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Electrochemical Studies At Room Temperature Ionic Liquid Of Choline Chloride/ Tartaric Acid

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We, examining committee, certify that we have read this thesis and examined the student in its content, and that in our opinion it is adequate with standing as a thesis for the Degree of M. Sc. in Chemistry.

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Dedication

To……

Dear Father and Mother…
For your love and prayers

Dear sister and brothers…
For your affection and tenderness

To each member of My Family,
My Friends and Colleagues…

ACKNOWLEDGMENTS

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List of abbreviations

Abbreviation	Name
R T I L	Room temperature ionic liquid
NTf_2	N,Ndialkyl- pyrrolidinium
BMIm	1-Butyl-3-methylimidazolium
BF_4	Tetrafluoroborate
CF_3COO	trifluoroacetate
$E_{1/2}$	Voltage of a half-cell
$E°$	Standard potential
k_e	rate constants
$\Delta G°$	free energies
η_{eff}	Current efficiency
e	Electron charge
I	Current
V O C	Volatile organic compound
UV-Vis	Ultraviolet- visible
O_h	Octahedral
T_d	Tetrahedral
B`	Racah parameter for complex
B	Racah parameter for free ion
β	Nephelauxetic factor

Abstract

The oxidation-reduction behavior of the newly prepared choline chloride/d-tartaric acid ionic liquid was studied by electrolysis at 25°C to 95°C with applied voltages of 0.5 to 5 volts. This ionic liquid was found stable up to 45°C and 5 volts as only showed small changes in current density. But, at 65°C the liquid showed noticeable unstable behavior particularly at or above 2.5 volt, which increased at higher temperature with increase conducting too.

Solution of $CuSO_4.5H_2O$ showed similar behavior to ionic liquid alone but with increased current density and conductivity which was attributed to viscosity changes and presence of copper (II) ions. However, $NiCl_2$ solution in ionic liquid decomposed at lower potential of (1 volt) at 65°C while giving a similar behavior of current density and conductivity to copper solution. The CrO_3 solution in ionic liquid was unstable from 65°C and 2.5 volts. However the conductivity was found to be similar than in ionic liquid alone up to 50°C which increased to more than ionic liquid at 60°C. This was attributed to the reduction of Cr (VI) to Cr (III) as was conformed by UV. Visible investigation.

It was found possible to carry out electroplating of copper, nickel, and chrome from their above solution at high potential and 85°C. The amount of coated metals was found to increase with potential of 2, 2.5, and 3 volts. The non uniform irregular shapes of the coated metal particles were found to adhere strongly to the substrate of stainless steel, nickel, and copper. In addition the current efficiency was found to be high

in case of chrome plating (~ 80%) while less than (50%) in copper and nickel plating.

UV.Vis examination of $CuSO_4.5H_2O$ indicate distorted octahedral coordination in this ionic liquid while $NiCl_2$ solution showed after electroplating process a mixed tetrahedral and octahedral spectra. However CrO_3 solution showed spectra of octahedral Cr (III) oxidation state when cooled from 85°C of the plating process indicating the reduction of Cr (VI) at around 60°C when its solution change color. Racah parameter, 10Dq , Nephelauxetic factor, and molar absorption were calculated to the above solutions.

CHAPTER ONE

INTRODUCATION

CHAPTER 1
Introduction

1.1 *Ionic liquids:*

Ionic liquids are solvents consisting entirely of ions resembling the ionic melts of metallic salts, however, ionic liquids are liquids at much lower temperatures (less than 100 C°)[1]. The ionic liquids generally consist of a combination of organic cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium and phosphonium and bulky and soft anions, such as $CF_3SO_3^-$, $NCF_3SO_2^-$, PF_6^- and BF_4^- [2].

Ionic liquid is also called the "designer's solvent" by changing the types and composition, positive ions and negative ions, it is possible to produce a limitless variety of chemical compounds. Therefore it makes possible the creation of electrolytes, which have new and non-conventional performance through modification of molecular design by changing types and combination of positive ions and negative. For this reason, research has advanced worldwide into various industrial applications which take advantage of ionic liquid characteristics[3] Ionic liquids have unique properties such as high thermal and electrochemical stability, high ionic conductivity, negligible vapor pressure, and non-flammability and resistance to moisture absorption. These properties

make ionic liquids potential benign solvent replacements for volatile organics traditionally used in organic synthesis and separation processes and electrochemical application[1].

Ionic liquids are fluids that consist entirely of organic cations and inorganic or organic anions[4] Figure (1.1). Seddon[5] speaks of about one trillion(10^{18}) possible cation / anion combinations to produce ionic liquids.

1.Common cations:-
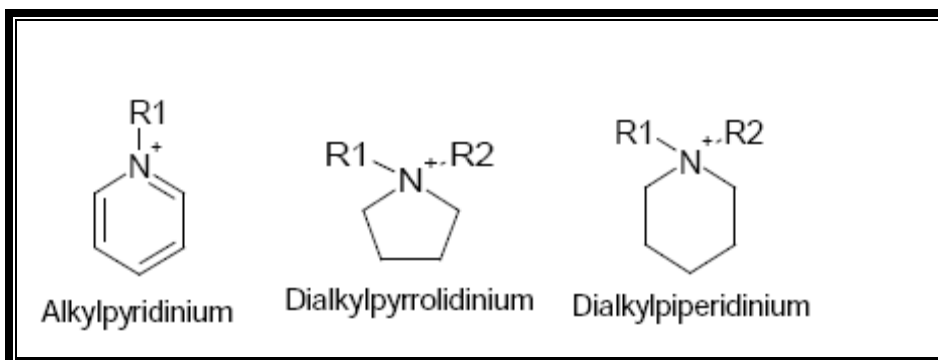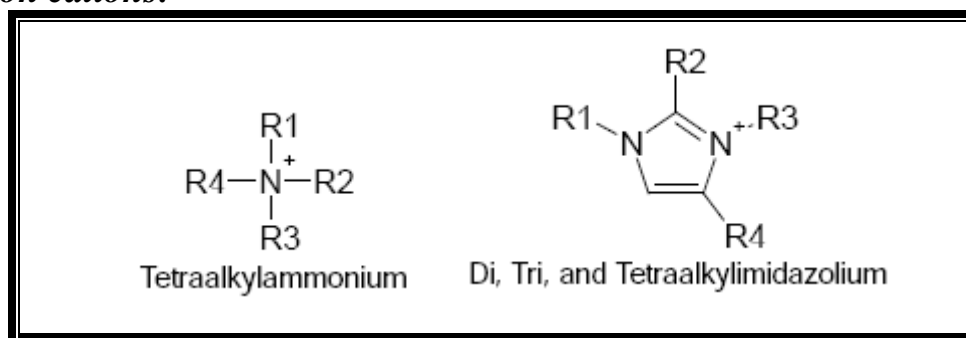
2. Common Anions:-

$[Cl]^-$, $[AlCl_4]^-$, $[N(SO_2CF_3)_2]^-$, $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$.

Figure (1.1):- (1) Common cations and (2) Common anions for ionic liquids.

1.1.1 *Historical review of ionic liquids:*

Ionic liquids may be considered as a new class of remarkable solvents, yet they have been around for many years dating back to the 1900s [6]. Ionic liquids were initially discovered by electrochemists many years ago while looking for ideal electrolytes for batteries [5]. The first recorded ionic liquid, ethylammonium nitrate $[C_2H_5NH_3^+]$ $[NO_3^-]$, which is a liquid at room temperature, was discovered by Walden in 1914 [7]. It was first developed by the military for use in liquid propellants [7]. Walden measured the physical properties of ethylammonium nitrate, $[C_2H_5NH_3^+]$ $[NO_3^-]$, which has a melting point of 12 ^0C, formed by the reaction of ethylamine with concentrated nitric acid. The modern history of ionic liquids started with the development of aluminum chloride based salts for electroplating in 1948 [8].

Then, Hurley and Weir [9] stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. Ionic liquids were in the some period discovered by US scientists Frank Hurley and Tom Weir at the Rice Institute in Texas in 1951while looking for a cheaper and easier way to electroplate aluminum. The ionic liquid they produced was an alkylpyridinium chloroaluminate [9]. The imidazolium cations were discovered by Hussey and Wilkes at the US Air Force Academy while looking for a replacement for the alkylpyridinium cations since they were relatively easy to reduce, both chemically and electrochemically, their particular favorite, [ethyl methyl imidazolium] $[AlCl_4]$ had a melting point below room temperature [10]. The chloroaluminate ionic liquids act as both catalyst and solvent in many processes, chemical reactions in the chloroaluminate ionic liquids, including Friedel-Crafts [11] and oligomerisation reactions [12] have been tested successfully. However,

they suffered a major drawback: they are air and water sensitive and therefore their use as solvents in transition metal catalysis is limited.

In 1970s and 1980s, Osteryoung [13] and Hussey [14] carried out extensive research on organic aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by Hussey [15]. The ionic liquids based on AlCl$_3$ can be regarded as the first generation of ionic liquids.

In 1992, Wilkes and Zaworotko[16] reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cations with either tetrafluoroborate or hexafluorophosphate as anions. The hexafluorophosphate ionic liquids are, however, less stable to moisture and are known to hydrolyse in the presence of water and heat to form HF and/or phosphoric acid. Therefore, ionic liquids based on more hydrophobic anions such as tri-fluoromethanesulfonate (CF$_3$SO$_3$), bis-(trifluoromethanesulfonyl) imide [(CF$_3$SO$_2$)$_2$NH] and tris (trifluoromethanesulfonyl) methide [(CF$_3$SO$_2$)$_3$CH] have been developed [17]. These ionic liquids have received extensive attention not only because of their low reactivity with water but also because of their large electrochemical windows.

1.1.2 *General advantages of ionic liquids:-*

Green chemistry concentrated its aims on the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [18]. With the rapid advancements in the field of synthetic organic chemistry, more and more environment friendly processes are being developed at rapid rate. Recently, there has been an upsurge in interest in ionic liquids. It is generally accepted that ionic liquids posses relatively low melting points and are less viscous than molten salts. Ionic liquids have low vapor pressures, are considered by

many authors to be environmentally friendly and can be applied in many organic reactions [19].

The very low vapor pressure of ionic liquids has led to their use as a green solvent in environmentally friendly reactions and separation processes [20]. This feature of ionic liquids permits their repeated use as benign solvents for green chemical syntheses without solvent loss to the environment due to evaporation [21]. Due to these excellent characteristics of ionic liquids which makes them superior to other organic solvents, scientists have done much work on their applications in electrochemistry, liquid-liquid extraction and catalysis, including biocatalysis and polymerization [22].

Ionic liquids have become very popular in recent years and have proven to be versatile alternatives to classic synthetic procedures using common organic solvents. Application in organic synthesis is enormous and still increasing. They have become of great importance in development of laboratory or industrial catalytic processes [23] and biocatalysis [24]. They have been used in various polymerization processes and preparation of ion conductive polymer electrolytes [25, 26]. Technical applications of ionic liquids present big diversity including preparation of photosensitizers [27], solar cells [28], lubricants for steel [29], improvement of aerogels production [30] and HPLC methods [31], and even embalming and tissue preservation for biological purposes [32].

B. Weyershausen and K. Lehmann [33] believe that due to their unique properties ionic liquids have a great potential to be used as performance additives in many materials and applications. The application of ionic liquids is in accordance with the chemical industry's guidelines and

principles concerning the initiatives sustainable development and responsible care [33].

1.1.3 *Ionic liquids based on choline chloride:-*

More recently, researchers have been moving away from $[PF_6]^-$ and $[BF_4]^-$ since they are highly toxic or even away from halogenated compounds completely. Moves towards less toxic cations have been growing, with compounds like ammonium salts such as choline being just as flexible a scaffold as imidazole [34]. Choline chloride is a quaternary amine salt, Ethanaminium, 2-hydroxy-N, N, N-trimethyl-, chloride, $C_5H_{14}NO.Cl$. It dissociates in water into the corresponding positively charged quaternary hydroxyl alkylammonium ion and the negatively charged chloride ion.

Eutectic mixtures of salts have been utilized for a long time to decrease the temperature for molten salt applications. Ambient temperature molten salts have been formed by mixing quaternary ammonium salts with metal salts.

Halide salts can also form complexes with hydrogen bond donors and previous work has shown that mixtures of urea with alkali metal halides form eutectics with melting points of < 150 °C [35]. While a few reports also exist for adducts of urea with other metal salts, their use as solvents has been limited to high temperature applications [36]. Recent work [37] showed that mixtures of substituted quaternary ammonium salts such as choline chloride with urea produce eutectics that are liquid at ambient temperature and have unusual solvent properties when compared to most molecular solvents and are more typical of the properties observed for ionic liquids. Choline chloride-urea ionic liquids are highly conducting,

confirming that the ionic species are dissociated in the liquid and can move independently.

The viscosity and conductivity are strongly affected by the amide and quaternary ammonium salt and hence the fluid properties could be tailored for specific applications [37]. The mixtures of amides with quaternary ammonium salts form low melting point eutectics that have unusual solvent properties, additional advantages of this type of mixture is that it is sustainable, biodegradable and a large number of variants can be produced from readily available materials.

1.2 *Electrochemistry in ionic liquids:-*

The physical and electrochemical properties of air stable room-temperature molten salts have been extensively studied for electrochemical application as electrolytes for batteries and capacitors [38]. It possesses several properties which make them attractive alternatives to traditional nonaqueous electrolytes and attractive candidates for various electrochemical devices [39]. Ionic liquids with different organic cations have also been suggested for electrolyte applications such as metal surface, finishing batteries, capacitors, fuel cells, electrosynthesis, actuators and nuclear waste treatment [40].

Ionic liquids containing various nonchloroaluminate anions, which are stable in air and moisture, are receiving much attention due to their potential applications in many diverse fields [40, 41].

As a large number of combinations of cations and anions are possible, so the physicochemical properties of ionic liquids can be controlled by a suitable choice of the composition of ionic liquid. The physicochemical properties of different hydrophobic and hydrophilic ionic liquids based on imidazolium cations have been reported to depend upon the alkyl chain length of the imidazolium cation and nature of the anion [42].

Central Research Institute of Electric Power Industry has focused on room temperature ionic liquid because it may be useful for producing inherently safer lithium secondary batteries if used as electrolyte due to its superior flame resistance compared to flammable organic liquid electrolytes [43]. The applications of ionic liquid as an alternative to more classical non aqueous electrolytes because of their intrinsic properties the hydrophobic ionic liquid can successfully be used as solvents for lithium salts leading to hydrophobic lithium electrolytes of high conductivity [44].

A change in viscosity, density, ion size and degree of dissociation also affects the conductivity of ionic liquid; however it is difficult to estimate the contribution of each parameter separately. However, most of the studies are mainly on ionic liquids containing various fluoroanions and both cations and anions have been reported to be mobile in such ionic liquids, as electrolytes in various electrochemical applications [45].

1.2.1 *Conductivity:-*

For any electrochemical process, the conductivity is a property of primary importance and the conductivity of the RTILs has been reviewed on several occasions, for example refs[46-48], Being composed entirely of ions, RTILs are supposed to be among the most concentrated electrolytic fluids with many charge carriers per unit volume. When these charge carriers are mobile, very high conductivities are possible. Room-temperature ionic liquids exhibit conductivities in the broad range 0.1-20 mS cm^{-1}[46,49,50]. Rather high conductivities of the order of 10 mS cm^{-1} can be found in the imidazolium family[51]. Quaternary ammonium ionic liquids are always characterized by lower conductivities; 2 mS cm^{-1} is thus the highest conductivity found for a *N,N*dialkyl- pyrrolidinium [NTf2] salt[50-52]. It is worth mentioning that ionic liquids incorporating the tricyanomethanide anion and the dicyanamide anion possess some of

the highest conductivities (up to 36 mS cm^{-1}) [53–55]. But these values are considerably lower than those of concentrated aqueous electrolytes (for example, the aqueous KOH solution (29.4 wt %) applied in alkaline battery is 540 mS cm^{-1}). The high viscosity of the RTILs has a major impact on the conductivities because the conductivity is inversely linked to the viscosity.[56-59]. The less viscous [NTf2] salts usually exhibit among the highest conductivities.[50] Although a correlation between viscosity and conductivity is generally observed, the viscosity alone cannot account for the conductivity behavior. For instance, [EMIm][OTf] and [BMIm][NTf2] display similar viscosities and densities, but their conductivities differ by a factor of 2 many others factors contribute to the conductivity.[49] Besides the effects of the ion size,[49,56] of the anionic charge delocalization, and of the RTILs' density,[56,57] aggregation and correlated ionic motions have to be stressed.[52,51] Transport properties and conductivities in a family of dialkylimidazolium RTILs were examined by varying the alkyl chain or the anion.[56] Increasing the length of the alkyl chains results in a higher viscosity and a lower conductivity. Increasing the size of the anions lowered the viscosity, but the conductivities, directly measured, were similar for any of the anions. However, conductivities calculated from the diffusion coefficients of the anions and the cations gave higher conductivities for the less viscous salts (larger anion)[57]. The inconsistency between calculated conductivities from diffusion measurements and measured conductivities was attributed to correlated ion motion or the diffusion of neutral species or both. Strong ionic association (ion pairing) was found for the more viscous salts. While the diffusion coefficients of such neutral species or ion pairs can be measured, they do not contribute to conductivity due to their lack of net ionic charge.[58]

1.2.2 *Electrochemical windows:-*

RTILs generally exhibit a wide potential window, which is a highly desirable property for applying the RTILs as electrochemical solvents. Typical windows of 4.5-5 V have been reported for the RTILs[52,59,60], and even an enlarged electrochemical window, up to 7 V, was found for [BMIm][BF4] and

[BMIm][PF6] by Gonc̦alves[60] . this potential window range is equal to slightly wider than that observed in conventional organic electrolytes but largely exceeds that accessible in aqueous electrolytes. It has been shown that the oxidation of the anions and the reduction of the cations, respectively, are responsible for the anodic and cathodic limits observed in the ionic liquids. The potentials at which these processes start determine the Electrochemical Reactivity in RTILs Chemical Reviews. The purity of the ionic liquids has a great influence on the width of the electrochemical window. But the nature of the material that is used for the working electrode may modify the decomposition potentials of the electrolyte. Thus, the electrochemical window of 1-butyl-3-methylimidazolium trifluoroacetate, [BMIm][CF3COO], is reported to be shorter with platinum than with glassy carbon, probably due to catalytic activity of the platinum metal. And the potentials values are often referred against different quasi-references, and consequently, the data cannot be compared with a high level of accuracy.[61]

However, general trends can be brought out. Quaternary ammonium and pyrrolidinium salts are reported to be more stable toward reduction than the corresponding imidazolium salts, due to the improvement of cathodic stability of

ammonium and pyrrolidinium cations[61,62] . The reduction of the imidazolium cation is related to the "high" acidity of the C2-H proton (Figure1.2), the reduction of 1,3-dialkylimidazolium cation leading to the

formation of a carbene. By comparing [NTf2] salts, MacFarlane et al.[56] noticed that pyrrolidinium salts extended their cathodic limit by 0.5 V with respect to the corresponding quaternary ammonium salts[56]. This electrochemical window is one of the widest ever reported for RTILs. Comparable large electrochemical

stability was also observed by Buzzeo et al. [63]for tris[(Nhexyl)-tetradecyl)]-phosphonium trifluoro-tris(pentafluoroethyl)- phosphate. On the oxidative side, ionic liquids take advantage of the very stable fluoroanions, such as PF_6^-,BF_4^- or NTf_2^- However, BF_4^- in [BMIm][BF4] was found to decompose into BF3 and fluorocarbons at the anode. In addition, [PF6] and [BF4] anions are susceptible to hydrolysis, which may release toxic hydrogen fluoride. In this context, [NTf2] is set as a strongly robust anion and has become widely used. But, very recent work clearly suggests that the [NTf2] anion engages in a series of reductive reactions beginning at approximately -2.0 V vs Fc/Fc+, well before the usually reported cathodic limit. The process is shown to cause cleavage of a S-N bond in the anion.

$$(CF_3SO_2)_2N^- + e^- \rightarrow \bullet NSO_2CF_3^- + SO_2CF_3^- \qquad \textit{(1-1)}$$
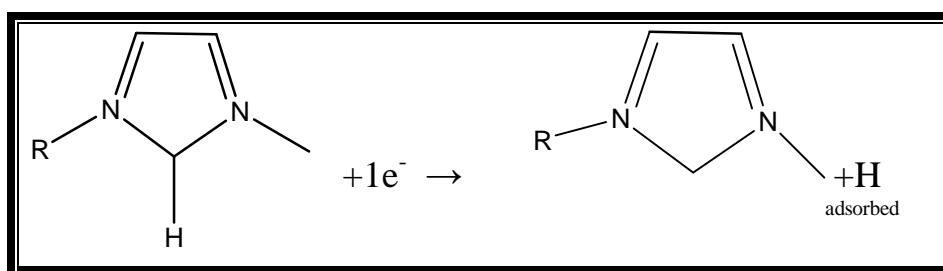
Figure (1.2)Proposed Electrochemical Reduction of Imidazolium cation.

The wide available electrochemical window provided by the ionic liquids was also suggested to be exploited in molecular solvents to extend the corresponding potential window[60,61]. A careful analysis of such

RTIL/organic solvent system potentialities has been undertaken and concluded that this combination provided an advantage over the commonly used tetrabutylammonium perchlorate/acetonitrile electrolyte with regard to extending the anodic limit but no improvement on the cathodic side[62].

1.2.3   *Electrochemical behavior in ionic liquids:-*

The first reported investigations were related to the oxidation or reduction of one-electron reversible couples, for which the initial purpose was to compare the voltammetric response of simple electrochemical systems with their corresponding behaviors in organic solvents. The main part of these works concerns the comparison between the diffusion coefficients in RTILs and in classical solvent. Ferrocene, cobaltocene, or tetrathiafulvalene in common RTILs, [BMIm][PF6] and [EMI][BF4], were investigated, showing the same general patterns in RTILs as those in molecular solvent containing an electrolyte [60,61] .Later, cyclic voltammetry experiments of the oxidation of ferrocene to ferricenium (Fc/Fc+) in RTILs were completed by using a large range of scan rates (typically from 0.1 V· s^{-1} to 1000 V s^{-1}) and confirmed that well-defined waves were observed for the whole range of scan rates. In all these ionic liquids, the peak currents for the reduction/oxidation of ferrocene were found to vary linearly with the square root of the scan rate, showing that the electrochemical process is diffusion controlled [62,63]. In common RTILs, the Fc/Fc^{+} couple is electrochemically reversible with small peak-

potential differences (ΔE) between the forward and backward scans (typically 57 and 73 mV at scan rates of 0.1 and 1000 V s^{-1}, respectively), which corresponds to a relatively fast electron-transfer kinetics. The standard potentials, $E°$, were classically derived from the half-sum between the forward and reverse peak potentials. In this case, it was considered that half-wave potentials, $E_{1/2}$, are close to the standard potentials $E°$, neglecting the possible difference on D coefficients between the neutral and charged species ($E_{1/2}$)

(E° + RT/(2F) ln (Dr/Do)). **(1-2)**

1.2.4 *Electron transfer thermodynamic and kinetic analyses:-*

The evolution of the reactivity is a major question when a reaction is transferred from a conventional organic medium to an ionic liquid. This has led several authors to use electrochemical methods for investigating how model electrochemical reactions are going to be affected by ionic liquids[64].

