Appendix:

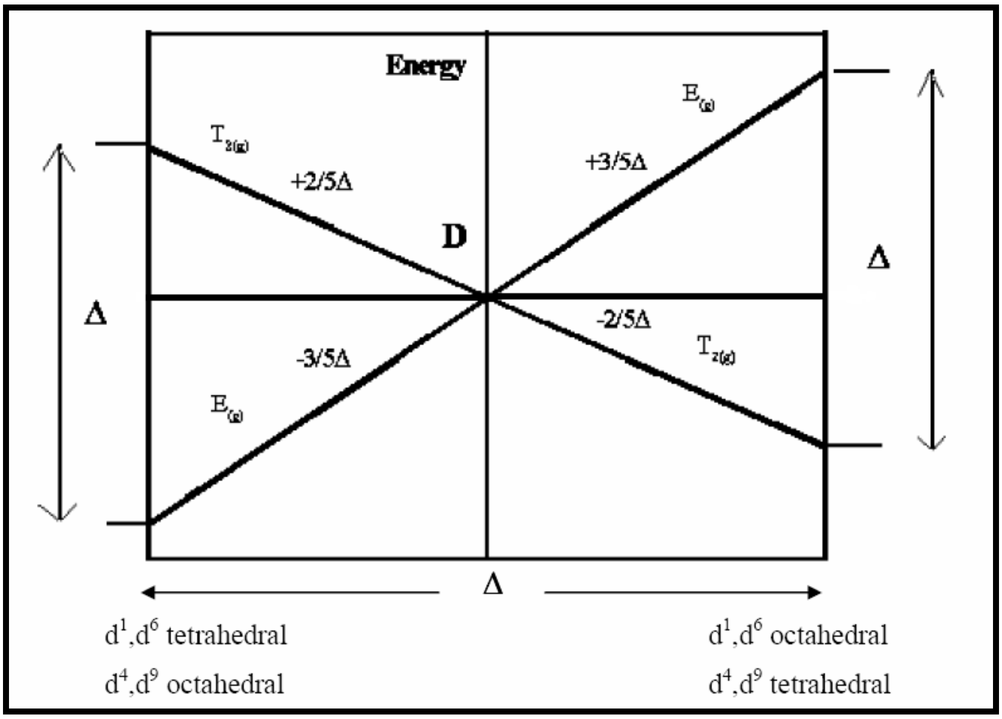
A.1 Determination of spectra:

The samples were prepared as described in section (2.3.3). At elevated temperature, the heated solution was packed in the quartz cell and was quickly transferred to the instrumental apartment and the spectra were recorded while the solution still hot. The variation in temperature was recorded before and after the measurement and the average value was considered. Normally the variation in temperature never exceeded 6 °C.

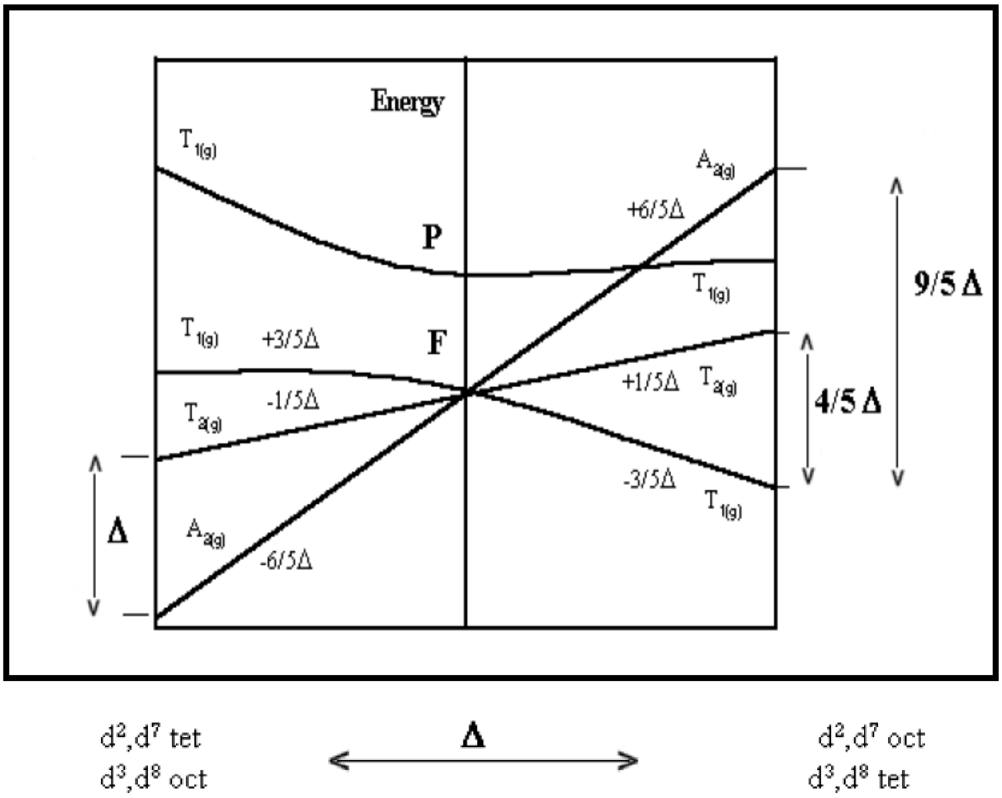
A.1.1 Orgel diagrams:

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 (A-1) the other for $d^{2, 3, 7, 8}$ Figure (A-2) 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. (85, 42)



Figure(A-1):- The splitting of free-ion D terms in octahedral and tetrahedral fields(85)



Figure(A-2):- The splitting of free-ion F and P term in octahedral and tetrahedral field. (85)

A.1.2. 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). (85,42)

A.2 Equations:

The equations that have been used in the determination of spectra of each complex were different from metal to another according to the splitting of terms for d^n configurations as shown in Figure (A-3) and in Table (A-1).

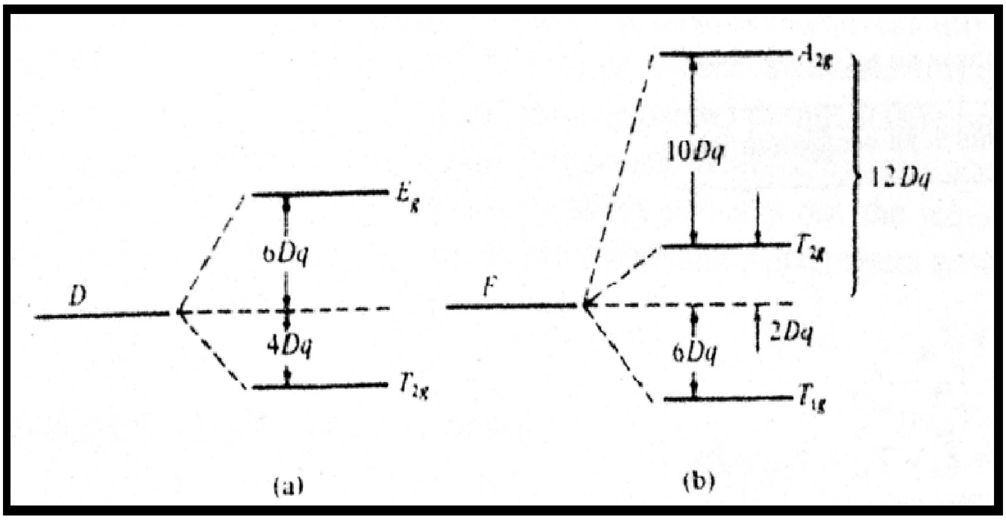


Figure (A-3): Splitting of terms for d^n configurations in to (a) and (b).

Table (A-1): Splitting of terms for d^n configuration. (54)

Configuration of free-ion	*Ground state of free-ion*	*Energy level diagram*	*Predicted in Figure (A-3)*
d^3	^4F	Inverted (b)	ν_1=10 Dq ν_2=18Dq-x ν_3=12Dq+15B`+x
d^7	^4F	(b)	ν_1=8Dq ν_2=18Dq ν_3=6Dq+15B`
d^8	^3F	Inverted (b)	ν_1=10 Dq ν_2=18Dq-x ν_3=12Dq+15B`+x
d^9	^2D	Inverted (a)	ν_1=10Dq

Also to measure the tendency of metal ion to form a complex Jorgenson rule have been used, the *g* factors provide an estimate of the value of 10Dq for an octahedral complex when combined with the *f* value for the appropriate ligands: **(54)**

$10Dq = f_{ligand} \times g_{ion}$ ………………………….……….(4-1)

Table (A-2):- Values of *g* and *f* factors for metal ions and various ligands

Transition metal ion	***Value of g factor***	***Various ligands***	***Value of f factor***
Cr(III)	17.4	Cl^-	0.78
Co(II)	9.00	tartaric acid	1.14 (this work)
Ni(II)	8.7	H_2O	1
Cu(II)	12.5		

In units of k (k=1000 cm^{-1}).

If all three transitions are observed, it is a simple matter to assign a value to B`, since the following equation must hold; (B` is in cm^{-1} units).

$15B` = \nu_3 + \nu_2 – 3\,\nu_1$ ……………………………………(4-2)

The nephelauxetic ratio *β* is given by:

$\beta = B`/B.$ ………………………………..…..(4-3)

Where ‘B’ is Racah parameter.

A.3 Example of calculations:

Consider an example application of a Tanabe-Sugano diagram for d^3 case. The absorption spectrum of a Cr^{+3} solution is shown below in Table (A-3). For example, the mathematical calculation of spectra, CrO_3 in choline chloride/tartaric acid room temperature ionic liquid.

Table (A-3):- Peak position of Chromium (III) ions in room temperature ionic liquid of Choline chloride/tartaric acid.

Ion	ν_1 cm^{-1}	ν_2 cm^{-1}	ν_3 cm^{-1}	ν_2/ν_1	ν_1/ν_2	Δ/B	Ref.
Cr^{+3}	17605	23419	?	1.33	0.752	32	This work

Two bands are observed within the range of measurement. They have maxima at 17605 and 23419 cm^{-1}. these are spin- allowed laporte-forbidden d-d transfers. Chromium is in the +3 oxidation state, so this is a d^3 system. Reference to Orgel diagram Figure (4-2) informs that three bands are expected and they can be assigned as:

$\nu_1 = {}^4A_2g\ (F) \rightarrow {}^4T_2g\ (F)$

$\nu_2 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (F)$

$\nu_3 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (P)$

Δ^o is taken to equal the absorption energy of 17605 cm^{-1}, and the intersect on the x-axis of Tanabe-Sugano diagram equal Δ^o/B. and by drawing a vertical line from this point it will intersect with other allowing electronic state of Tanabe-Sugano diagram for d^3 .

There are several goals sought in analyzing spectra using Tanabe-Sugano diagram:

1- To make correct band assignments. The two bands observed could be the first and second, or the second and third. Their assignment cannot be made by inspection.

2- To determine the magnitude of the ligand field splitting parameter, Δ^{o}.

3- To determine the magnitude of the e-e repulsion parameter (called a *Racah **B** parameter*).

Assumes bands are the first and second (so third band is not observed). Compare the two results. Tanabe-Sugano diagrams are unit less graphs showing energy ratios. The abscissa shows values for the ratio Δ^{o}/B (i.e., ligand field splitting parameter / e-e repulsion parameter).

Step (1): the calculated ratio of experimental band energy is: E (υ_2), E (υ_1),

Δ/B intersection with ^4T_2g at (E/B) = 32

Δ/B intersection with ^4T_1g at (E/B) = 42.53

B via ν_1 =17605 cm^{-1} /32.00 = 550 cm^{-1}.

B via ν_2 =23419 cm^{-1} /42.53 = 550.6 cm^{-1}.

Then B = 550.3 cm^{-1}.

$B_{\text{free-ion}}$ =918 cm^{-1}.

To determine the ν_3; Δ/B intersection with ^4T_1g (P) at (E/B) = 86.47

ν_3 = 86.47× 550 cm^{-1}

= 37702.7 cm^{-1}

= 265.23 nm

And by using the equations of splitting of term for d^3 in Table (A-2), we can determine the B` and β as following:

ν_1=10 Dq.

17605 cm^{-1}= 10 Dq

Dq = 1760.5 cm^{-1}.

ν_2=18Dq-x

23419 cm^{-1} = 18(1760.5 cm^{-1}) – x

x = 8270 cm^{-1}.

ν_3=12Dq+15B`+x

37702.7 cm^{-1} = 12 (1760.5 cm^{-1}) +15B`+ 8270cm^{-1}

15B`= 8306 cm^{-1}

B` = 553.7 cm^{-1}

Or we can use the following equation to determine the B`

15B`= ν_3+ ν_2-3 ν_1

15B`=37702.7 cm^{-1}+ 23419cm^{-1}-3(17605 cm^{-1})

B`=553.7 cm^{-1}

To determine the nephelauxetic ratio β:

β= B`/B, then β=553.7 cm^{-1}/918 cm^{-1}

β=0.6

Measurement of the tendency of metal ion to form complex with the probable existing ligand, using Jorgenson rule

10Dq= $f_{\text{ligand}} \times g_{\text{ion}}$

And the data in Table (A-3) and Table (A-2),

17605 = f_{ligand} ×17.4 ×1000 cm^{-1}

f_{ligand} = 1.01 cm^{-1}

Chapter One

Introduction

1.1: Green Chemistry:

1.1.1 Introduction to Green Chemistry:

‘‘Green chemistry is the use of chemical principles and methodologies for source reduction i.e. incorporates pollution prevention in the manufacture of chemicals, and promotes pollution prevention and industrial ecology.’’ It may also be defined as ‘‘the invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.’’ (1,2) Green chemistry is in other words the use of chemistry for pollution prevention. More specifically, it is the design of chemical products and processes that are environmentally benign. At its best, green chemistry is environmentally benign, linking the design of chemical products and processes with their impacts on human health and the environment. (3)

Chemistry is undeniably a very prominent part of our daily lives. From plastics to pharmaceuticals to dry cleaning, many of life’s comforts would be impossible without the chemical industry.

Food and drink has been made safe to consume, the development of cosmetics has enabled us to beautify and admire our appearances and the whole area of pharmaceuticals has allowed the development and synthesis of new cures for illnesses and diseases, all as a result of chemistry.

However, additional chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for ‘greener’ chemical products. (4)

Most processes that involve the use of chemicals have the potential to cause a negative impact on the environment. It is therefore essential that the risks involved be eliminated or at least reduced to an acceptable level. In its most simple form, risk can be expressed as:

$$Risk = Hazard.X.Exposure$$ (5)

Green chemistry looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of chemistry in our world today and the implications it can how on our environment. (4)

1.1. 2 ***<u>The Green Chemistry Program:</u>*** (1,6)

The Principles of Green Chemistry have been distilled from a diverse set of practices and emerging research.

In 2006, the Environmental Protection Agency (EPA), (7) developed 12 principles of green chemistry, which help to explain what the definition means in practice. The principles cover such concepts as:

- The design of processes to maximize the amount of raw material that ends up in the product.
- The use of safe, environment-benign solvents where possible.
- The design of energy efficient processes.
- The best form of waste disposal, aiming not to create it in the first place.

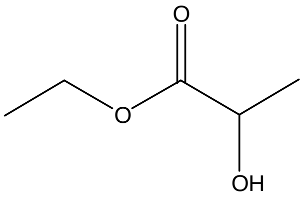
The Green Chemistry program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances. This program works very closely with the twelve principles of Green Chemistry as shown below:

1. Prevent waste: It is better to prevent waste rather than to treat it.
2. Atom economy: Aim to maximize the incorporation of all materials used in the chemical process into the final product. For example, minimize the production of by-product and wastes.
3. Less hazardous chemical synthesis: Design methods such that any chemical substances produced have the least toxic effect on human health and the environment as possible.
4. Safer chemical design: Aim to produce chemicals which fulfill the desired function but have minimal toxicity.
5. Safer solvents and auxiliaries: Minimize the use of chemical solvents and related substances (which may be flammable, toxic and/or environmentally unsafe). If unavoidable, use non-hazardous solvents wherever possible.
6. Design for energy efficiency: Reduce the amount of energy resources required to perform a chemical process.
7. Renewable feedstock: Use renewable raw materials and agents whenever possible.
8. Reduce derivatives: Chemical derivatives are often produced as temporary intermediate molecules between the start and end products. Such multistage processes require the input of more resources and chemical reagents. Therefore, the minimization of such steps is desirable.
9. Catalytic agents: Use catalytic agents (small amounts required, reusable) rather than stochiometric reagents (larger amounts required, non-reusable).
10. Degradable design: Design products to be degradable after completing their function.

11. Pollution reduction by real-time analysis: It is necessary to ensure that new methods are truly safe and nonpolluting. This requires proper monitoring of reactions to identify potential short-term and long-term by-product and their consequences. In order to achieve this, new analytical technologies may need to be developed.
12. Safer Chemistry: Reduce the use of dangerous chemicals and substances to minimize the risk of accidents.

1.1. 3: Green Solvents:

Green solvents are environmentally friendly solvents or bio solvents, which are maybe derived from the processing of agricultural crops. Ethyl lactate, for example whose structure is shown below, is a green solvent derived from processing corn. (8)



Ethyl lactate

Ethyl lactate is the ester of lactic acid. Lactate esters solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages including being 100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic and non-ozone depleting. (9)

Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low vapour pressure and low surface tension. It is a desirable coating for wood, polystyrene and metals and also acts as a very effective paint stripper and graffiti remover. Ethyl lactate has replaced solvents including toluene, acetone and xylene, which has resulted in the work place being made a great deal safer. (10)

The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment. The use of toxic solvents contributes to air emission of volatile organic compounds (VOC's); they are now considered as environmentally unacceptable. (11)

The Montreal Protocol identified the need to re-evaluate chemical processes with regard to their use of VOC's and the impact theses VOC's has on the environment. Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents. (12)

Alternative promising areas of research in the replacement of the use of VOCs in industry include the application of supercritical carbon dioxide and ***ionic liquids*** as alternative solvents. Both of which have proved to have valuable applications. (13)

Ionic liquids (IL) are novel solvents composed of organic cations and inorganic anions which are liquid at room temperature, or just above. A negligible vapour pressure (and an associated high thermal stability) makes IL promising replacements for volatile organic solvents in industrial processes. This has lead to IL being labeled as "green" and environmentally friendly. (14)

1.2 Ionic Liquids:

1.2.1 History of ionic liquid IL:

The history of IL's may be viewed as a relatively recent one, or one extending back to 19th century.

A working definition suitable for a historical review of ionic liquids, is that the an ionic liquid is a salt with melting temperature below the boiling point of water (100˚C).

The roots of ionic liquids are firmly planted in traditional high temperature molten salt. (15)

The early history of ionic liquids being in 1914. One of the earlier known ionic liquids (room temperature molten salt) was reported by Walden (16). He reported the physical properties of ethylammonium nitrate, $[EtNH_3]^+$ $[NO_3]^-$, which has a melting point of 12C^o, formed by the reaction of ethylamine with concentrated nitric acid. (17)

Much later, series of ionic liquids based on mixtures of 1,3-dialkylimidazolium or 1-alkylpyridinium halides and trihalogeno aluminates, initially developed for use as electrolytes, were to follow. (16,(18)

Hurley and Weir (19) who stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride.

Another progenitor of current ionic liquids was the work of Prof. John Yoke at Oregon State University. (20) In 1960□`s he found that mixtures of copper (1) chloride and alkyl ammonium chloride were liquid near room temperature when mixed as in equation (20)

$CuCl_{(s)} + Et_3NHCl_{(s)} \rightarrow Et_3NHCuCl_2$ ……………………… (1.1)

In 1970s, 1980s, Osretyoung et al. (17,21) And Hussey et al.(18,22) carried out extensive research on organic chloride-aluminum chloride ambient temperature ionic liquid. The ionic liquid based on $AlCl_3$ can be regarded as the first generation of ionic liquids. (23,24)

In 1992, Wilkes and Zawarotko (25) reported the preparation of ionic liquids with alternative, 'neutral' anions such as hexafluorophosphate ($[PF_6]^-$) and tetrafluoroborate ($[BF_4])^-$, allowing a much wider range of applications for ionic liquids. It was not until recently that a class of new, air- and moisture stable, neutral ionic liquids was available that the field attracted significant interest from the wider scientific community. (25)

More recently, people have been moving away from $[PF_6]^-$ and $[BF_4]^-$ since they are highly toxic, and towards new anions such as bistriflimide $[(CF_3SO_2)_2N]^-$ or even away from halogenated compounds completely. Moves towards less toxic cations have also been growing, with compounds like ammonium salts (such as choline) being just as flexible a scaffold as imidazole. (26)

The histogram of Figure (1-1) shows the increase of the number of publications on ionic liquid during the last decade up to the time being.

As seen, the average number of publications in the last decade is about 40 papers per year while in 2004 about 1000 papers and in 2005 about 1500 papers where published .

