Selective Removal of Gallium from Aqueous Solutions Using Organophosphorus Ligands.

By

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To my dear Wife and to my Parents

ABSTRACT

The removal and recovery of gallium (III) from aqueous solutions was investigated using different ligands. Sodium di-(n-octyl) phosphinate was found to be the most effective ligand. The metal-ligand complexes formed had the advantages of being highly insoluble in water and allowing a good regeneration of the ligand at the end of the cycle. The effect of time, pH, mole ratio of ligand to metal, temperature and the presence of other ions, such as Na^+, NO_3^-, Cl^- and SO_4^{2-}, was also studied. At the end of the removal process, gallium was recovered from the insoluble complexes using a solvent. The gallium was concentrated in an aqueous phase. The ligand was extracted in the organic phase and regenerated. Other organophosphorus ligands such as sodium di-(n-dodecyl) phosphinate, sodium mono-octyl ester phosphinate and O,O-di-(octyl) dithiophosphoric acid were also synthesised and studied. They were less efficient for the removal of gallium than the sodium di-(n-octyl) phosphinate ligand. The possibility of using compounds with a carboxylic group on the removal of gallium was also investigated using humic and fumaric acids.

The removal with sodium di-(n-octyl) phosphinate of other metals such as aluminum, indium, iron, calcium and zinc, found in the mining and electronic effluents with gallium, was considered. A good selectivity of the ligand for the gallium over the other metals was obtained. A process was proposed for the electronics industry to treat gallium arsenic effluent.

Finally a mathematical model was established to describe the removal behavior of the metals with the sodium di-(n-octyl) phosphinate ligand.

RESUME

L'enlèvement du gallium (III) de solutions aqueuses et sa récupération ont été étudiés avec différents ligands. De ces ligands, le di-(n-octyl) phosphinate de sodium est le plus efficace. Le complexe métal ligand formé a l'avantage d'être insoluble dans l'eau et de permettre la régénération du ligand en fin de cycle. L'effet du temps, du pH, du ratio molaire ligand/ métal, de la température et de la présence d'autres ions tels que Na^+, NO_3^-, Cl^- et SO_4^{2-}, a été étudié. Après élimination du gallium, le complexe ligand gallium formé est dissous dans un solvant. Le ligand, soluble dans la phase organique, est séparé du métal qui est concentré dans une solution aqueuse. Le solvant est évaporé et le ligand régénéré. D'autres ligands organophosphorés tels que le di-(n-dodecyl) phosphinate de sodium, l'ester mono-octyl phosphinate de sodium et l'acide O,O-di-(octyl) dithiophosphorique ont été aussi synthétisés et étudiés. L'enlèvement du gallium par ces ligands a été moindre qu'avec le di-(n-octyl) phosphinate de sodium. L'enlèvement du gallium d'une solution aqueuse par des composés avec des groupes carboxyliques tels que les acides humique et fumarique a été aussi investiguée.

L'enlèvement d'autres métaux tels que l'aluminium, l'indium, le fer, le calcium et le zinc, avec le di-(n-octyl) phosphinate de sodium a été considéré dans cette étude. Ces métaux sont généralement trouvés combinés avec le gallium dans les effluents miniers et dans ceux de l'industrie électronique. Une bonne sélectivité du ligand pour le gallium a été obtenue par rapport à tous ces métaux. Un procédé a été alors proposé pour traiter les effluents de l'industrie électronique contenant de l'arsenic et du gallium.

Finalement, un modèle mathématique a été établi pour simuler le comportement de l'enlèvement des métaux avec le di-(n-octyl) phosphinate de sodium.

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NOMENCLATURE

C° : initial molar concentration in the volume V°.

C : molar concentration.

Equilibrium pH : calculated or measured pH of a solution at equilibrium.

Final pH : final pH measured at the end of the experiment.

K_{1,CO_2} : equilibrium constant for the dissolution of CO_2.

K_{2,CO_2} : mass stability constant for the HCO_3^- complex.

K_{3,CO_2} : mass stability constant for the CO_3^{2-} complex.

$K_{j\text{-}M}$: mass stability constant for the hydroxide complex of metal M with

$$K_{j\text{-}M} = \frac{C_{M^{m+}} C_{OH^-}^{j}}{C_{M(OH)_j^{m-j}}}$$ where j is the number of OH^-; m is the charge of M.

K_{ML_m} : mass stability constant for the metal-ligand complex, ML_m, where m is the charge of metal M.

$K_{sp,M}$: solubility product of an insoluble metal-hydroxide complex.

$K_{sp,ML}$: solubility product of an insoluble metal-ligand complex.

K_w : water dissociation constant.

L_C : percentage loss of carbon (percentage of carbon remaining in solution) associated to a carboxylic ligand (humic or fumaric acid).

L_L : percentage loss of ligand (percentage of ligand remaining in solution).

M : metal (gallium, aluminum, indium, iron, calcium, zinc, arsenic).

MW : molecular weight.

n_C° : total initial number of moles of carbon (associated to a carboxylic ligand) added to the aqueous solution.

n_C : total number of moles of carbon present in the aqueous solution after filtration.

$n_{C_{R_2POONa}}$: total number of moles of carbon, associated to the R_2POONa ligand, present in the aqueous solution after filtration.

n_L° : total initial number of moles of ligand added to the aqueous solution.

n_L : total number of moles of ligand present in the aqueous solution after filtration.

n_M° : total initial number of moles of metal added to the aqueous solution.

n_M : total number of moles of metal present in the aqueous solution after filtration.

n_M^P : number of moles of metal in the insoluble complex at the end of the experiment.

$n_{ML_{3(s)}}$: total number of moles of insoluble metal-ligand complex.

$n_{M(OH)_{m(s)}}$: total number of moles of insoluble metal-hydroxide complex.

$n_{HL_{(s)}}$: total number of moles of insoluble acidic form of ligand.

pH° : calculated pH of the mixture of the ligand stock solution and of the initial metal solution before any complexation.

pH_A : calculated pH of the metal solution (metal stock solution+ distilled water + acid or base + salts), assuming that the metal is in its ionic form without hydroxyl complex formation.

pH_i : pH of the metal solution measured immediately after mixing the metal stock solution, the distilled water, HNO_3 or NaOH and in some cases, salts.

pH_X : pH of the mixture of the ligand stock solution and of the initial metal solution measured after X days (after complexation).

r° : initial mole ratio of ligand to total metals.

R_C : percentage removal of carbon.

R_L : percentage removal of the ligand.

$r^\circ_{M_1/M_2}$: initial mole ratio of compound M_1 to compound M_2.

R^*_M : fractional removal of metal.

R_M : percentage removal of metal.

V° : total volume of the solution.

V_a : volume of acid solution.

V_b : volume of base solution.

V_i : volume of the metal solution (metal stock solution+ distilled water + acid or base + salts).

V_L : volume of ligand stock solution.

V_{ms} : volume of metal stock solution + volume of distilled water.

w_o : water uptake.

$wt\%_{KF}$: weight percent of water in organic phase measured with Karl Fisher titrator.

$\alpha_{Ga/M}$: molar selectivity for Ga relative to an other metal M.

$\Delta\nu$: difference between the asymmetric and the symmetric POO^- infrared stretching frequencies [$\nu_{asym}(POO^-)$- $\nu_{sym}(POO^-)$].

Φ : ionic potential of the metal ion defined as [charge /ionic radius].

ρ : density of the ligand (g/L).

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INTRODUCTION

1.1 Gallium

Discovered in 1875, gallium is now mainly used in the electronics industry. The physical and electrical properties of its crystalline compounds (mostly GaAs and GaP) make them unique semiconductors that have found applications in numerous integrated circuits, where high speed and high operation frequencies are demanded (Kramer, 2002). Gallium arsenide, for example, is used in optoelectronic devices such as light emitting diodes (LEDs) due to its electro-luminescence. It is also used for laser, solar cell, and microwave devices. Kramer (2002) also reports a number of new promising developments such as the use of gallium nitride in lasers, the use of GaAlAs alloy in quantum dot lasers emitting visible light, and the use of an In-Ga-P-As combination in photovoltaic devices. Due to this increasing demand for gallium in electronics, the recovery of Ga (III) from different primary and secondary sources is of importance. While gallium is not rare and its abundance in the earth's crust is equivalent to that of lead, gallium occurs in very small amounts in rocks and ores of other metals making its recovery challenging.

The main sources of gallium are from the waste streams of the aluminum and zinc industries where it is recovered as a by-product (Puvvada, 1999; Nishihama *et al.*, 1999; Carvalho *et al.*, 2000). In the aluminum industry, gallium is associated with aluminum in bauxite ores to the extent of 0.002-0.008 % (20 to 80 mg/kg) (Chaves *et al.*, 2000). Puvvada (1999) reported a Bayer process liquor containing ≈ 450 g/L (7300 mM) of Na_2O, ≈ 80 g/L (800 mM) of Al_2O_3 and ≈ 0.2 g/L (1.1 mM) of Ga_2O_3. A solution from a Brazilian aluminum plant had an average composition of 0.1-0.11 g/L (0.5-0.6 mM) of Ga_2O_3, 10-25 g/L (100-250 mM) Al_2O_3 and 108-120 g/L (1700-1900 mM) Na_2O (Borges and Masson, 1994). At these concentrations, the gallium can be recovered from the liquor. It should be noted that a certain percentage of gallium co-precipitates with aluminum hydroxide, the degree of co-precipitation depending on the characteristics of the aluminum solution.

In zinc refinery residue, gallium is present at a trace level. Zinc, iron, lead, copper, cadmium, calcium and aluminum are present in the residues at higher concentrations (Lee *et al.*, 1994; Chegrouche *et al.*, 2001). For this reason, the recovery of gallium from waste of the zinc industry is a more complex process than the recovery from the aluminum industry. The conventional hydrometallurgical process used for recovering zinc and the other metals consists in leaching the zinc ore (ZnS) with H_2SO_4, followed by a separation where the pH is raised to favor the precipitation of the metals.

Electronics industry scrap contains a limited number of impurities, and gallium can be as much as 48 % of the scrap (Lee and Nam, 1998). Various trace metal elements such as indium are reported in Table 1.1. The manufacture of wafer compound semiconductors requires the use of gases such as arsine (AsH_3), phosphine (PH_3) and trimethyl (or triethyl) gallium to deposit thin metal layers on the surface of the wafer. Unconsumed gases may be treated by combustion followed by wet scrubbing (Van Gompel, 2001). However, this process produces a heavily contaminated wastewater containing arsenic (H_3AsO_4) and salts of indium, gallium and aluminum. Treatment of this waste stream is necessary before discharge. The arsenic released in water is strictly regulated with a maximum contaminant level of 0.01 mg L^{-1}, while gallium has a low toxicity but its recovery is desirable for its economic value (Meshalkin *et al.*, 1998; EPA, 2002).

Table 1.1: Chemical analysis of gallium arsenide scrap (Lee and Nam, 1998)

	Ga	As	P	In	Sn	Mg	Ca	Pb	Al	Mn
Content wt %	48.6	51.2	$\times 10^4$							
			24.0	17.0	6.0	2.9	2.7	1.6	1.3	0.9

Other potential sources of gallium are from ash, which can contain as much as 100 mg/kg of the metal (Fang and Gesser, 1996). The dusts generally contain some trace of gallium along with high amount of Al, Fe and Ca, but due to the high concentrations of impurities, the removal of gallium is difficult (Fang and Gesser, 1996; Gutierrez *et al.*, 1997). Gutierrez *et al.* (1997) reported concentrations of gallium between 10 and 30 mg/L (0.14 and 0.43 mM) and between 20 and 100 mg/L (0.30 and 1.53 mM) of zinc in the leachate of coal ash.

Chloride, sulfate, sodium and calcium are some of the common ions found in aqueous waste streams containing gallium. Mining liquors, from which gallium can be recovered, usually contain around 10 mg/L (0.25 mM) of calcium. This impurity is also found in the final gallium product (Lee *et al.*, 1994).

Due the high price of gallium in 2000-2001, companies such as Canyon Resources Inc. and Win-Eldrich Mines Ltd prospected for properties where gallium could be recovered as the principal product. Levels from 20 to 224 mg/L (0.3 to 3.2 mM) were found but no commercial production resulted (Kramer, 2002).

1.2 Removal methods

Due to the variety of sources of gallium, different processes are used to separate and concentrate it. The recovery of metals from aqueous solutions can be achieved by different types of processes (Liu, 1997; Nakayama and Egawa, 1997; Robins et al., 2001; Bhattacharyya *et al.*, 1999; Chegrouche and Bensmaili, 2002):

- Precipitation
- Oxidation /reduction
- Membrane technology
- Ion exchange
- Solvent extraction
- Adsorption

In order to treat GaAs wastewater, the gallium is removed first followed by the arsenic (Jadvar *et al.*, 1991; Lee and Nam, 1998; Peterson, 2000; Gompel, 2001). In solution, arsenic exists in the -3, 0, +3, and +5 oxidation states but the predominant aquatic forms are trivalent arsenite (+3) and pentavalent arsenate (+5). Depending of the pH and its oxidation state, the arsenic forms different complexes in aqueous solution such as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} for the arsenate (Fields *et al.*, 2000).

Precipitation, adsorption and cementation are some of the processes generally adopted for the removal and disposal of arsenic (Mortazavi *et al.*, 1999; Riveros *et al.*, 2001). The most common methods to precipitate arsenic from aqueous process streams are as calcium arsenate, arsenic sulfide or ferric arsenate (Bhattacharyya *et al.*, 1979;

Robins *et al.*, 2001). Arsenic sulfide, As_2S_3, has its lowest solubility below pH 4 but it is generally not disposed of as such, as it is easily oxidized and its solubility increases above pH 4 (Nishimura *et al.*, 2000). Calcium arsenate, on the other hand, precipitates at basic pH (> 8) but is not stable with respect to CO_2 in the atmosphere. The calcium arsenate is converted into calcium carbonate releasing soluble arsenic acid through the following reaction (Riveros *et al.*, 2001):

$$Ca_3(AsO_4)_2 + 3\ CO_2 + 3\ H_2O \longleftrightarrow 3\ CaCO_3 + 2\ H_3AsO_4 \qquad (1.1)$$

Calcium arsenate synthesized at higher temperatures exhibits solubility similar to compounds such as pharmacolite ($CaHAsO_4.2H_2O$) and guerinite ($Ca_5H_2(AsO_4)_4.9H_2O$) formed at lower temperature.

Thus for arsenic disposal, industry currently favors the formation of insoluble ferric arsenate compounds which are removed by filtration (Filippou and Demopoulos, 1997). The Fe(II) and As(III) can be first oxidized, as the metal arsenate is generally less soluble. The As(V) is then removed by adsorption and/or co-precipitation with iron hydroxide. The removal efficiency is directly related to the iron concentration (Fields *et al.*, 2000). This adsorption and/or co-precipitation process is also used for the treatment of GaAs polishing wastes where As is removed from the aqueous solution by ferric hydroxide (Sturgill *et al.*, 2000).

In solvent extraction, a mixture of metals is separated from an aqueous solution into an immiscible organic phase by formation of an organic salt or a chelate compound (Mihaylov and Distin, 1992 a). Solvent extraction has attracted significant attention due to its ability to recover selectively metals at low concentration. The first commercial operations using solvent extraction for gallium involved the recovery from acid chloride leach solutions into ethers by Sheka *et al.*, (1966). In their study, gallium was extracted from the aqueous phase into the organic solvent as the acid complex $HGaCl_4$. Complete removal of the gallium into the diethyl ether was obtained with 5.5 – 6 M HCl giving a good selectivity over the main co-existing elements except for germanium, gold and iron (III) (Sheka *et al.*, 1966). The organophosphorus acids have been used in solvent extraction and hydrometallurgy for the separation and recovery of metals (Owusu, 1998; Nishihama *et al.*, 1998). As an example, American Cyanamid developed phosphinic acid reagents for cobalt-nickel separation (Dreisinger and Cooper, 1984). Preston (1982) showed the importance of the solvent by studying the effect of xylene compared to *n*-heptane. Organophosphorus compounds, such as octyl phenyl acid phosphate (OPAP) mono and di-2-ethylhexyl phosphoric acid, M2EHPA and D2EHPA, respectively, are also suitable extractants for gallium (Mihaylov and Distin, 1992 b and 1995). The solvent extraction process can be combined with other processes such as ion exchange or precipitation to provide selective separation and concentration of individual metals. However, the extraction and the back extraction process can be slow (Sekine and Hasegawa, 1977), and also undesirable in industry due to the use of a flammable organic phase (Mihaylov and Distin, 1992 a). Furthermore, extraction cannot be used at high temperature because the solvents are generally volatile and the distribution coefficient generally decreases with temperature (Mihaylov and Distin, 1992 b). Another limitation of this process is the residual organic solvent and expensive extractant that can remain in the treated wastewater.

1.3 Affinity of a ligand for metal ions

The affinities of metal ions for ligands containing negatively charged oxygen donor atoms are strongly related to their affinity for the hydroxide ion. The value of log $K_{1,M}$ for a particular metal ion is therefore useful for describing its complexing behaviour with ligands containing negative oxygen donors. For the following reaction:

$$M^{m+} + OH^{-} \overset{K_{1,M}}{\longleftrightarrow} M\,(OH)^{m-1} \qquad (1.2)$$

where M is a metal, m is the charge and $K_{1,M} = \frac{C_{M^{m+}} C_{OH^-}}{C_{MOH^{m-1}}}$, the size and the charge of a metal ion are important in determining the affinity of hydroxide for a metal ion and the associated stability constant. The greater the charge on the ions and the smaller the ions, the greater should be the affinity. From this point of view, small ions of the same charge are favored and the stability of complexes should increase with the charge on the metal ions. An illustration of the effect of the charge is shown in Table 1.2. The stability of hydroxide complexes increases with the charge of the metal ion as the logarithm of $K_{1,M}$ decreases (becomes more negative). While an effect of the charge on the stability constant is obvious in Table 1.2, there is not a simple dependence between the metal ion radius and log $K_{1,M}$ for ions of the same charge. In Table 1.3, log $K_{1,In}$ value does not follow the expected trend.

Another approach to estimating the preference of individual metal ions for ligands depends on the charge density of the metal and ligand. Different classifications are proposed in the literature. In early studies, metal ions were classified under A and B type depending on their relative affinity for ligands in aqueous solutions (Schwarzenbach, 1961). These two types, A and B, were later renamed as hard and soft, respectively, as

Pearson developed the Hard and Soft Acids and Bases principle (HSAB) (Pearson, 1963 and 1987). The HSAB concept is a simple and useful method to estimate relative stabilities of complex ions. According to this principle, H^+ is a very small ion and it has a very high charge density. So, species that react strongly with it are called strong bases. Metals that are like H^+ should behave in a similar way. These metals are called class A metals or hard metals. Following this classification, metal ions referenced as soft or B type (e.g. Cd^{2+}, Hg^{2+}) prefer to complex with soft bases such as phosphorus which are less electronegative donor atoms. The hard metal ions, such as Ga^{3+} and Al^{3+}, form complexes with hard bases such as oxygen which are more electronegative donor atoms.

Table 1.2: Effect of the charge of the metal ion on $K_{1,M}$ (Martell and Hancock, 1996)

Metal	log $K_{1,M}$
Li^+	-0.36
Mg^{2+}	-2.58
Y^{3+}	-6.3
Th^{4+}	-10.8

Table 1.3: Effect of the radius of the metal ion on $K_{1,M}$ (Martell and Hancock, 1996)

Metal	Ionic Radius (Å)	log $K_{1,M}$
Al^{3+}	0.54	-9.1
Ga^{3+}	0.62	-11.4
Fe^{3+}	0.65	-11.8
In^{3+}	0.8	-10.0
Ti^{3+}	0.89	-13.4

Metal ions at the borderline show no preferences and can complex with hard or soft bases. Most stable complexes are formed when the metal and ligand have similar charge densities, i.e., hard with hard; soft with soft. In a similar way, metals with low charge densities (soft or class B) prefer large, polarizable ligands, for they too have low charge density. The classifications of some Lewis acids and bases are given in Table 1.4.

Table 1.4: Classifications of Lewis acids an bases

Classification of some Lewis Acids (Pearson, 1963)

Hard	**Borderline**	**Soft**
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}, Co^{3+}, As^{3+}, Si^{4+}, Ti^{4+}, Zr^{2+}	Fe^{2+}, Co^{2+}, Ni^{2+} Cu^{2+}, Zn^{2+}, Pb^{2+}	Cu^+, Ag^+, Au^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, $Co(CN)_5^{2-}$, Pt^{4+}, BH_3, $GaCl_3$, I_2, Br_2, ICN

Classification of some Lewis Bases (Pearson and Songstad, 1967)

Hard	**Borderline**	**Soft**
H_2O, OH^-, F^-, $CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, ClO_4^-, NO_3^-, ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_3^- NO_2^-, SO_3^{2-}	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, CN^-, CO, $(RO)_3P$, C_2H_4, H^-, R^-

where R is an alkyl chain

Finally the consideration of the electronic interactions of metals and ligands is also useful in interpreting their affinity. For example, the presence of the $3d^{10}$ electron core in zinc makes the cation much more strongly polarizing than the corresponding ion of Group 2, Ca^{2+}. Thus zinc tends to have many of the properties associated with tripositive Group 13 ions such as Al^{3+} and Ga^{3+} (Massey, 2000).

1.4 Organophosphorus acids and sodium phosphinates

The extraction of metal ions (Mason *et al.,* 1970) from an aqueous phase into an organic solution using organophosphorus acids is well established. Organophosphorus acids are generally viscous liquids, slightly soluble in water but highly soluble in many organic solvents (De *et al.*, 1970). Thus, different media and different solvents were used to enhance the extraction of metal ions with organophosphorus ligands.

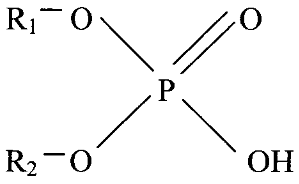
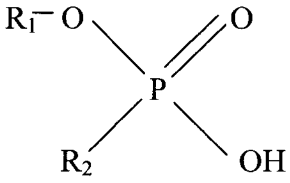
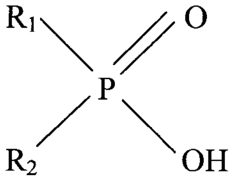
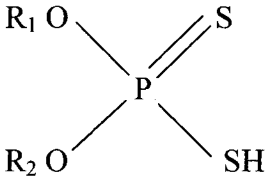
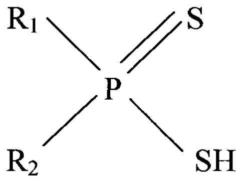
The structure of the organophosphorus extractant is important as the extractant can have a better affinity for the metal and thus increase the extraction efficiency. The generic formulas and their corresponding names are shown in Table 1.5. Peppard *et al.* (1959) and Preston (1982) reported that the direct C-P bond enhances the liquid-liquid extraction properties of the extractant and thus the extraction efficiency follows the order (Preston, 1982): Di-alkyl phosphinic > Di-alkyl phosphonic > Di-alkyl phosphoric

Using a phosphinic acid and its sulfur analogues, Wang *et al*, (1996) showed a good affinity of these organophosphorus extractants for gallium.

However, the use of organophosphorus compounds in the extraction processes can be limited by:

- the oxidation of the organophosphorus compounds which produces new but generally less efficient organophosphorus compounds (Rickelton *et al.*, 1998).
- the formation of a dimer in the organic phase (Danesi *et al.*, 1985), as depicted in Figure 1.1, which inhibits the removal of the metal.

Table 1.5: Various families of organophosphorus compounds (R_1 and R_2 are alkyl chains). Asterisks indicate the references where the use of a compound is mentioned.

Acid's Name	Formula
Di-(alkyl) phosphoric*	
Di-(alkyl) phosphonic*	
Di-(alkyl) phosphinic*	
Di-(alkyl) dithiophosphoric**	
Di-(alkyl) dithiophosphinic***	

*Danesi *et al.*, 1985

** Marcu *et al.*, 1977

*** Khoshkbarchi and Vera, 1995

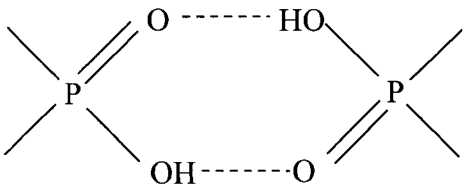


Figure 1.1: Dimeric form of the organophosphosphorus ligand present in a solvent (Danesi et al., 1985).

- the formation of a crud at the solvent/aqueous phase interface which inhibits the extraction and represents a loss of the extractant and of metal.

As an example, Rickelton *et al.* (1998) reported that the oxidation of the dithiophosphorus compounds forms a sulfur-sulfur bond in presence of ferric ions at concentrations below 2 mg/L.

Based on the properties of these organophosphorus compounds, Esalah *et al.* (2000 a) used sodium phosphinate ligands to form insoluble complexes with heavy metal ions (Pb^{2+}, Cd^{2+} and Zn^{2+}) in an aqueous solution. Esalah (1997) investigated the removal of these heavy metals with two different ligands, sodium di-(n-octyl) phosphinate and sodium di-(n-dodecyl) phosphinate, both with straight alkyl chains but, different chain lengths. The purpose of Esalah's studies was to overcome some disadvantages associated with other techniques, such as the formation of soluble metal sulfide species at excess dosage of sulfide, the long equilibrium time for the precipitation of metals as hydroxides, the sensitivity of the membrane material to acid or salt solutions for the membrane process, and the interference of other metal ions in ion exchange resins (Volesky, 1990; EPA, 1997).

The ligands reacted with the metal ions following the reaction:

$$M^{2+} + 2\,L^{-} \longleftrightarrow ML_{2\,(S)} \qquad (1.3)$$

where M^{2+} is Pb^{2+}, Cd^{2+} or Zn^{2+} and L^{-} is the sodium phosphinate ligand (Esalah, 1997). The ligand was selective to these metals in the order Zn > Pb > Cd and the insoluble ligand-metal complex was easily filtered.

Increasing the chain length of the sodium di-(n-alkyl) phosphinate gave more complete removal of the heavy metals (Esalah, 1997). At low pH (below 3), the ligands became insoluble and the metal removal decreased. Similar effects of the chain length and the pH were also obtained with the di-(alkyl) dithiophosphoric acids in the extraction process (Marcu *et al.*, 1977), but no study has examined the complexation of these acidic compounds or their sodium salts with metal ions.

Some studies were performed on the magnetic concentration and polymorphism of the metal-di-(n-alkyl) phosphinate complex (Haynes *et al.*,1985). Due to the lack of precise structural data from X-ray diffraction studies, infrared spectra were used by Ferraro *et al.* (1998) and Haynes *et al.* (1985). In the infrared spectrum, two POO^{-} stretching modes are present in organophosphorus metal complexes and are designated as the asymmetric and the symmetric POO^{-} stretching vibrations, denoted $\nu_{asym}(POO^{-})$ and $\nu_{sym}(POO^{-})$, respectively. The frequency difference between these two bands, $[\nu_{asym}(POO^{-}) - \nu_{sym}(POO^{-})]$, is denoted $\Delta\nu$ (cm^{-1}). The POO^{-} stretching region is generally observed between 950 and 1300 cm^{-1} in the infrared spectrum. These two POO^{-} stretching modes are useful in making comparisons between different metal ions complexed with the phosphinic ligands. However, the correlation between $\Delta\nu$, the ratio of the charge over the radius of the ion, Φ, and the type of bond between the ligand and the metal has some limitations. While both oxygen atoms of the ligand must interact with the metal ion to form the $\nu_{asym}(POO^-)$ and $\nu_{sym}(POO^-)$ bands, structural differences such as the formation of complex polymeric species can affect the absorption bands (Haynes *et al.*, 1985).

The other stretching mode that can be of interest for phosphinate groups is the PC_2 with a stretching region between 700 and 800 cm^{-1}. Like the POO^-, the PC_2 has an asymmetric and a symmetric stretch band. Haynes *et al.* (1985) studied the infrared spectum of the $Cu[(n\text{-}C_8H_{17})_2PO_2]_2$ and reported the $\nu_{asym}(PC_2)$ band in the 770-805 cm^{-1} region and the $\nu_{sym}(PC_2)$ band at around 725 cm^{-1}.

In the case of the metal-O stretching band, the vibrations are generally below 400 cm^{-1} and thus required the use of a Far-infrared. However, the bands associated with the metal-O are not very strong and can be difficult to identify (Pitts *et al.*, 1969; Haynes *et al.*, 1985; Ferraro *et al.*, 1998).

1.5 Carboxylic group: humic and fumaric acids

Both fumaric and humic acids are known to form complexes with metals (Navon *et al.*, 1997; Oste *et al.*, 2002). While humic acid is generally a result of the decay of vegetation, fumaric acid ($C_4H_4O_4$) is an organic acid widely found naturally in many plants. Fumaric acid contains two acid carbonyl groups (Figure 1.2). It is used widely in chemical manufacture, in the food processing and feed additive industries (Felthouse *et al.*, 2001).

Humic acid is composed of a mixture of compounds. Typically, humic acid contains both hard (e.g. carboxylic, phenolic) and soft (e.g. nitrogen- and sulfur-containing) complexing sites (Filella and Town, 2001).

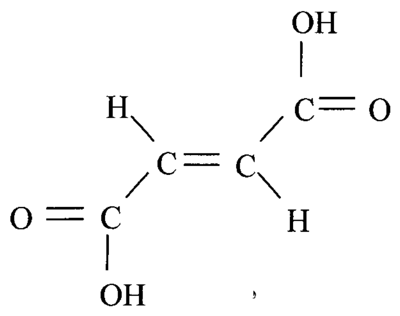


Figure 1.2: Structure of fumaric acid.

However, carboxylic and phenolic groups are the most important ionizable sites present in humic substances and are likely to determine many of the properties of proton and metal ion binding exhibited by these materials in natural waters, soils and sediments. Humic substances are active in binding ions, organic molecules, and mineral surfaces and are thereby potentially important to soil structure, soil fertility, and transport of pollutants in natural waters. Humic substances influence soil and water properties by interaction with other molecules and ions (complexation/decomplexation), with solid surfaces (adsorption/desorption), and among themselves (aggregation/disaggregation). They can act, for example, as effective chelating agents for metal ions, particularly Fe (III) but also Cu (II) and Pb (II) (Christl *et al.*, 2001 a). The humic substances are generally extractable in NaOH, and some of its compounds precipitate at acidic pH (Swift, 1996).

1.6 Motivation

Due to the growing demand for gallium and its high price, its recovery is important (Mihaylov and Distin, 1992 a; Hirayama *et al.*, 2001). The main sources of gallium are from the mining industry where it can be recovered from solutions of the aluminum and zinc industries and from electronic scrap where it is mainly used in semiconductor materials. While the mining solutions contain impurities such as calcium, iron and traces of indium, the electronic wastes are mainly composed of gallium and arsenic. The removal of gallium from aqueous solutions by formation of an insoluble complex with a ligand rather than by extraction is promising because it allows the reduction in the use of a hazardous organic solvent and in the loss of expensive extractant in the aqueous phase.

1.7 Objectives

The thesis aimed at:

- Investigating the use of different organophosphorus ligands on the removal by complexation of gallium from aqueous solutions and selecting the best ligand.
- Separating the gallium from the ligand and regenerating the ligand.
- Studying the selectivity of the ligand for gallium over other metals.
- Investigating the application of the best ligand for mining and electronic applications.
- Describing the removal of metals using a stability constant approach.

Based on the affinity of organophosphorus extractants for gallium (Wang *et al.*, 1996), the sodium di-(n-alkyl) phosphinate, referred to as R_2POONa, and two other organophosphorus ligands, O,O-di-(alkyl) dithiophosphoric acid, referred to as $(RO)_2PSSH$ and sodium mono-alkyl ester phosphinate, referred to as (RO)POOHNa were investigated. All of these ligands had straight alkyl chains. While the octyl and a dodecyl carbon chains of R_2POONa were used to see their effect on the removal of the metal, only the octyl forms of $(RO)_2PSSH$ and (RO)POOHNa were studied.

Commercial humic and fumaric acids, which have lower molecular weights than the organophosphorus ligands, were also tested to study the affinity of the carboxylic group for metals and its effect on the removal of the metal from a solution. The results were compared to the organophosphorus ligands.

Further studies were performed to investigate the use of the ligand with the best gallium removal efficiency for the mining and electronic industries.

1.8 Outline of the thesis

Chapter 2 describes the experimental methods for the synthesis and purification of the different ligands used, as well as the experimental procedure for the removal of a metal ion with a ligand, the recovery of the metal and the regeneration of the ligand. The analytical methods and the notation and quantities calculated from the data are also described in this chapter.

Chapter 3 includes the results for the removal of single metal ions from an aqueous solution. The results are organized into three parts: the removal of gallium with the sodium di-(n-octyl) phosphinate ligand under different conditions, the removal of gallium with other ligands (organophosphorus and carboxylic) and the removal of other metal ions with the sodium di-(n-octyl) phosphinate ligand.

Chapter 4 presents the selective removal of gallium from multi-metal ion solutions using the sodium di-(n-octyl) phosphinate ligand. Four solutions are considered: solutions containing zinc, aluminum, or calcium and wafer wastewater solution. The affinity of the ligand for a metal is then discussed.

Chapter 5 describes the removal of metal ions from an aqueous solution using the sodium di-(n-octyl) phosphinate ligand based on the “stability constants” approach. The model assumptions and the reaction mechanisms are discussed. The predictions of the model are compared with the experimental data.

Finally, the conclusions, original contributions to knowledge and suggestions for future work are the subject of Chapter 6.

CHAPTER 2

EXPERIMENTAL METHODS

This chapter describes the materials used and the experimental procedure to synthesize and purify three different organophosphorus ligands: the sodium di-(n-alkyl) phosphinate, referred to as R'_2POONa, the O,O-di-(alkyl) dithiophosphoric acid, referred to as $(RO)_2PSSH$ and the sodium mono-alkyl ester phosphinate, referred to as (RO)POOHNa. The preparation of the stock solutions using commercial natural ligands, humic and fumaric acids, is reported. Experimental procedures for the removal and the recovery of metals are also discussed.

2.1 Materials

The specifications and suppliers of all chemicals are listed in Table 2.1. The chemicals were used without further purification. Deionized water with a conductivity less than 0.8 $\mu S\ cm^{-1}$, prepared with a Barnstead Easy pure RF, Compact Ultrapure Water system (Fisher Scientific, Montréal, QC) was used when studying the effect of other ions on the removal of metal with the sodium di-(n-octyl) phosphinate ligand.

2.2 Synthesis and purification of ligands

2.2.1 Synthesis and purification of sodium di-(n-alkyl) phosphinates

Two compounds, di-(n-octyl) and di-(n-dodecyl) phosphinic acid, were synthesized by peroxide catalyzed reactions between the appropriate 1-alkene (octene or dodecene) and hypophosphorus acid following the procedure described by Williams and Hamilton (1952) and modified by Peppard *et al.* (1965).

Table 2.1: Chemical reagents and suppliers.

Synthesis of ligands		
Chemical	**Specification**	**Supplier***
Benzene	Laboratory grade	5
Benzoyl Peroxide	98 %	1
Diethyl Ether (Anhydrous)	A.C.S.	5
1-Dodecanol	98 %	3
1-Dodecene	95 %	3
Ethanol	USP	4
n-Heptane	98 %	5
Hydrochloric Acid	6 N	5
Hypophosphorus Acid, 50%	A.C.S.	1
Nitric Acid	Trace Metal Grade	5
Nitrogen	Extra Dry	6
1-Octanol	99 %	3
1-Octene	98 %	3
Phosphorus Oxychloride	99 %	5
Phosphorus Pentasulfide	99 %	3
Sodium Hydroxide	0.125 N	2
Sodium Hydroxide	A.C.S.	5
Sulfur	USP	5
Toluene	99.8 %	5
Experiments		
Chloroform D ($CDCl_3$)	99.8 atom % D	5
Deuterium Oxide (D_2O)	99.8 atom % D	5
Fumaric Acid	99%	3
Humic Acid	Technical grade	3
Sodium Chloride	A.C.S.	5

Sodium Nitrate Certified	A.C.S.	5
Sodium Sulfite Anhydrous	A.C.S.	3
Sulfuric Acid	Trace Metal Grade	5
Aluminum Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Aluminum (III) Chloride	99.99 %	3
Aluminum (III) Sulfate	99.999 %	3
Arsenic Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Calcium Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Gallium Nitrate (1 wt % Nitric Acid)	1000 mg/L	3
Gallium Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Gallium (III) Chloride	99.99 %	3
Gallium (III) Sulfate	99.999 %	3
Indium Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Iron Nitrate (2 wt % Nitric Acid)	1000 mg/L	5
Zinc Nitrate (2 wt % Nitric Acid)	1000 mg/L	5

* Suppliers

1. A&C American Chemicals (Montreal, QC)
2. ACP (Montreal, QC)
3. Aldrich Chemical Co. (Montreal, QC)
4. Commercial Alcohols Inc. (Brampton, ON)
5. Fisher Scientific (Montreal, QC)
6. Megs (Montreal, QC)

The ligands were then converted to their sodium salts. The procedure described below is also based on the more recent work of Esalah (1997):

1. A mixture of 4.2 moles of 1-alkene (471 g for the 1-octene and 707 g for the 1-dodecene), 2 moles of H_2PO_2H (254 g of 50 wt % aqueous hypophosphorus acid), 132 g water, 700 mL of 95 wt % ethanol (solvent), and 0.1 mole (24.2 g) of benzoyl peroxide (one third of the total mass of benzoyl peroxide being added every 8 hours) was refluxed for 1 day at a temperature of 80°C.
2. After cooling the mixture to approximately 20°C, two layers appeared. The top organic layer contained a white solid precipitate at the interface with the lower aqueous solution. The white solid was separated by filtration and dissolved in a separatory funnel by addition of 0.5 L of benzene. The addition of 2 L of 1.0 M of hydrochloric acid acidified the solution.
3. After removing the lower aqueous phase, the benzene phase (upper layer) was contacted with two 0.5 L portions of 1.0 M HCl to form the acidic form of the ligand. The benzene was removed by evaporation and a mixture of a white solid and oil was produced. The main product was a mono-n-alkyl (octyl or dodecyl) phosphinic acid.
4. The sodium salt of the ligand was produced by dissolving the unpurified acid in 1.5 L of 2 M NaOH. The solution was mixed thoroughly.
5. The two-phase solution (a clear aqueous and a white suspension of the ligand) was cooled to 10°C.

6. The cooled solution was mixed with 2 L of diethyl ether to remove the mono-n-alkyl phosphinic acid from the solid disubstituted compounds. The lower aqueous phase was discarded.
7. The diethyl ether phase containing the sodium salt of the product was contacted successively with six 1.0 L portions of 1.0 M NaOH. Each volume of NaOH added was agitated and the lower aqueous phase was discarded removing with it unwanted single chain compounds (re-extracted into the aqueous NaOH solution). The ligand was in its sodium form at the end of this step.
8. The ligand was then converted in its acid form by contacting the diethyl ether phase with 1.0 L of 3 M HCl. The acid form, insoluble in the organic solution formed a white solid suspension in the upper phase. Following thorough agitation and subsequent phase disengagement, the lower aqueous phase was discarded. The diethyl ether phase was contacted with two additional 1.0 L volumes of 1 M HCl. After each contact, the lower aqueous phase was again discarded.
9. The diethyl ether phase was evaporated and about 500 g of a white precipitate [di-(n-alkyl) phosphinic acid] was obtained.
10. The white precipitate was recrystalized from n-heptane to separate the higher melting, less soluble di-n-alkyl phosphinic acids. Approximately 3 L of n-heptane were needed. To completely dissolve the white precipitate, the solution was heated to 35-40 °C. Once the solution was homogeneous, it was cooled to 7-10 °C, and held at that temperature for approximately 10 minutes, enabling the product to re-precipitate. The solid phase was separated by vacuum filtration using Fischer brand fast flow filter paper and the filtrate was discarded.

11. The product was converted back to its sodium form, by following steps 4 through 7.
12. Finally, the sodium form of the ligand was dried in a vacuum oven at a temperature of 40-45°C and a pressure of 68 kPa (20" HgV) for approximately 1 day. The final product was stored in a desiccator.

After synthesizing the ligands, the water content of the compounds was measured using a Karl Fischer titrator, Model 701 (Metrohm Ltd., Herisau, Switzerland). Details are given in Appendix 1. No water was detected in the final product.

The purity of the sodium di-(n-octyl) phosphinate was determined by potentiometric titration with a 0.1 N nitric acid solution. The solution was titrated using a Metrohm Dosimat Model 665 and the pH was recorded simultaneously using a Metrohm Brinkmann 691 pH meter. A second test on the purity of the ligands was carried out by Phosphorus Nuclear Magnetic Resonance (P-NMR) analysis using Varian XL300 (Varian, Palo Alto, CA) instrument with H_3PO_4 as an external standard. The sodium form of the ligands (R_2POONa where R= octyl and dodecyl) was dissolved in D_2O while the acidic form was dissolved in $CDCl_3$. As shown in Table 2.2, a single peak at 47.53 ppm for sodium di-(n-octyl) phosphinate and 32.88 ppm for sodium di-(n-dodecyl) phosphinate was observed in the ^{31}P spectra. A value of 46.78 ppm for sodium di-(n-octyl) phosphinate was previously reported by Esalah (1997). No phosphorus impurities were detected by the P-NMR analyses.

Table 2.2: P-NMR analysis of two sodium di-(n-alkyl) phosphinates dissolved in D_2O.

Ligand	Peak value (ppm)	
	This study	Esalah (1997)
Sodium di-(n-octyl) phosphinate	47.53	46.78
Sodium di-(n-dodecyl) phosphinate	32.88	-

The carbon content, denoted as C, was analyzed with a Dohrmann DC-183 Total Carbon Analyzer combined with a Detector module Dohrmann DC-85 NDIR (Dohrmann, Santa Clara, CA). The sodium (Na) and phosphorus (P) analyses were performed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a Thermo Jarrel Ash Trace Scan (Thermo Jarrel Ash, Waltham, MA) axial torch sequential ICP. The results correspond to the calculated composition of sodium di-(n-octyl) phosphinate, 7.4 % mol, 10 % mol and 61.6 % mol for Na, P , C, respectively, and of sodium di-(n-dodecyl) phosphinate, 5.4 % mol, 7.3 % mol and 68 % mol for Na, P , C, respectively.

Based on the different analyses, it was concluded that the small amount of impurities of the R_2POONa were not basic and that they did not contain phosphorus.

Finally, an x-ray powder diffraction analysis (Diffractometer PW 1710, Philips, Holland) was performed for the sodium di-(n-octyl) phosphinate and the sodium di-(n-dodecyl) phosphinate. The ligands showed a crystalline structure in their sodium form with sharp narrow diffraction peaks as observed in Figures 2.1 and 2.2. The diffraction patterns were compared to the JCPDS (Joint Committee for Powder Diffraction Standards) database and no match was found.

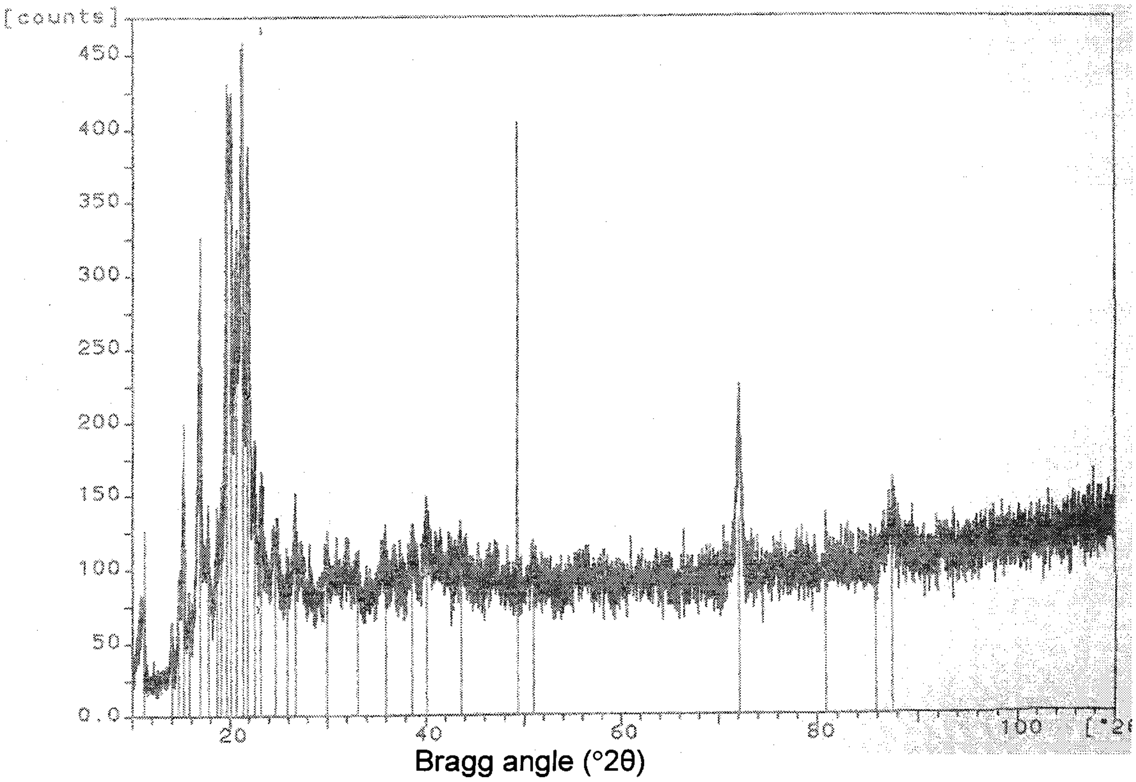


Figure 2.1: X-ray diffraction of the sodium di-(n-octyl) phosphinate

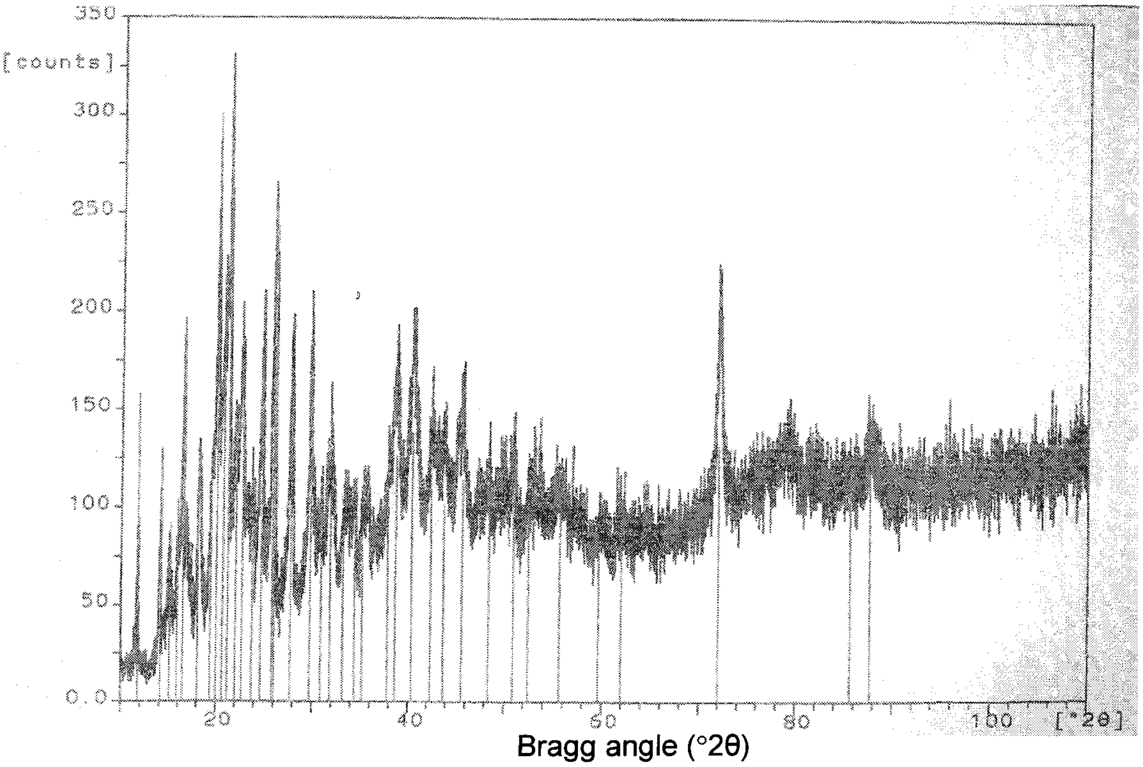


Figure 2.2: X-ray diffraction of the sodium di-(n-dodecyl) phosphinate

2.2.2 *Synthesis of O,O-di-(octyl) dithiophosphoric acid ($[RO]_2PSSH$ with R being an octyl chain) and sodium mono-octyl ester phosphinate ([RO]POOHNa)*

The O,O-di-(alkyl) dithiophosphoric acids were synthesized following the procedures described by Hoegberg and Cassaday (1951) and Van Wazer *et al.* (1966):

1. Finely ground phosphorus pentasulfide (0.5 mole or 111.14 g) was weighed in a glove box purged with dry nitrogen. The powder was suspended in about 500 mL of toluene. As the sulfur to phosphorus atomic ratio should be at least 2.6, 3 g of sulfur was added to the solution.
2. Two moles of the appropriate alcohol (65 g for octanol and 106 g for dodecanol) were gradually mixed with the phosphorus sulfide solution while the reaction temperature was maintained at 150°C. During the course of the reaction, dry nitrogen was passed into the vessel to sweep out the evolved hydrogen sulfide. Also a moderate stirring continued for about 1 hour after completion of the alcohol addition.
3. Upon completion of the reaction, the mixture was filtered in the fumehood with a water aspiration apparatus to remove unreacted phosphorus pentasulfide.
4. The solvent was removed from the filtrated solution using a rotary evaporator.
5. The approximate purity of the residual O,O-di-(alkyl) dithiophosphoric acid was determined by titration with standard alkali.
6. The sodium salt of the O,O-di-(alkyl) dithiophosphoric acid was produced by adding to the reaction mixture an equivalent quantity of sodium hydroxide (anhydrous).

7. The sodium mono-octyl ester phosphinate was produced by oxidizing the O,O-di-(octyl) dithiophosphoric acid. The O,O-di-(octyl) dithiophosphoric acid was solubilized in diethyl ether (about 200 mL per mole of salt) before adding the alkali in pellet form in order to prevent the salt from caking on the sides of the flask. A solid phase precipitated and was separated by vacuum filtration using Fischer brand fast flow filter paper. The filtrate was discarded. The precipitate, which is the sodium form of the ligand, was dried in a vacuum oven at a temperature of 40-45°C and a pressure of 68 Kpa (20" HgV) for approximately 1 day. The final product was stored in a desiccator.

2.2.3 Humic and fumaric acids

Humic and fumaric acids were purchased from Aldrich (Montreal, QC) and used as received. The humic acid was analyzed with a Total Organic Carbon (TOC) Analyzer and showed that the stock solution of humic acid (3000 mg/L) had a concentration of 800 mg/L of carbon.

2.3 Removal and recovery of gallium and other metals

At least two replicates were run in parallel for each experiment. The experiments were generally carried out at 22 ± 1°C with the exception of experiments on the effect of temperature, where the temperature was varied from 5 to 80 ± 1°C.

A metal stock solution was initially prepared at a concentration of metal of 1 g/L. Two metal stock solutions were used, both with the same concentration of metal:

- A metal salt (nitrate, chloride and sulfate) was dissolved in water and the solution was acidified with 2 wt % of HNO_3, HCl or H_2SO_4 depending on the counter ion desired.

- Solutions of metal nitrate were purchased. The solution contained generally 2 wt % of HNO_3 with the exception of the gallium stock solution used for the study described in Appendix 3 (1 wt % HNO_3).

The metal solutions were acidified to avoid the formation of metal-hydroxide complexes and titrated.

A ligand stock solution was prepared for all the ligands except for the sodium di-(n-dodecyl) phosphinate. Due to the low solubility of the sodium di-(n-dodecyl) phosphinate, the solid powder form of the ligand was added directly to the metal-containing solution. The procedure to prepare the aqueous stock solution of each ligand is described below:

- The sodium di-(n-octyl) phosphinate ligand in its powder form was dissolved in distilled water. The stock solution generally contained 8 g/L of ligand. The concentration of phosphorus in the stock solution, and thus of organophosphorus ligand, was measured by ICP-AES.
- The sodium mono-octyl ester phosphinate ligand in its powder form was dissolved in distilled water. The stock solution contained 5 g/L of ligand. The concentration of phosphorus in the stock solution, and thus of organophosphorus ligand, was also measured by ICP-AES.
- Humic or fumaric acid in its powder form was dissolved in distilled water at a concentration of 3 g/L.

All pH measurements were performed with an accuTupH reference/pH electrode (Fisher Scientific, Montreal, QC) filled with saturated potassium chloride solution. An OAKTON pH/mV Benchtop Meter model WD-35616-00 (Fisher Scientific, Montreal, QC) with a resolution of 0.1 mV and accuracy of ± 0.2 mV was used to measure pH. The pH meter was calibrated from 1.07 to 12, the practical lower and upper limit for accurate pH measurements, with standard pH solutions. For lower and higher pH values, solutions with known hydrogen or hydroxide ion concentration were prepared and used to calibrate the pH meter.

The metal solution was prepared by mixing the metal stock solution with distilled water, a salt (when required), and an acid or a base, depending on the pH desired. The amount of acid or base necessary to adjust the pH of the metal solution was based on the titration of the metal stock solution. For acidic solutions, the pH was adjusted using HNO_3, HCl or H_2SO_4 depending on the salts used during the preparation of the metal stock solution (metal nitrate, chloride or sulfate stock solution, respectively) and/or the counter ions desired. Dionized water was used, instead of distilled water, when studying the effect of other ions on the removal of metal with the sodium di-(n-octyl) phosphinate ligand. The volume of the metal solution (metal stock solution + distilled water + salts + acid or base) is designated by V_i and the pH measured immediately after mixing the metal solution is called the initial pH, and denoted by pH_i. For pH_i below 3.5 or above 12, the ratio of the molar concentration of the base (NaOH) added to adjust the pH over the concentration of metal added, denoted by $r^{\circ}_{NaOH/Ga}$, is also given. Details are given in the Appendix 3. The initial pH, pH_i, was measured immediately after mixing the metal stock solution with distilled water and an acid or a base. For pH_i between 3 and 12, the molar concentration of NaOH added to the solution can be calculated using Equation A3.17 presented in Appendix 3.

Having the initial volume of the metal solution, V_i, the ligand was added either initially diluted in an aqueous solution (sodium di-(n-octyl) phosphinate, sodium mono-octyl ester phosphinate, fumaric and humic acid) or directly in its powder form (sodium di-(n-dodecyl) phosphinate). The amount of ligand stock solution added was denoted by V_L and was a function of the desired ligand to metal(s) molar ratio. The total volume ($V°$) of the final solution was constant and generally fixed at 20 mL. The initial concentrations of ligand, $C^{\circ}_{\text{Ligand}}$, and metal, C°_{Metal}, were based on the final volume $V°$. The final pH of the solution is denoted by pH_X, where X representing the number of days after which the pH was measured, i.e 1, 2, 3, 5 , 6 and 91, respectively. When no ligand solution was added to the metal solution, V_i was $V°$ and pH_i was $pH°$. This case occurred when studying the formation of insoluble metal hydroxide without addition of ligand. A schematic diagram of the procedure is shown in Figure 2.3.

After the addition of the ligand as a solution or as a powder, the solution was mixed slowly and a minimum reaction time of 30 seconds was allowed. For the 1 day and longer experiments, the solution was mixed continuously. The solutions were filtered with 0.2 μm filters (Fisher Scientific, Montréal, QC) before analysis. The ICP-AES was used to determine the concentration in the aqueous solution of phosphorus and of the different metals (gallium, aluminum, indium, iron, calcium, zinc and arsenic). The wavelengths characteristic of the elements analyzed are reported in Table 2.3. The solid complexes were analyzed by x-ray diffraction (Diffractometer PW 1710, Philips) and by Fourier Transform Infrared spectrophotometer (FTIR MB 100, ABB Bomem Inc.). The infrared spectra were obtained on a KBr disk.