The thermodynamics ($E°$ measurements) and the kinetics through the measurement of apparent heterogeneous standard electrontransfer rate constants, ke. Investigations can be separated into two categories depending on the charge carried by the electrogenerated species (positive of negative). About the properties of a radical anion and thus the possible interactions with the cation of the ionic liquid, a series of substituted nitrobenzene and an aliphatic nitro compound was studied both in acetonitrile and in [BMIm][NTf2] and [Et3BuN][NTf2] using cyclic voltammetry. As found for the metallocenes, the general electrochemical

patterns for the reduction of NO$_2$ compounds in RTILs were not too different from the well-known behavior reported in organic solvents. These molecules display chemically reversible monoelectronic voltammograms (Figure1.3)[65]. The kinetics of electron transfer, the standard heterogeneous rate constants, k_e, were measured assuming that the Butler-Volmer law is valid and that the diffusion coefficients are equal for the reduced and oxidized species of the redox couple. The k_e values were generally derived from classical cyclic voltammetry measurements based on the variation of ΔE_p (difference between the anodic and the cathodic peak potentials) with the scan rate or from steady state methods.
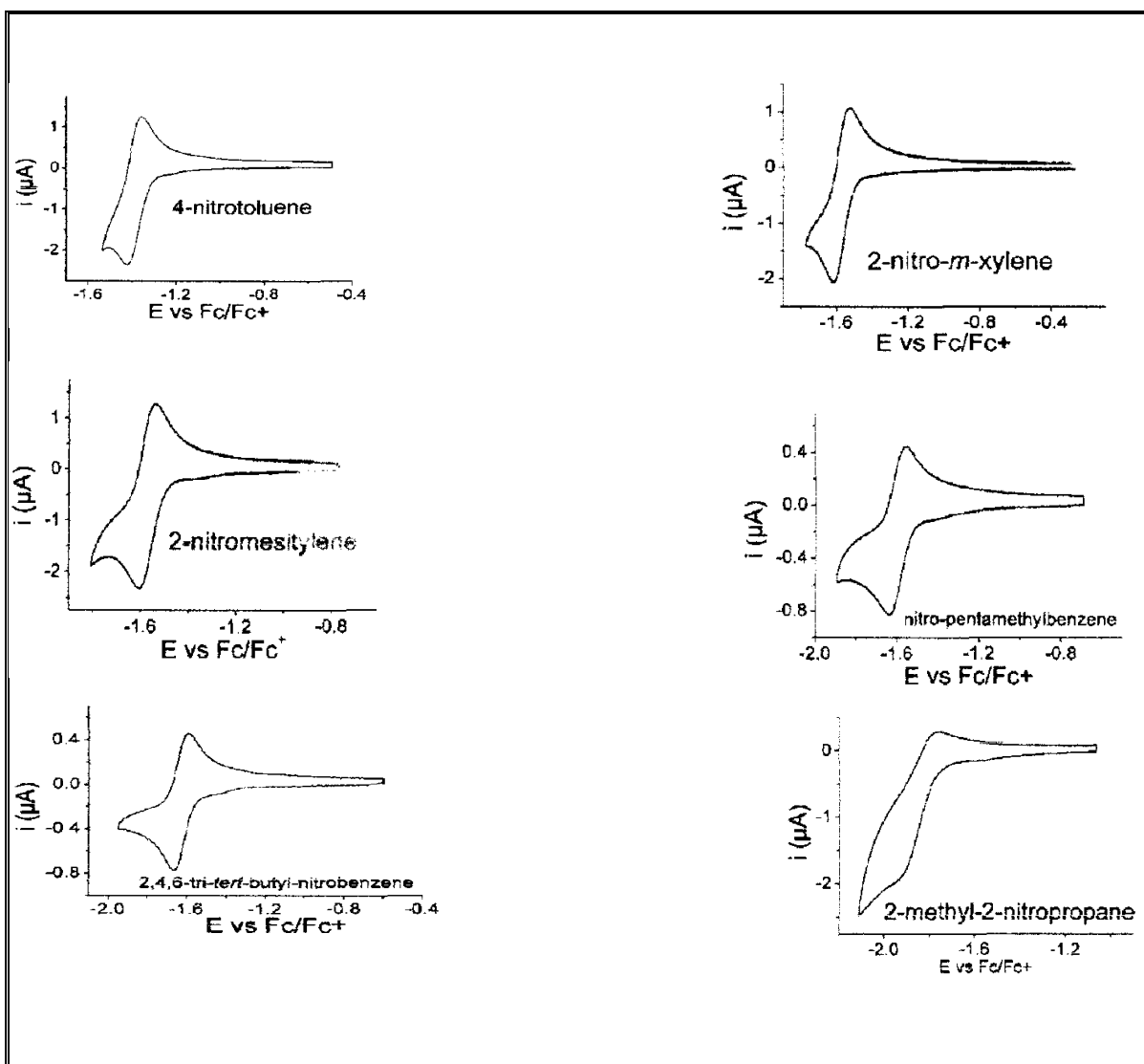
Figure (1-3) Cyclic voltammetry in ionic liquids, reduction of nitro compounds on a glassy carbon electrode. Scan rate =0.2 Vs⁻¹. All voltammograms were recorded in [BMIm][NTf2] except for the 2,4,6-tri-tert-butyl-nitrobenzen, which is in[Et3Bun][NTf2].

As explained previously, the lack of knowledge of the metal-RTIL interface makes difficult any correction for effect of the interface. Thus, for both oxidation and reduction investigations, only apparent ke values were determined without correction from the double layer effect and investigations focused on the relative effect for a given compound and a given electrode[66]. For example, the nitrotoluene reduction is fast in acetonitrile (ke > 1 cm s⁻¹) and becomes sluggish in the [Et3BuN][NTf2]

(ke≈ 0.01 cm s^{-1}). Similarly, for the reduction of benzaldehyde in [BMIm][NTf2], similar effects to those reported for the reduction of nitro compounds were detected, that is, a large decrease of the heterogeneous electron transfer rate constant by comparison with classical molecular solvent. In contrast, in [Pyr4][NTf2], the electron transfer kinetics for the same redox couple was found to be similar to that measured in a noninteracting molecular solvent containing quaternary ammonium electrolytes. This difference of behavior observed between these two types of ionic liquids suggests more complex interactions than simple electrostatic ion pairing, which could also involve π-π interactions or H-bonding that are possible with imidazolium and not possible with pyrrolidinium cations. To explain the lower kinetics, it was also suggested that ordering in the RTIL may play a role in the kinetics slowing[66]. Ordering would lead to higher solvent reorganization and slower double-layer interface relaxation, which would both result in apparent slow heterogeneous kinetics [67].

1.2.5 *Electrochemical reactivites of inorganic systems:-*

Electrochemical oxidation of ammonia has been examined in several RTILs by Compton et al.[68] In the first investigations, voltammograms obtained in [EMIm][NTf2] and in DMF have shown that similar responses are observed in each solvent with a broad oxidative wave and a new reductive process after the oxidation. It was deduced that the ammonium cation was formed after oxidation of ammonia, which is followed by deprotonation of ammonium to form ammonia and protons eq (1-3)(1-4). Comparison of the response in several ionic liquids with different anions established the influence of the anion of the RTILs in the global oxidation mechanism. Depending on the anion of the RTILs (A$^-$), subtle changes in the mechanisms are observed. In most cases, the protonated anion (AH) of the RTIL is formed in a first step corresponding

to the oxidation of NH_3 to N_2, followed by the protononation of NH_3 by the generated acid of the RTIL anion to form NH_4^+. In contrast, in [BMIm][PF_6], NH_4^+ is formed prior to the formation of HPF_6.[69]

$$NH_3 + 3A^- \rightarrow \tfrac{1}{2} N_2 + 3\,HA + 3e^- \qquad\qquad (1\text{-}3)$$

$$HA + NH_3 \rightarrow NH_4^+ + A^- \qquad\qquad (1\text{-}4)$$

The oxidations of halides, Cl^- and Br^-, display some different behaviors in RTILs than those observed in organic media. Oxidation of Cl^- in [BMIm][PF_6], with large concentrations of [BMIm][Cl], displays an irreversible process both on platinum and on graphite electrode. The main feature was that this oxidation does not lead to chlorine gas evolution but to the formation of oxidation products that stay in the RTILs in the form of complexes between Cl_2 molecule and chloride ion where the Cl_3^- is the major product [70,71].

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad\qquad (1\text{-}5)$$

$$Cl_2 + Cl^- \rightarrow Cl_3^- \qquad\qquad (1\text{-}6)$$

Oxidation of Br^- was investigated in an imidazolium RTIL but with a different anion, [NTf2]. The proposed mechanism was the same as for Cl^-, involving first the direct oxidation of bromide, Br^-, to bromine, Br_2, followed by the homogeneous formation of tribromine anion, Br_3^-.[72] However, the equilibrium constant corresponding to the formation of Br_3^- was found to be 3 orders of magnitude smaller in the ionic liquid than in acetonitrile. However, direct comparison between results obtained with Cl^- and Br^- are difficult because the nature of the anion, which was different in each study, may influence this type of equilibrium. A few works report on the behavior of metallic halides in RTILs. A part of this research was dedicated to the behavior of actinides in nonchloroaluminate RTILs. RTILs allow investigations on actinide chemistry without the unwanted side reactions existing in chloroaluminate ionic liquids.[72,73] For the first time, it was shown by a

spectroscopic and voltammetric analysis in [BMIm][NTf$_2$] that some actinides(IV) (Np(IV) and Pu(IV)) are able to form chloride complexes with a Cl$^-$/An(VI) ratio above 6/1. The electrochemistry of gold was studied in detail in [BMIm][NTf$_2$] over different electrode materials: gold, platinum, and glassy carbon. The reduction of AuCl$_4^-$ salt forms in a first step AuCl$_2^-$ before deposition as Au(0)[73].

1.2.6 Electrolysis behavior :-

Electrolysis is the process in which electric currents from an external source supply the energy necessary to make a chemical reaction take place. It is just the opposite of what occurs in a battery, where the energy of a chemical reaction is converted into electrical energy. Although electrolysis occurs in charging and discharging a battery, the term electrolysis is usually used only when the primary interest is in the chemical products of the process. If two copper electrodes immersed in a copper sulfate solution, the reaction caused by a current is simply the transfer of copper from one electrode to the other. This very simple system –illustrates the principles of electrolysis, and permits us to investigate further the subtleties of electrode processes.[74,75]

When a source is connected to the cell, one plate is made positive with respect to the other, so there is a current through the cell, as Cu^{2+} ions. As a result copper is removed from the positive plate, and deposited on the negative plate. By maintaining this potential difference across the cell we have considerably changed the potential distribution in the cell. This applied voltage, Vcell, is equal to the sum of three components.[75]

(1) There is an interface potential at the positive electrode which is less than the Nernst value. The rate at which copper dissolves is greater than the rate at which it is deposited on the electrode. so there is a net flow of copper into the electrolyte.

(2) At the negative electrode the interface potential now exceeds the Nernst value, and there is a net flow of Cu^{2+} ions from the solution to the electrode, where a deposit of copper is built up.

(3) There is a potential gradient across the electrolyte and an associated electric field within the electrolyte which drives the flow of Cu^{2+} ions between the electrodes. The difference between the Nernst equilibrium potentials and the actual potential difference at the electrode when there is an electric current is called the **overpotential** of the electrode. These overpotentials and the resistive potential drop across the cell must be established to make the reaction proceed. However they represent wasted energy. They can be minimised by suitable cell design and a low electrolysis rate, but some potential difference is required, and hence some energy must be dissipated to make the process proceed at a finite speed.[75,76]

However the electrolysis of molten sodium chloride (which melts at 801°C), sodium ions (Na^+) and chloride ions (Cl^-) are free to move around in the melt.   When carbon electrodes, connected to a battery, are dipped into the melt. The cathode, because it is negatively charged, attracts the positive ions from the melt,[77] where the ions receive electrons supplied by the battery (the ions are **discharged**). Sodium atoms are formed and molten sodium metal forms at the cathode:

$$Na^+{}_{(l)} + e^- \rightarrow Na_{(l)} \qquad\qquad (1\text{-}7)$$

The anode attracts the negatively charged Cl^- ions, where they each give up one electron. The electrons go into the anode and pass back along the wire to the battery. In this way, the circuit is completed.[78]

$$Cl^- \rightarrow Cl + e^- \qquad\qquad (1\text{-}8)$$

Chlorine atoms join together to form diatomic molecules:

$$Cl + Cl \rightarrow Cl_{2(g)} \qquad\qquad (1\text{-}9)$$

Note that these two stages are usually written as one half-reaction:

$$2Cl^-{}_{(l)} \rightarrow Cl_{2(g)} + 2e^- \qquad\qquad (1\text{-}10)$$
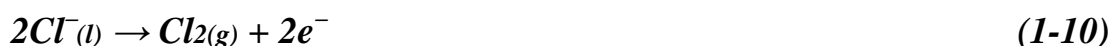
Therefore, sodium metal is formed at the cathode and bubbles of chlorine gas formed at the anode. Chemical changes take place at both electrodes, sodium ions are reduced and chloride ions are oxidized.[78] Electrons do not actually pass through the liquid, but an equal number of electrons are given up at the cathode as are received at the anode. The overall chemical equation for the reactions that take place is[79]

$$2NaCl(l) \rightarrow 2Na(l) + Cl_{2}(g) \qquad\qquad (1\text{-}11)$$

1.2.7 *Electroplating in ionic liquids:-*

Ionic liquids are useful alternative electrolytes for metal deposition because they have the following attributes:-[80]

- Wide potential windows.

- Avoidance of water and metal/water chemistry.

- High conductivity compared to non-aqueous solvents.

-Simple to handle.

The electrodeposition of most technologically important metals has been shown to be possible from a wide range of room temperature ionic liquids.and the processes have been developed for the deposition of Cr, Mn,Co,Ni, Cu, Zn, Sn, Pb, Pd and Ag.[81] Alloys such as Cu/Zn, Cr/Mn, Zn/Co and Zn/Sn have also been deposited on a wide range of substrates without special pretreatment. The air and moisture stable ionic liquids should operate at approximately the same conditions as conventional plating.[80,81]

1.2.7.1 *Electroplating of chromium:-*

Hard chrome is traditionally produced from solutions containing chromium trioxide and sulphuric acid. It is used in a variety of applications due to its hardness and wear resistance.[82] In addition, its micro cracked structure give it good oil retention properties producing a

low friction surface. Unlike decorative chrome plating which is limited in thicknesses that can be applied, hard chrome can be applied many hundreds of microns thick, producing a load bearing surface.[82] Due to Health, Safety and Environmental pressures, a search for alternatives to hexavalent hard chrome plating has been in progress for many years.[82,83] The search for alternatives also covers other traditional hexavalent

chrome processes such as passive. Cr(III) salts are not classified as hazardous and are ideal alternatives. The Current Alternatives to Cr(VI)For decorative applications (a thin layer of electroplated chrome on top of electroplated nickel), aqueous solutions based on Cr(III) salts have been, commercially available for many years.[83] Hard chrome deposits produced from aqueous Cr(III) systems have produced thick, hard or micro cracked deposits. The combination all 3 has proved elusive. The current preferred option for hard chrome replacement in Aero pace is HVOF (High Velocity Oxy Fuel) sprayed There are some major problems with use of HVOF coatings as hard chrome replacement, amongst which are:

-Limited geometry parts can be coated.

-Health and Safety concerns are now being raised about the post spray grinding of such coatings.[84]

The industrial objectives of Cr(III) from Ionic Liquid ,Produce a coating from a trivalent chrome system with identical properties to deposits produced from traditional aqueous hexavalent chrome baths: Appearance, Hardness, Wear resistance, Corrosion resistance, Microstructure.[85] Coatings produced from an Ionic Liquid containing chrome (III) chloride hexahydrate, choline chloride and an additive. Black coatings were produced from the original formulations. Deposits

had a similar appearance to black Chrome coatings produced from sulphate free hexavalent aqueous solutions. .[85]

1.2.7.2 Electroplating of copper

Electrolysis can be used for purifying a metal through the electrolytic dissolution of an impure anode and the subsequent recentralization of the pure metal on the cathode[85]. The impurities are left behind in solution. Copper is refined commercially by this electrolytic technique. Electrolysis is often used for electroplating a metal to another material acting as the cathode. The other material must also be electrically conducting. Nonconducting materials, such as leaves, can also be plated by first being painted with a metallic conductive paint.   Silver plating can be done with a silver anode and the object to be plated as the cathode. Electrolytic reduction (cathodic reduction) has developed into a useful technique for the restoration of artifacts such as corroded nails and encrusted silver.In the case of silver the degradation is usually due to the surface formation of insoluble (black) silver sulfide (Ag_2S).[86]

In this process, you will construct an electrolytic cell with copper electrodes. By comparing the mass of the cathode before and after the electrolysis reaction, you will be able to determine Avogadro's number and an experimental value for the information you must acquire from your experiment is the change in mass of the cathode and the total electrical charge that was used. Electrical charge (q) in coulombs is the product of the current, I, in amperes and the time, t, in seconds:

q = I x t   **(1-12)**

The electrolysis cell consists of two copper pieces (electrodes) and copper(II) sulfate solution, an external power supply, and an ammeter to

measure current. The electrode you choose as the cathode should be cleaned and weighed before the electrolysis begins. The initial mass (before electrolysis) is m_i and the final mass (after electrolysis) is m_f. The difference is the mass plated out, m, in the definitions above. Both the current and the time of electrolysis must be recorded.   To obtain better adherence of copper on the cathode, it is necessary to run the electrolysis backward for a short time (t_a) before connecting the chosen copper as the cathode (t_c). The net Xplating time, t, is proportional to the mass of copper plated out:[86,87]

t = tc – ta   **(1-13)**

1.2.7.3   Electroplating of nickel:-

Nickel is a hard, silvery white metal. It is produced by mining and refining sulphide and oxide ores. Nickel is also recycled from scrap metal. Electrolysis nickel plating is an auto-catalytic reaction used to deposit a coating of nickel on a substrate. it is not necessary to pass an electric current through the solution to form a deposit. this plating technique is to   prevent corrosion and wear. Electroplating of nickel technique can also be used to manufacture composite coating by suspending powder in the bath.[88] Products which contain nickel include rechargeable (NiCd) batteries, coins, welding rods and wires, electronic or computer equipment, and pigments for paints or ceramics. Nickel is also used in electroplating, electroforming and sintered metal coatings.[88]

1.3 *Interaction of the ligands with the metal ions:*

The tendency of metal ion to from a stable complex with ligands depend on many rules such as the hard and soft acids and bases (HSAB) rule of Pearson[89] which imply that metal ion tend to coordinate with certain functional groups of the ligand to from a stable complex. On the other hand, the tendency of transition metal ion of a special oxidation states is affected by the coordination to certain ligands. This phenomenon is called (symbiosis) [90,91].

Increasing the positive charge on the central transition metal ions strengthens the metal –ligands bond. The metal ion prefers to bind with atoms of high electron density such as N^{3-} , O^{2-} , P^{3-} , S^{2-} and C^{4-} . The ligand should have certain characteristic properties to make it convenient to form stable complex with transition metal ions. The size, geometrical shape, number and geometrical arrangement of ligand and donor atoms play the important role in the stability of the resultant complex. Metal centers, being positively charged, are favored to bind to negative charged biomolecules, the constituents of proteins and nucleic acid offer excellent ligands for binding to metal ions [92]. The Irving Williams series of stability for a given ligand shows a good criterion for the stability of complexes with dipositive metal ions which follows the order:

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
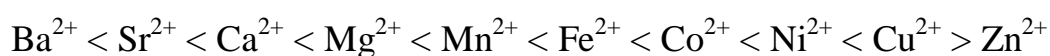
This order arises in part from a decrease in size across the series and in part from ligand field effect. A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^+, Hg^{2+} and Pt^{2+}, but other ligands seem to prefer ions such as Al^{3+}, Ti^{4+}, and Co^{3+}. Ligands and metal ions were classified as class (a) or (b) according to their preferential bonding. Class (a) metal ions includes those of alkali metals, alkaline earth metals, and lighter transition metals in higher oxidation states such as Ti^{+4} ,Cr^{+3} , Fe^{+3} ,Co^{+3} and the hydrogen ion, H^+.

Class (b) metal ions include those of the heavier transition metals, and those in lower oxidation states such as Cu^+, Ag^+, Hg^{+2}, Pd^{+2}, and Pt^{+2}. According to their preference toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b), respectively. Stability of these complexes may be summarized as follows [93]:

Tendency of ligands to complex with Class (a) metal ions	Tendency of ligands to complex with Class (b) metal ions
N >> P > As > Sb	N << P < As < Sb
O >> S > Se > Te	O << S < Se ~ Te
F > Cl > Br > I	F < Cl < Br < I

The ligand should have certain characteristic properties to make it convenient to form a stable complex with transition metal ions. The size, geometrical shape, number and geometrical arrangement of ligand donor atoms play the important role in stability of the resultant complex [93].

One of the important aspects of CFT is that all ligands are not identical when it comes to a causing separation of the d-orbital. For transition metal compounds, we are well aware of the multitude of colors available for a given metal ion when the ligands or stereochemistry are varied. In octahedral complexes, this can be considered a reflection of the energy difference between the higher dz^2, dx^2-y^2 (eg subset) and the dxy, dyz, dxz (t_2g subset).

It has been established that the ability of ligands to cause a large splitting of the energy between the orbitals is essentially independent of the metal ion and the spectrochemical series is a list of ligands ranked in order of their ability to cause large orbital separations.

A shortened list includes:

($I^- <$ Br$^- <$ SCN$^- \sim$ Cl$^- <$ F$^- <$ OH$^- \sim$ ONO$^- <$ C$_2$O$_4$$^{2-} <$ H$_2$O $<$ NCS$^- <$ EDTA$^{4-} <$ NH$_3 \sim$ pyr $\sim$ en $<$ bipy $<$ phen $<$ CN$^- \sim$ CO)

When metal ions that have between 4 and 7 electrons in the d orbitals form octahedral compounds, two possible electron allocations can occur. These are referred to as either weak field - strong field or high spin - low spin configurations.

The CFT method has provided a quantitative measure of the d-splitting. The eg/t$_2$g splitting (called the octahedral ligand field splitting $\Delta_0 = 10$Dq) Follows the general trend.

Point to consider about the Δ_0 splitting:

1- Charge on the metal:-

As charge increase, electrostatic attraction between M and L increases, M-L bond distance decreased and S$_{ML}$ increased. Also as charge increase, metal becomes more electronegative, decreasing ΔE_{ML}. Both trends lead to greater field strength for the more highly charged ion.

2- The nature of the metal ion, radial extension of 2nd and 3rd row transition metals are greater, thus S$_{ML}$ larger, leading to the following trend in Δ_0: 1st row transition metal $<<$ 2nd row transition metal $\sim$ 3rd row transition metal.

3- Nature of ligand:-

Different ligands have different S$_{ML}$ for a given metal ion. Can assess by measuring Δ_0 for different ligands about a given metal ion of given charge

Cl$^- <$ F$ <$ OH$_2 <$ CN$^-$ Cl$^- <$ OH$_2 <$ NH$_3 <$ CN$^-$

From experiments such as these, may deduce a general ranking of ligands in terms of field strength… this ranking is called the spectrochemical series:

($I^- <$ Br$^-$ < S^{2-} < SCN$^-$ < Cl$^-$ < F$^-$ < O^{2-} < OH$^-$ < H$_2$O < NH$_3$ < CN$^-$ < CO

< NO$^+$)   Strong field strength (largeΔ_0)

 Weak field strength (small Δ_0)   σ-only   π-accepter

 π-donors

In the above series, the ligand type has been overlayed onto the spectrochemical series. As is readily apparent from the energetic disposition of Δ_0, π-donors give weak ligand fields, σ-only ligands give intermediate fields and π-acceptors ligands give strong fields. [90-93]

1.4 The Aim of the present work:

Ionic liquids are growing materials and their excellent properties such as negligible vapor pressure, high degradation temperature, large electrochemical windows and high ionic conductivities make them growing widely. In the last two decades, many scientists have studied the electrical behavior of modified electrochemical process [23]. Thus, the present work aimed to establish the electrolysis of the newly prepared choline chloride/d-tartaric acid ionic liquid and the solution of $CuSO_4$, $NiCl_2$, CrO_3 in this solvent, all from room temperature up to 100 °C. The resultant behavior of these solutions will be used to electroplating the corresponding metals of each solution on a suitable substrate such as copper, stainless steel, and nickel. As a result, it would be possible therefore to determine the suitable conditions for practical application of this newly plating process.

In addition, the coordination of the dissolved metal ions in this solvent will be investigated by Uv.-Visible spectroscopy.

CHAPTER TWO

EXPERIMENTAL

CHAPTER 2

Experimental part

1.2 Chemicals:-

The chemicals used in this work and their purity and supplier are listed in Table (2-1)

Table (2-1) Chemicals and their purities and suppliers

Chemicals	Purity %	Supplied from
Choline chloride	99	Merck
Chromic oxide	99	BDH
Copper sulfate pentahydrate	99	BDH
Nickel chloride	99	BDH
Sulphuric acid conc.	98	Thomas Baker
d-tartaric acid	99	BDH
Potassium hydroxide	99	BDH

2.2. Setting of heating apparatus:-

Working in room temperature ionic liquid solvents offer a simplicity of apparatuses arrangements, in contrast to high temperature molten salts

apparatuses which requires heating equipments that withstand the high temperature used (i.e. heating to > 100 °C). Therefore illustrate the apparatuses used with room temperature ionic liquid, which is similar to those might be used with aqueous system.

1. Hot plate.
2. Oil bath.
3. Stand
4. Clamp.
5. Thermometer.
6. Reaction beaker.
7. Glass rod.

2.3 Methods:

2.3.1 Drying method:

All materials were dried in drying oven at 80°C for 4 hours before used. The dried samples where stored in a sealed container which was kept in a desiccators for further use.

2.3.2 Preparation of choline chloride/ d- tartaric acid ionic liquid:

The appropriate ratio of choline chloride/d-tartaric acid compounds were weighted out the dried samples which were milled together and introduced into an appropriate beaker. The beaker was gradually heated from room temperature with continuous mixing of the solid mixture until it reached liquid state when further heating to nearly 10 ^{o}C above melting point was applied to insure complete melting. The temperature of melting was recorded and the heating was cut-off allowing the melt to cool gradually when the mixture was still in the liquid state near by or close to room temperature.

2.3.3 Preparation of metal salts in (choline chloride/d-tartaric acid) ionic liquid:-

A general procedure which was adopted for all added solid materials to ionic liquid was as fallow:-

A known dry solid compound was weighted out (0.05g), and added to appropriate volume of ionic liquid at room temperature, the mixture was left to stand for 72 hours with occasional stirring to enhance dissolution of materials, as in Table (2-2) .

