REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY PRECIPITATION WITH SODIUM DI-(n-OCTYL) PHOSPHINATE

by

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ABSTRACT

Two organophosphorus compounds: sodium di-(n-octyl) phosphinate and sodium di-(n-dodecyl) phosphinate, were synthesized and purified. Sodium di-(n-octyl) phosphinate was used both as a surfactant to form reverse micelles and as a precipitating agent to remove heavy metals from aqueous nitrate and chloride solutions.

The heavy metals lead, cadmium, and zinc were precipitated from aqueous solutions with sodium di-(n-octyl) phosphinate (NaL) in the form of $PbL_{2(s)}$, $CdL_{2(s)}$, and $ZnL_{2(s)}$. The mole ratio of NaL to lead in the feed was varied from 0.1 to 6.5, depending on the acidity of the feed. The effects of the feed pH, concentration of chloride, concentration of calcium, and of the chain length of the precipitating agent on the removal of lead, were investigated. Adding acid to the feed solution reduced the removal of lead as some of the phosphinate precipitated in the acid form as $HL_{(s)}$. The presence of chloride or calcium in the feed solution, up to mole ratios to lead of 250 and 2.75, respectively, had no effect on the removal of lead. The solubility of the precipitate $PbL_{2(s)}$ was reduced by increasing the length of the alkyl group of the phosphinate. The removal of cadmium, zinc, and a mixture of lead, cadmium and zinc was investigated. Behavior similar to that of lead was observed. The selectivity of the precipitating agent for the three metals was in the order $Zn > Pb > Cd$.

The precipitating agent was completely regenerated by adding NaOH to the precipitate, and then contacted with diethyl ether to extract the reagent. The lead was completely recovered from the $PbL_{2(s)}$. Pure lead-free precipitating agent, and an aqueous solution of lead at a concentration 100 times its concentration in the feed, were obtained.

Using measured solubility products of the precipitates and literature values of the stability constants for the other expected reactions, the removal of metal, the loss of precipitating agent, and the equilibrium pH were predicted.

RÉSUMÉ

Deux composés organophosphorés: le phosphinate di-(n-octyl) de sodium et le phosphinate di-(n-dodécyl) de sodium ont été synthétisés et purifiés. Le phosphinate di-(n-octyl) de sodium a été utilisé à la fois comme surfactant dans la formation de micelles réversibles et comme agent précipitant de métaux lourds dans des solutions aqueuses de nitrates et de chlorures.

Les précipités obtenus pour les métaux lourds suivants: plomb, cadmium et zinc, ainsi que pour le di-(n-octyl) de sodium (NaL), ont pris la forme respective de $PbL_{2(s)}$, $CdL_{2(s)}$ et $ZnL_{2(s)}$. Le rapport molaire entre NaL et le plomb dans la solution d'alimentation a été varié de 0.1 à 6.5, tout dépendant de l'acidité de cette dernière. Les effets du pH, des concentrations en chlorure et calcium de la solution d'alimentation, ainsi que l'effet de la longueur de la chaîne alkyl de l'agent précipitant sur l'extraction du plomb, ont été étudiés. L'ajout d'acide à la solution d'alimentation a réduit l'efficacité de l'extraction du plomb dû à la précipitation d'un peu de phosphinate sous forme acide $HL_{(s)}$. La présence de chlorure et de calcium dans la solution d'alimentation, jusqu'à des rapports molaires de plomb de 250 à 2.75, respectivement, n'ont eu aucun effet dans l'élimination du plomb. La solubilité du précipité $PbL_{2(s)}$ a été réduite en augmentant la longueur du groupe alkyl du phosphinate. L'extraction du cadmium, du zinc, ainsi que l'extraction d'un mélange de plomb, cadmium et zinc ont également été étudiés. Des comportements similaires à ceux observés pour le plomb ont été obtenus. La sélectivité de l'agent précipitant pour les trois métaux est par ordre croissant: Zn > Pb > Cd.

L'agent précipitant a été complètement régénéré par addition de NaOH au précipité, puis par mise en contact avec de l'ether diethyl afin d'en extraire le réactif. Le plomb a été complètement extrait du $PbL_{2(s)}$. L'agent précipitant pur, sans plomb, et une solution aqueuse de Pb, à une concentration 100 fois sa concentration dans la solution d'alimentation, ont été obtenus.

En utilisant les produits de solubilité des précipités mesurés et les valeurs de constantes de stabilité de la littérature pour les autres réactions prévues, l'extraction des métaux, la perte de l'agent précipitant et le pH d'équilibre ont été prédits.

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Nomenclature

$n_{L_{(ad)}}$: overall equilibrium concentration of calcium

C^{o}_{Ca} : overall feed concentration of calcium

C^{*}_{Ca} : total initial number of moles of calcium, per unit volume of final mixture, $C^{o}_{Ca}(\frac{V^{o}}{V})$

C_{Cd} : overall equilibrium concentration of cadmium

C^{o}_{Cd} : overall feed concentration of cadmium

C^{*}_{Cd} : total initial number of moles of cadmium, per unit volume of final mixture, $C^{o}_{Cd}(\frac{V^{o}}{V})$

C_{Cl} : overall equilibrium concentration of chloride

C^{o}_{Cl} : overall feed concentration of chloride

C^{*}_{Cl} : total initial number of moles of chloride, per unit volume of final mixture, $C^{o}_{Cl}(\frac{V^{o}}{V})$

C_{Na} : overall equilibrium concentration of sodium

C^{o}_{Na} : overall feed concentration of sodium

C^{*}_{Na} : total initial number of moles of sodium, per unit volume of final mixture, $C^{o}_{Na}(\frac{V^{o}}{V})$

C_{NO_3} : overall equilibrium concentration of nitrate

$C^o_{NO_3}$: overall feed concentration of nitrate

$C^*_{NO_3}$: total initial number of moles of nitrate, per unit volume of final mixture, $C^o_{NO_3}(\frac{V^o}{V})$

C_{Pb} : overall equilibrium concentration of lead

C^o_{Pb} : overall feed concentration of lead

C^*_{Pb} : total initial number of moles of lead, per unit volume of final mixture, $C^o_{Pb}(\frac{V^o}{V})$

C_L : overall equilibrium concentration of di-(n-octyl) phosphinates

C^*_L : total initial number of moles of the precipitating agent, per unit volume of final mixture, $\frac{n_{NaL_{(ad)}}}{V}$

C_{Zn} : overall equilibrium concentration of zinc

C^o_{Zn} : overall feed concentration of zinc

C^*_{Zn} : total initial number of moles of zinc, per unit volume of final mixture, $C^o_{Zn}(\frac{V^o}{V})$

K's : mass-stability constants

K_a : acidity constant of di-(n-octyl) phosphinic acid

$K_{sp_{(CdL_2)}}$: solubility product of cadmium di-(n-octyl) phosphinate

$K_{sp_{(HL)}}$: solubility product of di-(n-octyl) phosphinic acid

$K_{sp_{(PbL_2)}}$: solubility product of lead di-(n-octyl) phosphinate

$K_{sp_{(ZnL_2)}}$: solubility product of zinc di-(n-octyl) phosphinate

K_w : dissociation constant of water

L : di-(n-octyl) phosphinate

L_D : di-(n-dodecyl) phosphinate

L_L : percentage loss of the precipitating agent

n^o_{Cd} : total initial number of moles of cadmium, $C^o_{Cd}V^o$

$n_{CdL_{2(s)}}$: moles of cadmium di-(n-octyl) phosphinate precipitate

n^o_{Cl} : total initial number of moles of chloride, $C^o_{Cl}V^o$

$n_{HL_{(s)}}$: moles of di-(n-octyl) phosphinic acid

$n_{NaL_{(ad)}}$: moles of sodium di(n-octyl) phosphinate added to the system

$n_{NaL_{D(ad)}}$: moles of sodium di-(n-dodecyl) phosphinate added to the system

$n^o_{NO_3}$: total initial number of moles of nitrate, $C^o_{NO_3}V^o$

n^o_{Pb} : total initial number of moles of lead, $C^o_{Pb}V^o$

$n_{PbL_{2(s)}}$: moles of lead di-(n-octyl) phosphinate

$n_{L_{(ad)}}$: moles of di(n-octyl) phosphinate added to the system

$n_{L_{D(ad)}}$: moles of di-(n-dodecyl) phosphinate added to the system

n^o_{Zn} : total initial number of moles of zinc, $C^o_{Zn}V^o$

$n_{ZnL_{2(s)}}$: moles of zinc di-(n-octyl) phosphinate

P_{CO_2} : partial pressure of carbon dioxiode in the atmosphere

pH : equilibrium pH

pH^o : pH of the feed

r^o_{Ca} : mole ratio of overall calcium to overall lead in the feed

r^o_{Cl} : mole ratio of overall chloride to overall lead in the feed

r^o_{L} : mole ratio of sodium di-(n-octyl) phosphinate added to the system to overall metal in the feed

$r^o_{L_D}$: mole ratio of sodium di-(n-dodecyl) phosphinate added to the system to overall metal in the feed

$r^o_{NO_3}$: mole ratio of overall nitrate to overall lead in the feed

R_{Ca} : percentage removal of calcium

R_{Cd} : percentage removal of cadmium

R_{Pb} : percentage removal of lead

R_{Zn} : percentage removal of zinc

V : final volume of the system

V^o : volume of the feed

CHAPTER 1
INTRODUCTION

Wastewater, encompasses many types of effluents, such as industrial waste, sewage effluent, and mining waste. Industrial wastewater is contaminated with a wide variety of potentially toxic chemicals, heavy metals and organics being the most significant of the potentially troublesome contaminants. These contaminants could lead to serious effects on human and animal health. There are many industrial processes that produce acidic wastewater streams containing low, yet significant concentrations of heavy metals. The increasing need for recovery of heavy metals from industrial wastewater, requires the development of new separation processes.

1.1 Heavy Metals

The term "heavy metals " has found its way into standard texts, although this term is loosely defined. Some technical dictionaries consider as heavy metals those which have specific gravities ranging from 4.5 to 22.5 (Nieboer and Richardson, 1980). Some times this expression is used with the connotation of toxicity. Volesky (1990), in his definition of heavy metals, included all metals of the periodic table except those in groups I and II. The heavy metals of particular concern in the treatment of industrial wastewater are lead, cadmium, mercury, zinc, copper, chromium, and nickel. The main reason for the concern is the risk of their entry into the food chain or into the water supply. The heavy metals considered in this work are lead, cadmium and zinc.

The toxicology of lead has been extensively studied. Lead is a cumulative poison and concentrates primarily in the bones. Inorganic lead (Pb^{2-}) is a general metabolic poison and enzyme inhibitor, and it has the ability to replace calcium in the bones. Cadmium has been established as extremely toxic to human beings. Cadmium acts synergistically with other elements such as copper and zinc, to increase toxicity. Zinc is the least toxic of the three metals considered.

There are numerous industrial activities involving these three metals, and as a result there are many sources of industrial effluents discharging these metals into the environment. The battery industry, electroplating industry, and smelting operations are the main sources of contamination of the environment with heavy metals.

Industries are generally required to adhere to local discharge limits on wastewater concentrations. The limits vary from region to region, but generally are in the range of 0.1 to 5 ppm (Volesky, 1990).

1.2 Removal Methods

Many separation and concentration processes are potentially applicable to metal removal from industrial wastewater. Most of these processes are well developed and many have been incorporated to commercial practice. Depending on the composition of the waste streams, the treatment plant may employ one or a combination of commercially available techniques for removal of heavy metals. Since metals exist in wastewater in many forms, the treatment process for metal removal must be either selected to remove the existing form of the metal, or the metal must be converted to a suitable form compatible with the removal process. In general, to be removed from wastewater, metals must be precipitated or otherwise attached to an insoluble material through adsorption or ion exchange. The available methods used for removal of heavy metals include: precipitation, ion exchange, membrane separations, solvent extraction, foam flotation, biosorption processes, etc. Peters et al.(1985), described various methods employed for heavy metal removal in industry and discussed advantages and disadvantages of these methods. Some of the limitations of the processes discussed below, are also limitations of the process described in this work. More information about the subject can be found elsewhere (Patterson, 1985).

Precipitation processes are widely used to remove metal ions from solution. The precipitation of a metal hydroxide is, by far, the most commonly used technique. Limitations associated with hydroxide treatment include: (1) hydroxide precipitates tend to solubilize if the solution pH is changed, (2) removal of metals by hydroxide precipitation in mixed metal wastes may not be effective since the minimum solubility for different metals occurs at different pH values. Patterson et al.(1977) investigated the use of carbonate precipitation to treat effluents containing heavy metals. The carbonate precipitation did not reduce the residual concentration below that obtained by hydroxide precipitation. An equivalent removal of metals could not be achieved at pH lower than those optimal for hydroxide precipitation. Carbonate precipitates have been reported to have better filtration characteristics than hydroxide precipitates (Patterson et al., 1977). Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing heavy metals. A high degree of separation was obtained by Battacharyya et al.(1979), using sulfide precipitation with sodium sulfide to remove lead, cadmium, and zinc from wastewater. The use of sulfide to treat metal waste water potentially generates some toxicity problems with excess residual sulfide reagent. Thus, the removal of the excess sulfide requires further treatment. In general, the disadvantages of the precipitation process are the large chemical consumption and the poor settling and filtering properties of the sludge.

In addition, the residual metal concentrations are not always as low as specified by the environmental authorities.

Organic reactants have also been used to precipitate metals in solution by formation of insoluble products. Tioacetamide, dialkyl dithiocarbonates, and starch xanthates have been used to remove soluble metals from waste effluents (Brooks, 1986). In general, poor regenerability and high costs discourage the use of most organic precipitating agents. Recently Husein (1996) used different compounds containing the sodium carboxylate group to remove lead from aqueous solutions. Sodium caprate produced the best filtration properties with the highest percentage removal. About 99% of sodium caprate was regenerated. The study of Husein (1996) was initiated based on preliminary results of the present project.

Ion-exchange has received considerable attention for separation and concentration of variety of metals from waste effluents. Ion-exchange is a process whereby ions held by chelating or electrostatic forces to functional groups of the insoluble material are exchanged for ions from the solution in which the insoluble material is immersed. This process continues until the solution being treated exhausts the exchange capacity of the ion exchange material. When this point is reached, the resin must be regenerated by replacing the ions given up in the ion exchange operation. Ion exchange is an attractive method for the removal of small amounts of impurities in wastewater. Problems typically involved with ion-exchange treatment include: (1) metallic fouling on the ion-exchange media, (2) fouling due to oil, grease, clay, etc., and (3) the presence of free acid reduces the operation efficiency of cation exchangers.

Membrane processes as applied to waste treatment are becoming increasingly attractive. Commercial membrane processes include electrodialysis, reverse osmosis, and ultrafiltration. In electrodialysis, pairs of ion exchange membranes are used. These membranes are permeable only to ionic species and are selective to a specific type of ion. In reverse osmosis, the size of the species as well as the chemical nature of the species are important. In ultrafiltration, the different chemical components are separated largely according to their size. The applications of this technology to the separation of heavy metals from industrial waste streams have been discussed by Huang and Kaseoglu (1993).

Electrodialysis is a separation technique that accomplishes the deionization of water streams by using a series of ion-exchange membranes placed between two electrodes, and a direct current as the driving force. Electrodialysis has been successfully applied in recovering various metals from electroplating waste streams that contain lead, cadmium and zinc (Gering and Scamehorn, 1988; Huang and Kaseoglu, 1993). One problem with the use of electrodialysis is the possibility of an extremely high voltage drop occurring at the membrane boundary layers which could ionize water and cause the precipitation of metal hydroxides that foul the membrane.

Reverse osmosis has been also applied for treating industrial wastewater. Reverse osmosis rejects dissolved components as small as 10^{-1} to 10^{-3} microns in size, which include ionic materials, dissolved salts, and most organics. Several studies on reverse osmosis treatability of industrial wastewater containing lead, cadmium, and zinc, have been conducted. The main limitation of reverse osmosis is the low permeate flux resulting from membrane fouling (Huang and Kaseoglu, 1993). A disadvantage of reverse osmosis is the relatively limited lifetime of the membrane, which results in higher operating costs.

Ultrafiltration cannot be applied directly to remove metals from industrial waste streams because of the relatively large pore size of the membranes. In general, ultrafiltration membrane processes are limited to the separation of pollutants with molecular weights from 300 to 300,000. In order to provide efficient separation of low molecular weight components of the mixture, such as heavy metals, membrane surface modification and/or the addition of surfactants may be necessary to increase the effective size of the metal ions. Christensen et al. (1982), studied the removal of heavy metals from electroplating rinsewaters by ultrafiltration. Zinc was removed, and the efficiency of the removal was strongly dependent on the pH of the waste stream. Strathman (1980) studied a process combining the macromolecular chelating agents or emulsified ion exchange resins with ultrafiltration for the selective removal of heavy metal ions from wastestreams. Rejections of 98% were obtained for cadmium and zinc. Goff and Benadda (1997) used ultrafiltration preceded by complexation to remove cadmium from industrial waste.

Micellar-enhanced ultrafiltration has also been proposed as a method for treating wastewater containing heavy metals (Huang and Kaseoglu, 1993). The underlying principle is to increase the size of the pollutant molecules so they can be removed when passed through a membrane with an appropriate pore size. A surfactant is added to a wastewater to promote the removal of smaller contaminants, such as heavy metals. Above a specific concentration level, called the critical micelle concentration (cmc), surfactant molecules will aggregate to form micelles. The metal ions are then bound electrostatically to the micelles. When this mixture is ultrafiltrated through a compatible membrane, the resulting permeate will contain a low concentration of heavy metals. The concentration of residual surfactants present in the permeate is usually around 100 ppm. This concentration may be high for discharge to the environment.

Major limitations associated with the use of membrane processes include; membrane fouling, and the limited life of the membrane, caused dissolution or degradation of the membrane by strong oxidizing agents, solvents or other organic compounds.

Solvent extraction or liquid-liquid extraction is an industrial process of separation of the components of a solution by preferential distribution between two immiscible liquid phases (Sedvic and Meider-Gorican, 1972; Fitoussi and Musikas, 1980, Curtui and Haiduc, 1981). Solvent extraction makes it possible to transfer selectively certain ionic species present in an aqueous solution to an organic solvent. A metal-bearing aqueous feed solution is contacted with an extractant-containing, non-polar organic phase so that a metal-extractant complex forms. Since these complexes are more soluble in the organic diluent, the metal transfers to the organic phase. Solvent extraction technology has been used for the separation and concentration of metals from terrestrial or oceanic sources as well as from industrial wastewaters. Examples of some metals extracted by solvent extraction are Cu, U, Co, Ni, Cr and Nb. The solvent extraction process becomes uneconomical in the handling of large volumes of solutions containing low metal concentrations since a large volume of solvent is necessary. This process has problems such as phase separation difficulties and reagent losses.

The use of liquid membranes containing a carrier material has been proposed as an alternative to solvent extraction for the selective separation and concentration of metals from dilute solutions (Weiss et al., 1982; Fuller and Li, 1984; Kim, 1984; Cox et al.,1987). A liquid membrane is a thin liquid film which acts as a diffusional barrier between the phase containing the species to be removed and the stripping phase. Unlike traditional membranes, liquid membranes extract a target pollutant from bulk solution by chemistry rather than by size. In many ways, liquid membranes is similar to solvent extraction. The supported liquid membrane is placed between the feed solution and the stripping solution (Danesi et al, 1984 & 1987; Chiarizia et al., 1990). For permeation to proceed, the metal in the continuous aqueous phase must find its way to the aqueous-membrane interface where the formation of metal-carrier complex occurs. The complex then diffuses across the membrane to the other side where it decomposes to recover the metal and to regenerate the carrier. This method is still immature and substantial research is needed before it becomes a viable alternative.

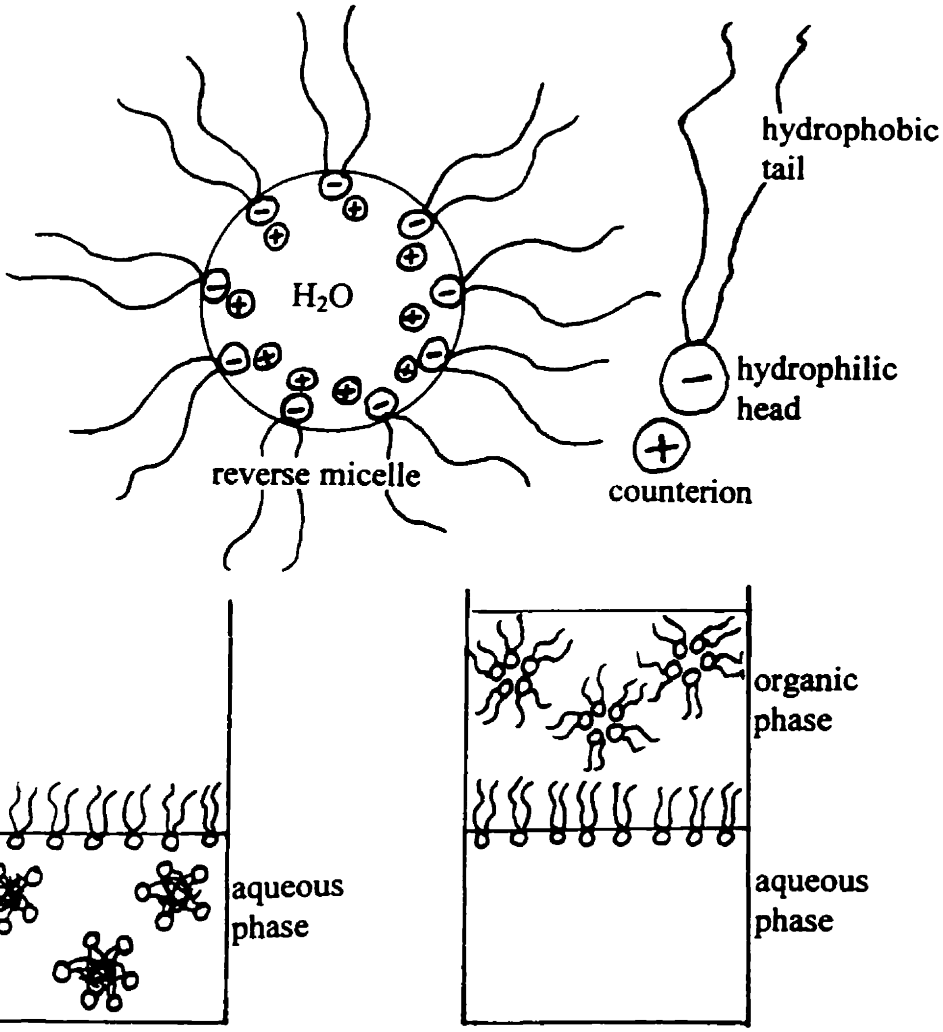
A combination of solvent extraction and ion exchange was developed by the introduction of solvent impregnated resins (Kauczor and Meyer, 1978; Warshawasky, 1981; Zipperian and Raghavan, 1985). In this approach, the extractant molecules are adsorbed onto a high surface area, macroporous polymeric support to produce solvent impregnated resins. In this process, the carrier (extractant) is immobilized and the feed solution is continuously fed and withdrawn.

Recently, reverse-micellar systems have been used to extract metal ions from aqueous solutions. (Goaker and Neuman, 1987; Osseo-Asare 1988; Paatero et al., 1990; Ashrafizadeh et al., 1993). Reverse micelles are thermodynamically stable isotropic mixtures that typically consist of four components: surfactant, co-surfactant, organic solvent, and aqueous salt solution. Surfactants are compounds containing hydrophilic and hydrophobic groups in the same molecule. These molecules tend to aggregate at the interface between an aqueous phase and other phases of the system where they reduce the surface or interfacial tension. Surfactants are generally classified by the charge of their hydrophilic groups as anionic, cationic, and nonionic. The hydrophobic group generally is a radical containing from 10 to 20 carbon atoms in a single or double chain configuration. In the presence of water, surfactants can associate into a variety of structures such as micelles, reverse micelles, and bilayers. The intermolecular forces that keep the aggregates together arise from weak van der Waals forces, hydrophobic interactions, screened electrostatic interactions and hydrogen bonds.

At relatively high concentrations in water, aqueous-soluble surfactants self-associate to form micelles which are aggregates characterized by a non-polar core formed by the hydrocarbon groups and hydrophilic groups facing outwards towards the water. When this aqueous solution contacted with organic phase, the surfactant molecules could migrate to the organic phase and aggregate forming reverse micelles. The reverse micelle is a water core surrounded by amphiphilic groups oriented towards the core and the hydrocarbon groups outwards towards the organic phase as shown in Figure 1.1. Water plays a decisive role in the formation of reverse micelles, and they are formed only with the mediation of water. The surfactant molecules could aggregate in bilayers forming a middle phase in equilibrium with an excess organic phase and an excess aqueous phase. The transition from micellar to reverse-micellar system is generally driven by a decrease of the surfactant hydrophilicity. Increasing the salinity of the aqueous constituent or adding medium-chained alcohol (cosurfactant), decrease the surfactant hydrophilicity.

The reverse-micellar system has the ability to transfer hydrophilic solutes from the aqueous phase into organic phase thereby circumventing the usually slow dehydration step at the interface between the organic phase and the excess aqueous phase (Osseo-Asare, 1988). In metal extraction research, the use of reverse micelles is gaining attention. These systems, when compared with solvent extraction processes, have been found to enhance both the percent extraction as well as the rate of extraction (Paatero and Sjoblom, 1990).

The foam flotation process may be described as the removal of a colloidal particle and its adsorbed material by flotation with a surfactant. Adsorbing colloid foam flotation involves the addition of a coagulant, usually ferric chloride or alum, to form a floc, usually positively charged. The dissolved heavy metals are then adsorbed onto the floc particle and/or coprecipitate with it. The addition of a surfactant of opposite charge, renders the floc particles hydrophobic, and the floc (with the adsorbed metal) is removed by air flotation, (McIntyre et al., 1983).



(a) (b)

Figure 1.1: Aggregation of surfactants:

(a) micelles; (b) reverse micelles

Ferguson et al. (1974) and Slapik et al. (1982) used foam flotation process to remove heavy metals from aqueous systems.

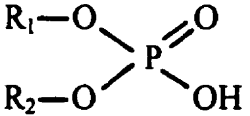
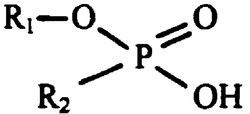
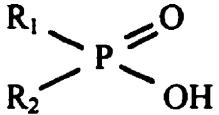
Biosorption is a technique in which biomass adsorbs ions from solution. It appears to offer considerable scope for applications in water purification as well as in hydrometallurgy. These processes and their applications have been reviewed by Vegliò and Beolchini (1997) and by Volesky (1990).

The increasing need to recover heavy metals from wastewater, requires the development of new separation processes that overcome the disadvantages of the present techniques. In this context, the objective of the present work was to investigate the removal of lead, cadmium and zinc from aqueous solutions by new separation technique that is believed to overcome some of the problems associated with other methods. In this technique, an organophosphorus compound, sodium di-(n-octyl) phosphinate, was used as the separating agent.

1.3- Sodium Di-(n-alkyl) Phosphinates and their Use in Separation Processes

Organophosphorus compounds fall into three distinct structural groups, namely: phosphoric, phosphonic and phosphinic acid-based derivatives having the structures shown in Table 1.1 (Danesi et al., 1985).

Table 1.1 : Organophosphorus compounds

Name	Structure
phosphoric	
phosphonic	
phosphinic	

The R1 and R2 groups are usually branched alkyl hydrocarbon chains, containing between eight and twelve carbon atoms. Organophosphorus reagents are well known in solvent extraction. These compounds are considered to be the most suitable extractants for the recovery and separation of cobalt and nickel from acidic leach solutions (Preston,1982; Rickelton, 1984; Danesi et al. 1985; Sastre et al., 1990). The sodium salts of these extractants are capable of solubilizing a large amount of water in organic solvents due to the formation of reverse micelles. Organophosphorus acids and/or their sodium salts, specifically, di-(2-ethylhexyl) phosphoric acid and di-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) form reverse micelles (Faure et al., 1985; Bhattacharyya 1987; Paatero and Sjoblom, 1990; Khoshkbarchi, 1994). Nickel is known to be extracted by di-(ethylhexyl) phosphoric acid and by its sodium salt reverse micelles (Neuman and Park, 1992). Di-(n-octyl) phosphinic acid has been used as an extractant in solvent extraction processes using aromatic solvents such as benzene and toluene (Peppard et al.,1965; Elizalde et al., 1987).

1.4 Behavior of Heavy Metals in Aqueous Solutions

Many metal ions form complexes in solution with a variety of substances that have free electrons capable of satisfying the coordination number of the metal. These complexing agents, called the ligands, could be inorganic or organic compounds. The behavior of heavy metals in aquatic system is largely governed by the speciation (the existing species and their concentrations). Speciation influences heavy metal availability and toxicity, its transportation and mobilization , and its interaction with the environment. The factors that influence the speciation of the heavy metals in water are: solubility of the compound, availability of the complexing agent, complex formation, ion-pair formation, adsorption or desorption onto particulate material, the redox and pH conditions of the environment (Hahne and Kroontje, 1973). The choice of a treatment method for a particular wastewater requires a knowledge of the speciation of the system.

When organic ligands are not available or their concentrations are low, metal ions are normally hydrated with water molecules, and combined with hydroxyl ions or chlorine ions to form hydroxo- or chloro- complexes (Hahne and Kroontje, 1973; Long et al. 1977; Stumm and Morgan, 1981). Some of the likely inorganic species of lead in water are; $PbOH^+$, $Pb(OH)_2$, $PbCl^+$, and $PbCl_2$. Only in acidic conditions or at low chloride concentration, is the Pb^{2+} ion likely to be present in reasonable amounts. In basic conditions, or at high chloride concentrations, $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, $PbCl_3^-$, and $PbCl_4^{2-}$ are expected to be present. At high lead concentration and high pH, polynuclear hydro-complexes such as $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ are expected to be present (Olin, 1961). The speciations of cadmium and zinc are similar to that of lead (Stumm and Morgan, 1981).

In general, because various species in aqueous solution are in a formation-dissociation equilibrium, displacement reactions of one metal or ligand by another are possible. Since different metal-ligand complexes have different stabilities in aqueous solutions, the extent of displacement and formation depends on the relative stabilities of the complexes in water.

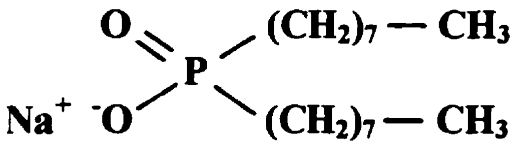
The formation and existence of complex species affect the thermodynamic as well as the kinetic behavior of metal ions in aqueous solutions. A quantitative determination of the distribution of various species in the system would provide valuable insight into reaction mechanisms and equilibrium states. Various theoretical approaches have been proposed for determining the speciation of specific elements in different aqueous systems. In general, there are two methods to calculate the equilibrium state of a multicomponent system: the 'free energy minimization' and the "equilibrium constant" methods, (Papangelakis, 1993). The "free energy minimization" method is employed in F.A.C.T (Facility for the Analysis of Chemical Thermodynamics),and HSC (Outokumpu HSC Chemistry for Windows).

Several models have been proposed show the changes in chemical speciation that accompany changes in ionic strengths or in the concentrations of the individual ions (Jansz, 1983; Papangelakis, 1993; Filippou et al., 1995). Use of these models usually involves simultaneous solution of several mass balance and complexation equilibrium equations using stability constant data.

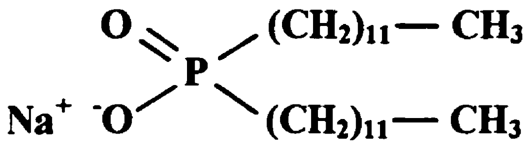
1.5 Motivation

In solvent extraction using organophosphorus extractants, both the chain structure and the head group have effect on the metal extraction, on the selectivity of different ions, and on the solubility of the extractant in water. The sodium salts of di-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), di-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex301), and di-(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex302), are capable of solubilizing large amounts of water in an organic phase in the form of reverse micelles (Khoshkbarchi, 1994). The effects of the chain length and the chain structure of the surfactant on reverse-micellar systems have not been investigated. Branching increases the solubility of the hydrocarbons in water. Increasing the chain length of n-alkane decreases its solubility in water. Using a surfactant with straight long chains in reverse micellar systems, is expected to reduce its solubility in water, and hence its residual concentration in the treated aqueous phase.

Based on these factors, two organophosphinic compounds: di-(n-octyl) and di-(n-dodecyl) phosphinic acids were synthesized and purified, and then converted to their sodium salts. The structures are shown in Figure 1.2. The first compound



Sodium di-(n-octyl) phosphinate (NaL)



Sodium di-(n-dodecyl) phosphinate (NaL_D)

Figure 1.2: Structure of the separating agents studied in this work

was used as the main separating agent in this work, while the second compound was used to investigate the effect of the chain length of the separating agent on the removal of heavy metals. It was first decided to test the extraction of heavy metals from aqueous solutions using reverse micelles of these anionic surfactants. Reverse micelles were formed with sodium di-(n-octyl) phosphinate and the preliminary experiments performed to extract heavy metals from aqueous solutions showed that this particular surfactant precipitated the heavy metal into the aqueous phase instead of extracting it to the reverse micellar phase. The phases were separated and analyzed. Based on the results of these analyses, the direction of the research is shifted toward the use of sodium di-(n-octyl) phosphinate as a precipitating agent. The formation of reverse micelles with this surfactant is described first, in chapters 2 & 3, due to its intrinsic novelty and to the possibility of using these reverse micelles in other applications.

1.6 Objectives

The prime objective of this work was to try to develop a process which can produce consistent and reproducible residual concentrations of lead, cadmium and zinc below the maximum accepted level for wastewater effluents. In North America, the levels are in the range of (0.2-2), (0.001-1), and (0.2-5 ppm) for lead, cadmium, and zinc, respectively. Calcium is a common ion in wastewater and may consume the separating agent. Thus, this process must be selective for heavy metals over calcium, and it should have the ability to remove heavy metals from different media at different conditions. A second objective was to regenerate the separating agent and to reduce its loss. A third objective was to develop a model which predicts the concentration of the species at equilibrium, from which the percentage removal and the equilibrium pH can be calculated.

After some preliminary trials, a detailed study of the precipitation of lead with sodium di-(n-octyl) phosphinate was conducted. The effect of the pH of the feed, the concentration of chloride and calcium in the feed, and the chain length of the precipitating agent were examined. In this study, solutions of lead and other cations in nitrate and chloride media are considered.

1.7 Outline of the Thesis

Chapter 2 describes the experimental work, including the chemicals used, the preparation and purification of the two di-(n-alkyl) phosphinic compounds, and the procedures followed for the formation of reverse micelles and for the removal of the heavy metals by precipitation as well as the regeneration of the precipitating agent. The analyses conducted for the di-(n-alkyl) compounds are included.

Chapter 3 presents the experimental results and discussion of the reverse micelles formation, and the removal of heavy metals by precipitation. The regeneration of the precipitating agent is also included in this chapter. The main part of this chapter describes the removal of lead, where the effect of some important variables on the removal of lead were investigated.

Chapter 4 presents a model for the calculation of the species concentrations in nitrate and in chloride aqueous solutions for a single metal and for a mixture of metals, where the " equilibrium constants " method was employed. The predictions of the model and their comparison with the experimental data are presented. The computational flowchart is presented in Appendix B.

The conclusions, claims to originality, and suggestions for future work are presented in chapter 5.

CHAPTER 2

EXPERIMENTAL WORK

2.1 Materials

The specifications and suppliers of all chemicals are listed in Table 2.1. The chemicals were used without further purification. Two compounds, di-(n-octyl) and di-(dodecyl) phosphinic acids, were synthesized and purified, and then converted to their sodium salts.

Di-(n-octyl) phosphinic acid was synthesized by the peroxide catalyzed reaction between 1-octene and hypophosphorus acid following the procedure described by Williams and Hamilton (1952) as modified by Peppard et al. (1965):

1- A mixture of 471 g of 1-octene, 264 g of "50%" aqueous hypophosphorus acid, 132 g of water, 700 mℓ of (95%) ethanol and 24.2 g of bezoyel peroxide was refluxed for 24 hr.

2- 500 mℓ of benzene and 2.0 ℓ of 1M HCl were added to the cooled mixture (approximately 20°C).

3- The lower (aqueous) phase was removed and the upper (benzene) phase containing the product was scrubbed with two 500 mℓ portions of 1M HCl. Benzene was then removed by evaporation.

Table 2.1 : Specifications and suppliers of the chemicals

Chemical	Specification	Company
benzoyl peroxide	97-99% (purity)	A&C (Montreal, QC)
cadmium nitrate $Cd(NO_3)_2.4H_2O$	≥ 99%	Anachemia (Montreal, QC)
calcium nitrate $Ca(NO_3)_2.4H_2O$	≥ 99%	A&C
decanol	A.C.S. (grade)	A&C
diethyl ether	A.C.S.	Anachemia
1-dodecene	≥ 99%	Sigma (Mississauga,ON)
ethanol	≥ 95%	Anachemia
n-heptane	A.C.S.	Anachemia
hydrochloric acid	A.C.S.	Anachemia
hypophosphorus acid, 50%	A.C.S.	Anachemia
isooctane	A.C.S.	Anachemia
lead chloride	≥ 99%	Anachemia
lead nitrate	≥ 99%	Anachemia
nitric acid	A.C.S.	Anachemia
1-octene	≥ 99%	A&C
sodium chloride	≥ 99%	Anachemia
sodium hydroxide	A.C.S.	Anachemia
sodium nitrate	≥ 99%	Anachemia
toluene	A.C.S.	Anachemia
zinc nitrate $Zn(NO_3)_2.6H_2O$	≥ 99%	Anachemia

4- The product was converted to its sodium salt by dissolution in 1.5 ℓ of 2M NaOH.