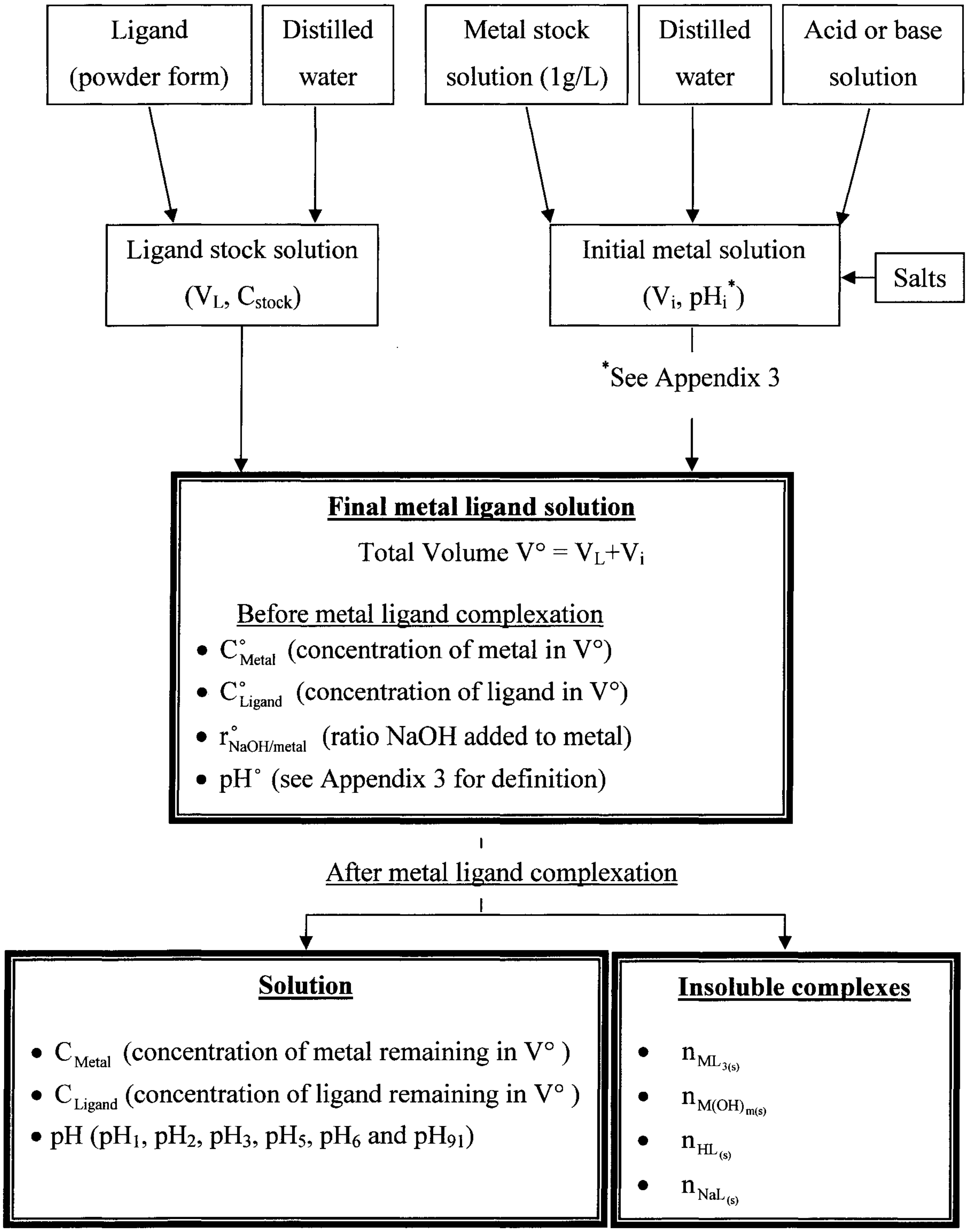


Figure 2.3: Schema of the experimental procedure. For sodium di-(n-dodecyl) phosphinate experiments, the dry ligand was added, hence $V° = V_i$.

The regeneration of the sodium di-(n-octyl) phosphinate ligand and the recovery of the metal were performed for gallium, aluminum, gallium + aluminum and gallium + zinc solutions. The solid metal ligand complexes were first formed and washed two times with distilled water at 5°C. The solids were separated each time from the aqueous phase by decanting. The insoluble complexes were then dried in an oven at 40°C. The separation of the metal from the ligand was performed at different pH using HNO_3 and NaOH by contact with a solvent (diethyl ether or chloroform). After agitation and phase disengagement, the metal was concentrated in the aqueous phase while the ligand, in its acidic or sodium form, was generally extracted into the solvent. The solvent was evaporated using a rotary evaporator to regenerate the ligand. In the case of diethyl ether, the soluble solvent remaining in the aqueous solution was evaporated using a vacuum oven. The regenerated ligand, as well as the aqueous phase, was analyzed by ICP-AES for metal and phosphorus content. Any insoluble complex remaining during the regeneration was separated from the solvent and the aqueous solution using 0.2 μm filters. The insoluble complex was then solubilized and analyzed by ICP-AES.

Table 2.3: Characteristic wavelengths of the ICP-AES for the different elements

Element	Wavelength (nm)	Element	Wavelength (nm)
P	177.50	Ga	294.36
S	180.73	Al	309.27
As	189.04	In	325.61
Zn	213.86	Ca	393.37
Pb	220.35	Na	589.59
Fe	259.94		

For gallium, the insoluble complexes were prepared by mixing 19.17 mL of 0.374 mM (26.1 mg/L) gallium nitrate solution with 0.83 mL of a 22.4 mM (7000 mg/L) sodium di-(n-octyl) phosphinate solution, giving a ratio of ligand to gallium of 3. The total concentration of gallium was 0.359 mM (25 mg/L) in the total volume of 20 mL and the final pH was 2. The solid complexes were separated from the aqueous phase as explained previously. The solid complexes were then mixed with:

- 20 mL of an aqueous solution at a fixed pH and 10 mL of a solvent (diethyl ether or chloroform)

or

- 5 mL of 3 N NaOH and 5 mL of diethyl ether.

For the regeneration of the ligand from the aluminum-ligand complex, a solid complex ($AlL_{3(S)}$) was first formed at $r^{\circ}_{L/Al} = 3$, by adding 5 mL of a 22.4 mM (7000 mg/L) sodium di-(n-octyl) phosphinate solution to 15 mL of a 2.48 mM (67 mg/L) aluminum nitrate solution. The total concentration of aluminum was 1.85 mM (50 mg/L) in the total volume of 20 mL and the final pH was 3. The aluminum-di-(n-octyl) phosphinate solid complex was separated from the aqueous solution following the method explained previously and then dissolved in 5 mL of 3 M NaOH. A volume of 3 mL of diethyl ether was added to the solution and the mixture was agitated vigorously as previously explained.

The recovery and the regeneration were also performed for the gallium-zinc system and the gallium-aluminum system. The solid complexes were formed at a ratio of ligand to the total metal $r^{\circ} = 1.25$ and a $pH_i = 2$ for the gallium zinc solution and at a ratio $r^{\circ} = 3$ and a $pH_i = 1.7$ for the gallium aluminum solution. For gallium-zinc system, the total concentrations of metal nitrate in the 20 mL solution was C°_{Ga} = 0.359 mM (25 mg/L) and C°_{Zn} = 1.15 mM (75 mg/L). For gallium-aluminum, the total concentration of metal nitrate in the 20 mL solution was C°_{Ga} = 0.359 mM (25 mg/L) and C°_{Al} = 0.925 mM (25 mg/L). In both cases, the solid complex was separated from the aqueous solution, then dissolved in 5 mL of 3 M NaOH and contacted with 5 mL of diethyl ether with vigorous agitation.

2.3.1 *Effect of mixing*

The effect of mixing on the equilibrium time was investigated at $pH^{\circ} = 2$ and $r^{\circ} = 3$. Metal nitrate was used and the pH adjustment was made using nitric acid. Two different mixing procedures were tested over a period of 10 minutes and 1 day; a fast stirring of the solution giving a homogenized solution, or the solution of metal into contact with the ligand and mixed slowly during 5 seconds to have a homogeneous dispersion of the ligand in the solution. The solution became whitish and was not stirred until the end of the 10 minutes period. After a contact time of 10 minutes, the solution was mixed vigorously for 5 seconds. Both solutions were then stirred for 1 day. The results are shown in Appendix 2.

2.3.2 *Metal recovery from GaAs wafer*

GaAs wafers were obtained from M/A-COM Advanced Materials, a division of Tyco electronics (Lowell, MA). To remove surface oxide, the wafers were washed using concentrated nitric acid (30 wt % trace element) and rinsed three times with deionized water. These operations were carried out under a nitrogen atmosphere. In order to simulate the wastewater from M/A-COM Advanced Materials, 0.2 g of the wafer was crushed and dissolved in 10 mL of 30 wt % nitric acid.

The ICP-AES analysis of wafer stock solution showed 49.1 wt % of gallium and 50.9 wt % of arsenic, somewhat different from the 48 wt % of gallium and 52 wt % of arsenic reported by M/A-COM Advanced Materials. While the difference can be partly due to experimental error, some loss in arsenic occurred due to the formation of arsine gas (AsH_3), as confirmed by the analysis of the gas using an arsine detector tube coupled to a Dräger accuro handheld bellows pump.

2.4 Notation and quantities calculated from the data

The curves in the figures are generally hand drawn unless otherwise specified. The concentrations of the species are expressed in molarity (M), and/or mg/L. The superscript ° is used for the properties of the aqueous solution before any complexation. The mole ratio of ligand to total metals is denoted r°; the mole ratio of ligand to an individual metal, M, is $r^{\circ}_{L/M}$.

The percentage removal of the metal, R_M, is defined as:

$$R_M = \frac{n^{o}_{M} - n_M}{n^{o}_{M}} \times 100 \tag{2.1}$$

where M stands for gallium, aluminum, indium, iron, calcium, zinc or arsenic; n^{o}_{M} is the initial total number of moles of the element M in the aqueous solution and n_M is the number of moles remaining in the aqueous solution.

The percentage removal of the ligand, R_L, is defined as:

$$R_L = \frac{n_L^\circ - n_L}{n_L^\circ} \times 100 \tag{2.2}$$

where n_L° is the total initial number of moles of ligand added to the solution, and n_L is the number of moles of ligand remaining in the aqueous solution after filtration.

The percentage loss of ligand, L_L, is the percentage of ligand remaining in aqueous solution:

$$L_L = \frac{n_L}{n_L^\circ} \times 100 = 100\text{-}R_L \tag{2.3}$$

The percentage loss of carboxylic ligands, humic or fumaric acid, was denoted as L_C, and was calculated using the Total Organic Carbon (TOC) measured before and after the complexation:

$$L_C = \frac{n_C - n_{C_{R_2POONa}}}{n_C^\circ} \times 100 \tag{2.4}$$

where n_C° is the initial total number of carbon associated to the carboxylic ligand added to the aqueous solution, n_C is the total number of moles of carbon remaining in the aqueous solution after filtration and $n_{C_{R_2POONa}}$ is the number of moles of carbon, associated to the R_2POONa ligand, remaining in the aqueous solution after filtration. The $n_{C_{R_2POONa}}$ was calculated using the concentration of phosphorus measured with the ICP-AES. When no R_2POONa ligand is added, n_C is the total number of moles of carbon, associated to the carboxylic ligand, remaining in the aqueous solution after filtration. In the following chapters, L_C is referred as the loss of carbon associated to the carboxylic ligand.

In order to express the selectivity of the gallium over calcium, zinc, aluminum, iron or indium, the fractional removal of each metal, R^*_M, and the molar selectivity $\alpha_{Ga/M}$ for Ga relative to the other metal M present in the solution, are defined as:

$$R^*_M = \frac{n^P_M}{n^o_M} \tag{2.5}$$

where n^P_M is the number of moles of M in the precipitate at the end of the experiment, and

$$\alpha_{Ga/M} = \frac{R^*_{Ga}/(1-R^*_{Ga})}{R^*_M/(1-R^*_M)} \tag{2.6}$$

From Equation 2.6, good selectivity for gallium over a metal M is indicated by $\alpha_{Ga/M}$ >>1.

CHAPTER 3

REMOVAL OF SINGLE METAL IONS

This chapter first describes the removal of gallium from aqueous solutions by complexation with sodium di-(n-octyl) phosphinate, sodium di-(n-dodecyl) phosphinate, O,O-di-(octyl) dithiophosphoric acid and sodium mono-octyl ester phosphinate; and with two carboxylic ligands: fumaric and humic acids.

The removal of aluminum, indium, iron and calcium was performed using sodium di-(n-octyl) phosphinate. The percent removal of metals was studied as a function of pH, the mole ratio of the ligand to metal and of Na^+, NO_3^-, Cl^- and SO_4^{2-} ions.

3.1 Removal of gallium with sodium di-(n-octyl) phosphinate

3.1.1 Effect of time

The effect of time on the removal of gallium using sodium di-(n-octyl) phosphinate ligand was established by varying the time (30 s, 5 min, 20 min, 1 h, 2 h, 1 day and 2 days) for different initial concentrations of metal in an acidic solution.

The initial concentration of gallium nitrate was 0.014, 0.052, 0.072, 0.119, 0.359 and 1.434 mM (1, 3.6, 5, 8.3, 25 and 100 mg/L, respectively) at a mole ratio of ligand to gallium, $r^{\circ}_{L/Ga}$, of 3 and at an initial pH, pH$_i$, of 2. The concentration of gallium was varied by increasing the total volume of the solution from 20 mL for 0.359 mM (25 mg/L) to 500 mL for 0.014 mM (1 mg/L). For 0.359 (25 mg/L) and 1.434 mM (100 mg/L), the total volume was kept constant at 20 mL and the amount of gallium added was increased 4 times. An example of the removal over time of gallium at different initial concentrations is given in Figure 3.1. For gallium at a concentration of 0.359 mM (25 mg/L), removal was complete in less than a minute and did not change after 2 hours and 1 day. For higher concentrations of gallium, the same high removals were obtained. After 1 day, a complete removal of gallium was obtained for all concentrations of gallium except for 0.014 mM (1 mg/L) where the removal was 81 ± 2 %. After 5 days, the gallium removal from the 0.014 mM (1 mg/L) solution increased to 89 ± 1 %.

Similar experiments were conducted with a concentration of gallium nitrate of 0.014 mM (1 mg/L) but with two larger mole ratios of ligand to metal: $r^{\circ}_{L/Ga} = 6$ and 9. As Figure 3.2 shows, at a fixed time, larger removals were achieved with larger $r^{\circ}_{L/Ga}$. After 5 days, about 0.0007 mM (0.05 mg/L) remained in solution which was the detection limit of the ICP-AES for gallium.

In subsequent experiments, a time of 1 day and a minimum initial concentration of gallium of 0.359 mM (25 mg/L) were used.

3.1.2 *Effect of pH on the removal of gallium without ligand and of ligand without gallium*

The effect of pH on the removal of gallium from an aqueous solution without ligand and on the removal of the ligand from an aqueous solution without gallium was investigated. Figure 3.3 shows the percent removal of gallium-hydroxide complex from a gallium nitrate solution with C°_{Ga} of 0.359 mM (25 mg/L). The final pH was measured after 1 day and after 6 days, and denoted as pH_1 and pH_6, respectively. No organophosphorus ligand was present in the solution.

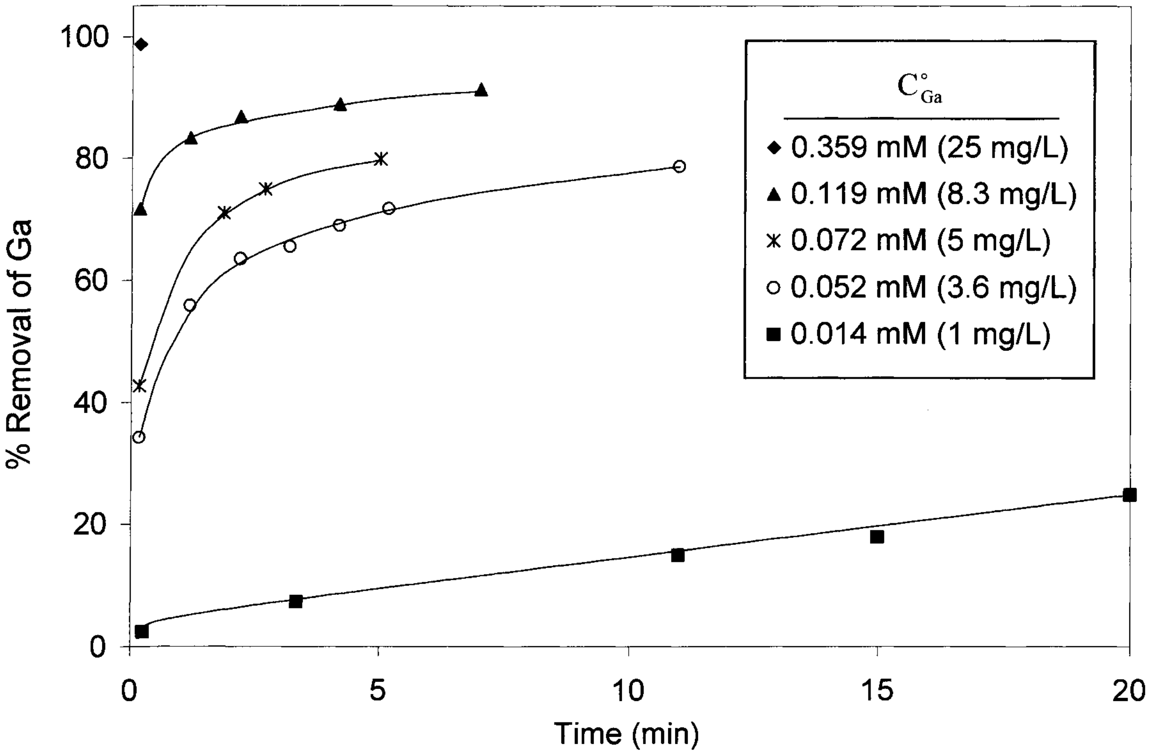


Figure 3.1: Effect of time on the removal of gallium using sodium di-(n-octyl) phosphinate for different initial concentrations of gallium [$r^{\circ}_{L/Ga} = 3$ and $pH_i = 2$ ($r^{\circ}_{NaOH/Ga} = 0$)].

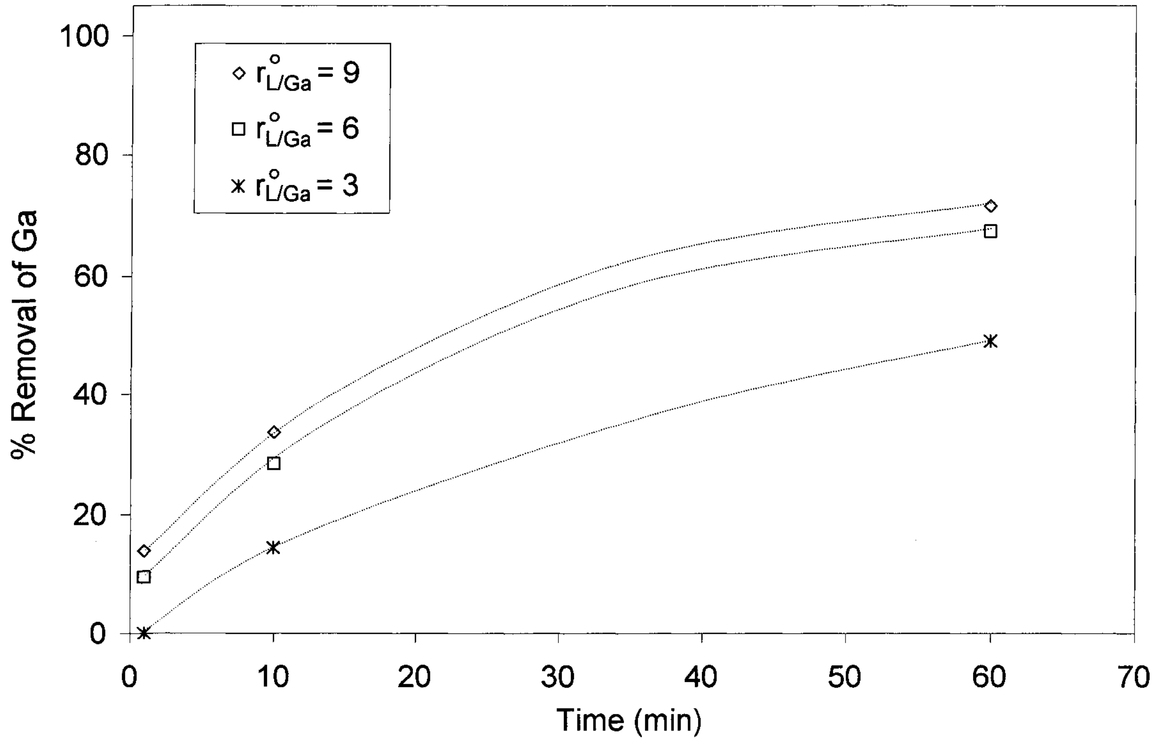


Figure 3.2: Effect of time on the removal of 0.014 mM (1 mg/L) of gallium using sodium di-(n-octyl) phosphinate for different initial mole ratio [$pH_i = 1.88$].

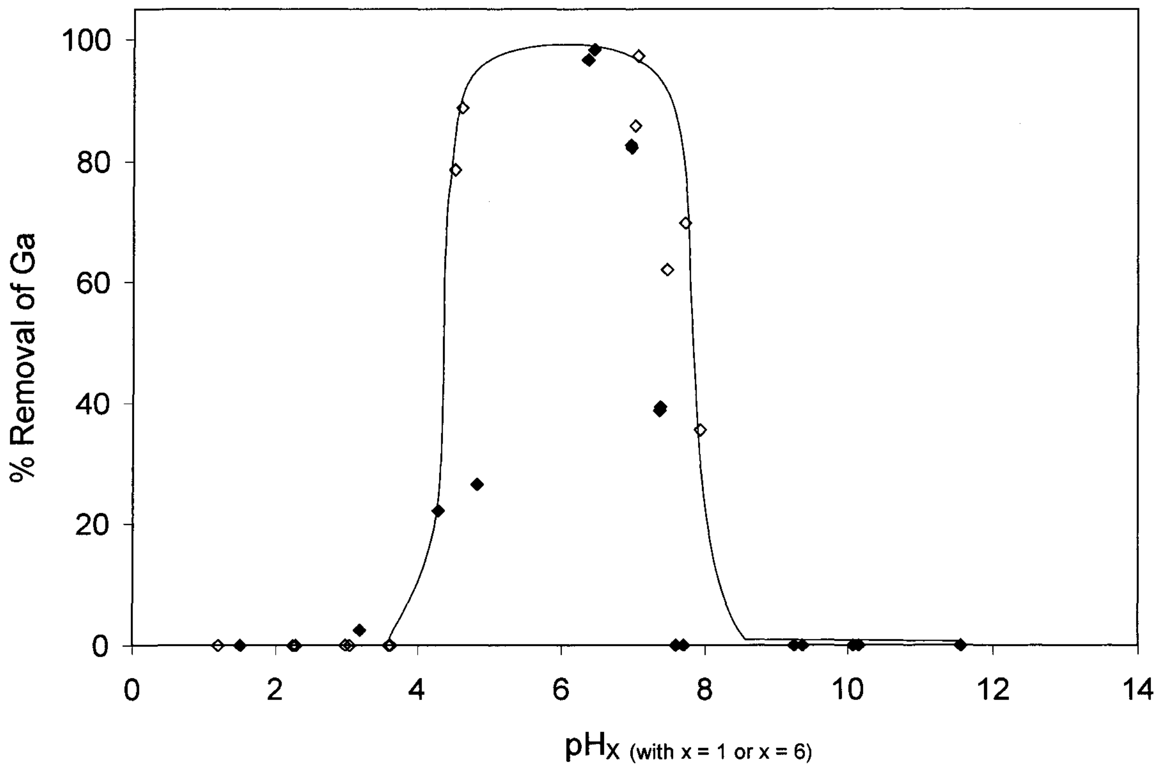


Figure 3.3: Precipitation of gallium in aqueous solution as a function of pH and time: after 1 day (◆), after 6 days (◇) [C^{o}_{Ga} = 0.359 mM].

After 1 day, gallium precipitated between a pH of 4 and 7.5. In this pH range, gallium forms the insoluble hydroxyl complex $Ga(OH)_{3(s)}$. Depending on the pH and the concentration of gallium, different hydroxyl-complexes are formed with gallium:

$$Ga^{3+} + n\,OH^- \longleftrightarrow Ga\,(OH)_n^{3-n} \tag{3.1}$$

where n = 1, 2, 3 and 4 at the low concentrations of gallium in this study. At pH below 3, gallium is in the form of Ga^{3+}; the soluble complexes $Ga(OH)^{2+}$ and $Ga(OH)_2^+$ form at higher pH values. For a pH above 7.5, the soluble complex $Ga(OH)_4^-$ becomes predominant (Baes and Mesmer, 1986). As a result, the removal of gallium decreases, and the pH decreases as OH^- is consumed:

$$H_2O \longleftrightarrow H^+ + OH^- \tag{3.2}$$

More details regarding the formation of hydroxyl complexes are given in Appendix 3. After 6 days, gallium was precipitated over a wider pH range than after 1 day. Around a final pH of 4, the formation of the $Ga(OH)_{3(s)}$ precipitate was not favored as few OH^- ions were present. As the pH increased to around pH 8, more precipitation occurred. Furthermore, by increasing the reaction time from 1 to 6 days, more gallium was removed from the solution. At a final pH = 4.55 ± 0.3, about 24 ± 3 % of gallium precipitated as $Ga(OH)_{3(s)}$ after 1 day, while 83 ± 6 % precipitated after 6 days. The precipitation of gallium hydroxide may take up to 2 or 3 months to reach equilibrium (Uchida and Okuwaki, 1997).

The effect of the pH on the percent loss of sodium di-(n-octyl) phosphinate ligand from an aqueous solution without gallium is shown in Figure 3.4 for two initial concentrations of ligand, 1 mM (310 mg/L) and 2 mM (650 mg/L). The natural pH of the ligand in aqueous solution was around 8. By decreasing the pH of the solution below this

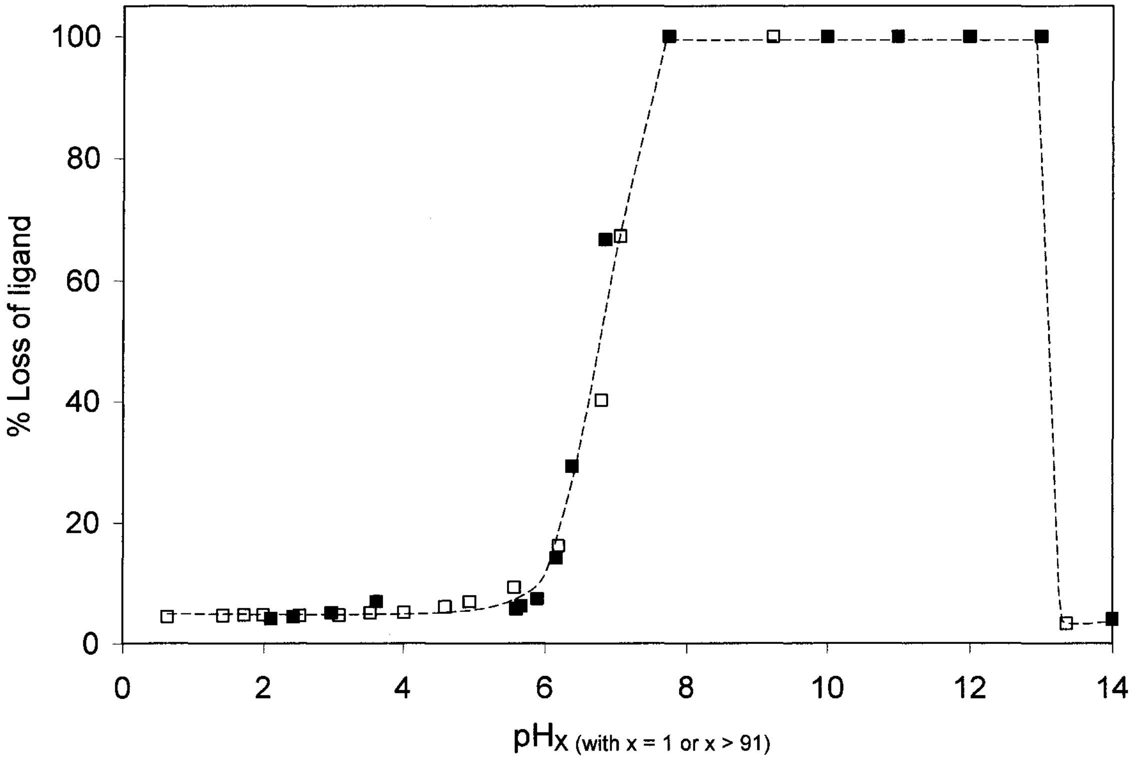


Figure 3.4: Percent loss of sodium di-(n-octyl) phosphinate in aqueous solution as a function of pH_x [C_L°: 1 mM (■), 2 mM (□)]. For values of pH lower than 10, $pH_X = pH_1$; for values of pH higher than 10, $pH_X > pH_{91}$ (pH measured after 13 weeks).

pH, the ligand was removed from the aqueous solution in the form of the water insoluble di-(n-octyl) phosphinic acid, $HL_{(s)}$:

$$H^+ + L^- \longleftrightarrow HL_{(s)} \tag{3.3}$$

Less than 10 % of the ligand remained in solution at pH < 6. A complete loss of ligand was observed in the pH range of 8 to 13. As the sodium hydroxide concentration increased, the concentration of Na^+, the counter ion of the ligand, increased. At large Na^+ concentration, the amount of ligand solubilized in the aqueous solution decreased due to precipitation of the sodium form of the ligand:

$$Na^+ + L^- \longleftrightarrow NaL_{(s)} \tag{3.4}$$

In acidic solution, the removal of the ligand in its acidic form reached equilibrium after 1 day, while at pH > 13, weeks were necessary for sodium di-(n-octyl) phosphinate to reach equilibrium. The effect of the concentration of sodium on the removal of the ligand was confirmed by adding a 1.09 M solution of $NaNO_3$ to a solution with a ligand concentration of 0.86 mM (270 mg/L) to give a mole ratio of sodium to ligand of 1260. At pH of 6.9 ± 0.1, the percent loss of ligand was 15 % compared to around 70 % when no sodium was added.

3.1.3 Effect of the mole ratio, pH and temperature on the removal of gallium

The effect of $r^{\circ}_{L/Ga}$ was investigated by mixing V_i of initial gallium solution and V_L of the sodium di-(n-octyl) phosphinate stock solution. The pH_i was at 2.64 and the initial concentration of gallium nitrate in the ligand-gallium mixture was $C^{\circ}_{Ga} = 0.473$ mM (33 mg/L). At this pH and concentration of gallium, no insoluble gallium hydroxide complex forms. As observed in Figure 3.5, a complete removal of gallium was obtained

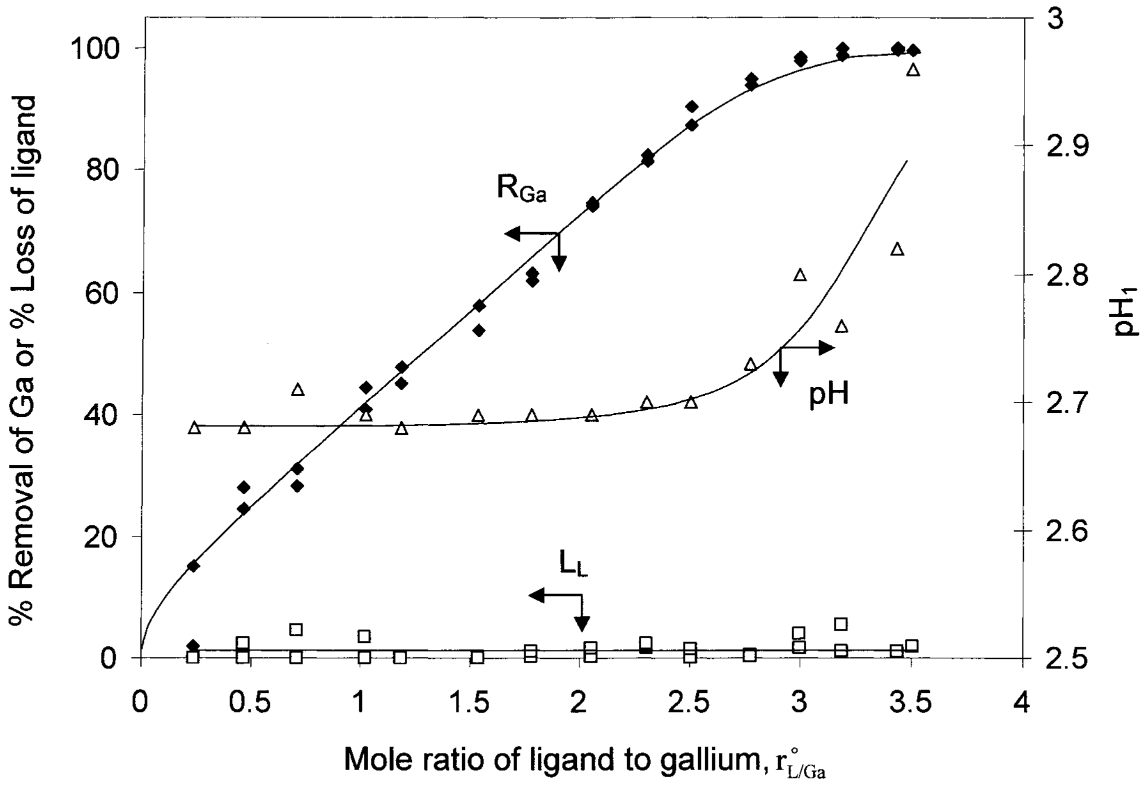


Figure 3.5: Effect of mole ratio of sodium di-(n-octyl) phosphinate to gallium on the percent removal of gallium (◆); percent loss of sodium di-(n-octyl) phosphinate (□); and the value of pH_l (Δ) [C°_{Ga} = 0.473 mM, pH_i = 2.64 ($r^{\circ}_{NaOH/Ga}$ = 18.3)].

by complexation at a mole ratio of ligand to gallium around 3. The final concentrations of gallium and ligand remaining dissolved in the aqueous solution were $C_{Ga} = 0.58 \pm 0.1$ mg/L and $C_L = 1.3 \pm 0.5$ mg/L. The following reaction describes the formation of the insoluble complex, $GaL_{3(s)}$, where the symbol L^- represents the radical $(C_8H_{17})_2POO^-$:

$$Ga^{3+} + 3\,L^- \longleftrightarrow Ga\,L_{3(S)} \tag{3.5}$$

Increasing the mole ratio above 3.2 decreased the level of soluble gallium below the detection limit of the ICP-AES. Further addition of ligand increased the final pH due to the formation of the acidic form of the ligand.

Figure 3.6 shows the removal of gallium at $pH_i = 3.34$. At this pH_i, complete removal of gallium was obtained at $r^{\circ}_{L/Ga} = 2$. In comparison, when pH_i was set at 2.64 as shown in Figure 3.5, the percent removal of gallium from the solution was about 74.3 ± 0.3 % at this ligand to gallium mole ratio. This phenomenon can be explained by the formation of gallium-hydroxide complex at higher pH_i as discussed in Appendix 3. As more hydroxide was added to increase the pH_i, the amount of gallium forming an insoluble complex with hydroxide increased, and thus, less ligand was required to remove the gallium in solution. As the ligand was in excess at $r^{\circ}_{L/Ga} > 2$, an increase in pH_l is also observed in Figure 3.6, which is due to the formation of insoluble hydrogen-ligand complex.

The effect of the pH on the removal of gallium is shown in Figure 3.7 at a mole ratio of ligand to gallium of 3 and an initial gallium nitrate concentration, C°_{Ga}, of 0.359 mM (25 mg/L). The pH_2 indicates the final pH measured after 2 days at the end of the experiment. The highest removal was obtained at a final pH between 2 and 7.

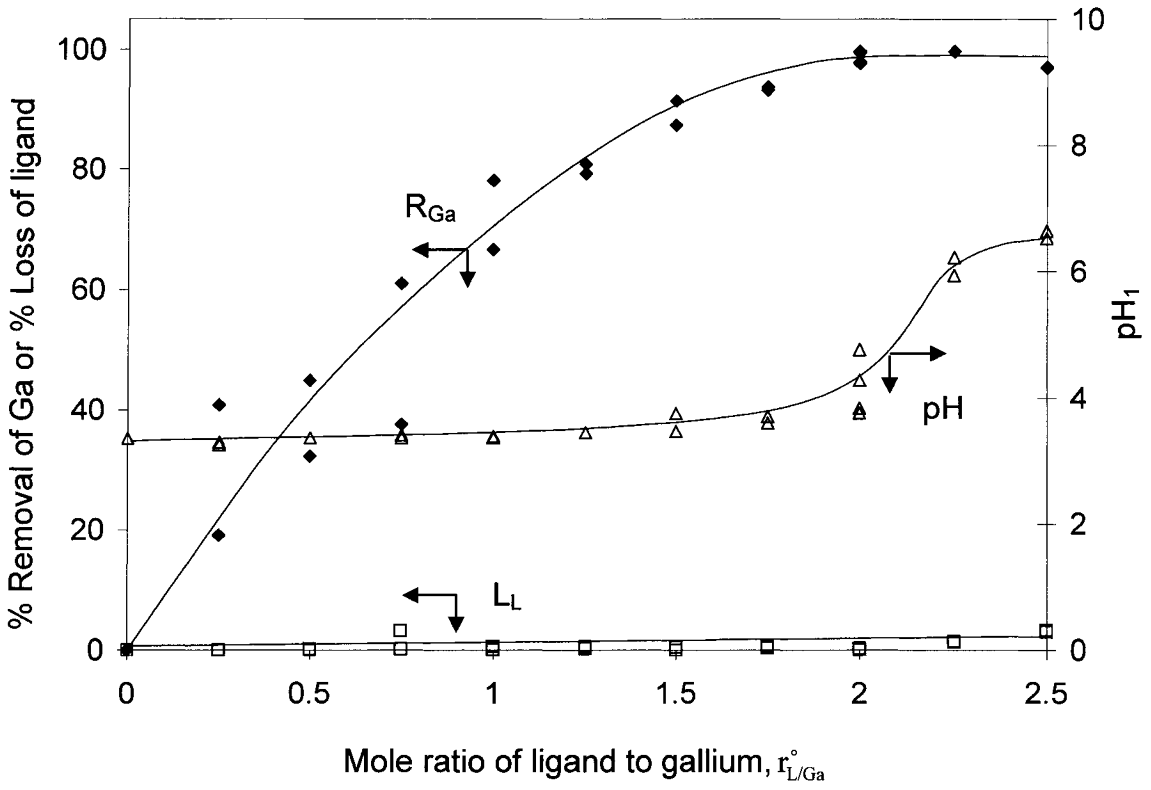


Figure 3.6: Effect of mole ratio of sodium di-(n-octyl) phosphinate to gallium on the percent removal of gallium (◆); percent loss of sodium di-(n-octyl) phosphinate (□); and the value of pH_l (Δ) [C°_{Ga} = 0.359 mM, pH_i = 3.34 ($r^{\circ}_{NaOH/Ga}$ = 23.4)].

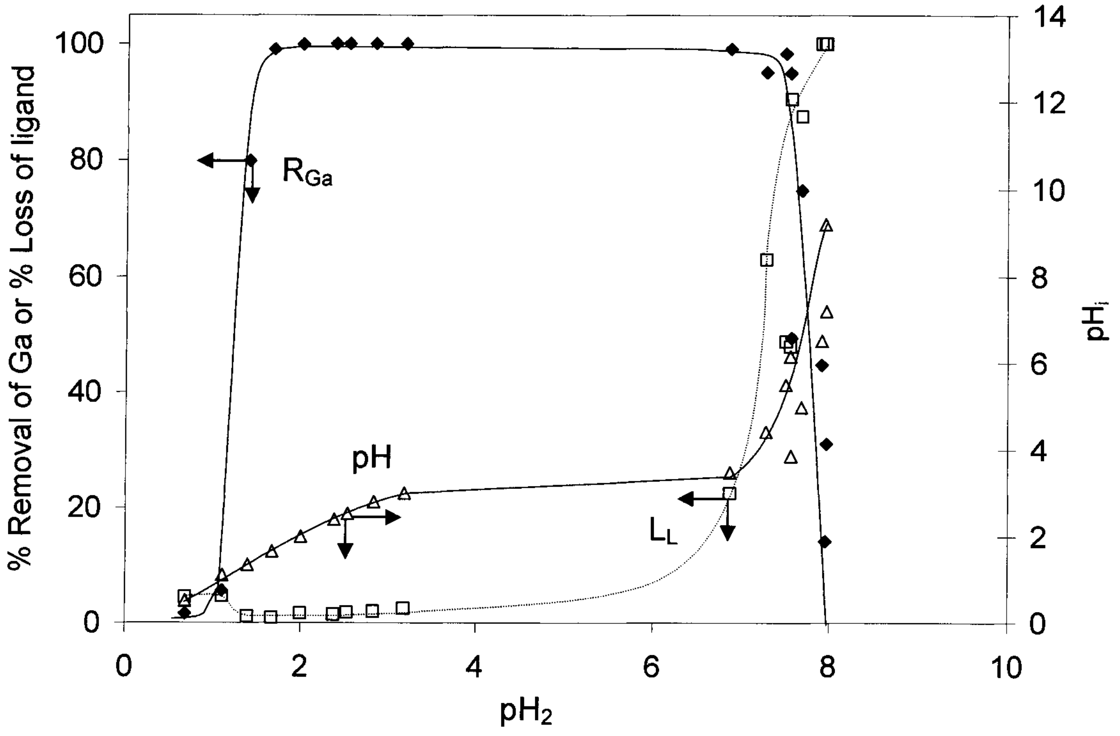


Figure 3.7: Effect of pH (△) on the percent removal of gallium (◆) and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{Ga} = 0.359 mM, $r^{\circ}_{L/Ga}$ = 3].

In this pH range, the concentration of gallium remaining in the aqueous solution was below the ICP-AES detection limit. For pH between 2 and 3, the gallium was removed by complexation with the ligand, since the gallium trihydroxide ($Ga(OH)_{3(s)}$) did not precipitate in this pH range, as shown in Figure 3.3. For pH below 1.1, the gallium remained in the aqueous solution, and the ligand was removed in its acidic insoluble form. Due to the strong acidity and the small amount of ligand added, the difference between the initial and final pH was small in this area. Also, due to the acidity constant of the soluble HL complex, some soluble HL remained in solution below pH 1.1 and the loss of the ligand increased from 1 % to 4.5 %. More details are given in Chapter 5. For a basic solution with a final pH close to 8 (the natural pH of the ligand), gallium was removed mainly by forming the insoluble complex $Ga(OH)_{3(s)}$, as previously shown in Figure 3.3. The formation of $Ga(OH)_{3(s)}$ favored the removal process. The precipitation of $Ga(OH)_{3(s)}$ did not reach equilibrium after 2 days because 2 to 3 months can be necessary as explained previously. Also, for pH close to 8, the ligand remains in the solution because less ligand reacts with gallium and fewer H^+ ions are available to remove the ligand in its acidic form.

Finally, at the final pH between pH 3 and 7, the OH^- ions compete with the ligand for the gallium. As explained in Appendix 3, for pH between pH 3 and 7, in the absence of organophosphorus ligand, the measured pH_i was close to the equilibrium pH because the main gallium hydroxide complex, $Ga(OH)_3$, formed rapidly. By adding the ligand to the gallium solution at a ratio $r^{\circ}_{L/Ga} = 3$, the gallium reacts with the ligand and thus releases OH^- from its hydroxide form. This results in a higher pH_2 value than the pH_i value, as shown in Figure 3.7.

For a pH_X of the gallium-ligand solution below 3.5, the removal of gallium and ligand reached equilibrium after 1 day as shown in Figure 3.8 where the removal of gallium did not change with time.

Figure 3.9 shows the effect of temperature on the concentration of gallium and the ligand remaining in solution at $r^{\circ}_{L/Ga} = 3$ and at $C^{\circ}_{Ga} = 0.359$ mM (25 mg/L). In some cases 3 replicates were tested and the mean concentration and sample standard deviation are shown. The concentration of gallium in the aqueous solution decreased with increasing temperature and was below the detection limit of the ICP-AES above 40°C. On the other hand, at 20°C the concentration of ligand in the solution was approximately 1.5 mg/L (0.005 mM), and at 60°C it was between 10 to 12 mg/L (0.032-0.038 mM), which represents a 5 % loss of ligand. The ratio of ligand removed to gallium removed was about 2.9 at 60°C. For an initial acidic pH, two insoluble complexes are present: the acidic form of the ligand and a complex formed between the ligand and gallium. At low temperature, the ligand is removed in its acidic form, leaving some gallium dissolved in the aqueous solution. As the temperature is increased, the acid form of the ligand is more soluble making more ligand available to remove gallium.

3.1.4 Effect of other ions on gallium removal

The effect of ions commonly found in aqueous solutions such as sodium, nitrate, chloride and sulphate on the removal of gallium using the sodium di-(n-octyl) phosphinate was investigated.

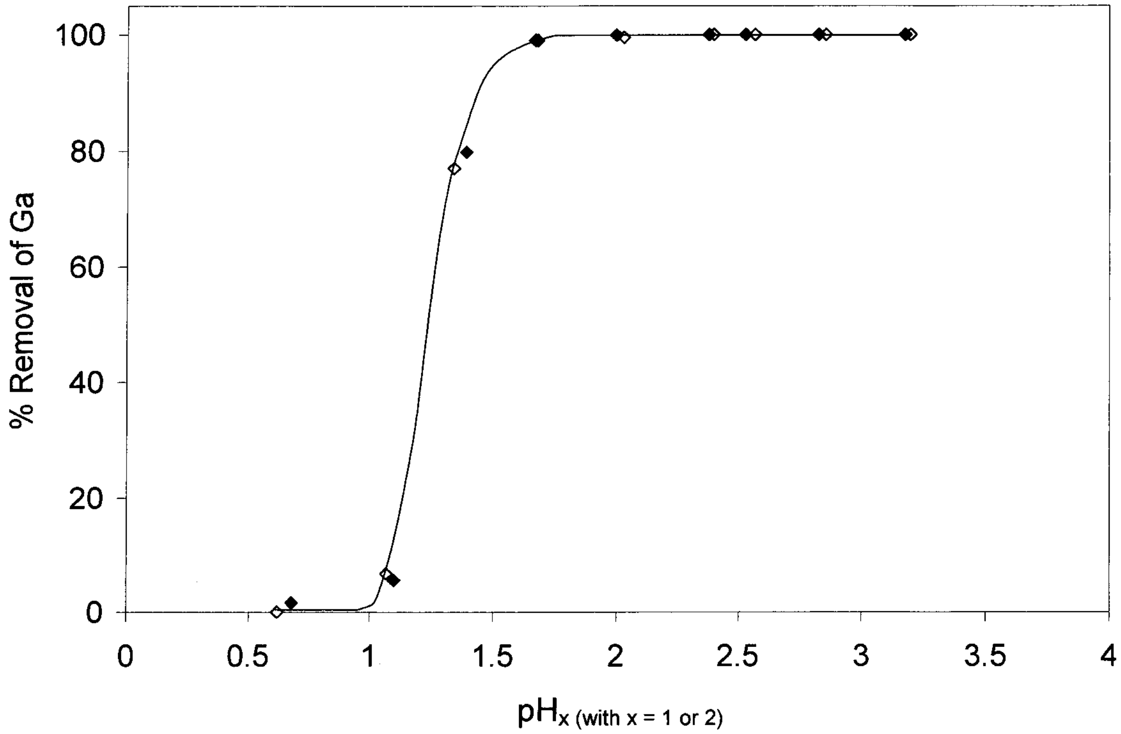


Figure 3.8: Effect of pH on the percent removal of gallium after 1 day (◇) and after 2 days (◆) [C°_{Ga} = 0.359 mM; $r^{\circ}_{L/Ga}$ = 3].

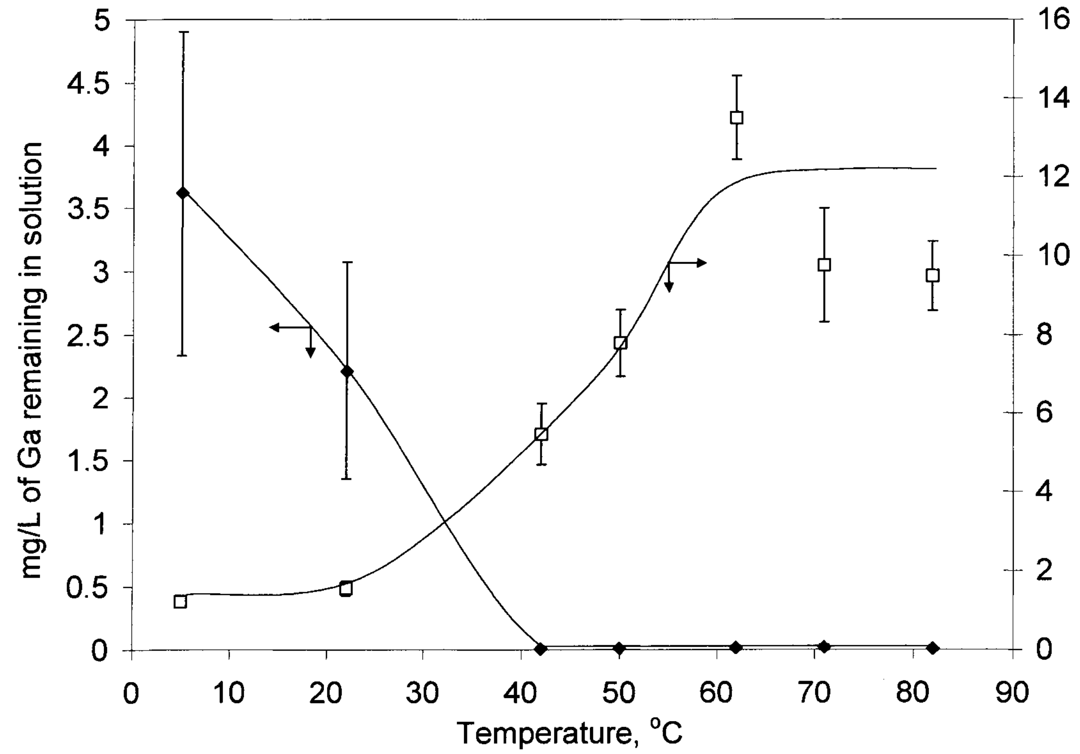


Figure 3.9: Effect of temperature on the residual concentration of gallium (◆) and sodium di-(n-octyl) phosphinate (☐) [pH_i = 2.2 ± 0.1; C°_{Ga} = 0.359 mM (25 mg/L); $r^{\circ}_{L/Ga} = 3$; $r^{\circ}_{NaOH/Ga} = 0$].

While chloride and sulphate can form soluble complexes with gallium, as shown in reactions 3.6 and 3.7, sodium can precipitate the ligand (reaction 3.4).

$$Ga^{3+} + n\,Cl^{-} \longleftrightarrow GaCl_n^{3-n} \tag{3.6}$$

$$Ga^{3+} + m\,SO_4^{2-} \longleftrightarrow Ga(SO_4)_m^{3-2m} \tag{3.7}$$

where n = 1 to 4 and m = 1 to 2 (Izatt *et al.*, 1969). The gallium ion does not form nitrate complexes in dilute solutions (Rudolph *et al.*, 2002).

Figure 3.10 shows the effect of 3 sodium salts, $NaNO_3$, NaCl and Na_2SO_4 on the percent removal of gallium for an initial concentration of $C^{\circ}_{Ga} = 0.359\,mM$. The mole ratio of ligand to gallium was between 2.25 and 3. The pH_i was adjusted using HNO_3, HCl or H_2SO_4 depending on the salts used during the preparation of the gallium stock solution, in order to avoid mixing of anions. In all cases, the concentration of ligand in the final solution was below the detection limit of the ICP-AES, representing essentially complete removal of the ligand from the solution. Since the final pH values were below 2.3, no insoluble hydroxyl complexes were formed.

The mole ratios of anion to gallium of 16, 40, 26 for $NaNO_3$, NaCl and Na_2SO_4, respectively, correspond to the amount of anion (NO_3^-, Cl^- or SO_4^{2-}) introduced from the gallium salt used in stock solution and from the acids used for pH adjustments. No additional sodium salt was added in these cases. For the case of $NaNO_3$, at the mole ratio of nitrate to gallium of about 16, the removal of gallium was 98.8 ± 1 %. Up to a ratio of nitrate to gallium of about 90, the removal of gallium was 98 ± 0.9 % and was not affected by the addition of $NaNO_3$. The gallium removal then decreased by 9 % for mole ratios of nitrate to gallium between 90 and 170.

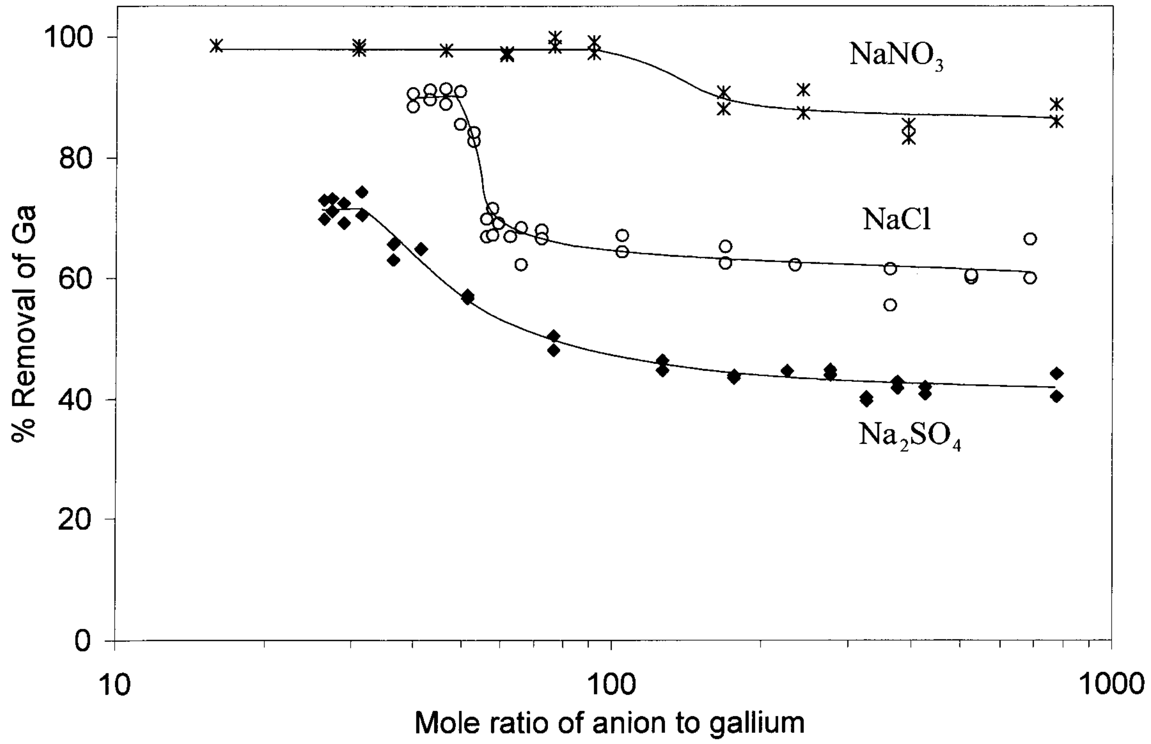


Figure 3.10: Effect of the sodium salts $NaNO_3$ (*), NaCl (O) and Na_2SO_4 (◆) on the percent removal of gallium [C°_{Ga} = 0.359 mM; for $NaNO_3$: $r^{\circ}_{L/Ga}$ = 3, pH_I with $NaNO_3$ = 2.3; for NaCl: $r^{\circ}_{L/Ga}$ = 2.5, pH_I with NaCl= 1.9; and for Na_2SO_4: $r^{\circ}_{L/Ga}$ = 2.25, pH_I with Na_2SO_4= 2.1].