Table (2-2):- Concentration and color of metal salts in choline chloride/ d-tartaric acid ionic liquid at room temperature.

Metal salts	Concentration in choline chloride/d-tartaric acid ionic liquid (M)	Solution color
$CuSO_4.5H_2O$	0.04	Yellow
$NiCl_2$	0.08	Pale green
CrO_3	0.1	Green

2.3.4

Determination of electrolysis (choline chloride/d-tartaric acid) ionic liquid alone and metal salts ($CuSO_4.5H_2O$, $NiCl_2$ and CrO_3) in ionic liquid:-

Electrolysis experimental of ionic liquid alone and with added metal salts of (0.05 g)of each of ($CuSO_4.5H_2O$, $NiCl_2$ and CrO_3) were carried out with a two-inert carbon electrodes with diameter (1cm). The electrodes were cleaned with sulphluric acid (H_2SO_4) and then with (KOH) solution, then rinsed thoroughly with deionized water. 5 ml of choline chloride/ d-tartaric acid ionic liquid was added in to a 10 ml beaker. The assembled apparatus shown in Fig (2-1). The current was measured with multi meter type (ASWAR D. T 9202 A) connected in series with the electrolytic cell. One carbon electrode was attached to the negative terminal of power supply type (Kepco), and another carbon electrode to the positive terminal of same power supply, both were connected to the ammeter device. When power supply was turned on the current was recorded at the variable voltages (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 volts) after 5 minutes at (25, 45, 65, 75, 85, 95 ^oC). Thermocouple was introduced in to the beaker to monitor the temperature and the solution was stirred by magnetic stirred to insure homogeneous mixing. Current density was calculated by dividing the current on the cross

sectional area of the electrodes immersed in the solution was using the following equation (2-1):-

cross sectional area = circle area   *(2-1)*

$$3.14 \times (r^2)$$
$$r = 0.5 \ cm$$
$$3.14 \times (0.5)^2$$
$$= 0.785 \ cm^2$$

Fig(2-1):-Electrolysis experiment setup.

2.3.5 Determination of conductivity (choline chloride/d-tartaric acid) ionic liquid alone and metal salts (CuSO₄.5H₂O,NiCl₂ and CrO₃) in ionic liquid:-

The conductivity was measured by (HANNA conductivity meter). The setting of the apparatus is illustrated in Fig (2-2) when contains the ionic liquid alone or with added salts in container (c) and recording the conductivities at variable temperatures (30, 40, 50, 60, 70, 80, 90, 100 $^{\circ}$C) with the used of the conductivity meter (a). The container (c) was placed in a another container (g) that contained an oil which was heated by hot plate (h) and the oil temperature was recorded by thermocouple (e). The oil bath was agitated by mechanical stirrer while the ionic liquid by glass rod to insure homogeneous distribution of the heat through out the liquids.

Fig(2-2):-Conductivity measurement experiment setup

2.3.6 Conditions of electrodeposition of (copper, nickel, and chrome)metals in choline chloride/d-tartaric acid ionic liquid:

The electrodeposition of copper, nickel, and chrome metals was carried out at 85 ^{o}C for one hour using the solution stated in section (2.3.3). However, Table (2-3) show the condition of the electrodeposition process for the three deposited metals.

Table (2-3):- Conc. of salts, color of solution, applied voltage, current voltage, metal cathode, and weight of metals before and after deposit at 85℃ for one hour in choline chloride/d-tartaric acid ionic liquid at different voltages.

Salts	Conc. of salts in ionic liquid (M)	Color of solution	Applied voltages (volt)	Measured current (mA)	Metal cathode	Weight of metal cathode before deposit (g)
$CuSO_4. 5 H_2O$	0.04	Yellow	2 2.5 3	1.15 1.60 2.50	Stainless steel	0.0777 0.0751 0.0780
$NiCl_2$	0.08	Pale green	2 2.5 3	1.15 1.25 1.70	Copper	0.0733 0.0762 0.0775
CrO_3	0.1	Green	2 2.5 3	0.35 0.60 0.75	Copper	0.0933 0.0700 0.0820
CrO_3	0.1	Green	2.5 3	0.40 0.60	Nickel	0.0382 0.0385
CrO_3	0.1	Green	3	0.8	Stainless steel	0.0765

2.3.7 Estimation of coating thickness:-

The estimation of thickness of these coated metals on the substrate, the specimens were mounted in a mold and a sufficient amount of powder epoxy resin was added, followed by the addition of the proper currying agent liquid (MEDICLS COLD CURE LIQUID). The resulting liquid was left to solidified and naturally cooled to room temperature. The specimens were, then removed from the mold and the top of each was smoothed by polishing machine. Each specimens was examined by optical microscope (EP type2 DDR) which has a maximum magnification power of (x620) and equipped with light intensity automatic controlled camera. The photos obtained from this camera was further investigated visually and for thickness measurements. Thickness of the plated metal on the substrate. This was carried out by magnifying the photo until suitable measurement can be obtained from the screen of the moniter. The scale shown on the photos was taken as reference scale in each time.

2.3.8 Determination of current efficiency:-

The amount of metal deposited was determined by the weight change (ΔW) observed in the cathode before and after electrolysis. The theoretical amount of metal that can be deposited for the quantity of electricity passed during the experiment was determined using the Faraday`s law:[94]

$$Wm = I \times t \times Am / n\, F \qquad\qquad (2\text{-}2)$$

where Wm is the theoretical amount of metal deposited, the term $I \times t$ (current $\times$ time) is the quantity of electricity supplied, n is the number of electrons transferred in the elementary act of the electrode reaction, Am is the atomic weight of the metal and F is the Faraday constant (96485 Coulombs). Current efficiency (ηeff), which is defined as the ratio of the actual amount of metal deposited to that expected theoretically was calculated by the following equation :[94]

$$\eta eff = \text{Actual amount of metal deposited } (\Delta W) / \text{ Theoretical amount of metal deposited } (Wm) \qquad (2\text{-}3)$$

2.3.9 Determination of spectra:

The solutions were prepared as described in section (2.3.3). And after electrodeposition of metals at room temperature, the quartz cell contained the cooled solution was transferred to the instrumental apartment and the spectra were recorded.

2.3.9.A Orgel diagrams:

Orgel diagrams are useful qualified means for showing the number of spin-allowed absorption bands expected, and their *symmetry state designations*, for *Td* and weak field *Oh* - complexes (d^5 not included). The two diagrams one for $d^{1, 4, 6, 9}$ Figure (2-3) the other for $d^{2, 3, 7, 8}$ Figure (2-4) pack a lot of information in very little space. Nevertheless, there are three major limitations to using Orgel diagrams:

They are restricted to weak field/high spin conditions and offer no information for $d^{4, 5, 6, 7}$ strong fields/ low spin cases. They only show symmetry states of same highest spin multiplicity. They are qualitative; energy values cannot be obtained /calculated from them.[93]
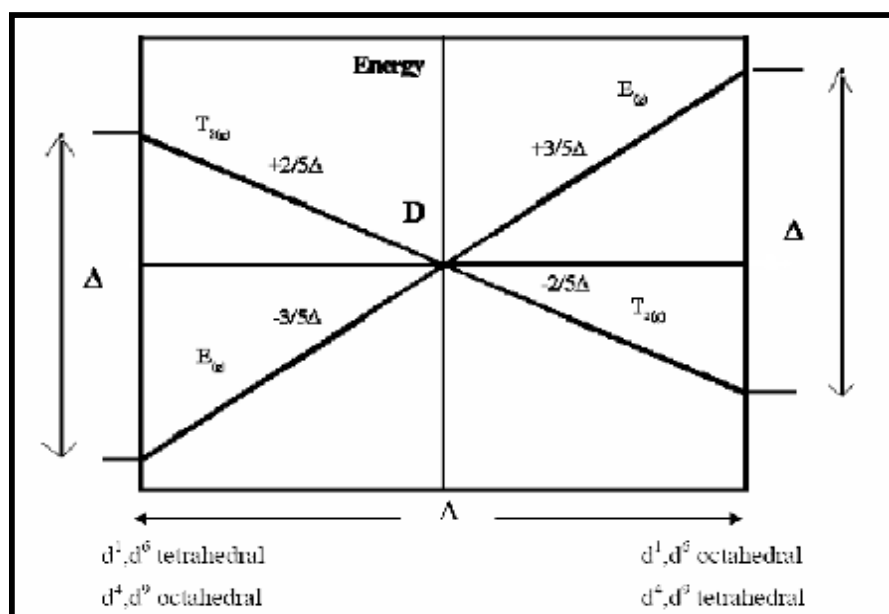
Figure(2-3):- The splitting of free-ion D terms in octahedral and tetrahedral fields[93]
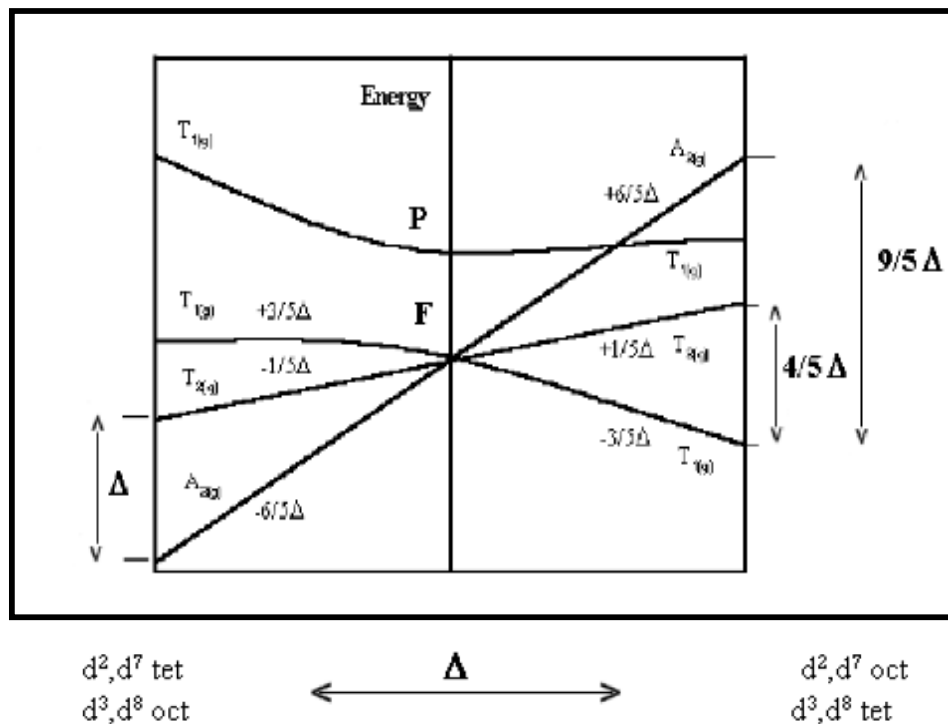
Figure(2-4):- The splitting of free-ion F and P term in octahedral and tetrahedral field. [93]

2.3.9.B Tanabe-Sugano diagrams:

Appear much more "busy" than Orgel diagrams because they contain all terms arising from a configuration, not just terms of highest spin-multiplicity. Appear different than Orgel diagrams because they use the ground symmetry state as a straight-line horizontal base, whereas Orgel diagrams place the parent term in a central location and direct ground symmetry states below it. Appear "split" for d^4, d^5, d^6, d^7, cases because both low and high spin symmetry states are included. Consequently, these diagrams appear to be discontinuous - having two parts separated by a vertical line. The left part pertains to the weak field /high spin condition and the right to strong field/ low spin.

First note why d^1 and d^9 cases have no T-S diagrams. A term description for an atom/ion is more informative than its electron configuration because terms account for e-e repulsion energies. However

there is no e-e repulsion for one "d" electron so the d^1 configuration gives rise to a single term, ^2D. In Oh and Td ligand fields this single term is split into T_2g, Eg, or E, T_2 symmetry states respectively. Only one absorption band is expected and energy of the observed band gives the Δ_o or Δ_{Td} value directly. No calculations are necessary, so no T-S diagram for d^1 (and d^9).[94]

2.3.9.C The molar absorptivity:-

Calculation of the molar absorptivity required the unit of concentration to be in molarity, therefore the determined solubility of the metal oxide and the molar absorptivity was calculated by using Beer's law ($A = \epsilon b c$), Where:-

A = absorbance

ϵ = molar absorpitivity (L cm^{-1} mol^{-1})

b = path length (1 cm)

c = concentration (Mol/ L)

CHAPTER THREE

RESULTS AND DISCUSSION

CHAPTER 3
Results & Discussion

3. *Introduction:*

Ionic liquids are salts that are liquid at ambient temperature. They are powerful solvents, capable of dissolving many different organic and inorganic materials, and work quite differently from conventional solvents, which are composed of molecules rather than ions. Environmental friendliness is an important attraction-ionic liquids are non volatile and so do not pollute the atmosphere. They can replace strong mineral acids and volatile organic solvents for many different applications. It was reported that a colorless, viscous liquid can be formed by mixing choline chloride with d-tartaric acid and the physical properties of this liquid are characteristic of an ionic liquid. The eutectic composition is found to be 1 : 2 choline chloride/d-tartaric acid. The use of this ionic liquid might offer an environmentally friendly process for electrodeposition of metals instead of the currently used aqueous acid based baths.[95]

3.1 Electrolysis in (choline chloride/tartaric acid) ionic liquid:-

3.1.1 Electrolysis of (choline chloride/tartaric acid) ionic liquid alone:-

The electrolysis process of choline chloride/ d-tartaric acid ionic liquid was studied from (0.5 to 5volts) at a temperature range of 25°C to 95°C to establish its stability over the stated conditions. The resulted current densities and current efficiency of this process were deduced and the resulted values were summarized in Table (3-1) and represented in Fig (3-1) and Fig (3-2). These results indicate an increase in current density with

increase the applied voltages at all temperatures. This increase was found to be larger for the high temperature which may be attributed to polarization effect.[96] The small changes in current densities at 25°C and 45°C could also be attributed to the high viscosity the ionic liquid which reduce the mobility of moiety that carrying the charges in ionic liquid. At elevated temperature of 65°C it was noticed that the current density increased markedly at 2.5 volt. This type of changes was also characterized at the reset of applied temperature ranges. Yet with more rate of increasing current density. This changes would expected to increase the electrode reaction rates.[96] The decomposition of ionic liquid was deduced from Fig (3-1) and Fig (3-2) and was found to range from 2 volt at 65°C to 2.5 volt at (75-95°C) with increased rate of electrolysis at the 95°C.

Table (3-1):- Electrolysis of choline chloride /d-tartaric acid ionic liquid alone at (a- 25℃, b- 45℃, c- 65℃, d- 75℃, e- 85℃ and f- 95℃).

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0	0
2	0.01	0.012
2.5	0.01	0.012
3	0.01	0.012
3.5	0.02	0.025
4	0.02	0.025
4.5	0.02	0.025
5	0.03	0.038

a-25℃

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.01	0.012
2	0.01	0.012
2.5	0.01	0.012
3	0.02	0.025
3.5	0.02	0.025
4	0.02	0.025
4.5	0.03	0.038
5	0.03	0.038

b-45℃

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.01	0.012
2	0.02	0.025
2.5	0.06	0.076
3	0.12	0.152
3.5	0.19	0.242
4	0.28	0.356
4.5	0.35	0.445
5	0.42	0.535

c-65℃

voltage	mA	mA\cm²
0.5	0	0
1	0.04	0.050
1.5	0.08	0.101
2	0.12	0.152
2.5	0.2	0.254
3	0.32	0.407
3.5	0.44	0.560
4	0.55	0.700
4.5	0.77	0.980
5	0.8	1.019

d-75℃

voltage	mA	mA\cm²
0.5	0.05	0.063
1	0.099	0.126
1.5	0.18	0.229
2	0.25	0.318
2.5	0.28	0.356
3	0.32	0.407
3.5	0.48	0.611
4	0.63	0.802
4.5	0.80	1.019
5	1.02	1.299

e- 85 ℃

voltage	mA	mA\cm²
0.5	0.004	0.005
1	0.02	0.025
1.5	0.12	0.152
2	0.26	o.331
2.5	0.33	0.420
3	0.67	0.853
3.5	0.94	1.197
4	1.30	1.656
4.5	1.55	1.974
5	1.72	2.191

f- 95℃
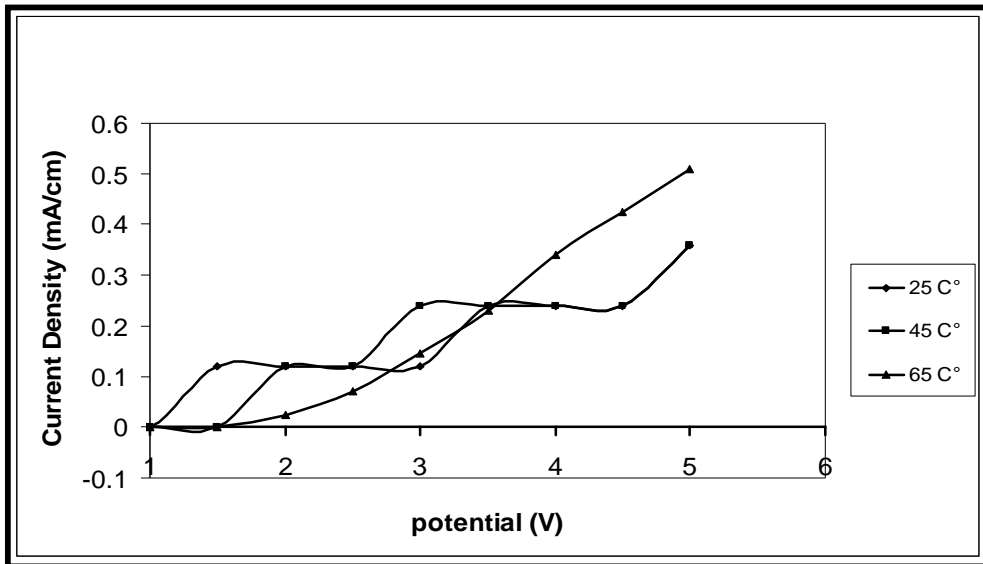
Fig (3-1)Current-voltage curve of choline chloride/d- tartaric acid ionic liquid alone at 25°C, 45 °C and 65 °C.

Fig (3-2)Current-voltage curve of choline chloride/d- tartaric acid ionic liquid alone at 75°C, 85 °C and 95°C.

The conductivity of choline chloride/d-tartaric acid ionic liquid was measured and it is found increasing with increased temperatures at (30°C to 100°C) which may be attributed to viscosity effect it is decrease with increasing temperatures, are represented in Table (3-2) and plotting the measured conductivity with temperatures as in Fig (3-3).

Table(3-2):- Calculated the conductivity of choline chloride/d-tartaric acid ionic liquid alone at (30°C -100°C).

Temperature (°C)	Conductivity (mS/cm)
30	0.02
40	0.055
50	0.073
60	0.099
70	0.109
80	0.120
90	0.130
100	0.140
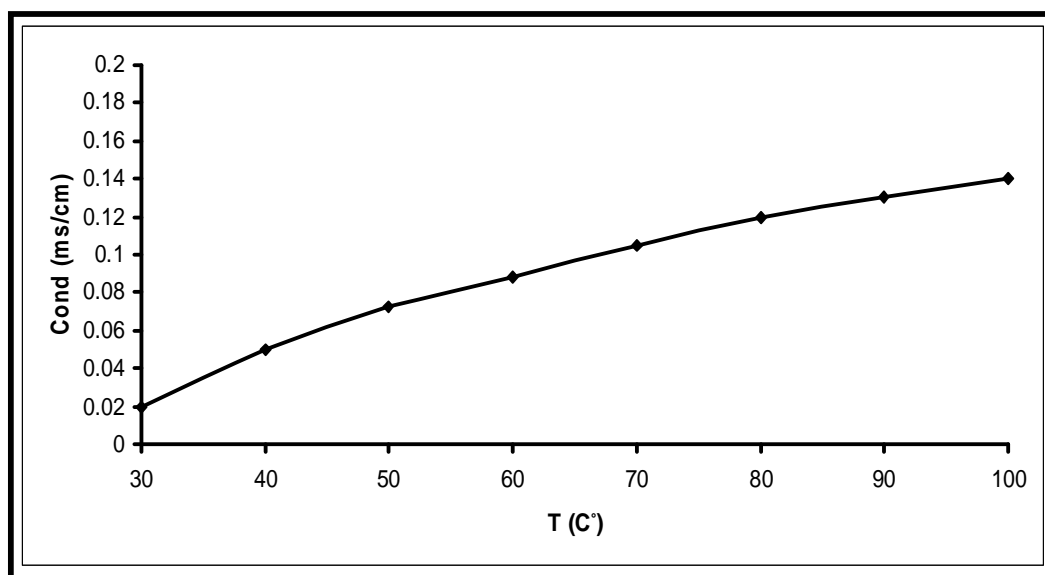
Figure(3-3) Conductivity vs. temperatures of choline chloride/d-tartaric acid ionic liquid alone at (30°C -100°C).

3.1.2 *Electrolysis of transition metals solution in choline chloride/d-tartaric acid ionic liquid:*

3.1.2.1 *Electrolysis of $CuSO_4.5H_2O$ in choline chloride/ d-tartaric acid ionic liquid:-*

The results of the electrolysis of $CuSO_4.5H_2O$ in choline chloride/d-tartaric acid ionic liquid at (25, 45, 56, 75, 85and 95°C) with a variable applied voltages of (0.5 to 5 volts) with 0.5 volt increments are presented Table (3-3) and plotting the measured current density with voltages as in Fig (3-4) and Fig (3-5).

As with choline chloride/d-tartaric acid ionic liquid alone, the changes in current density found to be small at low temperature of 25°C and 45°C but producing a much smoother curve than in ionic liquid alone compare Fig (3-1) and Fig (3-2). The latter could be attributed to the more ions mobility in the solution due to the soluble $CuSO_4.5H_2O$ and also to the less viscose solution produced. Which positively in hence the mobility of the ions.

Again as with ionic liquid alone at 65°C and 2.5 volt this solution showed a noticeable increasing in current density but much more than in ionic liquid alone which could also be related to the above reason, also, with the influence of the increased temperature too Fig (3-4).

Table (3-3):- Electrolysis of CuSO4.5H2O in choline chloride /d-tartaric acid ionic liquid at (a- 25℃, b- 45℃, c- 65℃, d- 75℃, e- 85℃ and f- 95℃).

