is added in small concentrations to H_2SO_4. The different extraction behavior of bis(2,4,4-trimethylpentyl)phosphinodithioic acid towards In(III) in HCl or H_2SO_4 solutions has been ascribed to the formation of asymmetrical In(III) aquochlorocomplexes in the former feed solution, which must be more labile than the $In(H_2O)_6{}^{3+}$ species, predominantly present in the latter medium (49). The results collected for this phosphinodithioic acid derivative compare generally well with data obtained for In(III) extraction by di-n-butylphosphorodithioic (51) and di-n-butylphosphorothioic acids (52).

Acidic Chelating-Type Extractants

Table 2 presents the most relevant information achieved for In(III) extraction by the use of acidic chelating-type extractants. A remarkable difference between this table and Table 1 is that there is less data on stripping of the metal ion from the organic phases for chelating extractants, as well as for its selective recovery from the feed aqueous solutions. This means that although more fundamental research has been carried out, there has been little commitment to technological applications. Consequently, these extraction reactions are better known and the involved equilibria are well understood, particularly for synergic mixtures. The structures of some of the most relevant organic compounds acting through a chelating-type reaction are presented in Fig. 1.

Substituted 4-acyl-5-hydroxypyrazoles have been particularly studied for the extraction of In(III), usually taking part in a synergic mixture (53–57). The composition of the complexes of In(III)-substituted 4-acyl-5-hydroxypyrazole derivatives is of the general type ML_3, M being In(III) and HL the chelating extractant. In the presence of a solvating compound S (e.g., TBP, TBPO, or TOPO), the structures are $ML_3{\cdot}S$ and ML_3S_2 (53). When In(III) is contained in a chloride–perchloric acid media, the extraction reactions of this sort of organic compound can be expressed again by Eq. (4), together with the equilibrium shown in Eq. (5) (54):

$$InCl^{2+}_{(aq)} + 2HL_{(org)} \leftrightarrow InClL_{2(org)} + 2H^{+}_{(aq)} \tag{5}$$

However, if tri-n-octylmethylammonium chloride ($TOMA^{+}Cl^{-}$) is added to the organic solvent when In(III) is present in a chloride–nitric acid solution, there is an enhancement of the metal ion extraction, explained by the occurrence of the equilibrium seen in Eq. (6).

$$InClL_{2(org)} + TOMA^{+}Cl^{-}_{(org)} \leftrightarrow TOMA^{+}InCl_2L^{-}_{2(org)} \tag{6}$$

The formation of this ion pair is either reduced if $TOMA^{+}Cl^{-}$ is replaced by tri-n-octylammonium chloride or suppressed if the aqueous solution contains

Table 2. Chelating Acidic-Type Extractants Used for Indium Extraction

Extractant	Aqueous Phase(s)	Stripping Phase(s)	References	Additional Comments
1-phenyl-3-methyl-4-acyl-5-hydroxy-pyrazoles	$HClO_4$ or $NaClO_4$, nitrate, chloride	—	53–57	Synergistic mixtures with solvating extractants, TBP, TOPO, MIBK, etc. (53–55)
3-hydroxy-2-methyl-4-pyridone derivatives	Aq. HNO_3, aq. HCl + NaCl	—	58–60	UV to follow formation of complexes (58)
Acetylacetone, benzoyl acetone (BA), and derivatives	Aq. $NaClO_4$ and different buffers	—	61–64	Good separation from Ga and Al (61–63); synergistic mixture with dichlorophenol (64)
2-thenoyl trifluoroacetone	Buffers	—	65–66	Synergistic mixture with TOPO
4-acyl-3-phenyl isoxazol-5-ones	Aq. HNO_3 and HCl	—	67–68	Synergistic mixture with TOPO (68)
N-nitroso-N-p-octadecyl-phenyl hydroxyl-amine ammonium salt	Aq. HCl and buffers	Aq. HCl and buffers	69	Separation factors In/Zn = 200–250 (10–100 folds); transport through impregnated polypropylene membrane
N-alkyl-carbonyl-N-phenyl-hydroxyl amines	—	—	70	Separation of In, Ga, Al
4-isopropyl tropolone	Aq. $NaNO_3$	—	71	Chloroform as diluent
"Pseudo calixarenes" (PCA)	Aq. chloride (pH = 3–5)	—	72	—
Hydroxyoxime derivatives, such as LIX63, 984, or 973N	Aq. HCl, buffers, aq. sulfate	—	22, 73–75	LIX 984 selectively separates In from Zn and Pb (74)