Above $r^{\circ}_{NO_3/Ga}$ = 170, the removal of gallium reached a plateau. Between $r^{\circ}_{NO_3/Ga}$ = 170 and 775 (4.6 and 22.9 g/L of $NaNO_3$ dissolved in the aqueous solution, respectively), the removal only decreased by an additional 2 %. While the nitrate ions did not inhibit the removal of gallium in the concentration range used, sodium competes more with gallium to form a complex with the ligand. The anions Cl^- and SO_4^{2-}, which compete with the ligand for gallium, inhibited the removal of gallium. The gallium salt solution was prepared 1 day before the addition of the ligand. To compare the effect of Cl^- and SO_4^{2-} on the removal of gallium with ligand, a blank was prepared with gallium nitrate salts acidified with nitric acid. No Cl^- and SO_4^{2-} were present. The pH_1 with HNO_3 was 2 and the removal of gallium with the ligand was 89.7 ± 2.2 % and 82.2 ± 1.2 % for $r^{\circ}_{L/Ga}$ = 2.5 and 2.25, respectively. As observed in Figure 3.10, the removal of gallium with the ligand with no addition of NaCl or Na_2SO_4 was 89.7 ± 2.2 % for the gallium chloride solution and 71.3 ± 2.3 % for the gallium sulphate solution for a ratio of anion to gallium of about 40 and 26, respectively. While the chloride ions did not initially inhibit the removal of gallium, the sulphate ions decreased the removal by 10 % as they form more stable soluble complexes with gallium (Mihaylov, 1991). By adding the NaCl or the Na_2SO_4 salts to the solution, the removal efficiency decreased for $r^{\circ}_{Cl/Ga} > 50$ (or $r^{\circ}_{Na/Ga} > 12$) for chloride and for $r^{\circ}_{SO_4/Ga} > 30$ (or $r^{\circ}_{Na/Ga} > 14$) for sulphate. The inhibition of the removal of gallium with the ligand is due to the chloride and sulphate ions, not the sodium ions, since no significant decrease in the removal of gallium was observed in the presence of $NaNO_3$. For $r^{\circ}_{Cl/Ga}$ between 56 and 680 (0.27 g/L of NaCl added and dissolved in the aqueous solution), the removal of gallium in the chloride solution reached a plateau as the removal only decreased by around 6 %. The percent removal in the sulphate solution decreased 20 % from $r^{\circ}_{SO_4/Ga} = 30$ up to $r^{\circ}_{SO_4/Ga} = 80$. Above this mole ratio till $r^{\circ}_{SO_4/Ga}$ around 1000, a decline of the removal of only 8 % was observed as the removal efficiency reached a plateau of around 45 %.

3.1.5 Recovery of gallium and regeneration of the ligand

Two phases, an organic (diethyl ether or chloroform) and an aqueous, were used to dissolve the gallium-ligand complex and separate the gallium from the ligand. The gallium was recovered in the aqueous phase, and the ligand was extracted into the organic phase. At low pH, the main species of gallium is Ga^{3+}. At high pH, the hydroxyl ions compete with the ligand for the gallium and form the hydroxyl-complexes $Ga(OH)_4^-$.

Initially, the insoluble $GaL_{3(s)}$ complex was formed by adding the ligand to an aqueous solution containing 0.359 mM of gallium nitrate at a mole ratio of ligand to gallium of 3 and $pH_I = 2$. The solid complex was then separated from the aqueous solution by decanting. Using this insoluble metal ligand complex, two approaches were developed; either an acidic aqueous solution or a basic aqueous solution was put into contact with the organic phase. The gallium was recovered in the aqueous solution while the ligand was extracted into the organic phase.

Figure 3.11 shows the percent recovery of gallium using a 20 mL acidic solution and 10 mL of a solvent (diethyl ether or chloroform). Over 80 % of the gallium was recovered in the aqueous phase at pH below 0.5 for diethyl ether and 1.5 for chloroform. The concentration of ligand in the aqueous phase was below the detection limit of the ICP-AES because the acidic form of the ligand is water insoluble.

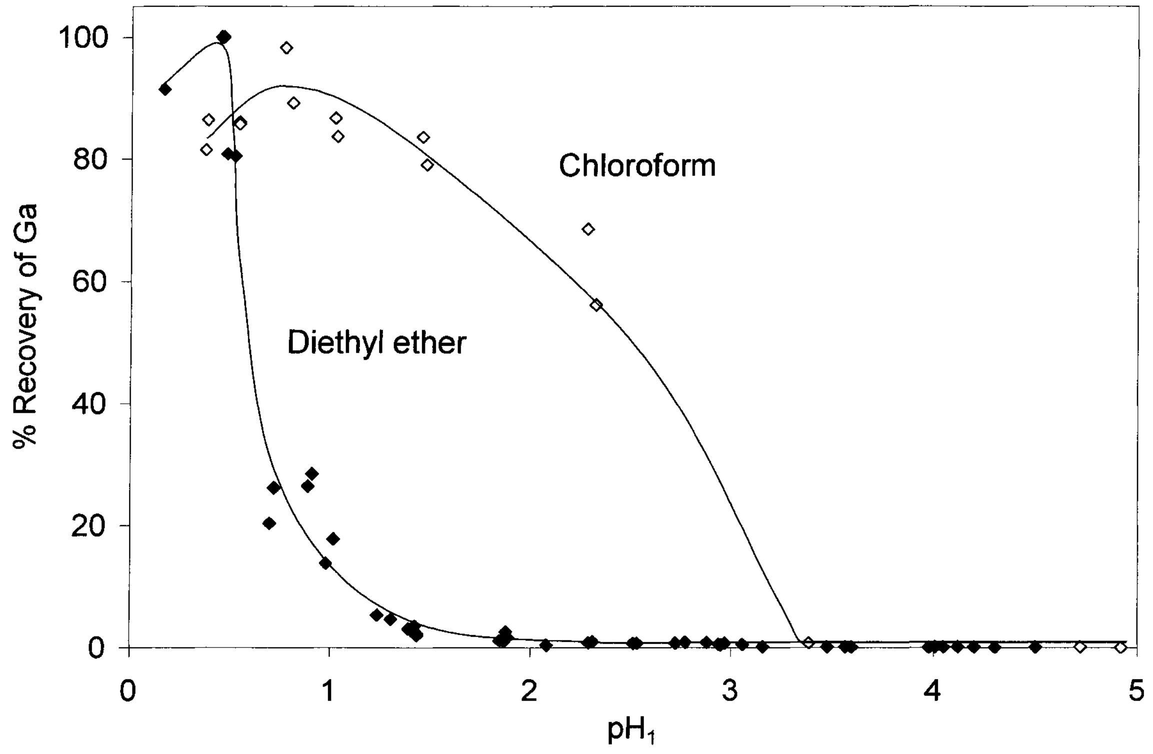


Figure 3.11: Percent recovery of gallium in the aqueous phase at different pH using diethyl ether (◆) or chloroform (◇).

A recovery between 90 to 100 % of gallium was obtained at pH_l around 0.5 and 0.8 for diethyl ether and chloroform, respectively. A further decrease in the pH resulted in a decrease of the percent recovery of gallium.

In the literature, gallium is extracted into an organic phase from an acidic solution (Sheka *et al.*, 1966). Thus, it is believed that gallium became more soluble in diethyl ether or chloroform phase as the pH decreased below 0.5. An increase in the pH of the aqueous solution resulted also in a decrease in the percent gallium recovery. As the pH increased, the concentration of gallium in the aqueous solution decreased and a precipitate containing both gallium and ligand formed at the water/solvent interface. The pH of the solution was close to the pH where the highest removal of gallium with the sodium di-(n-octyl) phosphinate ligand was obtained and thus can explain the formation of insoluble gallium-ligand complexes at the interface. While both solvents solubilized the ligand, the advantage of chloroform over diethyl ether is its lower solubility in water (8.2 g/L vs 75 g/L - see Table 3.1).

Table 3.1: Characteristics of different solvents (Perry and Green, 1997)

Solvent	Solubility (g/L)	Boiling Point (°C)
Chloroform	8.2	61.2
Diethyl ether	75	34.6
Benzene	0.70	80.1
Toluene	0.50	110.8

When smaller amounts of diethyl ether were added to dissolve the complex, the solubility of the solvent in the aqueous phase inhibited the complete extraction of the ligand. As a result, some ligand remained solubilized with the solvent in the aqueous phase. Another disadvantage of diethyl ether is that a lower pH is necessary to recover the gallium from the gallium/ligand complex. On the other hand, since the solvent must be evaporated to regenerate the ligand, the higher boiling point of chloroform is a disadvantage. For fast recovery or to concentrate the gallium removed from an acidic solution, chloroform can be used up to a pH of 1.5. The ligand in the organic phase requires further treatment with sodium hydroxide for regeneration.

Using a basic aqueous phase, the gallium was recovered and the ligand was regenerated at the same time in its sodium form. The complex was dissolved in an aqueous NaOH solution (5 mL of 3 N NaOH), then mixed with an organic phase (5 mL of diethyl ether). In this strong basic condition, the hydroxyl ions compete with the ligand for the gallium and the sodium ions compete with the gallium for the ligand. More than 98 % of the gallium was concentrated in the aqueous solution while all the ligand was extracted into the diethyl ether phase. The ligand was then regenerated by evaporating the diethyl ether phase. No gallium was detected in the regenerated ligand. The gallium was recovered at a concentration 4 times larger than its initial concentration. Higher gallium concentrations can be achieved by using a larger volume of gallium solution during the removal process and a smaller amount of NaOH during the regeneration. The recovery of the gallium using concentrated NaOH solution presents an advantage over the recovery in acidic solution because the ligand is regenerated in its sodium form and the amount of gallium recovered is higher.

3.1.6 Comparison of extraction and precipitation process for the gallium recovery

The extraction processes use solvents, such as benzene or toluene, in which the extractant is solubilized. The solvent is contacted directly with the solution to extract the metals from the aqueous solution. However, a part of the solvent remains in the treated aqueous solution with the extractant. The extraction processes are generally inhibited by the formation of insoluble metal-hydroxide precipitates as they remain in solution and thus are not extracted into the organic phase (Uchida and Okuwaki, 1997). In addition, the temperature used in the extraction process is limited by the boiling point of the organic solvent.

In the removal process using the sodium di-(n-octyl) phosphinate, the gallium is recovered from ligand complexes either in an acidic aqueous solution with a pH below pH 2 or in a basic aqueous phase with a pH > 14, while the ligand remains in the chloroform or diethyl ether phase. Hydrochloric acid should not be used for the recovery of the gallium as gallium can be extracted into the solvents by forming chloride complexes (Mihaylov and Distin, 1992 a). Although benzene and toluene have a lower solubility in water than chloroform and diethyl ether but a higher boiling point, as shown in Table 3.1, the volume of aqueous solution in contact with the solvent was less using the sodium di-(n-octyl) phosphinate. Thus, the total amount of organic phase lost in the aqueous phase was less compared to the extraction method. The lower boiling points of chloroform and diethyl ether make these solvent easier to remove from the aqueous solution than benzene and toluene. The formation of insoluble metal hydroxide supplements the removal of gallium with less amount of ligand. Furthermore, the removal of the metal using the sodium di-(n-octyl) phosphinate ligand increased by increasing temperature. Even at temperature above 40°C, the concentration of gallium in the aqueous solution remained undetectable.

3.2 Removal of gallium with other ligands

Based on the affinity of the sodium di-(n-octyl) phosphinate for the removal of metals by complexation, other organophosphorus ligands were investigated for the removal of gallium. The effect of the length of the carbon chain was studied with the sodium di-(n-dodecyl) phosphinate, while the effect of the sulfur and oxygen on the organophosphorus affinity for gallium were investigated using the O,O-di-(octyl) dithiophosphoric acid and the sodium mono-octyl ester phosphinate.

The affinity of the carboxylic group for gallium was investigated for different concentrations and different pH using the fumaric and humic acids. The removal of gallium by a mixture of two ligands, sodium di-(n-octyl) phosphinate and humic acid, was also tested.

3.2.1 Organophosphorus ligands

The removal of gallium using three organophosphorus ligands was studied in a nitrate solution at different pH using the ratio $r^{\circ}_{L/Ga} = 3$ for $C^{\circ}_{Ga} = 0.359$ mM. The removal of gallium using the octyl and dodecyl form of the sodium di-(n-alkyl) phosphinate ligand is shown in Figure 3.12. At pH > 1, the percent removal of gallium was lower with sodium di-(n-dodecyl) phosphinate than with the sodium di-(n-octyl) phosphinate. In acidic pH, up to 50 % of gallium was removed by the sodium di-(n-dodecyl) phosphinate ligand. At pH < 1, more gallium was removed by the sodium di-(n-dodecyl)

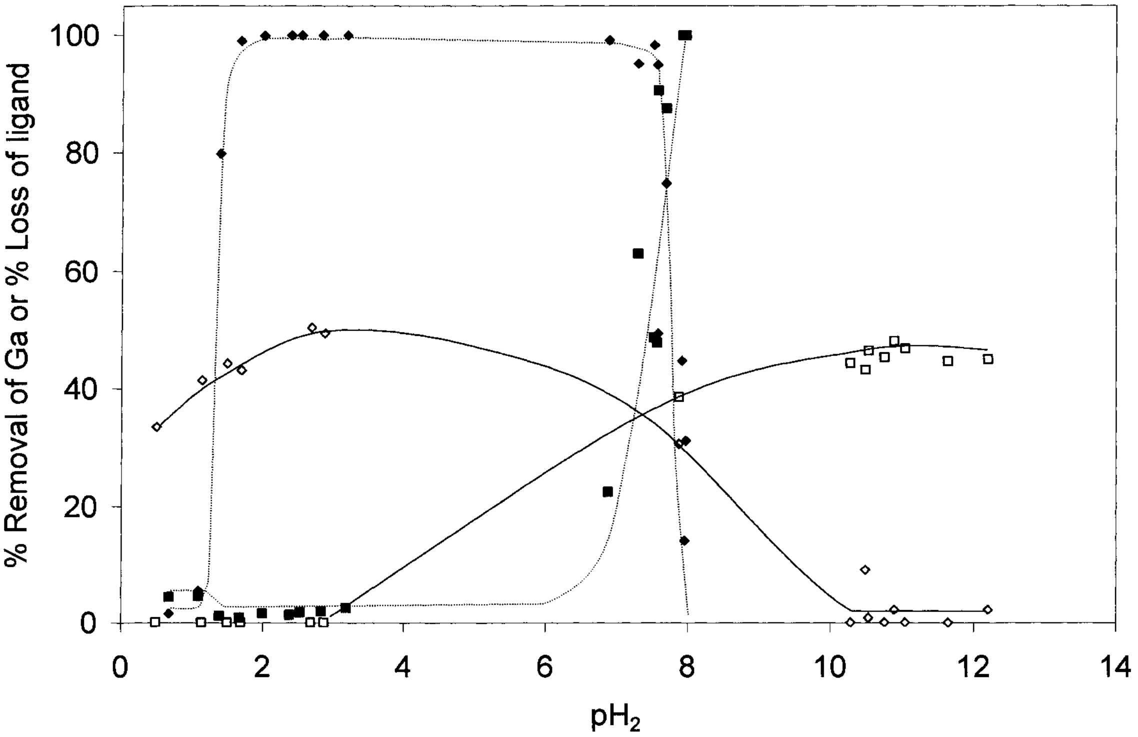


Figure 3.12: Effect of pH on the percent removal of gallium (◆,◇); percent loss of sodium di-(n-octyl) phosphinate (■); and percent loss of sodium di-(n-dodecyl) phosphinate (□) [$C^{\circ}_{Ga} = 0.359$ mM; $r^{\circ}_{L/Ga} = 3$].

phosphinate than with sodium di-(n-octyl) phosphinate. The sodium di-(n-dodecyl) phosphinate remaining in solution after the complexation with gallium was below the detection limit indicating that the ligands were removed either by complexation with the gallium or in its acidic form. At a pH higher than 8, as the ligand became more water soluble, about 50 % of the sodium di-(n-dodecyl) phosphinate ligand remained in solution. The solubility of the sodium di-(n-dodecyl) phosphinate in water is lower than that of the octyl form (Esalah, 1997), resulting in the remaining 50 % of the ligand in solid form (approximately 200 mg/L or 0.47 mM). The gallium remained in the aqueous phase at pH above 8 due to the formation of the soluble $Ga(OH)_4^-$.

Figure 3.13 shows the removal of gallium using the sodium mono-octyl ester phosphinate ligand. While some gallium was removed at pH below 3, essentially complete removal was obtained at pH between 4 and 6. In this pH range, insoluble $Ga(OH)_{3(s)}$ is formed as reported in Figure 3.3. Although most of the ligand, around 80 %, remained in solution in acidic conditions, more gallium was removed from the solution after 1 day using sodium mono-octyl ester phosphinate. It is believed that some of the ligand removed formed a ligand-metal complex which favored the removal of gallium. In basic solution, the ligand remained in the aqueous phase, similar to the sodium di-(n-octyl) phosphinate ligand.

Based on the affinity of dithiophosphinic acid extractant for gallium (Wang *et al.*, 1996), the removal of gallium by complexation using the O,O-di-(octyl) dithiophosphoric ligand was attempted in an aqueous solution. Although the structure of the thio organophosphorus extractants is stable in an organic phase, the sulfur groups of the ligand were oxidized in the aqueous solution.

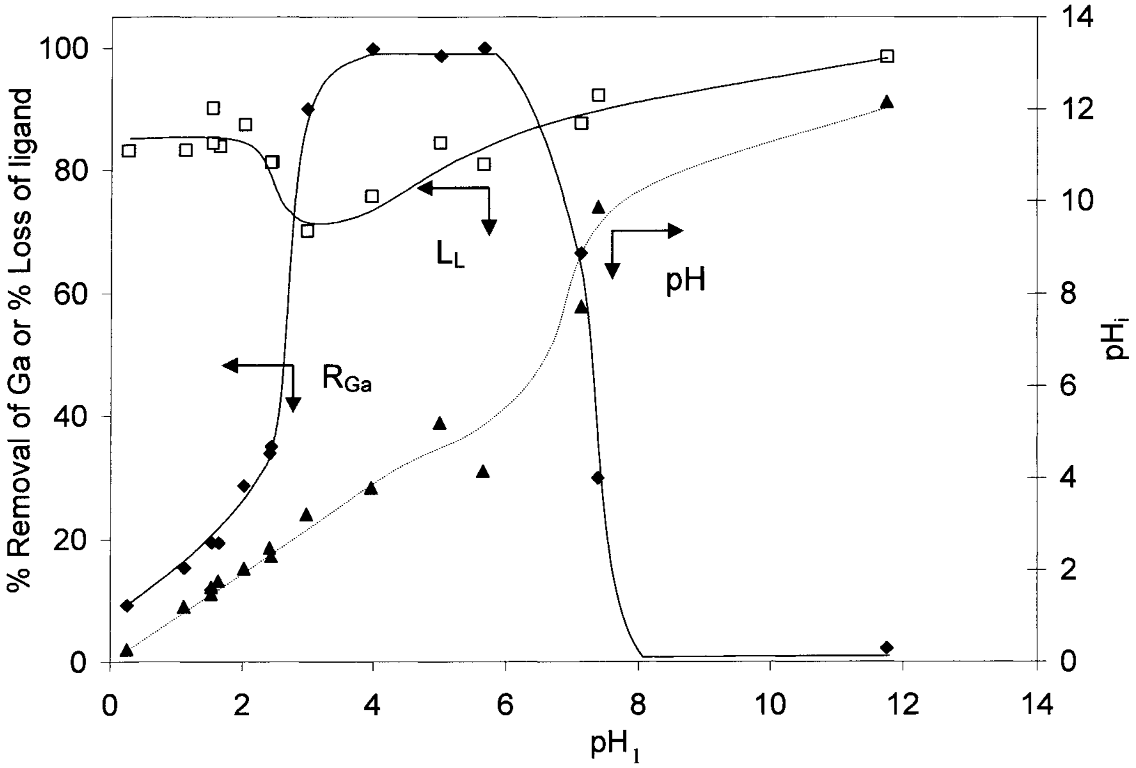


Figure 3.13: Effect of pH (▲) on the percent removal of gallium (◆); and percent loss of sodium mono-octyl ester phosphinate (□) [$C^{\circ}_{Ga} = 0.359$ mM; $r^{\circ}_{L/Ga} = 3$].

No further testing of this ligand was performed

3.2.2 Carboxylic group: fumaric and humic acids

The removal of gallium by fumaric acid was investigated at different pH in a nitrate solution. Two concentrations of fumaric acid at a molar ratio of fumaric acid to gallium of 3.6 and 18 were used. As shown in Figure 3.14, the gallium was removed after 1 day at a pH between 3 and 4 for both concentrations of fumaric acid. When no fumaric acid was added, the gallium remained in solution up to a pH above 4, and the insoluble $Ga(OH)_{3(s)}$ formed as the pH further increased. As explained previously, the precipitation of $Ga(OH)_{3(s)}$ does not reach equilibrium after 1 day. After 6 days, the removal of gallium trihydroxide was still occurring at a higher pH. As the concentration of fumaric acid increased, the pH range at which the gallium was removed became wider. The fumaric acid favored the removal of the gallium.

In order to study the removal of gallium using humic acid, the effect of pH on the removal of humic acid without the addition of metal was first investigated. A solution containing a fixed amount of humic acid (120 mg/L of carbon) was prepared. The concentration of carbon obtained by TOC analysis was used as an indication of humic acid concentration. As observed in Figure 3.15, about 20 % of carbon and thus of humic acid remained in solution at pH around 1. As reported by Swift (1996), the humic acid is composed of a mixture of compounds some of which are soluble in basic solutions but precipitate at pH 1. Also observed in Figure 3.15, there was no effect of the sodium di-(n-octyl) phosphinate on the removal of the humic acid from the solution. The organophosphorus ligand was removed in its acidic form up to a pH about 7, while the

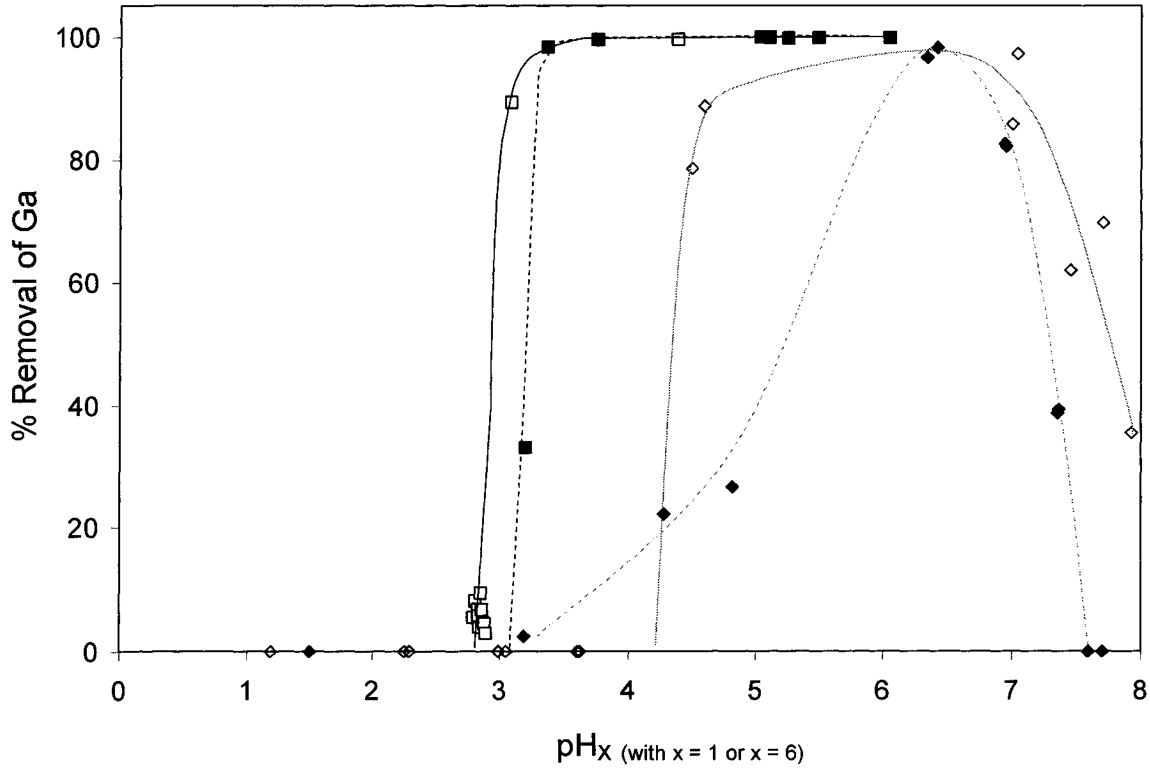


Figure 3.14: Effect of pH on the removal of gallium with and without fumaric acid [C°_{Ga} = 0.359 mM; no fumaric acid: 1 day (◆), 6 days (◇); fumaric acid after 1 day: $r^{\circ}_{L/Ga}$ = 3.6 (■) and 18 (□)].

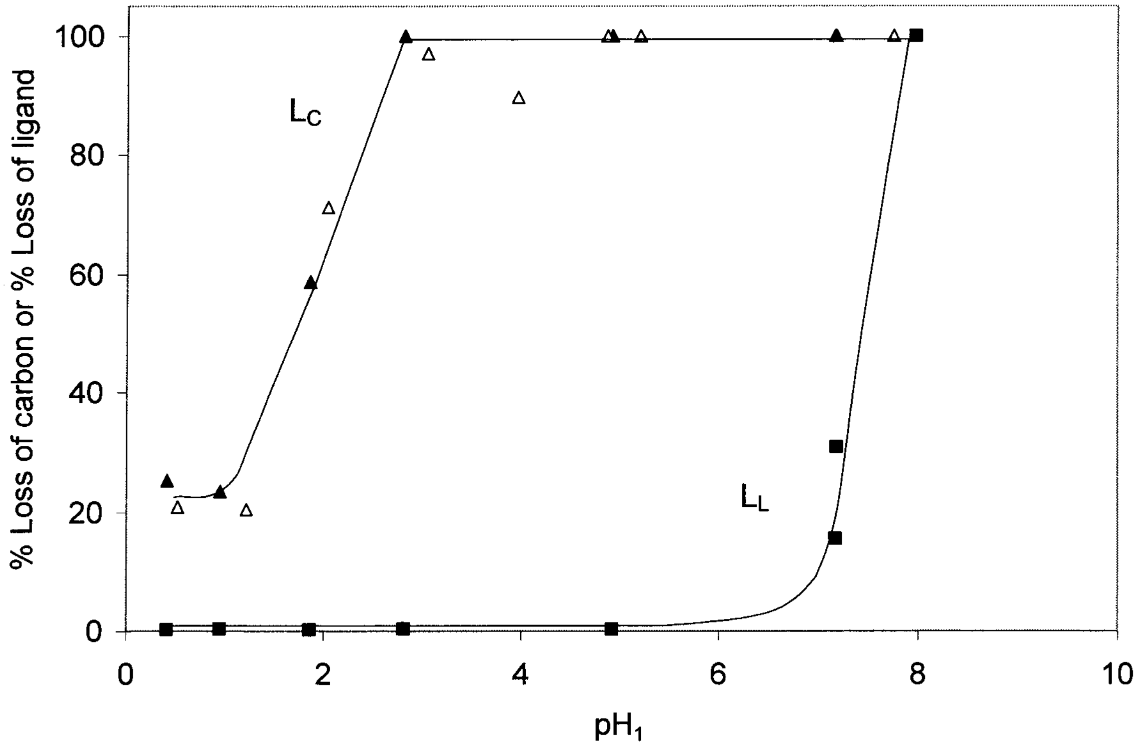


Figure 3.15: Effect of pH on the percent loss of carbon associated to humic acid in an aqueous solution with only humic acid (Δ); and percent loss of carbon associated to humic acid and sodium di-(n-octyl) phosphinate in an aqueous solution with humic acid (▲) and sodium di-(n-octyl) phosphinate (■) [humic acid: 120 mg/L of carbon; sodium di-(n-octyl) phosphinate: 1.08 mM].

humic acid precipitated in the same pH range with or without the addition of organophosphorus ligand.

The effect of the humic acid on the removal of gallium was investigated using two concentrations of humic acid, chosen arbitrarily at 40 and 120 mg/L of carbon. Figure 3.16 compares the removal with humic acid to the removal without humic acid. With 40 mg/L of carbon as humic acid, the removal of gallium increased for $3 < pH < 4$, but at the higher concentration of humic acid (120 mg/L of carbon), less gallium was removed. The gallium removal data from Figure 3.16 are shown with the carbon loss data in Figure 3.17 for solutions containing both gallium and humic acid. The carbon associated to the humic acid was removed from both solutions even at pH values where the humic acid was soluble. In the case of the solution containing 120 mg/L of carbon as humic acid, 5 % of the carbon was lost from the gallium solution at pH 1.2 compared to more than 20 % at the same pH with no gallium in the solution. In this pH range of 0.2 to 1.2, approximately 10 to 13 % of the gallium was removed. The soluble humic substances can bind metal (Christl *et al.*, 2001 a). For example, the metal complexes formed with fulvic acid, a compound found in humic acid, are generally insoluble around pH of 1, and thus removed from the solution. As the pH increased, more gallium was removed from the solution. For the concentration of humic acid = 40 mg/L, less than 20 % of the carbon was lost between pH 0.5 and 8. While the carbon and thus the humic acid remained in solution when no gallium was present as shown in Figure 3.15, less than 10 % of the organic carbon was lost at pH above 2. Also a decrease of 5 % of the organic carbon loss was observed above pH 4 when humic acid concentration equal to 40 mg/L.

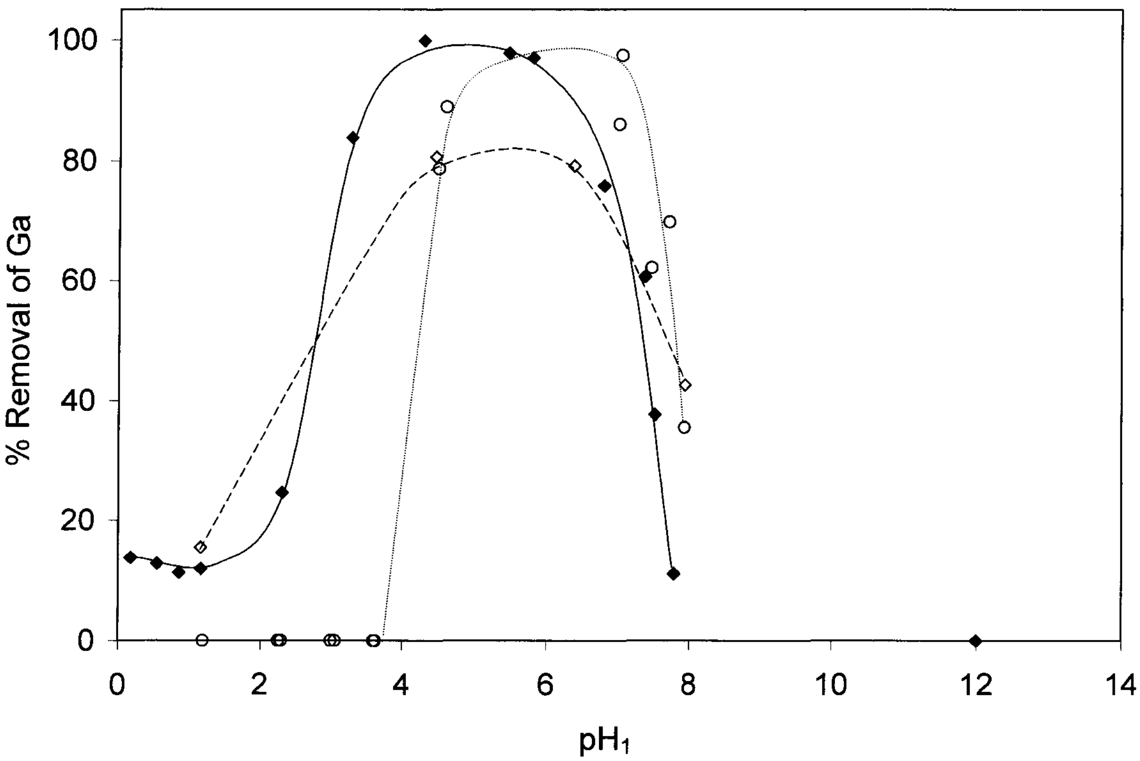


Figure 3.16: Effect of pH on the percent removal of gallium using humic acid [C°_{Ga} = 0.359 mM; no humic acid (○); humic acid: 40 mg/L of carbon (◆), 120 mg/L of carbon (◇)].

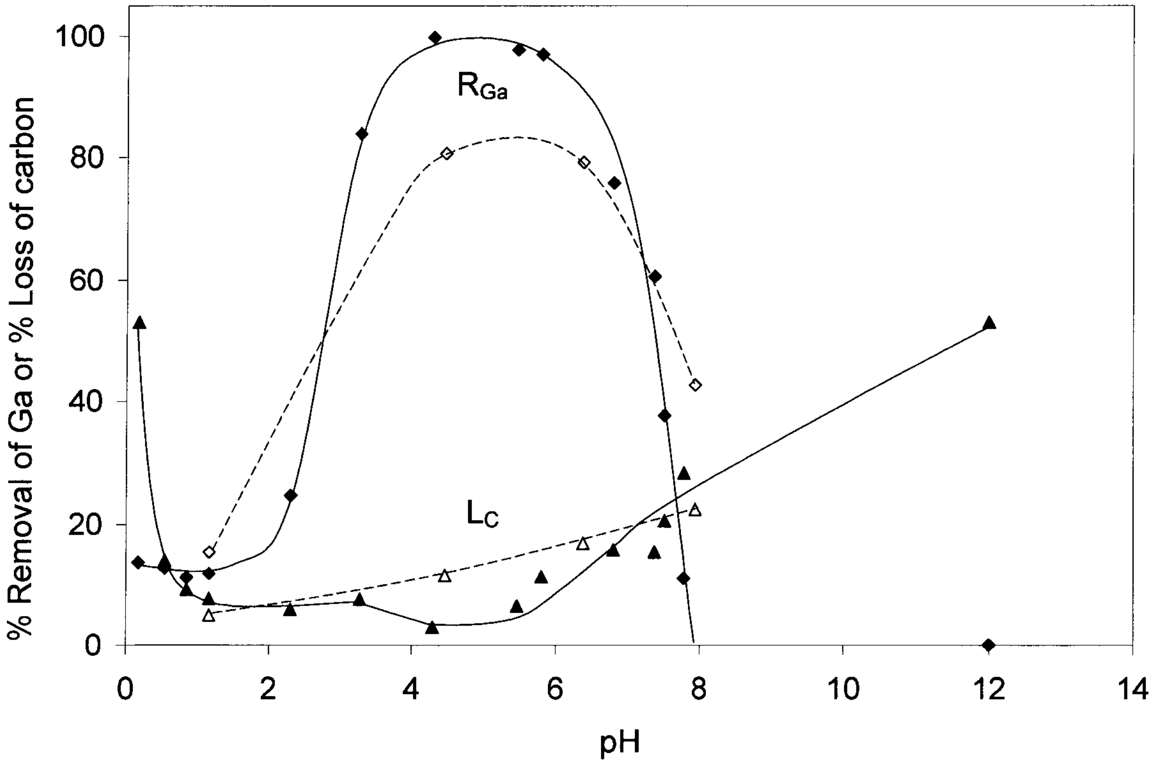


Figure 3.17: Effect of pH on the percent removal of gallium and percent loss of carbon associated to humic acid [humic acid = 40 mg/L of carbon (▲) and C°_{Ga} = 0.359 mM (◆); humic acid = 120 mg/L of carbon (△) and C°_{Ga} = 0.359 mM (◇)].

This pH corresponded to the highest removal of gallium from the solution indicating the interactions between the gallium, its hydroxide complexes and the humic acid. Christl *et al.* (2001 b) reported that the negative charge of the humic substances increases with pH due to the deprotonation of the acidic functional group. Thus, as pH increases, gallium and the humic substances bind forming an insoluble complex. Christl *et al.* (2001 a) suggested also the formation of different metal-ligand complexes depending on the metal and its concentration. The formation of these complexes can explain the decrease of the removal of the gallium with increasing amounts of humic acid. While some humic acid constituents are insoluble in acidic solution, others are insoluble in basic solution (Swift, 1996). At a pH of 12, approximately 50 % of the organic carbon remained in solution.

A solution containing 120 mg/L of carbon as humic acid, 0.359 mM of gallium nitrate and the sodium di-(n-octyl) phosphinate ligand at $r^{\circ}_{L/Ga} = 3$ was prepared. While the gallium can be removed by either the sodium di-(n-octyl) phosphinate ligand or the humic acid, their combination reduced the removal of gallium as shown in Figure 3.18. The percent removal of gallium decreased as the pH increased above 2 to 3 and as the humic acid became more soluble. At pH between 3 and 8, where the precipitation of gallium trihydroxide occurs, an increase of the removal of the gallium was observed. However, the removal was lower than the one obtained for gallium trihydroxide without the humic and the organophosphorus ligands. The formation of ligand-humic acid-gallium complexes can explain this lower removal. For all the experiments performed with the humic acid, the final solution was highly turbid. Thus, if this ligand were to be used with humic acid for metal complexation, further treatment would be required to clarify the aqueous solution.

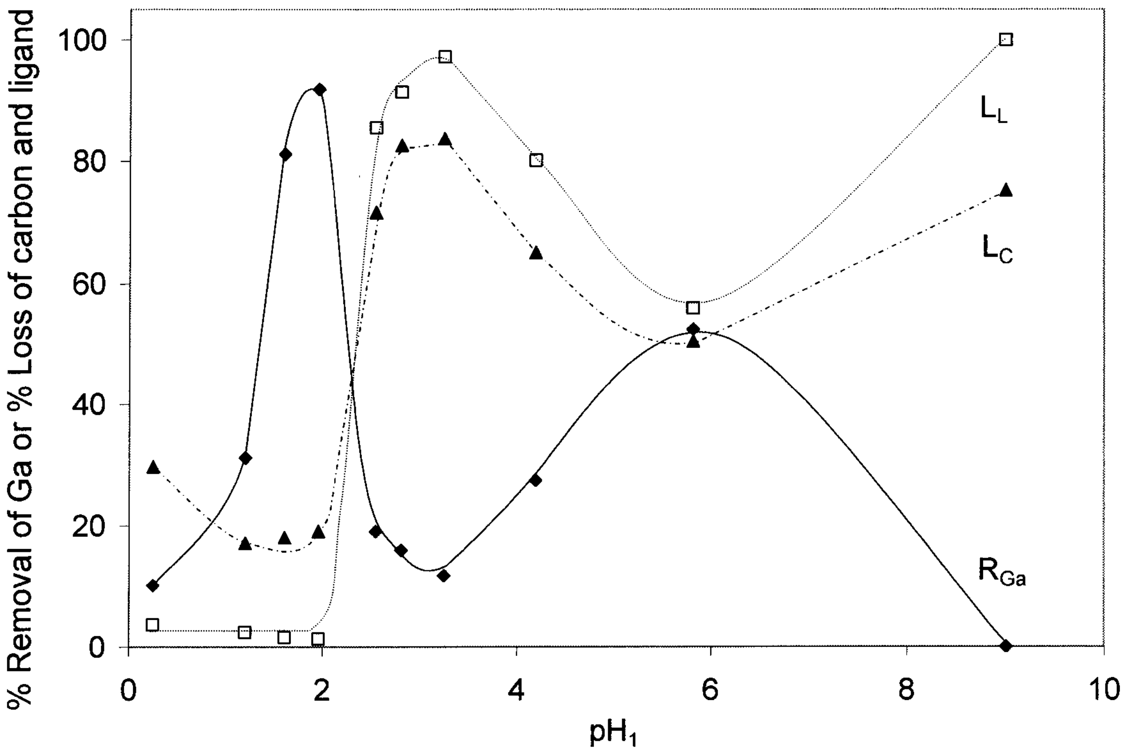


Figure 3.18: Effect of pH on the percent removal of Ga (◆); percent loss of carbon associated with humic acid (▲); and percent loss of sodium di-(n-octyl) phosphinate ligand (□) [$C^{\circ}_{Ga} = 0.359$ mM; humic acid = 120 mg/L of carbon; $r^{\circ}_{L/Ga} = 3$ for sodium di-(n-octyl) phosphinate].

3.3 Removal of other metal ions with sodium di-(n-octyl) phosphinate

3.3.1 Removal of aluminum

The separation of aluminum from an aqueous solution using sodium di-(n-octyl) phosphinate was studied at different pH, mole ratio of the ligand to metal and in the presence of different ions.

3.3.1.1 Hydrolysis of aluminum

The effect of pH on the removal of aluminum, from a nitrate solution with C°_{Al} = 0.925 mM (25 mg/L), is shown in Figure 3.19. Depending on the pH, different hydroxyl-complexes can be formed by Al^{3+} as follows:

$$Al^{3+} + n\,OH^{-} \longleftrightarrow Al\,(OH)_{n}^{3-n}, \qquad (3.8)$$

where n = 1, 2, 3 and 4. The speciation diagram of aluminum generated by using the mass stability constants reported by Baes and Mesmer (1986) is shown in Figure 5.3, in Chapter 5. In very acidic media, aluminum is present as soluble Al^{3+}. As the pH increases, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ are formed followed by $Al(OH)_3$ at pH above 4. The insoluble aluminum trihydroxide, $Al(OH)_3$, precipitates between pH 4 and 9, with a maximum removal at a pH of about 7. At pH around 9, the soluble $Al(OH)_4^{-}$ was formed, and the consumption of OH^{-} lowered the pH of the aluminum solutions.

3.3.1.2 Effect of the mole ratio of ligand to aluminum

The percent removal of aluminum and the percent loss of the ligand are shown in Figure 3.20 for a nitrate solution with C°_{Al} = 0.925 mM (25 mg/L) and pH_i = 2.75 ($r^{\circ}_{NaOH/Al}$ = 6.64). The solution contained the sodium di-(n-octyl) phosphinate at different $r^{\circ}_{L/Al}$.

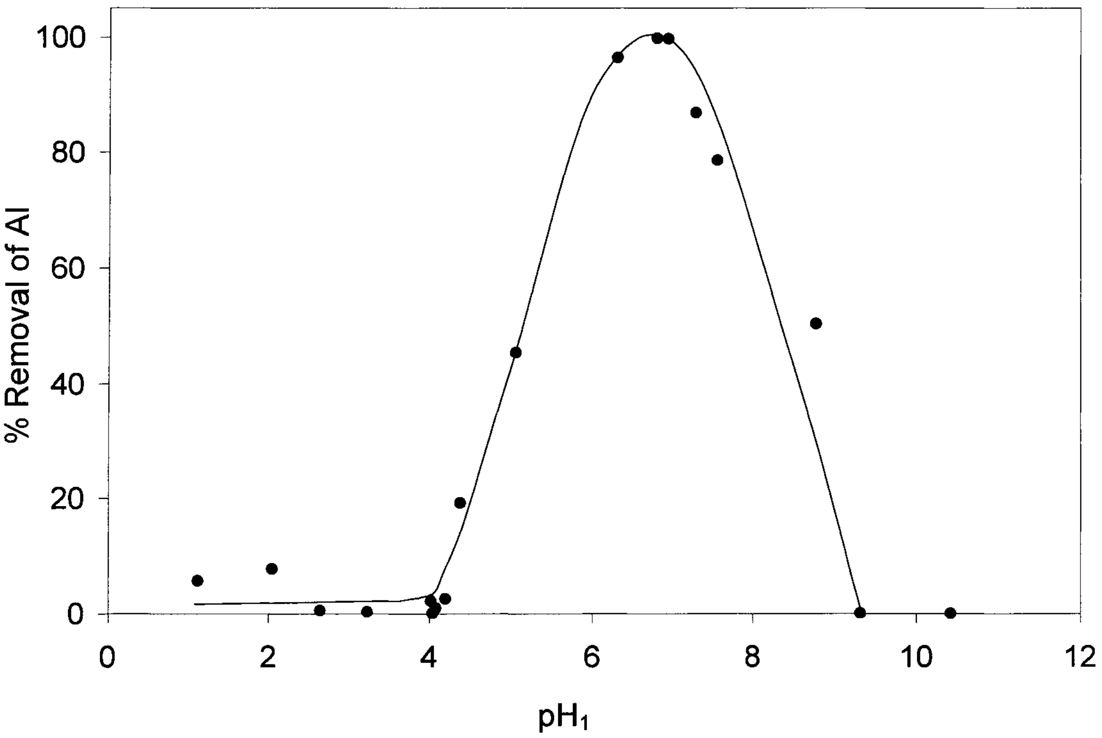


Figure 3.19: Precipitation of aluminum in aqueous solution as a function of pH [C^{o}_{Al} = 0.925 mM].

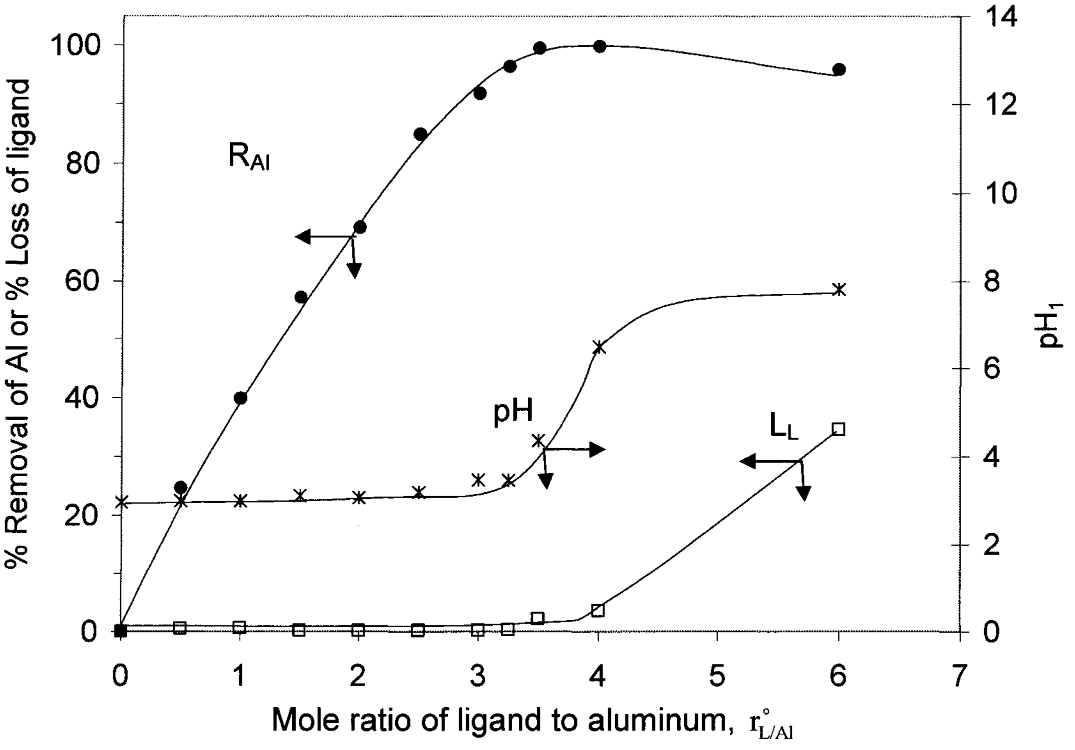


Figure 3.20: Effect of mole ratio of sodium di-(n-octyl) phosphinate to aluminum on the percent removal of aluminum (●), percent loss of sodium di-(n-octyl) phosphinate (□) and pH$_1$ (*) [C°_{Al} = 0.925 mM; pH$_i$ = 2.75 ($r^{\circ}_{NaOH/Al}$ = 6.64)].

The removal of aluminum increased linearly up to a value $r^{\circ}_{L/Al} = 3$ with a small increase in the final pH. At $r^{\circ}_{L/Al} = 3$, the mean concentrations of aluminum and ligand remaining in the solution (with 95 % confidence interval) were 0.7 ± 0.1 mg/L and 5 ± 0.5 mg/L, respectively. Based on these results, the following reaction describes the formation of the insoluble-complex $AlL_{3(s)}$ at a pH below 4:

$$Al^{3+} + 3\,L^{-} \longleftrightarrow Al\,L_{3(S)} \tag{3.9}$$

where the symbol L^{-} represents the radical $(C_8H_{17})_2POO^{-}$.

For pH > 4, competition between the hydroxyl and the ligand for the aluminum occurs. The highest percent removal with the lowest loss of ligand was observed at $r^{\circ}_{L/Al} = 3.25$. Higher mole ratios decreased the loss of ligand which precipitated in its acidic form (reaction 3.3). The consumption of the H^+ ions by the ligand increased the pH to a value near 8 where the ligand tends to remain in solution, thus the percent removal of aluminum decreased slightly.

3.3.1.3 Effect of the pH on the removal of aluminum

The effect of pH by addition of HNO_3 or NaOH on the removal of aluminum is shown in Figure 3.21. The initial solution had a concentration of aluminum nitrate C°_{Al} of 0.925 mM (25 mg/L) and the mole ratio of the ligand to aluminum ($r^{\circ}_{L/Al}$) was fixed at 3.1 for all the experiments. A complete removal of the aluminum was obtained for a final pH around 3. Decreasing pH below 3 lowered the percent removal of aluminum while the percent loss of the ligand remained constant. This result is attributed to the formation of the acidic form of the ligand, HL. The pH is always slightly higher than the initial pH because some H^+ ions are consumed in the formation of the acidic form of the ligand.

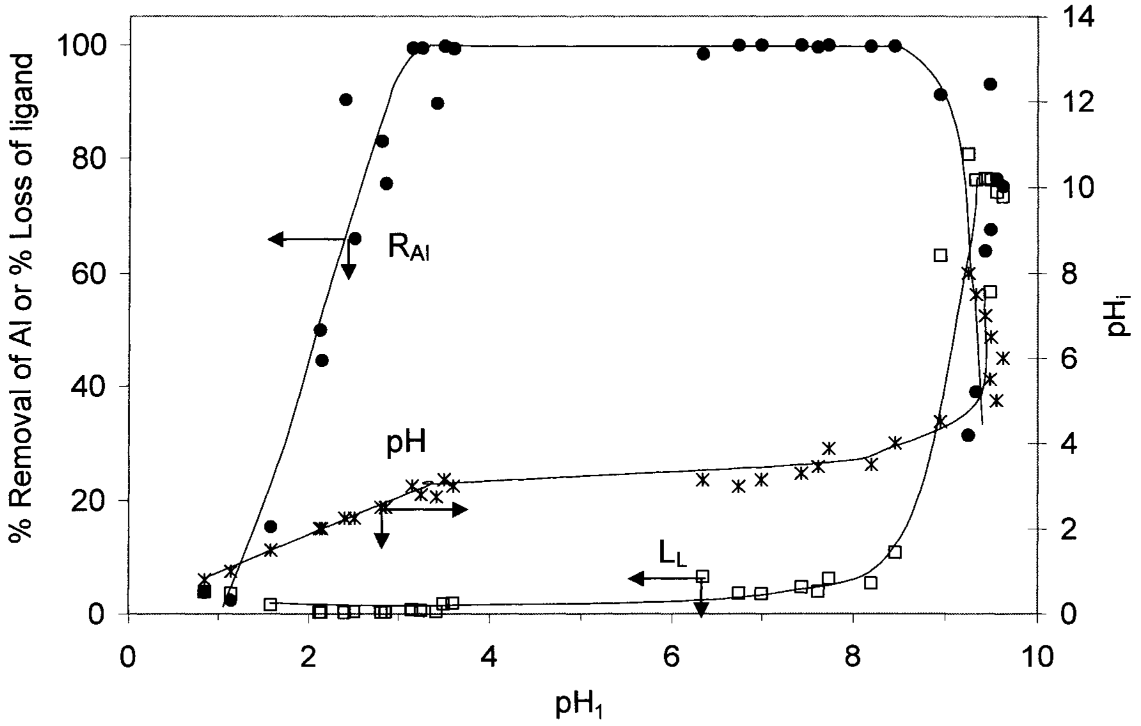


Figure 3.21: Effect of pH (*) on the percent removal of aluminum (●) and percent loss of sodium di-(n-octyl) phosphinate (□) [$C^{o}_{Al} = 0.925$ mM; $r^{o}_{L/Al} = 3.1$].

At pH below 1.2, the aluminum remained in solution while the acidic ligand was removed from the solution. As previously mentioned for gallium, some acidic ligand, HL, remained soluble due to the acidity constant of the complex. The acidity constant of HL being higher than the one of the soluble ligand-aluminum complex, an increase of the loss of the ligand to 4 % can be observed below pH 1.2. The values of the acidity constants of the aluminum-hydroxyl complexes are given in Chapter 5. As pH_i increased from 3 to 4, the percent removal of aluminum and the percent loss of the ligand remained constant, while the pH increased from around 3 to 8. In this pH range, the main species of aluminum is aluminum trihydroxide. As mentioned in Appendix 3, the formation of the soluble aluminum-hydroxyl complexes is fast and the complexes were already formed at pH_i. Thus, the ligand competes with the OH^- ions for the aluminum. The formation of the aluminum-ligand complexes frees more OH^- ions and pH increases. At pH above 8 which is the natural pH of the ligand, the percent removal of aluminum decreased due to the formation of the soluble $Al(OH)_4^-$ complex, and the excess ligand remains in the aqueous solution.

In Figure 3.22, the percent removal of aluminum and the pH for three sets of samples having an aluminum nitrate concentration of 0.925 mM (25 mg/L), and at pH_i values of 2, 2.5 and 2.75, are compared at different values of $r^{\circ}_{L/Al}$. For $pH_i = 2$, no pH adjustment was necessary, while for $pH_i = 2.5$ and 2.75, NaOH was added at $r^{\circ}_{Na/Al} = 5.40$ and 6.64, respectively. For a fixed value of $r^{\circ}_{L/Al}$, the removal of aluminum increased when pH_i increased from 2 to 2.75, because less ligand was removed as $HL_{(s)}$, and thus available to remove the aluminum. The highest percent removal of aluminum for each pH_i was obtained at a different value of $r^{\circ}_{L/Al}$.

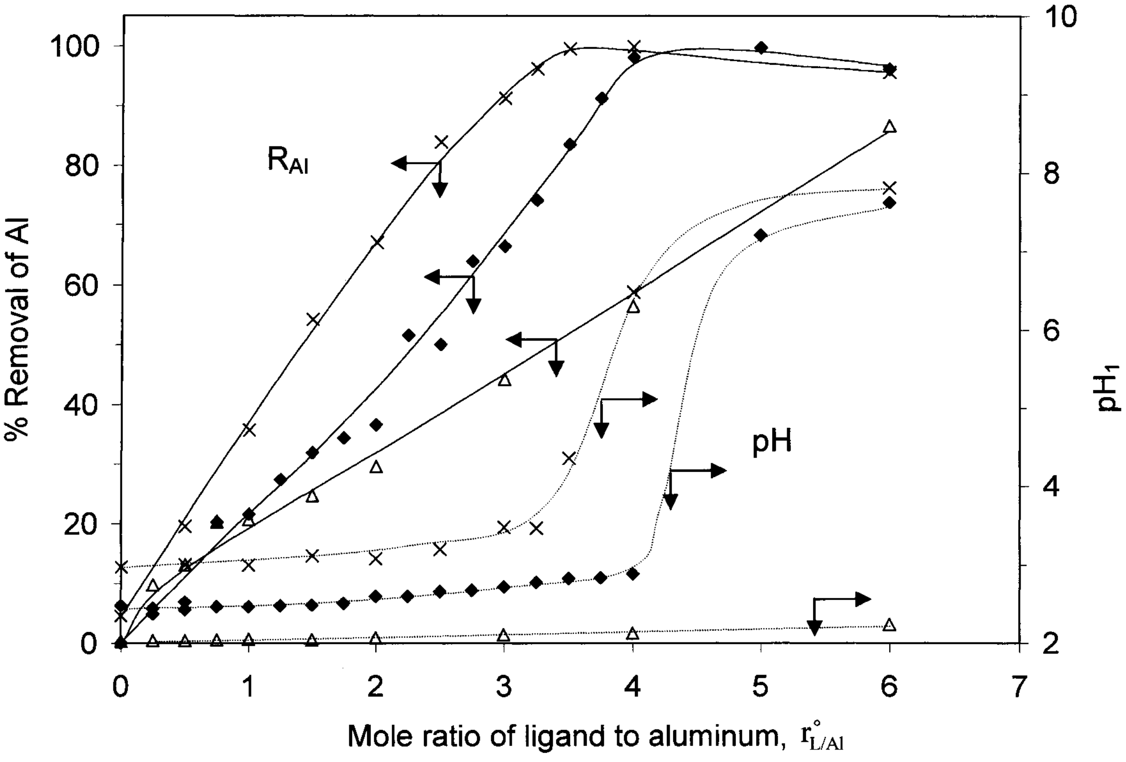


Figure 3.22: Effect of mole ratio of sodium di-(n-octyl) phosphinate to aluminum on the percent removal of aluminum (straight lines) and the pH (dashed lines) for different pH$_i$ [C°_{Al} = 0.925 mM; pH$_i$ = 2.75 ($r^{\circ}_{NaOH/Al}$ = 6.64) (×); pH$_i$ = 2.50 ($r^{\circ}_{NaOH/Al}$ = 5.4) (♦); pH$_i$ = 2.00 ($r^{\circ}_{NaOH/Al}$ = 0) (Δ)].

