Instituto Superior de Engenharia do Porto

Katholieke Hogeschool Sint-Lieven

Master in Chemical Engineering

Technologies for Environmental Protection

Mixed Extractant Systems for metal recovery

Sistema de Mistura de Extractantes para Recuperação de Metais

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Gent, July 2009

This thesis falls within the scope of the thesis of the Masters course in Masters in Chemical Engineering - Technologies for Environmental Protection from Instituto Superior de Engenharia do Porto held at Katholieke Hogeschool Sint-Lieven in Gent.

“Ninguém ignora tudo, ninguém sabe tudo. Por isso, aprenderemos sempre.”

"No one ignores all, nobody knows everything. So, always learn. "

Paulo Freire

I dedicate this work to my parents,
Joaquim Simões and Rosa Simões.

To my grandparents,
Moisés Simões (in memory),
Lucinda Nora,
António Costa (in memory),
Rosa Ferreira(in memory).

To all with all the affection.

Acknowledgments

The God, to be always doing the best for me.

My Supervisor Dr. Ing. Ilse Van de Voorde, thank you for what you have been provided to make this work, the entire support, for the extreme dedication and the valuable lessons provided.

As Dr. Hilde Lauwereys, thank you for the reception and support.

By Dr. Luc de Cooman, thank you for support and assistance.

I would like to thank Eng. Cristina Morais for her assistance during this Erasmus project.

I would like to thank Eng. Paula Cristina for her assistance during this Erasmus project.

By Davennck Martine thank you for the wonderful reception, support and assistance.

For the understanding and friendship, thanks to all colleagues and friends who accompanied me throughout this work and stay in Gent.

I thank especially my friend Diana for her great friendship, during this new experience in Gent. Thanks for the unconditional support. Without Diana I couldn't overcome the difficult moments during my stay in Gent.

For the unconditional support, love and presto emotional tribute to my family, who always walked beside me.

Expressed my sincere thanks to all those who in some way encouraged and contributed to this work.

Thank you all very much

Muito Obrigado a todos

Resumo

Hoje em dia, a prevenção dos resíduos de metais é uma questão muito importante para um grande número de empresas, pois necessitam optimizar o seu sistema de tratamento de águas residuais a fim de alcançarem os limites legais dos teores em iões metálicos e poderem efectuar a descarga das águas residuais no domínio hídrico público. Devido a esta problemática foram efectuados estudos inovadores relacionados com a remoção de iões metálicos de águas residuais, verificando-se que as tecnologias de membrana oferecem uma série de vantagens para o efeito. Uma dessas tecnologias, referida como Membrana Líquida de Suporte (SLM), é baseada num mecanismo de extracção. A membrana hidrofóbica, impregnada com uma solução extractora, funciona como barreira entre a água residual e uma solução, geralmente ácida. A diferença de pH entre a água residual e a solução actua como força motriz para o transporte de iões metálicos da água residual para a referida solução. Poderá ocorrer um problema de falta de estabilidade, resultante da possível fuga da solução extractora para fora dos poros das membranas.

Estudos anteriores mostraram que os ácidos alquilfosfóricos ou ácidos fosfónicos, como os reagentes D_2EHPA e CYANEX e hidroxioximas como o LIX 860-I podem ser muito úteis para a extração de iões metálicos como ferro, cobre, níquel, zinco e outros. A clássica extracção líquido-líquido também tem mostrado que a mistura de diferentes extractores pode ter um efeito sinergético. No entanto, não é claro que haja um efeito óptimo da razão de extractor ou que tipo de complexo é formado durante o processo de extracção.

O objectivo deste projecto é investigar este comportamento sinergético e as complexas formações por meio de um método espectrofotométrico, o “Job’s method” e “Mole-ratio method”. Estes métodos são utilizados para estimar a estequiometria dos vários complexos entre dois solutos, a partir da variação de absorvância dos complexos quando comparado com a absorvância do soluto. Com este projecto, o Job’s method e mole-ratio method serão aplicados a um sistema de três componentes, para conseguir mais informações sobre a complexação de níquel (II) e a fim de determinar a razão extractor: metal dos complexos formados durante a aplicação de mistura de extractores D_2EHPA e LIX 860-I.

Segundo Job’s method a elavada absorvância situa-se na região de 0,015-0,040 M de LIX 860-I e uma baixa concentração de D_2EHPA. Quando as diferentes experiências são encontradas num conjunto experimental foram avaliadas de acordo com o método de trabalho, o valor máximo do gráfico foi encontrado para uma baixa fração molar do ião metálico e uma maior concentração de D_2EHPA. Esta mudança foi encontrado de 0,50 até 0,30, que poderia apontar para a direção da formação de diferentes complexos.

Para o Mole-Ratio method, a estequiometria dos complexos metal pode ser determinada a partir do ponto de intersecção das linhas tangente do gráfico da absorbância versus a concentração do ligante. Em todos os casos, o máximo foi obtido em torno de uma concentração total de 0,010 M. Quando D_2EHPA foi aplicado sozinho, absorvâncias muito baixos foram obtidas.

Palavras-chave: Águas residuais, LIX, D_2EPHA, iões metálicos, Membrana Líquida de Suporte, Job's method, mole-ratio method

Abstract

Metal waste prevention is a very important issue for a lot of companies, because they need to optimize their wastewater treatment system in order to reach the legal disposal limits for metal ions. Therefore, a lot of innovative studies are dealing with the removal of metal ions out of wastewater. Membrane technologies offer a lot of advantages for this purpose. One of these membrane technologies are Supported Liquid Membranes (SLM). Supported Liquid Membranes are based on an extraction mechanism. A hydrophobic membrane is impregnated with an extractant solution and serves as a barrier between the wastewater and a strip solution. The strip solution is usually an acidic solution. The difference in pH between the wastewater and the strip solution acts as a driving force to transport the metal ions from the wastewater towards the strip solution. Sometimes a problem may occur due to a lack of stability resulting from the possible leakage of the extractant solution out of the pores of the membranes.

Previous studies showed that alkylphosphoric acids or – phosphonic acids such as D_2EHPA and CYANEX reagents and hydroxyoximes such as LIX 860-I can be very useful extractants for the extraction of metal ions such as iron, copper, nickel, zinc and so one. Classical liquid-liquid extractions have also shown that mixtures of different extractants can have a synergistic effect. However, it's not clear yet which extractant ratio has an optimal effect or which type of complex is formed during the extraction process.

The aim of this project is to investigate this synergistic behaviour and the complex formation by means of a spectrophotometric method, Job's method and Mole-ratio method. These methods are used to estimate the stoichiometry of the various complexes between two solutes, from the variation of light absorbance of the complexes when compared to the absorbances of the individual solutes. Within this project, Job's method and mole-ratio method will be applied for three-component systems, to achieve more information concerning the complexation of nickel (II) and in order to determine the extractant:metal ratio of the complexes formed during mixed extractant (D_2EHPA and LIX 860-I) applications.

For the Job's method the hisghest absorbance were situated in the region of 0.015-0.040 M of LIX 860-I and a low concentration of D_2EHPA. When the different sets which can be found within the experimental set-up are evaluated according to the method of Job, the maximum of the plot was shifted to a lower mole-fraction of metal ion when higher concentration of D_2EHPA were present in the mixture. A shift was found from 0.50 till 0.30 which could point into the direction of the formation of different complexes.

For the Mole-ratio method, the stoichiometry of the metal complexes can be determined from the intersection point of the tangent lines of the plot of the absorbance versus the

concentration of ligand. In all cases, the maximum was obtained around a total concentration of 0.010 M. When D_2EHPA alone was applied, very low absorbances were achieved.

Keywords: Wastewater, LIX, D_2EHPA, metal waste, Supported Liquid Membrane, Job's method, mole-ratio method

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Abbreviations and Symbols

LM.....Liquid Membranes

ELM.....Emulsion Liquid Membrane

ILM.....Immobilized Liquid Membrane

SLM.....Supported Liquid Membrane

FLM.....Flowing Liquid Membrane

CLM .....Contained Liquid Membrane

Kd .....Distribution ratio

Abs.....Absorbance

a .....wavelength-dependent absorptivity coefficient [$(M*cm)^{-1}$]

I_0.....intensity of incident light

I.....transmitted intensity

ε .....constant molar absorptivity [$(M*cm)^{-1}$]

b.....optical path [cm]

c.....molar concentration of the solution or analyte concentration [M]

MX .....Metal-Extractant Complex

HX.....Extractant

HL .....Second Extractant

M^{n+} .....Metal

X_M^{n+} .....Mole-fraction of metal ion

m.....Stoichiometric coeffcicent of metal

n.....Stoichiometric coefficent of extractant

o.....Stoichiometric coefficent of second extractant

C_M^{n+}.....Metal concentration [M]

C_X.....Extractant concentration [M]

C_L.....Second extractant concentration [M]

org.....Organic phase

C_{M0}.....Metal concentration before shaking [M]

C_{ME}.....Metal concentration after shaking [M]

λ.....wavelength [nm]

AAS.....Atomic Absorption Spectrophotometer

1. Introduction

Contamination in water by heavy metal ions leads to serious environmental problems. Industrial processes are responsible for a lot of water consumption. Almost all water which has been used in such processes is, in the end, in chemical or physical conditions which are unsuitable for return to the springs from which it was collected. The water released at the end of an industrial process can contain a variety of pollutants; for instance high levels of metal ions of high toxicity. Faced with this problem, companies need to optimize their wastewater treatment system in order to reach the legal disposal limits. The introduction of clean technologies in the industrial processes has helped in reducing the discharges of pollutants into the environment. However, there still can remain low concentrations of toxic chemicals in wastewater, including heavy metals. [1]

Several examples of classical physico-chemical processes to remove metal ions from wastewater are: precipitation, ion exchange, filtration or evaporation. However, these processes can be quite expensive (based on investment and required energy). [1]

A lot of innovative studies are dealing with the removal of metal ions out of wastewater, i.e. by means of membrane processes. One of these membrane technologies is SLM (Supported Liquid Membranes), which combines the benefits of liquid-liquid extraction and membrane processes. A microporous polymeric support is impregnated with carrier solution and is placed between two aqueous solutions: the feed solution, which initially contains the analytes, and the stripping solution, where the analytes are retained after their transport through the membrane. [2]

Previous studies showed that D_2EHPA and CYANEX reagents and LIX 860-I can be very useful extractants for the extraction of metal ions. Classical liquid-liquid extractions have also shown that mixtures of different extractants can have a synergistic effect. However, it's not clear yet which extractant ratio has an optimal effect or which type of complex is formed during the extraction process. [2]

Presented in this thesis are a series of experiments on the extraction of nickel (II). The extractants used in this work are LIX860-I (5-dodecylsalicylaldoxime) and D_2EHPA (Bis-(2-ethylhexyl)-phosphoric acid). The aim of this project is to investigate the synergistic behavior between those 2 extractants and to identify its complex formation by means of spectrophotometric methods. Job's method has been used already in previous work to identify the stoichiometry of metal complexes if individual extractant are applied.[25]

Within this project, Job's method and the Mole-ratio method will be applied to three component systems (i.e. mixed extractants systems), to study the interactions between two different extractants and the metal ion, nickel (II). Both methods can be used to establish the stoichiometry of complexes formed between pairs of species, typically an organic compound and a cation. [3,4]

2. Extraction Techniques

2.1. Liquid-Liquid Extraction

Liquid-Liquid Extraction is used for the removal of a certain component from a liquid phase into a second liquid phase.

Extractors bring about direct contact of the feed (solution to be separated) and extracting solvent in order to permit diffusional transfer of the constituents from the feed to the solvent. The rate of transfer depends upon the contact area of the two liquids and the degree of turbulence developed within them. The extractor disperses one of the liquids in the other to produce a large surface area. The extractor must also provide for the subsequent mechanical separation of the dispersion, based upon the different densities of the liquids, to permit withdrawal of the two effluent products, the extract (solvent containing the extracted constituents) and the raffinate (unextracted residue). [5]

Liquid-liquid extractions can be performed in a number of devices such as mixer settlers, packed towers, perforated-tray extractors and so one.

The success of liquid-liquid extraction processes depend on the appropriate choice of the solvent and/or extractant and the type of equipment.

2.1.1. Mixer Settlers

In a mixer-settler (figure 2.1), the feed and solvent flow continuously through the mixer, in which the rotating agitator disperses one of the liquids into small droplets immersed in the other. The size of this vessel must provide sufficient residence time for the liquids which makes the desired diffusional transfer to happen. The degree of agitation must be intense without, however, producing a so fine dispersion that subsequent settling is difficult. The dispersion flows then to the settler, most simply a drum, in which low velocity and lack of agitation promote gravital settling to provide clear effluents.

Since in such a single-stage apparatus, the extractable substance approaches concentration equilibrium in the effluents, nearly complete extraction requires a multiplicity of stages. [5]

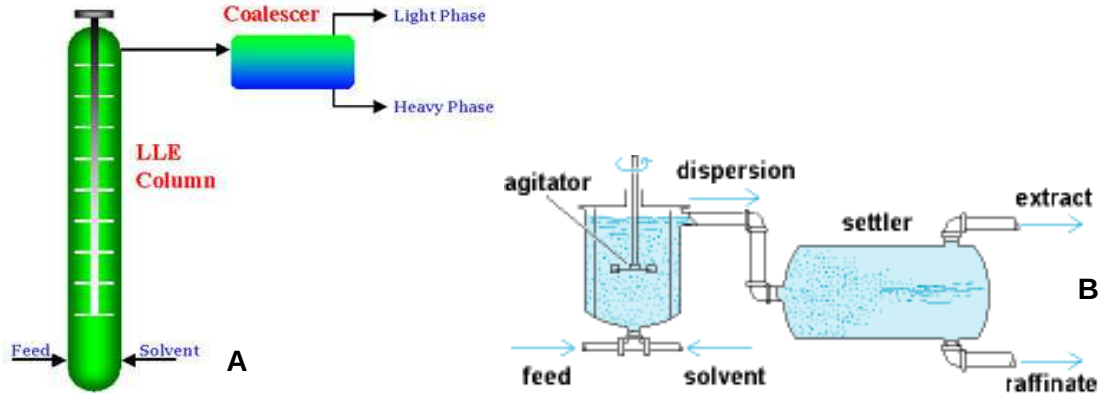

Figure 2.1 – Single Stage Mixer/Settler [A - 6,B - 7]

2.1.2. Packed Towers

A packed tower (figure 2.2) is a cylindrical shell, the bulk of which is filled with manufactured packing, such as rings, randomly arranged. The more dense liquid, introduced at the top, flows downward as a continuum. The less dense liquid enters at the bottom through small nozzles. The resulting small droplets rise through the heavy liquid, during which time extraction occurs. The packing serves to maintain the dispersion and provide moderate turbulence. [5]

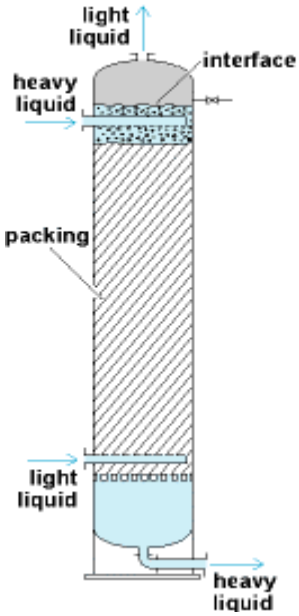

Figure 2.2 – Packed-tower extractor. [6]

2.1.3. Perforated-tray extractor

In perforated-tray towers (figure 2.3) the light liquid collects in a layer under each tray and is dispersed into droplets by the small perforations. The drops rise through the heavy liquid, which flows across each tray and through the downspout. The frequent redispersion achieved makes these towers very effective. Alternatively, by turning the tower upside down, the heavy liquid may be dispersed.[5]

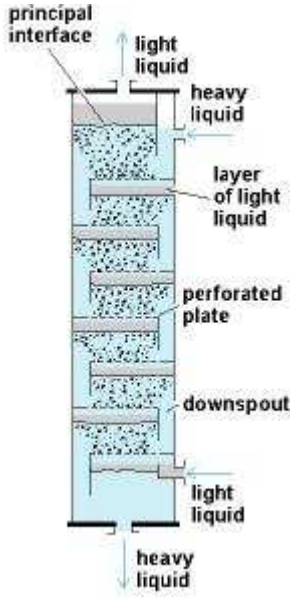

Figure 2.3 – Perforated-tray extractor. [6]

Conventional equipment has however some disadvantages:

- need for dispersion and coalescence;
- problems of emulsification;
- loading limits;
- high operation costs;
- high volumes of solvent and/or extractant necessary.

Membrane based solvent extractions can give an answer to some of these problems. [2]

3. Liquid Membranes

Liquid Membranes (LM) can a classified depending on the occurrence of the liquid membrane as a pure liquid or if polymeric support is involved in the process. [2] One of the benefits of using a liquid membrane is that liquid membranes can be highly selective. With the use of carriers for the transport mechanism, specific molecular recognition can be achieved. Liquid membranes can be relatively high in efficiency, and as such, are being looked into for industrial applications. It is however at this point that people run into the largest problems, Stability. Liquid membranes require stability in order to be effective. If the liquid is pushed out of the pores of the supporting material or ruptured in some way due to pressure differentials or turbulence, then they just do not work. [1] The most promising avenue for uses of liquid membranes resides mainly in the biochemistry and biological fields. The use of carriers utilizing proteins, antibiotics, or other molecules naturally found in cell membranes can provide fast, efficient, and almost continuous service for the researcher.[1,8] Other uses for liquid membranes can be situated in the treatment of wastewater, e.g. for the recovery of metals from dilute waste streams.

There are, in fact, three general types of liquid membranes Bulk Liquid Membranes (BLM), Emulsion Liquid Membranes (ELM) and Supported Liquid Membranes (SLM).

3.1. Bulk Liquid Membranes

Bulk liquid membranes are useful on laboratory scale, as preliminary experiments. Following figure 3.1, a U-tube cell can be used. The organic membrane phase containing the carrier is placed at the bottom of the tube. Two aqueous phases, the source and receiving phase, are placed in the arms of the U-tube, floating on top of the organic membrane phase. The amount of material transported is determined by the concentration in receiving phase. The stability is maintained as far as the agitator is not spinning too fast.

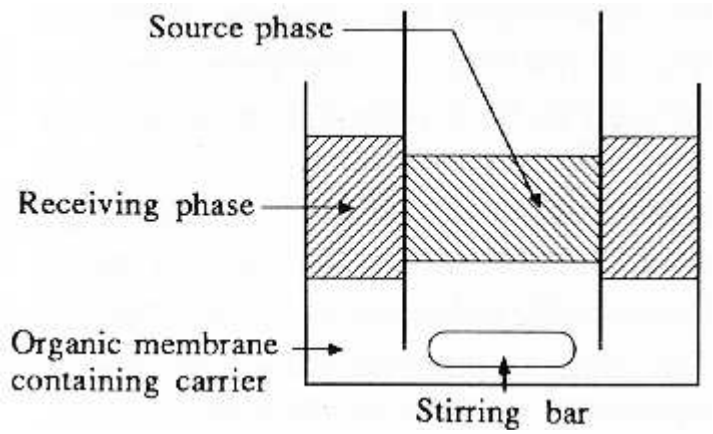

Figure 3.1 – Bulk Liquid Membrane [1]

3.2. Emulsion Liquid Membranes

Within this configuration, a large surface area per volume unit of source phase can be reached. The system (see figure 3.2) has however several drawbacks, all having to do with the formation of the emulsion. Emulsion stability should be controlled. i.e. ionic strengths, pH, etc. If for any reason, the membrane does not remain intact during the operation, the separation reached at that point is destroyed.

In order to recover the receiving phase, and to restore the carrier phase, the emulsion must be broken. This is a difficult task since, to make the stable emulsion, we have to work against the ease of breaking it back down.

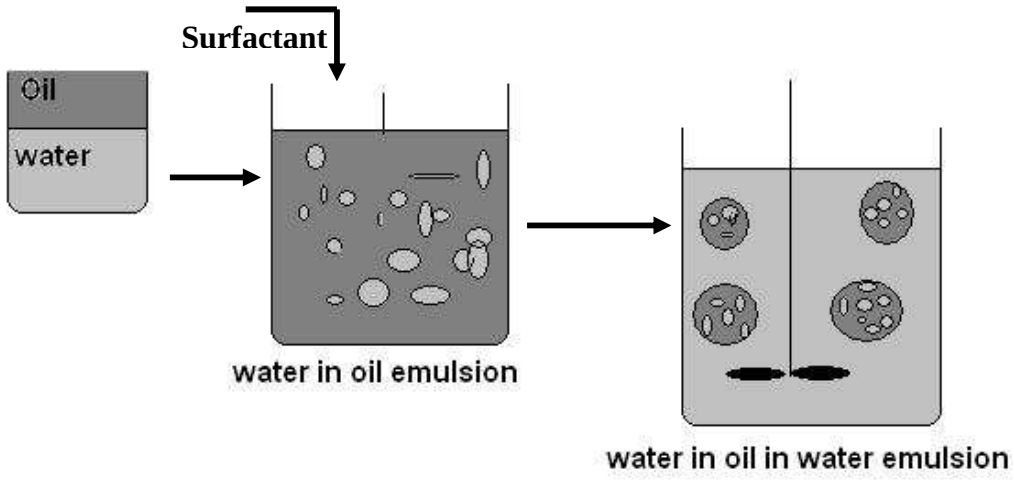

Figure 3.2 – Preparation of an emulsion liquid membrane (ELM) [9]

3.3. Supported Liquid Membranes

Different configurations have been investigated concerning SLM in an effort to increase the efficiency of the liquid membrane operation.

These configurations include Thin Sheet Supported Liquid Membranes, Hollow Fiber Supported Liquid Membranes, Flowing Liquid Membranes and Contained Liquid Membranes.

3.3.1. Thin Sheet Supported Liquid Membrane

The Thin Sheet Supported Liquid Membrane configuration (see figure 3.3) is the most simplistic in design and is often used on laboratory scale.

A hydrophobic membrane is impregnated with an extractant solution and serves as a barrier between the wastewater and a strip solution. The wastewater, initially containing all the metal ions, is referred to as the feed solution. The strip solution or receiving phase is usually an acidic solution in the case of an acidic extractant HX. The difference in pH between the wastewater and the strip solution acts as a driving force to transport the metal ions from the wastewater towards the strip solution.

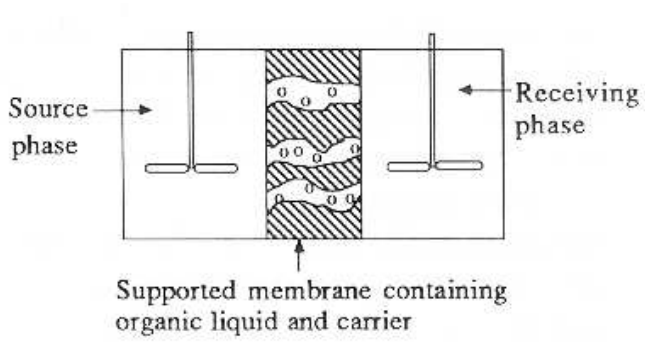

Figure 3.3 – Thin Sheet Supported Liquid Membrane [1]

The chemical reaction in the case of an acidic extractant and monovalent cation, can be schematized as [10]:

$$M^{n+} + nHX\,(membrane) \longleftrightarrow MX_n\,(membrane) + nH^+ \qquad (3.1)$$

The various steps that characterize the transport of metal species with an organic extractant solution through an SLM can be described by means of figure 3.4 [8]. Figure 3.4 shows an example of a counter- transport phenomenon.

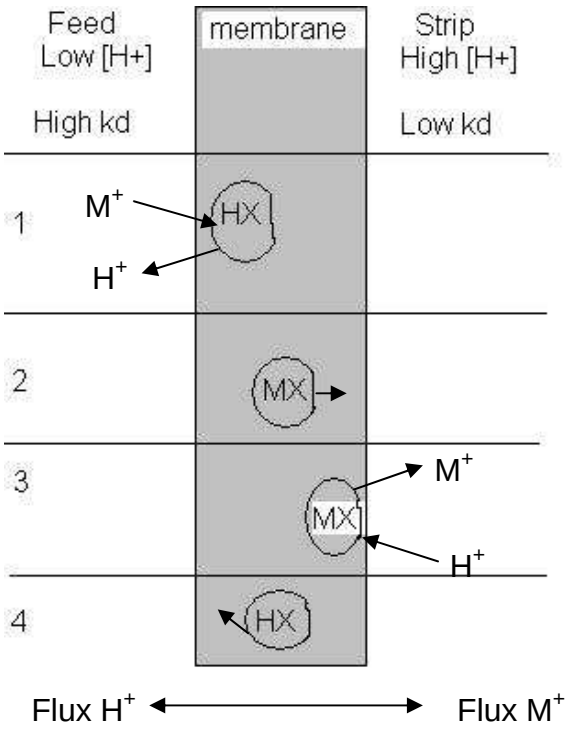

Figure 3.4 – Schematic description of the transport of a metal ion through a SLM with an acidic extractant HX. [10]

In the first step, the metal species in the feed solution diffuse towards the membrane interface where it reacts with the metal carrier. H^+ ions are simultaneously released into the feed solution (counter transport).

During the second step, the metal-carrier complex diffuses across the membrane.

In the third step, at the membrane-strip interface solution, the metal ions are released into the receiving phase. Then, the free carrier diffuses back across the membrane in order to repeat the complete cycle.