This reflects the increased interest in ionic liquids in general. (27)

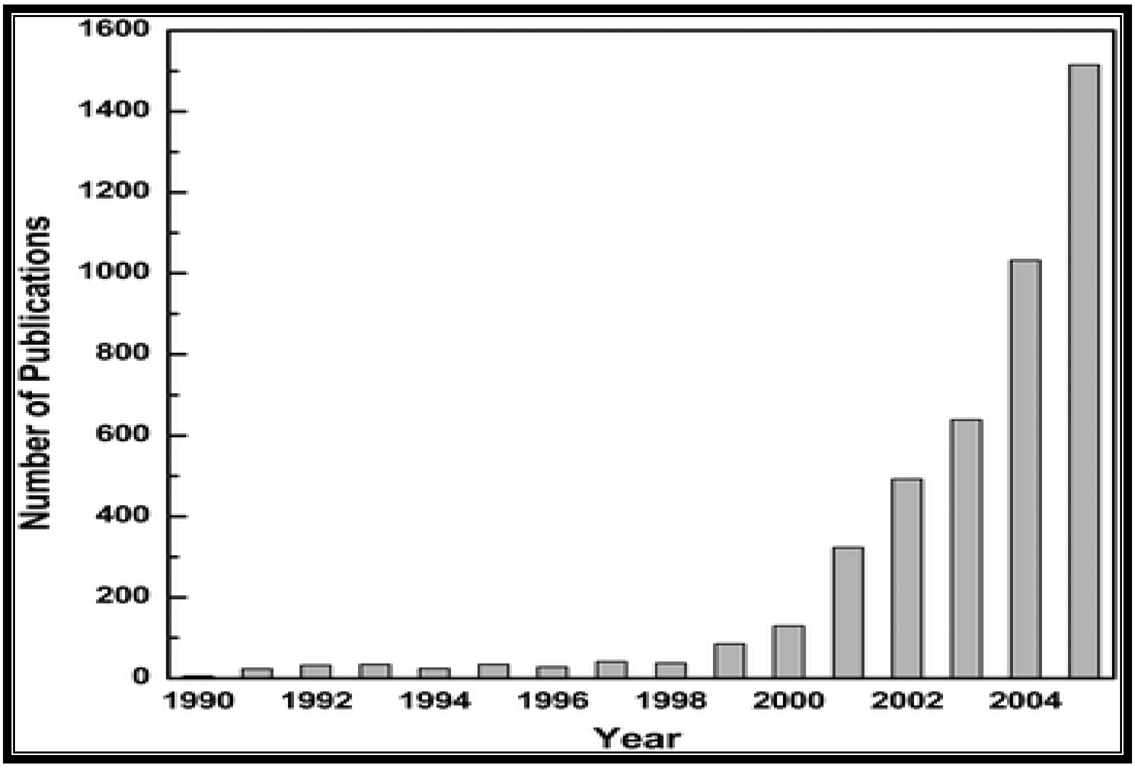


Figure 1-1 Publications containing the phrase (ionic liquid or ionic liquids) in the title; abstract and key words; determined by ISI web of science; as a function of time.

1.2.2 Ionic liquid definition:

An ionic liquid (IL) is a liquid consisting of ions only, but this definition is different from the classic definition of a molten salt. The latter is a high-melting, highly viscous, and highly corrosive liquid, while an ionic liquid is liquid at a much lower temperature (< 100 °C) and has a lower viscosity. (28)

1.2.2.1 Molten salt high temperature ionic liquid:

It is a rather dreadful name for an otherwise useful category of materials and processes. The term "Molten Salt" is self-descriptive; it is melted salt(s). Another common name is Fused Salt(s). The simplest example of a molten salt would be to take sodium chloride ("table salt") and heat it to a red heat (greater than 801° C, or 1474° F) where it would melt into a liquid. This liquid is stable, has a heat capacity similar to water (by volume) and flows much like water does. The major differences are the obvious higher temperatures attainable in the molten salt state and when the salt solidifies (freezes) it contracts versus expanding like water. Thus, molten salt freezing in a pipe would not burst the pipe as water would.(29,30)

The high temperatures (>100^{o}C) associated with most inorganic molten salt often limit their utilization as solvents for many applications. Whether practical or fundamental in nature. For example, few organic compounds possess sufficient thermal stability to be dissolved in inorganic molten salt and many potentially interesting inorganic solutes exhibit high vapor pressures at the elevated temperatures often encountered with some inorganic melts. In addition, the high temperature associated with some inorganic molten salts frequently place exceptional requirements on the design of apparatus used to study the neat melts or extraneous solutes dissolved in melts and often add extraordinary amount of nonessential experimental manipulation. Considerable interest has arisen in the last few years concerning aprotic molten salts that are liquid proximate to room temperature (25^{o}C) (31)

1.2.2.2 Room temperature ionic liquids (RTILs):

They are salts with melting points lower than 30^{o}C. They look like a classical liquid but they do not contain any molecules: they are made of ions. The structure of these liquids is completely different from the structure of any other solvents made of molecules. The properties of a given solvent depend on the interaction between the solvent molecules. If there are strong interactions between the solvent molecules, the solvent is called a “polar” solvent, e.g. water, methanol, ethanol. If the interactions between the solvent molecules are weak, it is an “apolar” solvent, e.g. hexane, heptane, petroleum ether. (30, 32)

Ionic liquids represent a novel class of non-aqueous solvents and may also be considered as a novel medium for liquid– liquid extraction. (33)

Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstanding good solvents for a variety of compounds, and their lack of a measurable vapor pressure makes them a desirable substitute for VOC’s. Ionic liquids are attractive solvents as they are non-volatile, non-flammable, have a high thermal stability and are relatively inexpensive to manufacture. They usually exist as liquids well below room temperature up to a temperature as high as 200^oC. The key point about ionic liquids is that they are liquid salts, which means they consist of a salt that exists in the liquid phase and have to be manufactured, they are not simply salts dissolved in liquid. Usually one or both of the ions is particularly large and the cation has a low degree of symmetry, these factors result in ionic liquids having a reduced lattice energy and hence lower melting points. (34)

1.2.3 Physical properties of ionic liquids:

1- Conductivity: ionic liquids have reasonably good ionic conductivities compared with those of organic solvents/ electrolyte systems (up to 10 mS cm^{-1}) .(35) at elevated temperature of e.g. 200^{o}C a conductivity of 0.1 Ω^{-1} cm^{-1} can be achieved for some system. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on the fact that ionic liquid are composed solely of ions, it would be expected that ionic liquids have high conductivities. This is not the case since the conductivity of any solution depends not only on the number of charge carried but also on their mobility. The large constituent ions of ionic liquids reduce the ion mobility which, in turn, leads to lower conductivities. Further more , ion pair formation and/or ion aggregation lead to reduced conductivity. The conductivity of ionic liquids of higher viscosity exhibit lower conductivity. Increasing the temperature increases conductivity and lowers viscosity. (36)

2- Viscosity: generally, ionic liquids are more viscous common molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature. The viscosities of some popular air and water stable ionic liquids at room temperature are: 312mPa s for [Bmim] PF_6; 154 mPa s for [Bmim] BF_4 (37); 52 mPa s for [Bmim] TF_2N (38); 85 mPa s for[BMP]TF_2N (39).

The viscosity of ionic liquids is determined by van der waals (VDW) force and hydrogen bonding. Electrostatic forces may also play an important role. Alkyl chain lengthening in the cation leads to an increase in viscosity (38). This is due to stronger (VDW) forces between cations leading to increase in the energy required for molecular motion. Also (38), the ability of anaions to form hydrogen bonding has a pronounced effect on viscosity.

The fluorinated anions such as BF_4^- and BF_6^- form viscous ionic liquids due to the formation of hydrogen bonding. In general all ionic liquids show a significant decrease in viscosity as the temperature increases. (40)

3- Density: Ionic liquid in general are denser than water with values ranging from 1 to 1.6 g cm^{-1} and their density decrease with increase in the length of the alkyl chain in the cation. The densities of ionic liquids are also affected by the identity of anions. (41) The order of increasing density for ionic liquids composed of single cation may be represent as:

$[CH_3SO_3]^- \approx [BF_4]^- < [CF_3CO_2]^- [CF_3SO_3]^- < [C_3F_7CO_2]^- < [(CF_3SO_2)_2N]^-$. (35)

4-Melting point: Ionic liquids have been defined to have melting point below 100 °C and most of them are liquid at room temperature. Both cations and anions contribute to the low melting points of ionic liquids. The increase in anion size leads to decrease in melting point. (42) cations size and symmetry make an important impact on the melting point of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction. (35)

5- Thermal stability: Ionic liquids can be thermally stable up to temperatures of 450 °C the thermal stability of ionic liquids is limited by the strength of their heteroatom- carbon and their heteroatom-hydrogen bonds, respectively. (41)

6- Electrochemical window: The electrochemical window is an important property and plays a key role in using ionic liquids in electrode position of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. As known, the electrodeposition 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] BF_6 at a platinium electrode, 4.10 V for [Bmim] BF_4 and 5.5 V for [BMP] TF_2N at a glassy carbon electrode. (43) In general, the wide electrochemical windows of ionic liquids have opened the door to electro-deposit metals and semiconductors at room temperature, which were formerly obtained only from high temperature molten salts. 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 presumable many other ones at elevated temperature. (44)

1.2.4 Advantages of ionic liquids: (45,46)

There is a dramatic need to search for alternatives to damaging solvents which are used in huge quantities and are usually volatile liquids that are difficult to contain .

One of these alternatives is ionic liquids that are liquid at room temperature and that have physical properties that make them very interesting as potential solvents for synthesis :

1. Good solvents for a wide range of inorganic and organic materials.
2. Often composed of poorly coordinating ions and can therefore be highly polar yet non coordinating. (47)
3. No effective vapour pressure. (21)
4. Liquid range of 300°C allowing tremendous kinetic control.
5. Thermally stable up to 200°C.
6. Their water sensitivity does not affect their industrial applications.
7. Immiscible with a number of organic solvents and provide non-aqueous polar alternatives for two-phase systems (48).

8. Relatively inexpensive/easy to prepare.
9. The ability to impart selective reactivity
10. Ionic liquids are attractive solvents as they are non-volatile, and non-flammable.

This has lead to IL being labeled as“ green” and environmentally friendly.

1.2.5 Applications of Ionic Liquids:

Ionic Liquids are of tremendous important to the chemical industry and they represent an innovation in the way chemistry is performed. As functional materials, they are being used in a wide variety of applications such as chemical engineering, synthesis, catalysis, batteries, fuel cells, biotechnology or analytical science. Numerous new combinations of ionic liquids are available. They can be designed specifically for every type of application since the selection of the ions determines their chemical and physical properties. The “unlimited” combination of the cations and anions is opening up new opportunities. (49)

Ionic liquids provide benefits particularly in the production area, since they optimize the reaction and preparation steps. They are very well suited as solvents for organic syntheses, because traditional solvents are for the most part toxic, volatile and readily combustible.

Additionally, they are used for applications in catalysis and for extractions. Production procedures, catalyses and enzyme catalyses are more efficient and longer lasting, since ionic liquids increase the yield and facilitate the isolation of the products from catalyst. They are also suitable for difficult aqueous preparation processes. (50)

1.2.6 Room temperature ionic liquid based on choline chloride:

Abott(51) has recently developed a range of ionic compounds, which are fluid at room temperature. These ionic liquids are based on simple precursors such us choline chloride (vitamin B_4) which is cheap and produced on a multi-ton scale and hence these ionic liquids/ deep eutectic solvents can be applied to large scale processes. (51)

Deep eutectic solvents (DES) can be formed between a range of carboxylic acids and choline chloride. The physical properties are significantly affected by the structure of the carboxylic acid but the phase behavior of the mixtures can be simply modeled by taking account of the mole fraction of carboxylic acid in the mixture. So, the physical properties and phase behavior are dependent upon the number of acid functionalities, the aryl/alkyl substitutions and the composition of mixture. The ease of synthesis, availability and biodegradability of the components makes these DES versatile alternatives to ionic liquid. (52)

1.3 Solvents:

Solvents may be defined as the component of a solution that is present in the greatest amount, or the substance in which the solute is dissolved. For examples: The solvent for sea water is water. The solvent for air is nitrogen. (53)

The vast majority of chemical reactions are performed in solution. The solvent fulfills several functions during a chemical reaction. It solvates the reactants and reagents so that they dissolve. This facilitates collisions between the reactant(s) and reagents that must occur in order to transform the reactant(s) to product(s). The solvent also provides a means of temperature control, either to increase the energy of the colliding particles so that they will react more quickly, or to absorb heat that is generated during an exothermic reaction. The selection of an appropriate solvent is guided by theory and experience. Generally a good solvent should meet the following criteria.

- It should be inert to the reaction conditions.
- It should dissolve the reactants and reagents.
- It should have an appropriate boiling point.
- It should be easily removed at the end of the reaction.

The second criterion invokes the adage "Like dissolves like". Non-polar reactants will dissolve in non-polar solvents. Polar reactants will dissolve in polar solvents. There are three measures of the polarity of a solvent:

- Dipole moment
- Dielectric constant
- Miscibility with water

Molecules with large dipole moments and high dielectric constants are considered polar. Those with low dipole moments and small dielectric constants are classified as non-polar. On an operational basis, solvents that are miscible with water are polar, while those that are not are non-polar; e.g. "Oil and water don't mix". (53)

1.3.1 Classification of solvents:

Solvents may be classified in three ways:

1.3.1.1: Aqueous and non aqueous solvents:

a- Aqueous solvents: Any solution in which water (H_2O) is the solvent. For examples: cola, saltwater, rain. (51)

b- Non aqueous solvents: An inorganic nonaqueous solvent is a solvent other than water, that is not an organic compound. Common examples are liquid ammonia as basic solvent, sulfuric acid as an acidic solvents ,bromine trifluoride as an aprotic solvent, and ionic liquids as polar non aqueous solvents. These solvents are used in chemical research and industry for reactions that cannot occur in aqueous solutions or require special environment. (54)

1.3.1.2: Polar and non-polar solvents:

Other type of classification, Chemists have classified solvents into three categories according to their polarity:

a- Polar protic

b- Dipolar aprotic

c- Non-polar.

a- Polar protic solvent:

Protic refers to a hydrogen atom attached to an electronegative atom, when electronegative atom is almost exclusively oxygen. In other words, polar protic solvents are compounds that can be represented by the general formula R-OH. The polarity of the polar protic solvents stems from the bond dipole of the O-H bond. The large difference in electronegativities of the oxygen and the hydrogen atom, combined with the small size of the hydrogen atom, warrant separating molecules that contain an OH group from those polar compounds that do not. Examples of polar protic solvents are water (HOH), methanol (CH_3OH), and acetic acid (CH_3CO_2H).

More generally, any molecular solvent which contains dissociable H^+, such as hydrogen fluoride, is called a **protic solvent**. The molecules of such solvents can donate an H^+ (proton). Conversely, **aprotic solvents** cannot donate hydrogen bonds.

Common characteristics of protic solvents:

1. Solvents display hydrogen bonding.
2. Solvents have an acidic hydrogen (although they may be very weak acids).
3. Solvents are able to stabilize ions.
4. Cations by unshared free electron pairs .
5. Anions by hydrogen bonding.

Examples are water, methanol, ethanol, formic acid, hydrogen fluoride and ammonia.

b- Dipolar Aprotic Solvents:

Solvents that share ion dissolving power with protic solvents but lack an acidic hydrogen. These solvents generally have high dielectric constants and high polarity. aprotic describes a molecule that does not contain an O-H bond. Typically this bond is a multiple bond between carbon and either oxygen or nitrogen. Most dipolar aprotic solvents contain a C-O double bond. Examples are acetone and ethyl acetate.

Polar protic solvents are favorable for S_N1 reactions, while polar aprotic solvents are favorable for S_N2 reactions. Apart from solvent effects, polar aprotic solvents may also be essential for reactions which use strong bases, such as reactions involving Grignard reagents or n-butyl lithium. If a protic solvent were to be used, the reagent would be consumed by a side reaction with the solvent. (55)

c- Non-Polar Solvents:

Non-polar solvents are compounds that have low dielecrtic constants and are not miscible with water. Examples include benzene (C_6H_6), carbon tetrachloride (CCl_4), and diethyl ether

All of these solvents are clear, colorless liquids.

1.3.1.3: Molecular and Ionic solvents:

Solvents can also be classified according to the constituent nature as moleculer and ionic solvents. All solvents whether aqueous , non aqueous, protic or aprotic solvents, are molecular solvents while those of molten salts such as RTIL are ionic solvent consisting anions and cations.

1.4 Solubility:

Solubility: A quantity expressing the maximum concentration of some material (the solute) that can exist in another liquid or solid material (the solvent) at thermodynamic equilibrium at specified temperature and pressure. Common measures of solubility include the mass of solute per unit mass of solution (mass fraction), mole fraction of solute, molality, molarity, and others. (56)

Solubility is a fundamental property of a compound and is useful in the investigation of many thermodynamic properties. (57)

Solubility is the intrinsic property of matter to form a homogeneous dispersion of one component, the solute, into another, the solvent. The solution phase can be gaseous, liquidus, or solidus. (38)

Saturated solution is a solution that contains all the solute that can be dissolved at a particular temperature.

Supersaturated solution: contains more solute than can be dissolved at the current temperature. (58)

1.4.1 Benefit and application of solubility:

Solubility is of fundamental importance in a large number of scientific disciplines and practical applications, the most obvious ones being in chemical engineering, material science and geology.

For example, solubility of a substance is useful when separating mixtures. A mixture of salt (sodium chloride) and silica may be separated by dissolving the salt in water, and filtering off the undissolved silica. The synthesis of chemical compounds, by the milligram in a laboratory, or by the ton in industry, both make use of the relative solubilities of the desired product, as well as unreacted starting materials, by-products, and side products to achieve separation.

Another example of this would be the synthesis of benzoic acid from phenylmagnesium bromide and dry ice. Benzoic acid is more soluble in an organic solvent such as dichloromethane or diethyl ether, and when shaken with this organic solvent in a separatory funnel, will preferentially dissolve in the organic layer. The other reaction products, i.e. the magnesium bromide will remain in the aqueous layer, clearly showing that separation based on solubility is achieved. (On a practical note, the benzoic acid obtained after evaporating the organic solvent should ideally be purified by recrystallizing from hot water.) (26)

The measurement of solubility is useful in determining the purity of compounds, especially when other methods failed, in identifying some macromolecules and in establishing separation schemes for a number of biochemicals and organic chemicals. Solubility measurements yield useful information regarding some thermodynamic properties of a molecule; this helps in our understanding of the various intermolecular forces at play solution.

One of the most important applications of solubility lies in the fact that conclusions regarding the purity and identity of a substance can be drawn by sophisticated solubility technique without ever having to know the chemical structure of the solid(s). One technique, phase solubility analysis (PTA), is described here briefly to point-out the powerful applications it has in the areas of food and organic chemistry. In principle, phase solubility analysis is derived from Gibbs phase rule. The technique involves the analysis of the composition in solution as a function of the total amount of solid added and yields a phase diagram. When phase equilibration and solubility analysis are used to prepare a pure solid, separated from its impurities, the process is often called “swish purification.” This technique can also be used to enrich impurities in solution phase, which helps to identifying them smith and downing, (1979) Garrett et al. (1963) (59) have described the practical aspects of phase solubility analysis and have used this technique to determine the solubility of steroids in mixtures of organic solvents. (59)

In addition the solubility is used to determine the **Lattice energy** and it is normally defined as The energy per ion pair required to separate completely the ions in a crystal lattice at a temperature of absolute zero. (43)

The lattice energy always the reverse process therefore it is always positive , the lattice energy of a crystal MX is the enthalpy of the process.(60)

$MX(s) \longrightarrow M^+ + X^- \qquad \Delta H^o = U$ ………………………(1.2)

The lattice energy of an ionic solid is a measure of the strength of bonds in that ionic compound. It is given the symbol U and is equivalent to the amount of energy required to separate a solid ionic compound into gaseous ions. Lattice energy can also be considered as the energy given off when gaseous ions form an ionic solid. It is dependent on ionic charge and the ionic radius: as the charge of the ions increases the lattice energy increases (becomes more negative), and as the radius decreases (the ions in the ionic solid are closer together) the lattice energy increases. (61)

The solubility curves were used to determine the enthalpy of fusion of the solute, which is expressed in cal/mol, by plotting logarithm of concentration in Molarity against the reciprocal of the absolute temperature (1/T). (62)

The following equation may be applied, assuming the solution is ideal:

$$Lnx = \frac{-\Delta H^{\circ}}{RT} + const. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 1.3$$

Where X = the concentration of the solute (mol kg^{-1})

R = the gas constant (1.987 cal K^{-1} mol^{-1})

T = the absolute temperature (K)

And ΔH° = the Enthalpy of fusion of the solute (cal mol^{-1})

1.4.2 Factors Affecting Solubility: (63)

There are three main factors that control solubility of a solute:

(1) Temperature

(2) Nature of solute or solvent

(3) Pressure

1.4.2.1 Effect of temperature:

The solubility of solutes is dependent on temperature. When a solid dissolves in a liquid, a change in the physical state of the solid analogous to melting takes place. Heat is required to break the bonds holding the molecules in the solid together. At the same time, heat is given off during the formation of new solute - solvent bonds.

Generally in many cases solubility increases with the rise in temperature and decreases with the fall of temperature but it is not necessary in all cases.

a: Decrease in solubility with temperature:

If the heat given off in the dissolving process is greater than the heat required to break apart the solid, the net dissolving reaction is exothermic (energy given off). The addition of more heat (increases temperature) inhibits the dissolving reaction since excess heat is already being produced by the reaction. This situation is not very common where an increase in temperature produces a decrease in solubility. In exothermic process solubility decrease with the increase in temperature.

For example: solubility of calcium oxide decreases with the increase in temperature.

b: Increase in solubility with temperature:

If the heat given off in the dissolving reaction is less than the heat required to break apart the solid, the net dissolving reaction is endothermic (energy required). The addition of more heat facilitates the dissolving reaction by providing energy to break bonds in the solid. This is the most common situation where an increase in temperature produces an increase in solubility for solids. In endothermic process solubility increases with the increase in temperature and vice versa. For example: solubility of potassium nitrate increases with the increase in temperature.

1.4.2.2 Nature of solute and solvent: (64)

Solubility of a solute in a solvent purely depends on the nature of both solute and solvent. For example, a polar solute dissolved in polar solvent,- Solubility of a non-polar solute in a solvent is large, or A polar solute has low solubility or insoluble in a non-polar solvent.

1.4.2.3 Effect of pressure: (64)

The effect of pressure is observed clearly in the case of gases.

An increase in pressure increases of solubility of a gas in a liquid.

For example carbon di oxide is filled in cold fizzy drink bottles (such as coca cola, Pepsi 7up etc.) under pressure.