5- 2.0 ℓ of diethyl ether was added to the cooled solution (approximately 10°C). Following thorough agitation and subsequent phase disengagement, the lower phase was discarded.

6- The ether phase of the sodium salt of the product was scrubbed with six 1.0 ℓ portions of 1M NaOH. This step removed the single chain compound which is preferentially re-extracted into the aqueous NaOH.

7- The ether phase was then contacted with 1.0 ℓ of 3M HCl. Following removal of the lower aqueous phase, the ether phase containing the product in the acid form was scrubbed with two 1.0 ℓ portions of 1M HCl.

8- The ether phase was removed by evaporation, and a white precipitate (di-(n-octyl) phosphinic acid) was obtained. This product was purified by crystallization from n-heptane.

9- Finally, the pure di-(n-octyl) phosphinic acid was converted to its sodium salt by following steps (4-6). The lower (aqueous) phase was discarded, and the ether was removed by evaporation to produce a white precipitate of sodium di-(n-octyl) phosphinate.

Di-(n-dodecyl) phosphinic acid was synthesized using a method described by Haynes et al.(1984). In place of step 1 above, a mixture of 1-dodecene (48.81 g), aqueous hypophosphorus acid (9.24 g), water (10 mℓ), ethanol (45 mℓ), and benzoyel peroxide (3.88 g) was refluxed for 24 hr. The benzoyel peroxide was added in three equal portions at 3-hour intervals. Following Steps (2-9), pure sodium di-(n-dodecyl) phosphinate was obtained.

The melting points of di-(n-octyl) and di-(n-dodecyl) phosphinic acids were measured using a Gallenkamp Melting Point Apparatus (Gallenkamp, England). The melting point of di-(n-octyl) phosphinic acid was measured as 83± 1°C. Values of 85° C were reported by Williams and Hamilton (1952), 84.0±0.2°C by Peppard et al. (1965), and 82-83.5°C by Haynes et al. (1985). The melting point of di-(n-dodecyl) phosphinic acid was measured as 94±1°C. Values of 93.8-94.8°C were reported by Williams and Hamilton (1955), and 93.5°C by Haynes et al. (1985).

X-ray powder diffraction was used to identify the compounds and to obtain information about their structures and compositions. X-ray diffraction was performed on Philips PW 1050/25 X-ray powder diffractometer (Philips, Holand), using a PW 11300/00 line focusing goniometer. The signal was recorded with a PW 1965/30 scintillation counter. Both compounds were found crystalline, and gave some very strong peaks at a very low angles as shown in Figure 2.1. A search match was performed on the peak list of each sample, using the appropriate chemical restrictions, however, no match was found for any of them, which indicates that their diffraction patterns have not been included in the JCPDS (Joint Committee for Powder Diffraction Standards) database.

The presence of water in the compounds (water of hydration) was also tested using a thermogravimetric analysis technique. This analysis is used to determine changes in sample weight, which may result from chemical or physical transformations, as a function of temperature. The thermogravimetric analysis was carried on a Stanton Redcraft PL-STA 1500 DTA/TGA instrument (PL Thermal Sciences, Mundelein, IL). This instrument allows the simultaneous measurement

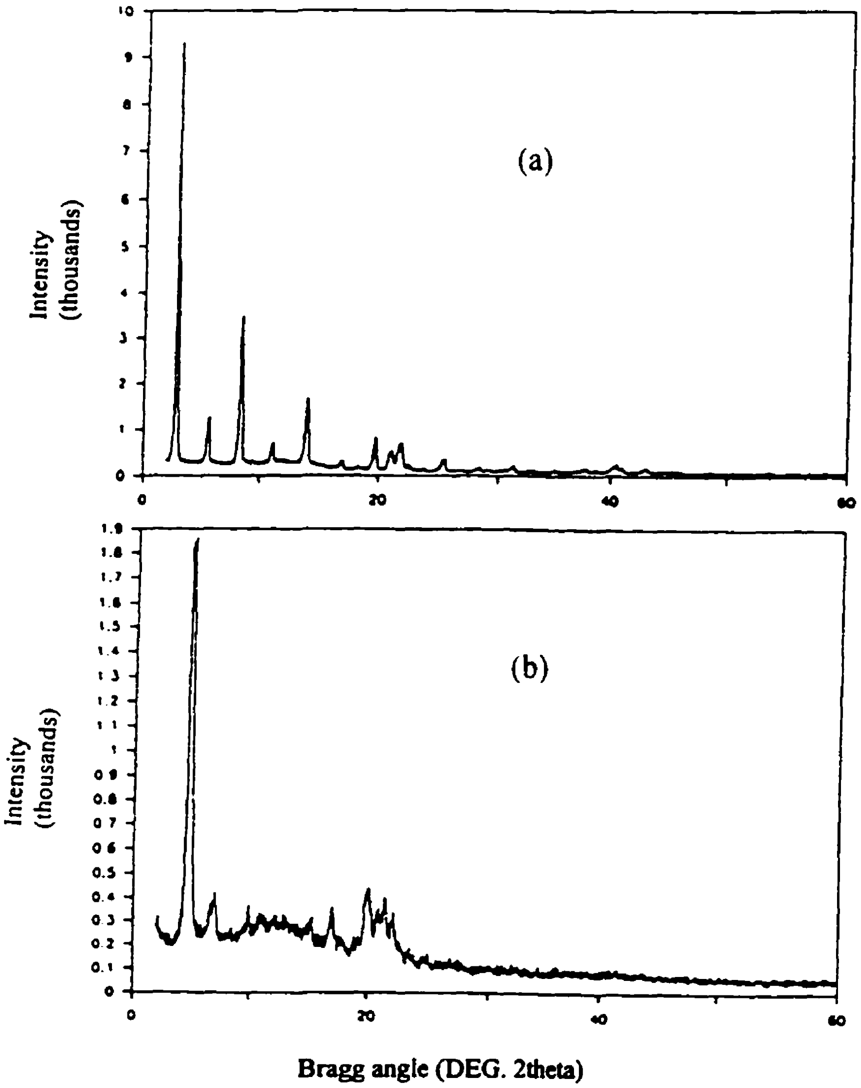


Figure 2.1: X-ray diffraction for: (a) di-(n-octyl) phosphinic acid, and (b) sodium di-(n-octyl) phospohinate

of the DTA signal (Differential Thermal Analysis), i.e. the difference of temperature between the sample and a reference, and of TGA signal (Thermogravimetric Analysis), i.e. the mass of the sample, when the temperature is varied. The two compounds were unlikely to be hydrated since no initial loss of mass was observed prior to the main decomposition as shown in Figure 2.2.

The purity of di-(n-octyl) phosphinic acid was determined by potentiometric titration of the acid in 75% aqueous ethanol with standard sodium hydroxide. The acid contained about 0.5% impurities. A test of the impurity was carried out by examining the ^{31}P- NMR of sodium di-(n-octyl) phosphinate, di-(n-octyl) and di-(n-dodecyl) phosphinic acids using Varian XL300 (Varian, Palo Alto, Ca) instrument with H_3PO_4 as an external standard. The samples of sodium di-(n-octyl)phosphinate were prepared in D_2O, and the samples of the two acids were prepared in $CDCl_3$. The ^{31}P spectrum, Figure 2.3, showed a single peak at 46.78 ppm for sodium di-(n-octyl) phosphinate, 60.63 ppm for di-(n-octyl) phosphinic acid, and 60.74 ppm for di-(n-dodecyl) phosphinic acid. Based on these analysis, it was concluded that the impurities of these compounds were not acidic and did not contain phosphorus.

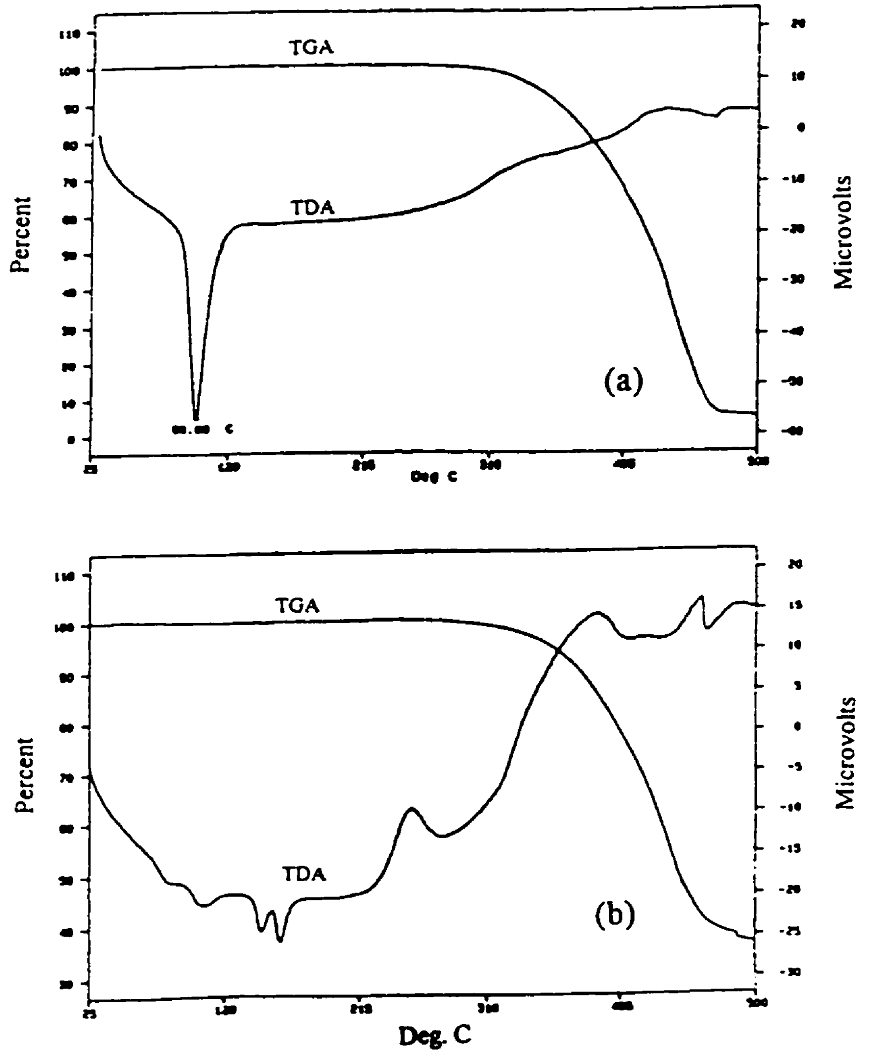


Figure 2.2: Thermogravimetric analysis for: (a) di-(n-octyl) phosphinic acid, and (b) sodium di-(n-octyl) phosphinate

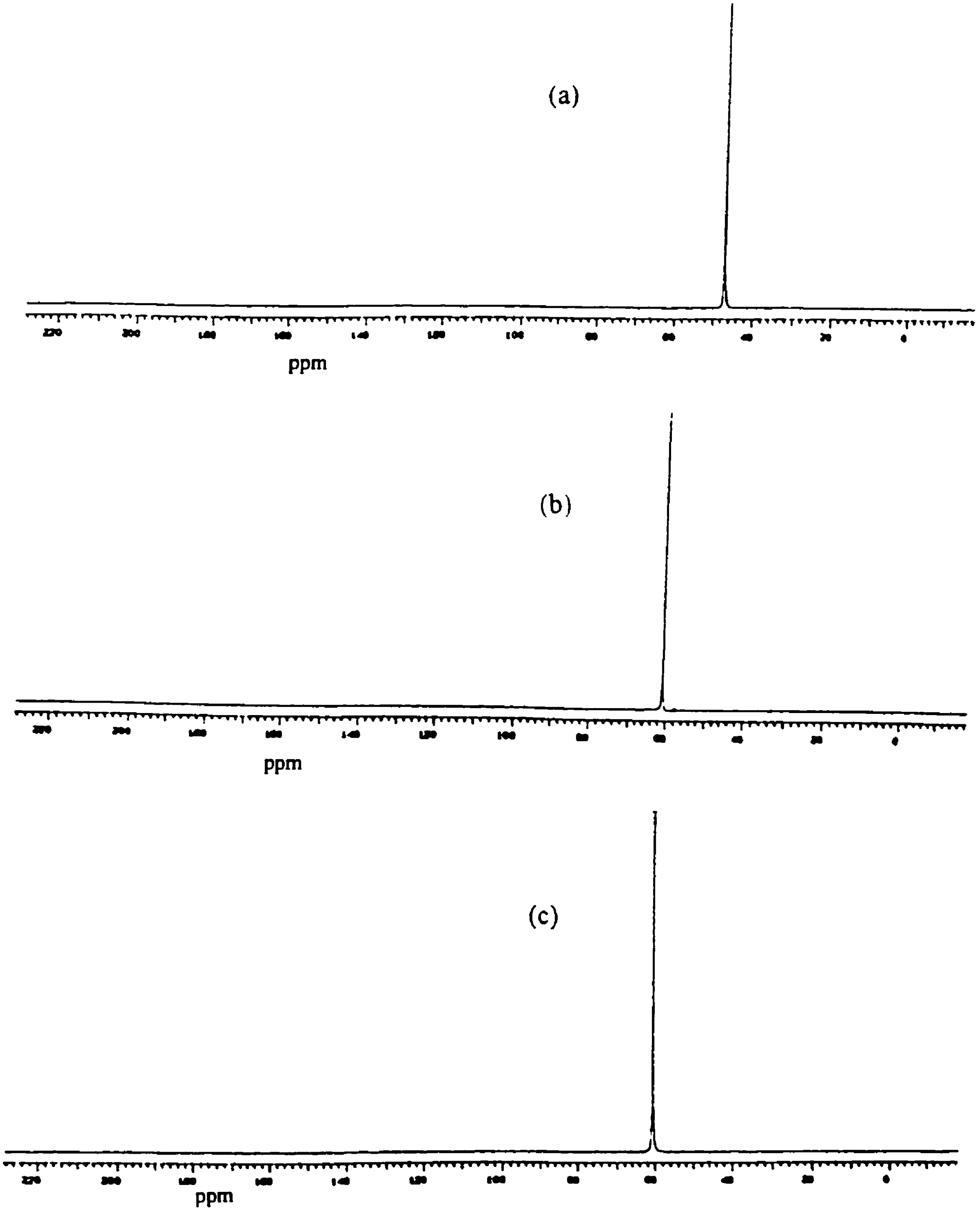


Figure 2.3: ^{31}P-NMR spectra of: (a) sodium di-(n-octyl) phosphinate; (b) di-(n-octyl) phosphinic acid, and (c) di-(n-dodecyl) phosphinic acid

2.2 Experimental Procedure

Di-(n-octyl) phosphinic acid is insoluble in water or in aliphatic hydrocarbons (e.g. iso-octane and decane). When the sodium di-(n-octyl) phosphinate and di-(n-octyl) phosphinic acid or the sodium di-(n-octyl) phosphinate and decanol were mixed in certain ratios and added to isooctane in contact with an aqueous solution, they dissolved in the organic phase, forming reverse micelles. Sodium di-(n-octyl) phosphinate is soluble in water. When a solution of lead, cadmium or zinc was mixed with a solution of sodium di-(n-octyl) phosphinate, a precipitate was formed. Based on this, sodium di(-n-octyl) phosphinate was used as a surfactant and as a precipitating agent .

2.2.1 Reverse Micelle Formation

Reverse-micellar systems were formed using sodium di-(n-octyl) phosphinate as a surfactant and di-n-(octyl) phosphinic acid or decanol as a co-surfactant. The systems were made by contacting equal volumes (20 mℓ) of an aqueous electrolyte (NaCl) solution and the organic solvent (**isooctane**) containing the surfactant and cosurfactant. The experiments were carried out in 100 mℓ jars. The jars were placed on a vibrating shaker and agitated for 1 hr. at constant temperature (22±1 °C), and then left to reach equilibrium. When equilibrium was established, the water content in the organic reverse-micellar phase, was determined by Karl Fischer titration using a Ω Metrohm-Brinkmann Model 701/1 KF Titrino (Ω Metrohm, Herisau, Switzerland).

2.2.2 Removal of Heavy Metal by Precipitation

The experiments were carried out at 22±1°C. The feed solution (35 mℓ) at a certain pH containing the metal ion, calcium, and nitrate or chloride at specific concentrations was treated with an aqueous solution (5 mℓ) of the precipitating agent at a specific concentration. All solutions were prepared with distilled water. The pH adjustment of the solution was made before the precipitation by addition of HNO_3 or HCl solution. All samples were shaken in tightly closed jars and then left to reach equilibrium. The equilibrium was tested by analyzing the system at different times (5 minutes, 30 minutes, one hour, 2 hours, one day, 2 days, and one week) and the same results were obtained. At equilibrium, two phases existed: a white precipitate and a clear aqueous phase. The two phases were separated using Fisher brand fast flow filter papers. After phase separation, the equilibrium pH was measured using Ω Metrohm 691 pH Meter (Ω Metrohm, Herisau, Switzerland). The metal content of the filtrate was determined by atomic absorption spectrometry using a Thermo Jarrel Ash model SH 11 (Thermo Jarrell Ash, Waltham, MA) surface beam atomic absorption spectrophotometer. The wavelegths were 283.3, 228.8, 213.9, and 422.7 nm for lead, cadmium, zinc, and calcium, respectively. For concentrations below 1 ppm, the metal content was measured by an Inductively Coupled Plasma using a Thermo Jarrel Ash Trace Scan (Thermo Jarrell Ash, Waltham, MA) axial torch sequential ICP. The wavelengths used for lead, cadmium, and zinc were 220.3, 214.4, and 213.8 nm, respectively. The sensitivity of the inductively coupled plasma instrument is higher of at least 10 times than that of the atomic absorption spectrophotometer. The concentration of the precipitating agent in the aqueous phase was measured by a Dohrmann DC-183 Total Carbon Analyzer (Dohrmann, Santa Clara, CA), in combination with a Dohrmann DC-85 NDIR Detector module. The schematic diagram of the removal of the heavy metals is shown in Figure 2.4.

The same procedure was used to remove the mixture of the three metals. In the case of the mixture, a feed solution containing lead, cadmium , and zinc at about equal concentrations was treated with the precipitating agent.

The mole ratio of the precipitating agent, sodium di-(n-octyl) phosphinate, to metal(s) was found to affect the properties of the system at equilibrium. When the mole ratio was less than or equal to two, a clear aqueous phase and filterable precipitate were obtained. When the mole ratio was higher than two, the liquid phase was turbid and either centrifuging or filtration through a 0.45 μm Millipore filter paper was required to clarify the solution. Adding calcium nitrate or calcium chloride to the turbid solution was found to clarify the aqueous phase and to improve the filtration characteristics. Shaking and/or centrifuging the samples was also found to improve the filtration characteristics.

The solubility of the precipitates in distilled water at 22 °C was measured and the solubility products were determined (Appendix A). X-ray powder diffraction was used to identify the three precipitates, lead-, cadmium-, and zinc-di-(n-octyl) phosphinates. The lead and cadmium compounds, were crystalline, and gave strong peaks at very low angles, as shown in Figure 2.5. The zinc compound contains a small amount of microcrytalline material as well as a major non-crystalline component (Denes, 1997-a). A search match was performed on the peak list of each sample, but no match was found, which indicates that these materials were unknown or that their diffraction patterns were not included in the JCPDS database. In the thermogravimetric analysis of the three compounds, there was a slow, small mass loss prior to decomposition, as shown in Figure 2.6. This could be due to the presence of very tightly bound water molecules in the

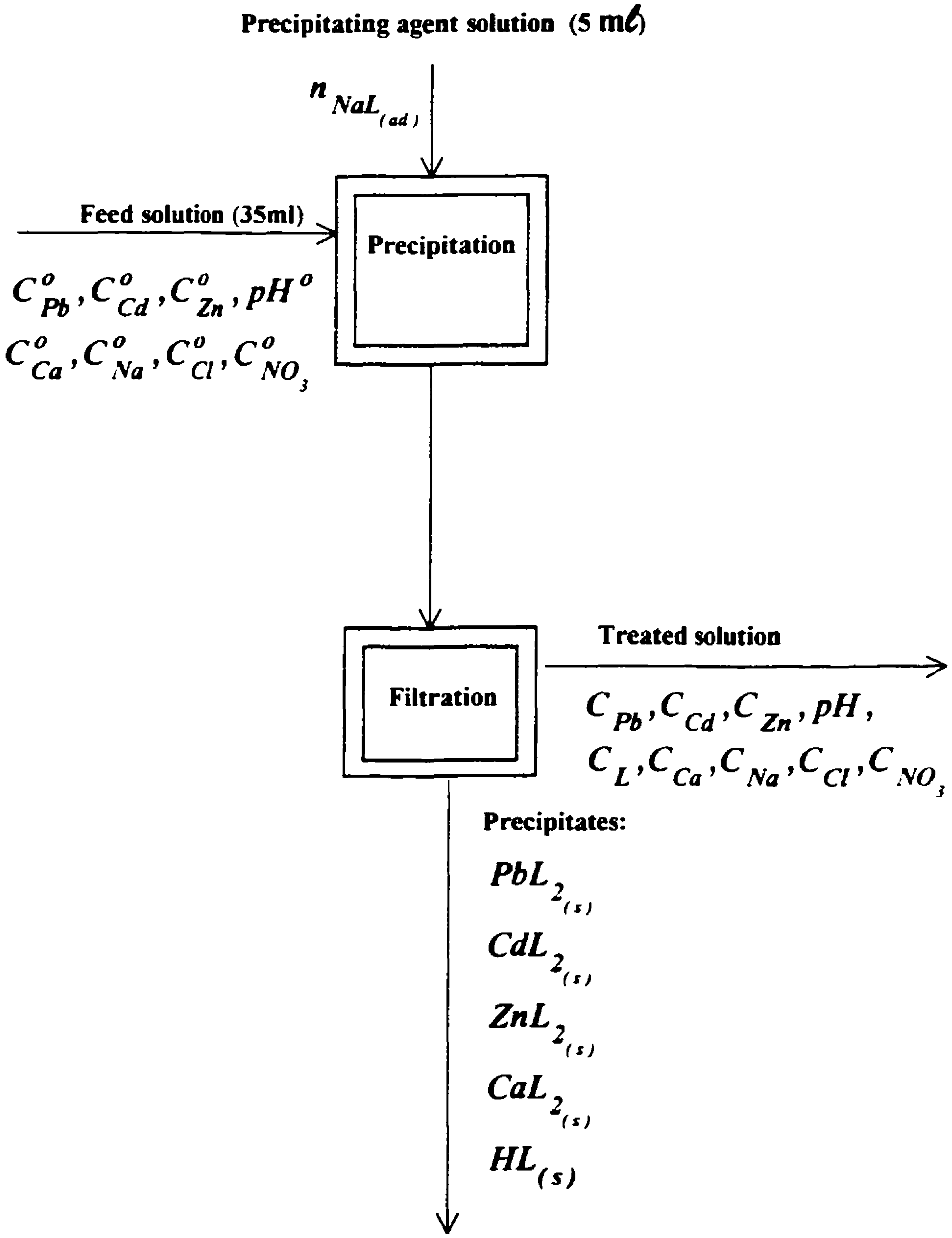


Figure 2.4 : Schematic diagram of the removal of the heavy metals

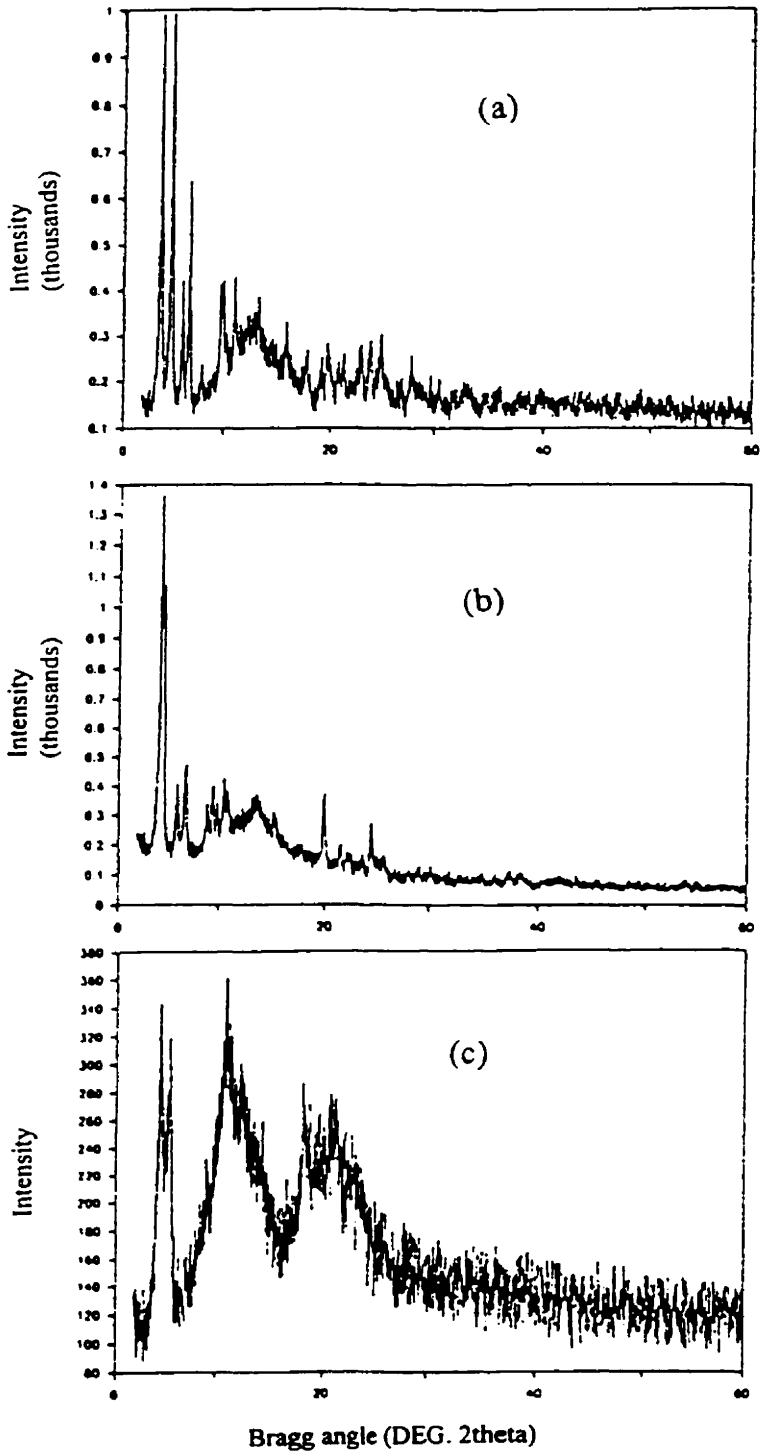


Figure 2.5: X-ray diffraction for, (a) lead di-(n-octyl) phosphinate, (b) cadmium di-(n-octyl) phosphinate, and (c) zinc di-(n-octyl) phosphinate.

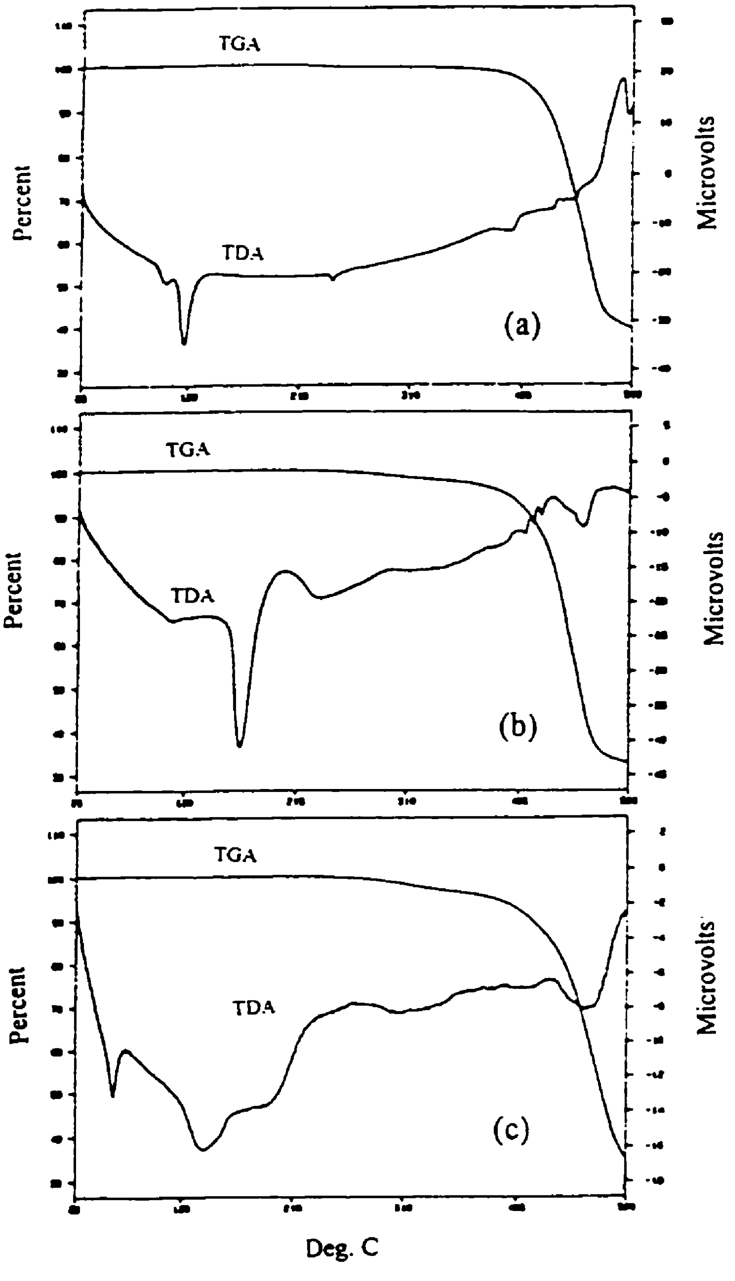


Figure 2.6: Thermogravimetric analysis for, (a) lead di-(n-octyl) phosphinate, (b) cadmium di-(n-octyl) phosphinate, and (c) zinc di-(n-octyl) phosphinate

solid lattice. The salt should be a hemihydrate, whereas the cadmium and zinc should be monohydrates (Denes, 1997-b). However, TGA alone cannot prove unambiguously that the initial slow small weight loss was due to dehydration. Infrared (IR) spectroscopy could confirm the presence of water in the samples.

2.2.3-Regeneration of the Precipitating Agent

After separating the precipitate from the aqueous phase, the precipitating agent was regenerated by adding 3M NaOH solution to the precipitate, followed by contact with diethyl-ether in a separatory funnel. After agitation and subsequent phase disengagement, two phases were present. The lower phase was an aqueous phase containing the metal with a concentration higher than that of the feed. The upper phase was the ether solution of the precipitating agent. The ether was evaporated, and sodium di-(n-octyl) phosphinate was regenerated. The regenerated compound was then analyzed for the metal content using the atomic absorption spectrometry. The schematic diagram of the regeneration process is shown in Figure 2.7.

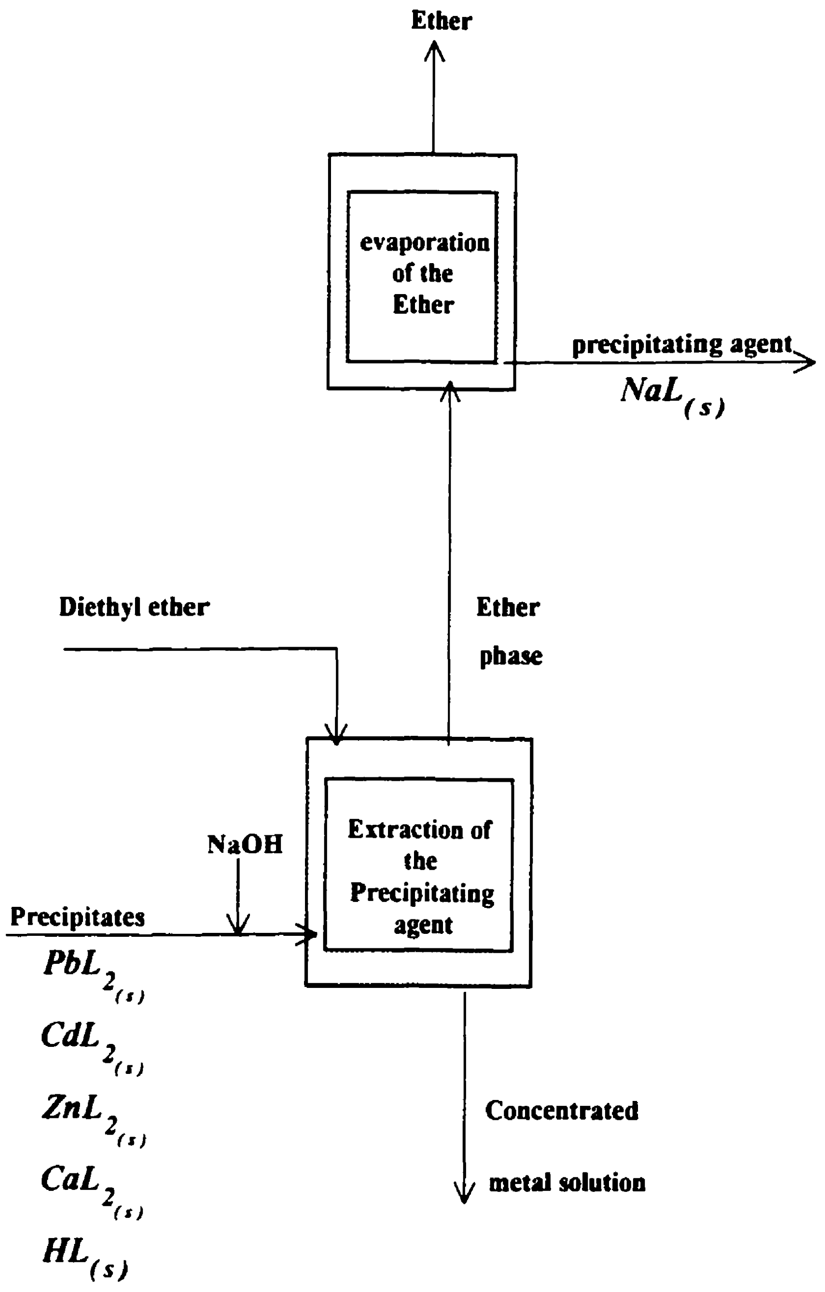


Figure 2.7 : Schematic diagram of the regeneration of the precipitating agent

CHAPTER 3

EXPERIMENTAL RESULTS AND DISCUSSION

The first section of this chapter presents the results obtained for sodium di-(n-octyl) phosphinate when it was used as a surface active agent, and the second section presents results for this compound when it was used as a precipitating agent. This chapter concentrates on the experiments conducted to precipitate heavy metals using sodium di-(n-octyl) phosphinate and the recovery of the precipitating agent.

3.1 Water Uptake of Sodium Di-(n-octyl) Phosphinate Reverse Micellar Systems

Experiments were conducted to study the effect of the nature and concentration of the cosurfactant on the water uptake with sodium di-(n-octyl) phosphinate as the surfactant. Two different cosurfactants; decanol and di-(n-octyl) phosphinic acid were used. The effect of the concentration of the surfactant was also investigated. The data are presented on the figures in terms of water uptake in organic phase, expressed as mass %, versus the mole ratio of cosurfactant to surfactant. Three replicates were run for each experiment. The maximum value of the 95% confidence intervals of the mass percentage of water uptake, was about ±3%.

3.1.1 Effect of Cosurfactant Concentration

Two cosurfactants, were investigated: decanol and di-(n-octyl) phosphinic acid. The concentration of the surfactant, and of the electrolyte, NaCl, were fixed at 0.15 m and 0.1 m, respectively. The water uptake results are shown in Figure 3.1. A minimum mole ratio of cosurfactant to surfactant was required to form reverse micelles and solubilize appreciable amount of water in the organic phase. The maximum water uptake was obtained at this critical mole ratio. The water uptake then decreased with increasing the mole ratio of cosurfactant to surfactant until a second critical mole ratio was reached above which no water was detected in the organic phase.