Sometimes a problem may occur due to a lack of stability resulting from the possible leakage of the extractant solution out of the pores of the membranes.

3.3.2. Hollow Fiber Supported Liquid Membranes

Instead of flat sheet membranes, the membranes are now configured as hollow fibers. Hollow Fiber Supported Liquid Membranes are compact modules, which contain many, many thin fibers. In this way, the surface area can be increased. What occurs is that the source phase is pumped through the fibers from bottom to top (lumen flow), while the receiving phase flows at the shell side. The pores in the fibers themselves are filled with the organic phase. The carriers in that phase then transport a component of the source phase across the membrane towards the receiving phase. Figure 3.5 represents this system.

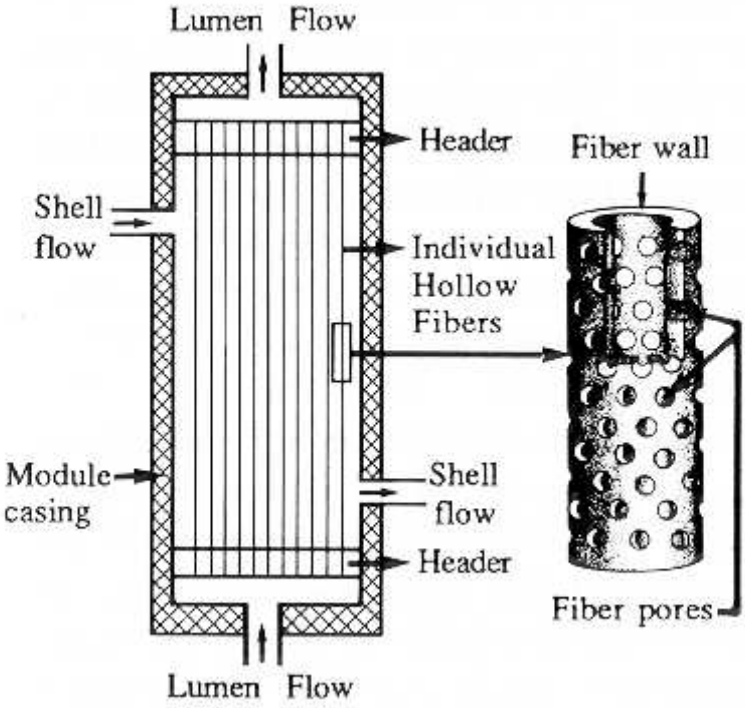

Figure 3.5 – Hollow Fiber Supported Liquid Membrane [1]

Likewise, there are a few problems associated with the flat and hollow fiber Supported Liquid Membrane as described above. Very hydrophobic membrane solvents and carriers are required to maintain the membrane stability. The systems must be cleaned between uses or there will be contaminant buildup.

In an effort to find solutions in order to improve the stability problems, researchers attempted to investigate other configurations. Such as a two module hollow fiber Supported Liquid Membranes (see figure 3.6) or Contained Liquid Membranes (CLM) and Flowing Liquid Mebranes (FLM). These configurations combine in fact the benefits of both Supported Liquid Membranes and Bulk Liquid Membranes. [11,12] In case of a two module configuration or Contained Liquid Membranes, the support is not impregnated with the extractant solution. The organic phase is present as bulk liquid which contain a series of fibers. The feed is sent through the lumen side of one set of fibers, as shown in figure 3.6.

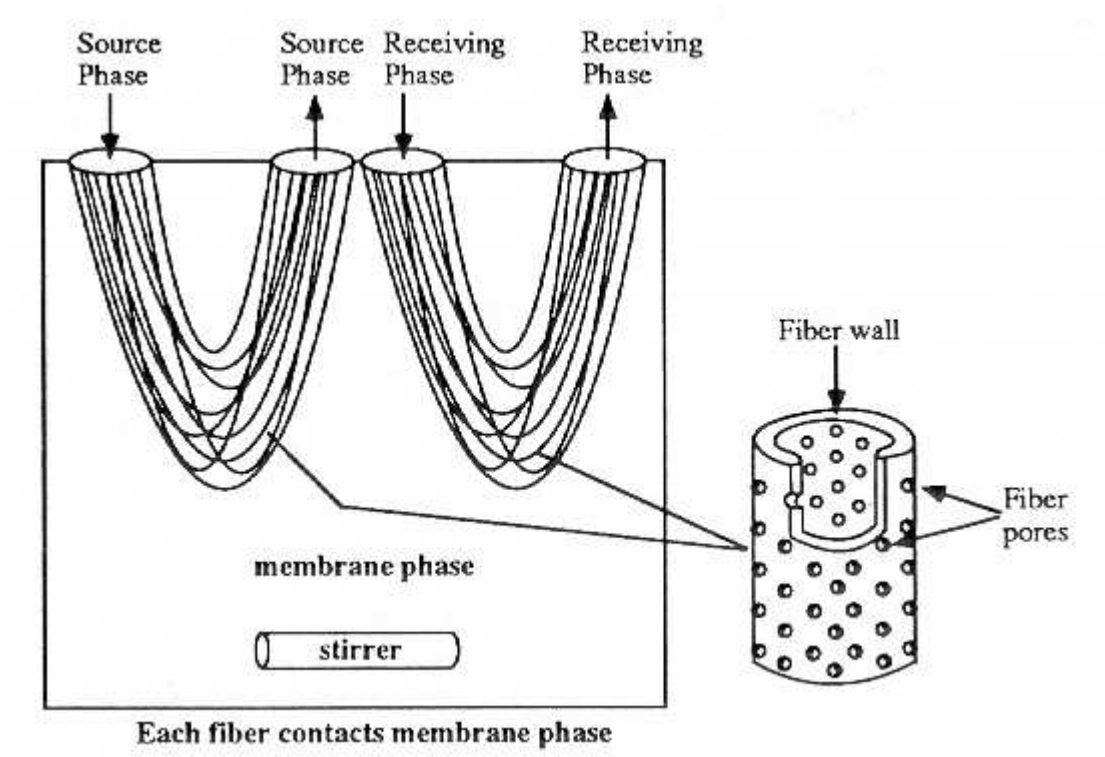

Figure 3.6 – Two Module Hollow Fiber Supported Liquid Membrane [1]

Whitin this set of fibers, the extraction step takes place. A second set of fibers is then necessary for stripping. These systems are also called “Contained Liquid Membranes”. Both aqueousphases flow through the lumen side of the fibers.(see figure 3.8)

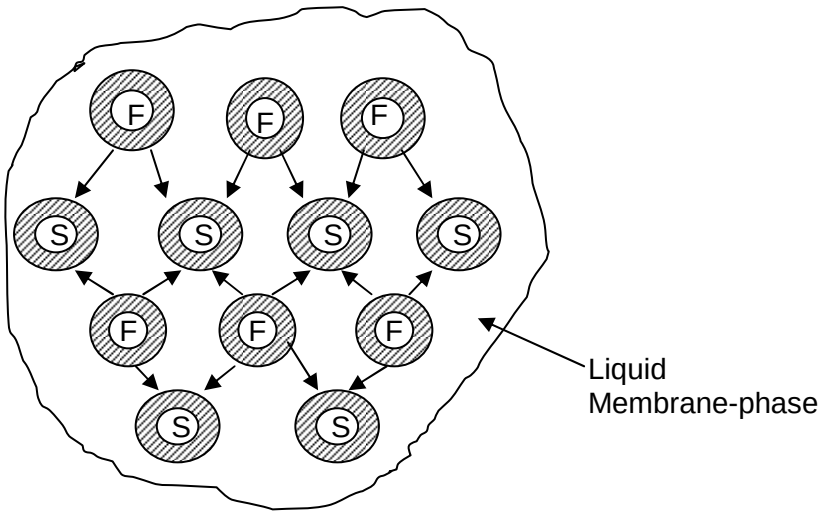

Figure 3.7 – Schematic drawing of Hollow Fiber Contained Liquid Membrane [11]

In FLM, a solution containing a liquid membrane carrier flows in thin channels between two hydrophobic microfiltration membranes that separate the liquid membrane from a feed solution and a strip solution. (see figure 3.7)

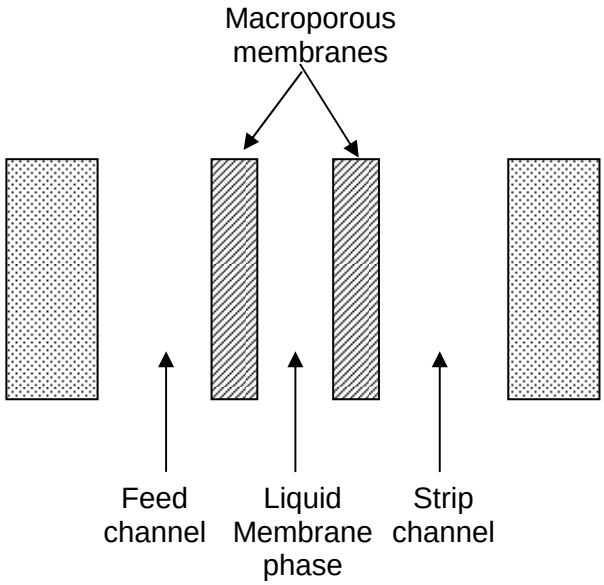

Figure 3.8 – Schematic drawing of Flowing Liquid Membrane [11]

3.3.3. Advantages and Limitations of SLM

Most important advantages of SLM are its high separation (facilitated transport), the low operating and energy costs, fewer moving parts resulting in lower maintenance and lower amount of organic membrane phase necessary compared to conventional extractions. When using a single hollow fiber module.

Likewise, there are a few problems associated with this technique, such as membrane instability which generally occurs because of the gradual loss of the liquid membrane towards the liquids on each side of the membrane. Such loss can occur because of the solubility of the carrier and its diluents in the feed and strip liquids or by capillary displacement as a result of an osmotic pressure differential between the two sides of the membrane. [13]

4. Extractants

Within this project, tthe synergism between the two extractants LIX 860-I and D_2EHPA will be investigated for nickel (II) extraction.

4.1. LIX 860-I

LIX 860-I (Cognis) is the commercial name of a 5-dodecylsalicylaldoxime solution diluted in a high flash point hydrocarbon diluent, needed for handling purposes. The structure of 5-salicylaldoxime is presented in figure 4.1.

This ligand is widely used as an extractant for copper. Even though a large number of molecules with a wide variety of extractive functionalities have been proposed as extractant to be used for the recovery of copper from sulfuric acid leach solutions, only the hydroxy oximes have been used in commercial copper extraction processes. LIX 860-I belongs to the class of the salicylaldoximes, which are very strong copper extractants. Ketoximes are weaker reagents. Very strong copper extractants extract substantial amounts of copper at pH values less than 1.0, while moderate strength copper extractants are most useful above a pH of 1.6-1.8. [14]

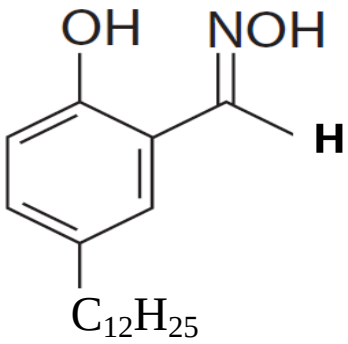

Figure 4.1 – Structure of LIX 860-I [14]

This aldoxime-based reagent has also been proposed as a reagent for the coextraction and selective stripping of copper and zinc. [14] If LIX 860-I is applied in a mixture with other classes of extractants, for instance organophosphoric acids, good extraction efficiencies can also be obtained for other metal ions, such as nickel (II). [14]

More specifications of this extractant can be obtained in appendix I_a.

For the experiments, the pure reagent with the commercial name Aloxime 800 has been applied.

4.2. D_2EHPA

D_2EHPA (VWR International) is a very efficient and versatile extraction agent in liquid-liquid extraction processes for purification, separation and enrichment processes, e.g. recovery of metal salts.

The structure of D_2EPHA or bis(2-ethylhexyl) phosporic acid is shown in figure 4.2.

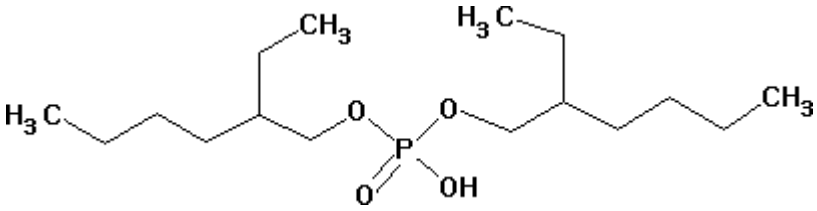

Figure 4.2 – Structure of D_2EHPA

D_2EHPA is soluble in common organic solvents such as aliphatic, aromatic and chlorinated hydrocarbons as well as in alcohol. D_2EHPA is only slighty soluble in water. However, it is very soluble in caustic soda with the formation of it's sodium di (2-ethylhexyl) phosphate salt.[15]

The most important extractions carried out with D_2EPHA in industry are: [15]

- Lanthanide extraction from HCl solution;
- Uranium(VI) extraction from H_3PO_4 solution;
- Zinc(II) extraction from chloridic solution;
- Zinc(II) extraction from Ca^{2+}/Cl^- solution;
- Zinc(II) extraction from $Na^+/H^+/SO_4^{2-}$ solution;
- Zinc(II) extraction from sulphuric acid solution containing Fe^{3+};
- Iron(III) extraction from $HF/HNO_3/Cr^{3+}/Ni^{2+}$, etc solutions;
- Calcium(II) extraction from $MgCl_2$ solution;
- Calcium(II) extraction from $Mg^{2+}/ Ni^{2+}/ Co^{2+}/SO_4^{2-}$ solution;
- Beryllium(II) extraction from sulphuric acid solution;
- Cobalt(II) extraction from $Ni^{2+}/Na^+/SO_4^{2-}$;
- Gallium(III) extraction from neutral sulphate solution;
- Molybdenum(VI) extraction from sulphuric acid solution.

More information about this extractant can be obtained in appendix I_b.

5. Spectrophotometric Methods for elucidation of the complexation process

Two spectrophotometric methods have been applied for investigation of the nickel (II) complexes, the method of continuous variation or Job's method and the Mole-ratio method.

5.1. Job's Method

Job's method, also called the method of continous variation, is a simple and effective approach to the determination of chemical reaction stoichiometry. Job's method is used to estimate the stoichiometry of the complexes formed between two solutes, from the variation in light absorbance of their mixtures when compared with the separate light absorbance of the individual constituents.

This method is widely used for the spectrophotometric determination of metal complexes. Consider the following reaction:

$$M^{n+} + nHX \rightarrow MX_n + nH^+ \tag{5.1}$$

The concentration of M^{n+} and X is varied, but the total combined analytical concentration is kept constant: [16]

$$c = C_{M^{n+}} + C_{HX} \tag{5.2}$$

The absorbance of the different solutions are measured and plotted against the mole-fraction of metal ion or ligand. (see figure 5.1)

The mole fraction of metal ion or ligand are calculated according equeation 5.3 and 5.4 respectively.

$$X_{M^{n+}} = \frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX}} \tag{5.3}$$

$$X_{HX} = \frac{C_{HX}}{C_{M^{n+}} + C_{HX}} \tag{5.4}$$

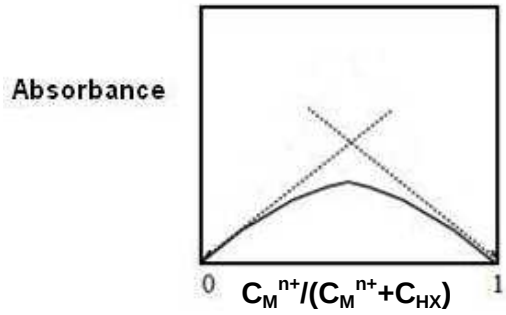

Figure 5.1 – Typical plot for a continuous variation experiment.[16]

This method is only reliable for solution conditions under which a single complex is formed. This method therefore uses diluted solutions of both reagents supposed to form complexes, to guarantee that for a given composition only one complex predominates.

If there is only one complex formed, e.g. MX_n and the absorbance is measured without interferences of the other compounds, then *n* can be determined from the maximum of the curve from the previous plot: [16]

$$n = \frac{1 - X_{\max}}{X_{\max}} \quad \text{or} \quad X_{\max} = \frac{1}{n+1} \tag{5.5}$$

Also stability constants can be deduced with this technique.

Job's method has already been extensively studied to elucidate the complex stoichiometry of single extractant solutions. [2]

However, also synergistic effects have been observed for mixed extractants systems, e.g. Ni (II) extraction with LIX 860-I and D_2EHPA.

Therefore, in this project, the method of continuous variation will be used for obtaining information of the complex formation in those mixed extractants processes. [3,4]

In the case of the extraction of a metal ion with a mixture of two extractants, a three-component system is obtained. Job´s method has already been applied for a three-component system by M. Bryce et al [17] for the study the interactions between two different compounds (phenylamine/catechol and phenol/catechol) and a complexant/flocculant cation, namely Al^{3+}.

In the case of a three component system, the following reaction can be written:

$$M^{n+} + nHX + oHL \rightarrow MX_nHL_o + nH^+ \tag{5.6}$$

HX and HL denote the extractant which neutralizes the metal ion and the extractant which is responsible for solvatation, respectively.

The concentration of M^{n+}, HX and HL is varied, but the total combined analytical concentration is kept constant:

$$c = C_{M^{n+}} + C_{HX} + C_{HL} \tag{5.7}$$

The mole fraction of metal ion, ligand HX and ligand HL can then be defined as:

$$X_{M^{n+}} = \frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}} \tag{5.8}$$

$$X_{HX} = \frac{C_{HX}}{C_{M^{n+}} + C_{HX} + C_{HL}} \tag{5.9}$$

$$X_{HL} = \frac{C_{HL}}{C_{M^{n+}} + C_{HX} + C_{HL}} \tag{5.10}$$

With three components, it is not possible to guarantee that a given maximum will correspond to an individual complex. As a consequence of this, the information to be obtained will be qualitative. [17]

5.2. Mole-Ratio Method

An alternative spectrophotometric method to distinguish the stoichiometry of a complex is the mole ratio method. A series of solutions are prepared containing an equal concentration of metal ion, but with a varying concentration of ligand. The absorbance of each solution is then measured and plotted against the ratio between the number of moles of ligand to the number of moles of metal ions (which is the same as the ratio of the corresponding total concentrations) as shown in figure 5.2.

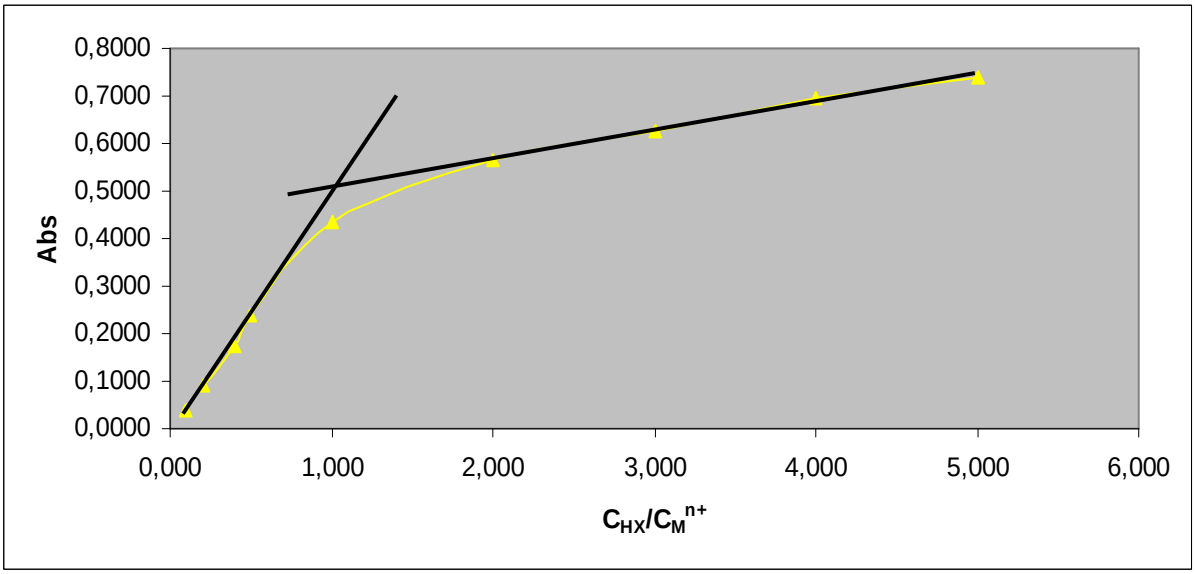

Figure 5.2 – Typical plot for a mole-ratio experiment

The stoichiometric formula of the complex can be found by extrapolating the straight-line portions of the graph, which is to say the point at which these lines cross each other, corresponds directly to the ratio of ligand to metal ion in the complex. This procedure works very well for weakly dissociated complexes. If the dissociation constant of the complex is too large, the mole-ratio plot will become a smooth continuous curve and it will be impossible to locate the stoichiometric point. In such cases, better results can often be secured by the continuous variation method.

6. Instrumentation

6.1. UV-Vis Spectrophotometry

Ultraviolet-Visible spectroscopy (UV-Vis) is the measurement of the attenuation of the beam of light after passing through a sample (see figure 6.1).

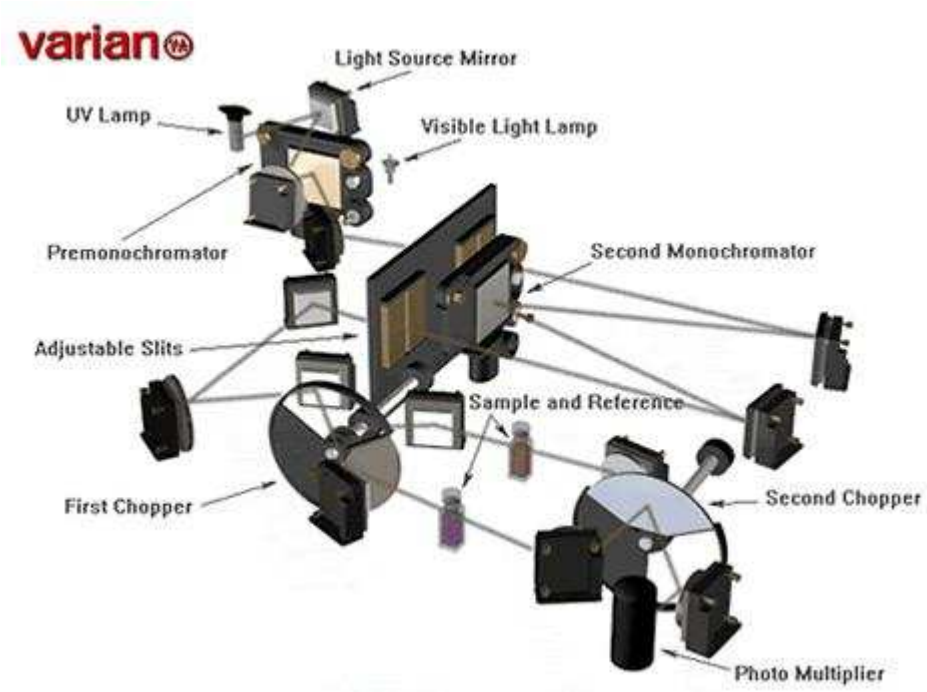

Figure 6.1 – Scheme of double beam UV-Vis spectrophotometric apparatus [18]

Absorption measurements can be on a single wavelength or over a broad spectral range. Ultraviolet and visible light have enough energy to promote external electrons to higher levels of energy, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra (spectral range see figure 6.2) have characteristics that are of limited use for large sample identification but are very useful for quantitative measurements.

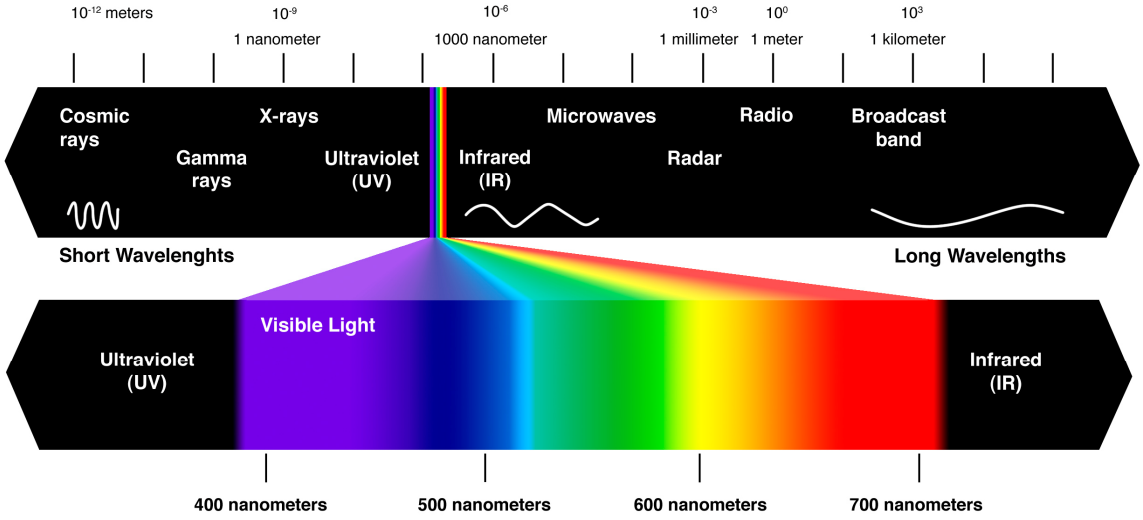

Figure 6.2 – Situation of Visible Spectrum within the spectroscopic techniques. [19]

The UV-Vis spectral range is situated approximately between 190 to 900 nm, as defined by the working set of typical commercial UV-Vis spectrophotometers (see figure 6.3). The short wavelength limit for the general UV-Vis spectrometer is the absorption of UV wavelength until 180 nm by atmospheric gases. A spectrometer purged with nitrogen extends this limit to 175 nm. Working beyond 175 nm requires a vacuum spectrometer and a suitable UV light source. The long-wavelength limit is usually determined by the wavelength response of the detector in the spectrometer.

