Master in Chemical Engineering

Environmental Protection Technologies

Metal deposition using Ionic Liquids
(Deposição de metais usando Liquidos Iónicos)

Departement of Chemical Engineering

Thesis performed by: Carlos Mota

Promoter: Prof. Dr. Edward Matthijs

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Dedicated to the memory of my grandfather

(Dedicado á memória do meu avô)

António Barroso da Mota

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Abstract

There is an interest to create zinc/tin alloys to replace cadmium as a corrosion protective coating material. Existing aqueous electroplating systems for these alloys are commercially available but have several limitations. Dangerous and highly toxic complexing agents are uses e.g. cyanides. To overcome these problems, ionic liquids could provide a solution to obtain an alloy containing 20 to 30% of zinc. Ionic liquids (IL's) often have wider electrochemical windows which allow the deposition of e.g. refractive metals that can not be deposited from aqueous solutions. In IL's it is often not necessary to add complexing agents. The Zn/Sn alloy deposition from IL's is therefore a promising application for the plating industry. Nevertheless, there are some issues with this alternative for aqueous systems. The degradation of the organic components, the control of the concentration of two metals and the risk of a two phase deposition instead of an alloy had to be overcome first.

It is the main purpose of this thesis to obtain a Zn/Sn alloy with 20% zinc using IL's as an electrolyte. First a separate study was performed on both the zinc and the tin deposition. Afterwards, an attempt to deposit a Zn/Sn alloy was made. An introduction to a study about the electrodeposition of refractive metals concludes this work. It initiated the research for oxygen-free IL's to deposit molybdenum or tungsten.

Several parameters (temperature, metal source and concentration, organic complexing agents,…) were optimized for both the zinc, tin and zinc/tin deposition. Experiments were performed both in a parallel plate cell and a Hull cell, so as to investigate the effect of current density as well. Ethaline200 was selected as electrolyte. As substrate, brass and iron were selected, while as anode a plate of the metal to deposit was chosen, tin for the alloy. The best efficiencies were always obtained on brass; however the iron substrate resulted in the best depositions. A concentration of 0.27M $ZnCl_2$, 0.07M $SnCl_2$ with 0.015M of K_3-HEDTA as complexant resulted in a deposition containing the desired alloy with the amount of 20% zinc and 80% tin with good appearance.

Refractory metals as molybdenum and tungsten cannot be electrodeposited from aqueous solutions without forming a co-deposition with Ni, Co or Fe. Here, IL's could again provide a solution. A first requirement is the dissolution of a metal source. MoO_3 could be suitable, however there are doubts about using oxides. Oxygen-free IL's were sought for. A first attempt was the combination of $ZnCl_2$ with chlormequat (CCC), which gave liquids below 150℃ in molar ratios of 2 : 1 and 3 : 1. Unfortunately, MoO_3 didn't dissolve in these IL's. Another route to design oxygen-free IL's was the synthesis of quaternary ammonium salts. None of the methods used, proved viable as reaction time was long and resulted in very low

yields. Therefore, no sufficient quantities were obtained to perform the possible electrochemical behavior of refractive metals.

Keywords: Ionic liquids, electrodeposition, zinc/tin alloys, refractory metals.

Resumo

Existe um interesse em criar ligas de zinco estanho para substituir o cádmio como um material de revestimento protector à corrosão. Existem sistemas aquosos de electrodeposição para estas ligas que estão disponíveis comercialmente, no entanto estes possuem algumas limitações. Agentes complexantes perigosos e altamente tóxicos são usados, como por exemplo cianetos. Para ultrapassar estes problemas, os líquidos iónicos (IL'S) podem fornecer uma solução para obter uma liga que contém 20-30% de zinco. Os líquidos iónicos (IL's) têm na sua maioria, uma ampla janela electroquímica que permite a deposição, por exemplo, de metais refractários que não podem ser depositados a partir de soluções aquosas. Com sistemas baseados em IL's muitas vezes não é necessário adicionar agentes complexantes. A deposição de ligas de Zn/Sn a partir de líquidos iónicos é, portanto, uma aplicação promissora para a indústria de electrodeposição. No entanto, existem alguns problemas com esta alternativa para os sistemas aquosos. A degradação dos componentes orgânicos, o controlo da concentração dos dois metais no electrólito e o risco de uma deposição com duas fases em vez de uma liga, tiveram de ser superados antes.

É o objectivo principal desta tese obter uma liga de Zn/Sn com 20% de zinco usando IL's com electrólito. Primeiramente, foi realizado o estudo da electrodeposição de zinco e estanho separadamente. Posteriormente, foi feita uma tentativa para depositar uma liga de Zn/Sn. Como parte final deste trabalho foi feita uma introdução ao estudo sobre a electrodeposição de metais refractários em que foi iniciada a investigação de IL's livres de oxigénio para depositar molibdénio ou tungsténio.

Vários parâmetros (temperatura, fonte de metais e concentração, agentes orgânicos complexantes, etc.) foram optimizados para o estudo da electrodeposição de zinco, estanho e ligas de zinco e estanho. As experiencias foram realizadas tanto numa célula electrolítica paralela como numa célula de denominada de Hull, a fim de ser também investigado o efeito da densidade de corrente. O Ethaline200 foi seleccionado como electrólito. Como substrato, foram escolhidos o latão e o ferro, enquanto como ânodo foi escolhida uma placa do metal a ser depositado sendo que para o estudo da deposição da liga de Zn/Sn foi escolhida uma placa de estanho. As melhores eficiências foram sempre obtidas para as experiencias com o latão, contudo as melhores deposições foram obtidas para as experiências em que foi usado ferro como substrato. O depósito com a liga desejada, ou seja com 20% de zinco e 80% de estanho foi obtido para o electrólito onde foi usada uma concentração de 0.27M $ZnCl_2$, 0.07 M $SnCl_2$ com 0.015M de K_3-HEDTA como agente complexante.

Metais refractários como molibdénio e tungsténio não podem ser electrodepositados a partir de soluções aquosas sem a formação de uma co-deposição de Ni, Co ou Fe. Aqui, IL's poderão novamente ser uma solução. A primeira exigência é a dissolução de uma fonte de metal. O MoO_3 poderia ser adequado, no entanto existem algumas dúvidas sobre o uso de óxidos. Sendo assim, IL's livres de oxigénio foram procurados. A primeira tentativa foi a combinação de $ZnCl_2$ com CCC, que resultou num líquido abaixo de 150 ° C na razão molar de 2:1 e 3:1. Infelizmente, o MoO3 não se dissolveu nestes IL. Outra forma usada para encontrar IL's sem oxigénio na sua composição foi a síntese de sais quaternários de amónio. Nenhum dos métodos utilizados se pode considerar viável, pois o tempo de reacção foi muito longo e foram obtidos rendimentos muito baixos. Portanto, estes sais não foram obtidos em quantidade suficiente para realizar e verificar o possível comportamento electroquímico de metais refractários.

Palavras-Chave: Líquidos iónicos, electrodeposição, ligas de Zn/Sn, metais refractários.

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Abbreviations and Symbols

Abbreviation/Symbol	Designation	Units
A	Area	m^2
AAS	Atomic absorption spectrometry	
C	Current	A
CC	Choline chloride	
CCC	Chlormequat chloride	
CV	Cyclic voltammetry	
DES	Deep eutectic solvent	
D.R	Dilution Ratio	
e^-	Electron	
H	Height	
h	Hours	h
IL	Ionic liquid	
L	Length	
M	Molar	mol/L
m	Mass	
MM	Molar mass	g/mol
min	Minutes	m
n	Moles	mol
nF	Number of electrons that are need to reduce or oxidize the metal	
P	Cell potential	V
ppm	Parts per million	mg/L
Q	Charge	C
quat	Quaternary ammonium salt	

Abbreviation/Symbol	Designation	Units
RTIL's	Room temperature ionic liquids	
s	Seconds	s
T	Temperature	ºC
t	Time	
V	Volume	m^3
VOC's	Volatile organic components	
W	With	
ρ	Density	g/m^3
Ø	Efficiency	%
η	Reaction yield	%

Subscripts:

Ano.	Anode
Cat.	Cathode
dep.	Deposition
dis.	Dissolution
exp.	Expected

1. Introduction

Electrochemistry has been used since the 16th century and is still an actual subject of modern chemistry. It can be defined as a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (electrolyte), and which involves electron transfer between the electrode and the electrolyte or species in solution. This scientific field covers all the chemical processes which involve the electron transfer between substances or in other words, the conversion of chemical energy in electric energy or vice versa. These chemical reactions where electrons are transferred between molecules or ions are called oxidation-reduction reactions (redox) [1].

In electrochemistry the redox reactions do not take place after direct contact of the chemicals but they occur via two electrodes, a cathode and an anode. The anode is defined as the electrode where oxidation occurs and the cathode is the electrode where the reduction takes place. Electrodes can be made from any sufficiently conductive materials, such as metals, semiconductors, graphite, and even conductive polymers. In between these electrodes is the electrolyte, which contains ions that can freely move [1]. The place where are the electrodes and electrolyte, and where the electrochemical reaction happens is called an electrolytic cell. Figure 1.1 shows a scheme of an electrolytic cell.

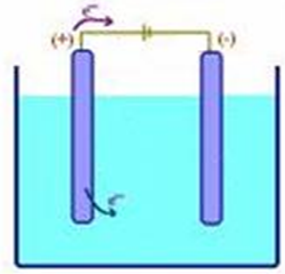


Figure 1.1 – Scheme of an electrolytic cell.

There are various important electrochemical processes in both nature and industry, like the detection of alcohol in the breath of drivers through the redox reaction of ethanol and the coating of metals on all kinds of substrates, (electroplating) [1]. The latter is the subject of this thesis.

Electroplating is an electrochemical process used to coat a conductive or a non-conductive object with a thin layer of the material, such as metal. Electroplating is primarily used for depositing a layer of material to apply a desired property (*e.g.* abrasion and wear resistance, corrosion protection, lubricity, etc) to a surface that otherwise hasn't that property.

In this process normally the part to be plated is the cathode, but electrodeposition at the anode is also possible (e.g. electrodeposition of PbO_2 from a Pb^{2+} solution). As anode two situations are possible. In one of them the anode is made of the metal to be plated (soluble anodes); in the other case inert anodes are used (insoluble anodes). In the latter case the anodic reaction is the oxidation of the solvent. Most commonly only one single metallic element is plated. However, alloys, such as brass and bronze, can be electrodeposited as well, but this process is more complicated than plating single metals [2].

An important parameter in an electroplating process is the current density. The higher the current density, the faster the deposition rate will be, which is advantageous from an economical point of view. Nevertheless, there is a practical limit enforced by poor adhesion and plating quality when the deposition rate is too high [2]. Moreover, current efficiency decreases at higher current densities. In any case, when developing new plating processes, the process should perform well at acceptable current densities.

The deposition properties at varying current densities can be checked just with a test cell. This test is called by hull cell. The hull cell was first defined in 1939 by R.O. Hull and with it, it is possible to examine the effects of the following [3]:

- Operational variables, such as pH, current densities, temperature and agitation
- Organics and metallic contaminations
- Salt constituents and addition agents
- Brightness range of plating deposit
- Covering power.

An important aspect to consider is that the hull cell just allows a qualitative analysis and not a quantitative analysis of the process.

The hull cell is a miniature plating tank with a trapezoidal configuration (see Figure 1.2). The angle of the inclination and the space between the cathode and the anode are critical to the study of the effects of the current density [3].

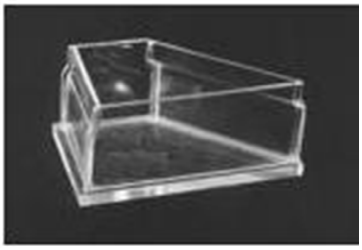


Figure 1.2 – Hull cell configuration.

As referred above, to construct an electrolytic cell two electrodes are necessary but also the electrolyte. The electrolyte is a specially designed chemical solution that contains

the desired metal, (such as gold, zinc, silver or tin) dissolved in a form of submicroscopic metallic particles (positively charged ions). Sometimes, various substances can be added (additives) in the bath to obtain smooth and bright depositions.

The most part of the electrolytes used in the electroplating sector are based on aqueous solutions. The electroplating methods based on aqueous solutions are often non-dangerous to the environment, but nevertheless have some limitations, including [4]:

- Limited potential windows
- Necessity for complexing agents such as cyanide
- Passivation of metals can cause difficulties with both anodic and cathodic materials
- All water must eventually be returned to the environment.

Then, to try overcoming these limitations, ionic liquids based solutions have been development. The use of ionic liquids (IL's) as electrolyte has some advantages compared with the use of water, such as [4]:

- IL's have a wide electrochemical window (often 5V), while water has only an electrochemical window of around 2V
- Some metals cannot be deposited from water solutions due to hydrolysis e.g. Al, Ti, Ta, Nb, Mo, W. But with IL these metals can be deposited
- There is potential for quality coatings to be obtained with IL's rather than with water
- The IL's offer the possibility to develop new plating baths for coating polymers without the necessity to add toxic and problematic organic complexants used in water
- Although the cost of IL's will be greater than aqueous solutions, the high conductivity and better efficiency will provide significant energy savings compared with water
- When strongly acidic aqueous electrolytes are used in electropolishing and electroplating process, large quantities of corrosive effluent full with metals are produced, whereas in IL's electrolytes normally the metals will precipitate and be readily separated and recycled
- The use of IL's allows the replacement of many toxic and hazardous materials used in water e.g. toxic form of chromium (VI), cyanide, caustic and corrosive electrolytes, etc.

For these and various other reasons, the use of IL's as electrolyte has received a highlighted research interest in the last decades.

2. Background

2.1 Ionic Liquids

The history of the Ionic liquids (IL) dates back to the 19th century. The last decades ionic liquids have known a true revival. The main interest stems from the possibility to use them as non-volatile solvents for green chemistry applications [5].

An ionic liquid can be defined as a salt with a melting temperature below the boiling point of water. Some salts identified as ionic liquids are liquid at room temperature and sometimes at even lower temperatures. In that case they are called 'Room Temperature Ionic Liquids' (RTIL's). There are a lot of synonyms used to define an IL, and the term 'Molten Salts' can be used as well, however the specific name 'Ionic liquid' was introduced to distinguish them from the 'molten salts' [5].

The IL's are formed of a cation and an anion. Often organic cations and anions are used. In figure 2.1 some commonly used cations and anions are shown [6].

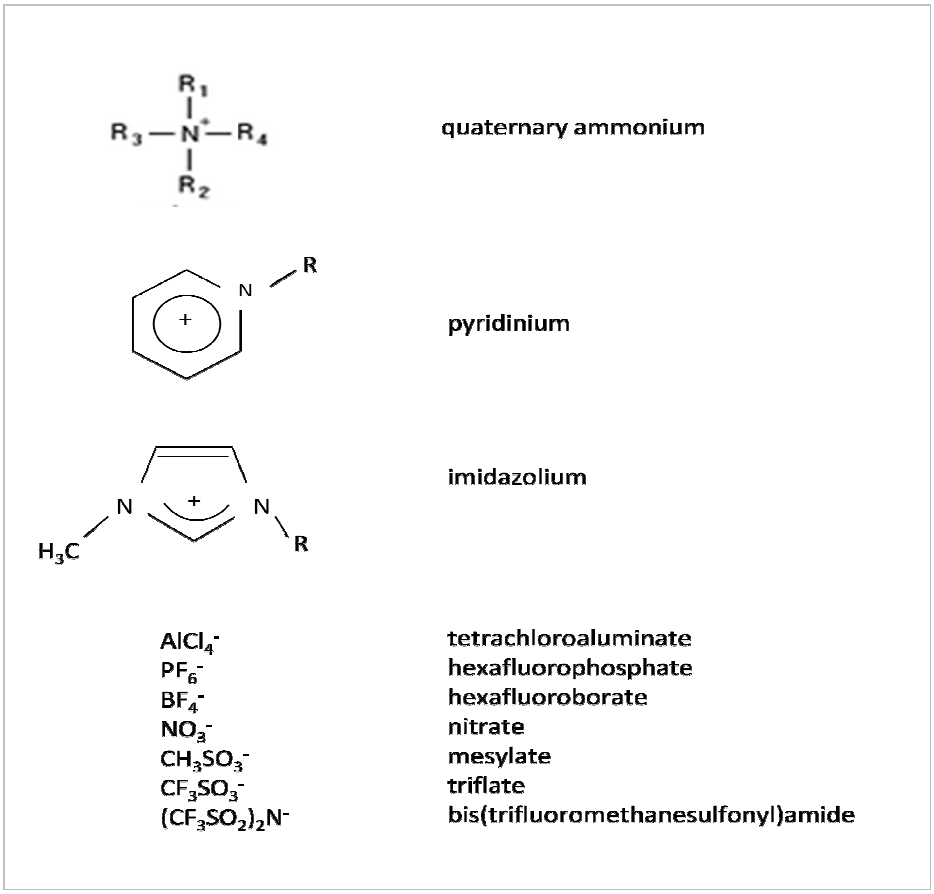


Figure 2.1 – Commonly used cations and anions.

2.1.1 Properties

A specific consequence of the organic nature of IL's is that their properties can be 'tuned'. In table 2.1 to the most common properties of IL's are listed. The physical and chemical properties of IL's depend on the combination of cation and anion used [6, 7, 8].

Table 2.1 – Properties of Ionic liquids.

A salt	Cation/Anion quite large
Freezing point	below 100ºC
Liquids range	Up to 400ºC
Thermal stability	Usually high
Viscosity	Normally between 20 and 1000 cP
Polarity	Moderate
Specific conductivity	Usually < 10mS/cm
Electrochemical window	Up to 5V (wide electrochemical window)
Solvent and/or catalyst	Excellent for many organic reactions
Vapour pressure	Not measurable at room temperature
Miscibility	Miscibility with water and organic solvents dependent on composition

2.1.2 A green alternative?

IL's are studied intensively for different applications. Normally, they are indicated as "green solvents" because of their low vapour pressure. The IL's reduce the gaseous emissions compared to volatile organic components (VOC's) used as solvent, nevertheless some aspects should be taken in consideration before they can be called "green solvents".

In recent years the biotoxicity and toxicity of IL's have been investigated, which proved that not all of the IL properties can be called "green" [7]. Some IL's are very toxic (*e.g.* with cyanide ions) and some of them are very persistent (*e.g.* fluorine containing anions).

Although the IL's are not "green solvents" on their own, they can be designed as such. IL's based on ammonium salts are less toxic than those based on imidazolium salts, so the former are to be preferred. A popular quaternary ammonium salt (quat) used as a starting point for IL's is choline chloride. It is one of the cheapest quats and used as an additive in chicken food. Therefore, it is not surprising IL's based on choline chloride have low toxicity so they are a good choice when large scale IL processes are targeted.

2.1.3 Choline Chloride

Choline chloride (CC) is an organic compound and a quaternary ammonium salt which is readily available on a large scale. It has a choline cation with chloride anion. CC can be prepared in the laboratory by methylation of dimethylethanolamine with methyl chloride.

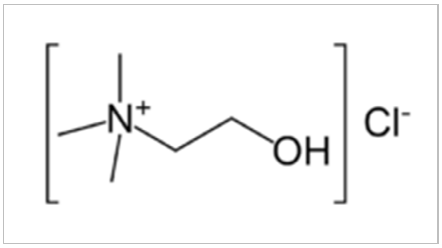


Figure 2.2 – Choline Chloride.

CC can be used as a constituent of true ionic liquids. For example, a mixture of $CuCl_2$ and choline chloride, both solids, results in a liquid consisting of an anion and choline as the cation. It can be used also to produce a range of IL analogues called 'deep eutectic solvents' (DES) [8, 10].

A DES is a type of IL composed of a mixture which forms a eutectic with a melting point much lower than each of the individual components. The complexing agent interacts with the anion, increasing its effective size. This in turn decreases the interaction with the cation and so decreases the melting point of the mixture [8]. DES based on choline chloride are produced by mixing CC with a hydrogen bond donor (*i.e.* complexing agent) such as urea, malic acid or ethylene glycol. A common DES that is used throughout this project is Ethaline200. It is formed by mixing ethylene glycol and choline chloride in a molar ratio 2:1. This DES is very easy to prepare, cheap (much cheaper than other IL's) and have a low viscosity [7]. Usually, the latter is a great problem found in similar DES.

2.1.4 Applications of Ionic Liquid

There are a lot of applications of IL's, among which we can highlight the use of IL's as alternative to non-volatile solvent and its use as an electrolyte in electrochemical applications. In the context of this thesis, the latter is the most interesting for our targeted application.

The use of IL's as an electrolyte has been thoroughly studied during the last few decades. Some examples of these researches are the study of these electrolytes for application in batteries, dye-sensitized solar cells, electrochemical capacitors, membrane additives for fuel cells, electrodeposition of reactive metals and nanomaterials, electro-polishing, electroplating in metal extraction processes. Some properties render IL's most attractive for use as an electrolyte: e.g. the non-volatility, the good solvent properties and the

excellent thermal, chemical and electrochemical properties. For electrochemical applications, IL's with a wide electrochemical window, low viscosity and high electric conductivity are being sought for [9].

2.2 Electrodeposition of metals from Ionic Liquids

As referred above, the electrodeposition of metals from IL's has received a big highlight in the last times. It is a novel method for the production of nanocrystallines metals and alloys because the grain size of the deposition can be adjusted by varying the electrochemical parameters such as potential, current density, and composition and temperature of the bath. Another important fact in the use of IL's for metal electrodeposition, is that IL's provides much higher health and safety standards for employees in the work place, i.e. elimination of hazardous vapors, elimination of highly corrosive acidic/basic solutions, and a big reduction of the use of hazardous chemical substances [4].

There are some metals that cannot be deposited from aqueous solutions but they can be deposited from IL's such as molybdenum and tungsten (refractory metals). It had been recognized that electrodeposition of refractory metals is possible only from high temperature IL's [12], but the electrodeposition of these metals at low temperatures has many advantages [12, 13]. One of the most promising applications of this metal electrodeposition is the LIGA (Lithographie – Galvanoformung – Abformung, German abbreviation), but for this process the electrodeposition of metals must be achieved at temperatures lower than 250ºC to avoid the softening and embrittlement of the substrate [13]. By this reason the electrodeposition of tungsten and molybdenum at low temperatures had been researched and is also an object of study of this work.

On the other hand, a lot of metals deposited from IL's can be also deposited from aqueous solutions such as Zinc and Tin. The great advantage is that with IL's are higher efficiencies of deposition than with water solutions are obtained. The Zinc and Tin can be deposited separately or together, if they are deposited together they form a Zinc-Tin alloy. This alloy is important from an engineering point of view because it offers better corrosion resistance than pure Zinc, particularly in high humidity conditions, and it is also important because it can be used to replace cadmium used as coating [11, 14].

2.3 Zinc/tin alloys as alternative for cadmium coatings

The metal finishing industry has been the target of several regulatory actions related with the use of hazardous materials that are used in coating processes. Environmental together with health and safety regulations were put up with the purpose to reduce the quantity of toxic and hazardous materials [14].

The cadmium and the hexavalent chromium are very toxic and carcinogenic materials heavily regulated by the Environmental Protection Agency (EPA). Due to the toxicity and the carcinogenicity some studies have been done with the aims to eliminate or reduce the use of cadmium in several applications, like for example its use in the military vehicles. Specifically the protective shells of electrical connectors currently used in military ground systems are cadmium plated and then chromated with chromate to provide additional corrosion protection [14].

Some studies have been performed to find alternatives to the currently used coating processes to reduce environmental and safety risks. However, the replacement of cadmium is not an easy task. Cadmium has been used as a protective coating for several applications for many years because of the numerous properties, such as the ease of manufacturing, ease to repair, low cost, temperature resistance and environmental resistance particularly corrosion resistance [14, 15]. Some of these properties are unique for these coating systems such as the corrosion resistance, and the cadmium coatings provide galvanic corrosion protection to electrical systems. Very few metals can provide a similar level of corrosion protection in this application. This is demonstrated by the position of cadmium in the galvanic series, shown in figure 2.3 [14].

Figure 2.3 shows also that zinc and zinc alloys, beryllium, manganese and aluminum alloys (circled area) are the most active metals in a corrosive environmental and, therefore are the only materials that can give a corrosion protection similar to cadmium. However, the beryllium is more hazardous that cadmium and the manganese and pure zinc both corrode too rapidly in several applications of engineering. However, zinc alloys and the aluminum alloys can be a great replacement for cadmium in several applications [14].

Of the existing zinc alloys, the most promising and with the best features is the zinc/tin alloy. The zinc-tin coatings have been considered promising for cadmium replacement and commercially there are electroplating systems that allow to deposit alloys of 20-30% of zinc using aqueous solutions as electrolyte [15, 16, 17].

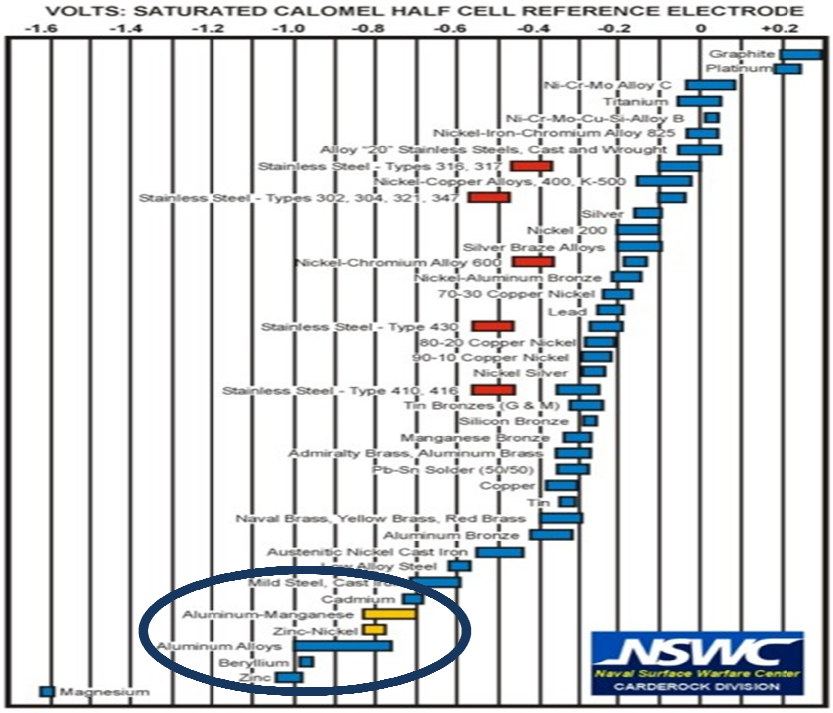


Figure 2.3 – Galvanic series, showing position of cadmium and viable alternative metals. (Circled area: materials providing galvanic corrosion protection.) [14]

However, there were some studies that noted that the deposited Zn/Sn coating was found to had an insufficient amount of zinc in the deposit to provide adequate corrosion protection (less than 1% zinc, versus the anticipated >20% zinc concentration found in more corrosion-resistant coatings that had been tested under related projects) [17]. This implies that, while the Zn/Sn alloys are promising for some applications, some electrolytic baths used are not good enough to provide a consistence coating composition and hence, are not good enough to provide sufficient corrosion resistance [17]. In response, new electrolytic baths based on Ionic liquids have been developed (also the main subject of this thesis) that can provide an electrodeposition of Zn/Sn alloys with a high content of zinc (20% zinc and 80% tin) and also a good consistent coatings and consequently a sufficient and a good corrosion resistance.

3. Analytical Determinations

3.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. The technique makes use of the wavelengths of light specifically absorbed by an element, that correspond to the energies needed to promote electrons from one energy level to another, higher, energy level [18]. An atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms (*i.e.* flame); and a means of measuring the specific light absorbed as illustrated in figure 3.1.

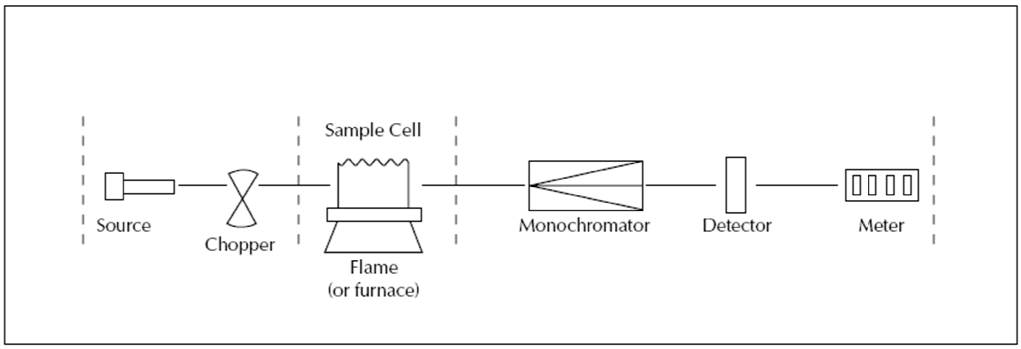


Figure 3.1 – Diagram illustrating the constitution of an AAS system.

The operation parameters of the AAS vary according the element to be measured, as may be observed in the Table 3.1.

Table 3.1- Operation parameters of the AAS to different elements.

Element	Light source	Flame description	Standard and Absorbance
Zinc	Hollow cathode	Air-Acetylene Oxidizing Fuel Lean Blue	A standard containing 0,25 µg/ml of Zn will give a reading of approximately 0,1A.
Tin	Hollow cathode	Nitrous oxide-Acetylene Fuel Rich Red cone 10 mm high	A standard containing 28 µg/ml of Sn will give a reading of approximately 0,1A.

Atoms of different elements absorb characteristic wavelengths of light. In AAS, the sample is atomized, this means that the sample is converted in free atoms in the vapour state, and a beam of electromagnetic radiation emitted from excited atoms is passed through the vaporized sample. A calibration curve is constructed by running several samples of known element concentration under the same conditions as the unknown. The amount of the standard absorption is compared with the calibration curve and this enables the calculation of the element concentration in the unknown sample [18]. For each element exists a specific range where the absorption is linearly related with the concentration according to the Lambert-Beer law (equation A).

$$A = \varepsilon.b.c \qquad \text{(A)}$$

Where:

A – Absorvance

ε – Molar absorptivity (constant characteristic of the species absorbing)

b – Optical path length (cm)

c – Molar concentration of solution (mol/L)

3.2 Cyclic Voltammetry

Cyclic Voltammetry (CV) is one of the most frequently used electrochemical methods because of its relative simplicity and its high information content. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process. Often, this technique is the first experiment performed in an electro-analytical study [19, 20].

In this technique the measurements are performed in a three-electrode cell:

- working electrode (substrate), where the reactions under study occurs;
- reference electrode with a fixed potential;
- counter or auxiliary electrode.

In figure 3.2 three examples of electrodes used in CV are shown.

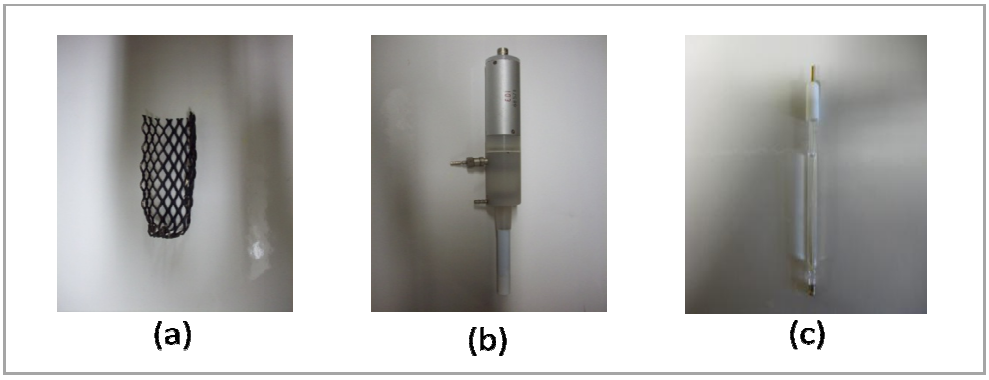


Figure 3.2 – Examples of electrodes used in CV: (a) counter electrode; (b) working electrode; and (c) reference electrode.

In CV the potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. The potential is varied linearly and the direction of the scan is reversed at a certain point. The data are plotted as current *vs.* potential in a graphic called a cyclic voltammogram [19]. In figure 3.3 a typical cyclic voltammogram is shown.

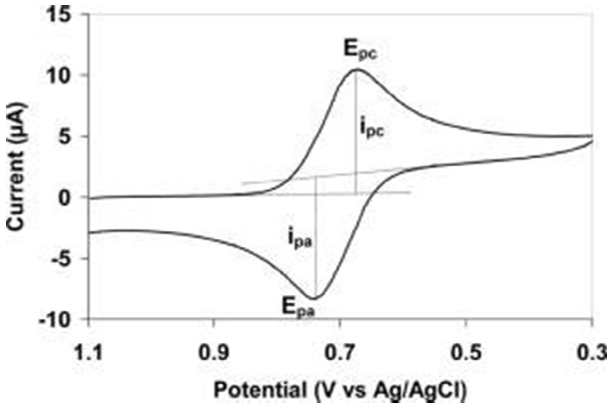


Figure 3.3 – A typical cyclic voltammogram where i_{pc} and i_{pa} show the peak cathodic and anodic current respectively.

As the waveform shows, the forward scan produces a current peak for any species that can be reduced (or oxidized depending on the initial scan direction) through the range of the potential scanned. As the potential reaches the reduction potential of the analyte, the current will increase but then falls off because the concentration of the analyte is depleted close to the electrode surface. If the redox couple is reversible then, when the applied potential is reversed, it will reach the potential that will oxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape as to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds are obtained [19, 20].

4. Materials and Methods

In this chapter the experimental procedures and the materials, reagents and equipments used in every experiments will be described.

4.1 Material

Besides the material commonly used in the lab, we used also:

- Brass plates
- Electrolytic cell
- Hull cell
- Iron plates
- Tin plates
- Zinc plates

4.2 Reagents

The reagents used were:

- 1-chloropropane 99% (Acros Organics)
- 1-iodopropane stabilized 99% (Acros Organics)
- Chlormequat chloride 66% (Taminco)
- Choline chloride 75%
- Citric acid (technical grade)
- DL-Malic acid 99% (Sigma – Aldrich)
- DL-Tartaric acid 99.5% (Acros Organics)
- Ethanol 96%
- Ethylene glycol >99% (Sigma – Aldrich)
- Hydrochloric acid fuming 37% (p.a., Merck)
- N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid or HEDTA ~98% (Aldrich Chemistry)
- Potassium hydroxide pellets (pure, Merck)
- Reline200 (made in lab)
- Tin(II) chloride anhydrous 98% (Acros Organics)
- Tin(II) hydroxide (made in lab)
- Triethylamine 99% (pure, Janssen Chimica)
- Zinc chloride >98% (extra pure, Acros Organics)
- Zinc nitrate hexahydrate 98% (extra pure, Acros Organics)
- Zinc oxide ~99% (extra pure, Merck)

- Zinc sulphate heptahydrate 99,5% (p.a., Acros Organics)

4.3 Equipments

In this work the following equipment was used:

- Analytical Scale (Mettler – Toledo, Acculab)
- Atomic absorption spectrometer (Unicam 989, Solaar)
- Hot plate and magnetic stirrer (RCT Basic)
- pH meter (Consort C861)
- Potentiostat (PGSTAT 12, Autolab)
- Power supply (EA – 3048B, Elektro)
- Ultrasonic bath (RK 103 H, Bandelin Sonorex)

4.4 Experimental Procedure

4.4.1 Electrodeposition of Zinc

The study of the zinc electrodeposition was performed in distinct set-ups. In one of them a normal parallel plate cell was used, and in the other one a hull cell was used. The parallel plate cell was a glass rectangular box and the hull cell was a miniature box with a trapezoidal configuration. The difference between the parallel plate cell and the hull cell used in this work can be seen in the figure 4.1 and their dimensions can be seen in appendix A.1.

Figure 4.1-Recipients used as electrolytic cell: (a) parallel plate cell; (b) hull cell.

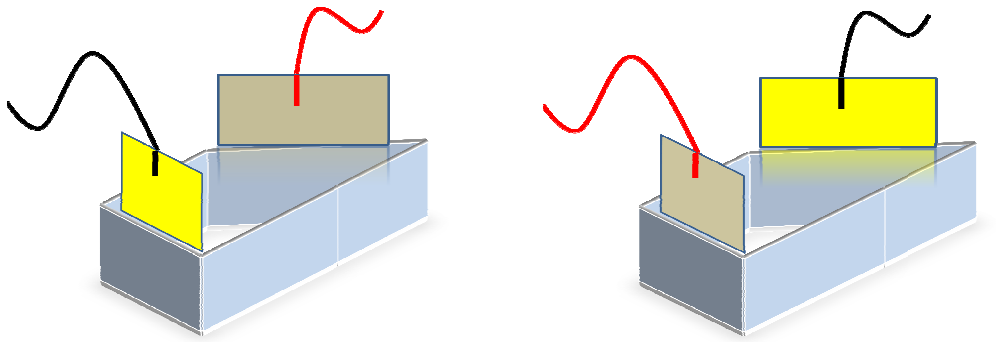
In both cells brass was used as the cathode material and zinc as the anode material. The brass plate was first washed to remove all the stains of dirt in order to make the surface for the deposition as clean as possible. After washing of the brass plate with acetone and water, the plate was dipped in a solution of 7.5% hydrochloric acid and then washed again with water. The cathode was connected to the negative pole of the power supply and the

anode was connected to the positive pole; in this way the oxidation reaction at the anode is the dissolution of the zinc and the reduction reaction at the cathode the deposition of the zinc.

Oxidation: $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (1)

Reduction: $Zn^{2+} + 2e^- \rightarrow Zn(s)$ (2)

If information on the electrodeposition of zinc was targeted, the cathode was placed at the slanted side. When information on the electrodissolution of zinc was targeted, the cathode and anode were switched sides in the hull cell. A scheme of this set-up is represented in the figure 4.2.



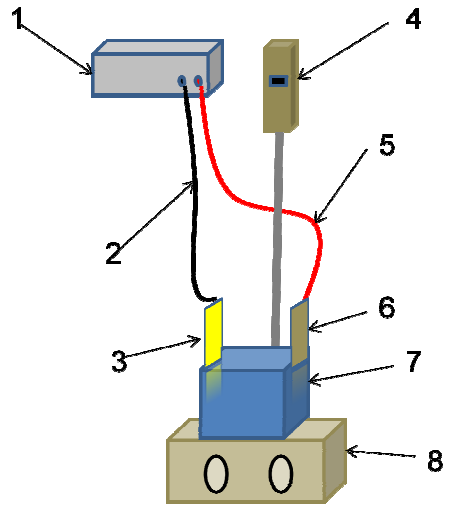
(a) (b)

Figure 4.2- Scheme of the set-up where the cathode and the anode are switched in the hull cell: in (a) the zinc plate (grey) occupies the slanted part and the brass plate (yellow) occupies the flat part; in (b) the opposite is shown.

The study of the electrodeposition of zinc was performed for different electrolytes. The solutions used were: 0.5 M $ZnCl_2$ in Ethaline200 and in Reline200 (1 CC **:** 2 Urea), 0.5 M ZnO in Ethaline200 and in Reline200, 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 and Reline200, 0.5 M $ZnSO_4.7H_2O$ in Ethaline200 and in Reline200. It was found that the solution of ZnO in Ethaline200 was an emulsion. Then, in order to turn it into a homogeneous solution and to improve the efficiency of the deposition three complexing agents were added one by one in order to study their effect separately. The complexing agents added were: 0.5 M malic acid, 0.5 M citric acid and 0.5 M tartaric acid. The solutions made with Ethaline200 were used for both set-ups (parallel plate cell and hull cell), whereas the solutions made with Reline200 were used just for the hull cell.

The effects of the cell potential and temperature on the deposition were also studied. The cell potentials used were: 2.25V, 17.6V and 35.3V and the temperatures used were:

50ºC, 60ºC, 65ºC, 75ºC, 80ºC. All the experiments had been running for 30 minutes, except one that had been running for 20 minutes in order to see the difference between the depositions obtained. All the experiments performed in the parallel plate cell were performed with stirring of the solutions; in the hull cell experiments one experiment was made with stirring and the rest without stirring. In figure 4.3 a scheme of the set-up used for the electrodeposition of zinc is shown.



Legend:

1 – Power supply
2 – Negative pole
3 – Brass plate (cathode)
4 – Thermometer
5 – Positive pole
6 – Zinc plate (anode)
7 – Electrolytic cell
8 – Hot plate and magnetic stirring

Figure 4.3 – Scheme of the set-up used for the electrodeposition of zinc.

4.4.2 Determination of the concentration of zinc in the electrolyte

The concentration of zinc in the electrolytic bath during the electrodeposition was also determined, but not for all the electrolytes. This measurement was done just for two solutions: 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 and 0.5 M ZnO with 0.5 M citric acid in Ethaline200. These experiments were performed in the glass parallel plate electrolytic cell at 50ºC and with a cell potential of 2.25V. For the first solution, the electrodeposition had been running for 4 hours; and for the second, the experiment had been running for 7 hours. Samples were taken of the electrolytic bath every hour in order to measure the pH of the solution and the concentration of zinc. The concentration of zinc was determined by AAS and for the calibration curve three standard solutions were used: 0.5 ppm, 1.0 ppm, 1.5 ppm. To determine the pH, the sample was diluted 10 times, in order to avoid damage to the pH-meter.

4.4.3 Electrodeposition of tin

The electrodeposition of tin was only studied in the hull cell. A slice of pure tin was used as the anode and a brass plate cleaned as described previously (see section 4.4.1) as the cathode.

The cathode was connected to the negative pole of the power supply and the anode was connected to the positive pole; in this way the oxidation reaction at the anode is the dissolution of the tin and the reduction reaction at the cathode the deposition of the tin. Note that tin can be oxidized either to Sn (II) or to Sn (IV).

