



University of Kerbala
College of Science
Department of Chemistry

**Electrodeposition of Zn,Co and their alloys from deep
eutectic solvents (DES)**

A Desertation

**Submitted to the Council of the College of Science/ University of Kerbala
In Partial Fulfillment of the Requirements for the Degree of Master of
Science in Chemistry**

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2022AD

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ لَقَدْ أَرْسَلْنَا رُسُلَنَا بِالْبَيِّنَاتِ وَأَنْزَلْنَا
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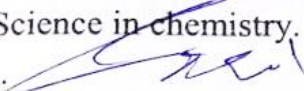
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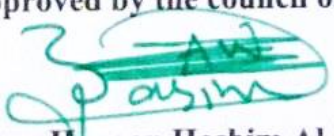
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Dedication

*Whoever conveyed the message and believed it to the
Prophet of Mercy, may God's prayers and peace be upon
him....*

To my dear husband...

And my children, Yasser, Farazdaq and nor al- Zahraa...

*Without whom this book would have been completed two
years earlier....*

Zena Jabbar Mohammed

Acknowledgments

*I would like to start my acknowledgements by expressing my heartfelt gratitude to Almighty Allah for sustaining, strengthening, guiding, and sparing my life to this point in my studies, it gives me great pleasure to express my gratitude to anybody who contributed in any way conveying this message. First, my gratitudes are extended to my supervisor **Prof. Dr. Luma Majeed Ahmed** and **Dr. Hasan Fisal Alesary** for their incessant helps, encouragements, supports, guidances and insightful feedbacks throughout the research time.*

*I would also like to thank **Dr. Azhar Al-Murshedi** ,Who helped me use the electrical properties measuring device cyclic voltammetry(C.V).Moreover, my gratitudes are extended as well to my colleagues and master students who have already graduated and to those of them who are about to graduate.In addition, to others in the department of Chemistry for their support and encouragement.*

Finally, it is important to note that this mission wonot be completed and finished without the love and patience of my family for whom I would like to present my work and special thanks to my husband for his support, encouragement, strength, and patience during these years. I dedicate this research for you, my family.

Zenia Jabbar Mohammed

Abstract

In the presence of varying quantities of water and additives, Zn -Co alloy coatings were electrodeposited on mild steel in a choline chloride (ChCl) :ethylene glycol (EG) based liquid. The conductivities of Zn ,Co , and Zn- Co electrolytes were found to improve through enhancing volumes of water, while conductivities of plating solution decreased as a result of using boric acid and nicotinic acid. The speciation of Co in a Zn -Co electrolyte was investigated using UV-visible spectroscopy. A blue shift in the Co species was detected when water was added to Zn -Co solutions. However no change was observed in the spectra of Co species when additives were introduced to the plating bath. The cyclic voltammetry was used to examine the redox potential of the plating solutions, from which it was found that when water was added to Zn ,Co, and Zn-Co electrolytes. The redox current peaks of Zn, Co and Zn -Co increased with increasing amount of water, while intensities of deposition peak were decreased when the boric acid, nicotinic acid and ascorbic acid added to the metals electrolytes. The morphologies of films were studied by using scanning electron microscopy (SEM). Improving in homogeneous the morphologies of the deposited Zn, Co and Zn-Co films was found with enhancing the amount of water and boric acid. Zn-Co coatings produced from the electrolyte with water had 19.83 wt% Zn and 80.13 wt% Co, according to the results. When the Zn- Co film was deposited in a bath containing 20% water, the roughness of the deposit was reduced to roughly 7.642 nm. To analyze the XRD pattern of the Zn -Codeposits, researchers used the X-ray Diffraction (XRD) technique.

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List of Abbreviations and Symbols

Abbreviations and Symbols	The Meaning
AFM	Atomic force microscopy
AS	Ascorbic acid
BA	Boric acid
CE	Counter electrode
ChCl	Choline chloride
CV	Cyclic voltammetry
DES	Deep eutectic solvent
E	Potential / Voltage
EDXS	Energy-dispersive X-ray spectroscopy
EG	Ethylene glycol
HBD	Hydrogen bond donor
IL	Ionic liquid
NA	Nicotinic acid
Ra	Roughness
RTILs	Room temperature ionic liquids
ARPE	Average Relative Percentage Errors
RF	Reference electrode
SEM	Scanning electron microscopy
EDX	Energy dispersive x-ray spectroscopy

T	time of release
UV-Vis	Ultra violet light in the range from 350 to 750 nm
WE	working electrode
XRD	X-ray diffraction
θ	Bragg angle
Λ	Wavelength(nm)
T	Temperature
i	Current (A)
i_{pc}	Cathodic peak current

CHAPTER ONE

INTRODUCTION

1. Introduction

1.1 Electrodeposition

Electrodeposition is the process of coating certain materials on surfaces from solution to produce a thin layer of material such as metals, polymers, etc., to change the physical properties of materials such as their corrosion resistance, roughness, brightness and hardness. Known that machines and tools made of metal and non-metallic materials have specific lifetimes due to their particular surrounding, such as environmental factors or their atomic structure, therefore covering these tools with layer metal necessary to protect them from External environmental influences [1].

Luigi Brugnatelli was the first who introduced electroplating for metals in 1805, when he utilized a Voltaic pile to deposit gold [2]. Following that, John Wright utilized a KCN electrolyte in silver and gold plating, in a procedure that is still used today, though this process was originally intended for the deposition of decorative metals. Using aqueous solutions, industrial electroplating can use metals (Cu, Zn Au, Ag, Ni, Cd, and Cr) and zinc alloys that are used to increase hardness and resistance to corrosion and give an attractive appearance to silver and gold, as these metals can be obtained from aqueous solution agreement with reported in reference [3]. There are disadvantages for electroplating of metals from an aqueous solutions where this due to formation of passivation of the layer on the electrodes (anode or cathode), uses toxic compounds such as cyanide, acids, and bases. It has a significant impact on the environment, as it needs large amounts of water to remove metals and electrolytes (and uses toxic materials. Aqueous solution has a narrow potential windows. In addition, metals such as Cr, Ni, and Cd are highly toxic, and thus out of preference are replaced where possible by Al, Ti, and W. The last three metals are

characterized by being highly resistant to corrosion; however, their oxides are insoluble in an aqueous solution. The solvents that are used in electroplating can be non-polar or polar. They were coated with organic solvents[4,5].

1.2 Ionic Liquids

Ionic liquids (ILs) are liquids that are totally made up of ions. They are known as room temperature ionic liquids (RTILs) because their liquid state is often below 100°C. Ethyl ammonium nitrate ([EtNH₃][NO₃]) was the first ionic liquid mentioned in the literature, as prepared in 1914 by Walden [6]. Almost 40 years after ionic liquids were discovered by Walden, the authors made efforts to prepare a lower temperature melt for the electrodeposition of aluminium, which was previously only accessible from high temperature molten salts. It was found that eutectic melts with freezing points close to 100°C could be formed when the composition of LiCl/ KCl/ AlCl₃ mixtures were changed [3].

The formation of bulky chloroaluminate ions (e.g. AlCl₄⁻ and Al₂Cl₇⁻) in the eutectic mixtures resulted in liquids with low melting points [6]. In the 1970, prepared ionic liquids by mixing AlCl₃ with the asymmetric 1-butylpyridinium cation, which forms a liquid at 20°C within a narrow compositional range of 60-67 mol% AlCl₃. It was found that the 1-butylpyridinium cation was easy to reduce, where previously this was restricting the electrochemical applications of this ionic liquid [3]. Later, Wilkes and Hussey noted that organic cations can be affected by the stability to reduction of ionic liquids. They prepared an AlCl₃:1-ethyl-3-methyl-imidazolium ionic liquid, whose physical properties, such as low viscosity and good conductivity, were found to be considerably improved over those of the 1-butylpyridinium system. However, applications of the liquids were limited due to their sensitivity to air, principally due to the rapid hydrolysis of AlCl₃ when in contact with moisture. Therefore AlCl₃ was ultimately replaced

with ZnCl_2 , which is far more stable to hydrolysis. The liquids that were formed from the mixing of organic cations with AlCl_3 and/or ZnCl_2 are often referred to as first generation ionic liquids. These types of liquids are fluid at low temperatures because of the creation of bulky chloroaluminate or chlorozincate ions at eutectic compositions of the mixture. This reduces the ions charge density, which can in turn reduce the lattice energy of the system, causing a reduction in the freezing point of the mixture. In general, delocalisation of charge on the ions reduces lattice energy and, thus, leads to the formation of an ionic liquid [3]. The properties of this generation of ionic liquids are easily affected by changing the composition of the liquid from that of Lewis basic, with an excess of the organic cation, and Lewis-acidic, with an excess of the metal halide. For example, Al speciation in the chloroaluminate ionic liquids can be altered through changing the composition of the liquid. The associated equilibria in these mixtures are ultimately dependent on the relative concentration of AlCl_3 , with higher-order Al ions dominating at lower AlCl_3 concentrations (indeed, it is this behaviour that lends this class of ionic liquids the name eutectic-based ionic liquids). Although Al ionic liquids are sensitive to moisture, and this limits their uptake outside the laboratory, they have nevertheless found use in the electroplating of a range of metals and alloys. The formation of these liquids and the speciation as a function of composition have recently been reviewed by Endres *et al* [7]. Wilkes and Hussey noted that organic cations can be affected by the stability to reduction of ionic liquids. They prepared an AlCl_3 :1-ethyl-3-methyl-imidazolium ionic liquid. The ionic liquids have the physical properties of low viscosities and generally good electrical conductivities optimized on the 1-butylpyridinium system [7]. However, because to its sensitivity to air and, in particular, the quick hydrolysis of AlCl_3 when exposed to moisture, its applications are limited. AlCl_3 has been replaced by ZnCl_2 , which is more stable for hydrolysis [8]. In the past ten years, the importance of ionic liquids at room temperature has increased in electroplating processes for metals and their alloys, due to:

-
- a) Wide potential windows exist for electrodeposition of metals with highly negative potentials prior to liquid breakdown due to IL.
 - b) It has compressible physical and chemical properties, which makes it possible to control the oxidation and reduction potentials and thus deposit new alloys.
 - c) Metal deposition at high temperatures for some materials, due to the low vapour pressure and good stability to the heat of ILs [9].

Cobalt is a well-known metal with hard magnetic properties, and its alloys have been used in procedures that require outstanding magnetic qualities for high-performance magnetic applications [10]. The electrodeposition of Zn-Co alloy in aqueous solution, however, is problematic due to the narrow electrochemical potential window of water. As a result, large electrochemical windows ionic liquids (ILs) are required as supporting electrolytes for the electrodeposition of Co-Zn alloys. The chloroaluminate-based ILs have been widely employed for the electrodeposition of various alloys due to the ability to alter Lewis acidity or basicity. The electrodeposition of cobalt-aluminum alloys from chloroaluminate ionic liquid, as well as the composition and shape of deposits, is said to be dependent on the applied potential. Katayama *et al.*[11] examined the influence of temperature on the electroplating of Co in ionic liquid in the presence of additives. By increasing the temperature, the excess potential for Co deposition was found to be diminished. As a new coating process, a variety of different room-temperature ionic liquids have been proposed. In ionic liquids, a number of investigations on the electrodeposition of Co have been reported [8-10]. Co electrodeposited on the substrate had poor adherence.

1.3 Deep Eutectic Solvents (DESS)

Ionic liquids containing discrete anions have difficulties such as high cost, toxicity, and availability, all of which will clearly limit their industrial utility. An alternative solution is to create a complex anion from the same liquids. The

mother (ionic liquids) with a quaternary ammonium halide and aluminum chloride. This method produced a series of halo aluminate anions [12]. Abbott *et al* [13] extend this idea at first to a metal halide and then complex compounds of quaternary anion ammonium salts with hydrogen bond donors (HBDs).

It was widely used for its ease of preparation, non-toxicity, cheapness, and biodegradability [13]. Deep eutectic solvents (DESs) are a type of IL that are made by mixing two compounds of the same or different phases with high melting points to generate a liquid compound with a melting point lower than the two ingredients[14], this degree called eutectic point. In general, at Eutectic point, when the components (C) are equal to 2 (A and B components), the phase (p) is 3 [(equilibrium state between A(solid) and B(solid)), [(equilibrium state between A(liquid) and B(liquid))], [equilibrium state between A(solid) with A(liquid) and equilibrium state between B(solid) with B(liquid)], so, the degree of freedom (F) at eutectic point is given zero value using the reduced rule phase equation $F = C - p + 1 = 2 - 3 + 1 = 0$, which indicated to no change in the chemical potential (molar free energy) at this point [129]. Figure 1.1 explains the phase behaviour of two blended components .

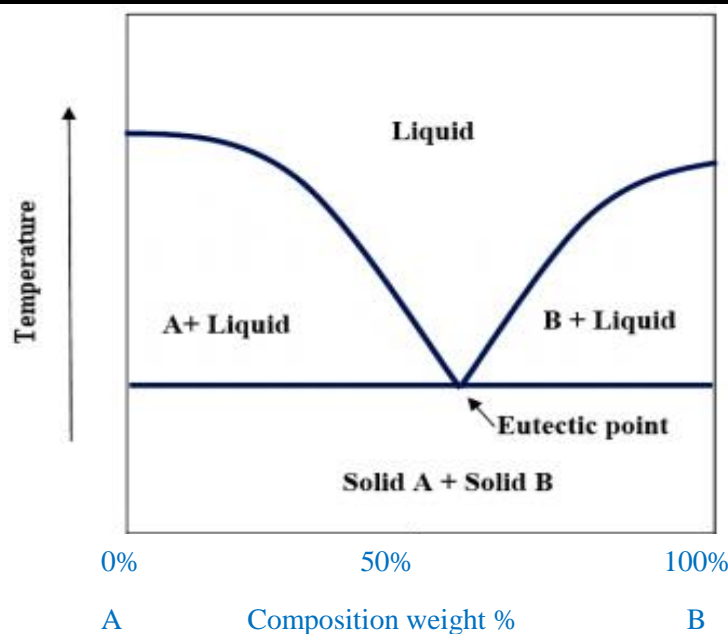
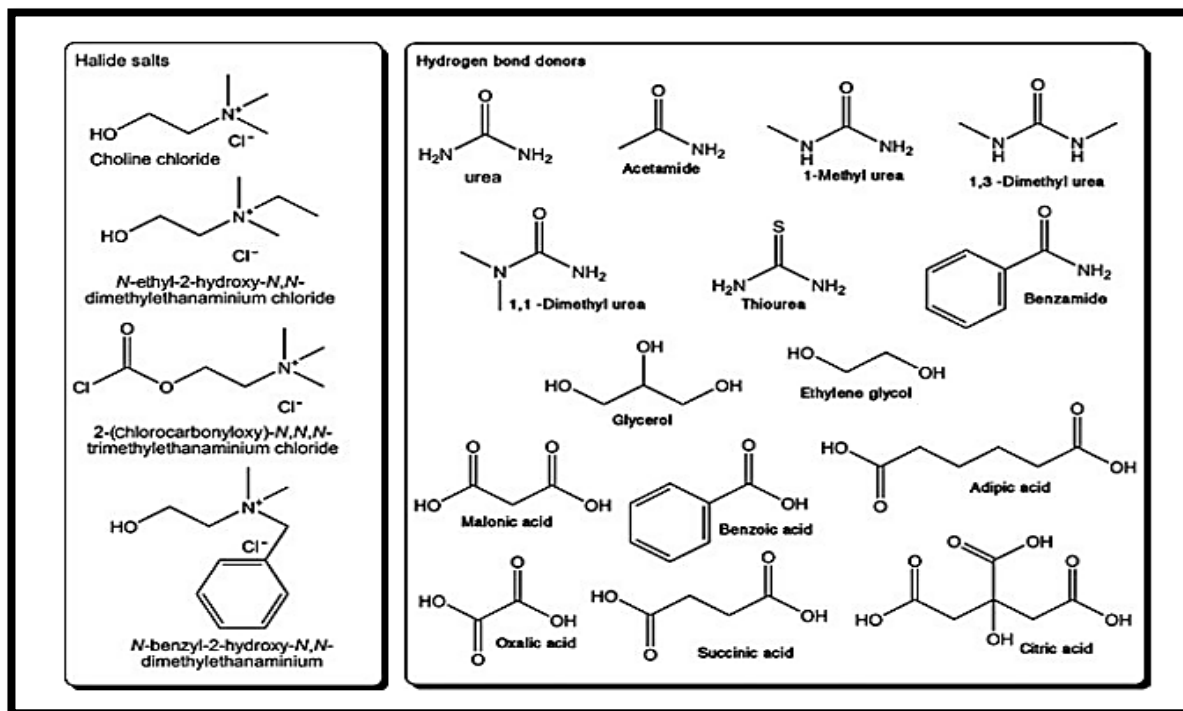


Figure [1.1] A drawing of a two-component phase diagram showing a melting points.

The deep eutectic solvents are made by mixing choline chloride and urea in a 1:2 ratio because choline chloride has a melting point of 302 °C and urea has a melting point of 133°C; yet, the resulting DES is liquid at less than 12°C due to the interaction between the halide and the hydrogen bond donor. The low melting points of DESs are due to large asymmetric ions with low energies[14]. It has been agreed that all ionic systems have some molecular component and thus the definition of ionic liquids has been expanded to include DESs because they are liquids that behave with ionic characteristics[15].

Since the usage of common salts with another hydrogen bond donor (HBD) such as alcohols, amides, amines, and carboxylic acids [14]. Figure 1.2 shows different types of donors for hydrogen bonding, an important note is that DES types of green ionic liquids are more frequently used because in the process of preparing them there is essentially no waste and no advanced technology is needed to prepare them. Many deep eutectic solvents have good properties, for instance, non-toxic[13], and their elements can be responsibly sourced, non-flammable, biodegradable, relatively affordable to synthesize, and can dissolve



A

B

Figure [1.2] The common structures of DESs as A)halide salts and B) hydrogen bond donors.

different metal oxides. Electroplating, electropolishing, recycling of metal, desulfurisation and synthesis of polymer are all domains where DESs are of great interest due to their particular physical properties[13].

According to the nature of the compound used, DESs can be classified into four types[19]:

Table[1.1] the four types of DESs.

Type 1	• Quaternary ammonium salt + metal chloride.
Type 2	• Quaternary ammonium salt + metal chloride hydrate.
Type 3	• Quaternary ammonium salt + hydrogen bond donor.
Type 4	• Metal chloride (hydrate) + hydrogen bond donor.