Figure 6.3 – Spectrophotometer (Cary 100 Bio UV-Vis Spectrophotometer).

The light source is usually a deuterium lamp for UV measurements and a tungsten-halogen or wolfraan lamp for visible measurements. The instruments automatically exchange lamps when scanning between the UV and visible. The wavelengths of these continuous light sources are typically dispersed in a single or double monochromator spectrograph. The

spectral band is determined by the monochromator slit width or the wide variety of elements in array-detector spectrometers. Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements. As detectors, photodiode or photomultipliers can be used. [20]
The main advantage of spectrophotometric methods is that small quantities of substances can be determined by simple means.

The concentration of an analyte in solution can be determined by measuring its absorbance in a range where the Lambert-Beer Law is applicable. Lambert-Beer law also called the Bouguer-Lambert-Beer law or simply Beer's law is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The Lambert-Beer law is written as:

$$\log \frac{I}{I_0} = Abs = a\ b\ c \tag{6.1}$$

where:
Abs - absorbance;
I_0 - intensity of the incident light;
I - transmitted intensity;
a - wavelength-dependent absorptivity coefficient [$(L*(g*cm)^{-1}$];
b - optical path [cm];
c - analyte concentration [g/L];

When working in concentration units of molarity, the equation of Lambert-Beer law is written as:

$$Abs = \varepsilon\ b\ c \tag{6.2}$$

where:
Abs - absorbance;
ε - constant molar absorptivity [$(M*cm)^{-1}$];
b - optical path [cm];
c - molar concentration of the solution [M];

For a given substance and a given wavelength, the absorbance is directly proportional to the concentration of the species concerned.

Usually cuvettes of 1 cm in path length are used, so equation 6.2 becomes:

$$Abs = \varepsilon \; c \tag{6.3}$$

The application of the Lambert-Beer Law is valid only for relatively dilute solutions and only for monochromatic light.

The linearity of the Lambert-Beer law is limited by chemical and instrumental factors. This linearity no longer occurs at very high concentrations (>0.01M) of the substance. In these cases, samples need to be diluted prior to measuring. It is therefore important to determine the range of concentrations allowed to keep a linear relationship. Once the linear relationship between the concentration of the substance in solution and its absorbance is established, the unknown concentration can be easily determined. [20]

6.2. Atomic Absorption Spectroscopy

The process of atomic absorption can be represented by figure 6.4:

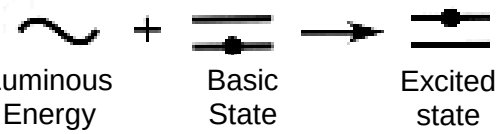

Figure 6.4 – Process of atomic absorption.

Atoms in the "basic state" are capable of absorbing light energy of a specific wavelength and reaching an "excited state".

By measuring the variation in the amount of light transmitted, the analyte present can be quantified. The amount of absorbed radiation is related to the concentration of the element of interest in the solution.

The AAS used in this project is displayed in figure 6.5.

Figure 6.5 – Atomic absorption spectrophotometry (Thermo Scientific S Series AA Spectrophotometer).

The different components of an AAS are shown in figure 6.6.

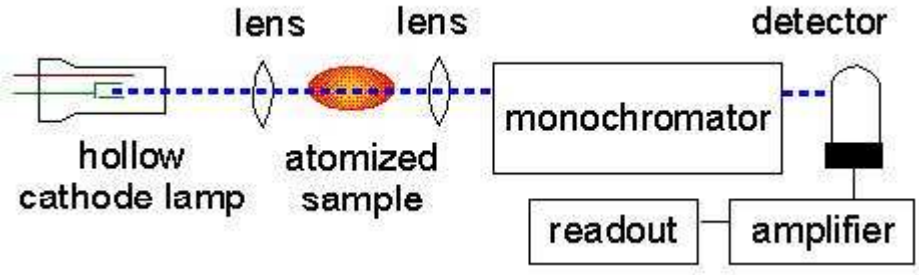

Figure 6.6 – Atomic Absorption Spectrometry [21]

The following components can be distinguished:

- The light source, emitting the spectrum of the element of interest;
- the "absorption cell," in which the atoms of the sample are produced;
- the monochromator;
- the detector, which measures the intensity of light, converts this light signal into an electrical signal and amplifies.

The most common source used in atomic absorption is the hollow cathode lamp (see figure 6.7).

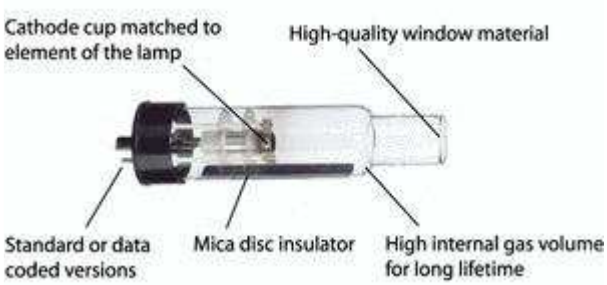

Figure 6.7 – Hollow cathode lamp [22]

The hollow cathode lamp is an excellent source for most elements due to their stability. However, for some more volatile elements, the hollow cathode lamps have low intensity emission and a very short life. For these elements, the discharge lamp can be used.
The anode (which can be a thread of tungsten) and cathode, made of the element of interest, are sealed in a glass capsule filled with an inert gas at low pressure, usually argon or neon. The best gas must be selected according to some criteria: (i) that generate less interference in the determination of the analyte, (ii) that gives greater intensity of the radiation source and (iii) that is more inert. The window through which the radiation passes is made of quartz, because glass absorbs within the ultraviolet range. There exist hollow cathode lamps for as much as 64 elements.

The function of the absorption cell is to convert the sample into atoms in the ground state. The sample must be, initially in liquid form. The process of nebulization is responsible for converting the sample into small droplets, which are directed to the flame, where the solvent is evaporated, producing dried particles. In the last stage, the molecules are split, producing the absorbing species. Some unwanted processes may occur, as (i) of atoms excited by the flame, with the consequent emission of energy of excitation, (ii) excited atoms can react with other atoms and molecules in the flame producing molecular species and / or radicals, which produce molecular spectra, (iii) ionization of atoms.

The method of pneumatic nebulization uses a gas that moves at high speed and perpendicular to the exit of capillary, dragging the net through the capillary by Venturi effect, and spray the liquid droplets at the exit of the capillary.
A common method of nebulization occurs by the use of a gas is moving at high speed and perpendicular to the exit of a capillary, dragging the net through the capillary by Venturi effect, and asparagus in the liquid droplets at the exit of the capillary: the pneumatic nebulization. The sample is aspirated into a chamber and produces small droplets of liquid, before the sample reaches the flame.
The figure 6.7 shows an image of a pre-mix burner:

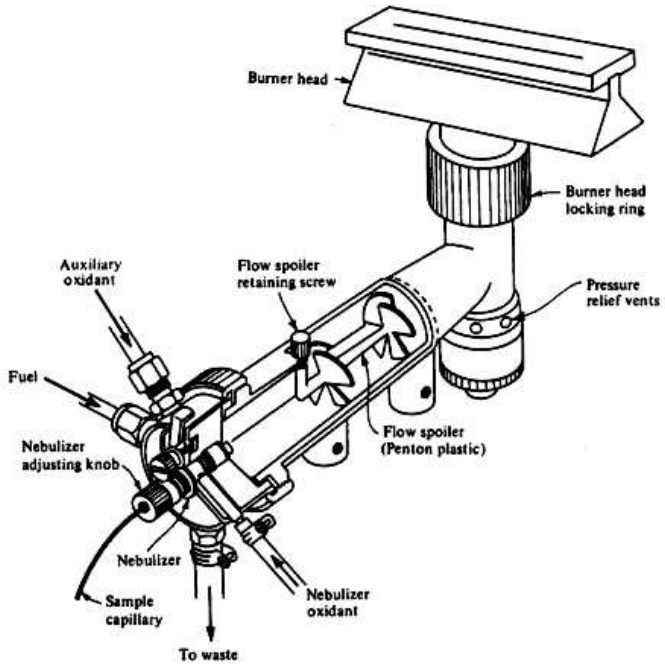

Figure 6.8 – Pre-mix burner [23]

The pre-mixing chamber is often made of polypropylene to avoid problems of corrosion and facilitates the efficient flow of the liquid (sample) that is drained during aspiration. The atmospheric pressure at which the sample is subjected is greater than the pressure at the outlet of the capillary, "pushing" the sample into the pre-mixing chamber. During this stage the small droplets are formed. Not all the droplets formed are directed to the flame. This step aims to select the insert of drops of uniform size, thus improving the accuracy of the measurements. The basic device used for the selection of the droplets to be injected is the flow spoiler constructed of polypropylene. Shields are arranged sequentially, which has the function to allow only the smaller droplets to reach the flame. In this process the larger drops, and therefore heavier, can not depart from the shields, bump into them and are being drained.

The flame (normally uses acetylene-air) is lined up in a beam of light of the appropriate wavelength (for Ni the primary wavelength is 232 nm). The atoms undergo a transition from the ground state to the first excited state by absorbing some of the light from the beam. The lamp must be perfectly aligned so the beam crosses the hottest part of the flame. The light passed through the flame is received by the monochromator. The detector then measures the intensity of the beam of light. When some of the light is absorbed by the metal, the beam's intensity is reduced. The detector records that reduction as absorption. That absorption is shown on an output device by the data system.

We can find the concentrations of metals in a sample running a series of calibration standards through the instrument. The instrument will record the absorption generated by a given concentration. By plotting the absorption versus the concentrations of the standards, a calibration curve can be plotted. We can then measure the absorption for an unknow sample solution and use the calibration curves to determine the concentration of the sample solution.
As with other analytical techniques, atomic absorption spectrometry requires careful calibration. The idealized calibration or standard curve is stated by Beer's law that the absorbance of an absorbing analyte is proportional to its concentration.
Unfortunately, deviations from linearity may occur, especially at higher concentrations of metallic analytes. Figure 6.9 shows an idealized and deviation of response curve. It is desirable to work in the linearity response range. The general rule is that a minimum of four standards and a blank should be prepared in order to have sufficient information to fit the standard curve appropriately. [24]

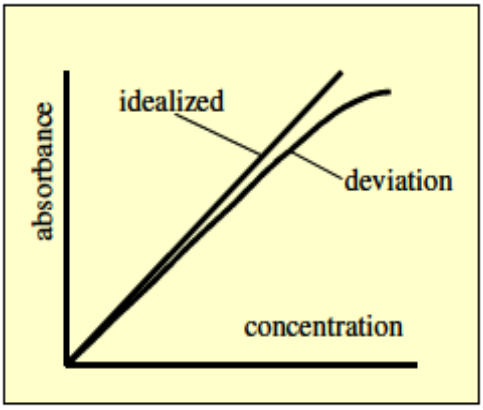

Figure 6.9 – Idealized/deviation response curve [24]

If the sample concentration is too high to permit accurate analysis in the linearity response range, samples must be diluted.

For this work, a blank and four standards with a concentration of respectively 1, 2, 4 and 5 ppm were used for making the calibration curve. (see figure 6.10)

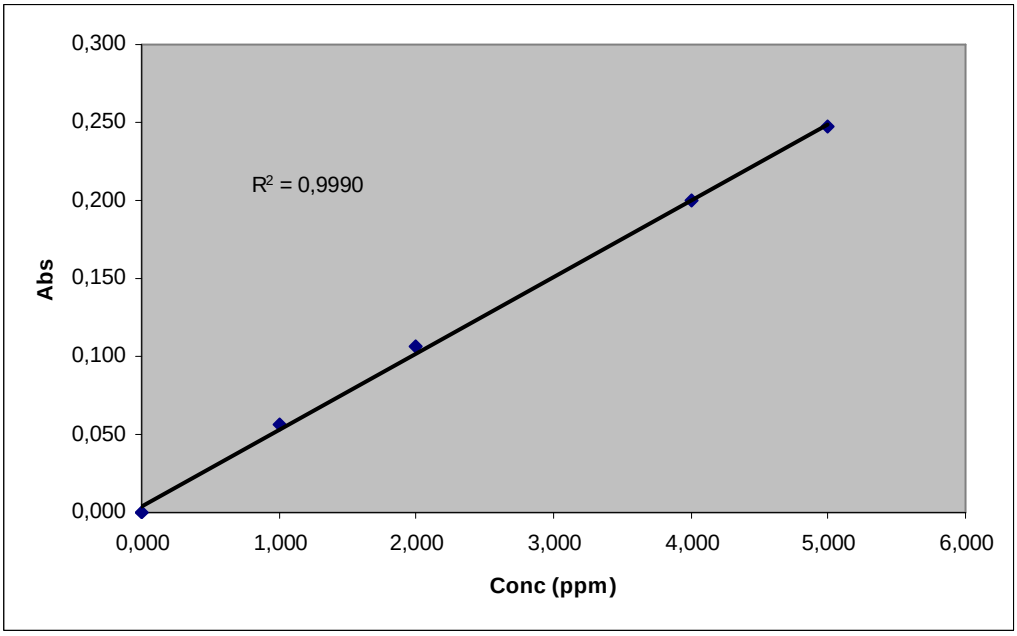

Figure 6.10 – Example of calibration curve.

7. Experimental Procedures

Two spectrophotometric methods, Job's method and Mole-ratio method will be investigated to achieve information concerning the complexation of the metal ion nickel (II) with a mixture of the extractants LIX 860-I and D_2EHPA.
These methods are used to estimate the stoichiometry of the various complexes between two solutes, from the variation of light absorbance of the complexes when compared to the light absorbances of the individual solutes. Therefore, only the extraction step is investigated within this project.

At first, it is necessary to prepare two stock solutions, the aqueous phase and organic phase. The aqueous phase is composed of the metal ion and the organic phase of the extractant(s). Separating funnels are filled with both phases (each 50ml) and are left shaking in an IKA Labortechnik HS501 digital shaking machine during night (approximately 16 hours) to ensure equilibrium. (see figures 7.1, 7.2 and 7.3)

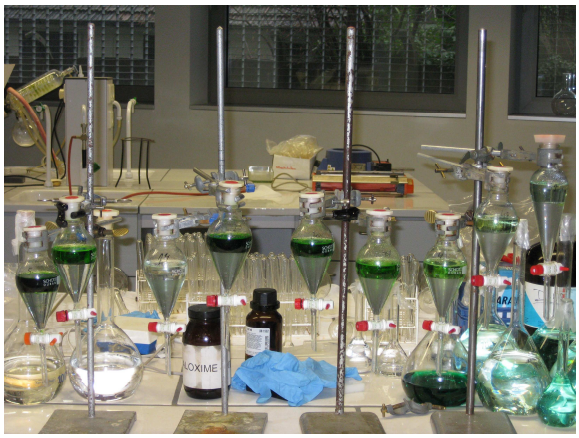

Figure 7.1 – Funnels before shaking

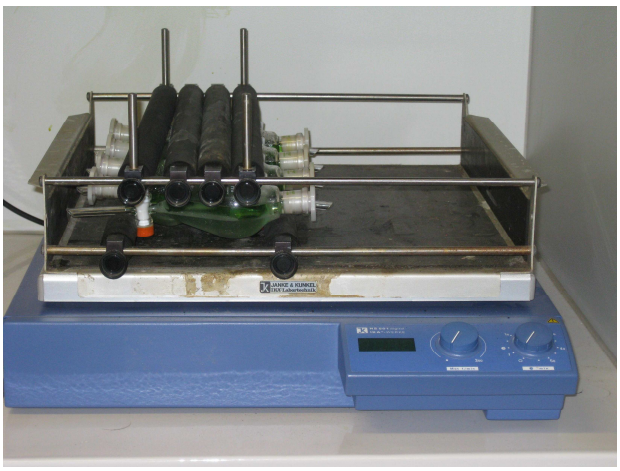

Figure 7.2 – IKA Labortechnik HS501 digital shaking machine

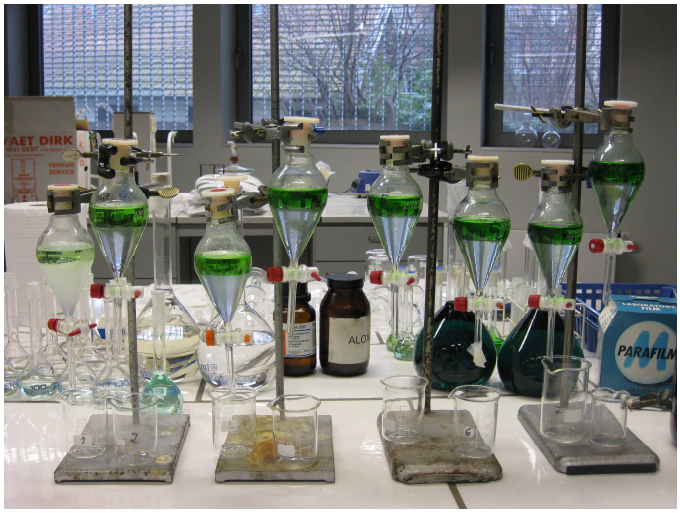

Figure 7.3 – Funnels after shaking

After shaking, the two phases are separated and analysed. From the aqueous phase, the metal concentrations are deduced with AAS. From the organic phase, a wavelength scan is made to determinate the wavelength at which maximum absorbance is obtained. Afterwards, the absorbance of all organic phases within one set of experiments are measured at the wavelength of maximum absorbance.

7.1. Buffered system

In this method, solutions with different ratios of metal ions and extractants have been prepared, while the total concentration of the three components (ligands and metal ion) is kept constant at a value of 0.05M (see equation 7.1 and table 7.2). The metal-to-ligand ratio is varied between 0 and 1.

$$[D_2EHPA]+[LIX\ \ 860-I]+[Ni^{2+}]=0.05M \quad (7.1)$$

Table 7.1 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 1:1[1].

Exp	D_2EHPA (M)	LIX 860-I (M)	Ni^{2+} (M)	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$
1	0.0225	0.0225	0.005	0.10
2	0.0200	0.0200	0.010	0.20
3	0.0175	0.0175	0.015	0.30
4	0.0150	0.0150	0.020	0.40
5	0.0125	0.0125	0.025	0.50
6	0.0100	0.0100	0.030	0.60
7	0.0075	0.0075	0.035	0.70
8	0.0050	0.0050	0.040	0.80
9	0.0025	0.0025	0.045	0.90

- **Preparation of aqueous phase**

Initially, a nickel (II) solution with a concentration of 1M was prepared from the chloride salt $NiCl_2.6H_2O$ (VWR International, 98%). The solution was buffered with sodium acetate trihydrate (VWR International, 99%) (1M) to ensure constant ionic strength and pH. The pH was set at 4.8 with a Consort R735 pH meter with a calibrated glass combination electrode assembly.

From this stock solution, a dilution serie was made to obtain different concentrations of nickel (II) as shown in table 7.2.

Table 7.2 – Set-up of the dilutions for the aqueous phase.

Concentration of diluted solutions (M)	Volume (ml) from stock solution of 1M[2]
0.045	45.00
0.040	40.00
0.035	35.00
0.030	30.00
0.025	25.00
0.020	20.00
0.015	15.00
0.010	10.00
0.005	5.00

[1] These ratios were used in the preliminary experiment with a D_2EHPA: LIX 860-I ratio of 1:1. Later, the experimental set up was extended with a variety of ratios. For more details (see Appendix II – Preliminary Experiments and Appendix III – Job's method).

[2] The dilutions were made in bottles of 1000ml.

From these dilutions, 50ml was pipetted into the shaking funnel.

In this way, several metal:ligand ratios are obtained while the total concentration stays constant at 0.05M.

- **Preparation of organic phase**

Extractant solutions were prepared with a concentration equal to 0.05 M, a D_2EHPA (Bis-(2-ethylhexyl)-phosphoric acid, VWR International, 95%) and LIX 860-I solution (5-dodecylsalicylaldoxime, Cognis) (see figure 7.4). As diluent, spectral grade hexane (after distillation) (Acros Organics, 98%) was used.

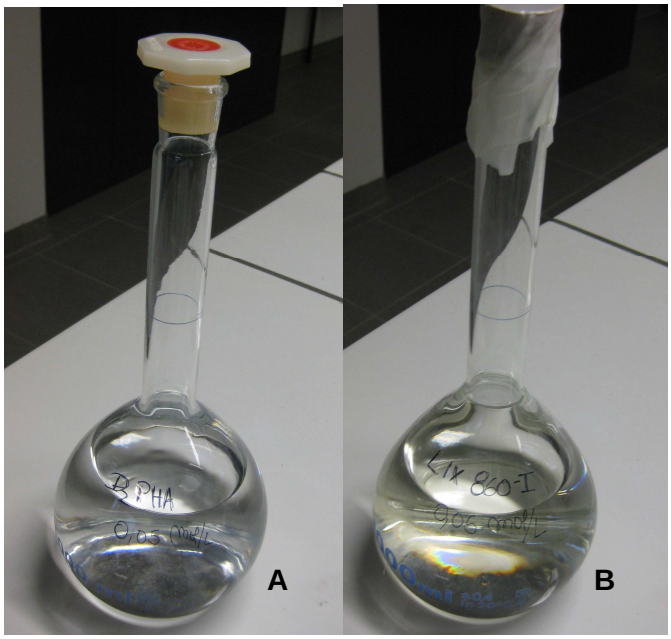

Figure 7.4 – Solutions of extractants (A – D2EPHA, B – LIX 860-I)

Dilutions of the organic phase were prepared directly in the shaking funnel.

Table 7.3 – Example for dilutions in shaking funnel[3]

Exp	Volume Ni^{2+} (ml)	Volume LIX 860-I (ml)	Volume D_2EHPA (ml)	Hexane
1	50.00	22.50	22.50	5.00
2	50.00	20.00	20.00	10.00
3	50.00	17.50	17.50	15.00
4	50.00	15.00	15.00	20.00
5	50.00	12.50	12.50	25.00
6	50.00	10.00	10.00	30.00

[3] These volumes were used in the preliminary experiment with a D_2EHPA: LIX 860-I ratio of 1:1. Later, the experimental set up was extended with a variety of volumes depending on the ratio.

Exp	Volume Ni^{2+} (ml)	Volume LIX 860-I (ml)	Volume D_2EHPA (ml)	Hexane
7	50.00	7.50	7.50	35.00
8	50.00	5.00	5.00	40.00
9	50.00	2.50	2.50	45.00

Then the funnels were shake during night at 305 rpm. After separation of the organic and aqueous phase, final analysis could be performed.

The organic phase is analysed spectrophotometrically (Cary 100 Bio UV-VIs Spectrophotometer). First, a scan is made between 350nm and 900nm to determine the wavelength of maximal absorbance. Later, this wavelength is used for the determination of the absorbance of each organic solution.

The aqueous phase is analyzed by Atomic Absorption Spectroscopy (Thermo Scientific S Series AA Spectrometer) before and after shaking to determine the extraction percentage. Through mass balance, the concentration of metal ion in the organic phase is determined.

The concentration of metal ion in the organic phase can be calculated for each sample by making the difference between the metal concentration in the aqueous phase before and after shaking, as shown in equation 7.2:

$$C_{org.} = C_{M_0} - C_{M_E} \tag{7.2}$$

The percentage of extraction is also calculated for each sample, by dividing the difference between the concentration of metal ion in the aqueous phase before and after shaking through the initial metal concentration in the aqueous phase. (see equation 7.3)

$$\%Extraction = \frac{C_{M_0} - C_{M_E}}{C_{M_0}} \times 100 \tag{7.3}$$

7.2. Not buffered system

The procedure is nearly identical as previously described.

A stock solution of nickel (II) with a concentration of 1M was prepared without the addition of acetate buffer.

The pH is now put at a value of 4.8 with a diluted sodium hydroxide solution (VWR International, 98%).

The rest of the procedure is similar as described in chapter 7.1.1..

7.3. Mole-ratio method buffered system

In this method, the metal concentration was kept constant at 0.010 M while the extractant concentration was varied. A complete set-up of 54 experiments was performed (see Appendix V). Some experiments of that set-up are shown in table 7.4 in order to explain the preparation procedure.

Table 7.4 – Experimental set-up of the different experiments

Exp	D_2EHPA (M)	LIX 860-I (M)	Ni^{2+} (M)	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
19	0.001	0.001	0.010	0.83
20	0.001	0.002	0.010	0.77
33	0.002	0.030	0.010	0.24
34	0.004	0.001	0.010	0.67
44	0.005	0.010	0.010	0.40
45	0.010	0.001	0.010	0.48
51	0.020	0.004	0.010	0.29
53	0.030	0.002	0.010	0.24
54	0.040	0.001	0.010	0.20

- **Preparation of aqueous phase**

Initially, a nickel (II) solution with a concentration of 0.010M was prepared from the chloride salt $NiCl_2.6H_2O$ (VWR International, 98%). The solution was buffered with sodium acetate trihydrate (VWR International, 99%) (0.010M) to ensure constant ionic strength and pH. The pH was set at 4.8 with a Consort R735 pH meter with a calibrated glass combination electrode assembly.