Oxidation: $Sn(s) \rightarrow Sn^{2+} + 2e^-$ (3)

Reduction: $Sn^{2+} + 2e^- \rightarrow Sn(s)$ (4)

or

Oxidation: $Sn(s) \rightarrow Sn^{4+} + 4e^-$ (5)

Reduction: $Sn^{4+} + 4e^- \rightarrow Sn(s)$ (6)

The set-up used in the electrodeposition of tin is the same as used for zinc and as before in the study of zinc electrodeposition, the cathode and the anode were switched in the hull cell in order to allow either the deposition of tin or the dissolution of tin to be studied (see figure 4.2).

In this case all the electrolytic baths were based on Ethaline200 with added $Sn(OH)_2$ or $SnCl_2$. The experiments were performed at different concentrations of these components. The concentrations used were: 0.1 M or 0.5 M of $Sn(OH)_2$ and 0.1 M or 0.5 M of $SnCl_2$. It was necessary to add complexing agents in order to obtain homogeneous solutions of $Sn(OH)_2$, as the addition of this component to Ethaline200 was an emulsion. Two complexing agents were added and their concentrations used were: 0.5 M and 0.8 M citric acid and 0.05 M, 0.1 M, 0.5 M, 0.8 M malic acid. The citric and malic acids were added separately (both 0.5 M) to $SnCl_2$ solutions and were investigated as well, in order to see if this improves the efficiency of the deposition. All the experiments were performed at 50ºC for 30 min. The only parameter that was varied was the cell potential that took values of 0.82V and 2.25V. All the experiments were performed without stirring.

4.4.4 Determination of the tin concentration in the electrolyte

The determination of the concentration of tin in the electrolyte was done for three different conditions of operation (three experiments). In the first Ethaline200 was used as electrolyte, with an applied cell potential of 0.82V and an experiment time of 6 hours. The electrolyte for the second experiment was also Ethaline200, but the cell potential was increased to 2.25V and the experiment time for the electrodeposition was 8 hours. The third experiment was done as well with Ethaline200, but this time 0.1 M K_3-HEDTA (potassium salt) was added as a complexing agent. At first a potential of 2.25V was applied and after 43

hours the potential was changed to 6.4V. The third experiment had a total duration of 130 hours. All the experiments were performed in the parallel plate cell with stirring at 50ºC.

AAS was the method of choice for the determination of the tin concentration in the electrolyte. For the calibration curve the following standard solutions of tin were used: 10 ppm, 50 ppm and 100 ppm. These solutions were made in 9% hydrochloric acid.

4.4.5 Preparation of the K_3-HEDTA (potassium salt)

The potassium salt was prepared by titration of HEDTA with KOH. During the titration KOH neutralizes the HEDTA causing the pH of the solution to increase. As HEDTA is a trivalent acid, three equivalence points can be distinguished in the titration curve as can be seen in figure 4.4. The blue point marks the point where the titration should be stopped; at that point HEDTA has been transformed quantitatively to K_3-HEDTA.

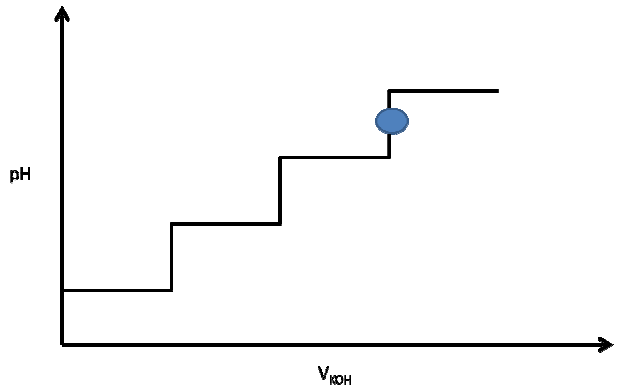
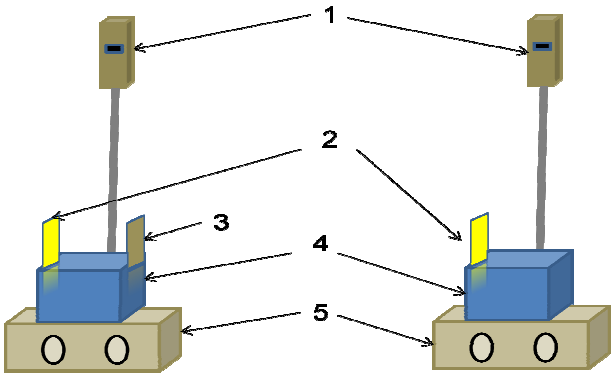


Figure 4.4– Variation of the pH with the addition of KOH.

4.4.6 Chemical dissolution of tin

The study of the chemical dissolution of tin was done in a glass box (the same glass box used to do the electrochemical deposition) and all the experiments were performed at 50ºC with stirring. In one experiment a plate of brass was put in the glass box to check if the tin present in the solution would deposited on it, and for all other experiments a plate of brass and a slice of tin were put in the cell to check if the dissolution or deposition of tin would occur. In figure 4.5 a scheme of the set-up with one plate and the set-up with the two plates are shown.



Legend:

1 – Thermometer
2 – Brass plate
3 – Tin plate
4 – Glass box (cell)
5 – Hot plate and magnetic stirring

Figure 4.5 – Scheme of the set-up used for the chemical deposition.

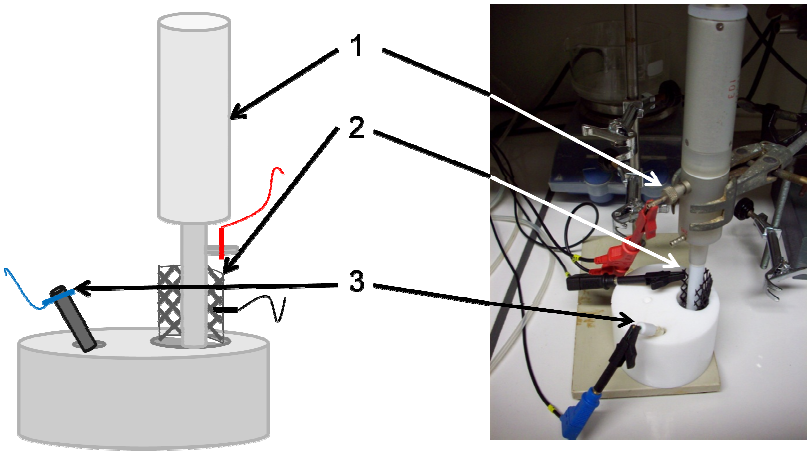
The chemical dissolution of tin in Ethaline200 with the following components added was checked: 0.5 M $Sn(OH)_2$ and 0.1 M $SnCl_2$. To the solution of $Sn(OH)_2$, 0.5 M malic acid was added as a complexing agent. The duration of the experiment was the main parameter changed and the experiments were performed for: 0.5 h, 17 h and 22 h.

4.4.7 Cyclic voltammetry analyses

After the study of the zinc electrodeposition in 0.5 M $ZnCl_2$ in Ethaline200 and in Reline200, these solutions were analyzed by cyclic voltammetry at room temperature. The measurements in CV are performed in a three-electrode cell (section 3.2), and the electrodes used were:

- Platinum disk Ø1 mm (working electrode)
- Ag/Ag^+ - cryptant in acetonitrile (0.01 M $AgNO_3$; 0.1 M Kryptofix 22) (reference electrode)
- D.S.A. RuO_2/IrO_2 coated Ti-grid (counter electrode)

In figure 4.6 an image and a scheme of the measuring set-up are shown.



Legend:

1 – Working electrode
2 – Counter electrode
3 – Reference electrode

Figure 4.6 - The three-electrode cell used in a cyclic voltammetry.

Pure Ethaline200 without any addition and after being used in the electrodeposition of tin was also analyzed by CV in different conditions. The first analysis was performed at room temperature and with the same set-up used for the CV of $ZnCl_2$ solutions (see figure 4.6), differing only in the working electrode used. The electrodes used in this case were:

- Tin 1,5 mm (working electrode)
- Ag/Ag^+ - cryptant in acetonitrile (0.01 M $AgNO_3$; 0.1 M Kryptofix 22) (reference electrode)
- D.S.A (counter electrode)

The second analysis of Ethaline200 was performed in a small vial at 50ºC and the electrodes used were:

- Platinum Ø0.5 mm (working electrode)
- Platinum (reference electrode)
- D.S.A (counter electrode)

A solution of K_3-HEDTA in Ethaline200 and a solution of 0.1 M $SnCl_2$ in Ethaline200 were also analyzed by cyclic voltammetry. These analyses were performed in the same conditions and with the same electrodes used in the second analysis of Ethaline200. The $SnCl_2$ solution was analyzed after being used in the tin electrodeposition, whereas the K_3-HEDTA solution was analyzed before and after being used in the electrodeposition of tin.

4.4.8 Electrodeposition of Zn/Sn alloy

All the experiments done in the study of the electrodeposition of Zn/Sn alloy were performed at 50ºC in the parallel plate cell. The investigated electrolytes were solutions of $ZnCl_2$ and $SnCl_2$ in different concentrations in Ethaline200. The solutions used were:

- 0.1 M $ZnCl_2$ with 0.07 M $SnCl_2$ in Ethaline200
- 0.27 M $ZnCl_2$ with 0.07 M $SnCl_2$ in Ethaline200
- 0.54 M $ZnCl_2$ with 0.07 M $SnCl_2$ in Ethaline200.

The salt 0.015 M K_3-HEDTA was added in all the solutions as complexing agent.

The tin plate was used as anode and as cathode brass or iron plates were used.

The current and the duration of electrodeposition were the parameters varied in this experiment. The values applied for the current were 0.25A and 0.51A and for the duration of the experiment: 1 min, 5 min, 10 min, 15 min, 20 min and 30 min. Almost all of the experiments were performed with stirring (except two that were performed without stirring), but this time the stirring wasn't performed with a magnetic stirrer bar (like in the electrodeposition of zinc and tin separately) but with an ultrasonic bath.

4.4.9 Determination of the content of zinc and tin in the deposition and in the electrolyte

The Zn/Sn depositions obtained in the previous procedures were scraped from the surface and dissolved in 37% hydrochloric acid. After that, the solutions were analyzed by AAS.

The concentration of zinc and tin in the electrolyte was determined in a solution of Ethaline200 with 0.27 M $ZnCl_2$, 0.07 M $SnCl_2$ and 0.015 M K_3-HEDTA. With this solution an experiment was done where the electrodeposition of Zn/Sn alloy was performed in the parallel plate cell at 50ºC, with a current of 0.51A and with an experiment duration of 18 hours. The cathode used was brass and the anode tin. Samples were taken from the electrolytic bath, and analysis performed with AAS.

In any case, the standard solutions used to make the calibration curve were the same described in the sections 4.4.2 and 4.4.4.

4.4.10 Preparation of IL's to dissolve molybdenum

The deposition of molybdenum from IL's is also subject of this thesis. Deposition of refractory metals such as molybdenum or tungsten is not an easy task. In first instance, it was tried to prepare IL's which dissolve molybdenum compounds. The most common Mo-compounds are MoO_3, Mo-chlorides or Mo-oxychlorides. The mixtures of substances and their molar ratios that were prepared for this purpose were:

A. 30 CCC **:** 1 $ZnCl_2$
B. 2 CCC **:** 1 $ZnCl_2$
C. 1 CCC **:** 2 $ZnCl_2$
D. 1 CCC **:** 3 $ZnCl_2$
E. 2 CC **:** 1 $Zn(NO_3)_2.6H_2O$

The deposition of molybdenum is hard to achieve in presence of oxygen, that's why the CCC was used to make the solutions, because it has no oxygen in its composition.
The mixtures A, B and E were not liquid below 150ºC, so these ones were discarded. Only the substances that were liquids below 150ºC were kept to study the dissolution of molybdenum.

4.4.11 Synthesis of quaternary ammonium salts

With the same purpose (to dissolve molybdenum or refractory metals) it was attempted to synthesize three quaternary ammonium salts (quats). These quats were synthesized by alkylation of a tertiary amine (triethylamine) with a halogenated alkane. This

reaction is referred to as the Menschutkin reaction. The compounds used to do the alkylation reaction with triethylamine were: 1-iodopropane and 1-chloropropane.

The 1-iodopropane was added to triethylamine and mixed during 1 hour at room temperature. The reaction of the synthesis is the following:

$$C_3H_7I + C_6H_{15}N \rightarrow (C_2H_5)_3CH_2CH_2CH_3N^+ + I^- \qquad (7)$$

After mixing, the product was dried by evaporating the remaining reactants, which were all volatile.

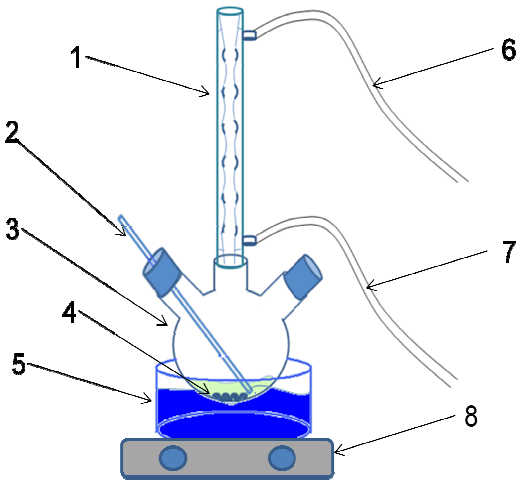
The reaction of 1-chloropropane with triethylamine was done at 60ºC with reflux of the mixture in order to avoid the loss of the reagents (1-chloropropane has a boiling point below of 60ºC). This reaction was performed in two different situations: using ethanol as solvent and with duration of 22 hours and without any solvent with duration of 29 hours. The latter case means that 1-chloropropane was actually used as the solvent. The reaction for the first situation is the following:

$$C_3H_7Cl + C_6H_{15}N \rightarrow (C_2H_5)_3CH_2CH_2CH_3N^+ + Cl^- \qquad (8)$$

In the second situation the reagents were added in a different molar ratio as can be seen by the following reaction:

$$2C_3H_7Cl + C_6H_{15}N \rightarrow (C_2H_5)_3CH_2CH_2CH_3N^+ + C_3H_7Cl + Cl^- \quad (9)$$

Figure 4.7 presents a scheme of the set-up used for the reaction with reflux.



Legend:

1 – Condensation column
2 – Thermometer
3 – Three neck flask
4 – Glass beads
5 – Warming bath (glycol)
6 – Water out
7 – Water in
8 – Hot plate

Figure 4.7 – Set-up used for the synthesis of quaternary ammonium salts.

5. Results and discussion

In this chapter the main results about the study of the electrodeposition of zinc, tin, and zinc/tin alloy will be shown and discussed. The results about the preparation of the IL's and the quat's for the electrodeposition of molybdenum or refractory metals will also be presented in this chapter. The cathodic and anodic efficiencies were calculated based on the Faraday's Law (see appendix A.3.1).

5.1 Electrodeposition of zinc

5.1.1 Study of the influence of the applied cell potential

The first group of experiments done for the electrodeposition of zinc had as objective to choose the potential indicated to perform the remaining experiments for the zinc electrodeposition. For this reason three experiments were done at three different potentials: 2.25V, 17.6V and 35.3V. These experiments were performed in the parallel plate cell at 50ºC with stirring and using 0.5 M $ZnCl_2$ in Ethaline200 as the electrolyte. The time intervals of the electrodepositions differed for each experiment: the experiment performed at 2.25V was run over 30 minutes, the experiment at 17.6V was run over 20 minutes and at 35.3V the experiment ran over 10 minutes. In figure 5.1 a graph is shown with the cathodic efficiencies (calculated based in Faraday's Law) obtained for each experiment.

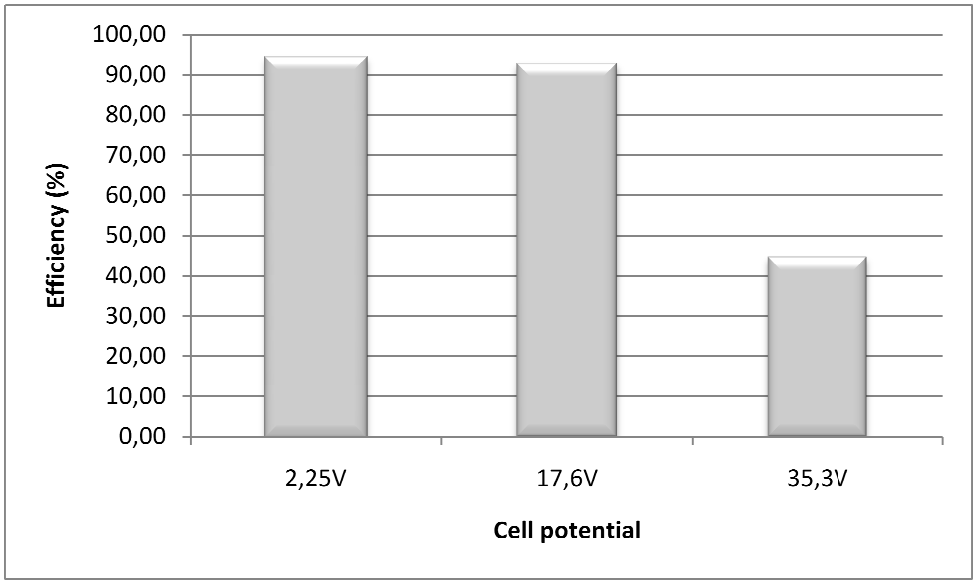


Figure 5.1 – Cathodic efficiencies of zinc electrodeposition for the experiments performed in the parallel plate cell with Ethaline200 based solutions at different cell potentials.

For the experiment performed at 2.25V an efficiency of the deposition of 94.22% was obtained; for the experiment at 17.6V an efficiency of 92.86% was obtained and for the

experiment performed at 35.3V a cathodic efficiency of 44.69% was obtained. However, as every experiment was performed over different time intervals, it is difficult to compare the efficiencies.

Nevertheless a cell potential of 2.25V was chosen for the next experiments because the best deposition was obtained with these conditions (very smooth). The other depositions obtained at the end of the experiments (i.e. with time intervals below those used for the experiment performed at 2.25V), were poor. These depositions appeared dark and the surface of deposition was covered with a black powder. It is clear if these experiments had been running for 30 minutes, the deposition would even be worse. It is concluded that the velocity of zinc deposition in these conditions is too high.

In figure 5.2 images of the depositions obtained in all conditions are shown.

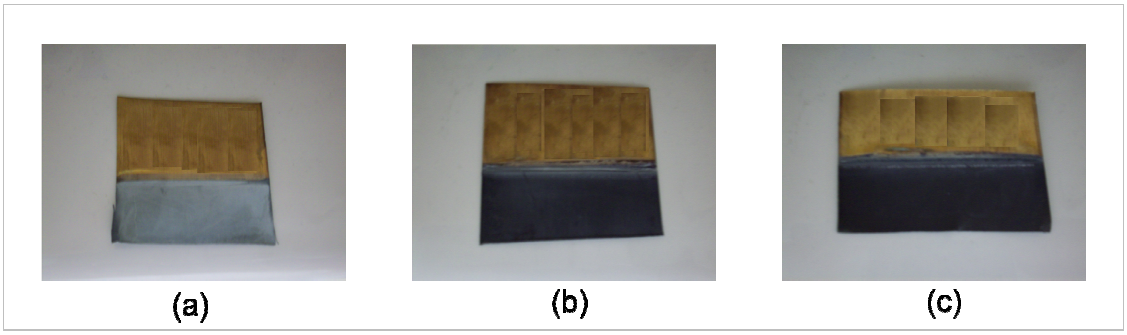


Figure 5.2 – Images of the zinc deposition obtained for different cell potentials: (a) 2.25V, (b) 17.6V and (c) 35.3V.

5.1.2 Study of the effect of stirring on the electrodeposition in the hull cell

The effect of stirring and the consequent increased mass-transport in the hull cell was just studied qualitatively and not quantitatively, in other words, the main interest was to check if there was any difference in the depositions obtained. For this purpose two experiments were performed: one with stirring and the other without stirring. Both were performed at 50ºC, with a cell potential of 2.25V and using 0.5 M $ZnSO_4.7H_2O$ in Ethaline200 as the electrolyte. In figure 5.3 images are shown of the depositions obtained for each experiment.

Figure 5.3 – Images of the deposition obtained in the hull cell for experiments: (a) without stirring and (b) with stirring.

On the figure it can be observed that the deposition without stirring was better than the deposition with stirring. Consequently all the remaining experiments in the hull cell were done without stirring.

5.1.3 Study of the influence of the types of electrolytic bath

In this section the results obtained for different electrolytic baths for the electrodeposition of zinc will be discussed.

In figure 5.4 the cathodic efficiencies (efficiencies of deposition) for the experiments performed in Ethaline200 solutions as the electrolyte are shown. These experiments were performed in the parallel plate cell at 50ºC, with stirring, during 30 min and an applied cell potential of 2.25V.

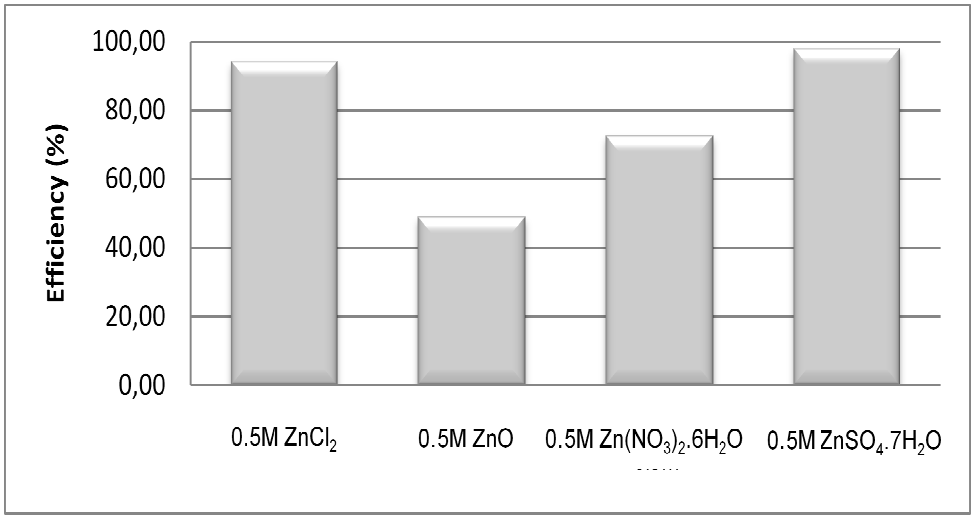


Figure 5.4 – Cathodic efficiencies of zinc electrodeposition for the experiments performed in the parallel plate cell with Ethaline200 based solutions.

The highest cathodic efficiency was 97.98% and the best deposition was obtained for the 0.5 M $ZnSO_4.7H_2O$. With 0.5 M $ZnCl_2$ the efficiency obtained was also good (94.22%), but the deposition obtained had a dark, burned appearance and compared to the deposition obtained with $ZnSO_4.7H_2O$ it was a little less smooth. The worst cathodic efficiency was obtained with 0.5 M ZnO. This solution was a white emulsion and despite having obtained an efficiency of 49.04%, there was no visible layer of zinc deposited on the brass plate. In relation to the 0.5 M $Zn(NO_3)_2.6H_2O$ solution, the cathodic efficiency obtained was relatively good (72.64%), but in the deposition two distinct zones were visible: a zone with a grayish color and a zone with a whitish color. This deposition did not show a good adhesion on the brass plate and after washing of the plate almost the entire deposition detached from the brass plate. In figure 5.5 images of the depositions obtained for these electrolytes are shown.

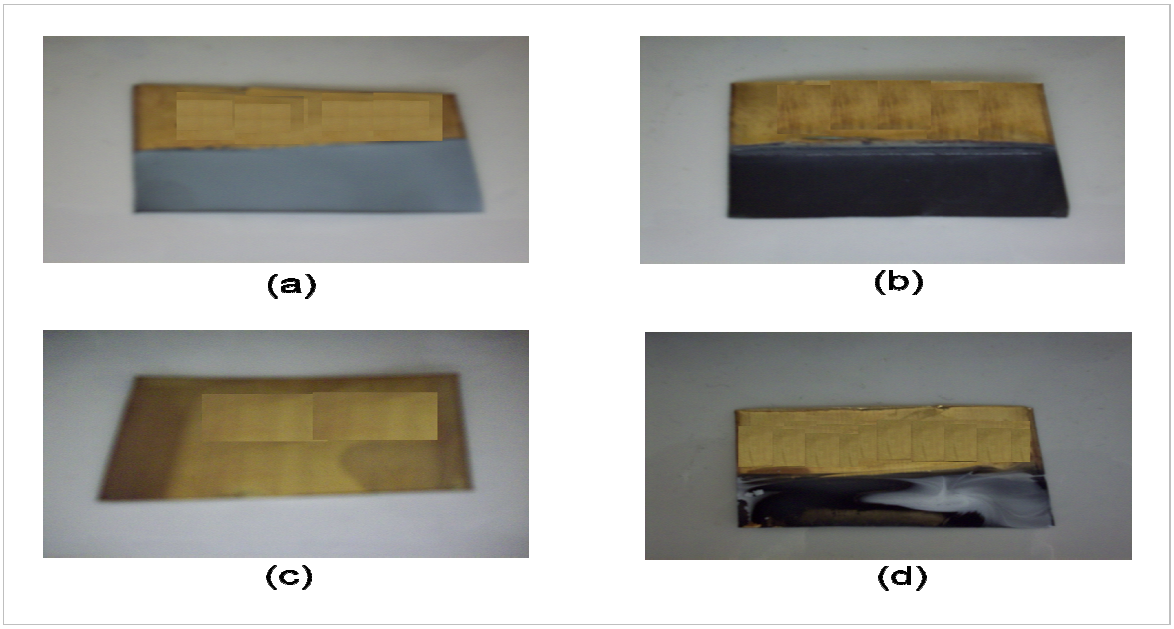


Figure 5.5 – Images of the deposition obtained in the parallel plate cell using as electrolyte: (a) 0.5 M $ZnSO_4.7H_2O$ in Ethaline200, (b) 0.5 M $ZnCl_2$ in Ethaline200, (c) 0.5 M ZnO in Ethaline200 and (d) 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200.

Figure 5.6 shows the cathodic efficiencies of the electrodeposition of zinc, for different electrolytes used in the hull cell. These experiments were performed at 50ºC, with a cell potential of 2.25V and an experiment time of 30 min.The experiments were done without stirring and with the brass plate placed at the slanted part of the hull cell. Because the deposition is not homogeneously spread over the surface of the electrode it is impossible to know the efficiency of the deposition at a specific location of the plate because the current densities varies with the angle of inclination of the plate

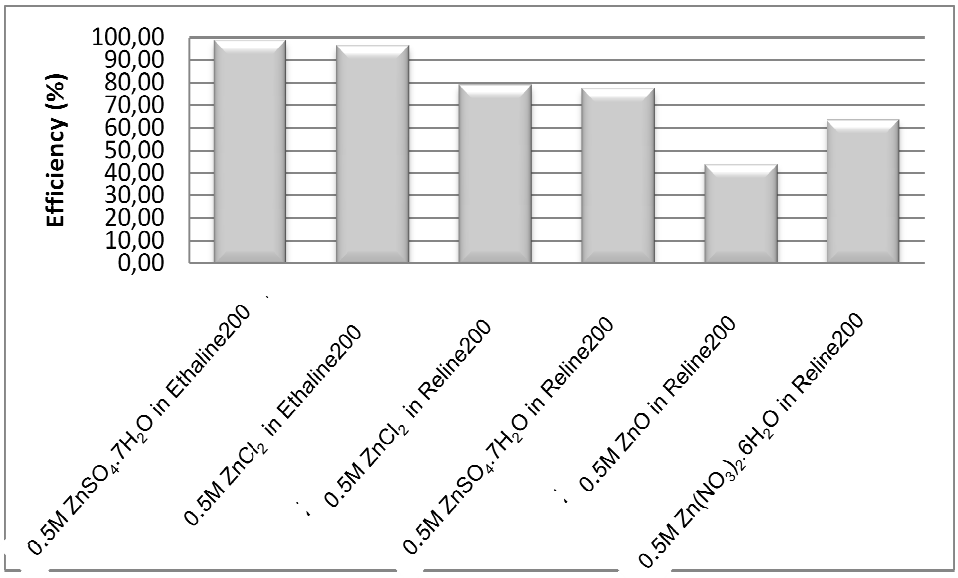


Figure 5.6– Cathodic efficiencies of zinc electrodeposition for the experiments performed in the hull cell with the brass plate in the slanted part.

The experiments performed for this set-up were done in two different solutions: Ethaline200 based solutions and Reline200 based solutions. The best cathodic efficiencies were found for the Ethaline200 based solutions, being that for 0.5 M $ZnSO_4.7H_2O$ an efficiency of 98.18% and for 0.5 M $ZnCl_2$ an efficiency of 95.84% was obtained. For both, the depositions obtained showed two distinct zones: the zone closest to the zinc plate shows a blackish deposition and the zone that was further from the zinc plate showed a grayish color. This means that there where the anode is closest to the cathode, the electrical resistance is lowest and consequently the current density at that location is higher, which causes a more intense deposition. At larger distances between anode and cathode, the resistance increases and the current density decreases. In this way distinct areas of deposition are obtained. The best, smooth electrodepositions of zinc are found at lower current densities.

For the Reline200 based solutions the cathode efficiencies obtained were: 78.37% for 0.5 M $ZnCl_2$, 76.86% for the 0.5 M $ZnSO_4.7H_2O$, 62.95% for the 0.5 M $Zn(NO_3)_2.6H_2O$ and 43.06% for the 0.5 M ZnO solution. The depositions obtained for $ZnCl_2$ and $ZnSO_4.7H_2O$ in Reline200 were smooth and better than the depositions obtained for the same salts in Ethaline200 solutions and present, as was expected, two distinct zones of deposition as well. For the ZnO solution, the deposition had a nearly black color. The deposition made in the $Zn(NO_3)_2.6H_2O$ solution was obviously bad, and as with the Ethaline200 solution, this deposition had a poor adhesion on the brass plate. Besides that, at the end of the experiment this solution contained black zinc particles in suspension. In figure 5.7 images are shown of the depositions obtained for these solutions.

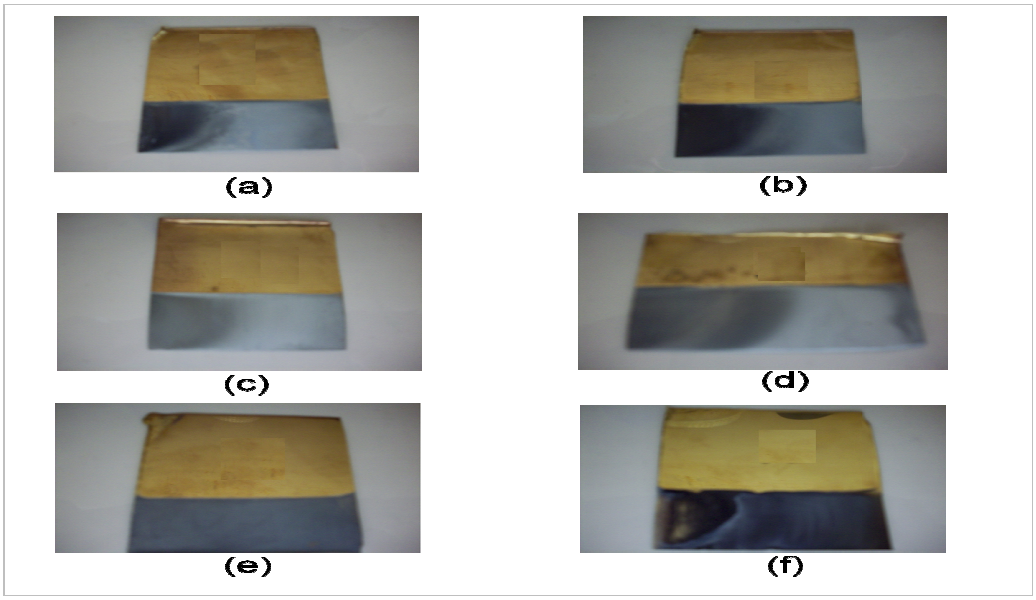


Figure 5.7 – Images of the deposition obtained in the hull cell with the brass plate in the slanted part using as electrolyte: (a) 0.5 M $ZnSO_4.7H_2O$ in Ethaline200, (b) 0.5 M $ZnCl_2$ in Ethaline200, (c) 0.5 M $ZnSO_4.7H_2O$ in Reline200, (d) 0.5 M $ZnCl_2$ in Reline200, (e) 0.5 M ZnO in Reline200 and (f) 0.5 M $Zn(NO_3)_2.6H_2O$ in Reline200.

The experiments in the hull cell were continued in the same conditions as before (50ºC, 2.25V, 30min and without stirring), but this time the zinc plate was positioned at the slanted part of the hull cell in order to check the efficiencies of dissolution (anodic efficiencies) of the zinc. The electrolytes used and the efficiencies for these experiments can be seen in figure 5.8.

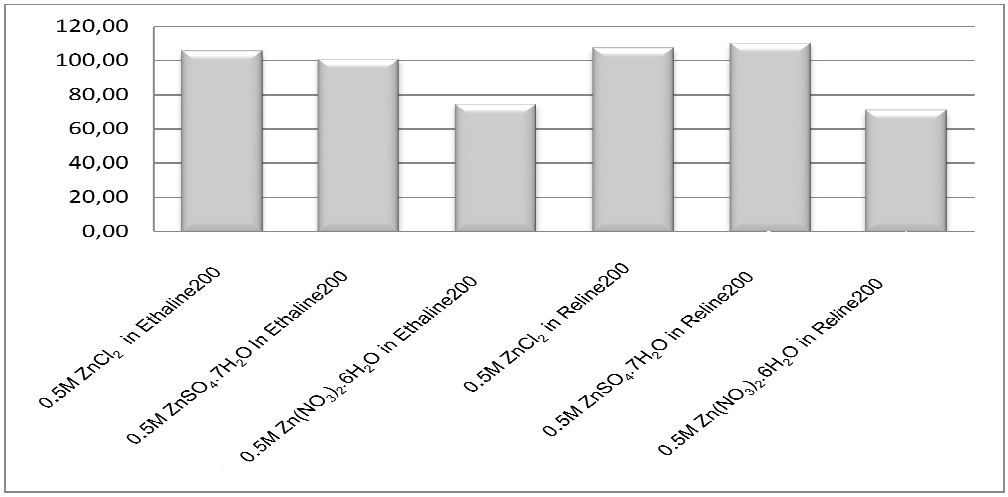


Figure 5.8 – Anodic efficiencies of zinc electrodeposition for the experiments performed in the hull cell with the zinc plate in the slanted part.

For this set-up Ethaline200 based solutions and Reline200 based solutions were used as well. The lowest efficiencies of dissolution were obtained for $Zn(NO_3)_2.6H_2O$, either in Ethaline200 (73.83%) as in Reline200 (70.52%). For $ZnSO_4.7H_2O$ anodic efficiencies of 100.20% were obtained for Ethaline200 solution and 109.65% for Reline200 solution. The efficiencies obtained for $ZnCl_2$ were 105.24% for Ethaline200 solution and 106.85% for Reline200 solution.

The anodic efficiencies obtained for $ZnCl_2$ and $ZnSO_4.7H_2O$ were higher than 100%, this may be due to small weighing errors.

After the experiments, the zinc plate always showed a blackish color. In figure 5.9 an image is shown of a zinc plate before and after the experiments.

Figure 5.9 – Images of the zinc plate: (a) before the experiments and (b) after the experiments.

Finally, from the study of the influence of the electrolyte in the zinc electrodeposition, it can be concluded that a solution of $Zn(NO_3)_2.6H_2O$ (Ethaline200 or Reline200) is not suitable for deposition of zinc because the results obtained with this solution are not satisfactory. Solutions of $ZnCl_2$ and $ZnSO_4.7H_2O$ are better for this purpose, because the qualitative and quantitative results obtained were good. Other experiments with different concentrations of these salts ($ZnCl_2$ and $ZnSO_4.7H_2O$) are to be performed to try optimize this process. Concerning the ZnO solutions, it is clear that these were always an emulsion. In order to solve this problem the study was extended by studying the influence of the addition of complexing agents on the quality and the efficiencies of the depositions.

5.1.4 Study of the influence of the addition of complexing agents

The study of the influence of the addition of complexing agents was performed for both cell types (parallel plate cell and hull cell) and just for the Ethaline200 based solutions. In the parallel plate cell the experiments were done in order to check the efficiencies of the deposition, whereas in the hull cell the experiments were performed with the purpose to find the efficiencies of dissolution. The substances that were used as complexing agents and their concentrations were: 0.5 M malic acid, 0.5 M citric acid and 0.5 M tartaric acid. All the experiments were performed at 50ºC, during 30 minutes and at an applied potential of 2.25V. The experiments in the parallel plate cell were done with stirring whereas in the hull cell the experiments were done without stirring and with the zinc occupying the slanted part of the cell. It is observed that after addition of any complexing agent, the ZnO solution turned from an emulsion to a homogeneous solution.

Figure 5.10 shows the efficiencies of deposition for the experiments performed in the parallel plate cell whereas figure 5.11 shows the efficiencies of dissolution for the experiments done in the hull cell.

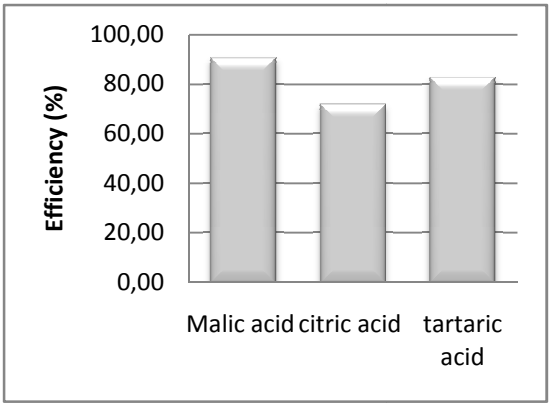


Figure 5.10 – Cathodic efficiencies of zinc electrodeposition for the experiments performed in the parallel plate cell for different complexing agents.

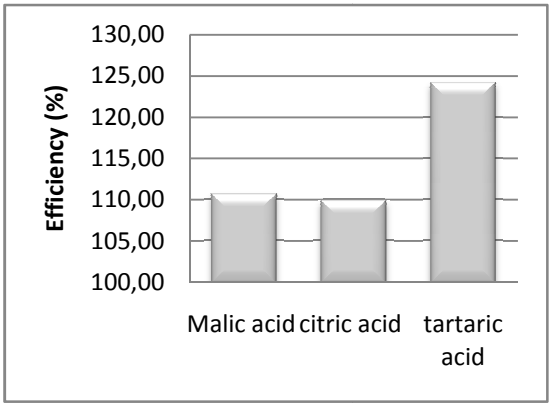


Figure 5.11 – Anodic efficiencies of zinc electrodeposition for the experiments performed in the hull cell for different complexing agents.

The best cathodic efficiency was obtained with addition of malic acid (89.97%). On addition of tartaric acid an efficiency of the deposition of 82.11% and for the citric acid a cathodic efficiency of 71.26% was obtained. Although the highest cathodic efficiency has been obtained after addition of malic acid, the appearance of the deposition was not the best. The best deposition was obtained after addition of tartaric acid (grayish color and smooth); the worst deposition was obtained after addition of citric acid (very dark). Figure 5.12 shows images of the depositions obtained during these experiments.

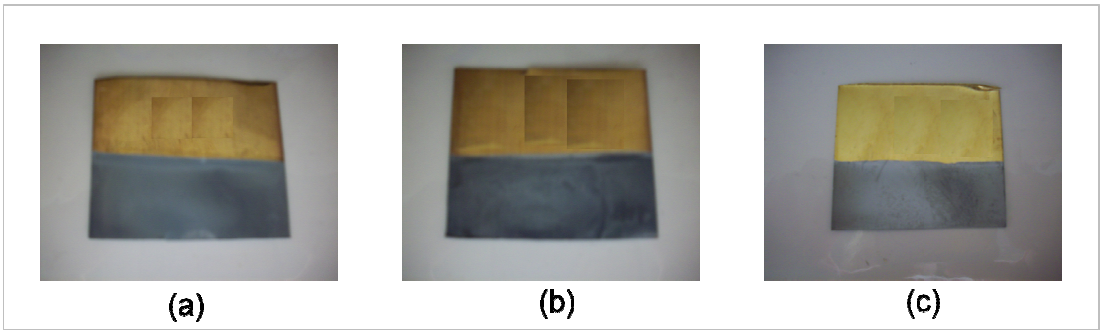


Figure 5.12 – Images of the deposition of zinc obtained using as complexing agents for the ZnO solutions in Ethaline200: (a) 0.5 M malic acid, (b) 0.5 M citric acid and (c) 0.5 M tartaric acid.

Concerning the anodic efficiencies, for all complexing agents, an efficiency higher than 100% was found. The explanation for this fact is discussed in section 5.1.3. The efficiency of dissolution obtained for malic acid was 110.56%, for citric acid 109.74% and for tartaric acid an anodic efficiency of 124.01% was obtained.

It is suggested to use tartaric acid as the complexing agent for the ZnO solutions in Ethaline200 because the deposition obtained with this electrolyte was quite good and the cathodic efficiency was relatively high.

