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ELECTRONIC SPECTROSCOPY OF SOME TRANSITION METAL ION COMPOUNDS IN A NEW IONIC LIQUID

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بسم الله الرحمن الرحيم

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Dedication:

To my :

Family and fiancé (Husam Ekrayym)

Zena

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Abstract:

The behavior of some transition metal cations [Cr (III), Fe (III), Fe (II), Co (II), Ni (II) and Cu (II)] were investigated in ammonium alum-urea ionic liquid. The study was followed by UV-Visible electronic spectroscopy to establish their coordination geometry in the liquid and estimate the ionic species attached to the transition metal cations.

The reactivity of the metal cations were found to vary from one to another. Chromium (III) cation was found, (as expected) to be in octahedral geometry with ionic liquid species and was inert toward the addition of ligands. Similarly iron (III) did not show a tendency to react with added ligands, yet charge transfer was prevailed. However, interesting iron (II) showed high spin octahedral coordination with thiocyanate ion but a low spin octahedral complex with nitrite ion.

Cobalt (II) showed an interesting behavior in alum-urea ionic liquid, as it coordinated in an octahedral geometry with its ionic species. A gradual geometrical changes were appeared as a major change in their spectra most probably forming a mixture of two species tetrahedral with some original octahedral complex when its solution was studied with increasing thiocyanate ion concentration up to 35 thiocyanate:1 cobalt mole ratio.

The solubility limit of nitrite in ionic liquid ceased the concentration ratio of nitrite : cobalt to be 5:1.

Nickel (II) also showed an octahedral geometry behavior in ionic liquid species. It reacts with added ligands particularly when the

concentration of thiocyanate ion : Ni (II) increased up to 30 to 1 mole ratio, the color changed from pale green to olive-green solution.

Cupper (II) cation showed a clear blue solution and its spectra are assigned to be octahedral geometry, while the added nitrite did not show color change but less absorbance was recorded. However, thiocyanate ion seems to react with cupper (II) ionic liquid solution producing suspended green solution with much less absorbance than with ionic liquid.

Interestingly, the water molecules present in the original ammonium alum was not found to coordinate with metal cations as their spectra was found to differ when compared with those obtained in aqueous solution.

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List of Abbreviations

Abbreviations	Name
VOCs	Volatile Organic Compounds
RTILs	Room Temperature Ionic Liquids
IL	Ionic Liquid
EMIM	1-Ethyl-3-Methyl Imidazolium
BMIM	1-Butyl-3-Methyl Imidazolium
CFT	Crystal Field Theory
MO	Molecular Orbital
LFT	Ligand Field Theory
UV-Vis.	Ultraviolet visible
Nm	Nanometer
Cm	Centimeter
DMSO	Dimethylsalfoxide
Td.	Tetrahedral
Oh.	Octahedral
B`	Racah parameter
B	Nephelauxetic factor
Tf_2N	Bis (trifluoromethylsulfonyl)imide
M	Concentration in unit of (mol/L) ' Molarity '
Y	Wavelength
E	Molar Absorptivity
En	Ethylene diamin
M	Number of moles
dm^3	Cubic decimetre

Chapter **1**

Introduction

1.1 Green chemistry:-

Green chemistry, (also called sustainable chemistry), is the use of chemistry for pollution prevention or, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry is a highly effective approach of pollution prevention because it applies innovative scientific solutions to real-world environmental situations. [1,2]

Green solvents are environmentally friendly solvents or bio solvents, which may be derived from the processing of agricultural crops. Ethyl lactate, for example is a green solvent derived from processing corn. [3]

Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low vapor 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 workplace being made a great deal safer. [4] 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 (VOCs); they are now considered as environmentally unacceptable. [5]

The Montreal Protocol identified the need to re-evaluate chemical processes with regard to their use of VOCs and the impact that VOCs has on the environment. Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents. [6]

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. [7] The use of new ionic liquid alum such as ($AlNH_4(SO_4)_2.XH_2O$, $Al_2(SO_4)_3.XH_2O$ and $AlK(SO_4)_2.XH_2O$) with urea considered useful as a green solvent because it has a low vapor pressure and stable when it is exposed to air or moisture.[8]

1.2 Molten salts ionic liquids:-

Molten Salt 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).[9]