The formation of reverse micelles using non-ionic amphiphilic cosurfactant, such as decanol, can be explained by the cosurfactant screening of the repulsive forces between the charged head groups of the surfactant at the interfacial region of the reverse micelles. At a certain concentration of alcohol, the surfactant molecules aggregated in the organic phase and formed reverse micelles. The decrease of the water uptake by further addition of cosurfactant has been explained in different ways. One explanation is that the polarity of the organic solvent increases by increasing the alcohol concentration. This increase in polarity favored the solubilization of the surfactant molecules in the organic solvent, thus decreasing the number of surfactant molecules available to form reverse micelles and decreasing the water uptake (Khoshkbarchi, 1994). Krie and Hustedt (1991) explained the decrease of water uptake with increasing alcohol concentration as due to the decrease in the size of the reverse micelles caused by reducing the repulsion between the surfactant head groups, thus allowing closer packing of surfactant molecules. Leodidis and Hatton (1989) proposed that increasing the concentration of the alcohol at the interface of the water pool of the reverse

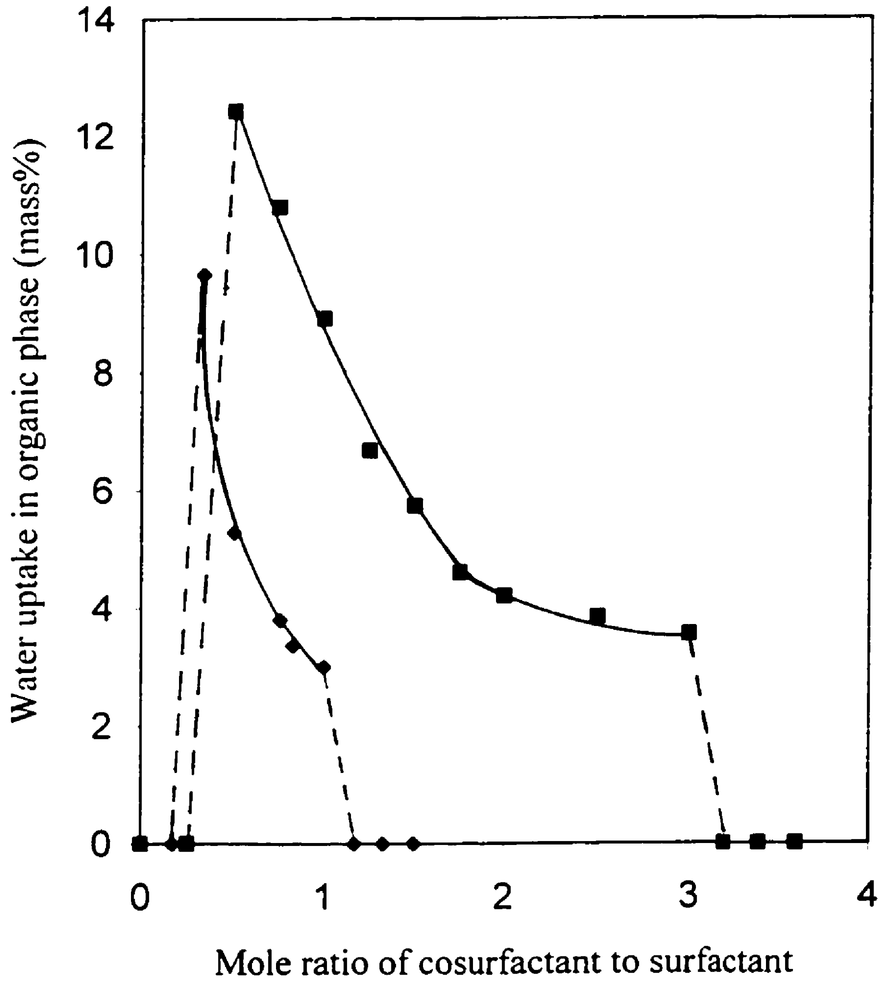
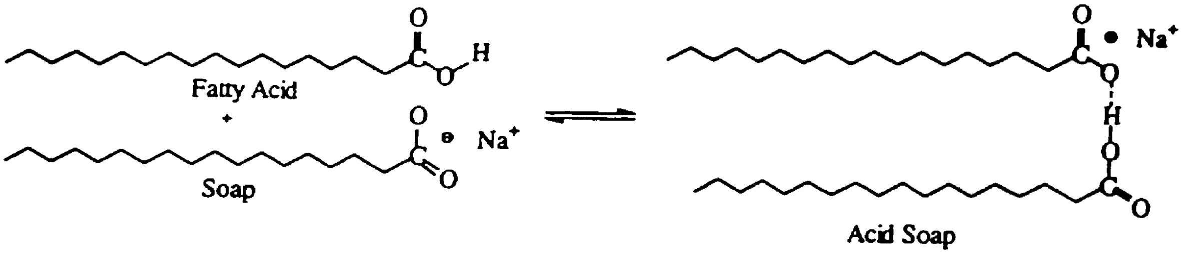


Figure 3.1: Effect of mole ratio of cosurfactant to surfactant. 0.15 m sodium di-(n-octyl) phosphinate at 0.1 m NaCl. (■) decanol; (◆) di-(n-octyl) phosphinic acid

micelle decreases the dielectric constant of the water pool. This decrease of the dielectric constant shifts the equilibrium of the surfactant from the ionic form to the undissociated form in the interfacial region of the reverse micelle. The undissociated form of the surfactant then migrates to the bulk organic phase, reducing the number of surfactant molecules constituting the reverse micelles and causing the decrease of water uptake (Wang et al., 1994).

When di-(n-octyl) phosphinic acid was used as a cosurfactant, similar behavior to decanol was observed, but with a smaller water uptake, as shown in Figure 3.1. Di-(n-octyl) phosphinic acid and its sodium salt are insoluble in aliphatic hydrocarbons. When mixed in certain ratios, they dissolve in isooctane. This behavior can be explained by the formation of an acid soap as described by Ekwall (1988) and by Laughlin (1994). The hydrolysis reaction of soaps produces, initially, fatty carboxylic acids. These fatty acids interact with soaps to form a number of compounds, which contain both molecules, and are commonly termed “acid soaps”. The equation for formation of the 1:1 acid soap is (Laughlin, 1994),



Acid soaps have been prepared in which the soap/ acid mole ratio is 1/2, 1/1, and 2/1. Ekwall (1969), attributed the high solubility of the sodium caprylate in caprylic acid to the formation of a soluble molecular compound. Its composition was established by viscosity measurement and infrared examination. He found that caprylate and caprylic acid molecules are bound to each other by an extremely firm hydrogen bond. Ekwall (1969) formed reverse micelles in ternary systems composed of water, soap and liquid fatty acid or alcohol. In three-component systems consisting of sodium caprylate (soap), caprylic acid (fatty acid), and water, reverse micelles were formed in caprylic acid media. The condition for the formation of this type of micellar system is the interaction between the two amphiphilic components to form a molecular compound that remains stable in the presence of water (Ekwall, 1969). These reverse micelles are composed of acrylic acid- sodium acrylate molecules with the composition $1NaC_8$ $.2HC_8$, around a water core. The components of the acid soap are linked by direct hydrogen bonds, and the acid soap molecules in the reverse micelles are linked via water molecules, which are bound to the sodium ions by ion-dipole forces, and to the carboxylate and hydroxyl groups by hydrogen bonds (Ekwall, 1969). Paatero and Sjoblom (1990), found that the sodium salt of di-(2,4,4-trimethyl pentyl) phosphinic acid can act as an anionic surfactant which can form reverse micelles in hexane with the aid of the free di-(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272). The maximum water uptake was obtained at mole ratio of sodium phosphinate/ phosphinic acid of 2/1. They concluded that while the sodium salt acts as the surfactant, the free acid is needed as a cosurfactant to modify the charge density at the aggregate interface, so that the reverse micelles can form.

3.1.2 Effect of Surfactant Concentration

The effect of surfactant concentration was studied by comparing two systems with different surfactant concentrations, at different mole ratios of cosurfactant to surfactant. The concentrations of surfactant were 0.15 m and 0.3 m. The concentration of sodium chloride was fixed at 0.1m. Decanol and di-(n-octyl) phosphinic acid were used as cosurfactants. The equilibrium water uptakes in the decanol system and in the di-(n-octyl) phosphinic acid system, are presented in Figure 3.2 and Figure 3.3, respectively.

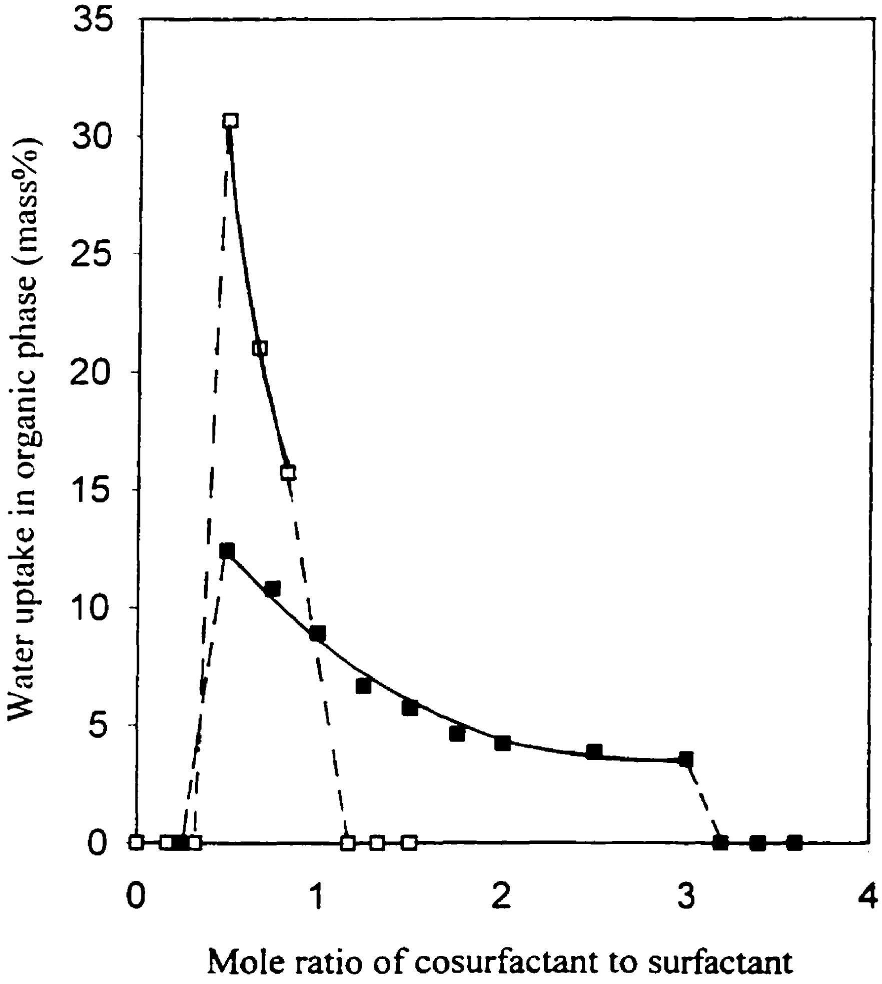


Figure 3.2: Effect of surfactant concentration on water uptake at different mole ratios of cosurfactant (decanol) to surfactant at 0.1 m NaCl.
(■) 0.15 m decanol; (□) 0.3 m decanol

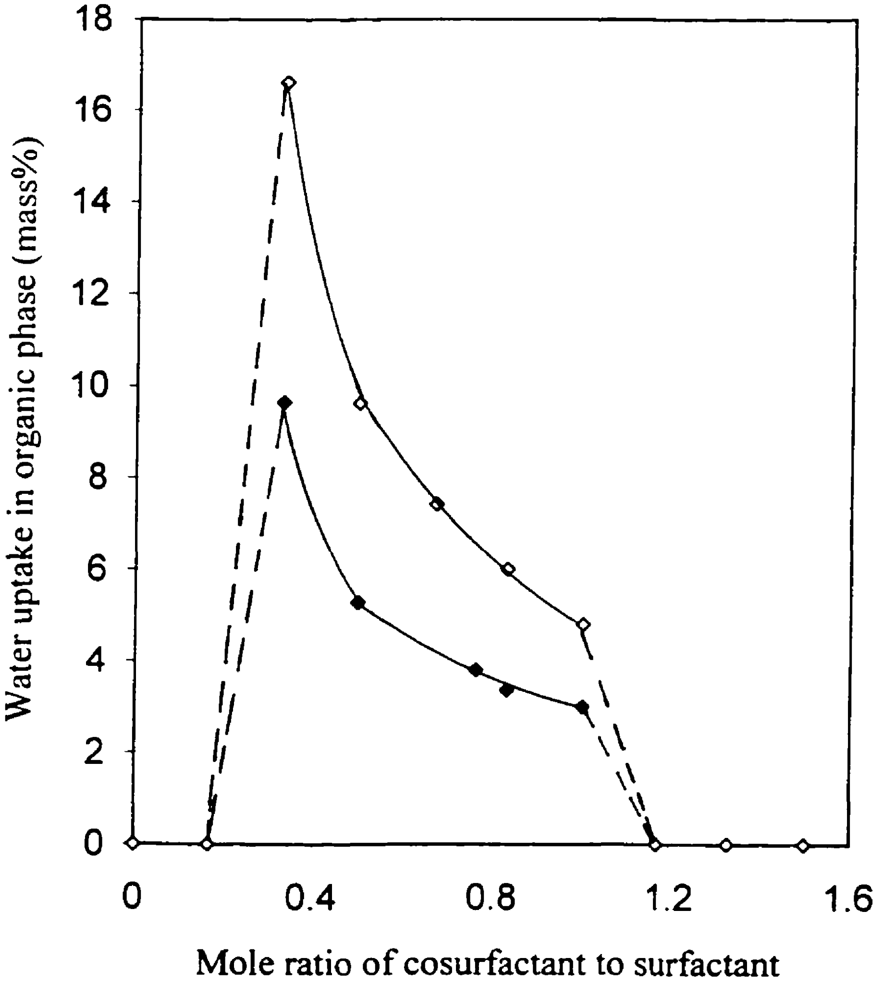


Figure 3.3: Effect of surfactant concentration on water uptake at different mole ratios of cosurfactant (di-(n-octyl) phosphinic acid) to surfactant at 0.1 m NaCl. (◆) 0.15 m di-(n-octyl) phosphinic acid; (◇) 0.3 m di-(n-octyl) phosphinic acid.

The water uptake increased with increasing surfactant concentration. The increase in the number of molecules of surfactant increased the number and/or size of the reverse micelles, thus increasing water uptake. For the decanol system, increasing the surfactant concentration: (1) increased the rate of the decrease in water uptake when the mole ratio of cosurfactant to surfactant increased, and (2) reduced the range of mole ratio of cosurfactant to surfactant in which water uptake in the organic phase was detected. For di-(n-octyl) phosphinic acid system, on the other hand, increasing the surfactant concentration had no noticeable effect on the rate of decrease in water uptake nor on the range of mole ratio of cosurfactant to surfactant in which water was solubilized in the organic phase. This difference in behavior between the two systems may be attributed to the formation of the acid soap type compound in the phosphinic acid system. As explained by Ekwall (1969), in the fatty acid system, the reverse micelles are composed of a molecular compound of soap and fatty acid linked by hydrogen bonds, and the relative amounts of the components in the micelles are constant. In the alcohol system, no molecular compounds are formed and the micelles are composed of the two amphiphilic components, and the relative amounts of components vary with the water-to-soap ratio.

Little attention has been paid to the formation of reverse micelles in metal extraction systems although some results demonstrate that reverse micelles enhance the rate of extraction (Gaonkar and Neuman, 1987; Neuman and Park, 1992). In this work, when the reverse micellar systems were contacted with aqueous solutions of lead, precipitates formed. The phases were separated and analyzed. The results of these analyses, shifted the direction of the research toward the use of sodium di-(n-octyl) phosphinate as a precipitating agent.

3.2 Removal of Heavy Metals by Precipitation

The first part of this section shows the effect of the mole ratio of the precipitating agent to lead, and describes the basis of this precipitation process. The second part studies the effects of feed variables, on the removal of lead. The effect of the chain length of the precipitating agent on the removal of lead was also investigated. The third part presents results for the removal of cadmium alone and zinc alone as well as for a mixture of the three metals. The nitrate salts of the metals were used in all cases, except when the effect of chloride concentration in the feed was studied. In this case, lead chloride was used. The last section describes the regeneration of the precipitating agent and the recovering of lead.

At least three replicates were run for each experiment. The maximum values of the 95% confidence intervals for the percentage removals of metal, the percentage loss of precipitating agent, and the equilibrium pH, were, ± 3%, ± 2%, and ±0.2, respectively. The concentrations of the species are expressed in molarity and/or parts per million by mass.

The data are presented on the figures in terms of percentage removal of the metal, percentage loss of the precipitating agent, and equilibrium pH versus each of the independent variables. The percentage removals of lead, cadmium, and zinc; R_{Pb}, R_{Cd}, and R_{Zn}, are defined as

$$R_{Pb} = \frac{C^*_{Pb} - C_{Pb}}{C^*_{Pb}} \times 100 \tag{3.1}$$

$$R_{Cd} = \frac{C^*_{Cd} - C_{Cd}}{C^*_{Cd}} \times 100 \tag{3.2}$$

$$R_{Zn} = \frac{C^*_{Zn} - C_{Zn}}{C^*_{Zn}} \times 100 \tag{3.3}$$

and the percentage loss of the precipitating agent; L_L, is defined as,

$$L_L = \frac{C_L}{C_L^*} \times 100 \tag{3.4}$$

3.2.1 Removal of Lead

A feed solution of 5.5 mM (1140 ppm) lead, at $pH^o = 4.2$, was treated with sodium di-(n-octyl) phosphinate. The percentage removal of lead and the percentage loss of the precipitating agent are shown in Figure 3.4 for different mole ratios of the precipitating agent to lead. The removal of lead was increased linearly up to a value of the mole ratio of two. At a mole ratio of two, the highest percentage removal with the lowest loss of precipitating agent was observed. The equilibrium concentrations of the lead and of the precipitating agent at this point were, 0.13 ± 0.04 ppm, 4.5 ± 0.1 ppm, respectively. At higher mole ratios, an increase in the mole ratio increased the loss of the precipitating agent and had no noticeable effect on the percentage removal of lead.

Based on these results, the stoichiometry of the overall precipitation reaction is believed to be:

$$Pb^{2+} + 2L^- \longleftrightarrow PbL_{2(s)} \qquad R-3.5$$

Aqueous solutions of lead salts are acidic. The decrease in the pH, when lead nitrate was added to water initially at $pH \approx 7$, resulted from the hydrolysis of Pb^{2+}, forming hydroxo-complexes and producing free protons according to the reactions;

$$nH_2O \longleftrightarrow nH^+ + nOH^- \qquad R-3.6$$

$$Pb^{2+} + nOH^- \longleftrightarrow Pb(OH)_n^{2-n} \qquad R-3.7$$

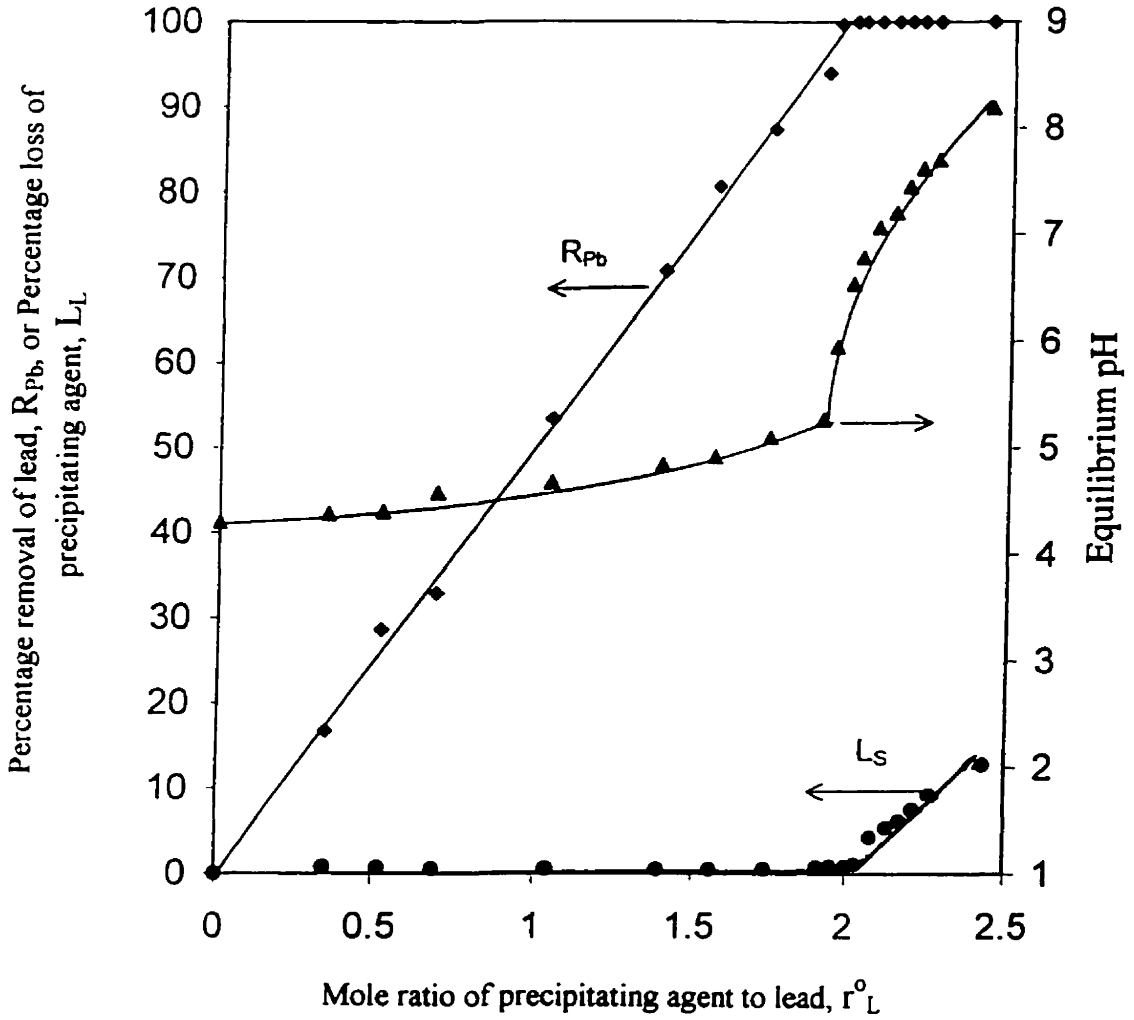


Figure 3.4: Effect of mole ratio of sodium di-(n-octyl) phosphinate to lead on the removal of lead, the loss of precipitating agent, and the equilibrium pH.

$C^o_{Pb} = 5.5$ mM, $pH^o = 4.2$, $r^o_{NO_3} = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

where n=1, 2, 3, and 4. The superscript (2-n) represents the charge of the complex.

The equilibrium pH was increased by increasing the mole ratio of the precipitating agent to lead. Up to a mole ratio of 2, the small increase observed in pH was due to reaction R-3.5, and the complex dissociation in reaction R-3.7, where consumption of Pb^{2+} in reaction R-3.5 shifted the reaction R-3.7 to the left. The sudden increase in pH at mole ratios above 2, was due to the formation of di-(n-octyl) phosphinic acid:

$$H^{+} + L^{-} \longleftrightarrow HL_{(s)} \qquad R-3.8$$

The percentage removal of lead and the equilibrium pH are shown in Figure 3.5 for three feed concentrations of lead: 0.46 mM (95 ppm); 5.50 mM (1140 ppm); and 10.62 mM (2200 ppm). The results are plotted as the percentage removal of lead and the equilibrium pH, versus the mole ratio of the precipitating agent to lead. At any specific mole ratio, increasing the concentration of lead in the feed had no effect on the percentage removal of lead, due to the stoichiometry of reaction R-3.5. The decrease in the pH caused by the increase of the lead concentration resulted from the hydrolysis reactions R-3.6 and R-3.7, where the concentration of hydrogen ions in the solution was increased. This behavior continued until a mole ratio of 2. At this mole ratio, the three systems gave the same equilibrium pH. The increase in pH with increasing feed lead concentration at mole ratios above 2 was caused by the increase of the amount of the precipitating agent added, which caused an increase of the amount of $HL_{(s)}$ formed, by the reaction R-3.8.

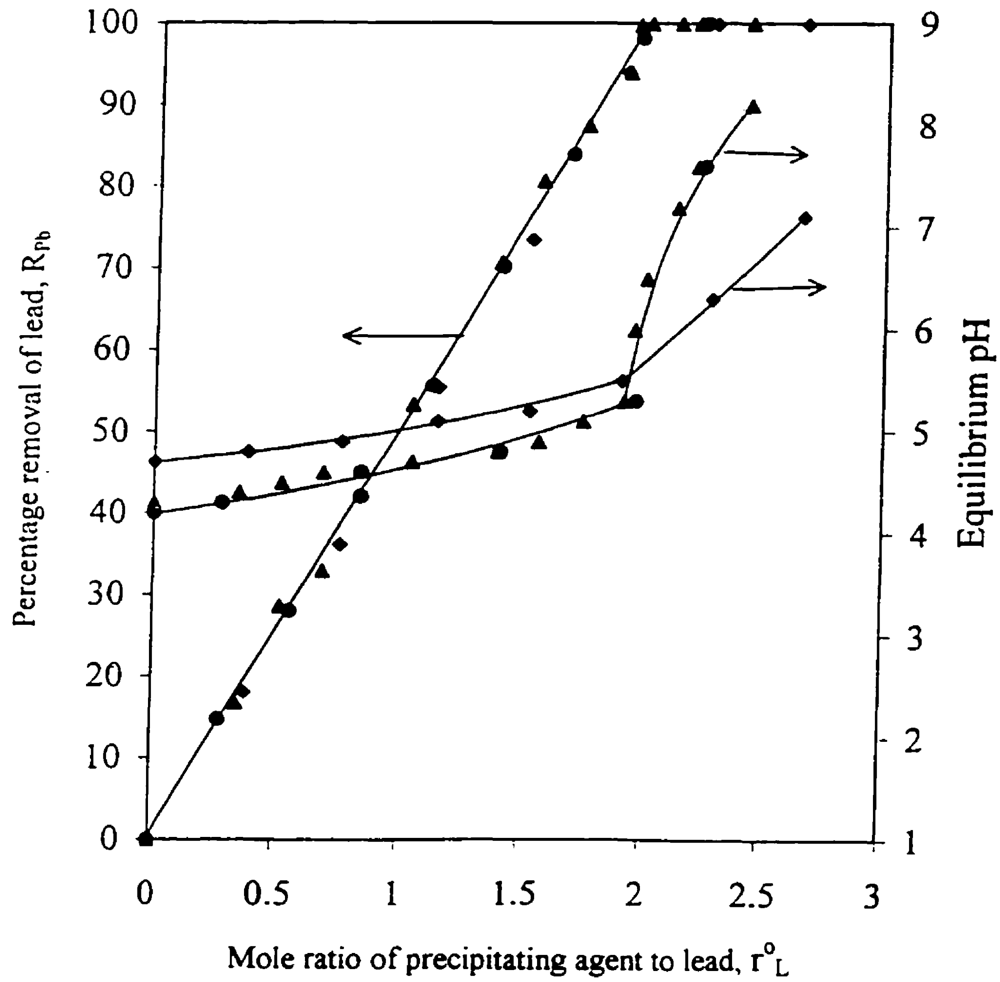


Figure 3.5: Effect of mole ratio of sodium di(n-octyl) phosphinate to lead on the removal of lead, and the equilibrium pH, at different feed concentration of lead. (♦)$C^o_{Pb_{(1)}}$ = 0.46 mM, $pH^o_{(1)}$ = 4.6; (▲)$C^o_{Pb_{(2)}}$ = 5.5 mM, $pH^o_{(2)}$ = 4.2; (●)$C^o_{Pb_{(3)}}$ = 10.62 mM, $pH^o_{(3)}$ = 4.1; $r^o_{NO_3}$ = 2.0, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

3.2.1.1 Effect of pH of the Feed

The effect of a decrease of the pH of the feed from 4.2 to 1.3 on the removal of lead and on the equilibrium pH was investigated. The pH of the feed was adjusted by adding HNO_3 solution. The concentration of lead in the feed was 7.1 mM (1460 ppm), and the mole ratio of the precipitating agent to lead (r_L^o) was 2.0. As shown in Figure 3.6, decreasing the pH of the feed (pH^o), decreased the percentage removal of lead and the equilibrium pH. The decrease in percentage removal of lead was due to the competition between lead and hydrogen ions for the ligand L^-, and the precipitation of the acid form ($HL_{(s)}$) according to reaction R-3.8. The decrease in pH was caused by the free acid left in the system. The equilibrium pH was higher than pH of the feed due to the precipitation of the acid (reaction R-3.8), and the hydroxo-complexation (reaction R-3.7).

Three sets of feed samples having the same lead concentration 6.75 mM (1400 ppm), and pH values of 4.1, 1.9, and 1.6, respectively, were compared at different mole ratios of precipitating agent to lead. No acid was added to the first set, and the initial pH of the other two was adjusted by adding nitric acid. The mole ratio of the precipitating agent to lead, r_L^o, was varied from 0 to 6.4. The percentage removal of lead, and the equilibrium pH plotted versus r_L^o are presented in Figure 3.7. For the first set of samples ($pH^o = 4.1$), because of low hydrogen concentration, only lead was precipitated as $PbL_{2(s)}$ according to reaction R-3.5. The highest percentage removal of lead was obtained at $r_L^o=2.0$. Addition of acid to the other sets ($pH^o = 1.9$, and $pH^o = 1.6$), reduced the removal of lead because an amount of acid precipitated as $HL_{(s)}$(reaction R-3.8). The highest percentage removal of lead for each set was obtained at different r_L^o for each set. The lower

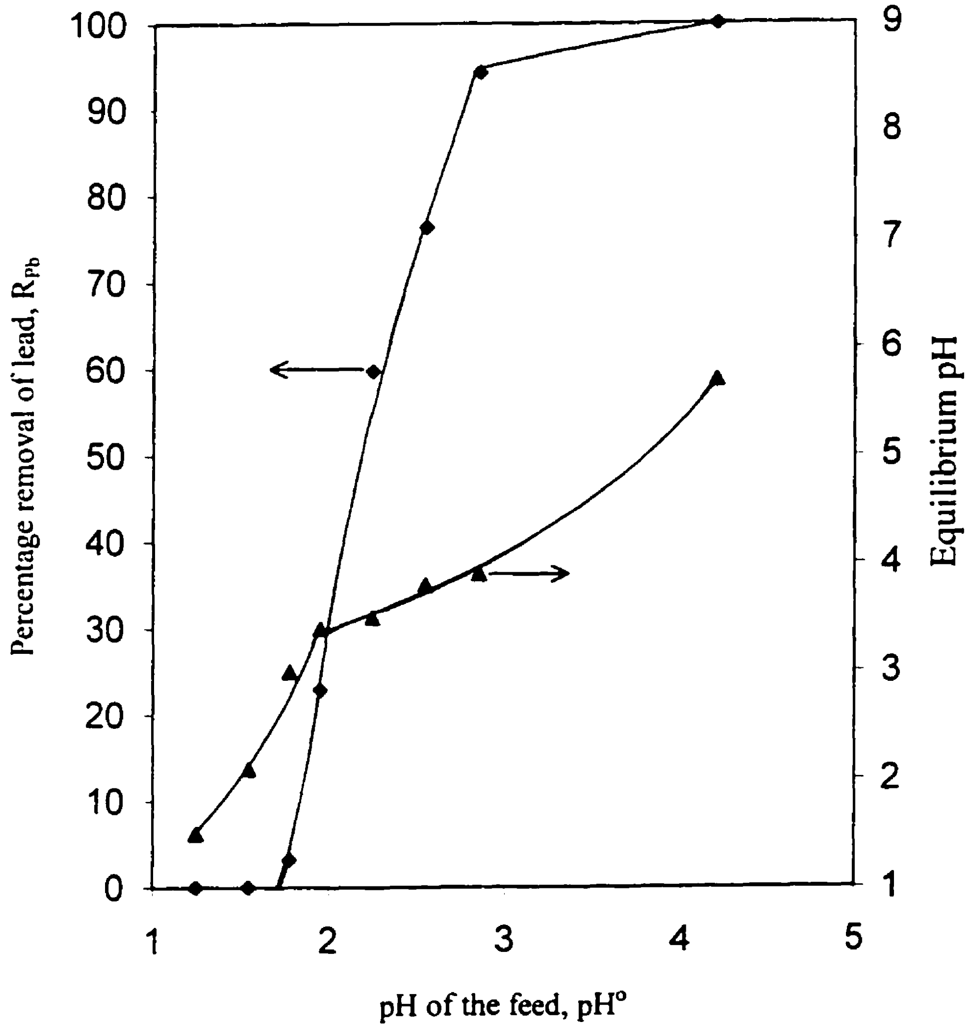


Figure 3.6: Effect of feed pH on the removal of lead, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Pb} = 7.1$ mM, $r^o_L = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

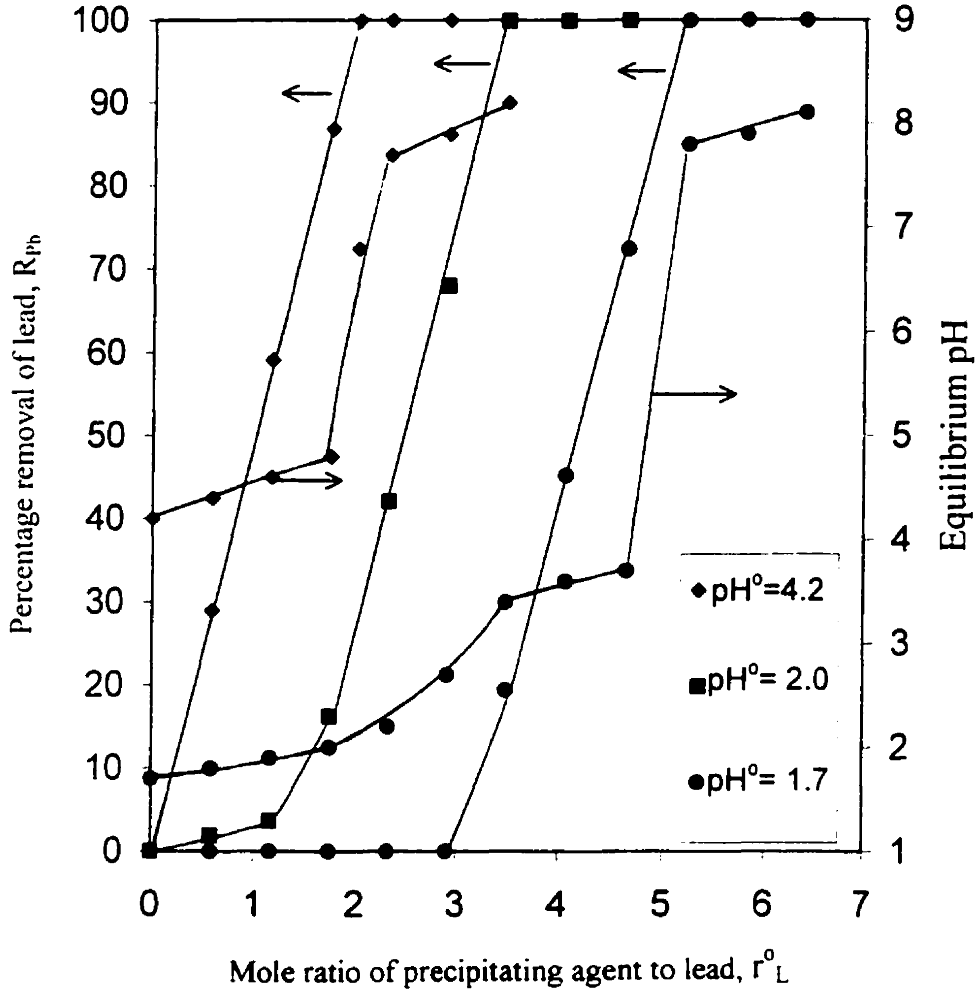


Figure 3.7: Effect of mole ratio of sodium di(n-octyl) phosphinate on the removal of lead, and the equilibrium pH, at different feed pH.

$C^o_{Pb} = 6.75$ mM , $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

the pH the higher the value of r_L^o required to produce the maximum removal.

For the third set ($pH^o = 1.6$), the behavior of the system can be divided into three regions. In the first region: from $r_L^o = 0$ up to $r_L^o = 3.2$, no lead was removed and all the precipitating agent was precipitated as $HL_{(s)}$. This caused an increase in the pH. In the second region from $r_L^o = 3.2$ to $r_L^o = 5.0$, only $PbL_{2(s)}$ was precipitated, and the increase in pH in this case resulted from the dissociation of hydroxo-complexes (reaction R-3.6). In the third region, $r_L^o > 5.0$, $HL_{(s)}$ precipitated again and the excess of the precipitating agent appeared in the aqueous phase. The first region did not appear in the first set, because no acid was added to the system. These regions are clearly defined by the prediction of the model presented in the next chapter

3.2.1.2 Effect of Chloride Concentration in the Feed

Chloride, which is present in most water streams, forms soluble chloro-complexes with lead:

$$Pb^{2+} + nCl^- \longleftrightarrow PbCl_n^{2-n} \qquad R-3.9$$

where n=1, 2, 3, and 4. The superscript (2-n) is the charge of the complex.