At a lower pH$_i$, higher $r^\circ_{L/Al}$ was required to remove the aluminum, because more ligand formed the complex HL$_{(S)}$.

3.3.1.4 Effect of nitrate, chloride, sulphate and sodium

Chloride and sulphate, which are present in most water streams, form soluble complexes with aluminum:

$$Al^{+3} + n\,Cl^{-} \longleftrightarrow Al(Cl)_n^{3-n} \tag{3.10}$$

$$Al^{+3} + m\,SO_4^{2-} \longleftrightarrow Al(SO_4)_m^{3-2m} \tag{3.11}$$

where $n = 1, 2, 3$, and 4 and $m = 1$ and 2.

An initial solution containing 0.925 mM (25 mg/L) of aluminum at pH$_i$ = 2.75 (around $r^\circ_{Na/Al} = 6.8$) was treated with sodium di-(n-octyl) phosphinate ligand at a ratio $r^\circ_{L/Al} = 2.5$. The mole ratio of anion to aluminum ($r^\circ_{NO_3/Al}$, $r^\circ_{Cl/Al}$ or $r^\circ_{SO_4/Al}$) was increased from 5 to 405 using $NaNO_3$, NaCL and Na_2SO_4 salts.

The percent removal of the aluminum and the final pH are shown in Figure 3.23 as a function of $r^\circ_{NO_3/Al}$, $r^\circ_{Cl/Al}$ or $r^\circ_{SO_4/Al}$. Chloride and nitrate solutions followed the same trend while the sulphate solutions were different. Using a metal stock solution prepared with $Al_2(SO_4)_3$ instead of $Al(NO_3)_3$ and no other added salt, the removal of aluminum was larger by about 10 % than the nitrate and chloride solutions. Adding more sulphate to the solution, using Na_2SO_4, formed more aluminum-sulphate complex and reduced the removal of aluminum by about 40 %. The increase of $r^\circ_{NO_3/Al}$ or $r^\circ_{Cl/Al}$ decreased the percent removal of aluminum by only 5 %. For all anion to aluminum ratios, the final pH was the same.

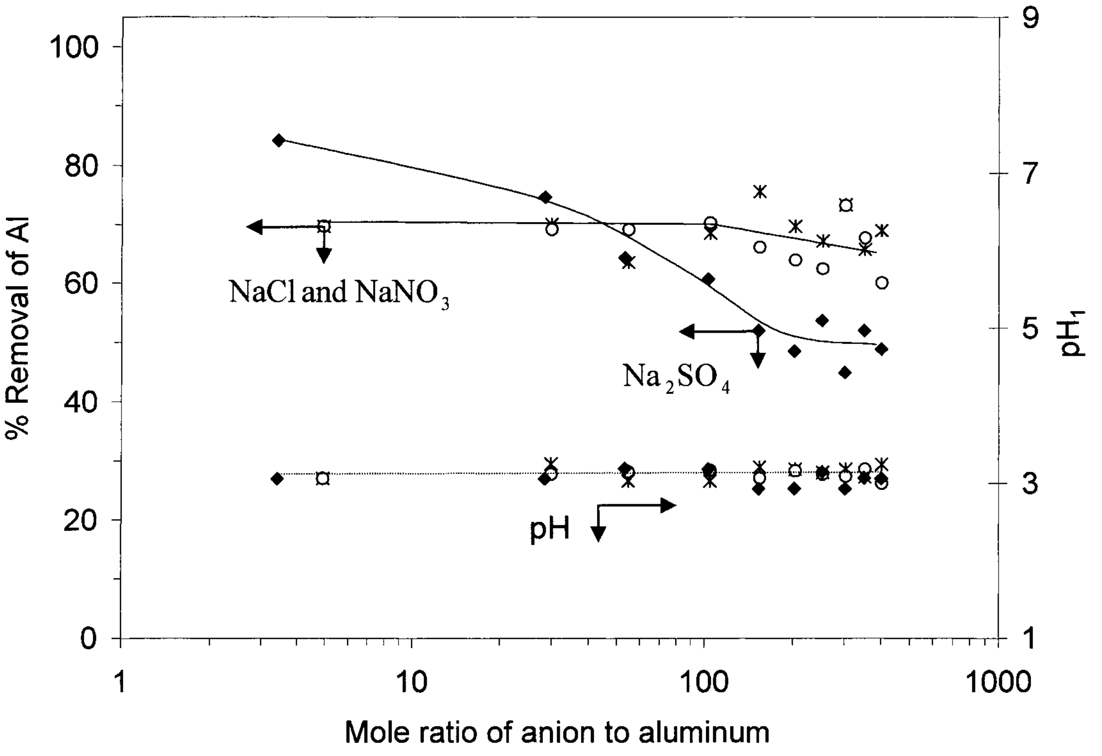


Figure 3.23: Effect of the sodium salts $NaNO_3$ (*), NaCl (O), and Na_2SO_4 (♦) on the percent removal of aluminum (straight line) and the pH (dashed line) [C°_{Al} = 0.925 mM; $r^{\circ}_{L/Al} = 2.5$; $pH_i = 2.75$ ($r^{\circ}_{NaOH/Al} = 6.8$)].

At a mole ratio of anion to aluminum of 405, over 60 % of the metal was removed from the nitrate and the chloride solution but only 40 % was removed from the sulphate solution. The effect of the sulphate on the removal of aluminum agree with the results for gallium where SO_4^{2-} strongly inhibited the removal. Aluminum forms similar sulphate complexes to gallium (Mihaylov, 1991; Ridley *et al.*, 1999). With sodium chloride addition, gallium removal was reduced by the chloride ions because gallium forms soluble complexes such as $GaCl_4^-$. The ligand was competing with the chloride ions for the gallium. Aluminum, on the other hand, forms the soluble complex $AlCl_4^-$ in non aqueous media only because in an aqueous solution it is easily hydrolyzed (Holleman and Wiberg, 2001), thus, the removal of aluminum with the sodium di-(n-octyl) phosphinate was similar in nitrate or chloride solutions. In all these cases, the increase in the sodium concentration due to the addition of sodium salts displaced reaction 3.4 to the right, resulting in a decrease in the availability of ligand to react with aluminum. For a weak electrolyte (such as $AlL_{3(S)}$ or $GaL_{3(S)}$), an increase in the ionic strength of the system, by addition of another electrolyte without a common ion (Al^{+3} or L^- for aluminum removal and Ga^{+3} or L^- for gallium removal), decreases the mean ionic activity coefficient of the weak electrolyte and thus increases its degree of dissociation, i.e. its solubility (Esalah *et al.*, 2000 b). Less metal is removed in this case. Finally, while not presented on the graph, all the ligand was removed from the aqueous solution either by complexation with the metal (reaction 3.5 or 3.9) or in its acidic form (reaction 3.3).

3.3.1.5 Regeneration of the ligand and recovery of the aluminum

To regenerate the ligand in its sodium form and recover the aluminum, sodium hydroxide and diethyl ether were used. A solid complex ($AlL_{3(S)}$) was formed by adding the sodium di-(n-octyl) phosphinate solution to an aluminum nitrate solution. The aluminum-di-(n-octyl) phosphinate solid complex was separated from the aqueous solution and then dissolved using NaOH. Diethyl ether was then added to the solution, and the mixture was agitated vigorously. After phase separation, two phases were formed: a lower (aqueous) phase, containing the aluminum and an upper (diethyl ether) phase, containing the ligand. The ligand was recovered from the organic phase by evaporating the diethyl ether. No aluminum was detected in the regenerated ligand, confirming the insolubility of aluminum-di-(n-octyl) phosphinate in diethyl ether. Over 95 % of the ligand added to the initial aluminum solution was recovered as a sodium di-(n-octyl) phosphinate solid. The volume of the aqueous basic solution, containing the aluminum, was about 5 mL, thus the concentration of aluminum was four times larger than its concentration in the initial solution.

3.3.2 Removal of indium, iron and calcium

The removal of three metals, indium, iron and calcium, at a concentration of 25 mg/L (0.22 mM), 20 mg/L (0.36 mM) and 45 mg/L (1.13 mM), respectively, was investigated with and without the sodium di-(n-octyl) phosphinate ligand. In all cases, only the nitrate salt was considered and the total volume of the solutions was 20 mL.

Figure 3.24 and 3.25 show the removal of indium and iron, respectively, without ligand added. In the case of indium, the precipitation of In $(OH)_{3(s)}$ started at around pH 3 and was essentially complete above pH 4. For iron, the precipitation of iron hydroxide began at around pH 2 and it was essentially complete at pH 4. Both indium and iron were removed from the aqueous solution up to pH 12.

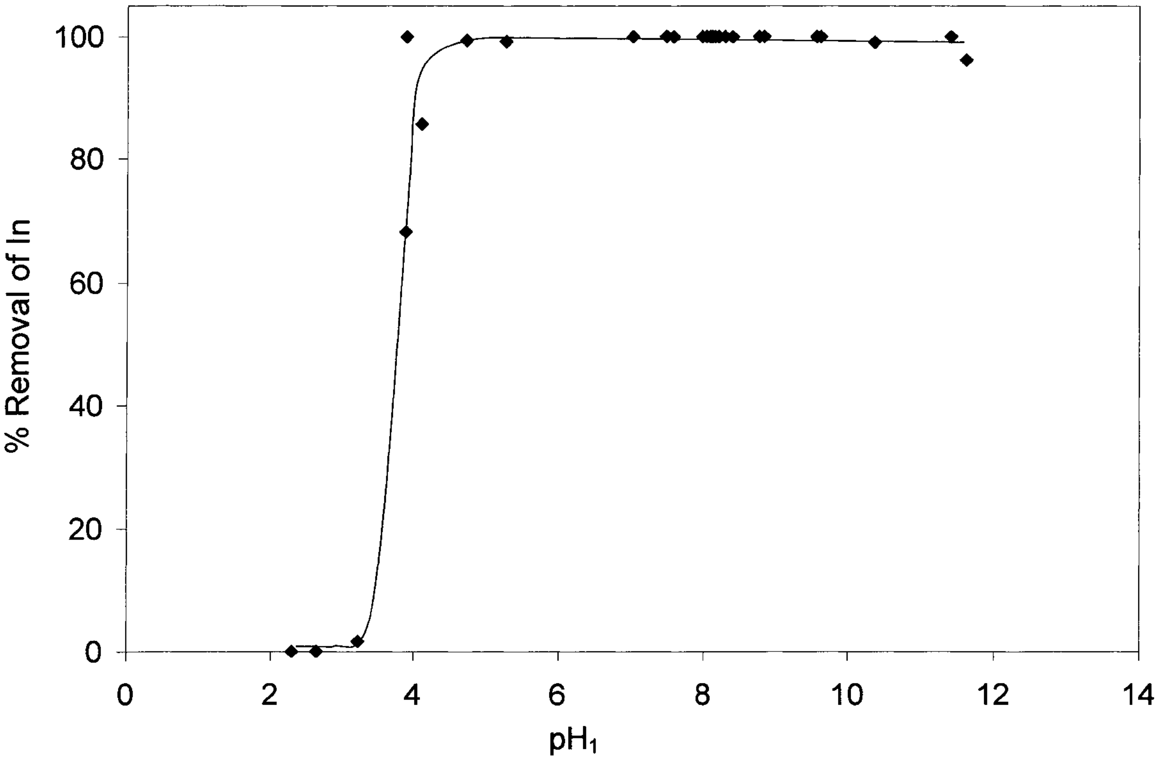


Figure 3.24: Precipitation of indium (◆) in aqueous solution as a function of pH [C°_{In} = 0.22 mM].

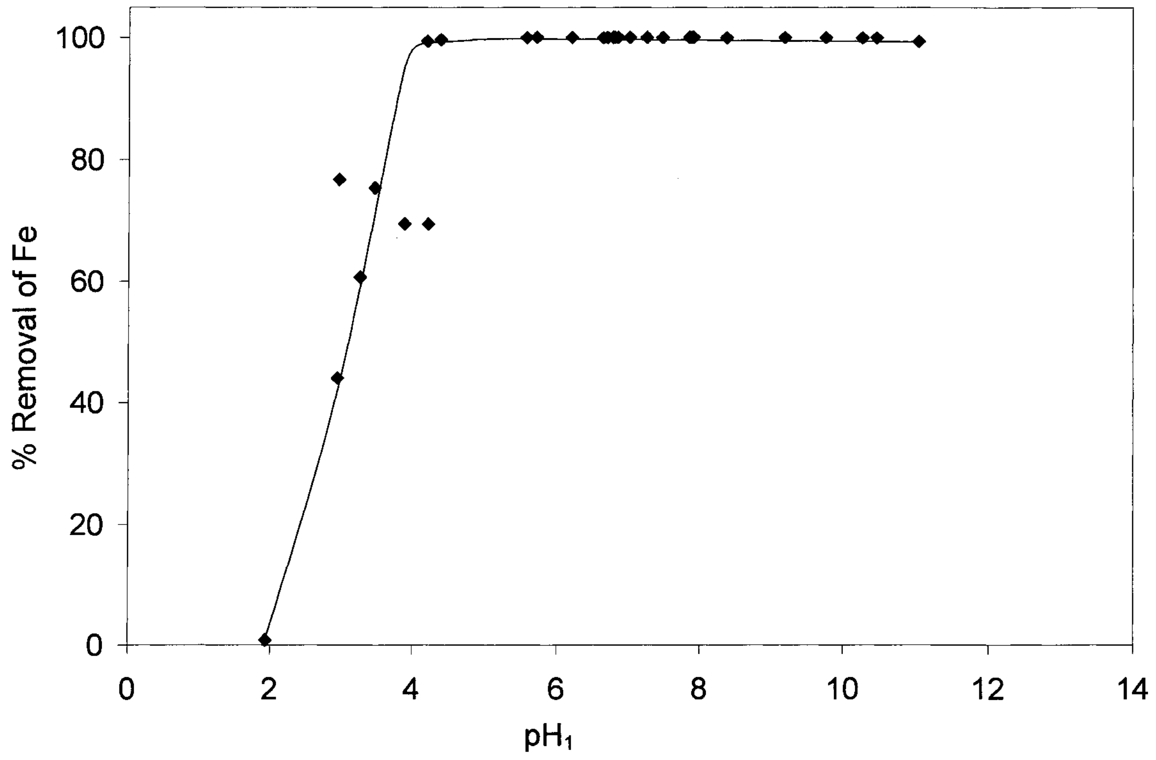


Figure 3.25: Precipitation of iron (◆) in aqueous solution as a function of pH [$C^{\circ}_{Fe} = 0.36$ mM].

These data are in good agreement with the speciation diagrams of indium and iron given in Figures 5.5 and 5.7 in Chapter 5, respectively. The formation of insoluble ferric hydroxide occurs in the pH range of the precipitation of iron and at the same concentration of iron used (Baes and Mesmer, 1986).

Since the indium and the iron precipitate in their hydroxide form at pH above 4, the removal of these metals with the sodium di-(n-octyl) phosphinate was considered only up to a pH_l of 5. In the case of calcium, higher pHs were considered as calcium does not form insoluble hydroxide complexes up to pH above 12 (Baes and Mesmer, 1986).

When mixing the metal solution (indium, iron or calcium) with the ligand solution, the behavior of the removal with time was similar to that reported for gallium in section 3.1. About 88 % of a concentration of 1 mg/L of indium was removed in less than 1 min at pH = 1 and at $r^{\circ}_{L/In} = 3$. In the case of iron, essentially complete removal was obtained in less than a day for $C^{\circ}_{Fe} \geq 0.36$ mM (20 mg/L) at a pH of 1.2 and $r^{\circ}_{L/Fe} = 3$.

Figure 3.26 shows the removal of indium by the sodium di-(n-octyl) phosphinate as a function of pH at $r^{\circ}_{L/In} = 3$. Essentially complete removal was obtained at a final pH > 0.6. The removal of the indium at a lower ratio, $r^{\circ}_{L/in} = 1$, is shown in Figure 3.27. Only 40 % of indium was removed for pH below 4 because insufficient ligand was added to the solution to form InL_3 for all of the indium. The removal of indium increased at pH above 4 due to the formation of the insoluble indium trihydroxide.

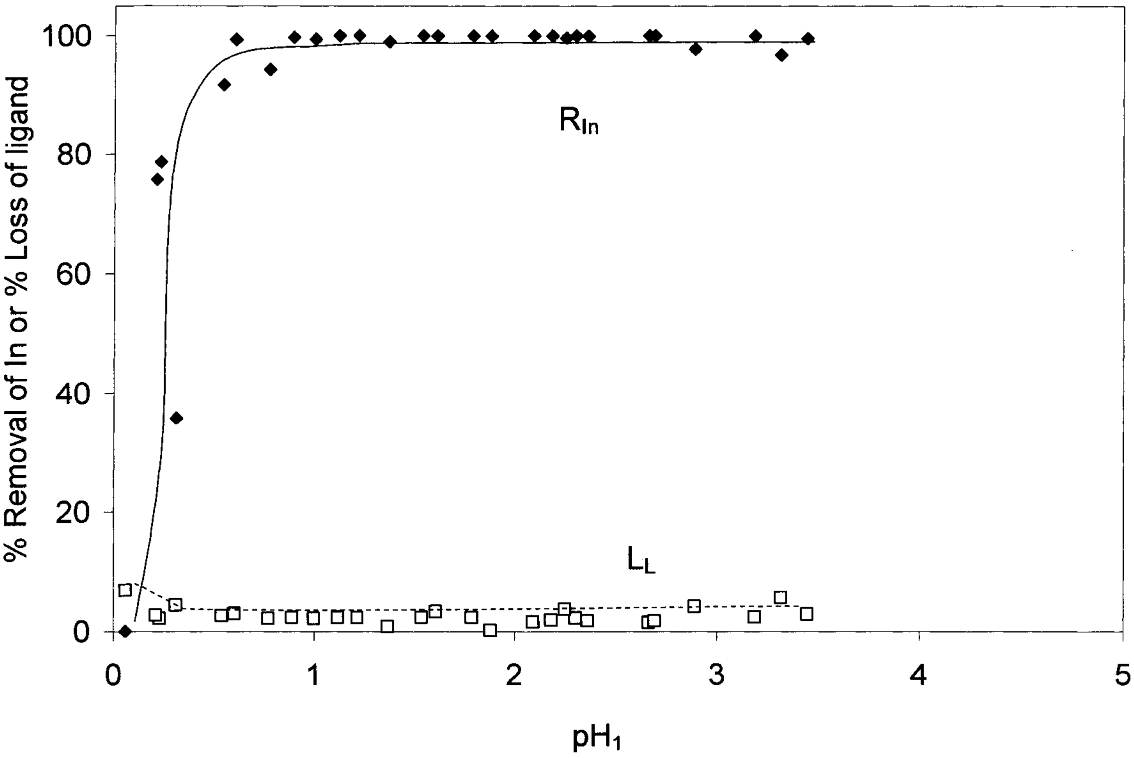


Figure 3.26: Effect of pH on the percent removal of the indium (◆); and percent loss of sodium di-(n-octyl) phosphinate (☐) [C°_{In} = 0.22 mM; $r^{\circ}_{L/In}$ = 3].

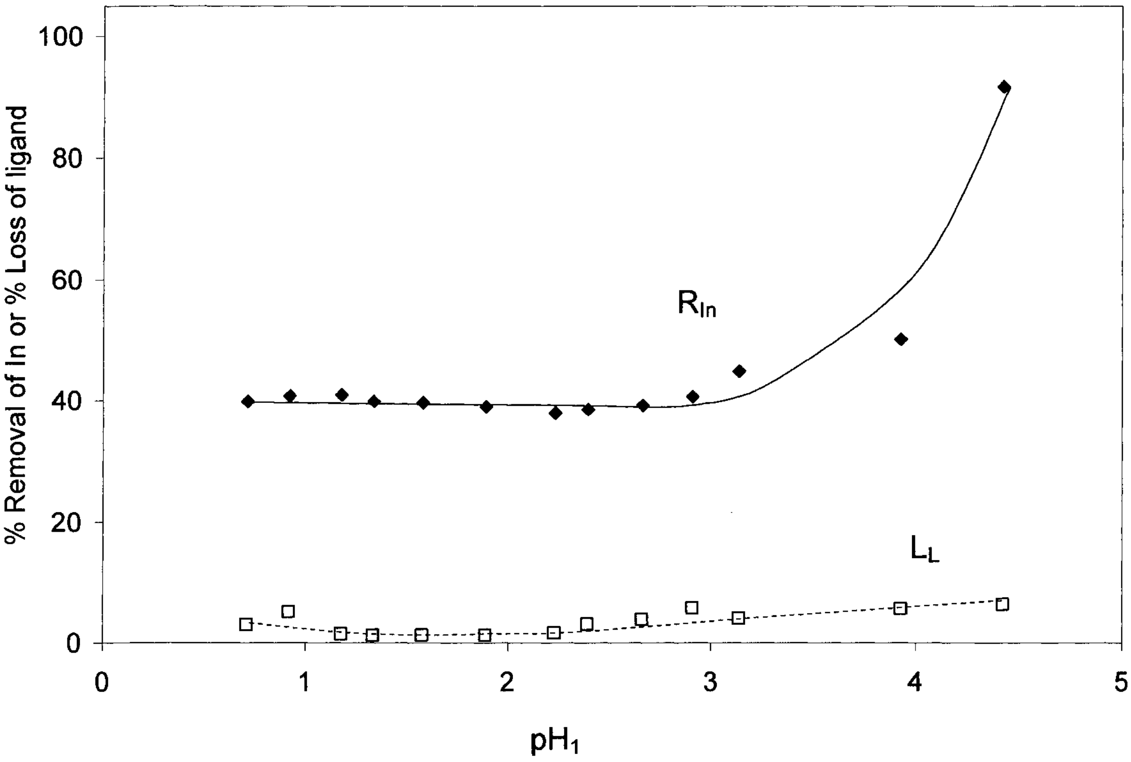


Figure 3.27: Effect of pH on the percent removal of the indium (◆); percent loss of sodium di-(n-octyl) phosphinate (☐) [C°_{In} = 0.22 mM; $r^{\circ}_{L/In}$ = 1].

Figure 3.28 shows the removal of iron with the sodium di-(n-octyl) phosphinate ligand. As the ratio $r^{\circ}_{L/Fe}$ increased from 1 to 3, more iron was removed in acidic condition. For $r^{\circ}_{L/Fe} = 3$, essentially complete removal of iron was obtained at a pH around 0.5. At pH = 1.1, while the iron was still completely removed at $r^{\circ}_{L/Fe} = 3$, about 50 % and 25 % of iron remains in solution for $r^{\circ}_{L/Fe} = 1$ and 2, respectively. Based on the assumption that 3 moles of ligand are necessary to remove 1 mole of ferric ion and 2 moles of ligand are necessary to remove one mole of ferrous ion, it was concluded that the iron in solution was ferric ion. At pH around 3, the ferric ion forms the insoluble hydroxide complex, increasing the removal of the metal at $r^{\circ}_{L/Fe} = 1$.

At pH between 1 and 2, both indium and iron have a higher removal than expected for ratios of ligand to metal of 1 and 2. This can be explained by the formation of metal-hydroxide complex before the addition of the ligand, as discussed in Appendix 3. The same behavior was observed for the gallium removal. While for gallium the formation of $Ga(OH)_{3(s)}$ was proposed, indium and iron solutions do not form insoluble metal-hydroxide complex between pH 1 and 2, as shown in Figures 5.5 and 5.7 in Chapter 5, respectively. An insoluble metal-ligand-hydroxyl complex, $M(OH)L_2$ or $M(OH)_2L$, is proposed to explain the higher removal of these two metals by the ligand.

The removal of calcium with the sodium di-(n-octyl) phosphinate ligand is shown in Figure 3.29. While calcium hydroxide is moderately soluble in water with a solubility of 0.02 M at 25°C (Baes and Mesmer, 1986), the addition of the ligand removed the calcium above a pH of 5. At $r_{L/Ca} = 2.6$, an excess of ligand was added to the solution. The ligand was in its acidic form until a pH around 5.

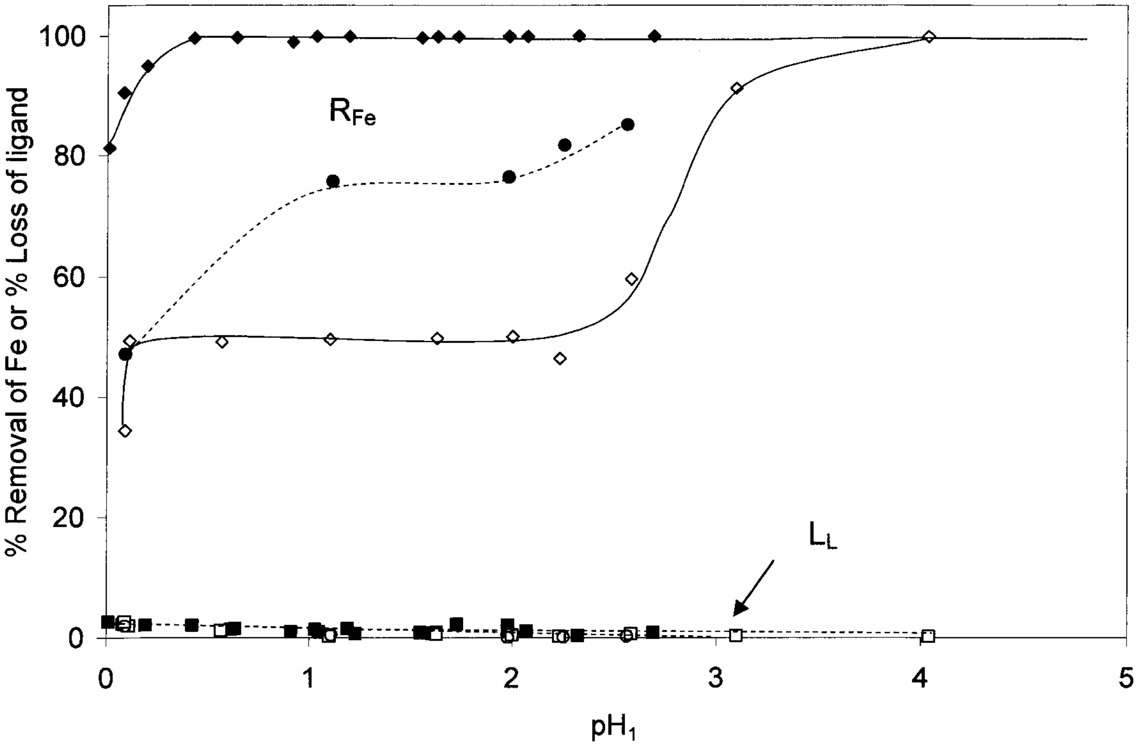


Figure 3.28: Effect of pH and $r^{\circ}_{L/Fe}$ on the percent removal of the iron (◇,●,◆); and percent loss of sodium di-(n-octyl) phosphinate (□,O,■) for different $r^{\circ}_{L/Fe}$ [C°_{Fe} = 0.36 mM; $r^{\circ}_{L/Fe}$ = 1 (◇, □); $r^{\circ}_{L/Fe}$ = 2 (●,O); $r^{\circ}_{L/Fe}$ = 3 (◆, ■)].

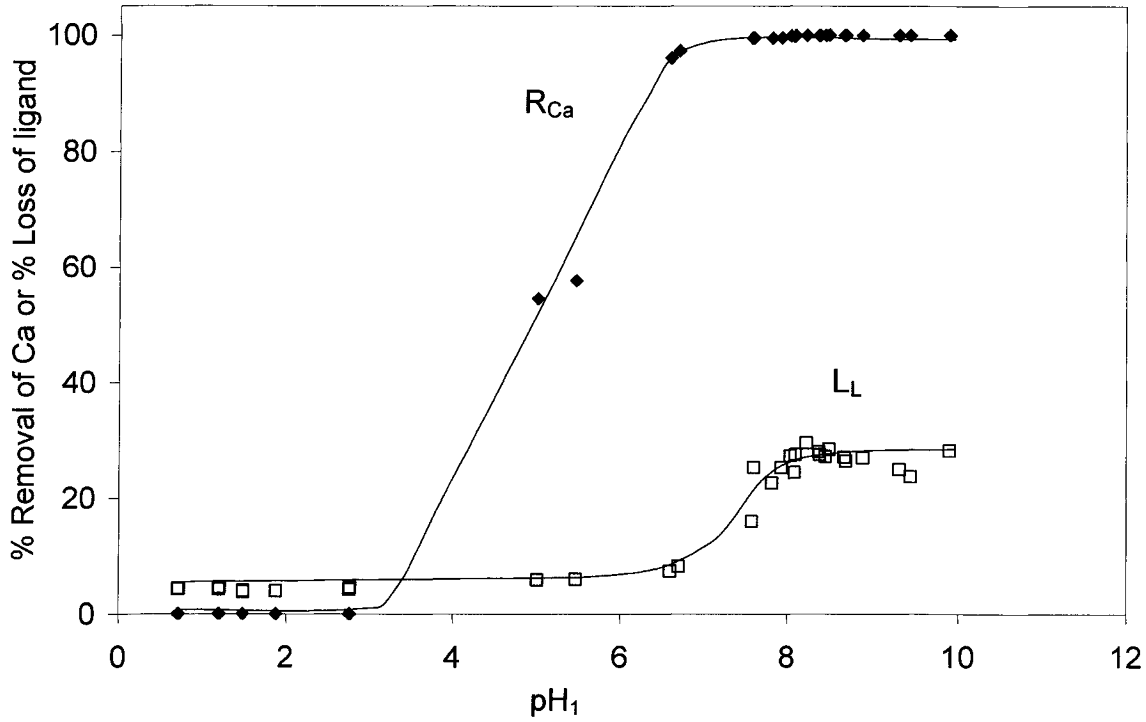


Figure 3.29: Effect of pH on the percent removal of calcium (◆); and percent loss of sodium di-(n-octyl) phosphinate ligand (☐) [C°_{Ca} = 1.13 mM, $r^{\circ}_{L/Ca}$ = 2.6].

Above pH 5, calcium started to form a complex with the ligand. The calcium was essentially completely removed from the solution at pH above 6. Above pH 8, the ligand, which tends to remain in solution at this pH, as seen with others metals, still formed complexes with the calcium. At pH = 8, the amount of ligand removed from the solution corresponded to $r_{L/Ca} = 2$. As the initial ratio of ligand to calcium, $r^{\circ}_{L/Ca}$, was 2.6, the excess of ligand remained in solution.

3.3.3 General features of the removal of single metal with sodium di-(n-octyl) phosphinate

The removal of a cationic metal, M^{m+}, with the anionic ligand, L^-, is written as:

$$M^{m+} + m\,L^{-} \longleftrightarrow M\,L_{m(s)} \tag{3.12}$$

In the case of gallium, aluminum, indium and iron where m = 3, the total removal of the metal by the ligand was obtained for a ratio $r^{\circ} = 3$. For calcium, where m = 2, the total removal of the metal by the ligand was obtained for a ratio $r^{\circ} = 2$. For this ratio, the effect of pH on the removal of the metals is shown in Figure 3.30.

The removal of the metal and of the ligand can be divided in 6 regions:

1 Removal of the ligand in its acidic form (Reaction 3.3). In this region, hydrogen ions compete with the metal ion for the ligand. Due to the high concentration of H^+, the ligand forms HL. Due to its low solubility in water, most of the HL complex precipitates as $HL_{(s)}$, but some ligand remains in solution as a weak acid, HL. In this region, the metal remains in solution. For gallium and aluminum solutions, region 1 was below pH_1 1.1.

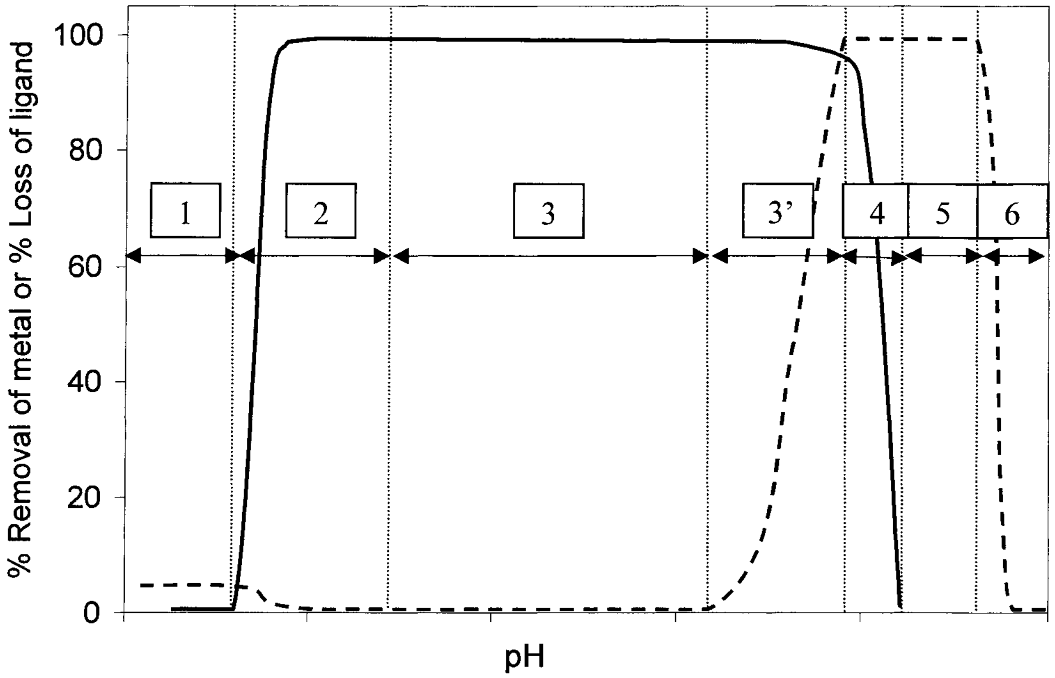


Figure 3.30: Effect of the pH on the percent removal of a metal; and percent loss of sodium di-(n-octyl) phosphinate at the optimum r° (--- Ligand, — Metal, X region X-see text).

2 Formation of the ligand-metal complex (Reaction 3.12). As the pH increases, the concentration of H^+ decreases, and the ligand reacts with the metal to form the insoluble ligand-metal complex. Unreacted ligand is still removed in its acidic form. For gallium solutions, pH_1 was between 1.1 and 3; for aluminum solutions, pH_1 was between 1.1 and 4.

3 & 3'. Removal of the metal with the ligand or in its insoluble hydroxide form (Reactions 3.1 and 3.5 for gallium, and Reactions 3.8 and 3.9 for aluminum). In this region, the ligand and the hydroxide ions compete for the metal. In the 3' region, the metal is removed mainly in its hydroxide form, hence more ligand remains in solution. For gallium solutions, pH_2 was between 3 and 8; for aluminum solutions, pH_1 was between 4 and 10.

4. Metal is removed in its hydroxide form (Reaction 3.1 for gallium and 3.8 aluminum). The soluble metal hydroxide complex (e.g. $Ga(OH)_4^-$ and $Al(OH)_4^-$) begins to form. The ligand remains in solution as it does not react with the hydroxide complex. For gallium solutions, pH_2 was around 8; for aluminum solutions, pH_1 and pH_6 were around 10.

5. Both metal and ligand remain in solution. The metal forms a soluble hydroxy complex, e.g. $Ga(OH)_4^-$ and $Al(OH)_4^-$. The ligand does not form an insoluble salt due to the low concentration of the cation from the base added to increase pH (Reaction 3.4). For gallium solutions, pH_2 was above 8; for aluminum solutions, pH_1 was above 11.

6. Removal of the ligand in its salt form (Reaction 3.4) caused by the high concentration of the cation from the base. The metal remains in solution

as a soluble hydroxide complex. Generally, the pH was above 12 as shown in Figure 3.4 and in Chapter 5.

3.4 Summary

The removal of single metal ions (gallium, aluminum, indium, iron and calcium) in solution by complexation using sodium di-(n-octyl) phosphinate was studied. For gallium, other organophosphorus ligands, such as sodium di-(n-dodecyl) phosphinate, O,O-di-(octyl) dithiophosphoric acid and sodium mono-octyl ester phosphinate, did not show a good removal.

The presence of humic and fumaric acids increased the removal of gallium when the metal was alone in an aqueous solution. However, the removal of the gallium was inhibited by the presence of both humic acid and sodium di-(n-octyl) phosphinate in solution. Due to the turbidity of the humic acid solutions, further treatment would be required.

Based on the high removal of the metal ions with the sodium di-(n-octyl) phosphinate, the following chapter discusses the use of this ligand for the selective removal of gallium. The mixture of metals considered is related to the mining and electronics industries in order to give a perspective of the potential applicability of this removal method.

CHAPTER 4

REMOVAL OF GALLIUM FROM MULTI-METAL ION SOLUTIONS

In the previous chapter, the sodium di-(n-octyl) phosphinate showed good removal capacity for single ions at a pH range between 2 to 4, except for calcium. Based on these results, the removal efficiency of sodium di-(n-octyl) phosphinate and its selectivity was investigated for mixture of gallium with:

- zinc and aluminum, for the recovery of gallium from the mining industry or from wastes;
- calcium, as an impurity;
- arsenic, indium and iron for the recovery of gallium from wafer wastes.

4.1 Separation of gallium from a zinc solution

Gallium is a byproduct in the production of zinc in the mining industry. Thus, the use of sodium di-(n-octyl) phosphinate for the separation of gallium from zinc was investigated. An initial solution of gallium and zinc nitrates, at $C^{\circ}_{Ga} = 0.359$ mM (25 mg/L) and $C^{\circ}_{Zn} = 1.15$ mM (75 mg/L) was treated with sodium di-(n-octyl) phosphinate. The mole ratio of ligand to gallium was increased up to $r^{\circ}_{L/Ga} = 21$ ($r^{\circ} = 5$, $r^{\circ}_{L/Zn} = 6.6$).

The percent removal of gallium and zinc, the percent loss of ligand and the final pH are shown in Figure 4.1, for different $r^{\circ}_{L/Ga}$ and at two initial pH values: $pH_i = 2$ ($r^{\circ}_{NaOH/Ga} = 0$) and $pH_i = 3.5$ ($r^{\circ}_{NaOH/Ga} = 13$). As observed, the percent removal of gallium and zinc increased with increasing $r^{\circ}_{L/Ga}$.

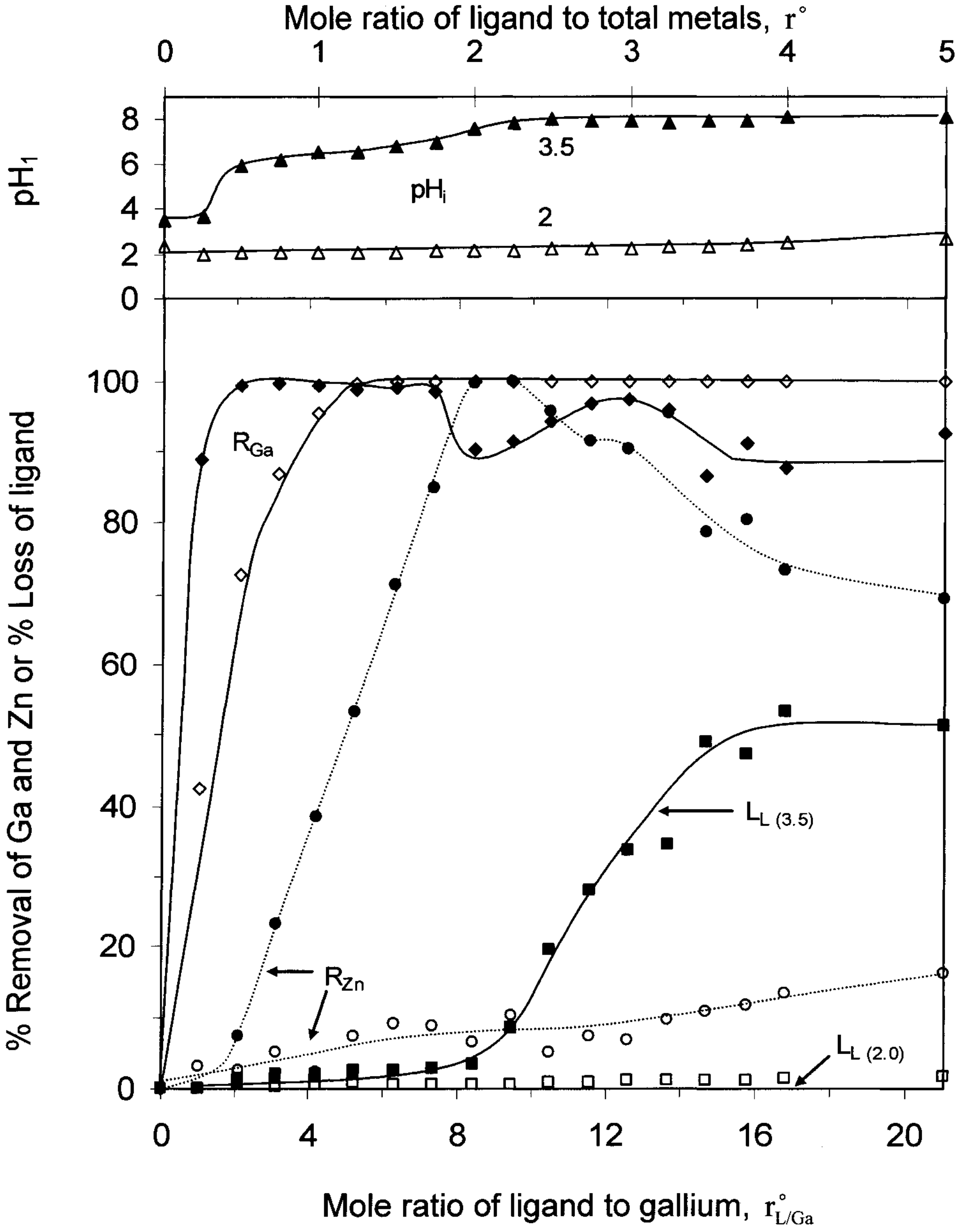


Figure 4.1: Effect of mole ratio of sodium di-(n-octyl) phosphinate to gallium on the percent removal of gallium (◇, ◆); percent removal of zinc (○, ●); percent loss of sodium di-(n-octyl) phosphinate (□, ■); and pH (△, ▲) [C°_{Ga} = 0.359 mM; C°_{Zn} = 1.15 mM; pH$_i$ = 2 ($r^{\circ}_{NaOH/Ga}$ = 0) (○, ◇, △, □); pH$_i$ = 3.5 ($r^{\circ}_{NaOH/Ga}$ = 13) (●, ◆, ▲, ■)].

For $pH_i = 2$, the species in solution of zinc and gallium are mainly Zn^{2+} and Ga^{3+}. When $r^{\circ}_{L/Ga}$ is greater than 5.25 ($r^{\circ} = 1.25$, $r^{\circ}_{L/Zn} = 1.64$ and pH = 2.1), essentially all of the gallium was removed. The removal of zinc was about 6 % and increased slightly as $r^{\circ}_{L/Ga}$ increased to 16.8. The molar selectivity, $\alpha_{Ga/Zn}$, was calculated using the value of the percent removal of each metal obtained from Figure 4.1 and using equation 2.6. At $r^{\circ}_{L/Ga} = 5.25$ and $pH_i = 2$, $\alpha_{Ga/Zn}$ was around 4700. For higher $r^{\circ}_{L/Ga}$, $\alpha_{Ga/Zn}$ increased above 20000 showing a clear affinity of the ligand for gallium over zinc. The percent loss of the ligand was less than 2 % for all values of $r^{\circ}_{L/Ga}$, since the excess ligand was removed as $HL_{(S)}$. In a single metal solution, zinc was removed by the same ligand at pH_i above 2 and at $r^{\circ}_{L/Zn}$ above 2.12 (Esalah, 1997).

At $pH_i = 3.5$, essentially all of the gallium was removed at $r^{\circ}_{L/Ga} = 2.1$ while zinc removal was only 7 %. In comparison when $pH_i = 2$, a complete removal of gallium was obtained at $r^{\circ}_{L/Ga} = 5.25$. In the case of pH_i 3.5, gallium forms hydroxyl complexes as seen in section 3.1.2, thus less ligand is required. The excess ligand formed $HL_{(S)}$, increasing the pH of the solution more significantly when $pH_i = 3.5$ compared to $pH_i = 2$. Due to the increasing pH of the solution, the metals form higher hydroxyl complexes:

$$M^{m+} + n\,OH^{-} \longleftrightarrow M\,(OH)_n^{m-n} \qquad (4.1)$$

with n = 1, 2 and 3 for m = 2 and n = 1,2,3 and 4 for m = 3. A complete removal of both zinc and gallium was obtained at $pH_i = 3.5$ when $r^{\circ}_{L/Ga} = 8.4$ ($r^{\circ} = 2$, $r^{\circ}_{L/Zn} = 2.6$). The removal of gallium decreased when $r^{\circ}_{L/Ga} > 8.4$ as more $Ga(OH)_4^-$ was formed. The unreacted ligand remained in solution as the pH was close to its natural pH where it is soluble.

Figure 4.2 shows the removals of gallium and zinc as a function of the pH of the solution. The mole ratio ligand to gallium was $r^{\circ}_{L/Ga} = 3.1$ ($r^{\circ} = 0.75$, $r^{\circ}_{L/Zn} = 1$). At pH around 2.6 ($pH_i = 2.5$), gallium and the ligand were removed while zinc remained in solution. At a low mole ratio of ligand to total metal of 0.75, the ligand showed a stronger affinity for gallium than for zinc. Also observed in Figure 4.2, at pH around 7, both zinc and gallium were removed from the aqueous solution. At this pH, the gallium precipitated by complexation with the hydroxyl ions forming insoluble $Ga(OH)_{3(s)}$. Since more ligand became available, zinc was then removed from the aqueous solution by the ligand. The loss of the ligand was less than 2 % for all pH values. The affinity of the ligand for gallium over zinc can be explained based on previous studies reporting that the extractability of metals using organophosphorus acids generally increases with the increasing number of the charges on the metal ion (Ritcey and Ashbrook, 1984).

To confirm the selectivity of the ligand for gallium, $r^{\circ}_{L/Ga}$ was increased from 3.1 to 8.4 in Figure 4.3. For a mole ratio of ligand to gallium of 8.4, $r^{\circ} = 2$ and $r^{\circ}_{L/Zn} = 2.6$, the ligand was in excess to form a complex with both metals. However, for both ratios, the gallium was removed preferably at low pH. At pH = 2, the molar selectivity, $\alpha_{Ga/Zn}$, was greater than 45000 for both $r^{\circ}_{L/Ga} = 3.1$ and $r^{\circ}_{L/Ga} = 8.4$. Above pH = 2, the molar selectivity decreased for the higher $r^{\circ}_{L/Ga}$ as the zinc was removed from the solution by the excess ligand. The zinc was removed in the same pH range from solution containing only zinc (Esalah *et al.*, 2000 b).

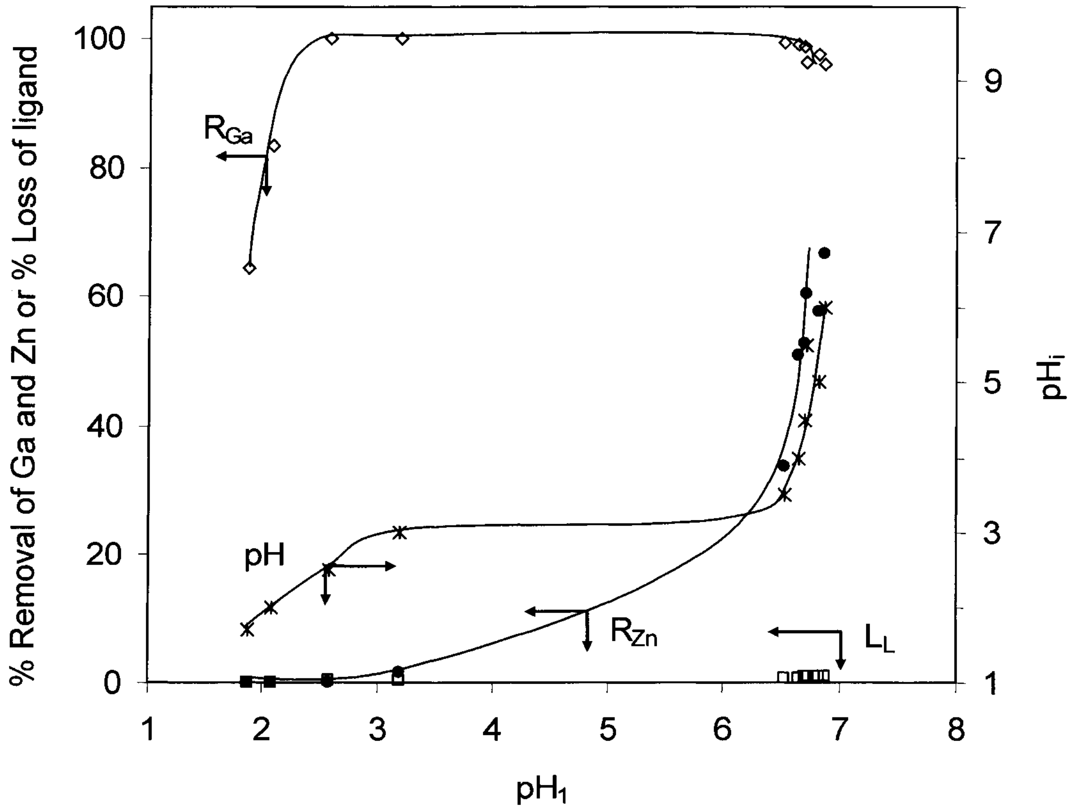


Figure 4.2: Effect of pH (*) on the percent removal of gallium (◇); percent removal of zinc (●); and percent loss of sodium di-(n-octyl) phosphinate (□) [$C^{\circ}_{Ga} = 0.359$ mM, $C^{\circ}_{Zn} = 1.15$ mM, $r^{\circ}_{L/Ga} = 3.1$].

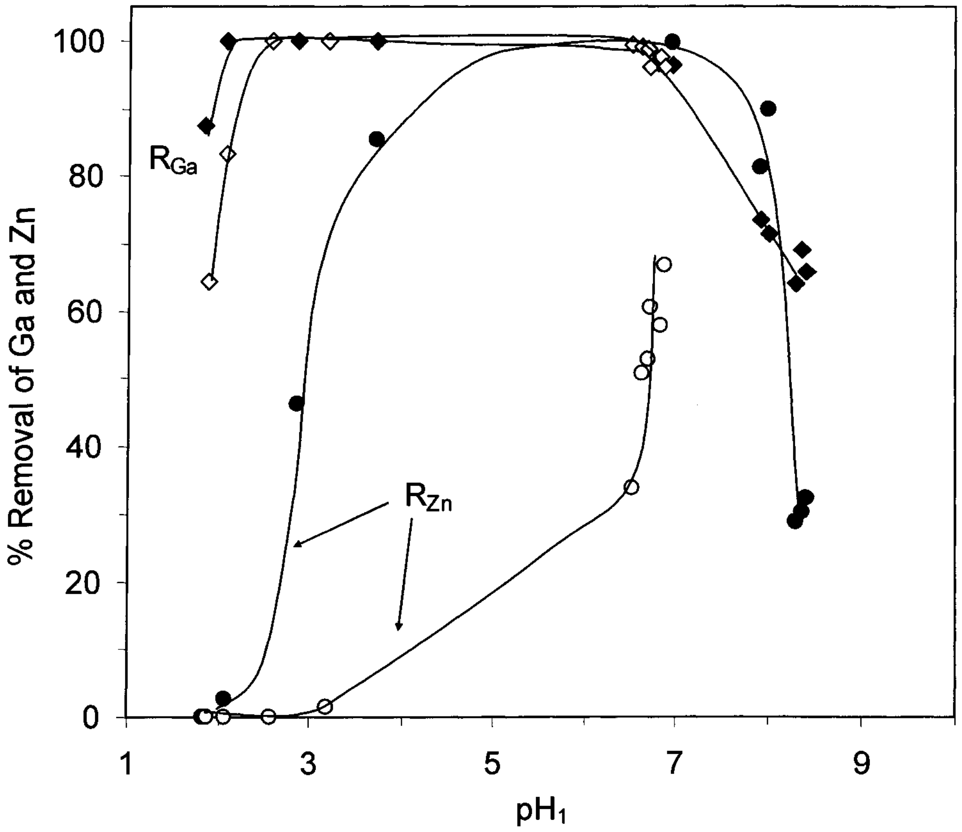


Figure 4.3: Effect of pH on the percent removal of gallium (◇ , ◆); and percent removal of zinc (○ , ●) using different mole ratios of sodium di-(n-octyl) phosphinate to gallium [C°_{Ga} = 0.359 mM; C°_{Zn} = 1.15 mM; $r^{\circ}_{L/Ga}$ = 3.1 (◇ , ○); $r^{\circ}_{L/Ga}$ = 8.4 (◆ , ●)].

Thus, good separation between gallium and zinc can be obtained by removing the gallium first at a pH around 2 with $r^{\circ}_{L/Ga} = 3$, then by increasing the pH above 3 to remove zinc with a mole ratio of ligand to zinc of 2.

4.2 Separation of gallium from an aluminum solution

Sodium di-(n-octyl) phosphinate was added to an initial solution containing 0.359 mM of gallium nitrate (25 mg/L) and 0.925 mM of aluminum nitrate (25 mg/L) to separate gallium from aluminum. The mole ratio of ligand to gallium, $r^{\circ}_{L/Ga}$, was varied up to 21.5 ($r^{\circ} = 6.0$, $r^{\circ}_{L/Al} = 8.3$).

Figure 4.4 shows the percent removal of gallium and aluminum, the percent loss of ligand and the pH for different mole ratios of ligand to gallium and for different initial pH. The pH of the initial solution was adjusted to $pH_i = 1.7$ ($r^{\circ}_{NaOH/Ga} = 8.7$), 2 ($r^{\circ}_{NaOH/Ga} = 26$) or 3 ($r^{\circ}_{NaOH/Ga} = 49$) with 1 M NaOH. At $pH_i = 1.7$, essentially complete removal of gallium was achieved at $r^{\circ}_{L/Ga} = 10.7$ ($r^{\circ} = 3.0$, $r^{\circ}_{L/Al} = 4.2$). The percent removal of aluminum for this ratio was approximately 6 %, giving a molar selectivity for Ga relative to Al, $\alpha_{Ga/Al}$, around 1200. For $r^{\circ}_{L/Ga} > 10.7$, the percent removal of aluminum increased, reaching 34 % at $r^{\circ}_{L/Ga} = 21.5$ ($r^{\circ} = 6.0$, $r^{\circ}_{L/Al} = 8.3$). The loss of ligand was less than 2 % for all $r^{\circ}_{L/Ga}$.