- **Type 1** solvents are metal halides, and have the general formula MCl_x , where M refers to the metal, for example, Fe, Ga, Sn, Zn, Al, and chlorine

salts, but these types are limited because their non-aqueous mineral salts are limited used in the preparation, such as (ZnCl₂+NaCl).

- **Type 2** can be prepared from choline chloride with hydrated metal salts, which is the same method as the first type but has lower melting points than the corresponding anhydrous salt, such as (ChCl+CoCl₂.6H₂O).
- **Type 3** DESs are the most widely studied because of their versatility. Some contain carboxylic acids, alcohols, and amides, as well as simple sugars, making them biodegradable, low cost, and are easy to prepare [18], such as(ChCl+EG).
- **Type 4** DESs are one of the most advanced types of metal halide that are used as hydrogen bond donors as this type is not suitable for giving cation and anions, such as(ZnCl₂+EG).

1.3.1 Properties of DESs.

Chemical characteristics differ between conventional ionic liquids and deep eutectic solvents. They do, however, share some physical characteristics, such as the ability to be used as tunable solvents that can be tailored to a specific type of chemistry. Whilst their chemical properties are different, the physical properties of both ionic liquids and DESs are similar, as:

1. Relatively wide potential windows
2. Low vapour pressures
3. Non-flammable.

DESs are distinguished from ionic liquids by their [18].

1. Low cost
2. Lower water sensitivity to transfer
3. Lower toxicity
4. Relative ease of preparation.

Where DESs are prepared by mixing two medium-heated compounds together and producing low-heating DESs for the two mixed compounds.

DESs can also be used for a variety of purposes. When it comes to toxicity, DESs are preferable over traditional ILs [12]. The constituent components of DESs are usually well-known. Furthermore, there is limited information on the toxicity of eutectic solvents themselves.

1.3.2 Density, viscosity, and conductivity

The densities of several forms of DES were determined by using the method proposed by Mjalli *et al.* [18]. The density's Average Relative Percentage Errors (ARPE), where DESs are roughly 1.9 percent. The effect of the molar ratio of salt to HBD on ARPE The conditions for the expected DES intensities were also explored effectively. That configure DESs from the interaction of phosphonium salts with a different number of (HBD).

The Density, pH, dissolved oxygen content, melting temperature, and viscosity form all have been measured temperature and conductivity. The molar ratio of salt was also found by the researchers, the hydrogen bond donor, and the effect of these components as it greatly affected DESs because they have viscosity, conductivity, density, and surface tension are examples of physical qualities. The parameters of different types of DES and ionic liquids with separated anions and the number of molecular solvents at 298 K are shown in the table below [3].

Table [1.2] At 298 K as the physical properties of DESs, ionic liquids, and molecular solvents [130].

Salt (mol equiv)	HBD (mol equiv)	Viscosity /cP	Conductivity /ms cm ⁻¹	Density /g cm ⁻³
ChCl	urea	632	0.75	1.24
ChCl	ethylene glycol	36	7.61	1.12
ChCl	glycerol	376	1.05	1.18
ChCl	malonic acid	721	0.55	1.33
ChCl	CrCl ₃ ·6H ₂ O	2346	0.37	1.43

In comparison to ionic fluids and molecular solvents, DESs can have high or low viscosities and conductivity, as shown in Table 1.2. The reason is due to their low free volume and the large volume of the constituent ions.

Moreover, the relationship between viscosity and molar conductivity was good [19,22] as noted by Walden's law: "A constant for a given electrolyte upon unlimited dilution in a group of solvents." As a result of hole theory, Abbott and colleagues were able to demonstrate this charge. Perforations (which can be indefinitely thinned) are used instead of ions for transport [18].

1.4 Hole theory

Due to the high viscosity and low conductivity of DESs, the focus has been on their extensive use when compared to aqueous liquids. Studies undertaken to understand the fluid properties of any of the standard Ionic liquids have also revealed a rise in the volume of the liquid and the free volume of the dissolving liquid, or DES, were developed to calculate the movement of ions at high temperatures. Ionic liquids and rationalize the movement of ions in DES using physical properties in hole theory [23-26]. Hole theory postulates that: "Suppose an ionic substance contains empty spaces that are created from thermally fluctuations were established in the local density of random size and location, and subject to constant flow" [23, 27].

The radius of the average sized void (r), relative to the surface tension of the liquid (γ), is given by [27]:

$$4 \pi (r_2) = 3.5kT / \gamma \quad \dots (1.1)$$

Where k is Boltzmann's constant and T is the absolute temperature.

The average size of the holes is similar dimensions to the matching ions in the case of molten salt, moreover, it was relatively easy to move to the vacuum position as the ion was small, meaning that the liquid contained less viscosity, at lower temperatures, the liquid has a higher viscosity because of the smaller hole size in comparison to the greater ion volumes, which further restricts the

movement of the ions and leads to a decrease in conductivity and an increase in viscosity [3].

1.5 Electroplating of metal surfaces by deep eutectic solvents

In the past few years, metallic electroplating has grown in popularity due to its benefits in industrial applications such as sensors, electronics, and optics, and the automotive industry. We mentioned earlier that previous electroplating of metals was carried out in an aqueous solution. However, aqueous solutions have disadvantages that hinder metal deposition. DES, As an ionic liquid, it's employed in metal electrodeposition to eliminate a lot of the issues that come with electrodeposition from both aqueous and non-aqueous solutions. Furthermore, the electrolyte must be [34]:

1. Highly soluble in metal salts
2. Low resistance to corrosion.
3. High conductivity.
4. High mass transport rates.
5. Low cost.
6. Non-flammable.
7. Good throwing power.
8. High electrochemical stability.

The problems with aqueous electrolytes in general include:

1. Low electrochemical stability
2. Gas evolution leads to hydrogen embrittlement due to limited potential windows
3. A passivation layer is formed on the surface of the electrodes, which leads to the reaction being halted.

The main properties of DESs that are advantageous over those of aqueous solutions and metal salts, metal oxides, and hydroxides are soluble in both organic and inorganic solvents [3].

Furthermore, one of the main issues with the formation of passivation layers in aqueous solution is that these layers are usually made up of insoluble oxides and/or hydroxides that appear on the electrode's surface, making the metal deposition process self-inhibitory and resulting in the formation of a thin metallic coating. In comparison, because DESs have high solubilities to metal oxides and hydroxides, they provide a thicker electrodeposition layer than commonly observed in aqueous solutions, deposition of metals from DESs does not result in the creation of a passivation layer. Dangerous complexing agents, like as cyanides, must be used in aqueous solutions; these are both highly toxic and extremely expensive. Water, however, does not naturally represent a green solvent; it is nontoxic, but all previously dissolved materials need to be removed from it before it can go back into the waterway [28]. Because DESs are characterized by low toxicity, low cost, in comparison to ionic liquids, they have a high metal melting ability and a low susceptibility to water. They must be able to create media that is appropriate for the industry's varied technological aims [5,18]. DESs are employed in the precipitation of metals with high corrosion resistance, such as Al, Ti, and W [29-31].

Furthermore, DES systems are also employed as an alternative to ecologically hazardous metals and coatings, as well as for the deposition of novel alloys and semiconductors [32, 33].

1.5.1 Zinc plating

Zinc is a popular metal surface coating that has been around for a long time. Zinc has a larger negative standard voltage (-0.76 V versus the SHE standard hydrogen electrode) than iron (-0.44 V versus SHE) and is therefore commonly

employed to protect steel from corrosion, as well as scratching and damage [34-37]. Moreover, zinc has the advantages of low cost, non-toxicity, and is easily recyclable, as a result of these qualities, it is widely used in a variety of industrial applications [38,39]. According to the International Zinc Association, more than 5 million tonnes of zinc are used to protect steel from corrosion each year around the world [8]. Zinc has a long lifespan and can produce excellent coatings from aqueous systems. Despite this, DES precipitation of zinc from the electrolyte on a copper substrate of ChCl: ethylene glycol, ChCl: urea as DESs, as initially obtained by Ryder *et al.*[40]. They replaced coating from aqueous and traditional ionic fluids in the last 10 years. Zinc is precipitated from DESs with a compact microcrystalline structure, but in the absence of a strong base in the bath, it exhibits a more dendritic shape in an aqueous solution. In addition, chemicals are added to aqueous solutions to improve the physical and mechanical qualities of the resulting metal plating.

Snowden investigated the effects of introducing formaldehyde as an organic component to a water zinc bath in 1907 [41]. Where it was found that adding a small amount of formaldehyde resulted in small grain size in the zinc deposits. Also, when many different organic additives are used to precipitate zinc electrically. As the purpose of the addition is:

- i. Brightness, roughness, and pressure plating properties should all be improved.
- ii. When organic additives like polyvinyl alcohol, aromatic amides, and quinine derivatives are added to the electrophoresis of zinc from acid and cyanide baths, the paint bath's operating performance, such as current efficiency, anodic depolarization, and throwing power, improve [42]. Abbott looked at the effects of ammonia, acetonitrile, and ethylene diamine on the zinc electrophoresis of 1:2 ChCl: ethylene glycol and 1:2 ChCl: urea a few years ago[40]. The same findings were observed after adding ethylene diamine and ammonia to the plating bath, where the zinc deposits were found to be glossy.

1.5.2 Cobalt plating

Cobalt is a hard, non-brittle magnetic metal that has been employed in magnetic processes due to its excellent qualities for high-performance magnetic applications[43]. Because the electrochemical window in water is narrow, electrostatic precipitation of cobalt and its alloys is problematic. Because ionic liquids (ILs) have large electrochemical windows, they can assist the electrostatic precipitation of cobalt or its alloys as electrolytes. The various ILs, chloroaluminate-based ILs are used on the large scale for electrodeposition of various alloys due to the ability to modify their Lewis acidity or basicity. Moreover, cobalt electroplating can be obtained from various ILs. Carlin *et al.* [44]. They found that cobalt electrodeposition could be achieved from liquid chloroaluminate IL. Pure cobalt is also deposited through progressive three-dimensional nucleation with diffusion-controlled development. It has also been noted that cobalt electroplating and cobalt-aluminium alloys of chloroaluminate IL, and the nature and form of the deposits are determined by the potential used [45]. Katayama and co-workers [29] studied the effects of temperature and additives on the electrodeposition of amide-type cobalt in ionic liquids [46]. This was done by increasing the effort to precipitate cobalt by raising the temperature with the addition of acetone.

Because of their numerous advantages, several alternative ionic liquids have been accepted as the new room temperature electroplating technology, including [29]:

- i.** A large electrochemical potential window is available.
- ii.** Vapor pressure is quite low.
- iii.** High ionic conductivity.

Several studies have been published on the electrostatic precipitation of carbon dioxide in ionic liquids [47-54]. When performing electrophoresis of

cobalt there was poor adhesion to the substrate [55]. However, the presence of acetone altered the co-ordinate of the Co^{2+} ion environment and reduced the over potential for electrodeposition of Co[46]. Since the electrodeposition of Co is strongly affected by the charge and coordination of Co^{2+} types in the ionic liquid. As mentioned previously, the electrophoresis of aluminium and aluminium alloys of ILs was performed by the Reddy group [56-59]. Nevertheless, the extremely hydrated nature of these chloroaluminate systems, the stability of urea in air and water, and the solubility of the choline chloride were examined by Abbott *et al.* [60]. It is made up of choline chloride and urea, with the interactions between the urea and chloride ions acting as donors in the creation of hydrogen bonds in a eutectic mixture characterized by:

1. The temperature at which it freezes is 12 degrees Celsius.
2. More than 2.5 volts in the electrochemical window.

They're also employed as an alternate solvent in many metal electroplating processes [61-66]. Several previous studies have demonstrated the effect of organic additives such as coumarin and thiourea on the electrochemical behaviour of Co electrodeposition in ionic liquids[67].The qualities of brightness, smoothness, changing the surface morphology, and absorption on the surface of the precipitant in aqueous solutions are what distinguishes these additives[68-72]. In addition, there have been many studies on additives in electrodeposition using ionic liquids, such as in Co electrodeposition where ethyl alcohol[48], propylene carbonate[48,50], were used, toluene[73], and lithium chloride (LiCl) [73] in Al electrodeposition.

The results in this field were demonstrated that the additives can affect on the grain size, surface morphology, and electrochemical behaviour. Also, cobalt deposition using ILs has been studied in a new way, very little is known about the mechanism of electrodeposition and pure cobalt reduction in choline chloride and ethylene glycol.

To determine the mechanism of cobalt reduction and nucleation, researchers used cyclic voltammetry to study the impacts of additives and morphological surface temperature.

1.6 Alloy plating

It is difficult to electroplate alloys electrically because of the difficulty in separating and reducing a potential between two elements in aqueous solution, and it is very difficult to electroplate two elements with different reduction potentials separately.

Therefore, to achieve stability of ionic solutions in water and air, a wide potential window must be found, so alloys of various types were produced in aqueous solution such as Cu-Mn [74], Cu-Li[75,76], Fe-Al[77], Fe-Si[78],Cu-Zn[79], and Cu-Zn-Al[79]. Among the conditions that can change the properties of electrodeposition of metal alloys are metal concentration in the plating solution, current density, temperature, and potential,Pd-Ni[80] and Pd-Sn[81] can be produced from conventional ILs by modifying the electrodeposition potential and the composition of the solution. Only a few studies have addressed the electroplating deposition of alloys from DESs under different conditions. There are examples of alloy coatings from DESs. Abbott and co-workers also studied the electrical deposition of Zn-Sn and mild steel for choline chloride, ethylene glycol or urea in DES[82]. And they used DESs in the deposition of alloys such as Ni-Co,[83] Ni-Zn, [84] Co-Sm[85], and Co-Pt[86].

1.6.1 Zn alloys

The electrodeposition of zinc is technologically simple, but electrodeposition of alloy is difficult in aqueous solution due to the difference in oxidation and reduction in the electrical potentials of the alloying elements. On the surfaces of active metallic substrates used in highly corrosive environments, coating these surfaces with zinc and its alloys [18]. The cathode in this alloy is less than that on the cathode surface when the electrode deposition is performed

to produce the Zn-Ni alloy[87]. Electrodeposition by aqueous systems is current limited by the requirement for strong acids and alkalis or toxic compounds in the plating baths. Many researchers have also attracted coating with Zn-Ni alloys when compared to other alloys, it has a higher corrosion resistance and better mechanical qualities [88]. The great interest in zinc alloys is due to the characteristics of such alloys, including [89-93] :

- i.** High corrosion resistance.
- ii.** More hardness and more resistance than pure zinc, so it is used in the automotive and aviation industries.

Zn-Ni alloys replaced Cd and Cd alloys due to their high toxicity[94,95].The electrodeposition of Zn-Ni alloys was also successful in aqueous baths. [96, 97] Nevertheless, it was observed that the throwing strength was weak in most such acid baths. The alloys, but the sediments in the alkaline cyanide bath were produced due to the severe toxicity of these two pigeons and their effect on the environment and humans.Cyanide baths were replaced with non-cyanide materials by adding various complexing agents to the plating bath to form less harmful precipitates such as sodium acetate[98, 99], amines [100], tartrates [101],Ethylene diamine[102],glycinate[103,104], triethanolamine, citrates, and urea[105].

However, the present efficiencies of this bath are quite poor. DESs are the successful solution electrophoresis of Zn-Ni to tackle this problem. Despite the addition of numerous complicated agents, it still has some electrostatic deposition issues, such as:

- i.** Due to excessive hydrogen emissions, there is a low current efficiency.
- ii.** High toxicity.
- iii.** Narrow potential window.

The researchers were interested in developing room temperature ionic liquids or ionic liquids that could be easily melted to precipitate electrodeposited minerals, as well as developing them as "green" solvents and effective substitutes

for toxic substances in baths,[106] where these types of liquids are characterized by[106]:

1. Good conductivity
2. The ability to dissolve mineral salts
3. Non-toxicity compared to aqueous solutions
4. Wide electrochemical windows.

As previously stated, the additives used in electroplating basins are intended to improve the coating's morphology while also having the potential to impact electrostatic deposition parameters such as brightness, grain size, thickness, roughness, hardness, and corrosion resistance [107].

Many studies in the literature have explained the effects of additives on the properties and mechanisms of metallic plating; in this paper, we will look at the electrostatic deposition of pure zinc and Zn-Co alloy from choline chloride and ethylene glycol in a 1:4 ratio, as well as the effect of additives on coatings (boric acid, nicotinic acid, ascorbic acid, and water) and the effects of electroplating with physical parameters. Different conditions (metal concentration, temperature, current density) will also be examined for the existing ionic eutectic liquid.

1.7 The role of additives on the electrodeposition processes of metals in eutectic solvents

The deposit's physical and chemical properties must be improved in order to perform it well as an electrodeposition. This can be accomplished by altering the paint bath's conditions, such as temperature, current density, mineral salt concentration, deposit time, and additives in the metal electroplating bath, which can make the metallic coating thicker, harder, corrosion-resistant, less rough, and brighter [42,108]. The types of additives used in electroplating vary, and their selection is based on the composition of the metal on which the coating is applied, as well as the temperature. The action of the

additives is complex, and decided by their interaction with metal ions in the solution by makes their reduction difficult or more or less absorbable on the surface of the electrode. The role of the addition agents in aqueous electroplating baths is very important owing mainly to the interesting and important effects they have on the structure, growth, and glossiness of the associated deposits [109,110].

The potential benefits of the additives include the brightening the deposit, reduction in grain size, and the tendency to tree, increasing the current density range, promotion of leveling, improvement of mechanical and physical properties, reducing stress and pitting, etc. Thus, organic additives and pulse control are an effective way to achieve grain refinement down to the nanoscale for mineral deposits. In the past five years, Guo *et al.*[111] have been studying the effects of nicotinic acid on Ni electroplating from DESs. They found that nicotinic acid can produce an Ni coating that is bright, smooth, and uniform. It was an effect of boric acid, nicotinic acid, and methylene nicotinate 5,5-Dimethylhydantoin on electroplating Ni from a choline chloride(ChCl)Ethylene glycol(EG) based on DES.This is the ChCl 1:2 EG. It was interesting to notice that the application of these chemicals resulted in the production of dazzling mirror Ni coatings[112].