5.1.5 Study of the influence of the temperature

The study of the influence of the temperature on the zinc electrodeposition was performed for both set-ups (parallel plate cell and hull cell) and for Ethaline200 and Reline200 based solutions. In the parallel plate cell experiments were done with 0.5 M $ZnCl_2$ in Ethaline200 and 0.5 M ZnO in Ethaline200, whereas in the hull cell 0.5 M $ZnSO_4.7H_2O$ in Etaline200 and 0.5 M $ZnCl_2$ in Reline200 were used as the electrolyte. Only the efficiencies of deposition were determined. This means that in the hull cell only experiments with the brass plate in the slanted part were performed. All the experiments were performed with a cell potential of 2.25V and with a duration of the experiment of 30 minutes. The experiments in the parallel plate cell were performed with stirring and in the hull cell without stirring. For

each electrolyte used two experiments were done at different temperatures, except for 0.5 M $ZnCl_2$ in Reline200 where three experiments where performed at different temperatures.

The aim of this study was not to compare the efficiencies of each electrolytic bath, but to know specifically for each electrolyte what the effect of the temperature on the deposition was and if some relation exists between the temperature and the cathodic efficiencies. In figure 5.13 the efficiencies of deposition obtained for 0.5 M $ZnCl_2$ in Ethaline200 at different temperatures are shown.

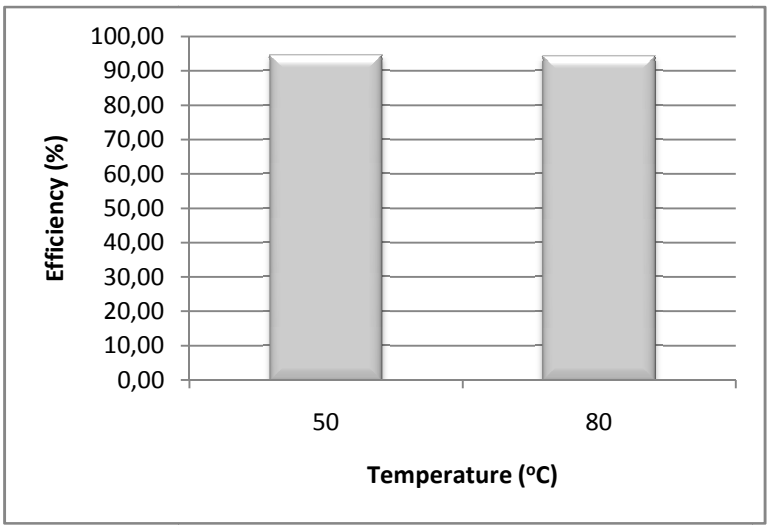


Figure 5.13 – Cathodic efficiencies for zinc electrodeposition at different temperatures with 0.5 M $ZnCl_2$ in Ethaline200 as the electrolyte in the parallel plate cell.

For 50ºC an efficiency of the deposition of 94.22% was obtained and for the experiment performed at 80ºC an efficiency of 93.98% was obtained. For both cases the deposition obtained was quite smooth and the only difference between them was that, for 50ºC the deposition presents a color a little bit more dark than for 80ºC. In this case, a temperature of 50ºC or a temperature of 80ºC is optimal to perform the zinc electrodeposition. Figure 5.14 shows images of the deposition obtained for each temperature.

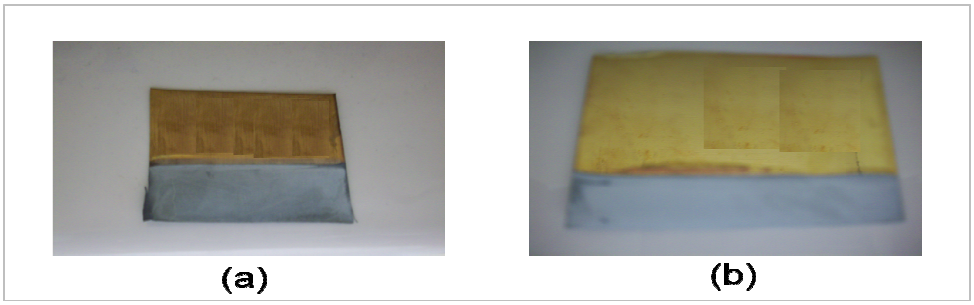


Figure 5.14 – Images of the deposition of zinc obtained with 0.5 M $ZnCl_2$ in Ethaline200 as the electrolyte for experiments performed at: (a) 50ºC and (b) 80ºC.

Figure 5.15 presents the cathodic efficiencies obtained for 0.5 M ZnO in Ethaline200 and at 50ºC and 75ºC.

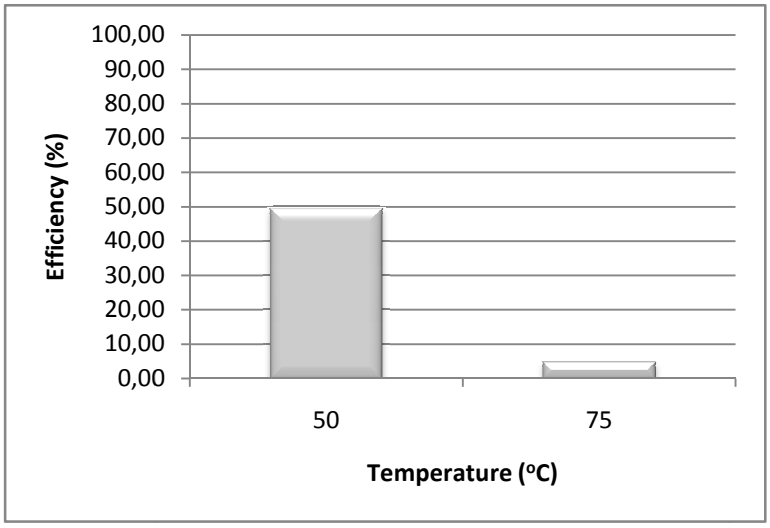


Figure 5.15 – Cathodic efficiencies for zinc electrodeposition at different temperatures using 0.5 M ZnO in Ethaline200 as electrolyte in the parallel plate cell.

For the experiment performed at 50ºC an efficiency of 49.04% and for the experiment performed at 75ºC an efficiency of 4.23% was obtained. The experiment performed at 75ºC was done with the purpose to check if the ZnO solution became a homogenous solution at higher temperatures, which did not happen. For both cases, and as happened before (section 5.1.3), there was no visible layer of zinc in the brass plate.

The efficiencies of deposition obtained for 0.5 M $ZnSO_4.7H_2O$ in Etaline200 for experiments done at 50ºC and 65ºC can be seen in figure 5.16.

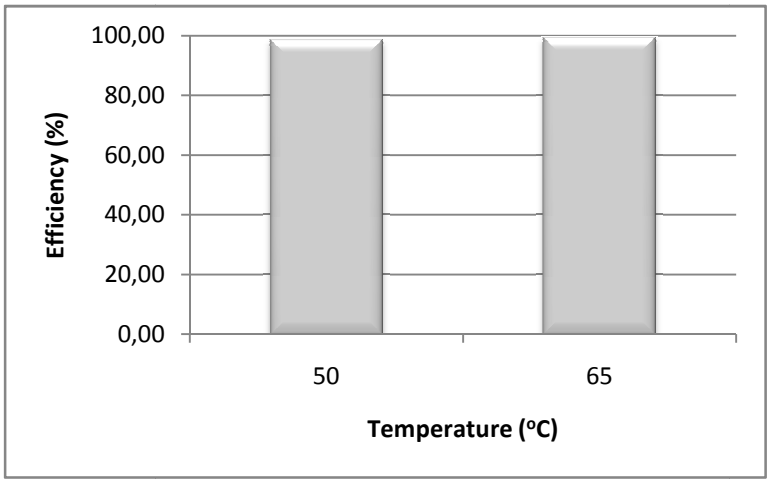


Figure 5.16 – Cathodic efficiencies for zinc electrodeposition at different temperatures using $ZnSO_4.7H_2O$ in Ethaline200 as the electrolyte in the hull cell.

For this electrolyte the efficiencies obtained were quite high independently of the temperature used to do the experiment. Efficiencies of 98.18% were obtained at 50ºC and 98.97% at 65ºC. The depositions that were obtained were smooth and a visible decrease of color grade was observed as the distance between the brass plate and the zinc plate increases. In figure 5.17 images of the depositions obtained for each temperature are shown.

Figure 5.17 – Images of the deposition of zinc obtained using 0.5 M $ZnSO_4.7H_2O$ in Ethaline200 as electrolyte for experiments performed at: (a) 50ºC and (b) 65ºC.

The results obtained for the experiments performed with 0.5 M $ZnCl_2$ in Reline200 at 50ºC, 60ºC and 65ºC can be seen in figure 5.18.

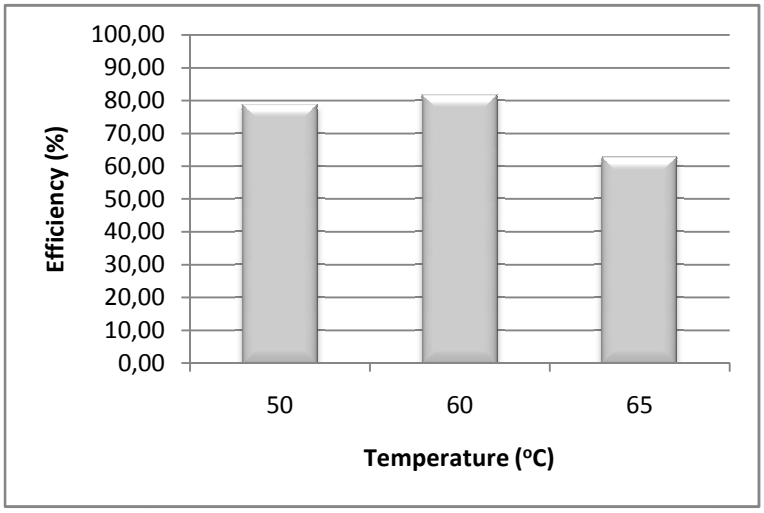


Figure 5.18 – Cathodic efficiencies for zinc electrodeposition at different temperatures using 0.5 M $ZnCl_2$ in Reline200 as electrolyte in the hull cell.

For this electrolyte, the best efficiency of the deposition was obtained at 60ºC (81.34%) and the worst for the experiment performed at 65ºC (62.32%). For the experiment done at 50ºC a cathodic efficiency of 78.37% was obtained. However, the worst deposition (dark) was obtained for the best efficiency of the deposition. For the other temperatures the

depositions obtained were similar (good deposition and smooth). The images of the depositions obtained for these experiments are shown in figure 5.19.

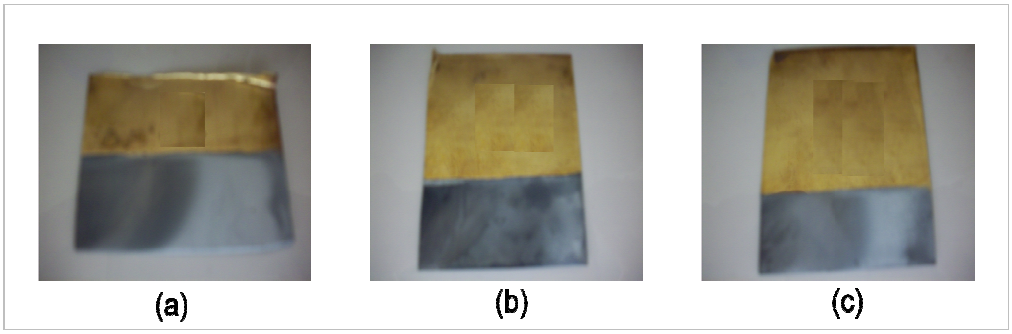


Figure 5.19 – Images of the deposition of zinc obtained using 0.5 M $ZnCl_2$ in Reline200 as the electrolyte for experiments performed at: (a) 50ºC, (b) 60ºC and (c) 65ºC.

Summarized, any electrolytic bath used (except ZnO) shows good depositions independently of the temperature. In the experiments performed in the hull cell, the depositions showed two distinct color zones (one bright and one dark). The dark depositions occur at high current densities and the bright depositions at low current densities.

With only two experiments for each electrolyte it was impossible to draw any conclusion about the variation of the efficiency with the temperature. Therefore, new experiments were performed in Reline200 at three different temperatures. Nevertheless it was impossible to draw any conclusion, because there was no linear relation between the temperature and the cathodic efficiency. It turns out the efficiency of the deposition behaves quite unpredictable in relation to the temperature.

5.1.6 Determination of the zinc concentration in the electrolyte

One of the important aspects in the study of the zinc electrodeposition was to know how the concentration of zinc varied in the electrolytic bath. The experiments were performed with two different electrolytes: 0.5M $Zn(NO_3)_2.6H_2O$ in Ethaline200 and 0.5 M ZnO + 0.5 M citric acid in Ethaline200. It can be stated that both solutions gave the worst depositions in all performed tests in this study (see sections 5.1.3 and 5.1.4). Then the concentration of zinc and the pH of the electrolyte were determined in order to check if these could have some influence on the results. The two experiments were performed in the parallel plate cell at 50ºC and with a cell potential of 2.25V. For the 0.5 M $Zn(NO_3)_2.6H_2O$ solution the experiment had been running over 4 hours and for the 0.5 M ZnO with 0.5 M citric acid solution the duration of experiment was 7 hours. In figure 5.20 the variation of the concentration of zinc over time for 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 is shown.

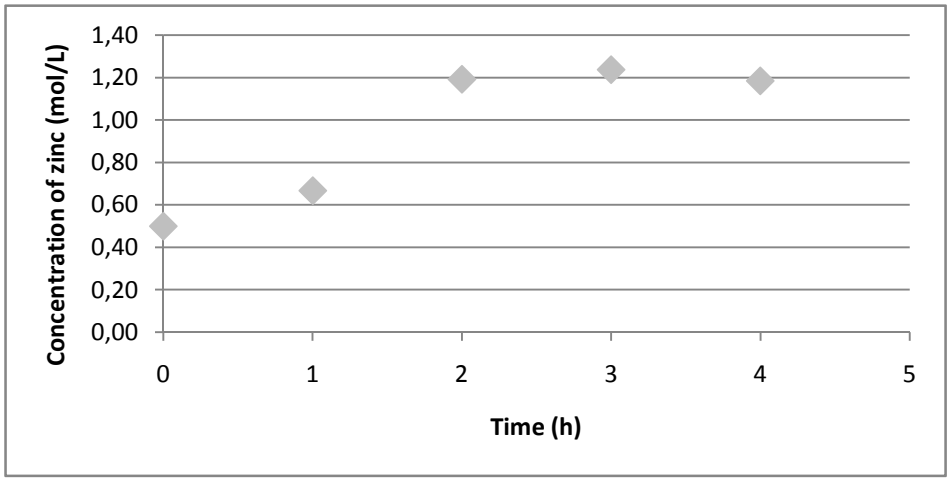


Figure 5.20 – Variation of the concentration of zinc over time for 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200.

The zinc concentration in the electrolyte increases for 2 hours and then reached a stable value of approximately 1.2 M of Zn. A mass balance was made in order to find out where the zinc is located: this is done by weighing anode and cathode at the end of each time interval and measuring the concentration in solution by AAS. Table 5.1 is shows the mass of zinc that really existed in solution (determined by AAS) and the expected mass of zinc in solution based on the mass balance (calculation - see appendix A.3.3) for different times.

Table 5.1 – Mass of zinc that really existed in 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 and mass of zinc that was supposed to exist in that solution for different times.

Time (h)	Real mass of zinc in the solution (g)	Expected mass of zinc in the solution (g)
0	6.5400	6.5400
1	8.6673	6.9909
2	15.4005	7.0770
3	15.8859	7.5276
4	15.1139	7.7099

For all time intervals it was verified that, taking in account the mass of dissolution at the anode and the mass of deposition at the cathode, more zinc than expected was present in the solution. This means that a great amount of zinc that dissolved stayed in the electrolyte instead of being deposited on the brass plate. Another explanation for this could be that organic compounds adhering on the electrodes are hard to remove from the plates even after washing, leading to weighing errors.

The pH, after 1 hour of experiment reached the value of 7.0 and remained so until the end of the experiment as can be seen in figure 5.21.

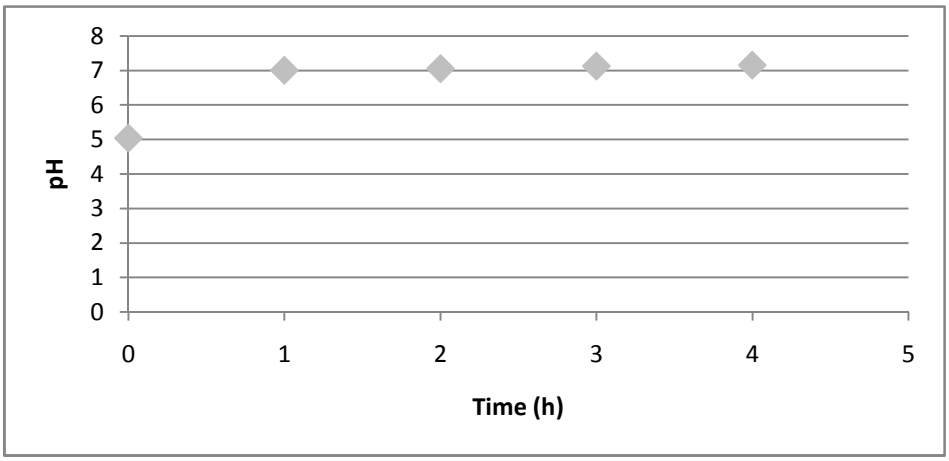


Figure 5.21 – pH variation over the time for 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200.

The deposition shows the same features than the depositions obtained for other experiments with the same electrolyte (see section 5.1.3). During the experiment the formation of bubbles closer to the brass plate was observed. The generation of these bubbles is ascribed to H_2 formation from the Ethaline200 or even from some water present in the electrolytic bath:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (10)$$

Eventually, some of the gas also might be formed because of the reduction of nitrate.

Figure 5.22 shows the variation of the zinc concentration over time for 0.5 M ZnO + 0.5 M citric acid in Ethaline200.

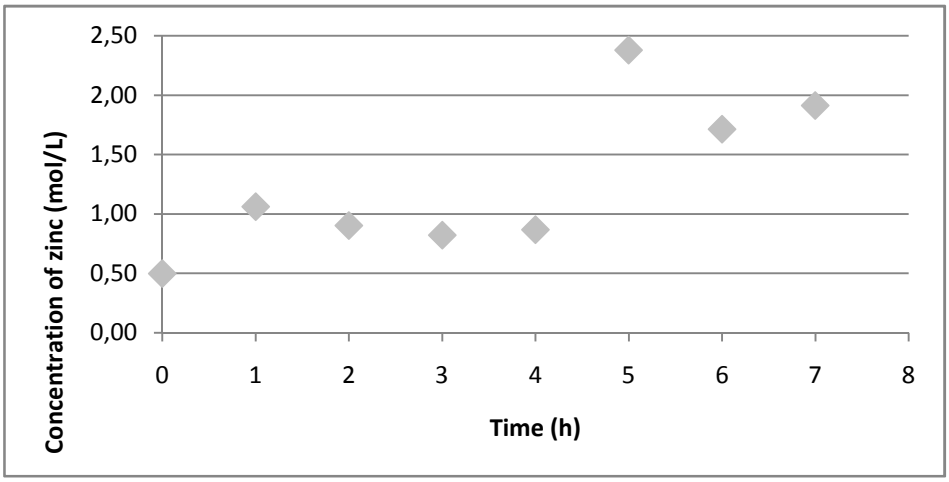


Figure 5.22 – Variation of the concentration of zinc over time for 0.5 M ZnO + 0.5M citric acid in Ethaline200.

The concentration of zinc in the electrolyte reached a maximum value of 2.40 M after 5 hours. Then, the concentration decreased further. In relation to the saturation concentration of zinc in the electrolytic solution no conclusions can be drawn because the concentration of

zinc did not reach a stable level, unlike with the solution of $Zn(NO_3)_2.6H_2O$. This experiment should have been done until the zinc concentration had reached a constant value, but due to the slow increase of the concentration and the increase of the viscosity to very high values, this was not done.

As been done for the previous solution, the content of the zinc in the solution was determined and compared to the expected value, in order to investigate if a solution with a stable zinc concentration could be obtained. The data of these determinations can be found in table 5.2.

Table 5.2 – Real mass of zinc in 0.5 M ZnO + 0.5 M citric acid in Ethaline200 and expected mass of zinc in that solution for different time intervals.

Time (h)	Real mass of zinc in the solution (g)	Expected mass of zinc in the solution (g)
0	6.5400	6.5400
1	13.7860	6.6416
2	11.6572	6.8879
3	10.5750	6.9668
4	11.0709	7.0851
5	30.1578	7.1396
6	21.6067	7.2177
7	23.9666	7.2730

For all time intervals the mass of zinc present in the solution was higher than the expected mass of zinc in the solution. This means that a great amount of zinc that was dissolved remained in the solution instead of being deposited, which is similar to the experiments with the $Zn(NO_3)_2.6H_2O$ solution.

The pH of the solution remained stable for 4 hours (value of approximately 3.9) and after that it increased to 6.0, as can be seen in figure 5.23. Note that the pH of the solution began to rise simultaneous with the zinc concentration.

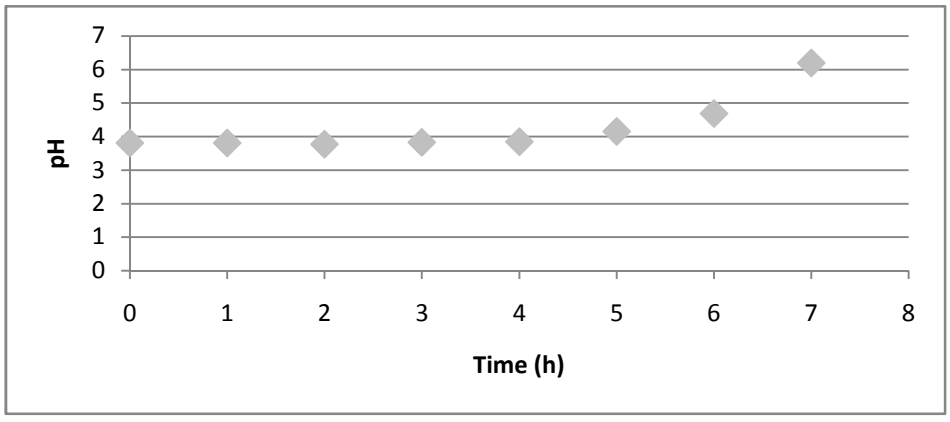


Figure 5.23 – pH variation over the time for 0.5 M ZnO + 0.5 M citric acid in Ethaline200.

The deposition was similar with the depositions obtained for other experiments performed with the same electrolytic bath (see section 5.1.4).

5.1.7 Cyclic voltammetry analyses

After the study of the zinc electrodeposition the solutions of 0.5 M $ZnCl_2$ in Ethaline200 and 0.5 M $ZnCl_2$ in Reline200 were analyzed by cyclic voltammetry (CV) at room temperature. The electrodes used for these determinations were: platinum (diameter = 1mm) as the working electrode, 0.01 M $AgNO_3$ + 0.1 M kryptofix22 / Ag in acetonitrile as reference electrode and a D.S.A as counter electrode. Figure 5.24 shows a cyclic voltammogram of 0.5 M $ZnCl_2$ in Ethaline200.

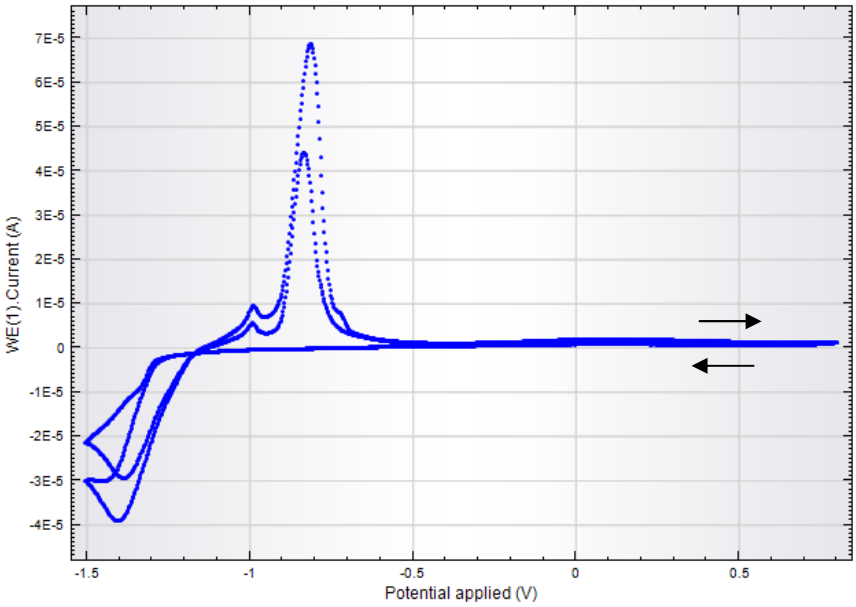


Figure 5.24 – A cyclic voltammogram of 0.5 M $ZnCl_2$ in Ethaline200 using a 1 mm diameter platinum disk as working electrode, 0.01 M $AgNO_3$ + 0.1 M kryptofix22 / Ag in acetonitrile as reference electrode and D.S.A. as counter electrode

As can be seen in figure 5.24, starting from positive potentials (+ 1.0 V) the Zn^{2+} is reduced to Zn around -1.4 V. On reversal, firstly a small peak appears that probably corresponds to oxidation of some reduced products presents in the solution and then a sharp stripping peak appears; this peak is related with the oxidation and dissolution of Zn to Zn^{2+}. The reduction of zinc occurs at potentials between -1.2V and -1.45V and the oxidation of zinc occurs between -0.9V and -0.8V.

In figure 5.25 a cyclic voltammogram of 0.5 M $ZnCl_2$ in Reline200 is shown.

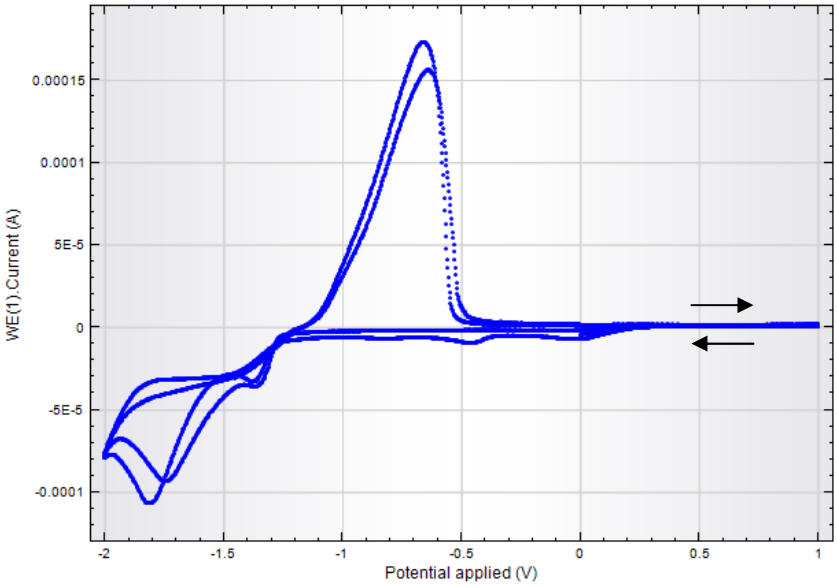


Figure 5.25 – A cyclic voltammogram of 0.5 M $ZnCl_2$ in Reline200 using a 1 mm diameter platinum disk as working electrode, 0.01 M $AgNO_3$ + 0.01 M kryptofix22 / Ag in acetonitrile as reference electrode and D.S.A. as counter electrode.

The graph in figure 5.25 shows firstly a reduction peak; there the Zn^{2+} is reduced to Zn (deposition of Zn). In the reverse way, a peak appears that corresponds to the oxidation of Zn to Zn^{2+}. The reduction of the zinc in this solution happens form -1.5V and the oxidation occurs between -1.1V and -0.6V.

In the Reline200 the zinc deposition occurs at more negative potentials than in Ethaline200.Tthe qualitative and quantitative results about the deposition of zinc are better in Ethaline200 solutions than in Reline200 solution.

5.2 Electrodeposition of tin

For the study of the electrodeposition of tin, all the electrolytic baths used were based on Ethaline200 solution. As the cathode a plate of brass was used and as anode a slice of tin. For this study, the efficiencies both cathodic and anodic were calculated taking into account that tin was oxidized or reduced with two electrons. The first set of experiments was performed in order to check the efficiencies and the depositions obtained for different electrolytes.

5.2.1 Study of the influence of the electrolytic bath used

For this study as electrolytes solutions of $Sn(OH)_2$, $SnCl_2$ and pure Ethaline200 were used. The $Sn(OH)_2$ solution was used with a concentration of 0.5 M whereas for the $SnCl_2$ two different concentrations were used: 0.5 M and 0.1 M. All the experiments were

performed at 50ºC, with a duration of 30 minutes and an applied cell potential of 2.25V, without stirring.

Firstly, and in order to determinate the cathodic efficiencies experiments were done with the brass plate occupying the slanted part of the hull cell. In figure 5.26 the efficiencies of the deposition for each electrolyte are presented.

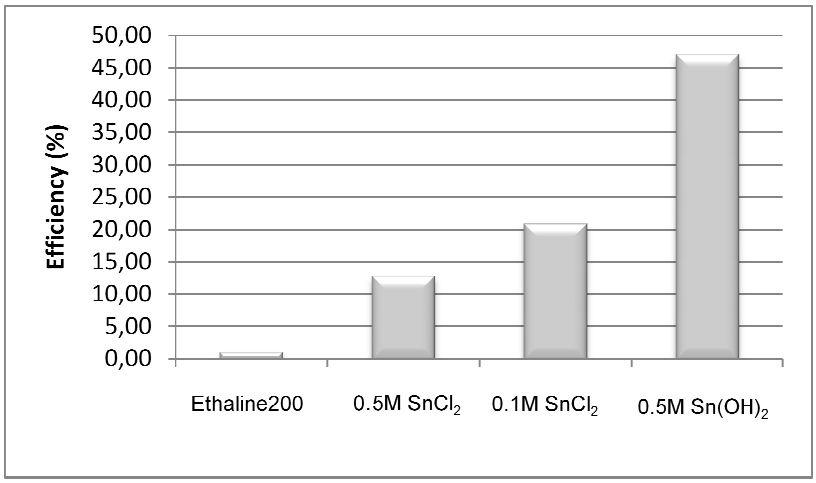


Figure 5.26– Cathodic efficiencies of tin electrodeposition for different electrolytes.

For the $SnCl_2$ solution, initially the experiment was done with a solution of a concentration of 0.5 M and the efficiency of the deposition was 12.65%; the deposition presented good features: very smooth and with a bright gray color. However, at the end of the experiment the existence of a great amount of tin dendrites was observed in the solution and on the brass plate. The formation of these dendrites indicates that the electrodeposition of tin occurs unhindered in this electrolyte. In order to try and solve this problem, the concentration of $SnCl_2$ in the solution was decreased to 0.1 M. In this case a cathodic efficiency of 20.75% was obtained, but the deposition was not so good as before. Moreover, the problem of the tin dendrites was not solved. In figure 5.27 an image of a deposition with tin dendrites is shown.

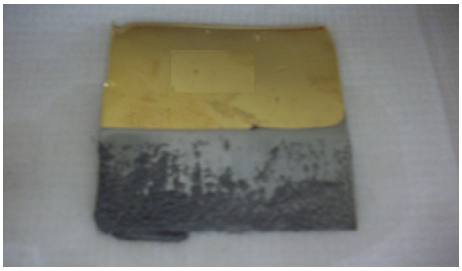


Figure 5.27– Image of the tin deposition with dendrites.

Another solution to try and overcome the problem of the dendrites was to use as electrolyte pure Ethaline200, which means that the only source of tin ions was the anodic dissolution from the slice of tin at the anode. For this experiment a cathodic efficiency of 0.87% was obtained. No deposition on the brass plate was observed.

With the $Sn(OH)_2$ solution an efficiency of 46.88% was obtained and the deposition showed a light dark color. Besides that, during the experiment the generation of bubbles close to the brass plate was checked (cfr. section 5.1.6). The solution was an emulsion showing at the end of the experiment a yellowish deposit at the bottom of the hull cell. In figure 5.28 images of the depositions for these experiments are shown.

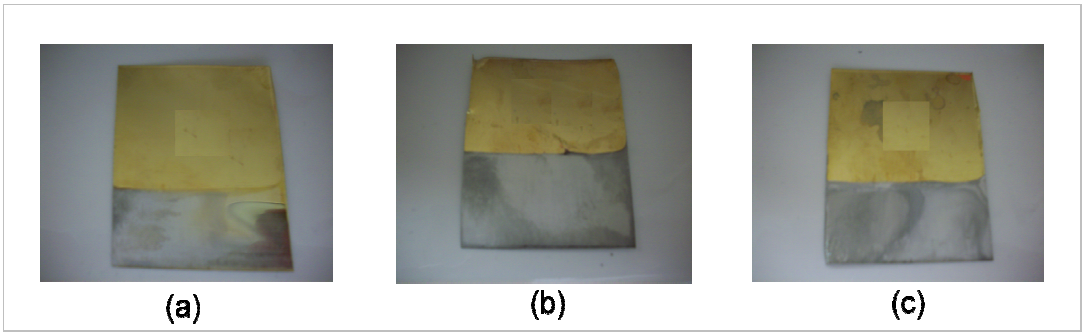


Figure 5.28 – Images of the deposition of tin using as electrolyte: (a) 0.5 M $SnCl_2$ in Ethaline200, (b) 0.1 M $SnCl_2$ in Ethaline200 and (c) 0.5 M $Sn(OH)_2$ in Ethaline200.

Although these experiments had been performed in the hull cell the decrease of color grade as a function of the distance between the brass plate and the slice of tin (anode), was not so pronounced as with the depositions of zinc.

For the determination of the anodic efficiencies for the tin electrodeposition a slice of tin was fixed in the slanted part of the hull cell. Only the efficiencies of the dissolution for the two solutions that gave the best cathodic efficiencies in previous experiments were determined. Figure 5.29 shows the anodic efficiencies for each electrolyte.

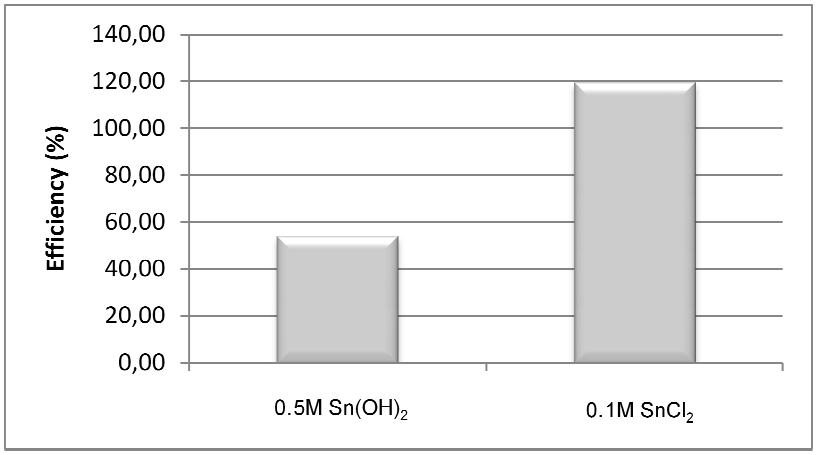


Figure 5.29– Anodic efficiencies of tin electrodeposition for different electrolytes.

For the $SnCl_2$ solution an efficiency of dissolution of 118.98% was obtained and for the $Sn(OH)_2$ an efficiency of 53.50% was obtained. The solution of $Sn(OH)_2$ was an emulsion and as in the previous experiment, at the end there was a yellowish precipitate at the bottom of the hull cell. In this experiment the generation of bubbles was also striking. For the $SnCl_2$ solution the only remark was the existence of tin dendrites in the solution and on the brass plate.

In summary, about the influence of the electrolytes for the tin electrodeposition it can be said that the pure Ethaline200 solution should not be used with this purpose because there was no deposition on the brass plate and the efficiency of deposition was low (practically zero), whereas the $SnCl_2$ solutions (both 0.1 M and 0.5 M) and the $Sn(OH)_2$ solutions are quite good for this electrodeposition. The main problem was, in the case of $Sn(OH)_2$ solution the fact that this solution was an emulsion and in the case of $SnCl_2$ solutions, the generation of tin dendrites in the solution occurred. So, to try and overcome these problems the influence of the addition of complexing agents was investigated as well as the study of the influence of the applied cell potential.

5.2.2 Study of the influence of the addition of complexing agents

To try and solve the aforementioned problems, citric acid and malic acid were added as complexing agents to the $Sn(OH)_2$ and $SnCl_2$ solution. The experiments done for this study were performed at 50ºC, with a duration of 30 minutes, without stirring and with an applied cell potential of 2.25V. Only the efficiencies of the deposition were calculated, which means that all the experiments were performed with the brass plate in the slanted part of the hull cell.

Firstly, the effect of the addition of complexing agents in the 0.5 M $SnCl_2$ solution was studied. Two experiments were done, one with the addition of 0.5 M citric acid and the other with the addition of 0.5 M malic acid. These substances were added to investigate if the generation of tin dendrites would disappear. Figure 5.30 shows the cathodic efficiencies for each complexing agent added to 0.5 M $SnCl_2$ solution.

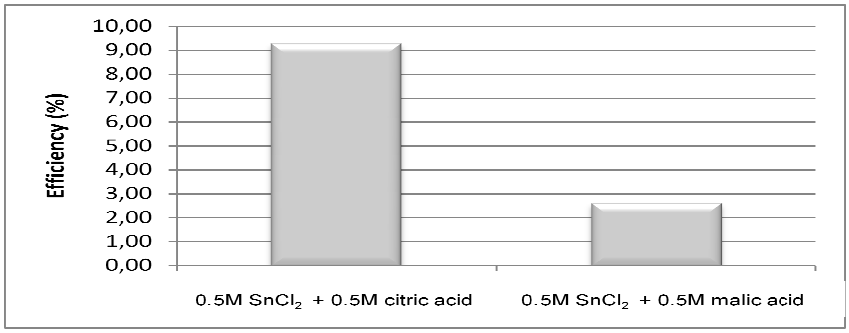


Figure 5.30– Cathodic efficiencies of tin electrodeposition for different complexing agents added to 0.5 M $SnCl_2$ in Etaline200.

For both cases the efficiencies of deposition were so much low; for the experiment where was added citric acid was obtained an efficiency of 9.23% and for the experiment with malic acid was obtained an efficiency of 2.56%. The depositions were similar between them, showing a bright gray color and an aspect very smooth. Unfortunately the problem of the tin dendrites was not resolved with the addition of these complexing agents and, in the end of the experiment performed with malic acid there was a whitish deposit in the bottom of the cell. In figure 5.31 is shown an image of the deposition for the experiment with the 0.5 M citric acid (as said before the deposition in the experiment with the malic acid was similar to the deposition in the experiment with citric acid).

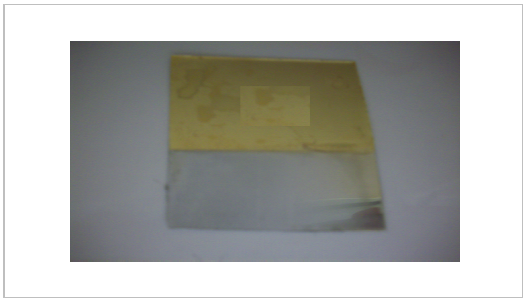


Figure 5.31– Image of the tin deposition for the experiment performed with 0.5 M $SnCl_2$ where 0.5M citric acid was added as complexing agent.

Then was studied the influence of the addition of complexing agents in 0.5 M $Sn(OH)_2$ solution in order to check if this solution became an homogeneous solution. For this effect were done two experiments, one with the addition of 0.5 M citric acid and the other with the addition of 0.5 M malic acid. In figure 5.32 is shown the cathodic efficiencies obtained for each experiment performed.

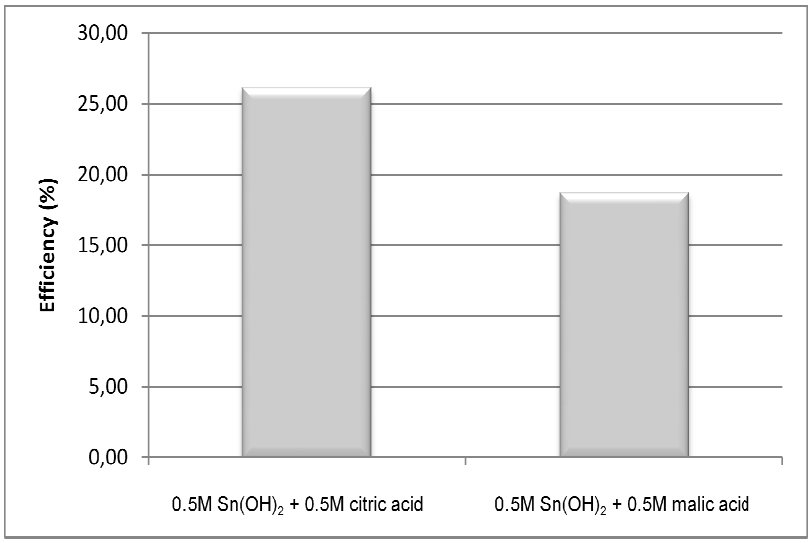


Figure 5.32– Cathodic efficiencies of tin electrodeposition for different complexing agents added to 0.5 M $Sn(OH)_2$ in Etaline200.

It was obtained a cathodic efficiency of 26.09% for the experiment performed with the citric acid and an efficiency of 18.66% for the experiment performed with the malic acid. The depositions for both experiments presented practically the same features (a bright gray color and smooth), the main difference between them was that in the deposition for the malic acid can be seen in the brass plate small areas without deposition. Figure 5.33 shows images of the deposition for each experiment.