An increase in the initial pH decreased the molar selectivity for gallium over aluminum; greater than 1200 for $pH_i = 1.7$ and less than 30 for $pH_i = 3$. At $pH_i = 3$ and $r^{\circ}_{L/Ga} = 10.7$ ($r^{\circ} = 3.0$, $r^{\circ}_{L/Al} = 4.2$), as more gallium-hydroxide complexes are formed, less ligand is necessary to remove the gallium as previously shown in Figure 3.6. Thus, the

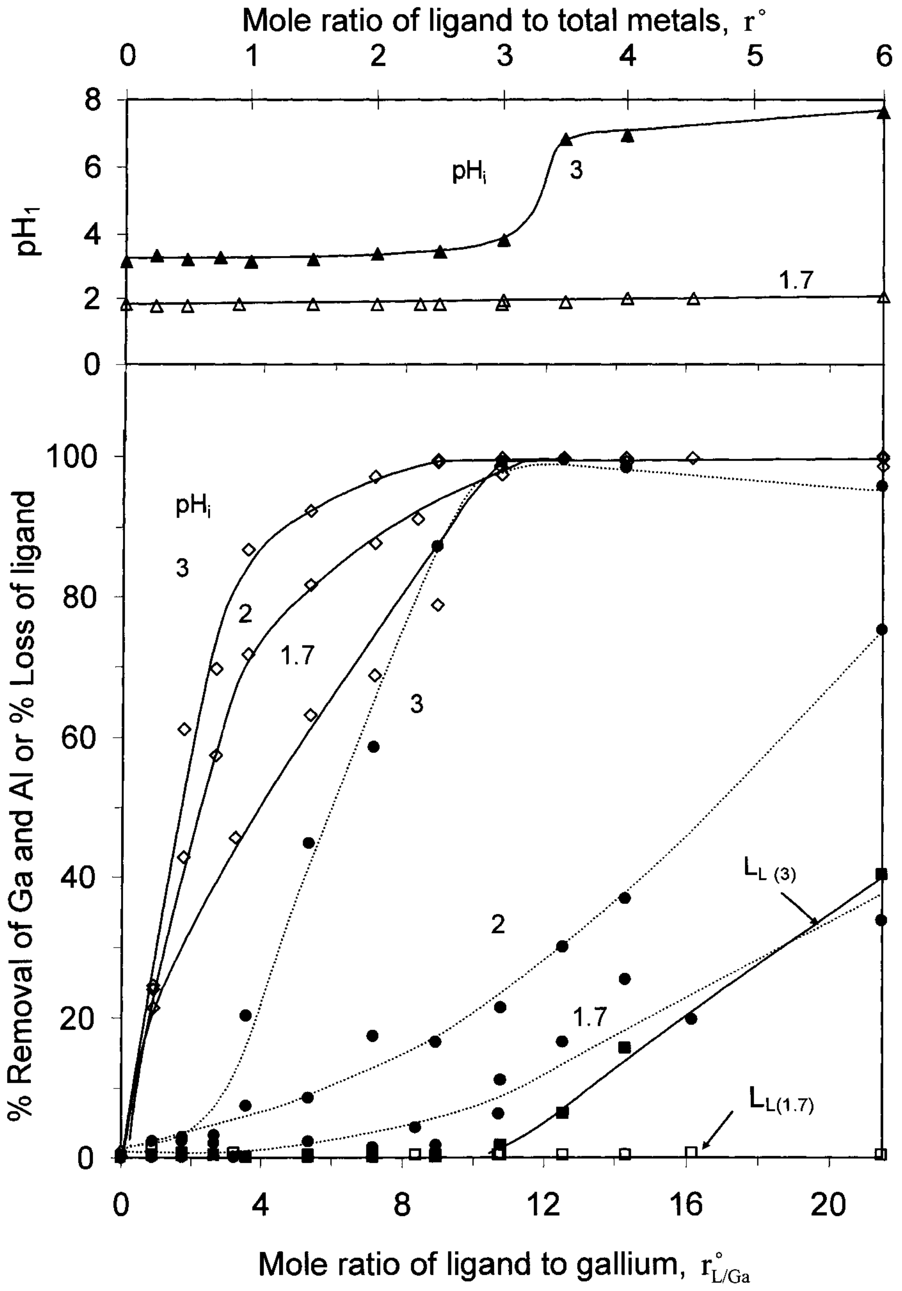


Figure 4.4: Effect of $r^{\circ}_{L/Ga}$ on the percent removal of gallium (◇); percent removal of aluminum (●); percent loss of sodium di-(n-octyl) phosphinate (□, ■); and pH (△, ▲) [C^{o}_{Ga} = 0.359 mM, C^{o}_{Al} = 0.925 mM; pH_i = 1.7 ($r^{\circ}_{NaOH/Ga}$ = 8.7), pH_i = 2 ($r^{\circ}_{NaOH/Ga}$ = 26), pH_i = 3 ($r^{\circ}_{NaOH/Ga}$ = 49)].

complexation was no longer selective for the removal of gallium and the percent removal for each metal (aluminum and gallium) was > 98 %. For values of $r^{\circ}_{L/Ga}$ above 10.7, more metals are removed in their hydroxyl form. Due to the increase of the pH up to pH around 8, the excess ligand remains in solution. Thus, the selective removal of gallium from an aqueous solution containing aluminum can be achieved for a solution with $pH_i < 2$ and with $r^{\circ}_{L/Ga} = 10.7$.

The effect of pH on the removal of gallium and aluminum is shown in Figure 4.5. The initial solution contained $C^{\circ}_{Ga} = 0.359$ mM and $C^{\circ}_{Al} = 0.925$ mM with $r^{\circ}_{L/Ga} = 3.6$ ($r^{\circ} = 1, r^{\circ}_{L/Al} = 1.4$). Enough ligand was added to remove completely only gallium. For pH = 1.8, the removal of gallium was 80 % and the removal of aluminum was 4 %. By increasing pH, the removal of both metals increased due to the formation of insoluble metal-hydroxide complexes, and the removal became less selective for gallium. The loss of the ligand was less than 2 % for pH between 1 and 8. The increase in the pH_i from 5 to 6 did not have any effect on the final pH which remained at 9.4. This phenomenon can be explained by the formation of a higher metal hydroxyl complex at $pH_i = 6$ which consumed the OH^- ions. As observed in Figure 4.5, the removal of the metals decreases for $pH_i = 6$ as $Ga(OH)_4^-$ and $Al(OH)_4^-$ are formed. While above its natural pH, pH = 8, the ligand still forms complexes with the metals as it is removed from the solution. The unreacted ligand remains in solution.

Figure 4.6 shows the removal of gallium and aluminum for pH values between 1.2 and 9.5 and for two mole ratios: $r^{\circ}_{L/Ga} = 3.6$ ($r^{\circ} = 1$, $r^{\circ}_{L/Al} = 1.4$) and $r^{\circ}_{L/Ga} = 8.05$ ($r^{\circ} = 2.26$, $r^{\circ}_{L/Al} = 3.15$). The initial solution contained $C^{\circ}_{Ga} = 0.359$ mM and $C^{\circ}_{Al} = 0.925$ mM.

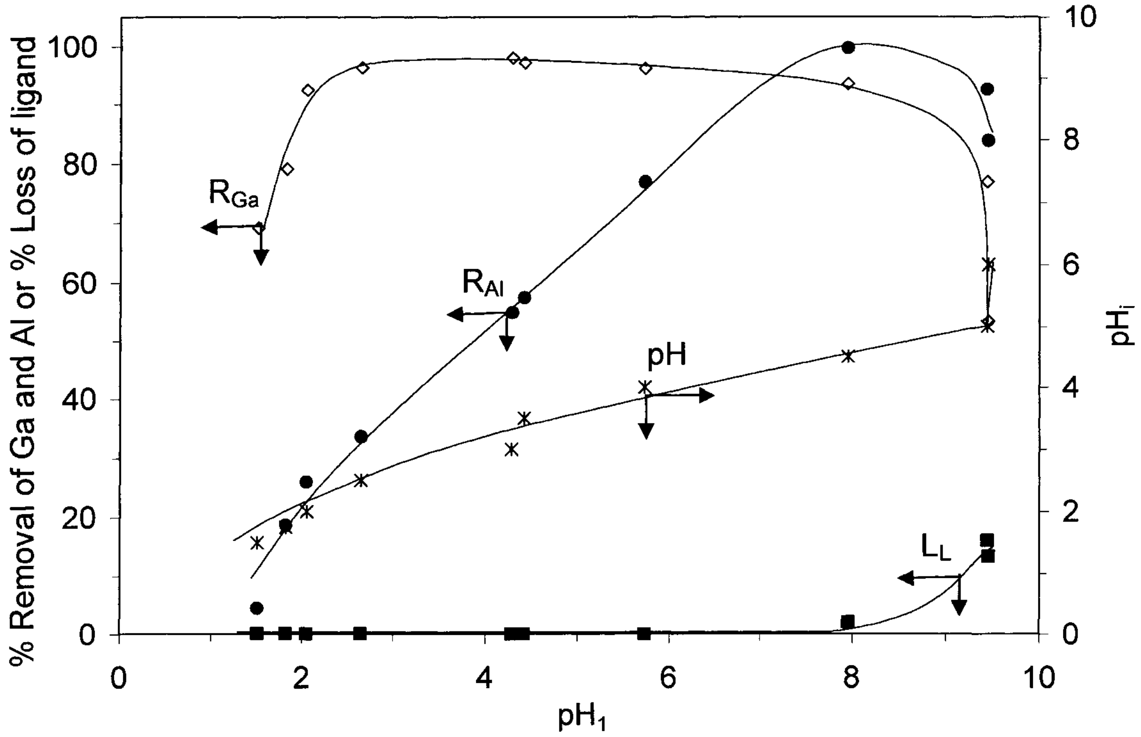


Figure 4.5: Effect of pH (*) on the percent removal of gallium (◇); percent removal of aluminum (●) and percent loss of sodium di-(n-octyl) phosphinate (■) [C°_{Ga} = 0.359 mM; C°_{Al} = 0.925 mM; $r^{\circ}_{L/Ga}$ = 3.6].

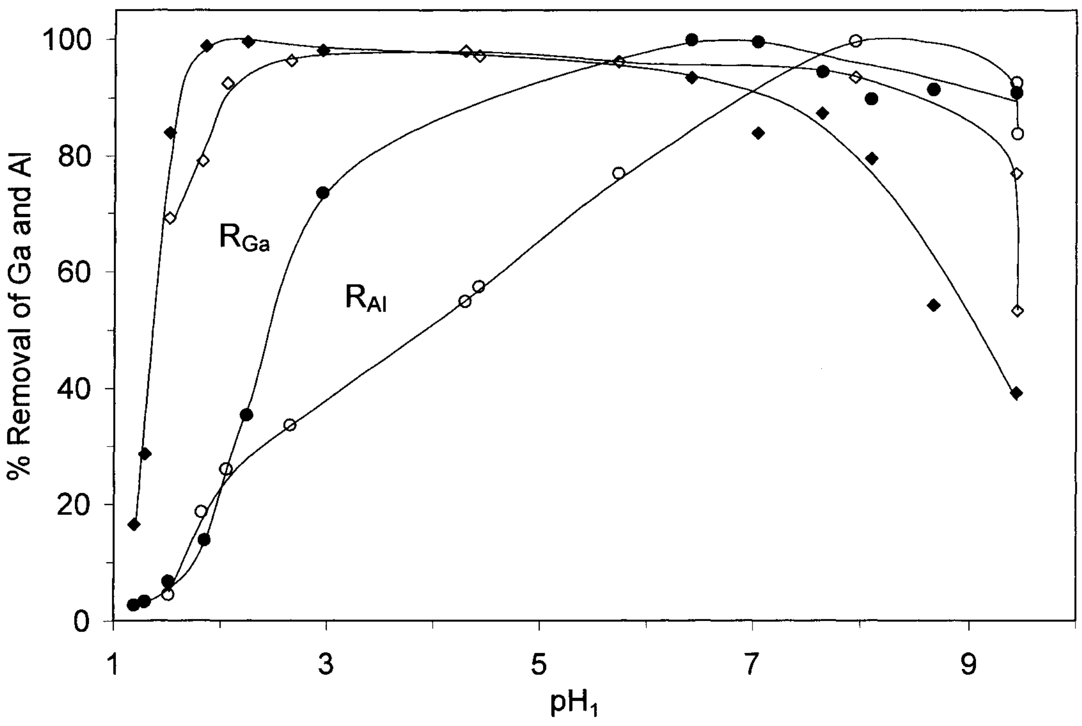


Figure 4.6: Effect of pH on the percent removal of gallium (◇, ◆) and percent removal of aluminum (○, ●) using different mole ratio of sodium di-(n-octyl) phosphinate to gallium [C°_{Ga} = 0.359 mM, C°_{Al} = 0.925 mM; $r^\circ_{L/Ga}$ = 3.6 (◇, ○), $r^\circ_{L/Ga}$ = 8.05 (◆, ●)].

Increasing the mole ratio increased the removal of both gallium and aluminum. The selectivity for gallium over aluminum decreased as $r^{\circ}_{L/Ga}$ increased to 8.5 at pH greater than 2.

4.3 Summary of the recovery of gallium from zinc and aluminum solutions

After selectively removing the gallium from the mixture of metals in solution by complexation with the ligand, the gallium was recovered and the ligand regenerated. The solid complex was dissolved in 3 M NaOH, and the resulting solution was contacted with diethyl ether to extract the ligand.

The solid complexes were formed at a ratio $r^{\circ} = 1.25$ for the gallium-zinc-nitrate solution at $pH_i = 2$. The total concentration in the 20 mL solution was $C^{\circ}_{Ga} = 0.359$ mM (25 mg/L) and $C^{\circ}_{Zn} = 1.15$ mM (75 mg/L). After 24 hours, essentially all of the gallium was removed from the solution, while 95 % of the zinc remained in solution. For the gallium-aluminum-nitrate solution, the solid complexes were formed at a ratio $r^{\circ} = 3$ and a $pH_i = 1.7$. The total concentration in the 20 mL solution was $C^{\circ}_{Ga} = 0.359$ mM (25 mg/L) and $C^{\circ}_{Al} = 0.925$ mM (25 mg/L). After 24 hours, essentially all the gallium was removed from the solution while 94 % of the aluminum remained in solution. The gallium-ligand solid complexes from both gallium-zinc and gallium-aluminum solutions were separated from the aqueous solution, then dissolved in 5 mL of 3 M NaOH and contacted with 5 mL of diethyl ether with vigorous agitation. No gallium was detected in the regenerated ligand, confirming the insolubility of the gallium-ligand complex in diethyl ether. Over 95 % of the ligand added to the initial gallium solution was recovered as a solid sodium di-(n-octyl) phosphinate in both cases. The volume of the NaOH added to dissolve the solid complex being 5 mL, the concentration of gallium was thus increased four times with respect to the initial solution. Some residual traces of zinc and aluminum were detected in the aqueous phase. A summary of the best values of the percent recovery of the different metals and the percent recovery of the ligand is given in Table 4.1.

Table 4.1: Summary of conditions for the removal and recovery of metals and ligand for the single metal solutions and for binary metal solutions:

Metals	pH_i	r°	pH_l	% Removal Metal	% Loss Ligand	% Recovery Metal	% Recovery Ligand
Ga	1.65	3	1.67	100 %	2.00 %	96 %	95 %
Zn^*	4.60	2	5.30	100 %	0.50 %	98 %	95 %
Al	2.75	3	3.50	100 %	0.30 %	95 %	95 %
Ga/Zn	2.00	1.25	2.10	100 % / 5 %	0.75 %	96 %	97 %
Ga/Zn	3.50	2.25	7.88	100 % / 90 %	2.00 %	-	-
Ga/Al	1.70	3	1.85	100 % / 6 %	0.25 %	95 %	96 %
Ga/Al	3.00	3	3.80	100 % / 99 %	1.70 %	-	-

* (Esalah *et al.*, 2000 b)

4.4 Removal of Ga^{3+} and Al^{3+} in the presence of Ca^{2+}

4.4.1 Effect of calcium on the removal of gallium

The selectivity of the ligand for gallium in the presence of calcium was studied as a function of pH. The initial solution contained 1.13 mM (45 mg/L) of calcium nitrate and 0.359 mM (25 mg/L) of gallium nitrate representing a mole ratio of calcium to gallium, $r^{\circ}_{Ca/Ga}$, of 3.15. In the initial aqueous solution, the mole ratio of ligand to calcium, $r^{\circ}_{L/Ca}$, was 2 giving a mole ratio of ligand to gallium, $r^{\circ}_{L/Ga}$, of 6.2. As shown in Figure 4.7, in the pH range from 2 to 5, gallium was removed from the aqueous phase through the formation of an insoluble complex with the ligand. Although the ligand was well in excess of the amount needed to completely remove gallium, no calcium was removed. As the pH increased from 5 to 8, excess ligand reacted with calcium to form an insoluble complex resulting in removal of calcium. At a pH 9 or higher, less than 3 % of the gallium was removed, whereas more than 90 % of the calcium and ligand were removed due to the formation of a calcium-ligand complex, $CaL_{2(s)}$. Thus, by using sodium di-(n-octyl) phosphinate ligand, the gallium can be selectively removed from aqueous phase in a pH range between 2 to 5 in presence of calcium.

4.4.2 Effect of calcium on the removal of aluminum

The selectivity of the ligand for aluminum, in presence of calcium, was investigated for an initial solution containing 0.925 mM (25 mg/L) of aluminum nitrate and 1.4 mM (56 mg/L) of calcium nitrate giving a mole ratio of calcium to aluminum of $r^{\circ}_{Ca/Al} = 1.5$. To this initial solution, the ligand was added at $r^{\circ}_{L/Al} = 4$.

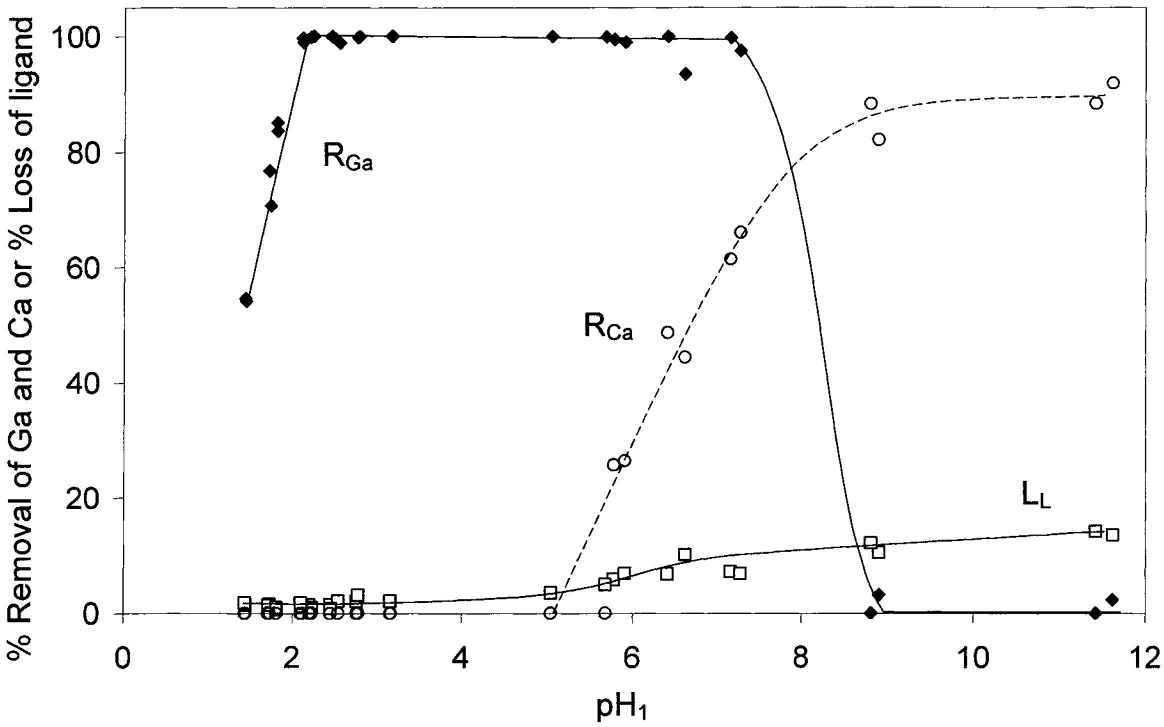


Figure 4.7: Effect of pH on the percent removal of gallium (◆), percent removal of calcium (○); and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{Ga} = 0.359 mM, C°_{Ca} = 1.13 mM; $r^{\circ}_{L/Ca}$ = 2].

As shown in Figure 4.8, a complete removal of aluminum was obtained in a pH range from 2 to 8, while the removal of calcium gradually increased from less than 2 % to about 20 % in the same pH range. The ligand had more affinity toward the aluminum than calcium. Finally, the final pH was always higher than the initial pH_i in the acidic region, pH < 7. In this region, the OH^- ions were released from the metal hydroxyl complexes as metal-ligand complexes were formed. Any extra ligand in this case was removed from the solution by forming the insoluble complex $HL_{(S)}$.

4.5 Application to the wafer industry

4.5.1 Removal of arsenic

An arsenic solution was treated with the ligand without any gallium. As observed in Figure 4.9, the arsenic (As) remained mainly in solution. Some loss of arsenic was also observed between replicates giving around 6 % of As removal. This loss was observed at various pH, even at pH where the ligand did not form an insoluble complex. No arsenic was detected in the insoluble ligand complex, and no arsine gas was detected with the arsine detector Dräger tube. Thus, this discrepancy in the As measurement between replicates was considered as experimental error.

Figure 4.10 shows the relationship between the amount of ferric ions in solution and the arsenic on the removal efficiency after three days. Three mole ratios of ferric ions to arsenic, 1, 2 and 3, were tested. As observed in Figure 4.10, the arsenic removal followed the same trends for the ratio 2 and 3 up to pH = 2, but only a maximum of 40 % of the arsenic was removed from the solution at ratio 1. The maximum removal was of As was obtained at pH around 2 for all three ratios. Sturgill *et al.* (2000) reported similar pH range for ferric arsenate removal.

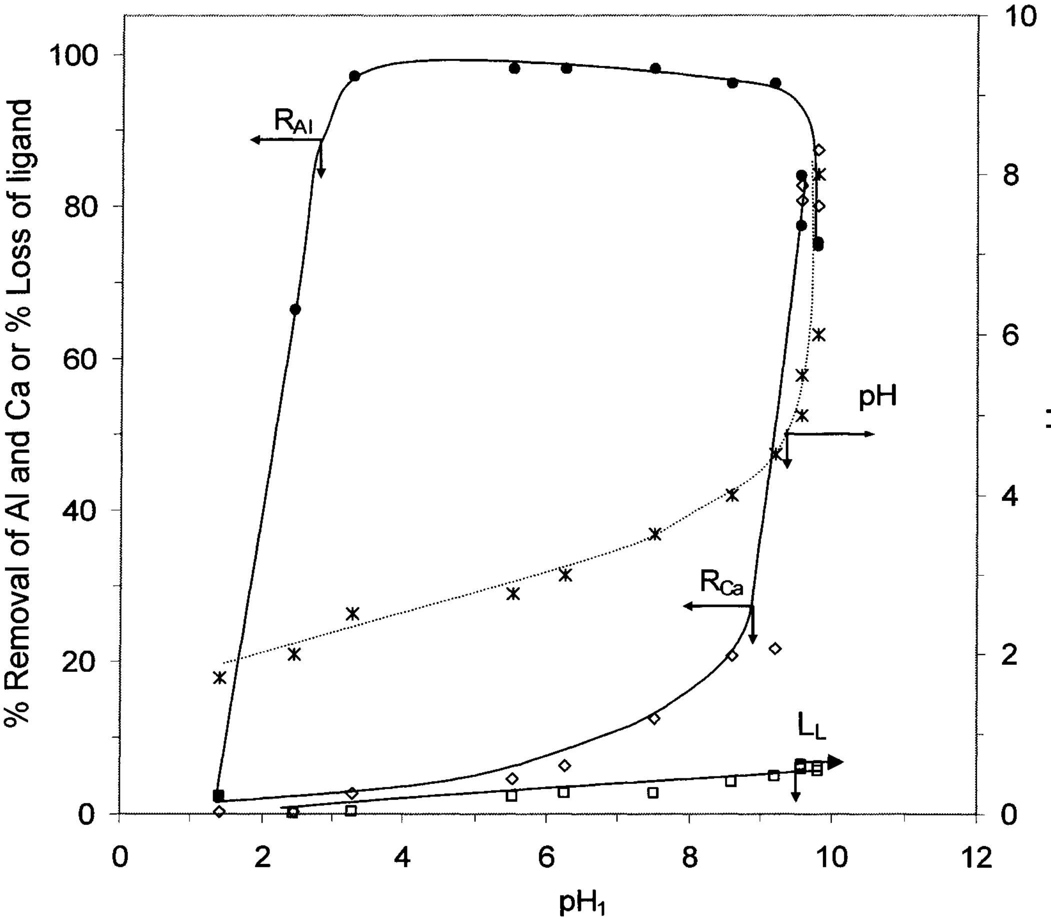


Figure 4.8: Effect of pH (*) on the percent removal of aluminum (●); percent removal of calcium (◇) and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{Al} = 0.925 mM; C°_{Ca} = 1.4 mM; $r^{\circ}_{Ca/Al}$ = 1.5; $r^{\circ}_{L/Al}$ = 4].

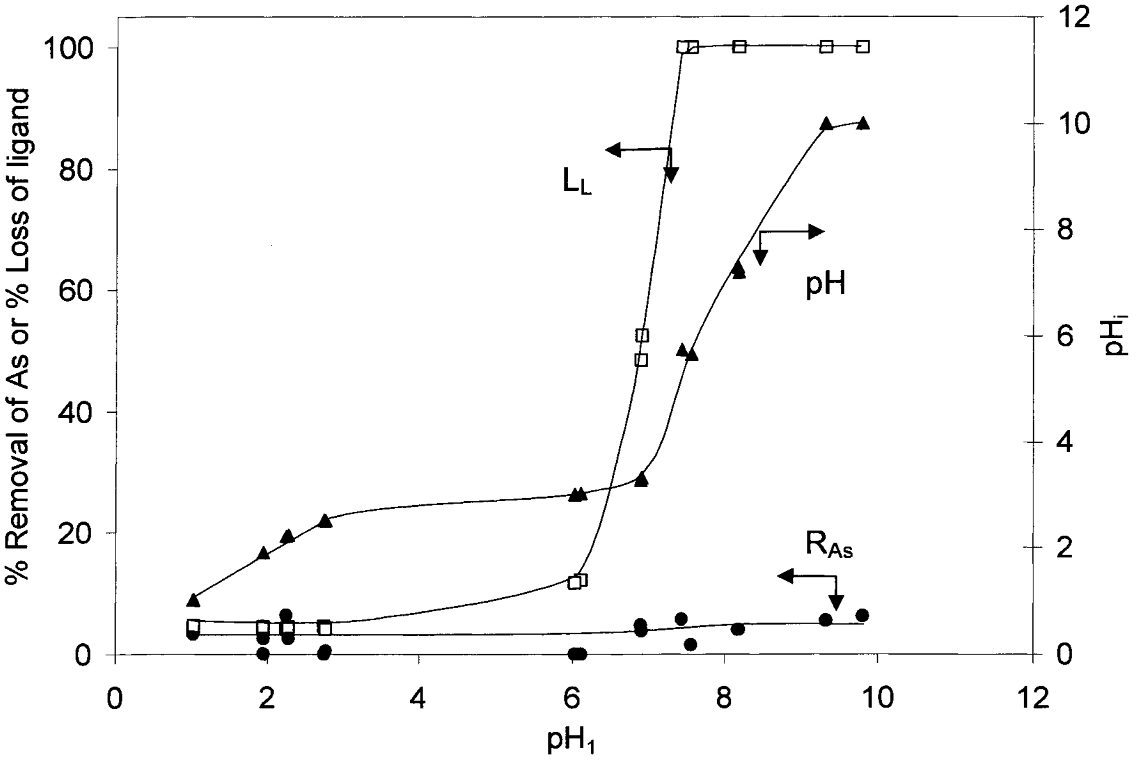


Figure 4.9: Effect of pH (▲) on the percent removal of arsenic (●) and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{As} = 0.33 mM; $r^{\circ}_{L/As}$ = 3].

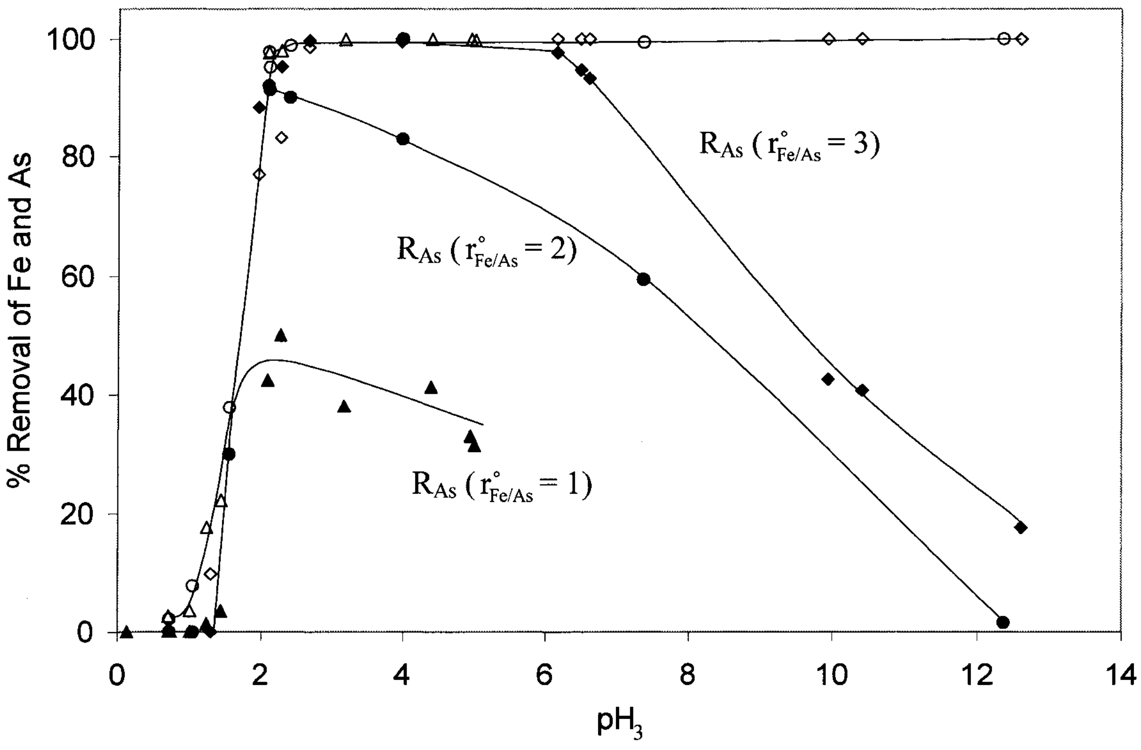


Figure 4.10: Effect of pH on the percent removal of arsenic (▲,●,◆), percent removal of iron (△,○,◇) at different iron to arsenic ratio, $r^\circ_{Fe/As}$ [$r^\circ_{Fe/As}$ = 1 (▲, △): C°_{As} = 1.33 mM and C°_{Fe} = 1.33 mM; $r^\circ_{Fe/As}$ = 2 (●, ○): C°_{As} = 1.33 mM and C°_{Fe} = 2.67 mM; $r^\circ_{Fe/As}$ = 3 (◆, ◇): C°_{As} = 1.33 mM and C°_{Fe} = 4 mM].

As the pH increased above 2, the ferric ions precipitated as ferric hydroxide and as ferric arsenate (Sturgill *et al.*, 2000). At $r^{\circ}_{Fe/As} = 3$, most arsenic was removed as ferric arsenate at pH range between 2 and 6 to yield a concentration of arsenic remaining in solution as low as 300 μg/L (4×10^{-3} mM). This concentration was still higher than the maximum contaminant level of 10 μg/L (1.3×10^{-4} mM) required by the Environmental Protection Agency (EPA, 2002). In industry, coagulant and flocculant agents are generally added to aid in the physical removal of the resultant precipitate (Sturgill *et al.*, 2000). Higher amounts of iron than the 1:1 arsenic to iron ratio are also generally required to stabilize and dispose of the arsenic iron precipitate (Riveros *et al.*, 2001).

The ferric arsenate experiments were repeated with sodium di-(n-octyl) phosphinate added to the solution. The percent removal of both metals and the percent loss of the ligand for two systems are shown in Figure 4.11. At $r^{\circ}_{L/Fe} = 1$ and $r^{\circ}_{Fe/As} = 2$ (closed symbols), there was not enough ligand to remove all the ferric ions. All of the ligand reacted with the ferric ions, removing around 40 % of this metal from the solution as expected considering that 3 moles of ligand are necessary to remove 1 mole of iron. By increasing the pH, the remaining iron was then removed in its hydroxide form, removing with it the arsenic from the solution. When $r^{\circ}_{L/Fe}$ increased to 3, by decreasing the amount of ferric ions in the solution, a complete removal of iron was obtained, while most of the As remained in solution at pH below 2. Thus, the iron selectively removed the ligand over As from the solution.

The same procedure was tested with calcium instead of ferric ions for the removal of the arsenic. Robins (1981) reported the formation of calcium arsenate at an optimum pH between 10.5 and 11.5 and optimum ratio calcium to arsenic of 2.

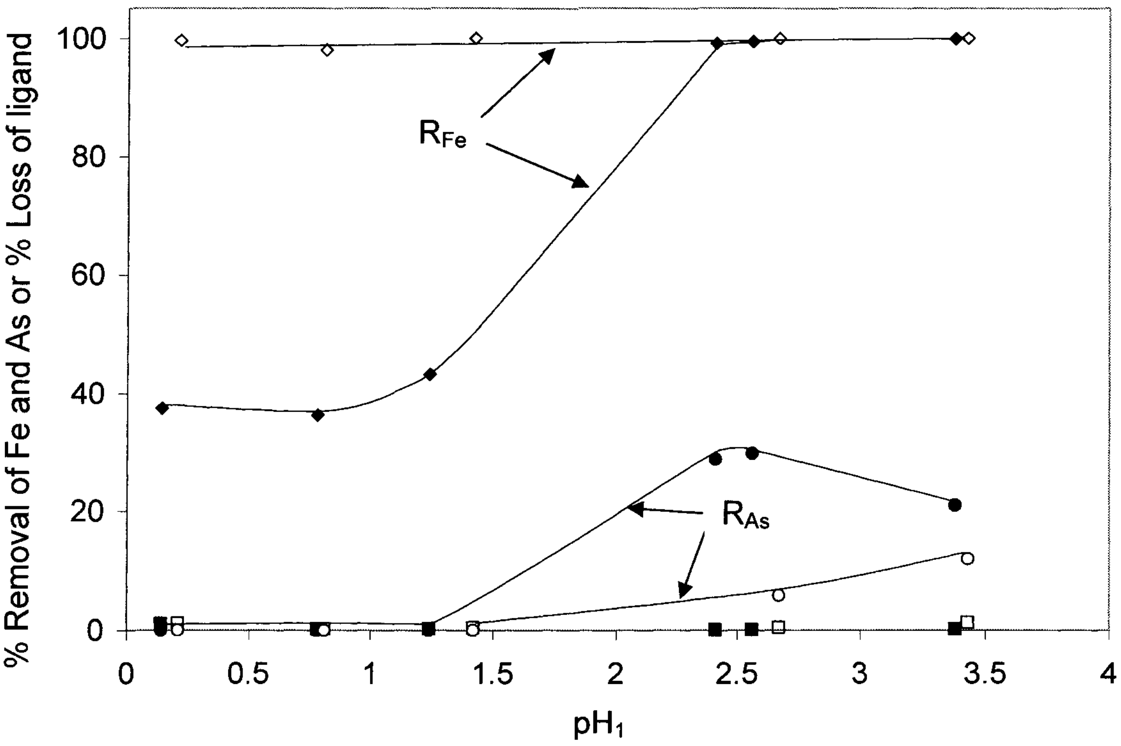


Figure 4.11: Effect of pH on the percent removal As (●,○); percent removal of Fe (◆,◇); and percent loss of sodium di-(n-octyl)phosphinate (■, □) [$r^{\circ}_{L/Fe} = 1$ and $r^{\circ}_{Fe/As} = 2$ (●,◆, ■): $C^{\circ}_{Fe} = 2.7$ mM, $C^{\circ}_{As} = 1.35$ mM; $r^{\circ}_{L/Fe} = 3$ and $r^{\circ}_{Fe/As} = 1$ (○,◇, □): $C^{\circ}_{Fe} = 1.35$ mM, $C^{\circ}_{As} = 1.35$ mM].

As described previously in this study, the ligand forms an insoluble complex with calcium at a pH above 7. Based on these data, the effect of the arsenic on the removal of sodium di-(n-octyl) phosphinate ligand with calcium was tested between pH 10.7 and 12. As reported in Table 4.2, all the arsenic remained in solution while the calcium selectively removed the ligand. However, the arsenic inhibited the removal of the ligand with the calcium. As the amount of initial ligand increased, more ligand remained in solution. The use of calcium to remove an excess of the ligand and then to treat an arsenic solution is also not recommended. The calcium arsenate precipitates are not stable with respect to the CO_2 in the atmosphere. Calcium carbonate can form, releasing back the arsenic from the precipitate (Robin *et al.*, 2001).

Table 4.2: Effect of sodium di-(n-octyl) phosphinate on arsenic (6.67 mM) and calcium nitrate (1.25 mM) system at an initial pH of 10.7.

Amount of ligand added		Ca		Ligand		As	
mM	mg/L	mM	mg/L	mM	mg/L (of P)	mM	mg/L
0	0	1.21	48.3	3×10^{-3}	0.1	1.31	98.5
1.3	39	0.65	25.9	0.14	4.3	1.33	99.6
2.5	78	0.13	5.4	0.31	9.5	1.33	99.5
6.3	195	0.02	0.62	1.03	32	1.31	98.1

4.5.2 GaAs wafer waste solution

A gallium arsenide solution was synthesized by dissolving a GaAs wafer in nitric acid. The ligand at a mole ratio ligand to gallium of 3 was added to the solution containing 2.91 mM of Ga (200 mg/L) and 2.67 mM (200 mg/L) of As. These concentrations correspond to the concentrations of dissolved arsenic and gallium found in waste streams (Sturgill *et al.*, 2000). Figure 4.12 shows the effect of pH on the percent removal of gallium and arsenic. A removal of 97.6 % of Ga was achieved at pH higher than 2 resulting in a maximum of 9.5×10^{-3} mM (or 5 mg/L) of gallium in solution. All the arsenic remained in the solution. A dilute solution containing 0.294 mM of Ga and 0.283 mM of As at a pH_i of 1.66 with a mole ratio ligand to gallium of 3 showed a removal of 98.4 ± 0.5 % of Ga. A maximum of 6×10^{-3} mM (or 0.44 mg/L) of gallium remained in solution.

Based on the selectivity of sodium di-(n-octyl) phosphinate for gallium over arsenic, a process is proposed in Figure 4.13 to treat GaAs effluents such as polishing wastes from the electronics industry. The treatment not only allows the removal of toxic arsenic and the desirable gallium from the waste stream but also allows their recovery and reuse. The polishing waste streams contain 3 to 10 wt % of an oxidizer (Sturgill *et al.*, 2000), thus the pH is first adjusted to pH 1.6 to 3 with sodium hydroxide. The sodium di-(n-octyl) phosphinate is added to the solution to remove the gallium, at an optimum ratio of 3 to minimize the sludge volume. The solid is separated from the aqueous solution and treated with diethyl ether to recover the gallium and regenerate the ligand. A soluble iron salt such as ferric nitrate is then added in excess to remove any remaining ligand from the solution. The pH can be decreased to avoid the formation of

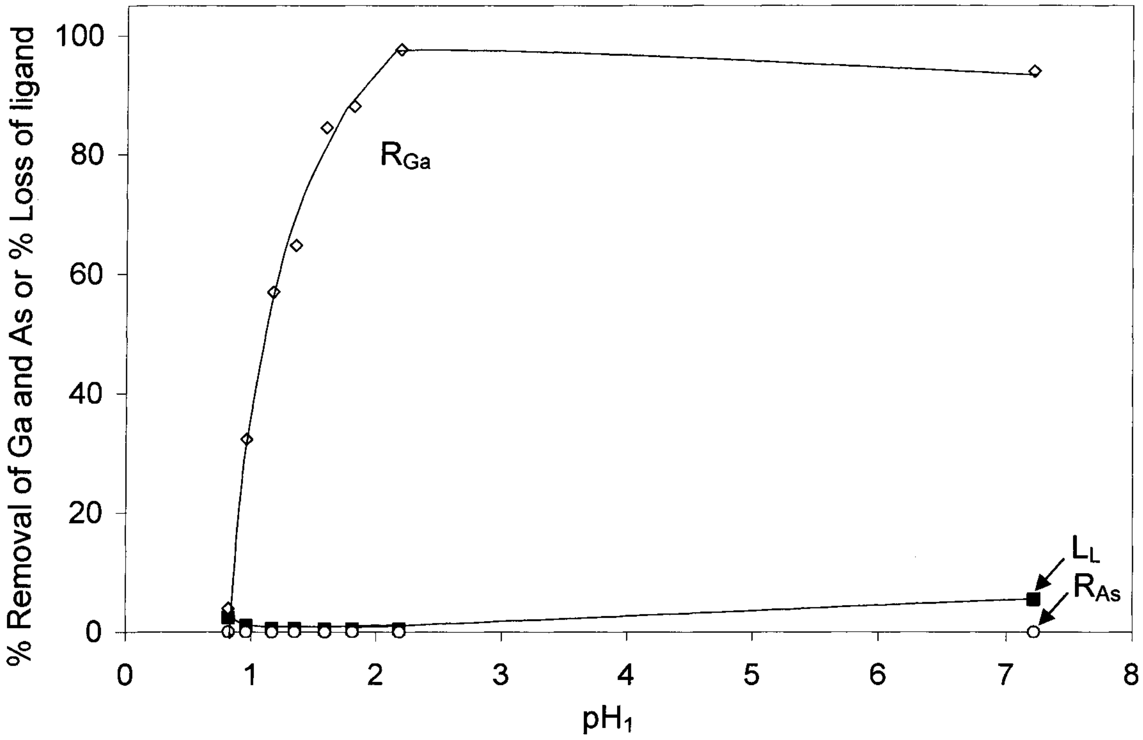


Figure 4.12: Effect of pH on the percent removal of gallium (◇); percent removal of arsenic (○); and percent loss of sodium di-(n-octyl) phosphinate (■) from a GaAs wafer solution [$r^{\circ}_{L/Ga} = 3$; $C^{\circ}_{Ga} = 2.91$ mM; $C^{\circ}_{As} = 2.67$ mM].

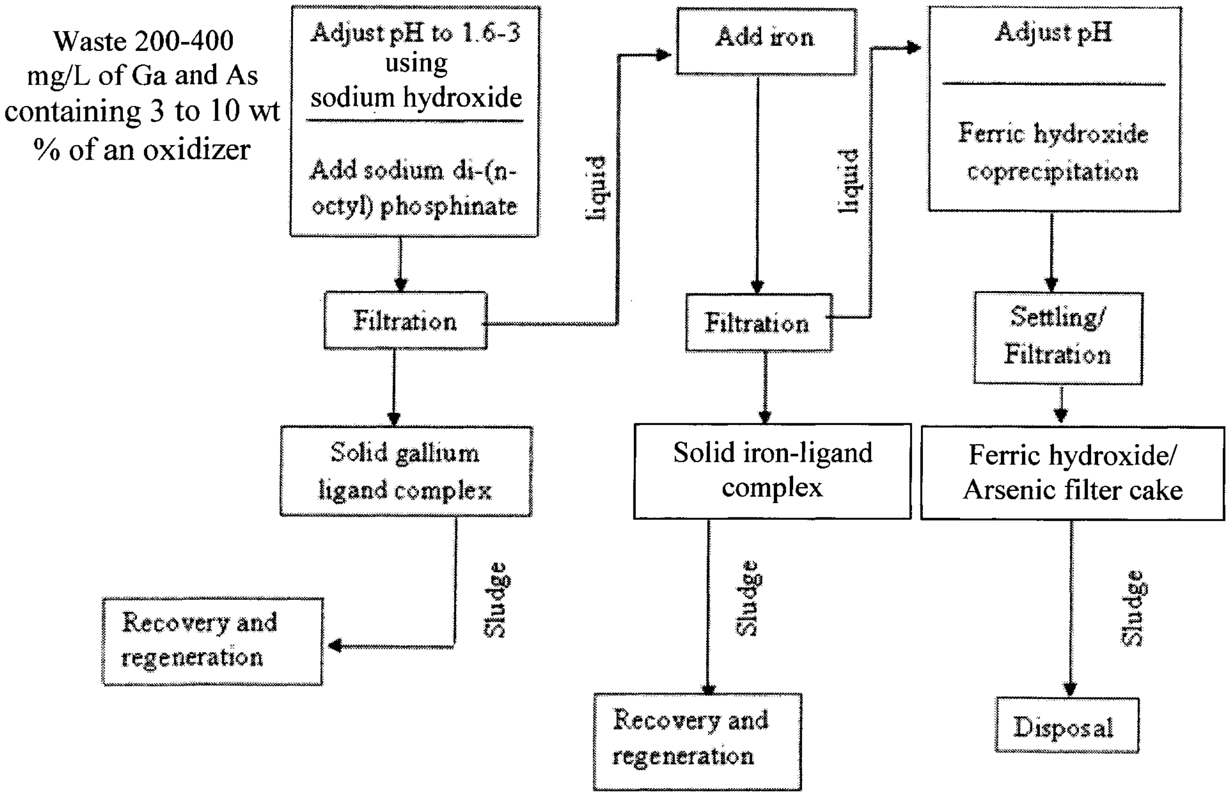


Figure 4.13: Suggested process for the recovery of gallium and arsenic from GaAs polishing wastes.

ferric hydroxide. Finally the pH is adjusted between 2 and 4 where the arsenic is removed as ferric arsenate. The removal process proposed in this study has a better selectivity for gallium than the precipitation by hydrolysis. The gallium-di-(n-octyl) phosphinate complexes are also easily separated from the solution.

The method can be used to remove traces of indium from the solution. From the previous observations on the removal of the indium with the sodium di-(n-octyl) phosphinate, a solution containing the same number of moles of indium (41 mg/L of indium nitrate or 0.357 mM) and gallium (25 mg/L of gallium nitrate or 0.359 mM) was prepared. Sodium di-(n-octyl) phosphinate was added to the solution at two mole ratios of ligand to total metal: $r^\circ = 1.5$ where only one metal can be removed with the ligand and $r^\circ = 3$ where both metals can be removed. The selectivity of the sodium di-(n-octyl) phosphinate ligand for indium over gallium is shown in Figure 4.14. For $r^\circ = 3$, at pH 0.7, the gallium concentration was 22 ± 0.2 mg/L while the indium concentration was 0.08 ± 0.01 mg/L or 7×10^{-4} mM yielding $\alpha_{In/Ga} \approx 4000$. As the pH increased, both gallium and indium were removed with the ligand at pH above 1.6. For a lower ratio of 1.5, most of the gallium remained in solution at pH below 3, and then was removed with the ligand as the indium forms hydroxide complexes at pH above 3. The ligand was completely removed from the solution either by the gallium or by the indium.

Finally, a solution containing 20 mg/L of indium nitrate (0.17 mM) and 200 mg/L of arsenic (2.67 mM) and gallium (2.87 mM) (dissolved GaAs wafer in nitric acid) at an initial pH of 0.86 was prepared. As explained in section 2.3.2 in Chapter 2, there was some loss of As during the preparation of the stock solution and the amounts of As and Ga used here reflect this fact.

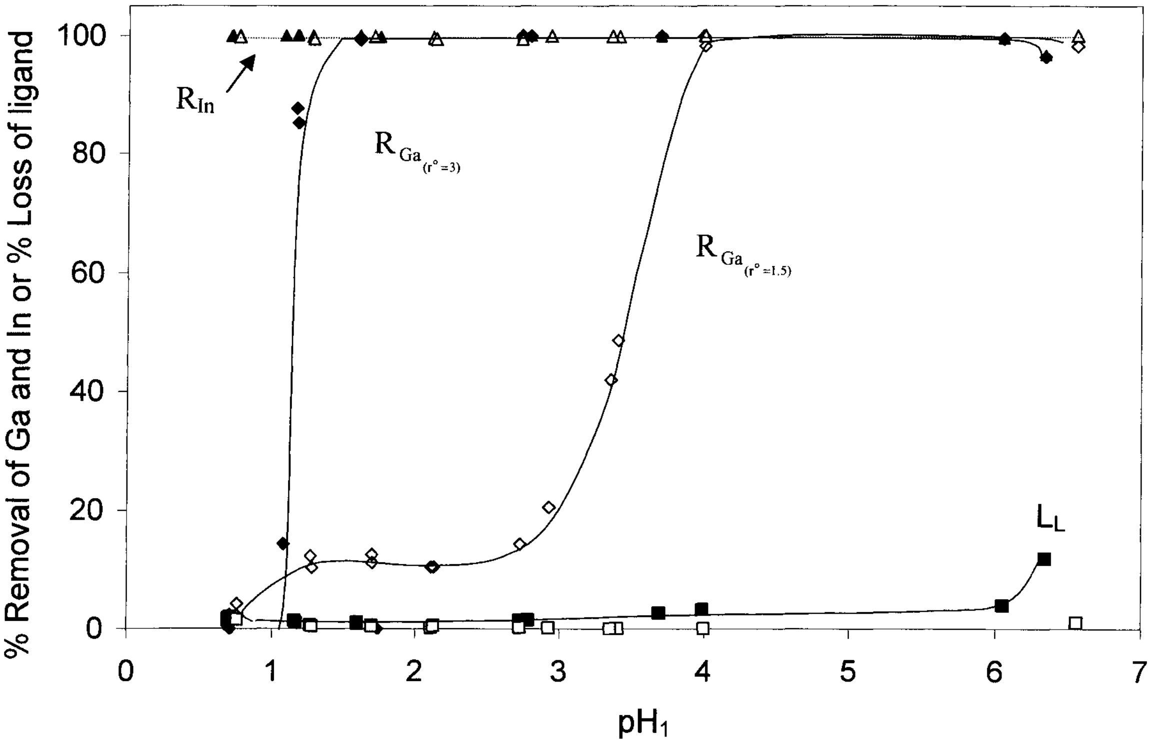


Figure 4.14: Effect of pH on the percent removal of gallium (◇ , ◆); percent removal of indium (△ , ▲); percent loss of sodium di-(n-octyl) phosphinate (□ , ■) for different mole ratio of ligand to metals (gallium + indium) [C°_{Ga} = 0.359 mM; C°_{In} = 0.357 mM; r° = 1.5 (◇, △ , □); r° = 3 (◆, ▲ , ■)].

The amount of indium, gallium and arsenic in the solution were related to the amount found in GaAs scraps (Sturgill *et al.*, 2000; Lee and Nam, 1998). Sodium di-(n-octyl) phosphinate was added to the solution at $r^{\circ}_{L/In} = 3$. Around 1 ± 0.2 mg/L (9×10^{-4} mM) of indium and 0.15 ± 0.15 mg/L of phosphorous (a maximum of 1×10^{-3} mM of ligand) remained in solution after three days. All the arsenic and the gallium remained in solution.

4.6 Affinity of sodium di-(n-octyl) phosphinate for metals

Based on the Hard and Soft Acids and Bases (HSAB) theory developed by Pearson (1963), Ca^{2+}, Fe^{3+}, Ga^{3+}, In^{3+} and As^{3+} are hard acids, Cd^{2+} is a soft acid and Zn^{2+}, Pb^{2+} and Cu^{2+} are part of the borderline, as previously mentioned in Table 1.4. The sodium di-(n-octyl) phosphinate ligand is also a hard base due to its oxygen groups. In the HSAB theory, hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.

The different affinities of the sodium di-(n-octyl) phosphinate for metals are reported in Table 4.3. As observed, the ligand has more affinity for the hard acid metals. However, metals ions bind strongly to ligands that are basic to protons whether the metal ions are hard or soft (Pearson, 1963). Thus Cd^{2+}, a soft acid, was also removed by complexation with the ligand (Esalah, 1997). In the case of metal of different charges, such as Ga^{3+} and Zn^{2+} or Ga^{3+} and Ca^{2+}, the affinity of the ligand increases with the increase of the charge of the metal ion. As mentioned previously, the same results were observed for the extractability of metals using organophosphorus acids (Ritcey and Ashbrook, 1984).

Table 4.3: Selectivity of sodium di-(n-octyl) phosphinate for metals

Selectivity	Reference
$Pb^{2+} > Ca^{2+}$ $Zn^{2+} > Pb^{2+} > Cd^{2+}$	Esalah (1997)
$Ga^{3+} > Al^{3+}$ $Ga^{3+} > Zn^{2+}$ $Ga^{3+} > Ca^{2+}$ $In^{3+} > Ga^{3+}$ $Fe^{3+} > Ga^{3+}$	This study

For ions of same charge, Esalah (1997) reported the importance of the ionic radius in the case of Zn^{2+}, Pb^{2+}, Cd^{2+}. The ionic radius of Pb^{2+} is bigger than Cd^{2+} and can explain the affinity of the ligand for Pb^{2+} (Pearson, 1963). The effect of the ionic radii and of the charge on the selectivity of the ligand can also be explained by a covalent character. The general rules of Fajans for covalent character according to Miessler and Tarr (1998) are:

1. For a given cation, covalent character increases with increase in size of the anion.
2. For a given anion, covalent character increases with decrease in size of the cation.
3. Covalent character increases with increasing charge on either ion.

4. Covalent character is greater for cations with a non-noble gas electronic configuration.

However, the ligand has a higher affinity for Zn^{2+} which has the same charge as Pb^{2+} and Cd^{2+} but a smaller radius (Esalah, 1997). Hard metal ions, such as gallium and aluminum, prefer ligands with hard donor atoms, such as the O contained in the sodium di-(n-octyl) phosphinate. Generally the affinities of metal ions for ligands containing negatively charged oxygen donor atoms are related to their affinity for the hydroxide ion. The value of log $K_{(OH-)}$ for a particular metal ion is therefore a good indicator of the complexing behaviour of the metal with a ligand containing negative oxygen donors (Martell and Hancock, 1996). For Al^{3+} and Ga^{3+}, log $K_{(OH-)}$ is -9.09 and -11.4, respectively (Baes and Mesmer, 1986). Thus, the ligand should have a stronger affinity for Ga^{3+}. The Ga^{3+} cation is also more strongly polarized than Al^{3+} due to the presence of the $3d^{10}$ electron core resulting in a high effective nuclear charge on the Ga^{3+} ion. The electronegativities of Al^{3+} and Ga^{3+} are 1.61 and 1.81, respectively (Huheey, 1983). Since the sodium di-(n-octyl) phosphinate ligand is an electron donor, the ligand again should have a stronger affinity for Ga^{3+}.

In order to explain the affinity of the ligand for metals of same charge, the use of the absorption bands of the metal-ligand complexes was investigated. Different stretching modes occurred in the metal-ligand insoluble complex. The P-O and the P-C stretching vibrations are considered to be the most informative regions (Pitts *et al.*, 1969; Haynes *et al.*, 1985; Ferraro *et al.*, 1998). The P-O has a strong absorption bands in the 1000-1200 cm^{-1} region while P-C has a lower absorption in the 700-800 range. Table 4.4 lists the frequencies assigned to the ν_{sym} and ν_{asym} stretching modes as well as the frequency difference associated Δν for different metal-di-(n-octyl) phosphinate complexes. The higher stretching band was associated to ν_{asym} and the lower one to ν_{sym}.

In the case of the P-C bands, ν_{sym}[PC] was virtually the same for all the complexes except for Cd^{2+} and Pb^{2+}, while ν_{asym}[PC] varied between 802 and 817. Haynes *et al.* (1985) reported two different structural forms α and β of the $Cu[(n\text{-}C_8H_{17})_2PO_2]_2$. The P-O bands of the 2 forms were close for this compound. However a significant difference was observed for the ν_{asym}[PC] where the stretch band of α was in the 770-775 cm^{-1} range and β was shifted to about 805 cm^{-1}.

Table 4.4: Absorption bands of the (POO^-) and (PC) stretching modes for different metal – di-(n-octyl) phosphinate complexes measured with Fourier Transform Infrared spectrophotometer.

Element	$\nu_{asym}[POO^-]$ (± 1 cm^{-1})	$\nu_{sym}[POO^-]$ (± 1 cm^{-1})	Δν (± 2 cm^{-1})	ν_{asym}[PC] (± 1 cm^{-1})	ν_{sym}[PC] (± 1 cm^{-1})	Δν (± 2 cm^{-1})
Na^+	1148	1041	107	815	720	95
Pb^{2+}	1089	1020	69	815	714	101
Cd^{2+}	1098	1022	76	813	714	99
Ca^{2+}	1137	1026	111	806	720	86
Zn^{2+}	1136	1049	87	808	720	88
Ga^{3+}	1126	1050	76	816	720	96
Al^{3+}	1149	1080	69	817	720	97
In^{3+}	1130	1052	78	815	720	95
Fe^{3+}	1102	1040	62	802	720	82

Thus, the removal of the metal using the soluble sodium di-(n-octyl) phosphinate produced mainly β for the metals charge (II). In the case of the (III) metals, a difference between the ν_{asym}[PC] of iron and the other metals can certainly be attributed to this polymorphism.

Also observed in Table 4.4, $\nu_{sym}(POO^-)$ increased when the charge of the metal ion varied from (II) to (III) except for Fe^{3+}. For the charge (II), larger energy variations were observed for Ca^{2+} and Zn^{2+}, while Al^{3+} and Fe^{3+} differed from the close bands of Ga^{3+} and In^{3+}. Overall, the $\nu_{asym}(POO^-)$ stretching mode of the sodium and aluminum di-(n-octyl) phosphinate appeared at the highest energy. Ferraro *et al.* (1998) reported that for the sodium form of the P,P'-di (2-ethylhexyl) methanediphosphinic acid, the highest energy indicated a weak interaction and a highly ionic Na-O bond. The bonds become more covalent as the value of the $\Delta\nu$ decrease. However, in this study, aluminum had a higher affinity for the ligand than the sodium. While the $\nu_{asym}(POO^-)$ stretching mode associated to aluminum was at the highest energy, the metal complex had a lower $\Delta\nu$ compare to gallium and indium. Ferraro *et al.* (1998) reported spectral complications due to structural differences between the metal complexes of interest. In order to verify if the sodium di-(n-octyl) phosphinate and the aluminum di-(n-octyl) phosphinate complexes have the same structure, an x-ray diffraction was carried out. As observed in Figure 4.15 and Figure 2.1, the sodium form of the ligand had sharp narrow diffraction peaks compared to the aluminum-ligand complex which had broader peaks (halo). These spectra showed a more amorphous behavior of the aluminum-ligand complex than the sodium-ligand complex. As sodium complexes differently than aluminum with the ligand, their bond with the ligand are certainly different and cannot be compared.