1.4.3 Some previous studies of solubility of transition metal in

various ionic liquids:

There has been a growing interest in the study of ambient- temperature ionic liquid as an amiable solvent for the study of transition metal oxides and transition metal chloro complexes. Ionic liquid represent an ideal nonaqueous environment for studying the reactions of these transition metal complxes free from the effects of solvation and solvolysis phenomena. (65)

Oxygen containing transition metal compounds have been used extensively in industrial as catalysts or as supports for other catalyst materials. For example, vanadium oxides and other related vanadium-containing compound are widely used as catalyst, especially for oxygen transfer reactions. (66)

The dissolution of vanadium (V) oxide V_2O_5 in various chloro_aluminate ionic liquids has been studied to determine the complexes formed with respect to melt composition and V_2O_5 concentration. V_2O_5 did not dissolve in either1-n-butyl-3-methylimidazolium tetrafluroaluminate or 1-n-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquids. V_2O_5 was found to dissolve at temperatures greater than 70 C^o in 1-ethyl- and 1-n-butyl-3-methylimidazolium tetrachloroaluminate. (67)

Additionally, the study of the solubility of a range of metal oxides in a eutectic mixture of choline chloride/ urea, showned that the dissolved metals can be reclaimed from a mixed metal oxide matrix using electrodepositing. (68)

The other one is measuring the solubility of some metal oxides in the elemental mass series Ti through Zn which have been determined in three ionic liquids based on choline chloride. The result was obtained are compared with aqueous solution of HCl and NaCl. (69) which showed in some instances a larger solubility in ionic liquid in comparison with those obtained from previous solvents.

1.5 .Chemistry of transition metal:

1.5.1 Copper (II) oxide or cupric oxide (CuO):

It is a black powder, insoluble in water. It dissolves in acids to give solutions of copper (II) salts. It is readily reduced to the metal by heating with hydrogen and is used to determine carbon and hydrogen in organic compounds (the carbon as carbon monoxide reduces the copper(II) oxide to copper). (70)

The water insoluble (55) copper (II) Oxide is the higher oxide of copper and is a basic oxide. It dissolves in mineral acids such as hydrochloric acid, sulfuric acid or nitric acid to give the corresponding copper (II) salts:

$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$ ……………………..…..1.4

$CuO + 2HCl \rightarrow CuCl_2 + H_2O$ ……………………..…..1.5

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$ …………………….....1.6

The ion configuration of this cation is $3d^9$.

1.5.2 Chromium (VI) Oxide (Chromium Trioxide):

Chromium trioxide is obtained as bright red crystals when concentrated sulphuric acid is added cautiously to a concentrated aqueous solution of a chromate or dichromate (VI). It can be filtered off through sintered glass or asbestos, but is a very strong oxidizing agent and so oxidises paper and other organic matter (hence the use of a solution of the oxide — "chromic acid' — as a cleansing agent for glassware). Chromium (VI) oxide is very soluble in water ; initially, "chromic acid', H_2CrO_4, may be formed, but this has not been isolated. If it dissociates as :

$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$ ……………………………….1.7

; then the $HCrO_4^-$ ions probably form dichromate ions :

$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$ ……………………………..…1.8

Chromium(VI) oxide is acidic, and the corresponding salts are the *chromates* and *dichromates*, containing the ions CrO_4^{-2} and $Cr_2O_7^{-2}$, i.e. $[CrO_4 + CrO_3]^{-2}$. The oxidation state of chromium is **+6** in each ion. (53) The ion configuration is of $3d^o$.

1.5.3 Cobalt oxide Co_3O_4:

This is $Co^{(II)}(Co^{(III)})_2O_4$ and has the normal spinel structure with $Co^{(II)}$ ions in tetrahedral and $Co^{(III)}$ ions in octahedral sites. (27)

It is obtained as a brown precipitate Co_3O_4. Aqueous when cobalt (II) hydroxide is oxidized in alkaline conditions (or when a cobalt (III) is decomposed by aqueous alkali). On heating it gives the black mixed oxide Co_3O_4. (53) the ion configuration of Co (II) is $3d^7$, and for Co (III) is $3d^6$

1.5.4 Zinc(II) oxide, ZnO:

it is prepared by heating the hydroxide $Zn(OH)_2$ or the carbonate $ZnCO_3$. It is a white solid, insoluble in water, but readily soluble in acids to give a solution containing the zinc(II) cation, and in alkalis to give a hydroxozincate(II) anion:

$ZnO + 2H_3O^+ \rightarrow Zn^{2+}_{(aq)} + 3H_2O$ …...………1.9

(e.g.) $ZnO + 2OH^- + 3H_2O \rightarrow [Zn(OH)_4(H_2O)_2]^{2-}$ ……..……..1.10

Zinc(II) oxide is therefore amphoterie. On heating, the oxide becomes yellow, reverting to white on cooling. When zinc oxide is heated, a little oxygen is lost reversibly. This leaves a non-stoichiometrie compound. The crystal lattice is disturbed in such a way that electrons from the excess zinc metal remaining can move in the crystal almost as freely as they can in a metal. This makes zinc oxide a semiconductor and gives it a yellow color, which is lost when oxygen is taken up again on cooling to give zinc oxide.(53) the ion configuration is $3d^{10}$.

1.5.5 Nickel oxide NiO:

Heating nickel (II) hydroxide $Ni(OH)_2$ gives the black oxide. NiO, which is also obtained by heating nickel(II) carbonate or the hydrated nitrate. (53) The grey or black color of nickel oxide arise from slight nonstiochiometry. It is a basic oxide dissolves easily in acids. But insoluble in water. (71) the ion configuration is $3d^8$.

1.6 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 (72)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) (27,54).

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 (71). 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 (69-70):

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 (69).

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:

($I^- < Br^- < SCN^- \sim Cl^- < F^- < OH^- \sim ONO^- < C_2O_4{}^{2-} < H_2O < NCS^- <$ $EDTA^{4-} < NH^3$ ~ pyr ~ en < bipy < phen < CN^- ~ 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 MOT method has provided a quantitative measure of the d-splitting. The eg/t_2g splitting (called the octahedral ligand field splitting Δ_0= 10Dq) 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 ~ 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:

($I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < O^{2-} < OH^- < H_2O < NH_3 < CN^- < CO < NO^+$)

Weak field strength (small Δ_0) π-donors

Strong field strength (largeΔ_0) σ-only π-accepter

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. (27-69-70)

1.7 Aim of the present work:

In view of the increasing interest in preparation of ionic liquids as they offer a new class of room temperature ionic liquids. It is planed to prepare an ionic liquid based on choline chloride/ carboxylic acid, as choline chloride based ionic liquids offer good air stable and moister in sensitive solvents.

In the current work, it was interested to prepare an ionic liquid from mixture of choline chloride with tartaric acid and to investigate their phase behavior, fluidity, solubility of some transition metal oxides, reactivity and conductivity. The purpose of chosen those compounds is their availability easy of preparation and non-toxic behavior as that the compounds are used as chicken food and humane consuming respectively.

To understand the behavior of the metal compound in solution and to determine their extent of dissolution in the solvents, as this knowledge would help in variable aspects such as solubility product, precipitation…etc, the following metal oxides CuO, ZnO, NiO, Co_3O_4, CrO_3 were chosen to be examined in the newly prepared ionic liquid in this work, particularly for their advantages application for electroplating as an example.

Chapter Three

Results and discussion

3.0 Introduction:

Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstanding good solvents for a variety of compounds, and their lack of measurable vapor pressure makes them a desirable substitute of VOC's. Ionic liquids are attractive solvents as they are non-volatile, have a high thermal stability, and are relatively inexpensive. (48)

Over the past few years, research and applications of ILs have expanded tremendously. The initial impetuses for this expansion were organic synthesis and the growth of green chemistry.

The principle of creating an ionic fluid by complexing a halide salt can be applied to mixtures of quaternary ammonium salts with a range of amides. (74) The charge delocalization is achieved through hydrogen bonding between the halide anion and with the amide moiety. It was shown that a eutectic mixture of choline chloride with urea gave a liquid with a freezing point of 12 °C. This liquid was found to have interesting solvent properties

that are similar to ambient temperature ionic liquids and a wide variety of solutes were found to exhibit high solubilities. (75)

This principle is not limited to amides, but can be applied to a wide variety of other hydrogen bond donors such as acids, amines and alcohols. (75,76)

Choline chloride or 2-hydroxy-N,N,N-trimethylethanaminium chloride is an organic compound and a quaternary ammonium salt. The counterion is chloride. In the laboratory choline can be prepared by methylation of dimethylethanolamine with methyl chloride. In the industrial Davy process choline chloride is produced from ethylene oxide, hydrochloric acid, and trimethylamine. (26) Choline chloride is mass produced and is an important additive in feed especially for chicken where it accelerates growth. With urea it forms a deep eutectic solvent. Other commercial choline salts are choline hydroxide and choline bitartrate. In foodstuffs the compound is often present as phosphatidylcholine. (77)

Tartaric acid is a white crystalline organic acid. It occurs naturally in many plants, particularly grapes, bananas, and tamarinds, and is one of the main acids found in wine. (26) It is added to other foods to give a sour taste, and is used as an antioxidant. Salts of tartaric acid are known as tartarates. (78)

However, the behavior of many dissolved compounds in solvent are not straight forward process, as they may either react with formation of soluble products or associated with gas evolution or solid precipitation.

Moreover, complex formation may also have a pronounced effect or the extend of solubility of particularly the transition metal cations. Therefor the solvation of transition metal oxides were also investigated by u.v. visible spectroscopy to follow the behavior of the dissolution of the metal oxide in the new hither to unreported Choline chloride/ tartaric acid ionic liquid which was prepared in this work.

3.1 Preparations of Choline chloride /tartaric acid ionic liquid and its phase behavior:

Tartaric acid was mixed with choline chloride in different mole ratio and heated up to 100°C, and then homogeneous colorless liquids were usually formed at different temperatures depending on the ratio of the tartaric acid to choline chloride, the starting temperatures of melting are shown in Table (3-1). The liquid was slowly cooled until it solidified; freezing point was taken as the temperature at which the first solid began to form, the results obtained are presented in Table (3-1), and graphically shown in Figure (3-1).

It is clear from Figure (3-1) that the addition of choline chloride had a significant effect on the melting point of pure tartaric acid. The depression of the melting point of tartaric acid was gradually increased with the addition of choline chloride until a eutectic point of the mixture was reached at 5°C when of the mixture was 66 mole% choline chloride **:** 33 mole% tartaric acid. Then increasing the adding of choline chloride showed an increase in the melting point of the mixture until the temperature of 302 °C represents the melting point of pure choline chloride salt.

Choline chloride /tartaric acid ionic liquids had been prepared at 74 °C. (79), but in this work it had been prepared at 5°C ,this maybe due to using the racemic tartaric acid (mp= 206 °C) instead of d-tartaric acid (mp=171-174 °C) that is used in this work.

The viscosity of all mole ratio of choline chloride / tartaric acid ionic liquid were found visually to have a high viscosity. Relatively, however, the viscosity increased as the mole ratio added tartaric acid increased.

However, the viscosity of the 3:1 mole ratio choline chloride / tartaric acid was also found to have a high viscosity too.

Table (3-1): Compositions and freezing points of choline chloride/ tartaric acid and temperature where melting started.

	Choline chloride (mole %)	*Tartaric acid (mole %)*	*Moles of the components Choline chloride: tartaric acid*	*Temperature of starting melting compounds °c*	*Freezing point °C*
1	75	25	3 : 1	70	8
2	66	33	2 : 1	60	5
3	60	40	1.5 : 1	60	5.5
4	50	50	1 : 1	70	7
5	40	60	1 : 1.5	80	8.5
6	33	66	1 : 2	80	9.5
7	25	75	1 : 3	90	11

During the preparation of these different mole ratios of the ionic liquids it was observed that all of them were clear viscous liquids between 5- 11 ^{o}C as shown in Table (3-1), all of them are and the viscosity decreases with temperature. No gas evolution or precipitate was found during the preparation of choline chloride/ tartaric acid ionic liquid.

It is well-known that pure choline chloride melts at 302 ^{o}C and tartaric acid melts at 170 ^{o}C. However these compounds were mixed in different mole ratios to prepare ionic liquids in an attempt to obtain room temperature ionic liquids.

It is possible to form compounds which are liquid at room temperature by reacting an amine salt, preferably a quaternary amine salt (choline chloride) which is capable of forming hydrogen bond with the anion of the amine salt. Compounds suitable for forming such hydrogen bonds include amides, such as urea, thiourea and acetamide, and carboxylic acids such as tartaric acid, oxalic acid, and cirtic acid, alcohol, and phenol. It is believed that hydrogen bonding of organic compound with the anion of the ammonium compound allows charge delocalization, which stabilizes the liquid form of the compound. (74)

Therefore, one of the methods of reducing the melting point of choline chloride is to use a hydrogen bond donor compound like tartaric acid which is a di-carboxylic acid. This mixture was prepared as illustrated in (2.3.2).

It was stated that fluidity is of key importance to the design of ionic liquids, as they tend to be more viscous than molecular liquids. It is shown that the fluid properties of these Deep Eutectic Solvents are linked to the size of the mobile species and the availability of holes of appropriate dimensions to allow mobility. This idea is found to be valid not only for other ionic liquids but also for molecular liquids and high-temperature molten salts. (52)

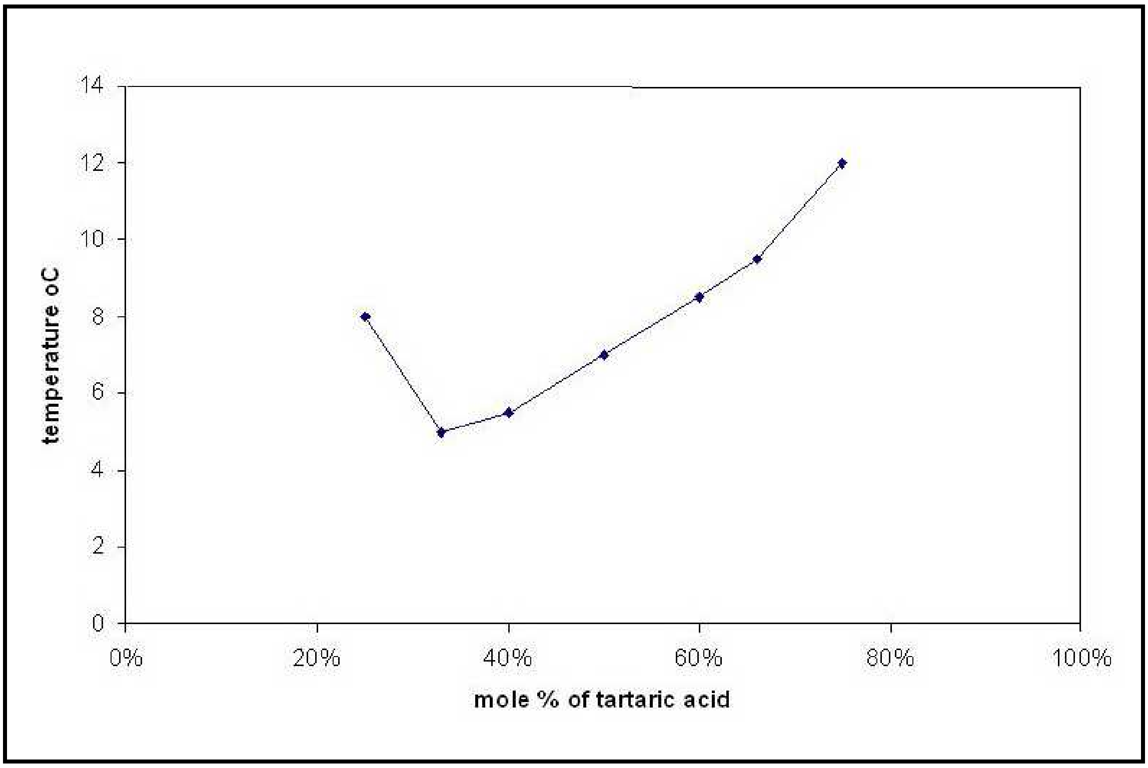


Figure 3-1: Phase diagram of the freezing points of Choline chloride/ Tartaric acid as a function of composition.

Figure (3-1) shows the phase diagram of the mixtures of tartaric acid with choline chloride as a function of composition. This diagram is of eutectic type. As mixing two compounds may leads to a different type of diagram these are eutectic, reaction system, and incongruent melting. (80)

The first type is the eutectic which is a liquid with the eutectic composition freezes at a single temperature, without previously deposition solid of its component A or B. A solid with eutectic composition melts, without change of composition, at the lowest temperature of any mixture solutions of composition to the right deposed B as they cool, and solution to the left deposed A: only the eutectic mixture (a part from pure B or pure A) solidifies at a single definite temperature

This system was constant and with three phases present, the phase rule tells us that there is a single Degree of freedom at the eutectic point according to phase rule since:

***Gibb's phase rule: F=1+C-P* (61), (80)**

F = the number of degrees of freedom.
C = number of components.
P = number of phases.

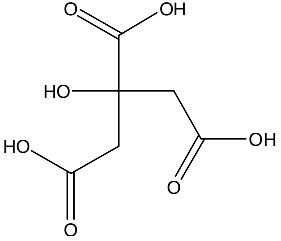
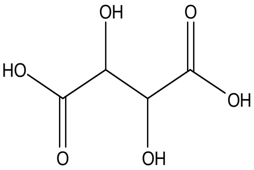
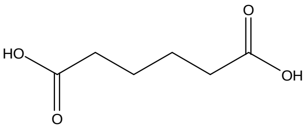
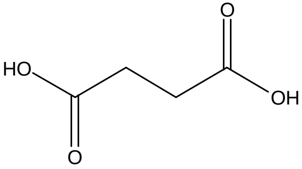
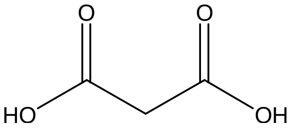
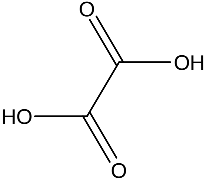
F=1+2-3=0

The conductivity of the DES of Choline chloride/ tartaric acid was measured and it is found to be 0.1 mS cm^{-1} which is in the lower range of the conductivities of different carboxylic acid ionic liquids which was reported to be in the range of 0.1 mS cm^{-1} - 10 mS cm^{-1} depending on the composition and temperature (51). These values are similar to Choline chloride/ urea DES (77).

It was also reported that the densities of ionic liquids are in the range of 1 to 1.6 g cm^{-3}. The obtained density of choline chloride/ tartaric acid ionic liquid of 1.6 g cm^{-3} is in the same range of densities.

It was reported that the lower the molecular weight of added carboxylic acids to choline chloride would increase the depression of freezing point of the mixture (51). This however, was not applied with tartaric acid, as it showed a much lower freezing point than other lower molecular weight carboxylic acid, Table (3-2). This maybe arises from the presence of additional 2 hydroxyl groups in comparison with succinic acid which may enhance the formation of hydrogen bonding there by increase the delocalization of the charge.

Table (3-2) Freezing point of several Choline chloride/ carboxylic acid (2:1) ionic liquids and the melting point with range of depression of melting point of several carboxylic acids (54).

	Structure	*Molecular weight (g/mol)*	*Freezing point (ionic liquid)^oC*	*Melting point (pure acid)^oC*	*Depression of melting point*
Citric acid		192.123	69	149	80
d-Tartaric acid		150.09	5	172	167
Adipic acid		146.14	85	153	68
Succinic acid		118.09	71	185	114
Malonic acid		104.03	10	135	125
Oxalic acid		90.03	34	190	156

3.2. Solubility of metal oxide in choline chloride/tartaric acid ionic liquid:

Metal oxides are usually insoluble in most molecular solvents and are generally only soluble in aqueous acid or alkali. The dissolution of metal oxides is a key to a range of important processes such as metal winning, corrosion remediation, and catalyst preparation.

A limit number of studies have shown that ambient temperature ionic liquids have potential as solvents for metal recovery. Whitehead et al.(81) have shown that imidazolium based ionic liquid can be used to extract gold and silver from mineral matrix. (81)

Some work has also been carried out on the elecrtowinning of metal, principally aluminum, from ionic liquids. (82,83)

In this work the choline chloride/ tartaric acid ionic liquid was investigated for its ability of dissolving some metal oxides (CuO, ZnO, NiO, Co_3O_4, CrO_3) hence metal oxides solubilities were determined in this melt.

Table (3-3) shows the data for the solubility of the metal oxide in IL at different temperatures and it can be seen that they tends to increase with temperature. It is evident that the solubility exhibits strong temperature dependent which may be put in the following order [$CuO > CrO_3 > NiO > Co_3O_4 > ZnO$]

Table (3-3): solubilities of the metal oxides in (molality X 10^2) and color of the solution in room temperature ionic liquid of choline chloride- tartaric acid at variable temperature.

Compound name	*Molecular formula*	*RT 27 °C*	*40 °C*	*60 °C*	*80 °C*	*100 °C*
Cupric oxide	CuO	10.5	12.7	20	29	38
Zinc oxide	ZnO	3.5	4.5	5.3	6.4	8.7
Nickel oxide	NiO	2.8	3.5	5.1	5.8	7.8
Chromic oxide	CrO_3	1.56	1.87	2.7	3.99	4.83
Cobalt oxide	Co_3O_4	0.76	0.88	1.14	1.46	1.96

The choline chloride/ tartaric acid ionic liquid is an acidic solvent as its pH was found to be 1.5, this may explain the higher solubility observed with the more basic oxide such as CuO.

The solubility curves were used to determine the lattice energy of the solute, which was expressed in cal/mol, by plotting logarithm of concentration against the reciprocal of the absolute temperature (1/T) using the following equation assuming the solution is ideal:

$$Lnx = \frac{-\Delta H^\circ}{RT} + const.$$

The results are represented in Figure (3-6)(3-7)(3-8)(3-9) and(3-10). As shown in Table (3-4)

Details of the results and discussion of each metal oxide is described in the following sections.

Table (3-4) Calculated lattice energy for each metal oxide.