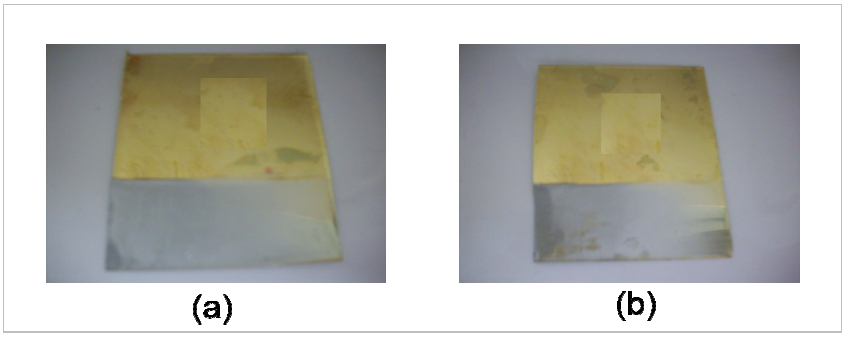


Figure 5.33– Images of the tin deposition for the experiment performed with 0.5 M $Sn(OH)_2$ where was added as complexing agent: (a) 0.5 M citric acid or (b) 0.5 M malic acid.

Even with the addition of these complexing agents the solution of $Sn(OH)_2$ did not become homogeneous and there was still the yellowish deposit at the bottom of the hull cell. Besides that, it was striking and for the first time for this solution, the generation of tin dendrites in the solution was observed. Then it was decided to reduce the concentration of $Sn(OH)_2$ to 0.1 M and two more experiments were done where the same complexing agents was added but with a different concentration (0.8 M citric acid and 0.8 M malic acid). The results for these experiments can be seen in figure 5.34.

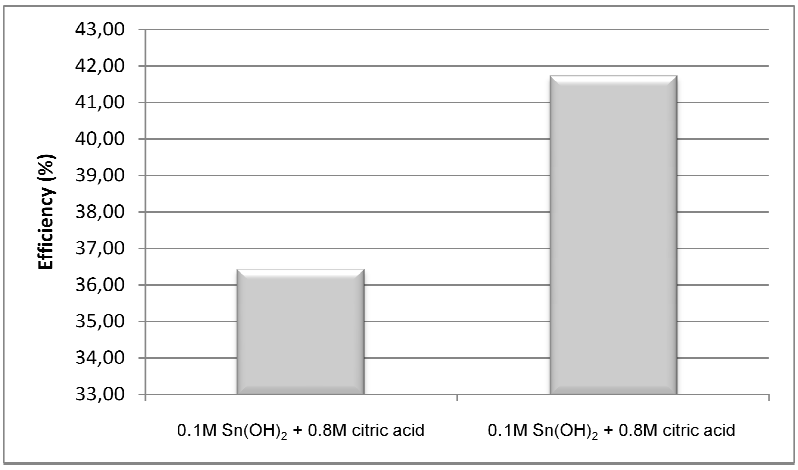


Figure 5.34– Cathodic efficiencies of tin electrodeposition for different complexing agents added to 0.1 M $Sn(OH)_2$ in Etaline200.

For the experiment where the citric acid was added an efficiency of deposition of 36.41% was obtained and for the experiment performed with the addition of malic acid an efficiency of 41.70% was obtained. The depositions for these experiments were better than the depositions for the experiments where complexing agents were added to the 0.5 M $Sn(OH)_2$ solution. In figure 5.35 images of the depositions are shown.

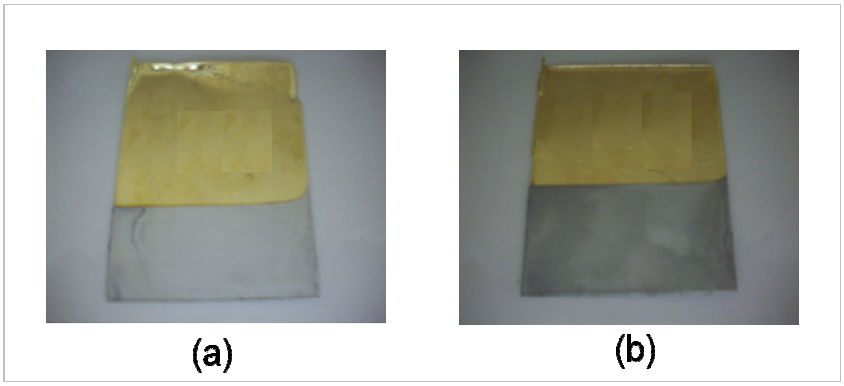


Figure 5.35– Images of the tin deposition for the experiment performed with 0.1 M $Sn(OH)_2$ where (a) 0.8 M citric acid or (b) 0.8 M malic acid were added as complexing agent.

Even with the decrease of the concentration of the $Sn(OH)_2$ and with the increase of the concentration of the complexing agents, the solutions were still an emulsion for both cases. The yellowish precipitate at the bottom of the cell remains. In these conditions there was no formation of tin dendrites.

Then, in a last attempt to obtain a homogeneous $Sn(OH)_2$ solution, more two experiments were performed where the concentration of malic acid was decreased to 0.1 M or 0.05 M. Malic acid was chosen in these experiments because it gave the best results in the previous experiments. In figure 3.36 the cathodic efficiencies for these experiments are shown.

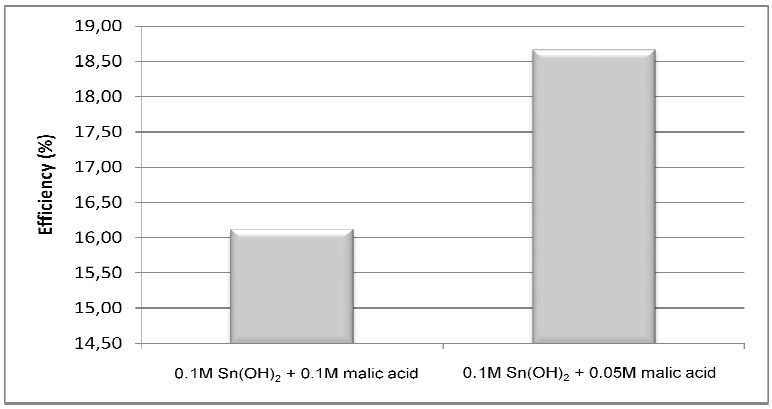


Figure 5.36– Cathodic efficiencies of tin electrodeposition for different concentrations of malic acid added as complexing agent to 0.1 M $Sn(OH)_2$ in Ethaline200.

A cathodic efficiency of 16.11% was obtained for the experiment with 0.1 M malic acid and a cathodic efficiency of 18.65 for the experiment with 0.05 M malic acid. The deposition for the experiment with the lowest concentration of malic acid was not good, showing a small zone where there was no deposition. In figure 5.37 images are shown of the depositions for both experiments.

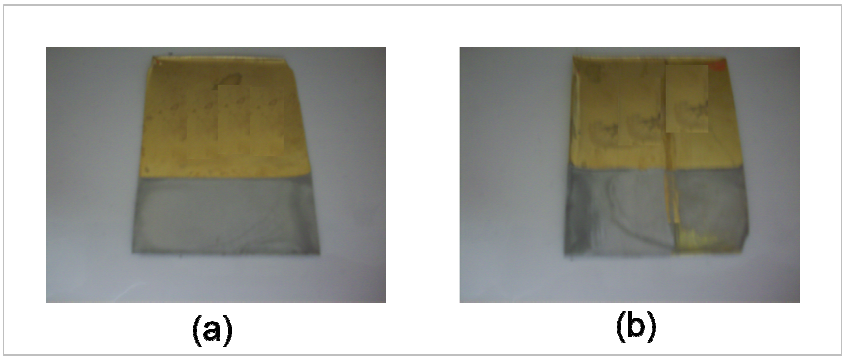


Figure 5.37– Images of the tin deposition for the experiment performed with 0.1 M $Sn(OH)_2$ where (a) 0.1 M malic acid or (b) 0.05 M malic acid was added as complexing agent.

The solution still turned into an emulsion at the end of the experiments with the same yellowish precipitate and in both experiments the formation of tin dendrites was striking.

In summary about the influence of the addition of complexing agents it can be said that independently of the complexing agent and its concentration added to the $Sn(OH)_2$ solution, the emulsion always occurred. The best depositions were obtained when the concentration of the complexing agent was higher than the concentration of the tin in solution; in these conditions there was no formation of tin dendrites, so it can be stated that the generation of tin dendrites could be avoided by adding an excess of complexing agent.

5.2.3 Study of the influence of the applied cell potential

As explained before the generation of tin dendrites could be due to a high concentration of tin in the electrolyte or, because of an unhindered reduction of Sn (II) at high applied cell potentials that allows a very fast reduction of Sn(II) to Sn(0) at the brass plate. Therefore, experiments were done with all the electrolytes that led to the formation of tin dendrites in previous experiments (performed at 2.25V), but this time the experiments were performed with an applied cell potential of 0.82V. All the experiments were done in the hull cell at 50ºC, during 30 minutes and without stirring.

The first experiments were done with the aim to calculate the cathodic efficiencies, which means that the brass plate was in the slanted part of the hull cell. In figure 5.38 the results are shown for the $SnCl_2$ solutions at potentials of 0.82V and 2.25V.

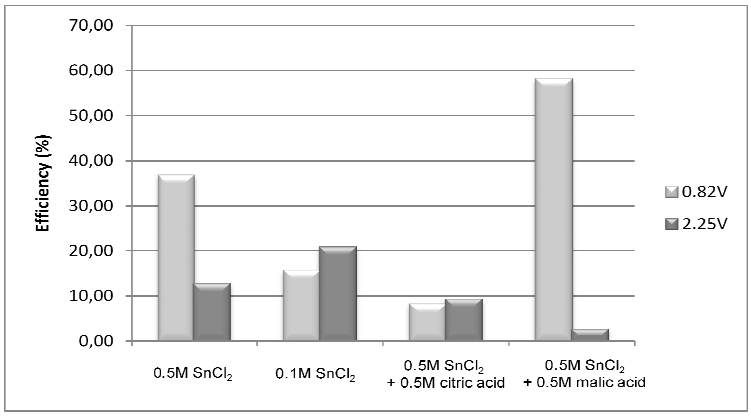


Figure 5.38– Cathodic efficiencies of tin electrodeposition for different electrolytic baths based on $SnCl_2$ and for different applied cell potential.

For the potential of 0.82V an efficiency of 36.75% was obtained for 0.5 M $SnCl_2$, 15.63% for 0.1 M $SnCl_2$, 8.18% for 0.5 M $SnCl_2$ with 0.5 M citric acid and 58.06% for 0.5 M $SnCl_2$ with 0.5 M malic acid. For the potential of 2.25V an efficiency of 12.65% was obtained for 0.5 M $SnCl_2$, 20.75% for 0.1 M $SnCl_2$, 9.23% for 0.5 M $SnCl_2$ with 0.5 M citric acid and 2.56% for 0.5 M $SnCl_2$ with 0.5 M malic acid.

The best depositions were obtained for the experiments performed at 2.25V. The experiment performed at 0.82V with 0.1 M $SnCl_2$ as electrolyte was the only experiment where there were no dendrites of tin on the brass plate or in the solution. For the experiment performed with 0.5 M $SnCl_2$ plus 0.5 M malic acid a whitish precipitate was visible at the bottom of the cell for both potentials. In figure 5.39 images of the depositions are shown.

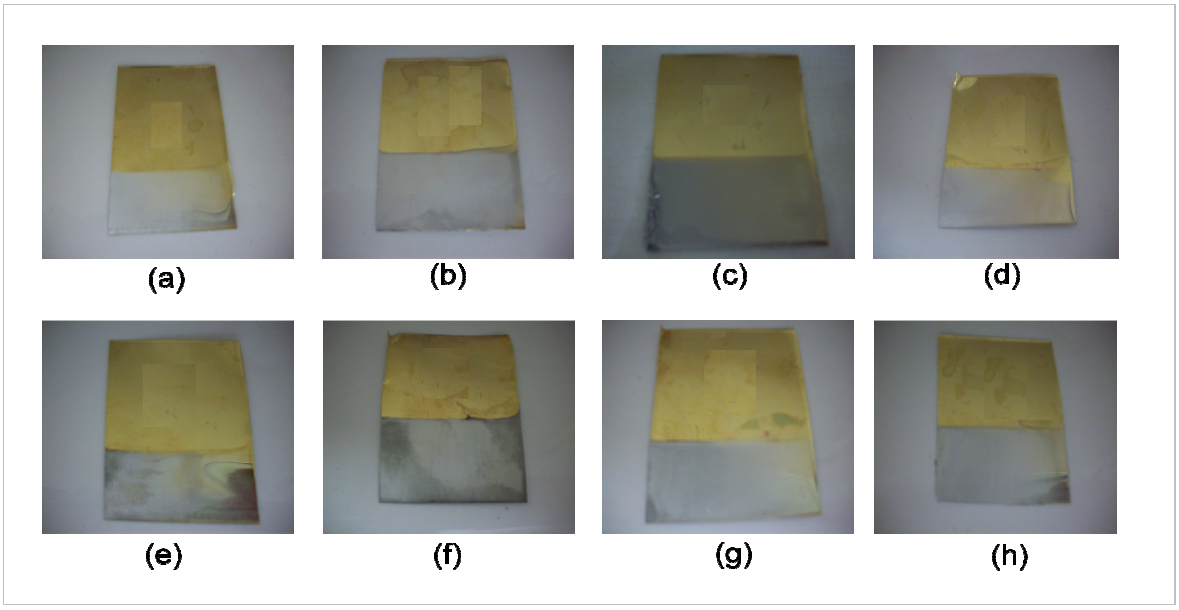


Figure 5.39– Images of the tin deposition for the experiment: (a) at 0.82V with 0.5 M $SnCl_2$, (b) at 0.82V with 0.1 M $SnCl_2$, (c) at 0.82V with 0.5 M $SnCl_2$ plus 0.5 M citric acid, (d) at 0.82V with 0.5 M $SnCl_2$ plus 0.5 M malic acid, (e) at 2.25V with 0.5 M $SnCl_2$, (f) at 2.25V with 0.1 M $SnCl_2$, (g) at 2.25V with 0.5 M $SnCl_2$ plus 0.5 M citric acid and (h) at 2.25V with 0.5 M $SnCl_2$ plus 0.5 M malic acid.

Following, experiments were performed for the $Sn(OH)_2$ solutions and the results for both potentials can be seen in figure 5.40.

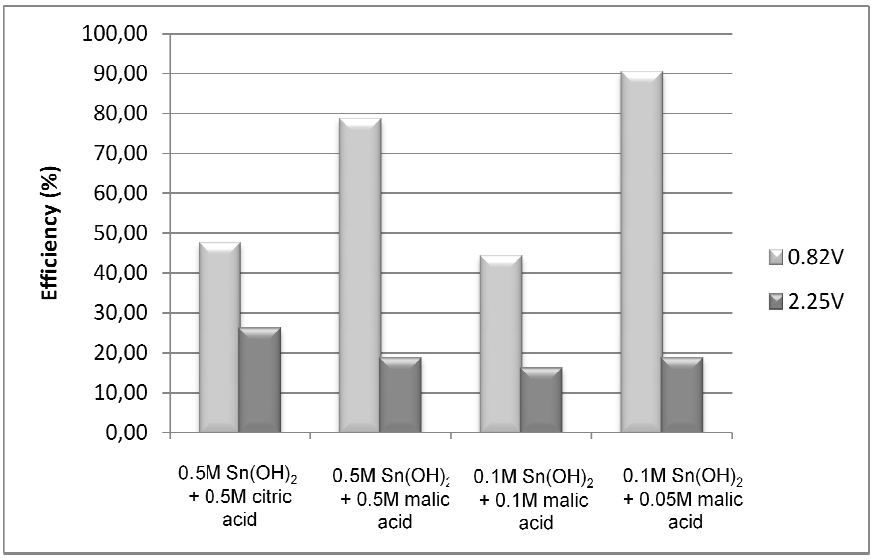


Figure 5.40– Cathodic efficiencies of tin electrodeposition for different electrolytic baths based on $Sn(OH)_2$ and for different applied cell potential.

For these solutions the cathodic efficiencies were higher for the experiments performed at 0.82V than for the experiments performed at 2.25V. For the solution of 0.5 M $Sn(OH)_2$ with 0.5 M citric acid an efficiency of 26.09% was obtained for the experiment performed at 2.25V and 47.48% for the experiment performed at 0.82V; for the solution of 0.5 M $Sn(OH)_2$ with 0.5 M malic acid an efficiency of 18.66% was obtained for the experiment at 2.25V and 78.55% for the experiment at 0.82V; for the solution of 0.1 M $Sn(OH)_2$ with 0.1 M malic acid an efficiency of 16.11% was obtained for the experiment at 2.25V and 44.19% for the experiment at 0.82V; and finally for the solution of 0.1 M $Sn(OH)_2$ with 0.05 M malic acid an efficiency of 18.65% was obtained for the experiment at 2.25V and 90.32% for the experiment at 0.82V.

The best depositions were obtained for the experiments performed at 0.82V and for all the experiments performed at 2.25V small areas without any deposition were visible on the brass plate. In figure 5.41 images of the depositions for these experiments are shown.

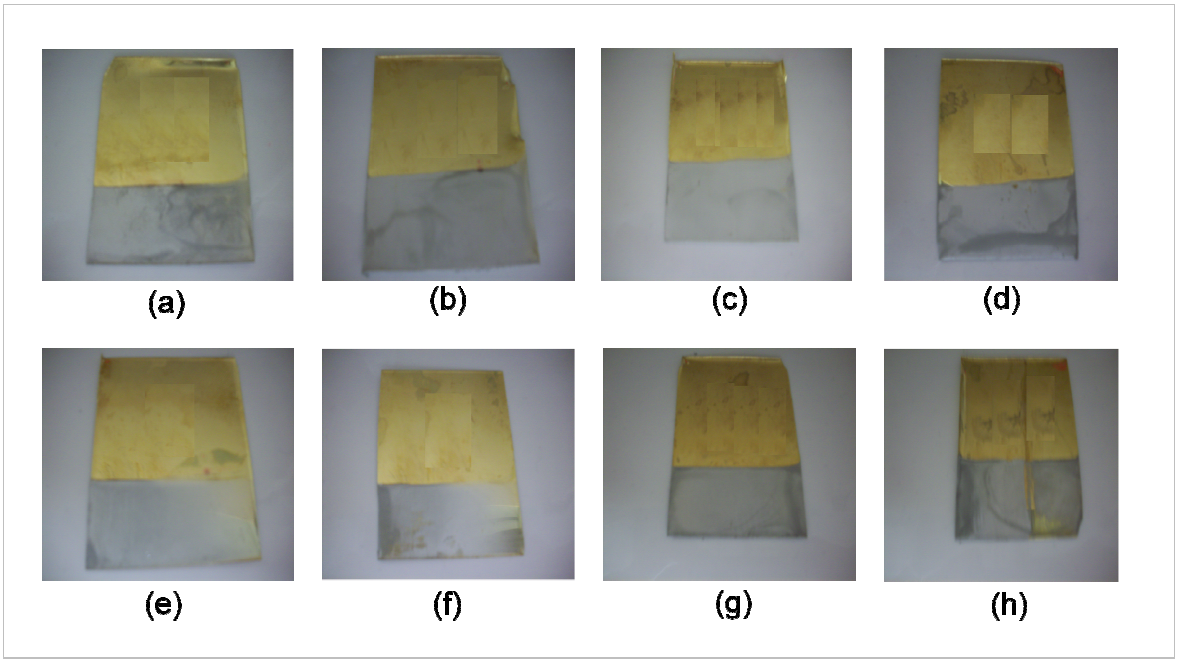


Figure 5.41– Images of the tin deposition for the experiment: (a) at 0.82V with 0.5 M $Sn(OH)_2$ plus 0.5 M citric acid, (b) at 0.82V with 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid, (c) at 0.82V with 0.1 M $Sn(OH)_2$ plus 0.1 M malic acid, (d) at 0.82V with 0.1 M $Sn(OH)_2$ plus 0.05 M malic acid, (e) at 2.25V with 0.5 M $Sn(OH)_2$ plus 0.5 M citric acid, (f) at 2.25V with 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid, (g) at 2.25V with 0.1 M $Sn(OH)_2$ plus 0.1 M malic acid and (h) at 2.25V with 0.1 M $Sn(OH)_2$ plus 0.05 M malic acid.

All the solutions used in previous experiments were emulsions. Only for the solution of 0.1 M $Sn(OH)_2$ with 0.05 M malic acid performed at 0.82V there was no generation of tin dendrites.

With the purpose to determinate the anodic efficiencies, the slice of tin was put in the slanted part of the hull cell and the efficiencies for the following solutions were calculated: 0.5 M $Sn(OH)_2$ with 0.5 M malic acid, 0.1 M $Sn(OH)_2$ with 0.1 M malic acid and 0.1M $Sn(OH)_2$ with 0.05 M malic acid. The efficiencies were only determined for experiments performed at 0.82V. In figure 5.42 the anodic efficiencies for these experiments are shown.

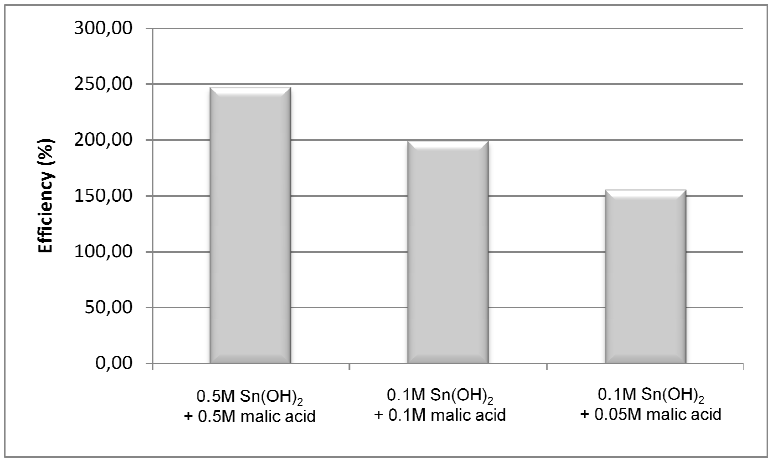


Figure 5.42– Anodic efficiencies of tin electrodeposition for different electrolytic baths based on $Sn(OH)_2$.

For the solution of 0.5 M $Sn(OH)_2$ with 0.5 M malic acid an anodic efficiency of 245.94% was obtained; for the solution of 0.1 M $Sn(OH)_2$ with 0.1 M malic acid an efficiency of 198.16% was obtained and for the solution of 0.1 M $Sn(OH)_2$ with 0.05 M malic acid an efficiency of deposition of 154.09% was obtained. As referred before, the values > 100% for anodic efficiencies can be due to weighing errors. However the values found at this time were high compared with other values found until now. This suggests that there might also be chemical dissolution of tin occurring simultaneously with the electro-dissolution. Therefore, it was investigated if and to what extent chemical dissolution of tin occurs.

5.2.4 Study of the chemical dissolution of tin

For this study experiments at 50ºC were performed in the parallel plate cell with stirring of the solution. The solutions which were found to have high anodic efficiencies in previous experiments (0.1 M $SnCl_2$ and 0.5 M $Sn(OH)_2$ with 0.5 M malic acid) were used; experiments with the 0.5 M $Sn(OH)_2$ were performed as well, because in these conditions an efficiency of dissolution bellow 100% was found in earlier experiments. For the first experiments a plate of brass and a slice of tin were placed in the solution.

Initially, an experiment was performed for each solution with a duration of 30 minutes (the same time used for the experiments performed for the electrochemical study). The anodic and cathodic efficiencies for these experiments were 0.00%, which means that there was no dissolution or deposition of tin.

As for the experiments performed with the duration of 30 minutes there was no dissolution of tin. One more experiment was done for each solution where the duration of the experiment was increased to 17 hours. Nevertheless, the anodic and cathodic efficiencies were still 0.00% and there was no dissolution or deposition of tin.

One more experiment was done with the 0.1 M $SnCl_2$ solution, but this time only a plate of tin was used in the parallel plate cell and the experiment was running over 22 hours. This experiment was performed with the aim to check if the tin present in the solution would be deposited chemically on the brass plate. At the end of the experiment the brass plate had lost a bit weight (0.0013 g), which means that some zinc or copper from the brass alloy had dissolved chemically into the solution. Possibly the small amount of the brass plate that had dissolved can be ascribed to the dissolution of the tiny metal oxide layer residing at the surface of the brass plate. Again, there was no deposition of tin on the brass plate.

It can be concluded that there was no chemical dissolution of tin in these experiments. Therefore, the high anodic efficiencies obtained for the electro-dissolution of tin can not be explained by the chemical dissolution of tin. The main reason for the efficiencies greater than 100% is still unknown.

5.2.5 Determination of the tin concentration in the electrolyte

The determination of the concentration of tin in the electrolyte experiments was performed in two different electrolytes: pure Ethaline200 and Ethaline200 with 0.1 M K_3-HEDTA as complexing agent. The experiments were performed at 50ºC in the parallel plate cell with agitation. With the pure Ethaline200 two experiments were done, one with an applied cell potential of 0.82V and with a duration of 6 hours and another with an applied cell potential of 2.25V and with a duration of 8 hours. For the Ethaline200 with 0.1 M K_3-HEDTA initially a potential of 2.25V was applied and after 43 hours the potential was changed to 6.4V. This experiment had a total duration of 130 hours. The Ethaline200 solution was chosen for this study because in earlier experiments (with a duration of 30 minutes), there was no tin deposition on the brass plate. Then, experiments were performed with longer duration of the experiments (more than 30 minutes) where it was checked how the concentration of tin varied over time in the solution. In figure 5.43 the variation of tin concentration over time for the experiment performed with Ethaline200 at 0.82V is shown.

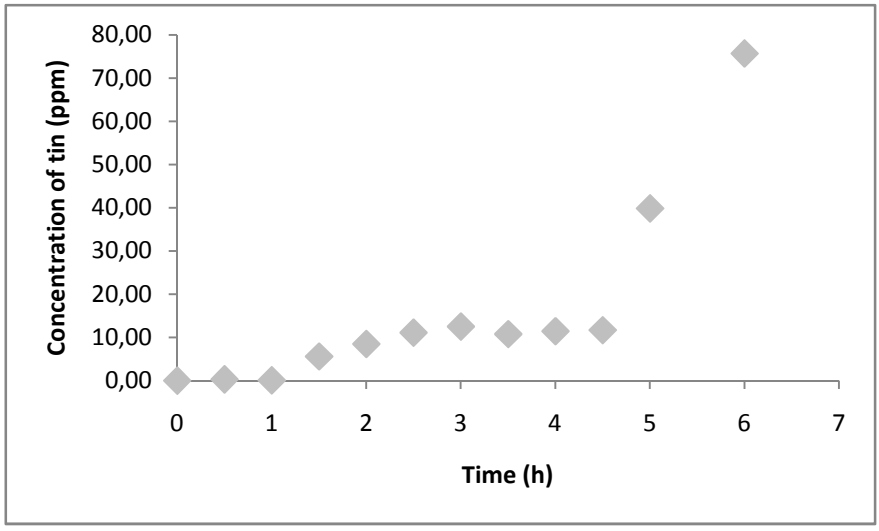


Figure 5.43 – Variation of the concentration of tin over time for the experiment performed at 0.82V and using pure Ethaline200 as electrolyte.

The concentration of tin in the electrolytic bath increased slowly until approximately 4.5 hours of experiment. After this time the concentration of tin increased sharply until the end of the experiment. At the end of 6 hours still no stable level of the tin concentration was reached in the electrolyte and there was no deposition on the brass plate, so it was decided to stop with this experiment and to restart with an applied cell potential of 2.25V. Figure 5.44 shows the variation of the concentration of tin over time for the experiment performed at 2.25V.

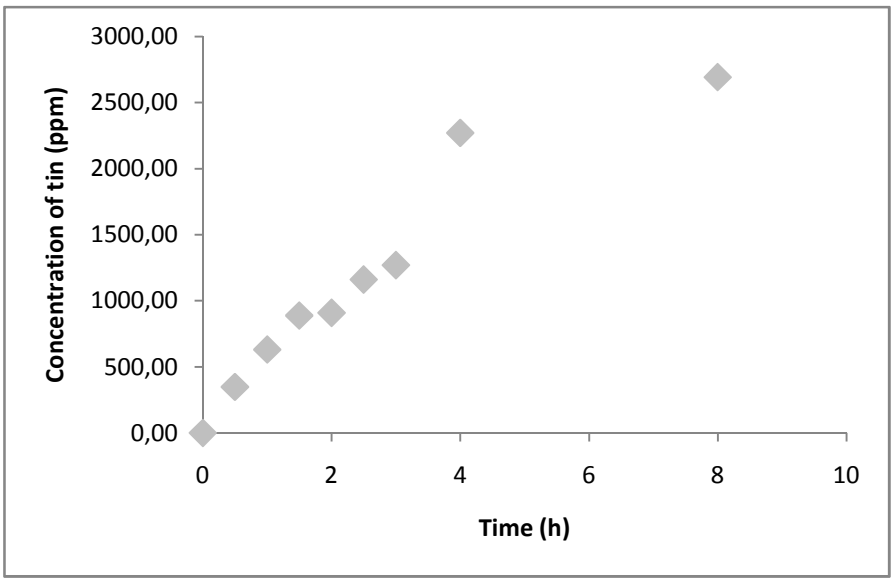


Figure 5.44 – Variation of the concentration of tin over time for the experiment performed at 2.25V and using pure Ethaline200 as electrolyte.

The tin concentration was increasing till 8 hours of experiment reaching a value of 2691.91 ppm. A stable level was never reached, even after 8 hours duration of the experiment. It has to be said that the increase of the tin concentration is slow. Therefore, no conclusions can be draw about the saturation concentration of tin in the electrolytic.

To try and find out how much of the dissolved tin was deposited or remained in the solution a mass balance was done for each time interval. In table 5.3 the mass of tin that really resided in the solution, as determined by AAS, is shown together with the expected mass of tin in the Ethaline200 solution based on the mass balance at different time intervals.

Table 5.3 – Real mass of tin in Ethaline200 and expected mass of tin in that solution for different time intervals.

Time (h)	Real mass of tin in the solution (g)	Expected mass of tin in the solution (g)
0.0	0.0000	0.0000
0.5	0.0693	0.1159
1.0	0.1250	0.2179
1.5	0.1750	0.3275
2.0	0.1780	0.4660
2.5	0.2264	0.5833
3.0	0.2463	0.7165
4.0	0.4375	0.9675
8.0	0.5155	1.9581

During the performance of the experiment the formation of tin dendrites was observed; dendrites often fall to the bottom. In this case some tin was thus deposited but stayed in the solution as a precipitate. As this amount of tin was not dissolved in the solution, it was not accounted in the real mass of tin in the electrolyte (measured by AAS). This results in the fact that the real mass of tin is lower than the expected mass of tin in the solution for these time interval.

With an increase of the applied cell potential from 0.82V to 2.25V it was possible to obtain a good tin deposition on the brass plate. The main problem was that in order to obtain this deposition it was necessary to make an experiment over 8 hours, which is too long to get a deposition in these circumstances. Besides that, as said before, there was the formation of tin dendrites in the solution and the generation of bubbles close to the brass plate. So, an experiment was performed where k_3-HEDTA was added as complexing agent to the Ethaline200 solution to try and decrease the time necessary to get the same deposition. At the same time it is also tried to avoid the formation of tin dendrites in the solution. In figure 5.45 the variation of the tin concentration over time for the Ethaline200 with 0.1 M K_3-HEDTA is shown.

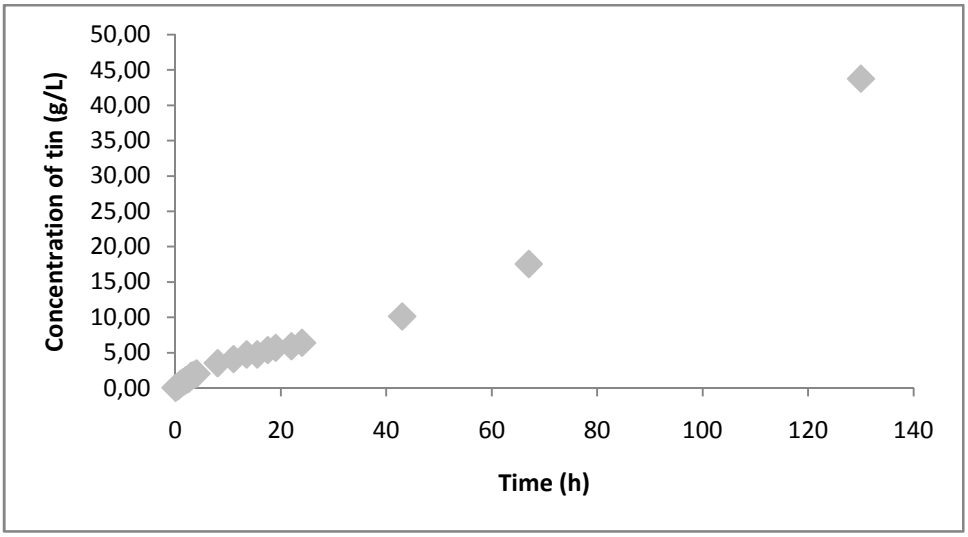


Figure 5.45 – Variation of the concentration of tin over time for the experiment performed using Ethaline200 with 0.1 M K_3-HEDTA as electrolyte.

This experiment was performed at 2.25V until an experiment time of 43 hours. Until here the concentration of tin in the solution was increasing slowly, but no stable level was reached. Then to accelerate the dissolution of tin from the anode to the solution the cell potential was increased to 6.4V. Nevertheless, after 130 hours of experiment a value of 43.8 g/L was reached for the tin concentration but still no stable level was reached. Therefore, no conclusions can be drawn about the saturation concentration of tin in this solution.

With the purpose to know where the tin was located a mass balance was calculated as well. In table 5.4 the mass of tin measured in solution and the expected mass of tin in the Ethaline200 with 0.1 M K_3-HEDTA based on the mass balance is shown for different time intervals

Table 5.4 – Real mass of tin in Ethaline200 with 0.1 M K_3-HEDTA and expected mass of tin in that solution for different time intervals.

Time (h)	Real mass of tin in the solution (g)	Expected mass of tin in the solution (g)
0.0	0.0000	0.000
0.5	0.0141	0.0505
1.0	0.0372	0.0910
1.5	0.0505	0.1268
2.0	0.0657	0.1678
2.5	0.0768	0.1973
3.0	0.0998	0.2299
3.5	0.1055	0.2544
4.0	0.1151	0.2804
8.0	0.1955	0.4719
11.0	0.2234	0.5918
13.5	0.2550	0.6748
15.5	0.2502	0.7465
17.5	0.2778	0.8133
19.0	0.2890	0.8529
22.0	0.2940	0.9450
24.0	0.3124	0.9927
43.0	0.4941	1.5569
67.0	0.8556	3.1080
130.0	2.1309	6.4152

For all the time interval, the expected mass was higher than the real mass present in the solution, due to the precipitation of tin dendrites similar as with the previous experiment.

With this solution there was no formation of tin dendrites in the same conditions as with the experiment with Ethaline200. In other words for 8 hours of experiment and with an applied cell potential of 2.25V there was no formation of tin dendrites. The formation of tin dendrites was checked after 67 hours and with an applied cell potential of 6.4V. For all experiments the generation of bubbles close to the brass plate was observed.

After 8 hours of experiment the deposition was better than the deposition for the experiment performed with pure Ethaline200. After 130 hours of experiment and because of the increase of the potential the deposition showed some grains of tin.

5.2.6 Cyclic voltammetry analyses

The electrodeposition of tin from pure Ethaline200 was analyzed as well with cyclic voltammetry (CV) at room temperature and at 50ºC. The electrodes used for the analyses at room temperature were: tin disk electrode (diameter = 1.5 mm) as the working electrode, 0.01 M $AgNO_3$ + 0.1 M kryptofix22 / Ag in acetonitrile as reference electrode and D.S.A. as counter electrode. Figure 5.46 shows a cyclic voltammogram of Ethaline200 in these conditions.

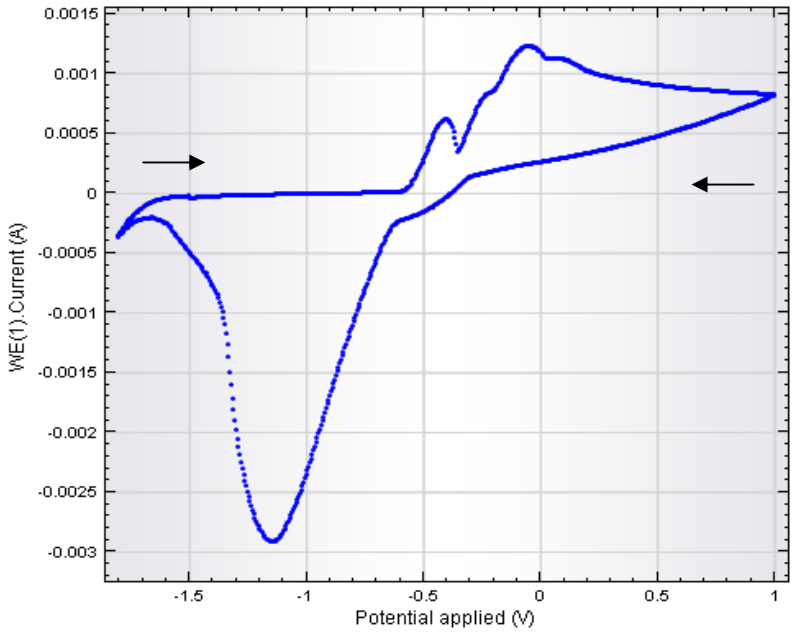


Figure 5.46 – A cyclic voltammogram of pure Ethaline200 using a 1.5 mm diameter tin disk as working electrode, 0.01 M $AgNO_3$ + 0.01 M kryptofix22 / Ag in acetonitrile as reference electrode and D.S.A. as counter electrode.

As can be seen in figure 5.46 starting from negative potentials (- 1.9V), two peaks appear that probably corresponds to the oxidation of Sn to Sn^{2+} and Sn^{4+}. On reversal, the Sn^{2+} or Sn^{4+} is reduced to Sn at around -1.1V. The reduction of tin occurs from -0.6V and the first peak of oxidation occurs between -0.6V and -0.3V and the second peak of oxidation occurs between -0.3V and 0.0V.

An analysis of Ethaline200 in which tin had been dissolved anodically for 30 minutes following the above procedure, was performed at 50ºC in a small vial and the electrodes used were: platinum (diameter = 1.0 mm) as the working electrode, platinum as reference electrode and D.S.A. as counter electrode. In figure 5.47 a cyclic voltammogram of Ethaline200 in these conditions is shown.

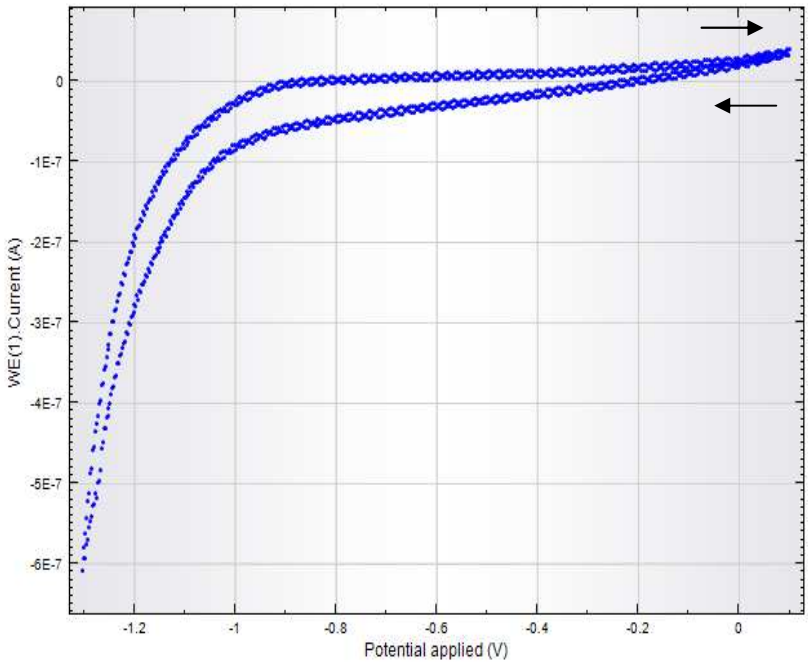


Figure 5.47 – A cyclic voltammogram of pure Ethaline200 using a 1.0 mm diameter platinum disk as working electrode, platinum as reference electrode and D.S.A. as counter electrode.

In figure 5.47 it can be seen that there is no peak of reduction or oxidation of tin. Therefore, it can be concluded that even after this solution has been used as electrolyte in an experiment over 30 minutes there were no reducible tin components in the solution.

A solution of 0.1 M $SnCl_2$ in Ethaline200 in which tin had been dissolved anodically for 30 minutes following the above procedure (section 4.4.3) was analyzed as well by CV. This analysis was performed in a small vial at 50ºC and the following electrodes were used: platinum (diameter = 1.0 mm) as the working electrode, platinum as reference electrode and D.S.A as counter electrode. In figure 5.48 a cyclic voltammogram of 0.1 M $SnCl_2$ in these conditions is shown.