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.011	0.014
2	0.016	0.020
2.5	0.021	0.026
3	0.029	0.036
3.5	0.039	0.049
4	0.049	0.062
4.5	0.075	0.095
5	0.105	0.133

ش

a- 25 ℃

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.020	0.025
2	0.035	0.044
2.5	0.064	0.081
3	0.090	0.114
3.5	0.120	0.152
4	0.170	0.216
4.5	0.230	0.292
5	0.301	0.383

b- 45 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.02	0.025
1.5	0.03	0.038
2	0.05	0.063
2.5	0.10	0.127
3	0.19	0.242
3.5	0.30	0.382
4	0.42	0.535
4.5	0.58	0.738
5	0.71	0.904

c- 65 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.02	0.025
1.5	0.05	0.063
2	0.09	0.114
2.5	0.17	0.216
3	0.30	0.382
3.5	0.42	0.535
4	0.55	0.700
4.5	0.70	0.891
5	0.85	1.082

d- 75 ℃

voltage	mA	mA\cm²
0.5	0.02	0.025
1	0.04	0.050
1.5	0.07	0.089
2	0.13	0.165
2.5	0.26	0.331
3	0.46	0.585
3.5	0.65	0.828
4	0.84	1.070
4.5	1.05	1.337
5	1.22	1.554

e- 85 ℃

| voltage	mA	mA\cm²
0.5	0.02	0.025
1	0.04	0.050
1.5	0.10	0.127
2	0.20	0.242
2.5	0.40	0.509
3	0.65	0.828
3.5	1	1.273
4	1.3	1.656
4.5	1.62	2.063
5	2	2.547

f- 95 ℃
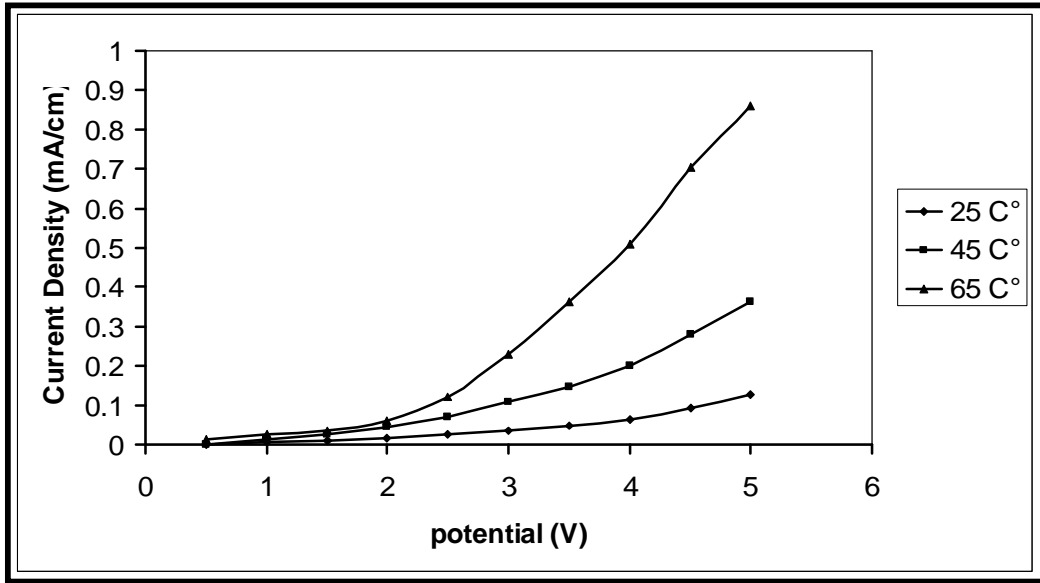
Fig (3-4)Current-voltage curve of CuSO₄.5H₂O in choline chloride/d- tartaric acid
ionic liquid at 25°C, 45 °C and 65 °C.
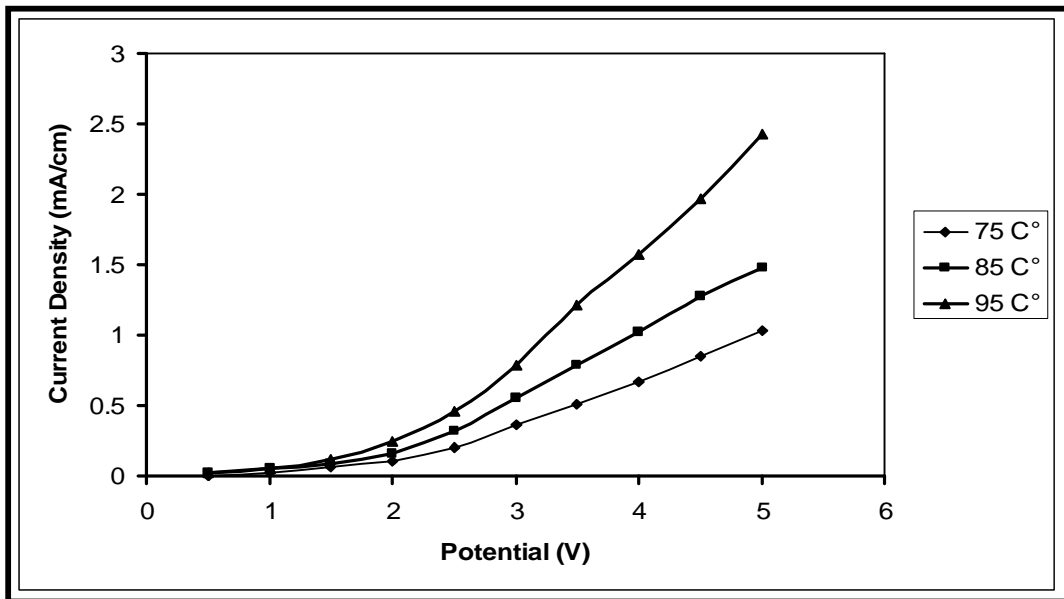
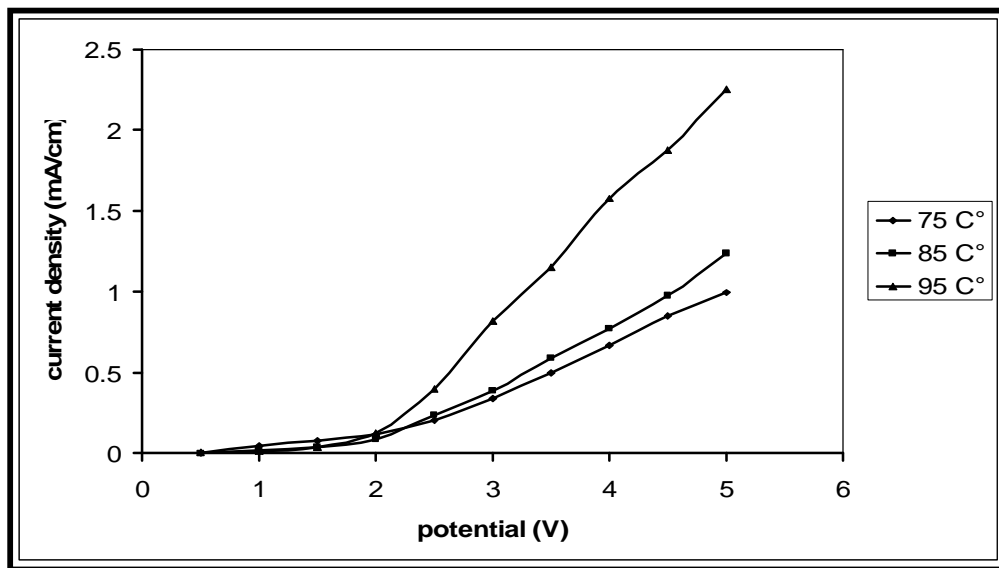*Fig (3-5)Current-voltage curve of CuSO₄.5H₂O in choline chloride/d- tartaric acid*
ionic liquid at 75°C, 85 °C and 95°C.

The conductivity of $CuSO_4.5H_2O$ solution in ionic liquid was found to be increased markedly with temperatures in Table (3-4), and when comparison with those of ionic liquid alone represented in Fig (3-6). This might be related to the presence of $CuSO_4$ ions. The conductivity increase with the acidity of the melt. The higher conductivity is attributed to a decrease in the viscosity of the melt and the increased percentage of Cu^{+2} ions and possibly a lower degree of ion pairing between the $CuSO_4$ in choline chloride/d-tartaric acid ionic liquid as compared to the choline chloride/d-tartaric acid ionic liquid alone.[98]

Table(3-4):- Calculated the conductivity of CuSO4.5H2O solution in choline chloride/d-tartaric acid ionic liquid at (30℃ -100℃).

Temperature (°C)	Conductivity (mS/cm)
30	0.08
40	0.28
50	0.60
60	0.88
70	1.20
80	1.56
90	1.90
100	2.25
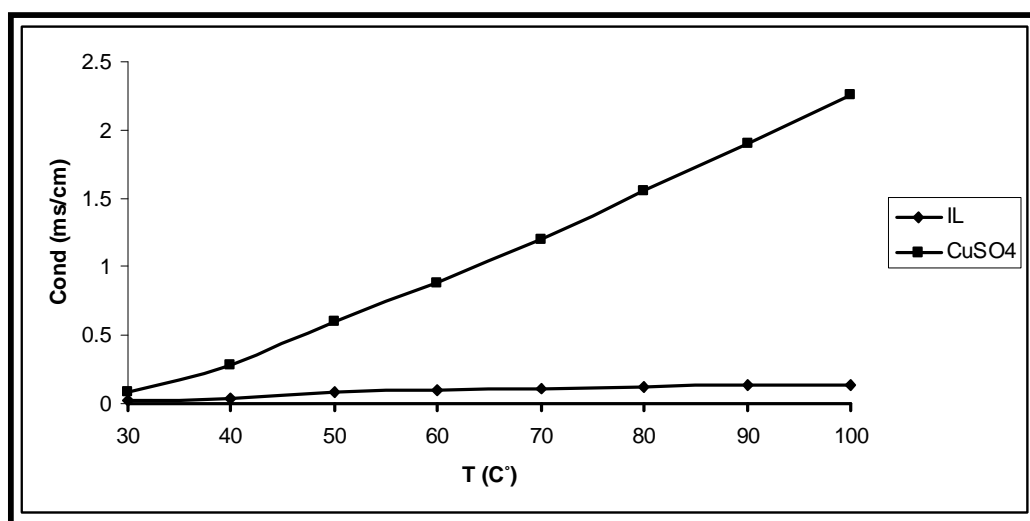
Figure(3-6) Conductivity vs. temperatures of choline chloride/d-tartaric acid ionic liquid alone and for CuSO4.5H2O solution in choline chloride/d-tartaric acid ionic liquid at 30℃ to 100℃.

3.1.2.2 *Electrolysis of NiCl$_2$ in choline chloride/ d-tartaric acid ionic liquid:-*

The results of the electrolysis of NiCl$_2$ in choline chloride/d-tartaric acid ionic liquid at (25, 45, 56, 75, 85and 95°C) with a variable applied voltages of (0.5 to 5 volts) with 0.5 volt increments are presented Table (3-5) and plotting the measured current density with voltages as in Fig (3-7) and Fig (3-8).

As with choline chloride/d-tartaric acid ionic liquid alone, the changes in current density found to be small at low temperature of 25°C and 45°C but producing a much smoother curve than in ionic liquid alone compare Fig (3-1) and Fig (3-2). The latter could be attributed to the more ions mobility in the solution due to the soluble NiCl$_2$ and also to the less viscose solution produced. Which positively in hence the mobility of the ions.

Again as with ionic liquid alone at 65°C and (1) volt this solution showed a noticeable increasing in current density but much more than in ionic liquid alone which could also be related to the above reason, also, with the influence of the increased temperature too Fig (3-7).

Table (3-5):- Electrolysis of NiCl₂ in choline chloride /d-tartaric acid ionic liquid at (a- 25℃, b- 45℃, c- 65℃, d- 75℃, e- 85a℃ and f- 95℃).

voltage	mA	mA\cm²
0.5	0	0
1	0.01	0.012
1.5	0.01	0.012
2	0.02	0.025
2.5	0.03	0.038
3	0.04	0.050
3.5	0.04	0.050
4	0.05	0.063
4.5	0.06	0.076
5	0.06	0.076

a- 25 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.02	0.025
1.5	0.04	0.050
2	0.04	0.050
2.5	0.05	0.063
3	0.08	0.101
3.5	0.10	0.127
4	0.12	0.152
4.5	0.15	0.191
5	0.18	0.229

b- 45 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.04	0.050
1.5	0.07	0.089
2	0.10	0.127
2.5	0.12	0.152
3	0.16	0.203
3.5	0.20	0.254
4	0.28	0.356
4.5	0.35	0.445
5	0.46	0.585

c- 65 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.05	0.063
1.5	0.07	0.089
2	0.10	0.127
2.5	0.17	0.216
3	0.27	0.343
3.5	0.39	0.496
4	0.50	0.636
4.5	0.63	0.802
5	0.75	0.955

d- 75 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.05	0.063
1.5	0.08	0.101
2	0.14	0.178
2.5	0.24	0.305
3	0.39	0.496
3.5	0.55	0.700
4	0.70	0.891
4.5	0.88	1.121
5	1.05	1.337

e- 85 ℃

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.05	0.063
1.5	0.09	0.114
2	0.16	0.203
2.5	0.25	0.318
3	0.45	0.573
3.5	0.55	0.700
4	0.80	1.01
4.5	1	1.273
5	1.20	1.528

f- 95 ℃

Fig (3-7)Current-voltage curve of NiCl$_2$ in choline chloride/d- tartaric acid ionic liquid at 25°C, 45 °C and 65 °C.

Fig (3-8)Current-voltage curve of NiCl$_2$ in choline chloride/d- tartaric acid ionic liquid at 75°C, 85 °C and 95°C.

The conductivity of NiCl$_2$ solution in ionic liquid was found to be increased markedly with temperatures in Table (3-6), and when comparison with those of ionic liquid alone represented in Fig (3-9). This might be related to the presence of NiCl$_2$ ions. The conductivity increase with the acidity of the melt. The higher conductivity is attributed to a decrease in the viscosity of the melt and the increased percentage of Ni^{+2} ions and possibly a lower degree of ion pairing between the NiCl$_2$ in choline chloride/d-tartaric acid ionic liquid as compared to the choline chloride/d-tartaric acid ionic liquid alone.[98]

Table(3-6):- Calculated the conductivity of NiCl$_2$ solution in choline chloride/d-tartaric acid ionic liquid at (30℃ -100℃).

Temperature °C	Conductivity (mS/cm)
30	0.03
40	0.10
50	0.17
60	0.25
70	0.33
80	0.40
90	0.48
100	0.60
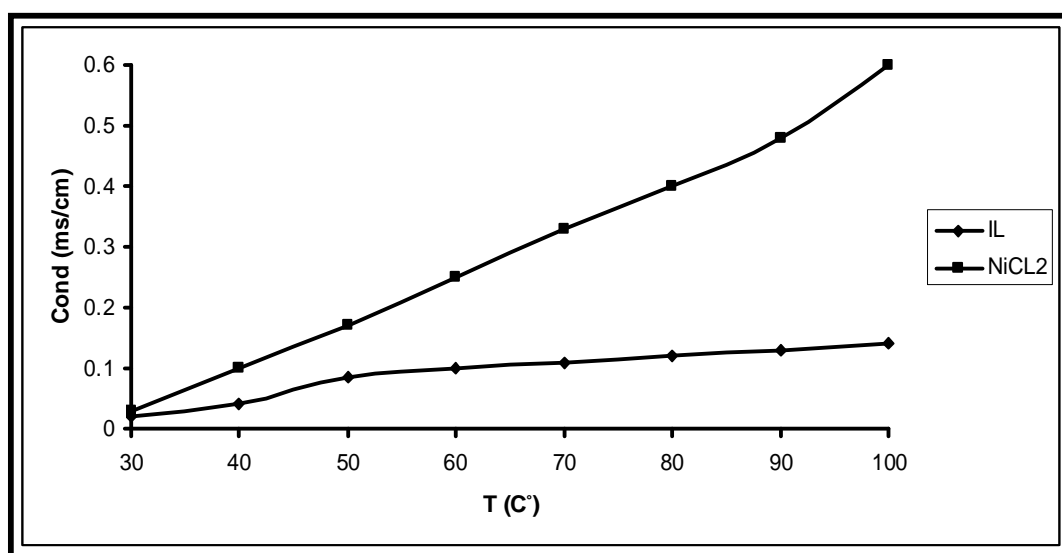
Figure(3-9) Conductivity vs. temperatures of choline chloride/d-tartaric acid ionic liquid alone and of NiCl$_2$ solution in choline chloride/d-tartaric acid ionic liquid at 30℃ to 100℃.

3.1.2.3 *Electrolysis of CrO₃ in choline chloride/ d-tartaric acid ionic liquid:-*

The results of the electrolysis of CrO_3 in choline chloride/d-tartaric acid ionic liquid at (25, 45, 56, 75, 85and 95°C) with a variable applied voltages of (0.5 to 5 volts) with 0.5 volt increments are presented Table (3-7) and plotting the measured current density with voltages as in Fig (3-10) and Fig (3-11).

As with choline chloride/d-tartaric acid ionic liquid alone, the changes in current density found to be small at low temperature of 25°C and 45°C but producing a much smoother curve than in ionic liquid alone compare Fig (3-1) and Fig (3-2). The latter could be attributed to the more ions mobility in the solution due to the soluble CrO_3 and also to the less viscose solution produced. Which positively in hence the mobility of the ions.

Again as with ionic liquid alone at 65°C and (2.5) volt this solution showed a noticeable increasing in current density but much more than in ionic liquid alone which could also be related to the above reason, also, with the influence of the increased temperature too Fig (3-10).

Table (3-7):- Electrolysis of CrO3 in choline chloride /d-tartaric acid ionic liquid at (a- 25℃, b- 45℃, c- 65℃, d- 75℃, e- 85℃ and f- 95℃).

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.01	0.012
2	0.01	0.012
2.5	0.01	0.012
3	0.01	0.012
3.5	0.02	0.025
4	0.02	0.025
4.5	0.02	0.025
5	0.02	0.025

voltage	mA	mA\cm²
0.5	0	0
1	0	0
1.5	0.02	0.025
2	0.04	0.05
2.5	0.05	0.063
3	0.07	0.089
3.5	0.08	0.101
4	0.1	0.127
4.5	0.13	0.165
5	0.15	0.191

a- 25 ℃   ***b- 45 ℃***

voltage	mA	mA\cm²
0.5	0	0
1	0.03	0.038
1.5	0.05	0.063
2	0.08	0.01
2.5	0.1	0.127
3	0.13	0.165
3.5	0.16	0.20
4	0.20	0.254
4.5	0.24	0.305
5	0.36	0.458

voltage	mA	mA\cm²
0.5	0	0
1	0.03	0.038
1.5	0.06	0.076
2	0.08	0.101
2.5	0.1	0.127
3	0.15	0.191
3.5	0.20	0.254
4	0.25	0.318
4.5	0.30	0.382
5	0.38	0.484

c- 65 ℃   ***d- 75 ℃***

voltage	mA	mA\cm²
0.5	0	0
1	0.03	0.038
1.5	0.06	0.076
2	0.08	0.101
2.5	0.12	0.152
3	0.22	0.280
3.5	0.34	0.433
4	0.45	0.576
4.5	0.65	0.828
5	0.80	1.019

voltage	mA	mA\cm²
0.5	0.01	0.012
1	0.04	0.050
1.5	0.06	0.076
2	0.1	0.127
2.5	0.2	0.254
3	0.35	0.445
3.5	0.50	0.636
4	0.75	0.955
4.5	1.05	1.337
5	1.30	1.656

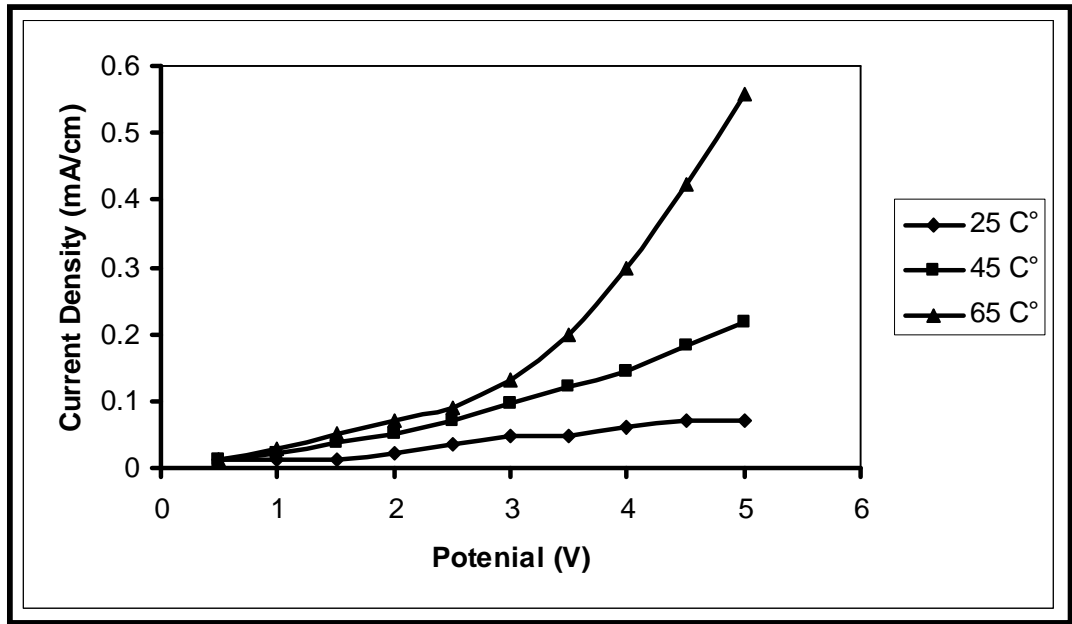***e- 85 ℃***   ***f- 95 ℃***
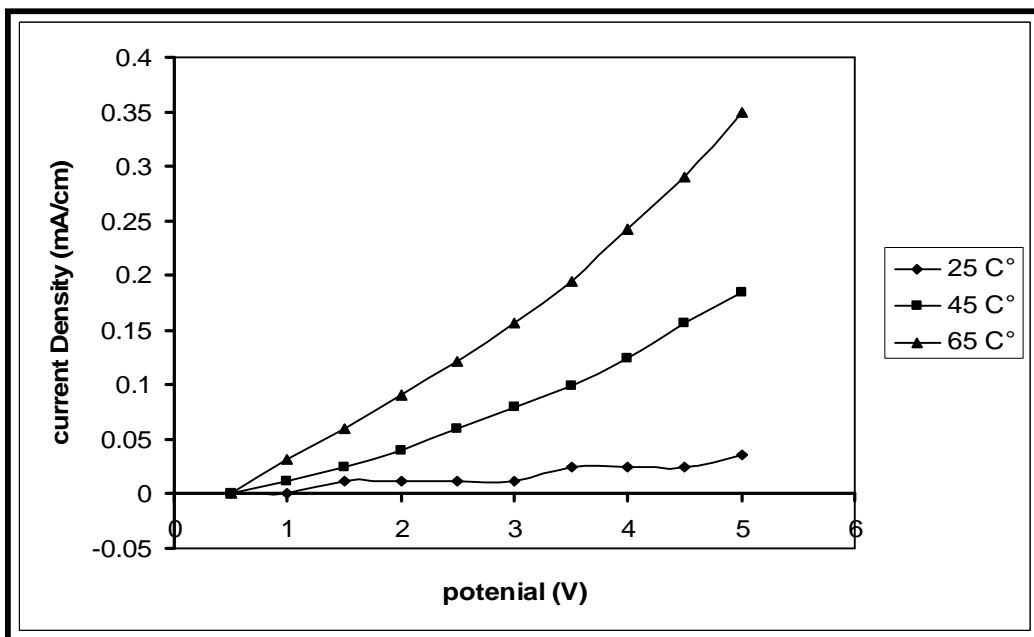
Fig (3-10)Current-voltage curve of CrO₃ in choline chloride/d- tartaric acid ionic liquid at 25°C, 45 °C and 65 °C.
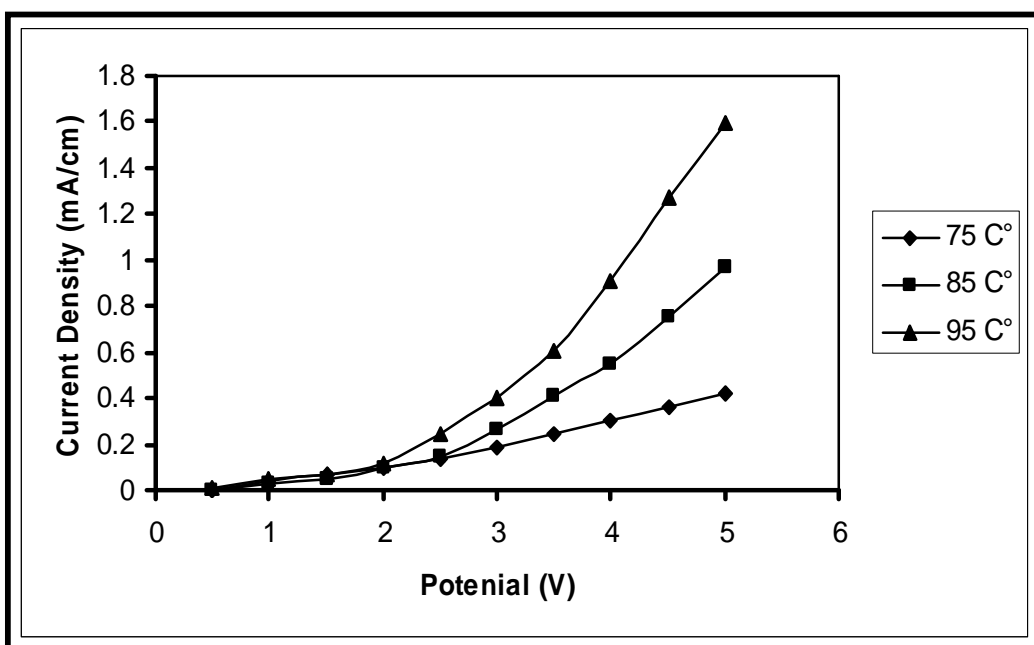
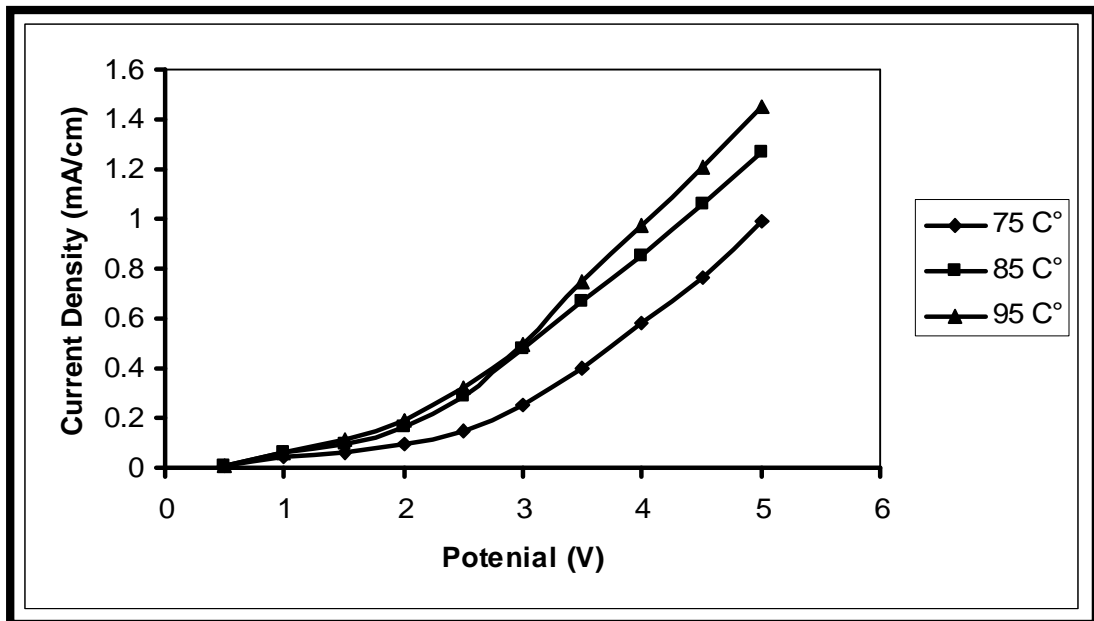*Fig (3-11)Current-voltage curve of CrO₃ in choline chloride/d- tartaric acid ionic liquid at 75°C, 85 °C and 95°C.*

The chromium (VI) oxide solution in ionic liquid showed a very small changes in conductivity in comparison with those of ionic liquid alone from 30 to 60°C. However at 60°C the conductivity showed noticeable increase Table (3-8). This was associated with a visual changes the color of the solution as it changed from green to deep green color. The ultraviolet visible investigation of the solution is represented in section (3.3.3) that indicate a redaction of chromium (VI) to chromium (III). At 60 °C to 100°C the conductivity of CrO_3 solution in ionic liquid was found to be increased markedly with temperatures in Table (3-8), and when comparison with those of ionic liquid alone represented in Fig (3-12). This might be related to the presence of CrO_3 ions. The conductivity increase with the acidity of the melt. The higher conductivity is attributed to a decrease in the viscosity of the melt and the increased percentage of Cr^{+3} ions and possibly a lower degree of ion pairing between the CrO_3 in choline chloride/d-tartaric acid ionic liquid as compared to the choline chloride/d-tartaric acid ionic liquid alone.[98]

Table(3-8):- Calculated the conductivity of CrO3 solution in choline chloride/d-tartaric acid ionic liquid at (30℃ -100℃).