From these solution, 25ml was pipetted into the shaking funnel.

- **Preparation of organic phase**

Extractant solutions were prepared with a concentration equal to 0.05 M, a D_2EHPA (Bis-(2-ethylhexyl)-phosphoric acid, VWR International, 95%) and LIX 860-I solution (5-dodecylsalicylaldoxime, Cognis) (see figure 7.4). As diluent, spectral grade hexane (after distillation) (Acros Organics, 98%) was used.

Dilutions of the organic phase were prepared directly in the shaking funnel as shown in table 7.5.

Table 7.5 – Example for dilutions in shaking funnel

Exp	Volume Ni^{2+} (ml)	Volume LIX 860-I (ml)	Volume D_2EHPA (ml)	Hexane (ml)
19	25.00	0.50	0.50	24.00
20	25.00	0.50	1.00	23.50
33	25.00	1.00	15.00	9.00
34	25.00	2.00	0.50	22.50
44	25.00	2.50	5.00	17.50
45	25.00	5.00	0.50	19.50
51	25.00	10.00	2.00	13.00
53	25.00	15.00	1.00	9.00
54	25.00	20.00	0.50	4.50

Then the funnels were shake during night at 305 rpm. After separation of the organic and aqueous phase, final analysis could be performed. (see also chapter 7.1)

8. Results and Discussion

8.1. Preliminary experiments

At first, some preliminary experiments were made with different ratios of D_2EHPA and LIX 860-I with Job's method. The total concentration of metal/D_2EHPA/LIX 860-I was kept constant at 0.05M. Five differents set-ups were undertaken with the following D_2EHPA:LIX 860-I ratios:

- D_2EHPA:LIX 860-I ratio of 1:1
- D_2EHPA:LIX 860-I ratio of 2:1
- D_2EHPA:LIX 860-I ratio of 1:2
- D_2EHPA:LIX 860-I ratio of 4:1
- D_2EHPA:LIX 860-I ratio of 1:4

The results are discussed in the following chapter.

These experiments were all carried out in a buffered system at pH 4.8 as explained in chapter 7.1.

8.1.1. D_2EHPA:LIX 860-I ratio of 1:1

This experiment was performed with a ratio of D_2EHPA:LIX 860-I of 1:1. The experimental set-up is shown in table 8.1. (see also chapter 7 and Appendix II_a for the results)

Table 8.1 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 1:1.

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
1	0.0225	0.0225	0.0050	4.5:4.5:1	0.10
2	0.0200	0.0200	0.0100	2:2:1	0.20
3	0.0175	0.0175	0.0150	3.5:3.5:3	0.30
4	0.0150	0.0150	0.0200	3:3:4	0.40
5	0.0125	0.0125	0.0250	2.5:2.5:5	0.50
6	0.0100	0.0100	0.0300	11:3	0.60
7	0.0075	0.0075	0.0350	1.5:1.5:7	0.70
8	0.0050	0.0050	0.0400	1:1:8	0.80
9	0.0025	0.0025	0.0450	0.5:0.5:9	0.90

In figure 8.1 and 8.2, the absorbance of the organic phase and the % extraction of nickel (II) are plotted in function of the mole fraction of metal ion.

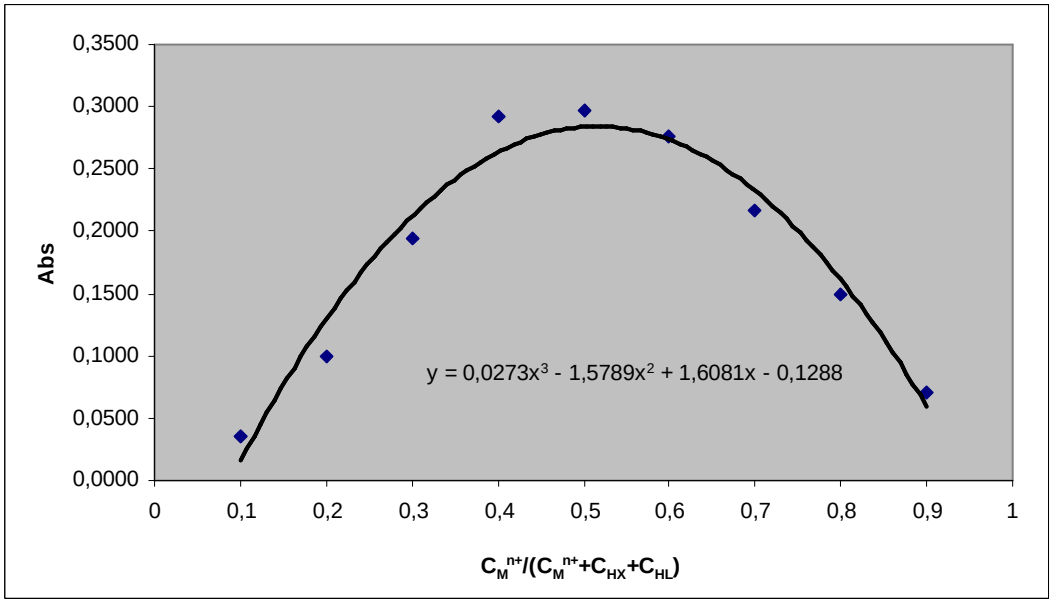

Figure 8.1 – Absorbance of the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:1 (λ=628nm).

The calculated maximum is found at a mole fraction of metal ion of 0.52. This corresponds with an absorbance of the organic phase of 0.284.

A maximum around a mole fraction of 0.5 indicates the formation of a M^{n+}:ligand complex with a ratio 1:1. Grapically, the maximum is also shown at a mole fraction of metal ion of 0.5.

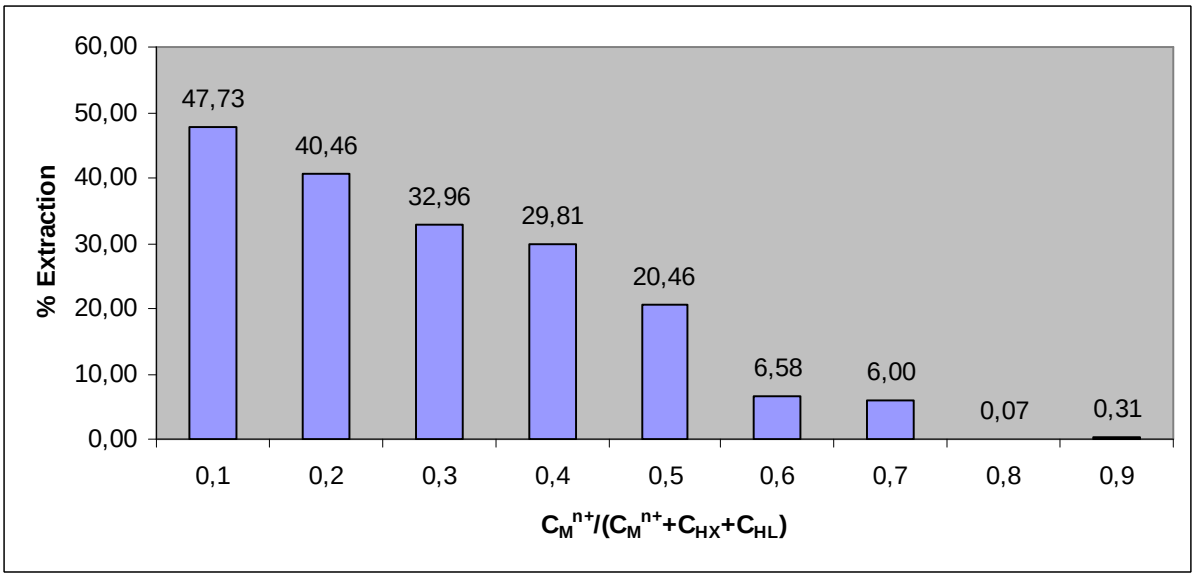

Figure 8.2 – %Extraction in function of the mole fraction of metal ion for D_2EHPA:LIX 860-I ratio of 1:1.

At a low mole fraction of metal ion, 47.73% of nickel can be extracted.

By mass balance data, it is possible to determine the concentration of Ni (II) in the organic phase. These results are displayed in figure 8.3 in function of the mole fraction of metal ion.

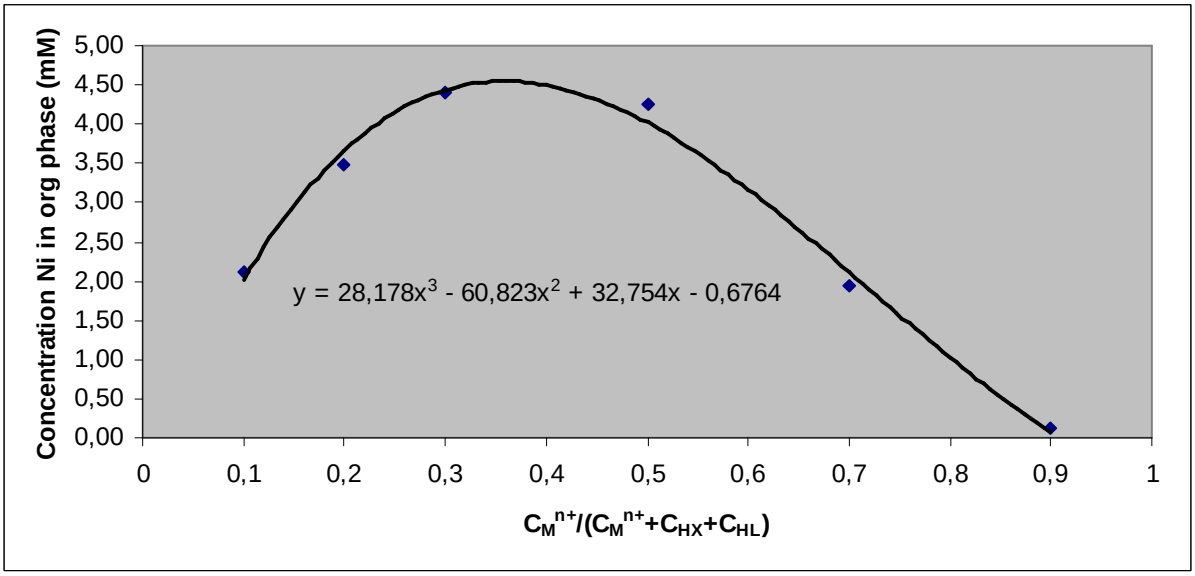

Figure 8.3 – Concentration of Ni (II) in the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:1.

When the maximum is calculated for figure 8.3, it is found at a value of 0.36. This corresponds with a nickel concentration in the organic of 4.55 mM.

A small shift towards a lower mole fraction of metal ion is found in figure 8.3 compared to figure 8.1.

8.1.2. D_2EHPA:LIX 860-I ratio of 2:1

A new set of experiments was performed with a D_2EHPA:LIX 860-I ratio of 2:1. A similar procedure was used as described in chapter 7, except for the concentration of D_2EHPA and LIX 860-I. The experimental set-up is shown below in table 8.2. More information concerning the results can be obtained in Appendix II_b.

Table 8.2 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 2:1.

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$
1	0.0300	0.0150	0.0050	6:3:1	0.10
2	0.0267	0.0133	0.0100	5.33:2.67:2	0.20
3	0.0233	0.0117	0.0150	5.67:2.33:3	0.30
4	0.0200	0.0100	0.0200	2:1:2	0.40
5	0.0167	0.0083	0.0250	3.33:1.67:5	0.50
6	0.0133	0.0067	0.0300	2.67:1.33:6	0.60
7	0.0100	0.0050	0.0350	2:1:7	0.70

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
8	0.0067	0.0033	0.0400	1.33:0.67:8	0.80
9	0.0033	0.0017	0.0450	0.67:0.33:9	0.90

In figure 8.4 and 8.5, the absorbance of the organic phase and the % extraction of nickel (II) are plotted in function of the mole fraction of metal ion.

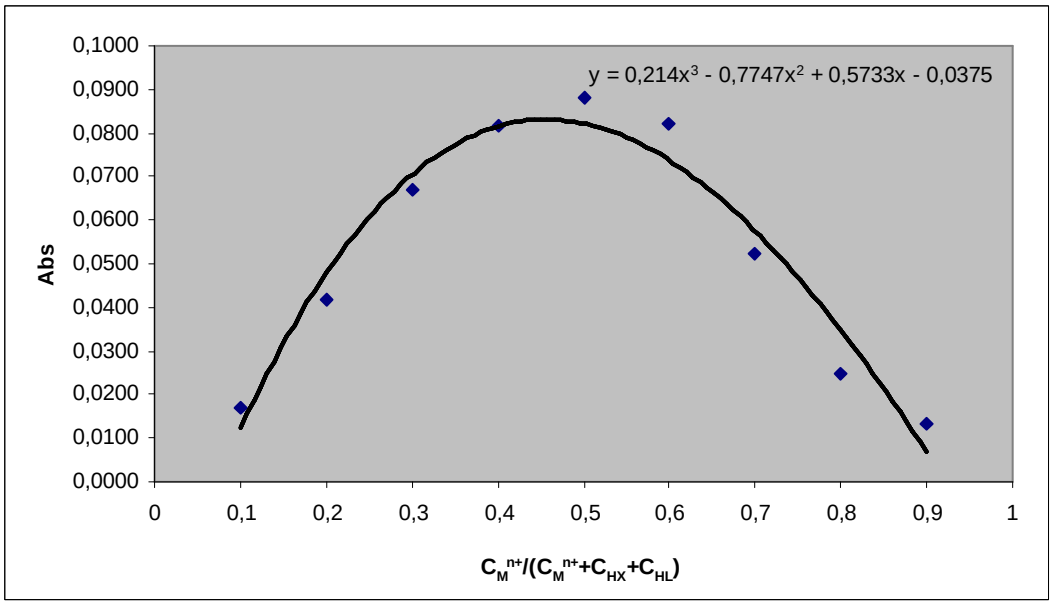

Figure 8.4 – Absorbance of the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 2:1 (λ=635nm).

The calculated maximum is found at a mole fraction of metal ion of 0.46. This corresponds with an absorbance of the organic phase of 0.083.

Also for a D_2EHPA:LIX 860-I ratio of 2:1, the maximum of the Job's method plot is found at a ratio of approximately 0.5.

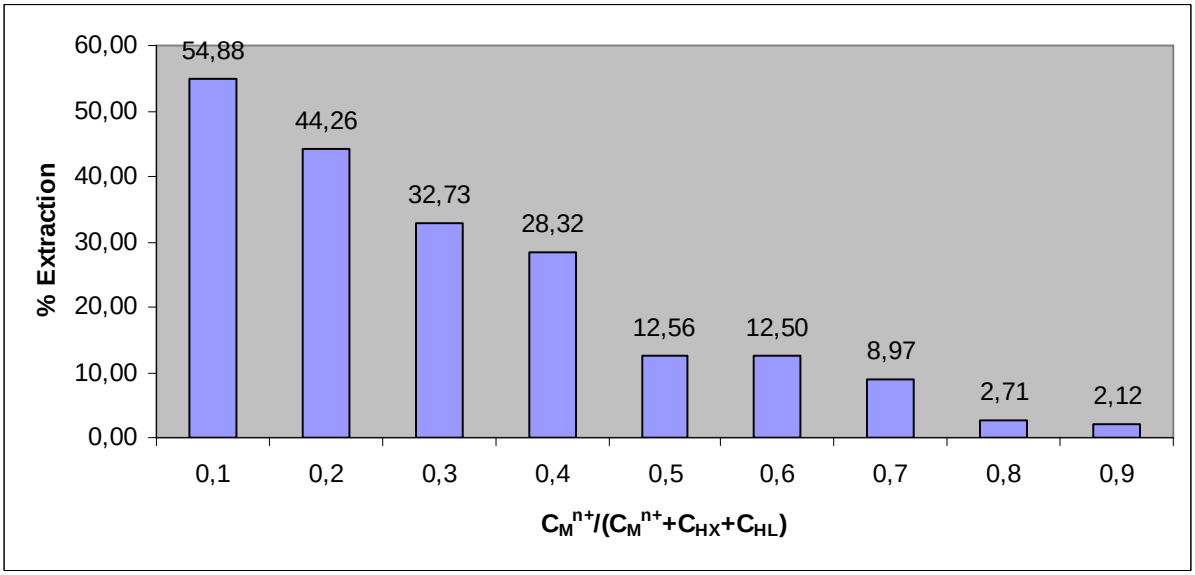

Figure 8.5 – %Extraction in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 2:1.

At a low mole fraction of metal ion, 54.88% of nickel can be extracted.

By mass balance data, it is possible to determine the concentration of Ni (II) in the organic phase. These results are displayed in figure 8.6 in function of the mole fraction of metal ion.

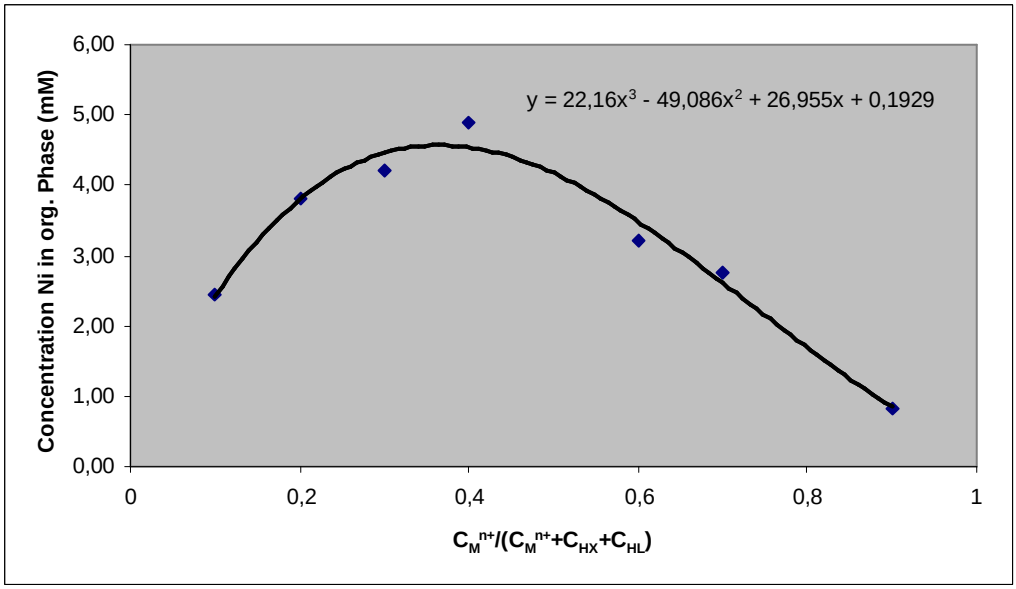

Figure 8.6 – Concentration of Ni (II) in the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 2:1.

When the maximum is calculated for figure 8.6, it is found at a value of 0.36. This correspond with a nickel concentration in the organic of 4.57 mM.

A small shift towards a lower mole fraction of metal ion is found in figure 8.6 compared to figure 8.4. The same trend is observed as for the experiment where the D_2EHPA:LIX 860-I ratio is kept constant at 1:1.

8.1.3. D_2EHPA:LIX 860-I ratio of 1:2

A new set of experiments was performed with a D_2EHPA:LIX 860-I ratio of 1:2. A similar procedure was used as described in chapter 7, except for the concentration of D_2EHPA and LIX 860-I. The experimental set-up is shown below in table 8.3. More information concerning the results can be obtained in Appendix II_c.

Table 8.3 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 1:2.

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
1	0.0150	0.0300	0.0050	3:6:1	0.10
2	0.0133	0.0267	0.0100	2.67:5.33:2	0.20
3	0.0117	0.0233	0.0150	2.33:5.67:3	0.30
4	0.0100	0.0200	0.0200	1:2:2	0.40
5	0.0083	0.0167	0.0250	1.67:3.33:5	0.50
6	0.0067	0.0133	0.0300	1.33:2.67:6	0.60
7	0.0050	0.0100	0.0350	1:2:7	0.70
8	0.0033	0.0067	0.0400	0.67:1.33:8	0.80
9	0.0017	0.0033	0.0450	0.33:0.67:9	0.90

In figure 8.7 and 8.8, the absorbance of the organic phase and the % extraction of nickel (II) are plotted in function of the mole fraction of metal ion.

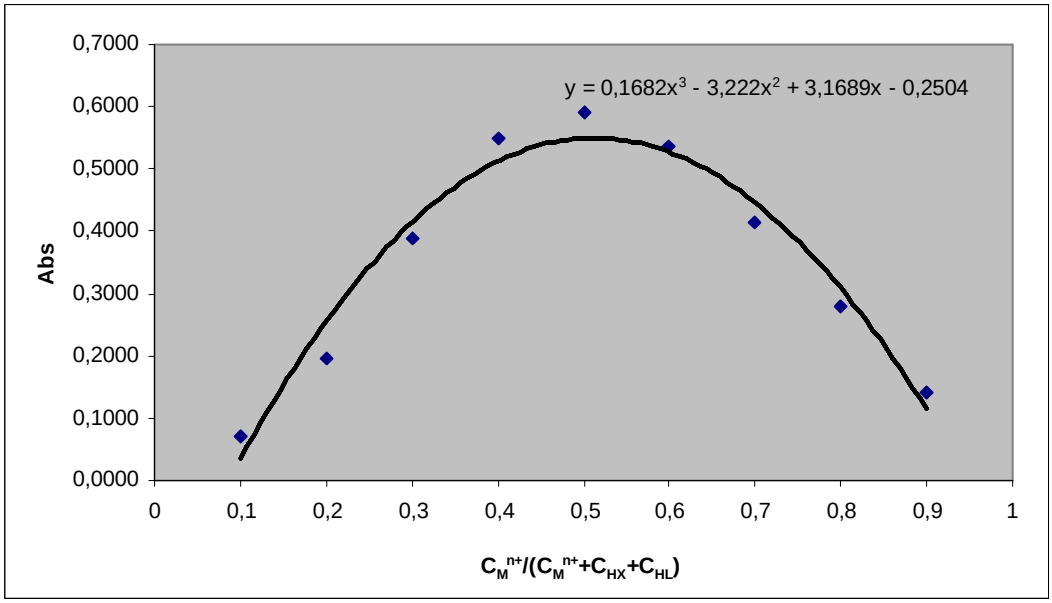

Figure 8.7 – Absorbance of the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:2 (λ=627nm).

The calculated maximum is found at a mole fraction of metal ion of 0.51. This corresponds with an absorbance of the organic phase of 0.550.

Also for a D_2EHPA:LIX 860-I ratio of 1:2, the maximum of the Job's method plot is found at a ratio approximately 0.5.

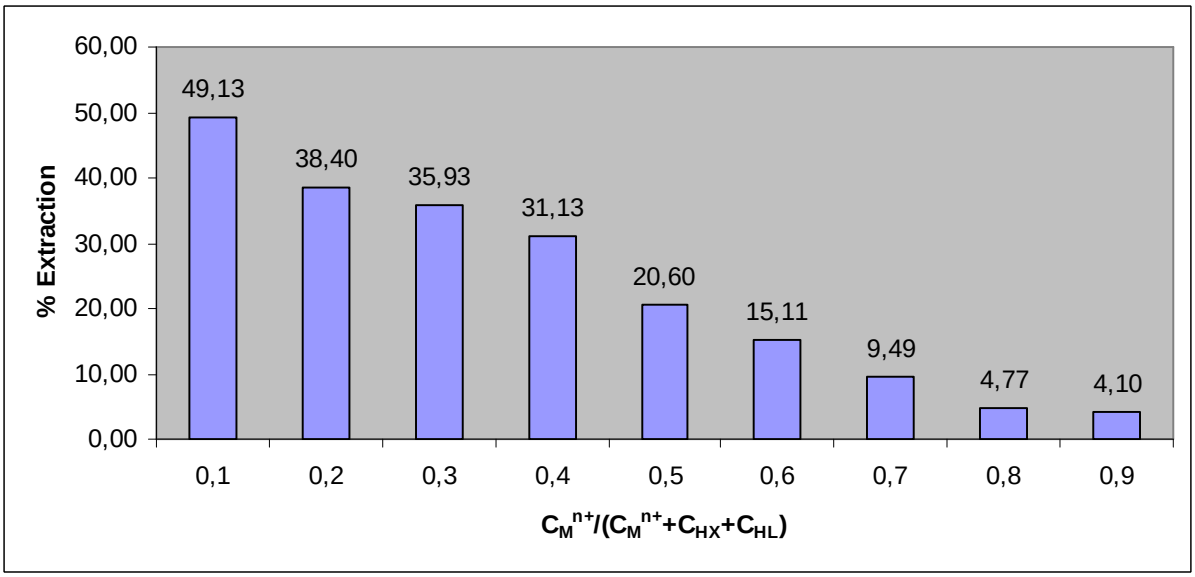

Figure 8.8 – %Extraction in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:2.

At a low mole fraction of metal ion, 49.13% of nickel can be extracted.

By mass balance data, it is possible to determine the concentration of Ni (II) in the organic phase. These results are displayed in figure 8.9 in function of the mole fraction of metal ion.