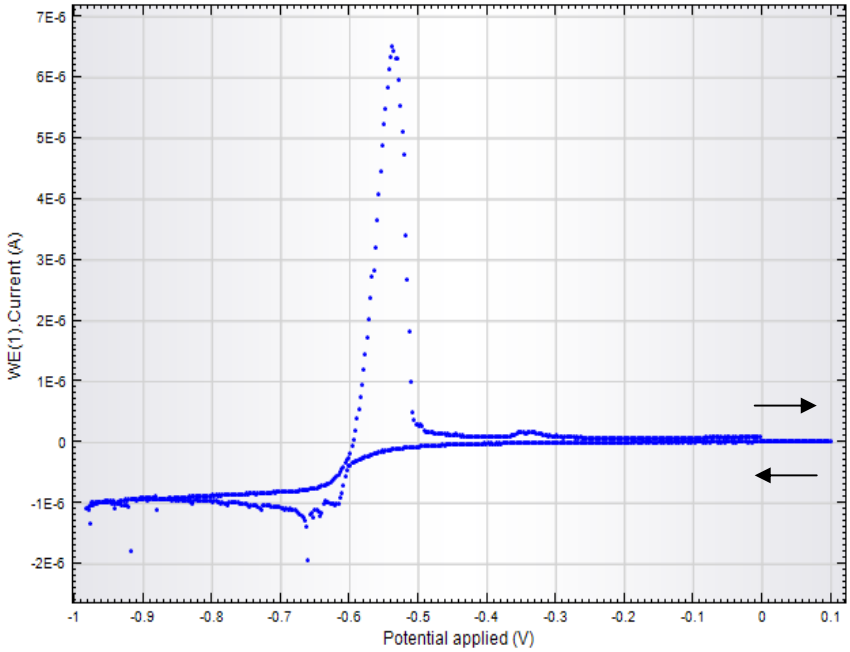


Figure 5.48 – A cyclic voltammogram of 0.1 M $SnCl_2$ in Ethaline200 using a 1.0 mm diameter platinum disk as working electrode, platinum as reference electrode and D.S.A. as counter electrode.

Starting from positive potentials (+0.1V), the peak that corresponds to the reduction of tin was expected but in reality it was not observed. In the reverse scan, a sharp stripping peak appears that corresponds to the oxidation of Sn to Sn^{2+} or Sn^{4+}. This means that although there was no visible peak of reduction, Sn^{2+} or Sn^{4+} must be present in some way as its reduction to Sn is observed in the reverse scan. The oxidation of tin occurs between -0.61V and -0.52V.

At the end, a solution of Ethaline200 with 0.1 M K_3-HEDTA in which tin had been dissolved anodically for 30 minutes following the procedure in 4.4.3, was analyzed as well by CV before and after it has been used for the study of the tin electrodeposition. These analyses were performed in the small vial at 50ºC and the electrodes used were: platinum (diameter = 1.0 mm) as the working electrode, platinum as reference electrode and D.S.A as counter electrode. In figure 5.49 a cyclic voltammogram of this solution before it has been used in the study of the tin electrodeposition is shown and in figure 5.50 a cyclic voltammogram of this solution after it has been used in the study of the tin electrodeposition is shown.

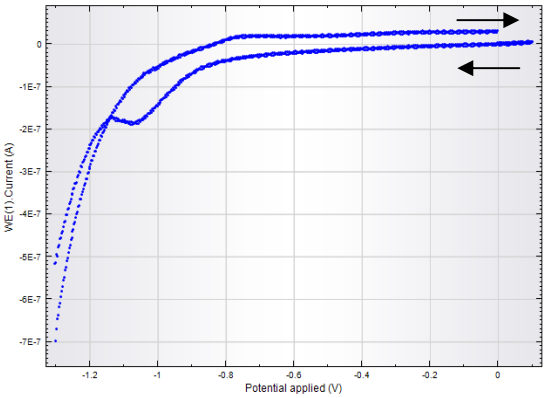


Figure 5.49 – A cyclic voltammogram of Ethaline200 with 0.1 M K_3-HEDTA before it was uses in the study of tin electrodeposition, with a 1.0 mm diameter platinum disk as working electrode, platinum as reference electrode and D.S.A. as counter electrode.

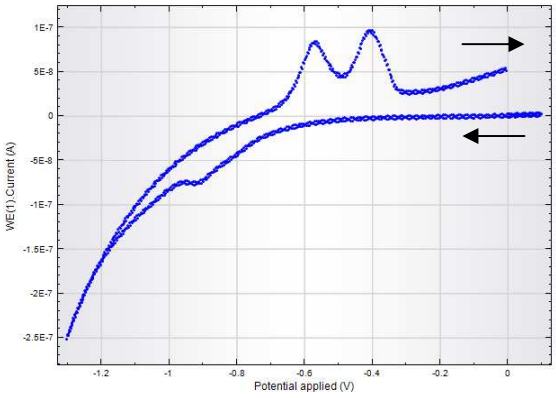


Figure 5.50 – A cyclic voltammogram of Ethaline200 with 0.1 M K_3-HEDTA after it was used in the study of tin electrodeposition, using a 1.0 mm diameter platinum disk as working electrode, platinum as reference electrode and D.S.A. as counter electrode.

The graph in figure 5.49 shows a small reduction peak that probably corresponds to reduction of some oxidized products or impurities present in the solution. There is no peak of reduction or oxidation of tin, because there was no tin dissolved in the solution.

The graph in figure 5.50 shows initially a small reduction peak; this peak has the same shape than the peak that appeared in figure 4.47. Therefore, it is complicated to know if this peak corresponds to the reduction of Sn^{2+} or to the reduction of Sn^{4+} to Sn or if it corresponds to the reduction of the same oxidized products present in solution. If this peak corresponds to the reduction of tin, this occurs between -0.80V and -0.95V. In the reverse scan, two peaks appear that correspond to the oxidation of Sn to Sn^{2+} and Sn^{4+}. The first oxidation peak occurs between -0.62V and -0.58V and the second oxidation peak occurs between -0.43V and -0.39V.

5.3 Electrodeposition of zinc/tin alloys

All the experiments done for the study of the electrodeposition of zinc/tin alloys were performed at 50ºC in the parallel plate cell. The aim was to obtain an alloy of 20% of zinc and 80% of tin, because the friction of this composition ressembles that of cadmium and thus this alloy is suitable for replacement of cadmium. This alloy offers a better corrosion resistance than pure zinc, particularly in high humidity conditions. Because of the high zinc content it is quite cheap. For this purpose $ZnCl_2$ and $SnCl_2$ in Ethaline200 are used as the electrolyte. To this solution K_3-HEDTA was added as complexing agent. The $ZnCl_2$ was chosen because the depositions obtained for this electrolyte in the study of the electrodeposition of zinc were good. This solution was not an emulsion and the cathodic efficiencies obtained for the

electrodeposition of zinc were high, which means that with this substance a zinc/tin alloy with a high content of zinc can be achieved. With the $SnCl_2$ solution good results were obtained as well in the study of the electrodeposition of tin, so this solution was also choosen for the electrodeposition of the alloy. Besides that, this was the only solution that was not an emulsion in the experiments done before. The K_3-HEDTA with a concentration of 0.015 M was added as complexing agent to avoid the formation of tin dendrites or/and to avoid that the solution became an emulsion.

As the anode a slice of tin was used and as the cathode a plate of brass or a plate of tin. In order to check with which electrode the best results were obtained the cathodic efficiencies, the thickness of the deposition and the content of zinc and tin in the deposition were determined. The cathodic efficiencies were calculated taking in account that the zinc and tin were oxidized and reduced with two electrons. in order to the determine the content of the metals, the deposition obtained in the experiments were scraped from the surface of the cathode and analyzed by AAS.

5.3.1 Study of the effect of stirring on the electrodeposition

With the aim to check the effect of the stirring, four experiments were performed: two with stirring and two without stirring. In two of the experiments brass was used as the cathode and in the other two iron was used as the cathode. The stirring was not performed with a magnetic stirrer bar (as happened with the study of the electrodeposition of zinc and tin, separately) but with an ultrasonic bath. All the experiments were performed with an applied current of 0.51A and with a duration of 15 minutes. The solution of 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 was used as the electrolyte in this study. In figure 5.51 the cathodic efficiencies obtained for each experiment are shown.

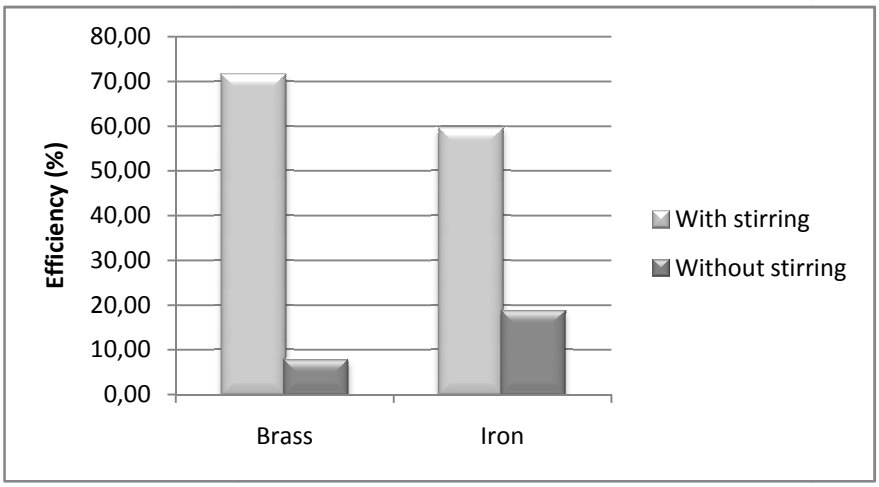


Figure 5.51– Cathodic efficiencies of zinc/tin alloys electrodeposition for experiments performed with or without stirring and using brass or iron as cathode.

The highest efficiencies of deposition were obtained for the experiments performed with stirring: for the experiment performed with the brass cathode an efficiency of 71.33% was obtained and for the experiment performed with iron an efficiency of 59.29% was obtained. For the experiments done without stirring a cathodic efficiency of 7.53% was obtained for the experiment performed with the brass cathode and 18.50% for the experiment performed with the iron cathode.

For all the experiments performed the generation of bubbles close to the cathode was striking (cfr. section 5.1.6); in the experiments performed without stirring these bubbles were present in such great quantity that a kind of foam formed along the cathode. It was also striking that the solution used as the electrolyte even with the addition of the complexing agent was an emulsion. The problem of the emulsion could be solved with an increase of the concentration of the complexing agent; the problem was that the concentration of 0.015 M was the highest possible concentration because of the solubility of the salt.

The depositions obtained for the experiments performed with stirring were better than the depositions obtained for the experiments performed without stirring as can be seen in figure 5.52.

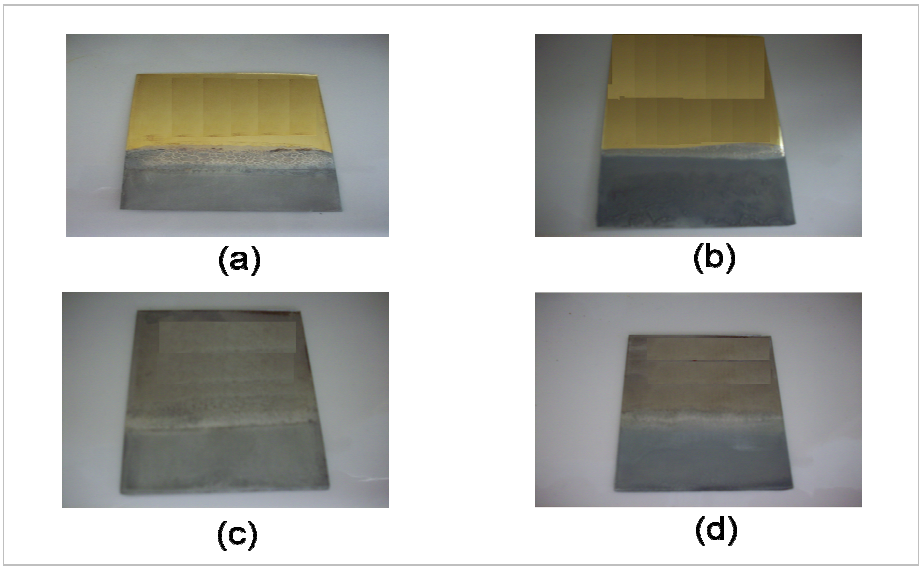


Figure 5.52– Images of the zinc/tin depositions obtained for the experiment performed: (a) without stirring and using brass as cathode, (b) with stirring and using brass as cathode, (c) without stirring and using iron as cathode and (d) with stirring and using iron as cathode.

For all experiments the content of zinc and tin in the deposition was determined with A.A.S. and also the thickness of the deposition (calculated). In table 5.5 the percentage of zinc and tin in the deposition and the thickness of the deposition is summarized for each experiment.

Table 5.5 – Percentage of zinc and tin in the deposition and thickness of the deposition for experiments performed with or without stirring and using brass or iron as cathode.

Experiment conditions	Cathode	Zinc (%)	Tin (%)	Thickness (µm)
With stirring	brass	22.6	77.4	14.3
	iron	44.9	55.1	14.5
Without stirring	brass	6.5	93.5	0.2
	iron	23.1	76.9	0.1

The alloys with a Zn/Sn content close to the desired 20% Zn and 80% Sn were obtained in the experiment with stirring and using brass as the cathode and for the experiment performed without stirring using iron as the cathode. The main problem of the deposition in the experiment with the iron cathode was the low thickness of the layer.
The depositions were scraped from the cathode surface, which means that the metals percentages obtained are rather an average over the whole surface and not to a specific point of the deposition. Therefore, it is not sure if the deposition is a true alloy or rather a 2-phase deposition of zinc and tin. In order to distinguish both X-ray analysis is required, which is not available in the lab.

It was decided to continue all further experiments with stirring because in these conditions the best cathodic efficiencies, the best deposition and also the best thicknesses were obtained.

5.3.2 Study of the influence of the concentration of $ZnCl_2$ in the electrolyte

In the study of the electrodeposition of Zn/Sn alloys the only parameter changed in the composition of the electrolytic bath was the concentration of $ZnCl_2$. The concentrations used were: 0.10 M, 0.27 M and 0.54 M. All the experiments were performed at a constant current of 0.51A and with stirring.

The first set of experiments was performed with a solution of 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 and as the cathode either brass or iron was used. In order to check how the content of zinc and tin and also the thickness of deposition varied over time the duration of the experiments was varied: 1 minute, 5 minutes, 15 minutes and 30 minutes were used. In figure 5.53 the cathodic efficiencies obtained for each experiment are shown.

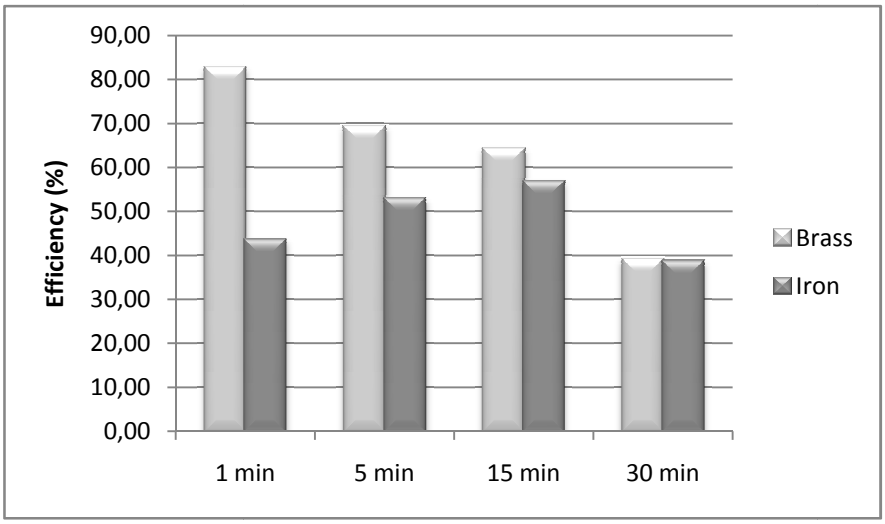


Figure 5.53– Cathodic efficiencies for electrodeposition of zinc/tin alloys for experiments with 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200, for different experimental times and using brass or iron as the cathode.

For the experiments with the brass cathode efficiencies of 82.65% for 1 minute experimental time, 69.32% for 5 minutes, 64.20% for 15 minutes and 39.06% for 30 minutes were obtained. For the experiments with the iron cathode efficiencies of 43.55% for 1 minute, 52.92% for 5 minutes, 56.78% for 15 minutes and 38.63% for 30 minutes were obtained. The efficiencies were always higher for the experiments with brass than for the experiments with iron and, as can be seen in figure 5.51, the cathodic efficiencies for the experiments with brass decreased with an increase of the experimental time; for the experiments with the iron cathode the efficiencies increased with an increase of the experimental time (with exception of the experiments performed over 30 minutes).

The solution used as electrolyte was an emulsion and for all the experiments performed with brass the generation of bubbles close to the brass plate was striking and for all the experiments with iron the generation of foam (great amount of bubbles) close to the cathode can be observed. The formation of tin dendrites was also remarkable for the experiments with a duration longer than 15 minutes.

The depositions for both the experiments with the brass and the iron cathode were good. Nevertheless, the best depositions were obtained for the experiments with the iron cathode. With the increase of the duration of the experiment the depositions became darker as can be seen in figure 5.54.

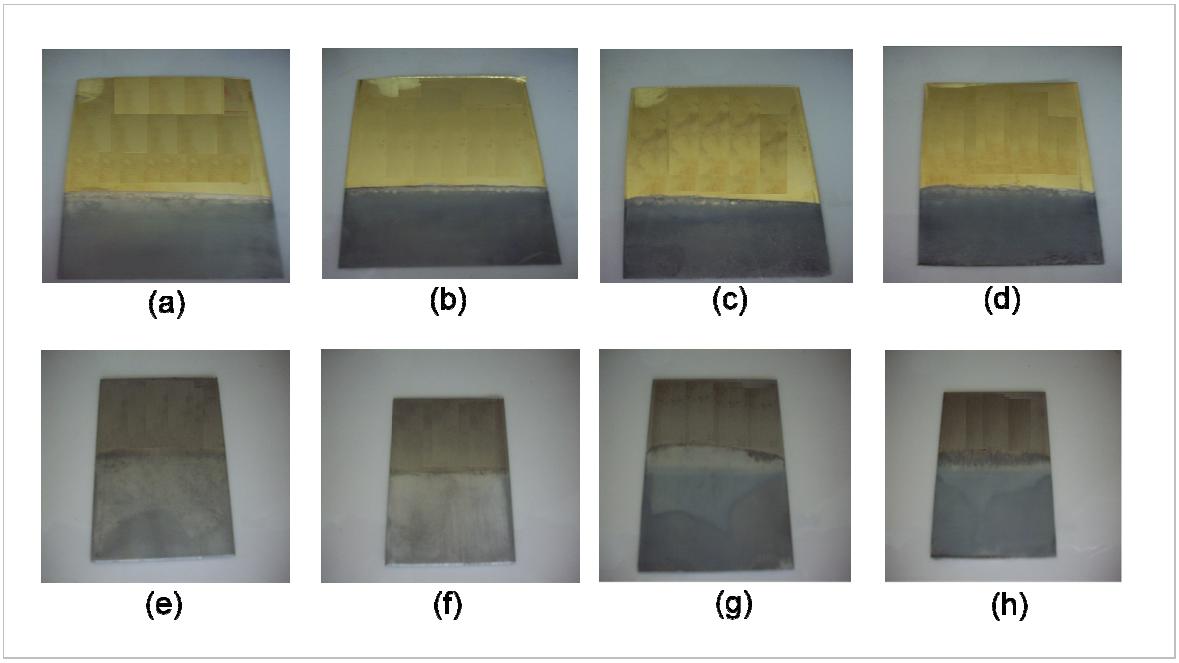


Figure 5.54– Images of the Zn/Sn deposition obtained for the experiment performed with 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 and (a) 1 min deposition with brass cathode (b) 5 min deposition with brass cathode (c) 15 min deposition with brass cathode (d) 30 min deposition with brass cathode (e) 1 min deposition with iron cathode (f) 5 min deposition with iron cathode (g) 15 min deposition with iron cathode and (h) 30 min deposition with iron cathode.

For these experiments the percentages of zinc and tin in the deposition and the thickness of the deposition were also determined. These results are shown in table 5.6.

Table 5.6 – Percentage of zinc and tin in the deposition and thickness of the deposition for experiments performed with 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 with a brass or iron cathode for different experimental times.

Cathode	Duration time (min)	Zinc (%)	Tin (%)	Thickness (µm)
Brass	1	26.5	73.5	1.4
	5	42.8	57.2	4.2
	15	32.6	67.4	12.1
	30	40.2	59.8	14.4
Iron	1	4.5	95.5	0.9
	5	0.5	99.5	4.7
	15	41.9	58.1	10.4
	30	25.6	74.4	17.7

For the experiments done with the brass cathode, the deposition with a content close to the desirable alloy was obtained for the experiment performed with an experimental duration of 1

minute. However, in this experiment the deposition was very thin. In any way the thickness is not sufficient to offer a suitable corrosion resistance. For the first experiments with an iron cathode (1 and 5 minutes) the Zn/Sn alloy had a high content of tin and for the experiments performed for 30 minutes the alloy contained just a little more zinc than the desirable amount, but on the other hand the thickness of the deposition was sufficient.

Two more experiments were performed with the concentration of $ZnCl_2$ increased to 0.54 M. This means the composition of the electrolytic bath was 0.54 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200. Both experiments were performed with a duration of 15 minutes. In one experiment brass was used as the cathode and in the other experiment an iron cathode was used. In figure 5.55 the cathodic efficiencies obtained for each experiment are shown.

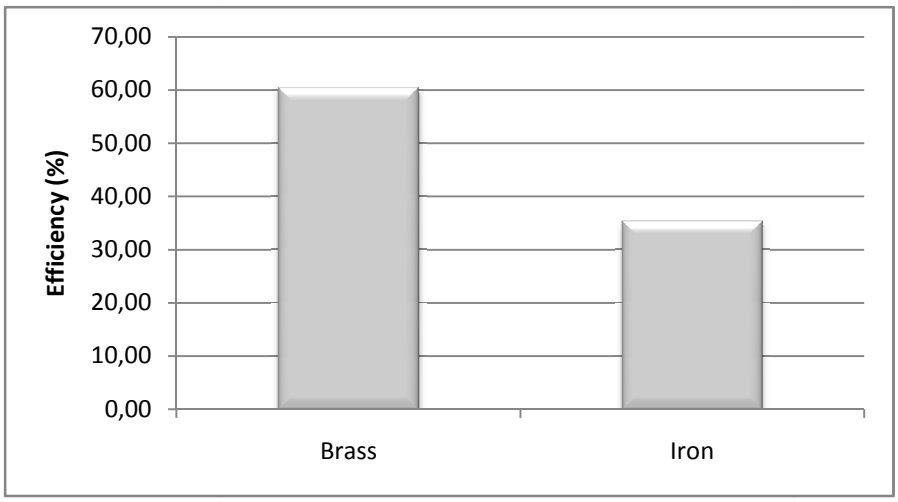


Figure 5.55– Cathodic efficiencies for electrodeposition of zinc/tin alloys for experiments performed with 0.54 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 with brass or iron as the cathode.

As happened in earlier experiments, the cathodic efficiency for the experiment with the brass cathode (60.19%) was higher than the cathodic efficiency for the experiment with iron (35.07%). Even with the addition of K_3-HEDTA the solution was an emulsion and the generation of a great amount of bubbles (foam) was striking for both experiments. With this solution the formation of tin dendrites in the solution was not observed.

The depositions obtained for each experiment can be seen in figure 5.56.

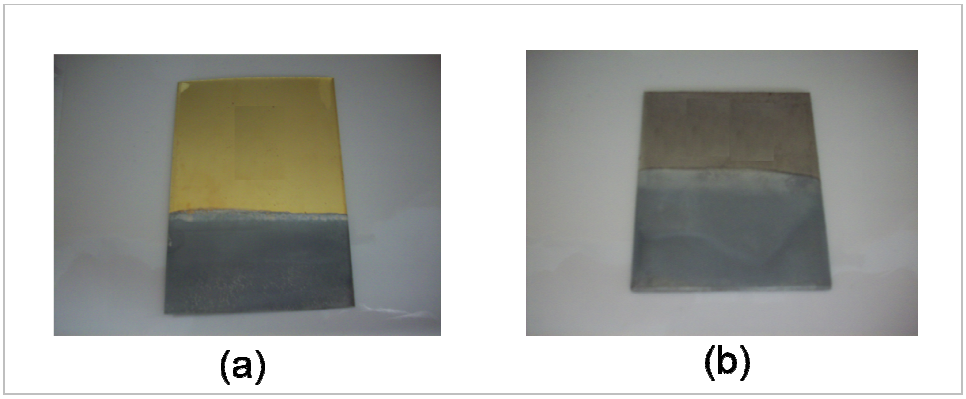


Figure 5.56– Images of the Zn/Sn deposition obtained for the experiment performed with 0.54 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 with (a) a brass and (b) an iron cathode.

The best deposition was obtained for the experiment with the iron cathode. This deposition was smoother and had a brighter gray color than the deposition obtained in the experiment with the brass cathode.

The thickness of the deposition and the percentage of zinc and tin in the deposition were also calculated; these results are shown in table 5.7.

Table 5.7 – Percentage of zinc and tin in the deposition and thickness of the deposition for experiments performed with 0.54 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 with a brass or iron cathode.

Cathode	Zinc (%)	Tin (%)	Thickness (µm)
Brass	52.4	47.6	10.1
Iron	45.1	54.9	7.3

For both experiments, the content of zinc in the deposition was too high which means that the concentration of $ZnCl_2$ used in the solution was too high to achieve a Zn/Sn alloy with 20% of zinc. The thickness of the deposition was quite good for both experiments.

At the end, experiments were performed where the concentration of $ZnCl_2$ was decreased to 0.10 M. So, the solution of 0.10 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 was used as electrolyte and for these experiments only iron cathodes were used. The iron was chosen because in earlier experiments with other concentrations of $ZnCl_2$ the best depositions were obtained for the experiments where the iron was used as cathode. With the purpose to check if some relation exists between the duration time of the experiments and the properties of the deposition experiments were performed for the following experimental times: 1 minute, 5 minutes, 10 minutes, 15 minutes, 20 minutes and 30 minutes. In figure 5.57 the cathodic efficiencies obtained for each experiment are shown.

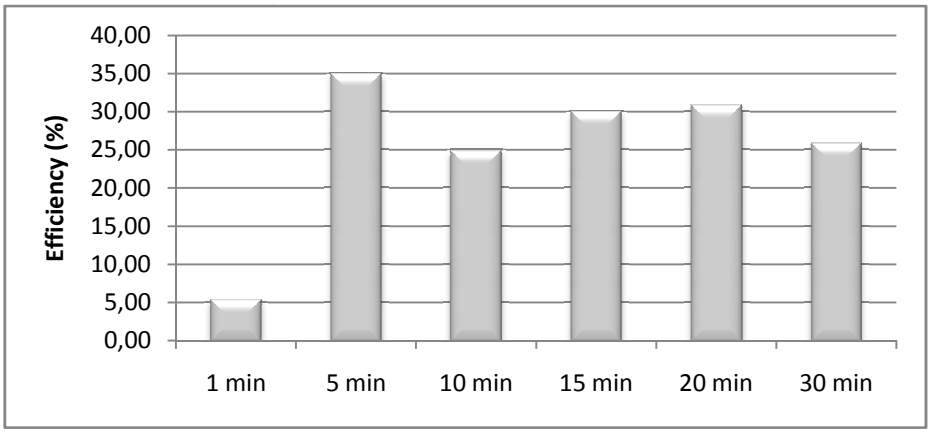


Figure 5.57– Cathodic efficiencies for electrodeposition of zinc/tin alloys for experiments performed with 0.10 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200, for different duration times with an iron cathode.

Efficiencies of the deposition of 5.25%, 34.81%, 24.75%, 29.88%, 30.71% and 25.70% were obtained for experiments of 1 minute, 5 minutes, 10 minutes, 15 minutes, 20 minutes and 30 minutes, respectively. These results show that there is no linear relation between the time of the experiment and the cathodic efficiencies.

The solution used as the electrolyte for these experiments was an emulsion and the generation of foam was striking for all the experiments. For the experiments with a duration above 10 minutes the appearance of tin dendrites in the solution was observed. The depositions obtained were good. The best deposition was obtained for the experiment with a duration of 30 minutes. In figure 5.58 images of the depositions are shown.

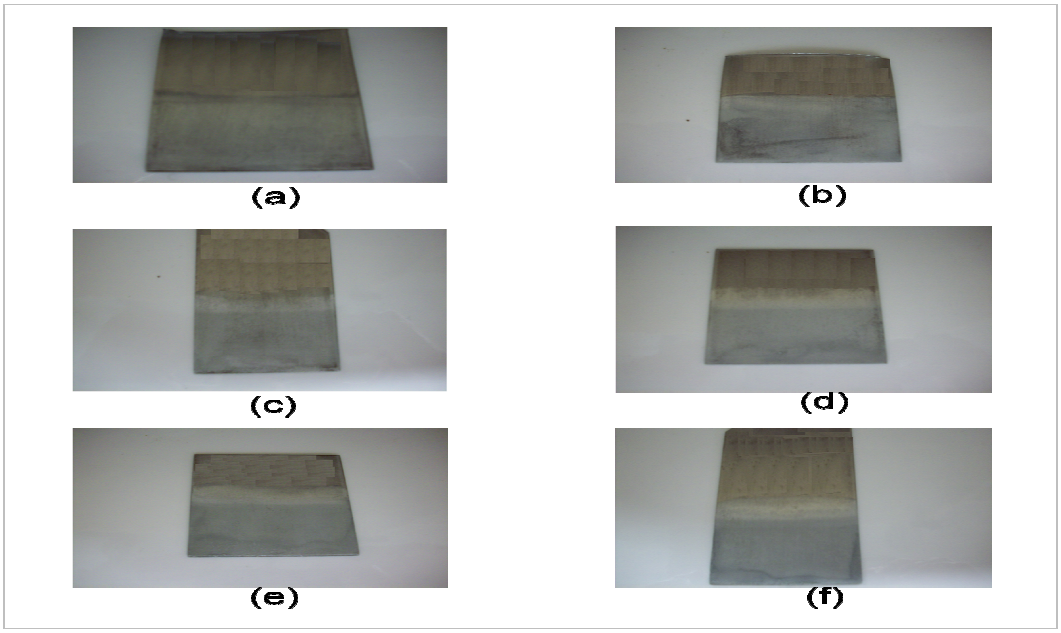


Figure 5.58– Images of the Zn/Sn deposition for the experiment performed with 0.10 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200, with iron as the cathode and with a duration of (a) 1 minute, (b) 5 minutes, (c) 10 minutes, (d) 15 minutes, (e) 20 minutes and (f) 30 minutes.

In table 5.8 the results about the determination of the thickness and the percentages of zinc and tin in the deposition are shown.

Table 5.8 – Percentage of zinc and tin in the deposition and thickness of the deposition for experiments performed with 0.10 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 and with iron as the cathode for different experimental times.

Duration time (min)	Zinc (%)	Tin (%)	Thickness (µm)
1	11.1	88.9	0.1
5	14.1	85.9	2.8
10	16.4	83.6	4.1
15	15.6	84.4	6.2
20	15.7	85.3	8.2
30	14.3	85.7	10.0

With a concentration of 0.10 M $ZnCl_2$ in the electrolyte, the content of zinc in the deposition was not sufficient to obtain a Zn/Sn alloy with 20% of zinc. As before, the thickness increased with an increase of the experimental time.

In summary, the best cathodic efficiencies were always obtained for experiments with a brass cathode but the best depositions were obtained for the experiments with an iron cathode. A concentration of 0.27 M $ZnCl_2$ was optimal for the study of the electrodeposition of Zn/Sn alloys, because with this concentration a content of zinc and tin in the deposition close to 20% and 80% respectively, was obtained. For the experiments with the electrolytic bath with a concentration of 0.54 M $ZnCl_2$ higher percentages of zinc were obtained in the deposition and for the experiments with the electrolyte with a concentration of 0.10 M $ZnCl_2$ lower percentages of zinc were obtained in the deposition.

5.3.3 Study of the influence of the applied current

A solution of 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 was used to study the influence of the applied current, because this was the solution that led to the best results in earlier experiments.

In order to investigate the effect of the current two experiments were performed at 0.25A and two were performed at 0.51A. Iron was used as the cathode in two of the experiments and brass in the other two. All the experiments were performed with stirring and with an experimental time of 30 minutes. In figure 5.59 the efficiencies of the deposition for each experiment are shown.

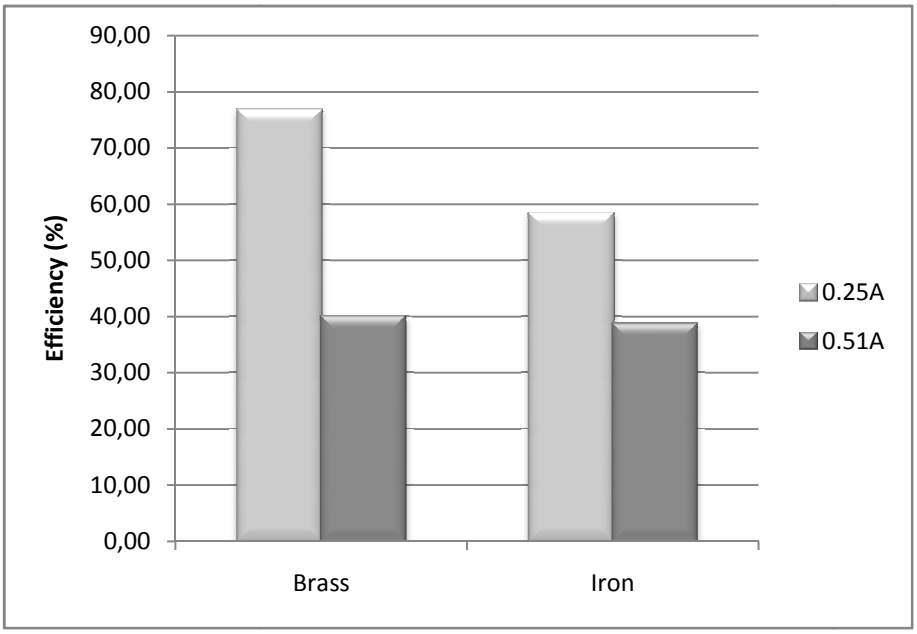


Figure 5.59– Cathodic efficiencies of zinc/tin alloys electrodeposition for experiments with an applied current of 0.25A or 0.51A and with brass or iron as the cathode.

The best cathodic efficiencies were obtained for the experiments performed with an applied current of 0.25A. In these conditions an efficiency of the deposition of 76.66% was obtained for the experiment with the brass cathode and 58.34% for the experiment with the iron cathode. For the experiments done with an applied current of 0.51A a cathodic efficiency of 39.96% was obtained for the experiment with the brass cathode and 38.63% for the experiment with the iron cathode.

In all the experiments performed the generation of bubbles was striking and only for the experiments with the iron cathode the formation of tin dendrites is observed. And as observed earlier, the electrolyte turned out to be an emulsion.

For the experiments performed at 0.51A the depositions were darker than the deposition for the experiments performed with an apllied current of 0.25A. Besides that, the depositions for the experiments where the iron cathode was used were smoother and better adhering than the depositions for the experiments with the brass cathode. In figure 5.60 images of the depositions obtained for this study are shown.

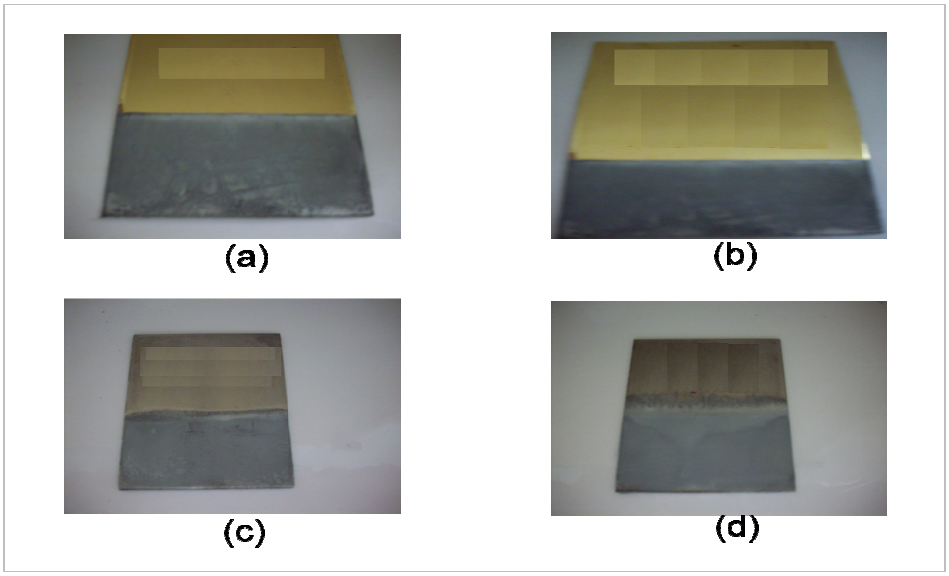


Figure 5.60– Images of the zinc/tin depositions for the experiment: (a) at 0.25A using a brass cathode, (b) at 0.51A using a brass cathode, (c) at 0.25A using an iron cathode and (d) at 0.51A using an iron cathode.

Finally, the thickness of the depositions and the percentages of zinc and tin in the deposition were determined as well. These results are shown in table 5.9.

Table 5.9 – Percentage of zinc and tin in the deposition and thickness of the deposition for experiments performed at an applied current of 0.25A or 0.51A using either a brass or iron cathode.

Cathode	Applied current (A)	Zinc (%)	Tin (%)	Thickness (µm)
Brass	0.25	23.4	76.6	14.6
	0.51	48.0	52.0	13.8
Iron	0.25	33.9	66.1	12.5
	0.51	25.6	74.4	17.7

From table 5.9 it can be concluded that there is no linear relation between the applied current and the thickness of the deposition or the percentage of zinc and tin in the deposition. For the experiments with the brass cathode and increasing current, the thickness of the deposition decreased and the percentage of zinc in the deposition increased. For the experiments with the iron cathode the opposite was observed; when the current increased, the thickness of the deposition increased and the percentage of zinc in the deposition decreased. Therefore, it is impossible to draw any conclusion about the effect of the applied current on the properties of the depositions (content of the metals and thickness). Depending

on the cathode used the thickness and the percentages of metals in the deposition behaved in different ways.

5.3.4 Determination of the zinc and tin concentration in the electrolyte

The concentration of zinc and tin in the electrolyte was determined for the solution which gave the best results in previous experiments. The solution used for this study contained 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200. A slice of tin was used as the anode and as the cathode a plate of brass was used. The experiment had a duration of 18 hours and was performed with an applied potential of 0.51A. In figure 5.61 the variation of the concentration of zinc and tin over time is shown.

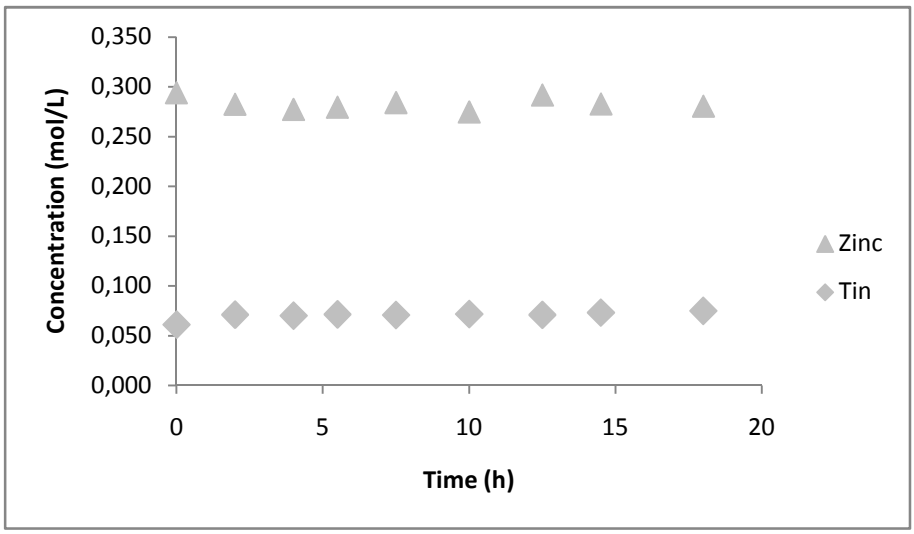


Figure 5.61 – Variation of the concentration of tin and zinc over time for the experiment performed with 0.27 M $ZnCl_2$ + 0.07 M $SnCl_2$ + 0.015 M K_3-HEDTA in Ethaline200 as the electrolyte.

The concentrations of zinc and tin were practically constant over time. The stability of the concentration indicates that all the tin that was dissolved anodically was deposited and did not lead to piling up of tin in the electrolyte. However, the tin that was dissolved anodically was not all deposited onto the brass plate, but sometimes the deposit was found on the bottom of the cell in the shape of tin lumps. The concentration of zinc was also stable during the experiment which means that only small amounts of zinc were transferred from the solution to the cathode.

For this study a mass balance was not calculated because it would be necessary in each time interval to know the content of zinc and tin in the deposition, which would be too laborious.

5.4 Electrodeposition of refractory metals

The electrodeposition of refractory metals such as molybdenum and tungsten at low temperatures (below 150ºC) was also subject of this thesis. Plating Mo or W is not an easy task. This study only intends to initiate this subject. Some possible routes will be explored even if this only means a small step in this difficult matter.

Two possible routes can be distinguished. One is to try and deposit these refractory metals from solutions that consist only of salts or other compounds of Mo or W. It is know that in this case the presence of oxygen in any form is disturbing. Mo and W are very 'oxiphilic' which means they attract oxygen from other compounds very strongly. The electrodeposition of Mo or W bonded to oxygen is very difficult or even impossible. When this route is followed the presence of oxygen in any form should be avoided. A second route is based on the fact that Mo or W can be deposited quite easily from aqueous solutions in a co-deposition with Ni, Co or Fe. The mechanism is not well understood, but the most likely explanation is that the refractory metals form a complex with Ni, Co or Fe and the electrodeposition of the refractory metal from this complex occurs unhindered. As Ni, Co or Fe deposit at more positive potentials than Mo or W, it can not be avoided that the former metals deposit simultaneously and a co-deposition of two metals occurs.