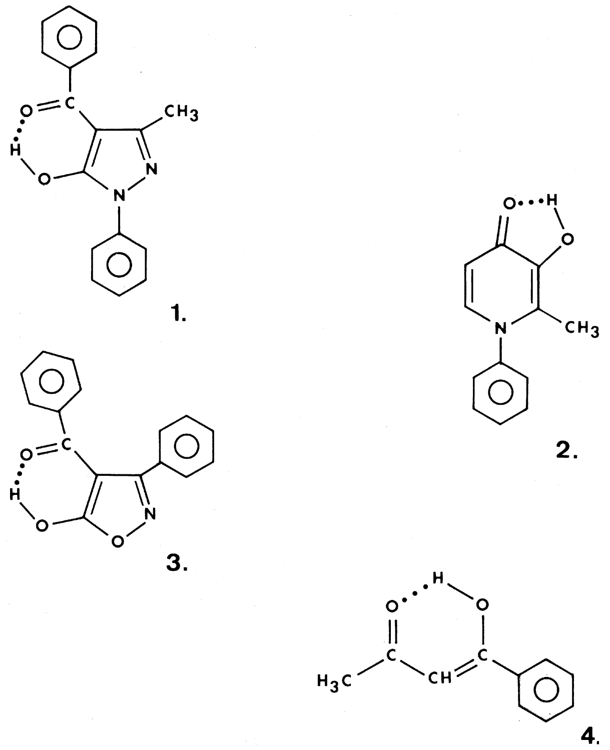

Figure 1. Structures of some chelating-type extractants for In(III) (1 tautomer shown for each case). **1.** 4-benzoyl-5-hydroxy-3-methyl-1-phenylpyrazole. **2.** 3-hydroxy-2-methyl-1-phenyl-4-pyridone. **3.** 3-phenyl-4-benzoyl-5-hydroxyisoxazol. **4.** benzoylacetone.

ClO_4^- instead of NO_3^- (54). With the help of IR, PMR, and ^{31}P NMR spectroscopies, the extraction of In(III) from Cl^-/ClO_4^- media by differently substituted 4-acyl-5-hydroxypyrazoles and TOPO (55) has been established to occur as in Eq. (7), with $0 < x < 3$.

$$\mathrm{InCl}_{x(\mathrm{aq})}^{(3-x)+} + (3-x)\mathrm{HL}_{(\mathrm{org})} + 2\mathrm{TOPO}_{(\mathrm{org})} \leftrightarrow \mathrm{InCl}_x\mathrm{L}_{3-x}(\mathrm{TOPO})_{2(\mathrm{org})} + (3-x)\mathrm{H}^+ \quad (7)$$

The 1-phenyl-3-methyl-4-benzoyl-5-hydroxypyrazole proved to be the most efficient extractant for In(III) among those tested (55). The In(III) complexes with a bis-derivative of this type, namely bis(1-phenyl-3-methyl-5-hydroxypyrazol-4-oyl)octane, have also been prepared and tentatively described by use of techniques such as IR, ^1H and ^{31}P NMR spectroscopies (56).

Substituted 3-hydroxy-4-pyridone derivatives have also been used for In(III) extraction from acidic chloride solutions (58–60); the chemical reactions involved are of the same type as that seen in Eq. (4). The 3-hydroxy-2-methyl-1-phenyl-4-pyridone compound and its respective In(III) complex (58,59) showed some degree of dissolution on the aqueous phase, therefore more hydrophobic extractants of a similar type have been synthesized and characterized, and their extraction properties towards In(III) have been evaluated (59).