The simplest example of a molten salt would be sodium chloride and heated to a red heat (greater than 801°C, or 1474°F) to 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 as water would. The other examples of molten salts are: LiCl/KCl which are melt at 450°C (binary system), LiCl/NaCl/KCl melt at 383°C (ternary system). Salts are simple, usually ionic (that is the chemical bonds are a simple ionic type) and stable compounds. The most common example is sodium chloride (NaCl). Both sodium and chlorine are notoriously reactive; sodium is one of the most electropositive substances (wants to lose an electron) and chlorine one of the most electronegative substances (wants to take an electron). These two opposite substances readily join to form stable sodium chloride via a strong ionic bond. [10]

Ionic liquids and room temperature ionic liquids (RTILs):-

An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salt whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). IL is largely made of ions and short-lived ion pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts or liquid salts. The ionic bond is usually stronger than the Vander Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Some salts are liquid at or below room temperature. **[11]**

Low-temperature ionic liquid can be compared with the ionic solutions, liquids that contain both ions and neutral molecules, and in particular so-called deep eutectic solvents, mixtures of ionic and non-ionic solid substances which have much lower melting points than the pure compounds. Certain mixtures of nitrate salts can have melting points below 100 °C. **[12]**

The discovery date of the "first" ionic liquid is disputed, along with the identity of its discoverer. Ethanol-ammonium nitrate (m.p. 52-55 °C) was reported in 1888 by S. Gabriel and J. Weiner.**[13]** One of the earliest truly room temperature ionic liquids was ethyl ammonium nitrate $[C_2H_5NH_3^+NO_3^-]$(m.p. 12 °C), synthesized in 1914 by Paul Walden.**[14]** In the 1970s and 1980s ionic liquids based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, were initially developed for use as electrolytes in battery applications.**[15,16]**

An important property of the imidazolium halogenoaluminate salts is that their physical properties: such as viscosity, melting point, and acidity, could be adjusted by changing the alkyl substituents and the imidazolium/pyridinium and halide/halogenoaluminate ratios.[17]

In 1992, Wilkes and Zaworotko obtained ionic liquids with 'neutral' weakly coordinating anions such as hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-), allowing a much wider range of applications.[18] Latter a new class of air and moisture–stable, ionic liquids based on 1-ethyl-3-methylimidazolium cation with either tetrafluoroborate or hexafluorophosphate as anions.[18] Unlike the chloroaluminate ionic liquids, these ionic liquids could be prepared and safely stored outside of an inert atmosphere. Generally, these ionic liquids are water insensitive, however, the exposure to moisture for a long time causes some change in their physical and chemical properties. [19]

Abbott et. al. [20] prepared a new class of air and moisture stable ionic liquids based on choline chloride, a green chemistry of such ionic liquids were demonstrated particularly in the metal process such as metal winding coating, this process offered much safer conditions and good quality for the manufacture .

Different type of choline chloride based on liquids with metal chlorides with hydrated or anhydrous were synthesized and each were used in particularly for their constituent, metal coating such as chrome, nickel, copper, zinc ….etc. [21,22]

Development of chloroaluminate was not halted at replacing the imidazolium or pyridinium by the less sensitive boron tetrafluoride or phosphate hexafluoride ions.

Most recently new ionic liquids based on aluminum chloride were prepared by Abood,[23] when it combined with either urea or acetamide or trimethyl urea. These ionic liquids are much stable than chloroaluminate ionic liquids, offering relatively cheaper, easily prepared ionic liquids with promising similar properties in at least its catalytic properties for organic reactions and aluminum metal coating on copper substrate .

In our laboratory a nother new type of ionic liquid were prepared from alum sulfate instead of alum chloride due to there ease of handling, cheaper, greener and availability of these compounds in variable industrial applications such as water purification. Alum of the type $NH_4Al(SO_4)_2.XH_2O$ and $KAl(SO_4)_2.XH_2O$ with urea or acetamide offered a room temperature ionic liquid with highly moisture and air stable characterization. As this is green ionic liquid as it expected to be used in variable process such as metal coating as it offer good media for some insoluble compounds in aqueous media to be dissolve easily this ionic liquid such as silver sulfate.[8]

There are many ways to prepare different types of ionic liquid such as:

1- Metathesis reactions: are good candidates to prepare new ionic liquids for the first time, however, they can leave the ionic liquids contaminated with small amounts of halide ions that may react with solute materials.[24]

$$[EMIM]I + Ag[BF_4] \rightarrow [EMIM][BF_4] + AgI \quad \text{m.p. } (12°C).$$ [25]

2- Acid-base neutralization reaction: tetraalkylammonium sulfonates have been prepared by mixing equimolar amounts of the sulfonic acid and the tetraalkylammonium hydroxide, the excess water was removed by vacuum.[24]

$$RSO_3H + [R_4N]\,[OH] \rightarrow [R_4N]\,[RSO_3] + H_2O$$

3- The final method for synthesis of ionic liquids is direct combination of a halide salt with a metal halide [24], such as:

$$AlCl_3 + [EMIM]Cl \rightarrow [EMIM]^+ + AlCl_4^- \text{ (basic part).}$$ [26]