1.7.1 Effect of water on electroplating of metal

Adding water to the bath electroplating containing DES systems improves the coating properties considerably [113-118], as water is a good hydrogen donor. Also, adding water to a sufficient amount of ionic liquid choline chloride-urea has been shown to reduce the viscosity of the liquid and give improved electrical conductivity[119]. Some of the benefits of adding water to ionic liquids are cuase decreasing in the conductivity and increasing in the

viscosity[120,121].Increasing the amount of water decreases the electrochemical window of the solution in water, as also noted by Compton *et al.*[120].

The nickel coatings deposited from systems containing ethylene and to which water had been added improved corrosion resistance due to the smoother surface of the negative films formed on the surface of the deposits[12]. In general, IL-water mixtures are of great importance in biochemical applications due to these mixtures' ability to dissolve a wide range of salts. From this perspective, it is important to understand the interactions in IL-water mixtures. With this, a study of the effect of water on zinc and cobalt electroplating will be given. It has been experimentally observed that small concentrations of water can change the morphology of zinc and cobalt deposits; the purpose of the study is to determine whether this is due to changes in the double-layer structure.

1.8 Aim this project's.

The research will focus on:

1. Electrodeposition of various metals, such as zinc and cobalt, and zinc-cobalt alloys, in Ethaline 400 as a deep eutectic solvent with a highly uniform layer of deep eutectic solvent(DES).
2. Studying of physical properties of plating liquids such as, conductivity and viscosity.
3. Studying of electrochemical properties of plating liquids using cyclic voltammetry method.
4. Studying the effect of water and additives such as nicotinic acid (NA), boric acid (BA) and ascorbic acid (AS) on the brightness and morphology of metals deposited from DES.
5. Studying of the mechanical and the physical properties of metal film such as morphology, roughness, and thickness .
6. Analyzing the samples by using XRD, AFM and SEM/EDX.

CHAPTER TWO
EXPERIMENTAL
PART

2. Experimental and Methods

2.1 Materials and Chemicals.

The used materials of chemical was listed in table[2.1]:

Table [2.1]: List of chemicals used in this project, their abbreviations and molecular weights and purities.

Chemicals	Abbreviation and Molecular Weight (g/mole)	Company supplied	Purity %and percentage
Choline chloride (ChCl)	$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ (139.63)	Aldrich- Sigma	99%
Ethylene Glycol (EG)	$\text{C}_2\text{H}_4(\text{OH})_2$ (62.07)	Aldrich- Sigma	99%
Zinc Chloride	ZnCl_2 (136.30)	Aldrich	$\geq 98\%$
Cobalt ChlorideHexahydrate	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (128,99)	Aldrich	$\geq 98\%$
Boric Acid (BA)	H_3BO_3 (61.83)	Analar	99.8%
Nicotinic Acid (NA)	$\text{C}_6\text{H}_5\text{NO}_2$ (123.11)	Sigma	99.5 %
Ascorbic acid	$\text{C}_6\text{H}_8\text{O}_6$ (176.12)	Fisher	$\geq 99\%$
Sulphuric acid	H_2SO_4 (82.07)	Fisher	$\geq 99\%$
Hydrochloric acid	HCl (36.46)	Fisher	≥ 36.5 - 38.0%
Alumina	Al_2O_3 (101.96)	Fisher	$\geq 100\%$
Ammonium persulphate	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (228.20)	Sigma	$\geq 98\%$

2.2 Preparation of Plating Solutions (Procedure)

2.2.1 Preparation of Electrolyte (Deep Eutectic Solvents)

The major solution of (Ethaline 400) was made as a DES by continuously mixing two chemical substances, choline chloride [$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$](ChCl), and ethylene glycol(EG), in a tiny beaker open to the air at 70 °C in a 1:4 ratio respectively. In just few minutes, the produced mixture was totally converted into a liquid that was homogeneous and colourless in nature[3].

2.2.2 Preparation of Plating Liquids

- a) A concentration of 0.3 M ZnCl_2 was prepared in Ethaline 400 liquid. The electrolyte that resulted was categorized as a zinc electrodeposition bath without additives. The additives were added individually to the zinc electrodeposition bath. At a temperature of 70°C, all electrodeposition experiments were carried out.
- b) The $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ electrodeposition solution was performed by mixing 100 mL (Ethaline 400) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at a concentration of 0.4 M, and heating the mixture at 70°C under continuous stirring.
- c) The Zn-Co alloy electrodeposition solution was done by mixing 100 mL (Ethaline 400) with 0.3 M ZnCl_2 0.4 M and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ under continuous stirring at 70°C [130]. See figure [2.1]:

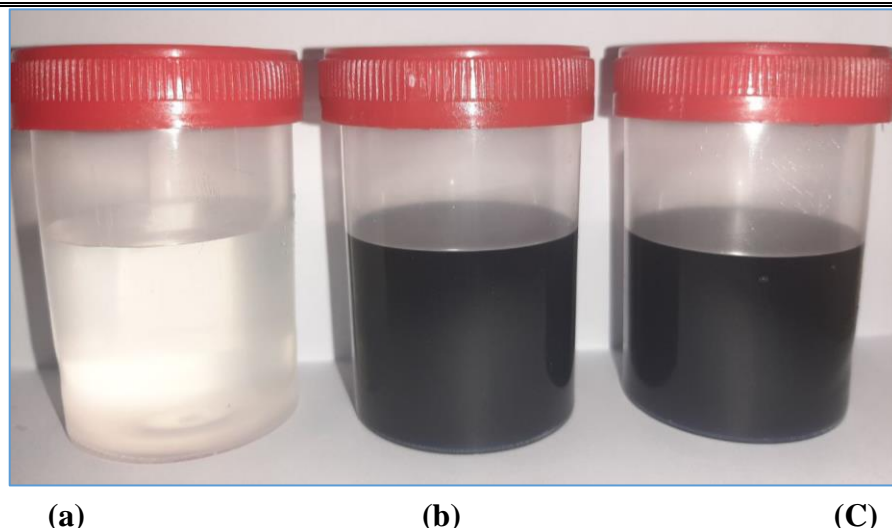


Figure [2.1]: Electrodeposition solutions (a) 0.3 M ZnCl₂ in 100 mL ethaline 400, (b) 0.4 M CoCl₂.6H₂O in 100 mL ethaline 400, (c) 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O in 100 mL (Ethaline 400). (All experiments were performed at 70°C).

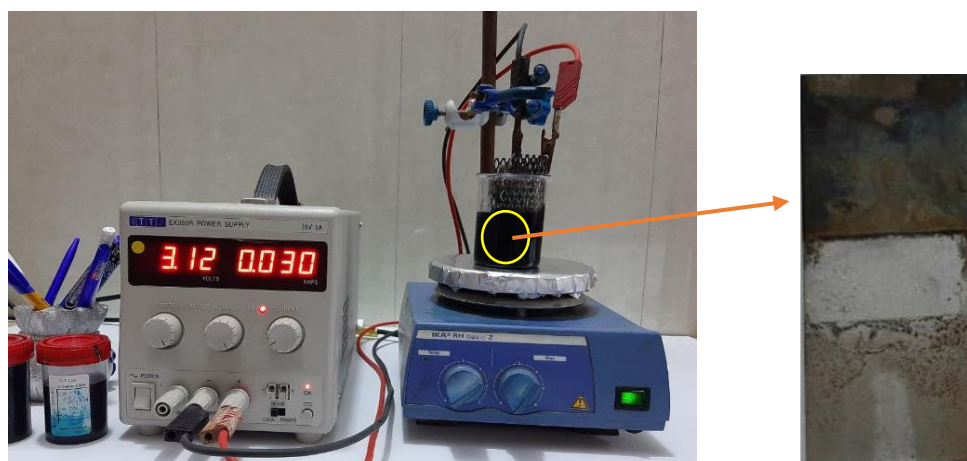
2.2.3 Prepare Plating solutions with additives:

0.6 M boric acid (BA), 0.5 M nicotinic acid (NA), and 0.03 M ascorbic acid were utilized as additives in the electrodeposition of Zn from Ethaline 400. Further, additives of 10%, 20%, 30% of H₂O to 90%, 80%, 70% from Zn solution in Ethaline 400. The concentrations of additives used in the electrodeposition of Co in Ethaline 400 were 0.6 M boric Acid (BA), 0.1 M nicotinic acid (NA), and 0.03 M ascorbic acid.

Also, the additives of 10%, 20%, 30% of H₂O to 90%, 80%, 70% from Co solution in Ethaline 400 were done. The concentrations of additives: 0.6 M boric Acid (BA), 0.1 M nicotinic acid (NA), and 0.03 M ascorbic acid were employed in the electrodeposition of Zn-Co alloy from Ethaline 400. Moreover, the additives of 10%, 20%, and 30% of H₂O to 90%, 80%, and 70% from Zn-Co alloy solution in Ethaline 400 were also employed[130].

2.3 Electrodeposition of Zn

After preparing the coating solution, which includes Zn in concentration 0.3M (Ethaline 400) into electrodeposit the Zn in the presence or absence of additives, the power supply current was regulated to 30 mA and the solution was heated at a fixed temperature at 70°C. The cathode was a mild steel substrate that had been cleaned using water before being immersed in strong HCl acid, rinsed with water, and dried with acetone. Before coating, it was weighed when it had completely dried. The anode was made of Ti mesh, and the electrodeposition was carried out for 2h [3,122], as shown in the figure below.



Figure[2.2] Under using Ethaline 400 containing 0.3M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ without and with additives on a mild steel substrate at 70°C for 2h at a current of 30 mA.

2.3.1 Electrodeposition of Co

Also, ready-to-coat solutions for the electrodeposition of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at a concentration of 0.4 M (Ethaline 400) was used to

electrodeposit Co in the existence or absence of additives, after which the power supply was adjusted to a current of 30 mA and heating the solution at fixed temperature at 70°C. The cathode was initially a mild steel substrate and, later, a copper substrate was used, which was cleaned with water and then placed in strong HCl acid, washed with water, and dried with acetone. After it had dried completely, it was weighed before coating. The second cathode electrode was cleaned with ammonium persulphate solution, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, washed with water, and then dried with acetone. The anode was made of Ti mesh, and the electrodeposition took 2 hours [123].

2.3.2 Electrodeposition of Zn-Co Alloy

The electrodeposition of Zn-Co alloy was conducted under different conditions, but at the same constant temperature (70°C), meaning that the concentrations of zinc ion were 0.3 and 0.4M, also the cobalt ion concentrations were 0.4 and 0.1M, the current densities used were 20,25,30, and 40 mA. The deposition times were 2 and 3h. In the existence and absence of additives, as well as the same steps for cleaning the substrate, whether mild steel or copper, the electrodeposition of the zinc-cobalt alloy was carried out [123].

2.4 Measurement of Physical Properties

2.4.1 Conductivity

The electrical conductivities of Zn and Co solutions as well as their Zn-Co alloys, were measured in the presence and absence of additives using an electrical conductivity device equipped with an electrode that is sensitive for temperature change, as the cell constant

is (1.01 cm^{-1}), the conductivities were found at temperatures ranging from (25-80)°C, where the measurement was at a decreasing of 5°C, and then the beaker containing the solution was shaken before each reading to ensure accurate readings [12].

2.5. UV-Visible Spectroscopy Measurements

Using UV-visible spectrophotometer device, analyses of the samples were carried out for the purpose of determining whether there were changes in the solution during dilution or addition of additives and the formation of new complexes.

Two types of liquids were prepared:

1:

- 5.0 mL of 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 0.0 mL of H_2O ,
- 4.5 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 0.5 mL of H_2O ,
- 4.0 mL of 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 1.0 mL of H_2O ,
- 3.5 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 1.5 mL of H_2O ,
- 3.0 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 2.0 mL of H_2O ,
- 2.5 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 2.5 mL of H_2O ,
- 2.0 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 3.0 mL of H_2O ,
- 1.5 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 3.5 mL H_2O ,
- 1.0 mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 4.0 mL H_2O ,
- 0.5mL of 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 4.5 mL H_2O ,
- 0.0 mL of 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 + 5.0 mL H_2O .

2:

- 0.4 M of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.6 M BA,
- 0.4 M of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.1 M NA,
- 0.4 M of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.03 M AS.

The cells used for examination are standard 1.0 cm quartz cuvettes.

2.6 Electrochemical Measurements

2.6.1 Cyclic Voltammetry Measurement

It was important to measure the electrical properties of the plating liquids with the addition of an orbital additive, which was accomplished using a periodic voltmeter with a software-controlled Autolab PGSTAT 20 with three electrodes:

1. 0.1 mm platinum wire as the working electrode
2. Silver wire as the reference electrode
3. Platinum sheet as the counter electrode.

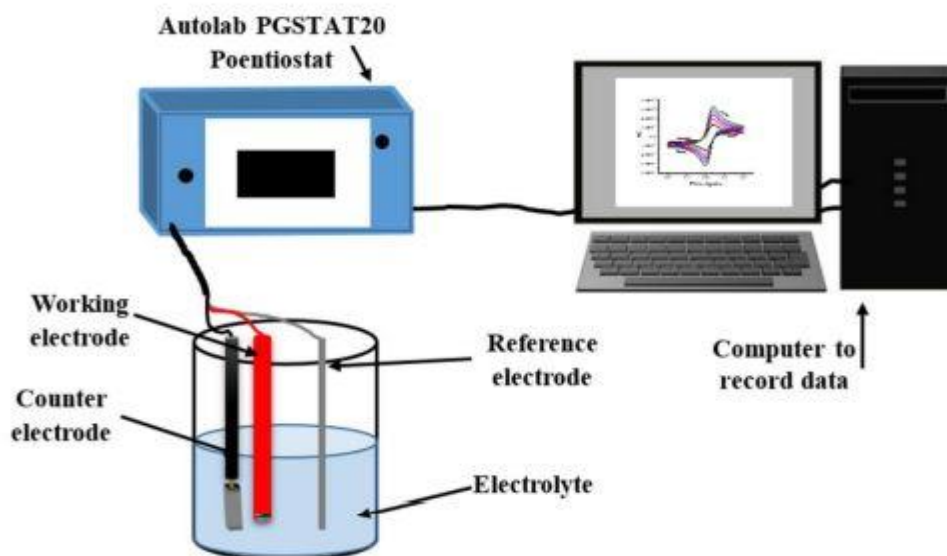


Figure [2.3]:A schematic digram for the cyclic voltammograms[12].

The voltammetric analysis of zinc was done with a potential window of 0.0V to -1.3V, while the cyclic voltammograms of cobalt were done with a potential window of +0.4V to -0.8V and back to 0.0 V. For the Zn-Co deposition, the cyclic voltammetry potential was set at +0.4 to 1.3V, then back to +0.4V. At a constant temperature of 70°C, cyclic voltammetry studies were performed at different scan

rates. The working electrode was polished with alumina paste, washed with water, and dried with acetone between each experiment in all experiments[78].

2.7 Surface Analysis

2.7.1 Atomic force microscope (AFM)

The purpose of surface analysis is to obtain the microscopic images that demonstrate the roughness of the particles forming during the coating on the surface of the sample. Atomic force microscopy (AFM) was employed to examine the samples in this manner.

2.7.2 Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (SEM, EDXA)

The morphology of surface was identified the shape of the paint granules, whether, they were spherical, cylindrical, or irregular in shape, using a SEM device, and the preliminary analysis by Energy dispersive x-ray spectroscopy (EDX)was also performed.

2.7.3. X-Ray Diffraction (XRD)

The X-ray powder diffraction of the samples was carried out using two instruments:

1. XRD XPERT PILIPS HILLAND.
2. XRD AB2700 HAOYUAN CHINA.

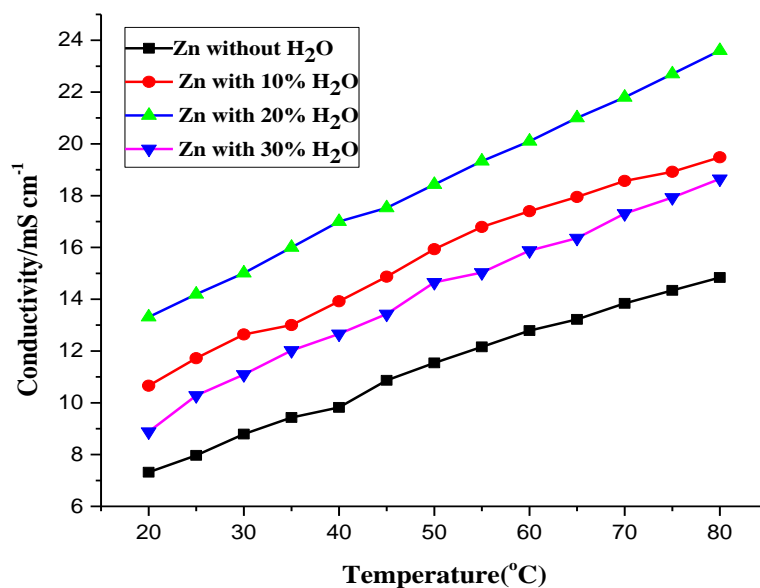
This technique used to detect the sutructural of prepared samples and proved the Zn-Co alloys are formed.