Simple β-diketones have also been applied to In(III) extraction. While acetylacetone and benzoylacetone efficiently extracted both Al(III) and In(III) from a sodium perchlorate solution, it has been shown that only Al(III) is extracted if α-phenylacetylacetone or α-phenylbenzoylacetone are used instead, under similar experimental conditions (61,62). This demonstrates the importance of the O···O distance in the chelate ring for metal ion size recognition (61–63). Equation (4) also applies for extraction of In(III) by these modified β-diketones (61,62). When acetylacetone was used in combination with 3,5-dichlorophenol for Ga(III) and In(III) extraction, it was found that the aromatic alcohol acted as synergist, leading to the formation of outer-sphere complexes with a composition of the type $ML_3{\cdot}nDCP$ ($1 < n < 3$), M being In(III) and Ga(III), and L the conjugated base of acetylacetone, HL. The synergic mixture can be used to separate the latter two metal ions from Al(III) (64).

Substituted 4-acylisoxazol-5-ones have also been applied to In(III) extraction (67,68), either from a nitrate or from a concentrated chloride media. Hence, five different 4-acyl-3-phenylisoxazol-5-ones have been synthesized and their particular characteristics as extractants for group 13 metal ions have been fully evaluated (67). It was found that complexes of the type InL_3 were always formed with the isoxazol derivatives tested. The same results were achieved when In(III) was extracted by 3-phenyl-4-benzoylisoxazol-5-one (HPBI), both from nitrate and concentrated chloride media (68). However, the presence of chloride anions dramatically decreased the free In^{3+} concentration in the aqueous phase, lowering the extraction efficiencies markedly. When TOPO was mixed with HPBI, there was always synergism for In(III) extraction: moderate for nitrate medium (68), as seen in Eq. (8),

$$In^{3+}_{(aq)} + 3HPBI_{(org)} + 2TOPO_{(org)} \leftrightarrow In(PBI)_3(TOPO)_{2(org)} + 3H^+ \qquad (8)$$

and strong for chloride solutions, whose equilibria can similarly be expressed by Eq. (7) (68), with HPBI = HL and $0 < x < 3$.

Compounds of the N-alkylcarbonyl-N-phenylhydroxylamine type have been synthesized and tested as extractants of several metal ions, including In(III) (70). It was found that the extracted complexes could be nonadduct, ML_3, or self-adduct, $ML_3(HL)_x$, with x varying between 1 and 3, but this data may not specifically refer to In(III) (70). The same ML_3 composition has also been observed for In(III)-alkyltropolone complexes (71).

Hydroxyoximes, specially known for their specific ability to extract Cu(II) from sulfuric solutions (3,4), have also been studied for In(III) extraction (22,73–75). For either LIX 973N (22) or LIX 984 (74), it was found that the extracted species had an InL_3 composition, L being the conjugated base of the hydroxyoxime, HL. The addition of neutral donors to β-hydroxynaphthaldoxime caused a synergistic effect on In(III) extraction, and the respective adduct formation constants have been calculated (75).

Finally, it must be mentioned that extractants such as 8-quinolinol derivatives (76,77) have been employed as a means to establish analytical methods for indium determination. Furthermore, In(III)-substituted dithiocarbamate complexes, obtained by SX (78–80), have also been reported.

Solvating Organic Reagents: Formation of Solvation Species

Tri-n-butylphosphate (TBP), tri-n-octylphosphine oxide (TOPO), and methylisobutylketone (MIBK) are the best-known solvating extractants, frequently used for extraction of several metal ions, including In(III). Table 3 presents a summary of the most relevant SX systems developed for indium recovery involving solvating extractants, and follows the same type of data presentation as the earlier tables.