In this project route 1 is explored and it is thus attempted to prepare IL's that contain no oxygen and that allow Mo or W compounds to dissolve. In first instance it is tried to dissolve MoO_3, because this product is easy to handle and cheap. In a later stage it will be necessary to transform MoO_3 in a product that does not contain oxygen e.g. $Mo(SCN)_6$.

The results about the preparation of IL's able to dissolve molybdenum and the results about the synthesis of quaternary ammonium salts for the same purpose are presented in this section.

5.4.1 Preparation of IL's to dissolve molybdenum

It was tried to prepare IL's to dissolve compounds of molybdenum. The most common compounds of Molybdenum are MoO_3, Mo-chlorides or Mo-oxychlorides. It was decided to investigate the possibilities of some mixtures that were liquid below 150ºC with the purpose to dissolve MoO_3. The mixtures of substances and their molar ratios that were prepared for this purpose were:

A. 30 CCC **:** 1 $ZnCl_2$
B. 2 CCC **:** 1 $ZnCl_2$
C. 1 CCC **:** 2 $ZnCl_2$
D. 1 CCC **:** 3 $ZnCl_2$
E. 2 CC **:** 1 $Zn(NO_3)_2.6H_2O$

When preparing mixture E one should be very careful because this mixture becomes explosive in the absence of water. Therefore, during its preparation the presence of water should always be ascertained. The CCC was used for all mixtures (except mixture E) because this is a substance that has no oxygen in its composition. In absence of other metallic compounds it is very difficult to deposit molybdenum in the presence of any kind of oxygen.

The mixtures A, B and E were discarded from this study because the main objective was to achieve an IL below 150ºC, and these mixtures were not a liquid below this temperature. The mixtures C and D were liquids below 150ºC, so it was tried to dissolve molybdenum in these solutions.

To dissolve the MoO_3, an amount of this compound was added to the mixtures C and D but no dissolution occurred. The solutions turned grayish and black particles could be observed. It is concluded with these mixtures it was impossible to dissolve molybdenum and because of the insolubility of MoO_3 it was impossible to do further studies of the electrodeposition.

5.4.2 Synthesis of quaternary ammonium salts

With the same purpose (to dissolve molybdenum or refractory metals) it was tried to synthesize three oxygen-free quaternary ammonium salts (quats). These quats were synthesized by alkylation of a tertiary ammine (triethylamine) with a halogenated alkane. As already mentioned this reaction is called the Menschutkin reaction. The compounds used to do the alkylation reaction with the triethylamine were: 1-iodopropane and 1-chloropropane.

The 1-iodopropane was added to triethylamine (equation 7) and mixed during 1 hour at room temperature. After mixing the product was dried by evaporation of the remaining reactants that were all volatile. A reaction yield of only 10.4% was obtained.

The reaction of 1-chloropropane with triethylamine was done at 60ºC with reflux of the mixture in order to avoid loss of reagents (1-chloropropane has a boiling point below 60ºC). This reaction was performed in two different situations: with ethanol as solvent and without any solvent. The latter case means that the 1-chloropropane was actually used as solvent. For the experiment where ethanol was used as the solvent the reagents were added stoichiometrically (equation 8). After 22 hours reflux a reaction yield of 3.19% was obtained. For the experiment where the 1-chloropropane was used as the solvent, an excess of it was used (equation 9). The experiment was run for 29 hours. In this case a reaction yield of 0.41% was obtained.

In summary, none of the methods used for the synthesis of quats is viable as only low reaction yields were obtained. It was not possible to prepare any quat in sufficient quantities as to study the dissolution of MoO_3. It was decided not to continue with the preparation of other quaternary ammonium salts.

6. Conclusions

The main purpose of this thesis was to create a zinc/tin alloy with high content of zinc (20% of zinc and 80% of tin) using electrolytes based on ionic liquids. In order to achieve this goal, the electrodeposition of zinc and tin were first studied separately.

The electrodeposition experiments of zinc, performed at 50ºC and at 2.25V both in the hull cell and in a parallel plate cell show good results both qualitatively (appearance of the deposition) and quantitatively (cathodic and anodic efficiencies).

The experiments were performed in Ethaline200 and Reline200 based solutions. The cyclic voltammogram of the Zn electrodeposition shows that for Reline200 solutions the zinc deposition occurs at more negative potentials than in Ethaline200. The qualitative and quantitative results are better in Ethaline200 based solutions than in Reline200 based solutions.

A solution of $Zn(NO_3)_2.6H_2O$ (Ethaline200 or Reline200) is not suitable for the deposition of zinc because the efficiency and the appearance of the deposition with this solution are not satisfactory. Solutions of $ZnCl_2$ and $ZnSO_4.7H_2O$ are better for this purpose, because the depositions with these solutions were smooth and the cathodic efficiencies were quite high. ZnO solutions were always an emulsion and the results obtained with it are not satisfactory either. When tartaric acid is used as a complexing agent for these solutions the deposition becomes quite good and the cathodic efficiency was relatively high.

Any of the tested electrolytic baths (except those containing ZnO) show good depositions independent of the temperature. It was found that there is no distinct relation between the temperature and the cathodic efficiency.

In this study anodic efficiencies above 100% were found. This may be due to weighing errors as the total amount that was weighed was only a few milligrams. In any way it is likely the true efficiency of the zinc electrodeposition is close to 100 %.

A mass balance revealed that zinc piles up in the electrolytic bath when a zinc anode is used. This means that a great amount of zinc that dissolved anodically remained in the electrolyte instead of being deposited on the brass cathode.

For the electrodeposition of tin, a pure Ethaline200 solution should not be used as the efficiency of the deposition on a brass cathode was practically zero. A cyclic voltammogram of a solution used earlier for the electrodeposition of Sn, shows that there is no reducible tin components in the solution. The $SnCl_2$ and $Sn(OH)_2$ solutions based on Ethaline200 are quite good for Sn electrodeposition. The main problem in the case of $Sn(OH)_2$ solutions is the

formation of an emulsion. In the case of $SnCl_2$ solutions, the generation of tin dendrites in the solution occurred.

Independently of the complexing agent and its concentration added to the $Sn(OH)_2$ solution, the emulsion still occurred. When the concentration of the complexing agents (e.g. K_3-HEDTA) was higher than the concentration of the tin in solution the best depositions were obtained and in these conditions there was no formation of tin dendrites. Therefore, it can be stated that the generation of tin dendrites could be avoided by adding an excess of complexing agent. K_3-HEDTA was also added to pure Ethaline200 as complexing agent. The depositions obtained with this solution were quite good and with an applied potential of 2.25V there was no generation of tin dendrites in this solution.

Anodic efficiencies greater than 100% were often encountered, but as mentioned earlier this is probably due to the small weights of the depositions. However, the values found for the tin depositions were a lot higher than 100% cfr. the values found for the zinc experiments which were only slightly over 100%. This suggests that there might also be chemical dissolution of tin occurring simultaneously with the electro-dissolution. A blanc experiment revealed the chemical dissolution of tin is not occurring. Therefore, the high anodic efficiencies obtained for the electro-dissolution of tin can not be explained by the chemical dissolution of tin. The main reason for the larger than 100% efficiencies is still unknown.

For the study of the electrodeposition of the zinc/tin alloys all the experiments were performed at 50ºC in the parallel plate cell. The electrolyte was a mixture of $ZnCl_2$, $SnCl_2$ and K_3-HEDTA in Ethaline200. The concentrations of $SnCl_2$ and K_3-HEDTA were fixed at 0.07 M and 0.015 M, respectively; only the concentration of $ZnCl_2$ was varied in this study. Either brass or iron plates were used as cathode.

The best cathodic efficiencies were always obtained for experiments performed with a brass cathode but the best appearances of the depositions were obtained for the experiments performed with an iron cathode. A concentration of 0.27 M $ZnCl_2$ turned out to be optimal as the content of zinc and tin in these depositions were close to the targeted 20% Sn and 80% Zn. For the experiments with the electrolytic bath with 0.54 M $ZnCl_2$ the Zn content in the deposition was too high and for the experiments with 0.10 M $ZnCl_2$ the Zn content in the deposition was too low.

The technique used to determine the contents of zinc and tin in the deposition (scraping of the deposition from the cathode) does not allow to distinguish between a true alloy or a 2-phase deposition of Zn and Sn. A genuine alloy should have the same content of the metals in any point of the deposition. Unfortunately, X-ray techniques are not available in

the lab to obtain a conclusive result. The A.A.S. measurements performed in these studies only give an average of the content over the whole surface.

It is difficult to draw any conclusion about the effect of the applied current on the properties of the deposition. Depending on the cathode material the thickness and the content of the metals in the deposition behaved in different ways.

A small study about the electrodeposition of refractory metals was also initiated in this thesis. However, this is not an easy task at all and it was not possible to perform any experiment about the electrodeposition of these metals. Nevertheless, some oxygen-free ionic liquids were prepared and the solubility of MoO_3 was investigated. The synthesis of oxygen-free quaternary ammonium salts was started with the same purpose.

It was targeted to obtain mixtures liquid at temperatures below 150 ℃. Some of the mixtures were discarded because no liquid could be obtained below this temperature. The mixtures that were liquid below 150ºC were: 1 CCC **:** 2 $ZnCl_2$ and 1 CCC **:** 3 $ZnCl_2$. However, no dissolution of MoO_3 occurred in these solutions. Consequently it was impossible to study the electrodeposition of Mo.

Only low reaction yields were obtained for the synthesis of oxygen-free quat's. Then, it was not possible to prepare sufficient quantities of the quats to study the dissolution or the electrodeposition of the refractory metals.

7. Suggestions for future works

For future works following suggestions are made:

- Concerning the Zn/Sn alloys the necessities for the whole galvanic process should be taken into account. In this project focus was on the electrodeposition of one single metal at the cathode and the dissolution of one single metal at the anode. In a viable process the replenishment of both metals must be considered as to maintain the concentration of both metals at a steady value. Moreover, the deterioration of organic compounds at the electrodes and the pretreatment before and rinse configuration after the galvanic process has to be considered.

- Concerning the refractory metals, as it is not the aim of the lab to start with elaborate organic synthesis, it seems advisable to start from commercially available quaternary ammonium salts. The range of these is already quite extended and it facilitates the use of these IL's on a larger scale. Aromatic quats such as trimethyl phenyl ammonium chloride and trimethyl benzyl ammonium chloride are in the crosshairs, because they also seem promising what concerns chemical stability. The fact that IL's based on aromatic quats are known for their high melting points is not such a problem in this study as the use of higher temperatures (targeted 150 ℃) can be justified because of the difficulty of electrodeposition of refractory metals and the guaranteed absence of water at these temperatures. The solubility of MoO_3 turned out to be poor. As the presence of oxygen is definitely not favorable, the use of molybdenum chlorides or a conversion of MoO_3 to oxygen-free compounds should be considered.

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A. Appendix

A.1 Dimensions of the electrolytic cells used

In this chapter are presented the dimensions of the cells used for the performance of this work. It was used three cells: one hull cell and two parallel plate cells.

A.1.1 Dimensions of the hull cell

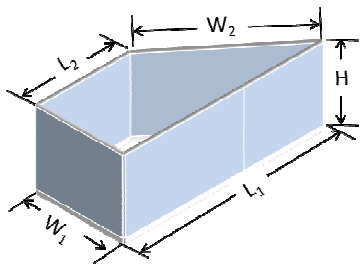

Figure A.1 – Dimensions of the hull cell.

Table A.1 – Dimensions of the hull cell.

L_1 (cm)	6.1
L_2 (cm)	2.4
W_1 (cm)	3.1
W_2 (cm)	4.8
H (cm)	3.1

A.1.2 Dimensions of the parallel plate cell

For the performance of the experiments it was used two different parallel plate cell: one for the experiments where were done the study of the electrodeposition of the metals and the other where was done the determination of the concentration of the metals in the electrolyte. Both had the same configuration; however the dimensions were different for each one.

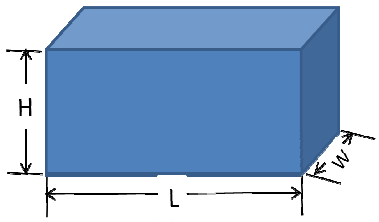

Figure A.2 – Dimensions of the parallel plate cell used for the experiments performed for the electrodeposition.

Table A.2 – Dimensions of the parallel plate cell used for the experiments performed for the electrodeposition of the metals and for the experiments performed for the determination of the concentration of the metals in the electrolyte.

	Electrodeposition of the metals	**Determination of the concentration**
L (cm)	9.5	7.8
W (cm)	7.5	6.0
H (cm)	6.0	3.2

A.2 Results

In this section, all the experimental results obtained and also the calculated results are presented.

A.2.1 Electrodeposition of zinc

In this chapter both the results obtained and the calculated results for the study of the electrodeposition of zinc are shown.

In table A.3 the results about the determination of the cathodic efficiencies for the study of the influence of the applied cell potential are shown.

Table A.3 – Cell potential, current, time, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the applied potential.

P (V)	C (A)	t (s)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
2.25	0.85	1800	0.0393	0,0431	123.06	61.53	$6.38x10^{-4}$	0,0417	94,22
17.6	1.28	1200	0.5666	0,8034	1800.10	900.05	$9.33x10^{-3}$	0,6101	92,86
35.3	2.71	600	0.2741	0,6353	1809.60	904.80	$9.38x10^{-3}$	0,6133	44,69

In table A.4 the results about the determination of the cathodic efficiencies for the study of the influence of the types of electrolytic bath in the parallel plate cell are shown.

Table A.4 – Electrolytic bath, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the types of electrolytic bath in the parallel plate cell.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	0.850	0.0393	0.0431	123.06	61.53	$6.38x10^{-4}$	0.0417	94.22
B	0.004	0.0013	0.0025	7.82	3.91	$2.65x10^{-3}$	0.0026	49.04
C	0.062	0.0276	0.0321	112.09	56.04	$3.80x10^{-2}$	0.0380	72.64
D	0.057	0.0342	0.0389	102.98	51.49	$3.49x10^{-2}$	0.0349	97.98

Note: The letters A, B, C and D correspond to the solutions of 0.5 M $ZnCl_2$ in Ethaline200, 0.5 M ZnO in Etaline200, 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 and 0.5 M $ZnSO_4.7H_2O$ in Ethaline200, respectively.

In table A.5 the results about the determination of the cathodic efficiencies for the study of the influence of the types of electrolyte bath in the hull cell are shown.

Table A.5 – Electrolytic bath, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the types of electrolytic bath in the hull cell.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	0.055	0.0332	0.0338	99.76	49.88	$5.16x10^{-4}$	0.0338	98.18
B	0.070	0.0408	0.0448	125.59	62.80	$6.51x10^{-4}$	0.0426	95.84
C	0.041	0.0199	0.0265	74.91	37.45	$2.54x10^{-2}$	0.0254	78.37
D	0.033	0.0154	0.0215	59.11	29.56	$2.00x10^{-2}$	0.0200	76.86
E	0.011	0.0029	0.0081	19.87	9.94	$6.74x10^{-3}$	0.0067	43.06
F	0.040	0.0155	0.0310	72.64	36.32	$2.46x10^{-2}$	0.0246	62.95

Note: The letters A, B, C, D, E and F correspond to the solutions of 0.5 M $ZnSO_4.7H_2O$ in Ethaline200, 0.5 M $ZnCl_2$ in Ethaline200, 0.5 M $ZnCl_2$ in Reline200, 0.5 M $ZnSO_4.7H_2O$ in Reline200, 0.5 M ZnO in Reline200 and 0.5 M $Zn(NO_3)_2.6H_2O$ in Reline200, respectively.

In table A.6 the results about the determination of the anodic efficiencies for the study of the influence of the types of electrolyte bath in the hull cell are presented.

Table A.6 – Electrolytic bath, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and anodic efficiency for the experiments performed for the study of the influence of the types of electrolytic bath in the hull cell.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{ano.}$ (%)
A	0.054	0.0318	0.0348	97.55	48.78	$5.06x10^{-4}$	0.0331	105.24
B	0.053	0.0316	0.0322	94.81	47.41	$4.91x10^{-4}$	0.0321	100.20
C	0.048	0.0056	0.0217	86.71	86.71	$4.49x10^{-4}$	0.0294	73.83
D	0.029	0.0092	0.0187	51.63	25.82	$2.70x10^{-4}$	0.0175	106.85
E	0.028	0.0073	0.0188	50.58	25.29	$2.60x10^{-4}$	0.0171	109.65
F	0.035	0.0061	0.0151	63.17	31.59	$3.30x10^{-4}$	0.0214	70.52

Note: The letters A, B, C, D, E and F correspond to the solutions of 0.5 M $ZnCl_2$ in Ethaline200, 0.5 M $ZnSO_4.7H_2O$ in Ethaline200, 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200, 0.5 M $ZnCl_2$ in Reline200, 0.5 M $ZnSO_4.7H_2O$ in Reline200 and 0.5 M $Zn(NO_3)_2.6H_2O$ in Reline200, respectively.

In table A.7 the results about the determination of the cathodic efficiencies for the study of the influence of the addition of complexing agents are shown.

Table A.7 – Electrolytic bath, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the addition of complexing agents in the parallel plate cell.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	0.063	0.0346	0.0347	113.46	56.73	$5.88x10^{-4}$	0.0384	89.97
B	0.049	0.0213	0.0220	88.18	44.09	$4.57x10^{-4}$	0.0299	71.26
C	0.049	0.0246	0.0366	88.39	44.20	$4.58x10^{-4}$	0.0300	82.11

Note: The letters A, B and C correspond to the solutions of 0.5 M ZnO plus 0.5 M malic acid in Ethaline200, 0.5 M ZnO plus 0.5 M citric acid in Ethaline200 and 0.5 M ZnO plus 0.5 M tartaric acid in Ethaline200, respectively.

In table A.8 the results about the determination of the anodic efficiencies for the study of the influence of the addition of complexing agents are shown.

Table A.8 – Electrolytic bath, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and anodic efficiency for the experiments performed for the study of the influence of the addition of complexing agents in the hull cell.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{ano.}$ (%)
A	0.037	0.0130	0.0281	66.85	33.43	$3.46x10^{-4}$	0.0226	124.01
B	0.036	0.0140	0.0246	65.64	32.82	$3.40x10^{-4}$	0.0222	110.56
C	0.031	0.0054	0.0204	54.84	27.42	$2.84x10^{-4}$	0.0186	109.74

Note: The letters A, B and C correspond to the solutions of 0.5 M ZnO plus 0.5 M tartaric acid in Ethaline200, 0.5 M ZnO plus 0.5 M malic acid in Ethaline200 and 0.5 M ZnO plus 0.5 M citric acid in Ethaline200, respectively.

In table A.9 the results about the determination of the cathodic efficiencies for the experiments performed in the parallel plate cell concerning to the study of the influence of the temperature, are presented.

Table A.9 – Electrolytic bath, temperature, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the temperature in the parallel plate cell.

Electrolytic bath	T (ºC)	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	50	0.850	0.0393	0.0431	123.06	61.53	$6.38x10^{-4}$	0.0417	94.22
	80	0.059	0.0337	0.0388	105.79	52.90	$5.48x10^{-4}$	0.0358	93.98
B	50	0.004	0.0013	0.0025	7.82	3.91	$4.05x10^{-5}$	0.0026	49.04
	75	0.016	0.0004	0.0088	27.88	13.94	$1.44x10^{-4}$	0.0094	4.23

Note: The letters A and B correspond to the solutions of 0.5 M $ZnCl_2$ in Ethaline200 and 0.5 M ZnO in Ethaline200, respectively.

In table A.10 the results about the determination of the cathodic efficiencies for the experiments performed in the hull cell concerning to the study of the influence of the temperature, are presented.

Table A.10 – Electrolytic bath, temperature, current, mass of deposition and dissolution of the zinc, charge, charge per electrons, mol of zinc, mass expected of zinc and cathodic efficiency for the experiments performed for the study of the influence of the temperature in the hull cell.

Electrolytic bath	T (ºC)	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Zn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	50	0.055	0.0332	0.0338	99.76	49.88	$5.17x10^{-4}$	0.0338	98.18
	65	0.065	0.0395	0.0414	117.75	58.88	$6.10x10^{-4}$	0.0399	98.97
B	50	0.041	0.0199	0.0265	74.91	37.46	$3.88x10^{-4}$	0.0254	78.37
	60	0.032	0.0160	0.0241	58.03	29.02	$3.00x10^{-4}$	0.0197	81.34
	65	0.050	0.0190	0.0318	89.94	44.97	$4.70x10^{-4}$	0.0305	62.95

Note: The letters A and B correspond to the solutions of 0.5 M $ZnSO_4.7H_2O$ in Ethaline200 and 0.5 M $ZnCl_2$ in Reline200, respectively.

In table A.11 the results about the determination of the zinc concentration in the electrolytic bath for the experiment where was used 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 as electrolyte, are shown.

Table A.11 – Time, pH, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of zinc in the diluted solution measured by AAS and real concentration of zinc in the electrolytic bath for the experiment where was used 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 as electrolyte.

t (h)	pH	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Zn\ diluted\ solution}$ (ppm)	$C_{Zn\ electrolyte}$ (g/L)	$C_{Zn\ electrolyte}$ (mol/L)
0	5.039	0.2212	$2.00x10^{-4}$	5.00	1.308	32.70	0.50
1	6.999	0.2173	$1.96x10^{-4}$	5.00	1.707	43.60	0.67
2	7.046	0.3223	$2.91x10^{-4}$	10.00	2.263	77.94	1.19
3	7.120	0.2230	$2.02x10^{-4}$	10.00	1.625	80.88	1.24
4	7.151	0.2364	$2.14x10^{-4}$	10.00	1.649	77.43	1.18

In table A.12 the results about the determination of the mass balance for the experiment where was used 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 as electrolyte, are shown.

Table A.12– Time, mass of the anode and the cathode, mass of dissolution and deposition accumulated, concentration of Zn in the electrolyte measured by AAS, volume of the electrolyte in the electrolytic cell, moles of Zn in the electrolyte, real mass of zinc in the solution and expected mass of zinc in the solution, for the experiment where was used 0.5 M $Zn(NO_3)_2.6H_2O$ in Ethaline200 as electrolyte.

t (h)	$m_{dis.}$ (g)	$m_{dis.}$ accumulate (g)	$m_{dep.}$ (g)	$m_{dep.}$ accumulate (g)	$C_{Zn\ electrolyte}$ (mol/L)	$V_{electrolyte}$ (L)	n_{Zn} (mol)	m_{real} (g)	$m_{exp.}$ (g)
0	0.000	0.000	0.000	0.000	0.50	0.200	0.100	6.5400	6.5400
1	0.4999	0.4999	0.0490	0.0490	0.67	0.199	0.132	8.6673	6.9909
2	0.1631	0.6630	0.0770	0.1260	1.19	0.198	0.235	15.4005	7.0770
3	0.5434	1.2064	0.0928	0.2188	1.24	0.196	0.243	15.8859	7.5276
4	0.1867	1.3931	0.0044	0.2232	1.18	0.195	0.231	15.1139	7.7099

In table A.13 the results about the determination of the zinc concentration in the electrolytic bath for the experiment where was used 0.5 M ZnO plus 0.5 M citric acid in Ethaline200 as electrolyte, are shown.

Table A.13 – Time, pH, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of zinc in the diluted solution measured by AAS and real concentration of zinc in the electrolytic bath for the experiment where was used 0.5 M ZnO plus 0.5 M citric acid in Ethaline200 as electrolyte.

t (h)	pH	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Zn\ diluted\ solution}$ (ppm)	$C_{Zn\ electrolyte}$ (g/L)	$C_{Zn\ electrolyte}$ (mol/L)
0	3.809	0.2224	$2.01x10^{-4}$	5.00	1.308	32.70	0.50
1	3.810	0.2417	$2.18x10^{-4}$	10.00	1.510	60.35	1.06
2	3.764	0.2335	$2.11x10^{-4}$	10.00	1.241	58.99	0.90
3	3.821	0.2346	$2.12x10^{-4}$	10.00	1.138	53.84	0.82
4	3.842	0.2374	$2.14x10^{-4}$	10.00	1.213	56.72	0.87
5	4.151	0.2542	$2.30x10^{-4}$	20.00	1.780	155.45	2.38
6	4.682	0.2391	$2.16x10^{-4}$	20.00	1.207	112.07	1.71
7	6.193	0.2293	$2.07x10^{-4}$	20.00	1.292	125.09	1.91

In table A.14 the results about the determination of the mass balance for the experiment where was used 0.5 M ZnO plus 0.5 M citric acid in Ethaline200 as electrolyte, are shown.

Table A.14– Time, mass of the anode and the cathode, mass of dissolution and deposition accumulated, concentration of Zn in the electrolyte measured by AAS, volume of the electrolyte in the electrolytic cell, moles of Zn in the electrolyte, real mass of zinc in the solution and expected mass of zinc in the solution, for the experiment where was used 0.5 M ZnO plus 0.5 M citric acid in Ethaline200 as electrolyte.

t (h)	$m_{dis.}$ (g)	$m_{dis.\ accumulate}$ (g)	$m_{dep.}$ (g)	$m_{dep.\ accumulate}$ (g)	$C_{Zn\ electrolyte}$ (mol/L)	$V_{electrolyte}$ (L)	n_{Zn} (mol)	m_{real} (g)	$m_{exp.}$ (g)
0	0.000	0.000	0.000	0.000	0.50	0.200	0.100	6.5400	6.5400
1	0.1740	0.1740	0.0724	0.0724	1.06	0.199	0.211	13.7860	6.6416
2	0.2891	0.4631	0.0428	0.1152	0.90	0.198	0.178	11.6572	6.8879
3	0.1641	0.6272	0.0852	0.2004	0.82	0.196	0.162	10.5750	6.9668
4	1.1761	0.8033	0.0568	0.2572	0.87	0.195	0.169	11.0709	7.0861
5	0.1177	0.9210	0.0642	0.3214	2.38	0.194	0.461	30.1578	7.1396
6	0.1380	1.059	0.0599	0.3813	1.71	0.193	0.330	21.6067	7.2177
7	0.1207	0.1207	0.0654	0.4467	1.91	0.192	0.366	23.9666	7.2730

A.2.2 Electrodeposition of tin

In this chapter both the results obtained and the calculated results for the study of the electrodeposition of tin are shown.

In table A.15 the results about the determination of the cathodic efficiencies for the study of the influence of the types of electrolytic bath used are shown.

Table A.15 – Electrolytic bath, current, mass of deposition and dissolution of the tin, charge, charge per electrons, mol of tin, mass expected of tin and cathodic efficiency for the experiments performed for the study of the influence of the types of electrolytic bath used.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Sn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	0.028	0.0147	0.0219	50.98	25.49	$2.64x10^{-4}$	0.0314	46.88
B	0.105	0.0148	0.0167	190.24	95.12	$9.86x10^{-4}$	0.1170	12.65
C	0.054	0.0123	0.0753	96.38	48.19	$4.99x10^{-4}$	0.0593	20.75
D	0.021	0.0002	0.0219	37.31	18.66	$1.93x10^{-4}$	0.0230	0.87

Note: The letters A, B, C and D correspond to the solutions of 0.5 M $Sn(OH)_2$ in Ethaline200, 0.5 M $SnCl_2$ in Etaline200, 0.1 M $SnCl_2$ in Ethaline200 and pure Ethaline200, respectively.

In table A.16 the results about the determination of the anodic efficiencies for the study of the influence of the types of electrolytic bath used are shown.

Table A.16 – Electrolytic bath, current, mass of deposition and dissolution of the tin, charge, charge per electrons, mol of tin, mass expected of tin and anodic efficiency for the experiments performed for the study of the influence of the types of electrolytic bath used.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Sn} (mol)	$m_{exp.}$ (g)	$Ø_{ano.}$ (%)
A	0.022	0.0070	0.0132	40.11	20.06	$2.08x10^{-4}$	0.0247	53.50
B	0.027	0.0044	0.0360	49.19	24.60	$2.55x10^{-4}$	0.0302	118.98

Note: The letters A and B correspond to the solutions of 0.5 M $Sn(OH)_2$ in Ethaline200 and 0.1 M $SnCl_2$ in Etaline200, respectively.

In table A.17 the results about the determination of the cathodic efficiencies for the study of the influence of the addition of complexing agents are shown.

Table A.17 – Electrolytic bath, current, mass of deposition and dissolution of the tin, charge, charge per electrons, mol of tin, mass expected of tin and anodic efficiency for the experiments performed for the study of the influence of the addition of complexing agents.

Electrolytic bath	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	n_{Sn} (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	0.123	0.0117	0.0211	206.05	103.02	$1.07x10^{-3}$	0.1267	9.23
B	1.162	0.0328	0.0764	2084.4	1042.2	$1.08x10^{-2}$	1.2821	2.56
C	0.055	0.0159	0.0263	99.08	49.54	$5.13x10^{-4}$	0.0609	26.09
D	0.055	0.0113	0.0368	98.44	49.22	$5.10x10^{-4}$	0.0606	18.66
E	0.031	0.0126	0.0074	56.26	28.13	$2.92x10^{-4}$	0.0346	36.41
F	0.033	0.0155	0.0353	60.43	30.22	$3.13x10^{-4}$	0.0372	41.70
G	0.043	0.0077	0.0388	77.69	38.84	$4.03x10^{-4}$	0.0478	16.11
H	0.031	0.0065	0.0383	56.65	28.32	$2.94x10^{-4}$	0.0348	18.65

Note: The letters A, B, C, D, E, F, G and H correspond to the solutions of 0.5 M $SnCl_2$ plus 0.5 M citric acid in Ethaline200, 0.5 M $SnCl_2$ plus 0.5 M malic acid in Ethaline200, 0.5 M $Sn(OH)_2$ plus 0.5 M citric acid in Ethaline200, 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid in Ethaline200, 0.1 M $Sn(OH)_2$ plus 0.8 M citric acid in Ethaline200, 0.1 M $Sn(OH)_2$ plus 0.8 M malic acid in Ethaline200, 0.1 M $Sn(OH)_2$ plus 0.1 M malic acid in Ethaline200 and 0.1 M $Sn(OH)_2$ plus 0.05 M malic acid in Ethaline200, respectively.

In table A.18 the results about the determination of the cathodic efficiencies concerning to the study of the influence of the applied potential are shown.

Table A.18 – Electrolytic bath, cell potential, current, mass of deposition and dissolution of the tin, charge, charge per electrons, mol of tin, mass expected of tin and cathodic efficiency for the experiments performed for the study of the influence of the applied potential.

Electrolytic bath	P (V)	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e$^-$)	nS_n (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
A	2.25	0.105	0.0148	0.0167	190.24	95.12	$9.86x10^{-4}$	0.1170	12.65
	0.82	0.029	0.0120	0.0135	26.54	26.54	$2.75x10^{-4}$	0.0326	36.75
B	2.25	0.054	0.0123	0.0753	96.38	48.19	$4.99x10^{-4}$	0.0593	20.75
	0.82	0.021	0.0037	0.0258	38.48	19.24	$1.99x10^{-4}$	0.0237	15.63
C	2.25	0.123	0.0117	0.0211	206.05	103.02	$1.07x10^{-3}$	0.1267	9.23
	0.82	0.019	0.0137	0.0115	272.42	136.21	$1.41x10^{-3}$	0.1676	8.18
D	2.25	1.162	0.0328	0.0764	2084.4	1042.2	$1.08x10^{-2}$	1.2821	2.56
	0.82	0.017	0.0110	0.0350	30.80	15.40	$1.60x10^{-4}$	0.0189	58.06
E	2.25	0.055	0.0159	0.0263	99.08	49.54	$5.13x10^{-4}$	0.0609	26.09
	0.82	0.008	0.0042	0.0071	14.38	7.19	$7.45x10^{-5}$	0.0088	47.48
F	2.25	0.055	0.0113	0.0368	98.44	49.22	$5.10x10^{-4}$	0.0606	18.66
	0.82	0.009	0.0076	0.0301	15.73	7.86	$8.15x10^{-5}$	0.0097	78.55
G	2.25	0.043	0.0077	0.0388	77.69	38.84	$4.03x10^{-4}$	0.0478	16.11
	0.82	0.013	0.0066	0.0254	24.28	12.14	$1.26x10^{-4}$	0.0149	44.19
H	2.25	0.031	0.0065	0.0383	56.65	28.32	$2.94x10^{-4}$	0.0348	18.65
	0.82	0.008	0.0081	0.0149	14.58	7.29	$7.56x10^{-5}$	0.0090	90.32

Note: The letters A, B, C, D, E, F, G and H correspond to the solutions of 0.5 M $SnCl_2$ in Ethaline200, 0.1 M $SnCl_2$ in Ethaline200, 0.5 M $SnCl_2$ plus 0.5 M citric acid in Ethaline200, 0.5 M $SnCl_2$ plus 0.5 M malic acid in Ethaline200, 0.5 M $Sn(OH)_2$ plus 0.5 M citric acid in Ethaline200, 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid in Ethaline200, 0.1 M $Sn(OH)_2$ plus 0.1 M malic acid in Ethaline200 and 0.1 M $Sn(OH)_2$ plus 0.05 M malic acid in Ethaline200, respectively.

In table A.19 the results about the determination of the anodic efficiencies concerning to the study of the influence of the applied potential are shown.

Table A.19 – Electrolytic bath, cell potential, current, mass of deposition and dissolution of the tin, charge, charge per electrons, mol of tin, mass expected of tin and anodic efficiency for the experiments performed for the study of the influence of the applied potential.

Electrolytic bath	P (V)	C (A)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e$^-$)	nS_n (mol)	$m_{exp.}$ (g)	$Ø_{ano.}$ (%)
A	0.82	0.007	0.0045	0.0177	11.70	5.85	$6.10x10^{-5}$	0.0072	245.94
B	0.82	0.013	0.0041	0.0294	24.12	12.06	$1.20x10^{-4}$	0.0148	198.16
C	0.82	0.006	0.0050	0.0100	10.55	5.28	$5.50x10^{-5}$	0.0065	154.09

Note: The letters A, B and C correspond to the solutions of 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid in Ethaline200, 0.1 M $Sn(OH)_2$ plus 0.1 M malic acid in Ethaline200 and 0.1 M $Sn(OH)_2$ plus 0.05 M malic acid in Ethaline200, respectively.

In table A.20 the results about the study of the chemical dissolution are presented.

Table A.20 – Electrolytic bath, plates used in the experiment, initial mass and final mass of the brass plate, initial mass and final mass of the tin slice, efficiency of deposition and efficiency of dissolution for the experiments performed for the study of the chemical dissolution of tin.

Electrolytic bath	Plates used	t (h)	$m_{inicial\ of\ brass}$ (g)	$m_{final\ of\ brass}$ (g)	$m_{inicial\ of\ tin}$ (g)	$m_{final\ of\ tin}$ (g)	$Ø_{dep.}$ (%)	$Ø_{dis.}$ (%)
A	brass and tin	0.5	7.5253	7.5253	50.8891	50.8816	0.00	0.01
	brass and tin	17	7.7190	7.7190	55.7735	50.7429	0.00	0.05
B	brass and tin	0.5	7.5253	7.5253	49.3431	49.3431	0.00	0.00
	brass and tin	17	7.5601	7.5601	49.3219	49.3145	0.00	0.02
C	brass and tin	0.5	7.5253	7.5253	49.3497	49.3230	0.00	0.05
	brass and tin	17	7.6244	7.6248	51.1784	51.1677	0.01	0.02
	brass	22	5.1172	5.1159	----------	----------	-0.02	-------

Note: The letters A, B and C correspond to the solutions of 0.5 M $Sn(OH)_2$ in Ethaline200, 0.5 M $Sn(OH)_2$ plus 0.5 M malic acid in Ethaline200 and 0.1 M $SnCl_2$ plus 0.5 M malic acid in Ethaline200, respectively.

In table A.21 the results about the determination of the tin concentration in the electrolytic bath for the experiment performed at 0.82V and where was used pure Ethaline200 as electrolyte, are shown.

Table A.21 – Time, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of tin in the diluted solution measured by AAS and real concentration of tin in the electrolytic bath for the experiment performed at 0.82V and where was used pure Ethaline200 as electrolyte.

t (h)	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Sn\ diluted\ solution}$ (ppm)	$C_{Sn\ electrolyte}$ (ppm)
0.0	1.0792	$9.76x10^{-4}$	0.010	0.000	0.00
0.5	1.4574	$1.32x10^{-3}$	0.010	0.043	0.33
1.0	1.0727	$9.70x10^{-4}$	0.010	0.008	0.08
1.5	1.0851	$8.80x10^{-4}$	0.010	0.550	5.61
2.0	1.0751	$9.72x10^{-4}$	0.010	0.826	8.50
2.5	1.0766	$9.73x10^{-4}$	0.010	1.082	11.12
3.0	1.0778	$9.74x10^{-4}$	0.010	1.222	12.54
3.5	1.0667	$9.64x10^{-4}$	0.010	1.040	10.79
4.0	1.0871	$9.83x10^{-4}$	0.010	1.125	11.45
4.5	1.1151	$1.01x10^{-3}$	0.010	1.178	11.69
5.0	1.0772	$9.74x10^{-4}$	0.010	3.877	39.81
6.0	1.0656	$9.63x10^{-4}$	0.010	7.288	75.66

In table A.22 the results about the determination of the tin concentration in the electrolytic bath for the experiment performed at 2.25V and where was used pure Ethaline200 as electrolyte, are shown.

Table A.22 – Time, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of tin in the diluted solution measured by AAS and real concentration of tin in the electrolytic bath for the experiment performed at 2.25V and where was used pure Ethaline200 as electrolyte.

t (h)	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Sn\ diluted\ solution}$ (ppm)	$C_{Sn\ electrolyte}$ (ppm)
0.0	1.0792	$9.76x10^{-4}$	0.010	0.000	0.00
0.5	1.0713	$9.68x10^{-4}$	0.010	33.724	348.24
1.0	1.0768	$9.73x10^{-4}$	0.010	61.444	631.23
1.5	1.0928	$9.88x10^{-4}$	0.010	87.734	888.12
2.0	1.0821	$9.78x10^{-4}$	0.050	15.810	808.42
2.5	1.0788	$9.75x10^{-4}$	0.050	22.636	1160.82
3.0	1.0755	$9.72x10^{-4}$	0.050	24.679	1269.51
4.0	1.3723	$1.24x10^{-3}$	0.050	56.312	2269.69
8.0	1.3396	$1.21x10^{-3}$	0.050	65.196	2691.91

In table A.23 the results about the determination of the mass balance for the experiment performed at 2.25V and where was used pure Ethaline200 as electrolyte, are shown.

Table A.23– Time, mass of the anode and the cathode, mass of dissolution and deposition accumulated, concentration of Sn in the electrolyte measured by AAS, volume of the electrolyte in the electrolytic cell, moles of Sn in the electrolyte, real mass of tin in the solution and expected mass of tin in the solution, for the experiment performed at 2.25V and where was used pure Ethaline200 as electrolyte.

t (h)	$m_{dis.}$ (g)	$m_{dis.\ accumulate}$ (g)	$m_{dep.}$ (g)	$m_{dep.\ accumulate}$ (g)	$C_{Sn\ electrolyte}$ (mol/L)	$V_{electrolyte}$ (L)	n_{Sn} (mol)	m_{real} (g)	$m_{exp.}$ (g)
0.0	0.000	0.000	0.000	0.000	0.00	0.200	0.00	0.000	0.000
0.5	0.1177	0.1177	0.0018	0.0018	$2.93x10^{-3}$	0.199	$5.83x10^{-4}$	0.0693	0.1159
1.0	0.1068	0.2245	0.0048	0.0066	$5.32x10^{-3}$	0.198	$1.05x10^{-3}$	0.1250	0.2179
1.5	0.1138	0.3383	0.0042	0.0108	$7.48x10^{-3}$	0.197	$1.47x10^{-3}$	0.1750	0.3275
2.0	0.1469	0.4852	0.0084	0.0192	$7.65x10^{-3}$	0.196	$1.50x10^{-3}$	0.1780	0.4660
2.5	0.1289	0.6141	0.0116	0.0308	$9.78x10^{-3}$	0.195	$1.91x10^{-3}$	0.2264	0.5833
3.0	0.1456	0.7597	0.0124	0.0432	$1.07x10^{-2}$	0.194	$2.08x10^{-3}$	0.2463	0.7165
4.0	0.2719	1.0316	0.0209	0.0641	$1.91x10^{-2}$	0.193	$3.69x10^{-3}$	0.4375	0.9675
8.0	1.0249	2.0565	0.0343	0.0984	$2.27x10^{-2}$	0.192	$4.36x10^{-3}$	0.5155	1.9581

In table A.24 the results about the determination of the tin concentration in the electrolytic bath for the experiment where was used 0.1 M K_3-HEDTA in Ethaline200 as electrolyte, are presented.