Temperature °C	Conductivity (ms/cm)
30	0.01
40	0.04
50	0.082
60	0.125
70	0.170
80	0.220
90	0.270
100	0.330
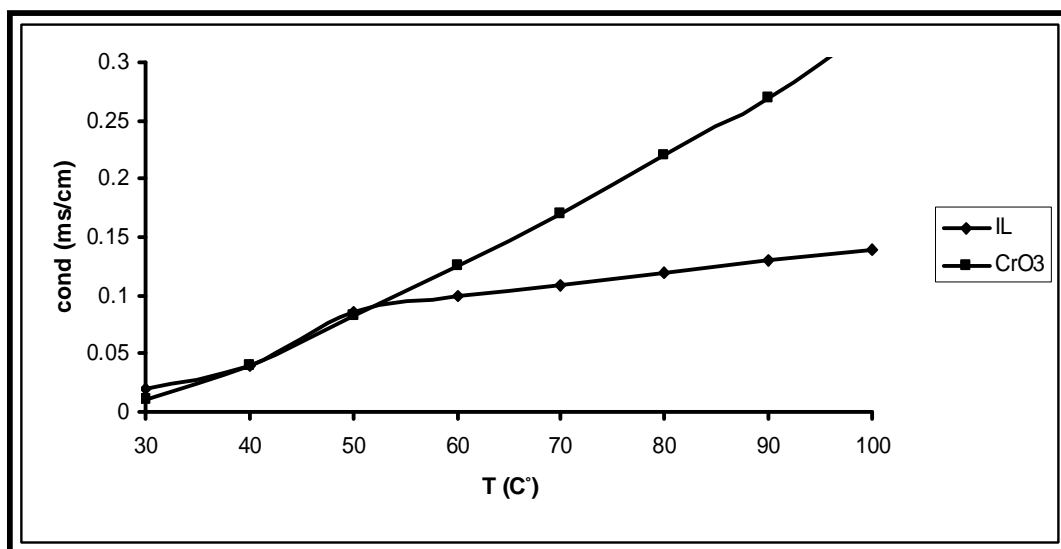
Figure(3-12) Conductivity vs. temperatures of choline chloride/d-tartaric acid ionic liquid alone and of CrO₃ solution in choline chloride/d-tartaric acid ionic liquid at 30°C to 100°C.

3.2 *Electro deposition of (copper, nickel, and chromium) in choline chloride/d-tartaric ionic liquid at 85°C:-*

The electro deposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V, but ionic liquids have significantly larger electrochemical windows, e.g., 4.15 V for [BMIm]PF₆ at a platinum electrode,[99] 4.10 V for [BMIm]BF₄ [99] and 5.5 V for [BMP]Tf₂N at a glassy carbon electrode.[100] This wide electrochemical widows of ionic liquids have opened the door to electrodeposit metals at room temperature which were formerly obtained only from high temperature molten salt For example, Al, Mg, Si, Ge, and rare earth elements can be obtained from room temperature ionic liquids. The thermal stability of ionic liquids allows to electrodeposit Ta, Nb, V, Se and presumably many other ones at elevated temperature.[100] This induced the aspect of investigations of electrodeposition in the newly prepared ionic liquids such as choline chloride/d-tartaric acid ionic liquid[101] of some metals such as copper, nickel, and chromium.

3.2.1 Electro deposition of copper on the stainless steel plate in choline chloride/d-tartaric acid ionic liquid at 85℃:-

The electrodeposition of copper on stainless steel was carried out at 85°C and an applied voltages of (2, 2.5, and 3 volts) in an electrolyte solution of (0.04 M) of $CuSO_4.5H_2O$ in choline chloride/d-tartaric acid ionic liquid. This electrodeposition was carried out for one hour at each applied voltages when the current out put was recorded and the resulted current density with the deposited weight of copper on stainless steel are shown in Table(3-9).   This weight was obtained from the differences between the weight of the stainless steel cathode before and after the one hour deposition time. In addition, it was observed that the electrolyte produced a tiny bubbles at the cathode electrode only when potential was applied, and the rate of their production increased with increasing the potential. These bubbles could be attributed the reduction of hydrogen ion that was produced possibly from tartaric acid (as the ionic liquid is normally acidic) at the cathode producing hydrogen gas. In addition, the absence of such bubbles at the anode which is expected to oxidize chloride ion in to chlorine gas, might be a rise from the formation of trichloride ion that was soluble in the ionic liquid solution.[70]

$$Cl^- + Cl_2 \rightarrow Cl_3 \qquad\qquad\qquad\qquad (3-1)$$

Table (3-12) shows that the weight of deposited copper on the stainless steel electrode increases with increasing applied voltages which in turn also increase the current density as is shown in Fig (3-13) which could be related to the polarization. Moreover the increase in voltage caused an increase in the rate of discharge (reduction) at the cathode that was noticeable for the increase production of bubbles which was related to the increase reduction of hydrogen ion too. The optical micrograph of the cross section view of copper deposited on stainless steel cathode, showed deposits thickness varied for 3 μm to 2 V, 4.5 μm to 2.5 V, and 6 μm to 3

ᴠ. The value of thickness is found to increase with increasing applied voltage at (85C°) and one hour time, shows that in Table(3-9), and represented in Figure(3-14). The current efficiency of the deposition of copper on stainless steel are listed in Table (3-9). The current efficiency was found to be less than 50% of the applied current to deposited copper metal on the cathode. This is possibly due to their reduction of hydrogen cation in the solution as was mentioned earlier that the electrolyte produced a colorless bubbles at the cathode. Which consumed the rest of the power. In addition, the small value of the current density might also attributed to the loss of some of the sample during cleaning especially if the deposition was dendritic as was reported by other workers.[102]

Table(3-9):- Applied voltages, current density, current efficiency and the weight and thickness deposited copper on stainless steel from CuSO₄.5H₂O in choline chloride/d-tartaric acid ionic liquid at 85°C and one hour time

Applied (voltages)	Current density(mA/cm^2)	Weight of copper deposit on stainless steel (mg)	Thickness of copper on stainless steel (µm)	Current efficiency (%)
2	1.15	0.3	3	48
2.5	1.6	0.4	4.5	46
3	2.5	0.6	6	44
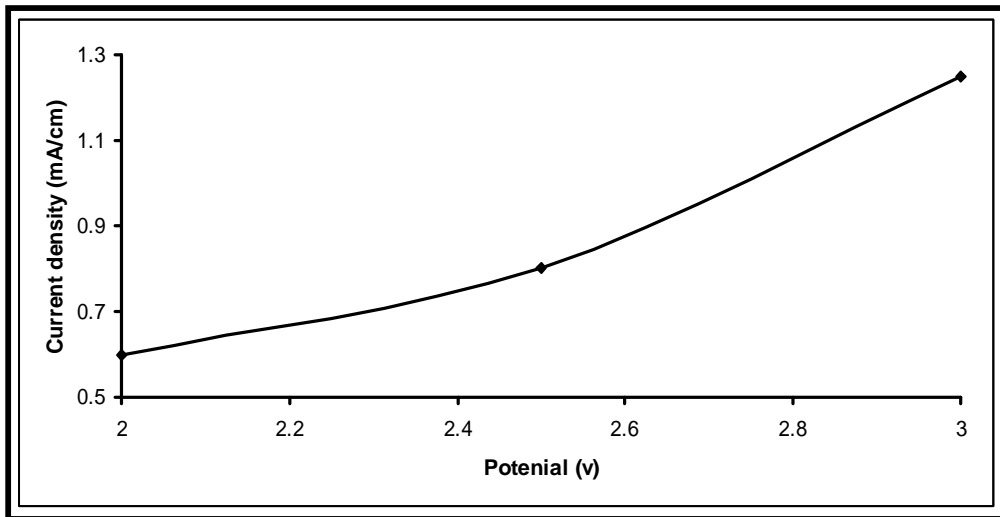
Figure (3-13) Current-voltage curve of electrodepositing of copper on stainless steel at (2,2.5,and 3volts) and 85℃.
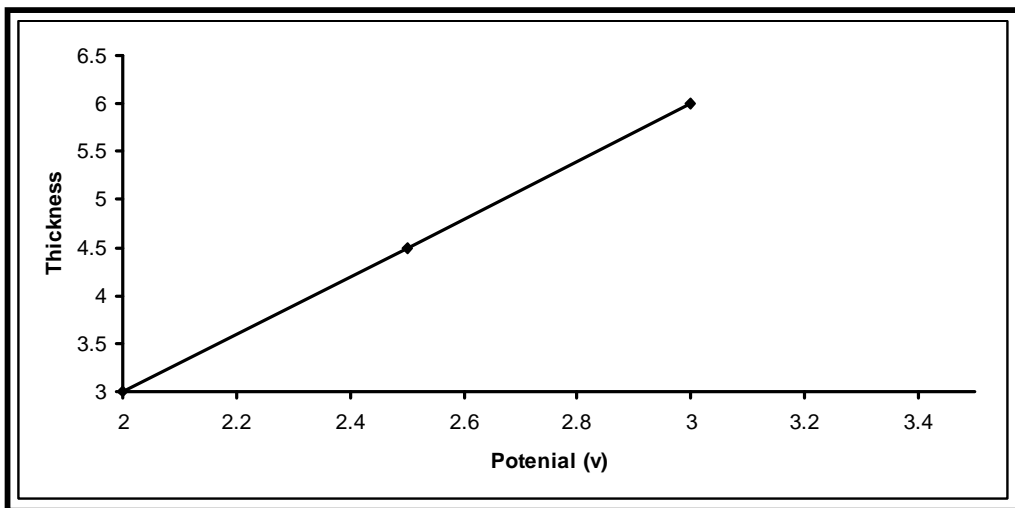
Figure (3-14) Thickness vs. potential of deposited copper on stainless steel in ionic liquid at (2,2.5,and 3volts) and 85℃.

3.2.1.1 *Morphology of copper deposited* on stainless steel:-

The optical micrograph image of copper on stainless steel at the applied voltages of (2, 2.5, and 3 volts) are represented in Fig (3-15). It can be noticed that the amount of deposited copper on stainless steel is increased with voltages as can be deduced from the density of deposited metal on the substrate (compare image a, b , and c). This shape of the deposited copper was found to have irregular spherical shape however the deposition seem not to have a homogeneous layer on the substrate which normally caused by the insufficient mixing of the solution or in case the viscose nature of the ionic liquid. The latter characterization required more vigorous mixing than in the aqueous solutions. However, the irregularity of deposition was less when the amount of deposited copper increased at 3 volt.

To determine the thickness of the deposited layer on the substrate another sample was prepared as mentioned in Fig (3-16). The deduced thickness Table (3-9) revealed that the highest thickness obtained was when the applied voltages was 3 volt, though all other conditions were similar. This increase can be explained as the current is normally increases with voltage, resulted in more deposited copper on substrate.

In addition, it can be noticed that the deposited copper filled all the surface of the substrate, although the surface of the latter was rough surface. This would be an advantages in the practical application of the process for mending pitted or eroded metal surfaces. The irregular surfaces of the specimens are a raised from the rough smoothing technique, however, the more irregular parts of image (b) of Fig (3-16) might occur during the necessary smoothing process of prepared specimens before taking an image for thickness measurements.
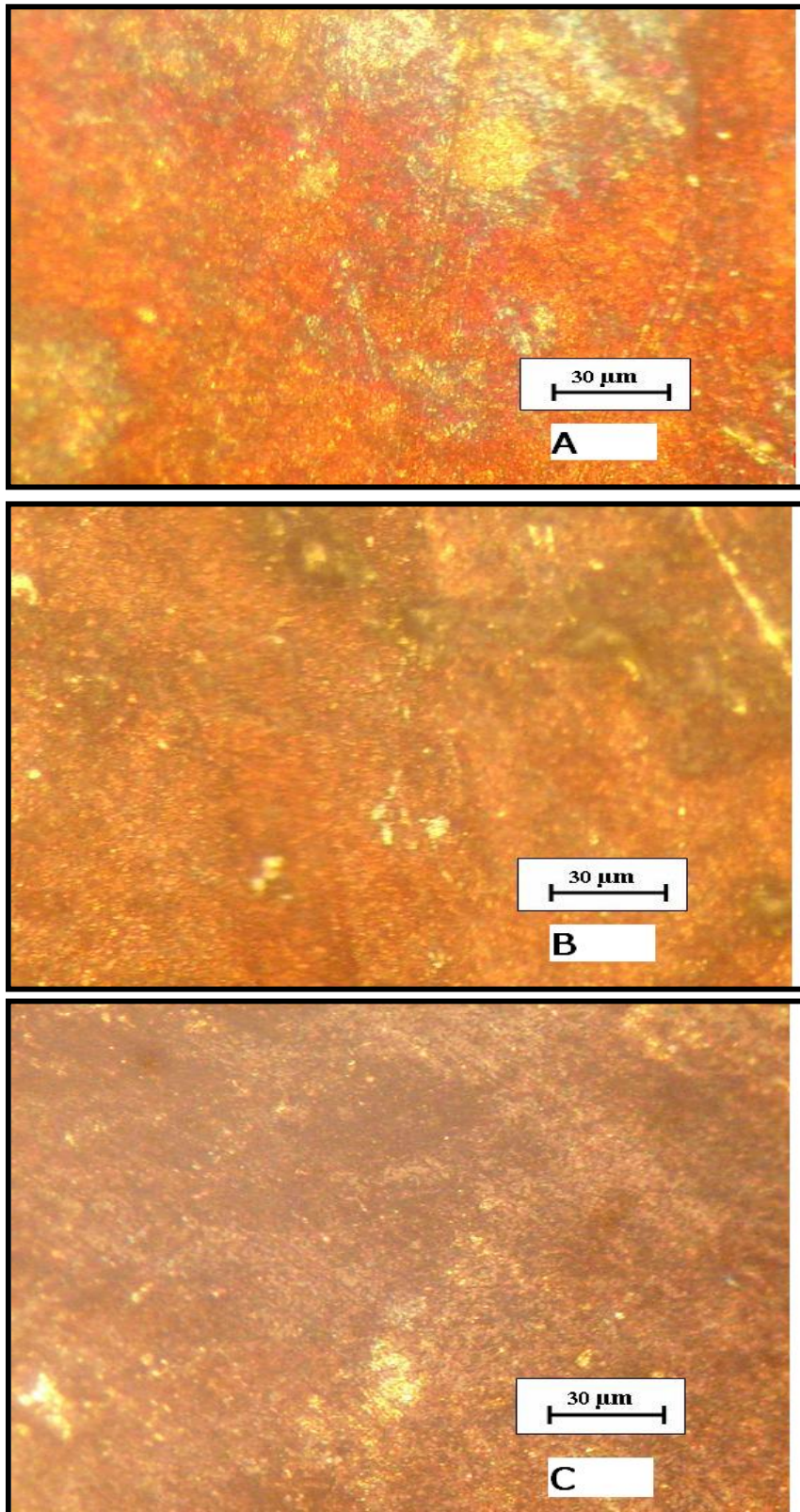
Figure (3-15) Electron micrographs of coated copper on stainless steel plate from 0.04 mole/l of CuSO4.5H2O in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2, (B)2.5, and(C)3 applied voltages.
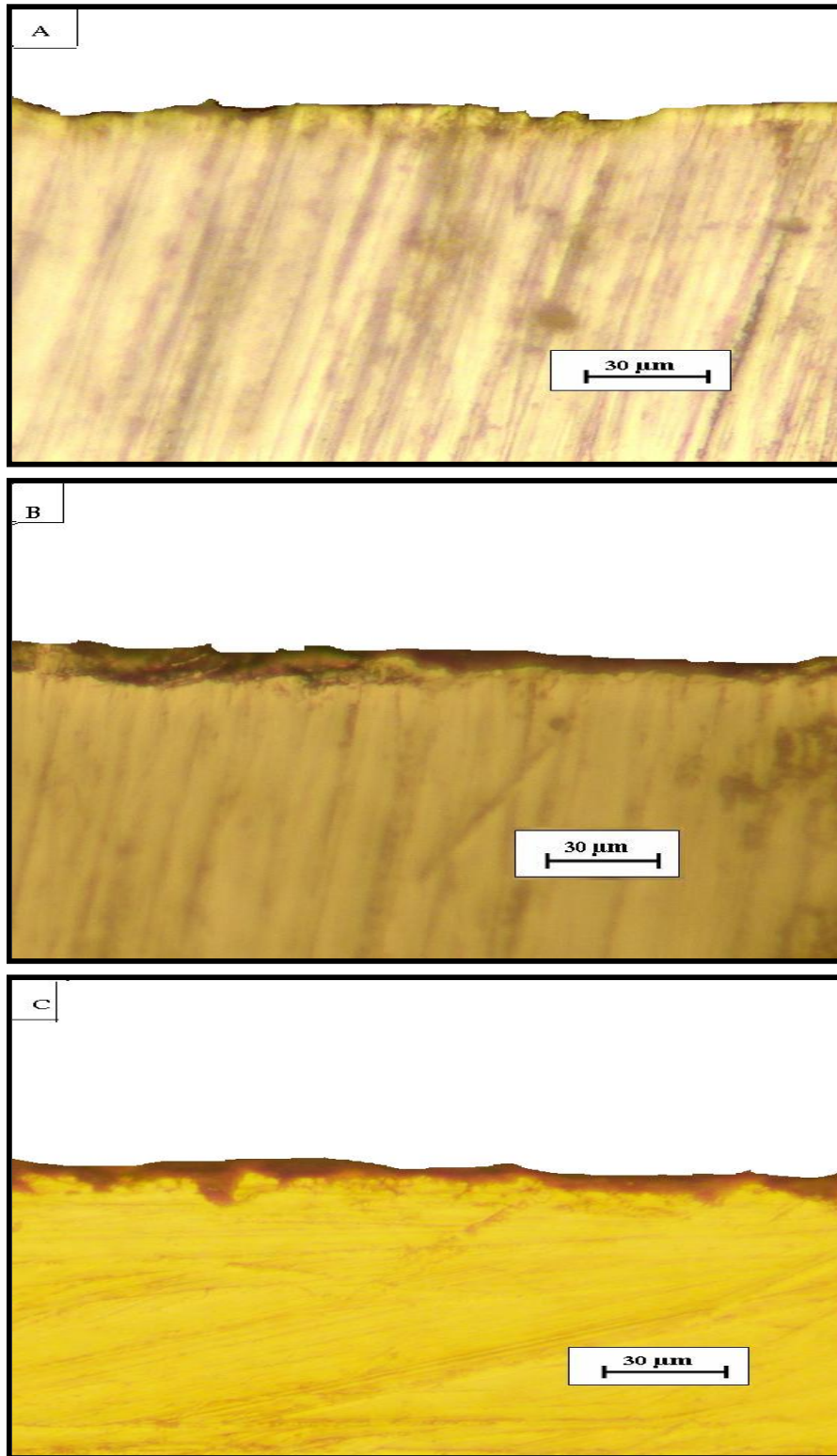
Figure (3-16) Cross sectioned electron images of copper coated on stainless steel plate from 0.04 mole/l of CuSO₄.5H₂O in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2, (B)2.5, and(C)3 applied voltages.

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3.2.2 Electro deposition of nickel on the copper plate in choline chloride/d-tartaric acid ionic liquid at 85°C:-

The electrodeposition of nickel on copper was carried out at 85°C and an applied voltages of (2, 2.5, and 3 volts) in an electrolyte solution of (0.08 M) of $NiCl_2$ in choline chloride/d-tartaric acid ionic liquid. This electrodeposition was during for one hour at each applied voltages when the current out put was recorded and the resulted current density with the deposited weight of nickel on copper are shown in Table(3-10). This weight was obtained from the differences between the weight of the copper cathode before and after the one hour deposition time. In addition, it was observed that the electrolyte produced a tiny bubbles at the cathode electrode only when potential was applied, and the rate of their production increased with increasing the potential. This bubbles appear it was less than from bubbles in copper deposited. These bubbles could be attributed the reduction of hydrogen ion that was produced possibly from tartaric acid (as the ionic liquid is normally acidic) at the cathode producing hydrogen gas. In addition, the absence of such bubbles at the anode which is expected to oxidize chloride ion in to chlorine gas, might be a rise from the formation of trichloride ion that was soluble in the ionic liquid solution.[70]

$$Cl^- + Cl_2 \rightarrow Cl_3 \qquad\qquad\qquad (3\text{-}2)$$

Table (3-10) shows that the weight of deposited nickel on the copper electrode increases with increasing applied voltages which in turn also increase the current density as is shown in Fig (3-17) which could be related to the polarization. Moreover the increase in voltage caused an increase in the rate of discharge (reduction) at the cathode that was noticeable for the increase production of bubbles which was related to the increase reduction of hydrogen ion too. The optical micrograph of the

cross section view of nickel deposited on copper cathode, showed deposits thickness varied for 2.4 μm to 2 V, 3 μm to 2.5 V, and 4.5 μm to 3 V. The value of thickness is found to increase with increasing applied voltage at $(85C^{\circ})$ and one hour time, shows that in Table(3-10), and represented in Figure(3-18). The current efficiency of the deposition of nickel on copper are listed in Table (3-10). The current efficiency was found to be less than 50% of the applied current to deposited nickel metal on the cathode. This is possibly due to their reduction of hydrogen cation in the solution as was mentioned earlier that the electrolyte produced a colorless bubbles at the cathode. Which consumed the rest of the power. In addition, the small value of the current density might also attributed to the loss of some of the sample during cleaning especially if the deposition was dendritic as was reported by other workers.[102]

Table(3-10):- Applied voltages, current density, current efficiency and the weight and thickness deposited nickel on copper from NiCl2 in choline chloride/d-tartaric acid ionic liquid at 85℃ and one hour time.