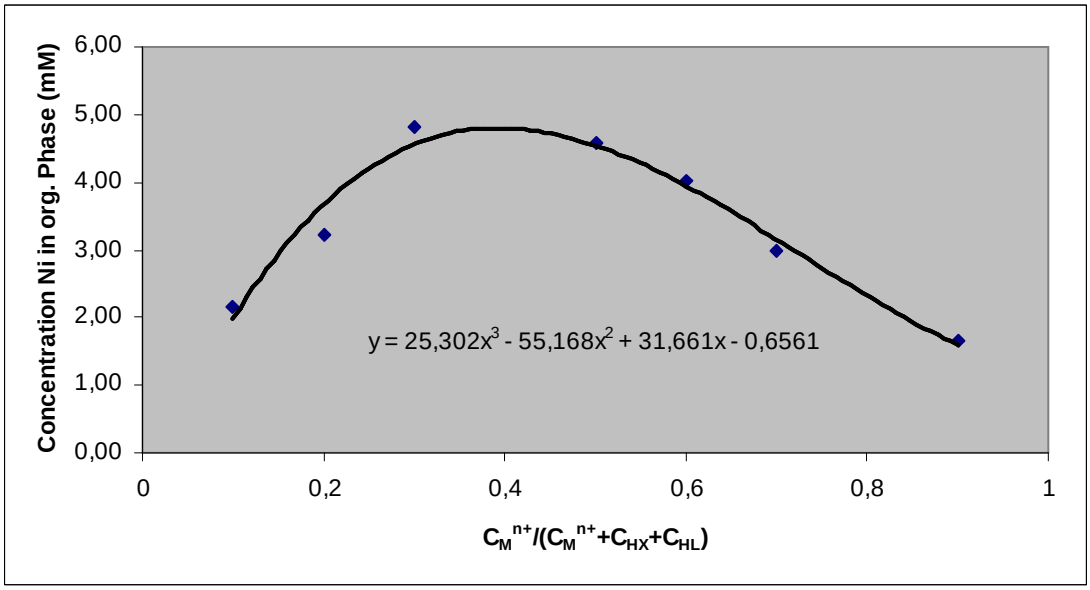

Figure 8.9 – Concentration of Ni (II) in the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:2.

When the maximum is calculated for figure 8.9, it is found at a value of 0.39. This corresponds with a nickel concentration in the organic of 4.80 mM.

A small shift towards a lower mole fraction of metal ion is found in figure 8.9 compared to figure 8.7. The same trend is observed as for the experiment where the D_2EHPA:LIX 860-I ratio is kept constant at 1:1.

8.1.4. D_2EHPA:LIX 860-I ratio of 1:4

A new set of experiments was performed with a D_2EHPA:LIX 860-I ratio of 1:4. A similar procedure was used as described in chapter 7, except for the concentration of D_2EHPA and LIX 860-I. The experimental set-up is shown below in table 8.4. More information concerning the results can be obtained in Appendix II_d.

Table 8.4 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 1:4.

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$
1	0.0090	0.0360	0.0050	1.8:7.2:1	0.10
2	0.0080	0.0320	0.0100	1.6:6.4:2	0.20
3	0.0070	0.0280	0.0150	1.4:5.6:3	0.30
4	0.0060	0.0240	0.0200	1.2:4.8:4	0.40
5	0.0050	0.0200	0.0250	1:4:5	0.50

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
6	0.0040	0.0160	0.0300	0.8:3.2:6	0.60
7	0.0030	0.0120	0.0350	0.6:2.4:7	0.70
8	0.0020	0.0080	0.0400	0.4:1.6:8	0.80
9	0.0010	0.0040	0.0450	0.2:0.8:9	0.90

In figure 8.10 and 8.11, the absorbance of the organic phase and the % extraction of nickel (II) are plotted in function of the mole fraction of metal ion.

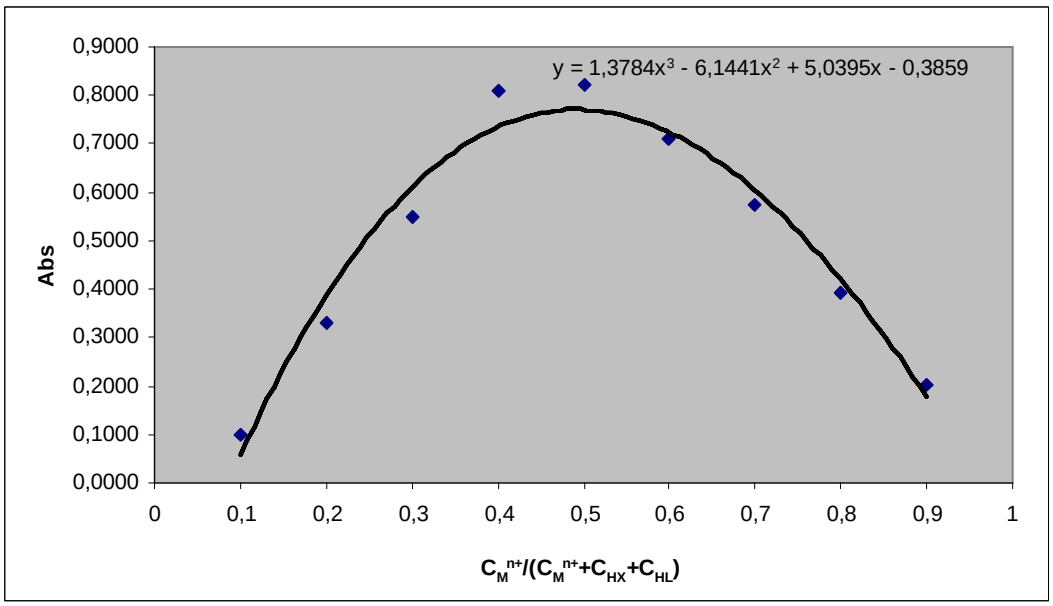

Figure 8.10 – Absorbance of the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:4 (λ=627nm).

The calculated maximum is found at a mole fraction of metal ion of 0.49. This corresponds with an absorbance of the organic phase of 0.770.

Also for a D_2EHPA:LIX 860-I ratio of 1:4, the maximum of the Job's method plot is found at a ratio of approximately 0.5, indicating the formation of a M^{n+}:ligand complex of 1:1.

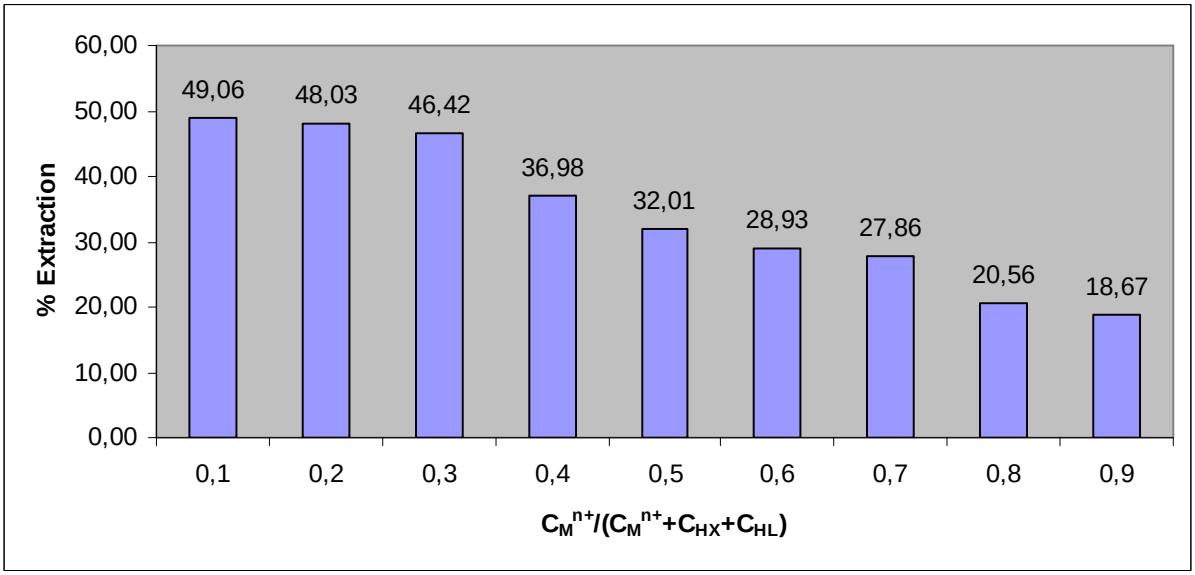

Figure 8.11 – %Extraction in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:4.

At a low mole fraction of metal ion, 49.06% of nickel can be extracted.

By mass balance data, it is possible to determine the concentration of Ni (II) in the organic phase. These results are displayed in figure 8.12 in function of the mole fraction of metal ion.

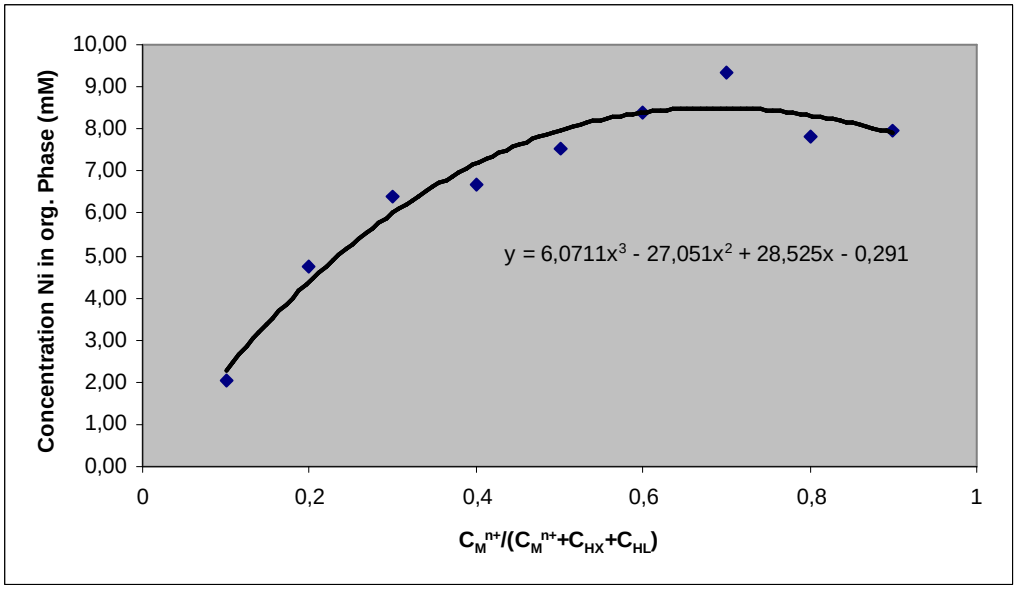

Figure 8.12 – Concentration of Ni (II) in the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 1:4.

Within this experiment, a completely different pattern was observed concerning the concentration of Ni (II) taken up in the organic phase. If seems that a plateau is reached at a mole fraction of metal ion higher than 0.6.

8.1.5. D_2EHPA:LIX 860-I ratio of 4:1

A new set of experiments was performed with a D_2EHPA:LIX 860-I ratio of 4:1. A similar procedure was used as described in chapter 7, except for the concentration of D_2EHPA and LIX 860-I. The experimental set-up is shown below in table 8.5. More information concerning the results can be obtained in Appendix II_e.

Table 8.5 – Experimental set-up for a D_2EHPA:LIX 860-I ratio of 4:1.

Exp.	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:Ni^{2+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$
1	0.0360	0.0090	0.0050	7.2:1.8:1	0.10
2	0.0320	0.0080	0.0100	6.4:1.6:2	0.20
3	0.0280	0.0070	0.0150	5.6:1.4:3	0.30
4	0.0240	0.0060	0.0200	4.8:1.2:4	0.40
5	0.0200	0.0050	0.0250	4:1:5	0.50
6	0.0160	0.0040	0.0300	3.2:0.8:6	0.60
7	0.0120	0.0030	0.0350	2.4:0.6:7	0.70
8	0.0080	0.0020	0.0400	1.6:0.4:8	0.80
9	0.0040	0.0010	0.0450	0.8:0.2:9	0.90

For this experiment, the absorbance of the organic phase were too low for interpretation. Nevertheless, the % extraction of nickel (II) is displayed in figure 8.13.

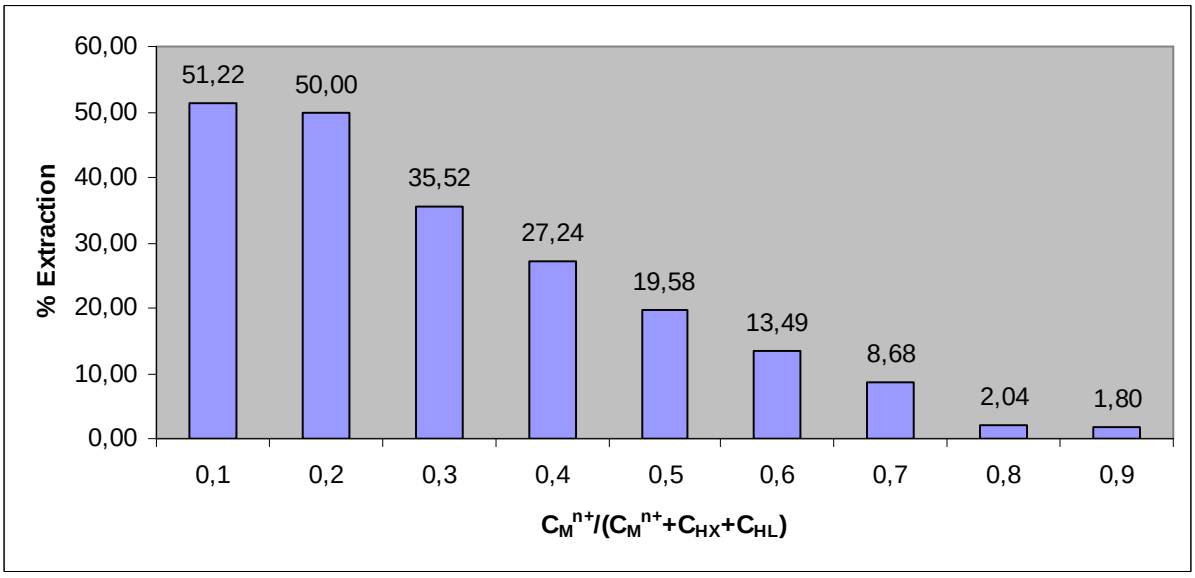

Figure 8.13 – %Extraction in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 4:1.

At a low mole fraction of metal ion, 51.22% of nickel can be extracted.

By mass balance data, it is possible to determine the concentration of Ni (II) in the organic phase. These results are displayed in figure 8.14 in function of the mole fraction of metal ion.

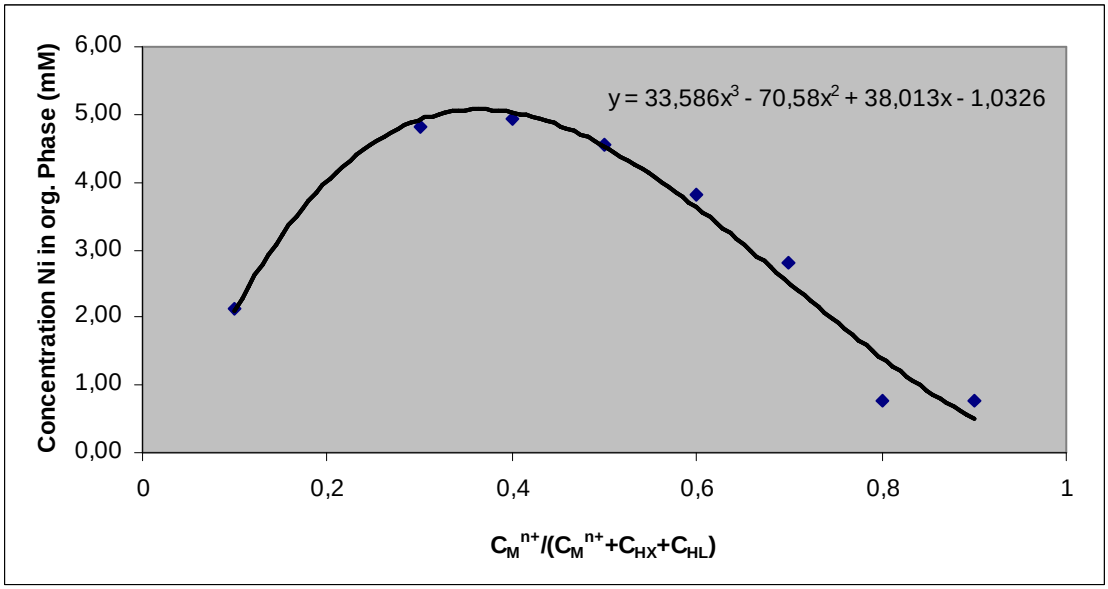

Figure 8.14 – Concentration of Ni (II) in the organic phase in function of the mole fraction of metal ion for a D_2EHPA:LIX 860-I ratio of 4:1.

When the maximum is calculated for figure 8.18, it is found at a value of 0.36. This corresponds with a nickel concentration in the organic of 5.07 mM.

8.1.6. Comparison of the different extractant ratios

As far as the Job's method plots are considered, the maxima were mostly shown at an X_M^{n+} value of around 0.5 or 0.36 as shown in the table 8.6 below.

Table 8.6 – Comparison of the calculated maxima of the Job's method plots for the different ratios.

D_2EHPA:LIX 860-I ratio	X_M^{n+} (based in absorbance)	X_M^{n+} (based on concentration of Ni(II) in organic phase)
1:1	0.51	0.36
2:1	0.46	0.36
1:2	0.51	0.39
1:4	0.49	-
4:1	-	0.36

For one example, namely a D_2EHPA:LIX 860-I ratio of 4:1, no Job's method plot could be made because of too low absorbances.

In figure 8.15, the % extraction for each set of experiments are compared.

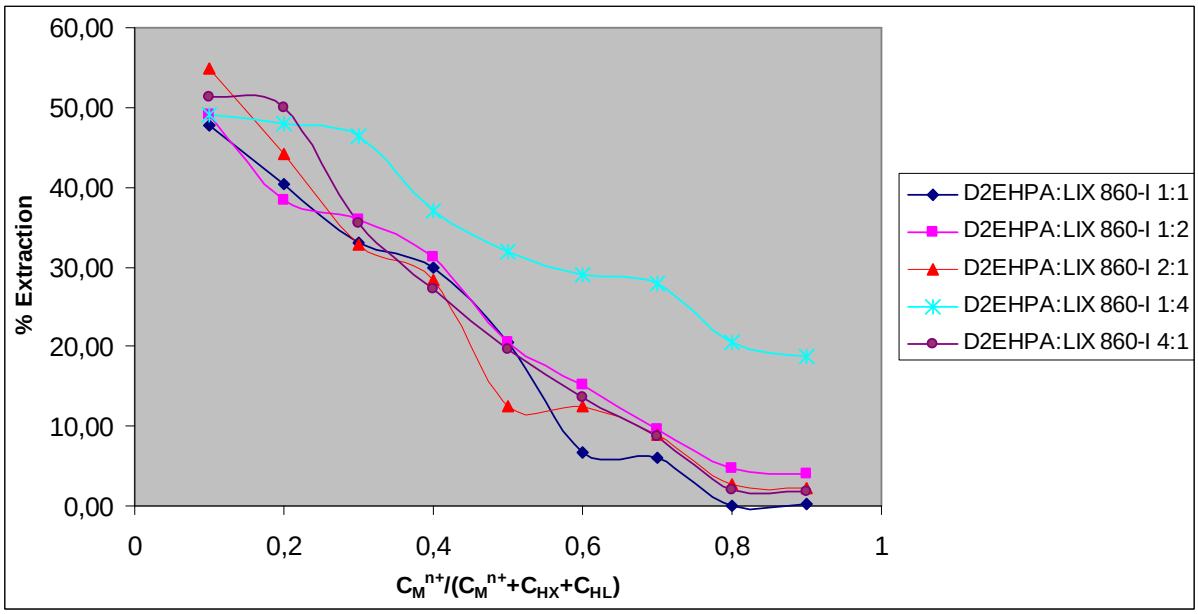

Figure 8.15 – Comparison of the % extraction as a function of the mole fraction of metal ion for the different ratios.

Similar results are obtained with a maximum of 50% extraction which can be reached for a mole fraction of metal ion of 0.1. Only the experiments with a D_2EHPA:LIX 860-I ratio of 1:4 show also higher extractions at higher mole fractions of metal ion.

8.1.7. Comparison of the visible spectra for a mole fraction of metal ion of 0.5 and 0.3.

According to the plot of Job's method, a maximum was generally found at a mole fraction of metal ion of 0.5. However, based on the amount of Ni (II) taken up in the organic phase the maximum is shifted towards a lower mole fraction.

Therefore, a comparison of the visible spectra are included for each set of experiments at a mole fraction of 0.5 (see figure 8.16) and 0.3 (see figure 8.17).

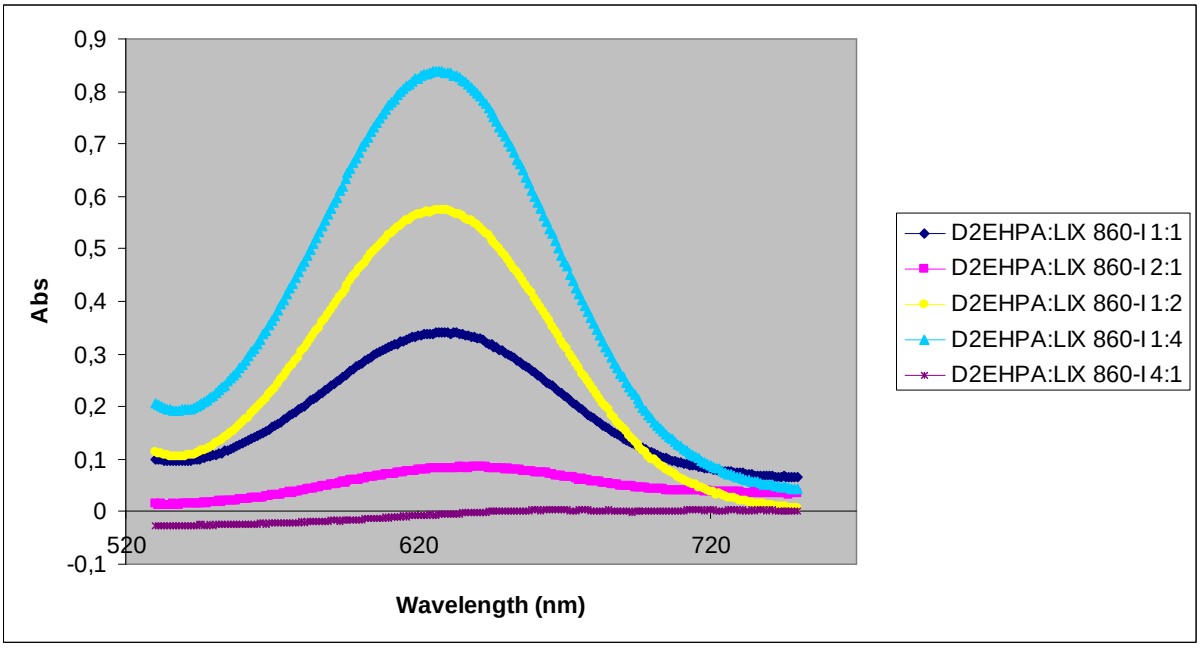

Figure 8.16 – Comparison of the visible spectra for a mole fraction of 0.5.

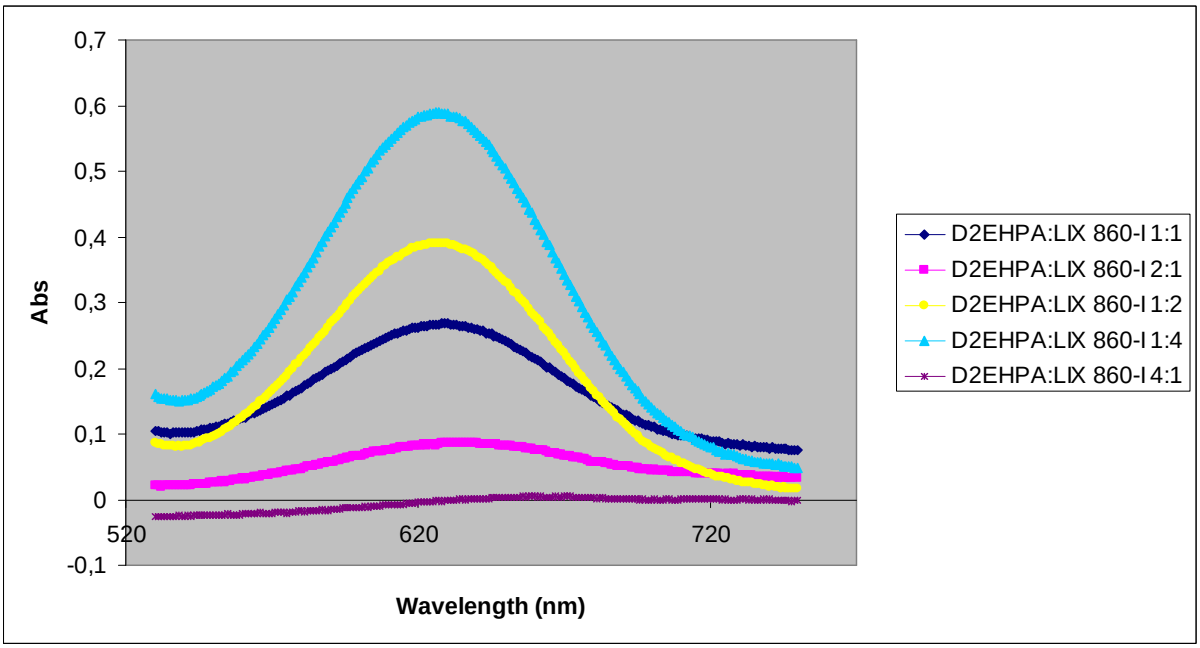

Figure 8.17 – Comparison of the visible spectra for a mole fraction of 0.3.