Comp. name	***Molecular formula***	***slope***	***linearity***	***Intersept (constant)***	***Lattice energy* (cal mol^{-1})**
Cupric oxide	CuO	-٢٠٤٢,٣	٠,٩٩٥١	٤,٥١٣٢	4058.05
Nickel oxide	NiO	-١٥٤٠,٣	٠,٩٩٢٨	١,٥٦٠١	3060.5761
Zinc oxide	ZnO	-١٤٦٧,٣	٠,٩٧٢١	١,٥٢٨٦	2915.525
Chromic oxide	CrO_3	-١٨٢٥,٣	٠,٩٩٢	١,٨٨٦٨	3626.8711
Cobalt oxide	Co_3O_4	-١٤٤٤,٩	٠,٩٨٩٦	-٠,١٠٤٧	2871.06

3.2.1 Chromium oxide (CrO_3):

The saturated solution of the deep brown chromium oxide in choline chloride/ tartaric acid deep eutectic solvents (DES) was prepared as described in section (2.3.3). At the initial addition of metal oxide the solid material was not dispersed easily in the liquid state of DES due to the viscose nature of the solvent which required more time to show a noticeable dissolution of chromium in the solvent. This was visually indicated by the color of the solution when it changed from colorless to dark green. The latter color was intensified with time and stirring as it changed to bluish green when the mixture was left for 7 days to insure complete dissolution of the oxide with the aid of occasionally stirring. However, the undissolved deep brown chromium oxide remains unchanged at the end of the seven days.

To determine the solubility of the melt in this solution at variable temperatures, it was heated to 40, 60, 80 and 100 ^{o}C. As described in section (2.3.3.) The viscosity of the solution changed with temperature as it decreased and finally reached almost similar fluidity of water at 100 ^{o}C. At the end of the 4 hours of heating without further stirring was applied and it required only 5-10 minutes to separate the solid undissolved chromium oxide from the clear soluble chromium solution in choline chloride/ tartaric acid system. A sample was taken as described in section (2.3.3) and analyzed for metal content by atomic absorption spectrometry.

The resulted solubilities at variable temperatures are represented in Table (3-3) and plotted in Figure (3-2),

ln molality vis reciprocal absolute temperature (1/T) was also plotted as showen in Figure (3-3). The determined slope from Figure (3-3) was applied in equation (1-1) to deduce the lattice energy of chromium oxide which was fond to be 3626.87 cal mol^{-1}, Table (3-4).

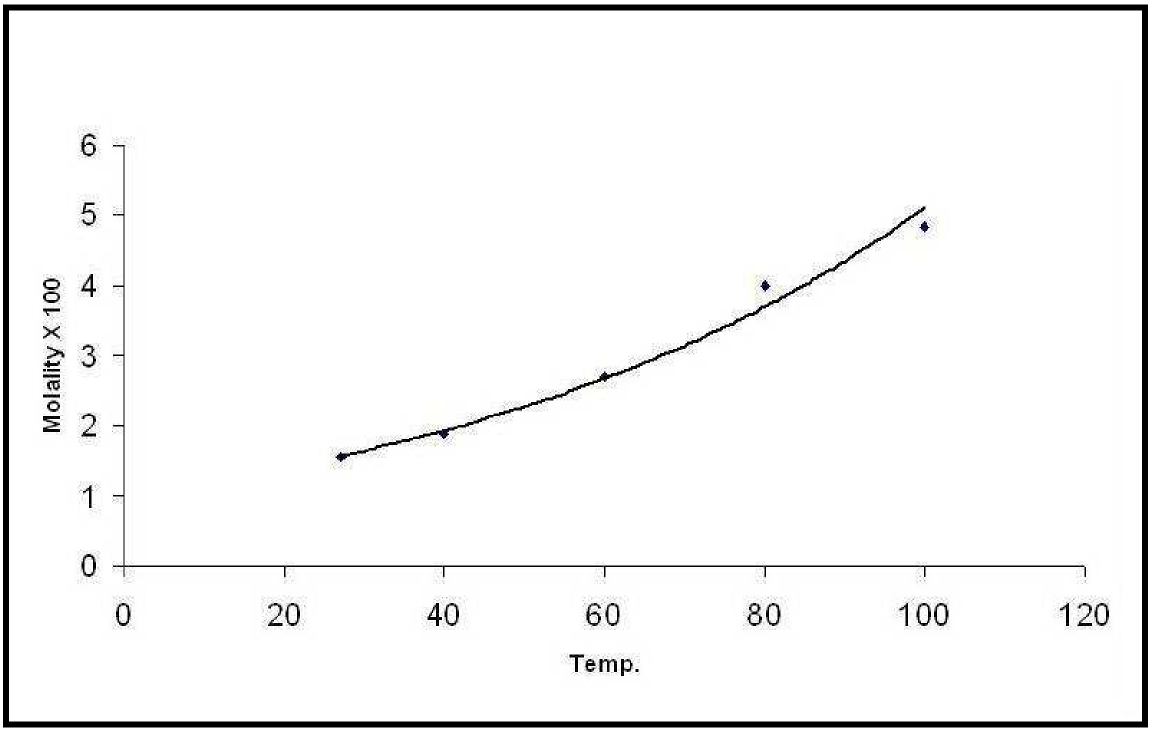


Figure 3-2: Solubility of CrO_3 in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in °C.

Referring to Figure (3-2), the solubility was found to increase with increasing the temperature as it reached 0.0483 m at 100 ^{o}C.

The increasing solubility with temperature indicates an exothermic process which arises from the dissolution of the oxide in the ionic liquid solvent.

The solubility of metal oxide would be expected to be larger when for example, dissolving basic metal oxide in acidic solvent or vis versa. There for the solubility of chromium oxide (CrO_3) which is known to have an acidic characterization, expected to show low solubility in the acidic choline chloride/ tartaric acid ionic liquid as the solubility observed in basic ionic liquid was reported to be higher than in this melt (0.108 M) in choline chloride/ urea ionic liquid (69) as shown in Table (3-5) .

Chromium (VI) oxide showed smaller solubilities in choline chloride/ tartaric acid room temperature ionic liquid, 0.025 M at 27^{o}C in comparison with that water at same temperature which is 0.063 M. (56)

However, at 60°C the solubility of chromium oxide obtained in this ionic liquid was found to be larger than that reported in hydrochloric acid solution (0.043 M , 0.02 M respectively). (69)

In a close compression the solubility in other ionic liquid of choline chloride/malonic acid at 60°C was found to be closer to that obtained in ionic liquid of this work (0.064 M and 0.043 respectively). (69)

The color change derived from the dissolution of CrO_3 in this ionic liquid was further studies in section 3.3.1.

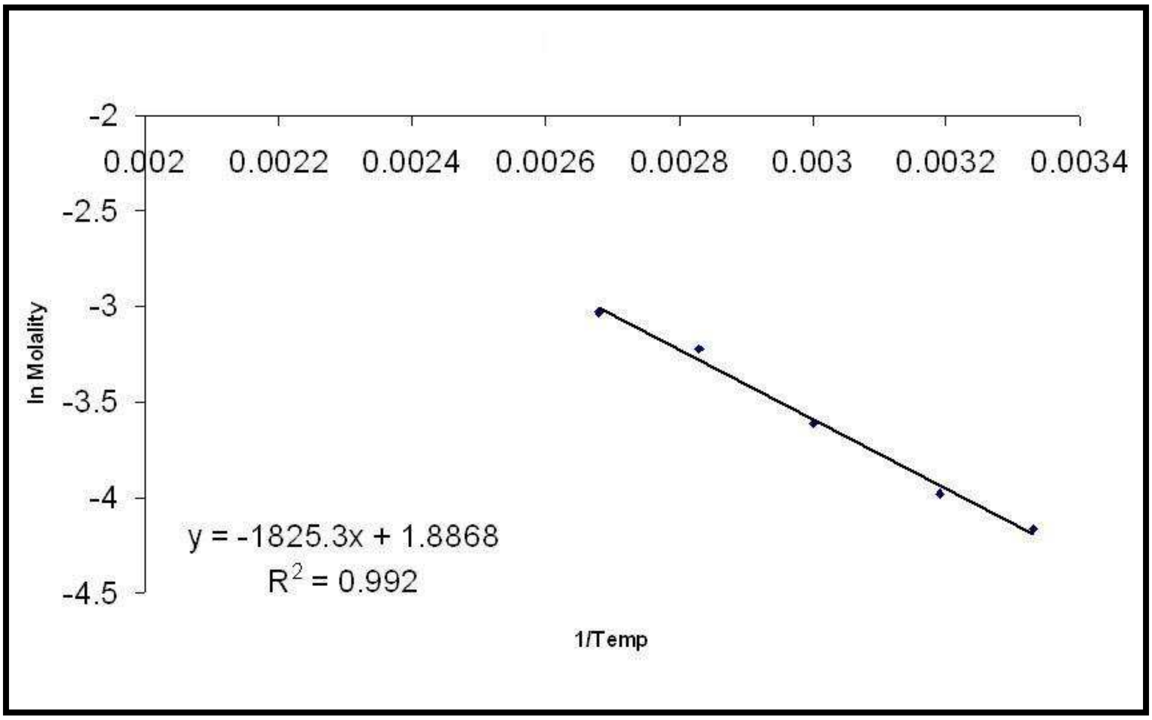


Figure 3-3: Log plot of solubilities of CrO_3 in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in K.

3.2.2 Cobalt oxide (Co_3O_4):

A saturated solution of black cobalt oxide in Choline chloride/ tartaric acid deep eutectic solvents (DES) was prepared as shown in section (2.3.3); the initial addition of metal oxide shows a slow dispersed in the liquid state of DES because of the viscose nature of the solvent which needed more time to show a notable dissolution of cobalt in the solvent. A visual indication is recognized by color changing from colorless to light green, which becomes more intense with time as it changed to lighter green when the mixture was left for 7 days to insure complete dissolution of the oxide with the aid of occasionally stirring. However, a black undissolved cobalt oxide remained unchanged at the end of the seven days.

The solubility of the melt in this solution was determined at a variable temperatures, it was heated to 40, 60, 80, 100 ^{o}C; as described in section 2.3.3. The viscosity of the solution is reversely proportion with the temperature ; and finally it reached almost similar fluidity of the water at 100 ^{o}C.

After the 4 hours of heating, no further stirring was applied and it required only 5-10 minutes to separate the clear soluble cobalt solution from solid undissolved cobalt oxide in Choline chloride/ tartaric acid. A sample was taken as described in section (2.3.3) and atomic absorption was used to analyze the metal content. The resulted solubilities at variable temperatures are represented in Table (3-4) and plotted in Figure (3-4).

ln molality vis reciprocal absolute temperature (1/T) was also plotted as shown in Figure (3-5). The determined slope from Figure (3-5) was applied in Equation (1-1) to deduce the lattice energy of cobalt oxide that was found to be 2871.06 cal mol^{-1}, Table (3-4).

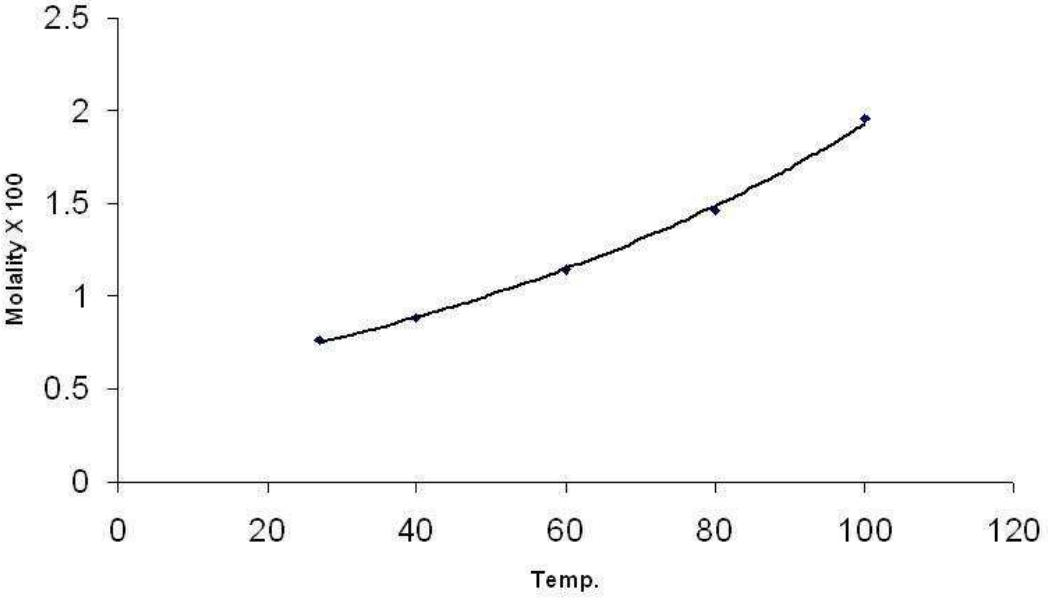


Figure 3-4: Solubility of Co_3O_4 in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in °C.

According to Figure (3-4), the solubility was found to increase with increasing the temperature as it reached 0.0196 m at 100 ^oC; that's indicates that the process of the dissolution of the metal oxide in this ionic liquid solvent is an exothermic process.

Cobalt oxide showed good solubilities in choline chloride/ tartaric acid room temperature ionic liquid, 0.0122 M at 27^{o}C in comparison with water at room temperature which is insoluble (56).

The solubility of metal oxide would be expected to be larger when dissolving basic metal oxide in acidic solvent or vice versa; that's why, the solubility of cobalt oxide (Co_3O_4) which is known to have a basic characterization, expected to show high solubility in the acidic choline chloride/ tartaric acid ionic liquid (0.0122 M) while the solubility as reported is drooped to (1.2 X 10^{-4} M) when dissolved in choline chloride/ urea ionic liquid (69)as shown in Table (3-5) .

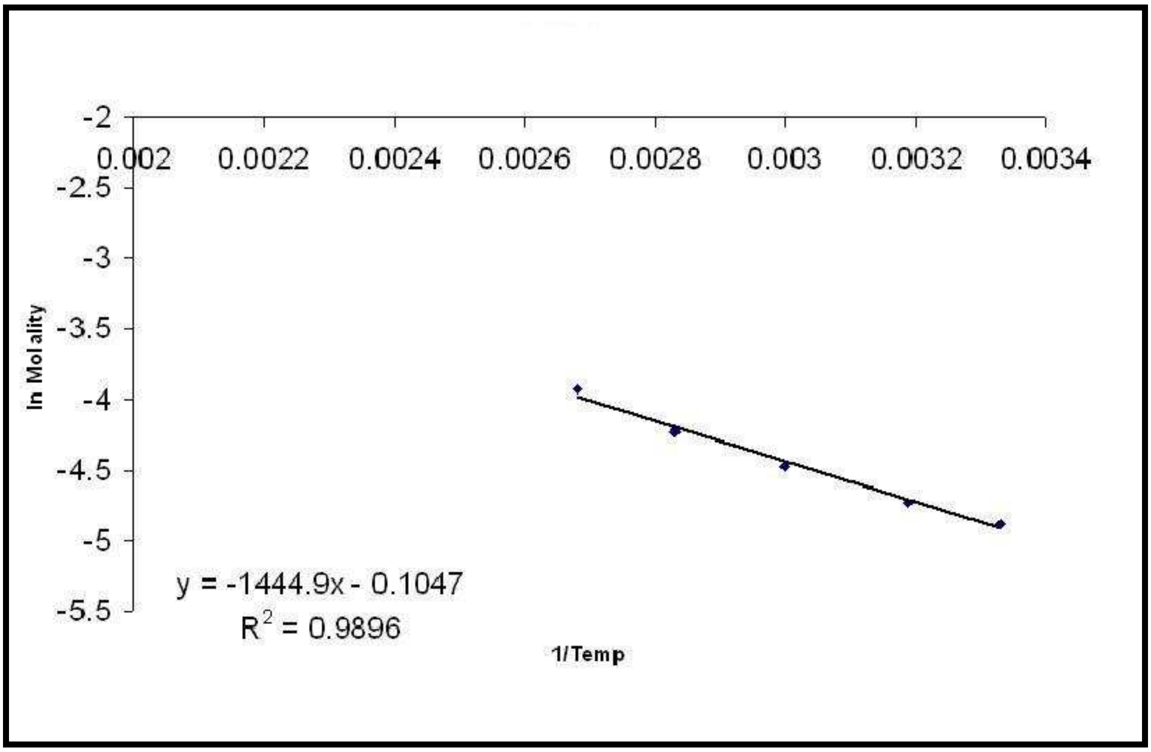


Figure 3-5: Log plot of solubilities of Co_3O_4 in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in K.

And in the acidic media, at 60 °C the solubility of cobalt oxide obtained in this ionic liquid was found to be smaller than that reported in hydrochloric acid solution (0.0183 M with 0.59 M respectively) (69).

In a closer comparison the solubility in other ionic liquid of example choline chloride/malonic acid was found to be very close to that obtained in ionic liquid of this work (0.0182 M with 0.02 respectively) (69).

The color change derived from the dissolution of Co_3O_4 in this ionic liquid was further studies in section 3.3.2.

3. 2.3 Nickel (II) oxide (NiO):

The saturated solution of nickel oxide in Choline chloride/ tartaric acid deep eutectic solvents (DES) was prepared as shown in section 2.3.3. The dispersed of the solid metal oxide in the liquid state of (DES) was not fast due to the high viscosity of the solvent ,which required a period of time to dissolute completely then it possible to make a visual identification when the color change from the colorless into green. The bluish-green colored solution was set up with time by means of occasionally stirring for seven days to insure a complete dissolution of the oxide in the solvent; nevertheless, an undissolved black nickel oxide is remained unchanged at the end of the seven days.

The solubility of the melt in the solution was verified at different temperatures 40 ,60 ,80 and 100°C as described in section (2.3.3.). it was obvious that the viscosity becomes lower when the temperature goes higher as it reaches a parallel fluidity to that of water at 100°C.

An easy separation of the undissolve nickel oxide was applied without stirring, from the clear soluble nickel solution in choline chloride / tartaric acid ionic liquid. A sample was taken as described in (2.3.3.) and analyzed for the metal contents by using atomic absorption.

The resulted solubilities at variable temperatures are represented in Table (3-4) and plotted in Figure (3-6).

ln molality vis reciprocal absolute temperature (1/T) was also plotted as shown in Figure (3-7). The determined slope from Figure (3-7) was applied in Equation (1-1) to deduce the lattice energy of nickel oxide which was fond to be 3060.57 cal mol^{-1}, Table (3-4).

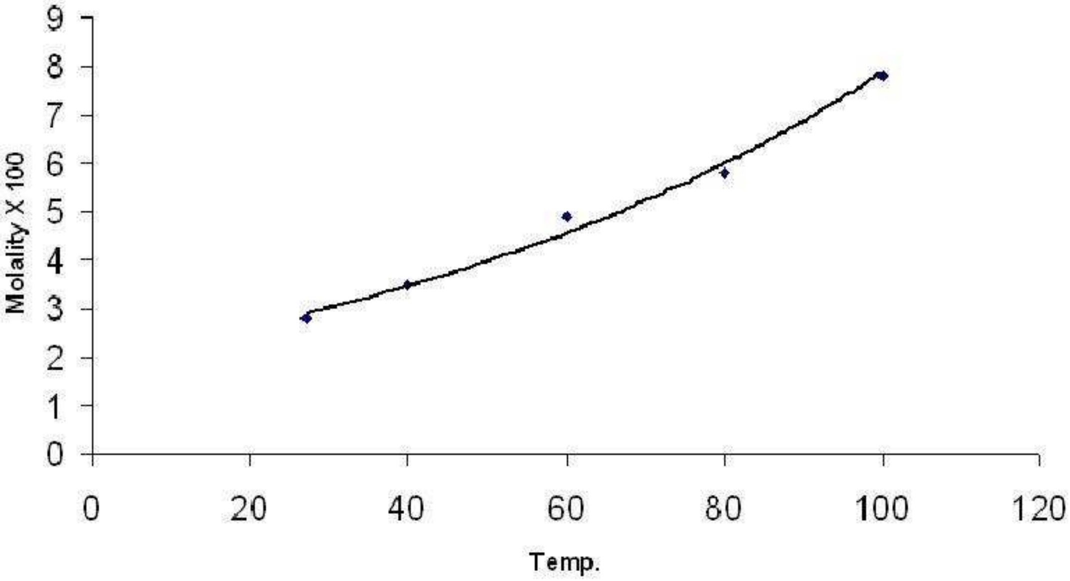


Figure 3-6: Solubility of NiO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in °C.

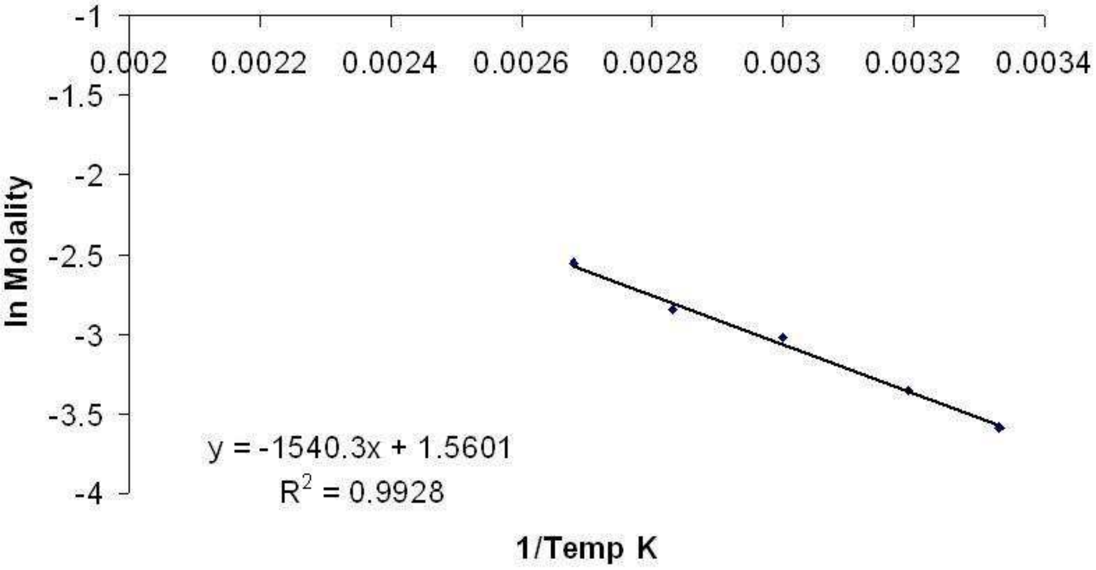


Figure 3-7: Log plot of solubilities of NiO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in K.

Referring to Figure (3-6), the solubility was found to increase with increasing the temperature as it reached 0.078 m at 100 ^{o}C.
The increasing solubility with temperature indicating an exothermic process arise from the dissolution of the oxide in the ionic liquid solvent.