CHAPTER THREE
RESULTS AND
DISCUSSION

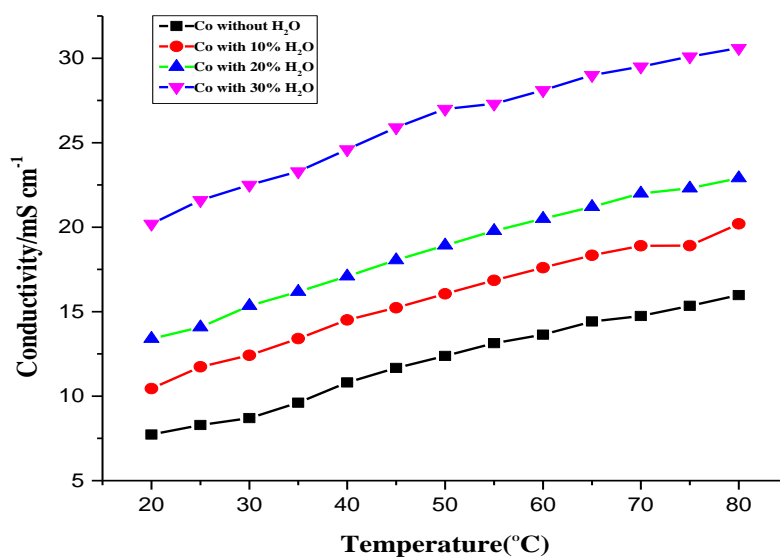
Physical properties

3.1 Conductivity

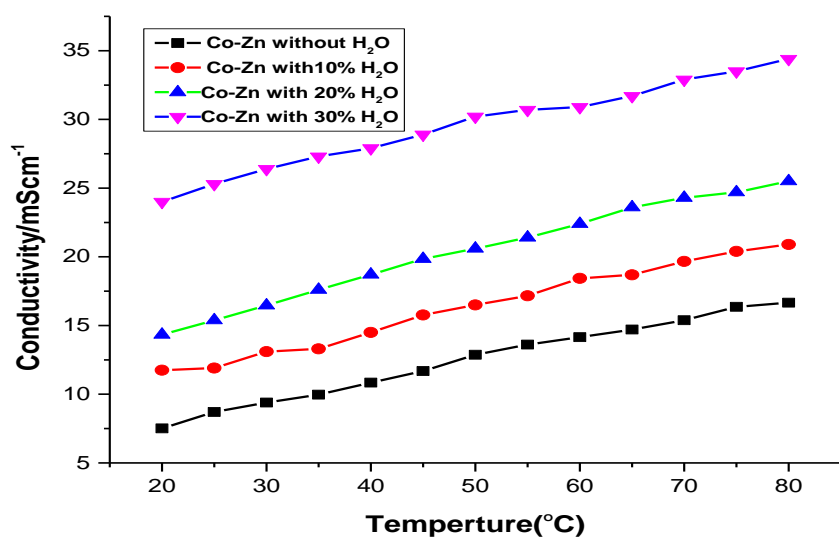
The conductivity of the plating liquid has a significant impact on the characteristics of the coating when electroplating metals are in a deep eutectic solvent. Given the relevance of conductivity, it is critical to investigate the conductivity of the coating liquid. Figures 3.1, 3.2, and 3.3 display the conductivity of ZnCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and Zn-Co in (Ethaline 400) as different of temperature in without and with of water and the additives BA, NA, and AS. Here, the conductivities of the Zn, Co, and Zn-Co solutions were found to increase with increasing amounts of water, where clear increases in the conductivities of the Zn, Co, and Zn-Co electrolytes were observed, but with additives the conductivity of Zn is decreasing. This could be because, as shown in Figure 3.4, increasing the viscosity of the Zn solution with additives decreased the conductivity of the liquid. The increase in the viscosity of Zn solution in (Ethaline 400) with NA and BA was inversely proportional to a decrease in the conductivity of the electrolyte. Also found that these additives increased the viscosity and decreased the conductivity of the Zn electrolyte. It should be noted that additives have little effect on conductivities, which is in line with the statement of the source [3].



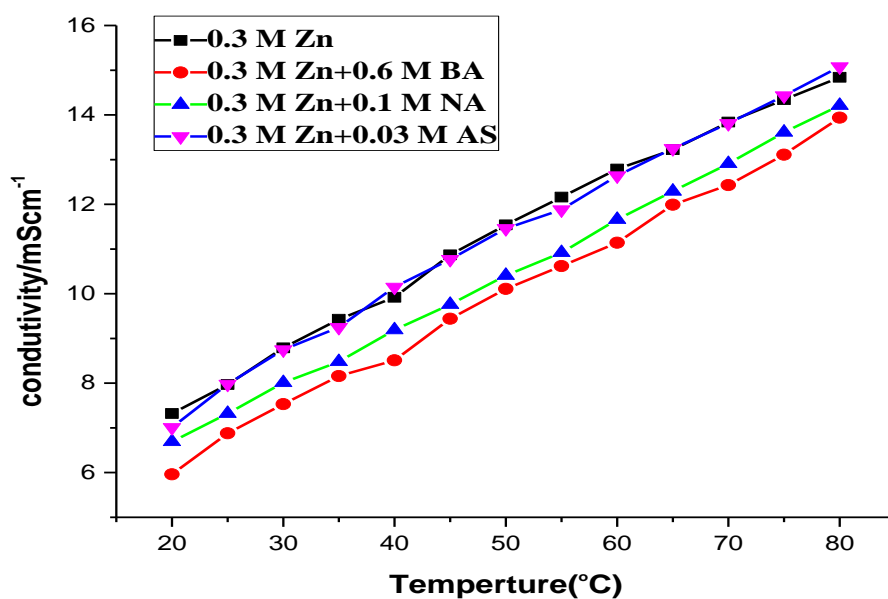
Figure[3.1] The conductivity in (Ethaline 400) of 0.3M ZnCl₂ as a different of temperature and various ratios of water.



Figure[3.2] The conductivity in Ethaline 400 of 0.4M CoCl₂.6H₂O as a different of temperature and various ratios of water.



Figure[3.3] The conductivity in Ethaline 400 of Zn-Co as a function of temperature and various ratios of water.

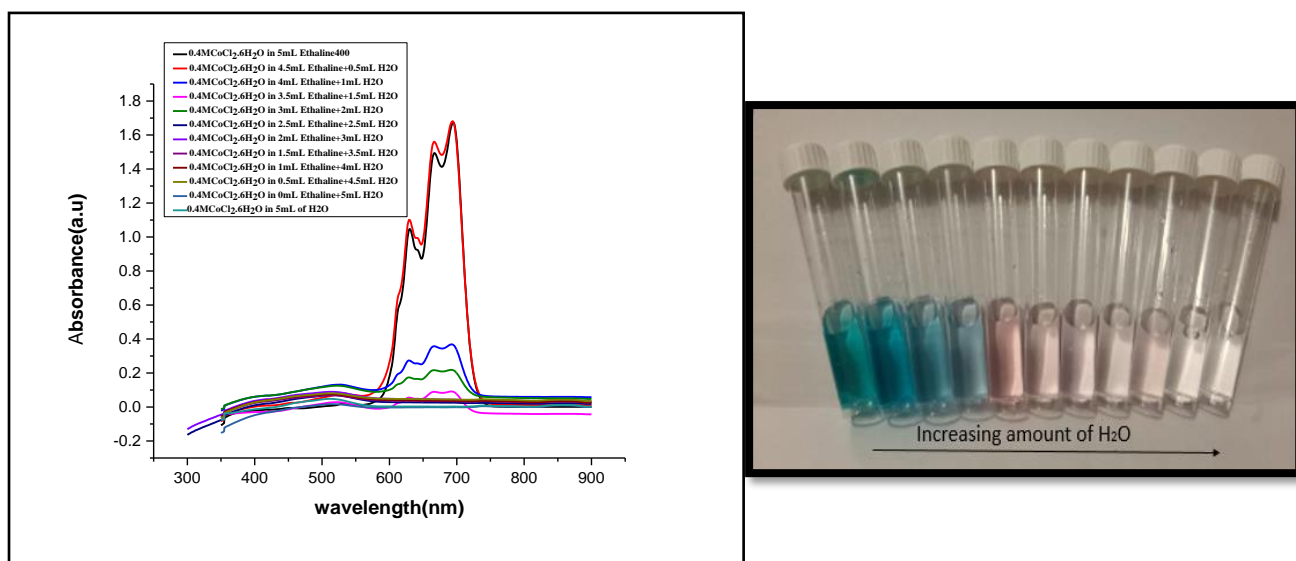


Figure[3.4]The conductivity in Ethaline 400 of 0.3 M ZnCl₂ as a function of temperature and various additives.

3.2 Speciation

In most co plating solutions, organic additives and varying volumes of water are added to the plating solution. This results in the appearance of metal ion speciation. The UV-visible spectro was employed to identify species of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (Ethaline 400) in the absence and presence of additives such as BA, NA, and AS, as well as water. The UV-visible spectra of solutions containing 0.4M of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (Ethaline 400) in without and with of various ratios of water and concentrations of BA, NA, and AS (0.6M, 0.1M, and 0.03M), respectively, as appears in figure 3.5. (a). Without H_2O , the color of 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (Ethaline 400) was blue. However, it was seen that the color shifted from blue to light blue with time, then the light blue changes to pink.

The addition of increasing the water amounts shall turn from pink to colourless as the intensity of the peaks disappears, as appears in Figure. 3.5. The blue colour indicates the production of $[\text{CoCl}_4]^{2-}$ complexes in the solution, i.e., peaks with pronounced intensity. Light blue and pink can be assigned to a mixture of $[\text{CoCl}_4]^{2-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. It is clear from Figure 3.5. (a) that the colourlessness is indicative of the formation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complexes.

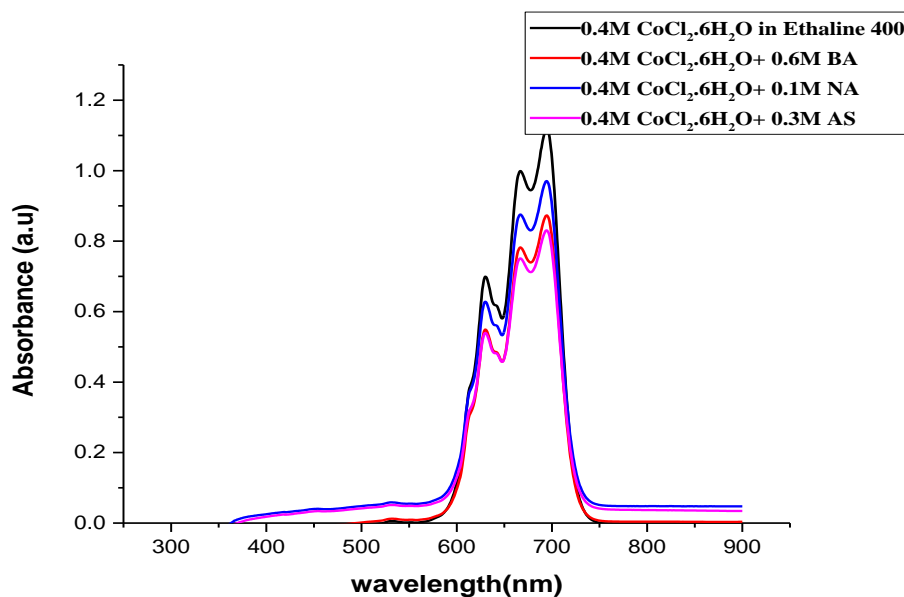


(a)

(b)

Figure [3.5] (a) UV-Visible spectra in Ethaline 400 for 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and addition of increasing amounts of H_2O , (b) photographic image in Ethaline 400 of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with increasing amounts of H_2O .

Figure 3.5 (b) explains the coordination environment of Co^{2+} : the coordination environment of metal species dissolved in an ionic liquid affects, to a certain extent, its electrochemical behaviour. Figure 3.6 shows the absorption spectra of (Ethaline 400) containing 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with different additives (0.6M BA, 0.1M NA, and 0.03M AS) at room temperature. There was no difference between the speciation before and after the addition of those additives, indicating that these additives do not tend to change the coordination environment of Co.



Figure[3.6] UV-visible spectra measured at 25 °C from ChCl:EG using 0.4M CoCl₂.6H₂O.

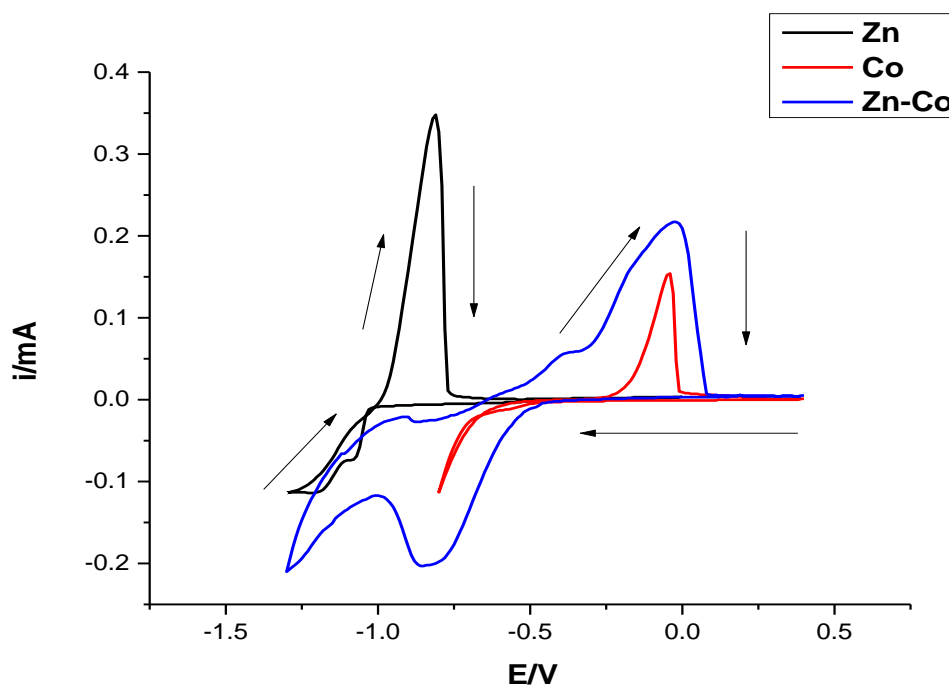
3.3 Electrochemical properties:

3.3.1 Cyclic voltammetric (CV) studies

The current section deals with studying the electricalchemical properties of coating liquid containing of Zn, Co, and Zn-Co in (Ethaline 400) by cyclic voltammetry. Figure 3.7 explains the cyclic voltammograms for 0.3M ZnCl₂ and 0.4M CoCl₂.6H₂O in (Ethaline 400), by using three electrodes (a Pt electrode of the working electrode (1mm diameter), the reference electrode an Ag wire, and the counter electrode a Pt flag)the experiments for which were achieved at 30 mV s⁻¹ and 70°C. These initially scanned cathodic from 0.0V to -0.6V, Figure 3.7 referes, the reduction of Co started at -0.6V on the electrode surface, At the same time the maximum oxidation current peak for Co was at approximately -0.2V, where this was smaller than the electrochemical behaviour of Co in a choline chloride-based liquid, From than Zn voltammograms clear in Figure 3.7 [2]. In these moments, it the Zn species began to

reduce at -1.1V , while the maximum oxidation current peak for Zn was at -1V . This result is in agreement with that demonstrated by Pereira *et al.*[43]. It is noticeable that the voltammograms of Zn differ from the voltammograms of Co, where, the Zn species require more energy to be deposited than the energy required to reduce the Co species; this is referred to in Figure 3.7. As Co started to reduce at -0.6V , while Zn started to reduce at -1.1V . This means that Co metal is deposited first on the cathode from a solution containing Zn and Co ions when a certain potential is applied. Zn metal started to oxidize at -1.1V , while dissolution of Co began at -0.2V , as can also be seen in figure 3.7. This indicates that Co metal needs a high potential to dissolve compared to that needed to oxidize Zn metal from the electrode surface. This means that the Co has a greater resistance to corrosion than Zn. However, the CVs of (Ethaline 400) containing 0.3M ZnCl_2 and $0.4\text{M CoCl}_2 \cdot 6\text{H}_2\text{O}$ recorded at 70°C are shown in Figure 3.7. Two deposition peaks are apparent in the CVs of Zn-Co recorded on a polished Pt electrode at a sweep rate of 30 mV/s versus an Ag wire reference electrode. The first reduction peak, which was observed at -0.8V , corresponds to the deposition of Co, while the deposition peak that appeared at -1.4V , corresponds to the reduction of Zn. The anodic branch also shows two peaks that start at about -0.8V and -1.4V , which correspond to the dissolution of Zn and Co, respectively, from the electrode surface. Recorded using an additive-free electrolyte, there were two separated reduction peaks for Zn and Co at potentials identical to those found previously for these metals in Figure 3.7. Therefore, it can't initially be inferred that a Zn-Co alloy has actually formed as this could potentially be a co-deposition of Zn and Co; to allow for a more in-

depth investigation, the XRD technique should be used in this regard.

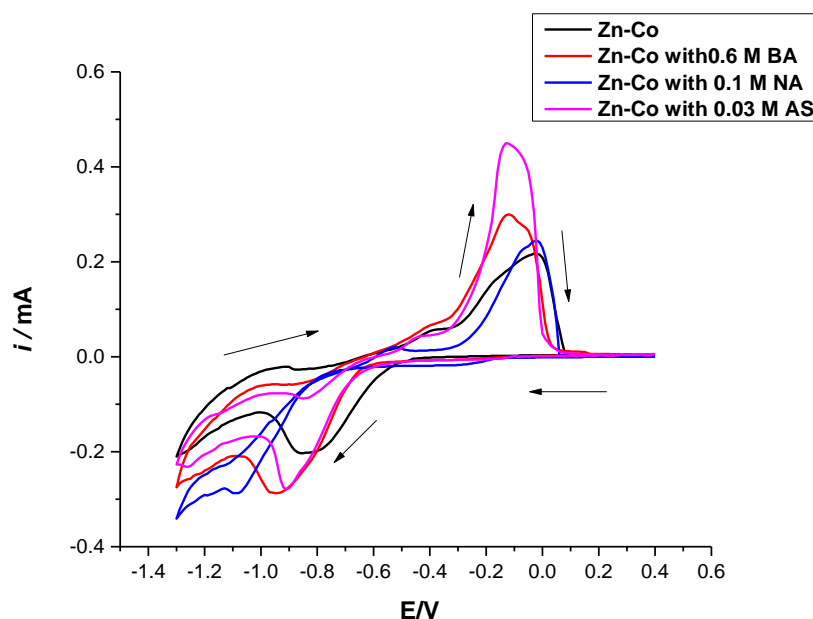


Figure[3.7] Cyclic voltammograms of 0.3 M ZnCl_2 (black) and 0.4 M CoCl_2 (red) and Zn-Co (blue) in Ethaline 400 at 70°C , using 30 mV/s scan rates and a Pt disc working electrode (1mm diameter), Pt flag counter electrode, and an Ag wire reference electrode.