The effect of chloride concentration on the removal of lead was investigated by adding sodium chloride to the feed solution. A feed solution of 6.85 mM (1420 ppm) lead, at $pH^o = 4.0$, was treated with precipitating agent at mole ratio, $r_L^o = 2.0$. Lead chloride ($PbCl_2$) was used as the source of the lead. The mole ratio of chloride to lead (r_{Cl}^o) was increased from 2 to 250. The percentage removal of lead, and the equilibrium pH are plotted versus the mole ratio of chloride to lead in Figure 3.8. To account for the ionic strength, this system was compared with a

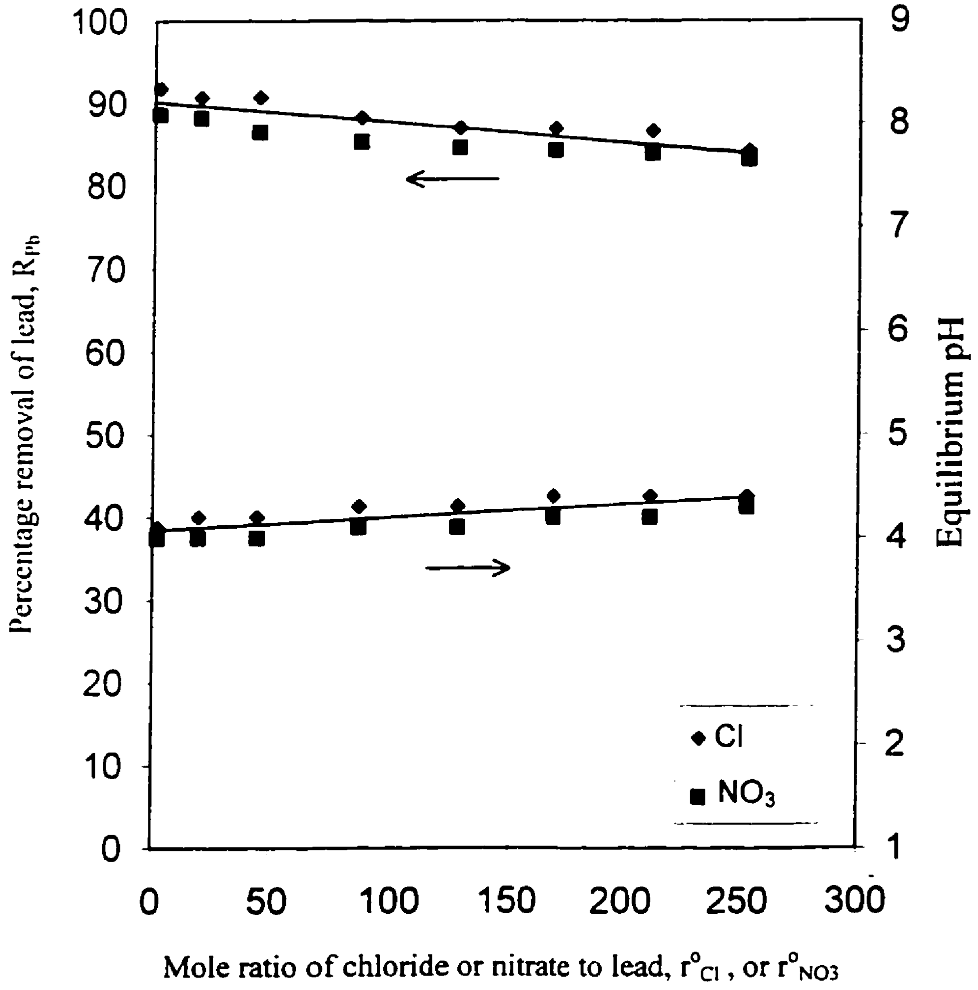


Figure 3.8 : Effect of chloride concentration (using NaCl) on the removal of lead, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Pb} = 6.85$ mM, $pH^o = 4.0$, $r^o_L = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = 0$

similar system where lead nitrate was used as the source of the lead and the nitrate concentration was adjusted with sodium nitrate. The percentage removal of lead and the equilibrium pH for the nitrate system are plotted against the mole ratio of nitrate to lead ($r^{o}_{NO_3}$) in Figure 3.8. There was no significant difference in the percentage removal or in the equilibrium pH in these two systems. Increasing r^{o}_{Cl} or $r^{o}_{NO_3}$ decreased slightly the percentage removal of lead and increased slightly the equilibrium pH. The decrease in the percentage removal was caused by the effect of the electrolyte added to the system on the solubility of the precipitate ($PbL_{2(s)}$). For a weak electrolyte (such as $PbL_{2(s)}$), an increase in the ionic strength of the system, by addition of another electrolyte which does not contain a common ion (Pb^{2+} or L^-), decreases the mean ionic activity coefficient and increases the degree of dissociation of the electrolyte. In general, the solubility changes as the constituents of the solution in equilibrium with the solid change. In addition, the decrease in the percentage removal of lead may be caused by the increase in Na^+ concentration which competed with Pb^{2+} for L^-, and shifted the following reaction to the left forming $NaL_{(s)}$ precipitate:

$$NaL_{(s)} \longleftrightarrow Na^+ + L^- \qquad R-3.10$$

The increase in the ionic strength of the solution reduced the activity coefficient of the hydrogen and hence increased the pH.

The effect of chloride concentration on the removal of lead was also investigated by adjusting the chloride concentration with a solution of HCl. Lead chloride was used as the source of lead. In this case, the system was compared with a similar nitrate system, where lead nitrate was used as the source of the lead and HNO_3 solution was used to adjust the nitrate concentration. In each system, a feed of 7.0 mM (1440 ppm) lead was treated with a precipitating agent solution at a mole ratio $r_L^o = 2.0$.

Figure 3.9 shows the percentage removal of lead and the equilibrium pH plotted versus r_{Cl}^o or $r_{NO_3}^o$. No difference was found in the percentage removal and in the equilibrium pH between the two systems. The decrease in the percentage removal and the equilibrium pH was caused by the effect of the pH of the feed, as discussed in section 3.1.1.1.

3.2.1.3 Effect of Calcium Concentration in the Feed

Effective removal methods must be selective for the target metal against the alkaline earth metals. Calcium is one of the metals that exists in most water streams. When calcium competes with lead, some of the precipitating agent Combined with calcium, forming $CaL_{2(s)}$:

$$Ca^{2+} + 2S^- \longleftrightarrow CaS_{2_{(s)}} \qquad R-3.11$$

The effect of mole ratio of the precipitating agent to lead on the removal of lead, removal of calcium, and the equilibrium pH was also investigated. The mole ratio of calcium to lead in the feed was $r_{Ca}^o = 1.0$. The concentration of lead in the feed was 10 mM (2070 ppm) at $pH^o = 4.3$, and the mole ratio of the precipitating agent to lead was increased from $r_L^o = 0$ up to $r_L^o = 2.75$. Figure 3.10 shows that, up to $r_L^o = 2.0$, only lead was precipitated. At mole ratio of two, the maximum percentage removal of lead was obtained. The increase of r_L^o higher than 2, increased the equilibrium pH and the percentage removal of calcium, which indicates that both $HL_{(s)}$ and $CaL_{2(s)}$ were formed.

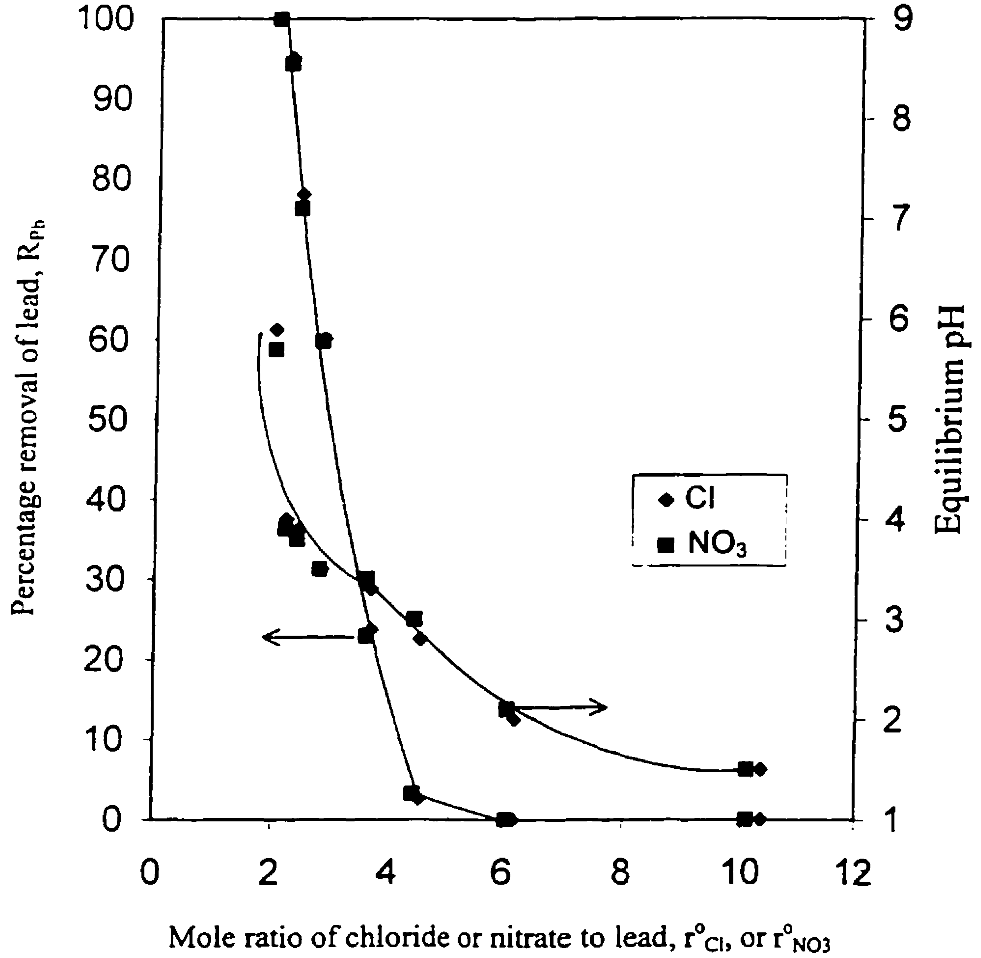


Figure 3.9: Effect of chloride concentration (using HCl) on the removal of lead, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Pb} = 7.0$ mM, $r^o_L = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = 0$

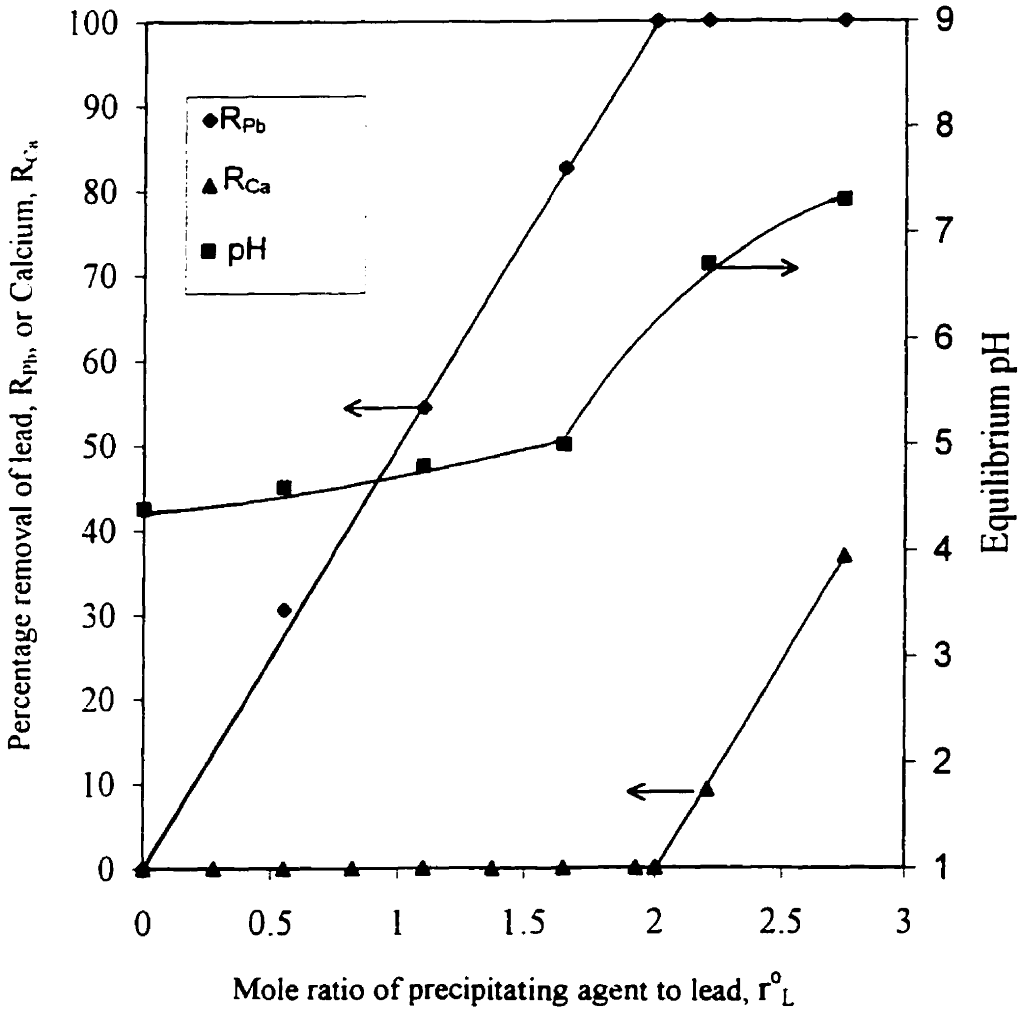


Figure 3.10: Effect of mole ratio of sodium di-(n-octyl) phosphinate to lead on the removal of lead, and the equilibrium pH, in the presence of calcium.

C^o_{Pb} = 10 mM, r^o_{Ca} = 1.0, pH° = 4.3, $r^o_{NO_3}$ = 4.0, $C^o_{Cd} = C^o_{Zn} = C^o_{Na} = C^o_{Cl} = 0$

The effect of calcium concentration on the removal of lead was investigated by addition of calcium nitrate to the feed solution. A feed solution containing 10 mM (2070 ppm) lead at $pH^o = 4.5$ was treated with a precipitating agent solution at mole ratio $r_L^o = 1.1$. The mole ratio of calcium to lead (r_{Ca}^o) was increased from 0 to 2.5. The percentage removal of lead and the equilibrium pH are presented in Table 3.1 versus the mole ratio of calcium to lead. The presence of calcium in the feed, in the range of mole ratio of calcium to lead considered, had no effect on the removal of lead. The precipitating agent showed a higher selectivity for lead over calcium. This could be attributed to the acidity and electronegativity of the cations, where Pb^{2+} is more acidic and electronegative than Ca^{2+}. The electronegativity of lead and calcium are 1.8 and 1.0, respectively.

Table 3.1: Effect of calcium on the removal of lead using sodium di-(n-octyl) phosphinate. $C_{Pb}^o = 10$ mM (2070 ppm), $pH^o = 4.5$, $r_L^o = 1.1$, $C_{Cd}^o = C_{Zn}^o = C_{Na}^o = C_{Cl}^o = 0$

r_{Ca}^o	$\%R_{Pb}$	$\%R_{Ca}$	pH
0	54.5	0	4.6
0.5	54.7	0	4.7
1.0	54.9	0	4.8
1.5	54.8	0	5.0
2.0	54.7	0	5.0
2.5	54.3	0	5.0

3.2.1.4 Effect of the Chain Length of the Precipitating agent

The effect of the chain length of the precipitating agent on the removal was studied by treating a feed solution containing 4.97 mM (1030 ppm) lead at pH^o = 4.1 with sodium di-(n-dodecyl) phosphinate. This system was compared with a similar system in which sodium di-(n-octyl) phosphinate was used as the precipitating agent. In both systems, the mole ratio of the precipitating agent (r_L^o or $r_{L_D}^o$) was increased from $r_L^o = r_{L_D}^o = 0$ up to $r_L^o = r_{L_D}^o = 2.87$. Due to the low solubility of sodium di-(n-dodecyl) phosphinate, the two reagents were added in a solid form to 40 mℓ of feed solution.

Figure 3.11 shows the percentage removal of lead and the equilibrium pH plotted versus the mole ratio of the precipitating agent to lead. There was little difference in the percentage removal or in the equilibrium pH between the two systems. Similarly, the stoichiometry of the overall precipitation reaction using sodium di-(n-dodecyl) phosphinate is suggested to be:

$$Pb^{2+} + 2L_D^- \longleftrightarrow Pb(L_D)_{2_{(s)}} \qquad R-3.12$$

The difference between the two system was found in the residual concentrations of lead and precipitating agent at $r_L^o = r_{L_D}^o = 2.0$. At this mole ratio, the equilibrium concentrations of the lead and the precipitating agent were 0.15 ± 0.05 ppm and 4.5 ± 0.2 ppm, respectively for the di-(n-octyl) phosphinate system, and 0.05 ± 0.02 ppm and 6.5 ± 0.4 ppm, respectively for the di-(n-dodecyl) phosphinate system. The increase in the chain length of the precipitating agent increased the stability of the precipitate (complex), and hence the solubility (dissociation) of the precipitate in water was decreased.. For the same hydrophilic group, increasing the number of carbon atoms in the hydrophobic group, increases the intermolecular forces between the chains, and decreases the solubility of the compound in water.

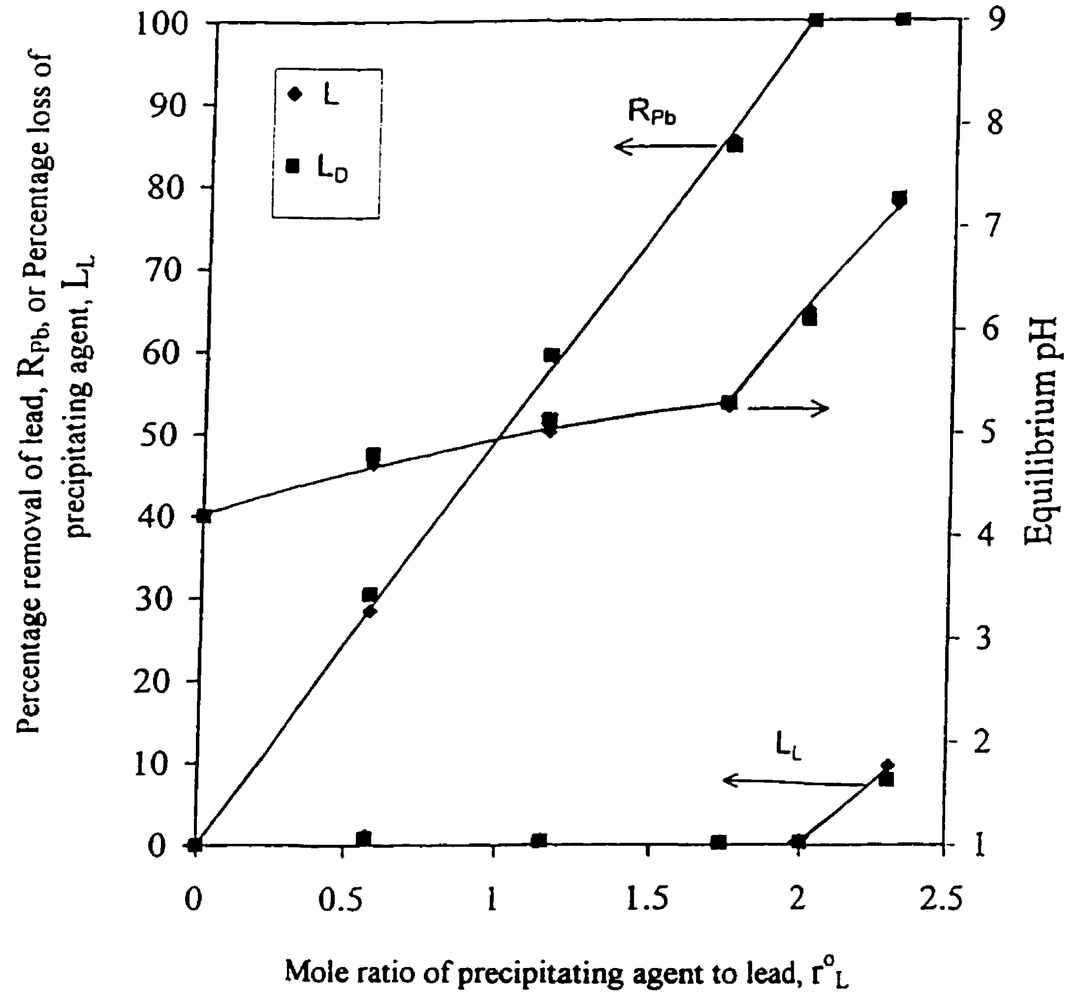


Figure 3.11: Effect of mole ratio of sodium di-(n-alkyl) phosphinate to lead on the removal of lead, and the equilibrium pH.

$C^o_{Pb} = 4.97$ mM, $pH^o = 4.1$, $r^o_{NO_3} = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

The solubilities of the two acids ($HL_{(s)}$ and $HL_{D_{(s)}}$) and their lead salts ($PbL_{2_{(s)}}$ and $Pb(L_D)_{2_{(s)}}$) in distilled water at 22 ± 1°C are presented in Table 3.2.

Table 3.2: Solubilities of di-(n-octyl) phosphinic acid ($HL_{(s)}$), di-(n-dodecyl) phosphinic acid ($HL_{D_{(s)}}$), lead di-(n-octyl) phosphinate ($PbL_{2_{(s)}}$), and lead di-(n-dodecyl) phosphinate ($Pb(L_D)_{2_{(s)}}$) in distilled water at 22±1°C

	$HL_{(s)}$	$HL_{D_{(s)}}$	$PbL_{2_{(s)}}$	$Pb(L_D)_{2_{(s)}}$
C_{H^-} (M)	$(4.11\pm0.1)\times10^{-6}$	$(6.72\pm0.13)\times10^{-7}$		
C_L (M)	$(1.81\pm0.07)\times10^{-5}$		$(1.11\pm0.06)\times10^{-5}$	
C_{L_D} (M)		$(1.55\pm0.14)\times10^{-5}$		$(5.73\pm0.21)\times10^{-6}$
C_{Pb} (M)			$(7.39\pm0.11)\times10^{-7}$	$(2.41\pm0.17)\times10^{-7}$

3.2.2 Removal of Cadmium

A feed solution of 5.9 mM (660 ppm) cadmium at pH^o = 4.7 was treated with sodium di-(n-octyl) phosphinate. Cadmium nitrate was used as the source of cadmium. The mole ratio of the precipitating agent to lead was varied from $r_L^o=0$ to $r_L^o=2.8$.

The percentage removal of cadmium and the equilibrium pH are shown in Figure 3.12 for different mole ratios of the precipitating agent to cadmium. Behavior similar to that of lead was observed, where the percentage removal of cadmium increased linearly with an increase in the mole ratio up to $r_L^o=2.0$. The highest percentage removal with the lowest loss of the precipitating agent was found at $r_L^o=2.0$. At this mole ratio, the equilibrium concentrations of the cadmium and the precipitating agent were 0.24 ± 0.03, and 4.5 ± 0.3, respectively.

Similarly, the stoichiometry of the overall precipitation reaction is

$$Cd^{2+} + 2L^- \longleftrightarrow PbL_{2_{(s)}} \qquad R-3.13$$

The equilibrium pH increased with increasing mole ratio of the precipitating agent to cadmium. The small increase in pH below $r_L^o = 2$, was due to dissociation of the hydroxo- complexes of cadmium in reaction:

$$Cd^{2+} + nOH^- \longleftrightarrow Cd(OH)_n^{2-n} \qquad R-3.14$$

The larger increase in pH at $r_L^o > 2.0$ was caused by the formation of di-(n-octyl) phosphinic acid (reaction R-3.4).

The effect of pH of the feed (pH^o) on the removal of cadmium and equilibrium pH was also investigated. The pH of the feed was decreased from 4.7 to 1.7 by addition of nitric acid. A feed solution containing 5.9 mM (660 ppm)

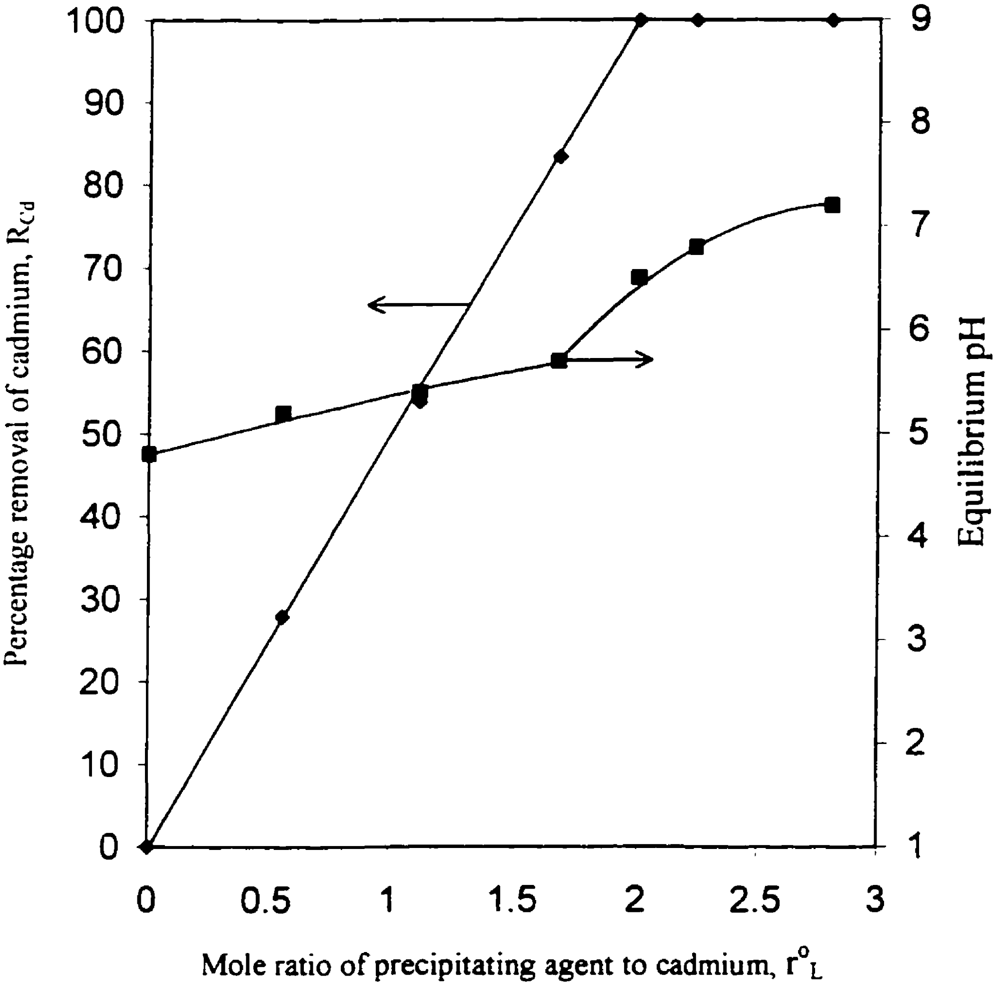


Figure 3.12: Effect of mole ratio of sodium di-(n-octyl) phosphinate to cadmium on the removal of cadmium, and the equilibrium pH.

$C^o_{Cd} = 5.9$ mM, $pH^o = 4.7$, $r^o_{NO_3} = 2.0$, $C^o_{Pb} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

cadmium was treated with the precipitating agent at a mole ratio $r_L^o = 2.2$. The percentage removal and the equilibrium pH are plotted in Figure 3.13 against the pH of the feed. The percentage removal and the equilibrium pH were decreased by decreasing the pH of the feed. Some of the acid was precipitated as $HL_{(s)}$, thus reducing the removal of cadmium. The decrease in equilibrium pH was due to the presence of excess free acid. The equilibrium pH was always higher than the pH of the feed because of the dissociation of the hydroxo- complexes in reaction R-3.14.

3.2.3 Removal of Zinc

Zinc was removed from a feed solution of 6.3 mM (410 ppm) zinc at $pH^o = 4.6$. by sodium di-(n-octyl) phosphinate. The mole ratio of the precipitating agent to zinc was varied from $r_L^o = 0$ to $r_L^o = 2.65$.

Figure 3.14 shows the percentage removal of zinc and the equilibrium pH plotted versus the mole ratio of the precipitating agent to zinc. A behavior similar to that of lead and cadmium was observed. The removal of zinc increased linearly with the increase of the mole ratio up to $r_L^o = 2.0$. The highest percentage removal of zinc with lowest percentage of loss of the precipitating agent was obtained at $r_L^o = 2.0$. At this point, the equilibrium concentrations of zinc and the precipitating agent were 0.08 ± 0.02 ppm, and 4 ± 1 ppm, respectively.

The stoichiometry of the overall precipitation reaction is

$$Zn^{2+} + 2L^- \longleftrightarrow PbL_{2_{(s)}} \qquad R-3.15$$

The equilibrium pH increased with increasing r_L^o. The increase in the pH between r_L^o and $r_L^o = 2$ was due to the dissociation of hydroxo-complexes of zinc in reaction:

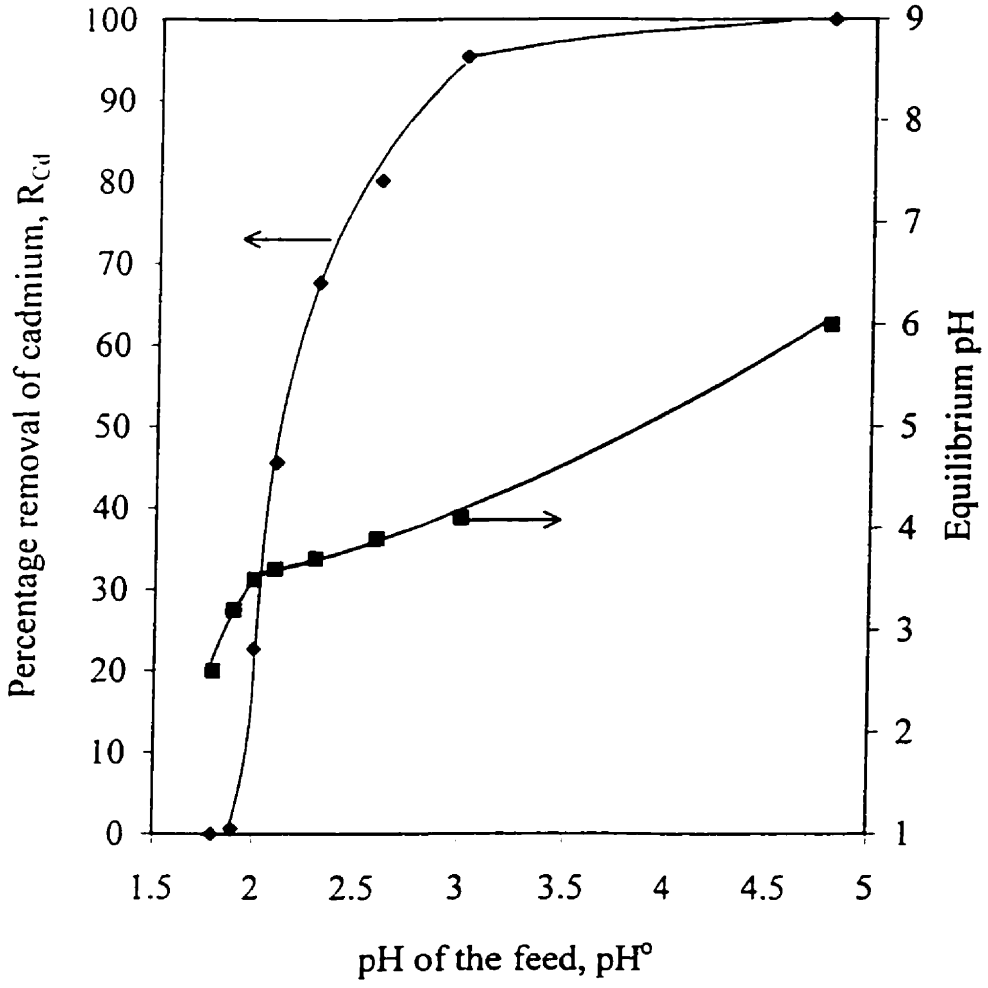


Figure 3.13: Effect of feed pH on the removal of cadmium, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^{o}_{Cd} = 5.9$ mM, $r^{o}_{L} = 2.2$, $C^{o}_{Pb} = C^{o}_{Zn} = C^{o}_{Ca} = C^{o}_{Na} = C^{o}_{Cl} = 0$

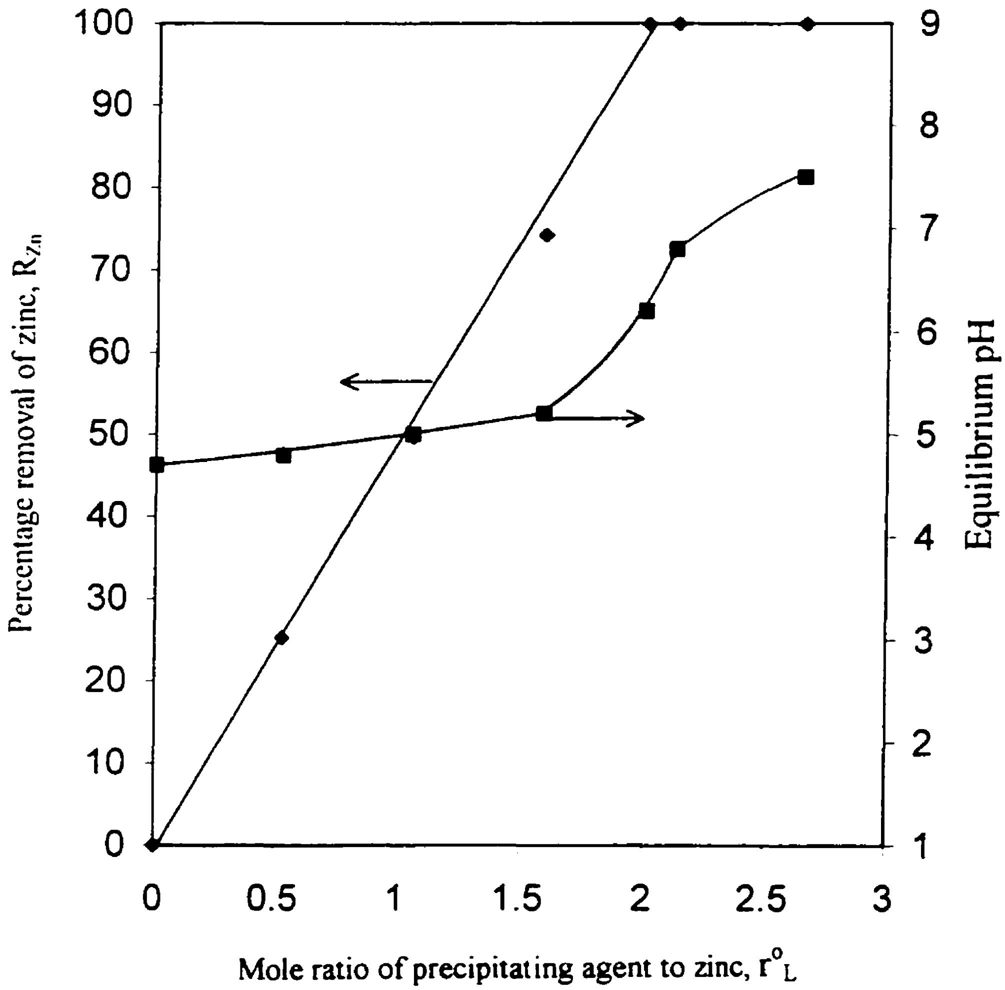


Figure 3.14: Effect of mole ratio of sodium di-(n-octyl) phosphinate to zinc on the removal of zinc, and the equilibrium pH.

$C^o_{Zn} = 6.3$ mM, $pH^o = 4.6$, $r^o_{No_3} = 2.0$, $C^o_{Pb} = C^o_{Cd} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

$$Zn^{2+} + nOH^{-} \longleftrightarrow Zn(OH)_{n}^{2-n} \qquad R-3.16$$

At r_L^o > 2, di-(n-octyl) phosphinic acid was formed, yielding a large increase in equilibrium pH.

The effect of pH of the feed on the removal of zinc was also investigated using sodium di-(n-octyl) phosphinate as the precipitating agent. A feed solution containing 6.3 mM (410 ppm) zinc was treated with the precipitating agent at mole ratio r_L^o = 2.12. The pH of the feed (pH°) was decreased from 4.6 to 1.7 with HNO_3. Figure 3.15 shows the effect of pH° on the percentage removal of zinc and the equilibrium pH. The percentage removal and the equilibrium pH were decreased with the decrease of pH°, because some of the added acid precipitated as $HL_{(s)}$.

3.2.4 Treatment of a Feed Containing Lead, Cadmium, and Zinc

A feed solution containing 2.0 mM (420 ppm) lead, 2.0 mM (220 ppm) cadmium, and 2.1 mM (140 ppm) zinc, at pH° = 4.3 was treated with sodium di-(n-octyl) phosphinate. The mole ratio of the precipitating agent to the total number of moles of metals was varied up to r_L^o = 2.7.

The percentage removal of each metal and the equilibrium pH are shown in the Figure 3.16 for different mole ratios. The percentage removal of each metal and the equilibrium pH increased with increasing the mole ratio up to r_L^o=2. In this range of mole ratios, the percentage removal of zinc was the highest, followed by lead and cadmium. At a mole ratio of 2.0, the maximum percentage removal of each metal with the lowest percentage loss of the precipitating agent was obtained. Increasing the mole ratio above 2 had no effect on the removal but increased the loss of the precipitating agent.