1.4. General characteristics of ionic liquids:-

Ionic liquids are often moderate to poor conductors of electricity, non-ionizing (e.g. non-polar), highly viscous and frequently exhibit low vapor pressure, their other properties are diverse: many have low combustibility, excellent thermal stability: some ionic liquids (such as 1-butyl-3-methylimidazolium nitrate) generate flammable gases on thermal decomposition, thermal stability and melting point depend on the liquid's components. [27]

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 causes the low melting points of ionic liquids and the increase in anion size leads to decrease in melting point. [28]

Ionic liquid have wide liquid regions, and favorable solvating properties for a range of polar and non-polar, useful in many classes of chemical reactions, such as Diels-Alder reactions and Friedel-Crafts reactions, which can be performed by using ionic liquids as solvents. Recent work showed that ionic liquids can serve as solvents for biocatalysis, and the miscibility of ionic liquids with water or organic solvents vary with side chain lengths on the cation and with choice of anion, they can be functionalized to act as acids, bases or ligands, and have been used as precursor salts in the preparation of stable carbenes because of their distinctive properties, they have low nucleophilicity and capability of providing week coordinating or non-coordinating environment. The stability of ionic liquids, at least at a certain extent, is crucial for optimum process performance. Several studies have indicated that although not 100% inert, certain ionic liquids incorporating 1,3-dialkyl imidazolium cations are generally more resistant than traditional solvents under certain harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes.[27]

High quality ionic liquids incorporating $[BMIM]^+$ cation and a variety of anions, such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[CF_3CO_2]^-$ and $[(CF_3SO_2)_2N]^-$ have been reported to be colorless, even though they are not 100% pure, the color of less pure ionic liquids generally ranges from yellowish to orange, the formation of the color was attributed to the use of raw materials with color or excessive heating during the synthesis, a number of precautions for synthesis of colorless ionic liquids have been described, and a procedure for removal of color from impure ionic liquids using acidic alumina and activated charcoal has also been proposed. [29,30]

Ionic liquids are attracting increasing attention in many fields, including organic chemistry, electrochemistry, catalysis, physical chemistry, and engineering.

1.5. Some applications of ionic liquid:-

1- Homogeneous and heterogeneous catalysts:-

Ionic liquids offer the advantage of both homogeneous and heterogeneous catalysts because selected ionic liquids can be immiscible with the reactants and products but dissolve the catalysts.[31]

This has the advantages of a solid for immobilizing the catalyst, with the advantages of a liquid to allow the catalyst to move freely.

2- Biological reactions media:-

Enzymes are also stable in ionic liquids, giving the possibility for ionic liquids to be used in biological reactions, such as the synthesis of pharmaceuticals. [31]

3- Treatment of high-level nuclear wastes:-

Ionizing radiation does not affect ionic liquids, so they could be used to treat high-level nuclear wastes. [31]

4- Removing of metal ions:- In another application, Davis and Rogers have designed and synthesized several new ionic liquids to remove cadmium and mercury from contaminated water, when the water-insoluble ionic liquids come in contact with contaminated water, they snatch the metal ions out of water and sequester them in the ionic liquid.[31]

5- Purification of gases :-

Ionic liquids can selectively dissolve and remove gases and could be used for air purification on submarines and spaceships.[31]

6- Synthesis of coordination complexes:-

Reports of direct synthesis of coordination complexes in ionic liquids are oxo-exchange chemistry, exposure of chloroaluminate ionic liquid to water leads to formation of aluminum oxo- and hydroxo-containing species, dissolution of more oxophilic metals than aluminum will generate metal oxohalide species. Hussey et al. used phosgene [$COCl_2$] to deoxochlorinate $[NbOCl_5]^{2-}$, as shown in equation (1): [32]

$$[NbOCl_5]^{2-} \underset{O^{2-}}{\overset{COCl_2}{\rightleftharpoons}} [NbCl_6]^{-}$$

……………(1)