The process of extracting In(III) with TBP has been known for a long time (81–89). When the metal ion is extracted from hydrochloric acid or chloride solutions, its distribution coefficient is enhanced by increasing concentrations of HCl. Proposals have been made for the composition of the extracted species such as $InCl_3 \cdot n\mathrm{TBP}$ ($2.3 < n < 2.5$) until 6 M HCl and $HInCl_4 \cdot n\mathrm{TBP}$ at higher HCl concentrations (83). The extraction reaction proposed in Eq. (9) (86,88) is in general accordance with those data.

$$InCl_{3(aq)} + 3TBP_{(org)} \leftrightarrow InCl_3 \cdot 3TBP_{(org)} \tag{9}$$

A salting-out effect occurred in In(III) extraction by TBP when ammonium or magnesium chloride were present in the aqueous phase (86). For the metal extraction from HCl, HBr, and thiocyanate media, stoichiometries such as $HInCl_4 \cdot 2TBP$, $HInBr_4 \cdot 2TBP$, $In(SCN)_3 \cdot 3TBP$, and $NH_4In(SCN)_4 \cdot 2TBP$ have been determined. The treatment and analysis of distribution data in these instances has been completed by use of conductimetric extraction–titrations (87).

TOPO has also been tested for In(III) extraction, always from an HCl medium (55,88–91). The stoichiometries found for the extracted species were $InCl_3 \cdot 2TOPO$ (88–90) and $HInCl_4 \cdot 2TOPO$ (89,91). Similar stoichiometries have been determined for the In(III) species extracted by tri-n-butylphosphine oxide (TBPO) (89). Triphenylphosphine oxide (TPPO) did not extract In(III) from HCl

Table 3. Solvating-type Extractants Used for Indium Extraction

Extractant	Aqueous Phase(s)	Stripping Phase(s)	References	Additional Comments
Tri-n-butyl phosphate (TBP)	Aq. HCl	Aq. HCl	10, 81–89	Separation factor: Sn/In = 100 (82); interference of several ions (10,81); supported liquid membrane (85)
Tri-n-butyl phosphate (TBP)	Aq. bromide, iodide, thiocyanate	—	87	—
Tri-n-octyl phosphine oxide (TOPO)	Aq. HCl	—	55, 88–91	IR (86), IR, and NMR studies (91)
Tri-n-butyl phosphine oxide TBPO)	Aq. HCl	—	89	Several organic diluents
Triphenyl phosphine oxide (TPPO)	Aq. HCl	—	15, 89	In not extracted, but separated from Ga and Tl
Cyclohexanone	Aq. bromide, iodide, thiocyanate	—	87	—
Methylisobutyl ketone (MIBK)	Aq. chloride, iodide, HBr, H_2SO_4	Aq. HNO_3	16, 87, 92–94	Interference of Sn, Bi, Sb, Ga, As, and other metal ions (16, 92–94)
Mesityl oxide	Aq. HCl, and HBr	—	95	Sb(III), SCN^-, and $C_2O_4^{2-}$ interfere; separation and determination of Ga, In, and Al
Diethylether, diisopropylether	Aq. HCl, and HBr	6M HCl	4, 11, 96	Raman studies (11)
Tris(2-ethylhexyl phosphate)	Aq. sodium salicylate	H_2O	97	Separation and determination of Ga, In, and Al
Triphenylarsine oxide (TPASO)	Aq. sodium salicylate	H_2O	98	Separation and determination of Ga, In, and Al

solutions as the other phosphine oxides did (15,89); this fact easily allowed the separation of Ga(III) and Tl(III) from In(III), with the latter remaining in the aqueous phase (15).

Methylisobutylketone (MIBK) has also been used as an efficient extractant for In(III), but SX is normally included only in an analytical method (16,92–94). This may explain why adequate stripping media have been developed, even while any information related to the extraction reactions is still missing.