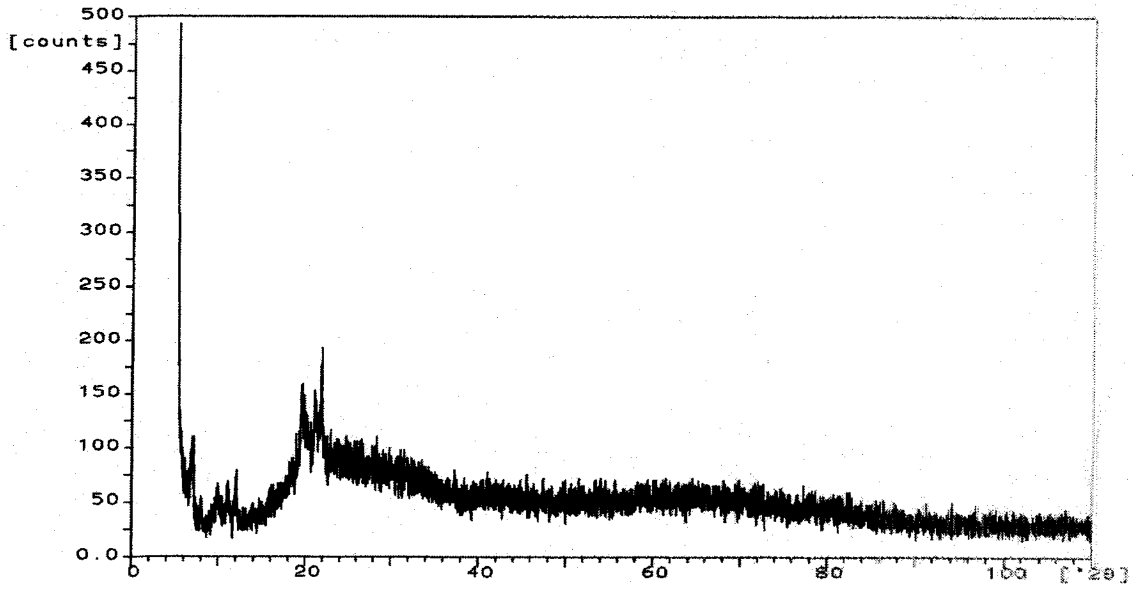


Figure 4.15: X-ray diffraction of the insoluble complex formed between aluminum and the sodium di-(n-octyl) phosphinate ligand at a mole ratio of 3.

Ferraro *et al.* (1998) also reported a good correlation between the ionic potential Φ and Δv. Using the same notation, Figure 4.16 shows Φ vs Δv. While the affinity of the ligand for the highest charges and biggest ionic radius is represented in the ionic potential, the metal (II) and the metal (III) had two different behaviors with the ligand. For the metal (II), the small linear slope is generally indicative of a similar bonding across the series. In the case of the metal (III), a more disperse behavior was observed. No correlation could be obtained between the two parameters, Φ and Δv. This can be explained again using the x-ray diffraction of the aluminum and gallium complexes. Figure 4.17 shows a crystalline structure with its sharp narrow diffraction peaks for the gallium complex as obtained for the sodium form of the ligand. The different amorphous structure of the aluminum complex observed previously in Figure 4.16 make the correlation more difficult (Ferraro *et al.*, 1998). In this case, the affinity of the ligand for the gallium over the aluminum is more related to the structure of the metal-ligand complex. The same explanation can be given for the affinity of the ligand for the Fe (III) over the Ga (III) considering the large difference, Δv, of the respective P-O and P-C bands of the metal-ligand complexes. This effect of the structure on the selectivity was also observed for the extraction of Co (II) and Ni (II) using the same ligand, di-(n-octyl) phosphinic acid, in toluene solutions (Danesi *et al.*, 1985).

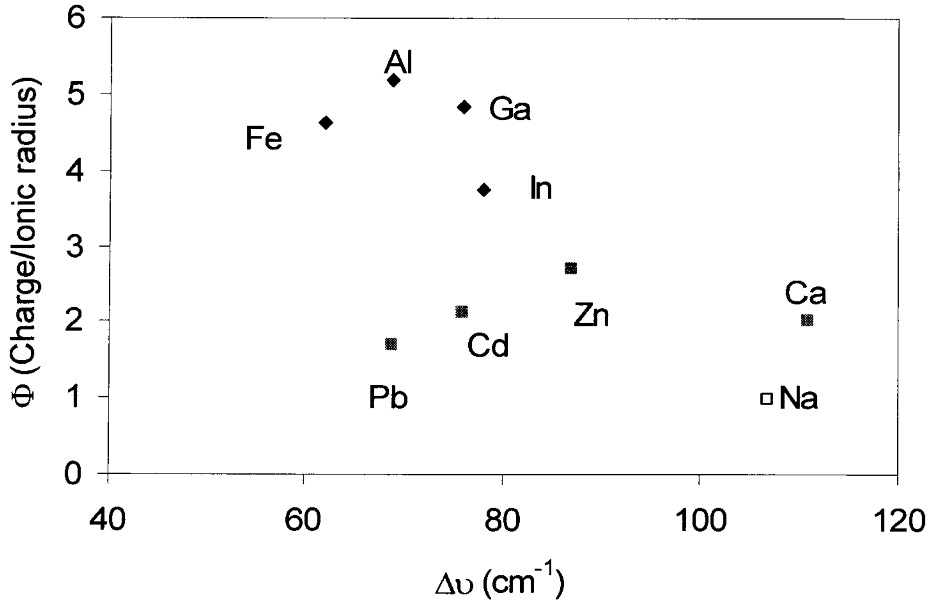


Figure 4.16: Ionic potential (Φ) of the metal ion vs Δν for various insoluble di-(n-octyl) phosphinate/ metal complexes formed at r° = 3 (◆ : Elements charged 3+; ■ : Elements charged 2+; □ : Element charged 1+).

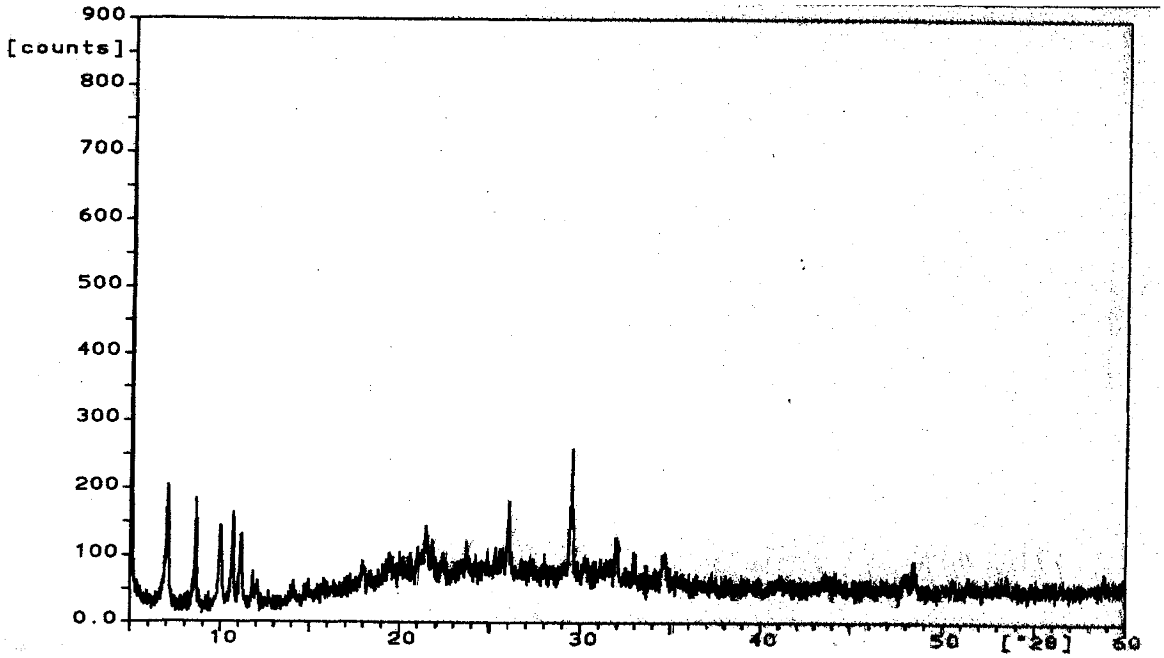


Figure 4.17: X-ray diffraction of the insoluble complex formed between gallium and the sodium di-(n-octyl) phosphinate ligand at a mole ratio of 3.

4.7 Summary

Gallium was selectively removed from zinc and aluminum solutions using sodium di-(n-octyl) phosphinate. A good separation between zinc and gallium was obtained while the separation range between aluminum and gallium was narrower. A good selectivity for gallium and aluminum over calcium was also obtained.

A process was proposed to treat GaAs effluents from the electronics industry. The gallium was removed by complexation with the sodium di-(n-octyl) phosphinate while the arsenic was precipitated with ferric ions. The excess ligand in solution was removed and recovered from the solution either in its acidic form or by complexation with the ferric ions.

Finally, of the many factors determining the affinity of the sodium di-(n-octyl) phosphinate for the metal, the following factors are significant:

- the hard and soft theory (the hard ligand reacts with the hard metals)
- the charge of the metal (higher charges have more affinity)
- the ionic radius (larger is the radius, better the affinity)
- the structure of the complex
- the electronegativity of the metals (including the influence of the orbital)

CHAPTER 5

MODELING OF THE COMPLEXATION AND PRECIPITATION OF METALS

The affinity of the different metals considered in this work and their complexation with sodium di-(n-octyl) phosphinate ligand were studied in Chapters 3 and 4. The following summarizes the phenomena observed and the conclusions:

- The sodium di-(n-octyl) phosphinate was removed from aqueous solutions in its acidic or sodium form or by complexation with a metal ion.
- Complete removal of metal was obtained when the metal ion and the ligand were oppositely charged. The formation of metal complexes with counter ions, such as chloride and sulfate, inhibited the removal of metals.
- Better removal of the metals with the ligand was generally obtained in acidic conditions. In basic solutions, metal hydroxide precipitates formed. Under these conditions, the addition of the ligand helped increasing the size of the precipitated particles, hence allowing better separation between the aqueous phase and the solid phase.

Based on these observations, a model on the complexation of gallium, aluminum, indium and iron with the sodium di-(n-octyl) phosphinate ligand that takes into account the presence of competing ions was developed for different pH. The effect of the hydroxide counter ions on the removal efficiency is considered in this model. The CO_2 from air and the possible formation of carbonate complexes is also considered. Finally, the model prediction is compared to the experimental values and comments on the possible sources of errors are made. In this section, sodium di-(n-octyl) phosphinate is called ligand.

5.1 Model assumptions

The following assumptions were made in order to obtain a workable model:

a. The phases are in equilibrium.

b. The total volume of the reaction mixture is constant throughout the reaction time and equal to 0.02 L.

c. The temperature is constant at 25°C, thus the stability constants at this temperature are considered.

d. The concentration of CO_2 in air and the atmospheric pressure are constant at 370 mg CO_2/L of air (Keeling and Whorf, 2003) and 1 atm, respectively.

e. The liquid phase is a dilute solution, and the activity coefficients of the different solutes are equal to 1.

f. The gas is ideal and the density of water is 1 g/mL.

g. Sodium di-(n-octyl) phosphinate and the metal nitrates are strong electrolytes, i.e. dissociate completely into their positive and negative ions.

5.2 Complexes and their stability constants

The successive equilibrium from the reaction of a cation M^{m+} reacting with an anion A^- is represented by:

$$M^{m+} + n\,A^- \longleftrightarrow M\,(A)_n^{m-n} \tag{5.1}$$

with n = 1, 2 and 3 for m = 2 and n = 1, 2, 3 and 4 for m = 3.

Based on this reaction, the stability constant, $K_{n,M}$, was defined as:

$$K_{n,M} = \frac{C_{M^{m+}} C_{A^-}{}^{n}}{C_{MA_n}{}^{m-n}} \tag{5.1a}$$

where C is molar concentration (moles per liter of solution) of given species. The solubility product was defined as:

$$K_{sp,MA_n} = C_{M^{m+}} C_{A^-}{}^{n} \tag{5.1b}$$

The number of moles of M, n_M, is given by:

$$n_M = VC_M \tag{5.1 c}$$

where V is the total volume in liter of the solution.

5.3 CO_2 from the air

Carbon dioxide dissolves in aqueous solutions to an extent determined by its partial pressure and its interaction with other solutes in water. Reaction 5.2 is an equilibrium reaction between the gaseous and the aqueous forms of CO_2.

$$CO_{2\,(g)} \xleftrightarrow{K_{1,CO_2}} CO_{2\,(aq)} \tag{5.2}$$

This equilibrium can be described by Henry's law. The concentration of CO_2 in the aqueous solution, $C_{CO_{2(aq)}}$, is proportional to the partial pressure of gaseous CO_2:

$$C_{CO_{2(aq)}} = K_{1,CO_2} P_{CO_2} \tag{5.2a}$$

where $K_{1,CO_2} = 10^{-1.464}$ mol/kg.atm for an ionic strength equal to 0 and at ambient temperature (Butler, 1998) with P_{CO_2} in atm.

In acidic solutions (pH < 5), the main species present in aqueous solutions at equilibrium is $CO_{2(aq)}$. At higher pH, bicarbonate and carbonate ions form according to reactions (5.3) and (5.4):

$$CO_{2\,(aq)} + 2\,H_2O \xleftrightarrow{K_{2,CO_2}} HCO_3^- + H_3O^+_{(aq)} \qquad K_{2,CO_2} = 10^{-6.363} \qquad (5.3)$$

and

$$HCO_3^- + H_2O \xleftrightarrow{K_{3,CO_2}} CO_3^{2-} + H_3O^+_{(aq)} \qquad K_{3,CO_2} = 10^{-10.329} \qquad (5.4)$$

where $K_{2,CO_2} = \frac{C_{HCO_3^-} C_{H^+}}{C_{CO_{2(aq)}}}$ and $K_{3,CO_2} = \frac{C_{CO_3^{2-}} C_{H^+}}{C_{HCO_3^-}}$ are obtained from literature (Butler, 1998).

5.4 Hydrolysis of metal

5.4.1 Gallium hydroxide complexes

The formation of gallium hydroxide complexes is mainly pH and concentration of gallium dependent. In gallium solutions with more than 100 mg/L Ga (1.4 mM), one or more polynuclear species, such as $Ga_{26}(OH)_{65}^{13-}$, can exist at pH above 3. However, for solutions where Ga is below 10 mg/L (0.14 mM), four mononuclear complexes can form according to equations (5.5) to (5.8) (Baes and Mesmer, 1986; Martell and Motekaitis, 1988).

$$Ga(OH)^{2+} \longleftrightarrow Ga^{3+} + OH^- \qquad K_{1,Ga} = 10^{-11.4} \qquad (5.5)$$

$$Ga(OH)_2^+ \longleftrightarrow Ga^{3+} + 2\,OH^- \qquad K_{2,Ga} = 10^{-22.1} \qquad (5.6)$$

$$Ga(OH)_3 \longleftrightarrow Ga^{3+} + 3\,OH^- \qquad K_{3,Ga} = 10^{-31.7} \qquad (5.7)$$

$$Ga(OH)_4^- \longleftrightarrow Ga^{3+} + 4\,OH^- \qquad K_{4,Ga} = 10^{-39.4} \qquad (5.8)$$

where $K_{1,Ga} = \frac{C_{Ga^{3+}} C_{OH^-}}{C_{Ga(OH)^{2+}}}$, $K_{2,Ga} = \frac{C_{Ga^{3+}} C^2_{OH^-}}{C_{Ga(OH)_2^+}}$, $K_{3,Ga} = \frac{C_{Ga^{3+}} C^3_{OH^-}}{C_{Ga(OH)_3}}$ and

$K_{4,Ga} = \frac{C_{Ga^{3+}} C^4_{OH^-}}{C_{Ga(OH)_4^-}}$ (Baes and Mesmer, 1986).

If $Ga(OH)_3$ precipitates, an additional relationship must be satisfied:

$$Ga(OH)_{3\,(s)} \longleftrightarrow Ga^{3+} + 3\,OH^- \qquad K_{sp,Ga} = 10^{-37} \tag{5.9}$$

where $K_{sp,Ga} = C_{Ga^{3+}} C^3_{OH^-}$ (Baes and Mesmer, 1986).

The precipitation of $Ga(OH)_{3(s)}$ occurs when the concentration of soluble gallium in saturated solution, $C_{Ga_{soluble}}$, is superior to the initial concentration of gallium (i.e. $C_{Ga_{soluble}} = \frac{K_{sp,Ga}}{C^3_{OH}} > C^\circ_{Ga}$). The gallium hydroxide precipitate was assumed to be the amorphous form $Ga(OH)_{3(s)}$ (eq. 5.9) and not the oxyhydroxide GaO(OH) form (eq. 5.10 and 5.11):

$$GaO(OH)_{(s)} + H_2O \longleftrightarrow Ga^{3+} + 3\,OH^- \qquad K_{sp_2,Ga} = 10^{-39.1} \tag{5.10}$$

where $K_{sp_2,Ga} = C_{Ga^{3+}} C^3_{OH^-}$ (Baes and Mesmer, 1986).

While GaO(OH) is a more stable complex than $Ga(OH)_{3(s)}$, it forms by aging $Ga(OH)_{3(s)}$. The oxyhydroxide form solubilizes in water according to:

$$GaO(OH)_{(s)} + H_2O \longleftrightarrow Ga(OH)_3\,(aq) \qquad K_{sp_3,Ga} = 10^{-7.4} \tag{5.11}$$

where $K_{sp_3,Ga} = C_{Ga(OH)_3\,(aq)}$ (Baes and Mesmer, 1986).

5.4.2 Aluminum hydroxide complexes

In dilute solutions, four mononuclear complexes of aluminum can form depending on the pH of the solution: $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$.

$$Al(OH)^{2+} \longleftrightarrow Al^{3+} + OH^- \qquad K_{1,Al} = 10^{-9.09} \qquad (5.12)$$

$$Al(OH)_2^+ \longleftrightarrow Al^{3+} + 2\ OH^- \qquad K_{2,Al} = 10^{-18.7} \qquad (5.13)$$

$$Al(OH)_3 \longleftrightarrow Al^{3+} + 3\ OH^- \qquad K_{3,Al} = 10^{-27} \qquad (5.14)$$

$$Al(OH)_4^- \longleftrightarrow Al^{3+} + 4\ OH^- \qquad K_{4,Al} = 10^{-33.3} \qquad (5.15)$$

where $K_{1,Al} = \frac{C_{Al^{3+}} C_{OH^-}}{C_{Al(OH)^{2+}}}$, $K_{2,Al} = \frac{C_{Al^{3+}} C^2_{OH^-}}{C_{Al(OH)_2^+}}$, $K_{3,Al} = \frac{C_{Al^{3+}} C^3_{OH^-}}{C_{Al(OH)_3}}$ and $K_{4,Al} = \frac{C_{Al^{3+}} C^4_{OH^-}}{C_{Al(OH)_4^-}}$

(Baes and Mesmer, 1986).

Gibbsite is the stable form of aluminum hydroxide at room temperature. The following solubility constant was estimated in a supersaturated acid in solution seeded with gibbsite (Baes and Mesmer, 1986). The equilibrium, as described in equation 5.16, was reached after one to three months:

$$Al(OH)_{3\,(s)} \longleftrightarrow Al^{3+} + 3\ OH^- \qquad K_{sp,Al} = 10^{-33.5} \qquad (5.16)$$

where $K_{sp,Al} = C_{Al^{3+}}\ C^3_{OH^-}$.

5.4.3 Indium hydroxide complexes

For the hydrolysis of indium, four mononuclear complexes of indium, $In(OH)^{2+}$, $In(OH)_2^+$, $In(OH)_3$, and $In(OH)_4^-$, can form depending on the pH of the solution:

$$In(OH)^{2+} \longleftrightarrow In^{3+} + OH^- \qquad K_{1,In} = 10^{-10} \qquad (5.17)$$

$$In(OH)_2^+ \longleftrightarrow In^{3+} + 2\ OH^- \qquad K_{2,In} = 10^{-20.18} \qquad (5.18)$$

$$In(OH)_3 \longleftrightarrow In^{3+} + 3\ OH^- \qquad K_{3,In} = 10^{-29.6} \qquad (5.19)$$

$$In(OH)_4^- \longleftrightarrow In^{3+} + 4\ OH^- \qquad K_{4,In} = 10^{-33.93} \qquad (5.20)$$

where $K_{1,In}=\dfrac{C_{In^{3+}}C_{OH^-}}{C_{In(OH)^{2+}}}$, $K_{2,In}=\dfrac{C_{In^{3+}}C^2_{OH^-}}{C_{In(OH)_2^+}}$, $K_{3,In}=\dfrac{C_{In^{3+}}C^3_{OH^-}}{C_{In(OH)_3}}$ and $K_{4,In}=\dfrac{C_{In^{3+}}C^4_{OH^-}}{C_{In(OH)_4^-}}$

(Baes and Mesmer, 1986).

The solubility constant of $In(OH)_3$ precipitate was estimated from precipitates aged for more than 2 months (Baes and Mesmer, 1986):

$$In(OH)_{3\,(s)} \longleftrightarrow In^{3+} + 3\,OH^- \qquad K_{sp,In}= 10^{-36.93} \tag{5.21}$$

where $K_{sp,In}= C_{In^{3+}}\, C^3_{OH^-}$.

5.4.4 *Iron hydroxide complexes*

The hydrolysis of ferric ion was considered for iron. Four mononuclear complexes $Fe(OH)^{2+}, Fe(OH)_2^+$, $Fe(OH)_3$, and $Fe(OH)_4^-$, can form depending on the pH of the solution:

$$Fe(OH)^{2+} \longleftrightarrow Fe^{3+} + OH^- \qquad K_{1,Fe}=10^{-11.81} \tag{5.22}$$

$$Fe(OH)_2^+ \longleftrightarrow Fe^{3+} + 2\,OH^- \qquad K_{2,Fe}=10^{-22.33} \tag{5.23}$$

$$Fe(OH)_3 \longleftrightarrow Fe^{3+} + 3\,OH^- \qquad K_{3,Fe}=10^{-30} \tag{5.24}$$

$$Fe(OH)_4^- \longleftrightarrow Fe^{3+} + 4\,OH^- \qquad K_{4,Fe}=10^{-34.94} \tag{5.25}$$

where $K_{1,Fe}=\dfrac{C_{Fe^{3+}}C_{OH^-}}{C_{Fe(OH)^{2+}}}$, $K_{2,Fe}=\dfrac{C_{Fe^{3+}}C^2_{OH^-}}{C_{Fe(OH)_2^+}}$, $K_{3,Fe}=\dfrac{C_{Fe^{3+}}C^3_{OH^-}}{C_{Fe(OH)_3}}$ and $K_{4,Fe}=\dfrac{C_{Fe^{3+}}C^4_{OH^-}}{C_{Fe(OH)_4^-}}$

(Baes and Mesmer, 1986).

The solubility constant of the amorphous FeO(OH) precipitate was considered:

$$FeO(OH)_{(s)} + H_2O \longleftrightarrow Fe^{3+} + 3\,OH^- \qquad K_{sp,Fe}= 10^{-39.5} \tag{5.26}$$

where $K_{sp,Fe}= C_{Fe^{3+}}\, C^3_{OH^-}$ (Baes and Mesmer, 1986).

5.4.5 *Model of the hydrolysis*

For an aqueous solution of gallium at different pH values, and when the pH is adjusted by the addition of NaOH or HNO_3, a total of 14 different species, listed in Table 5.1, exist in solution. At room temperature and atmospheric pressure, the proton and the hydroxide ions are related by:

$$H_2O \longleftrightarrow H^+ + OH^- \qquad K_{1,w} = 10^{-14} \qquad (5.27)$$

where $K_{1,w} = C_{H^+} C_{OH^-}$ (Butler, 1998).

Table 5.1: Possible species in an aqueous solution of gallium nitrate at different pH values adjusted by HNO_3 or NaOH.

Liquid	Total	Solid	Total	Gas	Total
Ga^{3+}, $GaOH^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3$, $Ga(OH)_4^-$, H^+, OH^-, CO_2, HCO_3^-, CO_3^{2-}, NO_3^-, Na^+	12	$Ga(OH)_{3(s)}$	1	CO_2	1

For this system, the following equations apply:

Mass Balance Equations

Mass Balance of Ga(III)

$$n^\circ_{Ga} = n_{Ga^{3+}} + n_{GaOH^{2+}} + n_{Ga(OH)_2^+} + n_{Ga(OH)_3} + n_{Ga(OH)_4^-} + n_{Ga(OH)_{3(s)}} \qquad (5.28)$$

Mass Balance of Nitrate (acidic conditions: pH below 7)

$$n^\circ_{NO_3} = 3n^\circ_{Ga} + n^\circ_{HNO_3} = n_{NO_3^-} \qquad (5.29)$$

$n^{\circ}_{NO_3}$ was obtained from the acid added to adjust the pH and from the metal nitrate added to the solution. In basic conditions, the $n^{\circ}_{NO_3}$ came only from the metal nitrate and in the case of gallium:

$$n^{\circ}_{NO_3} = n_{NO_3^-} = 3n^{\circ}_{Ga} \tag{5.29a}$$

Mass Balance of Sodium (basic conditions: pH above 7)

The sodium was added to the solution with NaOH to adjust the initial pH.

$$n^{\circ}_{Na} = n_{NaOH} = n_{Na^+} \tag{5.30}$$

Charge Balance

$$3n_{Ga^{3+}} + 2n_{GaOH^{2+}} + n_{Ga(OH)_2^+} + n_{Na^+} + n_{H^+} = n_{Ga(OH)_4^-} + n_{NO_3^-} + n_{OH^-} + n_{HCO_3^-} + 2n_{CO_3^{2-}} \tag{5.31}$$

The quantities in equations 5.28 to 5.31 were expressed in terms of concentration using equation 5.1c. The values of $K_{1,Ga}$, $K_{2,Ga}$, $K_{3,Ga}$, $K_{4,Ga}$, $K_{sp,Ga}$ for gallium and K_{1,CO_2}, K_{2,CO_2}, K_{3,CO_2} for carbon dioxide are the knowns. The value of P_{CO_2} was considered as equal to 2.057 × 10^{-4} atm. The unknowns were $C_{Ga^{3+}}$, $\frac{n_{Ga(OH)_{3(s)}}}{V}$ and C_{OH^-}.

The input values to the model are V, C°_{Ga} and the initial pH ($C^{\circ}_{HNO_3}$ or C_{NaOH}). All the derived species were expressed in terms of $C_{Ga^{3+}}$, C_{Na^+}, $C_{NO_3^-}$ and C_{OH^-}.

Using equations 5.2 to 5.8, 5.27, 5.29 and 5.30, the charge balance can be written as:

$$C_{Ga^{3+}}\left(3+2\frac{C_{OH^-}}{K_{1,Ga}}+\frac{(C_{OH^-})^2}{K_{2,Ga}}-\frac{(C_{OH^-})^4}{K_{4,Ga}}\right)+\frac{10^{-14}}{C_{OH^-}}+C^{\circ}_{NaOH}=$$
$$C_{OH^-}+3C^{\circ}_{Ga}+C^{\circ}_{HNO_3}+\frac{C_{OH^-}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}}+2\frac{(C_{OH^-})^2K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2} \tag{5.32}$$

Knowing C°_{Ga}, the total volume V and the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$), equation 5.32 can be solved for C_{OH^-} by considering:

- $C_{Ga^{3+}} = \frac{K_{sp,Ga}}{(C_{OH^-})^3}$ (5.9) whenever the value of $C_{Ga^{3+}} C^3_{OH^-}$ was larger than $K_{sp,Ga}$. The solution was saturated and gallium precipitated as $Ga(OH)_{3(s)}$. Thus, by replacing equations 5.5 to 5.8 in equation 5.28, the following equation was obtained:

$$\frac{n_{Ga(OH)_{3(s)}}}{V} = C^{\circ}_{Ga} - C_{Ga^{3+}} X_{GaOH} \tag{5.33}$$

  where $X_{GaOH} = 1 + \frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}} + \frac{(C_{OH^-})^3}{K_{3,Ga}} + \frac{(C_{OH^-})^4}{K_{4,Ga}}$ and $C_{Ga^{3+}} = \frac{K_{sp,Ga}}{(C_{OH^-})^3}$

- For $C_{Ga^{3+}} C^3_{OH^-}$ equal or smaller than $K_{sp,Ga}$, the solution was unsaturated. Equation 5.9 was dropped, and the precipitated $Ga(OH)_{3(s)}$ was not considered in the equations 5.28. By replacing equations 5.5 to 5.8 in equation 5.28, the following equation was obtained:

$$C_{Ga^{3+}} = \frac{C^{\circ}_{Ga}}{X_{GaOH}} \tag{5.34}$$

  where X_{GaOH} is defined in equation 5.33.

The parameter $C_{Ga^{3+}}$, defined in equation 5.9 or 5.34, was substituted into equation 5.32, which in turn was solved for C_{OH^-}. In acidic conditions, no sodium was added. Thus, the equation 5.30 was not used and replaced by equation 5.29 (pH was adjusted with HNO_3). In basic conditions, Equation 5.29a and 5.30 were used instead of Equation 5.30. The source of nitrate was from the initial amount of metal nitrate, and the source of sodium was the NaOH added to adjust the initial pH of the solution. By solving equation 5.32 for C_{OH^-}, the equilibrium pH of the solution and the concentrations of the different forms of gallium were determined.

The speciation of gallium as a function of pH is presented in Figure 5.1. The calculation was made for a total concentration of gallium of 0.359 mM (25 mg/L). $Ga(OH)_{3(s)}$ precipitated at a pH between 3 and 8 while a small amount of $Ga(OH)_3$ remained in solution in its soluble form. Experimental data are compared with the computed values in Figure 5.2. As more time was given to the phase to reach equilibrium, the experimental data approached the computed values. Due to the small amount of gallium used in these experiments and the fact that the solution was not seeded with $Ga(OH)_{3(s)}$ to favor the precipitation, a smaller amount of precipitate formed after 1 day. The difference between the experimental and computed values is expected because the values of the stability constants and the solubility products reported by Baes and Mesmer (1986) were obtained using seeded solutions and a longer contact time.

The same procedure was followed for the hydrolysis of aluminum where V, C°_{Al} and the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$) are the input parameters. The aluminum species were Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$ in the aqueous phase, and $Al(OH)_{3(s)}$ constituted the solid phase. From the charge balance, equation 5.35 was obtained:

$$C_{Al^{3+}}\left(3+2\frac{C_{OH^-}}{K_{1,Al}}+\frac{(C_{OH^-})^2}{K_{2,Al}}-\frac{(C_{OH^-})^4}{K_{4,Al}}\right)+\frac{10^{-14}}{C_{OH^-}}+C^{\circ}_{NaOH}=$$

$$C_{OH^-}+3C^{\circ}_{Al}+C^{\circ}_{HNO_3}+\frac{C_{OH^-}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}}+2\frac{(C_{OH^-})^2K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2} \qquad (5.35)$$

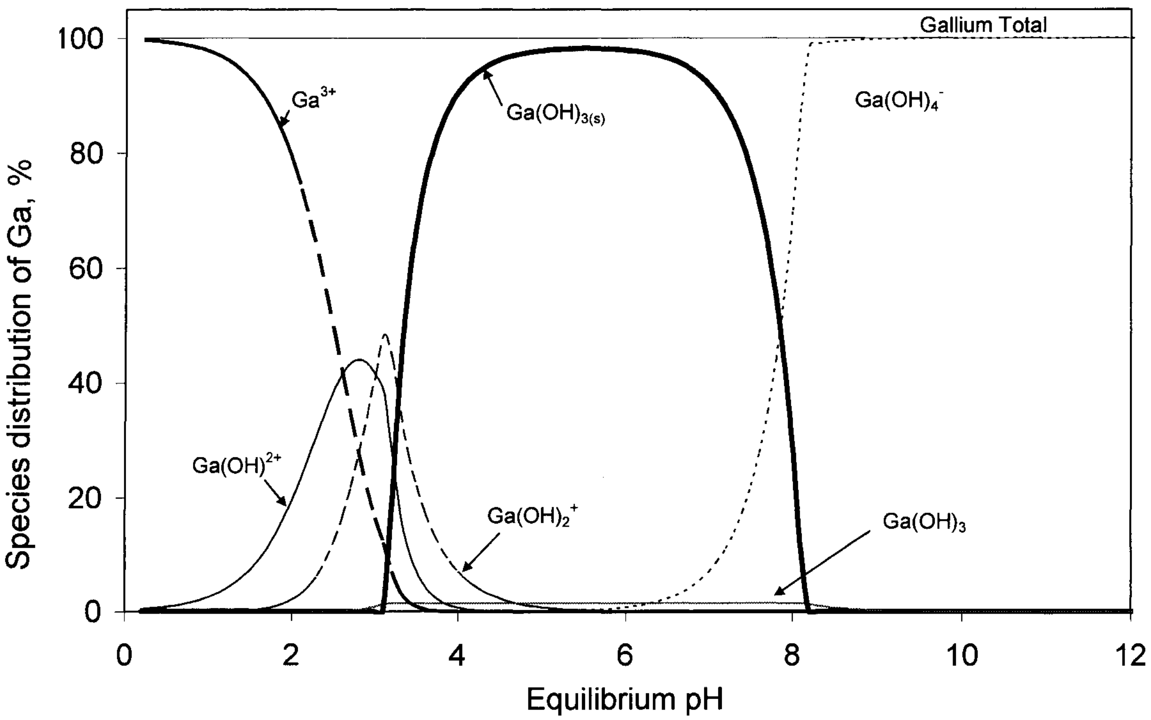


Figure 5.1: Distribution of gallium species in aqueous solutions at different pH [C°_{Ga} = 0.359 mM, values calculated with parameters from Baes and Mesmer (1986)].

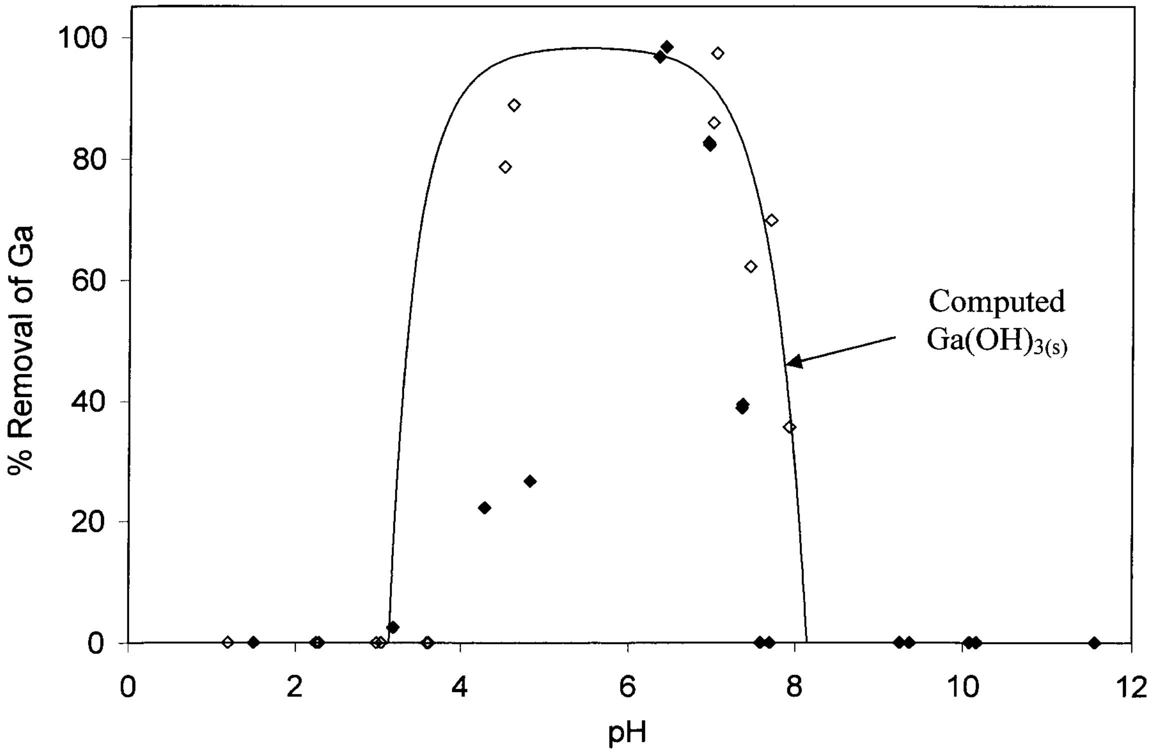


Figure 5.2: Precipitation of gallium in aqueous solution at different pH values. [C°_{Ga} = 0.359 mM; experimental removal of $Ga(OH)_{3(s)}$ obtained after: 1 day (◆), 6 days (◇); line: computed $Ga(OH)_{3(s)}$].

Knowing C°_{Al}, the total volume V and the initial pH (C°_{NaOH} or $C^\circ_{HNO_3}$), equation 5.35 was solved for C_{OH^-}. If the solubility product is exceeded, i.e. $C_{Al^{3+}} C^3_{OH^-} > K_{sp,Al}$, aluminum precipitates. The following equations were obtained from the solubility product (equation 5.16) and the mass balances of aluminum:

$$C_{Al^{3+}} = \frac{K_{sp,Al}}{(C_{OH^-})^3} \tag{5.16}$$

$$\frac{n_{Al(OH)_{3(s)}}}{V} = C^\circ_{Al} - C_{Al^{3+}} X_{AlOH} \tag{5.36}$$

where $X_{AlOH} = 1 + \frac{C_{OH^-}}{K_{1,Al}} + \frac{(C_{OH^-})^2}{K_{2,Al}} + \frac{(C_{OH^-})^3}{K_{3,Al}} + \frac{(C_{OH^-})^4}{K_{4,Al}}$

For $C_{Al^{3+}} C^3_{OH^-} \le K_{sp,Al}$, the $Al(OH)_{3(s)}$ precipitate was dropped, $n_{Al(OH)_{3(s)}} = 0$, giving:

$$C_{Al^{3+}} = \frac{C^\circ_{Al}}{X_{AlOH}} \tag{5.37}$$

where X_{AlOH} is defined in equation 5.31.

The parameter $C_{Al^{3+}}$, defined in equation 5.16 or 5.37, was substituted into equation 5.35, which in turn was solved for C_{OH^-}. The equilibrium pH of the solution and the concentrations of the different forms of aluminum were then determined from the value of C_{OH^-}.

The speciation of aluminum as a function of pH is presented in Figure 5.3 for a total concentration of aluminum of 0.925 mM. The main species present were Al^{3+} up to pH 4, the insoluble $Al(OH)_{3(s)}$ from pH 4 to around 11 and for pH above 11, $Al(OH)_4^-$. In Figure 5.4, the calculated values are compared to experimental data obtained after 1 day.

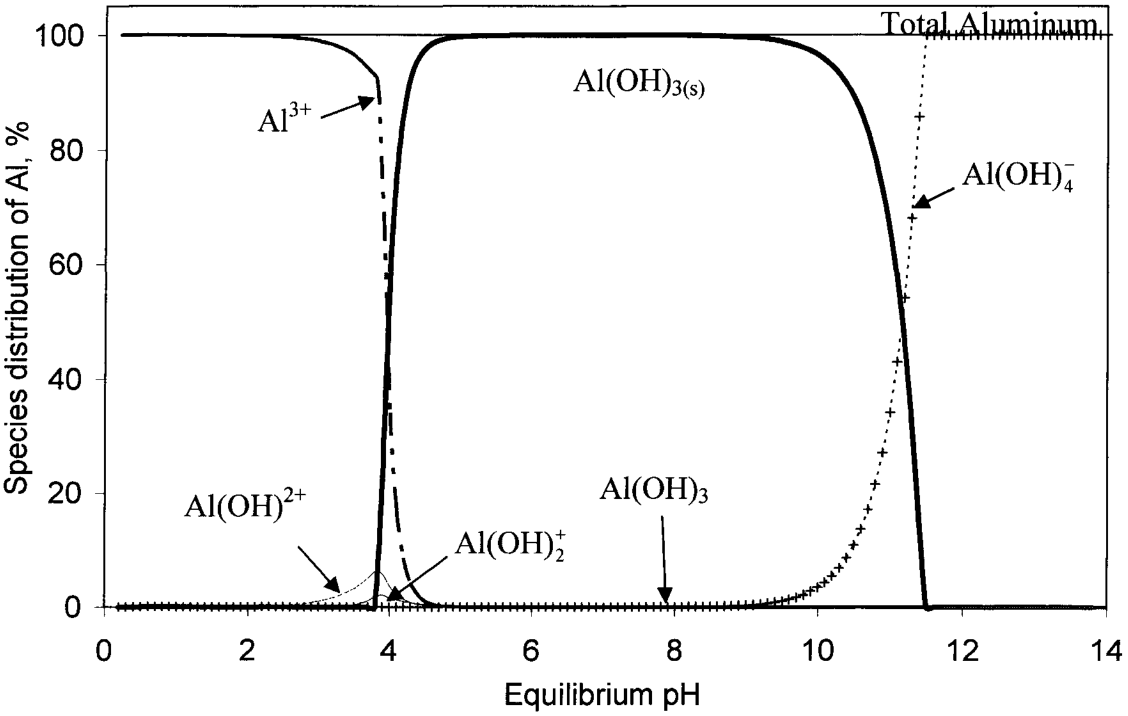


Figure 5.3: Distribution of aluminum species in aqueous solutions at different pH [C°_{Al} = 0.925 mM; values calculated with parameters from Baes and Mesmer (1986)].

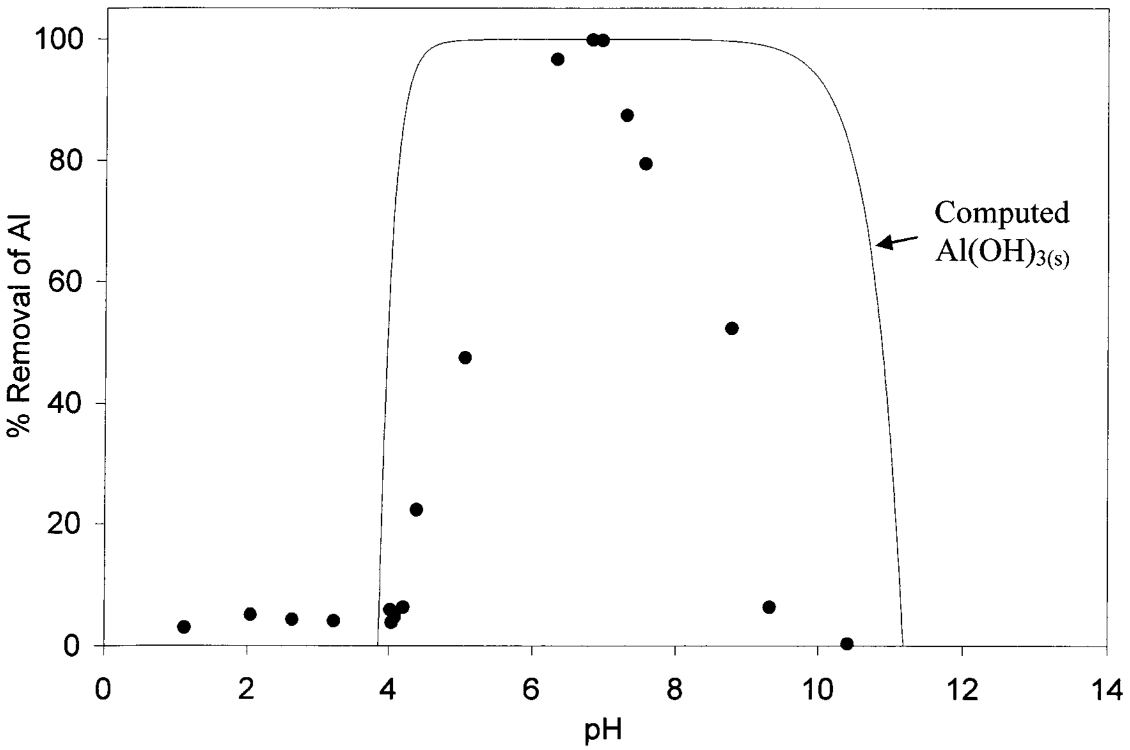


Figure 5.4: Precipitation of aluminum in aqueous solution at different pH values [C°_{Al} = 0.925 mM; experimental removal of $Al(OH)_{3(s)}$ obtained after 1day (●); line: computed $Al(OH)_{3(s)}$].

A noticeable difference, observed between the computed and experimental values, is due to the fact that the experimental values are not at equilibrium.

For the hydrolysis of indium and iron, the input parameters were V, C°_{In} or C°_{Fe} and the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$). No ligand was added to the solution. The same procedure for gallium was also followed for the hydrolysis of indium and iron. Equations 5.17 to 5.21 and 5.22 to 26 were considered for indium and iron, respectively. Based on the equations 5.27 to 5.34, where the gallium term was replaced by indium or iron, equation 5.32 was solved for C_{OH^-}. The equilibrium pH of the solution and the concentrations of the different forms of indium or iron were determined from the value of C_{OH^-}.

The speciation of indium is presented in Figure 5.5 for a total concentration of indium of 0.22 mM. The main species present were In^{3+} up to around pH 3, the insoluble $In(OH)_{3(s)}$ from pH 3 to around 13 and for pH above 13, $In(OH)_4^-$. In Figure 5.6, the calculated values of the precipitation of $In(OH)_{3(s)}$ are compared to experimental data obtained after 1 day. The discrepancy between computed and experimental values for indium is due to the fact that the experimental values were not at equilibrium. The time to reach equilibrium can take several months (Baes and Mesmer, 1986).

The speciation of iron is presented in Figure 5.7 for a total concentration of iron of 0.36 mM. The main species present were Fe^{3+} up to around pH 2, and above this pH, the insoluble $FeO(OH)_{(s)}$. Some $Fe(OH)^{2+}$ was formed between pH around 0.3 and 2.9. In Figure 5.8, the calculated values of the precipitation of $FeO(OH)_{(s)}$ are compared to experimental data obtained after 1 day. Again, the experimental values for iron were not at equilibrium, explaining the discrepancy with the computed data in the acidic pH.

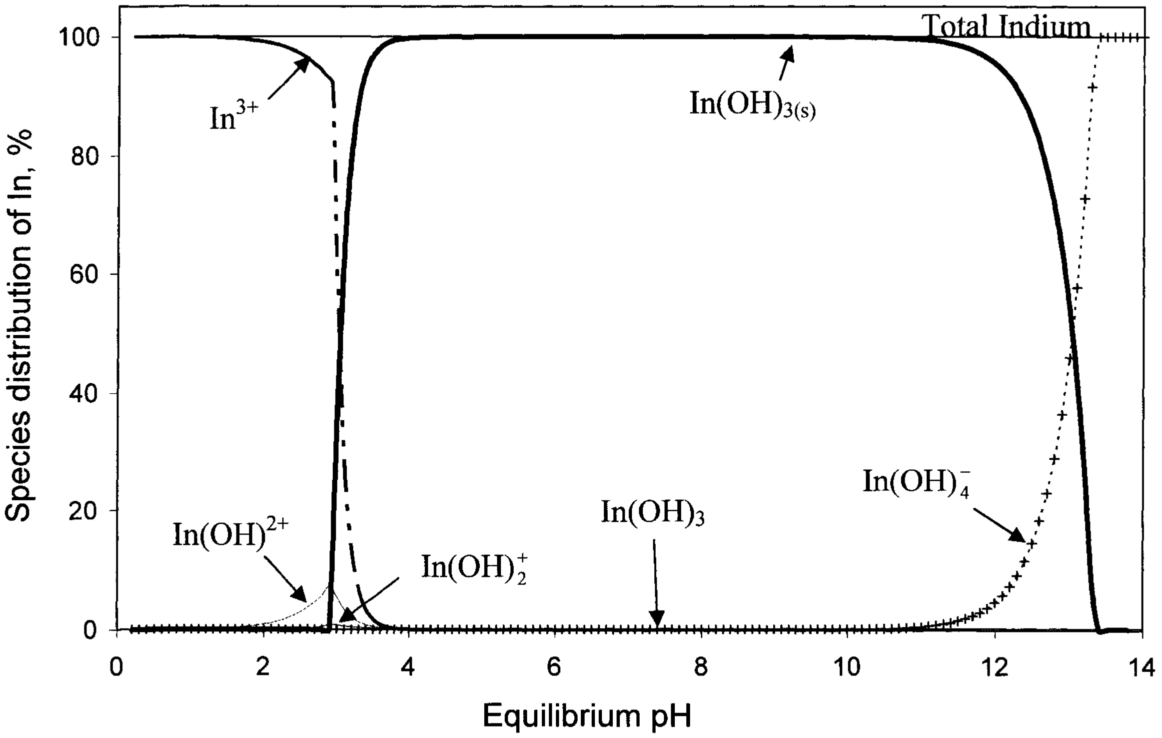


Figure 5.5: Distribution of indium species in aqueous solution at different pH [C°_{In} = 0.22 mM; values calculated with parameters from Baes and Mesmer (1986)].

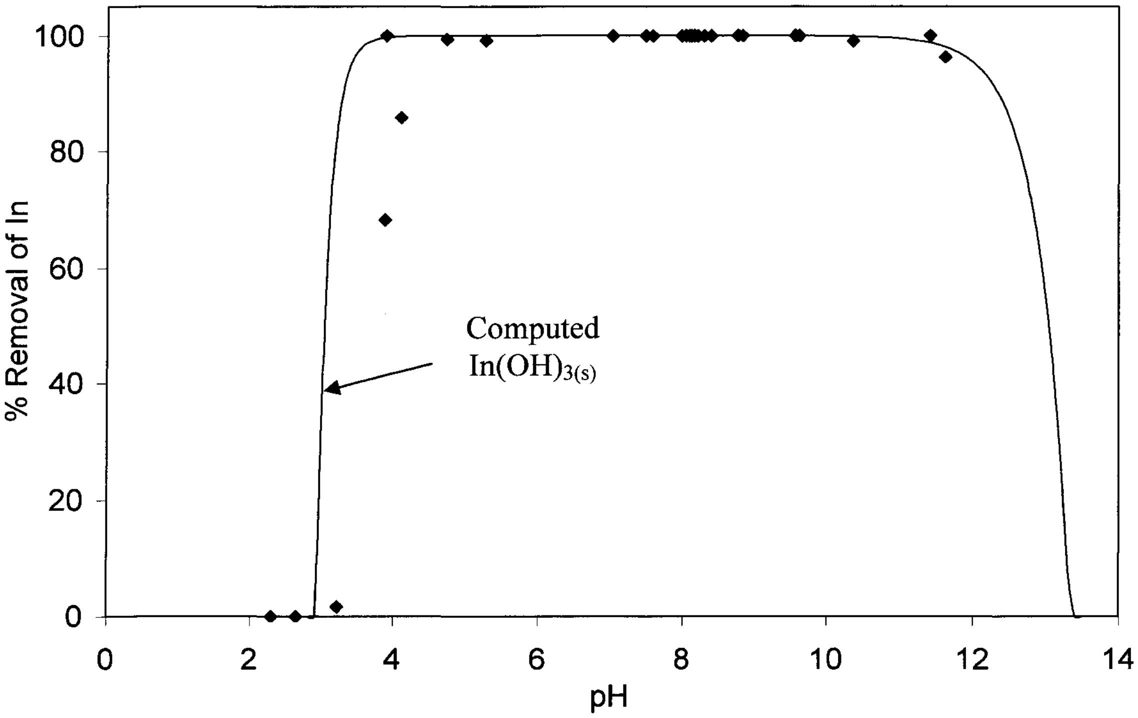


Figure 5.6: Precipitation of indium in aqueous solution at different pH values [$C^{\circ}_{In} = 0.22$ mM; experimental removal of $In(OH)_{3(s)}$ obtained after 1day (◆); line: computed $In(OH)_{3(s)}$].

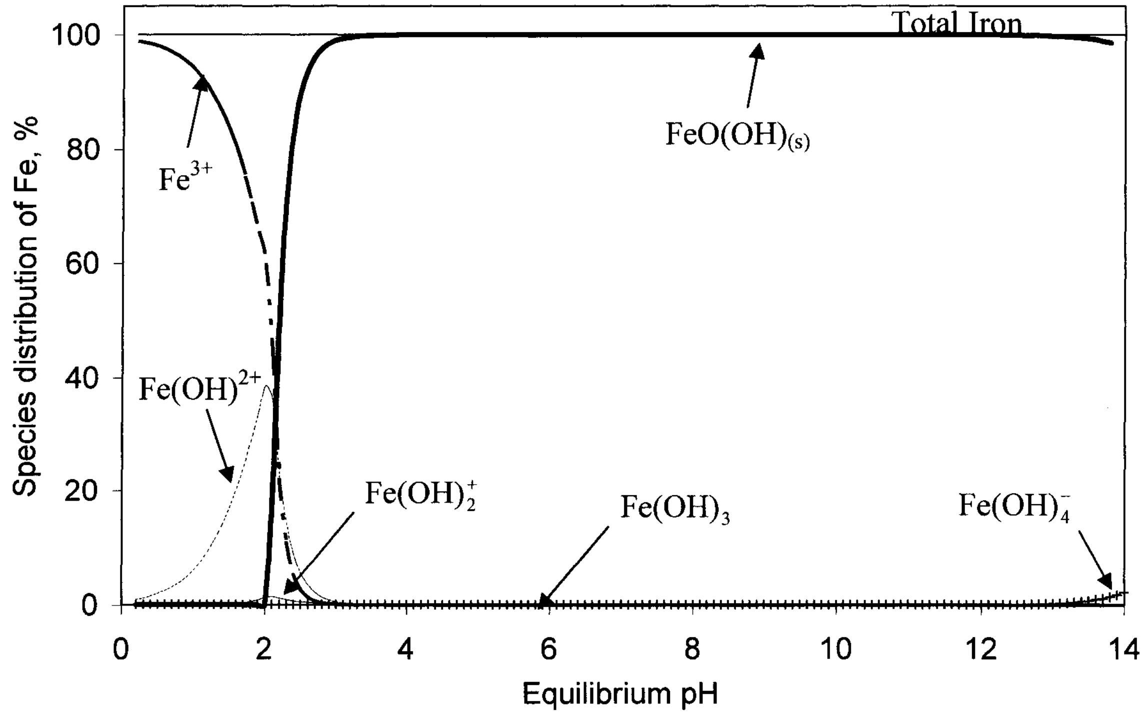


Figure 5.7: Distribution of iron species in aqueous solution at different pH [C°_{Fe} = 0.36 mM; values calculated with parameters from Baes and Mesmer (1986)].

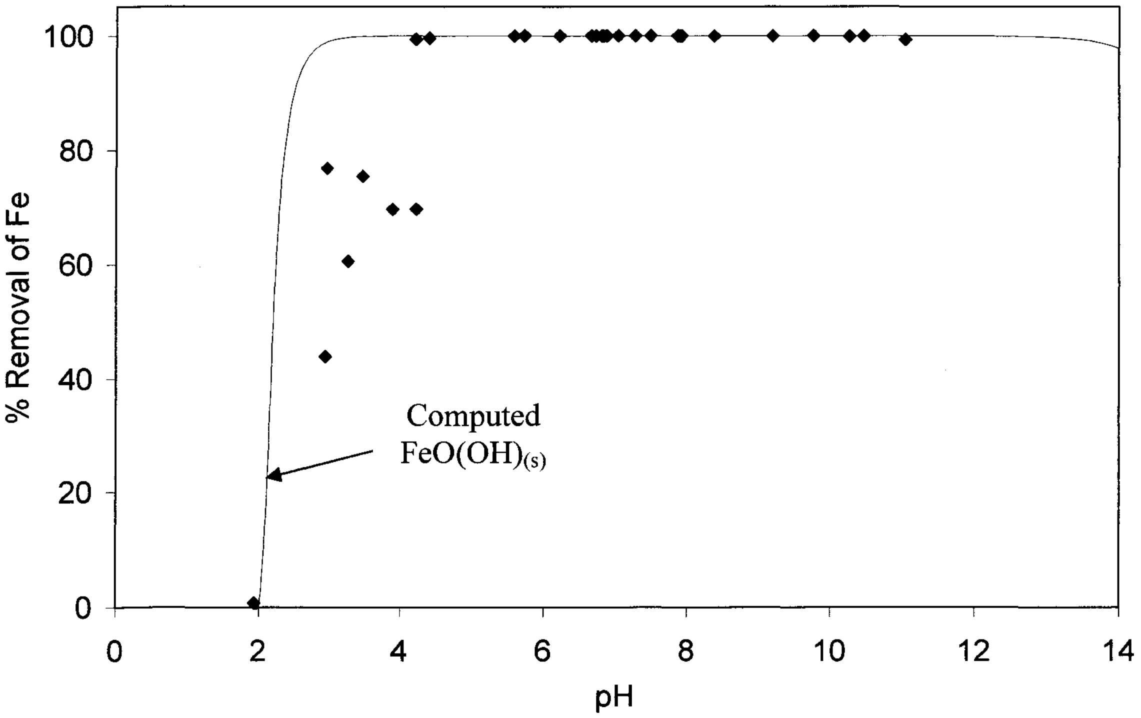


Figure 5.8: Precipitation of iron in aqueous solution at different pH values [C°_{Fe} = 0.36 mM; experimental removal of ferric hydroxide obtained after 1day (◆); line: computed $FeO(OH)_{(s)}$].