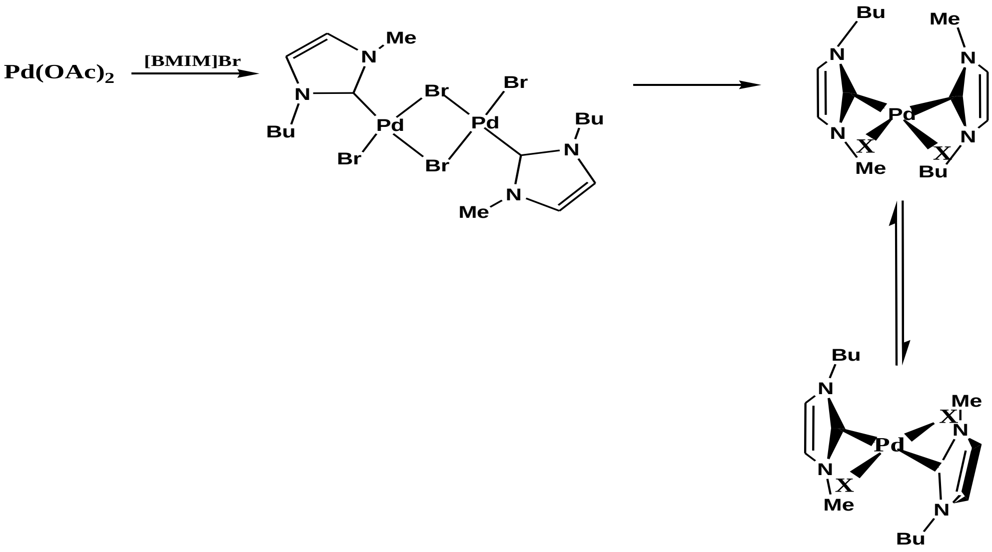
Triphosgene has been used to deoxochlorinate $[VO_2Cl_2]^-$ to $[VOCl_4]^{2-}$ then to $[VCl_6]^{3-}$ in both cases the deoxochlorination was accompanied by spontaneous reduction of the initial products, as shown in equation (2): [32]

$$[VO_2Cl_2]^{-} \underset{PhIO}{\overset{\text{triphosgene}}{\rightleftharpoons}} [VOCl_4]^{2-} \underset{O_2}{\overset{\text{triphosgene}}{\rightleftharpoons}} [VCl_6]^{3-}$$

………………..(2)

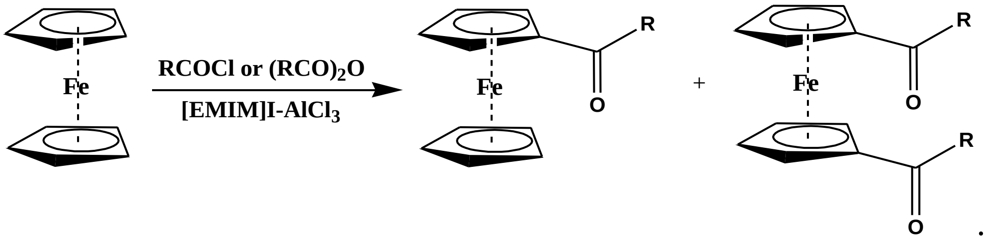
7- Synthesis of organometallic compounds:-

The imidazolium-based ionic liquids being used to prepare metal imidazolylidene complexes. The first came from Xiao et al., who prepared bis(imidazolylidene) palladium(II) dibromide in [BMIM]Br, as shown in equation (3): [32]



..(3)

And [BMIM]I-$AlCl_3$ used in acylation of ferrocene, as shown in equation (4):



……(4)

8- Formation of oxides:-

Recently, there has been some attention given to the preparation of oxides from solutions in ionic liquids. The first of these was the formation of a silica aerogel in [EMIM] [Tf_2N], as shown in equation (5): [32]

$$2HC(O)OH + (CH_3O)4Si \xrightarrow[\text{[EMIM] [Tf}_2\text{N]}]{} SiO_2 + 2CH_3OH + 2HC(O)OCH_3$$

………..(5)

1.6.1. Coordination chemistry:-

Coordination chemistry or metal complex, is an atom or ion (usually metallic), bonded to a surrounding array of molecules or anions, that are in turn known as ligands or complexing agents. Many metal-containing compounds consist of coordination complexes. [33,34]

The central atom or ion, together with all ligands comprises the coordination sphere. The central atoms or ion and the donor atoms comprise the first coordination sphere. [35,36]

The ions or molecules surrounding the central atom are called ligands. Ligands are generally bound to the central atom by a coordinate covalent bond (donating electrons from a lone electron pair into an empty metal orbital), and are said to be coordinated to the atom.[37]

In coordination chemistry, a structure is first described by its coordination number, the number of ligands attached to the metal (more specifically, the number of donor atoms). Usually one can count the ligands attached, but sometimes even the counting becomes ambiguous. Coordination numbers are normally between two and nine, but large numbers of ligands are not uncommon for the lanthanides and actinides. The number of bonds depends on the size, charge, and electron configuration of the metal ion and the ligands. Metal ions may have more than one coordination number.[36]