The solubility of metal oxide would be expected to be larger when for example, dissolving basic metal oxide in acidic solvent or vis versa. The nickel oxide (NiO) shows a low solubility of 6.6 X 10^{-5} M at 27°C ,when it dissolved in basic media like choline chloride / urea ionic liquid (69);while it shows a high solubility of (0.0448 M) at 27°C when it dissolved in choline chloride / tartaric acid ionic liquid in comparison with water which is insoluble at room temperature (56) as in Table (3-5).

At 60 ^{o}C the solubility was much higher when it dissolved in choline chloride / tartaric acid ionic liquid than that reported in hydrochloric acid (0.0816 M with 0.08 M respectively)(69).

In a closer compression the solubility in other ionic liquid of choline chloride/malonic acid was found to be that the solubility in the prepared choline chloride/tartaric acid is much higher than that obtained in choline chloride/malonic acid ionic liquid (0.0816 M compared to 0.002 M respectively) (69).

The color change derived from the dissolution of NiO in this ionic liquid was further studies in section 3.3.3.

3.2.4 Cupric(II) oxide:

The saturated solution of cupric (II) oxide in Choline chloride/ tartaric acid deep eutectic solvents (DES) was prepared as described in section 2.3.3. At the initial addition of metal oxide the solid material was not dispersed easily in the liquid state of DES due to the viscose nature of the solvent which required more time to show a notable dissolution of cupric (II) in the solvent when the color of the solution changed from colorless to yellow , the latter color was intensified with time when the mixture was left for 7 days to insure complete dissolution of the oxide with the aid of occasionally stirring. However, a black undissolved cupric (II) oxide remains unchanged at the end of the seven days.

Using different temperatures (40 ,60 ,80 and 100)°C to establish a clear idea about the solubility of the melt in the solution ,as we know the viscosity decreased at higher temperatures , yet at 100°Cthe viscosity of the melt approaches to the viscosity of water.

A (5-10) minutes was enough to isolate the undissolved cupric oxide from the soluble cupric oxide in choline chloride / tartaric acid ionic liquid. A sample was taken as described in section (2.3.3) and analyzed in atomic absorption.

The resulted solubilities at variable temperatures are represented in Table (3-4) and plotted in Figure (3-8).

As shown in Figure (3-8) we notice a directly proportional relationship between the solubility and the temperature ; yet at 100°C the solubility reaches to 0.38 m.

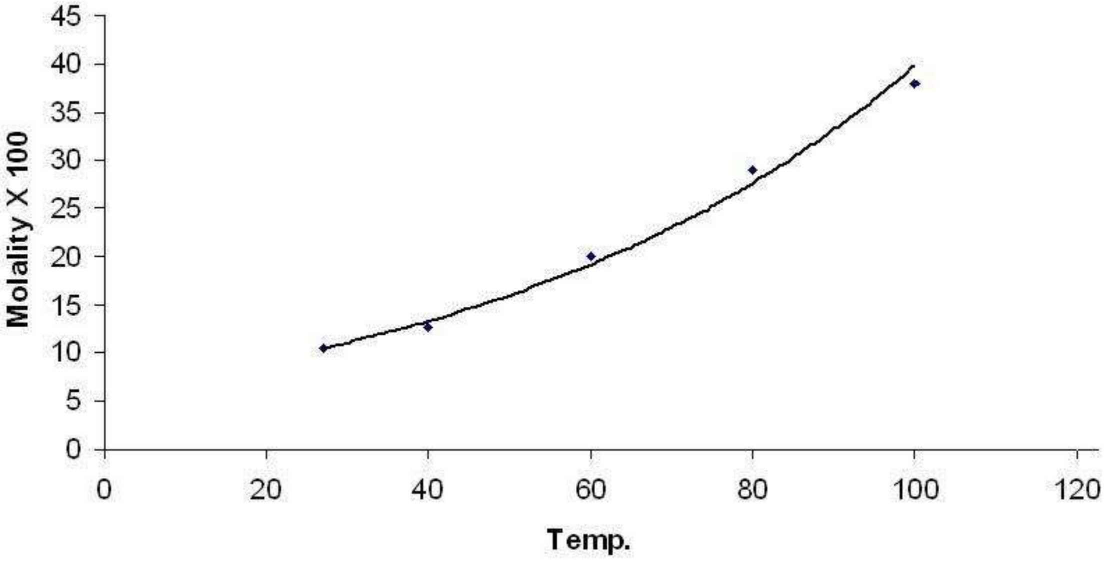


Figure (3-8): Solubility of CuO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in °C.

ln molality vis reciprocal absolute temperature (1/T) was also plotted as shown in Figure (3-9). An exothermic process will exist from the dissolution of the cupric oxide in the ionic liquid solvent , when the lattice energy of 4058.05 cal mol^{-1} is obtained from the slop applying in equation (1-1) as shown in Figure (3-9), Table (3-4).

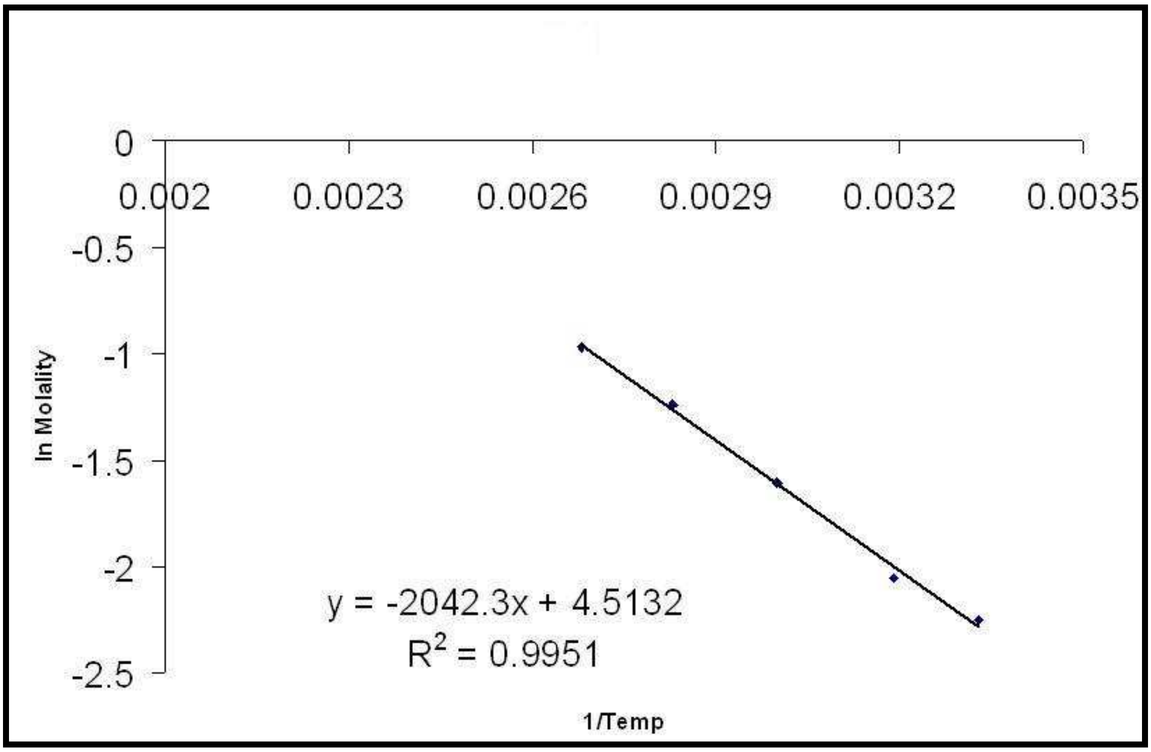


Figure (3-9): Log plot of solubilities of CuO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in K.

The solubility of metal oxide would be expected to be larger when for example, dissolving basic metal oxide in acidic solvent or Vice versa; therefore a high solubility are obtained when the cupric oxide is dissolved in acidic media of choline chloride / tartaric acid ionic liquid (0.168 M) at 27^{o}C in comparison with water at room temperature which it is insoluble $^{(56)}$; While in basic solvent of choline chloride / urea ionic liquid $^{(69)}$ the solubility is dropped to 5.5 X 10^{-3}M as shown in Table (3-5).

At moderated temperature of 60°C the solubility of cupric oxide become higher when a hydrochloric acid is used as a solvent (compare 0.32 M with 0.65 M respectively. $^{(69)}$

In a closer compression the solubility in other ionic liquid of choline chloride/malonic acid was found that the obtained ionic liquid in this work is much higher than choline chloride/malonic acid (0.32 M compared to 0.176 respectively) $^{(69)}$.

The color change derived from the dissolution of CuO in this ionic liquid was further studies in section 3.3.4.

3.2.5 Zinc oxide:

The saturated solution of zinc oxide in Choline chloride/ tartaric acid deep eutectic solvents (DES) was prepared as in section 2.3.3; the mixture was left for 7 days to insure complete dissolution of the oxide with the aid of occasionally stirring. However, no color changes after the addition of metal oxide to the Choline chloride/ tartaric acid ionic liquid, even at the end of the seven days.

To determine the solubility of the melt in this solution at a variable temperatures, it was heated to 40, 60, 80, 100 ^{o}C as described in section 2.3.3. The viscosity of the solution decreased and finally reached almost similar fluidity of the water at 100 ^{o}C. At the end of the 4 hours, no further stirring was applied and it required only 5-10 minutes to separate the solid undissolved white zinc oxide from the clear soluble zinc solution in Choline chloride/ tartaric acid. A sample was taken as described in 2.3.3 and analyses for metal content by atomic absorption. The resulted solubilities at variable temperatures are represented in Table (3-4) and plotted in Figure (3-10).

ln molality vis reciprocal absolute temperature (1/T) of solubilities is also plotted as shown in Figure (3-11). The determined slope from Figure (3-11) was applied in Equation (1-1) to deduce the lattice energy of zinc oxide that was fond to be 2915.525 cal mol^{-1}, Table (3-4).

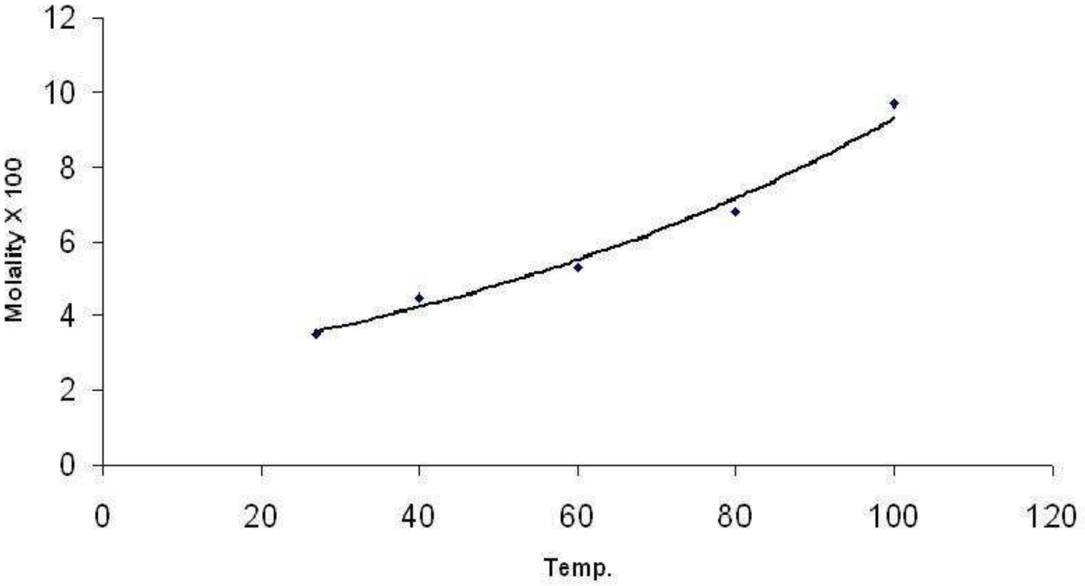


Figure 3-10: Solubility of ZnO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in °C.

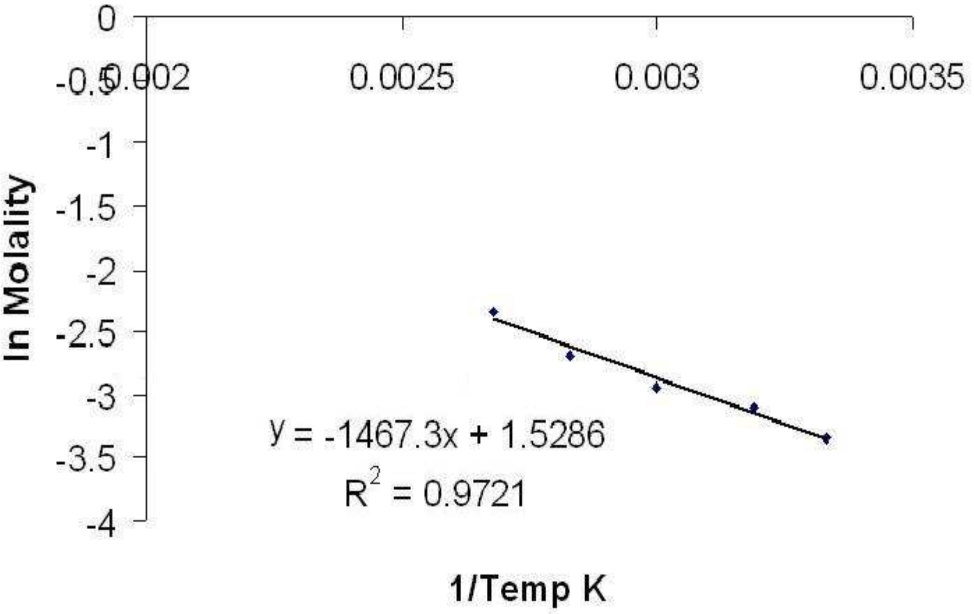


Figure 3-11: Log plot of solubilities of ZnO in Choline Chloride-Tartaric Acid ionic liquid with the absolute temperature in K.

Referring to Figure (3-10), the solubility was found to increase with increasing the temperature as it reached 0.87 m at 100 °C.

The increasing solubility with temperature indicating an exothermic process arises from the dissolution of the oxide in the ionic liquid solvent

The solubility of metal oxide would be expected to be larger when for example, dissolving basic metal oxide in acidic solvent or vis versa.

There for the solubility of cupric oxide (ZnO) which is known to have an amphoterie characterization, expected to show high solubility in the acidic choline chloride/ tartaric acid ionic liquid and high solubility in basic ionic liquids too, as in choline chloride/urea ionic liquids which was 0.023 M. (69) as in Table (3-5).

Zinc (II) oxide showed good solubilities in choline chloride/ tartaric acid room temperature ionic liquid, 0.056 M at 27°C in comparison with water at room temperature which it is insoluble (56) .

However, at 60 °C the solubility of zinc oxide obtained in this ionic liquid was found to be smaller than that reported in hydrochloric acid solution (compare 0.0848 M with 0.78 M respectively) (69).

In a closer compression the solubility in other ionic liquid of choline chloride/malonic acid was found to be higher to that obtained in ionic liquid of this work (0.199 M compared to 0.0848 M respectively) (69).

Table (3-5): Solubilities of metal oxides in Morality in different solvents.

Metal oxide	H_2O	*Choline chloride/ tartaric acid*	*Choline chloride/ malonic acid*	*Choline chloride/ urea*	*HCl (0.65 M)*
CrO_3	0.064	0.043	0.064	0.108	0.02
Co_3O_4	insoluble	0.0182	0.02	1.2×10^{-4}	0.59
NiO	insoluble	0.0816	0.002	6.6×10^{-5}	0.08
CuO	insoluble	0.32	0.176	6×10^{-5}	0.65
ZnO	insoluble	0.0848	0.199	0.025	0.78

3.3 Electronic spectroscopy of transition metal oxides in choline chloride/ 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. The range of the spectra is (190-1100) nm. using choline chloride/ tartaric acid ionic liquid as a solvent.

3.3.1 Electronic spectroscopy of chromium trioxide in choline chloride/ tartaric acid ionic liquid:

When deep brown chromium trioxide dissolved in choline chloride/ tartaric acid ionic liquid, showed a green color solution. This solution was investigated by U.V. Visible spectroscopy at room temperature and at elevated temperature up to 100 ^{o}C when the color changed into bluish green color.

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. (27) 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 at 568 nm (17605cm^{-1}) and 427 nm (23419cm^{-1}) which were considered (υ_1),(υ_2) respectively, as shown in Figure (3-12) , the high energy spectra observed indicated that chromium oxide in Choline chloride/ tartaric acid ionic liquid consist of octahedral coordination.

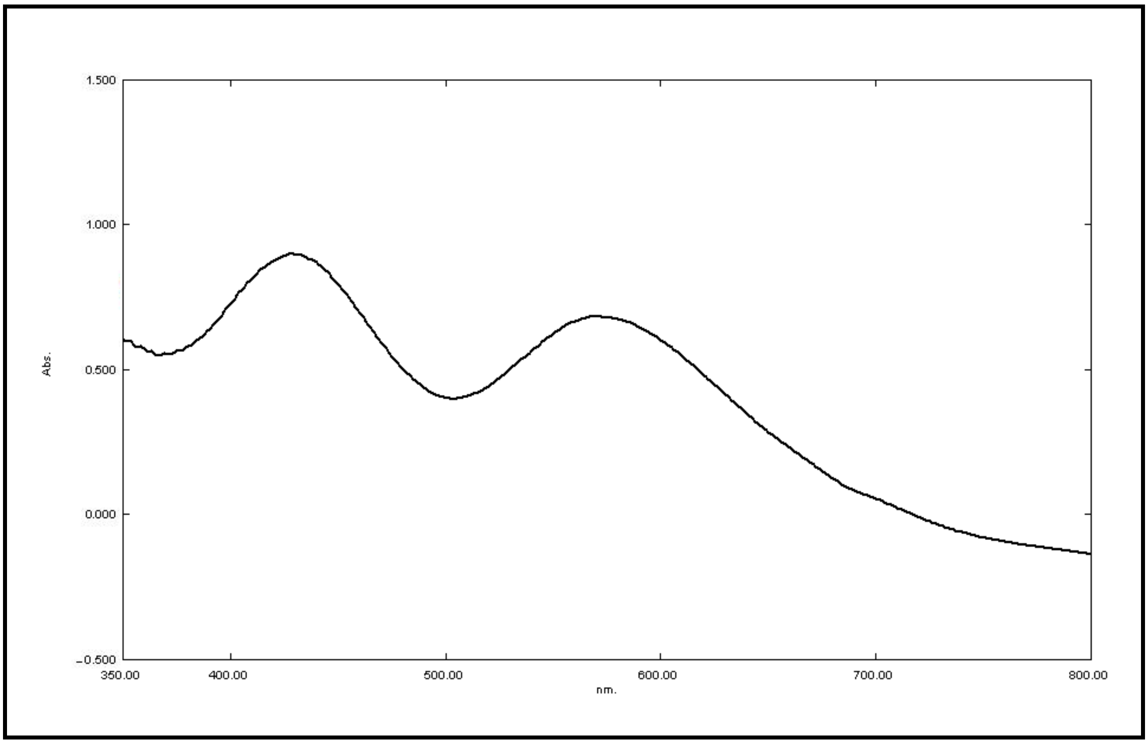


Figure (3-12) The UV- Vis. Spectrum of Chromium (III) oxide in Choline chloride/ tartaric acid ionic liquid at room temperature.

The third band of the octahedral coordination (υ_3) which normally occur at higher energy was deduced by using Tanabe- Sugano diagram Figure (3-13) of d^3 electronic configuration and it is found to be 265 nm (37702 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 (3-14)

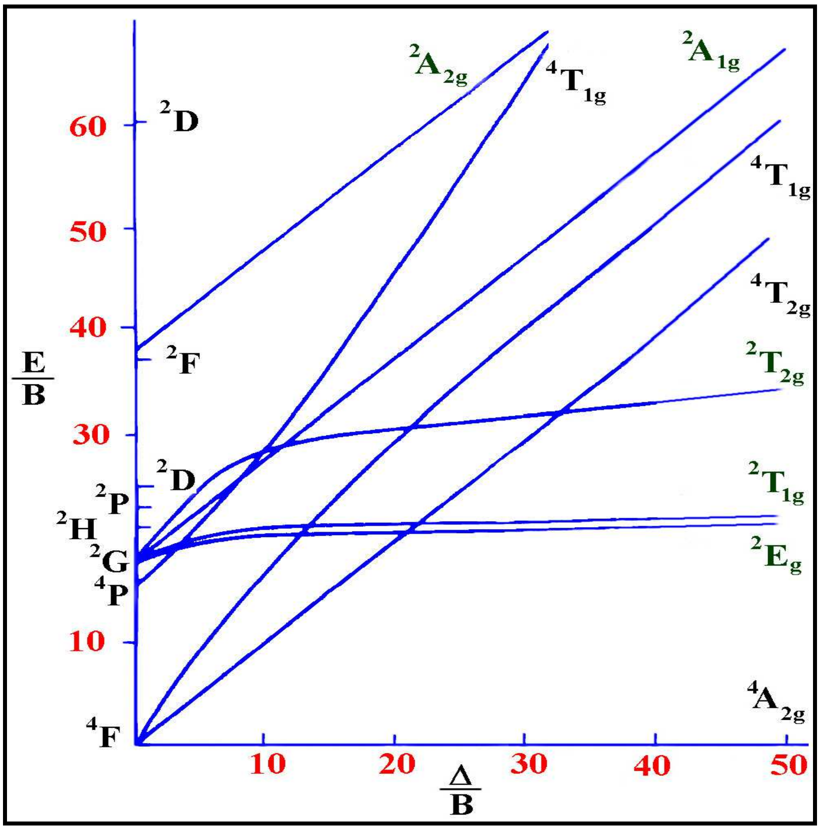


Figure (3-13) Tanabe-Sugano diagram for d^3 ion configuration.