5.5 Removal of metals with the sodium di-(n-octyl) phosphinate ligand

In this section, the complexation of the sodium di-(n-octyl) phosphinate alone in an aqueous solution is first considered. The complexation between the ligand and a metal (gallium, aluminum, indium or iron) in a solution containing one metal is then illustrated. Finally, the selective removal of gallium from a solution containing both gallium and aluminum is considered using the sodium di-(n-octyl) phosphinate ligand.

5.5.1 *Parameters for ligand-metal complexes*

As mentioned in section 3.1.2, the organophosphorus ligand can be removed from aqueous solutions containing no metals either in its acidic form or in its sodium form. A stability constant of the ligand in its acidic form was used in this case as it was observed in Figure 3.4 that a small amount of ligand remained in solution. The following reactions were considered to model the solubility of the organophosphorus ligand in aqueous solutions at different pH values:

$$HL \longleftrightarrow H^+ + L^- \qquad K_{1,HL} = 10^{-5.8} \qquad (5.38)$$

$$HL_{(S)} \longleftrightarrow H^+ + L^- \qquad K_{sp,HL} = 10^{-10} \qquad (5.39)$$

$$NaL_{(S)} \longleftrightarrow Na^+ + L^- \qquad K_{sp,NaL} = 10^{-4.7} \qquad (5.40)$$

where $K_{1,HL} = \dfrac{C_{H^+}C_{L^-}}{C_{HL_{(aq)}}}$, $K_{sp,HL} = C_{H^+}C_{L^-}$ and $K_{sp,NaL} = C_{Na^+}C_{L^-}$. All values of these constants were parameters fitted in this work.

The following metal-ligand complexes were considered for the removal of gallium, aluminum and indium by the sodium di-(n-octyl) phosphinate ligand:

$$GaL_3 \longleftrightarrow Ga^{3+} + 3\,L^- \qquad K_{GaL_3} \text{ negligible} \qquad (5.41)$$

$$\mathrm{GaL_{3\,(s)}} \longleftrightarrow \mathrm{Ga^{3+}} + 3\,\mathrm{L^-} \qquad K_{sp,GaL_3} = 2.5\times10^{-30} \qquad (5.42)$$

$$\mathrm{AlL_3} \longleftrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{L^-} \qquad K_{AlL_3} = 5\times10^{-22} \qquad (5.43)$$

$$\mathrm{AlL_{3\,(s)}} \longleftrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{L^-} \qquad K_{sp,AlL_3} = 2\times10^{-27} \qquad (5.44)$$

$$\mathrm{InL_3} \longleftrightarrow \mathrm{In^{3+}} + 3\,\mathrm{L^-} \qquad K_{InL_3} = 5\times10^{-29} \qquad (5.45)$$

$$\mathrm{InL_{3\,(s)}} \longleftrightarrow \mathrm{In^{3+}} + 3\,\mathrm{L^-} \qquad K_{sp,InL_3} = 3.7\times10^{-35} \qquad (5.46)$$

$$\mathrm{FeL_3} \longleftrightarrow \mathrm{Fe^{3+}} + 3\,\mathrm{L^-} \qquad K_{FeL_3} = 6\times10^{-30} \qquad (5.47)$$

$$\mathrm{FeL_{3\,(s)}} \longleftrightarrow \mathrm{Fe^{3+}} + 3\,\mathrm{L^-} \qquad K_{sp,FeL_3} = 9\times10^{-36} \qquad (5.48)$$

where $K_{GaL_3} = \frac{C_{Ga^{3+}}C^3_{L^-}}{C_{GaL_3}}$, $K_{sp,GaL_3} = C_{Ga^{3+}}C^3_{L^-}$, $K_{AlL_3} = \frac{C_{Al^{3+}}C^3_{L^-}}{C_{AlL_3}}$, $K_{sp,GaL_3} = C_{Ga^{3+}}C^3_{L^-}$, $K_{InL_3} = \frac{C_{In^{3+}}C^3_{L^-}}{C_{InL_3}}$, $K_{sp,InL_3} = C_{In^{3+}}C^3_{L^-}$, $K_{FeL_3} = \frac{C_{Fe^{3+}}C^3_{L^-}}{C_{FeL_3}}$ and $K_{sp,FeL_3} = C_{Fe^{3+}}C^3_{L^-}$. Again, all these constants were adjusted parameters in this work. The formation of soluble GaL3 was neglected, thus the value of K_{GaL_3} was not reported in equation 5.41.

5.5.2 *Description of the removal of metals with the sodium di-(n-octyl) phosphinate ligand*

The inputs to the model are the initial pH of the solution (without metal or ligand), the total number of moles of metal and ligand added (n°_{Ga}, n°_{Al} n°_{In}, n°_{Fe}, n°_{L}) and the total volume of the solution. All the different forms of metals, including the complexes with hydroxide and the ligand, were accounted for in the mass balance except for the soluble GaL3 ($n_{GaL_3} = 0$). The following case is for a solution containing gallium nitrate, aluminum nitrate and the ligand:

Mass Balance Equations

Mass Balance of Ga(III)

$$n^{\circ}_{Ga} = n_{Ga^{3+}} + n_{GaOH^{2+}} + n_{Ga(OH)_2^+} + n_{Ga(OH)_3} + n_{Ga(OH)_{3(s)}} + n_{Ga(OH)_4^-} + n_{GaL_{3(s)}} \qquad (5.49)$$

Mass Balance of Al(III)

$$n^{\circ}_{Al} = n_{Al^{3+}} + n_{AlOH^{2+}} + n_{Al(OH)_2^+} + n_{Al(OH)_3} + n_{Al(OH)_{3(s)}} + n_{Al(OH)_4^-} + n_{AlL_{3(s)}} + n_{AlL_3} \qquad (5.50)$$

Mass Balance of Nitrate

The nitrate in solution came from the nitric acid used to adjust the initial pH and/or from the metal nitrate.

$$n^{\circ}_{NO_3} = 3n^{\circ}_{Ga} + 3n^{\circ}_{Al} + n^{\circ}_{HNO_3} = n_{NO_3^-} \qquad (5.51)$$

Mass Balance of Sodium

The sodium was added to the solution either in the form of NaOH to adjust the initial pH or in the form of sodium di-(n-octyl) phosphinate.

$$n^{\circ}_{Na} = n_{Na^+} + n_{NaL_{(S)}} \qquad (5.52)$$

Mass Balance of Ligand

$$n^{\circ}_{L} = n_{L^-} + n_{NaL_{(s)}} + n_{HL_{(s)}} + n_{HL} + 3n_{GaL_{3(s)}} + 3n_{AlL_{3(s)}} + 3n_{AlL_3} \qquad (5.53)$$

Charge Balance

$$3n_{Ga^{3+}} + 2n_{GaOH^{2+}} + n_{Ga(OH)_2^+} + 3n_{Al^{3+}} + 2n_{AlOH^{2+}} + n_{Al(OH)_2^+} + n_{Na^+} + n_{H^+} = n_{Ga(OH)_4^-} + n_{Al(OH)_4^-} + n_{L^-} + n_{NO_3^-} + n_{OH^-} + n_{HCO_3^-} + 2n_{CO_3^{2-}} \qquad (5.54)$$

All species in equations 5.49 to 5.54 were expressed in terms of the unknown concentrations $C_{Ga^{3+}}$, $C_{Al^{3+}}$, $C_{NO_3^-}$, C_{Na^+}, C_{L^-}, $\frac{n_{HL_{(S)}}}{V}$, $\frac{n_{NaL_{(S)}}}{V}$, $\frac{n_{GaL_3\,(s)}}{V}$, $\frac{n_{AlL_{3(S)}}}{V}$,

$\frac{n_{Ga(OH)_{3(s)}}}{V}$, $\frac{n_{Al(OH)_{3(s)}}}{V}$ and C_{OH^-} using equations 5.2 to 5.9, 5.12 to 5.16, 5.27 and 5.38 to 5.44. The final forms of the equations are:

Mass Balance Equations

Mass Balance of Ga(III)

$$C^{\circ}_{Ga} = C_{Ga^{3+}}\left(1 + \frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}} + \frac{(C_{OH^-})^3}{K_{3,Ga}} + \frac{(C_{OH^-})^4}{K_{4,Ga}}\right) + \frac{n_{Ga(OH)_{3(s)}}}{V} + \frac{n_{GaL_{3(s)}}}{V} \tag{5.55}$$

Mass Balance of Al(III)

$$C^{\circ}_{Al} = C_{Al^{3+}}\left(1 + \frac{C_{OH^-}}{K_{1,Al}} + \frac{(C_{OH^-})^2}{K_{2,Al}} + \frac{(C_{OH^-})^3}{K_{3,Al}} + \frac{(C_{OH^-})^4}{K_{4,Al}} + \frac{(C_{L^-})^3}{K_{AlL_3}}\right) + \frac{n_{Al(OH)_{3(s)}}}{V} + \frac{n_{AlL_{3(s)}}}{V} \tag{5.56}$$

Mass Balance of Nitrate

$$C^{\circ}_{NO_3} = 3 \times C^{\circ}_{Ga} + 3 \times C^{\circ}_{Al} + C^{\circ}_{HNO_3} = C_{NO_3^-} \tag{5.57}$$

Mass Balance of Sodium

$$C^{\circ}_{Na} = C_{Na^+} + \frac{n_{NaL_{(S)}}}{V} \tag{5.58}$$

Mass Balance of Ligand

$$C^{\circ}_{L} = C_{L^-} + \frac{n_{NaL_{(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}} + \frac{3 \times n_{GaL_{3(s)}}}{V} + \frac{3 \times n_{AlL_{3(s)}}}{V} + 3 \times \frac{C_{Al^{3+}}C^{3}_{L^-}}{K_{AlL_3}} \tag{5.59}$$

Charge Balance

$$\begin{aligned}
&C_{Ga^{3+}}(3+2\frac{C_{OH^-}}{K_{1,Ga}}+\frac{(C_{OH^-})^2}{K_{2,Ga}})+C_{Al^{3+}}(3+2\frac{C_{OH^-}}{K_{1,Al}}+\frac{(C_{OH^-})^2}{K_{2,Al}})+C_{Na^+}+C_{H^+}= \\
&\quad C_{Ga^{3+}}\frac{(C_{OH^-})^4}{K_{4,Ga}}+C_{Al^{3+}}\frac{(C_{OH^-})^4}{K_{4,Al}}+C_{L^-}+C_{NO_3^-} \\
&\quad +C_{OH^-}(1+\frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}}+2\frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})
\end{aligned} \tag{5.60}$$

From this general form of the model, different cases were considered:

a) Gallium or aluminum in solution with no ligand (limited condition replicating the data previously mentioned) (C°_{Ga} = 0.359 mM and C°_{Al} = 0.925 mM) (Chapter 5, equations 5.27 to 5.37).

b) Ligand alone in solution (C°_{L} = 1 mM and 2 mM) (Appendix 4, equations A4.1 to A4.4).

c) Ligand and gallium in solution (C°_{Ga} = 0.359 mM, $r^{\circ}_{L/Ga}$ = 3) (Appendix 4, equations A4.5 to A4.9).

d) Ligand and aluminum in solution (C°_{Al} = 0.925 mM, $r^{\circ}_{L/Al}$ = 3) (Appendix 4, equations A4.10 to A4.14).

e) Ligand, gallium and aluminum in solution (C°_{Ga} = 0.359 mM, C°_{Al} = 0.925 mM, r° = 3) (Chapter 5, equations 5.55 to 5.60).

The experimental values showed that the ligand was precipitating in its sodium form above a pH of 12. The equilibrium pH was varied up to 12 in all the cases, except for case (b), where the ligand was alone in solution. Thus the formation of the insoluble $NaL_{(s)}$ was not considered in cases (a), (c), (d) and (e). In the cases of the ligand and one metal in solution (c and d), the equilibrium pH range was between 0.1 up to 12. In case (e), where gallium and aluminum were in solution with the ligand, the model prediction was limited to an equilibrium pH of 5. Thus, the formation of $Ga(OH)_4^-$ and $Al(OH)_4^-$ complexes was neglected.

The solution of the model for these systems was divided into two steps:

- From the initial pH and the total concentration of ligand and metal added, the concentration of total sodium and nitrate added to the solution was calculated.
- When the desired compounds (in case a, gallium or aluminum; and in case e, ligand, gallium and aluminum) were added to the solution, different cases were considered. The cases are illustrated here only for a solution with ligand and gallium:
    1) No insoluble complexes formed and $n_{HL_{(s)}}$, $n_{GaL_{3\,(s)}}$, $n_{Ga(OH)_{3\,(s)}} = 0$.
    2) Insoluble acidic ligand complex formed; concentration of L^- is calculated from $C_{L^-} = \frac{K_{sp,HL}}{C_{H^+}}$; gallium remained in solution and $n_{GaL_{3\,(s)}}$, $n_{Ga(OH)_{3\,(s)}} = 0$.
    3) Insoluble gallium hydroxide complex formed; concentration of Ga^{3+} is calculated from $C_{Ga^{3+}} = \frac{K_{sp,Ga(OH)_3}}{(C_{OH^-})^3}$; ligand remained in solution and $n_{HL_{(s)}}$, $n_{GaL_{3\,(s)}} = 0$.
    4) Insoluble gallium-ligand complex formed; concentration of Ga^{3+} is calculated from $C_{Ga^{3+}} = \frac{K_{sp,GaL_3}}{(C_{L^-})^3}$; and $n_{HL_{(s)}}$, $n_{Ga(OH)_{3\,(s)}} = 0$.

5) Insoluble gallium-ligand and acidic ligand complexes formed; concentration of Ga^{3+} is calculated from $C_{Ga^{3+}} = \frac{K_{sp,GaL_3}}{(C_{L^-})^3}$ and that of L^- is calculated from $C_{L^-} = \frac{K_{sp,HL}}{C_{H^+}}$; and $n_{Ga(OH)_{3(s)}} = 0$.

6) Insoluble gallium hydroxide and acidic ligand complexes formed; concentration of Ga^{3+} is calculated from $C_{Ga^{3+}} = \frac{K_{sp,Ga(OH)_3}}{(C_{OH^-})^3}$ and that of L^- is calculated from $C_{L^-} = \frac{K_{sp,HL}}{C_{H^+}}$; and $n_{GaL_{3(s)}} = 0$.

7) Insoluble gallium hydroxide and gallium-ligand complexes formed; the concentration of Ga^{3+} has to satisfy $C_{Ga^{3+}} = \frac{K_{sp,Ga(OH)_3}}{(C_{OH^-})^3}$ and $C_{Ga^{3+}} = \frac{K_{sp,GaL_3}}{(C_{L^-})^3}$; and $n_{HL_{(S)}} = 0$.

The formation of insoluble gallium hydroxide, gallium-ligand and acidic ligand complexes, all of them forming at the same time, was not considered. Such a case can be observed by adding an excess of ligand to the solution.

5.5.2.1 Effect of pH on solubility of the ligand

In this system, the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$) and the total number of moles of ligand added C°_{L} were known. The unknowns were $C_{NO_3^-}$, C_{Na^+}, C_{L^-}, C_{OH^-}, $\frac{n_{HL_{(S)}}}{V}$ and $\frac{n_{NaL_{(S)}}}{V}$. Different conditions were then considered. Based on the different forms of the ligand found in an aqueous solution without any metals the following hypotheses were used for the equations 5.38 to 5.40:

- $C_L^\circ \times C_{Na}^\circ > K_{sp,NaL}$ and $C_L^\circ \times C_{H^+}^\circ > K_{sp,HL}$ then the ligand precipitated both in its acidic form and in its sodium form (eq. 5.38, 5.39 and 5.40 considered).
- $C_L^\circ \times C_{Na}^\circ \leq K_{sp,NaL}$ and $C_L^\circ \times C_{H^+}^\circ > K_{sp,HL}$ then the ligand precipitated in its acidic form (eq. 5.38 and 5.39 considered).
- $C_L^\circ \times C_{Na}^\circ > K_{sp,NaL}$ and $C_L^\circ \times C_{H^+}^\circ \leq K_{sp,HL}$ then the ligand precipitated in its sodium form (eq. 5.38 and 5.40 considered).
- $C_L^\circ \times C_{Na}^\circ \leq K_{sp,NaL}$ and $C_L^\circ \times C_{H^+}^\circ \leq K_{sp,HL}$ then the ligand did not precipitate and only equation 5.38 was considered.

Depending on which condition was satisfied, the corresponding set of equations was used. The equilibrium pH and the different concentrations of the ligand were calculated based on the adjusted constants defined in equations 5.38, 5.39 and 5.40. The results are shown in Figure 5.9. At low pH, the ligand is mainly removed in its insoluble acidic form. The small loss of ligand was due to the formation of its soluble acidic form as described by equation 5.38. At higher pH, the ligand remained in solution at its natural pH. The ligand is removed in its sodium form at pH above 12 due to the excess of sodium from the sodium hydroxide. Also shown on the graph is the effect of the concentration of ligand on the percent loss.

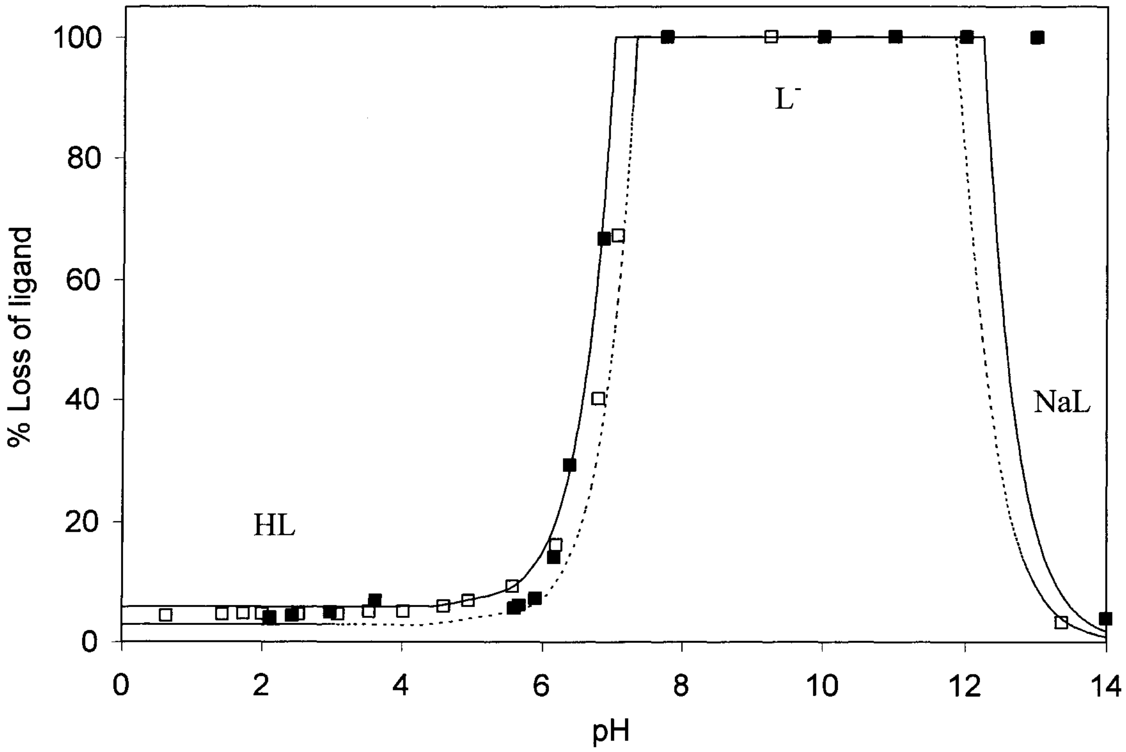


Figure 5.9: Comparison between the computed and the experimental values of the percent loss of sodium di-(n-octyl) phosphinate for two concentrations of the ligand [C_L° = 1 mM (■) and 2 mM (□); model: line C_L° = 1 mM, dashed line C_L° = 2 mM].

The model showed a slight shift as the ligand concentration increased from 1 mM to 2 mM. For example, a 20 % loss of ligand was observed at a pH around 6.2 for a ligand concentration of 1 mM and at a pH around 6.6 for a ligand concentration of 2 mM. The experimental values agreed with the computed values indicating the differences in the percent loss of ligand as the concentration increased from 1 to 2 mM was only marginal. The difference between the computed and experimental value at pH 13 is due to the slow formation of the sodium form of the ligand. Longer time should be required to reach equilibrium. It should be noted that the CO_2 from the air dissolved in the aqueous solution did not affect the calculated removal. While the dissolution of the CO_2 decreased the pH of the solution, the loss of the ligand remained the same for the same value of equilibrium pH with or without CO_2.

5.5.2.2 Removal of gallium by the ligand

In the case of the gallium alone in solution with the ligand, the aluminum parameters were nil and equations A4.5 to A4.9 from Appendix 4 were used. The total amount of gallium and ligand, the total volume and the initial pH were defined. The value of the solubility product of the gallium-ligand complex was adjusted. Figure 5.10 shows the comparison between the experimental data and the model based on the values of the constants from equation 5.38 to 5.40 for the ligand, 5.2 to 5.4 for CO_2 and 5.5 to 5.9 and 5.42 for gallium. The ligand was initially removed in its acidic form below a pH of 1. When the gallium formed a complex with the ligand, the removal of the ligand from the solution increased as the soluble ligand was removed either with gallium or in its acidic form. Between pH around 7 and 8, the model showed that the gallium is mostly removed in its hydroxide form while the ligand remains in solution.

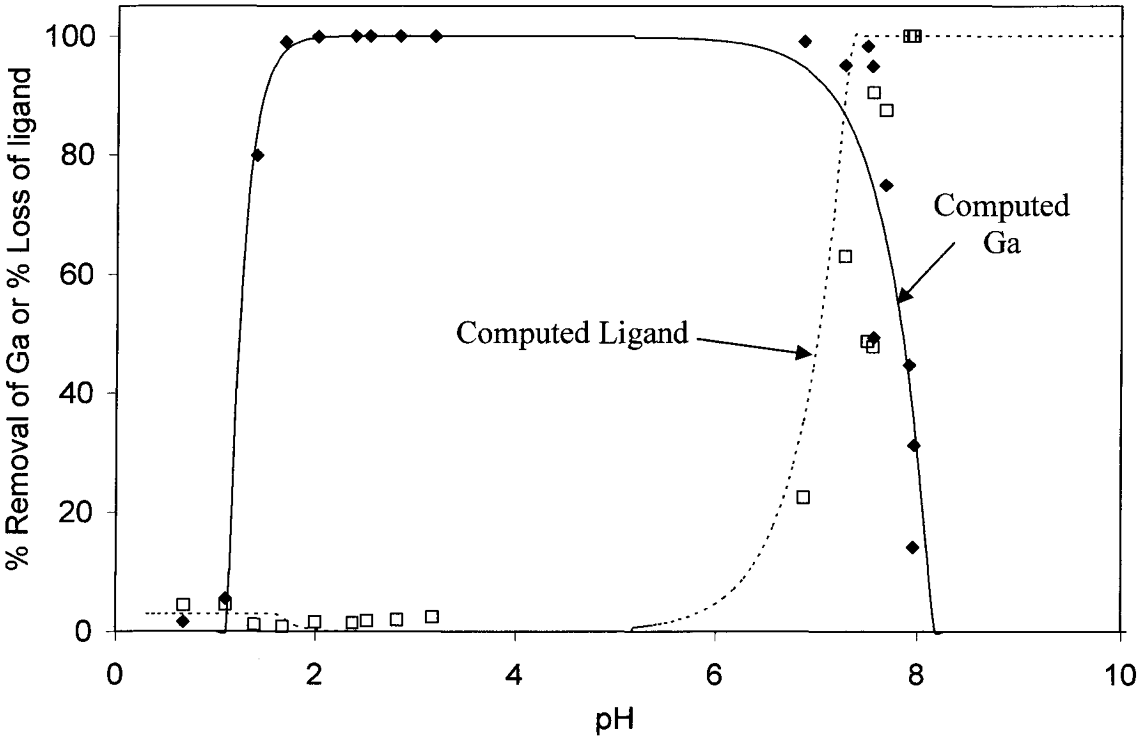


Figure 5.10: Comparison between the computed and the experimental values for the effect of the pH on the percent removal of gallium (◆); and percent loss of sodium di-(n-octyl) phosphinate (□) [$C^{\circ}_{Ga} = 0.359$ mM, $r^{\circ}_{L/Ga} = 3$; experimental values after 2 days].

5.5.2.3 Removal of aluminum by the ligand

In the case of the aluminum alone in solution with the ligand, the gallium parameters were nil and equations A4.10 to A4.14 from Appendix 4 were used. The total amount of aluminum, the total volume and the initial pH were defined. The value of the acidity constant and the value of the solubility product of the aluminum-ligand complex were adjusted. Figure 5.11 shows the comparison between the experimental data and the computations based on the values of the constants from equation 5.38 to 5.40 in the case of the ligand alone and 5.43 and 5.44 for the aluminum ligand complex. At pH < 2, the experimental data showed that some aluminum was removed from the solution, while the model indicated a removal of the aluminum only above a pH of 2. The discrepancy between the computed and the experimental values is believed to be due to the fact that some ligand was removed with the aluminum in this acidic condition. When the ligand is introduced to the metal solution, some metal could be exposed to a concentrated ligand solution until the homogeneous mixing is established. Since the formation of aluminum-ligand complex is instantaneous, a fraction of the Al was removed as metal-ligand complex. The remaining ligand was removed as HL complex. Between a pH around 2 and 10, the model indicated that the ligand was removed from the aqueous solution by forming a complex with the aluminum. As the pH increased, the aluminum can precipitate in its hydroxide form as predicted by the computed values in Figure 5.4 between a pH around 4 to 11. While the model indicated nearly total removal of the aluminum with the ligand between a pH of 4 to 9 and a removal of about 90 % $Al(OH)_{3(s)}$ at pH 10, the data showed a sharp decrease in the removal efficiency of the aluminum between pH 9 and 9.5.

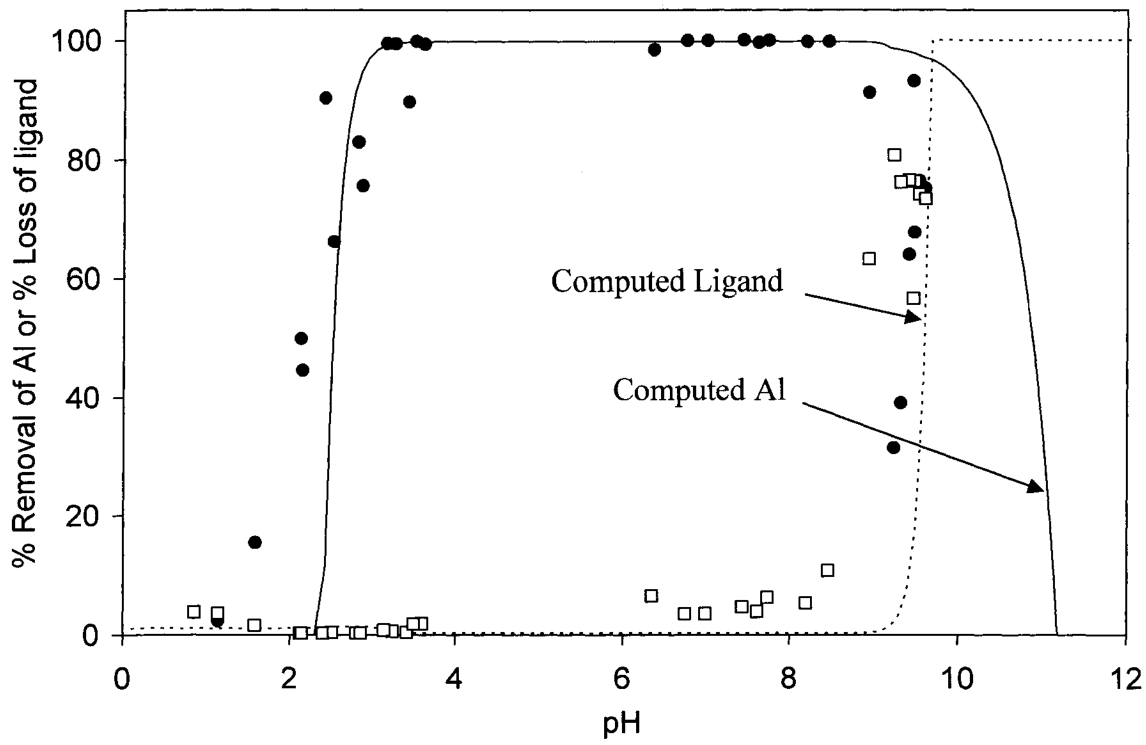


Figure 5.11: Comparison between the computed and the experimental values for the effect of pH on the percent removal of aluminum (●); and percent loss of sodium di-(n-octyl) phosphinate (□) [$C^{\circ}_{Al} = 0.925$ mM, $r^{\circ}_{L/Al} = 3$; experimental values after 1 day].

As explained previously, the experimental data were not at equilibrium after 1 day. Longer contact time and seeding are generally necessary (Baes and Mesmer, 1986).

To show the effect of the contact time on the experimental removal values obtained in basic solutions, a solution of ligand and aluminum was mixed at different pH during 6 days. The results are presented in Figure 5.12. By increasing the contact time, the aluminum removal agreed more closely with the computed values.

5.5.2.4 Removal of indium by the ligand

The same procedure used for gallium and aluminum was followed for the removal of indium with the sodium di-(n-octyl) phosphinate. Indium (0.22 mM) was mixed with the ligand at two mole ratios of ligand to indium: 1 and 3. Based on the experimental data in Section 3.3.2 in Chapter 3, the pH range was limited to pH up to 5. Since the pH studied was less than 12, the NaL complex was neglected. The inputs are V, C°_{In}, $n^{\circ}_{NaL_{(s)}}$ and the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$). The mass and charge balance equations used are shown in the Appendix 4, Table 4.4. In addition to the constants from the hydrolysis of indium (equation 5.17 to 5.21) and the constants from the acidic form of the ligand (equation 5.38 and 5.39), two indium-ligand complexes (1 soluble and 1 insoluble complex) were considered (equation 5.45 and 5.46).

The removal of indium by the sodium di-(n-octyl) phosphinate at a ratio of ligand to indium of 1 is shown in Figure 5.13. The model prediction can be divided into sections depending of the final pH of the solution:

1. For pH below 0.3, the ligand is removed from the aqueous solution in its acidic form, the indium remains in solution in its ionic In^{3+} form.

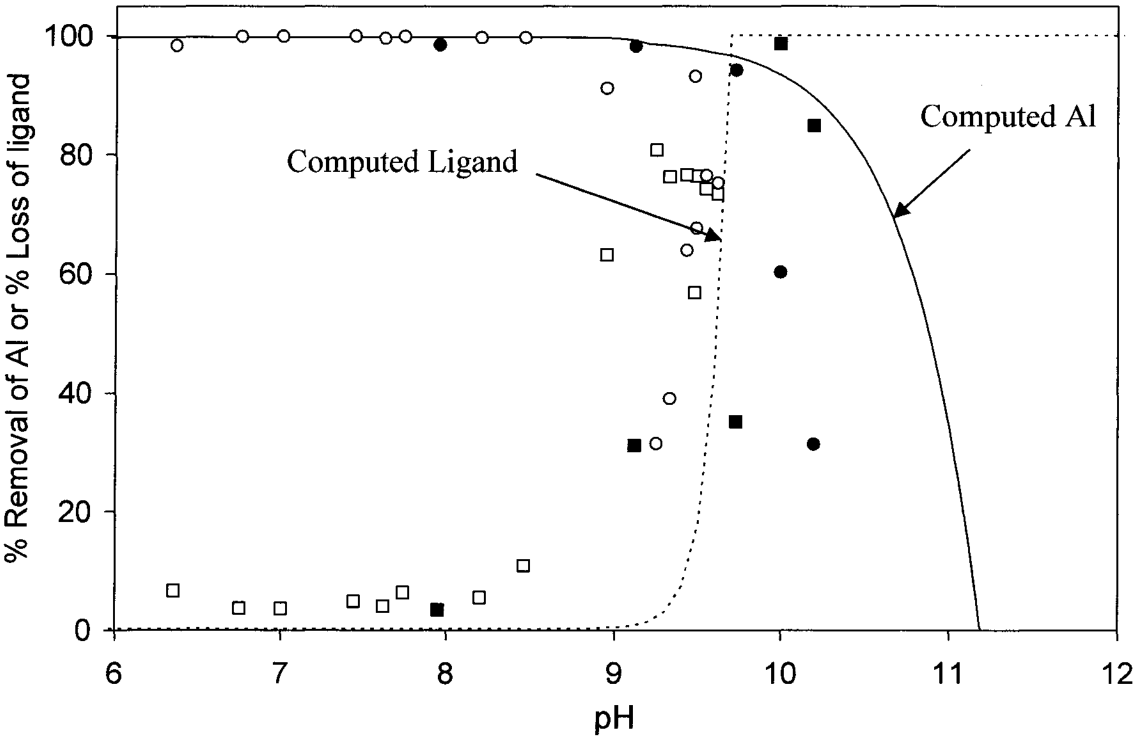


Figure 5.12: Comparison between the computed and the experimental values for the effect of pH on the percent removal of aluminum (●, ○); and percent loss of sodium di-(n-octyl) phosphinate (■, □) at two different times [$C^{\circ}_{Al} = 0.925$ mM, $r^{\circ}_{L/Al} = 3$; experimental values after 1 day (○, □), 6 days (●, ■)].

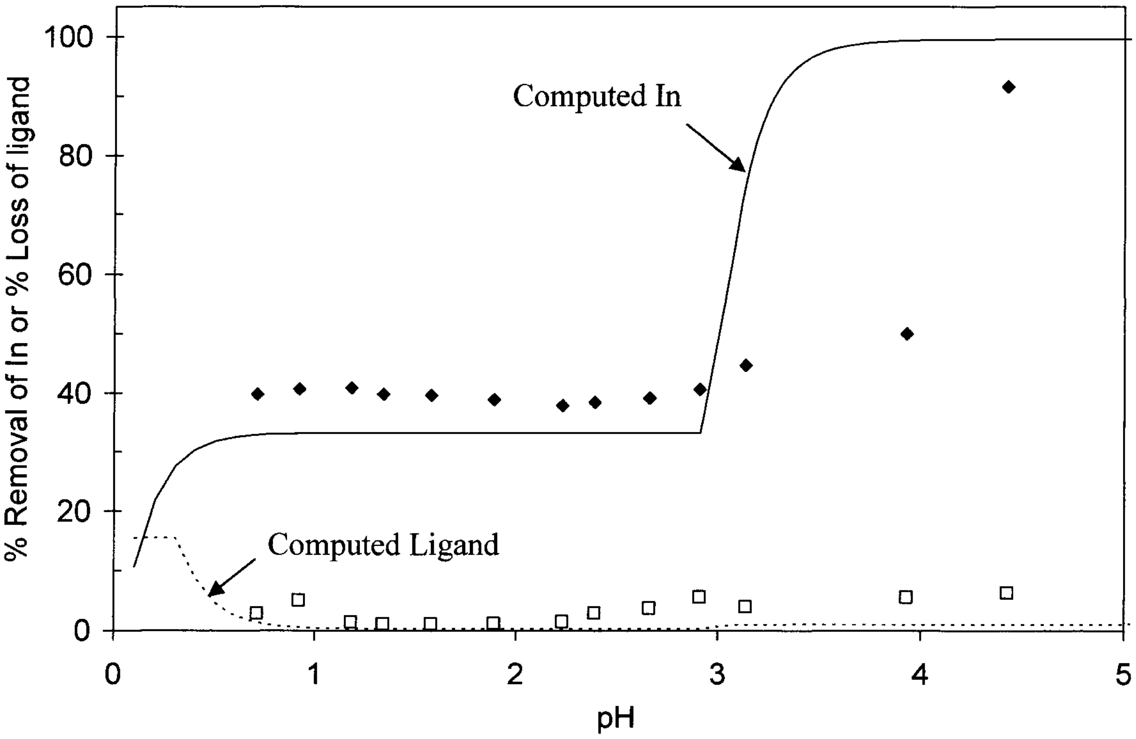


Figure 5.13: Comparison between the computed and the experimental values for the effect of pH on the percent removal of indium (◆); and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{In} = 0.22 mM, $r^{\circ}_{L/In}$ = 1; experimental values after 1 day (◆,□)].

2. For pH between 0.3 and about 2.9, indium is removed by the ligand following equation 5.46. Since the mole ratio of ligand to indium is 1, 33 % of indium was removed. The amount of soluble indium-ligand complex remaining in solution is negligible.
3. Above pH 2.9, indium is removed both in its insoluble ligand indium form (equation 5.46) and in its hydroxide form (5.21). The percent removal of indium increases to complete removal as more indium trihydroxide precipitated. Again the amount of soluble indium-ligand complex remaining in solution is negligible.

Above pH 2.9, while 33 % of the indium is removed with the ligand, the indium in excess is removed in its hydroxide form. Due to the small amount of indium in excess, longer contact time is required to form the insoluble $In(OH)_3$. This explains the discrepancy between the experimental and the predicted values.

As shown in Figure 5.14, by increasing the ratio of ligand to indium to 3, all the indium is removed from the solution by the ligand. A good agreement between the experimental data and the computed values is obtained.

5.5.2.5 Removal of iron by the ligand

The same procedure used for gallium and aluminum was followed for the removal of iron with the sodium di-(n-octyl) phosphinate. Iron (0.36 mM) was mixed with the ligand at a ratio of 3 and the pH range was limited to pH up to 5. Since the pH studied was less than 12, the NaL complex was neglected. The inputs are V, C°_{Fe}, $n^{\circ}_{NaL_{(s)}}$ and the initial pH (C°_{NaOH} or $C^{\circ}_{HNO_3}$). The mass and charge balance equations used are shown in the Appendix 4, Table 4.5.

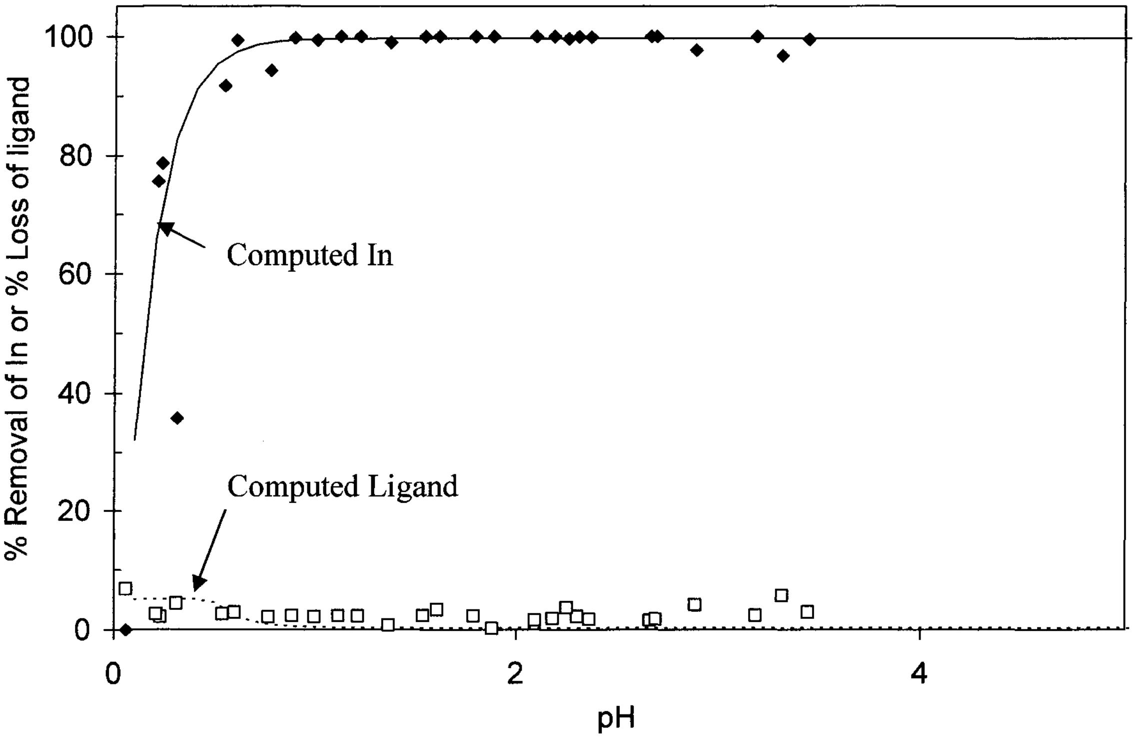


Figure 5.14: Comparison between the computed and the experimental values for the effect of pH on the percent removal of indium (◆); and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{In} = 0.22 mM, $r^{\circ}_{L/In}$ = 3; experimental values after 1 day (◆,□)].

In addition to the constants from the hydrolysis of iron (equation 5.22 to 5.26) and the constants from the acidic form of the ligand (equation 5.38 and 5.39), two iron-ligand complexes (1 soluble and 1 insoluble complex) were considered (equation 5.47 and 5.48). The removal of iron by the sodium di-(n-octyl) phosphinate at a ratio of ligand to iron of 3 is shown in Figure 5.15. The experimental data and the computed values were in good agreement in the pH range considered.

5.5.2.6 Removal of gallium and aluminum mixture by the ligand

Gallium (0.359 mM) and aluminum (0.925 mM) were mixed with the sodium di-(n-octyl) phosphinate at a mole ratio of ligand to total metals of 3. Due to the formation of hydroxide-metal complex in basic conditions making the use of the ligand unnecessary, only the acidic condition was considered. Equations 5.55 to 5.60 were used to model the system using the acidity constants and the solubility products of the metal-ligand complex (equations 5.41 to 5.44) and of the acidic form of the ligand (equations 5.38 and 5.39). As observed in Figure 5.16, the computed values showed the selectivity of the ligand to gallium over aluminum. Discrepancy between the computed and the experimental values was also observed for the gallium aluminum mixture in acidic pH. For the same reasons as for the aluminum solution, it is believed that while the ligand mainly formed the HL complex, a fraction was removed with the metal as ML_3.

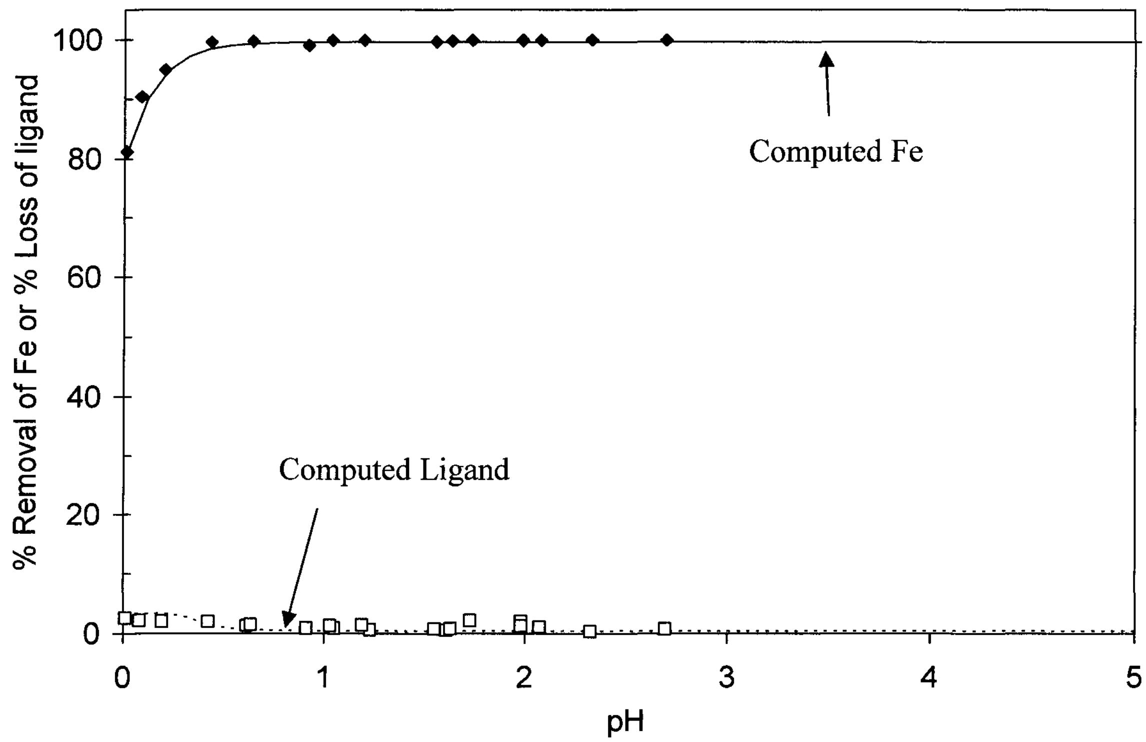


Figure 5.15: Comparison between the computed and the experimental values for the effect of pH on the percent removal of iron (◆); and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{Fe} = 0.36 mM, $r^{\circ}_{L/Fe}$ = 3; experimental values after 1 day (◆,□)].

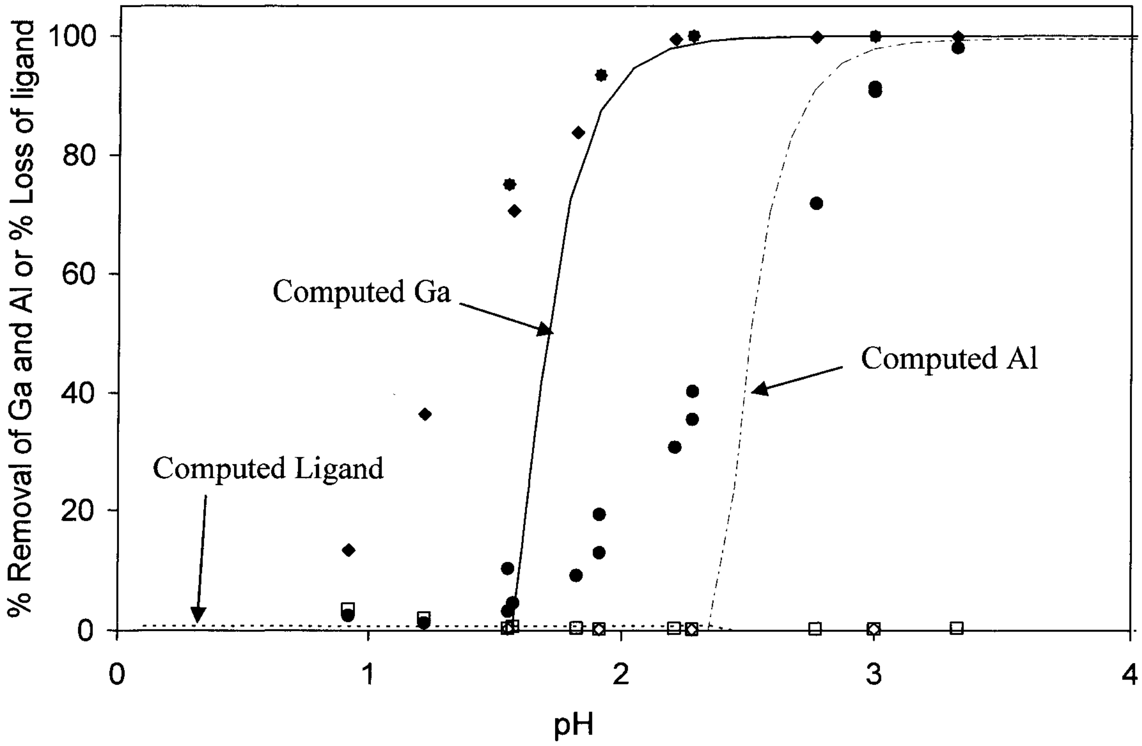


Figure 5.16: Comparison between the computed and the experimental values for the effect of pH on the percent removal of gallium (◆); percent removal of aluminum (●); and percent loss of sodium di-(n-octyl) phosphinate (□) [C°_{Ga} = 0.359 mM, C°_{Al} = 0.925 mM, r° = 3; experimental values after 1 day].

CHAPTER 6

CONCLUSIONS, CONTRIBUTIONS AND RECOMMENDATIONS

6.1 Conclusions

Four different organophosphorus ligands, sodium di-(n-octyl) phosphinate, sodium di-(n-dodecyl) phosphinate, sodium mono-octyl ester phosphinate and O,O-di-(octyl) dithiophosphoric acid were synthesized and used to remove gallium. Only the sodium di-(n-octyl) phosphinate showed good removal efficiency for gallium.

Gallium was removed from aqueous solution using sodium di-(n-octyl) phosphinate at an optimum ratio $r^{\circ}_{L/Ga} = 3$. Less di-(n-octyl) phosphinate ligand was used to remove the gallium when hydroxide complexes were formed. At higher temperature, a better removal of the metal was obtained. The initial concentration of gallium in solution and the removal time were related. The higher the initial concentration, the faster the metal was removed.

From the insoluble metal-ligand complex, the ligand was extracted in an organic phase and regenerated while the metal was concentrated in an aqueous phase. Chloroform and diethyl ether showed a good separation of the two compounds. Furthermore, while the metals and the ligand were generally separated in a caustic solution, it was shown that acidic conditions can be used to recover the metal.

Carboxylic groups, humic and fumaric acids, inhibited the removal of gallium by the sodium di-(n-octyl) phosphinate.

The removal of gallium was inhibited in chloride and sulfate solutions while only the sulfate solution inhibited the removal of aluminum.

A good selectivity of sodium di-(n-octyl) phosphinate for gallium was obtained over metals such as zinc, aluminum, calcium, iron and indium. The main parameters that defined the affinity of the ligand for the metals were explained by:

- the hard and soft theory (the hard ligand reacts with the hard metals)
- the charge of the metal (higher charges have a better affinity)
- the ionic radius (higher is the radius, better the affinity)
- the structure of the complex
- the electronegativity of the metals (including the influence of the orbital)

A process was proposed to treat GaAs effluents from the electronics industry. Gallium and indium were removed by complexation with sodium di-(n-octyl) phosphinate while the arsenic was precipitated with ferric ions. The excess ligand in solution was removed and recovered from the solution either in its acidic form or by complexation with the ferric ions.

A mathematical model based on stability constants was developed to describe the removal of the metals and of sodium di-(n-octyl) phosphinate ligand from an aqueous solution. Based on the initial concentration of the different compounds and the initial pH of the solution, the equilibrium pH and the final concentrations of the compounds were predicted. The effect of the hydrolysis of the metals was also considered.

6.2 Contributions to knowledge

1. Gallium was removed from aqueous solution as an insoluble complex with sodium di-(n-octyl) phosphinate but not as efficiently with sodium di-(n-dodecyl) phosphinate, sodium mono-octyl ester phosphinate or O,O-di-(octyl) dithiophosphoric acid.

2. The removal of gallium and ligand was determined as a function of pH. The gallium was removed in the pH range where insoluble gallium-hydroxide complexes form. The metal hydroxide enhanced the process as less sodium di-(n-octyl) phosphinate ligand was necessary to remove the metal.
3. The removal of gallium using humic and fumaric acids was demonstrated. Both acids removed gallium in a pH range close to the formation of the $Ga(OH)_{3(s)}$. In the case of humic acid, higher concentration of this compound decreased the removal of gallium. The removal of the metal using sodium di-(n-octyl) phosphinate was also inhibited by the humic acid.
4. Aluminum, indium, iron and calcium were removed from aqueous solution as insoluble complexes with sodium di-(n-octyl) phosphinate.
5. The removal of metals using sodium di-(n-octyl) phosphinate was achieved at higher temperature, decreasing the residual metal concentration. Chloride and sulfate ions inhibited the removal of metals with sodium di-(n-octyl) phosphinate.

6.3 Recommendations for future work

1. Test removal and recovery of gallium from GaAs effluents, such as the one of M/A-COM Advanced Materials, using the procedure described in Figure 4.13. Investigate the removal of impurities such as indium and the co-precipitation of metals to obtain a better selectivity.
2. Perform an economical analysis on the effluent of M/A-COM Advanced Materials comparing the extraction process with the sodium di-(n-octyl) phosphinate removal process.
3. Test the process for other industrial application, for example the separation of Co and Ni in the mining industry.

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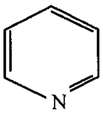
APPENDIX 1

KARL FISCHER TITRATOR

The Karl Fischer titrator calculates the mass percent of water in an organic phase. A known mass of dried ligand is dissolved in an organic solvent. The solution is then injected to the reaction vessel through the injection port. As Karl-Fischer solvent (Hydranal Composite 5) is added, the water contained in the ligand sample is consumed as shown below:

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightarrow [RNH]SO_4CH_3 + 2\,[RNH]I \qquad \text{(A1.1)}$$

Where **RN**: Pyridine



An electrode placed in the reaction vessel monitors the conductivity of the solution. By using a calibration curve, the water uptake number, w_o, can be calculated by the concentration ratio of water to the ligand written as:

$$w_o = \frac{[Water]}{[Ligand]} = \frac{\dfrac{\rho \times \dfrac{wt\%_{KF}}{100}}{MW_{water}}}{[Ligand]} \qquad \text{(A1.2)}$$

where ρ is defined as the density of the ligand (g/L), and $wt\%_{KF}$ is defined as the weight percent of water in organic phase which was obtained from the Karl Fischer titrator.

APPENDIX 2

EFFECT OF MIXING

The effect of mixing on the time to approach the equilibrium was also investigated using two procedures. The ligand solution was added rapidly to the metal solutions. This was followed by:

1) stirring at high speed for 10 minutes

or

2) slow mixing of 10 seconds followed by 10 minutes without stirring.

After 10 minutes, both solutions were stirred slowly for 24 hours. As observed in Table A2.1, after 10 minutes, the no stirring procedure removed more gallium. After 24 hours, the same removal was obtained using either procedure as equilibrium was approached. It should be noted that while the removal of the gallium increased after 24 hours, most of the ligand was removed from the aqueous solution after 10 minutes. The ligand that did not complex with the metal was removed from the solution by forming the insoluble di-(n-octyl) phosphinic acid, $HL_{(s)}$.

Table A2.1: Effect of stirring on the equilibrium time.

First 10 minutes	% Removal of Ga after		% Removal of di-(n-octyl) phosphinate after	
	10 minutes	24 hours	10 minutes	24 hours
1) Rapid stirring	88.1	99.1	99.5	99.8
2) No stirring	94.7	99.5	99.6	99.6

APPENDIX 3

DEFINITION OF INITIAL pH

The purpose of this appendix is to show:

- That the pH of the metal solution depends upon the rate of formation of metal hydroxide complexes.
- The effect of the distilled water from the ligand stock solution on the initial pH of the metal solution.

A3.1 Notation

The notation of Chapter 2 is used in this appendix. To obtain different values of $r^{\circ}_{L/Ga}$ or $r^{\circ}_{L/Al}$, different volumes V_L of di-(n-octyl) phosphinate ligand stock solution were added to a volume V_i of the metal solution to give a total volume V°. The percentage of V° coming from the ligand stock solution was a linear function of $r^{\circ}_{L/Ga}$ or $r^{\circ}_{L/Al}$:

$$\frac{V_L}{V^\circ} \times 100 = b\, r^{\circ}_{L/M} \qquad \text{(A3.1)}$$

where M represents either Ga or Al and b is a constant.