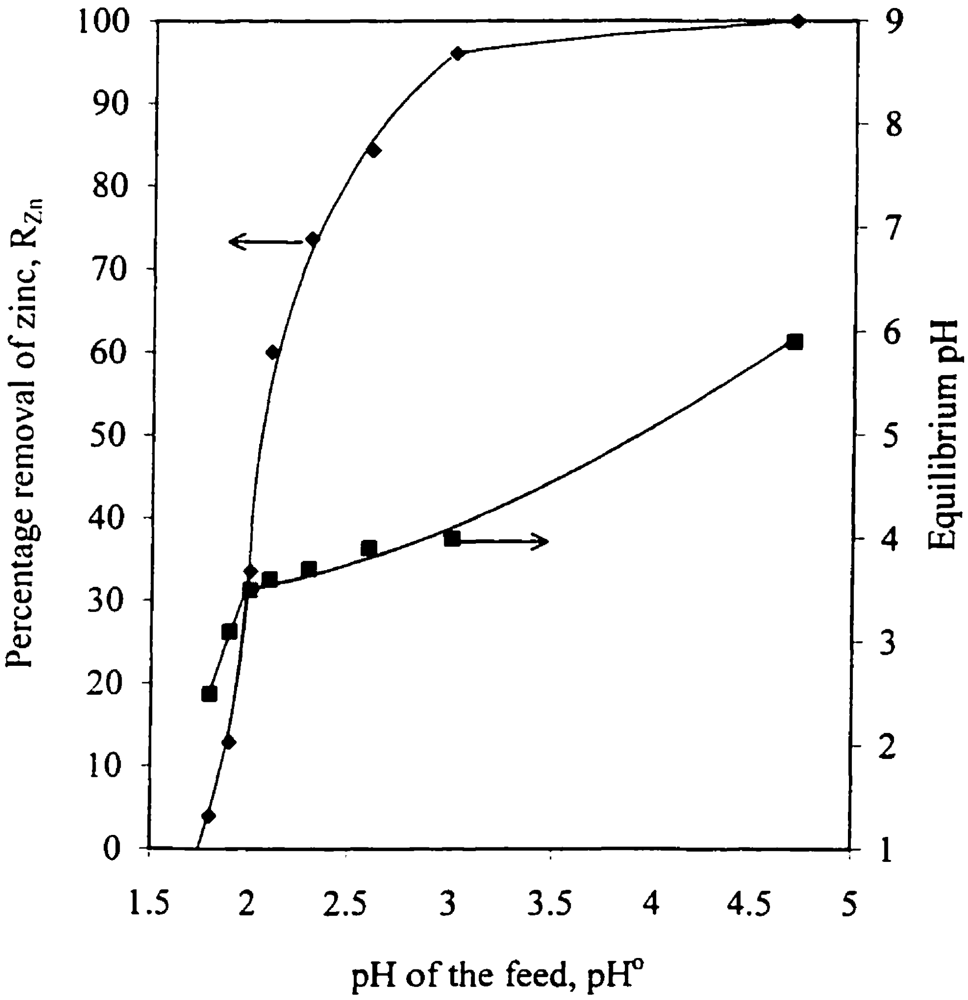


Figure 3.15: Effect of feed pH on the removal of zinc, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Zn} = 6.3$ mM, $r^o_L = 2.12$, $C^o_{Pb} = C^o_{Cd} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

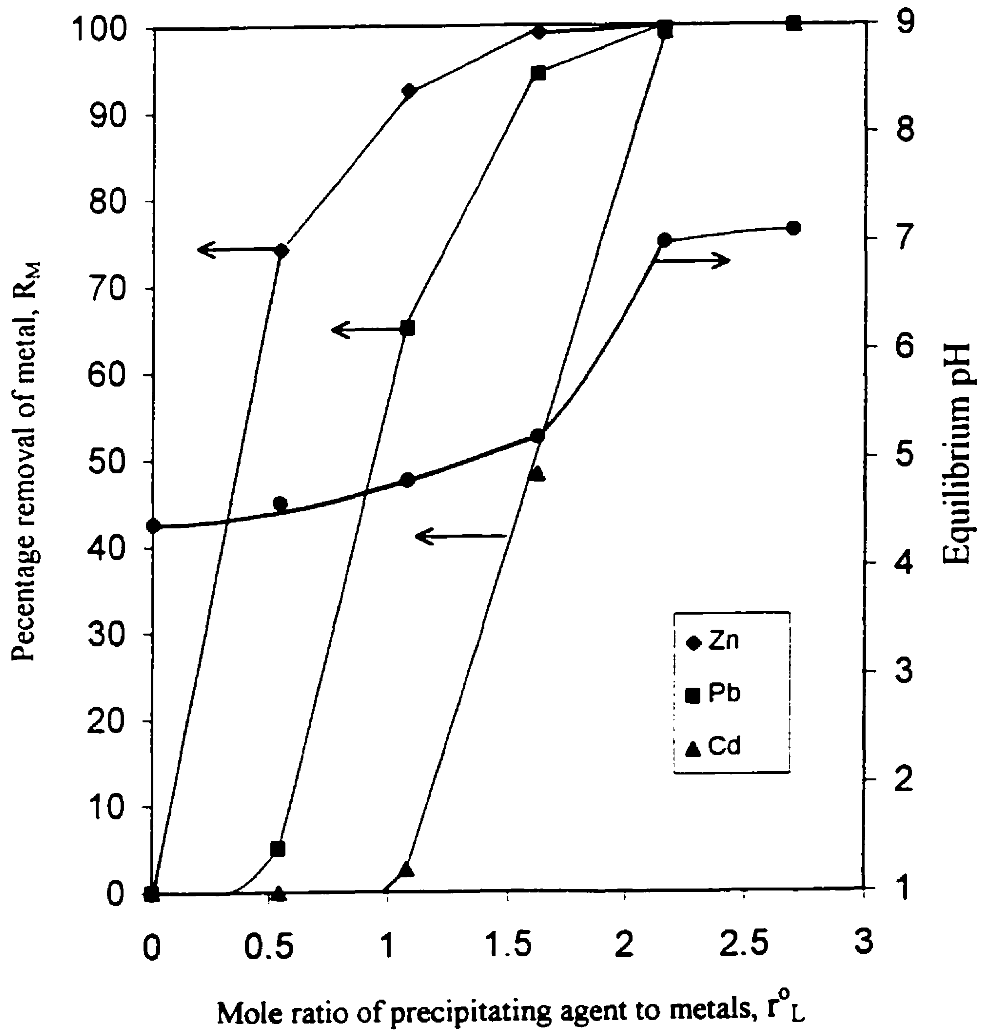


Figure 3.16: Effect of mole ratio of sodium di-(n-octyl) phosphinate to mixture of Pb, Cd, and Zn on the removal of metals, and the equilibrium pH.

$C^o_{Pb} = 2.0$ mM, $C^o_{Cd} = 2.0$ mM, $C^o_{Zn} = 2.1$ mM, $pH^o = 4.3$, $C^o_{NO_3} = 12.2$ mM,

$C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

The preference of the precipitating agent for a particular ion among others present in a solution depends both on the precipitating agent and the ion. Metal ions exist in aqueous solution with a certain number of water molecules bound to them. The larger the ionic radius, the smaller the hydrated radius and the lower the hydration energy. Smaller hydrated ions bind more strongly to the ligand. This may explain the selectivity of sodium di-(n-octyl) phosphinate for lead over cadmium, since the ionic radii of Pb^{2+} and Cd^{2+} are 1.16 and 0.97 Å, respectively. Although Zn^{2+} is smaller than Pb^{2+} and Cd^{2+} ions (the ionic radius of Zn^{2+} is 0.74 Å), the precipitating agent showed the highest selectivity for zinc. In this system, the effect of association and complex formation (e.g. hydroxo-complexation) in the solution on the selectivity is doubtless important because the same behavior was observed at low pH as shown in Figure 3.17. At low pH, only Pb^{2+}, Cd^{2+}, and Zn^{2+} are expected to be present in the solution.

The effect of pH of the feed on the removal of lead, cadmium and zinc from a solution containing the three metals was investigated. A feed solution of 2.0 mM lead, 2.0 mM cadmium, and 2.1 mM zinc was treated with sodium di-(n-octyl) phosphinate with $r_L^o = 2.2$. The pH of the feed was decreased from 4.3 to 1.7 with nitric acid.

The percentage removal of each metal and the equilibrium pH decreased by decreasing pH of the feed. This can be explained by combining the explanations that used for the effect of pH^o on the removal of the individual metals in the previous sections. The percentage removal of zinc was always the highest and the percentage removal of cadmium was the lowest, in the range of pH^o considered in this work.

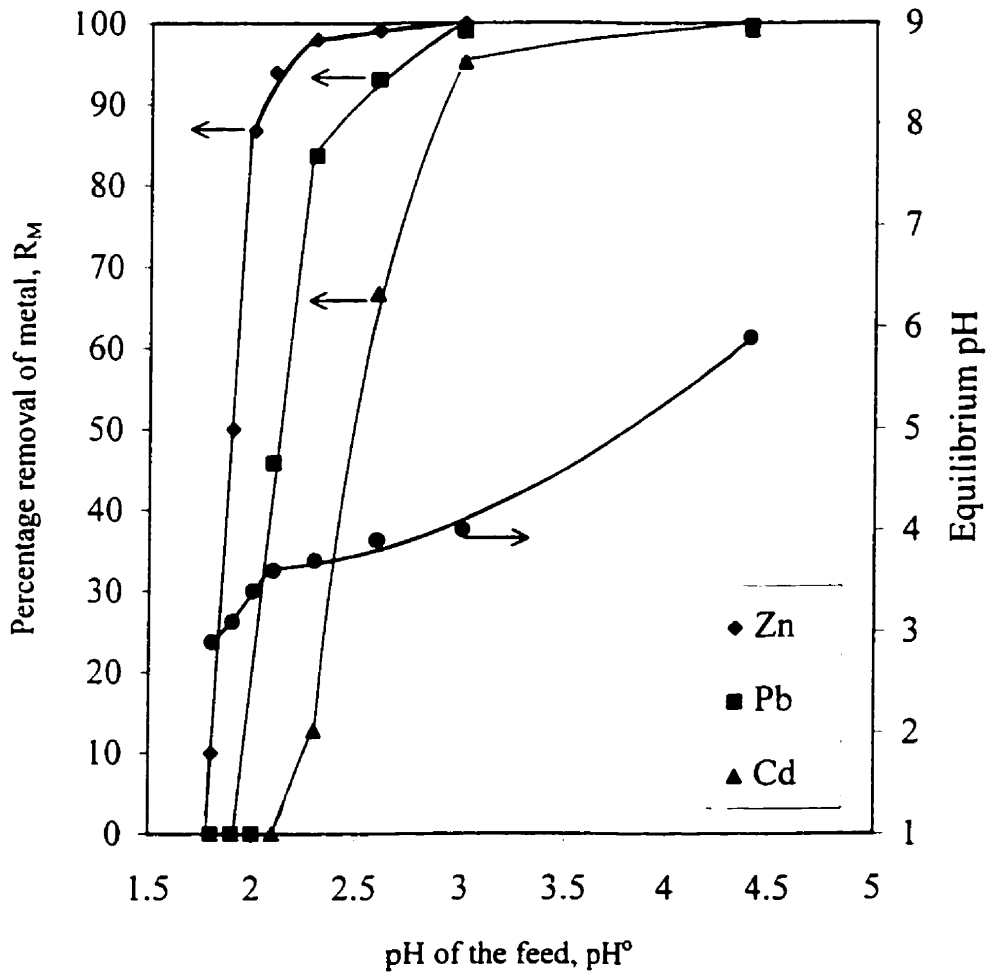


Figure 3.17: Effect of feed pH on the removal of mixture of Pb, Cd, and Zn and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Pb} = 2.0$ mM, $C^o_{Cd} = 2.0$ mM, $C^o_{Zn} = 2.1$ mM, $r^o_L = 2.2$, $C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$

3.2.5 Regeneration of the Precipitating Agent

The regeneration step was conducted by adding sodium hydroxide to the precipitate and then contacted it with an organic solvent capable of extracting the precipitating agent. Addition of sodium hydroxide solution to the precipitate ($PbL_{2(s)}$) increases the solubility of the precipitate, and the pH of the solution. At high pH, the hydroxyl ions compete with the precipitating agent for lead and form the hydroxo-complexes, $Pb(OH)_{2(s)}$, $Pb(OH)_3^-$, and $Pb(OH)_4^{2-}$. The sodium cations (which are at high concentration) compete with lead cations for the di-(n-octyl)-phosphinic anions. As a result, the selectivity of the precipitating agent for sodium over lead is increased.

The precipitate ($PbL_{2(s)}$) was formed by treating a liter of feed solution containing 5 mM lead with 50 mℓ solution containing 200 mM (3.12 g) sodium di-(n-octyl) phosphinate. The lead di-(n-octyl) phosphinate precipitate was separated and treated with 10 mℓ of 3M NaOH. Subsequently, the solution was contacted with 100 mℓ of diethyl ether in a separatory funnel and agitated rigorously. Two phases were formed. The lower (aqueous) phase containing the lead was separated. The upper phase (ether phase) containing the precipitating agent, was left for evaporation. When the ether was completely removed, sodium di-(n-octyl) phosphinate was obtained. No lead was detected in the regenerated precipitating agent because lead di-(n-octyl) phosphinate is insoluble in diethyl ether, on the other hand, sodium di-(n-octyl) phosphinate is soluble in diethyl ether. The percentage loss of the precipitating agent in the precipitation step was about 0.3%, and the amount of the regenerated precipitating agent was 3.09 ± 0.02 g. This means that 99% of the precipitating agent was regenerated. The volume of the aqueous solution containing the lead in different forms, was about 10 mℓ, which means that the concentration of lead was increased 100 times.

CHAPTER 4

MODELING THE PRECIPITATION OF HEAVY METALS

A model was developed to study the chemical speciation of lead, cadmium, and zinc in aqueous solution. The association of each metal with the ligands L . NO_3.OH^- , and Cl^- was considered. The effect of CO_2 from air was considered in the calculations. An algorithm to find the distribution of complexes and hence the concentrations of the reacting species was developed. The predictions of the model were compared with the experimental data.

4.1 Model Derivation

An aqueous solution containing lead, cadmium, and zinc was considered. The available ligands for complex formation in this solution are; OH^-, and NO_3^-, and L^-. In the considered range of pH, The hydroxo-complexes expected to exist in solution are $PbOH^+$, $Pb(OH)_2$, $CdOH^+$, $Cd(OH)_2$, $ZnOH^+$, and $Zn(OH)_2$. The nitro-complexes expected to present in the solution are $PbNO_3^+$, $CdNO_3^+$, and $ZnNO_3^+$. The chloro-complexes expected to exist in this system are $PbCl_n^{2-n}$, $CdCl_n^{2-n}$, and $ZnCl_n^{2-n}$, where $n=1,2,3$, and 4. The superscript $(2-n)$ represents the charge of the complex. The precipitating agent NaL dissociates completely to Na^+ and L^-, where the ligand L^- associates with other cations; Pb^{2+}, Cd^{2+}, Zn^{2+}, and H^+ forming precipitates or dissolved species. In this system, the following reactions were considered :

$$\mathrm{PbOH^{+}} \xleftrightarrow{K_{1,Pb}} \mathrm{Pb^{2+}} + \mathrm{OH^{-}} \tag{R-4.1}$$

$$\mathrm{Pb(OH)_{2}} \xleftrightarrow{K_{2,Pb}} \mathrm{Pb^{2+}} + 2\mathrm{OH^{-}} \tag{R-4.2}$$

$$\mathrm{CdOH^{+}} \xleftrightarrow{K_{1,Cd}} \mathrm{Cd^{2+}} + \mathrm{OH^{-}} \tag{R-4.3}$$

$$\mathrm{Cd(OH)_{2}} \xleftrightarrow{K_{2,Cd}} \mathrm{Cd^{2+}} + 2\mathrm{OH^{-}} \tag{R-4.4}$$

$$\mathrm{ZnOH^{+}} \xleftrightarrow{K_{1,Zn}} \mathrm{Zn^{2+}} + \mathrm{OH^{-}} \tag{R-4.5}$$

$$\mathrm{Zn(OH)_{2}} \xleftrightarrow{K_{2,Zn}} \mathrm{Zn^{2+}} + 2\mathrm{OH^{-}} \tag{R-4.6}$$

$$\mathrm{PbNO_{3}^{-}} \xleftrightarrow{K_{3,Pb}} \mathrm{Pb^{2+}} + \mathrm{NO_{3}^{-}} \tag{R-4.7}$$

$$\mathrm{CdNO_{3}^{-}} \xleftrightarrow{K_{3,Cd}} \mathrm{Cd^{2+}} + \mathrm{NO_{3}^{-}} \tag{R-4.8}$$

$$\mathrm{ZnNO_{3}^{-}} \xleftrightarrow{K_{3,Zn}} \mathrm{Zn^{2+}} + \mathrm{NO_{3}^{-}} \tag{R-4.9}$$

$$\mathrm{PbCl^{+}} \xleftrightarrow{K_{4,Pb}} \mathrm{Pb^{2+}} + \mathrm{Cl^{-}} \tag{R-4.10}$$

$$\mathrm{PbCl_{2}} \xleftrightarrow{K_{5,Pb}} \mathrm{Pb^{2+}} + 2\mathrm{Cl^{-}} \tag{R-4.11}$$

$$\mathrm{PbCl_{3}^{-}} \xleftrightarrow{K_{6,Pb}} \mathrm{Pb^{2+}} + 3\mathrm{Cl^{-}} \tag{R-4.12}$$

$$\mathrm{PbCl_{4}^{2-}} \xleftrightarrow{K_{7,Pb}} \mathrm{Pb^{2+}} + 4\mathrm{Cl^{-}} \tag{R-4.13}$$

$$\mathrm{CdCl^{+}} \xleftrightarrow{K_{4,Cd}} \mathrm{Cd^{2+}} + \mathrm{Cl^{-}} \tag{R-4.14}$$

$$\mathrm{CdCl_{2}} \xleftrightarrow{K_{5,Cd}} \mathrm{Cd^{2+}} + 2\mathrm{Cl^{-}} \tag{R-4.15}$$

$$\mathrm{CdCl_{3}^{-}} \xleftrightarrow{K_{6,Cd}} \mathrm{Cd^{2+}} + 3\mathrm{Cl^{-}} \tag{R-4.16}$$

$$\mathrm{CdCl_{4}^{2-}} \xleftrightarrow{K_{7,Cd}} \mathrm{Cd^{2+}} + 4\mathrm{Cl^{-}} \tag{R-4.17}$$

$$ZnCl^{+} \xleftrightarrow{K_{4,Zn}} Zn^{2+} + Cl^{-} \qquad R-4.18$$

$$ZnCl_2 \xleftrightarrow{K_{5,Zn}} Zn^{2+} + 2Cl^{-} \qquad R-4.19$$

$$ZnCl_3^{-} \xleftrightarrow{K_{6,Zn}} Zn^{2+} + 3Cl^{-} \qquad R-4.20$$

$$ZnCl_4^{2-} \xleftrightarrow{K_{7,Zn}} Zn^{2+} + 4Cl^{-} \qquad R-4.21$$

$$PbL_{2_{(s)}} \xleftrightarrow{K_{sp(PbL_2)}} Pb^{2+} + 2L^{-} \qquad R-4.22$$

$$CdL_{2_{(s)}} \xleftrightarrow{K_{sp(CdL_2)}} Cd^{2+} + 2L^{-} \qquad R-4.23$$

$$ZnL_{2_{(s)}} \xleftrightarrow{K_{sp(ZnL_2)}} Zn^{2+} + 2L^{-} \qquad R-4.24$$

$$HL_{(s)} \xleftrightarrow{K_{sp(HL)}} H^{+} + L^{-} \qquad R-4.25$$

$$HL_{(aq)} \xleftrightarrow{K_a} H^{+} + L^{-} \qquad R-4.26$$

$$H_2O \xleftrightarrow{K_w} H^{+} + OH^{-} \qquad R-4.27$$

Where K_1 - K_8 are the mass stability constants for the complexes, the $K_{sp_{(i)}}$ are the solubility products of the precipitates, K_a is the acidity constant, and K_w is the water dissociation constant. These constants are defined in Table 4.1. The values of $K_{sp_{(i)}}$ were determined experimentally-see Appendix A. The values of the other equilibrium constants were obtained from literature. The values of these constants with their references are presented in Table 4.1.

Table 4.1: Equilibrium constants

Equilibrium	Value of the equilibrium constant
$K_{1,Pb} = \frac{C_{Pb^{2+}} \cdot C_{OH^-}}{C_{PbOH^+}}$ (4.1)	$10^{-7.82}$ (a)
$K_{2,Pb} = \frac{C_{Pb^{2+}} \cdot C^2_{OH^-}}{C_{Pb(OH)_2}}$ (4.2)	$10^{-10.9}$ (b)
$K_{1,Cd} = \frac{C_{Cd^{2+}} \cdot C_{OH^-}}{C_{CdOH^+}}$ (4.3)	$10^{-5.72}$ (c)
$K_{2,Cd} = \frac{C_{Cd^{2+}} \cdot C^2_{OH^-}}{C_{Cd(OH)_2}}$ (4.4)	$10^{-7.7}$ (b)
$K_{1,Zn} = \frac{C_{Zn^{2+}} \cdot C_{OH^-}}{C_{ZnOH^+}}$ (4.5)	$10^{-5.77}$ (c)
$K_{2,Zn} = \frac{C_{Zn^{2+}} \cdot C^2_{OH^-}}{C_{Zn(OH)_2}}$ (4.6)	$10^{-11.1}$ (b)
$K_{3,Pb} = \frac{C_{Pb^{2+}} \cdot C_{NO_3^-}}{C_{PbNO_3^+}}$ (4.7)	$10^{-1.17}$ (b)
$K_{3,Cd} = \frac{C_{Cd^{2+}} \cdot C_{NO_3^-}}{C_{CdNO_3^+}}$ (4.8)	$10^{-0.5}$ (b)
$K_{3,Zn} = \frac{C_{Zn^{2+}} \cdot C_{NO_3^-}}{C_{ZnNO_3^+}}$ (4.9)	$10^{-0.4}$ (b)
$K_{4,Pb} = \frac{C_{Pb^{2+}} \cdot C_{Cl^-}}{C_{PbCl^+}}$ (4.10)	$10^{-1.59}$ (b)
$K_{5,Pb} = \frac{C_{Pb^{2+}} \cdot C^2_{Cl^-}}{C_{PbCl_2}}$ (4.11)	$10^{-1.8}$ (b)
$K_{6,Pb} = \frac{C_{Pb^{2+}} \cdot C^3_{Cl^-}}{C_{PbCl_3^-}}$ (4.12)	$10^{-1.7}$ (b)
$K_{7,Pb} = \frac{C_{Pb^{2+}} \cdot C^4_{Cl^-}}{C_{PbCl_4^{2-}}}$ (4.13)	$10^{-1.4}$ (b)

Table 4.1 (Continued)

Equilibrium		Value of the equilibrium constant
$K_{4,Cd} = \frac{C_{Cd^{2+}} C_{Cl^-}}{C_{CdCl^+}}$	(4.14)	$10^{-1.98}$ (b)
$K_{5,Cd} = \frac{C_{Cd^{2+}} C^2_{Cl^-}}{C_{CdCl_2}}$	(4.15)	$10^{-2.6}$ (b)
$K_{6,Cd} = \frac{C_{Cd^{2+}} C^3_{Cl^-}}{C_{CdCl_3^-}}$	(4.16)	$10^{-2.4}$ (b)
$K_{7,Cd} = \frac{C_{Cd^{2+}} C^4_{Cl^-}}{C_{CdCl_4^{2-}}}$	(4.17)	$10^{-2.8}$ (b)
$K_{4,Zn} = \frac{C_{Zn^{2+}} C_{Cl^-}}{C_{ZnCl^+}}$	(4.18)	$10^{-0.43}$ (b)
$K_{5,Zn} = \frac{C_{Zn^{2+}} C^2_{Cl^-}}{C_{ZnCl_2}}$	(4.19)	$10^{-0.61}$ (b)
$K_{6,Zn} = \frac{C_{Zn^{2+}} C^3_{Cl^-}}{C_{ZnCl_3^-}}$	(4.20)	$10^{-0.5}$ (b)
$K_{7,Zn} = \frac{C_{Zn^{2+}} C^4_{Cl^-}}{C_{ZnCl_4^{2-}}}$	(4.21)	$10^{-0.2}$ (b)
$K_{sp_{(PbL_2)}} = C_{Pb^{2+}} C^2_{L^-}$	(4.22)	9.18×10^{-17} (d)
$K_{sp_{(CdL_2)}} = C_{Cd^{2+}} C^2_{L^-}$	(4.23)	9.52×10^{-16} (d)
$K_{sp_{(ZnL_2)}} = C_{Zn^{2+}} C^2_{L^-}$	(4.24)	2.7×10^{-17} (d)
$K_{sp_{(HL)}} = C_{H^+} C_{L^-}$	(4.25)	7.38×10^{-11} (d)

Table 4.1 (Continued)

Equilibrium	Value of the equilibrium constant
$K_a = \frac{C_{H^+} C_{L^-}}{C_{HL_{(aq)}}}$ (4.26)	$10^{-3.4}$ (e)
$K_w = C_{H^+} C_{OH^-}$ (4.27)	10^{-14} (b)
$K_{CO_2} = \frac{C_{CO_{2(aq)}}}{P_{CO_{2(g)}}}$ (4.28)	0.0337 (f)
$K_8 = \frac{C_{HCO_3^-} C_{H^+}}{C_{CO_{2(aq)}}}$ (4.28)	4.3×10^{-7} (f)
$K_9 = \frac{C_{CO_3^{2-}} C_{H^+}}{C_{HCO_3^-}}$ (4.30)	4.7×10^{-11} (f)

(a): Dean (1979)
(b): Smith and Martell (1974)
(c): Sillen (1964)
(d): this work; see Appendix A
(e): Martinez et al.(1992)
(f): Segal (1989)

Water in contact with the atmosphere will become slightly acidic due to absorption of CO_2. Carbon dioxide in the air is in equilibrium with dissolved CO_2 in water:

$$CO_{2_{(g)}} \xleftrightarrow{K_{CO_2}} CO_{2_{(aq)}} \qquad R-4.28$$

When CO_2 dissolves in water, the following reactions occur;

$$CO_{2_{(aq)}} + 2H_2O \xleftrightarrow{K_8} HCO_3^- + H_3O^+_{(aq)} \qquad R-4.29$$

The HCO_3^- reacts with water forming CO_3^{2-}

$$HCO_3^- + H_2O \xleftrightarrow{K_9} CO_3^{2-} + H_3O^+_{(aq)} \qquad R-4.30$$

where K_{CO_2}, K_8 and K_9 are defined in Table 4.1. Their values were obtained from literature, and they are presented in Table 4.1.

The algorithm to find the metal(s) removed, and the equilibrium pH as well as the concentrations of the other species is based on :

1) mass balance equation for lead:

$$n^o_{Pb} = n_{Pb^{2+}} + n_{PbOH^+} + n_{Pb(OH)_2} + n_{PbNO_3^+} + n_{PbCl^+} + n_{PbCl_2} + n_{PbCl_3^-} + n_{PbCl_4^{2-}} + n_{PbL_{2(s)}} \qquad (4.31)$$

2) mass balance equation for cadmium:

$$n^o_{Cd} = n_{Cd^{2+}} + n_{CdOH^+} + n_{Cd(OH)_2} + n_{CdNO_3^+} + n_{CdCl^+} + n_{CdCl_2} + n_{CdCl_3^-} + n_{CdCl_4^{2-}} + n_{CdL_{2(s)}} \qquad (4.32)$$

3) mass balance equation for zinc:

$$n^{o}_{Zn} = n_{Zn^{2+}} + n_{ZnOH^{+}} + n_{Zn(OH)_2} + n_{ZnNO_3^{+}} + n_{ZnCl^{+}} + n_{ZnCl_2} + n_{ZnCl_3^{-}} + n_{ZnCl_4^{2-}} + n_{ZnL_{2(s)}} \tag{4.33}$$

4) mass balance equation for nitrate in its various forms:

$$n^{o}_{NO_3^-} = n_{NO_3^-} + n_{PbNO_3^+} + n_{CdNO_3^+} + n_{ZnNO_3^+} \tag{4.34}$$

5) mass balance equation for chloride in its various forms:

$$n^{o}_{Cl} = n_{Cl^-} + n_{PbCl^+} + 2n_{PbCl_2} + 3n_{PbCl_3^-} + 4n_{PbCl_4^{2-}} + n_{CdCl^+} + 2n_{CdCl_2} + 3n_{CdCl_3^-} + 4n_{CdCl_4^{2-}} + n_{ZnCl^+} + 2n_{ZnCl_2} + 3n_{ZnCl_3^-} + 4n_{ZnCl_4^{2-}} \tag{4.35}$$

6) mass balance equation for precipitating agent in various forms:

$$n_{L_{ad}} = n_{L} + 2n_{PbL_{2(s)}} + 2n_{CdL_{2(s)}} + 2n_{ZnL_{2(s)}} + n_{HL_{(s)}} + n_{HL_{(aq)}} \tag{4.36}$$

7) change balance equation expressing electroneutrality of the solution :

$$2n_{Pb^{2+}} + 2n_{Cd^{2+}} + 2n_{Zn^{2+}} + n_{PbOH^+} + n_{CdOH^+} + n_{ZnOH^+} + n_{PbCl^+} + n_{CdCl^+} + n_{ZnCl^+} + n_{H^+} + n_{Na^+} = n_{PbCl_3^-} + n_{CdCl_3^-} + n_{ZnCl_3^-} + 2n_{PbCl_4^{2-}} + 2n_{CdCl_4^{2-}} + 2n_{ZnCl_4^{2-}} + n_{OH^-} + n_{L^-} + n_{HCO_3^-} + 2n_{CO_3^{2-}} \tag{4.37}$$

The species in equations (4.31) to (4.37) were expressed in terms of the concentrations $c_{Pb^{2+}}$, $c_{Cd^{2+}}$, $c_{Zn^{2+}}$, $c_{NO_3^-}$, c_{Cl^-}, c_{L^-}, and c_{H^+}, using equations (4.1) to (4.21) and (4.26) to (4.30). Seven non-linear algebraic equations were obtained with eleven unknowns; $C_{Pb^{2+}}$, $n_{PbL_{2(s)}}/V$, $C_{Cd^{2+}}$, $n_{CdL_{2(s)}}/V$, $C_{Zn^{2+}}$, $n_{ZnL_{2(s)}}/V$, C_{L^-}, $n_{HL_{(s)}}/V$, $C_{NO_3^-}$, C_{Cl} and C_{H^+}. The equations are:

the mass balance equation for lead:

$$\begin{aligned} C^*_{Pb} = {} & C_{Pb^{2+}} + K_{1,Pb}K_w\frac{C_{Pb^{2+}}}{C_{H^+}} + K_{2,Pb}K_w^2\frac{C_{Pb^{2+}}}{C^2_{H^+}} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} \\ & + K_{4,Pb}C_{Pb^{2+}}C_{Cl^-} + K_{5,Pb}C_{Pb^{2+}}C^2_{Cl^-} + K_{6,Pb}C_{Pb^{2+}}C^3_{Cl^-} \\ & + K_{7,Pb}C_{Pb^{2+}}C^4_{Cl^-} + \frac{n_{PbL_{2(s)}}}{V} \end{aligned} \tag{4.38}$$

the mass balance equation for cadmium:

$$\begin{aligned} C^*_{Cd} = {} & C_{Cd^{2+}} + K_{1,Cd}K_w\frac{C_{Cd^{2+}}}{C_{H^+}} + K_{2,Cd}K_w^2\frac{C_{Cd^{2+}}}{C^2_{H^+}} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} \\ & + K_{4,Cd}C_{Cd^{2+}}C_{Cl^-} + K_{5,Cd}C_{Cd^{2+}}C^2_{Cl^-} + K_{6,Cd}C_{Cd^{2+}}C^3_{Cl^-} \\ & + K_{7,Cd}C_{Cd^{2+}}C^4_{Cl^-} + \frac{n_{CdL_{2(s)}}}{V} \end{aligned} \tag{4.39}$$

the mass balance equation for zinc:

$$\begin{aligned} C^*_{Zn} = {} & C_{Zn^{2+}} + K_{1,Zn}K_w\frac{C_{Zn^{2+}}}{C_{H^+}} + K_{2,Zn}K_w^2\frac{C_{Zn^{2+}}}{C^2_{H^+}} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-} \\ & + K_{4,Zn}C_{Zn^{2+}}C_{Cl^-} + K_{5,Zn}C_{Zn^{2+}}C^2_{Cl^-} + K_{6,Zn}C_{Zn^{2+}}C^3_{Cl^-} \\ & + K_{7,Zn}C_{Zn^{2+}}C^4_{Cl^-} + \frac{n_{ZnL_{2(s)}}}{V} \end{aligned} \tag{4.40}$$

the mass balance equation for nitrate:

$$C^{*}_{NO_3} = C_{NO_3^-} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-} \tag{4.41}$$

the mass balance equation for chloride:

$$\begin{aligned} C^{*}_{Cl} = {} & C_{Cl^-} + K_{4,Pb}C_{Pb^{2+}}C_{Cl^-} + K_{5,Pb}C_{Pb^{2+}}C^{2}_{Cl^-} + K_{6,Pb}C_{Pb^{2+}}C^{3}_{Cl^-} \\ & + K_{7,Pb}C_{Pb^{2+}}C^{4}_{Cl^-} + K_{4,Cd}C_{Cd^{2+}}C_{Cl^-} + K_{5,Cd}C_{Cd^{2+}}C^{2}_{Cl^-} \\ & + K_{6,Cd}C_{Cd^{2+}}C^{3}_{Cl^-} + K_{7,Cd}C_{Cd^{2+}}C^{4}_{Cl^-} + K_{4,Zn}C_{Zn^{2+}}C_{Cl^-} \\ & + K_{5,Zn}C_{Zn^{2+}}C^{2}_{Cl^-} + K_{6,Zn}C_{Zn^{2+}}C^{3}_{Cl^-} + K_{7,Zn}C_{Zn^{2+}}C^{4}_{Cl^-} \end{aligned} \tag{4.42}$$

the mass balance equation for the precipitating agent:

$$C^{*}_{L} = C_{L^-} + 2\frac{n_{PbL_{2(s)}}}{V} + 2\frac{n_{CdL_{2(s)}}}{V} 2\frac{n_{ZnL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_a} \tag{4.43}$$

and the charge balance equation :

$$\begin{aligned} & 2C_{Pb^{2+}} + 2C_{Cd^{2+}} + 2C_{Zn^{2+}} + K_{1,Pb}K_w\frac{C_{Pb^{2+}}}{C_{H^+}} + K_{1,Cd}K_w\frac{C_{Cd^{2+}}}{C_{H^+}} + K_{1,Zn}K_w\frac{C_{Zn^{2+}}}{C_{H^+}} \\ & + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-} + K_{4,Pb}C_{Pb^{2+}}C_{Cl^-} \\ & + K_{4,Cd}C_{Cd^{2+}}C_{Cl^-} + K_{4,Zn}C_{Zn^{2+}}C_{Cl^-} + C_{H^+} + C_{Na^+} = \\ & \quad K_{6,Pb}C_{Pb^{2+}}C^{3}_{Cl^-} + K_{6,Cd}C_{Zn^{2+}}C^{3}_{Cl^-} + K_{6,Zn}C_{Zn^{2+}}C^{3}_{Cl^-} + 2K_{7,Pb}C_{Pb^{2+}}C^{4}_{Cl^-} \\ & \quad + 2K_{7,Cd}C_{Cd^{2+}}C^{4}_{Cl^-} + 2K_{7,Zn}C_{Zn^{2+}}C^{4}_{Cl^-} + \frac{K_w}{C_{H^+}} + C_{L^-} + \frac{K'_8}{C_{H^+}} + 2\frac{K'_9}{C^{2}_{H^+}} \end{aligned} \tag{4.44}$$

where, $K_8 = K_8 K_{CO_2} P_{CO_{2(g)}}$, and $K'_9 = \frac{K_9 K'_8}{C_{H^+}}$.

If a species precipitates, its solubility product equation is satisfied; if it does not precipitate, its term must be dropped from the equations. For example, if there is a precipitate $PbL_{2(s)}$, then the solubility product equation (4.22), must be satisfied, and $C_{Pb^{2+}} = K_{sp(PbL_2)} / C^2_{L^-}$. When there is no $PbL_{2(s)}$ precipitate, then $n_{PbL_{2(s)}} = 0$. The same is applied for the $HL_{(s)}$ precipitate, where either $C_{L^-} = K_{sp(HL)} / C_{H^+}$ or $n_{HL_{(s)}} = 0$.

The derived model is in its general form, where lead, cadmium, zinc, nitrate chloride, and precipitating agent exist in the solution. For the feed speciation, i.e. before adding the precipitating agent, the mass balance equation of the precipitating agent, and all the species containing this agent (including C_{Na^+}) in the other equations were dropped. For a solution containing only one metal, the mass balance equations for the other metals as well as their species in the other equations were eliminated. Similarly, if the precipitation is from nitrate solution, then the chloride mass balance equation and any chloride species in the other equations were dropped, and vise-versa. For example, when the precipitation of lead from nitrate solution was considered, equations (4.38) to (4.44) were reduced to equations (4.45) to (4.48) as presented in Table 4.2. The model of this system was divided into two steps. First, the speciation of the feed is determined. The precipitating agent balance equation, equation (4.47), as well as the species concentration, C_{L^-} and C_{Na^+}, in the charge balance equation, equation (4.48), were eliminated. C^*_{Pb} and $C^*_{NO_3}$ were replaced by C^o_{Pb} and $C^o_{NO_3}$, respectively. In a metal removal process, the total concentration of the metal, C^o_{Pb}, and the pH of the feed ($-\log C^o_{H^+}$), are known. Three equations with three unknowns, $C_{Pb^{2+}}$, $C_{NO_3^-}$, and

$C^{o}_{NO_3}$ were obtained. The concentration of total nitrate in the feed, $C^{o}_{NO_3}$, was calculated for every, C^{o}_{Pb} and C_{H^+}, and then corrected to $C^{*}_{NO_3}$ and used as an input to the other cases. Second, when the precipitating agent is added, there are four possible cases: no precipitate, $PbL_{2(s)}$ and/or $HL_{(s)}$ precipitate(s) could be formed. The model of this precipitation process was divided into the following four cases:

1) the precipitating agent was added to the system, but no precipitate was formed. Equations (4.45) to (4.48), at $n_{PbL_{2(s)}} = n_{HL_{(s)}} = 0$, were used.

2) two precipitates, $PbL_{2(s)}$ and $HL_{(s)}$, were formed. Equations (4.45) to (4.48) were solved at $C_{Pb^{2+}} = K_{sp_{PbL_2}} / C^{2}_{L^-}$ and $C_{L^-} = K_{sp_{(HL)}} / C_{H^+}$.

3) one precipitate, $HL_{(s)}$, was formed. Equations (4.45) to (4.48), at $n_{PbL_{2(s)}} = 0$ and $C_{L} = K_{sp_{(HL)}} / C_{H^+}$ were used.

4) one precipitate, $PbL_{2(s)}$, was formed. In this case, equations (4.45) to (4.48), with $n_{HL_{(s)}} = 0$, and $C_{Pb^{2+}} = K_{sp_{PbL_2}} / C^{2}_{L^-}$, were used.