Similar analytical purposes can be understood from research work on the use of SX to extract In(III) by mesityl oxide (95), diethyl and diisopropyl ethers (4,11,96), tris(2-ethylhexylphosphate) (97), and triphenylarsine oxide (TPASO) (98). However, for the two latter reagents, the equilibria involved in the extraction of the metal ion from salicylate medium has been established, as shown in Eqs. (10–12), and seem to be identical for both extractants (where L = extractant and Sal^{2-} = salicylate anion).

$$In^{3+}_{(aq)} + Sal^{2-}_{(aq)} \leftrightarrow InSal^{+}_{(aq)} \qquad (10)$$

$$InSal^{+}_{(aq)} + HSal^{-}_{(aq)} \leftrightarrow (InSal^{+}HSal^{-})_{(aq)} \qquad (11)$$

$$(InSal^{+}HSal^{-})_{(aq)} + 2L_{(org)} \leftrightarrow (InSal^{+}HSal^{-})\cdot 2L_{(org)} \qquad (12)$$

Although there are several examples of solvating reagents that can be used to extract In(III), this type of organic compound is also currently used as an extractant of many other metal ions (3,4), therefore selectivity patterns towards In(III) extraction involving the conventional solvating compounds only may be quite difficult to establish.

Basic Organic Reagents: Formation of Ion Pair Species

The most relevant work that describes the use of long-chain alkylamines to extract In(III) has usually been carried out when the metal ion is present in hydrochloric acid or chloride media. For In(III) extraction from these solutions, research related with the acidic- and solvating-type extractants that have been mentioned up to now, considered In^{3+}, $InCl^{2+}$, $InCl_2{}^{+}$, and $InCl_3$ to be the predominant species in weak to moderate concentrated chloride phases. In these cases, the In(III): chloride ratios, when they existed, were maintained in the correspondent extracted species (29,54,55,86–91). Early studies developed to establish the complex formation equilibria between In(III) and chloride ions found that they are, in fact, in accordance with that assumption (99,100).

However, equilibrium data obtained by SX studies on the extraction of In(III) from chloride solutions using long-chain alkylamines (12,14,101–106), ammonium salts (89), or diethyl ether (11), suggested the presence of species containing $InCl_4^{-}$, $InCl_5^{2-}$, and $InCl_6^{3-}$ moieties in the organic solution. These species motivated a certain polemics in the evaluation of In(III) speciation in aqueous chloride media. It is understood that features such as HCl concentration, amine structure, amine total concentration, and the nature of the organic diluent can lead to different SX equilibria. Sometimes, however, the diversity of results found for the stoichiometries of the ion pairs may be intrinsically related to the fact that the association of the extractant and extracted species in diluents of low dielectric constant has not been considered (107,108).

Different types of extraction reactions have been proposed to explain the collected equilibria; however, analysis of IR and Raman data of metal loaded organic extracts only gave evidence for the existence of $\mathrm{InCl_4^-}$ (11,103,104,106,108) and $\mathrm{InCl_5^{2-}}$ (104). For instance, in the extraction of In(III) by tri-n-octylamine reported by Aguilar (107), a composition such as $\mathrm{InCl_3(TOAHCl)_3}$ has been proposed for the extracted species, but equilibrium data could similarly suggest something such as $\mathrm{InCl_6^{3-}\cdot 3TOAH^+}$.

In summary, distribution and spectroscopic data point out that the reactions involved in In(III) extraction from concentrated chloride media by amine salts can be generally expressed by Eqs. (13) and (14) (103,105,106,108), neglecting any possible initial association of extractant molecules in organic phase or waters of hydration.

$$\mathrm{InCl_{3(aq)} + R_3NH^+Cl^-_{(org)} \leftrightarrow R_3NH^+InCl^-_{4(org)}} \tag{13}$$

$$\mathrm{R_3NH^+InCl^-_{4(org)} + R_3NH^+Cl^-_{(org)} \leftrightarrow R_3NH^+InCl_4^-R_3NH^+Cl^-_{(org)}} \tag{14}$$

In fact, for diluted organic solutions of In(III), ion pairs with a 1:2 metal ion/amine salt relationship have been found, whereas for loading experiments a 1:1 stoichiometry was observed (106). Equation (13) also shows that there is no exchange of anions; what actually occurs is an association of $\mathrm{Cl^-}$ from the amine salt with the neutral metal species, giving rise to $\mathrm{InCl_4^-}$ in the organic phase, frequently identified by IR or Raman (11,104,106). The association of another molecule of amine salt—shown in Eq. (14)—can explain a certain confusion caused by the proposal of extracted species such as $\mathrm{(R_3NH^+)_2InCl_5{}^{2-}}$ (12,102) when evidence for the existence of an In(III) anionic chloride species in aqueous solutions was missing (99,100). In spite of this, a quite recent work reports the identification of penta- and hexa- anionic chloride complexes of In(III) in chloride media, with a concentration up to 5 molal in chloride ion (109).