Applied (voltages)	Current density(mA/cm^2)	Weight of nickel deposit on copper (mg)	Thickness of nickel on copper (μm)	Current efficiency (%)
2	0.57	0.2	2.4	49
2.5	0.62	0.3	3	46
3	0.85	0.4	4.5	45
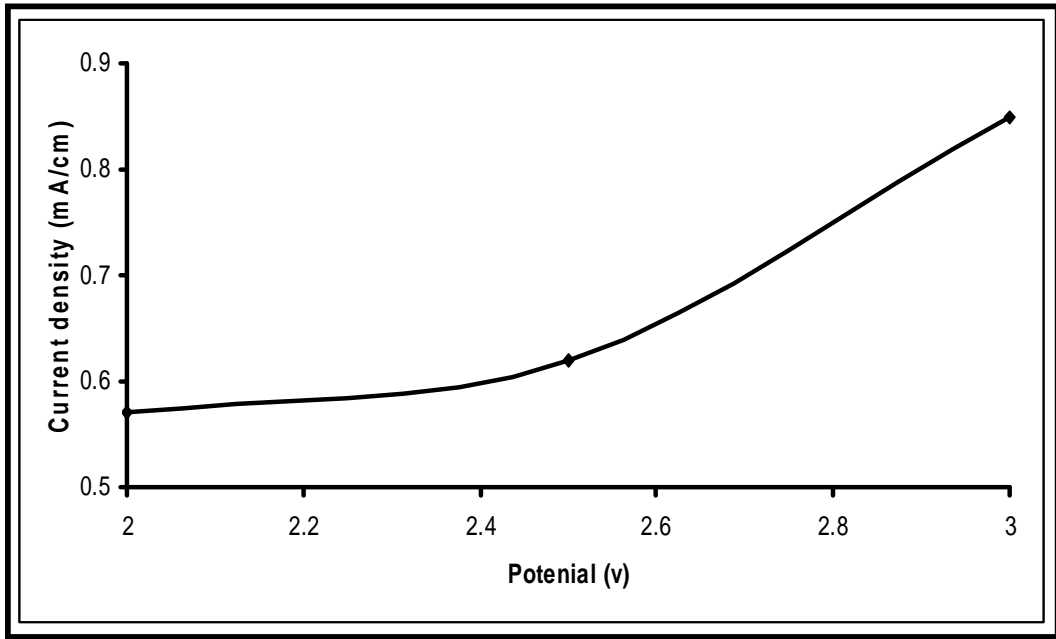
Figure (3-17) Current-voltage curve of electrodepositing of nickel on copper at (2,2.5,and 3volts) and 85°C.
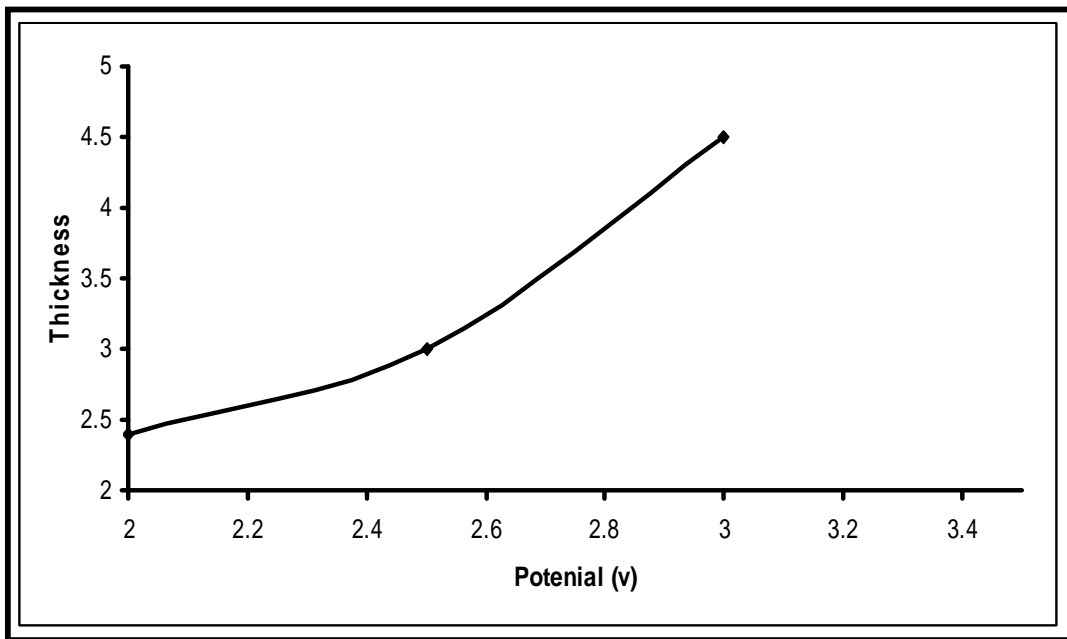
Figure (3-18) Thickness vs. potential of deposited nickel on copper in ionic liquid at (2,2.5,and 3volts) and 85°C

3.2.2.1 Morphology of nickel deposited on copper:-

The optical micrograph image of nickel on copper at the applied voltages of (2, 2.5, and 3 volts) are represented in Fig (3-19). It can be showed that the coated of deposited nickel on copper approximately to cover all the surface of copper substrate, and is increased with voltages as can be deduced from the density of deposited nickel on the substrate (compare image a, b , and c). This shape of the deposited nickel was found to have less irregular spherical shape from copper deposited, however the deposition seem have a homogeneous layer on the substrate which normally caused by the insufficient mixing of the solution or in case the viscose nature of the ionic liquid. The latter characterization required more vigorous mixing than in the aqueous solutions. However, the irregularity of deposition was less when the amount of deposited nickel increased at 3 volt. To determine the thickness of the deposited layer on the substrate another sample was prepared as mentioned in Fig (3-20). The deduced thickness Table (3-10) revealed that the highest thickness obtained was when the applied voltages was 3 volt, though all other conditions were similar. This increase can be explained as the current is normally increases with voltage, resulted in more deposited nickel on substrate.

In addition, it can be noticed that the deposited nickel filled all the surface of the substrate, although the surface of the latter was rough surface. This would be an advantages in the practical application of the process for mending pitted or eroded metal surfaces. The irregular surfaces of the specimens are a raised from the rough smoothing technique, however, the nickel deposited which used in avoiding the corrosion and erosion for the metal surface, by converting it to a planer surface.
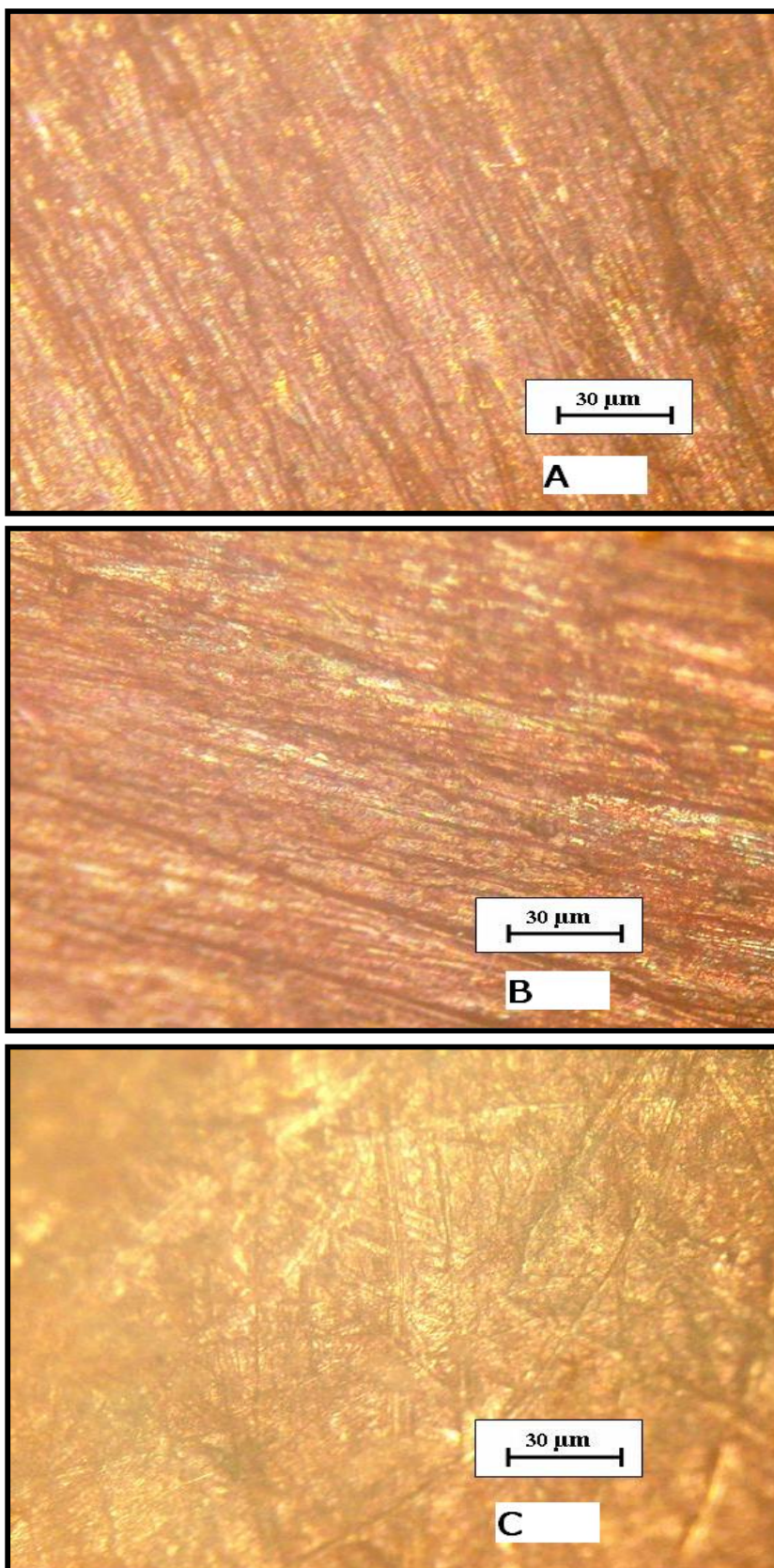
Figure (3-19) Electron micrographs of coated nickel on copper plate from 0.08 mole/l of NiCl2 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2, (B)2.5, and(C)3 applied voltages.
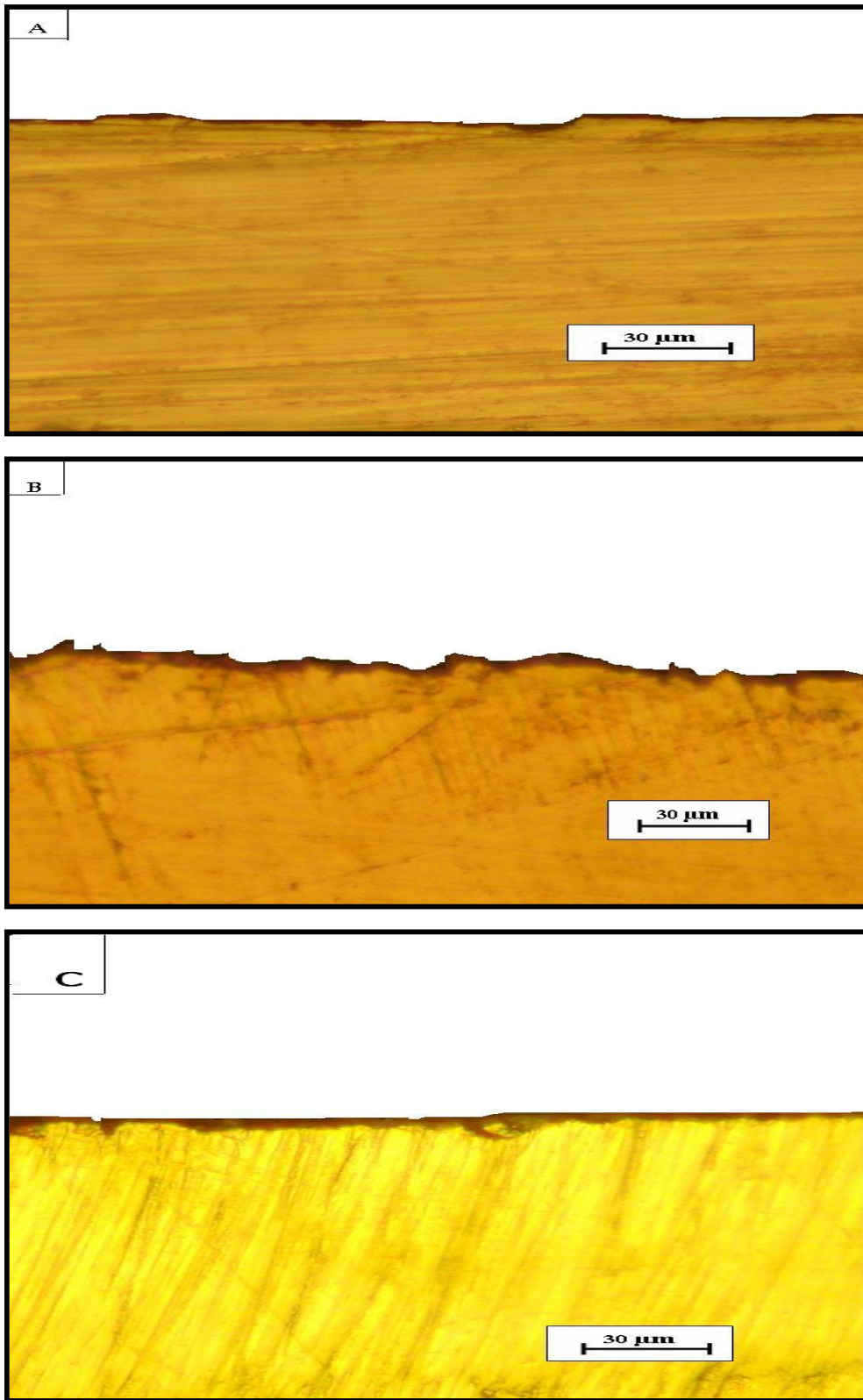
Figure (3-20) Cross sectioned electron images of nickel coated on copper plate from 0.08 mole/l of NiCl2 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2, (B)2.5, and(C)3 applied voltages. .

3.2.3 _Electro deposition of chromium on the (copper, nickel, and stainless steel) plate in choline chloride/d-tartaric acid ionic liquid at 85℃ :-_

Conventional chromium plating processes uses chromic acid, comprising hexavalent chromium, which is toxic and carcinogenic. Ionic liquids allow the use of trivalent chromium salts, which are far less toxic, and the conventional chromic acid process releases a large volume of hydrogen gas, which can make the coating brittle, reducing quality and yield.[102] With ionic liquids, only little amounts of hydrogen are generated, minimizing cracking and producing highly corrosion resistant deposits. However, conventional chrome electroplating is harder than pure chromium as it is effectively an alloy, chromium hydride. Plating with ionic liquids yields pure chromium deposits, although these have a nano-crystalline structure that improves hardness and can also deal with your waste issues by recycling the liquid when it comes to the end of its use.[103]

3.2.3.1 Electro deposition of chromium on the copper plate in choline chloride/d-tartaric acid ionic liquid at 85℃:-

The electrodeposition of chrome on copper was occurred at 85°C and an applied voltages of (2, 2.5, and 3 volts) in an electrolyte solution of (0.1 M) of CrO_3 in choline chloride/d-tartaric acid ionic liquid. This electrodeposition was during for one hour at each applied voltages when the current out put was recorded and the resulted current density with the deposited weight of chrome on copper are shown in Table(3-11). This weight was obtained from the differences between the weight of the copper cathode before and after the one hour deposition time. In addition, it was observed that the electrolyte produced a tiny bubbles at the cathode electrode only when potential was applied, and the rate of their production increased with increasing the potential. The bubbles formed at cathode less than bubbles showed in copper and nickel deposited, due to the applied voltages used in process is enough voltage to reduction of Cr(VI) to Cr (III). These bubbles could be attributed the reduction of hydrogen ion that was produced possibly from tartaric acid (as the ionic liquid is normally acidic) at the cathode producing hydrogen gas. In addition, the absence of such bubbles at the anode which is expected to oxidize chloride ion in to chlorine gas, might be a rise from the formation of trichloride ion that was soluble in the ionic liquid solution.[70]

$$Cl^- + Cl_2 \rightarrow Cl_3 \qquad\qquad (3\text{-}3)$$

Table (3-11) shows that the weight of deposited chrome on the copper electrode increases with increasing applied voltages which in turn also increase the current density as is shown in Fig (3-21) which could be related to the polarization. Moreover the increase in voltage caused an

increase in the rate of discharge (reduction) at the cathode that was noticeable for the increase production of bubbles which was related to the increase reduction of hydrogen ion too. The optical micrograph of the cross section view of chrome deposited on copper cathode, showed deposits thickness varied for 1.5 μm to 2 V, 3 μm to 2.5 V, and 5.4 μm to 3 V. The value of thickness is found to increase with increasing applied voltage at (85C°) and one hour time, shows that in Table(3-11), and represented in Figure(3-22). The current efficiency of the deposition of chrome on copper are listed in Table (3-11). The current efficiency was found to be less than 98% of the applied current to deposited chrome metal on the cathode. This is possibly due to amount less their reduction of hydrogen cation in the solution at the cathode.. In addition, the small value of the current density might also attributed to the loss of some of the sample during cleaning especially if the deposition was dendritic as was reported by other workers. In other ionic liquids the plating process of Cr(III) for depositing crack free chrome black which has high current efficiency (> 90 %).[102]

Table(3-11):- Applied voltages, current density, current efficiency and the weight and thickness deposited chrome on copper fromCrO₃ in choline chloride/d-tartaric acid ionic liquid at 85℃ and one hour time.

Applied (voltages)	Current density(mA/cm^2)	Weight of chrome deposit on copper (mg)	Thickness of chrome on copper (μm)	Current efficiency (%)
2	0.35	0.17	1.5	95
2.5	0.6	0.2	3	94
3	0.75	0.3	5.4	93
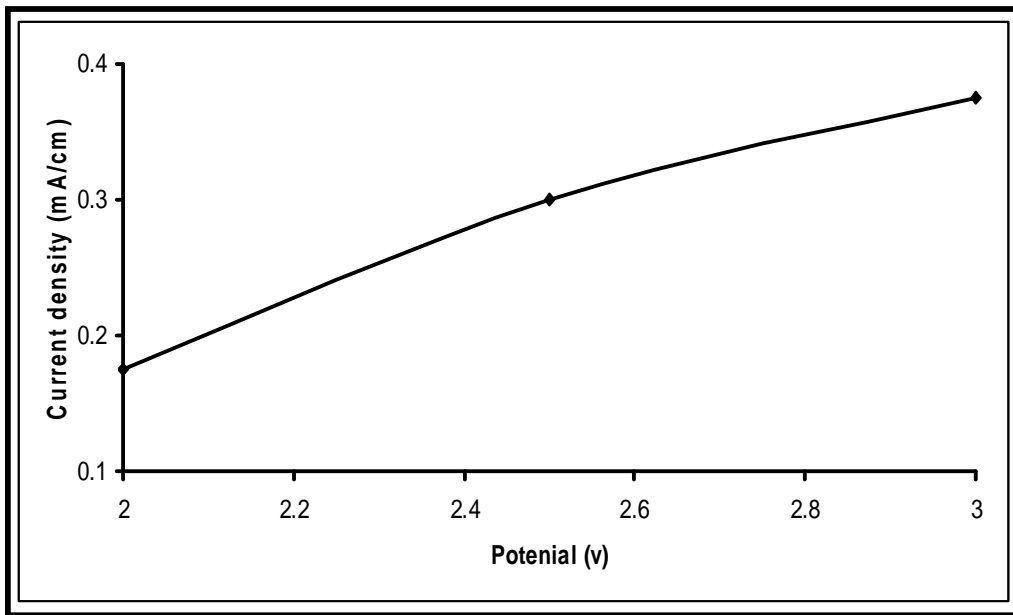
Figure (3-21) Current-voltage curve of electrodepositing of chrome on copper at (2,2.5,and 3volts) and 85℃.
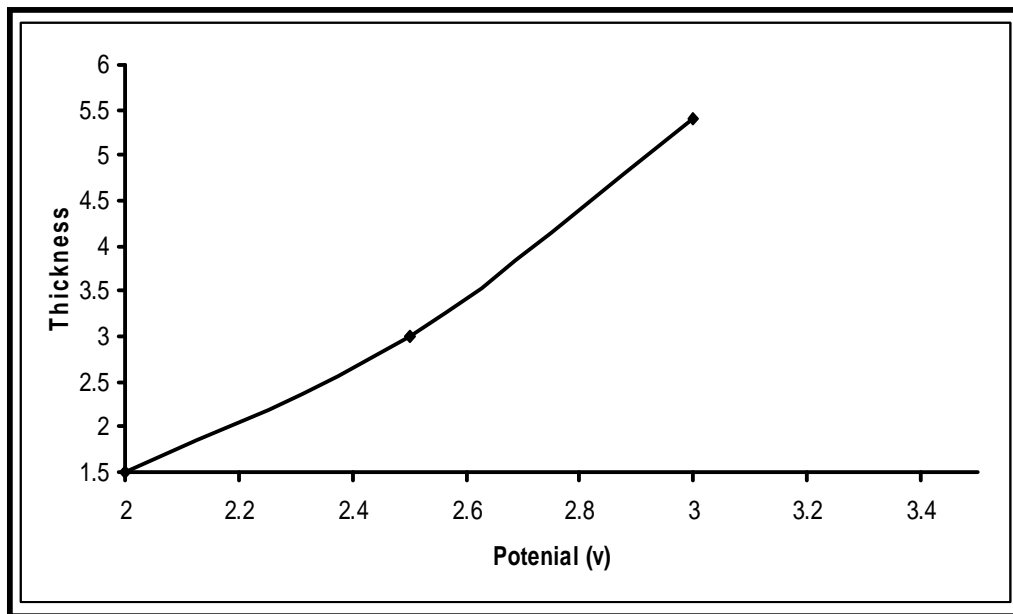
Figure (3-22) Thickness vs. potential of chrome deposited on copper in ionic liquid at (2,2.5,and 3volts) and 85℃

3.2.3.1.1 Morphology of chrome deposited on copper:-

The optical micrograph image of chrome on copper at the applied voltages of (2, 2.5, and 3 volts) are represented in Fig (3-23). It can be showed that the coated of deposited chrome on copper approximately to cover all the surface of copper substrate, and is increased with voltages as can be deduced from the density of deposited chrome on the substrate (compare image a, b , and c). Chrome which itself adheres very well to copper-combination corrosion protection resistance. This shape of the deposited chrome was found to have less irregular spherical shape from copper and nickel deposited, however the deposition seem have a homogeneous layer on the substrate which normally caused by the sufficient mixing of the solution or in case the high viscose nature of the ionic liquid. The latter characterization required more vigorous mixing than in the aqueous solutions. However, the irregularity of deposition was less when the amount of deposited nickel increased at 3 volt. To determine the thickness of the deposited layer on the substrate another sample was prepared as mentioned in Fig (3-24). The deduced thickness Table (3-11) revealed that the highest thickness obtained was when the applied voltages was 3 volt, though all other conditions were similar. This increase can be explained as the current is normally increases with voltage, resulted in more deposited chrome on substrate.

In addition, it can be noticed that the deposited chrome filled all the surface of the substrate, although the surface of the latter was rough surface. This would be an advantages in the practical application of the process for mending pitted or eroded metal surfaces. The irregular surfaces of the specimens are a raised from the rough smoothing technique, however, the chrome deposited which used in avoiding the corrosion and decorative for the metal surface, by converting it to a planer surface.

Figure (3-23) Electron micrographs of coated chrome on copper plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C˚, for one hour, and at (A)2, (B)2.5, and (C)3 applied voltages.   .
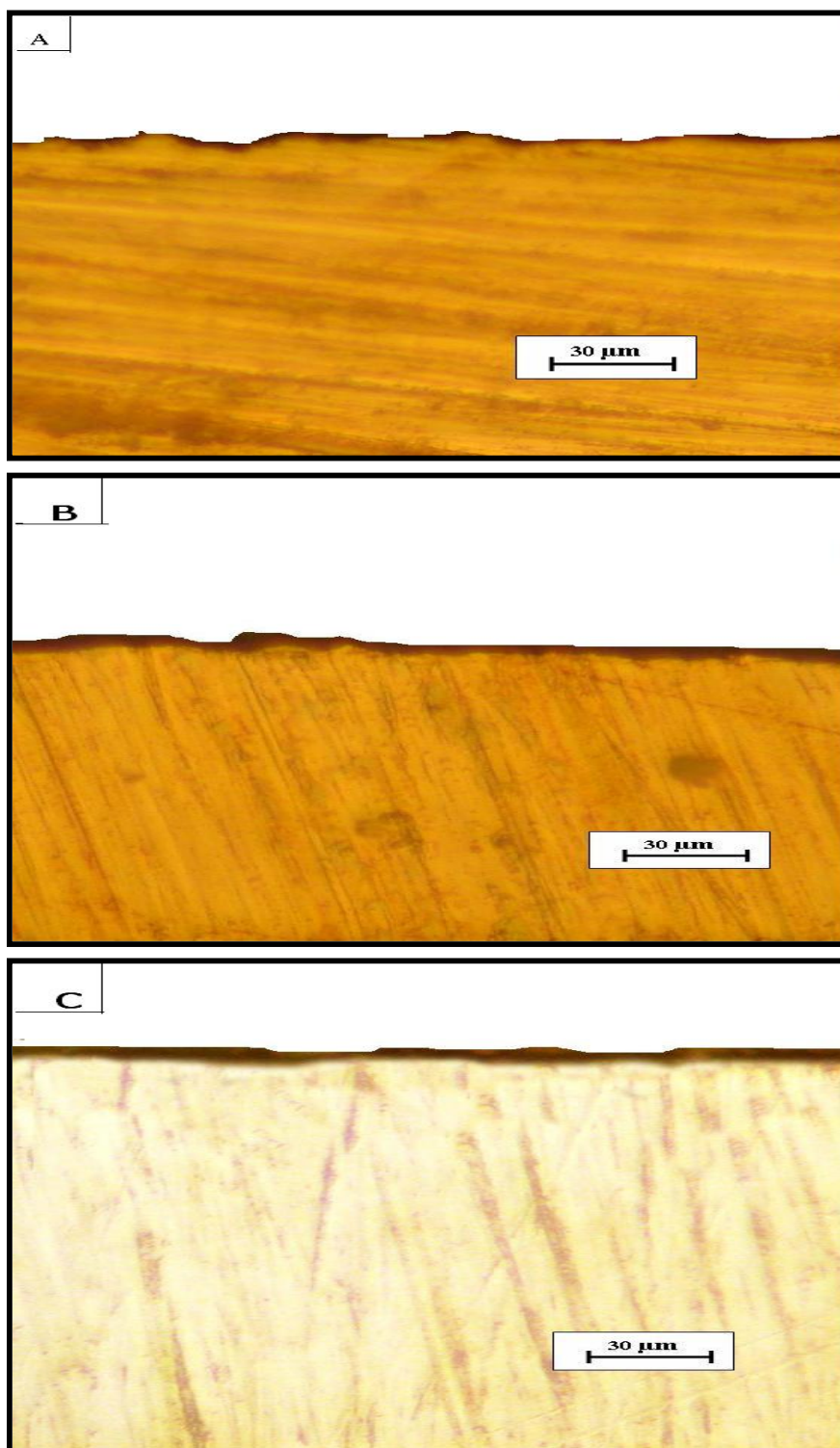
Figure (3-24) Cross sectioned electron images of chrome coated on copper plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2, (B)2.5, and(C)3 applied voltages.   .