Table A.24 – Time, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of tin in the diluted solution measured by AAS and real concentration of tin in the electrolytic bath for the experiment where was used 0.1 M K_3-HEDTA in Ethaline200 as electrolyte.

t (h)	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Sn\ diluted\ solution}$ (ppm)	$C_{Sn\ electrolyte}$ (g/L)
0.0	1.0869	$9.82x10^{-4}$	0.010	0.000	0.00
0.5	1.0846	$9.80x10^{-4}$	0.010	21.622	0.22
1.0	1.1168	$1.01x10^{-3}$	0.010	59.633	0.59
1.5	1.0764	$9.73x10^{-4}$	0.010	79.198	0.81
2.0	1.0747	$9.72x10^{-4}$	0.050	20.912	1.08
2.5	1.0741	$9.71x10^{-4}$	0.050	24.869	1.28
3.0	1.0822	$9.78x10^{-4}$	0.050	33.111	1.69
3.5	1.0647	$9.62x10^{-4}$	0.050	35.023	1.82
4.0	1.0814	$9.78x10^{-4}$	0.050	39.470	2.02
8.0	1.0404	$9.40x10^{-4}$	0.050	65.670	3.49
11.0	1.0920	$9.87x10^{-4}$	0.050	80.201	4.06
13.5	1.0961	$9.91x10^{-4}$	0.050	93.587	4.72
15.5	1.1099	$1.00x10^{-3}$	0.100	47.370	4.72
17.5	1.0945	$9.89x10^{-4}$	0.100	52.850	5.34
19.0	1.0755	$9.72x10^{-4}$	0.100	55.086	5.67
22.0	1.0546	$9.53x10^{-4}$	0.100	56.051	5.88
24.0	1.1017	$9.96x10^{-4}$	0.100	63.486	6.37
43.0	0.1036	$9.36x10^{-5}$	0.010	94.630	10.10
67.0	0.0855	$7.73x10^{-5}$	0.040	33.877	17.53
130	0.0165	$1.49x10^{-5}$	0.010	65.264	43.76

In table A.25 the results about the determination of the mass balance for the experiment where was used 0.1 M K_3-HEDTA in Ethaline200 as electrolyte, are shown.

Table A.25– Time, mass of the anode and the cathode, mass of dissolution and deposition accumulated, concentration of Sn in the electrolyte measured by AAS, volume of the electrolyte in the electrolytic cell, moles of Sn in the electrolyte, real mass of tin in the solution and expected mass of tin in the solution, for the experiment where was used 0.1 M K_3-HEDTA in Ethaline200 as electrolyte.

t (h)	$m_{dis.}$ (g)	$m_{dis.\ accumulate}$ (g)	$m_{dep.}$ (g)	$m_{dep.\ accumulate}$ (g)	$C_{Sn\ electrolyte}$ (mol/L)	$V_{electrolyte}$ (L)	n_{Sn} (mol)	m_{real} (g)	$m_{exp.}$ (g)
0.0	0.0000	0.0000	0.0000	0.0000	0.00	0.065	0.00	0.0000	0.0000
0.5	0.0510	0.0510	0.0005	0.0005	$1.86x10^{-3}$	0.064	$1.19x10^{-4}$	0.0141	0.0505
1.0	0.0416	0.0926	0.0011	0.0016	$4.98x10^{-3}$	0.063	$3.14x10^{-4}$	0.0372	0.0910
1.5	0.0387	0.1313	0.0029	0.0045	$6.86x10^{-3}$	0.062	$4.25x10^{-4}$	0.0505	0.1268
2.0	0.0450	0.1763	0.0040	0.0085	$9.07x10^{-3}$	0.061	$5.53x10^{-4}$	0.0657	0.1678
2.5	0.0339	0.2102	0.0044	0.0129	$1.08x10^{-2}$	0.060	$6.48x10^{-4}$	0.0768	0.1973
3.0	0.0374	0.2476	0.0048	0.0177	$1.42x10^{-2}$	0.059	$8.38x10^{-4}$	0.0998	0.2299
3.5	0.0299	0.2775	0.0054	0.0231	$1.53x10^{-2}$	0.058	$8.87x10^{-4}$	0.1055	0.2544
4.0	0.0311	0.3086	0.0051	0.0282	$1.70x10^{-2}$	0.057	$9.69x10^{-4}$	0.1151	0.2804
8.0	0.2152	0.5238	0.0237	0.0519	$2.94x10^{-2}$	0.056	$1.65x10^{-3}$	0.1955	0.4719
11.0	0.1443	0.6681	0.0244	0.0763	$3.42x10^{-2}$	0.055	$1.88x10^{-3}$	0.2234	0.5918
13.5	0.1134	0.7815	0.0304	0.1067	$3.98x10^{-2}$	0.054	$2.15x10^{-3}$	0.2550	0.6748
15.5	0.0934	0.8749	0.0217	0.1284	$3.98x10^{-2}$	0.053	$2.11x10^{-3}$	0.2502	0.7465
17.5	0.0829	0.9578	0.0161	0.1445	$4.50x10^{-2}$	0.052	$2.34x10^{-3}$	0.2778	0.8133
19.0	0.0526	1.0104	0.0130	0.1575	$4.77x10^{-2}$	0.051	$2.43x10^{-3}$	0.2890	0.8529
22.0	0.1158	1.1262	0.0237	0.1812	$4.95x10^{-2}$	0.050	$2.48x10^{-3}$	0.2940	0.9450
24.0	0.0681	1.1943	0.0204	0.2016	$5.37x10^{-2}$	0.049	$2.63x10^{-3}$	0.3124	0.9927
43.0	0.5982	1.7925	0.0340	0.2356	$8.51x10^{-2}$	0.049	$4.17x10^{-3}$	0.4941	1.5569
67.0	1.6071	3.3996	0.0560	0.2916	$1.48x10^{-1}$	0.048	$7.10x10^{-3}$	0.8556	3.1080
130	3.3475	6.7471	0.0403	0.3319	$3.69x10^{-1}$	0.048	$1.77x10^{-2}$	2.1309	6.4152

A.2.3 Electrodeposition of zinc/tin alloys

In this chapter both the results obtained and the calculated results for the study of the electrodeposition of zinc/tin alloys are shown.

In table A.26 the results about the determination of the cathodic efficiencies for the study of the effect of stirring in the electrodeposition are presented.

Table A.26 – Experimental conditions, cathode used in each experiment, applied potential, mass of deposition of zinc and tin, mass of dissolution of the tin, charge, charge per electrons, mol of zinc or tin, mass expected of zinc or tin and cathodic efficiency for the experiments performed for the study of the effect of stirring in the electrodeposition.

Experimental conditions	Cathode	P (V)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	$n_{Zn/Sn}$ (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
with stir	brass	4.6	0.1874	0.4161	475.37	237.69	$2.46x10^{-3}$	0.2627	71.33
	iron	4.6	0.1365	0.4038	468.85	234.42	$2.43x10^{-3}$	0.2302	59.29
without stir	brass	10	0.0205	0.4512	456.12	228.06	$2.36x10^{-3}$	0.2724	7.53
	iron	8.6	0.0086	0.1154	84.32	42.16	$4.37x10^{-4}$	0.0465	18.50

In table A.27 the results about the determination of the content of zinc and tin in the deposition, concerning to the study of the effect of stirring in the electrodeposition are presented.

Table A.27 – Experimental conditions, cathode used in each experiment, dilution ratio used to dilute the deposition, concentration of zinc and tin in the diluted solution, mass of zinc and tin in the deposition and percentage of zinc and tin in the deposition, for the experiments performed for the study of the effect of stirring in the electrodeposition.

Experimental conditions	Cathode	D.R		$C_{diluted\ solution}$ (ppm)		$m_{deposited}$ (g)		Content (%)	
		Zn	Sn	Zn	Sn	Zn	Sn	Zn	Sn
with stir	brass	250	50	1.145	19.583	0.007	0.024	22.6	77.4
	iron	500	10	0.744	45.572	0.009	0.011	44.9	55.1
without stir	brass	250	5	0.055	39.766	$3.44x10^{-4}$	0.005	6.5	93.5
	iron	50	1	0.096	16.004	$1.20x10^{-4}$	$4.00x10^{-4}$	23.1	76.9

In table A.28 the results about the determination of the thickness of the deposition, concerning to the study of the effect of stirring in the electrodeposition are presented.

Table A.28 – Experimental conditions, cathode used in each experiment, area of the deposition obtained, mass of the deposition obtained, average of the density of the deposition, volume of the deposition and thickness of the deposition for the experiments performed for the study of the effect of stirring in the electrodeposition.

Experimental conditions	Cathode	$A_{deposition}$ (m^2)	$m_{deposition}$ (g)	$\rho_{average}$ (g/m^3)	$V_{deposition}$ (m^3)	Thickness (µm)
with stir	brass	0.0018	0.1874	7271543.78	$5.58x10^{-8}$	14.3
	iron	0.0013	0.1365	7233597.35	$1.89x10^{-8}$	14.5
without stir	brass	0.0150	0.0205	7299004.14	$2.81x10^{-9}$	0.2
	iron	0.0090	0.0086	7270776.77	$1.18x10^{-9}$	0.1

In table A.29 the results about the determination of the cathodic efficiencies for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte are shown.

Table A.29 – Cathode used in each experiment, time, applied potential, mass of deposition of zinc and tin, mass of dissolution of the tin, charge, charge per electrons, mol of zinc or tin, mass expected of zinc or tin and cathodic efficiency for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	P (V)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	$n_{Zn/Sn}$ (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
brass	1	6.1	0.0184	0.0368	41.07	20.54	$2.13x10^{-4}$	0.0223	82.65
	5	6.5	0.0547	0.1172	158.80	79.40	$8.23x10^{-3}$	0.0789	69.32
	15	5.7	0.1586	0.3893	470.45	235.22	$2.44x10^{-3}$	0.2470	64.20
	30	6.5	0.1845	0.7600	936.73	468.36	$4.85x10^{-3}$	0.4723	39.06
iron	1	5.3	0.0094	0.0376	35.81	17.90	$1.86x10^{-4}$	0.0216	43.55
	5	5.9	0.0511	0.1240	157.33	78.66	$8.15x10^{-4}$	0.0966	52.92
	15	6.7	0.1316	0.3872	464.19	232.10	$2.40x10^{-3}$	0.2318	56.78
	30	6.6	0.1934	0.7357	919.43	459.72	$4.76x10^{-3}$	0.5006	38.63

In table A.30 the results about the determination of the content of zinc and tin in the deposition for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.30 – Cathode used in each experiment, time, dilution ratio used to dilute the deposition, concentration of zinc and tin in the diluted solution, mass of zinc and tin in the deposition and percentage of zinc and tin in the deposition, for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	D.R		$C_{diluted\ solution}$ (ppm)		$m_{deposited}$ (g)		Content (%)	
		Zn	Sn	Zn	Sn	Zn	Sn	Zn	Sn
brass	1	100	2	0.363	50.444	0.001	0.003	26.5	73.5
	5	400	10	0.582	31.108	0.006	0.008	42.8	57.2
	15	1000	20	0.546	56.445	0.014	0.028	32.6	67.4
	30	1000	20	0.571	42.526	0.014	0.021	40.2	59.8
iron	1	20	1	0.016	6.822	$8.00x10^{-6}$	$1.71x10^{-4}$	4.5	95.5
	5	1	1	0.291	56.771	$7.00x10^{-6}$	$1.42x10^{-3}$	0.5	99.5
	15	1000	20	0.653	45.225	0.016	0.023	41.9	58.1
	30	200	10	0.337	39.238	0.003	0.010	25.6	74.4

In table A.31 the results about the determination of the thickness of the deposition for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.31 – Cathode used in each experiment, time, area of the deposition obtained, mass of the deposition obtained average of the density of the deposition, volume of the deposition and thickness of the deposition for the experiments where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	$A_{deposition}$ (m^2)	$m_{deposition}$ (g)	$\rho_{average}$ (g/m^3)	$V_{deposition}$ (m^3)	Thickness (µm)
brass	1	0.0018	0.0184	7265017.93	$2.53x10^{-9}$	1.4
	5	0.0018	0.0547	7237233.95	$7.56x10^{-9}$	4.2
	15	0.0018	0.1586	7254581.77	$2.19x10^{-8}$	12.1
	30	0.0018	0.1845	7241713.94	$2.55x10^{-8}$	14.2
iron	1	0.0015	0.0094	7302383.09	$1.29x10^{-9}$	0.9
	5	0.0015	0.0511	7309133.05	$6.99x10^{-9}$	4.7
	15	0.0018	0.1316	7238725.52	$1.82x10^{-8}$	10.4
	30	0.0015	0.1934	7238725.52	$2.66x10^{-8}$	17.7

In table A.32 the results about the determination of the cathodic efficiencies for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte are shown.

Table A.32 – Cathode used in each experiment, time, applied potential, mass of deposition of zinc and tin, mass of dissolution of the tin, charge, charge per electrons, mol of zinc or tin, mass expected of zinc or tin and cathodic efficiency for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	P (V)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	$n_{Zn/Sn}$ (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
brass	15	8.5	0.1312	1.1144	463.31	231.66	$2.40x10^{-3}$	0.2180	60.19
iron	15	8.1	0.0789	0.3656	458.65	229.32	$2.38x10^{-3}$	0.2250	35.07

In table A.33 the results about the determination of the content of zinc and tin in the deposition for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.33 – Cathode used in each experiment, time, dilution ratio used to dilute the deposition, concentration of zinc and tin in the diluted solution, mass of zinc and tin in the deposition and percentage of zinc and tin in the deposition, for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	D.R		$C_{diluted\ solution}$ (ppm)		$m_{deposited}$ (g)		Content (%)	
		Zn	Sn	Zn	Sn	Zn	Sn	Zn	Sn
brass	15	1000	20	0.590	26.811	0.015	0.013	52.4	47.6
iron	15	200	5	0.735	35.757	0.004	0.004	45.1	54.9

In table A.34 the results about the determination of the thickness of the deposition for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.34 – Cathode used in each experiment, time, area of the deposition obtained, mass of the deposition obtained average of the density of the deposition, volume of the deposition and thickness of the deposition for the experiments where was used 0.54 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	$A_{deposition}$ (m^2)	$m_{deposition}$ (g)	$\rho_{average}$ (g/m^3)	$V_{deposition}$ (m^3)	Thickness (µm)
brass	15	0.0018	0.1312	7220941.02	$1.82x10^{-8}$	10.1
iron	15	0.0015	0.0789	7233292.97	$1.09x10^{-8}$	7.3

In table A.35 the results about the determination of the cathodic efficiencies for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte are shown.

Table A.35 – Cathode used in each experiment, time, applied potential, mass of deposition of zinc and tin, mass of dissolution of the tin, charge, charge per electrons, mol of zinc or tin, mass expected of zinc or tin and cathodic efficiency for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	P (V)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	$n_{Zn/Sn}$ (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
iron	1	4.3	0.0011	0.0630	35.81	17.91	$1.86x10^{-4}$	0.0209	5.25
	5	4.5	0.0311	0.1457	155.03	77.52	$8.03x10^{-4}$	0.0893	34.81
	10	4.4	0.0445	0.2620	315.55	157.78	$1.64x10^{-3}$	0.1798	24.75
	15	4.4	0.0829	0.3748	484.98	242.49	$2.51x10^{-3}$	0.2774	29.88
	20	4.4	0.1107	0.4999	630.64	315.32	$3.27x10^{-3}$	0.3605	30.71
	30	4.3	0.1378	0.7317	931.42	465.71	$4.83x10^{-3}$	0.5363	25.70

In table A.36 the results about the determination of the content of zinc and tin in the deposition for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.36 – Cathode used in each experiment, time, dilution ratio used to dilute the deposition, concentration of zinc and tin in the diluted solution, mass of zinc and tin in the deposition and percentage of zinc and tin in the deposition, for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	D.R		$C_{diluted\ solution}$ (ppm)		$m_{deposited}$ (g)		Content (%)	
		Zn	Sn	Zn	Sn	Zn	Sn	Zn	Sn
iron	1	200	5	0.022	7.082	$1.1x10^{-4}$	$8.9x10^{-4}$	11.1	88.9
	5	50	2	0.218	33.289	$2.7x10^{-4}$	$1.7x10^{-3}$	14.1	85.9
	10	250	5	0.225	57.281	$1.4x10^{-3}$	$7.2x10^{-3}$	16.4	83.6
	15	400	5	0.255	110.419	$2.6x10^{-3}$	$1.4x10^{-2}$	15.6	84.4
	20	400	5	0.254	108.781	$2.5x10^{-3}$	$1.4x10^{-2}$	15.7	84.3
	30	500	5	0.182	109.418	$2.3x10^{-3}$	$1.3x10^{5}$	14.3	85.7

In table A.37 the results about the determination of the thickness of the deposition for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 and concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte, are presented.

Table A.37 – Cathode used in each experiment, time, area of the deposition obtained, mass of the deposition obtained average of the density of the deposition, volume of the deposition and thickness of the deposition for the experiments where was used 0.10 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200, concerning to the study of the influence of the concentration of $ZnCl_2$ used in the electrolyte.

Cathode	t (min)	$A_{deposition}$ (m^2)	$m_{deposition}$ (g)	$\rho_{average}$ (g/m^3)	$V_{deposition}$ (m^3)	Thickness (µm)
iron	1	0.0015	0.0011	7291210.75	$1.51x10^{-10}$	0.1
	5	0.0015	0.0311	7286083.53	$4.27x10^{-9}$	2.8
	10	0.0015	0.0445	7282092.92	$6.11x10^{-9}$	4.1
	15	0.0018	0.0829	7283490.09	$1.14x10^{-8}$	6.2
	20	0.0015	0.1107	7283242.65	$1.52x10^{-8}$	8.2
	30	0.0019	0.1378	7285755.77	$1.89x10^{-8}$	10.0

In table A.38 the results about the determination of the cathodic efficiencies for the experiments performed for the study of the influence of the applied current are shown.

Table A.38 – Cathode used in each experiment, applied current and applied potential, mass of deposition of zinc and tin, mass of dissolution of the tin, charge, charge per electrons, mol of zinc or tin, mass expected of zinc or tin and cathodic efficiency for the experiments performed for the study of the influence of the applied current.

Cathode	C (A)	P (V)	$m_{dep.}$ (g)	$m_{dis.}$ (g)	Q (c)	Q/nF (c/e^-)	$n_{Zn/Sn}$ (mol)	$m_{exp.}$ (g)	$Ø_{cat.}$ (%)
brass	0.25	2.3	0.1907	0.3946	451.80	225.90	$2.34x10^{-3}$	0.2488	76.66
	0.51	4.6	0.1796	0.7491	931.36	465.68	$4.83x10^{-3}$	0.4495	39.96
iron	0.25	2.3	0.1219	0.3180	400.60	200.30	$2.08x10^{-3}$	0.2089	58.34
	0.51	6.6	0.1934	0.7357	919.43	459.72	$4.76x10^{-3}$	0.5006	38.63

In table A.39 the results about the determination of the content of zinc and tin in the deposition for the experiments performed for the study of the influence of the applied current are presented.

Table A.39 – Cathode used in each experiment, applied current, dilution ratio used to dilute the deposition, concentration of zinc and tin in the diluted solution, mass of zinc and tin in the deposition and percentage of zinc and tin in the deposition, for the experiments performed for the study of the influence of the applied current.

Cathode	C (A)	D.R		$C_{diluted\ solution}$ (ppm)		$m_{deposited}$ (g)		Content (%)	
		Zn	Sn	Zn	Sn	Zn	Sn	Zn	Sn
brass	0.25	50	50	1.045	3.430	0.001	0.004	23.4	76.6
	0.51	500	50	1.697	18.398	0.021	0.023	48.0	52.0
iron	0.25	1000	10	0.443	86.498	0.011	0.022	33.9	66.1
	0.51	400	10	0.337	39.238	0.003	0.010	25.6	74.4

In table A.40 the results about the determination of the thickness of the deposition for the experiments performed for the study of the influence of the applied current, are presented.

Table A.40 – Cathode used in each experiment, applied current, area of the deposition obtained, mass of the deposition obtained average of the density of the deposition, volume of the deposition and thickness of the deposition for the experiments performed for the study of the influence of the applied current.

Cathode	C (A)	$A_{deposition}$ (m^2)	$m_{deposition}$ (g)	$\rho_{average}$ (g/m^3)	$V_{deposition}$ (m^3)	Thickness (µm)
brass	0.25	0.0018	0.1907	7270301.68	$2.62x10^{-8}$	14.6
	0.51	0.0018	0.1796	7228431.92	$2.48x10^{-8}$	13.8
iron	0.25	0.0014	0.1219	7252422.67	$1.68x10^{-8}$	12.5
	0.51	0.0015	0.1934	7266530.98	$2.66x10^{-8}$	17.7

In table A.41 the results about the determination of the tin concentration in the electrolytic bath for the experiment where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 as electrolyte, are presented.

Table A.41 – Time, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of tin in the diluted solution measured by AAS and real concentration of tin in the electrolytic bath for the experiment where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 as electrolyte.

t (h)	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Sn\ diluted\ solution}$ (ppm)	$C_{Sn\ electrolyte}$ (mol/L)
0.0	0.5254	$4.75x10^{-4}$	0.100	34.463	0.061
2.0	0.2576	$2.33x10^{-4}$	0.050	39.385	0.071
4.0	0.2519	$2.28x10^{-4}$	0.050	37.975	0.070
5.5	0.2056	$1.86x10^{-4}$	0.050	31.512	0.071
7.5	0.2504	$2.26x10^{-4}$	0.050	38.034	0.071
10.0	0.2399	$2.17x10^{-4}$	0.050	36.959	0.072
12.5	0.2454	$2.22x10^{-4}$	0.050	37.383	0.071
14.5	0.2506	$2.26x10^{-4}$	0.050	39.383	0.073
18.0	0.2389	$2.16x10^{-4}$	0.050	38.489	0.075

In table A.42 the results about the determination of the zinc concentration in the electrolytic bath for the experiment where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 as electrolyte, are presented.

Table A.42 – Time, mass of sample that was pipeted from the bath, volume of the sample that was pipeted, volume used to dilute that sample, concentration of zinc in the diluted solution measured by AAS and real concentration of zinc in the electrolytic bath for the experiment where was used 0.27 M $ZnCl_2$ plus 0.07 M $SnCl_2$ with 0.015 M K_3-HEDTA in Ethaline200 as electrolyte.

t (h)	$m_{sample\ of\ solution}$ (g)	$V_{pipeted}$ (L)	$V_{to\ dilute\ the\ sample}$ (L)	$C_{Zn\ diluted\ solution}$ (ppm)	$C_{Zn\ electrolyte}$ (mol/L)
0.0	0.1139	$1.03x10^{-4}$	2.00	0.990	0.294
2.0	0.1074	$9.71x10^{-5}$	2.00	0.897	0.283
4.0	0.1059	$9.57x10^{-5}$	2.00	0.868	0.277
5.5	0.0972	$8.79x10^{-5}$	2.00	0.803	0.279
7.5	0.1056	$9.55x10^{-5}$	2.00	0.887	0.284
10.0	0.1065	$9.63x10^{-5}$	2.00	0.865	0.275
12.5	0.1061	$9.59x10^{-5}$	2.00	0.915	0.292
14.5	0.1119	$1.01x10^{-4}$	2.00	0.935	0.283
18.0	0.1032	$9.33x10^{-5}$	2.00	0.856	0.281

A.2.4 Electrodeposition of refractory metals

In this chapter, both the results obtained and the calculated results for the study of the electrodeposition of refractory metals are shown.

In table A.43 the results about the preparation of IL's to dissolve molybdenum are presented.

Table A.43 – Information about the preparation of IL's to dissolve molybdenum: mixtures that were done and if they were liquids or not below 150ºC and mass of MoO_3 to dissolve in the solutions that were liquids and if it dissolved or not.

Mixture	Liquid below 150ºC	$m_{MoO3\ to\ dissolve}$ (g)	Dissolution of molybdenum
30 CCC : 1 $ZnCl_2$	No	----------	----------
2 CCC : 1 $ZnCl_2$	No	----------	----------
1 CCC : 2 $ZnCl_2$	Yes	1.3132	No
1 CCC : 3 $ZnCl_2$	Yes	1.3781	No
2 CC : 1 $Zn(NO_3)_2.6H_2O$	No	----------	----------

In table A.44 the results about the synthesis of quaternary ammonium salts are shown.

Table A.44 – Operational conditions, mixtures that were done, mass of the tertiary ammine and mass of the halogenated alkane added, mass of the salts that were obtained and reaction yields for the synthesis of quaternary ammonium salts.

Operational conditions	Mixture	$m_{tertiary\ ammine}$ (g)	$m_{halogenated\ alkane}$ (g)	$m_{salt\ obtained}$ (g)	η (%)
molar ratio-1 : 1 t-1 h T-room temperature with stirring	1-iodopropane : triethylamine	14.0436	19.1510	1.6845	10.4
molar ratio-1 : 1 t-22 h T-60ºC Solvent-ethanol with reflux	1-chloropropane : triethylamine	15.6469	13.1570	0.7126	3.19
Molar ratio.2 : 1 t-29 h T-60ºC solvent-chloropropane with reflux	1-chloropropane : triethylamine	12.3241	18.6143	0.0698	0.41

A.3 Calculations

In this section, examples of the main calculations made in this thesis are presented.

A.3.1 Cathodic and anodic efficiencies

The cathodic and anodic efficiencies were calculated based on Faraday's Law and the following example is concerning to the experiment performed at 2.25V and for the study of electrodeposition of zinc (table 9.3).

During the performance of the experiments the variation of the current and potential over time were traceable by a computer. These data were exported for a excel file and after that the charge for each experiment were calculated.

With the data exported for the excel is possible to draw a graph with the variation of the current over time.

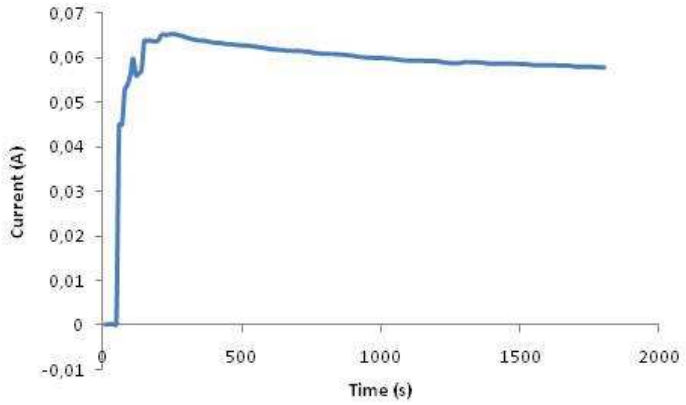

Figure A.3 – variation of the current over time.

The charge can be calculated by the following expression:

$$Q = C \times t(s)$$

But as there is a variation of the current over the time, the charge is calculated by the integration of the area below the curve and for this example the value of the charge is 123.06 C.

After that the charge is divided by the number of the electrons that are needed to oxidize or reduce the metal (for both tin and zinc was considered that the number of electrons needed is 2).

$$\frac{Q}{nF} = \frac{123.06}{2} = 61.53C / e^{-}$$

If the last result is divided by the Faraday constant it is obtained the moles of the metal.

$$n = \frac{61.53}{96485} = 6.38 \times 10^{-4} mol$$

The mass expected of the metal can be calculated multiplying the molar mass of the substance by the number of moles.

$$m_{\exp.} = 6.38 \times 10^{-4} \times 65.41 = 0.0417\, g$$

The cathodic efficiency or the anodic efficiency is calculated dividing the mass of deposition or dissolution respectively, by the mass expected of the metal.

$$\phi_{cat.} = \frac{0.0393}{0.0417} \times 100 = 94.22\%$$

A.3.2 Concentration of the metal in the electrolyte

The following example is concerning to the experiment performed during 1 hour for the study of the zinc electrodeposition (table 9.11).

The volume that was pipeted from the electrolytic bath was also weighted. With the mass of the sample that was pipeted and the density of the Ethaline200 is possible to know the exactly volume of the sample pipeted.

$$V_{pipeted} = \frac{m_{samplepipeted}}{\rho_{Ethaline200}} = \frac{0.2173}{1106.23} = 1.96 \times 10^{-4} L$$

Then the concentration of the metal in the electrolyte is calculated by the following expression.

$$C_{electrolyte} = \frac{C_{dilutedsolution} \times V_{dissolvethesample}}{V_{pipeted}} = \frac{1.707 \times 5.00}{1.96 \times 10^{-4}} = 43598.02 mg/L = 43.60 g/L$$

A.3.3 Mass balance

The following example is concerning to the experiment performed during 1 hour for the study of the zinc electrodeposition (table 9.12).

Firstly it needs to be calculated the accumulated mass of dissolution or deposition over time. In this case, the accumulated mass corresponds to the mass of dissolution or deposition obtained in the end of 1 hour of experiment.

Then, the mass expected of the metal in the electrolyte can be calculated by the following mass balance.

$$m_{\exp ected} = m_{beginning} + m_{dissolved} - m_{deposited} = 6.5400 + 0.4999 - 0.0490 = 6.9909\,g$$

A.3.4 Efficiency for the chemical dissolution of tin

The following example is concerning to the experiment performed during 0.5 hour with 0.5 M $Sn(OH)_2$ in Ethaline200 for the study of the chemical dissolution of tin (table 9.20).

The efficiency of the chemical dissolution of tin is calculated simply by the next expression.

$$\Phi = \frac{m_{initial} - m_{final}}{m_{initial}} \times 100 = \frac{50.8891 - 50.8816}{50.8891} \times 100 = 0.01\%$$

A.3.5 Content of zinc and tin in the deposition

The following example is concerning to the study performed with stir and with brass as cathode shown in table 9.27.

With the concentration measured by AAS and the molar ratio used for each metal, is possible to know the real concentration of the metal in the deposition. Following is shown an example of the calculation for the zinc.

$$C_{deposition} = C_{dilutedsol\,ution} \times D.R = 1.145 \times 250 = 286.250\,ppm$$

For the tin the value found was 979.150 ppm.

Then, the mass deposited of each metal can be calculated just multiplying the previously value by the volume of the volumetric flask used to do the dissolution of the deposition. For the zinc it was found a value of 0.007 g and for the zinc it was found a value of 0.024 g. This means that the total mass of the deposition is 0.031 g (0.007+0.024).

So, the content of the zinc and the tin in the deposition can be calculated by the following way (example just for the zinc).

$$Content = \frac{m_{zinc}}{m_{total}} \times 100 = \frac{0.007}{0.031} \times 100 = 22.6\%$$

A.3.6 Thickness of the deposition

The following example is concerning to the study performed with stir and with brass as cathode shown in table 9.28.

For the calculation of the thickness, firstly is need to calculate the average of the density of the deposition, as is shown following.

$$\rho_{average} = \rho_{Sn} \times Content_{Sn} + \rho_{Zn} \times Content_{Zn} \Leftrightarrow$$

$$\rho_{average} = 7310000 \times 0.774 + 7140000 \times 0.226 = 7271543.78 g/m^3$$

With the average of the density of the deposition and with the mass of deposition obtained, the volume of the deposition can be calculated.

$$V_{deposition} = \frac{m_{deposition}}{\rho_{average}} = \frac{0.1874}{7271543.78} = 5.58 \times 10^{-8} m^3$$

So, the thickness of the deposition can be calculated by the following equation.

$$Thickness = \frac{V_{deposition}}{A_{deposition}} = \frac{5.58 \times 10^{-8}}{0.0018} = 1.43 \times 10^{-5} m = 14.3 \mu m$$

A.3.7 Reaction yield

The following example is concerning to the synthesis of a quaternary ammonium salt using 1-iodopropane and triethylamine (table 9.44).

The equation of the reaction is the following.

$$C_3H_7I + C_6H_{15}N \rightarrow (C_2H_5)_3CH_2CH_2CH_3N^+ + I^-$$

For the performance of the experiment, 14.0436 g of $C_6H_{15}N$ was added to 19.1510 g of C_3H_7I. These mass correspond to 0.139 mol of $C_6H_{15}N$ and 0.113 mol of C_3H_7I. This means that in this experiment the limiting reagent is the C_3H_7I.

Because of the stoichiometrically of the reaction, the number of moles of C_3H_7I is the same that the number of moles of $(C_2H_5)_3CH_2CH_2CH_3N^+$ (0.113 mol). Then, the expected mass of the $(C_2H_5)_3CH_2CH_2CH_3N^+$ is 16.2728 g.

After this, the yield of the reaction can be calculated using the following equation.

$$\eta = \frac{m_{obtained}}{m_{\exp ected}} \times 100 = \frac{1.6845}{16.2728} \times 100 = 10.4\%$$

A.4 Safety data sheet

In this section, the safety data sheets of the substances used are presented.

A.4.1 Chloropropane

Material Safety Data Sheet

1-Chloropropane, 99%

Section 1 -Chemical Product and Company Identification

MSDS Name: 1-Chloropropane, 99%

Catalog Numbers: 10995-0000, 10995-0050, 10995-1000

Synonyms: n-Propyl chloride

Acros Organics BVBA

Company Identification: Janssen Pharmaceuticalaan 3a

2440 Geel, Belgium

Acros Organics

Company Identification: (USA) One Reagent Lane

Fair Lawn, NJ 07410

For information in the US, call: 800-ACROS-01

For information in Europe, call: +32 14 57 52 11

Emergency Number, Europe: +32 14 57 52 99

Emergency Number US: 201-796-7100

CHEMTREC Phone Number, US: 800-424-9300

CHEMTREC Phone Number, Europe: 703-527-3887

Section 2 -Composition, Information on Ingredients

CAS# Chemical Name: % EINECS#

540-54-5 1-Chloropropane 99% 208-749-7

Hazard Symbols: XN F

Risk Phrases: 11 20/21/22

Section 3 -Hazards Identification

EMERGENCY OVERVIEW

Highly flammable. Harmful by inhalation, in contact with skin and if swallowed.

Potential Health Effects

Eye: May cause eye irritation.

Skin: May cause skin irritation. Harmful if absorbed through the skin.

Ingestion: Harmful if swallowed. May cause irritation of the digestive tract.

Inhalation: Harmful if inhaled. May cause respiratory tract irritation.

Chronic:

Section 4 -First Aid Measures

Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get

Eyes:

medical aid.

Get medical aid. Flush skin with plenty of water for at least 15 minutes while removing contaminated

Skin:

clothing and shoes.

Ingestion: Get medical aid. Wash mouth out with water.

Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If

Inhalation:

breathing is difficult, give oxygen. Get medical aid.

Notes to

Physician:

Section 5 -Fire Fighting Measures

As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved

General

or equivalent), and full protective gear. Vapors can travel to a source of ignition and flash back. Will burn if

Information:

involved in a fire. Flammable liquid and vapor.

Extinguishing Use water spray to cool fire-exposed containers. Use foam, dry chemical, or carbon dioxide. Water may
Media: be ineffective.
Section 6 -Accidental Release Measures
General
Use proper personal protective equipment as indicated in Section 8.
Information:
Absorb spill with inert material (e.g. vermiculite, sand or earth), then place in suitable container. Remove
Spills/Leaks:
all sources of ignition. Use a spark-proof tool.
Section 7 -Handling and Storage
Handling: Use spark-proof tools and explosion proof equipment. Avoid breathing dust, vapor, mist, or gas. Avoid contact
with skin and eyes. Use caution when opening.
Storage: Keep away from sources of ignition. Store in a tightly closed container. Store in a dry area.
Refrigerator/flammables.
Section 8 -Exposure Controls, Personal Protection
Engineering Controls:
Use adequate general or local explosion-proof ventilation to keep airborne levels to acceptable levels.
Exposure Limits
CAS# 540-54-5:
Personal Protective Equipment
Eyes: Wear chemical splash goggles.
Skin: Wear appropriate protective gloves to prevent skin exposure.
Clothing: Wear appropriate protective clothing to prevent skin exposure.

Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a
Respirators: NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if
irritation or other symptoms are experienced.
Section 9 -Physical and Chemical Properties
Physical State: Clear liquid

Color: colorless

Odor: chloroform-like

pH: Not available

Vapor Pressure: 360 mbar @ 20 deg C

Viscosity: Not available

Boiling Point: 46 -47 deg C

Freezing/Melting Point: -123 deg C (-189.40..F)

Autoignition Temperature: 520 deg C (968.00 deg F)

Flash Point: -18 deg C (-0.40 deg F)

Explosion Limits: Lower: 2.60 vol %

Explosion Limits: Upper: 10.50 vol %

Decomposition Temperature: Not available

Solubility in water: 2.7g/l (20..C)

Specific Gravity/Density: 0.8920

Molecular Formula: C3H7Cl

Molecular Weight: 78.54

Section 10 -Stability and Reactivity

Chemical Stability: Stable under normal temperatures and pressures.

Conditions to Avoid: Incompatible materials, light, excess heat.

Incompatibilities with Other Materials Strong oxidizing agents, strong bases.

Hazardous Decomposition Products Hydrogen chloride, carbon monoxide, carbon dioxide.

Hazardous Polymerization Has not been reported.

Section 11 -Toxicological Information

RTECS#: CAS# 540-54-5: TX4400000

RTECS:

LD50/LC50: CAS# 540-54-5: Oral, rat: LD50 = >2 gm/kg; .

Carcinogenicity: 1-Chloropropane -Not listed as a carcinogen by ACGIH, IARC, NTP, or CA Prop 65.

Other: See actual entry in RTECS for complete information.

Section 12 -Ecological Information

Ecotoxicity: Not available

Section 13 -Disposal Considerations

Dispose of in a manner consistent with federal, state, and local regulations.

Section 14 -Transport Information

IATA IMO RID/ADR

Shipping PROPYL CHLORIDE(forbidden to ship via 1-PROPYL

Name: passenger air) CHLOROPROPANE CHLORIDE
Hazard Class: 3 3 3
UN Number: 1278 1278 1278
Packing
Group:
Section 15 -Regulatory Information
European/International Regulations
European Labeling in Accordance with EC Directives
Hazard Symbols: XN F
Risk Phrases:
R 11 Highly flammable.
R 20/21/22 Harmful by inhalation, in contact with skin and if swallowed.
Safety Phrases:
S 9 Keep container in a well-ventilated place.
S 29 Do not empty into drains.
WGK (Water Danger/Protection)
CAS# 540-54-5: 2
Canada
CAS# 540-54-5 is listed on Canada's DSL List
US Federal
TSCA
CAS# 540-54-5 is listed on the TSCA Inventory.
Section 16 -Other Information
MSDS Creation Date: 10/10/1996
Revision #1 Date 1/11/2002
Revisions were made in Sections: General revision.
The information above is believed to be accurate and represents the best information currently available
to us. However, we make no warranty of merchantibility or any other warranty, express or implied,
with respect to such information, and we assume no liability resulting from its use. Users should make
their own investigations to determine the suitability of the information for their particular purposes. In no
event shall the company be liable for any claims, losses, or damages of any third party or for lost profits

or any special, indirect, incidental, consequential, or exemplary damages howsoever arising, even if the
company has been advised of the possibility of such damages.

A.4.2 Chlormequat chloride

MATERIAL SAFETY DATA SHEET

Rev Date: 06/14/2006MSDS Date: 07/28/2000Supersedes: 01/14/1992

OHP, INC.

P.O. BOX 230

MAINLAND, PA 19451

800-659-6745

CYCOCEL® PLANT GROWTH REGULANT

EPA Registration Number: 241-74-59807

EMERGENCY AND PRODUCT INFORMATION

OHP, Inc.: . . . . . .(800)-356-4647

TRANSPORTATION EMERGENCY

CHEMTREC: . . . . . .(800)-424-9300

1

I. CHEMICAL PRODUCT INFORMATION

Trade Name . . . . . .: CYCOCEL® PLANT
GROWTH REGULANT

Chemical Name . . . . . .: 2-chloro-N,N,N,-
trimethylethanaminium chloride

Synonyms . . . . . .: chlormequat chloride,
CL38,555; CCC

Formula . . . . . .: C5 H13 C12 N

Chemical Family . . . . . .: quaternary ammonium

Mol Wt . . . . . .: 158.1

II. INGREDIENTS

COMPONENT CAS No. % PEL/TLV – SOURCE

chlormequat chloride 999-81-5 11.80 None established

Inerts N/A 88.20 None established

SARA Title III Section 313: Not listed

III. PHYSICAL DATA

Boiling/Melting Point@ 760mm Hg . . . . . .: 100℃

pH . . . . . .: 4.8 – 5.2

Vapor Pressure mmHg @ 20℃ . . . .: Similar to wate r

Specific Gravity or Bulk Density . .: 1.02 g/mL
Solubility in Water . . . . . .: Complete
Appearance . . . . . .: Pale yellow liquid
Odor . . . . . .: Fishy
Intensity . . . . . .: Slight
IV. FIRE AND EXPLOSION DATA
Flash Point (test method) . . . . . .: > 190℉ TCC
Autoignition Temp . . . . . .: N/D
Flammability Limits in Air (% by Vol):
Lower: N/D
Upper: N/D
NFPA 704 HAZARD CODES
Health: N/R Flammable: N/R Instability: 0 Other: N/R
NFPA 30 Storage Classification . . .: N/R
Extinguishing Medium . . . . . .: Use water fog, foam, CO(2),
or dry chemical extinguishing media.
Special Fire Fighting Procedures . .: Firefighters should be
equipped with self-contained breathing apparatus and
turnout gear.
Unusual Fire Explosion Hazards . .: None known.
Decomposition temperature for the technical = 245° C.
V. HEALTH DATA
TOXICOLOGICAL TEST DATA:
Data for the formulated product:
Rat, Oral LD50 (male) > 3915 mg/kg
Rat, Inhalation LC50 (4 hr, actual) – Not available
Rat, Inhalation LC50 (1 hr calculated) – Not available
Rabbit, Dermal LD50 (male) 5075
Rabbit, Eye Irritation – Not irritating
Rabbit, Skin Irritation – Not irritating
Guinea pig, Dermal Sensitizer – Not available
This product demonstrated a wide range of oral LD50’s among animal species, tending to be more toxic in higher species such as the dog and monkey than in lower species such as the mice and rat. It is prudent to assume that it may be at least moderately toxic to humans on ingestion.