3.3.2 Voltammetry of Zn-Co alloy with/without additives

Here, Compared the cyclic voltammetric response of a solution of 0.3 M ZnCl_2 and 0.04M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (Ethaline400) at 70°C without and with of the following additives: (Black)without additives, (red) with 0.6 M BA, (blue) with 0.1M NA, and (pick) with 0.0 M AS. Cyclic voltammetry was performed scanning a potential window from 0.0 V in the negative direction to -1.5 V, which was then reversed to the starting point. Figure 3.8 explian cyclic voltammograms of 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in (Ethaline 400) without and with of 0.6 M BA, It is worth noting that using the BA

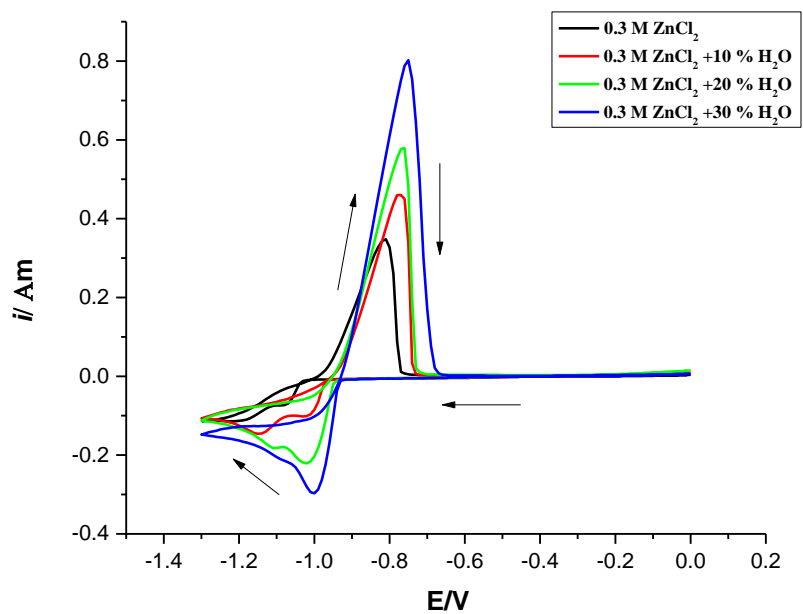
intensity the redox peaks and reduced Co where a negative shift at -0.1, when in the Co reduction peak was also observed. The behavior that due to the adsorption of BA on to the surface of the electrode, that due to the deposit of Co inhibit, On the other hand the use BA with the electrodeposition of Zn from (Ethaline 400) leads to adsorbed on electrode surfaces, and therefore impeding the reduction of Zn species this is consistent with what the source is referring [124]. It can be seen that rate of Zn-Co deposition increase when the additives (BA, NA and AS) were introduced to the plating solution. This is because the additive can be deposited on the electrode surface, also known as the "blocking surface" As a result, metal deposition cannot occur on organic molecule-occupied locations. The leveling molecules will be adsorbed on the active sites for H₂ evolution [125] or on the high points of the electrode surface. The diffusion layer thickness will be thinner in the main points than in the concavity, allowing organic molecules to travel faster. As a consequence, organic molecule adsorption in the concavity will be significantly reduced. As a result, metals tend to deposit in the electrode surface's conductivity.



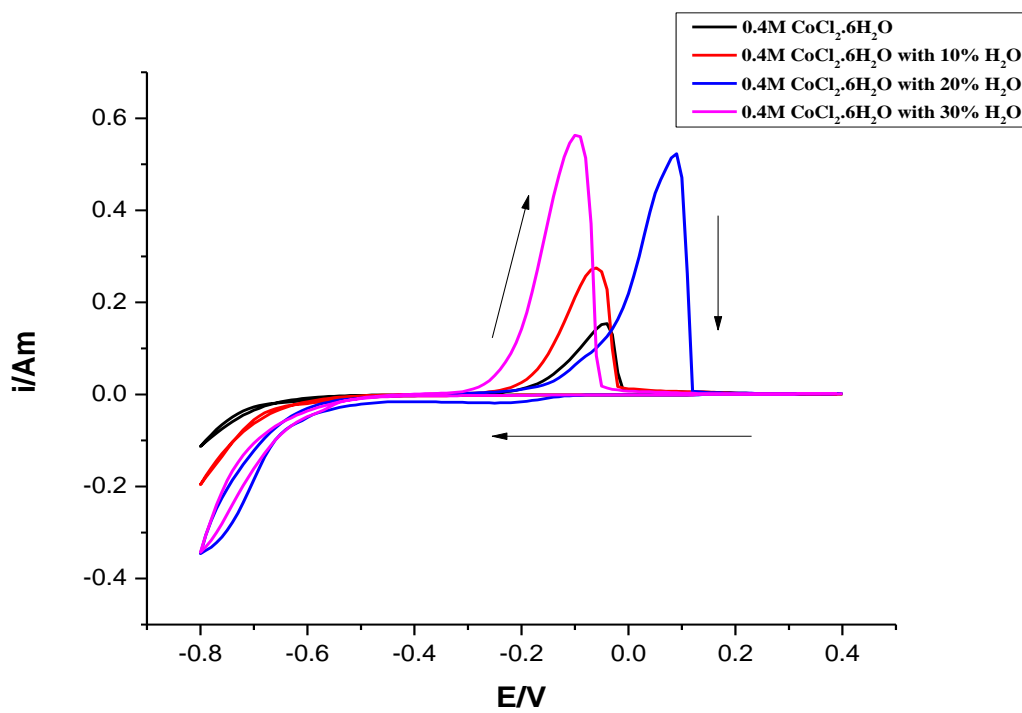
Figure[3.8] Cyclic voltammograms obtained for 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline400 without/with additives: (Black) without additives, (red) with 0.6 M BA, (blue) 0.1 M NA, and (pick) 0.03 M AS.

3.3.3 Voltammetry of Zn, Co, and Zn-Co alloy without/with H_2O .

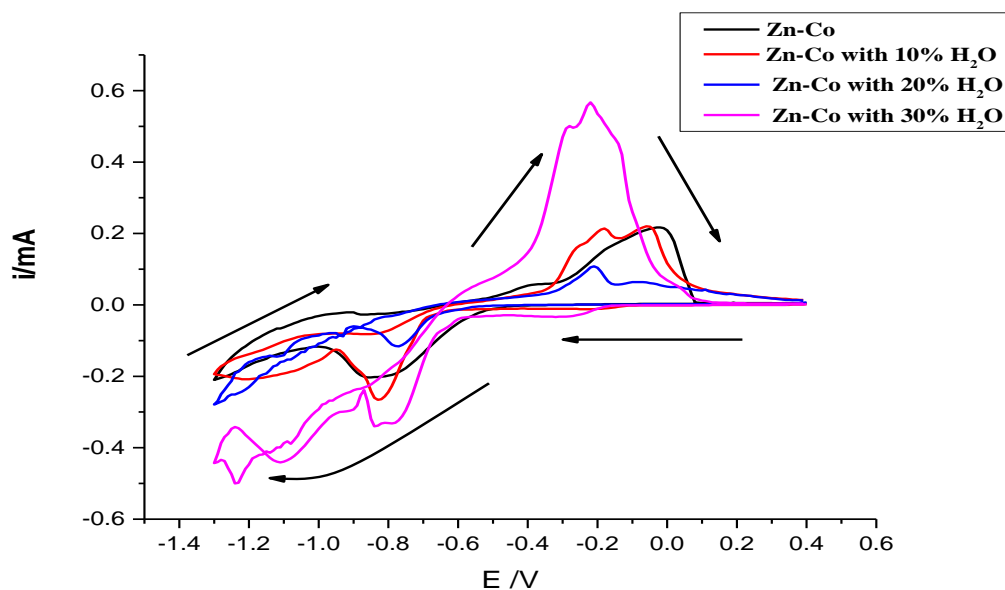
The effect of water on Zn, Co, and Zn-Co cyclic voltammograms in (Ethaline 400) was also investigated. Figure 3.9, from which one can see an increase in redox peak intensity of Zn with increasing amounts of water. The same effect was noted for Co on increasing the reduction. The redox potential of Co due to the increase in conductivity, as explained previously. The oxidation-reduction of Zn-Co was also studied, it can be detected a change in the redox potential of these metals with increasing amounts of water. The reduction potential shifted to more negative potentials with increasing amounts of water and also increasing in oxidation or desolation peak of Zn-Co appear so that water can be effect on the physical properties of Zn-Co and reduction –oxidation.



(a)



(b)

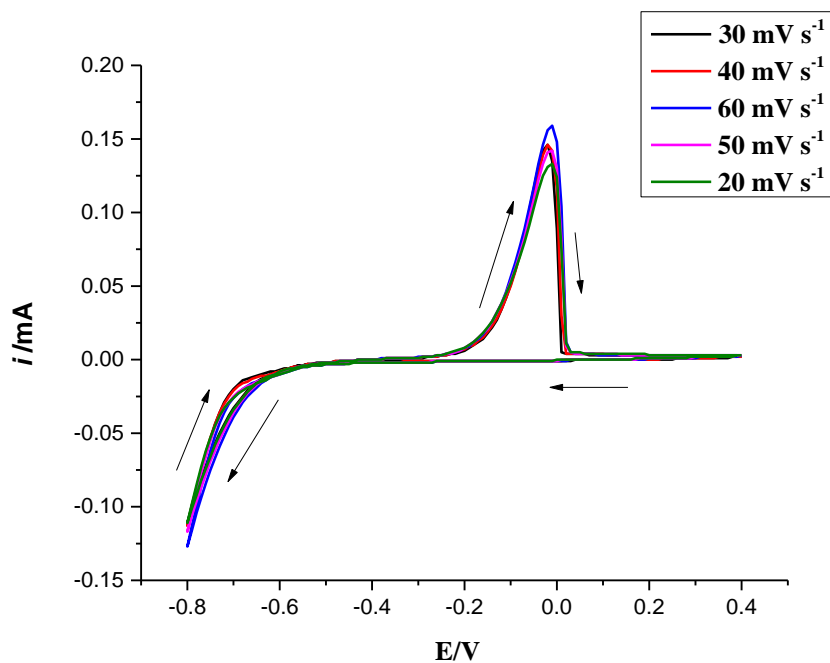


(c)

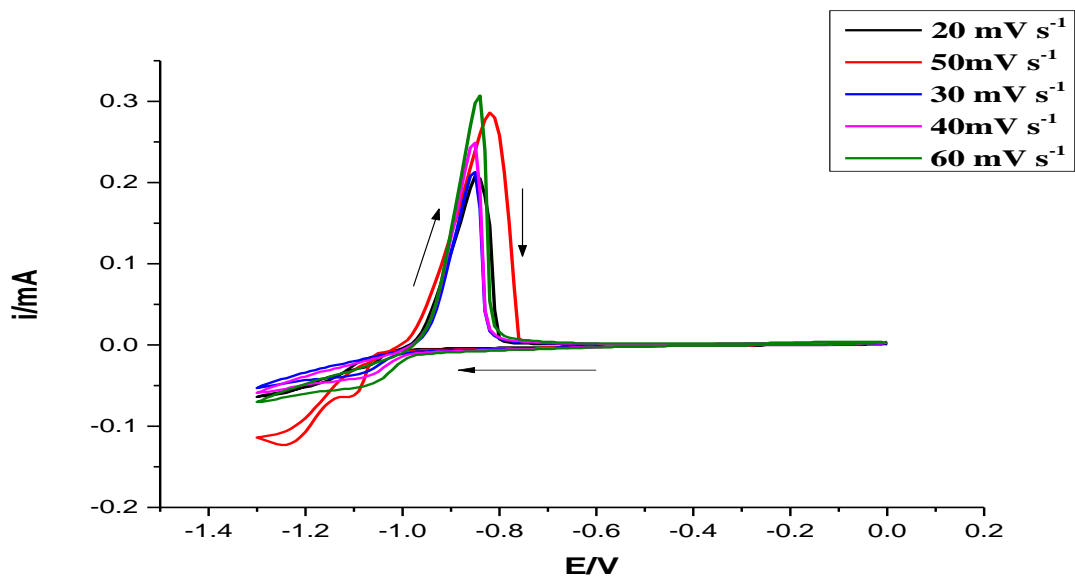
Figure [3.9] Voltammograms for of (a) 0.3 M ZnCl_2 , (b) 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and (c) a mix Zn-Co in (Ethaline 400) without/with H_2O , at a temperature of 70°C , under scan rate of 30 mV s^{-1} , and using a Pt working electrode and Ag wire reference electrode.

Figure 3.10 shows the effects of scan rate on the voltammetry of Zn, Co, and Zn-Co. (c), were investigated, and it was shown that when the scan rate increased, the Zn and Co reduction peaks migrated cathodically; In addition, we can observe that as the scan rate rose, the intensity of these peaks increased as well. With increased scan rate, the apparent shift in Zn and Co deposition potentials in Figure 3.10. (c) could be the result of the electrodeposition not experiencing any significant effects of mass diffusion, with electron transfer or surface chemical reaction steps acting as the controlling mechanisms. The shift in Zn and Co deposition potentials found for our system could be attributed to resistive organic electrolytes, as shown in Figure 3.10. (b) did not measure the resistance of the solution. The Double oxidation peaks emerged in the reverse scans, which correspond to the oxidation of pure Zn (Zn is oxidized in Ethaline (400) at roughly 1.5 V, as

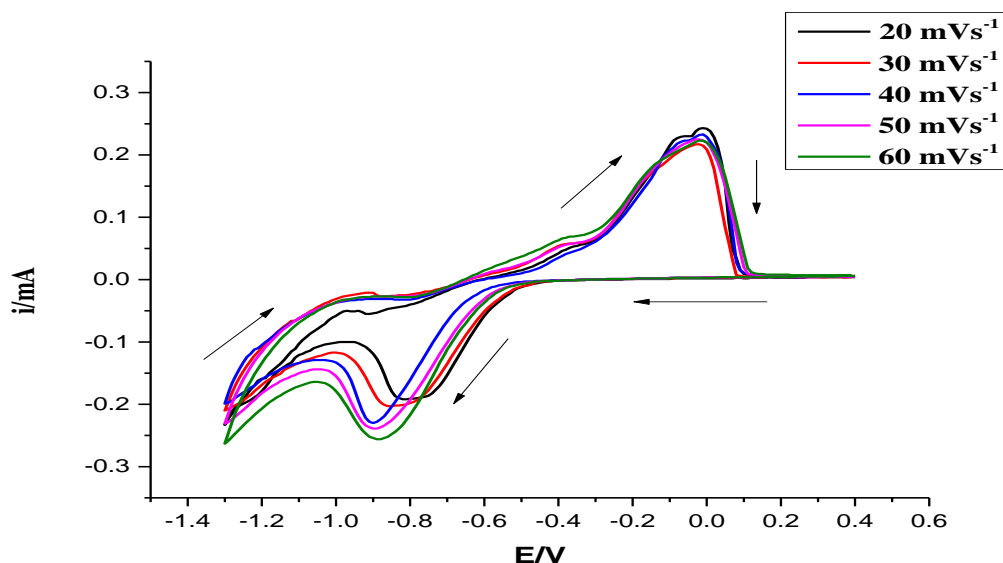
shown in Figure 3.8. The second stripping peak, which appeared at about -0.49 V, corresponds to the dissolution of pure Co.



(a)



(b)



(c)

Figure[3.10] (a) Voltammograms for Ethaline 400 containing 0.3 M $ZnCl_2$,(b) 0.4 M $CoCl_2 \cdot 6H_2O$, (c) The electrodeposition of Zn-Co. (electrolytes for under different scan rates, at a temperature of $70^\circ C$, and using a Pt working electrode and Ag wire reference electrode).

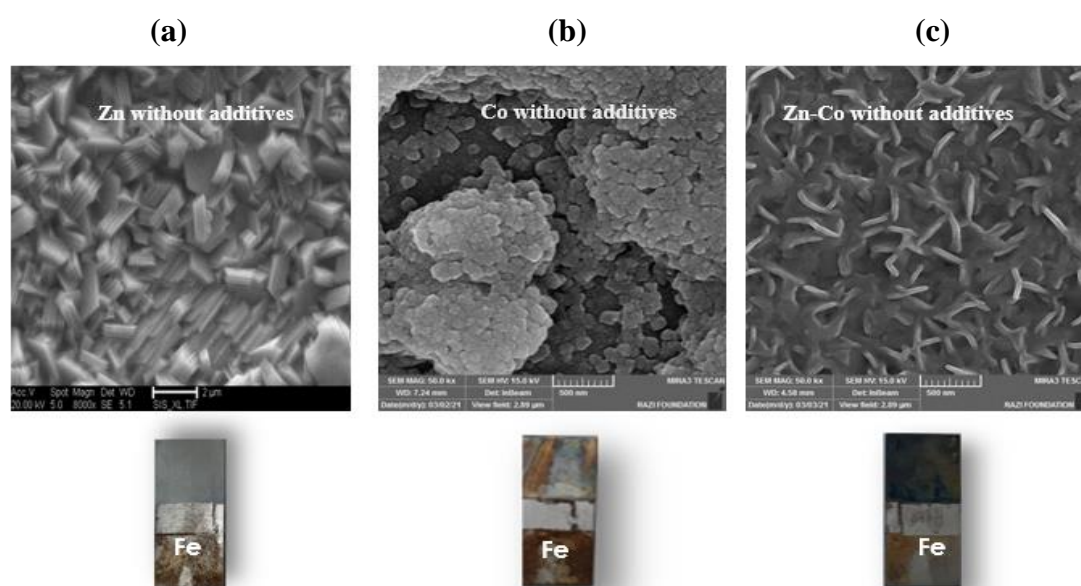
3.4 Surface analysis techniques.

3.4.1 Scanning electron microscopy (SEM).

The SEM image in Figure 3.11 (a) shows that a pure zinc film with irregular pentagonal crystals and a pure Co coating with spherical agglomerates as a Broccoli shape, which are shown in the SEM images in Fig.3.11a and 3.11b, whilst Fig. 3.11c explains the Co-Zn crystallites that resemble rice grains, pure Zn coating with hexagonal crystallites, a pure Co with spherical agglomerated crystallites, and Zn-Co crystallites similar to rice grains were observed in Ethaline 400 solution, as is typical of pure zinc electrodeposition [126].

Figure 3.11(b) shows a SEM image of Co deposition on a mild steel substrate where it is obvious that the particle sizes of the Zn and Co deposits are significantly different. In comparison to pure Zn and Co deposits, the SEM deposit in Figure 3.11. (c), which depicts the morphology of the Zn-Co coating, is dramatically different. This could be connected to changes in coating

compositions or electrolyte speciation. It should be highlighted that the Zn-Co deposit depicted in Figure 3.11(c) was proven to be a Zn-Co alloy. The morphology of the Zn-Co deposits obtained without additives looks to be a deposition of Zn and Co at the very least, Addition, the rice shape for Co-Zn coating in absence water alters to textile shape with increasing the amount of water that cause raise the Zn wt % deposite, but could also be a form of co-deposition. Because XRD may be used to investigate the crystal structure of the Zn-Co deposit, it may be the best tool for determining if this is an alloy or not. This indicates that when (Ethaline 400) was deposited without additions, a combination of the Zn and Co phases formed. The results of the EDX spectra showed the formation of precipitates in the electroplating process, as shown in (Figures 3.13,3.15,3.17) and (Tables 3.1,3.2,3.3). Where the Zn, Co and Zn-Co alloy was formed. Total it was discovered that atom% (A%) and weight% (W%) equal 100%.