In the case of the D_2EHPA:LIX 860-I ratio of 4:1, no Job's method plot could be made because of too low absorbances. No real difference in maximum can be observed.

8.1.8. Conclusion

Different experimental set-ups have been undertaken with Job's method to achieve more information concerning the complexation of nickel (II) with a mixture of the extractants D_2EHPA and LIX 860-I.

Different extractant ratios were tested. The total concentration of metal and ligands were however kept constant at 0.05 M.

The experiment with a D_2EHPA:LIX 860-I ratio of 1:4 showed higher extraction percentages, especially for the lower mole fractions of metal ion compared to the other procedures.

For the experiment with a D_2EHPA:LIX 860-I ratio of 4:1, the absorbance of the organic phase were too low in order to draw any relevant conclusion. A ligand:metal ratio of 2:1 seems however more plausible.

The plots of the absorbances versus the mole fraction generally indicate a similar maximum around 0.5 or 0.36.

8.2. Job's method

The preliminary experiments all indicated a similar maximum. However, a similar ratio between the two extractants was used within one set of experiments.

In accordance to M. Bryce et al. [17], a new experimental set-up was started with a much higher variety in molar ratios in order to define the most important regions of complex formation. [17]

8.2.1. Buffered system

A total set of 54 shaking experiments were made with different concentrations of D_2EHPA, LIX 860-I and nickel (II). The total concentration was constant (0.05 M), as was also the case for the preliminary experiments.

The experimental circunstances as well as the results are taken up in Appendix III and IV_a respectively.

In figure 8.18, the absorbance of the organic phases are depicted by means of a colour code (see also legend of figure 8.18), this in function of the different concentrations of LIX 860-I and D_2EHPA.

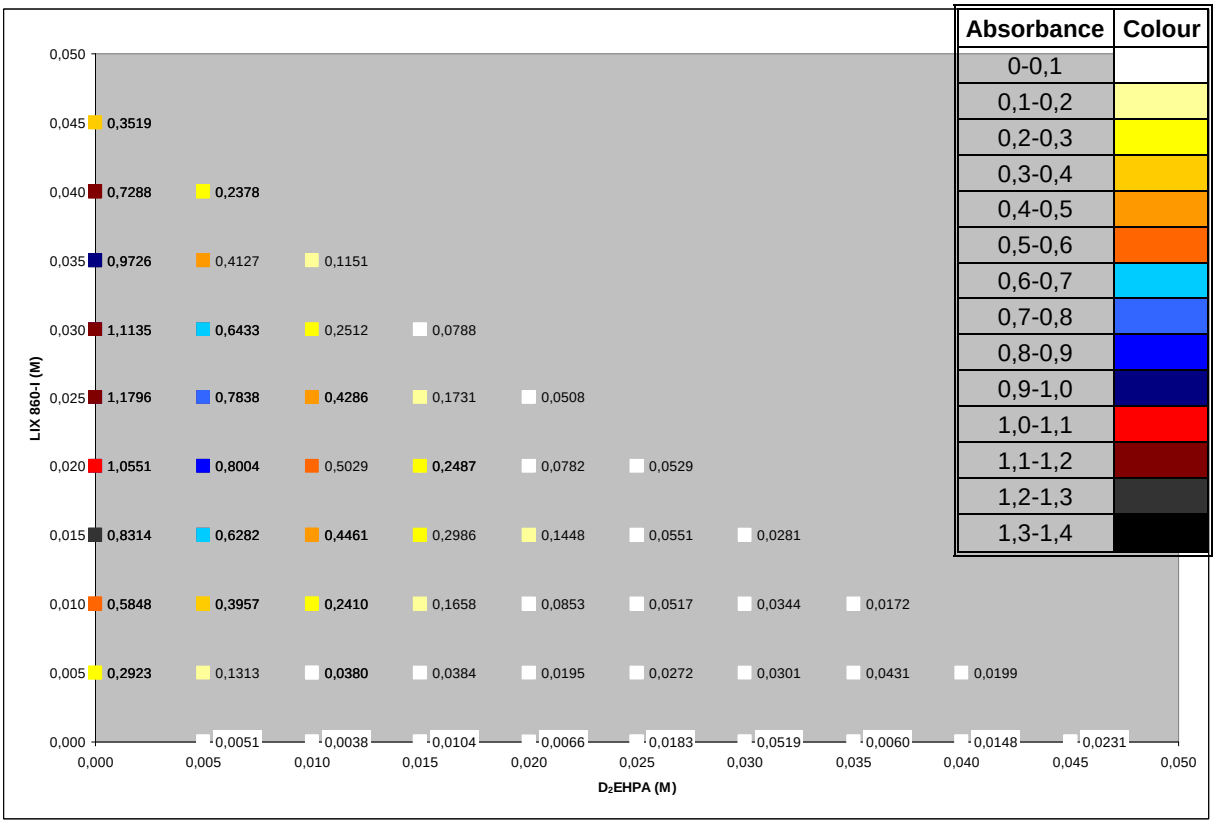

Figure 8.18 – Absorbance of the organic phases as a function of the concentration of D_2EHPA and LIX 860-I for a buffered system.

Figure 8.18 shows that the highest absorbances are situated in the region of LIX 860-I 0.015-0.040 M and for low D_2EHPA concentrations.

In figure 8.19, the results are displayed in function of the mole fraction of metal ion, for several sets of experiments which can be distinguished within the complete experimental set-up.

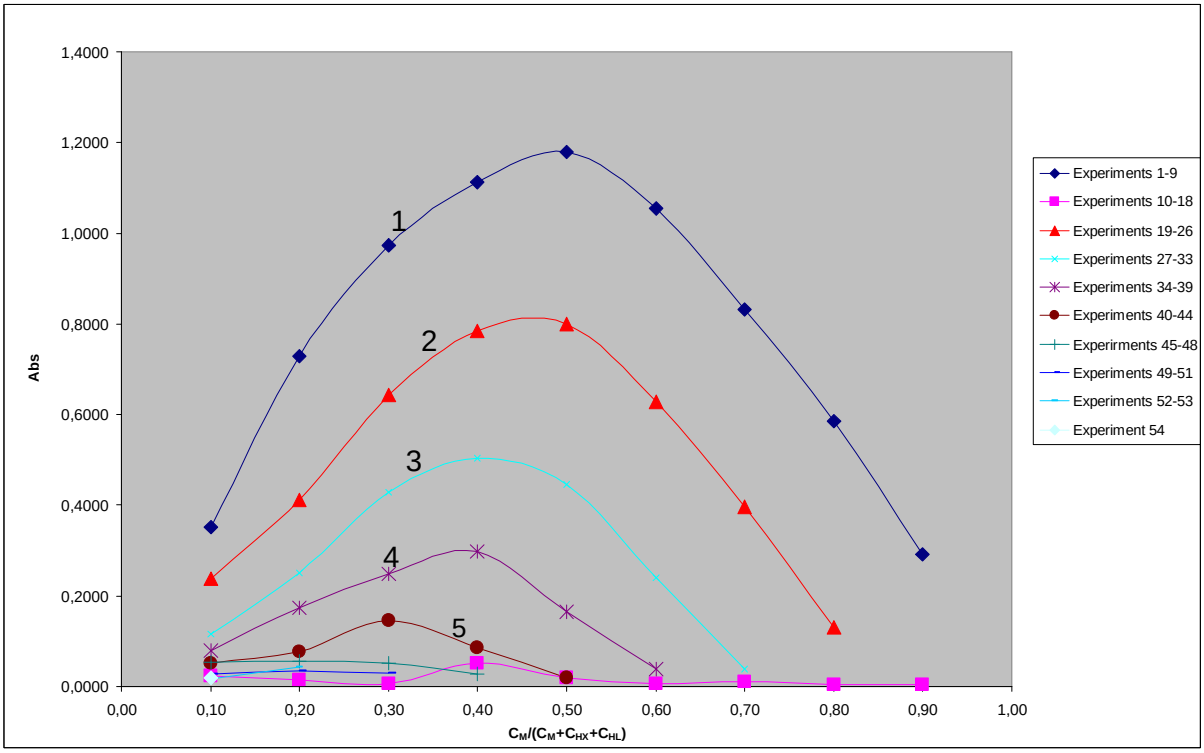

Figure 8.19 – Absorbance of the organic phases as a function of the mole fraction of metal ion for a buffered system.

The experiments 1 till 9 display the results with LIX 860-I alone as extractant, the experiments 10 till 18 represent the results of only D_2EHPA. As can be seen from figure 8.19, low absorbances are obtained with D_2EHPA.

Third order equations were drawn trough the experimental data obtained.

The following equations were obtained:

1 – (Experiment 1-9) $y = 2.1337x^3 - 8.3579x^2 + 6.3373x - 0.2121$ (8.1)

2 – (Experiment 19-26) $y = -1.528x^3 - 2.9034x^2 + 3.5084x - 0.1191$ (8.2)

3 – (Experiment 27-33) $y = -2.3444x^3 - 1.7924x^2 + 2.6411x - 0.1461$ (8.3)

4 – (Experiment 34-39) $y = -3{,}2444x^3 - 0.0613x^2 + 1.3495x - 0{,}0573$ (8.4)

5 – (Experiment 40-44) $y = -3.7806x^3 + 1.1713x^2 + 0.3909x - 0.0003$ (8.5)

In table 8.7, the calculated maxima are represented as well as the corresponding absorbances. For the experiments 10 till 18 and 45 till 54, no equation could be calculated because of the lower amount of experiments under the same conditions and/or lower absorbances obtained.

Table 8.7 – Calculated maxima.

	Equation 8.1	Equation 8.2	Equation 8.3	Equation 8.4	Equation 8.5
Experiment	1-9	19-26	27-33	34-39	40-44
Abs	1.142	0.765	0.474	0,269	0.121
$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$	0.46	0.45	0.41	0.37	0.32

Figure 8.19 and table 8.7 show that the mole fraction of metal ion is shifted towards lower values when higher concentrations of D_2EHPA are present. A shift is observed from approximately 0.50 till 0.30/0.33 which indicate the formation of different complexes.

In figure 8.20, the percentage extractions (in colour code, see legend of figure 8.20) are depicted in function of the concentration of D_2EHPA and LIX 860-I.

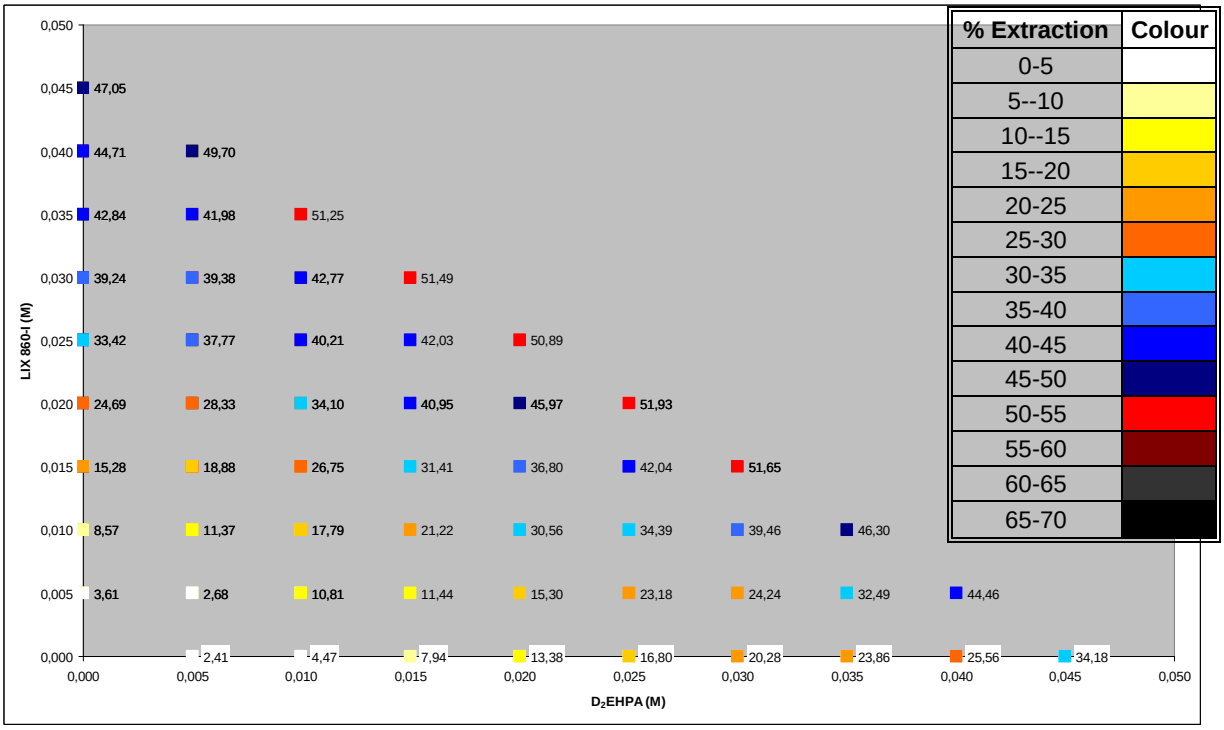

Figure 8.20 – % Extraction as a function of the concentration of D_2EHPA and LIX 860-I for a buffered system.

In figure 8.21, the % extractions are displayed in function of the mole fraction of the metal ion.

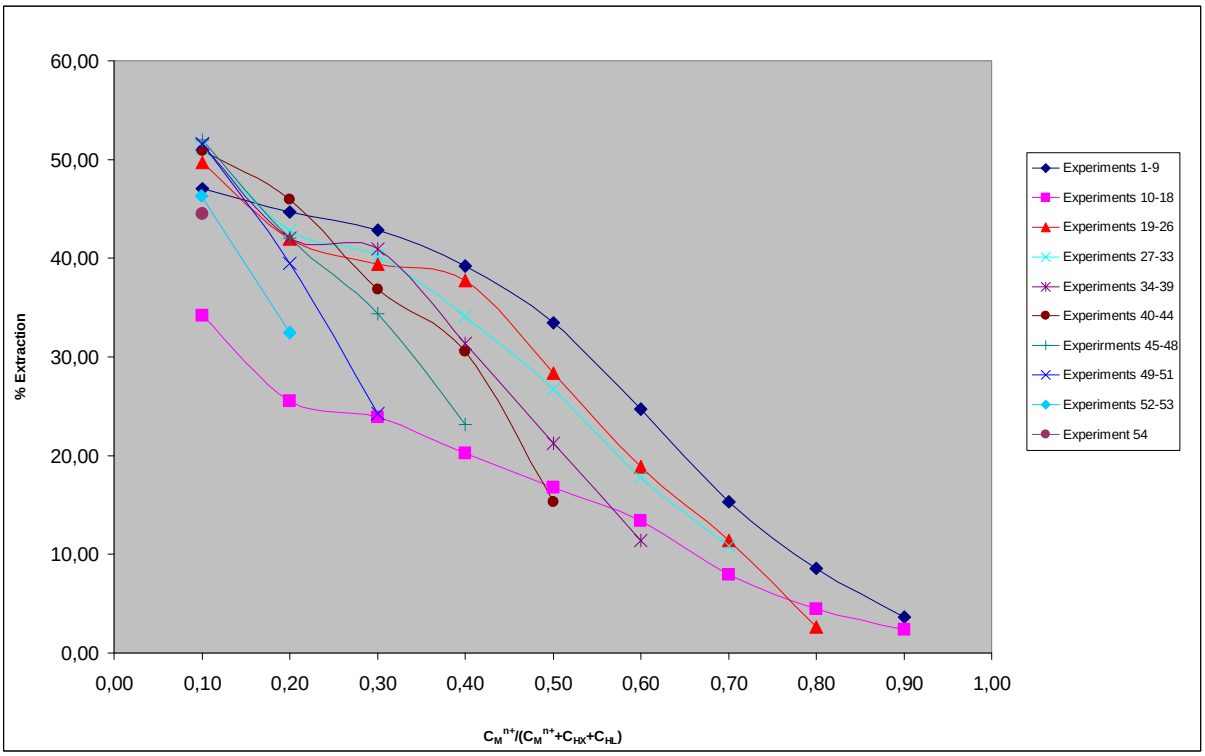

Figure 8.21 – % Extraction as a function of the mole fraction of metal ion for a buffered system.

This figure shows that with D_2EPHA alone as extractant, lower percentage extractions are being obtained.

As was also the case for the preliminary experiments, the concentration of Ni (II) can be calculated through mass balance. These results are displayed in figure 8.22.

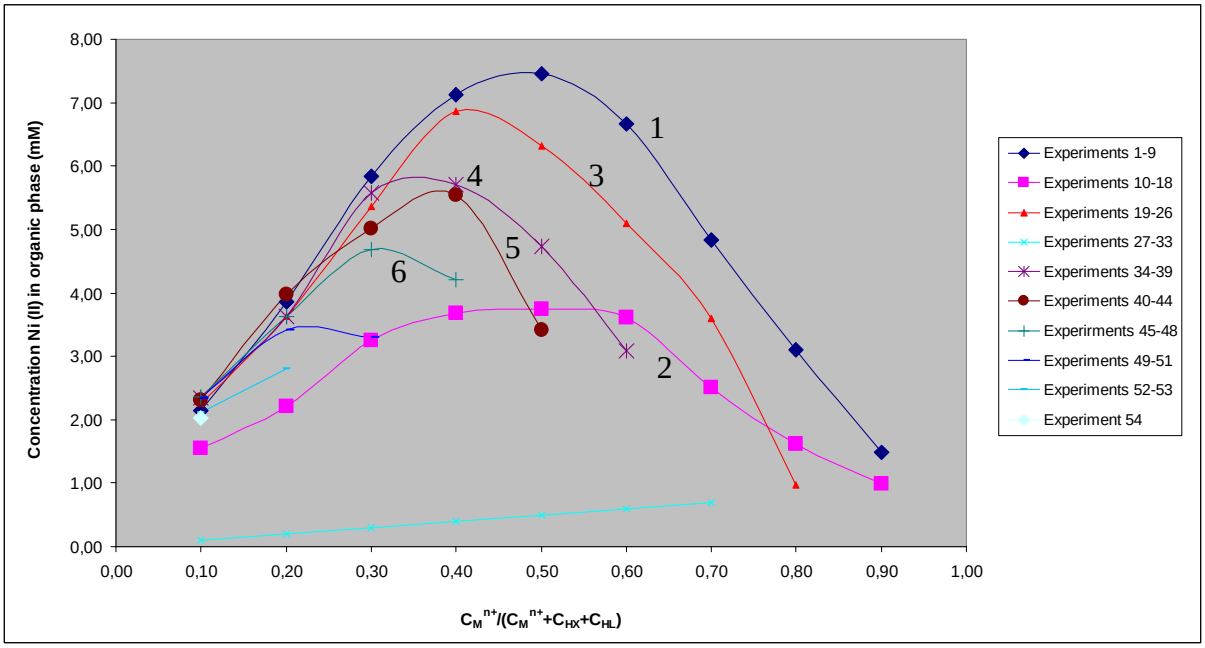

Figure 8.22 – Concentration of Ni (II) in the organic phase as a function of the mole fraction of metal ion for a buffered system.

Also third order equations can be determined.

The following equations were obtained:

1 – (Experiment 1-9) $y = 11.262x^3 - 51.364x^2 + 40.355x - 1.7257$ (8.6)

2 – (Experiment 10-18) $y = 5.5194x^3 - 24.175x^2 + 18.452x - 0.2389$ (8.7)

3 – (Experiment 19-26) $y = -13.515x^3 - 21.876x^2 + 27.892x - 0.5234$ (8.8)

4 – (Experiment 34-39) $y = -41.603x^3 - 3.3505x^2 + 21.775x + 0.1229$ (8.9)

5 – (Experiment 40-44) $y = -170{,}81x^3 + 96.009x^2 - 1.9036x + 1.7486$ (8.10)

6 – (Experiment 45-48) $y = -216.85x^3 + 118.99x^2 - 7.803x + 2.1696$ (8.11)

In table 8.8, the calculated maxima are represented as well as the corresponding absorbances. For the experiments 27 till 33, no equation could be calculated because of the low % extractions obtained.

Table 8.8 – Calculated maxima.

	Equation 8.6	Equation 8.7	Equation 8.8	Equation 8.9	Equation 8.10	Equation 8.11
Experiment	1-9	10-18	19-26	34-39	40-44	45-48
Concentration of Ni (II) in the organic phase (mM)	7.06	3.67	6.37	5.63	5.39	4.76
$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$	0.46	0.45	0.45	0.40	0.36	0.33

For the mixed extractant systems, different maxima are being observed with a trend towards a maximum at a lower mole fraction of metal ion. This shift was also found in the plot of the absorbances of the organic phases in function of the mole fraction of metal ion.

Therefore, a comparison of the visible spectra are included for each set of experiments at a mole fraction of 0.5 (see figure 8.23) and 0.3 (see figure 8.24) respectively.

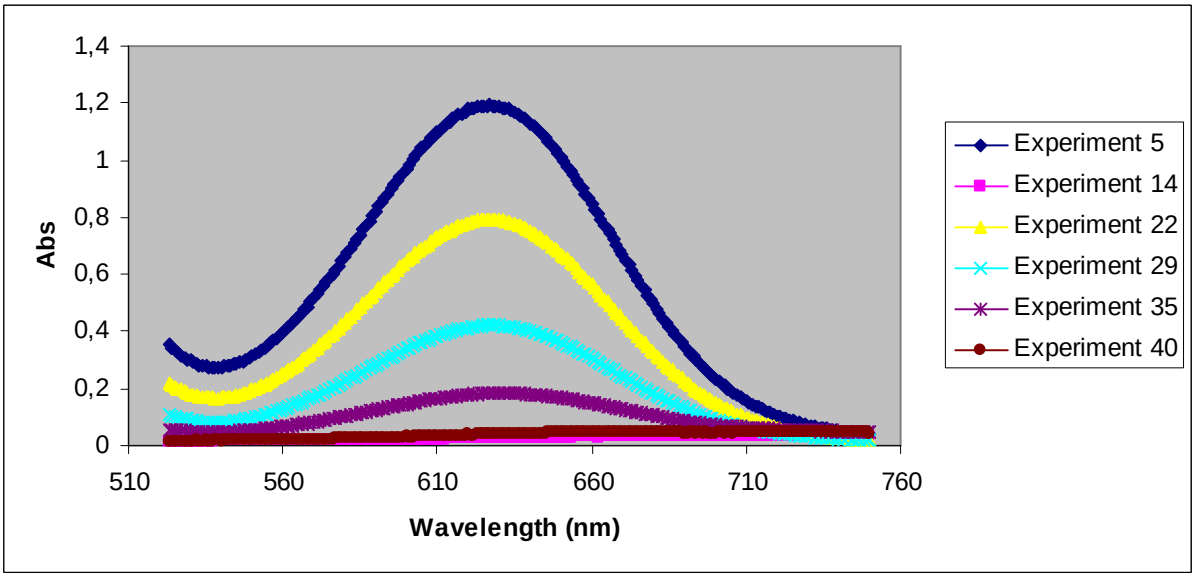

Figure 8.23 – Comparison of the visible spectra for a mole fraction of 0.5.

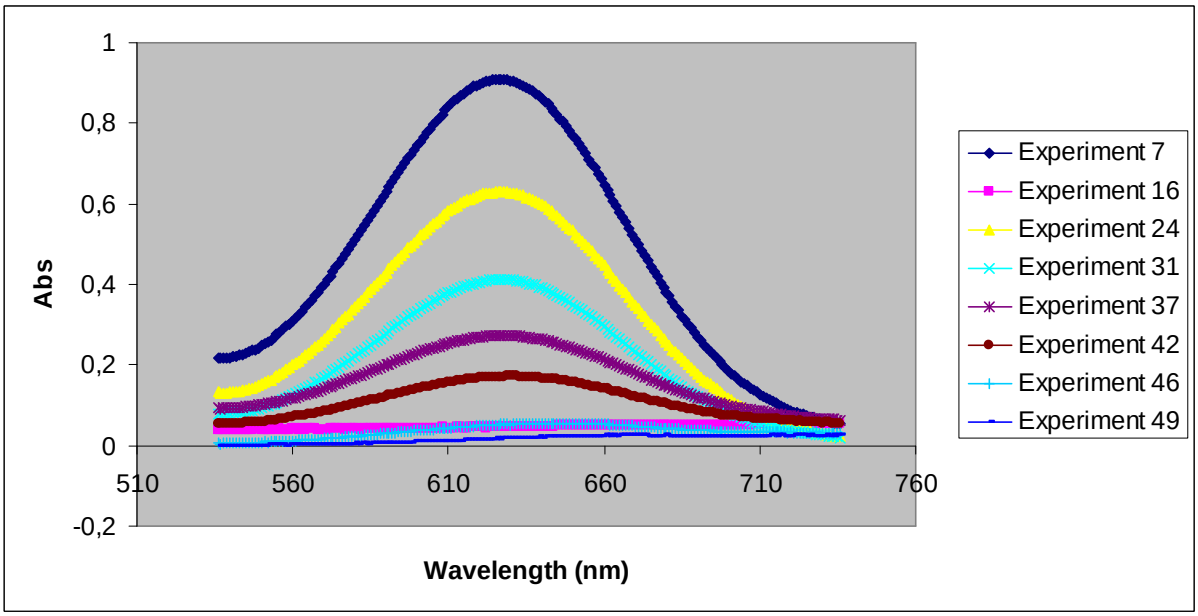

Figure 8.24 – Comparison of the visible spectra for a mole fraction of 0.3.