The mass- and charge balance equations of the other considered systems are presented in Tables 4.3 to 4.6. Similarly, the models of these systems were divided into cases, depending on the precipitate(s) formed.

Table 4.2: Mass- and Charge-balance equations for the precipitation of lead from nitrate solutions

lead mass balance	$C^{\bullet}_{Pb} = C_{Pb^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{2,Pb}K_{w}^{2}\frac{C_{Pb^{2+}}}{C_{H}^{2}} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + \frac{n_{PbL_{2(s)}}}{V}$ (4.45)
nitrate mass balance	$C^{\bullet}_{NO_3} = C_{NO_3^-} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-}$ (4.46)
precipitating agent mass balance	$C^{\bullet}_{L} = C_{L^-} + 2\frac{n_{PbL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_a}$ (4.47)
charge balance	$2C_{Pb^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + C_{H^+} + C_{Na^+} =$ $\frac{K_w}{C_{H^+}} + C_{L^-} + C_{NO_3^-} + \frac{K_4^{'}}{C_{H^+}} + 2\frac{K_5^{'}}{C_{H^+}^{2}}$ (4.48)

Table 4.3: Mass- and Charge-balance equations for the precipitation of lead from chloride solutions

lead mass balance	$C^{\bullet}_{Pb} = C_{Pb^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{2,Pb}K^{2}_{w}\frac{C_{Pb^{2+}}}{C^{2}_{H^{+}}} + K_{4,Pb}C_{Pb^{2+}}C_{Cl^{-}}$ $+ K_{5,Pb}C_{Pb^{2+}}C^{2}_{Cl^{-}} + K_{6,Pb}C_{Pb^{2+}}C^{3}_{Cl^{-}} + K_{7,Pb}C_{Pb^{2+}}C^{4}_{Cl^{-}} + \frac{n_{PbL_{2(s)}}}{V}$ (4.49)
chloride mass balance	$C^{\bullet}_{Cl} = C_{Cl^{-}} + K_{4,Pb}C_{Pb^{2+}}C_{Cl^{-}} + K_{5,Pb}C_{Pb^{2+}}C^{2}_{Cl^{-}} + K_{6,Pb}C_{Pb^{2+}}C^{3}_{Cl^{-}}$ $+ K_{7,Pb}C_{Pb^{2+}}C^{4}_{Cl^{-}}$ (4.50)
precipitating agent mass balance	$C^{\bullet}_{L} = C_{L^{-}} + 2\frac{n_{PbL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^{+}}C_{L^{-}}}{K_{a}}$ (4.47)
charge balance	$2C_{Pb^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{4,Pb}C_{Pb^{2+}}C_{Cl^{-}} + C_{H^{+}} + C_{Na^{+}} =$ $K_{6,Pb}C_{Pb^{2+}}C^{3}_{Cl^{-}} + 2K_{7,Pb}C_{Pb^{2+}}C^{4}_{Cl^{-}} + \frac{K_{w}}{C_{H^{+}}} + C_{L^{-}} + \frac{K'_{4}}{C_{H^{+}}} + 2\frac{K'_{5}}{C^{2}_{H^{+}}}$ (4.51)

Table 4.4: Mass- and Charge-balance equations for the precipitation of cadmium from nitrate solutions

Cadmium mass balance	$C^{*}_{Cd} = C_{Cd^{2+}} + K_{1,Cd}K_{w}\frac{C_{Cd^{2+}}}{C_{H^{+}}} + K_{2,Cd}K_{w}^{2}\frac{C_{Cd^{2+}}}{C_{H}^{2}} + K_{3,Cd}C_{Cd^{2+}}C_{NO_{3}^{-}} + \frac{n_{CdL_{2(s)}}}{V}$	(4.52)
nitrate mass balance	$C^{*}_{NO_{3}} = C_{NO_{3}^{-}} + K_{3,Cd}C_{Cd^{2+}}C_{NO_{3}^{-}}$	(4.53)
precipitating agent mass balance	$C^{*}_{L} = C_{L^{-}} + 2\frac{n_{CdL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^{+}}C_{L^{-}}}{K_{a}}$	(4.54)
charge balance	$2C_{Cd^{2+}} + K_{1,Cd}K_{w}\frac{C_{Cd^{2+}}}{C_{H^{+}}} + K_{3,Cd}C_{Cd^{2+}}C_{NO_{3}^{-}} + C_{H^{+}} + C_{Na^{+}} =$ $\frac{K_{w}}{C_{H^{+}}} + C_{L^{-}} + C_{NO_{3}^{-}} + \frac{K'_{4}}{C_{H^{+}}} + 2\frac{K'_{5}}{C_{H^{+}}^{2}}$	(4.55)

Table 4.5: Mass- and Charge-balance equations for the precipitation of zinc from nitrate solutions

zinc mass balance	$C^{\bullet}_{Zn} = C_{Zn^{2+}} + K_{1,Zn} K_w \frac{C_{Zn^{2+}}}{C_{H^+}} + K_{2,Zn} K_w^2 \frac{C_{Zn^{2+}}}{C_H^2} + K_{3,Zn} C_{Zn^{2+}} C_{NO_3^-} + \frac{n_{ZnL_{2(s)}}}{V}$ (4.56)
nitrate mass balance	$C^{\bullet}_{NO_3} = C_{NO_3^-} + K_{3,Zn} C_{Zn^{2+}} C_{NO_3^-}$ (4.57)
precipitating agent mass balance	$C^{\bullet}_L = C_{L^-} + 2 \frac{n_{ZnL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+} C_{L^-}}{K_a}$ (4.58)
charge balance	$2C_{Zn^{2+}} + K_{1,Zn} K_w \frac{C_{Zn^{2+}}}{C_{H^+}} + K_{3,Zn} C_{Zn^{2+}} C_{NO_3^-} + C_{H^+} + C_{Na^+} =$ $\frac{K_w}{C_{H^+}} + C_{L^-} + C_{NO_3^-} + \frac{K_4^{'}}{C_{H^+}} + 2 \frac{K_5^{'}}{C_{H^+}^2}$ (4.59)

Table 4.6: Mass- and Charge-balance equations for the precipitation of lead, cadmium and zinc from nitrate solutions

lead mass balance	$C^{\bullet}_{Pb} = C_{Pb^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{2,Pb}K^{2}_{w}\frac{C_{Pb^{2+}}}{C^{2}_{H}} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + \frac{n_{PbL_{2(s)}}}{V}$ (4.45)
cadmium mass balance	$C^{\bullet}_{Cd} = C_{Cd^{2+}} + K_{1,Cd}K_{w}\frac{C_{Cd^{2+}}}{C_{H^{+}}} + K_{2,Cd}K^{2}_{w}\frac{C_{Cd^{2+}}}{C^{2}_{H}} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} + \frac{n_{CdL_{2(s)}}}{V}$ (4.52)
zinc mass balance	$C^{\bullet}_{Zn} = C_{Zn^{2+}} + K_{1,Zn}K_{w}\frac{C_{Zn^{2+}}}{C_{H^{+}}} + K_{2,Zn}K^{2}_{w}\frac{C_{Zn^{2+}}}{C^{2}_{H}} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-} + \frac{n_{ZnL_{2(s)}}}{V}$ (4.56)
nitrate mass balance	$C^{\bullet}_{NO_3} = C_{NO_3^-} + K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-}$ (4.60)
precipitating agent mass balance	$C^{\bullet}_{L} = C_{L^-} + 2\frac{n_{PbL_{2(s)}}}{V} + 2\frac{n_{CdL_{2(s)}}}{V} 2\frac{n_{ZnL_{2(s)}}}{V} + \frac{n_{HL_{(s)}}}{V} + \frac{C_{H^+}C_{L^-}}{K_a}$ (4.61)
charge balance	$2C_{Pb^{2+}} + 2C_{Cd^{2+}} + 2C_{Zn^{2+}} + K_{1,Pb}K_{w}\frac{C_{Pb^{2+}}}{C_{H^{+}}} + K_{1,Cd}K_{w}\frac{C_{Cd^{2+}}}{C_{H^{+}}} + K_{1,Zn}K_{w}\frac{C_{Zn^{2+}}}{C_{H^{+}}}$ $+ K_{3,Pb}C_{Pb^{2+}}C_{NO_3^-} + K_{3,Cd}C_{Cd^{2+}}C_{NO_3^-} + K_{3,Zn}C_{Zn^{2+}}C_{NO_3^-} + C_{H^+} + C_{Na^+} =$ $\frac{K_w}{C_{H^+}} + C_{L^-} + C_{NO_3^-} + \frac{K'_4}{C_{H^+}} + 2\frac{K'_5}{C^2_{H^+}}$ (4.62)

4.2 Computational Procedure

Since the concentrations of species considered were low, it was assumed that the activity coefficients for all species are equal to one, and the mass-stability constants at ionic strength equal to zero were used. For high ionic strengths the mass-stability constants must be corrected. The main references for stability constants are reported in Table 4.1. Some of the constants in these references were experimentally measured, while others were obtained by extrapolation. Different values of each constant from these sources were tested, and similar results were obtained. The K_1 values had a small effect on the equilibrium pH, but not on the percentage removal. In this work, the values which produced the best prediction were selected. The solubility products of the precipitates were determined experimentally as explained in Appendix A.

The inputs to the model are the concentration of hydrogen in the feed ($C^{o}_{H^{+}}$), the total concentration of the metal in the feed (C^{o}_{Pb}, C^{o}_{Cd}, C^{o}_{Zn}), and the total number of moles of precipitating agent added ($n_{L_{st}}$). The equations of each case were reduced to a polynomial, two equations, or three equations. The polynomials were solved using MATLAB. When solved, one positive root was always obtained. The other roots were either negative or imaginary. The non-linear equations were solved simultaneously using the Newton-Raphson iterative method. The solutions of these equations depend on the initial guessed values. The sensitivity of the solution to the initial values was investigated. Positive roots were obtained when the initial values for the equilibrium concentration of hydrogen were equal to or higher than the initial concentration of hydrogen in the feed, and for the other species, were equal to or less than their total concentrations in the feed. In these ranges, the solutions of the equations converged to the same positive roots. Negative root(s) were obtained when the initial values for the hydrogen concentration were less than 10^{-7} and/or for the other species were higher than their total concentrations in the feed. When the concentration of hydrogen is less than 10^{-7}, other hydroxo-complexes, which are not considered in the model, are expected to present in the system. In general, all initial values which were consistent with the physics of the problem, produced the same positive roots. In this work, the following initial values were used:

$$C^{i}_{Pb^{2+}} = C^{o}_{Pb}$$

$$C^{i}_{Cd^{2+}} = C^{o}_{Cd}$$

$$C^{i}_{Zn^{2+}} = C^{o}_{Zn}$$

$$C^{i}_{H^{+}} = C^{o}_{H}$$

$$C^{i}_{L^{-}} = C^{*}_{L}$$

$$C^{i}_{NO_3^{-}} = 2 \times (C^{o}_{Pb}\ , C^{o}_{Cd}\ , \text{and/or } C^{o}_{Zn})$$

$$C^{i}_{Cl^{-}} = 2 \times (C^{o}_{Pb}\ , C^{o}_{Cd}\ , \text{and/or } C^{o}_{Zn})$$

The sensitivity of the model prediction to the values of the equilibrium constants was also investigated. The equilibrium constants were varied about the values in Table 4.1 by ± 50%. For the precipitation of a single metal, varying K_1's had only a small effect on the equilibrium pH. The variation of the other equilibrium constants had changed the percentage removal, loss of the precipitating agent or equilibrium pH by less than 1%. The prediction of the model became sensitive to the values of $K_{sp_{PbL_2}}$, $K_{sp_{CdL_2}}$, and $K_{sp_{ZnL_2}}$ when the precipitation of a mixture of lead, cadmium, and zinc was considered. A feed solution contain

2.0, 2.0, and 2.1 mM of lead, cadmium, and zinc, respectively, at pH^o=4.3, was considered. The mole ratio of the precipitating agent to the metals, r_L^o, was varied from 1.26 to 1.99. The results are presented in Tables 4.7 To 4.9. The maximum effect of the variation of K_{sp}'s was obtained at low percentage removal(s) of metal(s) or at low r_L^o, due to the competition among the metals. This effect diminished at the maximum percentage removal of the three metals. Variation of $K_{sp_{HL}}$ had no effect on the percentage removal or on the equilibrium pH.

The computational procedure is described in the flowchart (Appendix B), and the equations of each precipitation process (for each case) are illustrated in Table B.1 for precipitation of metals in nitrate solution. For precipitation in chloride solution, the mass balance equation for nitrate, and the nitrate species in the other equations and in the flowchart must be replaced by the chloride mass balance equation and chloride species. For example, the equations (4.45) to (4.48) in case (1) (X≡Pb), were replaced by equations (4.49) to (4.51), $C_{L^-}=0$, $C_{Na^+}=0$, and $n_{PbL_{2(s)}}=0$.

Table 4.7: Sensitivity of the model prediction to the values of $K_{sp_{PbL_2}}$

r_L^o	$K_{sp_{PbL_2}}$			$K_{sp_{PbL_2}}$ - 50%			$K_{sp_{PbL_2}}$ + 50%		
	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}
1.26	88.7	0.65	97.3	94.0	-0.45	97.2	84.0	5.3	97.5
1.37	90.4	15.7	97.7	94.8	11.4	97.6	86.4	19.6	97.8
1.48	92.1	30.7	98.1	95.7	27.2	98.1	88.7	34.0	98.2
1.59	93.7	45.8	98.5	96.6	43.0	98.5	91.1	48.3	98.6
1.71	95.4	60.8	99.0	97.5	58.7	98.9	93.5	62.6	99.0
1.82	97.1	75.8	99.4	98.4	74.5	99.3	95.9	77.0	99.4
1.93	98.9	90.8	99.8	99.4	90.3	99.7	98.4	91.2	99.8
1.99	99.8	98.1	99.9	99.9	98.0	99.9	99.7	98.2	99.9

Table 4.8: Sensitivity of the model prediction to the values of $K_{sp_{CdL_2}}$

r_L^o	$K_{sp_{CdL_2}}$			$K_{sp_{CdL_2}}$ - 50%			$K_{sp_{CdL_2}}$ + 50%		
	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}
1.26	88.7	0.65	97.3	80.1	11.4	95.3	92.1	-3.5	98.2
1.37	90.4	15.7	97.7	83.1	24.9	96.0	93.2	12.1	98.4
1.48	92.1	30.7	98.1	86.0	38.3	96.7	94.4	27.8	98.7
1.59	93.7	45.8	98.5	89.0	51.7	97.4	95.6	43.4	99.0
1.71	95.4	60.8	99.0	92.0	65.1	98.1	96.8	59.1	99.3
1.82	97.1	75.8	99.4	95.0	78.5	98.9	98.0	74.7	99.6
1.93	98.9	90.8	99.8	98.0	91.8	99.6	99.2	90.3	99.8
1.99	99.8	98.1	99.9	99.6	98.4	99.9	99.8	98.0	99.9

Table 4.9: Sensitivity of the model prediction to the values of $K_{sp_{ZnL_2}}$

r_L^o	$K_{sp_{ZnL_2}}$			$K_{sp_{ZnL_2}}$ - 50%			$K_{sp_{ZnL_2}}$ + 50%		
	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}	R_{Pb}	R_{Cd}	R_{Zn}
1.26	88.7	0.65	97.3	88.6	-0.59	98.7	88.8	1.9	96.1
1.37	90.4	15.7	97.7	90.3	14.6	98.9	90.5	16.7	96.7
1.48	92.1	30.7	98.1	92.0	29.9	99.1	92.1	31.6	97.3
1.59	93.7	45.8	98.5	93.7	45.1	99.3	93.8	46.4	97.8
1.71	95.4	60.8	99.0	95.4	60.3	99.5	95.5	61.3	98.4
1.82	97.1	75.8	99.4	97.1	75.5	99.7	97.2	76.1	99.0
1.93	98.9	90.8	99.8	98.8	90.7	99.9	98.9	90.9	99.6
1.99	99.8	98.1	99.9	99.8	98.1	99.9	99.8	98.2	99.9

4.3 Model Predictions

The predictions of the model are presented and interpreted for the precipitation of a single metal (lead, cadmium, or zinc), as well as a mixture of the three metals. The precipitation of lead in chloride solution was also predicted. The results of the model and the corresponding experimental data are presented in the same figure in terms of the percentage removal of the metal, percentage loss of the precipitating agent, and the equilibrium pH, versus the independent variable. The partial pressure of carbon dioxide, (P_{CO_2}), in the atmosphere was taken as 3.53×10^{-4} atm.

The model predictions for the effect of the mole ratio of the precipitating agent to lead (r_L^o) are compared to the experimental data in Figure 4.1, for feed solutions of lead at pH of 4.2 (no acid was added to the system). Figure 4.2 shows the effect of the mole ratio of the precipitating agent to lead, at different feed concentrations of lead. The effect of pH of the feed on the removal of lead and on the equilibrium pH was predicted by the model and is compared to the experimental data in Figure 4.3. The effect of mole ratio of the precipitating agent to lead on the removal of lead and on the equilibrium pH, in the presence of acid, is shown in Figure 4.4. The effect of chloride concentration in the feed on the removal of lead, and on the equilibrium pH is shown in Figure 4.5.

The model predictions for the effect of the mole ratio of the precipitating agent to metal on the removal of cadmium and zinc, are compared with the experimental data in Figures 4.6 and 4.7, respectively. Figures 4.8 and 4.9 show the prediction of the effect of initial pH on the removal of cadmium and of zinc, respectively. Finally, the effect of the mole ratio of the precipitating agent to total metals on the removal of lead, cadmium, and zinc was predicted by the model and compared with the experimental results in the Figure 4.10.

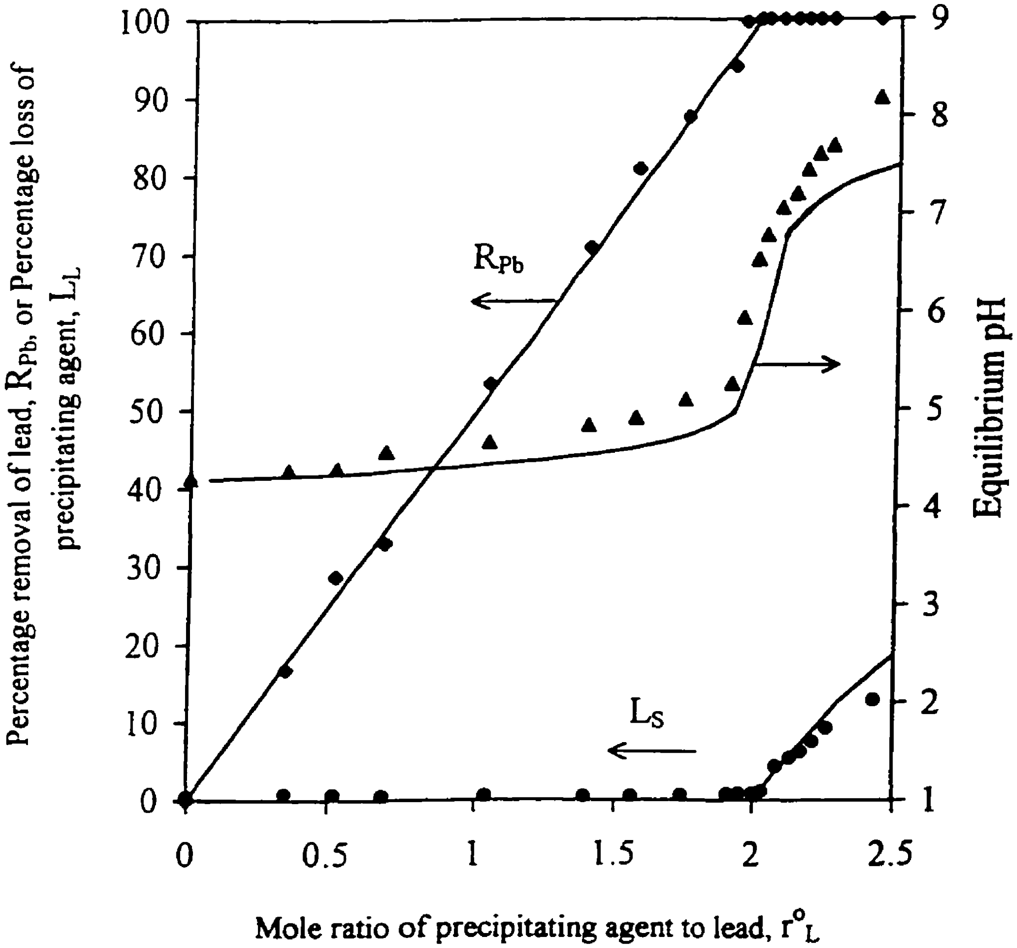


Figure 4.1: Effect of mole ratio of sodium di-(n-octyl) phosphinate to lead on the removal of lead, the loss of precipitating agent, and the equilibrium pH. $C^o_{Pb} = 5.5$ mM, $pH^o = 4.2$, $r^o_{NO_3} = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

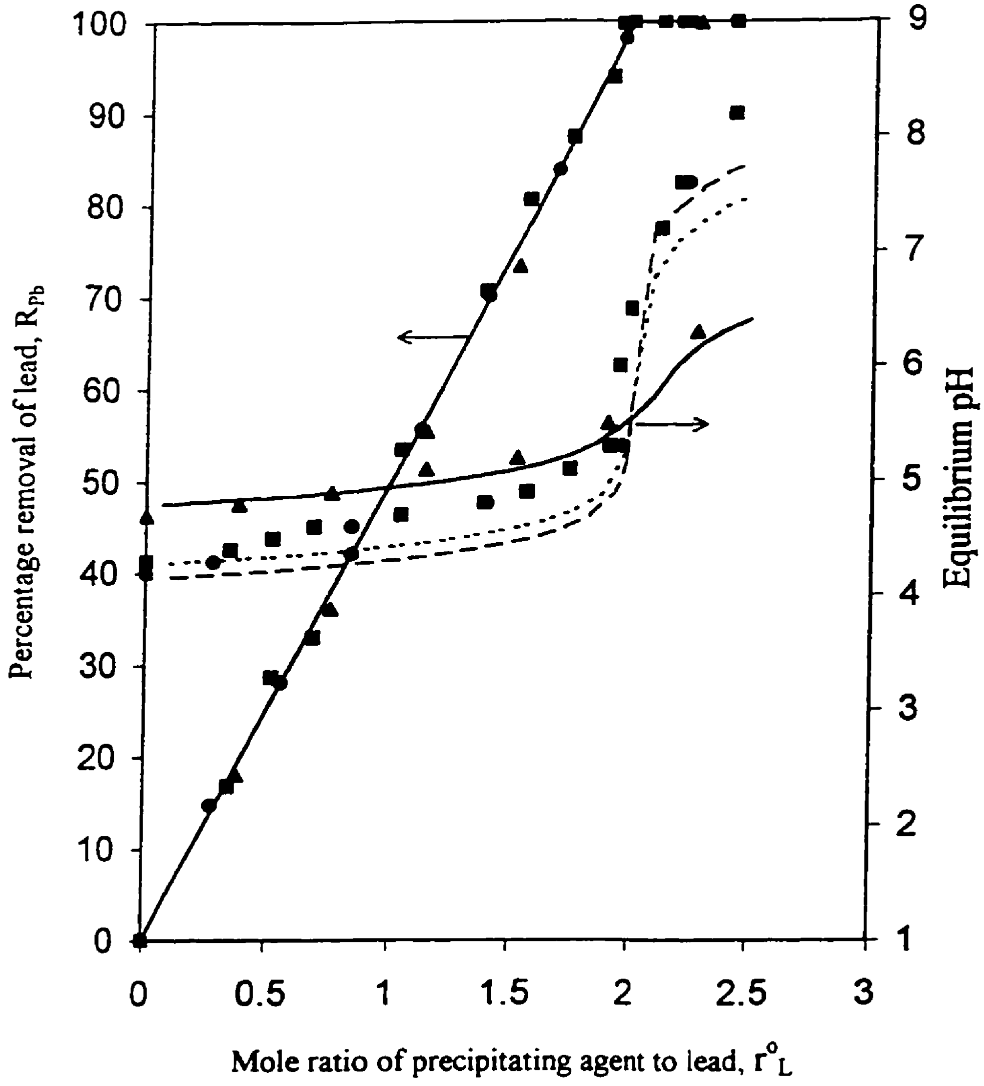


Figure 4.2: Effect of mole ratio of sodium di(n-octyl) phosphinate to lead on the removal of lead, and the equilibrium pH, at different feed concentration of lead (▲, ——) $C^o_{Pb} = 0.46$ mM, pH° = 4.6; (■, -----) $C^o_{Pb} = 5.5$ mM, pH° = 4.2; (●, —··—) $C^o_{Pb} = 10.62$ mM, pH° = 4.1; $r^o_{NO_3} = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

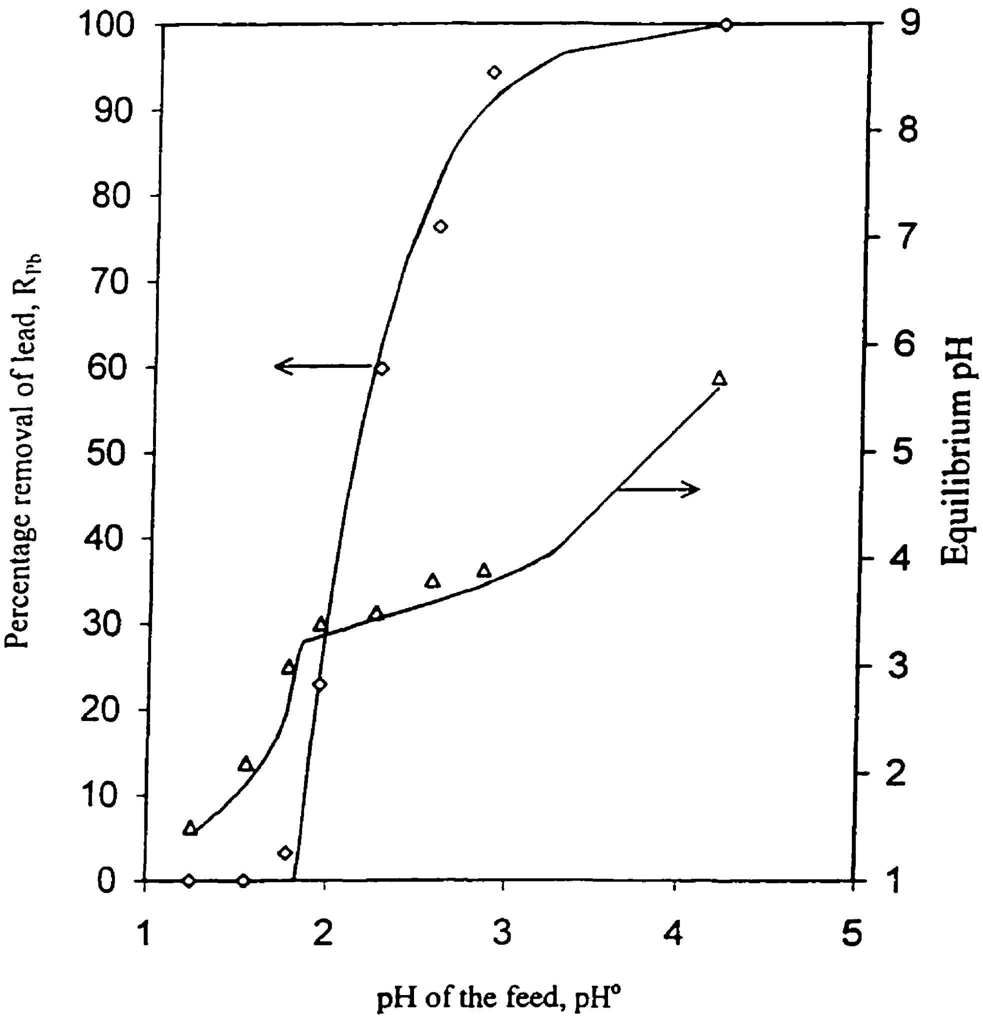


Figure 4.3: Effect of feed pH on the removal of lead, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^{o}_{Pb} = 7.1$ mM, $r^{o}_{L} = 2.0$, $C^{o}_{Cd} = C^{o}_{Zn} = C^{o}_{Ca} = C^{o}_{Na} = C^{o}_{Cl} = 0$. Points-experiments; lines-model.

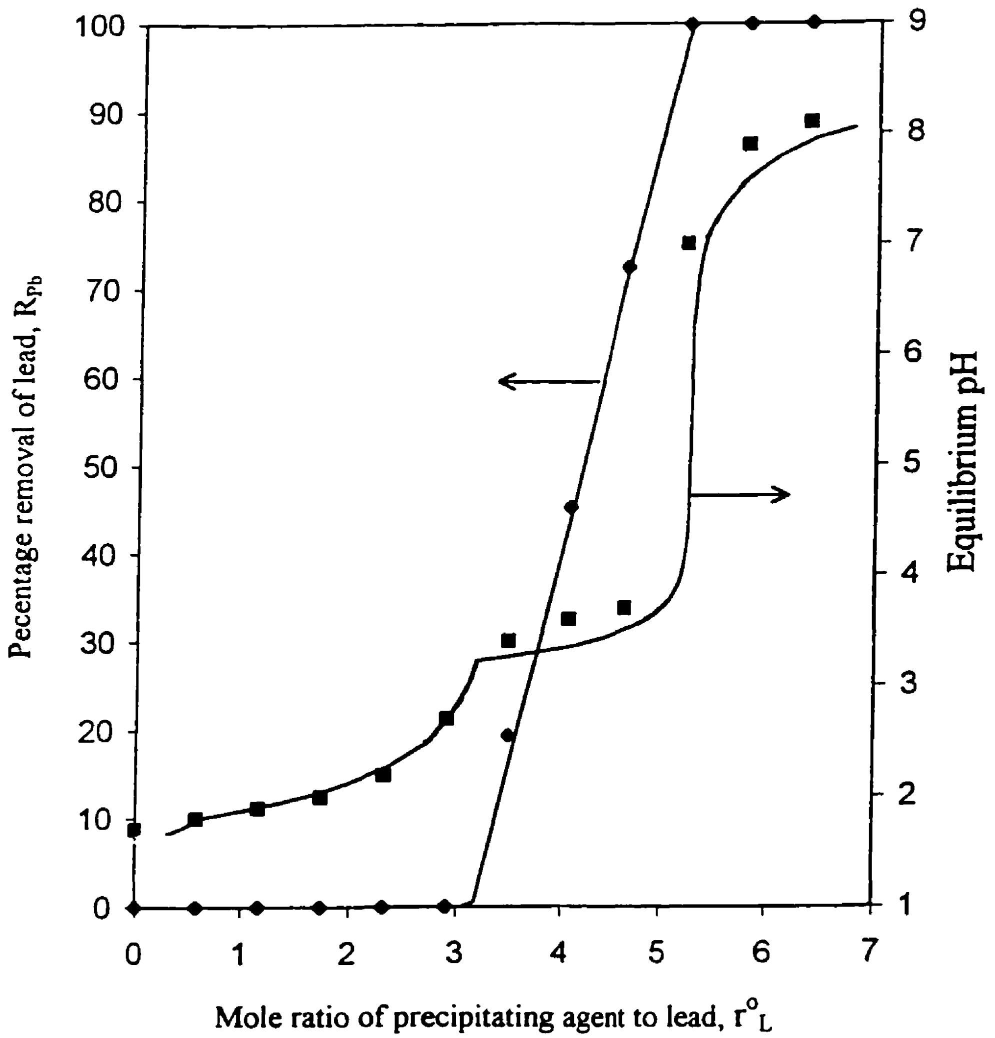


Figure 4.4: Effect of mole ratio of sodium di(n-octyl) phosphinate on the removal of lead, and the equilibrium pH, in the presence of free acid.

$C^o_{Pb} = 6.75$ mM, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

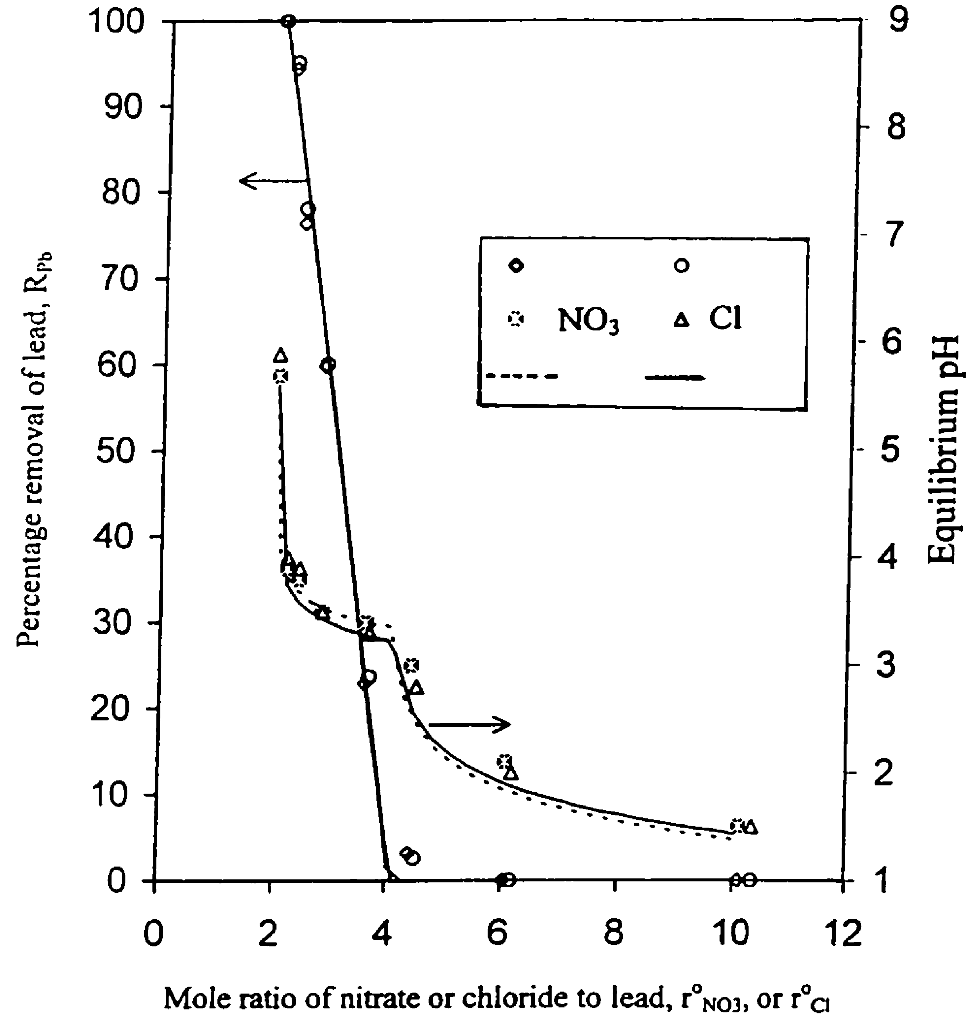


Figure 4.5: Effect of chloride concentration (using HCl) on the removal of lead, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Pb} = 7.0$ mM, $r^o_L = 2.0$, $C^o_{Cd} = C^o_{Zn} = C^o_{Ca} = C^o_{Na} = 0$. Points-experiments; lines-model.

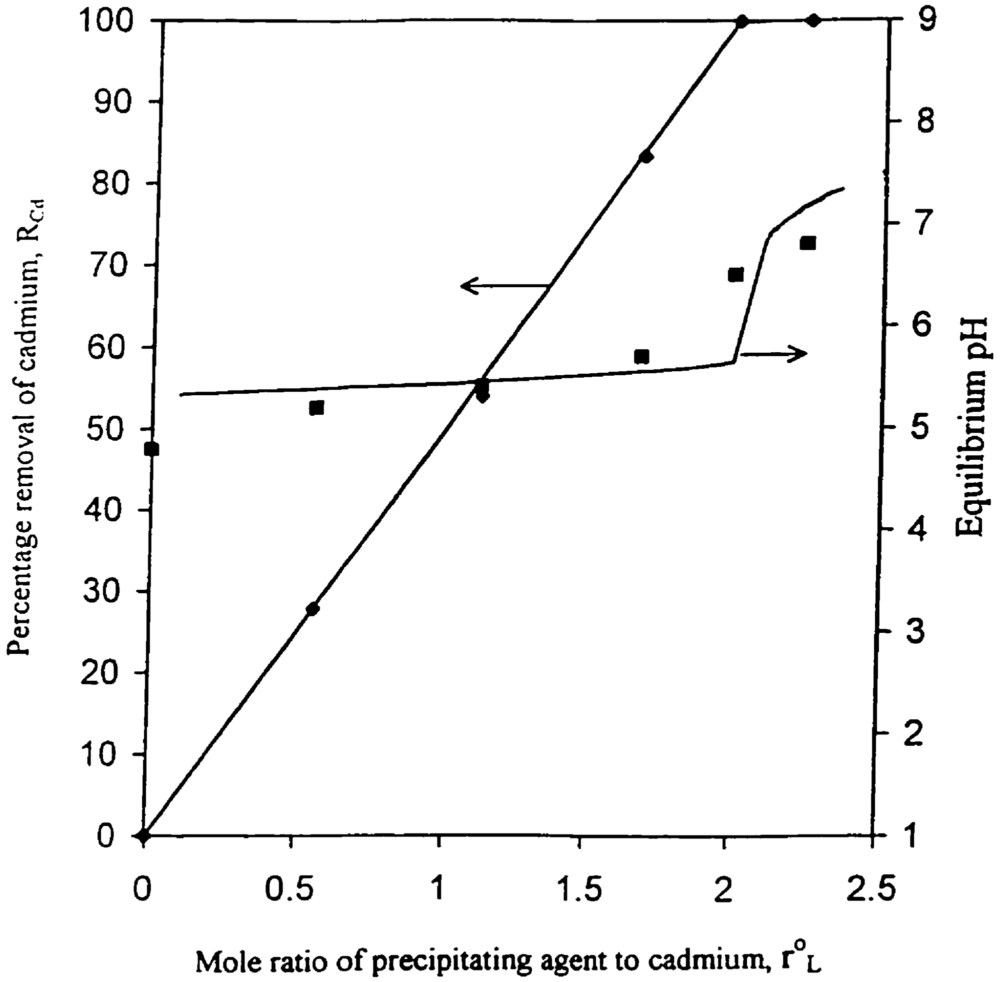


Figure 4.6: Effect of mole ratio of sodium di-(n-octyl) phosphinate to cadmium on the removal of cadmium, and the equilibrium pH.