The structures of several amines tested for In(III) extraction have been well explored, including tri-n-octylamine (12,103,106,107), tri-isooctylamine (101, 102,110), and tri-n-hexylamine (102,104). Commercial mixtures of tertiary amines such as Adogen 364 (108,111) have also been investigated, as well as a commercial primary amine, Primene 81R (102), and the aromatic n-octylaniline (14). Ammonium salts have also been widely used as In(III) extractants; examples of these are tetra-n-butylammonium chloride (89), n-hexylammonium halide (chloride, bromide, iodide, thiocyanate) (105), tetradecyldimethylbenzylammonium chloride (112), Alamine 336 (102), Aliquat 336 (104), and Aliquat (R)-336 (113).

The most recent work on In(III) extraction by tertiary amines involves Adogen 364 (ADG) (108). Assuming that ADG is the amine and ADGHCl the amine salt responsible for the metal ion extraction, evidence was collected for the presence of $ADGH^+InCl_4^-$, $(ADGHCl)ADGH^+InCl_4^-$, and $(ADGHCl)_2(ADGHCl)ADGH^+InCl_4^-$ in the organic phase, where their ratios depend directly on the concentration of ADG and HCl media used. Hence, for the formation of the two latter metal ion species, the presence of dimeric ADGHCl in kerosene solution must be considered. As before, identification of $InCl_4{}^-$ in organic phase has also been achieved by IR (108). The results of this investigation have been applied to the conception of a supported liquid membrane (111), which allowed the establishment of the most adequate conditions for quantitative permeation of In(III); a recovery of 98% for the metal ion has been achieved. Moreover, under the adopted experimental conditions, In(III) was effectively separated from Pb(II) and Cu(II), but not from Cd(II) (111).

The interference of some contaminating ions on In(III) extraction by basic reagents has only been considered in a few cases (14,110), but the efficiency of amine salts to extract other metal ions such as Fe(III) (12,103,104), Co(II) (104), and Ga(III) (102,104), just to mention only a few, is well known.

CONCLUSIONS

From a technological point of view, the acidic-type extractants for In(III) have been deeply explored and diverse SX schemes for the metal ion recovery from sulfuric acid solutions in presence of several other metallic contaminants have been developed and are easily available. Mixtures of phosphorus acids and a few solvating extractants showed interesting synergic effects for In(III) extraction, but fundamental research on that area is currently missing. On the other hand, the collected information on the extraction pathways involving chelating reagents and their synergic mixtures may be an important key feature for future technological developments, despite the lack of current knowledge on selectivity patterns and adequate stripping solutions for In(III) recovery.

One drawback to SX that is sometimes pointed out is that it is a potentially polluting process, due to the involvement of organic solvents. While SX cannot be considered a clean technology, some extraction substances can be more hazardous than others. A progressive replacement of the more toxic phosphorus compounds by specific chelating extractants such as hydroxyoximes or β-diketones would be an important contribution to better industrial waste management.

The chemical behavior of basic-type organic compounds for In(III) extraction from hydrochloric or chloride media is well known, as are the complexation characteristics of In(III) in those aqueous media. This collected information can likely add support for a broader utilization of chloride media in the hydrometallurgical processing of complex sulfide ores (114).

Finally, the knowledge acquired in conventional SX studies can be interestingly applied to relevant and innovative variations to the extraction method. The development of exchange resins and liquid membranes for indium recovery are certainly important approaches that can be economically feasible to treat small quantities of effluents containing the metal.

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