3.2.3.2 *Electro deposition of chromium on the nickel plate in choline chloride/d-tartaric acid ionic liquid at 85°C:-*

The electrodeposition of chrome on nickel was carried out at 85°C and an applied voltages of (2.5, and 3 volts) in an electrolyte solution of (0.1 M) of CrO_3 in choline chloride/d-tartaric acid ionic liquid. This electrodeposition was during for one hour at each applied voltages when the current out put was recorded and the resulted current density with the deposited weight of chrome on nickel are shown in Table(3-12). This weight was obtained from the differences between the weight of the nickel cathode before and after the one hour deposition time.

In addition, it was observed that the electrolyte produced a tiny bubbles at the cathode electrode only when potential was applied, and the rate of their production increased with increasing the potential. The bubbles formed at cathode less than bubbles showed in copper and nickel deposited, due to the applied voltages used in process is enough voltage to reduction of Cr(VI) to Cr (III). These bubbles could be attributed the reduction of hydrogen ion that was produced possibly from tartaric acid (as the ionic liquid is normally acidic) at the cathode producing hydrogen gas. In addition, the absence of such bubbles at the anode which is expected to oxidize chloride ion in to chlorine gas, might be a rise from the formation of trichloride ion that was soluble in the ionic liquid solution.[70]

$$Cl^- + Cl_2 \rightarrow Cl_3^- \tag{3-4}$$

Table (3-12) shows that the weight of deposited chrome on the copper electrode increases with increasing applied voltages which in turn also increase the current density as is shown in Fig (3-25) which could be related to the polarization. Moreover the increase in voltage caused an increase in the rate of discharge (reduction) at the cathode that was

noticeable for the increase production of bubbles which was related to the increase reduction of hydrogen ion too. The optical micrograph of the cross section view of chrome deposited on nickel cathode, showed deposits thickness varied for 1.5 µm to 2.5 V, and 2.4 µm to 3 V. The value of thickness is found to increase with increasing applied voltage at $(85C^{\circ})$ and one hour time, shows that in Table(3-12), and represented in Figure(3-26). The current efficiency of the deposition of chrome on nickel are listed in Table (3-12). The current efficiency was found to be less than 98% of the applied current to deposited chrome metal on the cathode. This is possibly due to amount less their reduction of hydrogen cation in the solution at the cathode. And the current efficiency less than when the chrome deposited on copper. In addition, the small value of the current density might also attributed to the loss of some of the sample during cleaning especially if the deposition was dendritic as was reported by other workers. In other ionic liquids the plating process of Cr(III) for depositing crack free chrome black which has high current efficiency (> 90 %).[102]

Table(3-12):- Applied voltages, current density, current efficiency and the weight and thickness deposited chrome on nickel fromCrO3 in choline chloride/d-tartaric acid ionic liquid at 85℃ and one hour time.

Applied (voltages)	Current density(mA/cm^2)	Weight of chrome deposit on nickel (mg)	Thickness of chrome on nickel (µm)	Current efficiency (%)
2	-	-	-	-
2.5	0.2	0.1	1.5	83
3	0.45	0.3	2.4	74
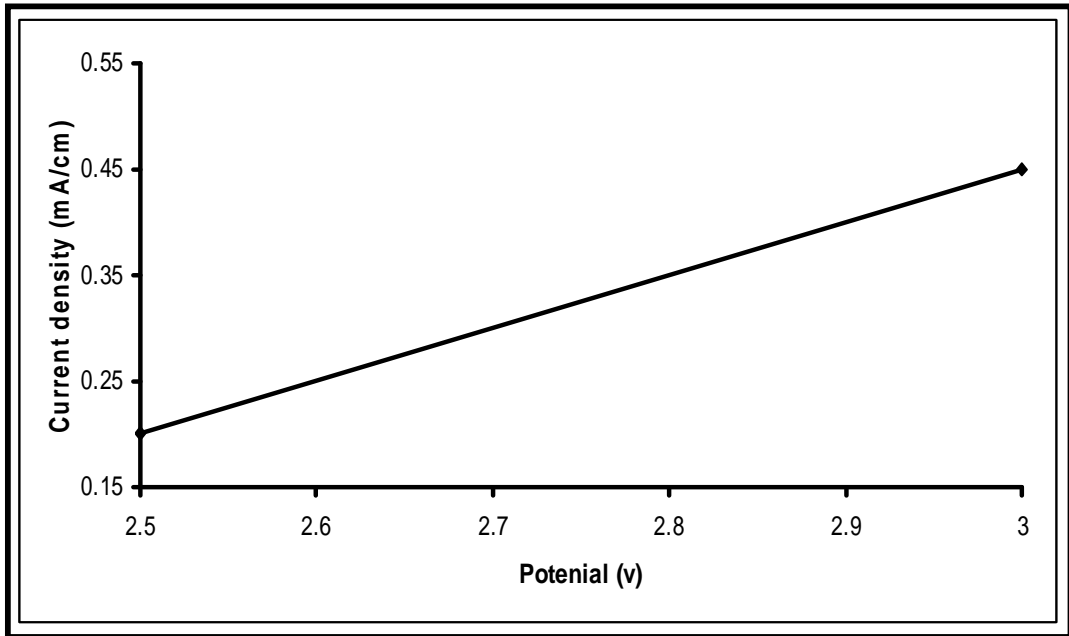
Figure (3-25) Current-voltage curve of electrodepositing of chrome on nickel at (2.5,and 3volts) and 85℃.
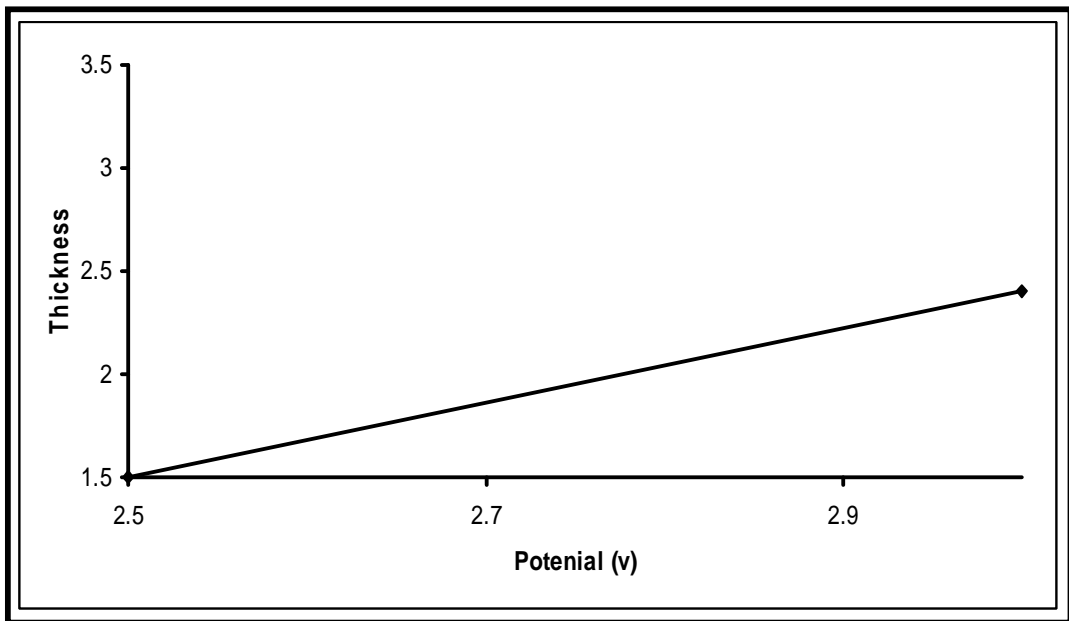
Figure (3-26) Thickness vs. potential of deposited chrome on nickel in ionic liquid at (2.5,and 3volts) and 85℃.

3.2.3.2.1 Morphology of chrome deposited on nickel:-

The optical micrograph image of chrome on nickel at the applied voltages of (2.5, and 3 volts) are represented in Fig (3-27). It can be showed that the coated of deposited chrome on nickel approximately to cover all the surface of nickel substrate, and is increased with voltages as can be deduced from the density of deposited chrome on the substrate (compare image a, and b). Chrome which very well adheres to nickel-combination corrosion protection resistance. This shape of the deposited chrome was found to have more irregular spherical shape from chrome deposited on copper, however the deposition seem have not a homogeneous layer on the substrate which normally caused by the insufficient mixing of the solution or in case the high viscose nature of the ionic liquid. The latter characterization required more vigorous mixing than in the aqueous solutions. However, the irregularity of deposition was less when the amount of deposited chrome increased at 3 volt. To determine the thickness of the deposited layer on the substrate another sample was prepared as mentioned in Fig (3-28). The deduced thickness Table (3-12) revealed that the highest thickness obtained was when the applied voltages was 3 volt, though all other conditions were similar. This increase can be explained as the current is normally increases with voltage, resulted in more deposited chrome on substrate.

In addition, it can be noticed that the deposited chrome filled all the surface of the substrate, although the surface of the latter was rough surface. This would be an advantages in the practical application of the process for mending pitted or eroded metal surfaces. The irregular surfaces of the specimens are a raised from the rough smoothing technique, however, the chrome deposited which used in avoiding the corrosion and decorative for the metal surface, by converting it to a planer surface.

Figure (3-27) Electron micrographs of coated chrome on nickel plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at (A)2.5, and (B)3 applied voltages.   .
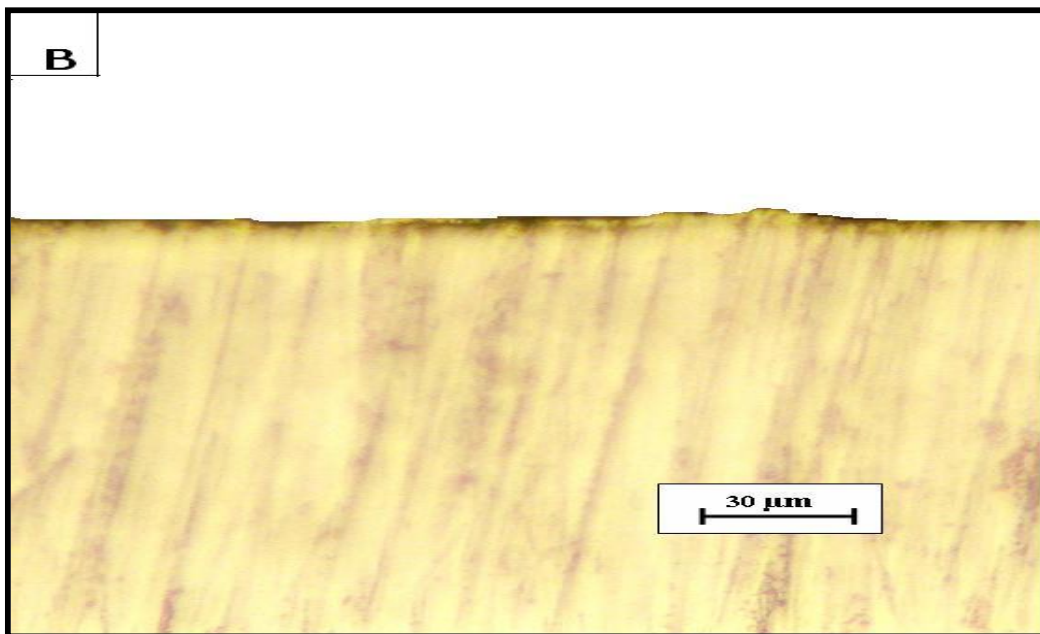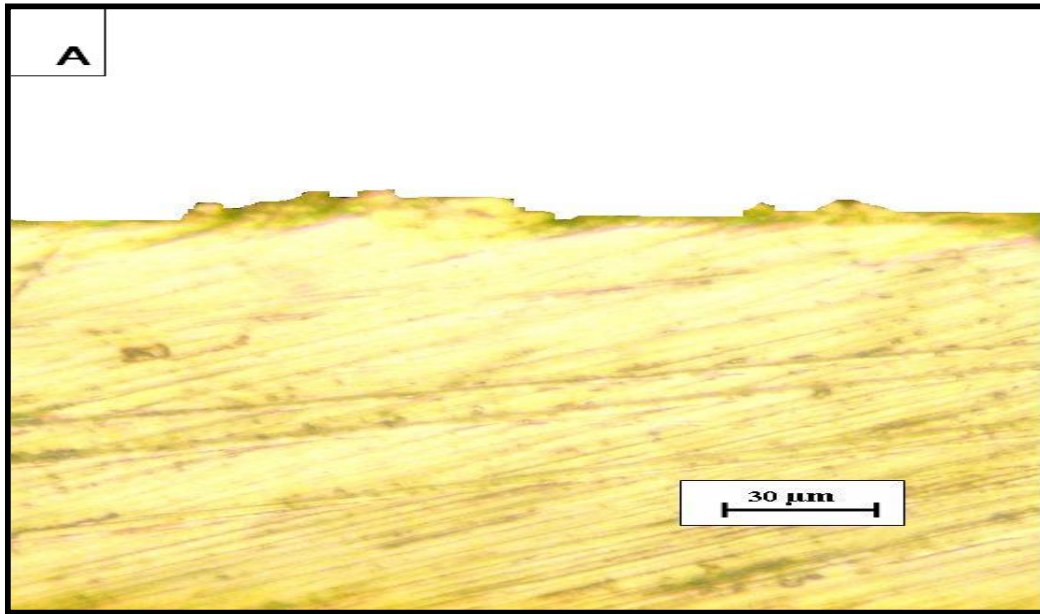
Figure (3-28) *Cross sectioned electron images of chrome coated on nickel plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C˚, for one   hour,   and   at   (A)2.5,   and(B)3   applied   voltages. .*
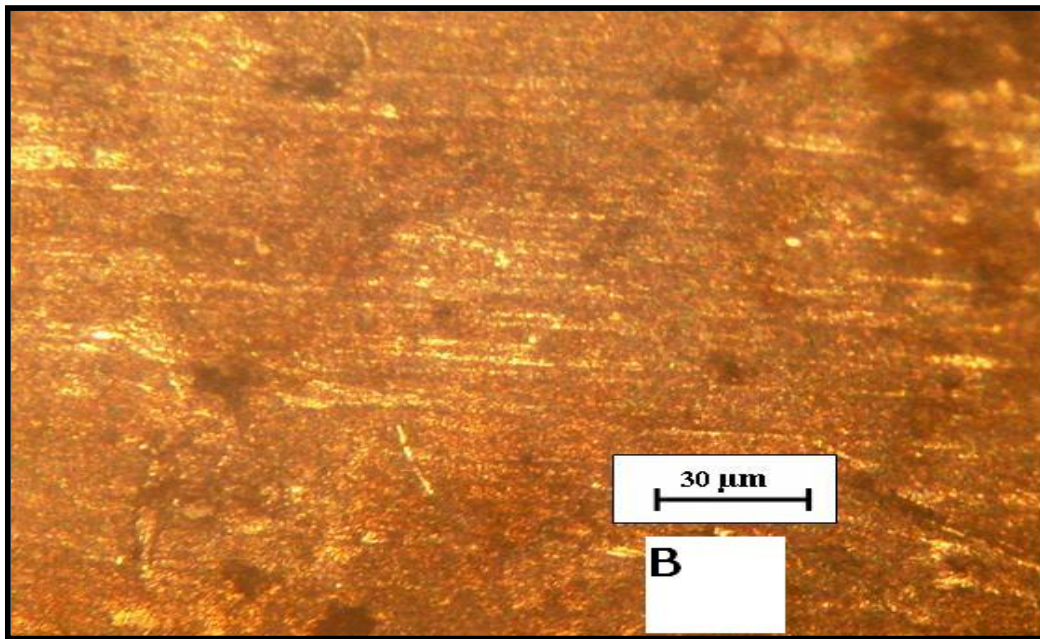
3.2.3.3 Electro deposition of chromium on the stainless steel plate in choline chloride/d-tartaric acid ionic liquid at 85℃:-

The electrodeposition of chrome on stainless steel was carried out at 85°C and an applied voltages of (3 volts) in an electrolyte solution of (0.1 M) of CrO_3 in choline chloride/d-tartaric acid ionic liquid. This electrodeposition was during for one hour at each applied voltages when the current out put was recorded and the resulted current density with the deposited weight of chrome on stainless steel are shown in Table(3-13). This weight was obtained from the differences between the weight of the stainless steel cathode before and after the one hour deposition time. In addition, it was observed that the electrolyte produced a tiny bubbles at the cathode electrode only when potential was applied, and the rate of their production increased with increasing the potential. The bubbles formed at cathode less than bubbles showed in copper and nickel deposited, due to the applied voltages used in process is enough voltage to reduction of Cr(VI) to Cr (III). These bubbles could be attributed the reduction of hydrogen ion that was produced possibly from tartaric acid (as the ionic liquid is normally acidic) at the cathode producing hydrogen gas. In addition, the absence of such bubbles at the anode which is expected to oxidize chloride ion in to chlorine gas, might be a rise from the formation of trichloride ion that was soluble in the ionic liquid solution.[70]

$$Cl^-+Cl_2 \rightarrow Cl_3 \qquad\qquad\qquad (3\text{-}5)$$

Table (3-13) shows that the weight of deposited chrome on the copper electrode increases with increasing applied voltages which in turn also increase the current density, which could be related to the polarization. Moreover the increase in voltage caused an increase in the rate of discharge (reduction) at the cathode that was noticeable for the increase

production of bubbles which was related to the increase reduction of hydrogen ion too. The optical micrograph of the cross section view of chrome deposited on stainless steel cathode, showed deposits thickness varied for 3 μm to 3 V. The value of thickness is found to increase with increasing applied voltage at ($85C^{\circ}$) and one hour time, shows that in Table(3-13). The current efficiency of the deposition of chrome on stainless steel are listed in Table (3-13). The current efficiency was found to be less than 98% of the applied current to deposited chrome metal on the cathode. This is possibly due to amount less their reduction of hydrogen cation in the solution at the cathode. And the current efficiency less than when the chrome deposited on stainless steel. In addition, the small value of the current density might also attributed to the loss of some of the sample during cleaning especially if the deposition was dendritic as was reported by other workers. In other ionic liquids the plating process of Cr(III) for depositing crack free chrome black which has high current efficiency (> 90 %).[102]

Table(3-13):- Applied voltages, current density, current efficiency and the weight and thickness deposited chrome on stainless steel fromCrO3 in choline chloride/d-tartaric acid ionic liquid at 85℃ and one hour time.

Applied (voltages)	Current density(mA/cm^2)	Weight of chrome deposit on nickel (mg)	Thickness of chrome on nickel (μm)	Current efficiency (%)
3	0.4	0.3	3	83

3.2.3.3.1 Morphology of chrome deposited on stainless steel:-

The optical micrograph image of chrome on stainless steel at the applied voltages of (3 volts) are represented in Fig (3-29). It can be showed that the coated of deposited chrome on stainless steel approximately to cover all the surface of stainless steel substrate, and is increased with voltages as can be deduced from the density of deposited chrome on the substrate.. This shape of the deposited chrome was found to have more irregular spherical shape from chrome deposited on copper and nickel, however the deposition seem have not a homogeneous layer on the substrate which normally caused by the insufficient mixing of the solution or in case the high viscose nature of the ionic liquid. The latter characterization required more vigorous mixing than in the aqueous solutions. However, the irregularity of deposition was less when the amount of deposited chrome increased at 3 volt. To determine the thickness of the deposited layer on the substrate another sample was prepared as mentioned in Fig (3-30). The deduced thickness Table (3-13) revealed that the highest thickness obtained was when the applied voltages was 3 volt, though all other conditions were similar. This increase can be explained as the current is normally increases with voltage, resulted in more deposited chrome on substrate. In addition, it can be noticed that the deposited chrome filled all the surface of the substrate, although the surface of the latter was rough surface. This would be an advantages in the practical application of the process for mending pitted or eroded metal surfaces. The irregular surfaces of the specimens are a raised from the rough smoothing technique, however, the chrome deposited which used in avoiding the corrosion and decorative for the metal surface, by converting it to a planer surface.

Figure (3-29) Electron micrographs of coated chrome on stainless steel plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at 3 applied voltage.
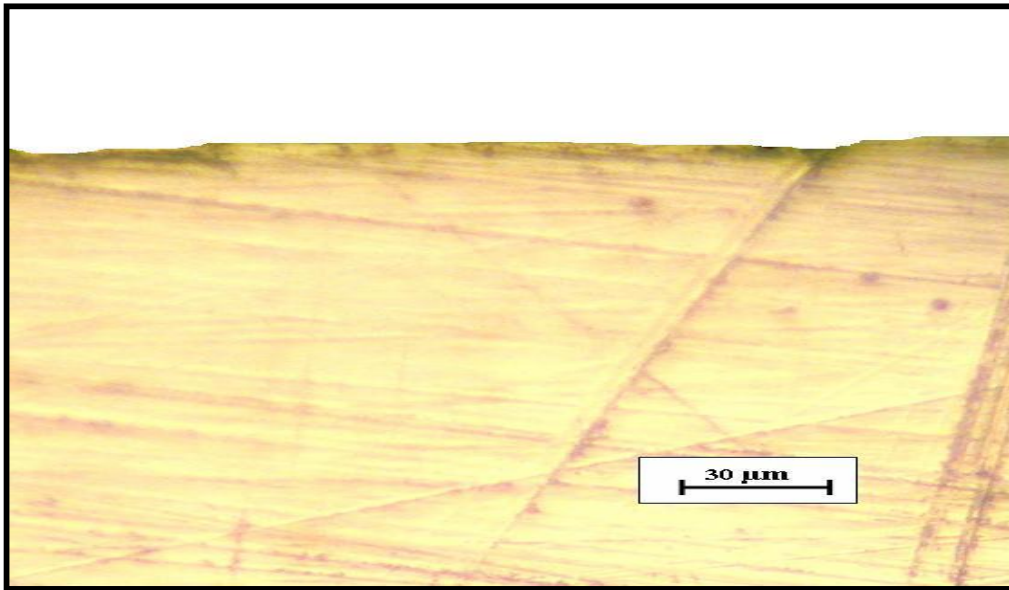
Figure (3-30) Cross sectioned electron images of chrome coated on stainless steel plate from 0.1 mole/l of CrO3 in choline chloride/d- tartaric acid ionic liquid at 85C°, for one hour, and at 3 applied voltage.

3.3 _Electronic spectroscopy of transition metals in choline chloride/d- tartaric acid room temperature ionic liquid:_

Electronic absorption of transition metal complexes are usually attributed to the partially filled d-orbital of the metal. The energy required for such transition is that of the near ultraviolet and visible region. While charge transfer spectra are due to transitions between metal and ligand. Studies of electronic spectra of complexes helps in the determination of structure of the complexes through the electronic interaction of the metal d-orbital and ligand orbital. However, it was intended to investigate the electrolyte solution of the metal deposition used this work to identify the nature of the formed complexes of those transition metal cation.