$C^{o}_{Cd} = 5.9$ mM, $pH^{o} = 4.7$, $r^{o}_{NO_3} = 2.0$, $C^{o}_{Pb} = C^{o}_{Zn} = C^{o}_{Ca} = C^{o}_{Na} = C^{o}_{Cl} = 0$. Points-experiments; lines-model.

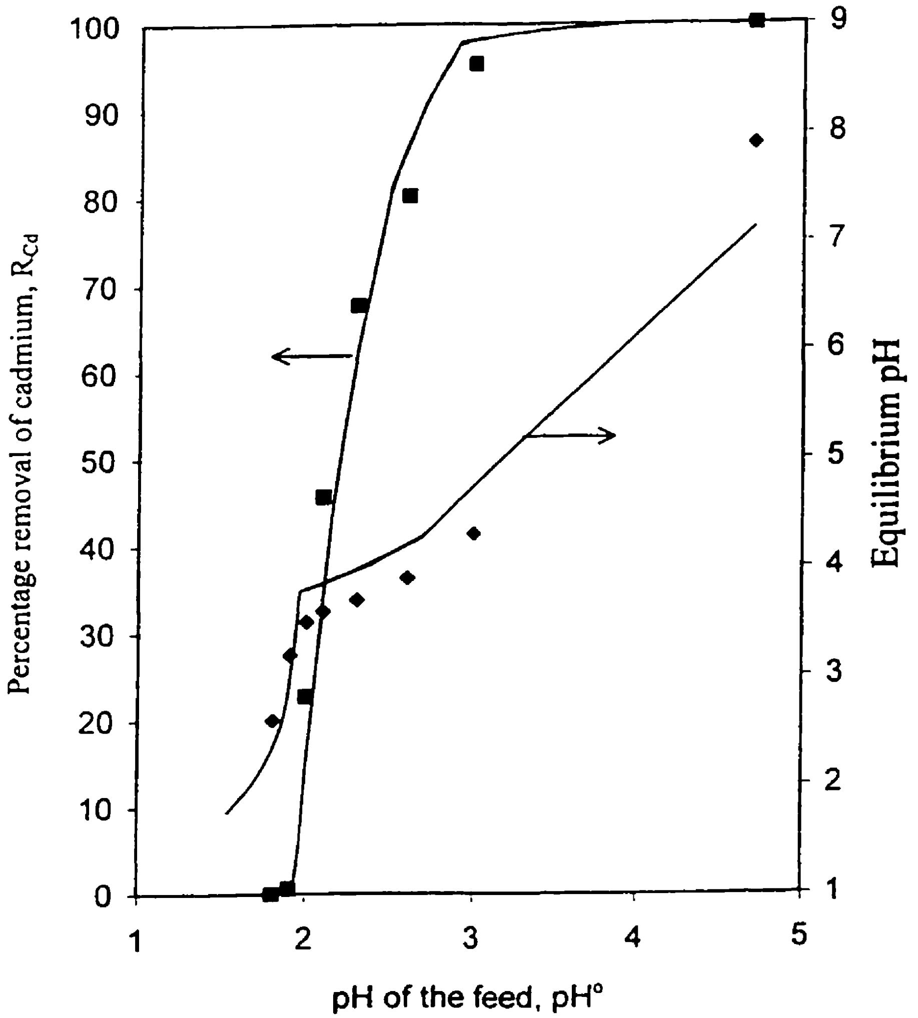


Figure 4.7: Effect of feed pH on the removal of cadmium, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^{o}_{Cd} = 5.9$ mM, $r^{o}_{L} = 2.2$, $C^{o}_{Pb} = C^{o}_{Zn} = C^{o}_{Ca} = C^{o}_{Na} = C^{o}_{Cl} = 0$. Points-experiments; lines-model.

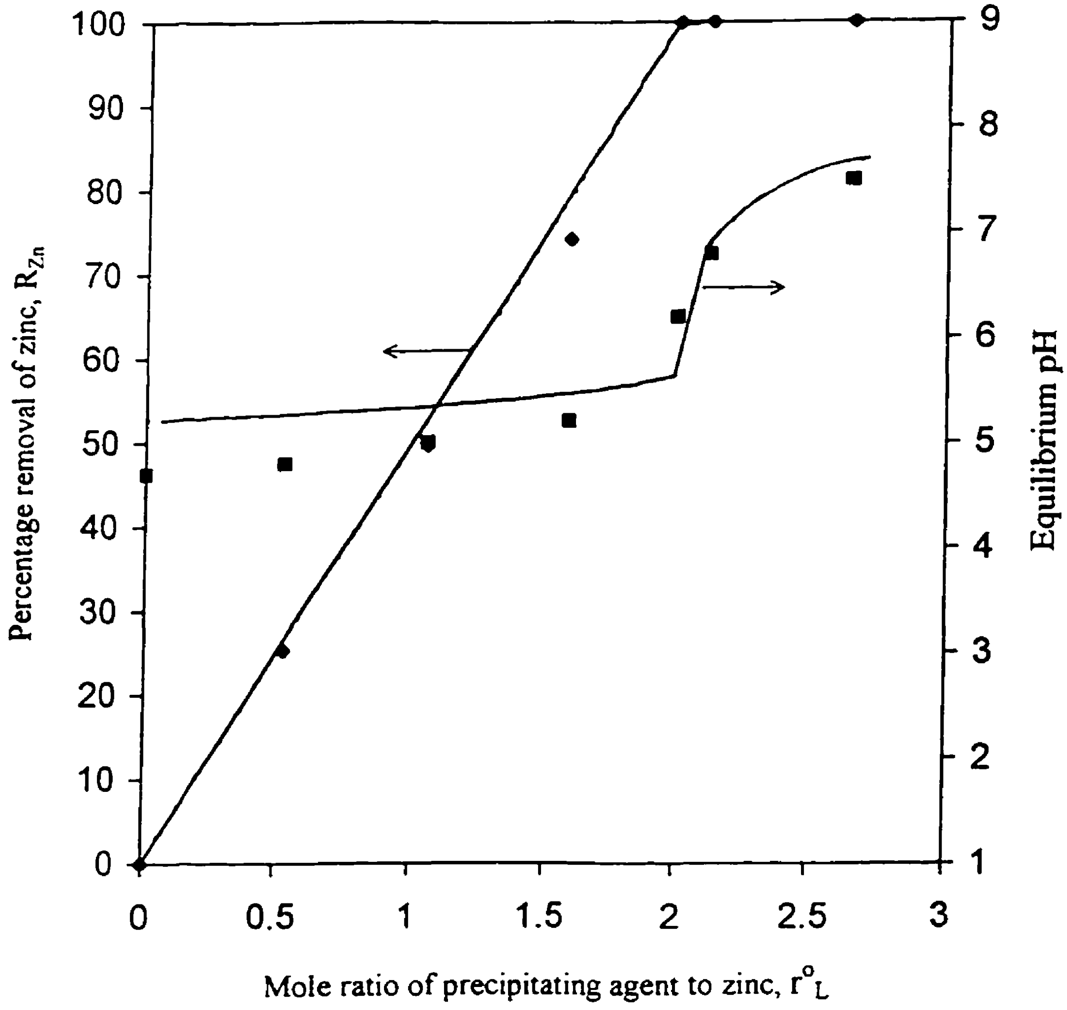


Figure 4.8: Effect of mole ratio of sodium di-(n-octyl) phosphinate to zinc on the removal of zinc, and the equilibrium pH.

$C^o_{Zn} = 6.3$ mM, $pH^o = 4.6$, $r^o_{NO_3} = 2.0$, $C^o_{Pb} = C^o_{Cd} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

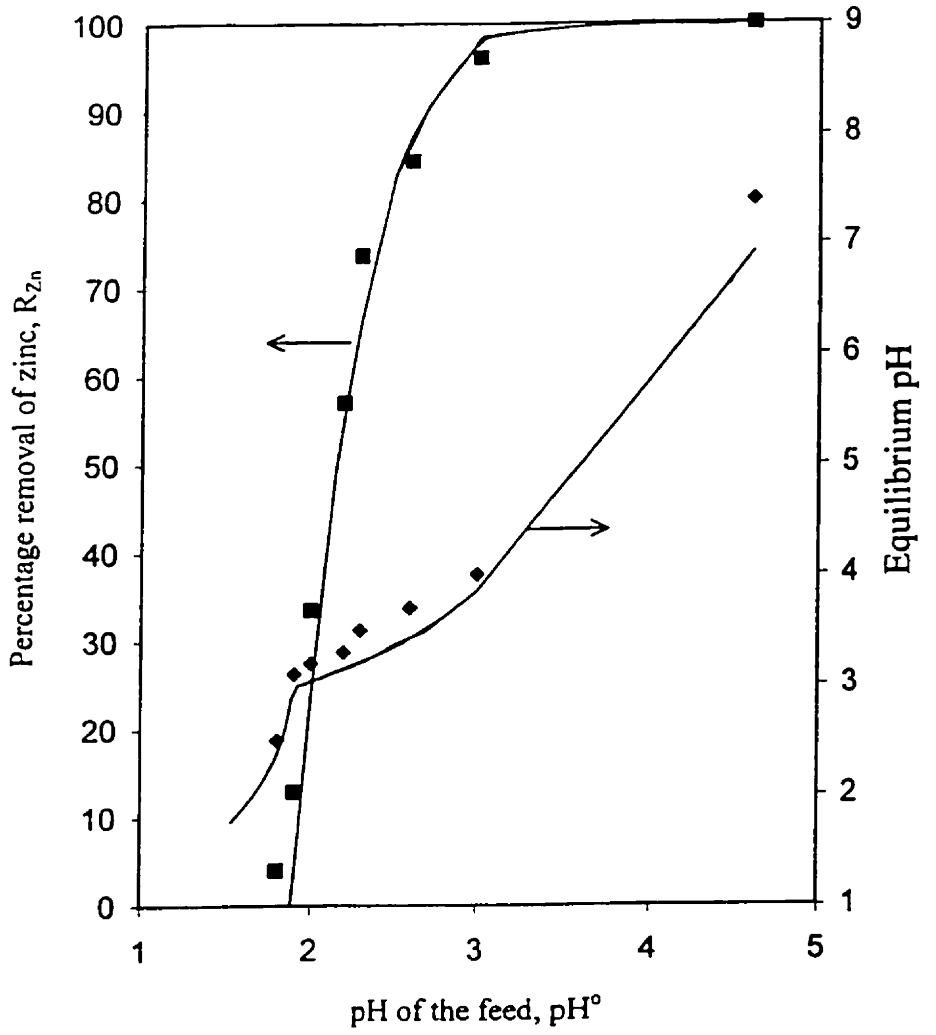


Figure 4.9: Effect of feed pH on the removal of zinc, and the equilibrium pH using sodium di-(n-octyl) phosphinate.

$C^o_{Zn} = 6.3$ mM, $r^o_L = 2.12$, $C^o_{Pb} = C^o_{Cd} = C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

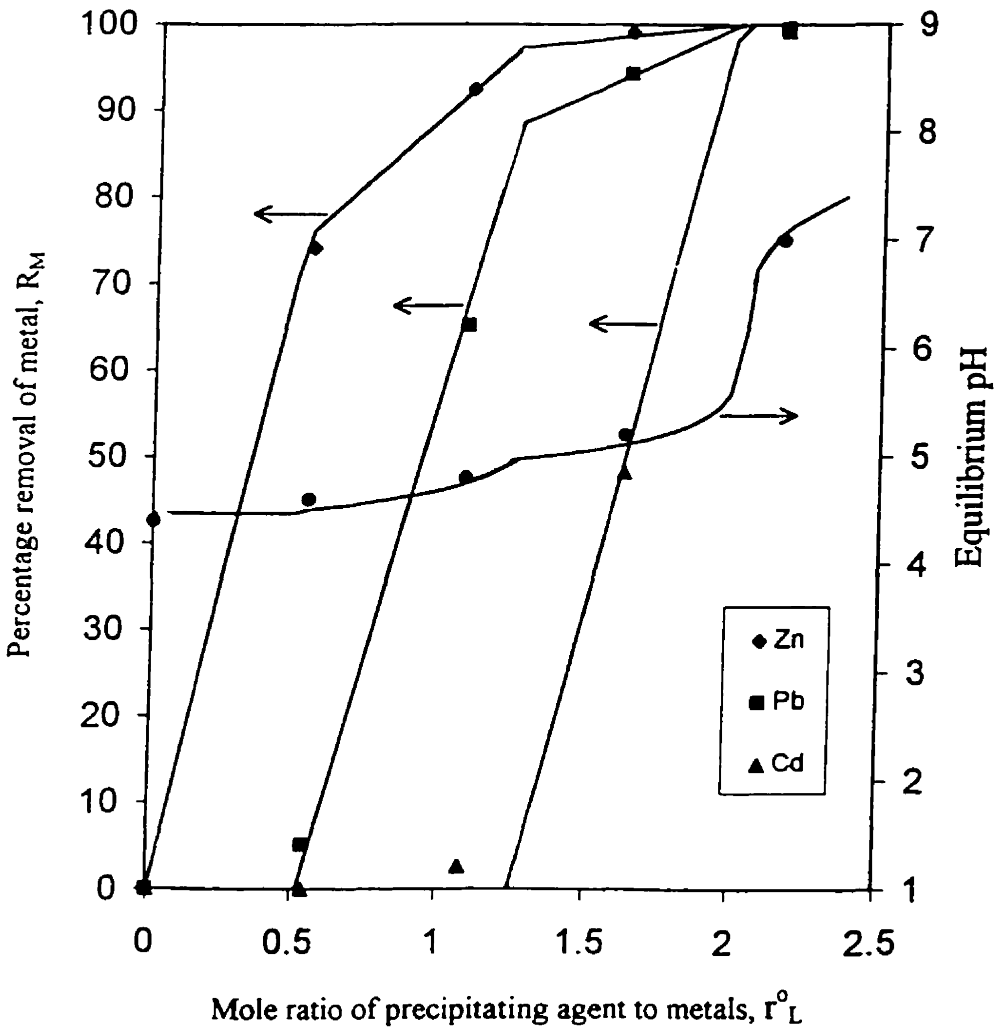


Figure 4.10: Effect of mole ratio of sodium di-(n-octyl) phosphinate to mixture of Pb, Cd, and Zn on the removal of metals, and the equilibrium pH.

$C^o_{Pb} = 2.0$ mM, $C^o_{Cd} = 2.0$ mM, $C^o_{Zn} = 2.1$ mM, $pH^o = 4.3$, $C^o_{NO_3} = 12.2$ mM, $C^o_{Ca} = C^o_{Na} = C^o_{Cl} = 0$. Points-experiments; lines-model.

There is a good agreement between the experimental results and the model predictions for the percentage removal of the metal, percentage loss of the precipitating agent, and the equilibrium pH. The observed close agreement between the predicted and the measured values shows that the assumptions in the model are reasonable and that the values of the solubility products and the mass-stability constants are correct. The difference between the predicted by the model and the measured equilibrium pH, up to pH≈6, is due to the effect of the values of the selected K_I's. Adjusting K_I improves the prediction of pH. The difference in equilibrium pH between the predicted and measured pH, at pH higher than 6, may be caused by the effect of the excess precipitating agent (colloid) on the measurement of pH.

The model results show abrupt changes in the slope of the percentage removal with corresponding changes in slope of the equilibrium pH at certain mole ratios of the precipitating agent to metal, or at certain initial pH-values. These changes resulted when a new species started to precipitate. The changes in slope of the equilibrium pH were caused by the dissociation of the hydroxo-complexes of the metal started to precipitate, or by the precipitation of di-(n-octyl) phosphinic acid $HL_{(s)}$,. Precipitation of lead as $PbL_{2(s)}$, in reaction R-4.22, caused the dissociation of $PbOH^+$ and $Pb(OH)_2$, reactions R-4.1 and R-4.2, and as a result the concentration of OH^- increased. Similarly, precipitation of cadmium and of zinc, reactions R-4.23 and R-4.24, respectively, caused the increase of the concentration of OH^- due to dissociation of $CdOH^+$, $Cd(OH)_2$, $ZnOH^+$, and $Zn(OH)_2$ in reactions R-4.3, R-4.4, R-4.5, and R-4.6, respectively.

In Figure 4.1, the maximum removal of lead was obtained at $r_L^o=2$. At this point, was change in the slope of the equilibrium pH due to the precipitation of $HL_{(s)}$, reaction R-4.25. Figure 4.2 shows that increasing the concentration of lead increased the difference between the predicted and measured equilibrium pH, because the selected stability constants are chosen at zero ionic strength. The change in the slope of equilibrium pH at $pH^{o} \approx 1.8$, in Figure 4.3, was caused by the precipitation of lead, reaction R-4.22, and the dissociation of the hydro-complexes of lead, reactions R-4.1 and R-4.2. In Figure 4.4, the slope of pH changed at $r_{L}^{o} \approx 3.1$ due to the precipitation of lead as $PbL_{2(s)}$, and at $r_{L}^{o} \approx 5$ due to precipitation of $HL_{(s)}$. The change in the slope of pH at $r_{Cl^-}^{o} = r_{NO_3^-}^{o} \approx 4.0$, in Figure 4.5, was caused by the precipitation of lead. Figure 4.6 shows that the maximum removal of cadmium was obtained at $r_{L}^{o}=2$. At this point, di-(n-octyl) phosphinic acid ($HL_{(s)}$) started to precipitate causing an abrupt change in the slope of the equilibrium pH. The change in the slope of the equilibrium pH at $pH \approx 1.8$, in Figure 4.7, was due to the precipitation of cadmium, reaction R-4.23, and the dissociation of the hydro-complexes of cadmium, reactions R-4.3 and R-4.4. At pH below 1.8, only $HL_{(s)}$ was formed. In Figure 4.8, the maximum removal of zinc was obtained at $r_{L}^{o}=2$. At this point, di-(n-octyl) phosphinic acid started to precipitate causing an abrupt change in the slope of the equilibrium pH. In Figure 4.9, up to $pH^{o} \approx 1.8$, only di-(n-octyl) phosphinic acid was formed causing an increase in the equilibrium pH. At $pH^{o} \approx 1.8$, zinc started to precipitate as $ZnL_{2(s)}$, reaction R-4.24, which caused an in the pH due to the dissociation of the hydro-complexes of zinc, R-4.5 and R-4.6.

Figure 4.10 shows changes in slope of the percentage removal of each metal with corresponding changes in the slope of pH. The changes in the slope of the percentage removal of zinc and of the pH at $r_{L}^{o} \approx 0.5$, were caused by the precipitation of lead, reaction R-4.22, and the hydroxo-complexes dissociation, reactions R-4.1 and R-4.2. The change in the slope of percentage removal of zinc and lead, and of pH, at $r_L^o \approx 1.25$, were caused by the precipitation of cadmium, reaction R-4.23, and the hydroxo-complexes dissociation, reactions R-4.3 and R-4.4. The abrupt change in slope of pH, at $r_L^o \approx 2$, was caused by the precipitation of $HL_{(s)}$.

CHAPTER 5

CONCLUSIONS, CONTRIBUTIONS, AND SUGGESTIONS

5.1 Conclusions

Reverse micelles were formed in isooctane with sodium di-(n-octyl) phosphinate using either decanol or di-(n-octyl) phosphinic acid as the cosurfactant.

Lead, was removed from nitrate and chloride solutions by precipitation with sodium di-(n-octyl) phosphinate to form PbL_2. Decreasing the pH of the feed decreased the percentage removal, because an amount of acid precipitated as $HL_{(s)}$. The presence of chloride or calcium had no effect on the removal of lead within the ranges of concentrations of chloride or calcium considered.

At optimal conditions, increasing the chain length decreased the residual concentrations of lead and of the precipitating agent in the aqueous phase.

Behavior similar to that for lead was found for cadmium or zinc, as well as for a mixture of the three metals. The precipitating agent was selective to these metals in the order; Zn > Pb > Cd.

The lead was completely recovered and the precipitating agent was completely regenerated. A concentrated lead solution (100 times the concentration of lead in the feed) was obtained.

A model based on the measured solubility products of the precipitates and the available literature data for stability constants of the other reactions, was developed. The model predictions were in good agreement with the experimental results.

5.2 Contributions to Knowledge

The removal of lead, cadmium, zinc, and mixture of the three metals from aqueous solution by precipitation with sodium di-(n-octyl) phosphinate was demonstrated. At optimum conditions, the residual metal concentrations meet the effluent quality limit. The precipitating agent was regenerated, and the metal was recovered in a concentrated metal solution.

The solubility of the lead di-(n-alkyl) phosphinate was reduced by increasing the length of the alkyl group from 8 to 12.

The solubility products of the precipitates were measured for lead-, cadmium-, and zinc- di-(n-octyl) phosphinates.

A model for the prediction of the removal of the metal, loss of the precipitating agent, and the equilibrium pH has been developed. No adjustable parameters are required.

Sodium di-(n-octyl) phosphinate formed reverse micelles in isooctane using either decanol or di-(n-octyl) phosphinic acid as a cosurfactant. Up to 30% (mass) water could be solubilized.

5.3 Suggestions for Future Work

This system is suggested to be tested for the removal of other heavy metals such as mercury.

Formation of reverse micelles using sodium di-(n-alkyl) phosphinates, and their applications in hydrometallurgy and biotechnology should be investigated.

Increasing the chain length of the alkyl group of the precipitating agent from 8 to 12 carbons, reduced its solubility in water significantly. further investigation of the effect of the chain length as well the chain structure is suggested.

Other organo-phosphorus compounds, especially organo-thiophosphorus compounds should be investigated. Replacement of the oxygens in the phosphinic acid by sulfur increases its acidity, the pK_a of the acid decreases, metal extraction at lower pH is possible.

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APPENDIX A

DETERMINATION OF SOLUBILITY PRODUCTS OF THE PRECIPITATES

The solubility product of di-(n-octyl) phosphinic acid was determined experimentally by dissolving the acid in distilled water at 22±1°C and stirred for 24 hrs. The precipitate was separated and the equilibrium pH was measured. The total carbon content in the aqueous solution was measured, and then the total concentration of the di-(n-octyl) phosphinic group (L), was calculated. This concentration represents the total solubility of L, including L^- and $HL_{(aq)}$,

$$C_{L_T} = C_{L^-} + C_{HL_{(aq)}} \tag{A.1}$$

The equilibrium constant for the acid, K_a, was determined by Martinez et al. (1992), and defined as,

$$K_a = \frac{C_{H^+} C_{L^-}}{C_{HL_{(aq)}}} \tag{4.26}$$

By using equation A.1, equation (4.26) becomes,

$$K_a = \frac{C_{H^+} C_{L^-}}{C_{L_T} - C_{L^-}} \tag{A.2}$$

The value of C_{L^-} (the only unknown) was calculated from equation A.2. The solubility product of di-(n-octyl) phosphinic acid, ($K_{sp_{(HL)}}$), was then calculated, where,

$$K_{sp_{(HL)}} = C_{H^-} C_{L^-} \tag{4.25}$$

and the $K_{sp_{(HL)}}$ value obtained was $(7.38 \pm 0.07) \times 10^{-11}$.

The solubility product of lead, cadmium and zinc phosphinates (PbL_2, CdL_2, and ZnL_2), were also obtained experimentally by dissolving each precipitate in distilled water at 22±1°C, and stirred for 24 hrs. The precipitate was separated and the equilibrium concentration of the metal was measured. The concentration was assumed to be the concentration of Pb^{2+}, Cd^{2+},or Zn^{2+}. The total carbon concentration in the aqueous solution was measured, and the total equilibrium concentration of L was calculated. This concentration, was assumed to be the concentration of L^-; C_{L^-} .

The solubility product values for the three precipitates were calculated from the following equations;

$$K_{sp_{(PbL_2)}} = C_{Pb^{2+}} C^2_{L^-} \tag{4.22}$$

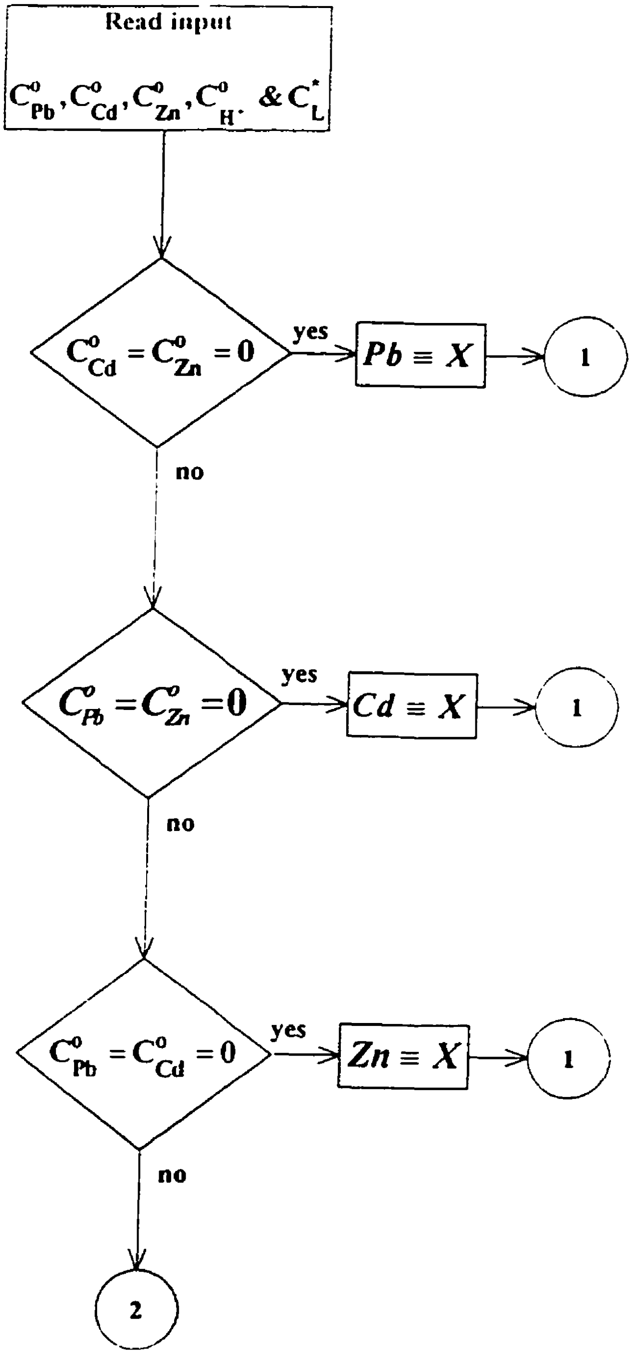
$$K_{sp_{(CdL_2)}} = C_{Cd^{2+}} C^2_{L^-} \tag{4.23}$$

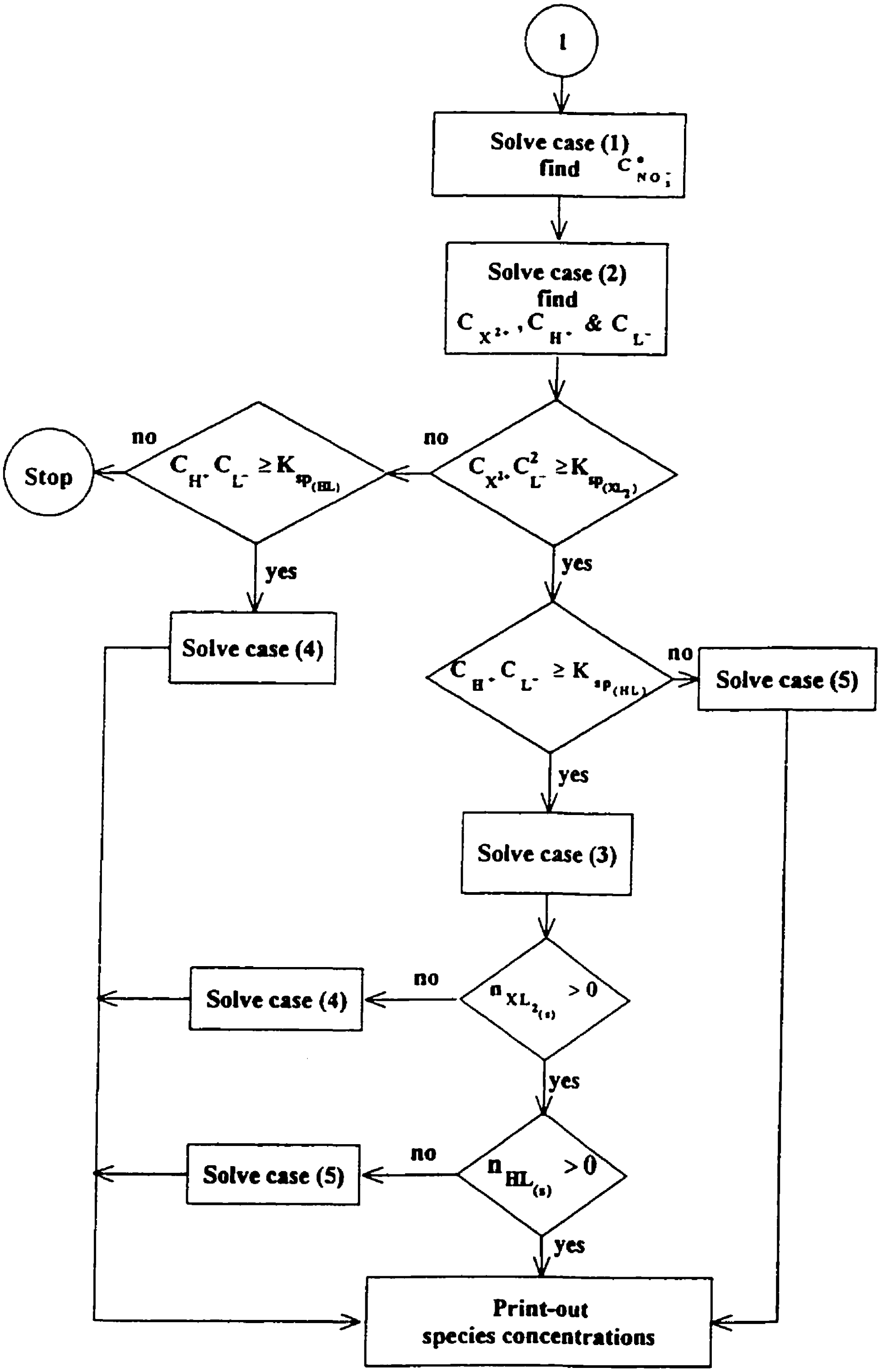
$$K_{sp_{(ZnL_2)}} = C_{Zn^{2+}} C^2_{L^-} \tag{4.24}$$

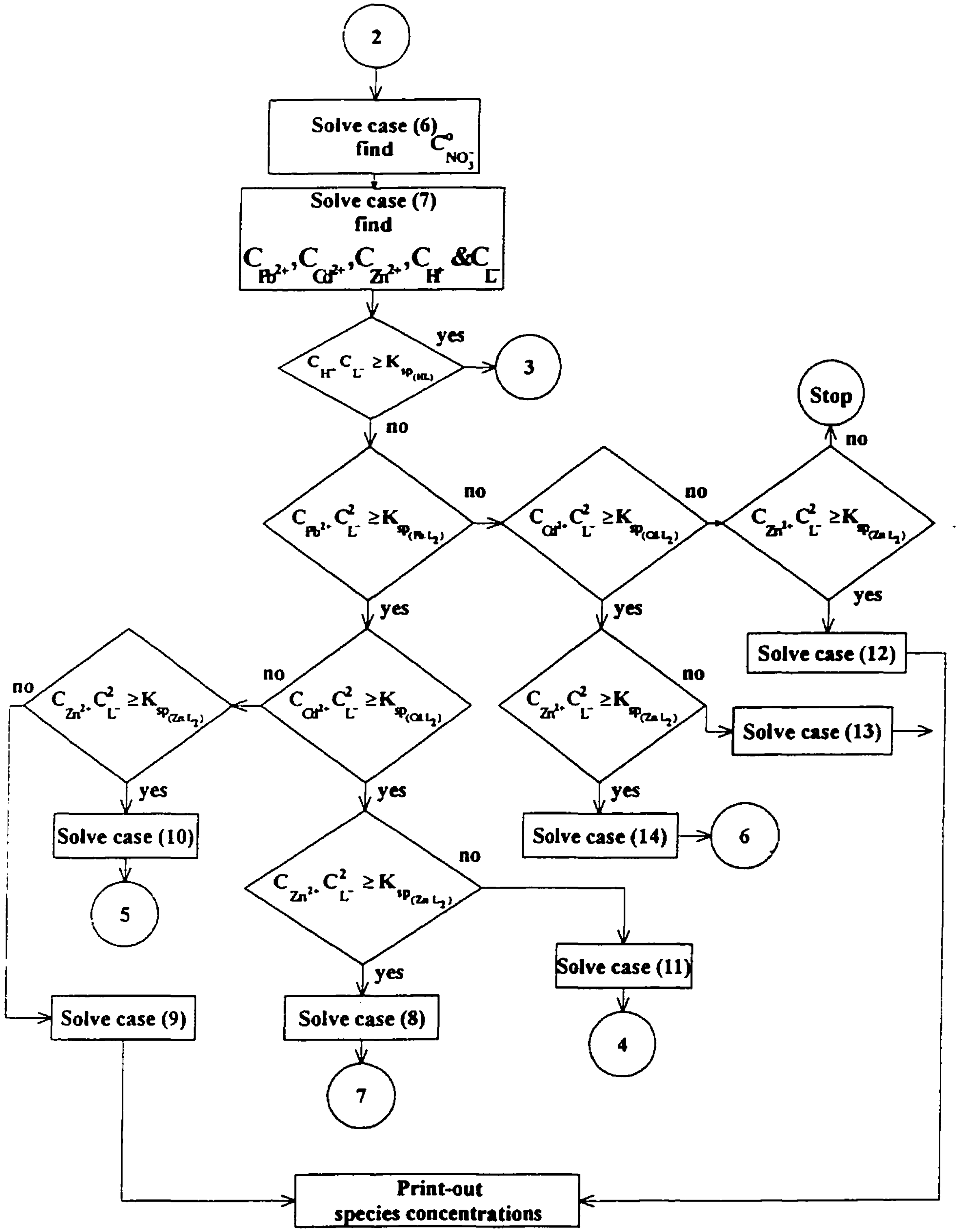
and the values obtained are; $(9.18 \pm 0.05) \times 10^{-17}$, $(9.52 \pm 0.07) \times 10^{-16}$, and $(2.7 \pm 0.1) \times 10^{-17}$, respectively.