To study the relation between the measured pH and calculated values of pH, a gallium solution was prepared by mixing the metal stock solution with distilled water and an acid or a base, depending on the pH desired. The volume of the gallium solution is designated by V_i and the pH measured immediately after mixing the 3 solutions (metal stock solution + distilled water + HNO_3 or NaOH) is called the initial pH, and denoted by pH_i. While the gallium in the metal stock solution was stabilized as Ga^{3+} at pH below 1 with 2 wt % of nitric acid, the dilution of the metal stock solution with distilled water and the addition of an acid or a base changed the proportion of hydroxide complexes formed by the metal. Due to the formation of these metal hydroxides, it was anticipated that the value of the measured pH could vary with time. Thus, the pH values of the solution measured after 1 day and after 5 days are denoted by pH_1 and pH_5, respectively. The calculated pH of the metal solution (metal stock solution+ distilled water + acid or base), assuming that the metal is in its ionic form (i.e. Ga^{3+}) without complex formation, is denoted by pH_A. The calculated pH value of the metal solution (metal stock solution+ distilled water + acid or base) obtained by allowing the metal to form hydroxide complexes at equilibrium is denoted as the equilibrium pH. Each value of pH_A is associated with a value of the equilibrium pH.

Finally, following the notation of Chapter 2, when no ligand solution was added to the metal solution, $V_i = V°$ and $pH_A = pH°$. This case occurred when studying the formation of insoluble metal hydroxide without addition of ligand.

A3.2 Effect of the hydrolysis on the initial pH of the metal solution

Figure A3.1 shows an example of the precipitation of gallium as $Ga(OH)_{3(s)}$ as a function of pH without the addition of ligand. The percent precipitation of gallium after 1 day is plotted against the pH measured after 1 day, pH_1. Also shown is the value of pH_i (pH measured immediately after mixing). The values of pH_i and pH_1 were essentially equal up to pH 4 and above pH 8. Between pH_i = 4 and 8, the metal formed insoluble hydroxide complexes and pH_i was less than from pH_1.

A model was developed to determine the range of pH at which the hydroxide complex formation has an effect on the measured pH. A volume V_{ms} of metal in solution was mixed with a volume V_a of acid solution or a volume V_b of base solution. When

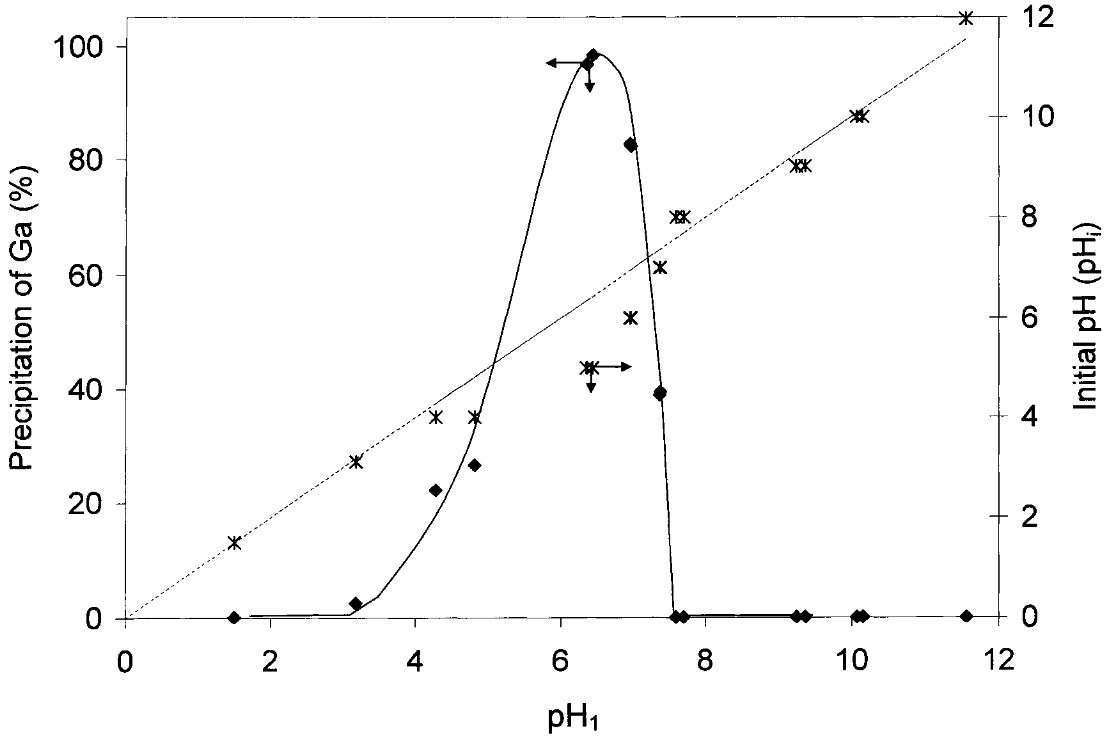


Figure A3.1: Precipitation of gallium (◆) in aqueous solution as a function of pH$_1$ [C°_{Ga} = 0.359 mM; V° = 20 mL]. Values of pH$_i$ (*) are presented on the right ordinate. Dashed line: pH$_i$ = pH$_1$. No ligand was added.

mixing the metal stock solution with distilled water, the symbol V_a is also used for the volume of the distilled water as its pH is below 7. Two cases were studied:

- The metal ions in solution did not form complexes.
- The metal formed hydroxide complexes at equilibrium.

Calculations were made for:

- Mixing of two acidic solutions:
  - The acidic metal solution $(H^+ NO_3^-)_{ms}$: V_{ms}, pH_{ms}, C°_{Ga}
  - A nitric acidic solution $(H^+ NO_3^-)_a$: V_a, $pH_a \leq 7$
- Mixing of an acidic and a basic solution:
  - The acidic metal solution $(H^+ NO_3^-)_{ms}$: V_{ms}, pH_{ms}, C°_{Ga}
  - A sodium hydroxide solution $(Na^+ OH^-)_b$: V_b, $pH_b > 7$

Assuming that no hydroxide complexes form and ignoring the difference between activity and concentration of ions, the equations for mixing two acidic solutions are:

$$K_w = C_{H^+} C_{OH^-} \tag{A3.2}$$

$$C_{H^+_{ms}} = 10^{-pH_{ms}} \tag{A3.3}$$

$$C_{H^+_a} = 10^{-pH_a} = C_{(NO_3^-)_a} \tag{A3.4}$$

Mass balance of Ga

$$C^{\circ}_{Ga} = \frac{V_{ms}}{(V_{ms} + V_a)} \times C_{Ga^{3+}} \tag{A3.5}$$

Mass balance of (NO_3^-)

$$\begin{aligned} C^\circ_{NO_3^-} &= \frac{V_{ms}}{(V_{ms}+V_a)} \times C_{(NO_3^-)_{ms}} + \frac{V_a}{(V_{ms}+V_a)} \times C_{(NO_3^-)_a} \\ &= \frac{V_{ms}}{(V_{ms}+V_a)} \times (10^{-pH_{ms}} + 3 \times C^\circ_{Ga}) + \frac{V_a}{(V_{ms}+V_a)} \times 10^{-pH_a} \end{aligned} \tag{A3.6}$$

Charge balance

$$C_{OH^-} + C^\circ_{NO_3^-} = C_{H^+} + 3 \times C^\circ_{Ga} \tag{A3.7}$$

Replacing eq A3.2, A3.5 and A3.6 in eq A3.7, the following equation is obtained:

$$C^2_{H^+} - \left(\frac{V_{ms}}{(V_{ms}+V_a)} \times 10^{-pH_{ms}} + \frac{V_a}{(V_{ms}+V_a)} \times 10^{-pH_a}\right) C_{H^+} - K_w = 0 \tag{A3.8}$$

The quadratic Eq A3.8 was solved for H^+ and the pH was determined from:

$$pH_A = -\log(C_{H^+}) \tag{A3.9}$$

Assuming that no hydroxide complexes form, the equations for an acidic solution mixed with a basic solution are:

$$C_{H^+_{ms}} = 10^{-pH_{ms}} \tag{A3.10}$$

$$C_{Na^+_b} = K_w 10^{pH_b} = C_{OH^-_b} \tag{A3.11}$$

Mass balance of Ga

$$C^\circ_{Ga} = \frac{V_{ms}}{(V_{ms}+V_a)} \times C_{Ga^{3+}} \tag{A3.12}$$

Mass balance of (NO_3^-)

$$C^\circ_{NO_3^-} = \frac{V_{ms}}{(V_{ms}+V_b)} \times C_{(NO_3^-)_{ms}} = \frac{V_{ms}}{(V_{ms}+V_b)} \times (10^{-pH_{ms}} + 3 \times C^\circ_{Ga}) \tag{A3.13}$$

Mass balance of (Na^+)

$$C^{\circ}_{Na^+} = \frac{V_b}{(V_{ms}+V_b)} \times C_{(Na^+)_b} = \frac{V_b}{(V_{ms}+V_b)} \times K_w 10^{pH_b} \tag{A3.14}$$

Charge balance

$$C_{OH^-} + C^{\circ}_{NO_3^-} = C_{H^+} + C^{\circ}_{Na^+} + 3 \times C^{\circ}_{Ga} \tag{A3.15}$$

Replacing eq A3.2, A3.12, A3.13 and A3.14 in eq A3.15, the quadratic equation for the mixing of an acid and a base solution was:

$$C^2_{H^+} + (\frac{V_b}{(V_{ms}+V_b)} \times K_w \times 10^{pH_b} - \frac{V_{ms}}{(V_{ms}+V_b)} \times 10^{-pH_{ms}})C_{H^+} - K_w = 0 \tag{A3.16}$$

and pH_A was computed from eq. A3.9.

The calculations for the compositions of the equilibrium solutions (i.e. allowing the formation of hydroxide complexes) used the model developed in Chapter 5 (section 4) for the hydrolysis of metal with the effect of carbon dioxide neglected. For each volume of acid (V_a) or base (V_b) added to the solution (V_{ms}= metal stock solution + distilled water), an equilibrium pH was computed. Thus, each value of pH_A had a corresponding equilibrium pH.

The relationship between the computed values of pH_A and equilibrium pH is shown in Figure A3.2 as the solid line. The dashed line represents pH = pH_A. Measured values of the pH are shown as filled symbols for the pH measured immediately after mixing, denoted pH_i, and by open symbols for the pH measured 5 days after mixing, pH_5. As observed in Figure A3.2 and in Table A3.1, the measured values of pH_i were generally close to the calculated equilibrium pH, indicating that the formation of the hydroxide complexes was fast. Four zones were defined for the calculated values of the equilibrium pH reported in Table 3.1 and compared to the speciation diagram of gallium

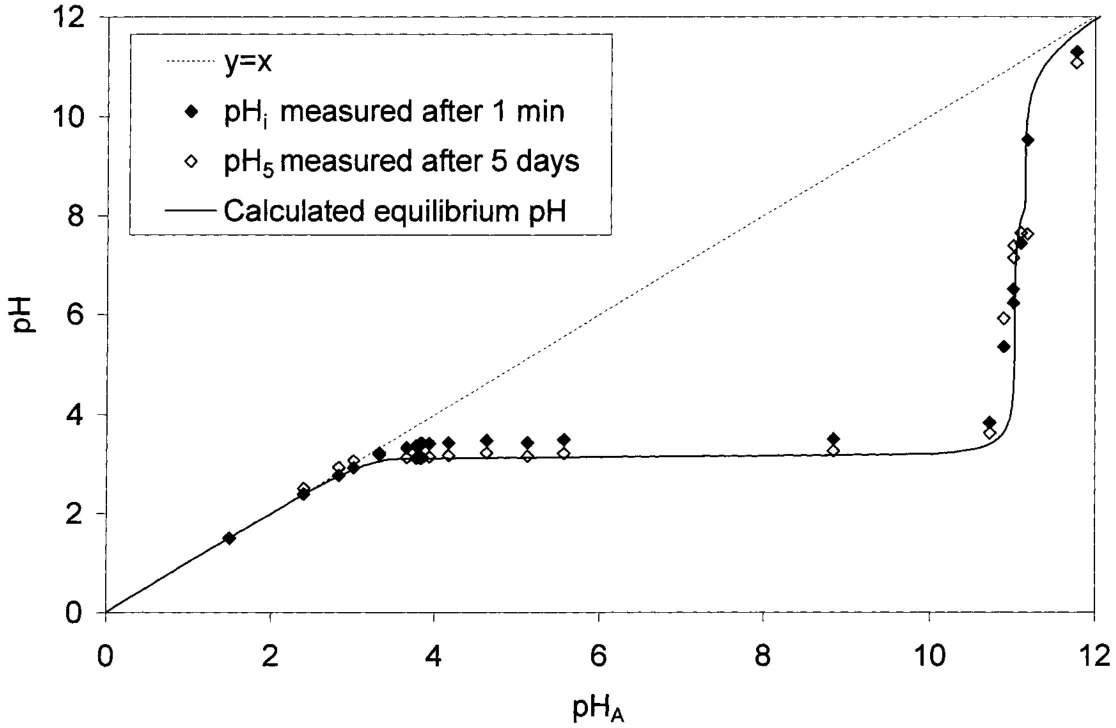


Figure A3.2: Comparison between experimental and calculated pH based on the amount of acid or base added to a gallium solution $[C^{\circ}_{Ga} = 0.359 \text{ mM}; V^{\circ} = 20 \text{ mL}]$. pH$_A$ is the value of pH calculated ignoring the formation of hydroxy-complexes.

Table A3.1: Calculated and associated experimental values of the pH for fixed volumes of NaOH [V° = 20 mL and C°_{Ga} = 0.359 mM]. Numbers in bold indicate replicate experiments (new solutions and new calibrations). The zones correspond to the areas defined in Figure A3.3.

Zone	mL of NaOH (0.1N)	Calculated pH		Measured pH		
		pH_A	Equilibrium pH	pH_i	pH 1 day	pH 5 days
1	0	2.40	2.39	2.39	2.48	2.50
	0	**2.40**	**2.39**	**2.52**	**2.61**	**2.41**
	0.5	2.83	2.76	2.77	2.91	2.93
	0.6	3.02	2.89	2.93	3.05	3.07
	0.7	3.33	3.06	3.19	3.23	3.23
2	0.75	3.66	3.17	3.33	3.24	3.13
	0.76	3.77	3.20	3.37	3.24	3.12
	0.762	3.80	3.20	3.36	3.25	3.14
	0.763	3.82	3.21	3.37	3.25	3.15
	0.764	3.83	3.21	3.42	3.24	3.12
	0.765	3.85	3.21	3.42	3.25	3.13
	0.77	3.93	3.23	3.42	3.26	3.14
	0.78	4.17	3.25	3.43	3.25	3.18
	0.789	4.63	3.28	3.48	3.32	3.23
	0.792	5.13	3.29	3.43	3.29	3.16
	0.793	5.57	3.29	3.49	3.36	3.22
	0.795	8.85	3.30	3.51	3.37	3.27
	0.9	10.73	3.40	3.83	3.77	3.62
	0.9	**10.73**	**3.40**	**3.91**	**3.81**	**3.65**
	0.9	**10.73**	**3.40**	**3.91**	**3.84**	**3.59**
3	0.95	10.89	3.63	5.35	5.80	5.91
	0.95	**10.89**	**3.63**	**4.91**	**4.99**	**4.69**
	0.95	**10.89**	**3.63**	**4.80**	**5.00**	**4.63**
	1	11.01	4.42	6.22	7.35	7.13
	1	11.01	4.42	6.49	7.36	7.38
	1	**11.01**	**4.42**	**6.30**	**6.79**	**6.94**
	1.05	11.11	7.91	7.43	7.82	7.64
	1.05	**11.11**	**7.91**	**6.79**	**7.34**	**7.63**
	1.05	**11.11**	**7.91**	**6.84**	**7.62**	**7.76**
	1.1	**11.19**	**10.00**	**7.28**	**7.73**	**8.08**
	1.1	**11.19**	**10.00**	**7.25**	**7.85**	**8.09**
4	1.1	11.19	10.00	9.52	8.80	7.62
	2	11.78	11.66	11.29	11.07	11.07

shown in Figure A3.3. The zones were:

- Zone 1 for calculated equilibrium pH up to around 3. The pH measured generally increased with time ($pH_i < pH_l < pH_5$).
- Zone 2 for calculated equilibrium pH between 3 and around 3.4. The pH measured generally decreased with time ($pH_i > pH_l > pH_5$).
- Zone 3 for calculated equilibrium pH between 3.4 and around 8. The pH measured generally decreased with time ($pH_i < pH_l < pH_5$).
- Zone 4 for calculated equilibrium pH above 8. The pH measured generally decreased with time ($pH_i < pH_l < pH_5$).

In the first zone, the pH measured (pH_i, pH_l, pH_5) increased with time as soluble hydroxide gallium species were formed. The formation of gallium hydroxide did not have an effect on the pH as the difference between pH_A and pH measured was within the experimental error as discussed below. Above $pH_A \approx 3.3$, the values of pH_A and the measured pH diverged; the measured pH was generally lower than the corresponding value of pH_A and closer to the calculated equilibrium pH. The second zone was defined by an increase of the pH measured with time and ranged from $pH_A \approx 3.3$ up to around 10.7. In this pH_A range, the measured pH and the equilibrium pH varied only from 3 to 3.8 as the hydroxide ions added to the solution formed insoluble gallium hydroxide complexes. The difference between the measured pH and the calculated equilibrium pH value was generally less than 0.2 pH units up to $pH_A = 8.85$ (calculated equilibrium pH = 3.3) . As observed in Figure A3.1, the precipitation of $Ga(OH)_{3(s)}$ in zone 2 was less than predicted by the speciation diagram. By increasing the time after which the pH was measured, the measured pH decreased slightly and tended toward the calculated

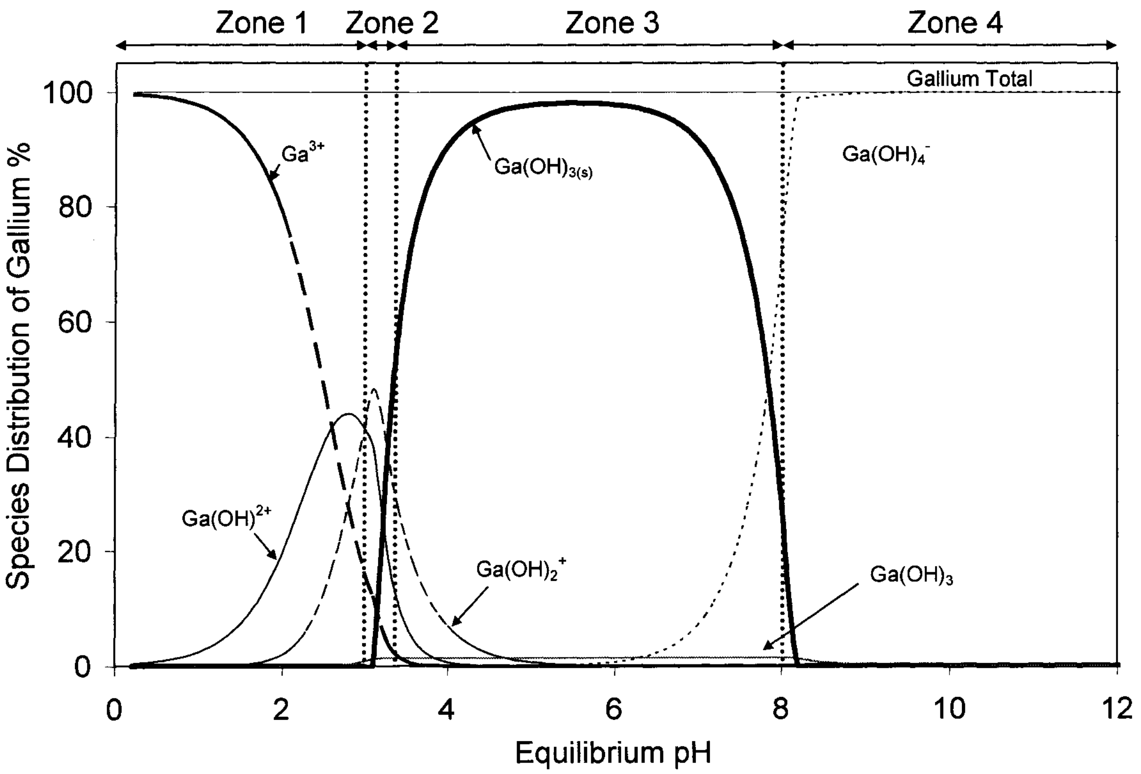


Figure A3.3: Distribution of gallium species in aqueous solution at different pH [$C^{\circ}_{Ga} = 0.359$ mM; $V^{\circ} = 20$ mL]. The zones correspond to the ones reported in Table A3.1 and are defined based on the calculated equilibrium pH.

equilibrium value.

More $Ga(OH)_{3(s)}$ precipitated with time as shown in Figure 3.3. Above pH_A = 10.73, the calculated equilibrium pH and the measured pH also diverged. For a small extra amount of NaOH added to the solution (0.2 mL), the pH_A increased from 10.7 to 11.2, while the calculated equilibrium pH and the measured pH increased from pH = 3.4 up to pH = 10. Between pH_i = 4 to around 8, the measured pH increased with time to reach a plateau after 1 day as observed in Table A3.1. In the third zone defined in Figure A3.3, insoluble $Ga(OH)_{3(s)}$ was precipitated from the solution after 1 day. In this zone 3, the percent precipitation varied less with time than in the zone 2. Above pH_i = 8, corresponding to a pH_A around 11.1, the main hydroxide gallium complex in the fourth zone is $Ga(OH)_4^-$. The transition between the insoluble $Ga(OH)_{3(s)}$ and the soluble $Ga(OH)_4^-$ generated a small deviation in the calculated pH shown in Figure A3.2. In this zone, the pH measured decreased slightly with time. The formation of $Ga(OH)_4^-$ affected the pH up to pH around 12 where values of pH measured and pH_A tend to coincide. Above pH values of 12, the amount of OH^- consumed to form $Ga(OH)_4^-$ was negligible compared to the amount of OH^- available. At pH = 12, the concentration of OH^- available was 7 times higher than the concentration of OH^- needed to form $Ga(OH)_4^-$.

In conclusion, the initial and final pH measured were close to equilibrium as the metal formed complexes relatively rapidly with the hydroxide ions. Below pH_i of 3.5 and above a pH_i of 12, $pH_i \approx$ equilibrium pH. However, from pH_i of 3.5 to 12, the pH varied with time as the difference between the pH calculated and the pH measured was higher than the experimental uncertainty, which was estimated at 0.2 pH.

As shown in Tables A3.2 and A3.3, small experimental errors can have a large effect on the calculated equilibrium pH or the corresponding amount of NaOH added to the solution. In Table A3.2, the effect of the apparatus precision and of the precision in the concentration is shown for 3 different ranges of equilibrium pH: for pH < 3 and for pH > 8, the gallium complexes are soluble while for pH between 3 and 8, the gallium precipitates as shown in Figure A3.3. As observed in these tables, for a small error on the volume of gallium stock solution or in the concentration of NaOH, the highest variation of the equilibrium pH was for pH between 3 to 8. On the contrary, as shown in Table A3.3, an error of 0.1 pH units results in a higher increase of the NaOH added for pH 2.5 and 12 compared to the case of pH of 5.5. While the reproducibility of the pH measured was poor when making new calibrations and preparing new solutions, it can be observed in Table A3.1 that the reproducibility of the pH of duplicate samples was good when the same titrating solutions and calibrations were used.

In conclusion, the measured initial pH, pH_i, was used in the body of the thesis for pH_i below 3.5 and above 12. For experiments with a fixed pH_i below 3.5, the amount of NaOH added to the solution was also reported using the mole ratio of sodium over metal to avoid the effect of the error on the pH measurement. Between a pH_i of 3.5 and a pH_i of 12, pH_i was used. In this area, the addition of a small amount of sodium hydroxide increased the pH significantly. The corresponding molar concentration of sodium hydroxide added to the solution can be deduced from equation 5.24:

$$C^{\circ}_{NaOH} = C_{OH^-} + 3C^{\circ}_{Ga} + C^{\circ}_{HNO_3} - C_{Ga^{3+}}\left(3 + 2\frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}} - \frac{(C_{OH^-})^4}{K_{4,Ga}}\right) - \frac{10^{-14}}{C_{OH^-}} \qquad \text{(A3.17)}$$

Table A3.2: Example of sources of error and their effect on the calculated equilibrium pH.

Sources of error	Case	mL of NaOH added (0.1 N)	Equilibrium pH range	Calculated equilibrium pH	
				0.5 mL	(-)/(+)
Precision of a 1 mL pipette (± 0.02 mL)	(0.5 ± 0.02) mL Ga stock solution (1 wt % HNO_3)	0.20	pH < 3	2.5	2.5/2.5
		1.01	3 < pH < 8	6.4	7/4.9
		3.08	pH > 8	12	12/12

Sources of error	Case	mL of NaOH added (0.1 N)	Equilibrium pH range	Calculated equilibrium pH	
				0.1 N	(-)/(+)
Precision in concentration	NaOH (0.1 ± 0.02 %) N	0.20	pH < 3	2.5	2.5/2.5
		1.00	3 < pH < 8	4.42	4.41/7.02
		3.08	8 < pH	12	12/12

Table A3.3: Effect of the error in the equilibrium pH on the corresponding amount of NaOH [0.5 mL of Ga stock solution (1 wt % HNO_3)].

Source of error	Case	Equilibrium pH	Calculated mL of NaOH added (0.1 N)
Precision of pH meter (± 0.1 pH unit)	pH = 2.5 ± 0.1	2.5	0.20
		2.4/2.6	0.03/0.34
	pH = 5.5 ± 0.1	5.5	1.01
		5.4/5.6	1.01/1.01
	pH= 12 ± 0.1	12	3.08
		11.9/12.1	2.67/3.60

where $C_{Ga^{3+}} = \frac{K_{sp,Ga}}{(C_{OH^-})^3}$ if Ga(OH)$_{3(s)}$ precipitate (i.e. $K_{sp,Ga} \leq C_{Ga^{3+}} \times (C_{OH^-})^3$) or

$$C_{Ga^{3+}} = \frac{C^{\circ}_{Ga}}{(1 + \frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}} + \frac{(C_{OH^-})^3}{K_{3,Ga}} + \frac{(C_{OH^-})^4}{K_{4,Ga}})} \text{ if } K_{sp,Ga} > C_{Ga^{3+}} \times (C_{OH^-})^3$$

In equation A3.17, OH^- represents the hydroxide ions at equilibrium, the acidity constants are those defined in Chapter 5 and the total concentrations of gallium and nitric acid are known.

A3.3 Effect of the distilled water added to the metal solution

The effect of the amount of distilled water from the ligand solution on the pH of the metal solution is of interest when the mole ratio of ligand to metal is increased. A schema of the experimental procedure is presented in Figure 2.3. For a single metal solution, the values of $r^{\circ}_{L/Ga}$ and $r^{\circ}_{L/Al}$, for the systems shown in Table A3.4, ranged from 0 to 3.5 and from 0 to 6, respectively. The corresponding maximum volume of sodium di-(n-octyl) phosphinate ligand solution added was around 1 mL for the removal of gallium and 4.3 mL for the removal of aluminum. The optimum removal was generally obtained for both metals at a ligand to metal ratio of 3, representing a volume of ligand solution added to the metal solution of 0.83 mL for gallium and 2.15 mL for aluminum. For a mixture of metals, r°_{Ga} was increased from 0 to 21 for the zinc/gallium solutions and from 0 to 21.5 for the aluminum/gallium solutions for the systems shown in Table A3.1. In all cases, the maximum volume of ligand solution added never exceeded around 6 mL or 30 % of a total volume of 20 mL.

Table A3.4: Relation between percentage of V° from ligand stock solution and $r^{\circ}_{L/M}$ for various metals. The associated figure(s) are presented in the body of the thesis.

System	V°, mL	$\frac{V_L}{V^\circ}\times 100$	Associated figure(s)
Gallium	15	$=1.85\, r^{\circ}_{L/Ga}$	3.5
Gallium	20	$=1.39\, r^{\circ}_{L/Ga}$	3.6 - 3.13
Gallium/zinc			4.1 - 4.3
Gallium/aluminum			4.4 - 4.6
Aluminum	20	$=3.59\, r^{\circ}_{L/Al}$	3.21-3.24

Values of the percent of V°, coming from the ligand solution for the removal of other metals with sodium di-(n-octyl) phosphinate ligand or the removal of gallium with other ligands, are reported in Table A3.5. The total volume V° was 20 mL. The maximum volume of ligand solution added to 14 mL of metal solution was 6 mL. This value was not exceeded in any of the mixtures of gallium/aluminum, gallium/zinc and iron/arsenic.

The effect on the initial pH of the metal solution of the distilled water from the ligand stock solution is considered here. A 14 mL metal solution was prepared by mixing distilled water, the metal stock solutions and an acid (HNO_3) or a base (NaOH). The pH, pH_i, was measured immediately after mixing. After the addition of the 6 mL of distilled water, corresponding to the maximum volume of ligand solution added in the cases shown in Table A3.5, the pH° was measured.

Table A3.5: Summary of the percent of V° from ligand stock solution for various metals with the associated figure(s) in the body of the thesis [V° = 20 mL].

Metal/ ligand		Ratio ligand to metal(s)	percent of V° from ligand solution	Associated figure(s)
Gallium/mono-octyl ester phosphinate		3	4.5	3.14
Gallium/fumaric acid		3.6	5	3.15
		18	25	
Gallium/humic acid	40 mg/L	-	5	3.17, 3.18
	120 mg/L	-	15	3.17, 3.18
Gallium/humic acid/di-(n-octyl) phosphinate		Humic acid (120 mg/L)	15	3.19
		di-(n-octyl) phosphinate ($r^{\circ}_{L/Ga} = 3$)	4.2	
Indium/di-(n-octyl) phosphinate		1	0.8	3.29
		5	4.2	3.28
Iron/di-(n-octyl) phosphinate		1	1.4	3.30
		3	4.2	
Calcium/di-(n-octyl) phosphinate		2.6	11.3	3.31

Gallium/calcium/di-(n-octyl) phosphinate	$r^{\circ}_{L/Ca} = 2$	8.7	4.7
Aluminum/calcium/di-(n-octyl) phosphinate	$r^{\circ}_{L/Al} = 4$	13.9	4.8
Arsenic/di-(n-octyl) phosphinate	3	3.9	4.9
Iron/arsenic/di-(n-octyl) phosphinate	$r^{\circ}_{L/Fe} =$ 1	10.4	4.11
	3	31.1	
Gallium/arsenic/di-(n-octyl) phosphinate	$r^{\circ}_{L/Ga} = 3$	16.9*	4.12
Gallium/indium/di-(n-octyl) phosphinate	1.5	4.2	4.14
	3	8.3	

* Stock ligand solution at 16 g/L

The metal concentrations of the solutions shown in Table A3.6 are based on a total volume of 20 mL. As observed in Table A3.6, the largest difference between the values, pH_i and pH°, was for the lower and higher values of pH_i of the metal solution. The difference between pH_i and pH° was generally below 0.15 pH units which is close to the detection limit of the pH meter used. Thus the effect of the addition of 6 mL of distilled water on the pH_i of a 14 mL of metal solution was neglected in the body of the thesis.

Table A3.6: Effect on the measured pH_i (of the metal solution) of the distilled water from the ligand stock solution [pH of the distilled water = 6.06].

Solutions	Measured pH_i	Measured pH°
	14 mL metal solution	20 mL (14 mL metal solution + 6 mL distilled water)
Gallium (0.359 mM)/aluminum (0.925 mM)	1.45	1.60
	1.85	2.00
	2.75	2.90
	3.75	3.83
	5.42	5.43
	8.93	8.92
Gallium (0.359 mM)/zinc (1.15 mM)	1.08	1.22
	1.23	1.36
	1.98	2.11
	5.80	5.83
	12.14	12.07

A3.4 Speciation diagram and initial pH of other metal solutions

The stability constants and solubility product of zinc and calcium are given in Table A3.7 and in Chapter 5 for aluminum, indium and iron. The speciation diagrams for zinc and calcium, calculated using the models developed in Chapter 5 and in Section A3.2 of this appendix, are shown in Figures A3.4 and A3.5. These speciation diagrams agreed with the ones reported by Baes and Mesmer (1986). Comparisons between the experimental pH and the equilibrium pH calculated using the model developed in Appendix 3 are also presented in this section for completeness in Figure A3.6, A3.7 and A3.8. As the results are similar to those obtained for gallium, it is not necessary to discuss them in detail.

Table A3.7: Mass stability constants and solubility products used for the speciation diagram of metals and the calculation of the equilibrium pH. The values reported follow the notation described in Chapter 5.

Species	Stability constant	log value of the stability constant (Baes and Mesmer, 1986)
$Zn(OH)^+$	$K_{1,Zn} = \frac{C_{Zn^{2+}} C_{OH^-}}{C_{Zn(OH)^+}}$	-5.04
$Zn(OH)_2$	$K_{2,Zn} = \frac{C_{Zn^{2+}} C^2_{OH^-}}{C_{Zn(OH)_2}}$	-11.1
$Zn(OH)_3^-$	$K_{3,Zn} = \frac{C_{Zn^{2+}} C^3_{OH^-}}{C_{Zn(OH)_3^-}}$	-13.6
$Zn(OH)_4^{2-}$	$K_{4,Zn} = \frac{C_{Zn^{2+}} C^4_{OH^-}}{C_{Zn(OH)_4^{2-}}}$	-14.8
$Ca(OH)^+$	$K_{1,Ca} = \frac{C_{Ca^{2+}} C_{OH^-}}{C_{Ca(OH)^+}}$	-1.15
Species	Solubility product	log value of the solubility product
$Zn(OH)_{2(s)}$	$K_{sp,Zn} = C_{Zn^{2+}} C^2_{OH^-}$	-16.86
$Ca(OH)_{2(s)}$	$K_{sp,Ca} = C_{Ca^{2+}} C^2_{OH^-}$	-5.2

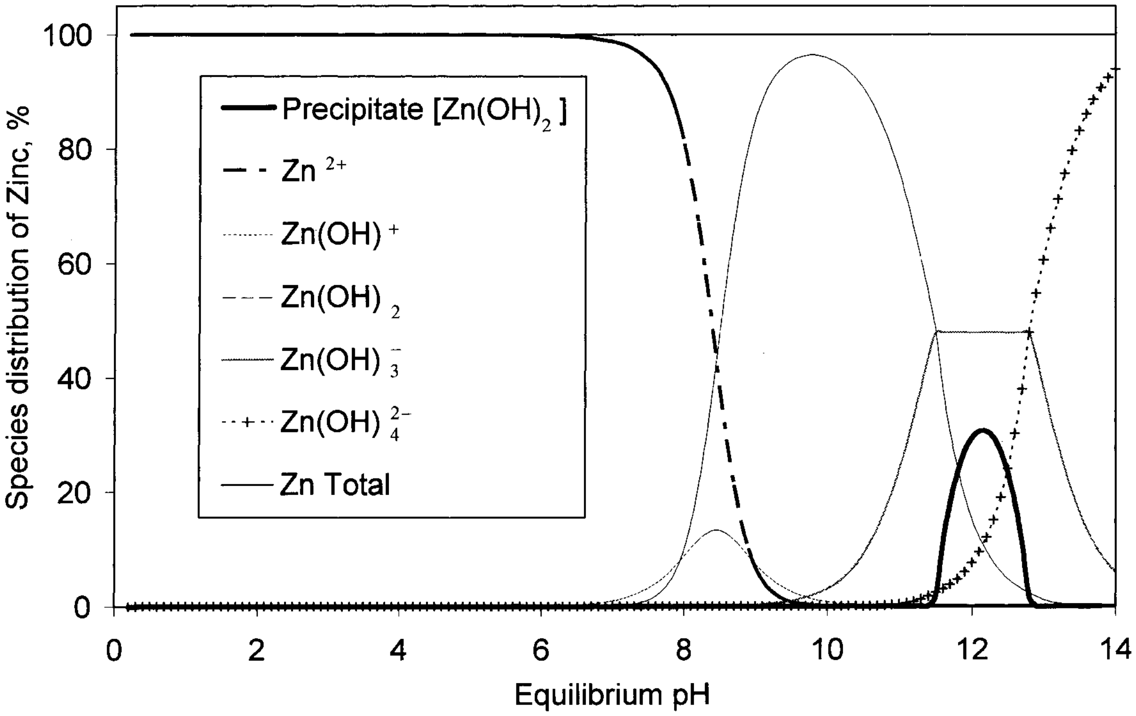


Figure A3.4: Distribution of zinc species in aqueous solution at different pH [C°_{Zn} = 1.15 mM; values calculated with parameters from Baes and Mesmer (1986)].

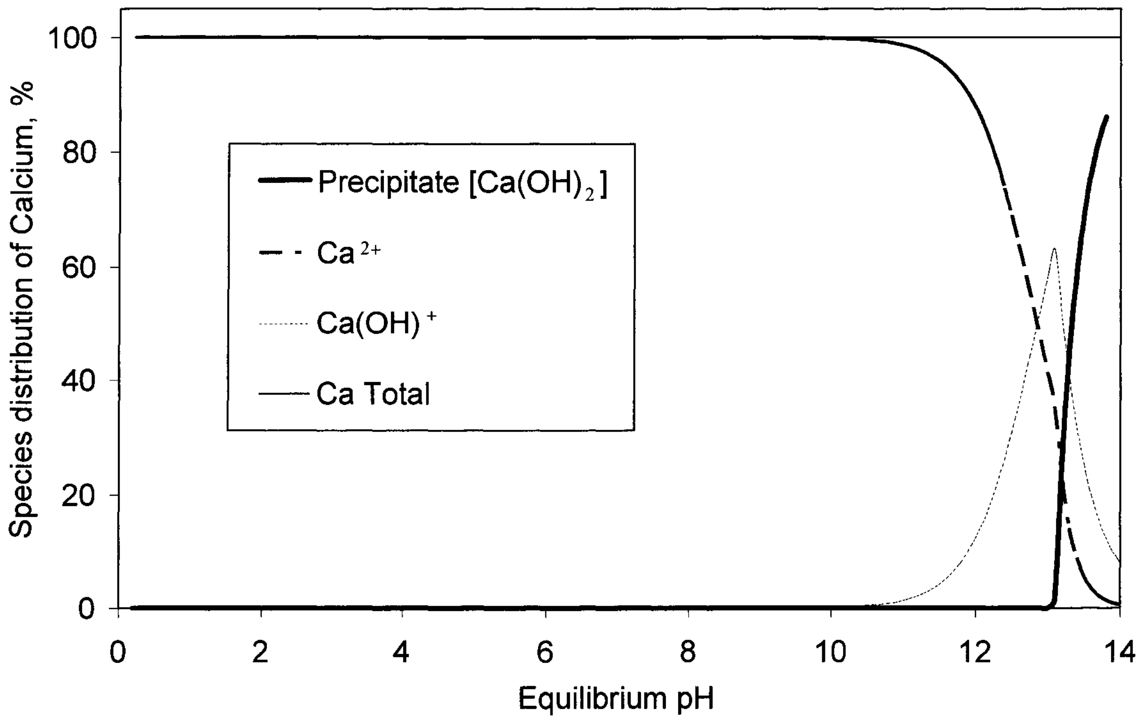


Figure A3.5: Distribution of calcium species in aqueous solution at different pH [C°_{Ca} =1.13 mM; values calculated with parameters from Baes and Mesmer (1986)].

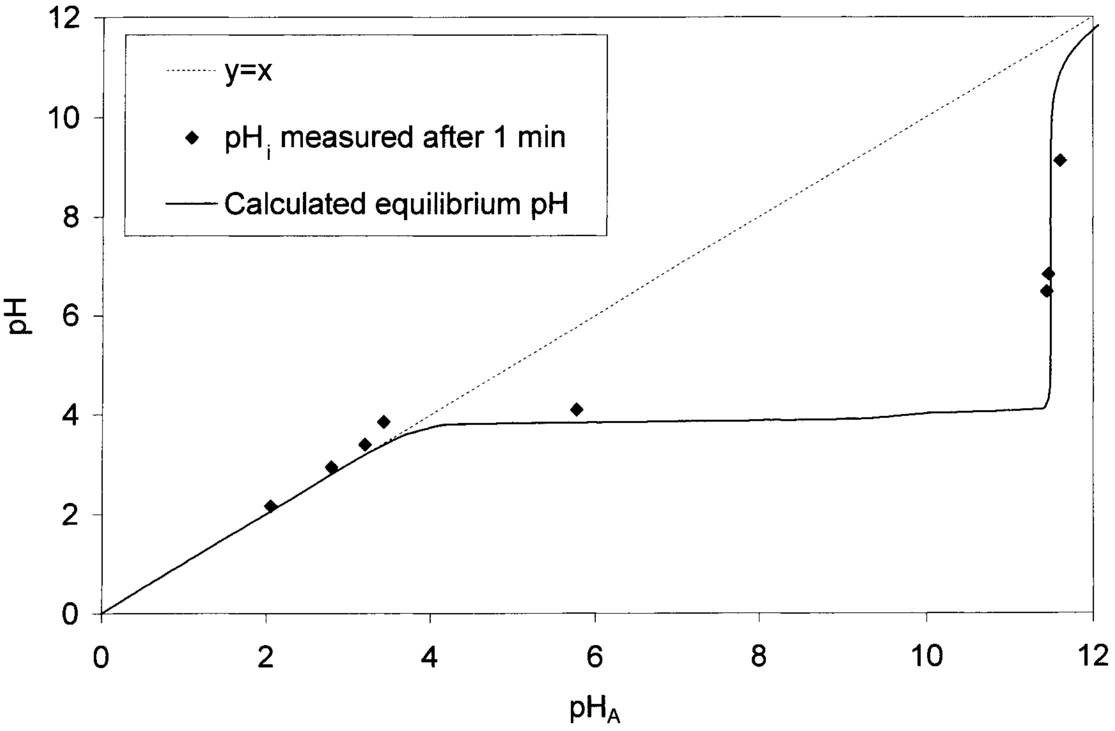


Figure A3.6: Comparison between experimental and calculated pH based on the amount of acid or base added to aluminum solutions $[C^{\circ}_{Al} = 0.925 \text{ mM}; V^{\circ} = 20 \text{ mL}]$. pH$_A$ is the value of pH calculated ignoring the formation of hydroxy-complexes.

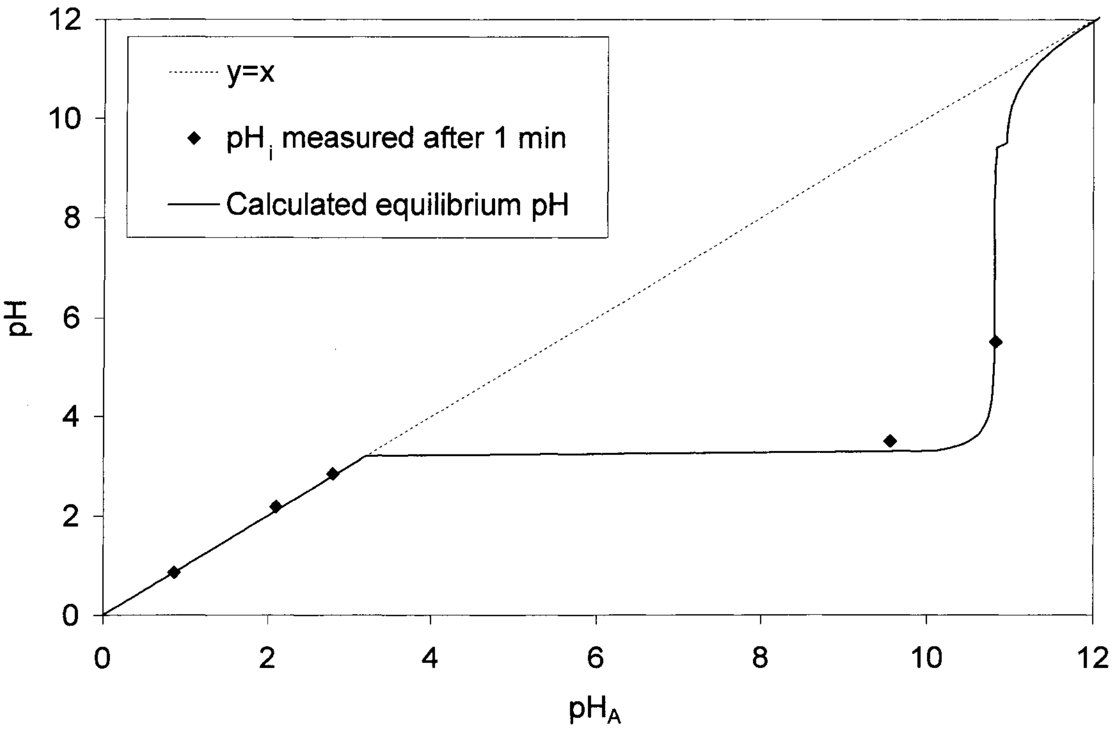


Figure A3.7: Comparison between experimental and calculated pH based on the amount of acid or base added to indium solutions [$C^{\circ}_{In} = 0.22$ mM; $V^{\circ} = 20$ mL]. pH_A is the value of pH calculated ignoring the formation of hydroxy-complexes.

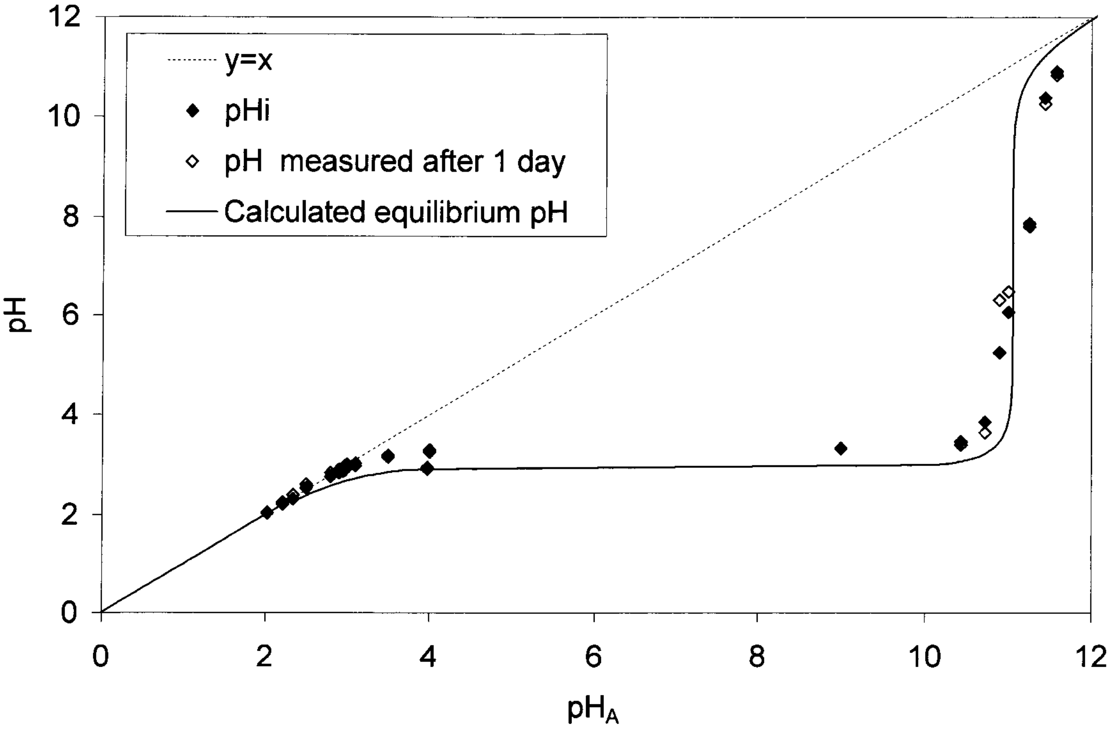


Figure A3.8: Comparison between experimental and calculated pH based on the amount of acid or base added to ferric iron solutions [$C^{\circ}_{Fe} = 0.36$ mM; $V^{\circ} = 20$ mL]. pH_A is the value of pH calculated ignoring the formation of hydroxy-complexes.

As previously observed for gallium metal solutions, the values of pH_i measured for these other metal solutions were generally close to the calculated equilibrium pH, indicating that the formation of the hydroxide complexes was fast. Thus, the following notation was used in the body thesis for these metal solutions:

- For experiments with a fixed pH_i, the amount of NaOH added to the solution is reported using the mole ratio of sodium over metal to avoid the effect of the error on the pH measurement.
- When studying the effect of the pH on the removal of the metal with a ligand, the measured final pH is generally used. The values of pH_i are reported to illustrate the evolution of the pH in comparison with the values of the calculated equilibrium pH.

APPENDIX 4

MASS AND CHARGE BALANCE EQUATIONS

Table A4.1: Mass and charge balance equations for the removal of sodium di-(n-octyl) phosphinate ligand alone in nitrate solution.

Mass Balance of Nitrate	$C^{\circ}_{NO_3} = C^{\circ}_{HNO_3} = C_{NO_3^-}$	(A4.1)
Mass Balance of Sodium	$C^{\circ}_{Na} = C^{\circ}_{NaOH} + \frac{n^{\circ}_{NaL_{(S)}}}{V} = C_{Na^+}$	(A4.2)
Mass Balance of Ligand	$C^{\circ}_{L} = C_{L^-} + \frac{n_{NaL_{(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}}$	(A4.3)
Charge Balance	$C_{Na^+} + C_{H^+} = C_{L^-} + C_{NO_3^-} + C_{OH^-}(1 + \frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}} + 2 \times \frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})$	(A4.4)

Table A4.2: Mass and charge balance equations for the removal of gallium using sodium di-(n-octyl) phosphinate ligand in nitrate solution.

Mass Balance of Ga (III)	$C^{\circ}_{Ga} = C_{Ga^{3+}}(1 + \frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}} + \frac{(C_{OH^-})^3}{K_{3,Ga}} + \frac{(C_{OH^-})^4}{K_{4,Ga}}) + \frac{n_{Ga(OH)_{3(s)}}}{V} + \frac{n_{GaL_{3(s)}}}{V}$ (A4.5)
Mass Balance of Nitrate	$C^{\circ}_{NO_3} = 3 \times C^{\circ}_{Ga} + C^{\circ}_{HNO_3} = C_{NO_3^-}$ (A4.6)
Mass Balance of Sodium	$C^{\circ}_{Na} = C^{\circ}_{NaOH} + \frac{n^{\circ}_{NaL_{(s)}}}{V} = C_{Na^+}$ (A4.7)
Mass Balance of Ligand	$C^{\circ}_{L} = C_{L^-} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}} + 3 \times \frac{n_{GaL_{3(s)}}}{V}$ (A4.8)
Charge Balance	$C_{Ga^{3+}}(3 + 2 \times \frac{C_{OH^-}}{K_{1,Ga}} + \frac{(C_{OH^-})^2}{K_{2,Ga}}) + C_{Na^+} + C_{H^+} = C_{Ga^{3+}} \frac{(C_{OH^-})^4}{K_{4,Ga}} + C_{L^-} + C_{NO_3^-}$ $+ C_{OH^-}(1 + \frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}} + 2 \times \frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})$ (A4.9)

Table A4.3: Mass and charge balance equations for the removal of aluminum using sodium di-(n-octyl) phosphinate ligand in nitrate solution.

Mass Balance of Al (III)	$C^{\circ}_{Al} = C_{Al^{3+}}(1 + \frac{C_{OH^-}}{K_{1,Al}} + \frac{(C_{OH^-})^2}{K_{2,Al}} + \frac{(C_{OH^-})^3}{K_{3,Al}} + \frac{(C_{OH^-})^4}{K_{4,Al}} + \frac{(C_{L^-})^3}{K_{AlL_3}}) + \frac{n_{Al(OH)_{3(s)}}}{V} + \frac{n_{AlL_{3(s)}}}{V}$ (A4.10)
Mass Balance of Nitrate	$C^{\circ}_{NO_3} = 3 \times C^{\circ}_{Al} + C^{\circ}_{HNO_3} = C_{NO_3^-}$ (A4.11)
Mass Balance of Sodium	$C^{\circ}_{Na} = C^{\circ}_{NaOH} + \frac{n^{\circ}_{NaL_{(s)}}}{V} = C_{Na^+}$ (A4.12)
Mass Balance of Ligand	$C^{\circ}_{L} = C_{L^-} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}} + 3 \times \frac{n_{AlL_{3(s)}}}{V} + 3 \times \frac{C_{Al^{3+}}(C_{L^-})^3}{K_{AlL_3}}$ (A4.13)
Charge Balance	$C_{Al^{3+}}(3 + 2 \times \frac{C_{OH^-}}{K_{1,Al}} + \frac{(C_{OH^-})^2}{K_{2,Al}}) + C_{Na^+} + C_{H^+} = C_{Al^{3+}} \frac{(C_{OH^-})^4}{K_{4,Al}} + C_{L^-} + C_{NO_3^-}$ $+ C_{OH^-}(1 + \frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}} + 2 \times \frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})$ (A4.14)

Table A4.4: Mass and charge balance equations for the removal of indium using sodium di-(n-octyl) phosphinate ligand in nitrate solution.

Mass Balance of In (III)	$C^{\circ}_{In} = C_{In^{3+}}(1 + \frac{C_{OH^-}}{K_{1,In}} + \frac{(C_{OH^-})^2}{K_{2,In}} + \frac{(C_{OH^-})^3}{K_{3,In}} + \frac{(C_{OH^-})^4}{K_{4,In}} + \frac{(C_{L^-})^3}{K_{InL_3}}) + \frac{n_{In(OH)_{3(s)}}}{V} + \frac{n_{InL_{3(s)}}}{V}$	(A4.15)
Mass Balance of Nitrate	$C^{\circ}_{NO_3} = 3 \times C^{\circ}_{In} + C^{\circ}_{HNO_3} = C_{NO_3^-}$	(A4.16)
Mass Balance of Sodium	$C^{\circ}_{Na} = C^{\circ}_{NaOH} + \frac{n^{\circ}_{NaL_{(s)}}}{V} = C_{Na^+}$	(A4.17)
Mass Balance of Ligand	$C^{\circ}_{L} = C_{L^-} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}} + 3 \times \frac{n_{InL_{3(s)}}}{V} + 3 \times \frac{C_{In^{3+}}(C_{L^-})^3}{K_{InL_3}}$	(A4.18)
Charge Balance	$C_{In^{3+}}(3 + 2 \times \frac{C_{OH^-}}{K_{1,In}} + \frac{(C_{OH^-})^2}{K_{2,In}}) + C_{Na^+} + C_{H^+} = C_{In^{3+}} \frac{(C_{OH^-})^4}{K_{4,In}} + C_{L^-} + C_{NO_3^-}$ $+ C_{OH^-}(1 + \frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}} + 2 \times \frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})$	(A4.19)

Table A4.5: Mass and charge balance equations for the removal of iron using sodium di-(n-octyl) phosphinate ligand in nitrate solution.

Mass Balance of Fe (III)	$C^\circ_{Fe} = C_{Fe^{3+}}(1 + \frac{C_{OH^-}}{K_{1,Fe}} + \frac{(C_{OH^-})^2}{K_{2,Fe}} + \frac{(C_{OH^-})^3}{K_{3,Fe}} + \frac{(C_{OH^-})^4}{K_{4,Fe}} + \frac{(C_{L^-})^3}{K_{FeL_3}}) + \frac{n_{FeO(OH)_{(s)}}}{V} + \frac{n_{FeL_{3(s)}}}{V}$	(A4.20)
Mass Balance of Nitrate	$C^\circ_{NO_3} = 3 \times C^\circ_{Fe} + C^\circ_{HNO_3} = C_{NO_3^-}$	(A4.21)
Mass Balance of Sodium	$C^\circ_{Na} = C^\circ_{NaOH} + \frac{n^\circ_{NaL_{(s)}}}{V} = C_{Na^+}$	(A4.22)
Mass Balance of Ligand	$C^\circ_{L} = C_{L^-} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_{1,HL}} + 3 \times \frac{n_{FeL_{3(s)}}}{V} + 3 \times \frac{C_{Fe^{3+}}(C_{L^-})^3}{K_{FeL_3}}$	(A4.23)
Charge Balance	$C_{Fe^{3+}}(3 + 2 \times \frac{C_{OH^-}}{K_{1,Fe}} + \frac{(C_{OH^-})^2}{K_{2,Fe}}) + C_{Na^+} + C_{H^+} = C_{Fe^{3+}} \frac{(C_{OH^-})^4}{K_{4,Fe}} + C_{L^-} + C_{NO_3^-}$ $+ C_{OH^-}(1 + \frac{K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{10^{-14}} + 2 \times \frac{(C_{OH^-})K_{3,CO_2}K_{2,CO_2}K_{1,CO_2}P_{CO_{2(g)}}}{(10^{-14})^2})$	(A4.24)