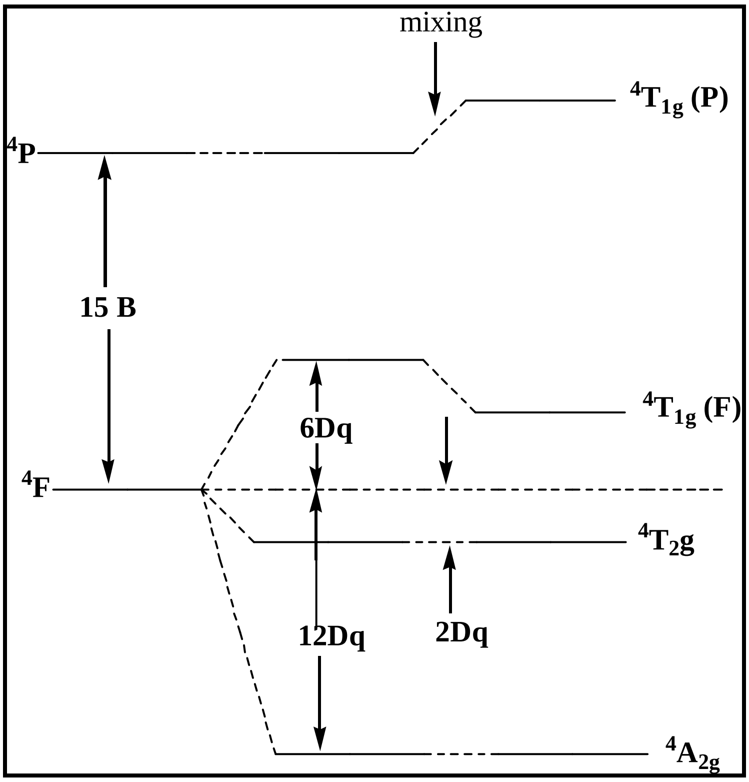


Figure (3-14) Crystal field splitting of the term of d^3 ion octahedral configuration.

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 (3-6). It is notice that Racah parameter (553 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 apparent value of B in complexes is always smaller than that of free ion. This phenomenon is known as nephelauxetic effect and is attributed to delocalization of the metal electrons around the ligand as well. As a result of this delocalization (cloud expansion) the average interelectronic repulsion is reduced and therefore B` is usually smaller. (56) This is also found in this work as β complex was found to have a small value as shown in Table (3-7).

Calculation by Jorgenson rule of average environment for Cr (III) ions in choline chloride/ tartaric acid ionic liquid did not support that the coordination is either of 6 chloride ions or three tartarate ions. The field factor value of the solvent ions with the metal was considered to be 1.14 as deduced from the nickel coordination in this ionic liquid section 3.3.3.

However, the calculation revealed that the coordination of Cr as of $2Cl^-$ and 2 of the solvent, the latter ion bonded to the central metal as bidentate ligand. This calculation indicated a non-uniform coordinated ligands around the Cr (III) ions as illustrated in Table (3-6) and shown in Figure (3-16); therefore, it may show irregular octahedral shape. This suggestion is supported by the large molar absorption value of (27 L/mol^{-1} cm^{-1}) as shown in Table (3-11), since the normal octahedral would show much less value (<10). (83)

As shown in Figure (3-15), increasing the temperature did not show significant changes in color as it is only increases the intensity of the green color and there was no change in bands positon.

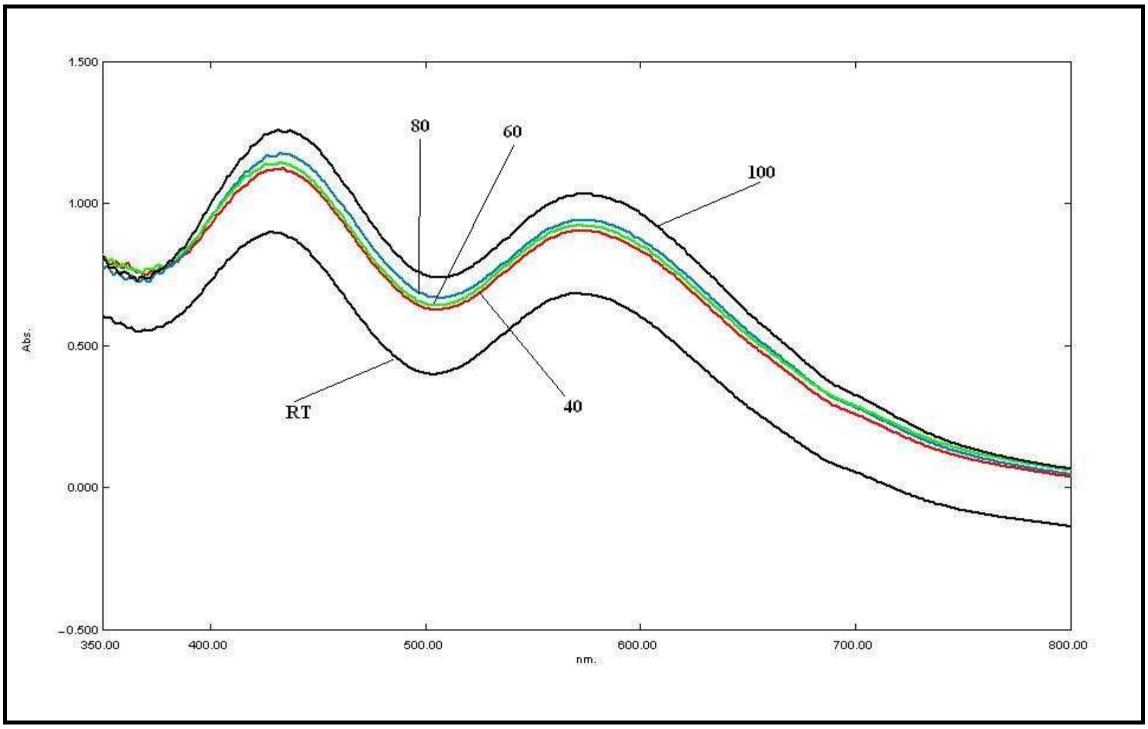


Figure (3-15) The UV- Vis. Spectra of chromium oxide in Choline chloride/ tartaric acid ionic liquid at different temperatures in °C.

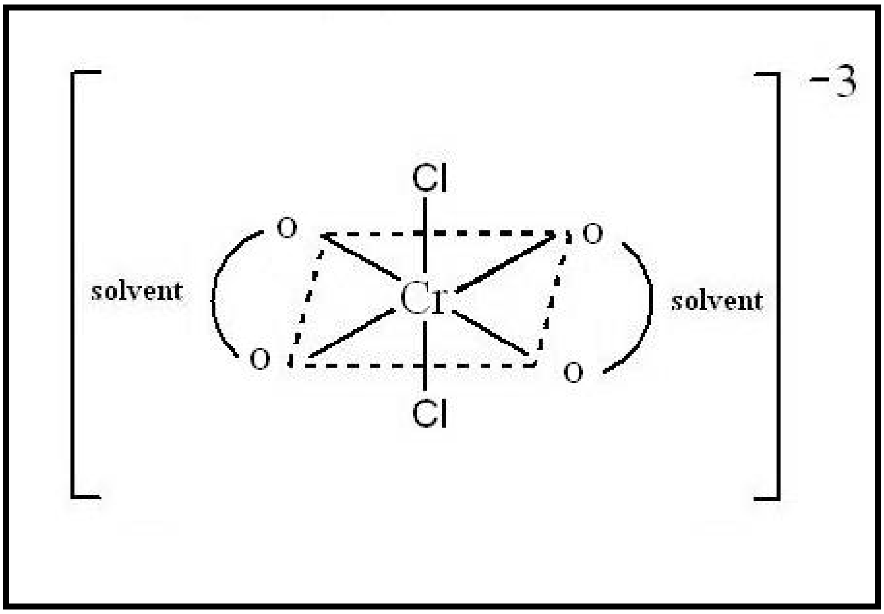


Figure (3-16): Suggested structure for chromium (III) in choline chloride/ tartaric acid ionic liquid.

Table (3-6): The observed 10Dq as comparison with the calculated 10dq in different ratio of ligands

Observed 10Dq	*Calculated 10Dq (6Cl-)*	*Calculated 10Dq (4cl with 1 tartarate ion)*	*Calculated 10Dq (2cl- with 2 tartarate ion)*	*Calculated 10Dq (3 tartarate ion)*
17605	13570	15660	17748	19835

Table (3-7) Chromium (III) oxide electronic spectra parameters

Chromium (III) oxide	*RT ^oC*	*40 ^oC*	*60 ^oC*	*80 ^oC*	*100 ^oC*
υ_1	17605	17513	17574	17361	17543
υ_2	23419	23148	23095	23148	23201
υ_3	37702	37388	37424	37205	37462
B free ion	918	918	918	918	918
B`	553	533	519	551	535
β	0.6	0.58	0.566	0.6	0.58

3.3.2 Electronic spectroscopy of cobalt oxide in choline chloride/ tartaric acid ionic liquid:

When cobalt oxide dissolved in choline chloride/ tartaric acid ionic liquid, showed a green color solution.

To understand the behavior of the cobalt oxide in choline chloride/ tartaric acid ionic liquid in different temperatures, the samples were investigated by U.V. Visible spectroscopy at room temperature and at elevated temperature up to 100 ^{o}C.

The ultraviolet visible spectra of the solution of the cobalt oxide shows one absorbance maxima band at 698 nm (14326cm^{-1}) which represent υ3, and two other absorbance at 667 nm (14992 cm^{-1}) and 643 nm (15552cm^{-1}) both represent a forbidden transitions ($^4A_2 \rightarrow {}^2A_1$ (^2G))and ($^4A_2 \rightarrow {}^4T_2$ (^2G)) respectively , as shown in Figure (3-17) .

Cobalt oxide normally spinel with Co^{+2} ions in tetrahedral interstices with green colored solution and Co^{+3} on in octahedral interstices with red colored solutions. It is known that Co^{+2} is more stable than $Co^{+3,}$ so it is expected that all Co^{+3} will reduced to Co^{+2} as in equation (3-1)

$Co^{+3} + e^{-} \rightarrow Co^{+2}$ …………………equation (3-1)

That is indicating that cobalt oxide in Choline chloride/ tartaric acid ionic liquid consists of tetrahedral coordination complex of cobalt (II).

The term symbol for the ground state of Co (II) ion F^4 can split in tetrahedral crystal field as following:

$\upsilon_1 = {}^4A_2 (F) \rightarrow {}^4T_2 (F)$ (10Dq)
$\upsilon_2 = {}^4A_2 (F) \rightarrow {}^4T_1 (F)$
$\upsilon_3 = {}^4A_2 (F) \rightarrow {}^4T_1 (P)$

And Figure (3-18) shows the assigned electronic transition of the term symbol for the ground state of Co(II) ion ^4F.

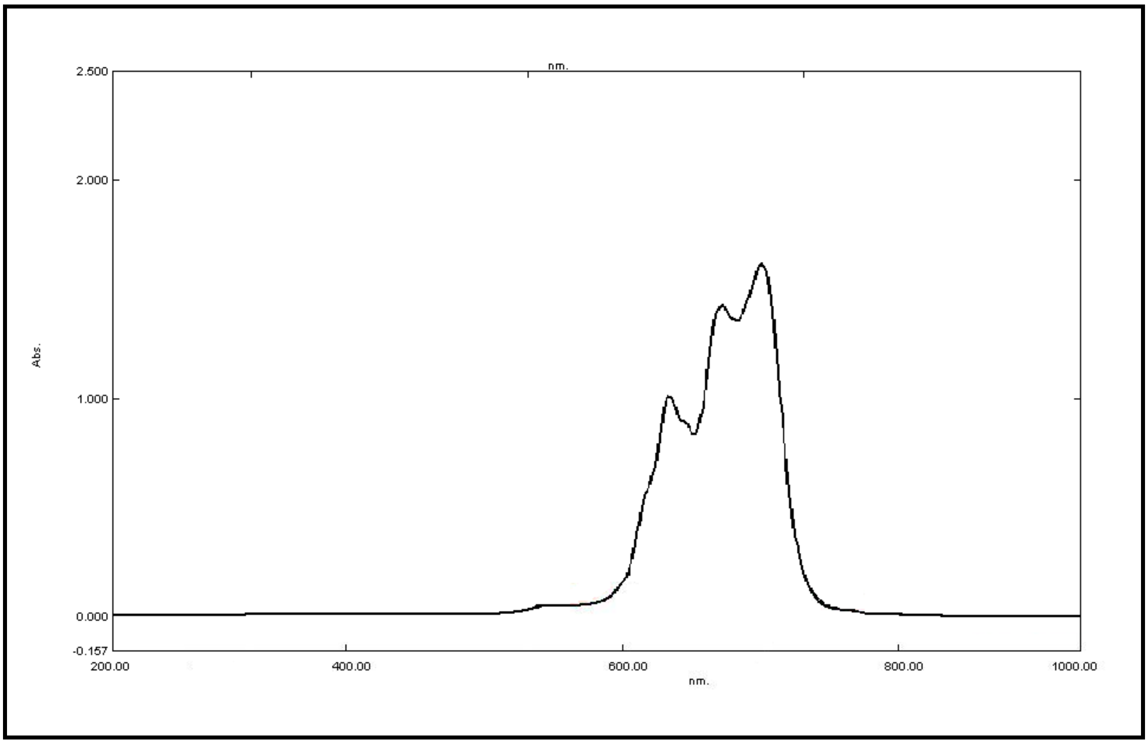


Figure (3-17): The UV- Vis spectrum of Co_3O_4 in Choline chloride/ tartaric acid ionic liquid at room temperature.

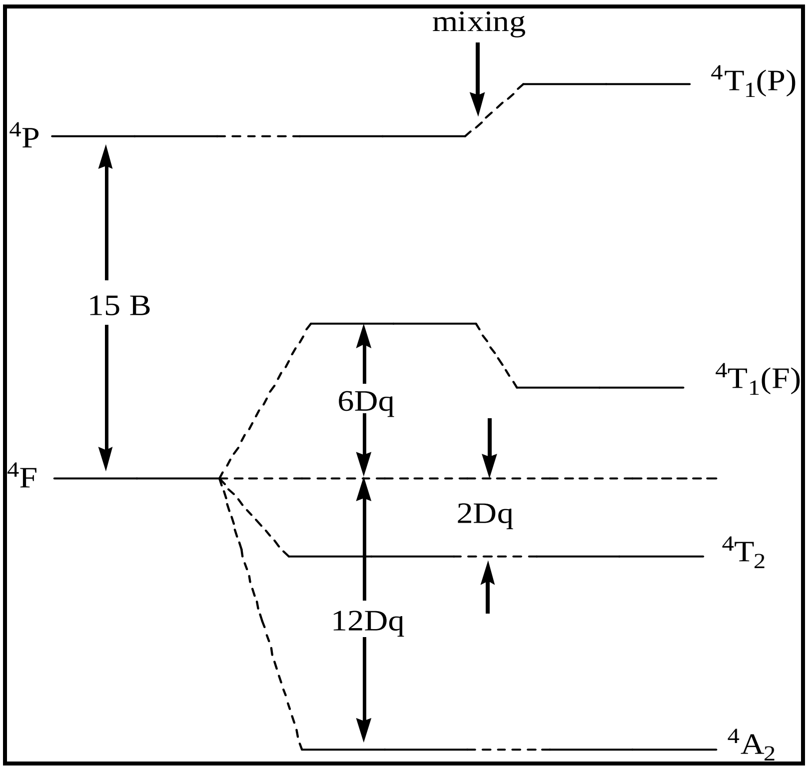


Figure (3-18) Crystal field splitting of ^{4}F term of d^7 ion tetrahedral configuration.

In this case, υ_1 should be in the IR region and υ_2 in near IR region. Examination of this part of the IR has some times indicated the presence of a band, though overlying vibrational bands make interpretation difficult.

As Jorgenson calculations of average environment for Co (II) ions in choline chloride/ tartaric acid ionic liquid suggests that the coordination is of four chloride ions. This calculation indicates uniform coordinated ligands around the Co (II) ions; therefore, it may show a regular tetrahedral shape as shown in Figure (3-19).

This suggestion is supported by the large molar absorption value of (6.3) since the normal tetrahedral would show less value (<10) as shown in Table (3-13).

Moreover, increasing the temperature did not show significant changes in color as it is only increases the intensity of the green color and there was no changes in band position as in Table (3-8). and this is indicated in Figure (3-20).

Table (3-8) Cobalt oxide Co_3O_4 electronic spectra parameters.

Cobalt oxide	***RT °C***	***40 °C***	***60 °C***	***80 °C***	***100 °C***
υ_3	14326	14285	14265	14144	14084

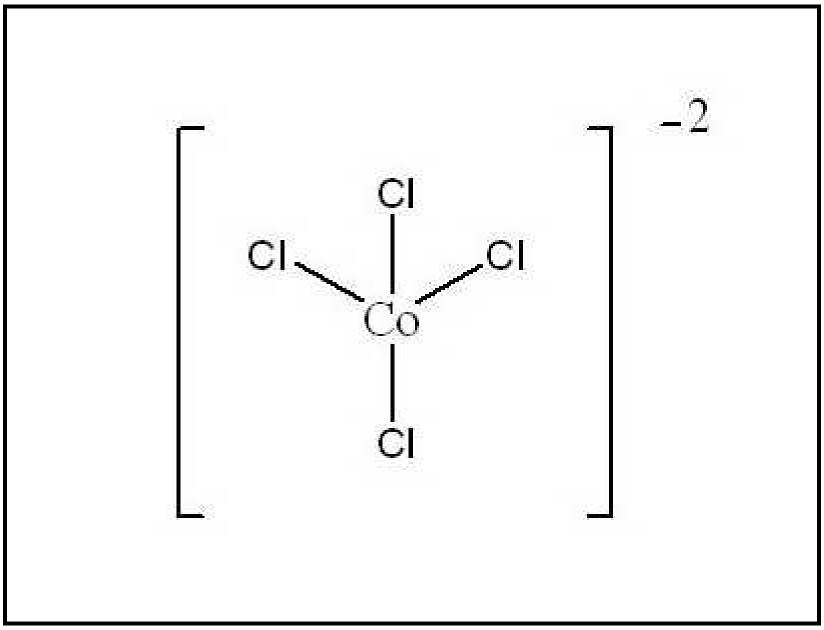


Figure (3-19): Suggested structure for cobalt (II) in choline chloride/ tartaric acid ionic liquid.

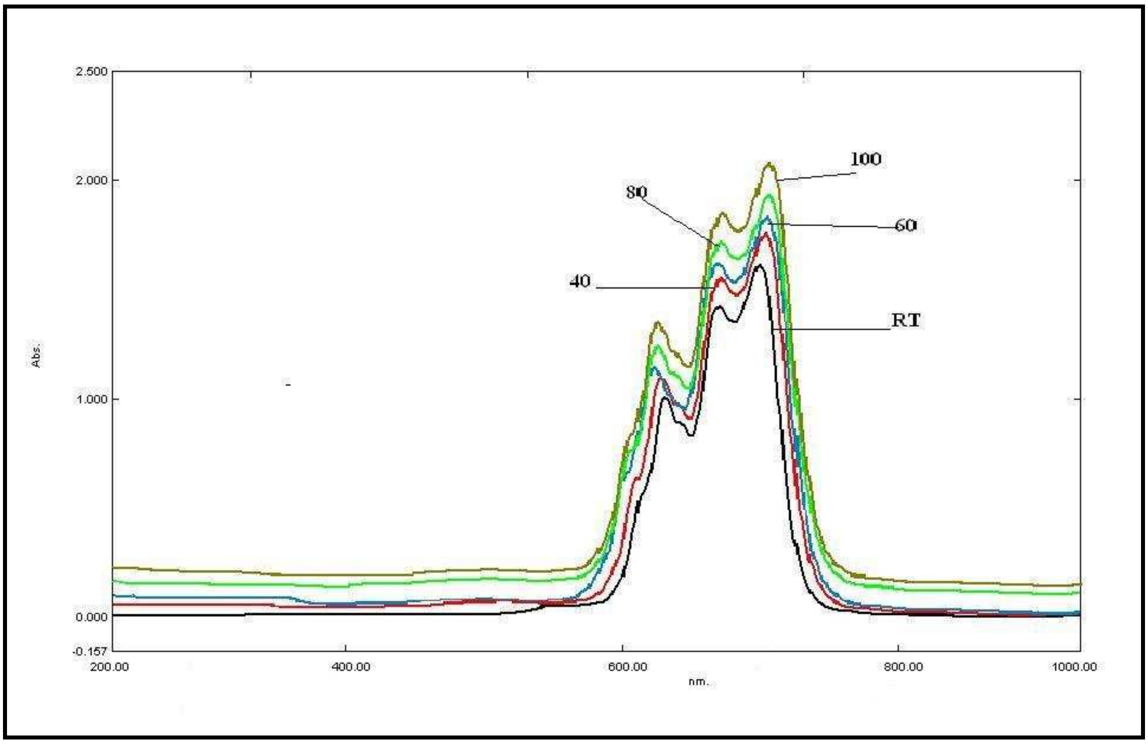


Figure (3-20) The UV- Vis spectra of Co_3O_4 in Choline chloride/ tartaric acid ionic liquid at different temperatures in °C.

3.3.3 ***Electronic spectroscopy of nickel (II) oxide in choline chloride/ tartaric acid ionic liquid:***

The green solution of nickel oxide and choline chloride / tartaric acid ionic liquid, was investigated by U.V-Vis spectroscopy at room temperature and at elevated temperature reaches up to 100°C, when the color changed into blue.

The recorded ultraviolet visible spectra of the green solution of the nickel (II) oxide shows two absorbance maxima bands at 655 nm (15267cm^{-1}) and 418 nm (23923 cm^{-1}) which was considered (υ_2),(υ_3) respectively as shown in Figure (3-21) While there is another band near the second absorbance band at 699 nm (14306 cm^{-1}) which represents a forbidden transition, that appeared due to spin-orbit coupling transition from the $^3A_2$ ground state to the singlet state of ^1E_g which are very close in energy, indicating that nickel (II) consisted of octahedral coordination complex.