Figure[3.11] SEM images for the electrodeposition of (a) 0.3 M ZnCl₂,(b) 0.4 M CoCl₂.6H₂O and (c) Zn-Co from Ethaline 400 containing 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O without other additives.(All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C at 2h a current of 30 mA).

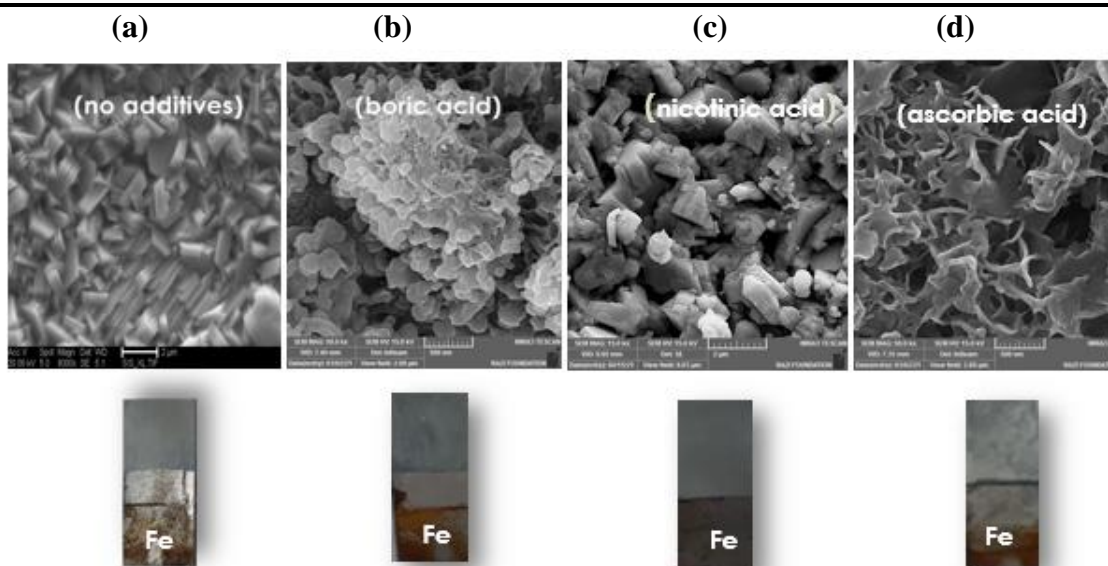


Figure [3.12] SEM of Zn electrodeposited from Ethaline 400 of 0.3 M ZnCl₂: (a) no additives, (b) 0.6 M BA, (c) 0.1 M NA, and (d) 0.03 M AS. (All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C at 2h a current of 30 mA).

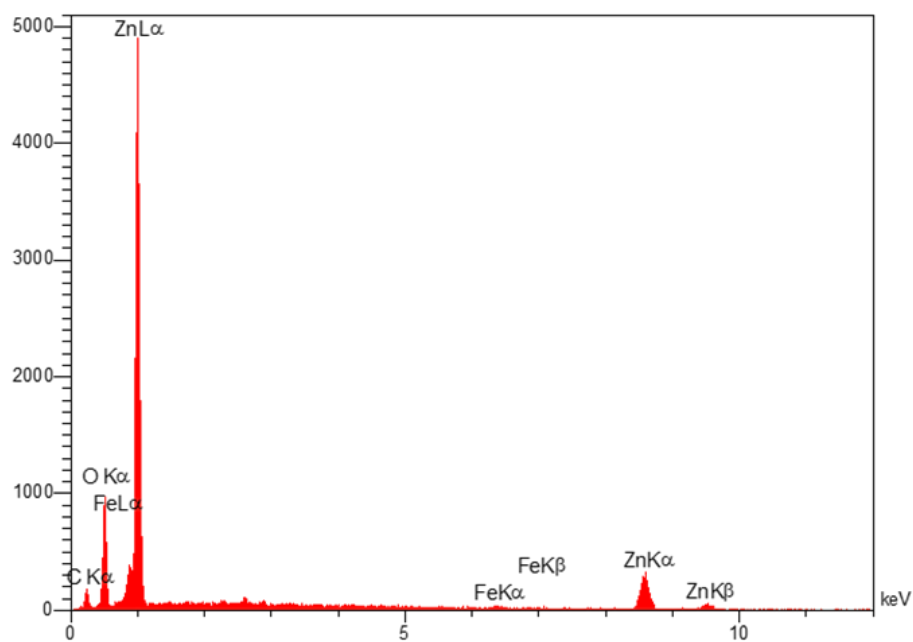


Figure [3-13]: EDX spectrum of 0.3 M ZnCl₂ on mild steel substrate.

Table [3-1]:The value of the chemical composition obtained from EDXspectrum for ZnCl₂ .

Elt	Line	Int	Error	K	Kr	W%	A%
C	Ka	23.4	8.4098	0.0478	0.0311	14.89	32.56
O	Ka	180.7	8.6878	0.1805	0.1175	0.223	43.97
Fe	Ka	7.5	0.2753	0.0123	0.0080	0.79	0.37
Zn	Ka	170.2	0.8304	0.7594	0.4941	84.1	23.10
				1.0000	0.6506	100%	100.00

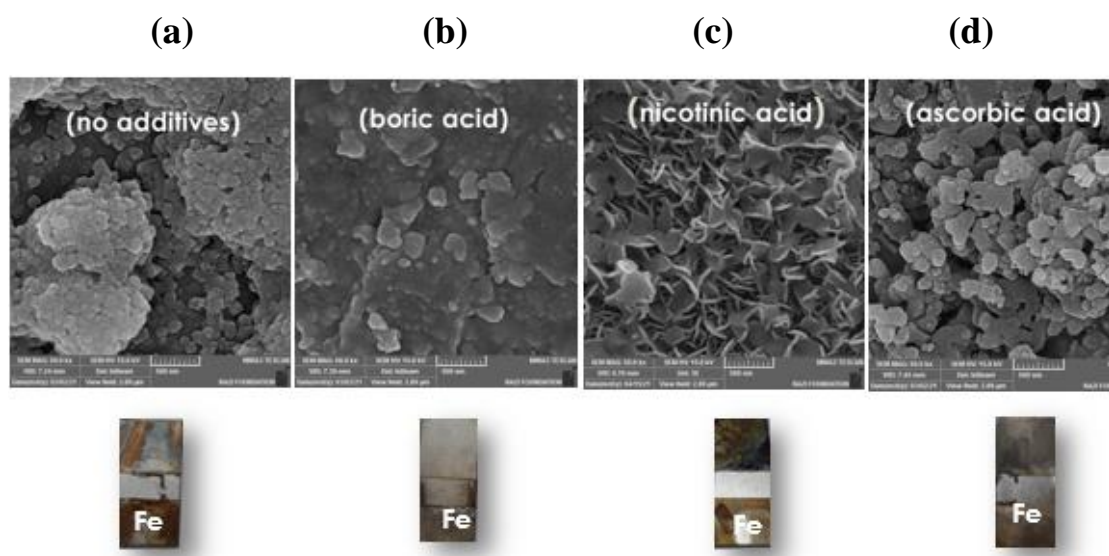


Figure [3.14] SEM of Co electrodeposited from Ethaline 400 of 0.4 M CoCl₂. 6H₂O: (a)no additives,(b) 0.6 M BA,(c) 0.1 M NA, and (d) 0.03 M AS.(All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C at 2h a current of 30 mA).

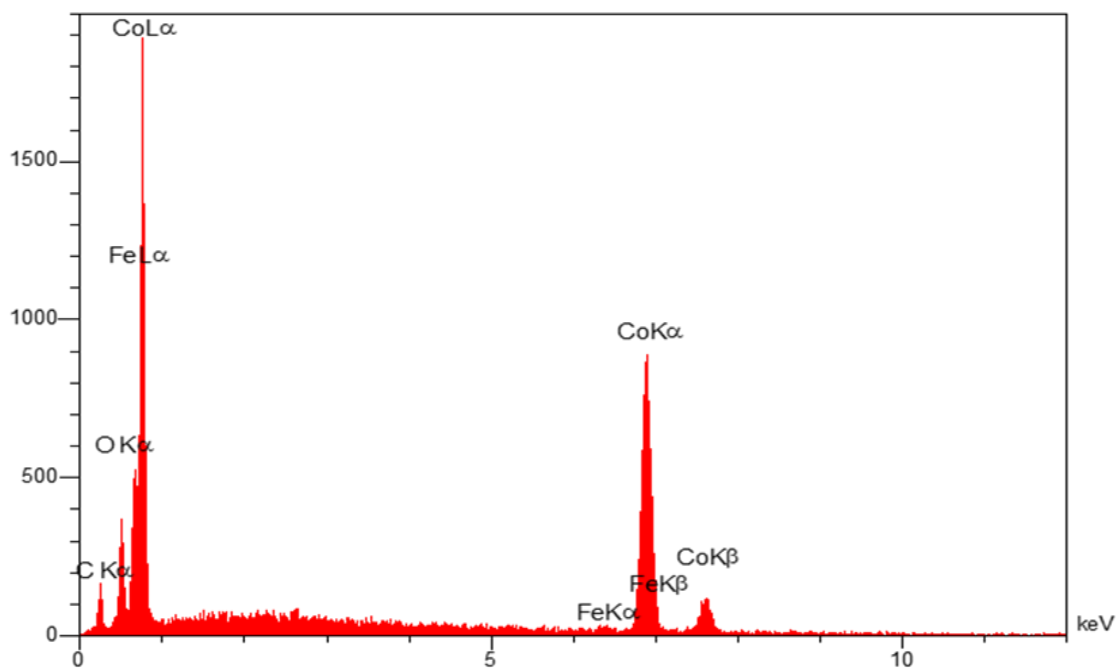


Figure [3-15]: EDX spectrum of 0.4M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ on mild steel substrate.

Table [3-2]: The value of the chemical composition obtained from EDX spectrum for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

Elt	Line	Int	Error	K	Kr	W%	A%
C	Ka	24.2	6.9244	0.0467	0.0374	13.62	37.77
O	Ka	60.7	7.1533	0.0574	0.0460	3.83	18.39
Fe	Ka	4.6	1.0587	0.0071	0.0057	0.57	0.34
Co	Ka	465.0	1.0718	0.8888	0.7127	82.98	43.50
				1.0000	0.8019	100%	100.00

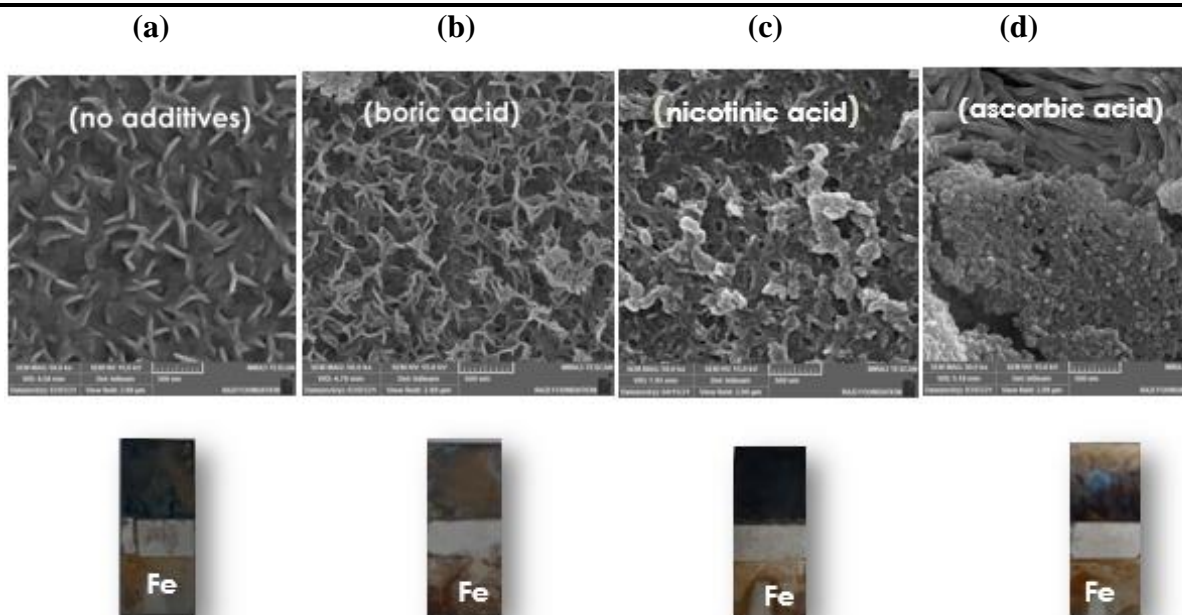


Figure [3.16] SEM of Zn-Co alloy electrodeposited from Ethaline 400: (a)no additives, (b) 0.6 M BA,(c) 0.1 M NA, and (d) 0.03 M AS.(All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C at 2h a current of 30 mA).

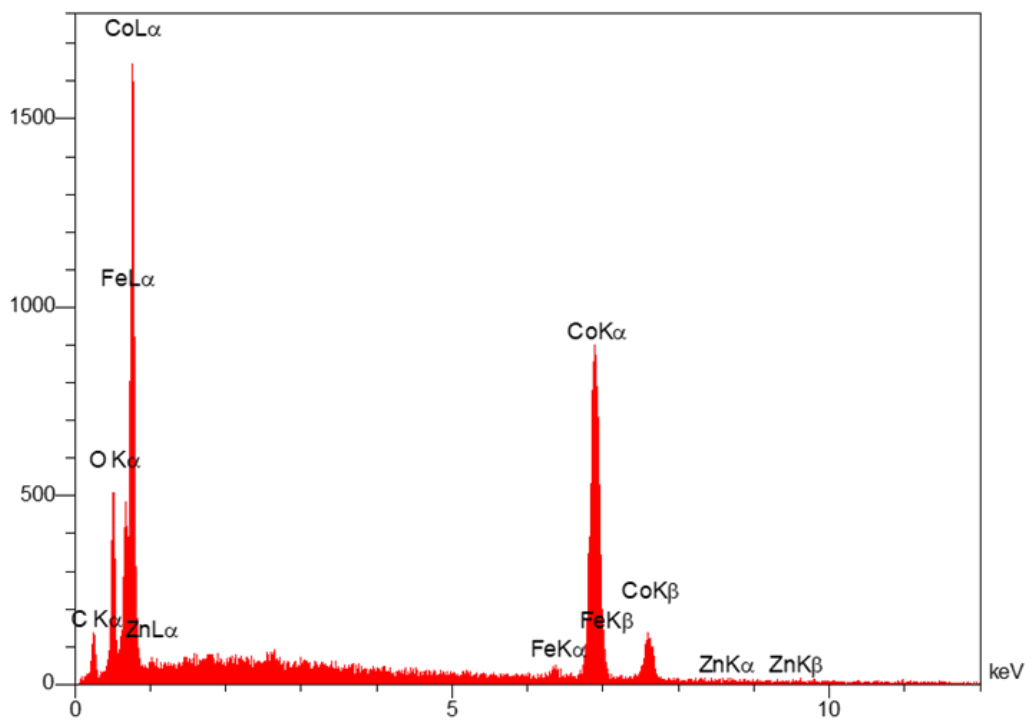


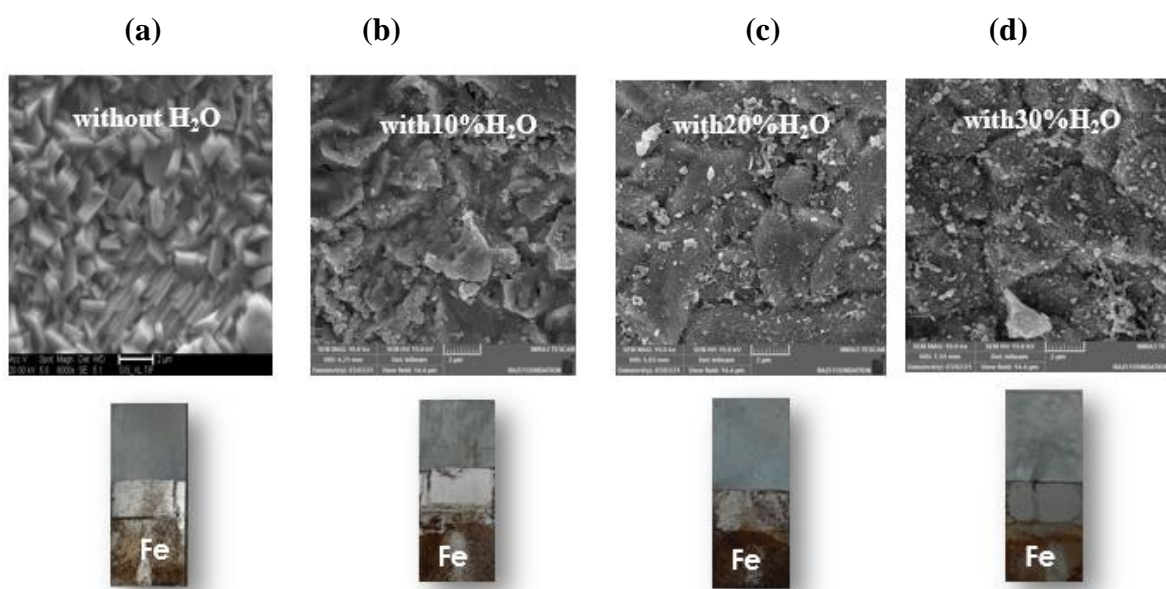
Figure [3-17]: EDX spectrum of Zn-Co alloy on mild steel substrate.

Table [3-3]: The value of the chemical composition obtained from EDX spectrum for Zn-Co.