3.3.1 _Electronic spectroscopy of copper sulfate in choline chloride/d- tartaric acid ionic liquid:_

A yellow solution was obtain when copper sulfate is dissolved in choline chloride / tartaric acid ionic liquid (0.04 M) this solution after electrodeposition was examined by U.V-Vis spectroscopy at room temperature. The recorded ultraviolet visible spectra of the yellow solution of the copper Sulfate showed one broad band with absorption maxima at $11751 cm^{-1}$ as shown in Figure (3-31).
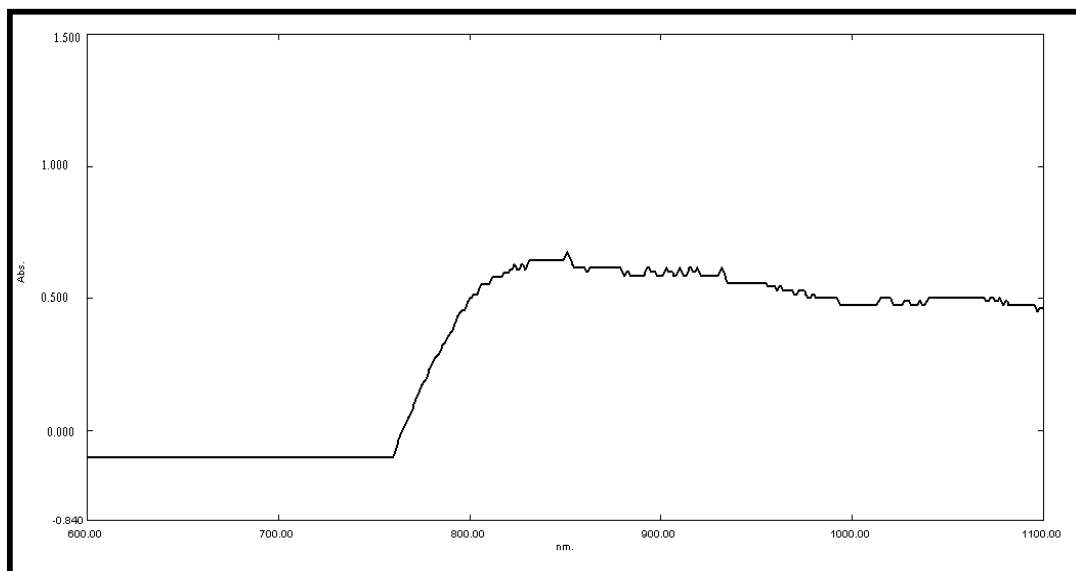
Figure (3-31) The UV- Vis. Spectrum of cupper sulfate(CuSO4) in choline chloride/ tartaric acid ionic liquid at room temperature.

The d^9 configuration makes Cu (II)subjected to John-Teller distortion if placed in an environment of cubic (i.e. regular octahedral, or tetrahedral) symmetry, and this has a profound effect on all its stereochemistry. The high absorption of copper (II) in choline chloride/ tartaric acid ionic liquid may indicates a large distortion in its geometry. The result of Cu(II) in choline chloride/ tartaric acid ionic liquid is similar to those taken for Cu (II) in molten chloride of LiCl/ KCl at 400 ^{o}C which showed one absorbance maxima at 9500 cm^{-1}, where it propose to be in distorted octahedral to tetrahedral coordination[103].

This suggestion is supported by the value of molar absorption (17.5) since the normal octahedral would show less value (<10) and normal tetrahedral (~100).

3.3.2 *Electronic spectroscopy of nickel (II)chloride in choline chloride/d- tartaric acid ionic liquid:*

The green solution of nickel chloride and choline chloride / tartaric acid ionic liquid (0.08M), was also investigated by U.V-Vis spectroscopy at room temperature. The recorded ultraviolet visible spectra of the green solution of the nickel (II) chloride shows two absorbance maxima bands at 13333cm^{-1} and 24449cm^{-1}) which was related (υ_2) and (υ_3) respectively as shown in Figure (3-32), While there is another band near the second absorbance band at 14100 cm^{-1} and 15000 cm^{-1} which were considered to be related to distorted tetrahedral coordination, In the case of nickel (II) the two bands were initially assigned to a distorted tetrahedral coordination though in the light of more detailed measurements by Smith [104] over a temperature range of (700-1000 C°) in (LiCl/KCl mixtures) was 15,200 and 14,100 cm^{-1} which are similar to those found in this work. Therefore the UV- Vis. spectra of Ni^{+2} indicating that nickel (II) consisted of octahedral and tetrahedral coordination complex.
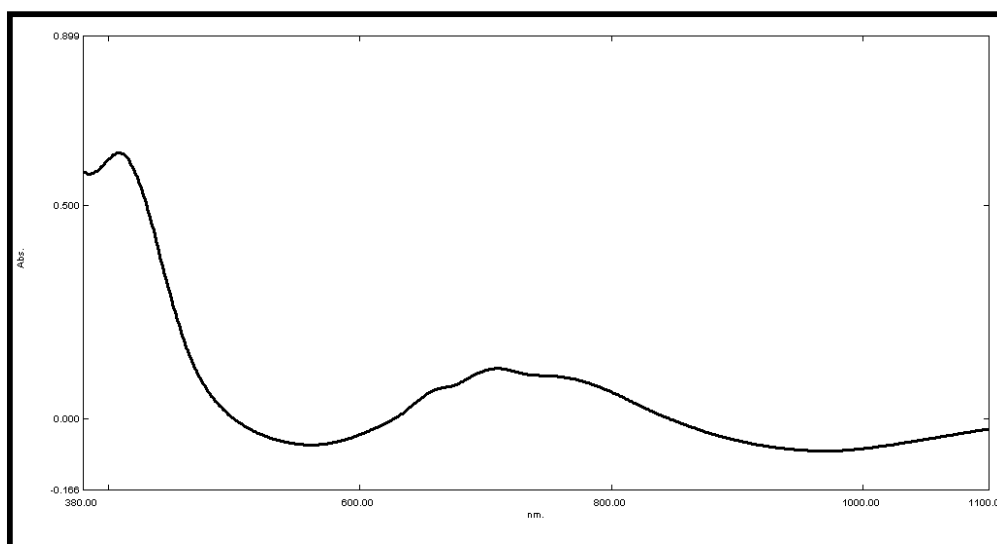
Figure (3-32): The UV- Vis spectrum of NiCL2 in choline chloride/ tartaric acid ionic liquid at room temperature.

The (υ_1) band of the octahedral geometry which normally occur at a low energy was deduced by using Tanabe- sugano diagram Figure (3-33) of d^8 electronic configuration and it's found to be 7964 cm^{-1}.

And the bands may be assigned as:

$\upsilon_1 = {}^3A_{2g} \quad\rightarrow\quad {}^3T_{2g}$ (F)

$\upsilon_2 = {}^3A_{2g} \quad\rightarrow\quad {}^3T_{1g}$ (F)

$\upsilon_3 = {}^3A_{2g} \quad\rightarrow\quad {}^3T_{1g}$ (P)

Since the terms of the d^8 configuration can split as illustrated in Figure (3-34)
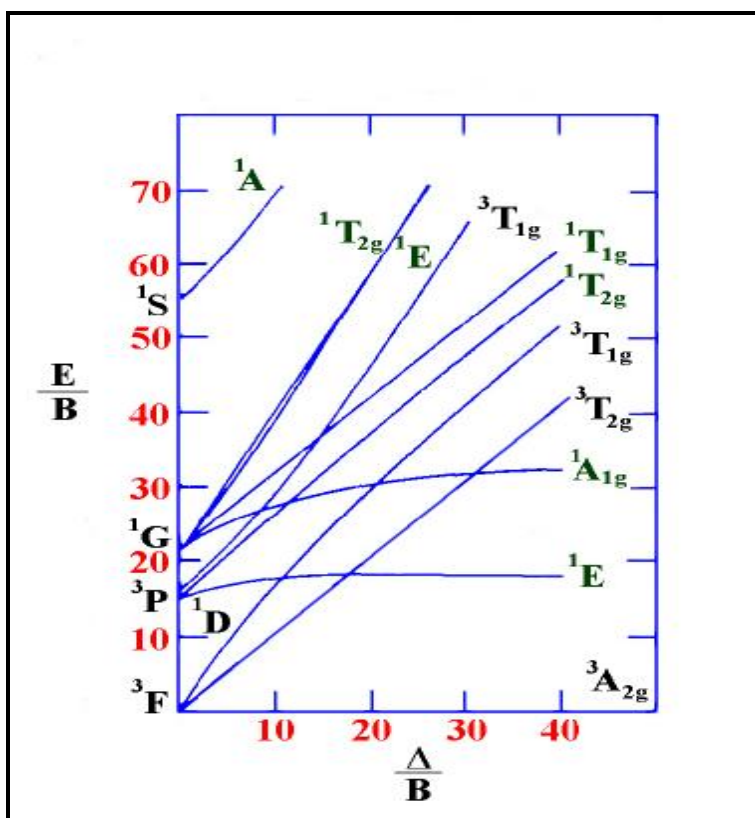
Figure (3-33) Tanabe-Sugano diagram for d^8 octahedral electronic configuration.

Figure (3-34) Crystal field splitting of ^3F term of d^8 ion octahedral configuration

The calculated values of interelectronic repulsion parameter (**Racah** parameter B`) in the complex formed in choline chloride/ tartaric acid ionic liquid with nickel (II) ion and that of **nephelauxetic** factor were represented in Table (3-14). It is notice that **Racah** parameter (926cm^{-1}) was found to be much less than that in free ion (1030 cm^{-1}) due to the expansion of d- electron charge on the complex which expected to reduce the metal inter electronic repulsion.

Table (3-14):- Electronic spectra of nickel (II) complexes ions in choline chloride/tartaric acid ionic liquid.

Absorption band cm^{-1}	B`(cm^{-1})	Calculated β	10 Dq	Δ_0/B	Є L / mol cm
v1cal=7964 v2=13333 v3=24449	926	0.89	7963.6	8.6	7.8

3.3.3 *Electronic spectroscopy of chromium trioxide in choline chloride/d- tartaric acid ionic liquid:*

When deep brown chromium trioxide dissolved in choline chloride/ tartaric acid ionic liquid (0.1M), showed a green color solution. This solution after electrodeposition was investigated by U.V. Visible spectroscopy at room temperature. The color change of chromium oxide before and after its dissolution in the ionic liquid indicated a reduction in the chromium (VI) into chromium (III), as the latter usually gives green solution of the octahedral coordination nature of this metal. [105] The color before dissolution usually attributed to ligand- metal charge transfer spectra. As this band cover the blue end of the visible region. The recorded ultraviolet visible spectrum of the green solution of the chromium oxide showed two bands with absorption maxima at17793cm^{-1} and 23094cm^{-1}which were considered (υ_1) and (υ_2) respectively, as shown in Figure (3-35).

The high energy spectra observed indicated that chromium oxide in choline chloride/ tartaric acid ionic liquid consist of octahedral coordination.
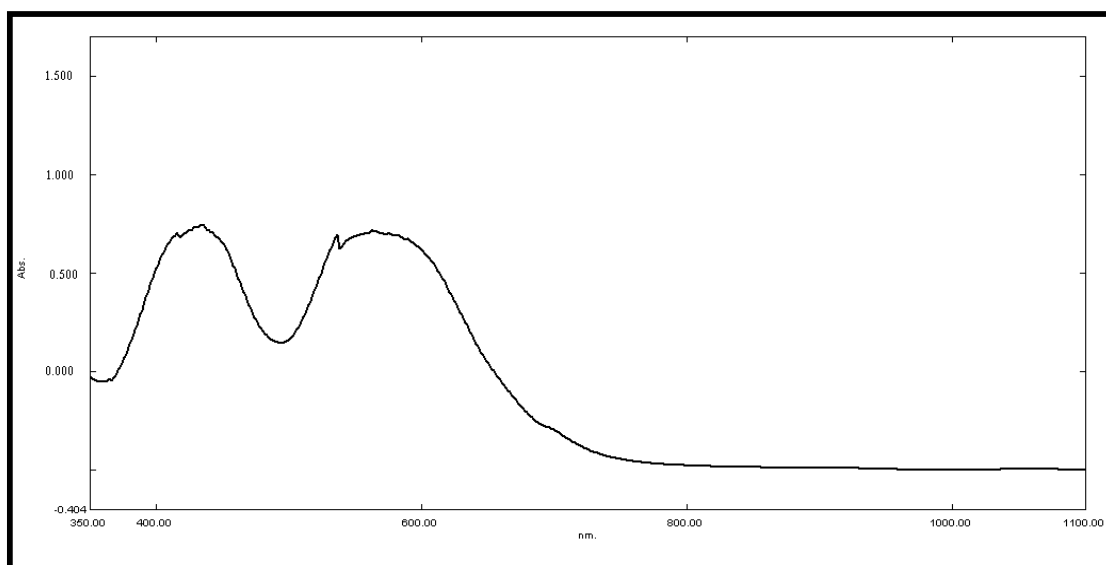
Figure (3-35) The UV- Vis. Spectrum of chromium (III) oxide in choline chloride/ tartaric acid ionic liquid at room temperature.

The third band of the octahedral coordination (υ_3) which normally occur at higher energy was deduced by using Tanabe- Sugano diagram Figure (3-36) of d^3 electronic configuration and it is found to be 37695 cm^1.

And the bands may be assigned as:

$\upsilon_1 = {}^4A_{2g} (F) \rightarrow {}^4T_{2g} (F) (10Dq)$

$\upsilon_2 = {}^4A_{2g} (F) \rightarrow {}^4T_{1g} (F)$

$\upsilon_3 = {}^4A_{2g} (F) \rightarrow {}^4T_{1g} (P)$

The terms of the d^3 splitting may also illustrated in Figure (3-37)
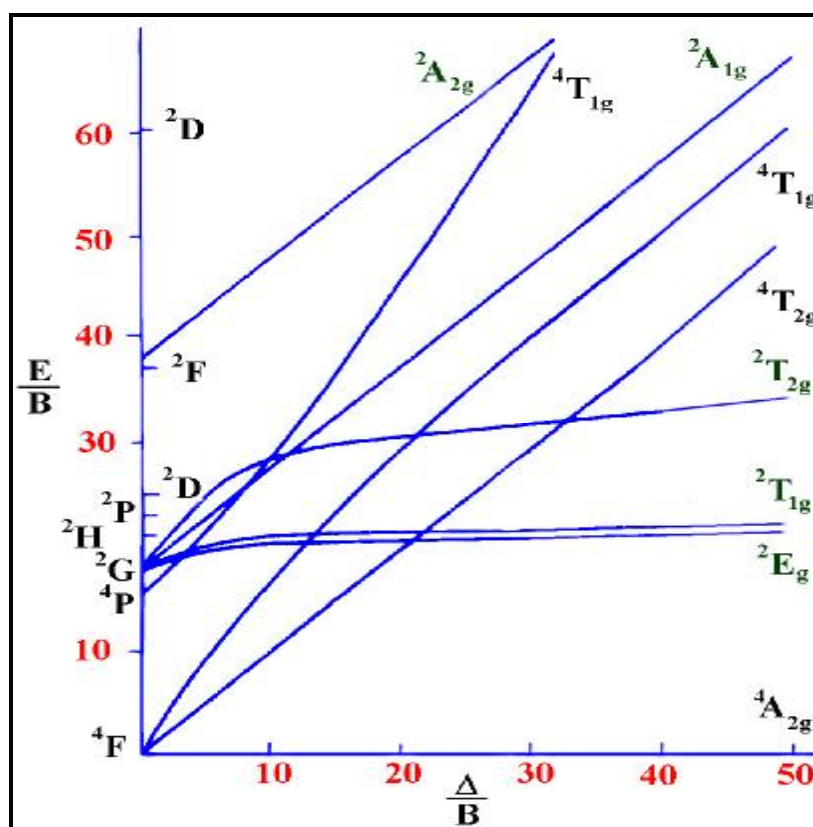
Figure (3-36) Tanabe-Sugano diagram for d^3 ion configuration.
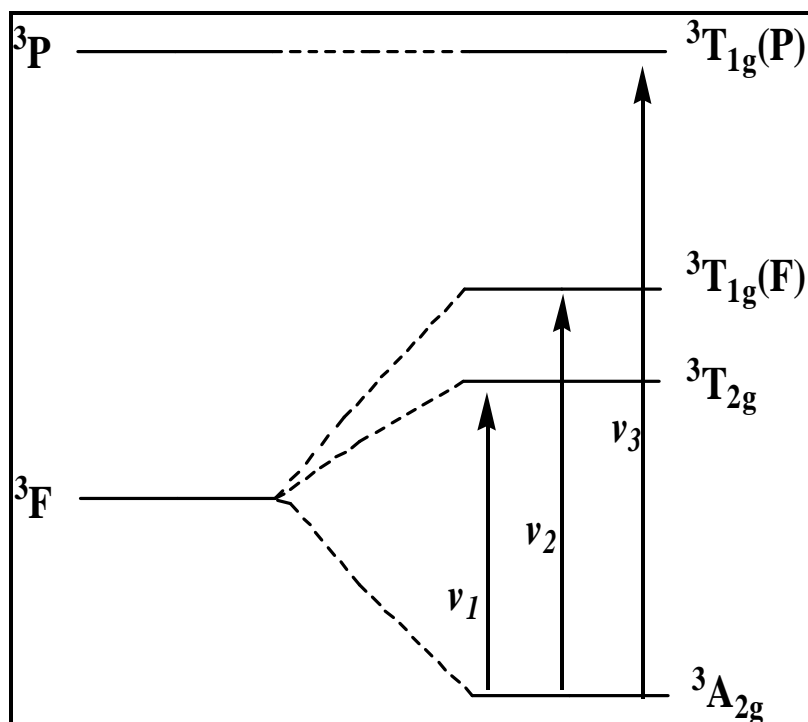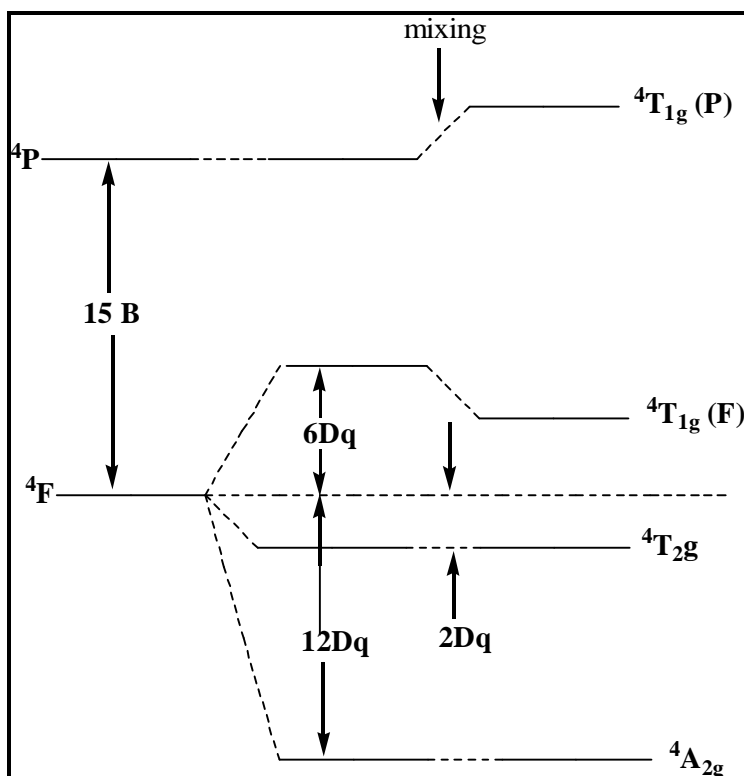
Figure (3-37) Crystal field splitting of the term of d^3 ion octahedral configuration.

The calculated values of interelectronic repulsion parameter (Racah parameter B) in the complex formed in choline chloride/ tartaric acid ionic liquid with chromium (III) ion and that of *nephelauxetic* factor were represented in Table (3-15). It is notice that Racah parameter (494 cm^{-1}) was found to be much less than that in free ion (918 cm^{-1}) due to the expansion of d- electron over the complex which expected to reduce the metal inter electronic repulsion. In addition the molar absorption obtained for this solution is in agreement with the known value of (< 10) for octahedral geometry.

Table (3-15):- Electronic spectra of chrome (III) complexes ions in choline chloride/tartaric acid ionic liquid.

Absorption band cm^{-1}	B`(cm[-1])	Calculated β	10 Dq	Δ_0/B	$\epsilon_{L / mol \, cm}$
ν_1=17793 ν_2=23094 $\nu_{3 \, cal}$=37695	494	0.53	1778.4	36	5.8

3.4 General Conclusions:

The following conclusions may be driven off from the results of this work:-

1. Choline chloride/d-tartaric acid ionic liquid was found to be much stable than aqueous solution as its electrolysis was noticeable at 2.5 volt.

2. $CuSO_4.5H_2O$, $NiCl_2$, and CrO_3 was soluble in this ionic liquid and showed a stable solutions except $NiCl_2$ which was decomposed at around (1 volt) while the others started at similar potential to of that ionic liquid (2.5 volt).

3. Copper, nickel, and chrome were successfully coated on stainless steel, copper, and nickel in this ionic liquid at 85°C offering a much more safer conditions in comparison to those of acidic solution of chrome.

4. The high voltage applied in these processes gave a much more coating in shorter time compared with corresponding aqueous solution as the allowed applied potential was higher in ionic liquid then in aqueous solutions.

5. The adherence of the coating was strong which offer a good practical characterization.

6. The coordination of the transition metal cation were of distorted octahedral of Cu^{+2} and mixed tetrahedral and octahedral of Ni^{+2} while Cr(VI) was reduced to Cr(III) of octahedral geometry.

3.5 Suggestion for future work:-

The following suggestions can be postulated to ensure completion of the study in this work:

1- The electrodeposition might be studied at different time to evaluate the efficiency of the solutions.

2- Studying the electrodeposition of transition metal at variable temperatures using the same prepared ionic liquid.

3- Examining the electrodeposition of other metals.

4- Examining of the resulted coated substrate with more efficient by microscopic instruments to evaluate the shape of coated particles and to establish the proper condition for selected shapes.

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الخلاصة

في هـذا البحـث تـم دراسـة سـلوك تفاعـلات الأكسـدة و الاختـزال مـع السـائل الأيـوني كلوريـد الكولين/حـامض التارتـارك، عـن طريـق دراسـة عمليـة التحليـل الكهربـائي للسـائل الأيـوني فـي درجـات الحـرارة (25الـى 95م°) مـع فولتيـات (0.5-5فولـت). حيـث وجـد أن اسـتقرار السـائل الأيوني فوق درجة حرارة 45 م° و 5 فولت. لكن لوحظ في حرارة 65 م °ان السـائل الأيوني أصبح أكثر أستقرار في 2,5 فولت. و تم قياس التوصيلية للسائل الأيوني و لوحظت أنها تـزداد بزيادة الحرارة.

وأيضا في هذا البحث استخدم الملح المنصهر المحضر كمذيب لا مائي لدراسـة سـلوك التحليل الكهربائي بعض أملاح العناصر الأنتقالية من السلسة الأولى.

حيث وجد أن محلول كبريتات النحاس مشابه لسلوك السائل الأيوني لوحده و لوحظ زيـادة كثافة التيار و التوصيلية بزيادة الحرارة وذلك بسبب كثافة المحلول.

وأيضا تم دراسة سلوك محلول كلوريد النيكل في السائل الأيوني و لوحظ أن فولتية التحليل كانت (1فولت) في درجة حرارة 65 م °بينما كان متشابه في سلوك كثافة التيـار و الفولتيـة مـع سـلوك محلول كبريتات النحاس.

و تم إيضاح سلوك محلول ا وكسيد الكروم في السائل الأيوني حيـث وجـد أنـه غيـر مسـتقر فـي درجة حرارة 65 م° و 2.5 فولت. لـذلك كانـت التوصيلية مشابهة إلـى توصـيلية السـائل الأيـوني لوحده في درجة حرارة(50 م°) لكن ازدادت عـن توصـيلية السـائل الأيـوني فـي حـرارة (60 م°)، وذلك بسبب عملية إختزال الكروم السداسـي إلـى كـروم ثلاثـي، و تـم دراسـة هـذه العمليـة عـن طريق جهاز الاشعة فوق البنفسجية – المرئية.

و لـوحظ أيضا فـي دراسـة عمليـة الترسيب للمحاليـل السـابقة فـي نفـس السـائل الأيـوني المحضـر بأسخدام فولتيات عالية، و حرارة ثابتة (85 م°) لمدة سـاعة. حيـث ظهـرت كميـة المـادة المترسـبة تـزداد بزيـادة الفولتيـة (2,2.5، و 3فولـت). حيـث لـوحظ أن شـكل الترسـيب بعـد التشـخيص غيـر منتظم

لكن جيد الالتصاق على المادة (نحاس، نيكل، و حديد). و تم حسـاب كفـاءة التيـار حيـث لـوحظ فـي عملية الترسيب للكروم(80%) و كان أقل في حالة ترسيب النيكل و انحاس(50%).

و تم تشخيص المحاليل السابقة في السائل الأيوني عن طريق جهاز الأشعة فوق بنفسجية-المرئية حيث وجد أن محلول كبريتات النحاس ثمانية السطوح، و ظهران محلول كلوريد النيكل هو مزيج بين ثماني و رباعي السطوح، ووجد أن محلولاوكسيد الكروم رباعي السطوح.

و تم حساب معامل راكاح (Racah) ، مقدار طاقة الانفصال، و حساب الامتصاصية لكل محلول من المحاليل السابقة.

بسم الله الرحمن الرحيم

لقد أرسلنا رسلنا بالبينات وأنزلنا معهم

الكتاب والميزان ليقوم الناس بالقسط

وأنزلنا الحديد فيه بأس شديد ومنافع للناس

وليعلم الله من ينصره ورسله بالغيب إن الله قوي

عزيز

صدق الله العظيم

سورة الحديد

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الكيمياء

دراسة كهروكيميائية المنصهر الأيوني المحضر بدرجة حرارة الغرفة لمزيج أملاح كلوريد الكولين/حامض الترتارك .

رسالة
مقدمة الى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قِبَلْ

نور جاسم محمد الزيدي
بكالوريوس (2006) (جامعة النهرين)

بأشراف
الدكتور هادي محمد علي عبود

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