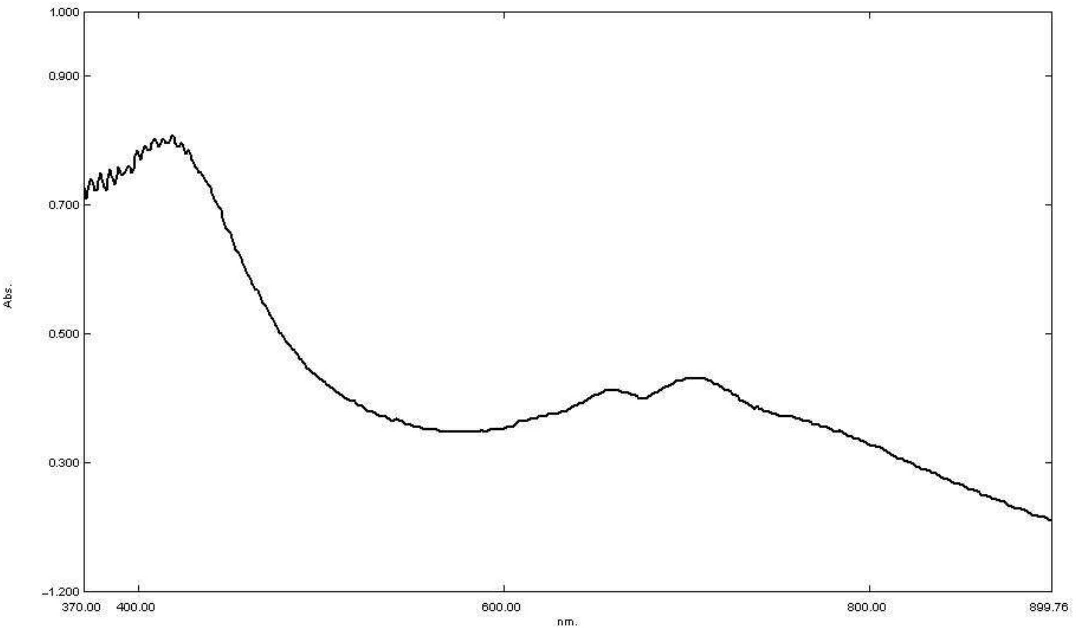


Figure (3-21): The UV- Vis spectrum of NiO in Choline chloride/ tartaric acid ionic liquid at room temperature.

The third band (υ_1) which normally occur at a low energy was deduced by using Tanabe- sugano diagram Figure (3-22) of d^8 electronic configuration and it’s found to be 1007 nm (9923 cm^{-1}).

And the bands may be assigned as:

$\upsilon_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$ (F)
$\upsilon_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
$\upsilon_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)

Since the terms of the d^8 configuration can split as illustrated in Figure (3-23)

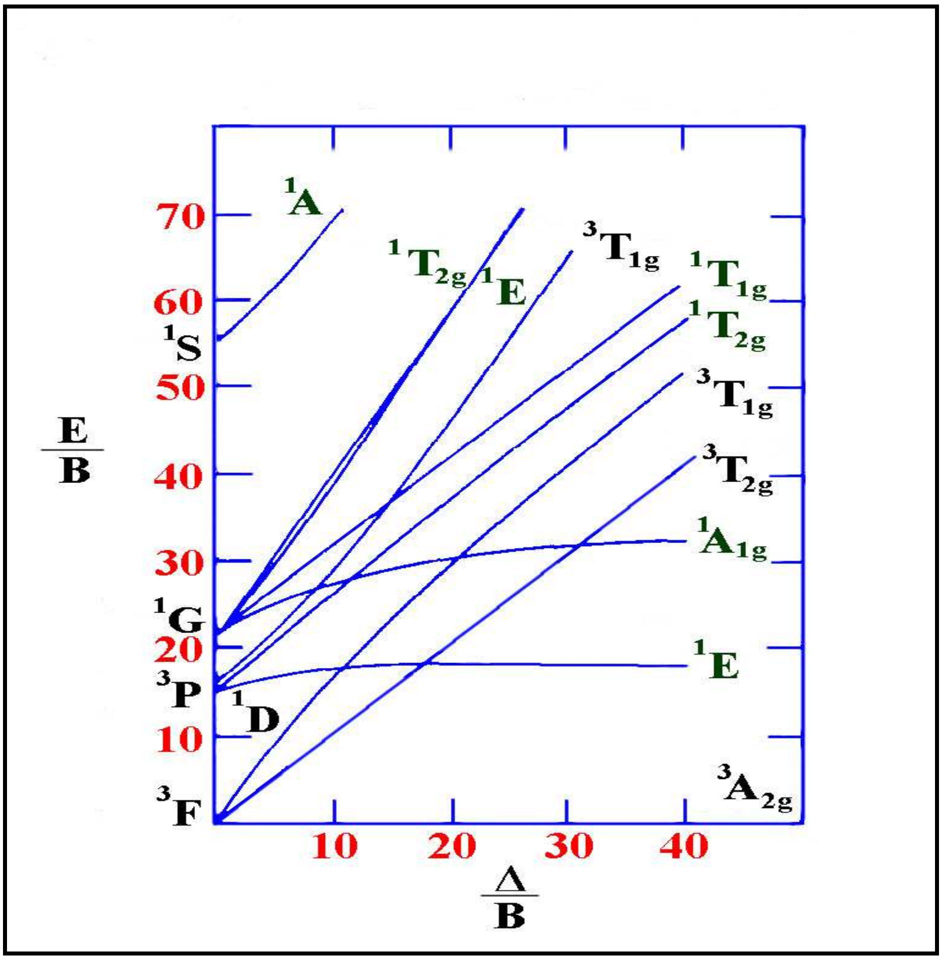


Figure (3-22) Tanabe-Sugano diagram for d^8 octahedral electronic configuration.

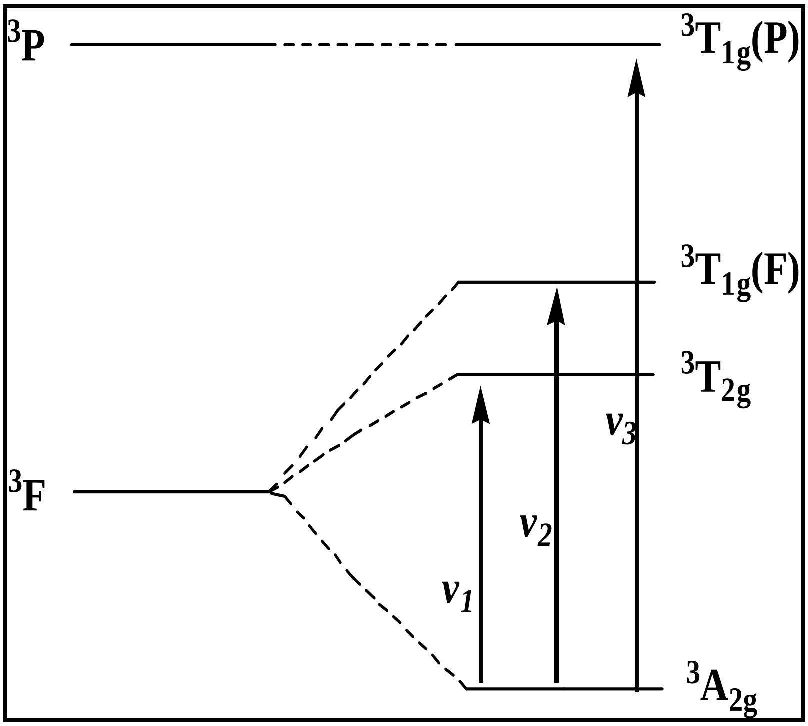


Figure (3-23) Crystal field splitting of ^3F term of d^8 ion octahedral configuration.

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 (3-9). It is notice that ***Racah*** parameter (627.9 cm^{-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.

In addition, the apparent value of B` in complexes is always smaller than that of free ion. This phenomenon is known as ***nephelauxetic*** effect and is attributed to delocalization of the metal electrons around the ligand as well. As a result of this delocalization (cloud expanding) the average interelectronic repulsion is reduced and therefore B` is usually smaller. (56) This is also found in this work as β complex was found to have a small value as shown in Table (3-9).

From the obtained spectra of nickel in this solvent it was deduced that the field factor of the coordinated part of the solvent was equal to 1.14. this large field may arise from the tartaric acid anions and it is assumed that the bond of tartaric acid to nickel was of bidentate and three molecules of the tartarate was attached to the central metal as illustrated in Figure (3-24)

And as Jorgenson calculations of average environment for Ni (II) ions in choline chloride/ tartaric acid ionic liquid it support that the coordination is of three tartarate ions. This calculation indicated uniform coordinated ligands around the Ni (II) ions; therefore, it may show a regular octahedral shape. As shown in Table (3-10).

This suggestion is supported by the small molar absorption value of (6.3) as shown in Table (3-13) since the normal octahedral would show less value (<10).

Moreover, the effect of increasing temperature was not recognized on the color changes but it increases the intense of the green color. and there is no change in the band position as shown in Figure (3-25).

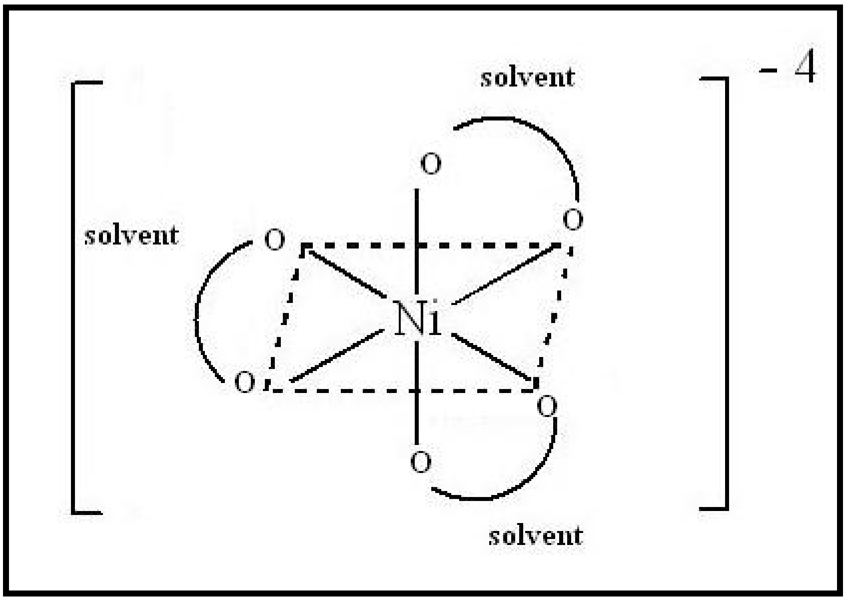


Figure (3-24): Suggested structure for nickel (II) in choline chloride/ tartaric acid ionic liquid

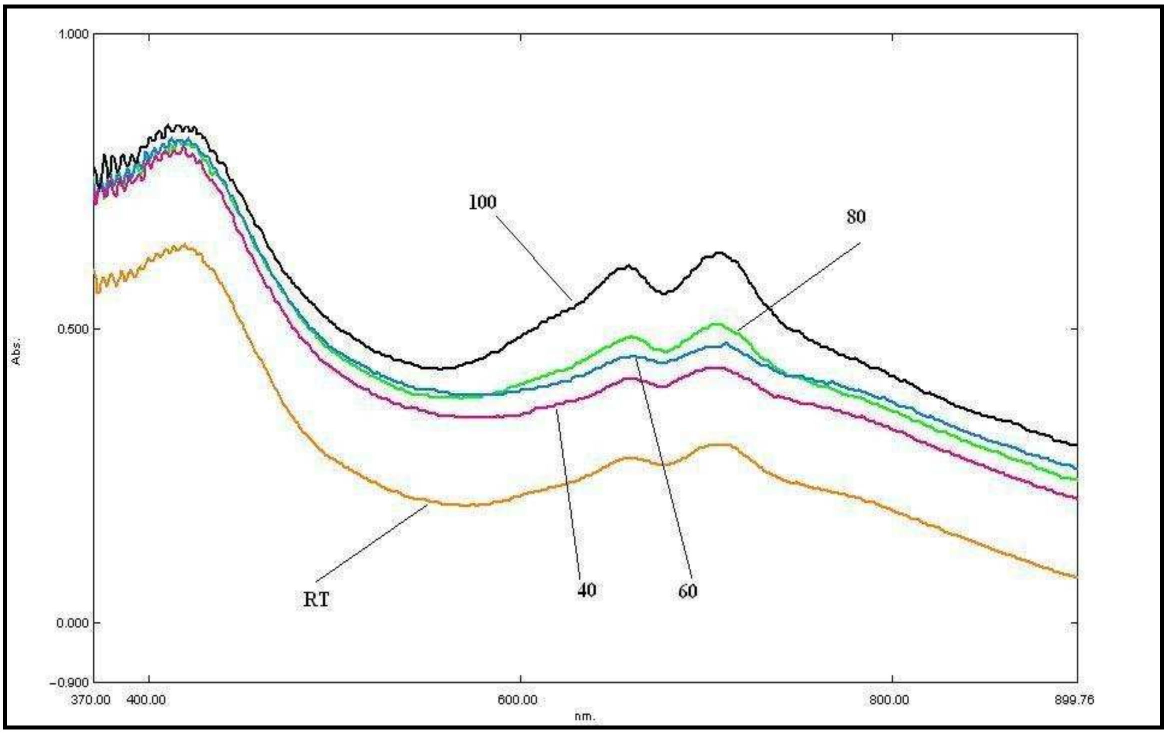


Figure (3-25) The UV- Vis spectra of NiO in Choline chloride/ tartaric acid ionic liquid at different temperatures in °C.

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Table (3-9) Nickel (II) oxide NiO electronic spectra parameters.

Nickel oxide	***RT ^{o}C***	***40 ^{o}C***	***60 ^{o}C***	***80 ^{o}C***	***100 ^{o}C***
υ_1	9923	9904	9908	9680	9688
υ_2	15267	15243	15174	15174	15197
υ_3	23923	23866	23752	24096	24096
B free ion	1030	1030	1030	1030	1030
B`	627.9	615.3	613.5	682	681
β	0.6	0.597	0.595	0.662	0.662

Table (3-10): The observed 10Dq as comparison with the calculated 10dq in different ratio of ligands

Observed 10Dq	***Calculated 10Dq (6Cl-)***	***Calculated 10Dq (4cl$^-$ with tartarate ion)***	***Calculated 10Dq (2cl- with 2 tartarate ion)***	***Calculated 10Dq (3 tartarate ion)***
9923	6786	6786	9220	9923

3.3.4 Electronic spectroscopy of cupric oxide in choline chloride/ tartaric acid ionic liquid:

A yellow solution was obtain when cupric oxide is dissolved in choline chloride / tartaric acid ionic liquid; this solution was examined by U.V-Vis spectroscopy at room temperature and at elevated temperature up to 100°C, where at this point the colure of the solution is changed into deep yellow.

The recorded ultraviolet visible spectra of the yellow solution of the cupric oxide showed one broad band absorption maxima at 1069 nm (9355cm^{-1}) as shown in Figure (3-26).

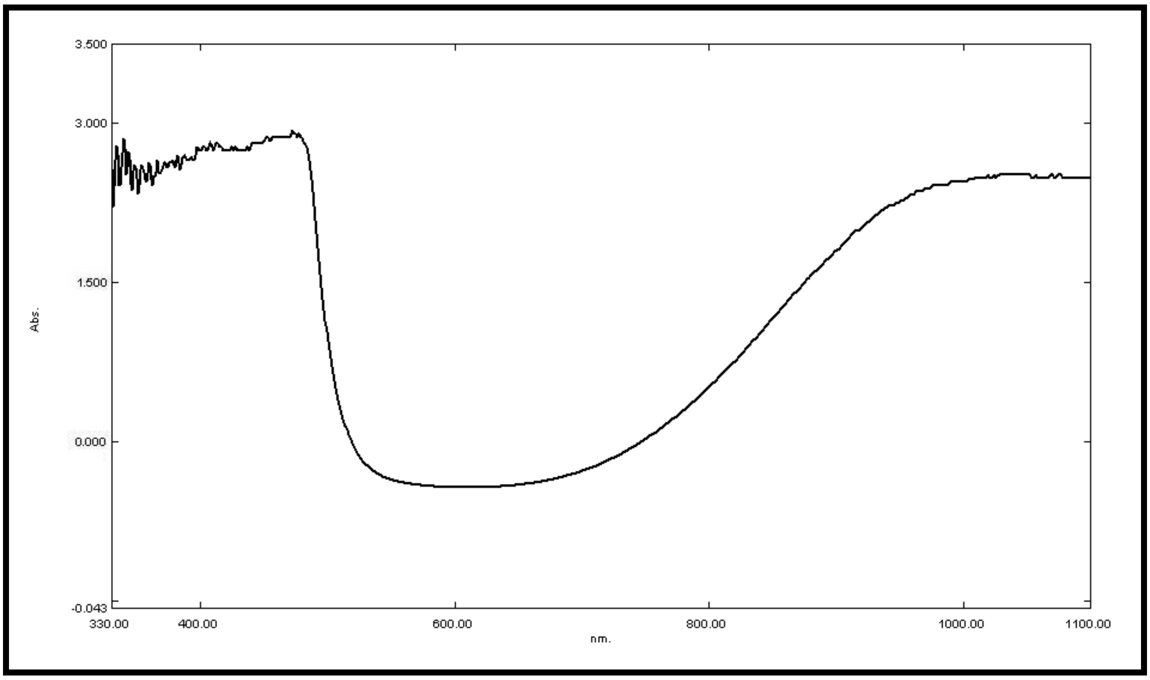

Figure (3-26) The UV- Vis. Spectrum of Cupric oxide (CuO) in Choline chloride/ tartaric acid ionic liquid at room temperature.

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 °C which showed one absorbance maxima at 9500 cm^{-1}, where it propose to be in distorted octahedral to tetrahedral coordination (84).

The suggested average environmental is that copper (II) in choline chloride/ tartaric acid was bonded with two chloride ions and one tartaric acid molecule. As shown in Figure (3-27). This suggestion is supported by the value of molar absorption (15.9) as shown in Table (3-14) since the normal octahedral would show less value (<10) and normal tetrahedral (~100).

As shown in Figure (3-28), increasing the temperature did not show significant changes in color as it is only increases the intensity of the yellow color and there was no change in bands positions.

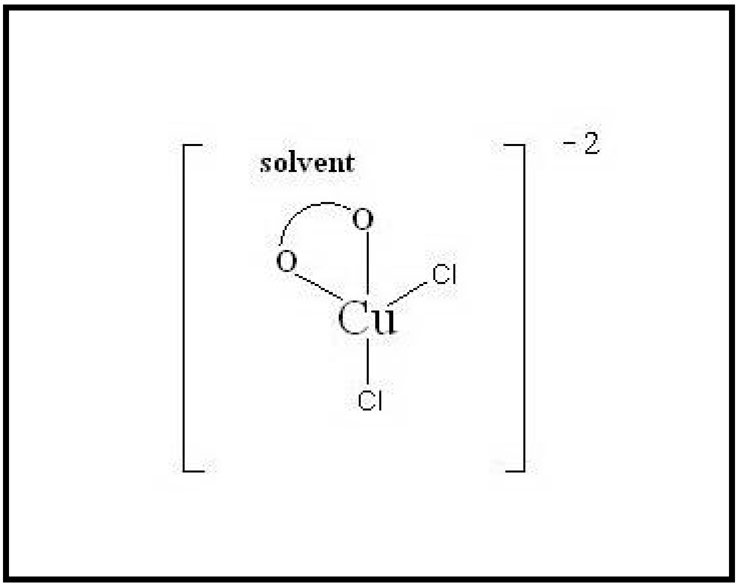

Figure (3-27): Suggested structure for copper (II) in choline chloride/ tartaric acid ionic liquid.

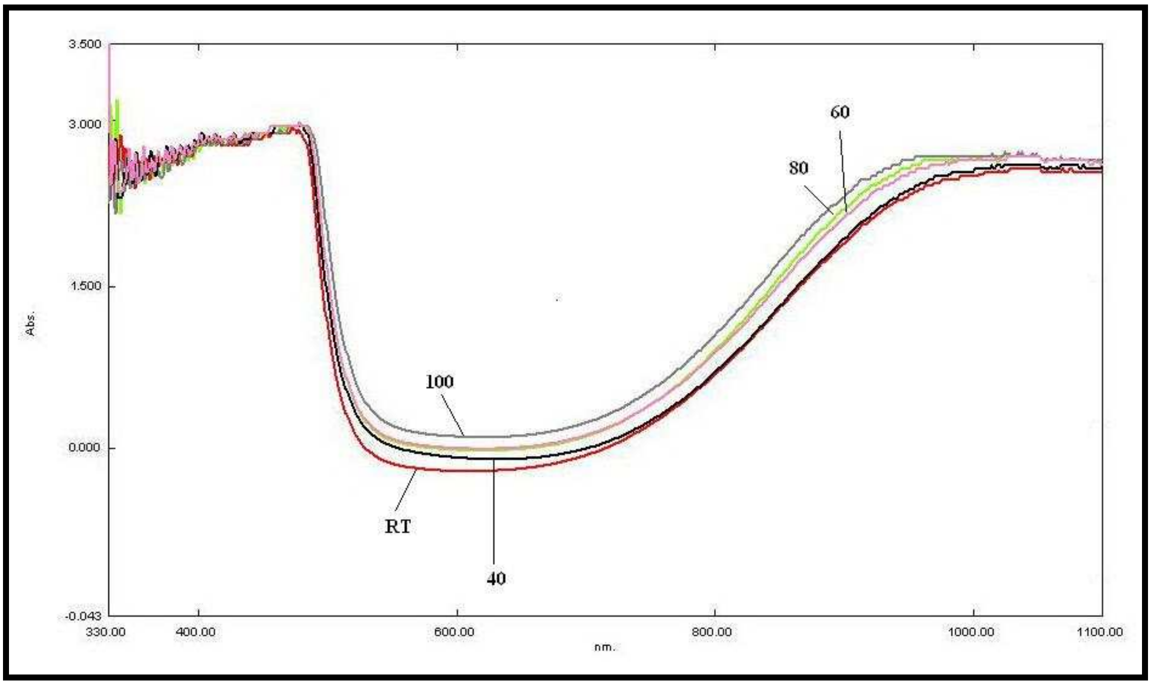

Figure (3-28) The UV- Vis spectra of Cupric oxide (CuO) in Choline chloride/ tartaric acid ionic liquid at different temperatures at °C.