Elt	Line	Int	Error	K	Kr	W%	A%
C	Ka	22.8	5.5009	0.0401	0.0321	11.68	31.98
O	Ka	98.4	5.6827	0.0847	0.0678	4.48	25.66
Fe	Ka	10.9	0.9314	0.0154	0.0123	1.24	0.73
Co	Ka	491.1	0.9429	0.8541	0.6835	54.08	41.36
Zn	Ka	1.5	0.2309	0.0057	0.0046	38.52	0.26
				1.0000	0.8002	100%	100

Figures 3.12,3.14,and 3.16 shows optical images and the morphologies of the Zn, Co, and Zn-Co alloy deposits obtained from an (Ethaline 400)based-liquid containing 0.3 M ZnCl₂ and 0.4M CoCl₂.6H₂O in the absence and presence of 0.6 M BA, 0.1 M NA and 0.03 M AS. The depositions were performed on Fe substrates at a current of 30 mA for 2h. Figures 3.12 and 3.14 (a) depict a rough and dark grey Co and Zn-Co deposit generated from an electrolyte without additions, with varied sized Co and Zn-Co particles and a rather random overall shape. When the additives were applied separately to the Zn and Zn-Co baths,clear changes in the roughnesses and morphologies of the Co and Zn-Co deposits were discovered, as illustrated in figures 3.14(b) and 3.16(b). BA is commonly used to improve the characteristics of coatings when metals are electrodeposited.Researchers believe that adding BA to the electroplating solution works as a buffering agent, preventing or at least reducing the alkalization process that happens at the cathodic electrode due to hydrogen evolution. The effects of BA and NA on the electrodeposition of Zn from DES have been studied previously [124]. They were discovered to restrict Zn deposition while also acting as brighteners, resulting in very uniform and smooth Zn deposits. When BA was used in the electrodeposition of Co and Zn-Co in this study, the morphology of the Co film changed significantly. When deposition was carried out in a bath containing BA, a

bright Co film was formed, with an improvement in the smoothness and refinement of the grain size of the coating when compared to the use of NA and AS, where it was discovered that BA was able to prevent the formation of a surface passivation layer during electrodeposition [127]. The mechanism by which BA functions in the electrodeposition of metals in DES, on the other hand, is currently being studied. Figure 3.14 depicts the situation (b). With the addition of these chemicals to the bath, the Co crystallites have morphologies that are more homogenous, flat, and glossy. When BA was added to the Co solution, a bright and smooth Co coating resulted, as well as a noticeable refinement in the Co deposit's crystal size



Figure[3.18] SEM images from Ethaline 400 systems of 0.3 M ZnCl₂ using the following additives:(a) without H₂O, (b) with 10% H₂O, (c) with 20% H₂O, (d) with 30% H₂O.(All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C formed 2h at a current of 30 mA).

Figure 3.18 shows images of Zn deposit with and without water; a clear, large particulate size in the resultant Zn deposit was observed when the deposition was achieved from (Ethaline 400) without water. The particulate size was found to be further refined when 10% water was added to the solution,

and when 20% and 30% water was added to the solution, homogeneous coatings were achieved.

Figure 3.19 demonstrates the effect of water on the Zn-Co coating. No significant change in the morphology just can see with 30% and 20% are like line grain these same and no change of colour of coting but the best results were for 20 % of added water because the roughness of the paint was very little [128].

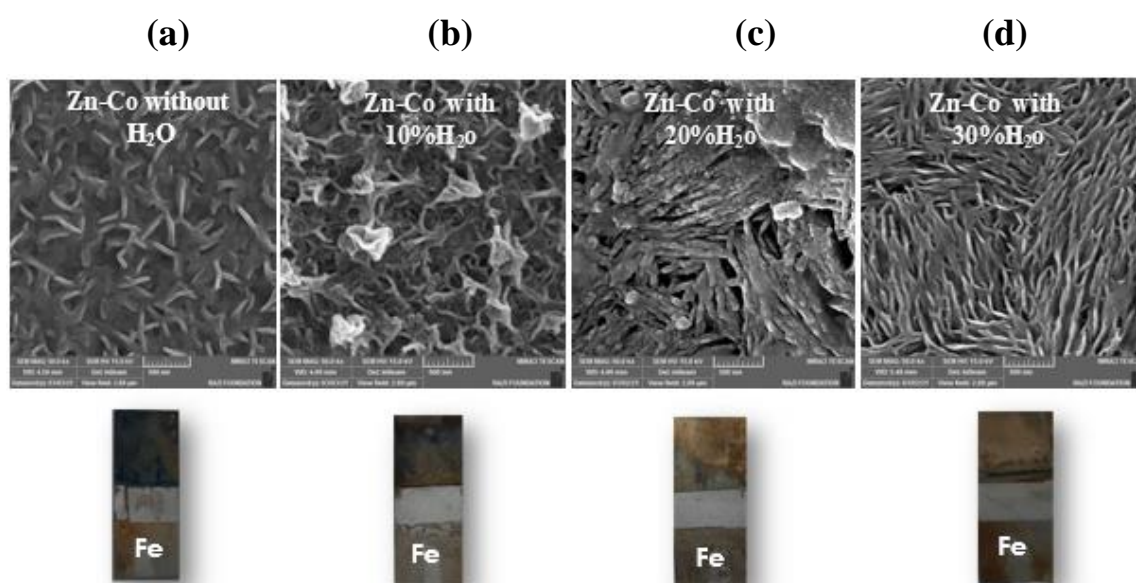
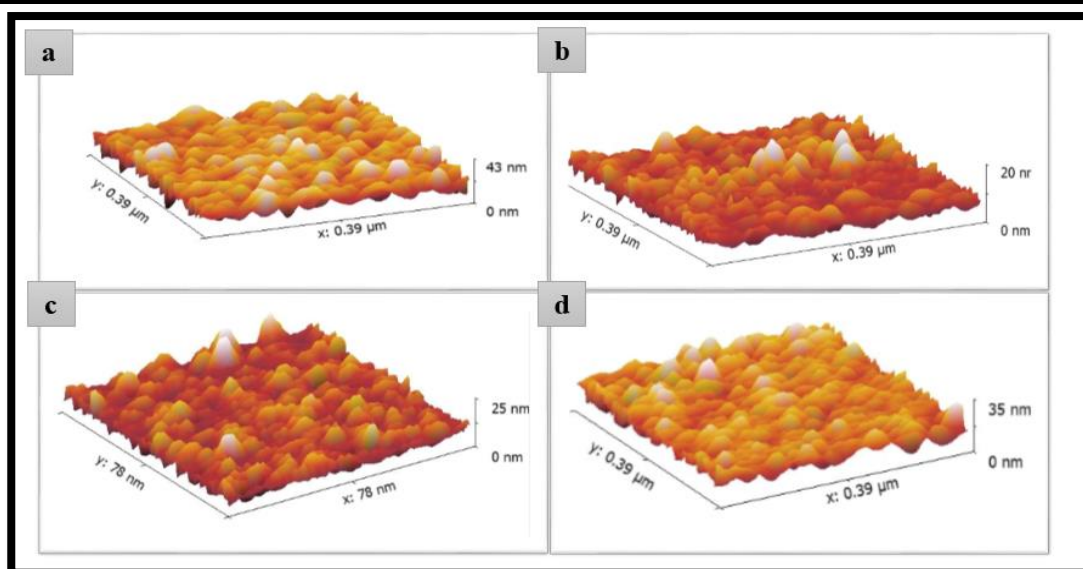


Figure [3.19] SEM images from Ethaline 400 systems of Zn-Co of :(a) without H₂O, (b) with 10% H₂O, (c) with 20% H₂O, (d) with 30% H₂O.(All depositions have been achieved from Ethaline 400 on a mild steel substrate at 70°C formed 2h at a current of 30 mA).

3.4.2 Atomic force microscopy (AFM).

Atomic force microscopy (AFM) is a surface probe technique that can be used to investigate the structure of conducting and insulating surfaces in both air and liquid. It's a crucial approach for studying topography and the formation of metal deposits. AFM has been used to analyze the morphology of Zn, Co, and Zn-Co alloy electrodeposited from Ethaline 400 in both the absence and presence of additives, in addition to scanning electron microscopy (SEM). The morphology of the Zn, Co, and Zn-Co deposits changes due to variances in their initial nucleation and growth mechanisms without and with the different additions, as measured by UV-visible data, conductivity data, and cyclic voltammetry. These features of Zn deposit surfaces were investigated by using AFM. Figure 3.20 shows a three-dimensional AFM image of a Zn deposit made from Ethaline 400 without and with several types of organic additives (BA, NA, and AS) at 70°C on a Fe substrate for 2 hours at 30 mA. The AFM and SEM results are nearly identical. The topography of the Zn deposit from (Ethaline 400) of 0.3M ZnCl₂ without additives is shown in Figure 3.20(a). The micrographs demonstrate that the Zn deposits are made up of grains of varying sizes. As shown in Figures 3.20 (b), (c), and (d), the deposition achieved from a system with additives results in a tiny Zn grain size, especially when BA, NA, and AS are used (d).



Figure[3.20]The AFM three dimension images showing samples from Ethaline 400 systems 0.3 M of $ZnCl_2$ of :(a) without additives,(b) 0.6 M BA,(c) 0.1 M NA, and (d) 0.03 M AS (All depositions achieved at $70^\circ C$ for 2h on a mild steel substrate and a current of 30 mA).

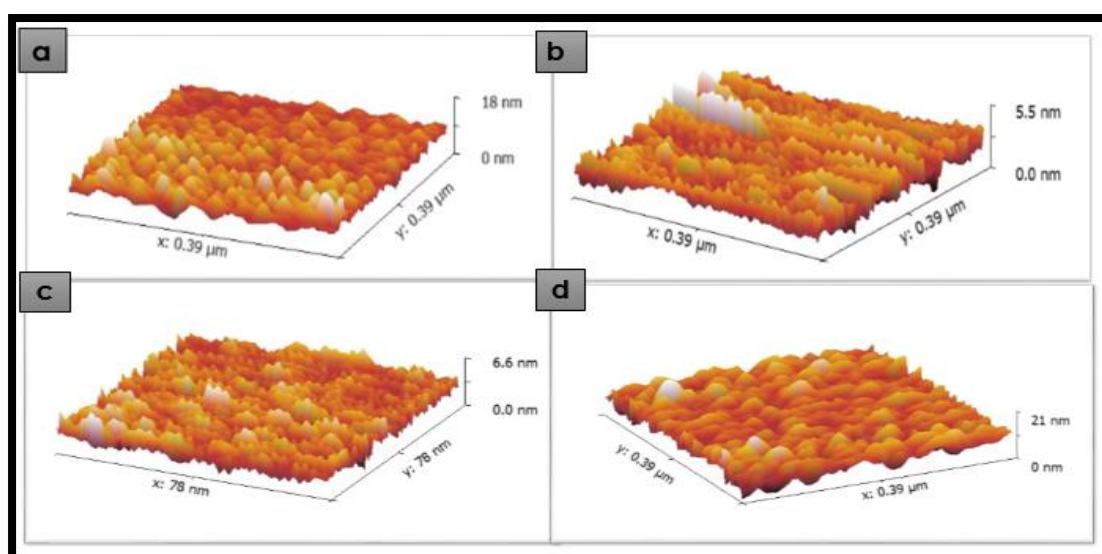


Figure [3.21] The AFM three dimension images showing samples from Ethaline 400 systems 0.4 M of $CoCl_2 \cdot 6H_2O$:(a) without additives, (b) 0.6 M BA, (c) 0.1 M NA, and (d) 0.03 M AS (All depositions achieved at $70^\circ C$ for 2h on a mild steel substrate and a current of 30 mA).

The roughness of the Zn, Co, and Zn-Co alloy films has been measured by using AFM. When electrodepositions were done with additives, smoother Co and Zn-Co films were created than when

electrodepositions were performed without additives. The roughness of Zn, Co, and Zn-Co deposits made from solutions with and without additions is reported in Tables 3.4, 3.5, and 3.6. The roughness of the Zn deposit obtained from a system without additions was around 49.5 nm, the Co deposit was around 6.17 nm, and the Zn-Co deposit was about 33.55 nm. The following tables report the roughnesses as well as the average particle sizes for the above three deposits.

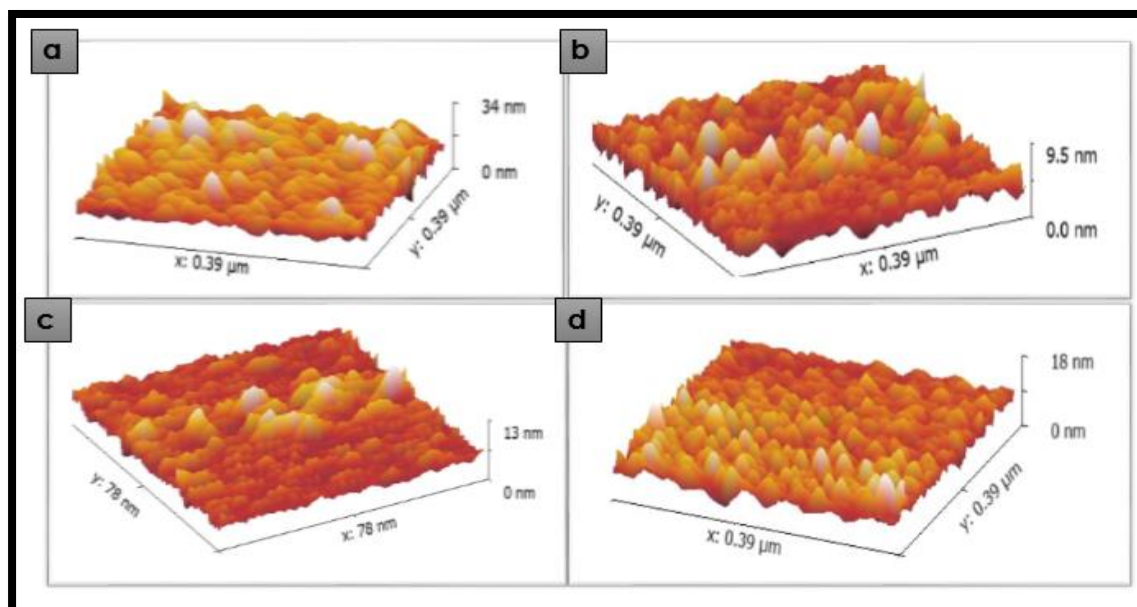


Figure [3.22] The AFM three dimension images showing samples from Ethaline 400 systems containing Zn-Co of :(a) without additives,(b) 0.6 M BA, (c) 0.1 M NA, and (d)0.03 M AS (All depositions achieved at for 70°C 2h on a mild steel substrate and a current of 30 mA).

Table[3.4]The surface roughness of Zn deposits from Ethaline 400 system containing 0.3 M ZnCl₂ without and with additives of (0.6 M BA, 0.1 M NA, and 0.03 M AS).(All experimental were achieved at 70°C for 2h on a mild steel substrate and applied current of 30 mA).

Metal salt	Additives	Roughness, Ra /nm
ZnCl ₂	None	49.5
ZnCl ₂	boric acid	16.49
ZnCl ₂	nicotinic acid	4.861
ZnCl ₂	ascorbic acid	38.35

Table[3.5]The surface roughness of Zn deposits from Ethaline 400 system containing 0.4 M of CoCl₂.6H₂O without and with additives of (0.6 M BA, 0.1 M NA, and 0.03 M AS)(All experimental were achieved at 70°C for 2h on a mild steel substrate and applied current of 30 mA).

Metal salt	Additives	Roughness,Ra /nm	Average particle size /nm
CoCl ₂ .6H ₂ O	none	6.173	23.77
CoCl ₂ .6H ₂ O	boric acid	6.803	23.91
CoCl ₂ .6H ₂ O	nicotinic acid	4.896	15.64
CoCl ₂ .6H ₂ O	Ascorbic acid	39.60	121.3

Table[3.6]The surface roughness of Zn deposits from Ethaline 400 system containing Zn-Co alloy without and with additives of (0.6 M BA, 0.1 M NA, and 0.03 M AS)(All experimental were achieved at 70°C for 2h on a mild steel substrate and applied current of 30 mA).

Metal salt	Additives	Roughness, Ra /nm	Average particle size /nm
Zn -Co	none	33.55	63.78
Zn -Co	boric acid	9.329	20.80
Zn -Co	nicotinic acid	4.561	12.72
Zn -Co	ascorbic acid	23.82	53.12

The effects of water on the roughness of the plating can be seen in Figure 3.23 below, which shows that the lowest possible roughness is obtained when 20% water is added to the plating bath.

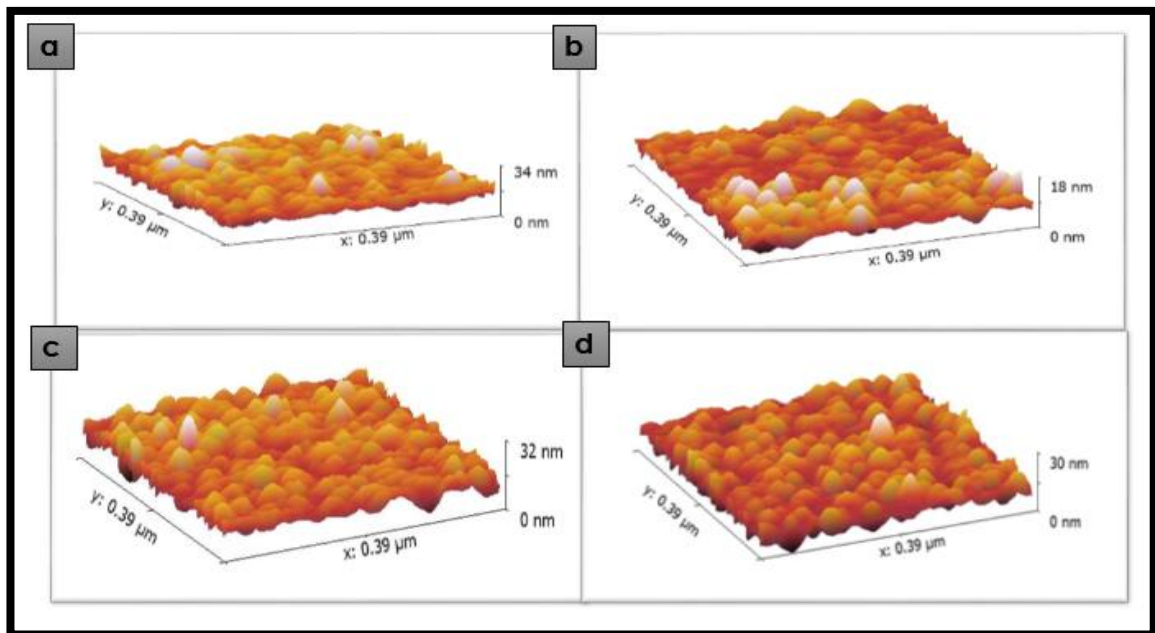


Figure [3.23] The AFM three dimension images showing samples from Ethaline 400 systems containing of mixtuer Zn-Co :(a) without H₂O,(b) with 10% H₂O, (c) with 20% H₂O,and (d) with 30% H₂O(All expremental were achieved at 70°C for 2h on a mild steel substrate and applied current of 30 mA).