As can be seen from figures 8.23 and 8.24, lower absorbances are obtained when you have a higher ratio of D_2EHPA. No difference in maximum wavelength was found between a mole fraction of metal ion of 0.5 and 0.3.

8.2.2. Not buffered system

A new set of experiments was performed wih a not buffered system in order to have a better view on the synergism.

The same experimental procedure was used as during the experiments with buffer (see Appendix III[4]). More information concerning the results obtained can be found in appendix IV_b.

The absorbances were however too low to withdraw any relevant conclusion. Also too much fluctuations were found on the extraction percentages.

No trend could be found in the results.

[4] In this experitmental procedure 25.00ml of aqueous phase and 25.00ml of organic phase were used instead of 50.00ml.

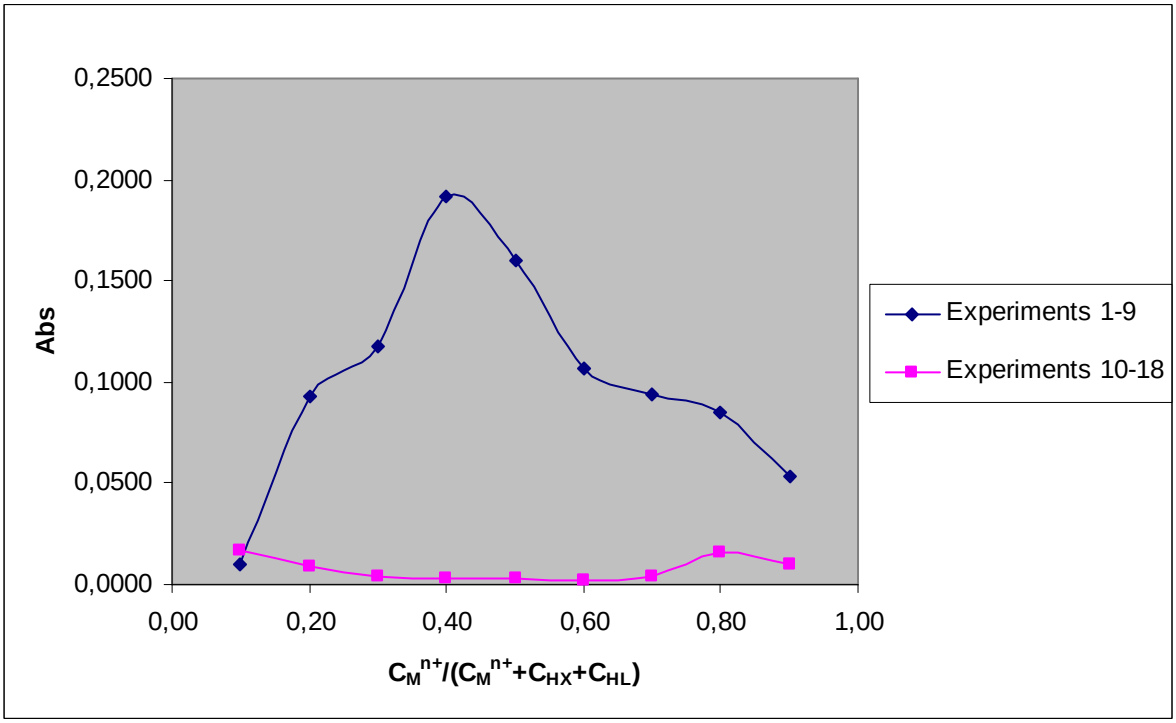

Figure 8.25 – Absorbance of the organic phases as a function of the mole fraction of metal ion for a not buffered system.

For obtaining better results, higher concentration should be used.

8.3. Mole-ratio method

A second spectrophotometric method, the mole-ratio method was tested in a buffered system.

For the experimental set-up and results is referred to Appendix V and VI, respectively.

Now, the concentration of metal ion was kept constant at a value of 0.010 M.

In figure 8.26, the absorbance of the organic phase is plotted in function of the total concentration of ligand.

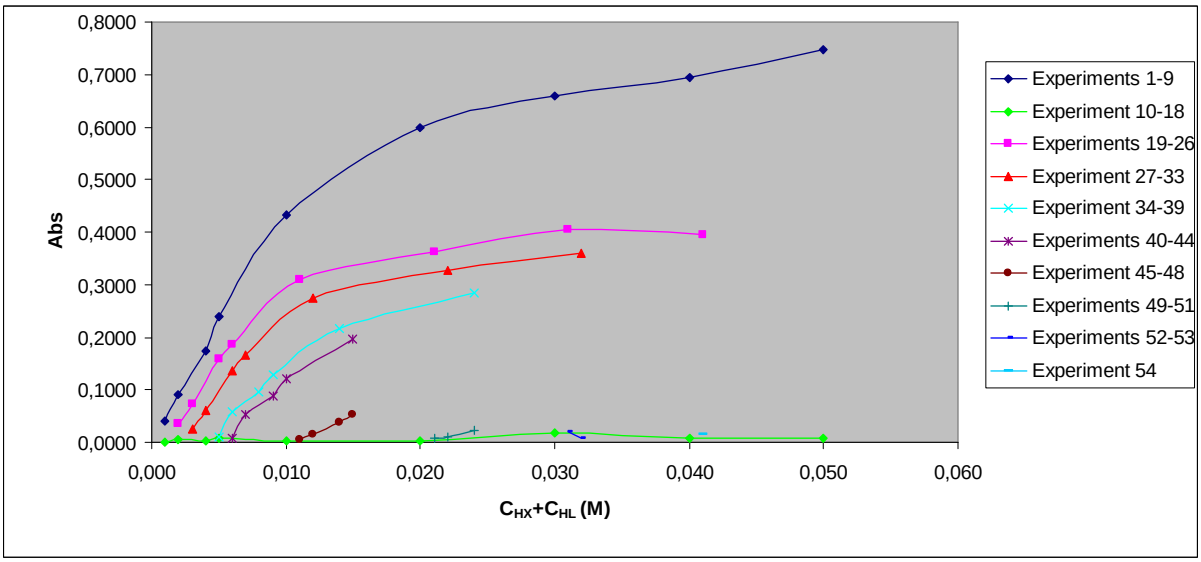

Figure 8.26 – Absorbance of the organic phases as a function of the total concentration of ligand.

For each set experiments, the tangent lines can be drawn in order to determine the point of intersection. An example is shown in figure 8.27.

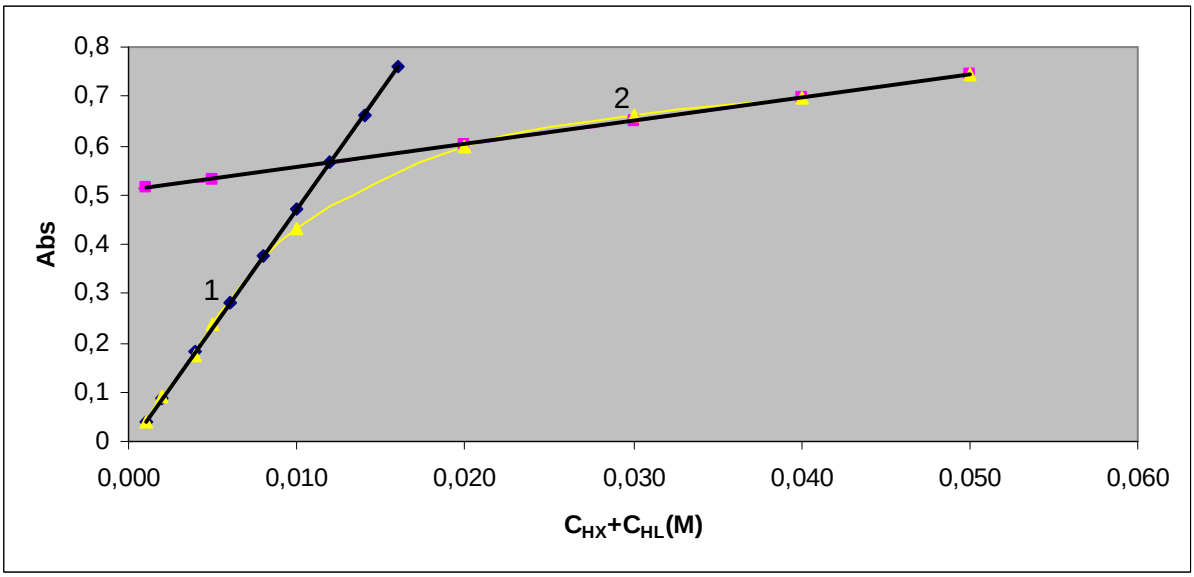

Figure 8.27 – Tangent lines marked on the absorbance versus total concentration of ligand plot for the experiment 1-9.

The following equations were obtained for the different set of experiments:

(Experiment 1-9) 1- $y = 47.91x - 0.0076$ (8.12)

2- $y = 4.7663x + 0{,}5802$ (8.13)

(Experiment 19-26) 1- $y = 41.507x - 0.0495$ (8.14)

2- $y = 3.1167x + 0{,}2592$ (8.15)

(Experiment 27-33) 1- $y = 35.277x - 0.0791$ (8.16)

2- $y = 4.2667x + 0{,}2738$ (8.17)

(Experiment 34-39) 1- $y = 29.367x - 0.1368$ (8.18)

2- $y = 6.9933x + 0{,}1176$ (8.19)

In table 8.9, the calculated points are represented as well as the corresponding absorbances. For the experiments 40 till 54, no equation could be calculated because the points for construction of the chart aren't sufficient. For the experiment with only D_2EHPA, the absorbance values were too low.

Table 8.9 – Calculated interception point.

Experiment	1-9	19-26	27-33	34-39
Absorbance	0.565	0.311	0.292	0.197
C_{HX}+ C_{HL} (M)	0.011	0.0087	0.011	0.011

Table 8.9 shows that the interception point of the tangent lines is found around a total concentration of ligand of 0.011 M. Only the result of experiment 19 till 26 deviate a little bit from this behaviour.

In figure 8.28, the concentration of Ni (II) in the organic phase is shown in function of the total concentration of ligand.

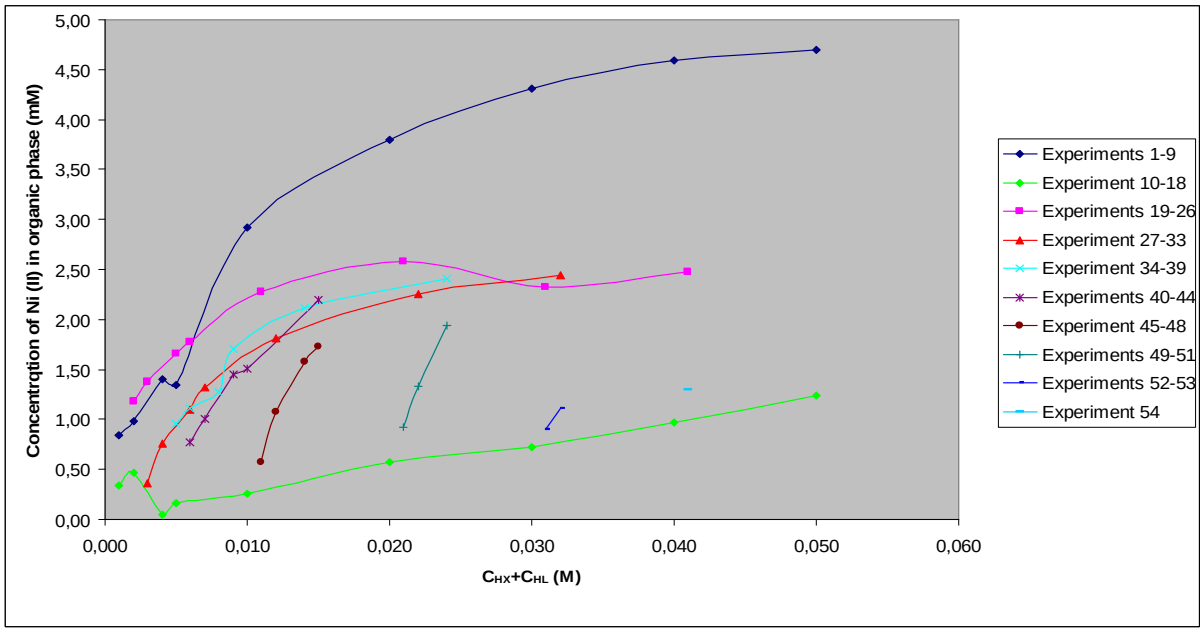

Figure 8.28 – Concentration of Ni (II) in the organic phase as a function of the total concentration of ligand.

Highest extraction percentages were found with LIX 860-I as extractant.

The following equations were calculated fot he tangent lines. the interception point were obtained:

(Experiment 1-9) 1- $y = 235.98x + 0.5318$ (8.20)

2- $y = 51.729x + 2.756$ (8.21)

(Experiment 19-26) 1- $y = 134.22x + 0.9773$ (8.22)

2- $y = 30.261x + 1.9449$ (8.23)

(Experiment 27-33) 1- $y = 184.75x + 0.0143$ (8.24)

2- $y = 18.947x + 1.833$ (8.25)

(Experiment 34-39) 1- $y = 190.65x - 0.012$ (8.26)

2- $y = 29.579x + 1.6953$ (8.27)

In table 8.10, the calculated interception points are represented as well as the corresponding concentration of Ni(II) in the organic phase. For the experiments 40 till 54, no equation could be calculated because the points for construction of the chart aren't sufficient. With D_2EHPA alone as extractant, the % extraction was too low.

Table 8.10 – Calculated interception point.

Experiment	1-9	19-26	27-33	34-39
Concentration of Ni (II) in the organic phase (mM)	3.38	2.23	2.04	2.01
C_{HX}+ C_{HL} (M)	0.012	0.0093	0.011	0.011

Table 8.10 shows that the interception point of the tangent lines is around the total concentration of ligand of 0.011 M. The same conclusion could also be drawn the absorbance plot.

9. Conclusion

The aim this project was to investigate the extraction behaviour of a mixed extractant system of LIX 860-I and D_2EHPA by means of two spectrophotometric methods, namely Job's method and Mole-ratio method.

Different preliminary experimental set-ups have been undertaken to achieve more information concerning the complexation of nickel (II) with a mixture of the extractants D_2EHPA and LIX 860-I.

Different extractant ratios were tested. While the total concentration of metal and ligands was kept constant at 0.05 M during Job's method.

The plots of the absorbances versus the mole fraction of metal ion all indicated a similar maximum around 0.5. The results based on uptake of metal ion into the organic phase showed however a maximum at a lower mole fraction of metal ion, around 0.36.

The experiment with a D_2EHPA:LIX 860-I ratio of 1:4 showed the highest extraction percentages, especially for the lower mole fractions of metal ion compared to the other procedures.

The experimental procedure was then extended into a bigger experimental design in order to achieve a more varied palet of ratios.

The hisghest absorbance were situated in the region of 0.015-0.040 M of LIX 860-I and a low concentration of D_2EHPA. When the different sets which can be found within the experimental set-up are evaluated according to the method of Job, the maximum of the plot was shifted to a lower mole-fraction of metal ion when higher concentration of D_2EHPA were present in the mixture. A shift was found from 0.50 till 0.30 which could point into the direction of the formation of different complexes.

When a not buffered system was applied, the absorbances were too low to withdraw any relevant conclusion. Also too much fluctuations were found on the extraction percentages.

Secondly, Job's method was compared with a second spectrophotometric method, the Mole-ratio method. Again, an experimental design was made. Now, the concentration of metal was kept constant at 0.010 M.

For the Mole-ratio method, the stoichiometry of the metal complexes can be determined from the intersection point of the tangent lines of the plot of the absorbance versus the concentration of ligand.

In all cases, the maximum was obtained around a total concentration of 0.010 M.

When D_2EHPA alone was applied, very low absorbances were achieved. Therefore, a suggestion of future work could be to repeat the experiment design at higher concentration of extractant.

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Appendix I – Technical bulletin of chemicals

Appendix I_a – 5-dodecylsalicylaldoxime

LIX 860-I, a solvent extraction reagent, consists of 5-dodecylsalicylaldoxime diluted with Kerosene. It is a very strong copper extractant requiring about 225g/l H_2SO_4 for stripping.

Suggested Uses

LIX 860-I can be blended with LIX 84 over a broad range to give copper extraction reagents of variable extractive strength. It extracts copper according to the equation below:

$$2RH_{org} + Cu^{2+}_{aq} \leftrightarrow R_2Cu_{org} + 2H^{+}_{aq}$$

LIX 860-I can also extract zinc from ammoniacal solutions.

Typical Properties

A. Physical Properties

Extractant Appearance	Fluid Amber Liquid
Specific Gravity (25º/25ºC)	0.91 – 0.93 g/ml
Flash Point[5]	Greater than 170ºF
Copper Complex Solubility	>30 g/l Cu at 25ºC

B. Performance Specifications[6]:

Maximum Copper Loading	5.4 to 5.8 g/l Cu
Extraction Isotherm Point	≥ 4.80 g/l Cu
Extraction Kinetics	≥ 95% (30 seconds)
Extraction Cu/Fe Selectivity	≥ 2500
Extraction Phase Separation	≤ 70 seconds
Strip Isotherm Point	≤ 2.90 g/l Cu
Strip Kinetics	≥ 95% (30 seconds)
Strip phase Separation	≤ 80 seconds

[5] The flash point is determined by Setaflash closed cup.
[6] The performance parameters were determined using the Standard Cognis Quality Control

Appendix I_b- Bis(2-ethylhexyl) phosporic acid

Product information			
Synonyms	HDEHP, Phosphoric acid bis (2-ethylhexyl) ester, Bis(2-ethylhexyl) phosphoric acid		
Formula	$C_{16}H_{35}O_4P$		
Categories of danger	harmful, corrosive		
Hazard Symbol	 C		
HS Code	2919 90 00	EC number	206-056-4
Molar mass	322.43 g/mol	CAS number	298-07-7
Chemical and physical data			
Ignition temperature	> 300 ℃	**Solubility in water**	1 g/l (20 ℃)
Melting point	-50 ℃	**Assay (acidimetric)**	≥ 95 %
Density	0.97 g/cm^3 (20 ℃)	**pH value**	~3 (< 1 g/l, H_2O)
Boiling point	48 ℃ (16 hPa)	**Vapor pressure**	< 0.1 hPa (20 ℃)
Flash point	150 ℃		
Safety information			
R Phrase	R 21-34 Harmful in contact with skin. Causes burns.		
S Phrase	S 26-36/37/39-45 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).		
RTECS	TB7875000		
Storage class (VCI)	8 A Flammable corrosive materials		
ADR Packing category	A		

WGK	1 (slightly polluting substance)		
Disposal	3 Relatively unreactive organic reagents should be collected in Category A. If halogenated, they should be placed in Category B. For solid residues use Category C.		
Toxicological data			
LD 50 oral	LD 50 oral rat 4940 mg/kg	**LD 50 dermal**	LD 50 dermal rabbit 1250 mg/kg

Appendix I_c – Hexane

General	
Product Name	Hexanes
CAS Number	92112-69-1
ACD Code	MFCD00009520
Molecular Formula	$C_6 H_{14}$
Molecular weight (g/mol)	86.18
Physical	
Density (g/ml)	0.65
Refractive index	1.378-0
Boiling Point (℃)	69
Melting Point (℃)	-95
Flash Point (℃)	-22
Safety	
Hazard	 F: Highly flammable  XN: Harmful  N: Dangerous for the environment
Risk	11: Highly flammable. 38: Irritating to skin. 48/20: Harmful : danger of serious damage to health by prolonged exposure through inhalation. 51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. 62: Possible risk of impaired fertility. 65: Harmful: may cause lung damage if swallowed. 67: Vapours may cause drowsiness and dizziness.
Safety	9: Keep container in a well-ventilated place. 16: Keep away from sources of ignition - No smoking. 29: Do not empty into drains. 33: Take precautionary measures against static discharges. 36/37: Wear suitable protective clothing and gloves. 61: Avoid release to the environment. Refer to special instructions / safety data sheets. 62: If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label.
Categories	Preparation, Purification and Analysis > Solvents

Other	
Parameter	EINECS 295-570-2
	Solubility: Solubility in water: insoluble Solubility in other solvents: soluble in alcohol, acetone, ether and chloroform
	Origin: synthetic
	Reference: Beilstein: 01,142
	Reference: Merck: 14,4694

Product Specifications	
Appearance	clear liquid
Color scale	<10 APHA
Separat. Techn. GC	>98.0 % (sum of isomers)
Free acid (CH3COOH)	<0.002 %
Residue after evaporation	<0.001 %
Sulfur compounds (as S)	<0.005 %
Thiophene	passes test

Appendix I_d – Nickel (II) Chloride Hexahydrate

Product information			
Chemical formula	$NiCl_2 * 6 H_2O$		
Categories of danger	toxic, sensitizing, dangerous for the environment		
Hazard Symbol	 **T**  **N**		
HS Code	2827 35 00	**EC number**	231-743-0
Molar mass	237.70 g/mol	**CAS number**	7791-20-0
Chemical and physical data			
Solubility in water	2540 g/l (20 ℃)	**Melting point**	1001 ℃ (anhydrous substance) decomposes
pH value	~4.9 (100 g/l, H_2O, 20 ℃)	**Density**	1.92 g/cm^3
Safety information			
R Phrase	R 25-43-50/53 Toxic if swallowed. May cause sensitization by skin contact. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.		
S Phrase	S 24-37-45-61 Avoid contact with skin. Wear suitable gloves. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). Avoid release to the environment. Refer to special instructions/Safety data sheets.		
Storage class (VCI)	6.1 B Non-flammable toxic materials		
ADR Packing category	G		
WGK	3 (highly polluting substance)		
Disposal	15 Solutions and solids containing heavy metals: Category E. Stir Raney **nickel** (also: Urushibara **nickel**) in the form of an aqueous suspension into Hydrochloric acid (Item No. 100312) until dissolved (Category E). Neither Raney **nickel** nor filter residues should be allowed to dry out, otherwise they will spontaneously ignite in air.		