3.3.5 Electronic spectroscopy of zinc oxide in choline chloride/ tartaric acid ionic liquid:

Zinc has two s electrons outside filled d shells. No lose of electron occur to gives ions or complexes, so it is regarded as non-transition elements, and since there are no electron transition, zinc complexes are colorless and cant be identify by U.V. Vis spectroscopy.

The results of molar absorptivity were obtained in Tables (3-11), (3-12), (3-13), and (3-14).

Table (3-11): Variable of molar absorbability (є) of the spectra for chromium oxide in choline chloride ionic liquid at variable temperature measured at λ =357.9 cm^{-1}.

υ_1	*A*	*Concentration in M (c)*	*b*	$\epsilon_{L\ /\ mol\ cm}{}^{3}$
RT ^{o}C	0.683	0.025	1	27.3
40 ^{o}C	0.904	0.025	1	36.16
60 ^{o}C	0.927	0.025	1	37.08
80 ^{o}C	0.943	0.025	1	37.72
100 ^{o}C	1.033	0.025	1	41.32
υ_2	*A*	*Concentration in M (c)*	*b*	$\epsilon_{L\ /\ mol\ cm}{}^{3}$
RT ^{o}C	0.898	0.025	1	35.92
40 ^{o}C	1.124	0.025	1	44.96
60 ^{o}C	1.146	0.025	1	45.84
80 ^{o}C	1.177	0.025	1	47.08
100 ^{o}C	1.260	0.025	1	50.4

Table (3-12): Variable of molar absorbability (ϵ) of the spectra for cobalt oxide in choline chloride ionic liquid at variable temperature measured at λ= 240.7 cm^{-1}.

At υ_3	*A*	*Concentration in M (c)*	*b*	$\epsilon_{L\ /\ mol\ cm^3}$
RT ^{o}C	1.62	0.01	1	162
40 ^{o}C	1.751	0.01	1	175.2
60 ^{o}C	1.816	0.01	1	181
80 ^{o}C	1.937	0.01	1	193.7
100 ^{o}C	2.090	0.01	1	209

Table (3-13): Variable of molar absorbability (ϵ) of the spectra for nickel oxide in choline chloride ionic liquid at variable temperature measured at λ= 232 cm^{-1}.

υ_2	*A*	*Concentration in M (c)*	*b*	$\epsilon_{L\ /\ mol\ cm^3}$
RT ^{o}C	0.28	0.044	1	6.36
40 ^{o}C	0.413	0.044	1	9.36
60 ^{o}C	0.452	0.044	1	10.2
80 ^{o}C	0.487	0.044	1	11.07
100 ^{o}C	0.607	0.044	1	13
υ_3	*A*	*Concentration in M (c)*	*b*	$\epsilon_{L\ /\ mol\ cm^3}$
RT ^{o}C	0.642	0.044	1	14.5
40 ^{o}C	0.806	0.044	1	18.3
60 ^{o}C	0.823	0.044	1	18.7
80 ^{o}C	0.817	0.044	1	18.5
100 ^{o}C	0.846	0.044	1	19.2

Table (3-14): Variable of molar absorbability (ϵ) of the spectra for copper oxide in choline chloride ionic liquid at variable temperature measured at λ=324.8 cm^{-1}.

At υ_{max}	*A*	*Concentration in M (c)*	*b*	ϵ *L / mol cm^3*
RT °C	2.683	0.168	1	15.97
40 °C	2.709	0.168	1	16.07
60 °C	2.767	0.168	1	16.47
80 °C	2.767	0.168	1	16.47
100 °C	2.799	0.168	1	16.66

3.4 Thermodynamic effect of d-orbital splitting:

It was found that the calculated lattice energies of the dissolved metal oxides in choline chloride/ tartaric acid ionic liquid did not have a straight increasing line when it plotted with atomic number Figure(3-29).

This was found to be in agreement with the lattice energies of the metal dichloride of the divalent element of the first transition series (29) Figure (3-30).

This would be attributed according to crystal field theory, to the d-orbitals splitting into t_2g and eg orbitals which stabilized by 4Dq and 6 Dq respectively. This would imply that the electrons are entering d-orbitals of different energies as progress through a transition series causing a non linear graph of for example lattice energy.

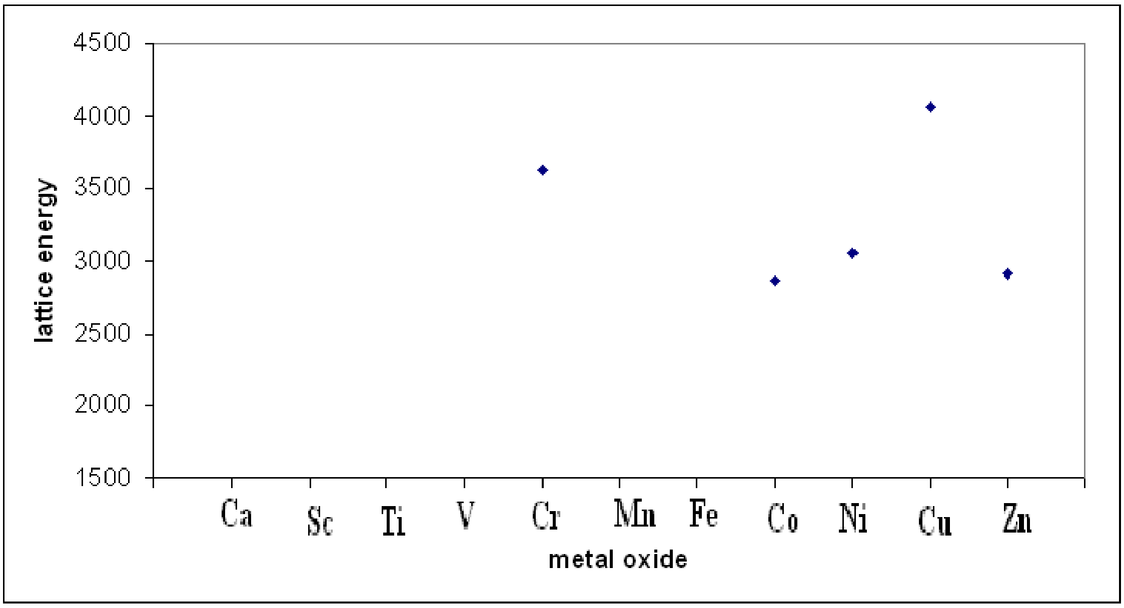

Figure (3-29) Lattice energies for Cr_2O_3, Co_3O_4, NiO, CuO, ZnO element of the first series of the transition metals.

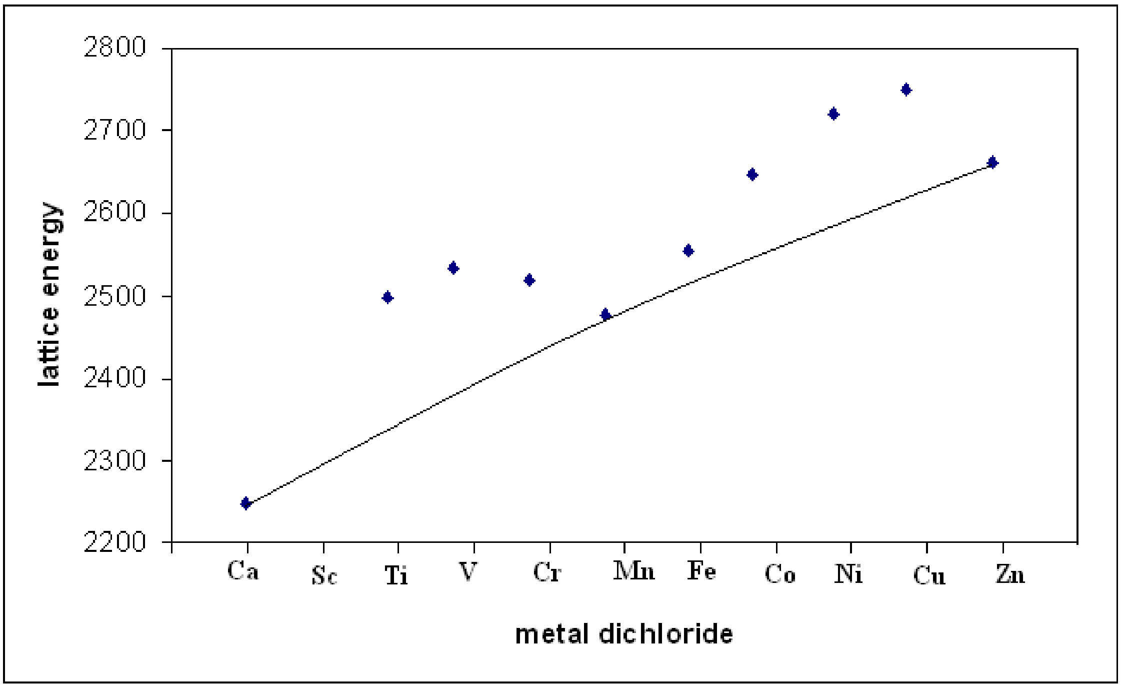

Figure (3-30) Lattice energies for the dichloride of the divalent elements of the first series of the transition metals.

3.5 ***Conclusion:***

1- The prepared room temperature ionic liquid was based on quaternary ammonium salt (choline chloride) that was mixed with hydrogen bond donor molecule [$(CH_2CHOHCOOH)_2$] in mole ratio of 2:1 showed different physical properties from other aqueous solvents.

2- The prepared ionic liquid was colorless, high viscosity, have low PH, and 5^oC freezing point.

3- This prepared ionic liquid has been used as non-aqueous solvents to study the solubilities of some first row transition metal oxides, CrO_3, Co_3O_4, CuO, NiO and ZnO, which showed promising properties to dissolve the oxides.

4- The prepared ionic liquid has been used as solvent to study the behavior of the metal oxide. The interaction when examined by UV-Vis that took place between transition metal ions and the possible ligand in each solution gave complexes with possibly variable mixed ligands of octahedral and tetrahedral geometry.

5- The calculated ligand field shows different strength (according to the 10 Dq value of each metal complexes), different Racah parameter (B`) and different electron repulsion parameter (β), which refers to different ionic character between the metal and the donor atom of the ligand.

6- The obtained lattice energies from the solubility measurements of the metal oxides were consistent with the enterelecrtonic repulsion normally showed by the transition metal complexes.

7- Heating the resultant metal solutions didn’t appear to have a noticeable geometrical deformation but merely increasing the intensity of the absorb visible energy bands.

3.6 Suggestion for future work:

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

1- Investigating the solubility and coordination of another set of transition metal complexes using another transition metals ions such as second or third rows of transition metal using the same prepared choline chloride/ tartaric acid ionic liquid.
2- Studying the solubility of metal chlorides in addition to the metal oxides that already studied.
3- Finding a suitable method to isolate the prepared complexes of the transition metal ions from their ionic liquid solution.
4- Identifications of the isolated complexes of the transition metal ions by using infrared spectroscopy, magnetic susceptibility or the x-ray diffraction.

Chapter Two

Experimental

2.1. Chemicals and Instruments:

2.1.1. 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
Cobalt oxide	98	Merck
Cupric oxide	99	BDH
Nickel oxide	99	BDH
Sulphuric acid conc.	98	Thomas Baker
d-tartaric acid	99	BDH
Zinc oxide	99	BDH

2.1.2 Instruments:

There were some instrumental analysis and procedures were applied in this work which will be described in the following section:

2.1.2.1- Metal analysis:

The metal content in complexes was measured by atomic absorption technique in PERKIN-ELMER-5000 Atomic Absorption Spectrophoto meter for the determination of (Co, Cu, Cr, Ni, and Zn), using air-acetylene lamp, of 240.7, 324.8, 357.9, 232, and 213.9 cm^{-1} wavelength respectively. the measurement was carried out in the laboratory of biology department/ college of science/ Baghdad University

2.1.2.2- UV-Vis spectroscopic:

The electronic spectra of complexes were obtained by using SIMADZU (Japan), UV-Vis 1650 PC ultra violet visible spectrophotometer from room temperature to 100^{o}Cusing quartz cells of 1.0 cm length and ionic liquid as solvent in the range of wave length 190-1100 nm (52632 – 9091 cm^{-1}). As the spectra were recorded and characterized. the measurement was carried out in the laboratory of chemistry department/ college of science/ Al-Nahrain University

2.1.2.3 Conductivity measurement:

The conductivity measurement was carried out at 27 °C using HANNA instrument 5000 µs/ cm. the measurement was carried out in the laboratory of chemistry department/ college of science/ Al-Nahrain University

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 Figure (2-1) illustirate the apparatuses used with room temperature ionic liquid, which is similar to those might be used with aqueous system. The apparatuses of Figure (2-1) consists of :

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

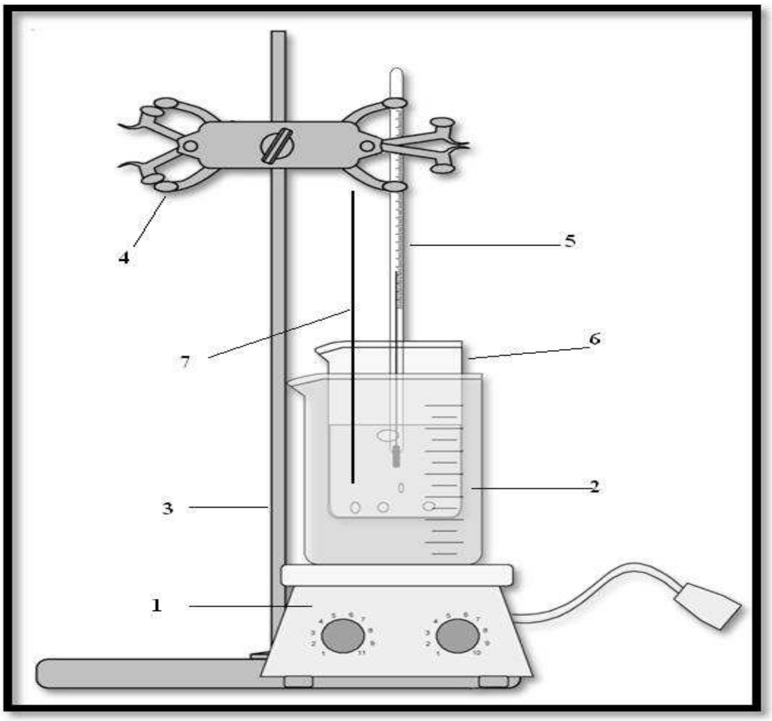

Figure (2-1):- Setting of heating apparatus

2.3 Methods:

2.3.1 Drying method:

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

2.3.2 Determination composition/ melting point, phase diagram of choline chloride/ d- tartaric acid ionic liquid:

The composition / melting point phase diagram was obtained for the melting points of the mixtures of choline chloride ($HOC_2H_4N\ (CH_3)_3{}^+Cl^-$) (m wt = 139.63 g/mol) / tartaric acid ($[CHOHCOOH]_2$) (m wt = 150.09 g/mol). The appropriate ratio of their compounds were prepared from 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 °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.

To determine the freezing point of their mixtures they were placed in an ice bath and the temperature at which the melt frozen was recorded.

2.3.3 Solubility determination:

Metal solubility was determined by adding 0.05 g of cupric, chromic, cobalt, nickel, and zinc oxide to 5 ml of Choline chloride/ Tartaric acid ionic liquid in 10 ml beaker in order to get five saturated solution. Each solution was left for one week with daily hand stirring to determine the solubility at room temperature (27 C^{o}), at the 7th day the solution left without stirring to insure settling of the undissolved metals, after that (1 g) of the soluble was taken from each solution and that is by inserting the glass rod in the beaker to reach the upper layer of the solution to take several drops and put in a volumetric flask, then dissolved in 10 ml of concentrated sulfuric acid. Then, the all solutions were taken for atomic absorption analyzing.

Solubility measurements at 40, 60, 80, and 100 ^{o}C were carried out for the metal oxides by heating the saturated solutions to those temperatures and kept for 4 hours then the last hour was with out stirring to allow settling of the undissolved oxides.

Finally, the determined metal content of these samples were used to calculate the metal oxide concentration in the ionic liquid at each temperature of analysis.

2.3.4 The molar absorptivity:(73)

Calculation of the molar absorptivity required the unit of concentration to be in molarity, therefore the determined solubility of the metal oxide was changed from molality to molarity 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)

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List of abbreviations

Abbreviation	***Name***
A A	Atomic absorption
UV-Vis	Ultraviolet- visible
Oh	Octahedral
Td	Tetrahedral
B`	Racah parameter for free ion
B	Racah parameter for complex
β	Nephelauxetic factor
Δ°	Crystal field splitting energy
nm	Nanometer
I L	Ionic liquid
R T I L	Room temperature ionic liquid
H T I L	High temperature ionic liquid
V O C	Volatile organic compound
D E S	Deep eutectic solvents
P T A	Phase solubility analysis
E P A	Environmental protection agency
C F T	Crystal field theory
M O T	Molecular orbital theory
V D W	Van der waals
HSAB	Hard and soft acids and bases
[Bmim]	1 1-butyl-3-methylimidazolium
[BMP]	1-butyl-1-methylpyrrolidinium

Abstract

Choline chloride / tartaric acid room temperature ionic liquid was prepared and the obtained phase diagrams of the mixture showed eutectic point at 5 ^{o}C. The ionic liquid showed a conductive properties, high density and low PH values.

Secondly, the dissolution of Co_3O_4, CrO_3, NiO, CuO, and ZnO. Were studied and found soluble in choline chloride / tartaric acid ionic liquid as their solubilities were determined by measuring the dissolved metal by atomic absorption from room temperature up to 100 ^{o}C. The lattice energies of the metal oxides were deduced and the effects of the d- orbital electrons on the lattice energy were compared.

In addition to their solubilities the above solution of metal oxides were investigates by ultraviolet visible spectroscopy. The spectra were measured and assigned to the expected coordination in the choline chloride/ tartaric acid ionic liquids, the effect of increasing temperature of the solution up to 100 ^{o}C were also studied and showed similar coordination but higher vibration with increasing temperature.

Racah factor for there complexes (B`) were determined together with field factor, crystal field splitting energy (Δ^{o}), *nephelauxetic* factors and molar absoptivities for each spectra at the variable temperatures.

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عنوان الاطروحه: دراسة الذوبان والكيمياء التناسقية لأكاسيد بعض العناصر ألانتقاليه للمنصهر ألايوني المحضر لمزيج كلوريد الكولين/ حامض التارتاريك.

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

من قِبَلْ
فرح أنور حسن
بكالوريوس٢٠٠٥ (جامعة النهرين)

بإشراف
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تموز ٢٠٠٨ **جمادي الثاني ١٤٢٩**

(بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ)

﴿ يُؤتِي الْحِكْمَةَ مَن يَشَاءُ وَمَن يُؤْتَ الْحِكْمَةَ
فَقَدْ أُوتِيَ خَيْراً كَثِيراً وَمَا يَذَّكَّرُ إِلاَّ أُوْلُواْ
الأَلْبَابِ﴾

صدق الله العلي العظيم

سورة البقرة، الآية { ٢٦٩ }

الخلاصه

في هذا البحث تم تحضير نوع جديد من الأملاح المنصهرة في درجة حرارة الغرفة ، عن طريق مزج احد أملاح جذر الامونيوم الرباعي وهو كلوريد الكولين مع احد المواد لها القابلية على تكوين أواصر هيدروجينية وهو الحامض الكاربوكسيلي الثنائي الكاربوكسيل وهو حامض ألتارتارك، تم تحضير عده محاليل بنسب مولية مختلفة. ومن المخطط ألطوري للمحلول تم الحصول على محلول بدرجه انصهار ٥ درجه مئوية.

ومن مواصفات هذا الملح المنصهر المحضر هي : له صفات توصيلية ، له كثافة عالية ، وقيمه الأس الهيدروجيني له واطئه.

وأيضا في هذا البحث استخدمه الملح المنصهر المحضر كمذيب لا مائي لدراسة قابليه ذوبان بعض أكاسيد العناصر ألانتقاليه من السلسلة الأولى وتشمل:

$$[Co_3O_4, CrO_3, NiO, CuO, ZnO]$$

حيث وجد أن لها ألقابليه على الذوبان في هذا الملح المنصهر المحضر، وتم قياس التركيز (الإذابة) عن طريق استخدام جهاز الامتصاص الذري وذالك بدرجه حرارة ألغرفه صعودا إلى المائة درجة مئوية.

إضافة إلى ذلك تم حساب الحرارة الكامنة للانصهار لكل واحد من أكاسيد العناصر و تم توضيح تأثير اوربيتال d على قيمة الحرارة الكامنة للانصهار.

تم تشخيص المحاليل السابق ذكرها عن طريق جهاز الأشعة ألفوق البنفسجية- المرئية (UV. Vis.) لغرض معرفه المعقدات المتكونة ومعرفة التغير في الصيغة التركيبية للأوكسيد . وتم اخذ بنظر الاعتبار تأثير زيادة الحرارة إلى درجه حرارة مائه درجه مئوية ، حيث ان زيادة درجه الحرارة ليس له تأثير على ألصيغه التركيبية إلا انه له تأثير على زيادة الاهتزاز الالكتروني.

تم حساب معامل راكاح (*Racah*) ،مقاييس المجال الليكندي ، مقدار طاقه الانفصال (Δ^o) و حساب الامتصاصية ألمولاريه لكل طيف في جميع درجات الحرارة.

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Solubility and coordination study of some transition metal oxides in new choline chloride/ tartaric acid ionic liquid

A Thesis
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إلى من جُعلت الجنة تحت أقدامها وتآنس روحي بقربها ويستنير دربي بدعائها وتغفو أحزاني بابتسامة عيناها

أمي حنان الدنيا كلها ورمز التضحية

إلى من شجعني على خوض التجربة وجعلني أمسك بدفة المَركب وبموج هذه الحياة

أبي العزيز

إلى من أشد به أزري في الحياة

أخي سيف

إلى كل من له مكانة في قلبي

إليكم ما وفقني إليه ربي

فرح

٢٠٠٨

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