Furthermore, no significant change was observed in the roughness when using different proportions of water in the Zn plating bath, as per figure 3.24:

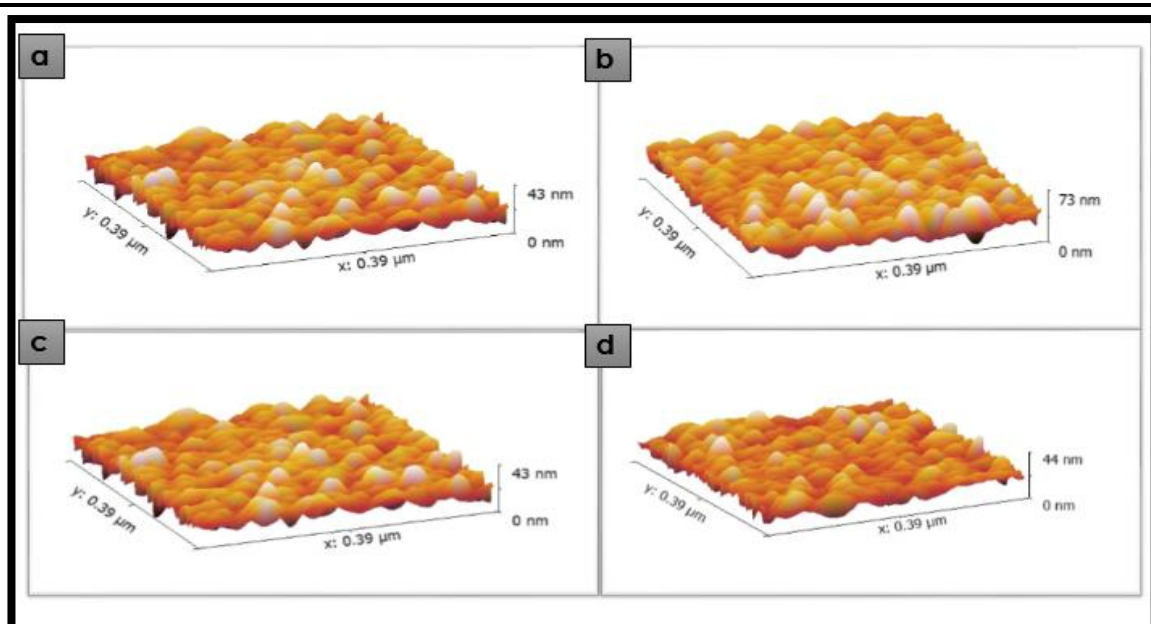


Figure [3.24] The AFM three dimension images showing samples from Ethaline 400 systems containing 0.3 M of $ZnCl_2$ of (a) without H_2O ; (b) with 10% H_2O ; (c) with 20% H_2O ; and (d) with 30% H_2O (All experimental were achieved at $70^\circ C$ for 2h on a mild steel substrate and applied current of 30 mA).

Table [3.7] The surface roughness of Zn-Co deposits from Ethaline 400 containing 0.3 M $ZnCl_2$ and 0.4 M $CoCl_2 \cdot 6H_2O$ in without and with different ratio of water (All experimental were achieved at $70^\circ C$ for 2h on a mild steel substrate and applied current of 30 mA).

Metal salt	Additives	Roughness, Ra /nm	Average particle size /nm
Zn-Co	Without H_2O	33.55	63.78
Zn-Co	With 10% H_2O	47.23	66.37
Zn-Co	With 20% H_2O	7.642	29.26
Zn -Co	With 30% H_2O	8.33	35.85

Table [3.8] The surface roughness of Zn-Co deposits from Ethaline 400 containing 0.3 M ZnCl₂ with different ratio of water (All experimental were achieved at 70°C for 2h on a mild steel substrate and applied current of 30 mA).

Metal salt	Additives	Roughness,Ra /nm	Average particle size /nm
Zn	With 10% H ₂ O	52.88	159.5
Zn	With 20% H ₂ O	53.32	146.6
Zn	With 30% H ₂ O	12.57	41.21

3.4.3 X-ray diffraction(XRD)

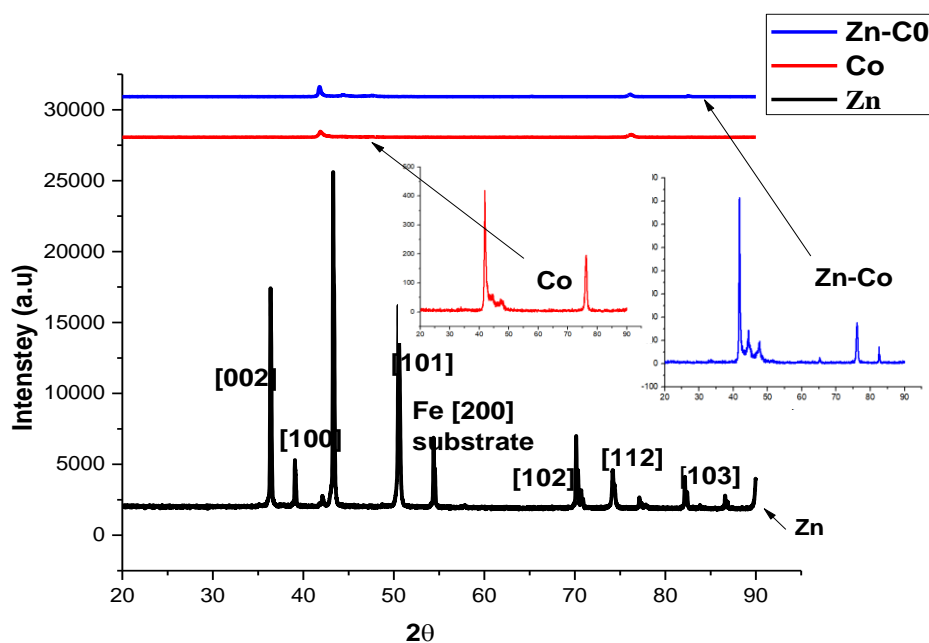
To determine whether an alloy has formed in each scenario, the crystal structures of the Zn,Co, and Zn-Co alloy deposits created from the electrolyte in the presence and absence of water must be examined, XRD was employed to do so. Figure 3.25 shows the XRD phase for pure Zn, pure hexagonal Co, and Zn-Co films devoid of water.(a) Using equal current densities, (Ethaline 400) was deposited on steel electrode at 70°C for 2hours. In the pure Zn deposit, the (002), (100), (102), (103), (112), and (201) planes were observed, while in the Co film the (110), (002), (101), (220), (110), and (200) planes were observed at 2θ angles of 41.6°, 47.5°, 50.7°, 74.4°, 75.9°, and 90.5°, respectively. Without water, XRD patterns for Zn-Co deposits revealed the (112), (002), (102), (100), (201) and (112) Zn planes.

No specific shifting was seen in the XRD patterns of the Zn-Co deposit formed in the solution in the abncences of water, despite the presence of Co phases such as at 44.6° and 47.5°. There is some evidence of other phases in figure 3.25 (b) and 3.25 (c) that could be Zn-Co alloys, but they are very minor in comparison to the pure metal phases. This suggests that a new plan has made in the deposition of water-

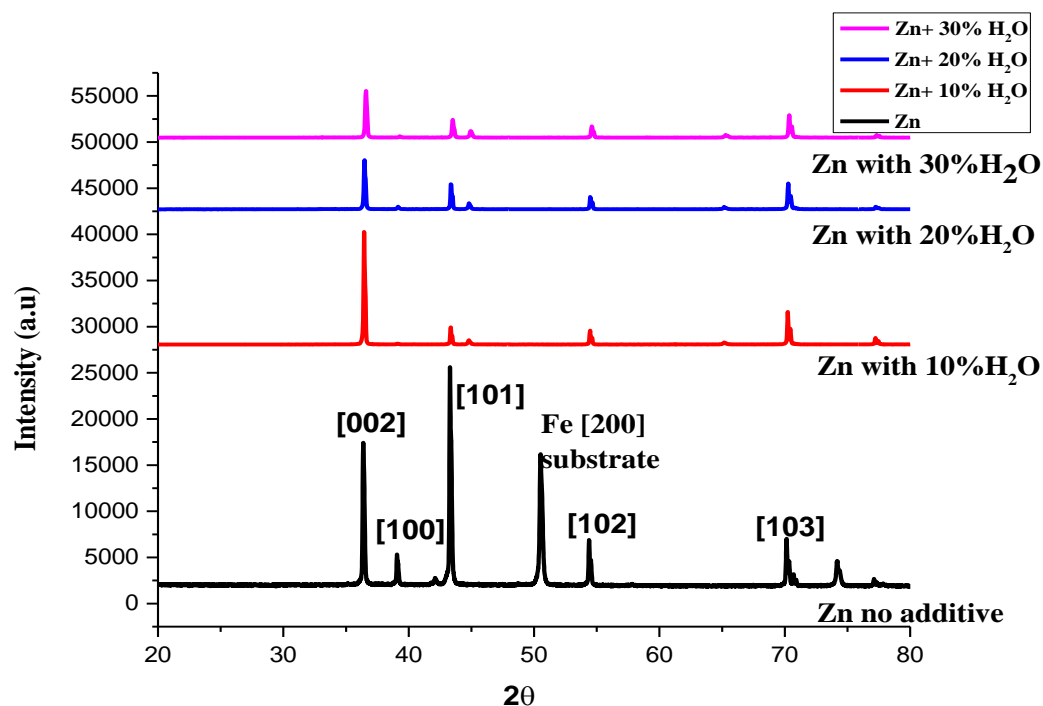
containing electrolytes. XRD results indicate that a Zn-Co alloy coating may be

formed on a mild steel substrate using (Ethaline 400) for 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 70°C and 30 mA on a mild steel substrate.

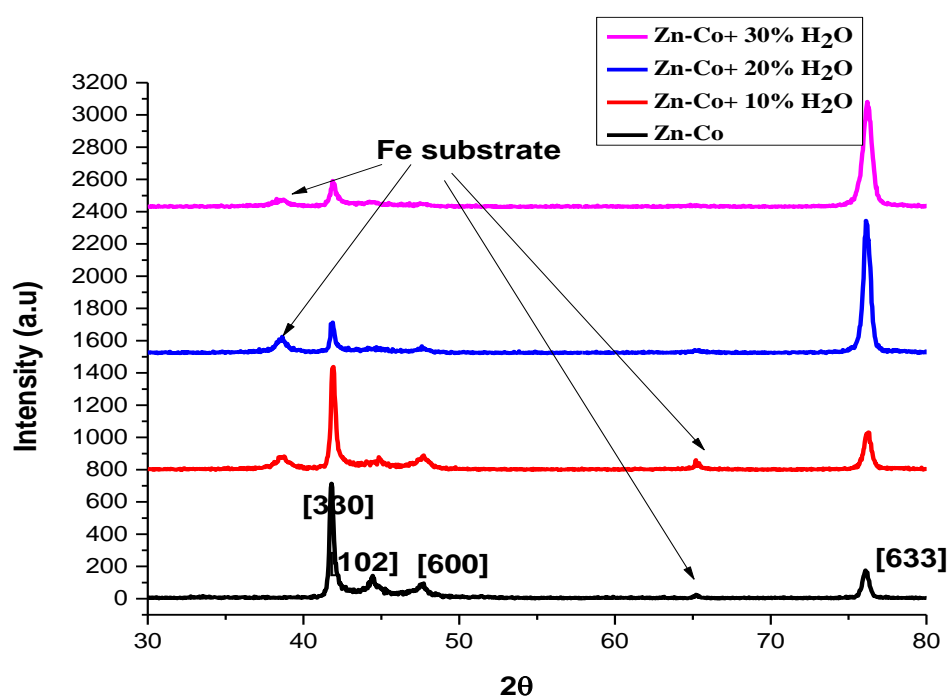
Moreover, in figures 3.25a and 3.25b, the red shift in 2θ value 42.04° and 70.09° occurs to more values of 2θ after increases the amount of water and forms alloy that proved the produced metallic bond between CoZn as Zn-Co alloy, and Zn is deposited firstly then Co.



(a)



(b)



(c)

Figure [3.25] (a) XRD patterns of Zn electrodeposited, Co electrodeposited, and Zn-Co electrodeposited without water using 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O, (b) XRD patterns of Zn electrodeposited in Ethaline 400 by presencing of water and , (c) XRD patterns of Zn-Co electrodeposited in Ethaline 400 by presencing of water.

Conclusion

3.5 Conclusion

The goal of this research was to see how water and additives affected the electrodeposition of Zn, Co, and Co-Zn on mild steel using a choline chloride (ChCl)1:4:ethylene glycol(EG) based liquid Ethaline 400 as deep eutectic solvent (DES), with boric acid, nicotinic acid, and ascorbic acid as the additives. The additives used were found to have a strong effect on the metal deposition described above.

The results show for the first time that Co-Zn deposits from ionic liquids can be prepared using water. It was found that the conductivity of the plating solution increases as the amount of water increases, but the conductivity decreases when an additive is used. It has been noted that conductivities of plating solution has been increased with increasing amount of water, while conductivities of these solution decreased by using additives. New species of Co were formed when water was added to the Co electrolyte where this was examined by using UV-visible spectroscopy. Electrochemical properties for Zn, Co and Zn-Co in 1:4 choline chloride (ChCl): ethylene glycol(EG)-based liquid (Ethaline 400) has been studied using cyclic voltammetry method. The redox current peaks of Zn, Co and Co-Zn increased with increasing amount of water, while intensities of deposition peak were decreased when the boric acid, nicotinic acid and ascorbic acid added to the metals electrolytes.

There is a reduction withinside the Zn, Co deposition height that takes place at bad ability withinside the presence of BA, nicotinic acid and ascorbic acid, in which this lower is because of the adsorption of those components onto the electrode surface, inhibiting metals deposition, additionally the anodic method for Zn and Co that befell at bad ability turned into decrease via way of means of one hundred μA withinside the presence of boric acid. This shows that, due to adsorption of boric acid onto the surface of the electrode, the nucleation of the steel increase mechanisms is affected, which hinders the stripping peak. Water coordinated to Co ions and inhibited the deposition of Co. Oxidation and

Conclusion

reduction of Zn-Co peaks got bigger when the water was added to the plating bath due to increasing the conductivity of the solution. ZnCo deposition morphology was improved when deposition was achieved from electrolytes containing water as an additive. In addition, the proportion of water has been found to affect the composition and morphology of Zn-Co deposits, and the proportion of Co in the Zn-Co membrane decreases as the amount of water in the bath increases.

The roughness of the Zn-Co membrane formed from the solution in the absence of water was 33.55 nm, while the roughness of the coating was reduced to 8.33 nm when deposited from 30% water electrolyte. XRD data showed that the Zn-Co deposits formed new diffraction peaks, which caused a structural change in the Zn-Co membrane. One of the most important applications of these coatings is coating oil pipelines, coating cars and aircraft, coating cooking utensils etc.

3.6 Recommendations.

Several recommendations can be outlined in the future:

1. Examination other metals to deposit on mild steel substance, like: Cu, Ag, Sn, and Mn.
2. Characterization XRD, SEM-EDX, and AFM.
3. Characterization plating liquid such as: conductivity and UV-visible spec

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الخلاصة:

تمت عملية الترسيب الكهربائي لسبيكة الكوبلت- خارصين (Co-Zn alloy) على النموذج mild steel من محلول كلوريد الكولين (ChCl):اثليين كلايكل (EG) كمحلول اساس وبوجود كميات مختلفة من الماء والمضافات. وجدت توصيلية المحاليل الالكتروليتيية متزايدة للـ Co و Zn و Co-Zn والتي تم تحسينها من خلال اضافة حجوم معينة من الماء، بينما قلت توصيليات محلول الطلاء عند اضافة حامض البوريك وحامض النيكوتين. خمنت اصناف الـ Co في محلول Co-Zn باستخدام مطيافية الاشعة المرئية وفوق البنفسجية. ظهرت ازاحة زرقاء لاصناف الـ Co عند اضافة الماء الى محلول Co-Zn . على اية حال، لم يظهر اي تغير باطيف اصناف الـ Co عند اضافة المضافات خلال استخدام حمام الطلاء.

تم قياس الجهد الكهربائي لفحص جهد الاكسدة والاختزال لمحلول الطلاء، والذي تم ايجاده عند اضافة الماء للالكتروليتيات الـ Co و Zn و Co-Zn. حيث وجد ان قمم تيار الاكسدة والاختزال للـ Co و Zn و Co-Zn تزداد بزيادة اضافة كميات من الماء، بينما تقل شدة قمم الترسيب عند اضافة حامض البوريك، و وحامض النيكوتين، وحامض الاسكوربيك الى الكترولينات هذه الفلزات.

درست مورفولوجية سطح الرقاقت باستخدام مجهر المسح الالكتروليتي (SEM). تم تحسين مورفولوجية سطوح الرقاقت المطلية بالـ Co و Zn و Co-Zn عن طريق دعمها بكميات من الماء وحامض البوريك. اذ وجد بان طلاء الـ Co-Zn من المحلول الالكتروليتي الحاوي على الماء بنسبة وزنية مئوية للـ Zn تساوي 19.83% و للـ Co تساوي 80.13%. كما وجد بان الخشونة لرقاقة الـ Co-Zn المترسبة بحمام يحوي 20% ماء، قد اختزلت الى 7.642 نانومتر. فحصت تقنية حيود الاشعة السينية الـ (XRD)، لتحديد نمط الـ XRD لترسيب الـ Co-Zn.



جامعة كربلاء

كلية العلوم

قسم الكيمياء

الطلاء الكهربائي للـ Co, Zn وسببكتهما من السوائل الأيونية
اليوتكتيكية (DES)

رسالة مقدمة الى

مجلس كلية العلوم – جامعة كربلاء

كجزء من استكمال متطلبات نيل درجة الماجستير

علوم في الكيمياء

تقدمت بها

زينة جبار محمد

بكالوريوس علوم في الكيمياء (٢٠٠٨) جامعة كربلاء

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