Toxicological data	
LD 50 oral	LD 50 oral rat 186 mg/kg
Specifications	
Assay (complexometric)	≥ 98.0 %
pH-value (5 %; water)	3.5 - 5.5
Sulphate (SO_4)	≤ 0.005 %
Ca (Calcium)	≤ 0.005 %
Co (Cobalt)	≤ 0.005 %
Cu (Copper)	≤ 0.001 %
Fe (Iron)	≤ 0.001 %
Na (Sodium)	≤ 0.01 %
Pb (Lead)	≤ 0.002 %
Zn (Zinc)	≤ 0.001 %

Appendix II - Preliminary Experiments

Appendix II_a – Experiment with D_2EHPA:LIX 860-I ratio of 1:1

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=628nm)
1	0.0225	0.0225	0.0050	4.5:4.5:1	0.10	261	137	125	2.12	47.73	3.24	0.0348
2	0.0200	0.0200	0.0100	2:2:1	0.20	506	301	205	3.49	40.46	3.55	0.1003
3	0.0175	0.0175	0.0150	3.5:3.5:3	0.30	785	526	259	4.41	32.96	3.81	0.1944
4	0.0150	0.0150	0.0200	3:3:4	0.40	1067	749	318	5.42	29.81	4.09	0.2929
5	0.0125	0.0125	0.0250	2.5:2.5:5	0.50	1221	971	250	4.26	20.46	4.32	0.2977
6	0.0100	0.0100	0.0300	11:3	0.60	1561	1458	103	1.75	6.58	4.60	0.2764
7	0.0075	0.0075	0.0350	1.5:1.5:7	0.70	1886	1772	113	1.93	6.00	4.80	0.2162
8	0.0050	0.0050	0.0400	1:1:8	0.80	2190	2188	2	0.03	0.07	5.00	0.1488
9	0.0025	0.0025	0.0450	0.5:0.5:9	0.90	2430	2422	8	0.13	0.31	5.28	0.0710

Appendix II_b – Experiment with D_2EHPA:LIX 860-I ratio of 2:1

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=635nm)
1	0.0300	0.0150	0.0050	6:3:1	0.10	261	118	143	2.44	54.88	3.37	0.0348
2	0.0267	0.0133	0.0100	5.33:2.67:2	0.20	506	282	224	3.82	44.26	3.68	0.1003
3	0.0233	0.0117	0.0150	5.67:2.33:3	0.30	754	507	247	4.20	32.73	3.94	0.1944
4	0.0200	0.0100	0.0200	2:1:2	0.40	1013	726	287	4.89	28.32	4.22	0.2929
5	0.0167	0.0083	0.0250	3.33:1.67:5	0.50	1222	1068	153	2.61	12.56	4.51	0.2977
6	0.0133	0.0067	0.0300	2.67:1.33:6	0.60	1504	1316	188	3.20	12.50	4.73	0.2764
7	0.0100	0.0050	0.0350	2:1:7	0.70	1809	1647	162	2.77	8.97	4.92	0.2162
8	0.0067	0.0033	0.0400	1.33:0.67:8	0.80	2101	2044	57	0.97	2.71	5.14	0.1488
9	0.0033	0.0017	0.0450	0.67:0.33:9	0.90	2312	2262	49	0.84	2.12	5.36	0.0710

Appendix II_c – Experiment with D_2EHPA:LIX 860-I ratio of 1:2

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=627nm)
1	0.0150	0.0300	0.0050	3:6:1	0.10	258	131	127	2.16	49.13	3.24	0.0712
2	0.0133	0.0267	0.0100	2.67:5.33:2	0.20	494	305	190	3.23	38.40	3.51	0.1972
3	0.0117	0.0233	0.0150	2.33:5.67:3	0.30	788	505	283	4.83	35.93	3.74	0.3872
4	0.0100	0.0200	0.0200	1:2:1	0.40	1107	762	344	5.87	31.13	3.99	0.5505
5	0.0083	0.0167	0.0250	1.67:3.33:5	0.50	1306	1037	269	4.58	20.60	4.26	0.5913
6	0.0067	0.0133	0.0300	1.33:2.67:6	0.60	1567	1330	237	4.03	15.11	4.53	0.5358
7	0.0050	0.0100	0.0350	1:2:7	0.70	1843	1668	175	2.98	9.49	4.78	0.4133
8	0.0033	0.0067	0.0400	0.67:1.33:8	0.80	2113	2013	101	1.72	4.77	5.00	0.2781
9	0.0017	0.0033	0.0450	0.33:0.67:9	0.90	2349	2253	96	1.64	4.10	5.26	0.1407

Appendix II_d – Experiment with D_2EHPA:LIX 860-I ratio of 1:4

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=627nm)
1	0.0090	0.0360	0.0050	1.8:7.2:1	0.10	245	125	120	2.05	49.06	3.27	0.0986
2	0.0080	0.0320	0.0100	1.6:6.4:2	0.20	578	301	278	4.73	48.03	3.51	0.3302
3	0.0070	0.0280	0.0150	1.4:5.6:3	0.30	808	433	375	6.39	46.42	3.72	0.5510
4	0.0060	0.0240	0.0200	1.2:4.8:4	0.40	1064	670	393	6.70	36.98	4.01	0.8082
5	0.0050	0.0200	0.0250	1:4:5	0.50	1386	942	444	7.56	32.01	4.29	0.8203
6	0.0040	0.0160	0.0300	0.8:3.2:6	0.60	1702	1210	492	8.39	28.93	4.53	0.7086
7	0.0030	0.0120	0.0350	0.6:2.4:7	0.70	1969	1421	549	9.35	27.86	4.77	0.5724
8	0.0020	0.0080	0.0400	0.4:1.6:8	0.80	2235	1775	460	7.83	20.56	5.00	0.3936
9	0.0010	0.0040	0.0450	0.2:0.8:9	0.90	2498	2031	466	7.94	18.67	5.24	0.2030

Appendix II_e – Experiment with D_2EHPA:LIX 860-I ratio of 4:1

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni (II) in organic phase (ppm)	Concentration of Ni in organic phase (mM)	Extraction (%)	pH after shaking
1	0.0360	0.0090	0.0050	7.2:1.8:1	0.10	245	120	126	2.14	51.22	3.24
2	0.0320	0.0080	0.0100	6.4:1.6:2	0.20	587	294	294	5.00	50.00	3.51
3	0.0280	0.0070	0.0150	5.6:1.4:3	0.30	797	514	283	4.83	35.52	3.74
4	0.0240	0.0060	0.0200	4.8:1.2:4	0.40	1066	776	290	4.95	27.24	3.99
5	0.0200	0.0050	0.0250	4:1:5	0.50	1369	1101	268	4.57	19.58	4.26
6	0.0160	0.0040	0.0300	3.2:0.8:6	0.60	1654	1431	223	3.80	13.49	4.53
7	0.0120	0.0030	0.0350	2.4:0.6:7	0.70	1902	1737	165	2.81	8.68	4.78
8	0.0080	0.0020	0.0400	1.6:0.4:8	0.80	2185	2141	45	0.76	2.04	5.00
9	0.0040	0.0010	0.0450	0.8:0.2:9	0.90	2468	2424	44	0.76	1.80	5.26

Appendix III – Experimental Set-up for Job's method

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
1	0.000	0.005	0.045	0:1:9	0.90
2	0.000	0.010	0.040	0:1:4	0.80
3	0.000	0.015	0.035	0:3:7	0.70
4	0.000	0.020	0.030	0:2:3	0.60
5	0.000	0.025	0.025	0:1:1	0.50
6	0.000	0.030	0.020	0:3:2	0.40
7	0.000	0.035	0.015	0:7:3	0.30
8	0.000	0.040	0.010	0:4:1	0.20
9	0.000	0.045	0.005	0:9:1	0.10
10	0.005	0.000	0.045	1:0:9	0.90
11	0.010	0.000	0.040	1:0:4	0.80
12	0.015	0.000	0.035	3:0:7	0.70
13	0.020	0.000	0.030	2:0:3	0.60
14	0.025	0.000	0.025	1:0:1	0.50
15	0.030	0.000	0.020	3:0:2	0.40
16	0.035	0.000	0.015	7:0:3	0.30
17	0.040	0.000	0.010	4:0:1	0.20
18	0.045	0.000	0.005	9:0:1	0.10
19	0.005	0.005	0.040	1:1:8	0.80
20	0.005	0.010	0.035	1:2:7	0.70
21	0.005	0.015	0.030	1:3:6	0.60
22	0.005	0.020	0.025	1:4:5	0.50
23	0.005	0.025	0.020	1:5:4	0.40
24	0.005	0.030	0.015	1:6:3	0.30
25	0.005	0.035	0.010	1:7:2	0.20
26	0.005	0.040	0.005	1:8:1	0.10
27	0.010	0.005	0.035	2:1:7	0.70
28	0.010	0.010	0.030	1:1:3	0.60
29	0.010	0.015	0.025	2:3:5	0.50
30	0.010	0.020	0.020	1:2:2	0.40
31	0.010	0.025	0.015	2:5:2	0.30
32	0.010	0.030	0.010	1:3:1	0.20
33	0.010	0.035	0.005	2:7:1	0.10
34	0.015	0.005	0.030	3:1:6	0.60
35	0.015	0.010	0.025	3:2:5	0.50
36	0.015	0.015	0.020	3:3:4	0.40
37	0.015	0.020	0.015	3:4:3	0.30
38	0.015	0.025	0.010	3:5:2	0.20
39	0.015	0.030	0.005	3:6:1	0.10
40	0.020	0.005	0.025	4:1:5	0.50
41	0.020	0.010	0.020	2:1:2	0.40
42	0.020	0.015	0.015	4:3:3	0.30
43	0.020	0.020	0.010	2:2:1	0.20
44	0.020	0.025	0.005	4:5:1	0.10
45	0.025	0.005	0.020	5:1:4	0.40
46	0.025	0.010	0.015	5:2:3	0.30
47	0.025	0.015	0.010	5:3:2	0.20
48	0.025	0.020	0.005	5:4:1	0.10
49	0.030	0.005	0.015	6:1:3	0.30
50	0.030	0.010	0.010	3:1:1	0.20
51	0.030	0.015	0.005	6:3:1	0.10
52	0.035	0.005	0.010	7:1:2	0.20
53	0.035	0.010	0.005	7:2:1	0.10
54	0.040	0.005	0.005	8:1:1	0.10

Appendix IV – Results of Job's method

Appendix IV$_a$ – Buffered system

Exp	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni (II) in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=627nm)
1	0:1:9	0.90	2409	2322	87	1.48	3.61	5.24	0,2923
2	0:1:4	0.80	2123	1941	182	3.10	8.57	4.98	0,5848
3	0:3:7	0.70	1854	1571	283	4.83	15.28	4.73	0,8314
4	0:2:3	0.60	1583	1192	391	6.66	24.69	4.44	1,0551
5	0:1:1	0.50	1309	872	438	7.46	33.42	4.05	1,1796
6	0:3:2	0.40	1065	647	418	7.12	39.24	3.79	1,1135
7	0:7:3	0.30	799	457	342	5.83	42.84	3.56	0,9726
8	0:4:1	0.20	507	280	227	3.86	44.71	3.49	0,7288
9	0:9:1	0.10	267	141	126	2.14	47.05	3.31	0,3519
10	1:0:9	0.90	2409	2351	58	0.99	2.41	5.24	0,0051
11	1:0:4	0.80	2123	2028	95	1.62	4.47	5.05	0,0038
12	3:0:7	0.70	1854	1707	147	2.51	7.94	4.83	0,0104
13	2:0:3	0.60	1583	1371	212	3.61	13.38	4.72	0,0066
14	1:0:1	0.50	1309	1089	220	3.75	16.80	4.62	0,0183
15	3:0:2	0.40	1065	849	216	3.68	20.28	4.51	0,0519
16	7:0:3	0.30	799	608	191	3.25	23.86	4.43	0,0060
17	4:0:1	0.20	507	378	130	2.21	25.56	4.34	0,0148
18	9:0:1	0.10	267	176	91	1.55	34.18	4.24	0,0231
19	1:1:8	0.80	2123	2066	57	0.97	2.68	5.02	0,1313
20	1:2:7	0.70	1854	1644	211	3.59	11.37	4.78	0,3957
21	1:3:6	0.60	1583	1284	299	5.09	18.88	4.50	0,6282
22	1:4:5	0.50	1309	938	371	6.32	28.33	4.21	0,8004
23	1:5:4	0.40	1065	663	402	6.86	37.77	3.87	0,7838
24	1:6:3	0.30	799	484	315	5.36	39.38	3.65	0,6433
25	1:7:2	0.20	507	294	213	3.63	41.98	3.49	0,4127
26	1:8:1	0.10	267	134	133	2.26	49.70	3.32	0,2378
27	2:1:7	0.70	1854	1654	200	3.41	10.81	4.98	0,0380
28	1:1:3	0.60	1583	1301	282	4.80	17.79	4.73	0,2410
29	2:3:5	0.50	1309	959	350	5.97	26.75	4.39	0,4461
30	1:2:2	0.40	1065	702	363	6.19	34.10	4.02	0,5029
31	2:5:2	0.30	799	478	321	5.47	40.21	3.81	0,4286
32	1:3:1	0.20	507	290	217	3.70	42.77	3.52	0,2512
33	2:7:1	0.10	267	130	137	2.33	51.25	3.24	0,1151
34	3:1:6	0.60	1583	1402	181	3.08	11.44	4.78	0,0384
35	3:2:5	0.50	1309	1032	278	4.73	21.22	4.46	0,1658
36	3:3:4	0.40	1065	731	335	5.70	31.41	4.13	0,2986
37	3:4:3	0.30	799	472	327	5.58	40.95	3.72	0,2487
38	3:5:2	0.20	507	294	213	3.63	42.03	3.50	0,1731
39	3:6:1	0.10	267	130	137	2.34	51.49	3.23	0,0788
40	4:1:5	0.50	1309	1109	200	3.41	15.30	4.65	0,0195
41	2:1:2	0.40	1065	740	326	5.55	30.56	4.22	0,0853
42	4:3:3	0.30	799	505	294	5.01	36.80	3.88	0,1448
43	2:2:1	0.20	507	274	233	3.97	45.97	3.52	0,0782
44	4:5:1	0.10	267	131	136	2.31	50.89	3.27	0,0508
45	5:1:4	0.40	1065	818	247	4.21	23.18	4.56	0,0272
46	5:2:3	0.30	799	524	275	4.68	34.39	4.09	0,0517
47	5:3:2	0.20	507	294	213	3.63	42.04	3.68	0,0551
48	5:4:1	0.10	267	128	139	2.36	51.93	3.24	0,0529
49	6:1:3	0.30	799	605	194	3.30	24.24	4.39	0,0301
50	3:1:1	0.20	507	307	200	3.41	39.46	3.76	0,0344
51	6:3:1	0.10	267	129	138	2.35	51.65	3.29	0,0281
52	7:1:2	0.20	507	342	165	2.81	32.49	4.08	0,0431
53	7:2:1	0.10	267	143	124	2.11	46.30	3.51	0,0172
54	8:1:1	0.10	267	148	119	2.02	44.46	3.73	0,0199

Appendix IV$_b$ – Not-buffered system

Exp	Molar ratio $D_2EHPA:LIX\ 860\text{-}I:M^{n+}$	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni (II) in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=627nm)
1	0:1:9	0.90	2475	2468	7	0.11	0.26	3.13	0.0532
2	0:1:4	0.80	2154	2141	13	0.22	0.61	2.93	0.0854
3	0:3:7	0.70	1848	1817	32	0.54	1.72	2.84	0.0943
4	0:2:3	0.60	1588	1564	24	0.40	1.50	2.81	0.1065
5	0:1:1	0.50	1322	1266	56	0.95	4.23	2.77	0.1605
6	0:3:2	0.40	1130	941	189	3.22	16.72	2.75	0.1135
7	0:7:3	0.30	840	728	112	1.91	13.33	2.84	0.1921
8	0:4:1	0.20	522	504	18	0.30	3.40	2.82	0.1178
9	0:9:1	0.10	260	253	7	0.12	2.63	2.80	0.0925
10	1:0:9	0.90	2475	2443	32	0.54	1.28	4.14	0.0097
11	1:0:4	0.80	2239	2160	79	1.35	3.55	4.00	0.0159
12	3:0:7	0.70	1962	1877	85	1.45	4.34	3.94	0.0040
13	2:0:3	0.60	1760	1582	177	3.02	10.08	3.87	0.0019
14	1:0:1	0.50	1376	1313	63	1.08	4.60	3.81	0.0032
15	3:0:2	0.40	1131	1092	39	0.66	3.44	3.74	0.0026
16	7:0:3	0.30	840	808	32	0.55	3.82	3.65	0.0044
17	4:0:1	0.20	522	520	2	0.03	0.33	3.75	0.0088
18	9:0:1	0.10	260	259	2	0.03	0.64	3.75	0.0164
19	1:1:8	0.80	2239	2200	39	0.67	1.76	3.08	0.0280
20	1:2:7	0.70	1848	1792	57	0.97	3.07	2.89	0.0344
21	1:3:6	0.60	1588	1537	51	0.97	3.19	2.81	0.0644
22	1:4:5	0.50	1322	1247	75	0.86	5.67	2.75	0.0508
23	1:5:4	0.40	1130	957	174	1.28	15.36	2.72	0.0437
24	1:6:3	0.30	809	699	111	2.96	13.67	2.72	0.0490
25	1:7:2	0.20	522	509	13	1.89	2.57	2.75	0.0777
26	1:8:1	0.10	260	248	12	0.21	4.80	2.82	0.0507
27	2:1:7	0.70	1962	1925	37	0.63	1.90	3.01	0.0155
28	1:1:3	0.60	1588	1561	27	0.46	1.69	2.83	0.0221
29	2:3:5	0.50	1322	1288	34	0.57	2.54	2.75	0.0211
30	1:2:2	0.40	1130	1004	127	2.16	11.20	2.68	0.0594
31	2:5:2	0.30	809	682	128	2.18	15.81	2.67	0.0237
32	1:3:1	0.20	514	377	136	2.33	26.55	2.70	0.0360
33	2:7:1	0.10	260	239	22	0.37	8.29	2.77	0.0413
34	3:1:6	0.60	1760	1666	94	1.60	5.34	2.98	0.0106
35	3:2:5	0.50	1376	1360	16	0.28	1.18	2.83	0.0187
36	3:3:4	0.40	1130	989	142	2.41	12.52	2.72	0.0173
37	3:4:3	0.30	809	673	137	2.33	16.86	2.68	0.0177
38	3:5:2	0.20	514	379	135	2.31	26.35	2.65	0.0205
39	3:6:1	0.10	260	229	31	0.54	12.10	2.77	0.0156
40	4:1:5	0.50	1376	1320	56	0.95	4.06	3.02	0.0203
41	2:1:2	0.40	1131	1049	82	1.40	7.28	2.83	0.0164
42	4:3:3	0.30	840	793	47	0.80	5.56	2.75	0.0222
43	2:2:1	0.20	522	502	21	0.35	3.94	2.73	0.0453
44	4:5:1	0.10	260	227	34	0.57	12.90	2.76	0.0507
45	5:1:4	0.40	1131	1041	90	1.53	7.92	2.98	0.0367
46	5:2:3	0.30	840	825	15	0.25	1.75	2.86	0.0224
47	5:3:2	0.20	522	501	21	0.36	4.07	2.80	0.0147
48	5:4:1	0.10	260	230	31	0.52	11.74	2.79	0.0316
49	6:1:3	0.30	840	821	19	0.32	2.23	2.96	0.0207
50	3:1:1	0.20	522	504	18	0.31	3.52	2.83	0.0242
51	6:3:1	0.10	260	243	17	0.29	6.52	2.82	0.0160
52	7:1:2	0.20	522	512	10	0.18	1.98	3.00	0.0131
53	7:2:1	0.10	260	246	14	0.24	5.35	2.93	0.0169
54	8:1:1	0.10	260	236	24	0.42	9.38	3.01	0.0117

Appendix V – Experimental Set-up for Mole-ratio method

Exp	[D_2EHPA] (M)	[LIX 860-I] (M)	[Ni^{2+}] (M)	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}} + C_{HX} + C_{HL}}$
1	0.000	0.001	0.010	0:1:10	0.91
2	0.000	0.002	0.010	0:1:5	0.83
3	0.000	0.004	0.010	0:2:5	0.71
4	0.000	0.005	0.010	0:1:2	0.67
5	0.000	0.010	0.010	0:1:1	0.50
6	0.000	0.020	0.010	0:2:1	0.33
7	0.000	0.030	0.010	0:3:1	0.25
8	0.000	0.040	0.010	0:4:1	0.20
9	0.000	0.050	0.010	0:5:1	0.17
10	0.001	0.000	0.010	1:0:10	0.91
11	0.002	0.000	0.010	1:0:5	0.83
12	0.004	0.000	0.010	2:0:5	0.71
13	0.005	0.000	0.010	1:0:2	0.67
14	0.010	0.000	0.010	1:0:1	0.50
15	0.020	0.000	0.010	2:0:1	0.33
16	0.030	0.000	0.010	3:0:1	0.25
17	0.040	0.000	0.010	4:0:1	0.20
18	0.050	0.000	0.010	5:0:1	0.17
19	0.001	0.001	0.010	1:1:10	0.83
20	0.001	0.002	0.010	1:2:10	0.77
21	0.001	0.004	0.010	1:4:10	0.67
22	0.001	0.005	0.010	1:5:10	0.63
23	0.001	0.010	0.010	0.1:1:1	0.48
24	0.001	0.020	0.010	0.1:2:1	0.32
25	0.001	0.030	0.010	0.1:3:1	0.24
26	0.001	0.040	0.010	0.1:4:1	0.20
27	0.002	0.001	0.010	2:1:10	0.77
28	0.002	0.002	0.010	1:1:5	0.71
29	0.002	0.004	0.010	1:2:5	0.63
30	0.002	0.005	0.010	2:5:10	0.59
31	0.002	0.010	0.010	2:5:5	0.45
32	0.002	0.020	0.010	0.2:2:1	0.31
33	0.002	0.030	0.010	0.2:3:1	0.24
34	0.004	0.001	0.010	4:1:10	0.67
35	0.004	0.002	0.010	2:1:5	0.63
36	0.004	0.004	0.010	2:2:5	0.56
37	0.004	0.005	0.010	4:5:10	0.53
38	0.004	0.010	0.010	2:5:5	0.42
39	0.004	0.020	0.010	0.4:2:1	0.29
40	0.005	0.001	0.010	5:1:10	0.63
41	0.005	0.002	0.010	5:2:10	0.59
42	0.005	0.004	0.010	5:4:10	0.53
43	0.005	0.005	0.010	1:1:2	0.50
44	0.005	0.010	0.010	1:2:2	0.40
45	0.010	0.001	0.010	1:0.1:1	0.48
46	0.010	0.002	0.010	5:1:5	0.45
47	0.010	0.004	0.010	5:2:5	0.42
48	0.010	0.005	0.010	2:1:2	0.40
49	0.020	0.001	0.010	2:0.1:1	0.32
50	0.020	0.002	0.010	2:0.2:1	0.31
51	0.020	0.004	0.010	2:0.4:1	0.29
52	0.030	0.001	0.010	3:0.1:1	0.24
53	0.030	0.002	0.010	3:0.2:1	0.24
54	0.040	0.001	0.010	4:0.1:1	0.20

Appendix VI – Results of Mole-Ratio method

Exp	Molar ratio D_2EHPA:LIX 860-I:M^{n+}	$\frac{C_{M^{n+}}}{C_{M^{n+}}+C_{HX}+C_{HL}}$	Initial concentration of Ni (II) (ppm)	Concentration of Ni (II) after shaking (ppm)	Concentration of Ni (II) in organic phase (ppm)	Concentration of Ni (II) in organic phase (mM)	Extraction (%)	pH after shaking	Abs of organic phase (λ=627nm)
1	0:1:10	0.91	524	475	49	0.84	9.39	4.70	0.0410
2	0:1:5	0.83	524	466	58	0.98	11.00	4.59	0.0904
3	0:2:5	0.71	524	441	82	1.40	15.70	4.37	0.1745
4	0:1:2	0.67	520	441	79	1.34	15.16	4.52	0.2385
5	0:1:1	0.50	520	348	171	2.92	32.97	4.21	0.4320
6	0:2:1	0.33	520	297	223	3.79	42.83	3.80	0.5987
7	0:3:1	0.25	520	267	253	4.31	48.67	3.62	0.6602
8	0:4:1	0.20	520	250	270	4.59	51.90	3.49	0.6951
9	0:5:1	0.17	520	244	275	4.69	53.01	3.39	0.7459
10	1:0:10	0.91	524	504	20	0.34	3.80	4.78	0.0012
11	1:0:5	0.83	524	496	28	0.47	5.28	4.78	0.0042
12	2:0:5	0.71	524	521	3	0.05	0.53	4.75	0.0036
13	1:0:2	0.67	524	514	10	0.17	1.86	4.74	0.0066
14	1:0:1	0.50	524	509	15	0.25	2.83	4.62	0.0028
15	2:0:1	0.33	524	490	34	0.57	6.43	4.46	0.0013
16	3:0:1	0.25	524	481	43	0.73	8.18	4.32	0.0180
17	4:0:1	0.20	524	467	57	0.97	10.84	4.24	0.0088
18	5:0:1	0.17	524	451	73	1.24	13.90	4.14	0.0068
19	1:1:10	0.83	524	455	69	1.17	13.17	4.66	0.0350
20	1:2:10	0.77	524	443	81	1.38	15.41	4.55	0.0728
21	1:4:10	0.67	524	426	98	1..66	18.63	4.33	0.1588
22	1:5:10	0.63	524	420	104	1.77	19.87	4.26	0.1863
23	0.1:1:1	0.48	524	390	134	2.28	25.53	3.87	0.3083
24	0.1:2:1	0.32	524	372	151	2.58	28.92	3.49	0.3634
25	0.1:3:1	0.24	524	387	136	2.32	26.02	3.23	0.4060
26	0.1:4:1	0.20	524	378	145	2.48	27.76	3.26	0.3949
27	2:1:10	0.77	524	502	21	0.36	4.07	4.63	0.0263
28	1:1:5	0.71	524	479	45	0.76	8.53	4.51	0.0616
29	1:2:5	0.63	524	459	64	1.10	12.31	4.30	0.1352
30	2:5:10	0.59	524	446	78	1.32	14.83	4.23	0.1658
31	2:5:5	0.45	524	417	106	1.81	20.31	3.90	0.2731
32	0.2:2:1	0.31	524	392	132	2.25	25.21	3.49	0.3277
33	0.2:3:1	0.24	524	381	143	2.44	27.34	3.35	0.3589
34	4:1:10	0.67	524	467	56	0.96	10.75	4.56	0.0100
35	2:1:5	0.63	524	459	65	1.11	12.41	4.46	0.0582
36	2:2:5	0.56	524	449	75	1.27	14.28	4.23	0.0960
37	4:5:10	0.53	524	423	100	1.71	19.16	4.15	0.1275
38	2:5:5	0.42	524	400	124	2.11	23.64	3.84	0.2155
39	0.4:2:1	0.29	524	383	141	2.41	26.96	3.49	0.2854
40	5:1:10	0.63	524	479	45	0.77	8.60	4.57	0.0068
41	5:2:10	0.59	524	465	59	1.00	11.24	4.44	0.0526
42	5:4:10	0.53	524	439	85	1.45	16.21	4.20	0.0874
43	1:1:2	0.50	524	435	89	1.51	16.93	4.10	0.1204
44	1:2:2	0.40	524	395	129	2.19	24.56	3.89	0.1954
45	1:0.1:1	0.48	524	490	34	0.57	6.44	4.55	0.0061
46	5:1:5	0.45	524	460	63	1.08	12.10	4.43	0.0145
47	5:2:5	0.42	524	431	93	1.58	17.70	4.15	0.0388
48	2:1:2	0.40	524	422	102	1.73	19.41	4.08	0.0539
49	2:0.1:1	0.32	524	469	54	0.93	10.37	4.45	0.0088
50	2:0.2:1	0.31	524	446	78	1.33	14.91	4.28	0.0110
51	2:0.4:1	0.29	524	410	114	1.94	21.69	3.98	0.0232
52	3:0.1:1	0.24	524	471	53	0.90	10.07	4.33	0.0205
53	3:0.2:1	0.24	524	458	65	1.11	12.45	4.20	0.0077
54	4:0.1:1	0.20	524	448	76	1.30	14.54	4.21	0.0161