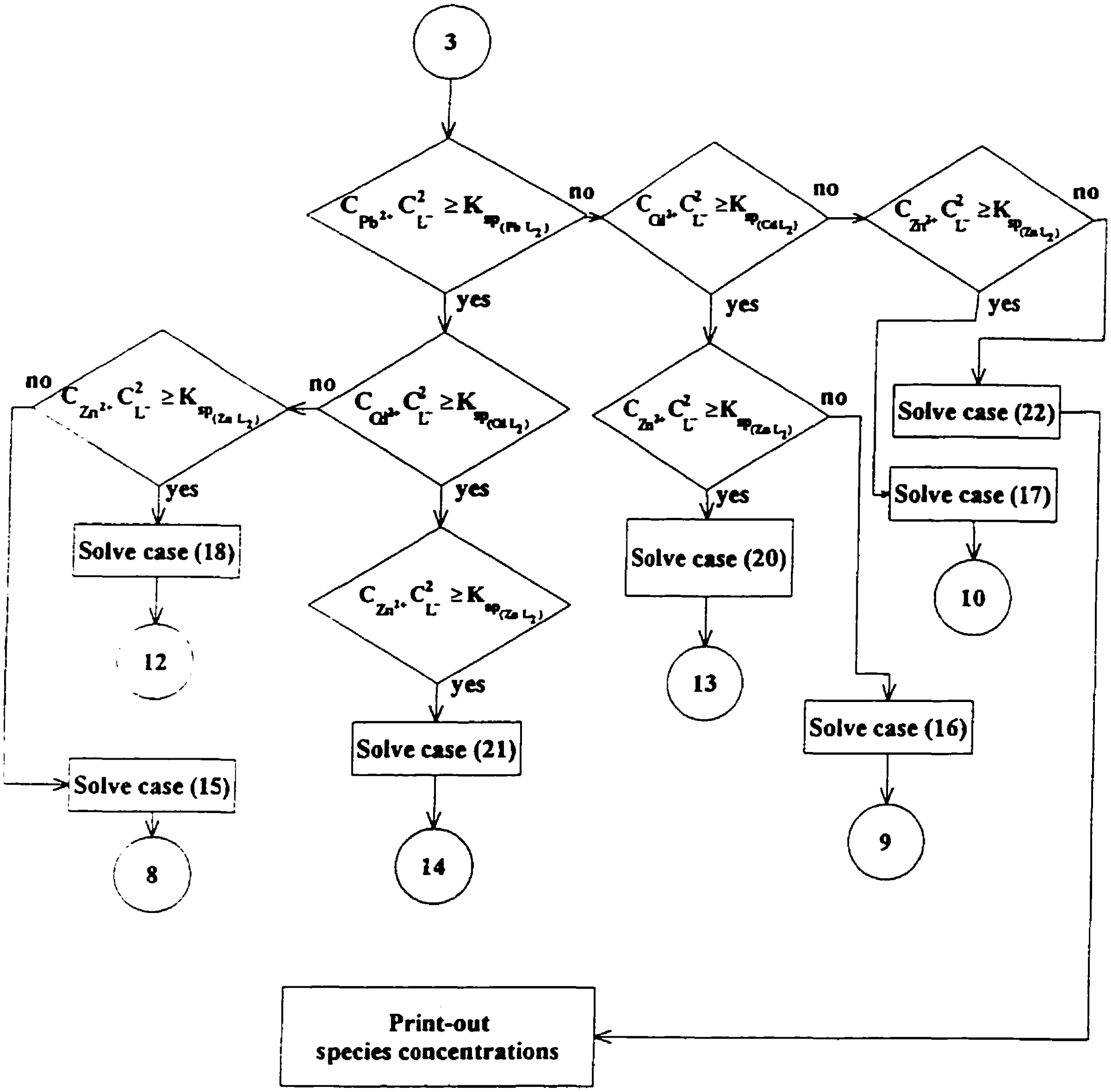
APPENDIX B

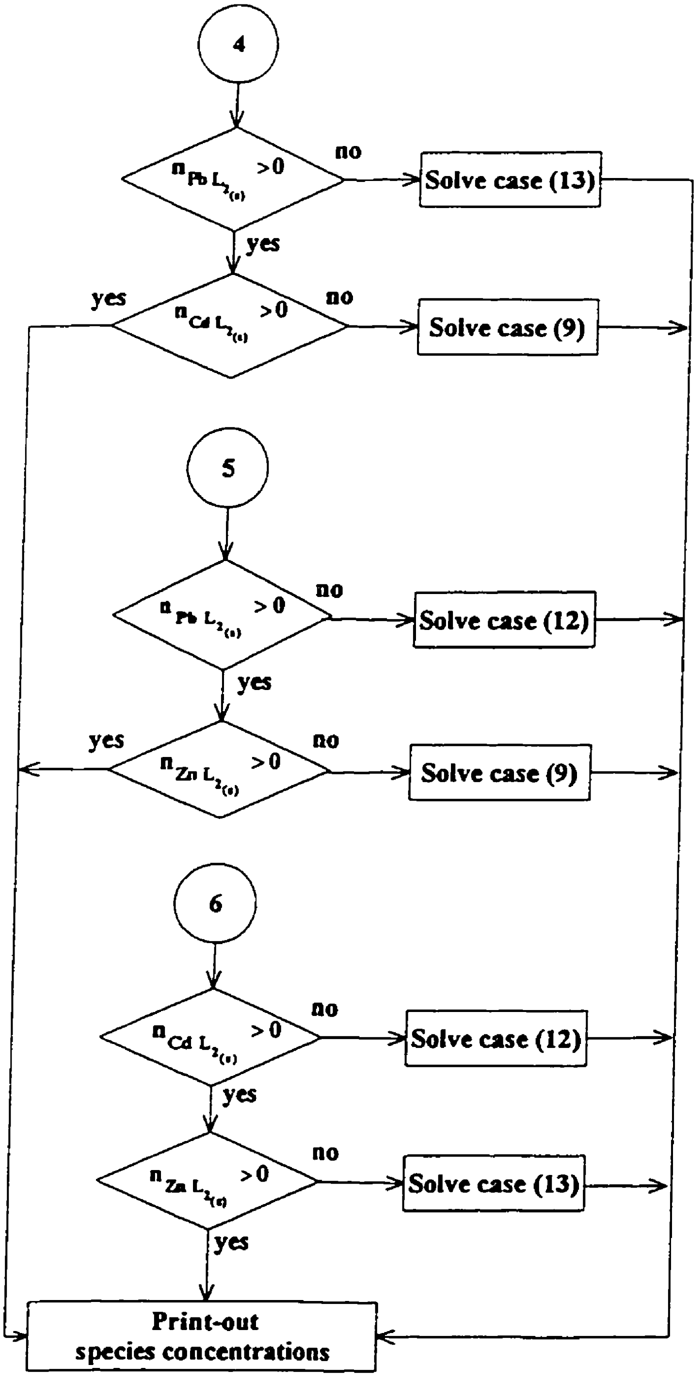
COMPUTATIONAL PROCEDURE FLOWCHART




1
Solve case (1) find $C^{*}_{NO_3^-}$
Solve case (2) find $C_{X^{2+}}$, C_{H^+} & C_{L^-}
$C_{X^{2+}} C^2_{L^-} \geq K_{sp(XL_2)}$
no
$C_{H^+} C_{L^-} \geq K_{sp(HL)}$
no
Stop
yes
Solve case (4)
yes
$C_{H^+} C_{L^-} \geq K_{sp(HL)}$
no
Solve case (5)
yes
Solve case (3)
$n_{XL_{2(s)}} > 0$
no
Solve case (4)
yes
$n_{HL_{(s)}} > 0$
no
Solve case (5)
yes
Print-out species concentrations


2
Solve case (6) find $C^{o}_{NO_3^-}$
Solve case (7) find
$C_{Pb^{2+}}, C_{Cd^{2+}}, C_{Zn^{2+}}, C_{H^+} \& C_{L^-}$
$C_{H^+} C_{L^-} \geq K_{sp(HL)}$
yes
3
no
$C_{Pb^{2+}} C^2_{L^-} \geq K_{sp(PbL_2)}$
no
$C_{Cd^{2+}} C^2_{L^-} \geq K_{sp(CdL_2)}$
no
$C_{Zn^{2+}} C^2_{L^-} \geq K_{sp(ZnL_2)}$
no
Stop
yes
Solve case (12)
yes
yes
no
$C_{Zn^{2+}} C^2_{L^-} \geq K_{sp(ZnL_2)}$
no
$C_{Cd^{2+}} C^2_{L^-} \geq K_{sp(CdL_2)}$
no
$C_{Zn^{2+}} C^2_{L^-} \geq K_{sp(ZnL_2)}$
Solve case (13)
yes
Solve case (10)
5
yes
$C_{Zn^{2+}} C^2_{L^-} \geq K_{sp(ZnL_2)}$
no
yes
Solve case (14)
6
Solve case (11)
4
yes
Solve case (9)
Solve case (8)
7
Print-out species concentrations


3
$C_{Pb^{2+}} C_{L^-}^2 \geq K_{sp(PbL_2)}$
no
$C_{Cd^{2+}} C_{L^-}^2 \geq K_{sp(CdL_2)}$
no
$C_{Zn^{2+}} C_{L^-}^2 \geq K_{sp(ZnL_2)}$
no
yes
yes
yes
no
$C_{Zn^{2+}} C_{L^-}^2 \geq K_{sp(ZnL_2)}$
no
$C_{Cd^{2+}} C_{L^-}^2 \geq K_{sp(CdL_2)}$
$C_{Zn^{2+}} C_{L^-}^2 \geq K_{sp(ZnL_2)}$
no
Solve case (22)
yes
yes
yes
Solve case (17)
Solve case (18)
Solve case (20)
10
$C_{Zn^{2+}} C_{L^-}^2 \geq K_{sp(ZnL_2)}$
12
13
yes
Solve case (16)
Solve case (21)
Solve case (15)
9
14
8
Print-out species concentrations



$n_{PbL_{2(s)}} > 0$

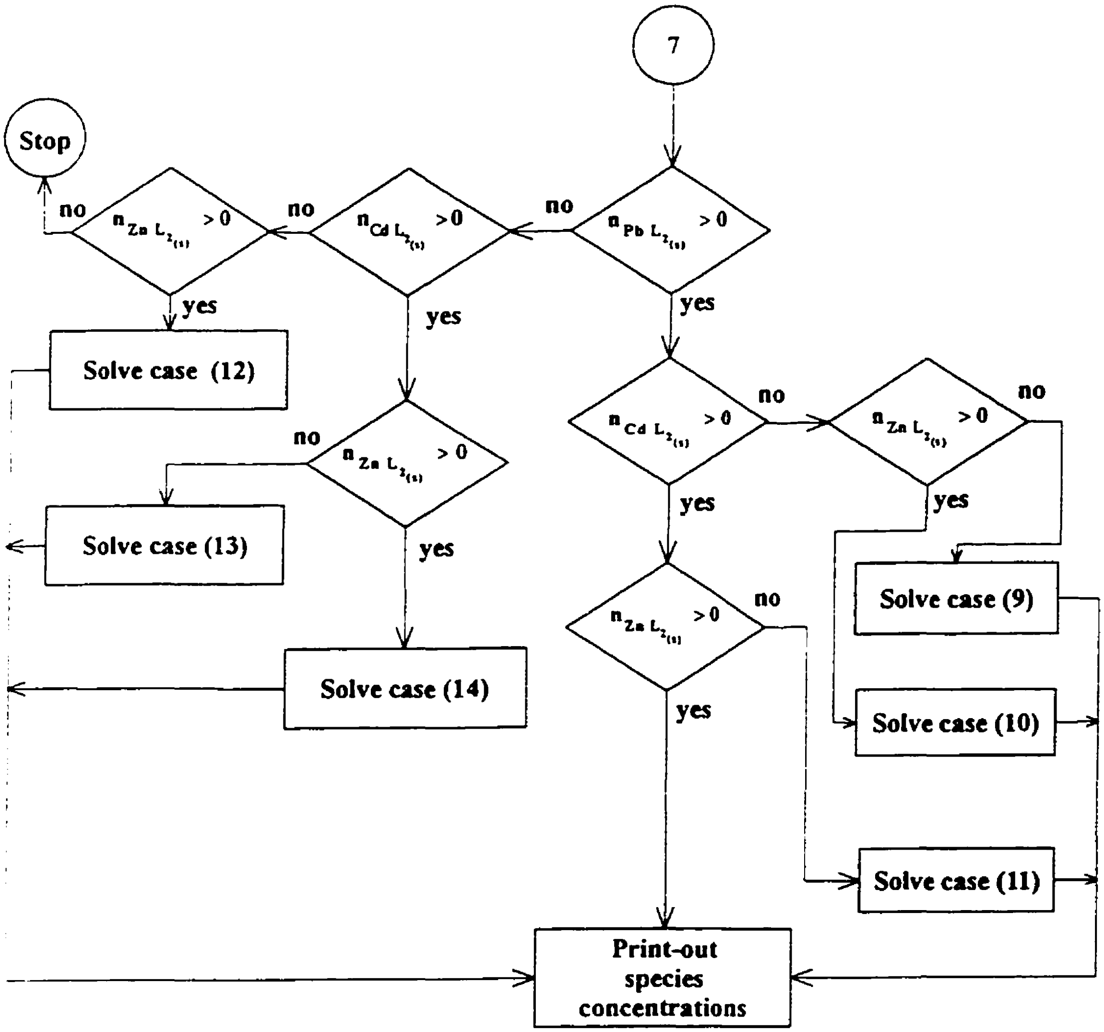
$n_{CdL_{2(s)}} > 0$

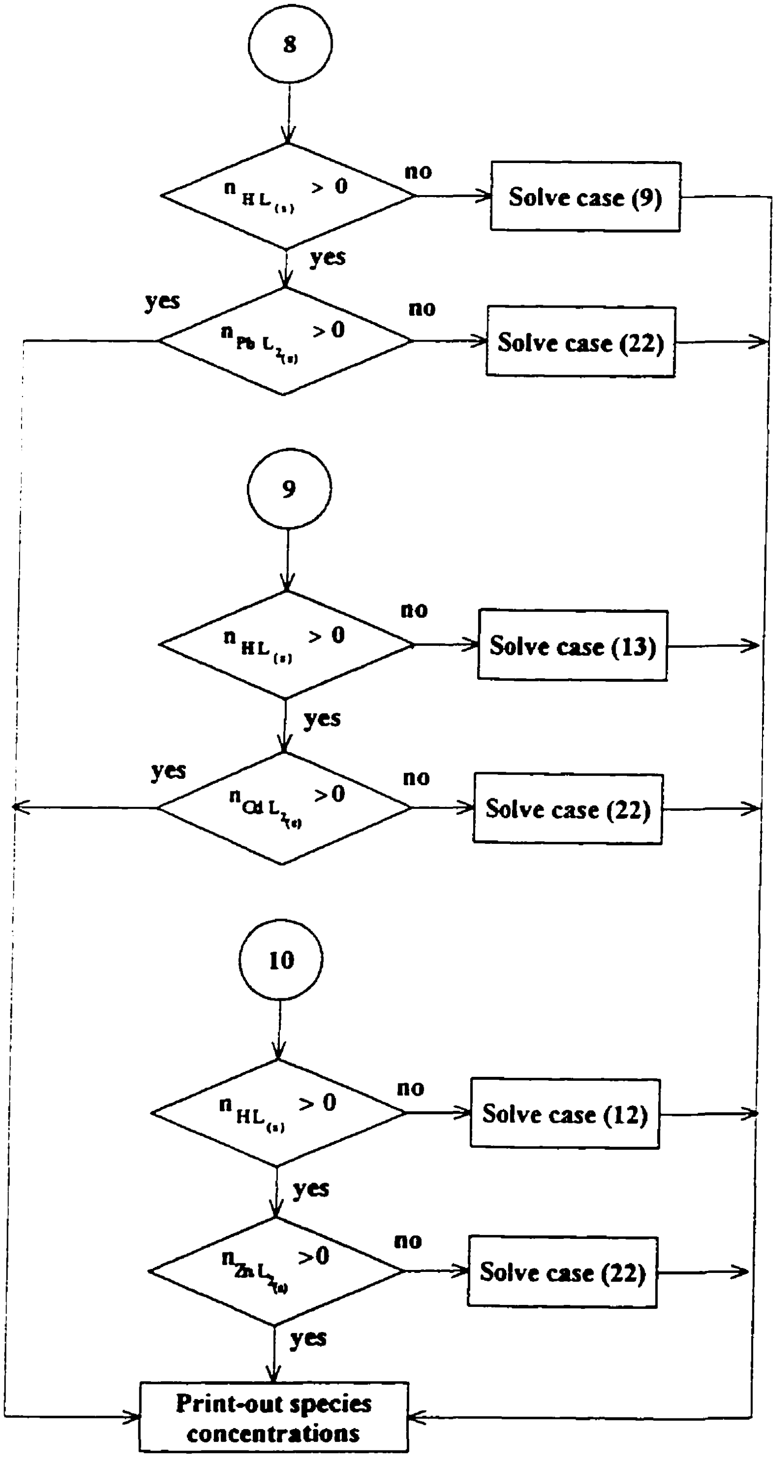
$n_{PbL_{2(s)}} > 0$

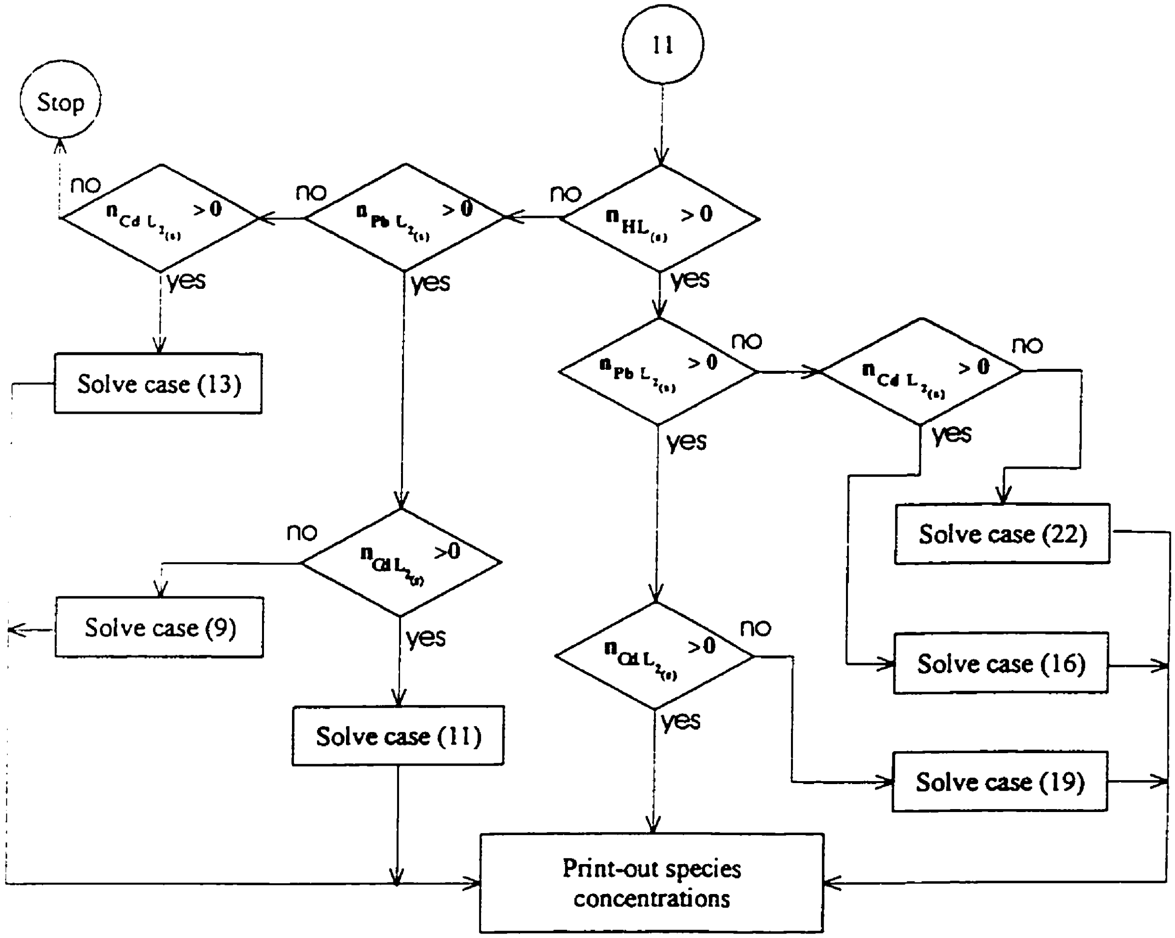
$n_{ZnL_{2(s)}} > 0$

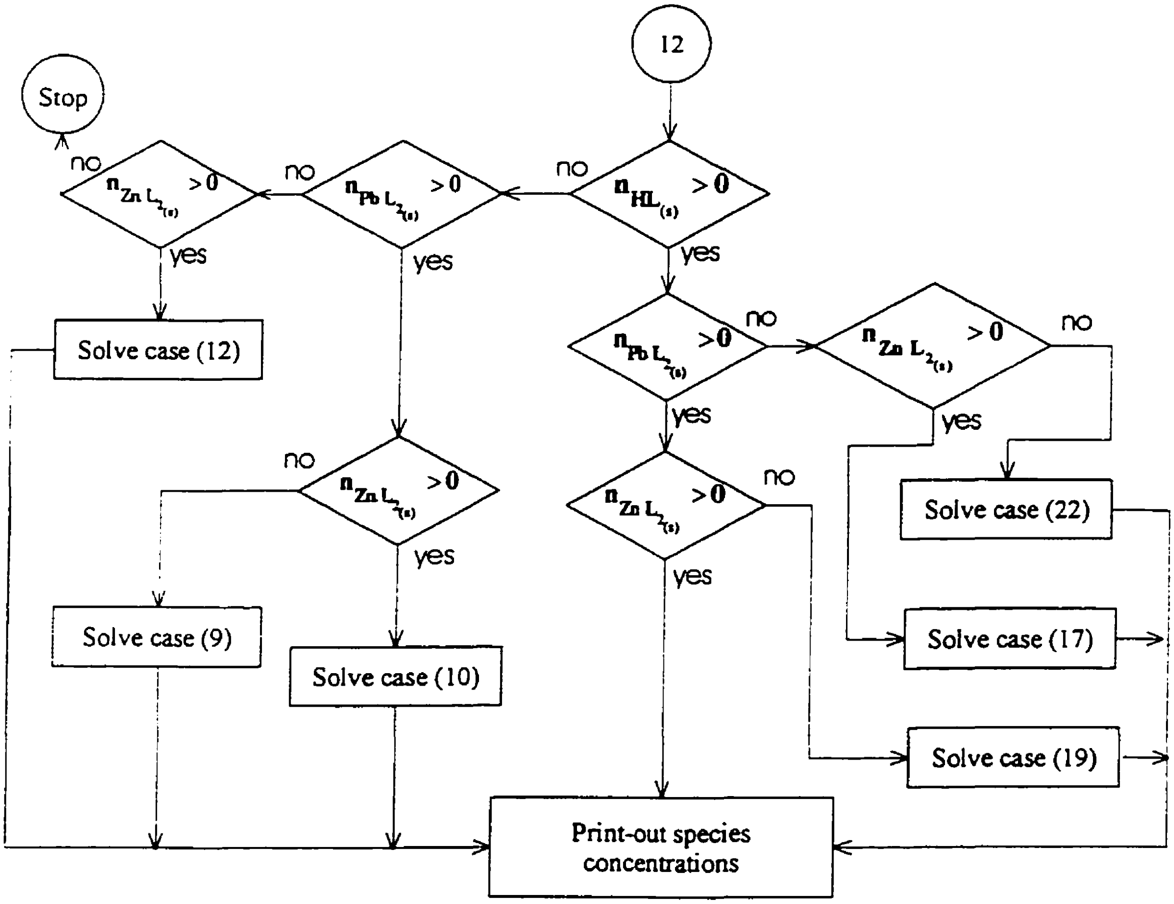
$n_{CdL_{2(s)}} > 0$

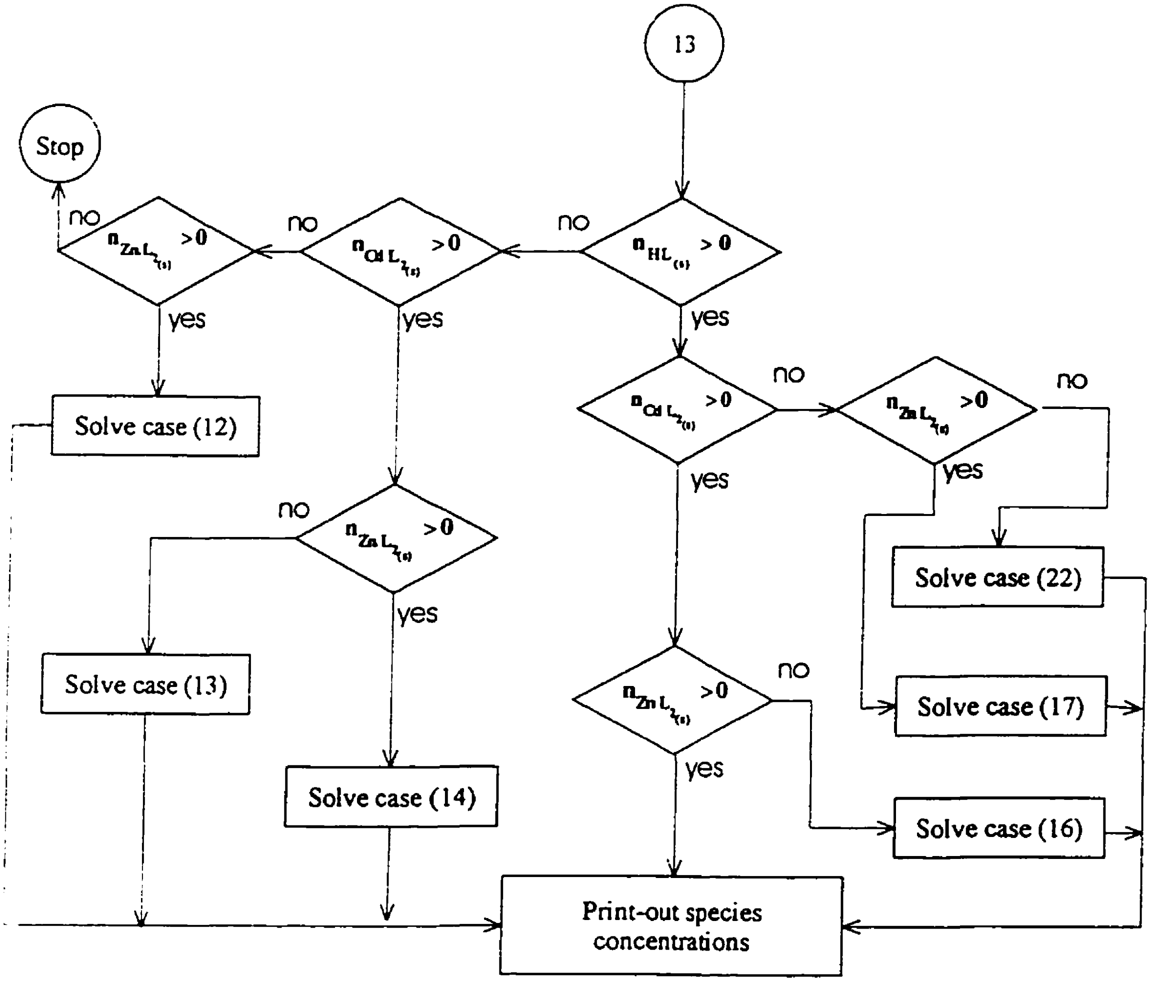
$n_{ZnL_{2(s)}} > 0$

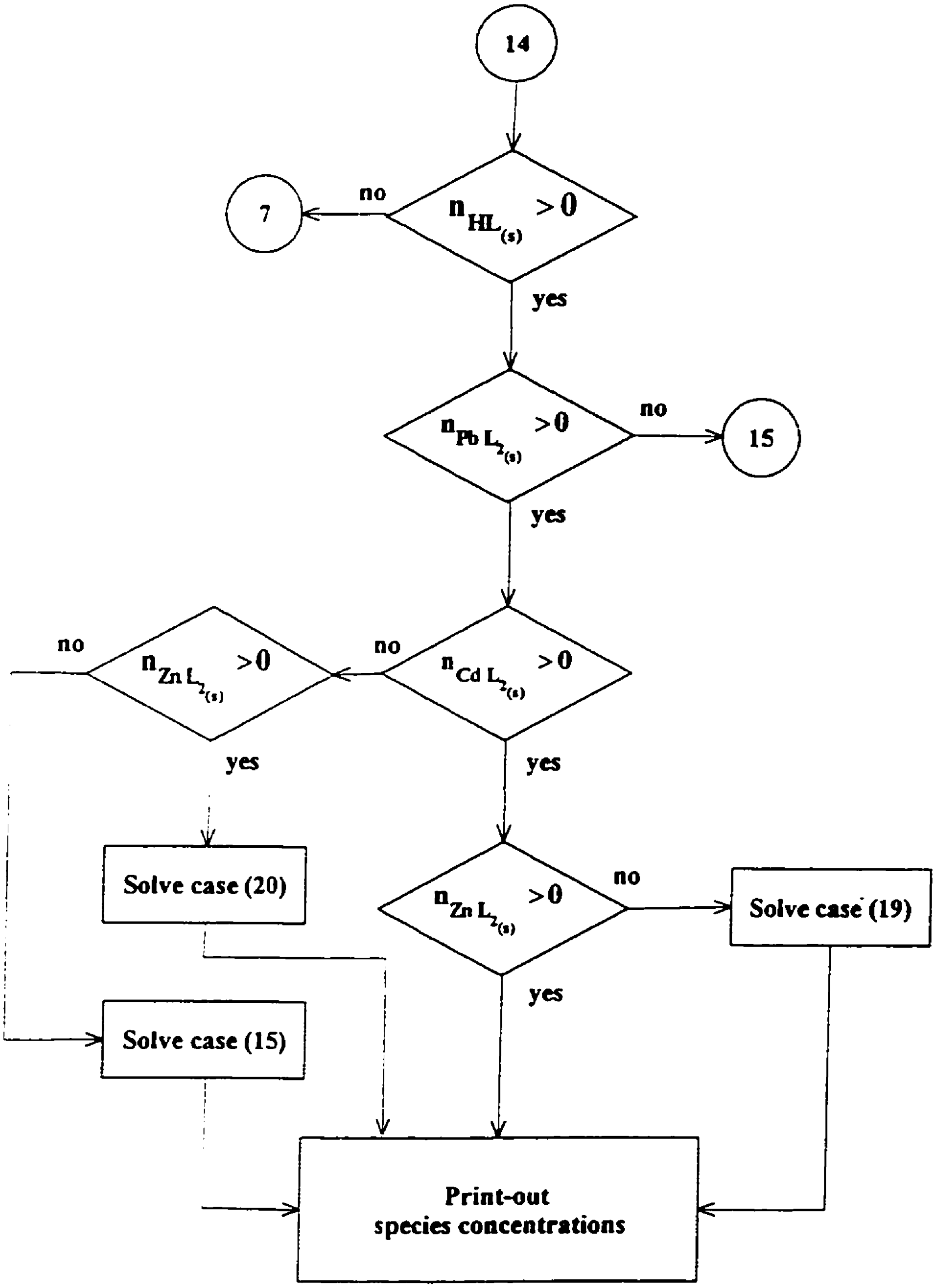

7
Stop
no
$n_{ZnL_{2(s)}} > 0$
no
$n_{CdL_{2(s)}} > 0$
no
$n_{PbL_{2(s)}} > 0$
yes
Solve case (12)
yes
yes
$n_{CdL_{2(s)}} > 0$
no
$n_{ZnL_{2(s)}} > 0$
no
no
$n_{ZnL_{2(s)}} > 0$
Solve case (13)
yes
yes
yes
Solve case (9)
$n_{ZnL_{2(s)}} > 0$
no
Solve case (14)
yes
Solve case (10)
Solve case (11)
Print-out species concentrations


8
$n_{HL_{(s)}} > 0$
no
Solve case (9)
yes
yes
$n_{PbL_{2(s)}} > 0$
no
Solve case (22)
9
$n_{HL_{(s)}} > 0$
no
Solve case (13)
yes
yes
$n_{CdL_{2(s)}} > 0$
no
Solve case (22)
10
$n_{HL_{(s)}} > 0$
no
Solve case (12)
yes
$n_{ZnL_{2(s)}} > 0$
no
Solve case (22)
yes
Print-out species concentrations


11
Stop
no
$n_{CdL_{2(s)}} > 0$
yes
no
$n_{PbL_{2(s)}} > 0$
yes
no
$n_{HL_{(s)}} > 0$
yes
$n_{PbL_{2(s)}} > 0$
no
yes
$n_{CdL_{2(s)}} > 0$
no
yes
Solve case (13)
no
$n_{CdL_{2(s)}} > 0$
yes
Solve case (9)
Solve case (11)
$n_{CdL_{2(s)}} > 0$
no
yes
Solve case (22)
Solve case (16)
Solve case (19)
Print-out species concentrations


12
Stop
$n_{HL_{(s)}} > 0$
$n_{PbL_{2(s)}} > 0$
$n_{ZnL_{2(s)}} > 0$
no
yes
Solve case (12)
Solve case (9)
Solve case (10)
Solve case (22)
Solve case (17)
Solve case (19)
Print-out species concentrations


13
Stop
no
yes
$n_{HL_{(s)}} > 0$
$n_{CdL_{2(s)}} > 0$
$n_{ZnL_{2(s)}} > 0$
Solve case (12)
Solve case (13)
Solve case (14)
Solve case (22)
Solve case (17)
Solve case (16)
Print-out species concentrations


14
7
no
$n_{HL_{(s)}} > 0$
yes
$n_{PbL_{2(s)}} > 0$
no
15
yes
no
$n_{ZnL_{2(s)}} > 0$
no
$n_{CdL_{2(s)}} > 0$
yes
yes
Solve case (20)
$n_{ZnL_{2(s)}} > 0$
no
Solve case (19)
yes
Solve case (15)
Print-out
species concentrations

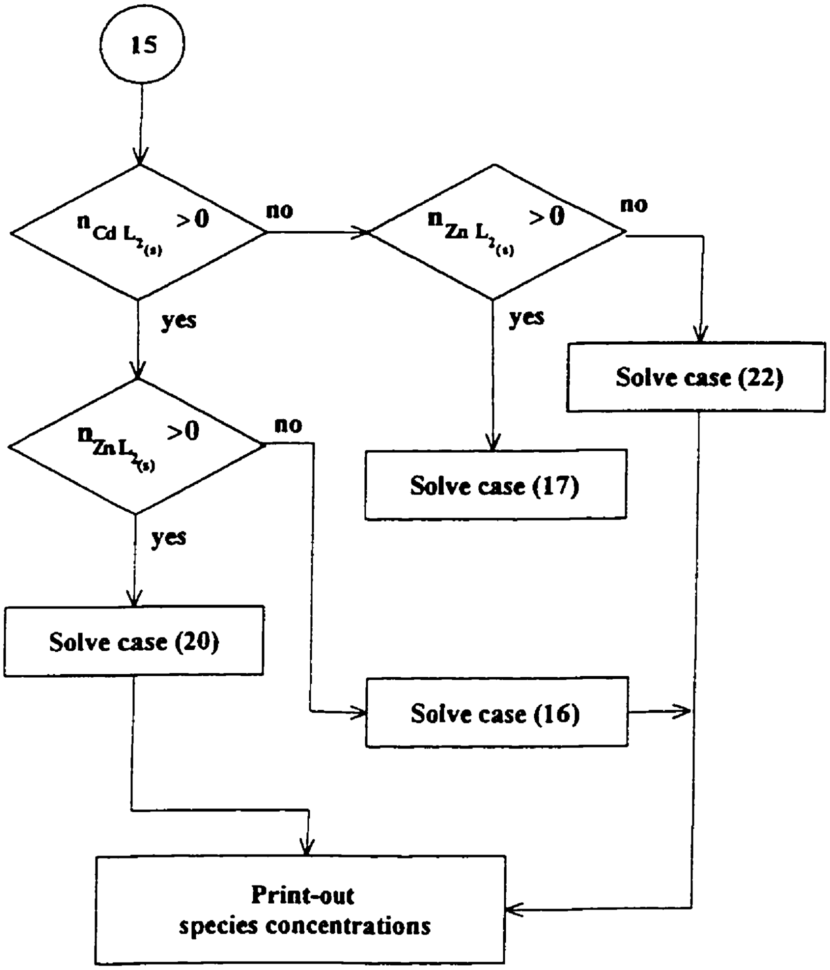

15
$n_{CdL_{2(s)}} > 0$
no
yes
$n_{ZnL_{2(s)}} > 0$
no
yes
$n_{ZnL_{2(s)}} > 0$
no
yes
Solve case (22)
Solve case (17)
Solve case (20)
Solve case (16)
Print-out
species concentrations

Table B.1: Equations considered for each precipitation process

Case		Equations
Pb≡ X	(1)	(4.45), (4.46), (4.48), ($C_{L^-} = 0$), ($C_{Na^+} = 0$), ($n_{PbL_{2(s)}} = 0$)
	(2)	(4.45 to 4.48), ($n_{PbL_{2(s)}} = 0$), ($n_{HL_{(s)}} = 0$)
	(3)	(4.22), (4.25), (4.45) to (4.48)
	(4)	(4.25), (4.45) to (4.48), ($n_{PbL_{2(s)}} = 0$)
	(5)	(4.22), (4.45) to (4.48), ($n_{HL_{(s)}} = 0$)
Cd≡ X	(1)	(4.52), (4.53), (4.55), ($C_{L^-} = 0$), ($C_{Na^+} = 0$), ($n_{CdL_{2(s)}} = 0$)
	(2)	(4.52) to (4.55), ($n_{CdL_{2(s)}} = 0$), ($n_{HL_{(s)}} = 0$)
	(3)	(4.25), (4.23), (4.52) to (4.55)
	(4)	(4.25), (4.52) to (4.55), ($n_{CdL_{2(s)}} = 0$)
	(5)	(A.23), (4.52) to (4.55), ($n_{HL_{(s)}} = 0$)
Zn≡ X	(1)	(4.56), (4.57), (4.59), ($C_{L^-} = 0$), ($C_{Na^+} = 0$), ($n_{ZnL_{2(s)}} = 0$)
	(2)	(4.56) to (4.59), ($n_{ZnL_{2(s)}} = 0$), ($n_{HL_{(s)}} = 0$)
	(3)	(4.24), (4.25), (4.56 to 4.59)
	(4)	(4.25), (4.56) to 4.59), ($n_{ZnL_{2(s)}} = 0$)
	(5)	(4.24), (4.56) to (4.59), ($n_{HL_{(s)}} = 0$)

Table B.1 (Continued)

Case	Equations
(6)	(4.45), (4.52), (4.56), (4.60), (4.62), ($C_{L^-}=0$), ($C_{Na^+}=0$), ($n_{PbL_{2(s)}}=0$), ($n_{CdL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$)
(7)	(4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{CdL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(8)	(4.22) to (4.24), (4.45), (4.52), (4.56), (4.60) to (4.62)
(9)	(4.22), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{CdL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(10)	(4.22), (4.24), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{CdL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(11)	(4.22), (4.23), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{ZnL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(12)	(4.24), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{CdL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(13)	(4.23), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(14)	(4.23), (4.24), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{HL_{(s)}}=0$)
(15)	(4.22), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{CdL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$)
(16)	(4.23), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{ZnL_{2(s)}}=0$)
(17)	(4.24), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{CdL_{2(s)}}=0$)
(18)	(4.22), (4.24), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{CdL_{2(s)}}=0$)
(19)	(4.22), (4.23), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{ZnL_{2(s)}}=0$)
(20)	(4.23), (4.24), (4.25), (4.45), (4.52), (4.56), (4.600 to (4.62), ($n_{PbL_{2(s)}}=0$)
(21)	(4.22), (4.23), (4.24), (4.25), (4.45), (4.52), (4.56), (4.60) to (4.62)
(22)	(4.25), (4.45), (4.52), (4.56), (4.60) to (4.62), ($n_{PbL_{2(s)}}=0$), ($n_{CdL_{2(s)}}=0$), ($n_{ZnS_{2(s)}}=0$)