OSHA, NTP, or IARC Carcinogen . .: Not listed.
Effects of Overexposure:
See Product Label and Directions For Use for additional
precautionary statements.
CAUTION: KEEP OUT OF REACH OF CHILDREN
HARMFUL IF SWALLOWED OR ABSORBED THROUGH THE SKIN.
AVOID CONTACT WITH THE SKIN, EYES, AND CLOTHING.
Prolonged exposure to this product may be irritating to the respiratory
tract.
Existing medical conditions aggravated by this product: None known.
FIRST AID PROCEDURES
If swallowed . . . . . .: Call a physician or Poison
Control Center. Drink 1 or 2 glasses of water and
induce vomiting by touching back of throat with finger.
If person is unconscious, do not give anything by mouth
and do not induce vomiting. Avoid alcohol.
If in eyes . . . . . .: Flush eyes with plenty of
water. Call a physician if irritation persists.
If on skin . . . . . .: Wash with plenty of
soap and water. Get medical attention if irritation
persists.
If inhaled . . . . . .: Move person to fresh air. If
person is not breathing, call 911 or an ambulance, then
give artificial respiration, preferably mouth-to-mouth, if
possible. Call a poison control center or doctor for fur-
ther treatment advice.
Note to physician . . . . . .: Chlormequat chloride is a
weak ganglionic stimulant with an action similar to that
of nicotine. An effective antidote has not been estab-
lished. Based on animal studies, atropine is definitely
contraindicated as it may act synergistically with this
choline derivative once poisoning has taken place.
Note . . . . . .: Have the product container
or label with you when calling a poison control center or
MATERIAL SAFETY DATA SHEET
Rev Date: 06/14/2006MSDS Date: 07/28/2000Supersedes: 01/14/1992

OHP, INC.

P.O. BOX 230

MAINLAND, PA 19451

800-659-6745

CYCOCEL® PLANT GROWTH REGULANT

EPA Registration Number: 241-74-59807

EMERGENCY AND PRODUCT INFORMATION

OHP, Inc.: . . . . . .(800)-356-4647

TRANSPORTATION EMERGENCY

CHEMTREC: . . . . . .(800)-424-9300

1

I. CHEMICAL PRODUCT INFORMATION

Trade Name . . . . . .: CYCOCEL® PLANT GROWTH REGULANT

Chemical Name . . . . . .: 2-chloro-N,N,N,-trimethylethanaminium chloride

Synonyms . . . . . .: chlormequat chloride, CL38,555; CCC

Formula . . . . . .: C5 H13 C12 N

Chemical Family . . . . . .: quaternary ammonium

Mol Wt . . . . . .: 158.1

II. INGREDIENTS

COMPONENT CAS No. % PEL/TLV – SOURCE

chlormequat chloride 999-81-5 11.80 None established

Inerts N/A 88.20 None established

SARA Title III Section 313: Not listed

III. PHYSICAL DATA

Boiling/Melting Point@ 760mm Hg . . . . . .: 100℃

pH . . . . . .: 4.8 – 5.2

Vapor Pressure mmHg @ 20℃ . . . .: Similar to wate r

Specific Gravity or Bulk Density . .: 1.02 g/mL

Solubility in Water . . . . . .: Complete

Appearance . . . . . .: Pale yellow liquid

Odor . . . . . .: Fishy

Intensity . . . . . .: Slight

IV. FIRE AND EXPLOSION DATA

Flash Point (test method) . . . . . .: > 190℉ TCC
Autoignition Temp . . . . . .: N/D
Flammability Limits in Air (% by Vol):
Lower: N/D
Upper: N/D
NFPA 704 HAZARD CODES
Health: N/R Flammable: N/R Instability: 0 Other: N/R
NFPA 30 Storage Classification . . .: N/R
Extinguishing Medium . . . . . .: Use water fog, foam, CO(2), or dry chemical extinguishing media.
Special Fire Fighting Procedures . .: Firefighters should be equipped with self-contained breathing apparatus and turnout gear.
Unusual Fire Explosion Hazards . .: None known.
Decomposition temperature for the technical = 245° C.
V. HEALTH DATA
TOXICOLOGICAL TEST DATA:
Data for the formulated product:
Rat, Oral LD50 (male) > 3915 mg/kg
Rat, Inhalation LC50 (4 hr, actual) – Not available
Rat, Inhalation LC50 (1 hr calculated) – Not available
Rabbit, Dermal LD50 (male) 5075
Rabbit, Eye Irritation – Not irritating
Rabbit, Skin Irritation – Not irritating
Guinea pig, Dermal Sensitizer – Not available
This product demonstrated a wide range of oral LD50's among animal species, tending to be more toxic in higher species such as the dog and monkey than in lower species such as the mice and rat. It is prudent to assume that it may be at least moderately toxic to humans on ingestion.
OSHA, NTP, or IARC Carcinogen . .: Not listed.
Effects of Overexposure:
See Product Label and Directions For Use for additional precautionary statements.
CAUTION: KEEP OUT OF REACH OF CHILDREN
HARMFUL IF SWALLOWED OR ABSORBED THROUGH THE SKIN.

AVOID CONTACT WITH THE SKIN, EYES, AND CLOTHING.
Prolonged exposure to this product may be irritating to the respiratory tract.
Existing medical conditions aggravated by this product: None known.
FIRST AID PROCEDURES
If swallowed . . . . . .: Call a physician or Poison Control Center. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger. If person is unconscious, do not give anything by mouth and do not induce vomiting. Avoid alcohol.
If in eyes . . . . . .: Flush eyes with plenty of water. Call a physician if irritation persists.
If on skin . . . . . .: Wash with plenty of soap and water. Get medical attention if irritation persists.
If inhaled . . . . . .: Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible. Call a poison control center or doctor for further treatment advice.
Note to physician . . . . . .: Chlormequat chloride is a weak ganglionic stimulant with an action similar to that of nicotine. An effective antidote has not been established. Based on animal studies, atropine is definitely contraindicated as it may act synergistically with this choline derivative once poisoning has taken place.
Note . . . . . .: Have the product container or label with you when calling a poison control center or
MATERIAL SAFETY DATA SHEET
CYCOCEL® PLANT GROWTH REGULANT
EPA Registration Number: 241-74-59807
doctor or going for treatment.
Hazardous Waste 40CFR261 . . . . .: No
VI. REACTIVITY DATA
Hazardous Waste Number . . . . . .: None
Stability . . . . . .: Stable. Do not store

Container Disposal . . . . . .: For Plastic Containers: below 32℉.
Triple rinse (or equivalent) and add rinsate to the spray
Conditions to Avoid . . . . . .: Store in original container in tank. Then offer for recycling or reconditioning, or
cool, dry well ventilated place away from ignition puncture and dispose of in a sanitary landfill, or by
sources, heat or flame. incineration, or if allowed by state and local authorities, by burning. If burned, stay out of smoke.
Chemical Incompatibility . . . . . .: Oxidizing agents, strong alkalies, KMNO4, carbon steel
IX. SHIPPING DATA -PACKAGE
Hazardous Decomposition
Products . . . . . .: Oxides of carbon and nitro-D.O.T. Proper Shipping Name (49CFR172.101-102):
gen, HCl and alkylamines
Hazardous Substance (49CFR CERCLA List):
Hazardous Polymerization . . . . . .: Does not occur.
RQ(lbs) . . . . . .: None
Conditions to Avoid . . . . . .: Does not polymerize.
D.O.T. Hazard Classification
Corrosive to Metal . . . . . .: carbon steel (CFR 172.101-102) . . . . . .: Primary
Oxidizer . . . . . .: No
Secondary
D.O.T. Labels Required (49CFR172.101-102):
VII. PERSONAL PROTECTION
D.O.T. Placards Required (CFR172.504):
PESTICIDE APPLICATORS & WORKERS must refer to the
Poison Constituent (49CFR172.203(K)):
Product Label and Directions for Use attached to the product for
Bill of Lading Description . . . . . .: This section has been left
Agricultural Use Requirements in accordance with the EPA
blank intentionally.
Worker Protection Standard 40 CFR part 170.
CC NO.:
RECOMMENDATIONS FOR MANUFACTURING, COMMERCIAL
BLENDING, AND PACKAGING WORKERS: UN/NA Code:
Respiratory Protection . . . . . .: Supplied air respirators
should be worn if large quantities of mist/dust are gen-X. ADDITIONAL INFORMATION

erated or prolonged exposure possible.
Agricultural Use Requirements
Eye Protection . . . . . .: Chemical goggles when res-
Use this product only in accordance with its labeling and with pirator does not provide eye protection.
the Worker Protection Standard, 40 CFR part 170. Refer to sup-
Protective Clothing . . . . . .: Gloves and protective cloth-plemental labeling under ‘Agricultural Use Requirements’ in the
ing as necessary to prevent skin contact. Directions for Use section for information about this standard.
Ventilation . . . . . .: Whenever possible, engineering
controls should be used to minimize the need DISCLAIMER
for personal protective equipment.
IMPORTANT: WHILE THE DESCRIPTIONS, DESIGNS, DATE AND
INFORMATION CONTAINED HEREIN ARE PRESENTED IN GOOD FAITH
AND BELIEVED TO BE ACCURATE, IT IS PROVIDED FOR YOUR GUID
VIII. ENVIRONMENTAL DATA
ANCE ONLY. BECAUSE MANY FACTORS MAY AFFECT PROCESSING
Environmental Toxicity Data
OR APPLICATION/USE, WE RECOMMEND THAT YOU MAKE TESTS TO
See the product label for information regarding environmental toxicity.
DETERMINE THE SUITABILITY OF A PRODUCT FOR YOUR PARTICULAR
PURPOSE PRIOR TO USE. NO WARRANTIES OF ANY KIND,
SARA 311 / 312 REPORTING
EITHER EXPRESS OR IMPLIED, INCLUDING WARRANTIES OF MERFIRE:
N PRESSURE: N REACTIVITY: N CHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, ARE
MADE REGARDING PRODUCTS DESCRIBED OR DESIGNS, DATA OR
ACUTE: Y CHRONIC: N TPQ(lbs): N/R
INFORMATION SET FORTH, OR THAT THE PRODUCTS, DESIGNS, DATA
Spill and Leak Procedures . . . . . .: In case of large scale
OR INFORMATION MAY BE USED WITHOUT INFRINGING THE INTELspillage
of this product, avoid contact, isolate area and
LECTUAL PROPERTY RIGHTS OF OTHERS. IN NO CASE SHALL THE
keep out animals and unprotected persons. Call

DESCRIPTIONS, INFORMATION, DATA OR DESIGNS PROVIDED BE
CHEMTREC (800) 424-9300 or OHP, INC. (800)-356-CONSIDERED A PART OF OUR
TERMS AND CONDITONS OF SALE.
4647. For a small spill, wear personal protective equip-FURTHER, YOU EXPRESSLY
UNDERSTAND AND AGREE THAT THE
ment as specified on the label. DESCRIPTIONS, DESIGNS, DATA, AND INFORMATION
FURNISHED BY
For a Liquid Spill: Dike and contain the spill with inert OHP, INC. HEREUNDER ARE GIVEN
GRATIS AND OHP, INC. ASSUMES
material (sand, earth, etc.) and transfer the liquid and NO OBLIGATION OR LIABILTY FOR
THE DESCRIPTION, DESIGNS,
solid diking materials to separate containers for disposal.
DATA AND INFORMATION GIVEN OR RESULTS OBTAINED, ALL SUCH
BEING GIVEN AND ACCEPTED AT YOUR RISK.
Hazardous Substance Superfund .: No
Cycocel is a registered trademark of BASF Corp.
RQ(lbs) . . . . . .: None
Waste Disposal Method . . . . . .: Pesticide wastes are acutely
hazardous. Wastes resulting from this product may be
disposed of on site or at an approved waste disposal
facility. Improper disposal of excess pesticide, spray
mix or rinsate is a violation of federal law. If these
wastes cannot be disposed of according to label
instructions, contact the state agency responsible for
pesticide regulation or the Hazardous Waste representative
at the nearest EPA Regional Office for guidance.
OHP 981660 / 981661 / 981662 06/06

A.4.3 Citric acid

Safety information according to GHS

Hazard Statement(s)	H319: Causes serious eye irritation.
Precautionary Statement(s)	P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Warning

Hazard Pictogram(s)	
RTECS	GE7350000
Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering
Disposal	3 Relatively unreactive organic reagents should be collected in container A. If halogenated, they should be collected in container B. For solid residues use container C.

Safety information

R Phrase	R 36 Irritating to eyes.
S Phrase	S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
Categories of danger	irritant
Hazard Symbol	 Irritant

Transport information

Declaration (railroad and road) ADR, RID	Kein Gefahrgut
Declaration (transport by sea) IMDG-Code	No Dangerous Good
Declaration (transport by air) IATA-DGR	No Dangerous Good

Toxicological data

LD 50 oralLD50 rat 3000 mg/kg

Specifications

Assay (alcalimetric, calculated on anhydrous substance)	99.5 - 100.5 %
Identity (IR-spectrum)	passes test
Appearance	white to almost white, fine-granular powder
Appearance of solution (200 g/l; water)	clear (≤ 3 NTU) and not more intense in color than reference solution Y_7, BY_7 or GY_7
Sulfate (SO_4)	≤ 0.005 %
Heavy metals (as Pb)	≤ 0.0005 %
Al (Aluminium)	≤ 0.00002 %
As (Arsenic)	≤ 0.0001 %
Hg (Mercury)	≤ 0.0001 %
Pb (Lead)	≤ 0.00005 %
Oxalates (as $C_2H_2O_4$)	≤ 0.01 %
Residual solvents (Ph. Eur./USP/ICH)	excluded by manufacturing process

Readily carbonisable substance	passes test
Sulfated ash (600 °C)	≤ 0.05 %
Water (according to Karl Fischer)	≤ 0.5 %
Bacterial endotoxins	≤ 0.5 I.U./mg

Corresponds to Ph. Eur., BP , JP, USP, E 330, FCC
Conforms to the purity criteria on food additives according to European Commission directive 96/77/EC.

A.4.4 Ethanol

Safety information according to GHS

Hazard Statement(s)	H225: Highly flammable liquid and vapour.
Precautionary Statement(s)	P210: Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
Signal Word	Danger
Hazard Pictogram(s)	
RTECS	KQ6300000
Storage class	3 Flammable Liquids
WGK	WGK 1 slightly water endangering
Disposal	1 Strongly contaminated halogen-free organic solvents: container A.

Safety information

R Phrase	R 11 Highly flammable.
S Phrase	S 7-16 Keep container tightly closed.Keep away from sources of ignition - No smoking.
Categories of danger	highly flammable
Hazard Symbol	 Flammable

Transport information

Declaration (railroad and road) ADR, RID	UN 1170 *Ethanol*, 3, II
Declaration (transport by sea) IMDG-Code	UN 1170 *ETHANOL*, 3, II
Declaration (transport by air) IATA-DGR	UN 1170 *ETHANOL*, 3, II

Toxicological data

LD 50 oralLD50 rat 6200 mg/kg

Specifications

Purity (GC)	≥ 99.9 %
Identity (IR)	conforms

Appearance	conforms
Colour	≤ 10 Hazen
Solubility in water	conforms
Acidity or alkalinity	< 30 ppm
Titrable acid	≤ 0.0002 meq/g
Titrable base	≤ 0.0002 meq/g
Density (d 20 °C/20 °C)	0.790 - 0.793
UV absorption	conforms
Aldehydes (as Acetaldehyd)	≤ 0.001 %
Fusel oils	conforms
Substances reducing potassium permanganate (as O)	≤ 0.0002 %
Carbonyl compounds (as CO)	≤ 0.003 %
Readily carbonizable substances	conforms
Acetone (GC)	≤ 0.001 %
Ethylmethylketone (GC)	≤ 0.02 %
Isoamyl alcohol (GC)	≤ 0.05 %
2-Propanol (GC)	≤ 0.003 %
Higher alcohols (GC)	≤ 0.01 %
Volatile impurities (GC)	
- Acetaldehyde and Acetal	≤ 10 ppm
- Benzene	≤ 2 ppm
- M*ethanol*	≤ 100 ppm
- Total of other impurities	≤ 300 ppm
- disregard limit	≤ 9 ppm
Chloride (Cl)	≤ 0.3 ppm
Nitrate (NO_3)	≤ 0.3 ppm
Phosphate (PO_4)	≤ 0.3 ppm
Sulphate (SO_4)	≤ 0.3 ppm
Ag (Silver)	≤ 0.000002 %
Al (Aluminium)	≤ 0.00005 %
As (Arsenic)	≤ 0.000002 %
Au (Gold)	≤ 0.000002 %
Ba (Barium)	≤ 0.00001 %
Be (Beryllium)	≤ 0.000002 %
Bi (Bismuth)	≤ 0.000002 %
Ca (Calcium)	≤ 0.00005 %
Cd (Cadmium)	≤ 0.000005 %
Co (Cobalt)	≤ 0.000002 %
Cr (Chromium)	≤ 0.000002 %
Cu (Copper)	≤ 0.000002 %
Fe (Iron)	≤ 0.00001 %
Ga (Gallium)	≤ 0.000002 %

In (Indium)	≤ 0.000002 %
Li (Lithium)	≤ 0.000002 %
Mg (Magnesium)	≤ 0.00001 %
Mn (Manganese)	≤ 0.000002 %
Mo (Molybdenum)	≤ 0.000002 %
Ni (Nickel)	≤ 0.000002 %
Pb (Lead)	≤ 0.00001 %
Pt (Platinum)	≤ 0.000002 %
Sb (Antimony)	≤ 0.000002 %
Sn (Tin)	≤ 0.00001 %
Ti (Titanium)	≤ 0.000002 %
Tl (Thallium)	≤ 0.000002 %
V (Vanadium)	≤ 0.000002 %
Zn (Zinc)	≤ 0.00001 %
Zr (Zirconium)	≤ 0.000002 %
Evaporation residue	≤ 0.0005 %
Water	≤ 0.1 %

A.4.5 Ethylene glycol

Safety information according to GHS

Hazard Statement(s)	H302: Harmful if swallowed.
Signal Word	Warning
Hazard Pictogram(s)	
Storage class	10 Combustible liquids not in Storage Class 3
WGK	WGK 1 slightly water endangering

Safety information

R Phrase	R 22 Harmful if swallowed.
Categories of danger	harmful
Hazard Symbol	 Harmful

Toxicological data

LD 50 oral LD50 rat > 2000 mg/kg

Specifications

Purity (GC)	≥ 99.0 %
Identity (IR)	conforms
Density (d 20 °C/ 4 °C)	1.112 - 1.114
Chloride (Cl)	≤ 0.0002 %
Fe (Iron)	≤ 0.0002 %
Water	≤ 0.3 %

A.4.6 HEDTA

SIGMA-ALDRICH

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 3.0 Revision Date 03.12.2009

Print Date 31.05.2010

GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

Product name : N-(2-Hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid

Product Number : H8126

Brand : Aldrich

Company : Sigma-Aldrich N.V./S.A.

K. Cardijnplein 8

B-2880 BORNEM

Telephone : +3238991301

Fax : +3238991311

Emergency Phone # : 070 245245

E-mail address : eurtechserv@sial.com

2. HAZARDS IDENTIFICATION

Risk advice to man and the environment

Irritating to eyes, respiratory system and skin.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : HEEDTA

HEDTA

N-Carboxymethyl-N'-(2-hydroxyethyl)-N,N'-ethylenediglycine

Formula : C10H18N2O7

CAS-No. EC-No. Index-No. Classification Concentration

N-(2-Hydroxyethyl)ethylenediaminetriacetic acid

150-39-0 205-759-3 -Xi, R36/37/38 >= 99,5 %

Nitrilotriacetic acid

139-13-9 205-355-7 -Xn, R22 - R36 - R40 < 0,1 %

For the full text of the R-phrases mentioned in this Section, see Section 16.

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4. FIRST AID MEASURES

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters

Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions

Use personal protective equipment. Avoid dust formation. Avoid breathing dust. Ensure adequate ventilation.

Environmental precautions

Do not let product enter drains.

Methods for cleaning up

Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling

Avoid contact with skin and eyes. Avoid formation of dust and aerosols.

Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire

protection.

Storage

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

hygroscopic

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a dust mask type N95 (US) or

type P1 (EN 143) respirator. Use respirators and components tested and approved under appropriate

government standards such as NIOSH (US) or CEN (EU).

Hand protection

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the

standard EN 374 derived from it. Handle with gloves.

Eye protection

Safety glasses with side-shields conforming to EN166

Skin and body protection

Choose body protection according to the amount and concentration of the dangerous substance at the work

place.

Hygiene measures

Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at

the end of workday.

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9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form powder

Colour white

Safety data

pH no data available

Melting point 212 ℃

Boiling point no data available

Flash point no data available

Ignition temperature no data available

Lower explosion limit no data available

Upper explosion limit no data available

Water solubility no data available

10. STABILITY AND REACTIVITY

Storage stability

Stable under recommended storage conditions.

Materials to avoid

Strong bases, Strong oxidizing agents

Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Carbon oxides, nitrogen oxides (NOx)

11. TOXICOLOGICAL INFORMATION

Acute toxicity

LD50 Intraperitoneal - rat - 337 mg/kg

Irritation and corrosion

no data available

Sensitisation

no data available

Chronic exposure

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as

probable, possible or confirmed human carcinogen by IARC.

Signs and Symptoms of Exposure

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly

investigated.

Potential Health Effects

Inhalation May be harmful if inhaled. Causes respiratory tract irritation.

Skin May be harmful if absorbed through skin. Causes skin irritation.

Eyes Causes eye irritation.

Ingestion May be harmful if swallowed.

Additional Information

RTECS: MB9185000

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12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

no data available

Ecotoxicity effects

Toxicity to fish mortality LC50 - Lepomis macrochirus (Bluegill) - 766 - 852 mg/l - 96 h

Further information on ecology

no data available

13. DISPOSAL CONSIDERATIONS

Product

Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION

ADR/RID

Not dangerous goods

IMDG

Not dangerous goods

IATA

Not dangerous goods

15. REGULATORY INFORMATION

Labelling according to EC Directives

Hazard symbols

Xi Irritant

R-phrase(s)

R36/37/38 Irritating to eyes, respiratory system and skin.

S-phrase(s)

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

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16. OTHER INFORMATION

Text of R-phrases mentioned in Section 3

R22 Harmful if swallowed.

R36 Irritating to eyes.

R36/37/38 Irritating to eyes, respiratory system and skin.

R40 Limited evidence of a carcinogenic effect.

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used
only as a guide. The information in this document is based on the present state of our knowledge and is
applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee
of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from
handling or from contact with the above product. See reverse side of invoice or packing slip for additional
terms and conditions of sale.
Aldrich -H8126 www.sigma-aldrich.com Page 5 of 5

A.4.7 Hydrochloric acid fuming

Safety information according to GHS

Hazard Statement(s)	H314: Causes severe skin burns and eye damage. H335: May cause respiratory irritation. H290: May be corrosive to metals.
Precautionary Statement(s)	P280: Wear protective gloves/eye protection/face protection. P301 + P330 + P331: IF SWALLOWED: rinse mouth. Do NOT induce vomiting. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	8 B Non combustible, corrosive substances
WGK	WGK 1 slightly water endangering
Disposal	12 Inorganic *acids* and anhydrides thereof should first be diluted or hydrolyzed by stirring carefully into ice water and then neutralized (protective gloves, fume cupboard!) with sodium hydroxide solution

(Cat. No. 105587). Before filling into container D, check the pH with pH universal indicator strips (Cat. No. 109535). *Fuming sulfuric acid* should be carefully stirred dropwise into 40 % *sulfuric acid* (Cat. No. 109286). Ensure that plenty of ice is available for cooling! When sufficiently cool, treat the highly concentrated *sulfuric acid* as described above. Analogous to this procedure, other anhydrides can be converted into their corresponding *acids*. *Acid* gases (e.g. hydrogen halide, chlorine, phosgene, sulfur dioxide) can be introduced into dilute sodium hydroxide solution and after neutralization disposed of in container D.

Safety information

R Phrase	R 34-37 Causes burns.Irritating to respiratory system.
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).
Categories of danger	corrosive
Hazard Symbol	 Corrosive

Transport information

Declaration (railroad and road) ADR, RID	UN 1789 Chlorwasserstoffsäure, 8, II
Declaration (transport by sea) IMDG-Code	UN 1789 *HYDROCHLORIC ACID*, 8, II, Segregation Group: 1 (*Acids*)
Declaration (transport by air) IATA-DGR	UN 1789 *HYDROCHLORIC ACID*, 8, II

Specifications

Assay (*acid*imetric)	36.5 - 38.0 %
Identity	passes test
Appearance	passes test
Colour	≤ 10 Hazen
Bromide (Br)	≤ 50 ppm
Free chlorine (Cl)	≤ 1 ppm
Heavy metals (as Pb)	≤ 1 ppm
Sulphate (SO_4)	≤ 1 ppm
Sulfite (SO_3)	≤ 1 ppm
As (Arsenic)	≤ 0.01 ppm
Fe (Iron)	≤ 0.2 ppm
NH_4 (Ammonium)	≤ 3 ppm
Extractable organic substances	≤ 5 ppm
Residue on ignition (as SO_4)	≤ 5 ppm

A.4.8 Iodopropane

Safety information according to GHS

Hazard Statement(s)	H226: Flammable liquid and vapour. H331: Toxic if inhaled.
Precautionary Statement(s)	P210: Keep away from heat/sparks/open flames/hot surfaces. - No smoking. P304 + P340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
Signal Word	Danger
Hazard Pictogram(s)	
RTECS	TZ4100000
Storage class	3 Flammable Liquids
WGK	WGK 1 slightly water endangering
Disposal	3 Relatively unreactive organic reagents should be collected in container A. If halogenated, they should be collected in container B. For solid residues use container C.

Safety information

R Phrase	R 10-20 Flammable.Harmful by inhalation.
S Phrase	S 24/25 Avoid contact with skin and eyes.
Categories of danger	flammable, harmful
Hazard Symbol	 Harmful

Transport information

Declaration (railroad and road) ADR, RID	UN 2392 Iodpropane, 3, III
Declaration (transport by sea) IMDG-Code	UN 2392 *IODOPROPANES*, 3, III, Segregation Group: 10 (Liquid halogenated hydrocarbons)
Declaration (transport by air) IATA-DGR	UN 2392 *IODOPROPANES*, 3, III

Specifications

Assay (GC, area%)	≥ 98 %
Density (d 20 °C/ 4 °C)	1.740 - 1.750
Identity (IR)	passes test

A.4.9 Malic acid

Safety information according to GHS

Hazard Statement(s)	H319: Causes serious eye irritation.
Precautionary Statement(s)	P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Warning
Hazard Pictogram(s)	
RTECS	ON7175000
Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering
	3
Disposal	Relatively unreactive organic reagents should be collected in container A. If halogenated, they should be collected in container B. For solid residues use container C.

Safety information

R Phrase	R 36 Irritating to eyes.
Categories of danger	irritant
Hazard Symbol	 Irritant

Transport information

Declaration (railroad and road) ADR, RID	Kein Gefahrgut
Declaration (transport by sea) IMDG-Code	No Dangerous Good
Declaration (transport by air) IATA-DGR	No Dangerous Good

Toxicological data

LD 50 oral LD50 rat > 3200 mg/kg

Specifications

Assay (*acid*imetric)	≥ 99 %
Melting range	
- lower value	≥ 129 °C
- upper value	≤ 132 °C
Identity (IR)	passes test

A.4.10 Potassium hydroxide

Safety information according to GHS

Hazard Statement(s)	H314: Causes severe skin burns and eye damage. H302: Harmful if swallowed. H290: May be corrosive to metals.
Precautionary Statement(s)	P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + P330 + P331: IF SWALLOWED: rinse mouth. Do NOT induce vomiting. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Danger
Hazard Pictogram(s)	
RTECS	TT2100000
Storage class	8 B Non combustible, corrosive substances
WGK	WGK 1 slightly water endangering
Disposal	13 Bases and alcoholates should be diluted if necessary by carefully stirring them into water and then neutralized (protective gloves, fume cupboard!) with hydrochloric acid (Cat. No. 100312). Before placing in container D, check the pH with pH universal indicator strips (Cat. No. 109535).

Safety information

R Phrase	R 22-35 Harmful if swallowed.Causes severe 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).
Categories of danger	harmful, corrosive
Hazard Symbol	 Corrosive

Transport information

Declaration (railroad and road) ADR, RID	UN 1813 Kaliumhydroxid, fest, 8, II
Declaration (transport by sea) IMDG-Code	UN 1813 *POTASSIUM HYDROXIDE*, SOLID, 8, II, Segregation Group: 18 (Alkalis)
Declaration (transport by air) IATA-DGR	UN 1813 *POTASSIUM HYDROXIDE*, SOLID, 8, II

Toxicological data

LD 50 oralLD50 rat 273 mg/kg

Specifications

Assay (acidimetric, KOH)	≥ 85.0 %
Carbonate (as K_2CO_3)	≤ 1.0 %
Chloride (Cl)	≤ 0.0005 %
Phosphate (PO_4)	≤ 0.0005 %
Silicate (SiO_2)	≤ 0.005 %
Sulphate (SO_4)	≤ 0.0005 %
Total nitrogen (N)	≤ 0.0005 %
Heavy metals (as Pb)	≤ 0.0005 %
Al (Aluminium)	≤ 0.001 %
Ca (Calcium)	≤ 0.001 %
Cu (Copper)	≤ 0.0002 %
Fe (Iron)	≤ 0.0005 %
Na (Sodium)	≤ 0.5 %
Ni (Nickel)	≤ 0.00025 %
Pb (Lead)	≤ 0.0005 %
Zn (Zinc)	≤ 0.0025 %

A.4.11 Tartaric acid

Safety information

R Phrase	R 36 Irritating to eyes.
S Phrase	S 24/25 Avoid contact with skin and eyes.
Categories of danger	irritant
Hazard Symbol	 Irritant
Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering
Disposal	3 Relatively unreactive organic reagents should be collected in container A. If halogenated, they should be collected in container B. For solid residues use container C.

A.4.12 Tin chloride

Safety information according to GHS

Hazard Statement(s)	H302: Harmful if swallowed. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H319: Causes serious eye irritation. H335: May cause respiratory irritation.
Precautionary Statement(s)	P280: Wear protective gloves. P302 + P352: IF ON SKIN: Wash with plenty of soap and water. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Warning
Hazard Pictogram(s)	
RTECS	XP8700000
Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering
Disposal	14 Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-Universal indicator strips (Item No. 109535).

Safety information

R Phrase	R 22-36/37/38-43 Harmful if swallowed.Irritating to eyes, respiratory system and skin.May cause sensitization by skin contact.
S Phrase	S 24-26-37 Avoid contact with skin.In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.Wear suitable gloves.
Categories of danger	harmful, irritant, sensitizing
Hazard Symbol	 Harmful

Toxicological data

LD 50 oralLD50 rat 700 mg/kg

Specifications

Assay (iodometric)≥ 97 %

A.4.13 Triethylamine

Safety information according to GHS

Hazard Statement(s)	H225: Highly flammable liquid and vapour. H332: Harmful if inhaled. H312: Harmful in contact with skin. H302: Harmful if swallowed. H314: Causes severe skin burns and eye damage. H335: May cause respiratory irritation.
Precautionary Statement(s)	P210: Keep away from heat/sparks/open flames/hot surfaces. - No smoking. P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + P330 + P331: IF SWALLOWED: rinse mouth. Do NOT induce vomiting. P302 + P352: IF ON SKIN: Wash with plenty of soap and water. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Danger
Hazard Pictogram(s)	
RTECS	YE0175000
Storage class	3 Flammable Liquids
WGK	WGK 1 slightly water endangering

Safety information

R Phrase	R 11-20/21/22-35 Highly flammable.Harmful by inhalation, in contact with skin and if swallowed.Causes severe burns.
S Phrase	S 3-16-26-29-36/37/39-45 Keep in a cool place.Keep away from sources of ignition - No smoking.In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.Do not empty into drains.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).
Categories of danger	highly flammable, harmful, corrosive
Hazard Symbol	 Flammable  Corrosive

Transport information

Declaration (railroad and road) ADR, RID	UN 1296 Triethylamin, 3 (8), II
Declaration (transport by sea) IMDG-Code	UN 1296 *TRIETHYLAMINE*, 3 (8), II
Declaration (transport by air) IATA-DGR	UN 1296 *TRIETHYLAMINE*, 3 (8), II

Toxicological data

LD 50 oral	LD50 rat 460 mg/kg
LD 50 dermal	LD50 rabbit 416 mg/kg

Specifications

Assay (GC, area%)	≥ 99 %
Density (d 20 °C/ 4 °C)	0.726 - 0.728
Water (K. F.)	≤ 0.2 %
Identity (IR)	passes test

A.4.14 Zinc chloride

Safety information according to GHS

Hazard Statement(s)	H302: Harmful if swallowed. H314: Causes severe skin burns and eye damage. H335: May cause respiratory irritation. H410: Very toxic to aquatic life with long lasting effects.
Precautionary Statement(s)	P273: Avoid release to the environment. P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + P330 + P331: IF SWALLOWED: rinse mouth. Do NOT induce vomiting. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Signal Word	Danger
Hazard Pictogram(s)	

RTECS	ZH1400000
Storage class	8 B Non combustible, corrosive substances
WGK	WGK 3 highly water endangering
	14
Disposal	Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-Universal indicator strips (Item No. 109535).

Safety information

R Phrase	R 22-34-50/53 Harmful if swallowed.Causes burns.Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
S Phrase	S 26-36/37/39-45-60-61 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).This material and its container must be disposed of as hazardous waste.Avoid release to the environment. Refer to special instructions/ Safety data sheets.
Categories of danger	harmful, corrosive, dangerous for the environment
Hazard Symbol	 Corrosive  Dangerous for the environment

Transport information

Declaration (railroad and road) ADR, RID	UN 2331 Zinkchlorid, wasserfrei, 8, III
Declaration (transport by sea) IMDG-Code	UN 2331 *ZINC CHLORIDE*, ANHYDROUS, 8, III, Marine Pollutant: P, Segregation Group: 1 (Acids), 7 (Heavy metals and their salts (including their organometallic compounds))
Declaration (transport by air) IATA-DGR	UN 2331 *ZINC CHLORIDE*, ANHYDROUS, 8, III

Toxicological data

LD 50 oralLD50 rat 350 mg/kg

Specifications

Assay (complexometric, $ZnCl_2$)	98.0 - 100.5 %
Identity	passes test
Insoluble substances	≤ 0.005 %
pH-value (10 %; water)	4.6 - 5.5

Nitrate (NO_3)	≤ 0.003 %
Oxide *chloride* (as ZnO)	≤ 1.2 %
Sulphate (SO_4)	≤ 0.002 %
Total nitrogen (N)	≤ 0.002 %
Aluminium,Calcium,Magnesium,Heavy metals,Iron	passes test
Ca (Calcium)	≤ 0.001 %
Cd (Cadmium)	≤ 0.0005 %
Cu (Copper)	≤ 0.001 %
Fe (Iron)	≤ 0.0005 %
K (Potassium)	≤ 0.02 %
Mg (Magnesium)	≤ 0.01 %
Na (Sodium)	≤ 0.005 %
NH_4 (Ammonium)	≤ 0.005 %
Pb (Lead)	≤ 0.001 %

A.4.15 Zinc nitrate

Safety information

R Phrase	R 8-22-36/37/38-50/53 Contact with combustible material may cause fire.Harmful if swallowed.Irritating to eyes, respiratory system and skin.Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
S Phrase	S 26-61 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.Avoid release to the environment. Refer to special instructions/ Safety data sheets.
Categories of danger	oxidizing, harmful, irritant, dangerous for the environment
Hazard Symbol	 Oxidising  Harmful  Dangerous for the environment
Storage class	5.1 B Oxidizing agents (TRG 515 Group 2+3)
WGK	WGK 3 highly water endangering
	14
Disposal	Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-

	Universal indicator strips (Item No. 109535).

Transport information

Declaration (railroad and road) ADR, RID	UN 1514 Zinknitrat, 5.1, II
Declaration (transport by sea) IMDG-Code	UN 1514 *ZINC NITRATE*, 5.1, II, Segregation Group: 7 (Heavy metals and their salts (including their organometallic compounds))
Declaration (transport by air) IATA-DGR	UN 1514 *ZINC NITRATE*, 5.1, II

Toxicological data

LD 50 oralLD50 rat 1190 mg/kg

Specifications

Assay (complexometric)	≥ 98.5 %
Chloride (Cl)	≤ 0.001 %
Sulphate (SO_4)	≤ 0.005 %
Ca (Calcium)	≤ 0.001 %
Cd (Cadmium)	≤ 0.0005 %
Cu (Copper)	≤ 0.0005 %
Fe (Iron)	≤ 0.0005 %
Na (Sodium)	≤ 0.001 %
Pb (Lead)	≤ 0.002 %
Identity	passes test

A.4.16 Zinc oxide

Safety information according to GHS

Hazard Statement(s)	H410: Very toxic to aquatic life with long lasting effects.
Precautionary Statement(s)	P273: Avoid release to the environment.
Signal Word	Warning
Hazard Pictogram(s)	
RTECS	ZH4810000
Storage class	10 - 13 Other liquids and solids
WGK	WGK 2 water endangering
Disposal	14 Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-Universal indicator strips (Item No. 109535).

Safety information

R Phrase	R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

S Phrase	S 60-61 This material and its container must be disposed of as hazardous waste.Avoid release to the environment. Refer to special instructions/ Safety data sheets.
Categories of danger	dangerous for the environment
Hazard Symbol	 Dangerous for the environment

Transport information

Declaration (railroad and road) ADR, RID	UN 3077 Umweltgefährdender Stoff, fest, n.a.g.(ZINKOXID), 9, III
Declaration (transport by sea) IMDG-Code	UN 3077 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.(*ZINC OXIDE*), 9, III, Marine Pollutant: P, Segregation Group: 7 (Heavy metals and their salts (including their organometallic compounds))
Declaration (transport by air) IATA-DGR	UN 3077 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.(*ZINC OXIDE*), 9, III

Toxicological data

LD 50 oralLD50 rat > 5000 mg/kg

Specifications

Assay - complexometric, ZnO calculated on calcined substance	99.0 - 100.5 %
- complexometric, ZnO	≥ 99.0 %
Identity	passes test
Carbonate and color of solution	passes test
Substances insoluble in diluted sulfuric acid	≤ 0.01 %
Free Alkali	passes test
Chloride (Cl)	≤ 0.001 %
Nitrate (NO_3)	≤ 0.003 %
Sulfur compounds (as SO_4)	≤ 0.01 %
Total nitrogen (N)	≤ 0.0005 %
As (Arsenic)	≤ 0.0001 %
Ca (Calcium)	≤ 0.001 %
Cd (Cadmium)	≤ 0.0005 %
Cu (Copper)	≤ 0.0005 %
Fe (Iron)	≤ 0.0005 %
K (Potassium)	≤ 0.01 %
Mg (Magnesium)	≤ 0.005 %
Mn (Manganese)	≤ 0.0005 %
Na (Sodium)	≤ 0.001 %
Pb (Lead)	≤ 0.002 %
Substances reducing potassium permanganate (as O)	≤ 0.001 %
Loss on	≤ 1.0 %

ignition (500 °C)

A.4.17 Zinc sulphate

Safety information according to GHS

Hazard Statement(s)	H302: Harmful if swallowed. H318: Causes serious eye damage. H410: Very toxic to aquatic life with long lasting effects.
Precautionary Statement(s)	P280: Wear protective gloves/protective clothing/eye protection/face protection. P273: Avoid release to the environment. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P301 + P330 + P331: IF SWALLOWED: rinse mouth. Do NOT induce vomiting.
Signal Word	Danger
Hazard Pictogram(s)	  
RTECS	ZH5300000
Storage class	10 - 13 Other liquids and solids
WGK	WGK 3 highly water endangering
Disposal	14 Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-Universal indicator strips (Item No. 109535).

Safety information

R Phrase	R 22-41-50/53 Harmful if swallowed.Risk of serious damage to eyes.Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
S Phrase	S 22-26-39-46-60-61 Do not breathe dust.In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.Wear eye/face protection.If swallowed, seek medical advice immediately and show

	this container or label.This material and its container must be disposed of as hazardous waste.Avoid release to the environment. Refer to special instructions/ Safety data sheets.
Categories of danger	harmful, irritant, dangerous for the environment
Hazard Symbol	 Harmful  Dangerous for the environment

Transport information

Declaration (railroad and road) ADR, RID	UN 3077 Umweltgefährdender Stoff, fest, n.a.g.(ZINKSULFAT), 9, III
Declaration (transport by sea) IMDG-Code	UN 3077 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.(ZINC SULFATE), 9, III, Marine Pollutant: P, Segregation Group: 7 (Heavy metals and their salts (including their organometallic compounds))
Declaration (transport by air) IATA-DGR	UN 3077 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.(ZINC SULFATE), 9, III

Toxicological data

LD 50 oralLD50 rat 1260 mg/kg

Specifications

Assay (complexometric)	99.5 - 103.0 %
Identity	passes test
Clarity of solution	passes test
Insoluble matter	≤ 0.01 %
pH-value (5 %; water, 25 °C)	4.4 - 5.6
Chloride (Cl)	≤ 0.0005 %
Total nitrogen (N)	≤ 0.0005 %
Nitrate (NO_3)	≤ 0.002 %
As (Arsenic)	≤ 0.00005 %
Ca (Calcium)	≤ 0.001 %
Cd (Cadmium)	≤ 0.0005 %
Cu (Copper)	≤ 0.0005 %
Fe (Iron)	≤ 0.0005 %
K (Potassium)	≤ 0.001 %
Mg (Magnesium)	≤ 0.001 %
Mn (Manganese)	≤ 0.0003 %
Na (Sodium)	≤ 0.001 %
NH_4 (Ammonium)	≤ 0.001 %
Pb (Lead)	≤ 0.001 %