Typically the chemistry of complexes is dominated by interactions between s and p molecular orbitals of the ligands and the d orbitals of the metal ions. The s, p, and d orbitals of the metal can accommodate 18 electrons. The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion (to be more specific, the number of empty orbitals) and to the ratio of the size of the ligands and the metal ion. Large metals and small ligands lead to high coordination numbers, e.g. $[Mo(CN)_8]^{4-}$. Small metals with large ligands lead to low coordination numbers, e.g. $Pt[P(CMe_3)]_2$. Due to their large size, lanthanides, actinides, and early transition metals tend to have high coordination numbers.[38]

Different ligand structural arrangements result from the coordination number. Most structures follow the points-on-a-sphere pattern (or, as if the central atom were in the middle of a polyhedron where the corners of that shape are the locations of the ligands), where orbital overlap (between ligand and metal orbitals) and ligand-ligand repulsions tend to lead to certain regular geometries, but there are many cases that deviate from a regular geometry, e.g. due to the use of ligands of different types (which results in irregular bond lengths; the coordination atoms do not follow a points-on-a-sphere pattern), due to the size of ligands, or due to electronic effects.[39]

The idealized descriptions of 5-, 7-, 8-, and 9- coordination are often indistinct geometrically from alternative structures with slightly different L-M-L (ligand-metal-ligand) angles. The classic example of this is the difference between square pyramidal and trigonal bipyramidal structures.[39]

Due to special electronic effects such as (second-order) Jahn-Teller stabilization, certain geometries are stabilized relative to the other possibilities, e.g. for some compounds the trigonal prismatic geometry is stabilized relative to octahedral structures for six-coordination. [38]

1.6.2. Electronic properties:-

Many of the properties of metal complexes are dictated by their electronic structures. The electronic structure can be described by a relatively ionic model that ascribes formal charges to the metals and ligands.

The electronic configuration of the complexes gives them some important properties: [40]

1.6.2.1. **Color**:-

Metal complexes often have spectacular colors caused by electronic transitions by the absorption of light. For this reason they are often applied as pigments. Most transitions that are related to colored metal complexes are either d-d transitions or charge transfer. In a d-d transition, an electron in a d orbital on the metal is excited by a photon to another d orbital of higher energy. A charge transfer band entails promotion of an electron from a metal-based orbital into an empty ligand-based orbital (Metal-to-Ligand Charge Transfer or MLCT). The converse also occurs: excitation of an electron in a ligand-based orbital into an empty metal-based orbital (Ligand to Metal Charge Transfer or LMCT). This phenomena can be observed with the aid of electronic spectroscopy, also known as UV-Vis. For simple compounds with high symmetry, the d-d transitions can be assigned using Tanabe-Sugano diagrams. These assignments are gaining increased support with computational chemistry.[38,40]

1.6.2.2. **Magnetism**:-

Metal complexes that have unpaired electrons are magnetic. Considering only monometallic complexes, unpaired electrons arise because the complex has an odd number of electrons or because electron pairing is destabilized. Thus, monomeric Ti(III) species have one "d-electron" and must be (para)magnetic, regardless of the geometry or the nature of the ligands. Ti(II), with two d-electrons, forms some complexes that have two unpaired electrons and others with none. This effect is illustrated by the compounds $TiX_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$: when X = Cl, the complex is paramagnetic (high-spin configuration), whereas when

$X=CH_3$, it is diamagnetic (low-spin configuration). It is important to realize that ligands provide an important means of adjusting the ground state properties.

In bi- and polymetallic complexes, in which the individual centers have an odd number of electrons or that are high-spin, the situation is more complicated. If there is interaction (either direct or through ligand) between the two (or more) metal centers, the electrons may couple (antiferromagnetic coupling, resulting in a diamagnetic compound), or they may enhance each other (ferromagnetic coupling). When there is no interaction, the two (or more) individual metal centers behave as if in two separate molecules. [40]

1.6.2.3. Reactivity:-

Complexes show a variety of possible reactivities, some of them are: [40]

1- Electron transfers :

A common reaction between coordination complexes involving ligands are inner and outer sphere electron transfers. They are two different mechanisms of electron transfer redox reactions, largely defined by the late Henry Taube. In an inner sphere reaction, (a ligand with two lone electron pairs acts as a bridging ligand, a ligand to which both coordination centres can bond), through this, electrons are transferred from one centre to another.

2- ligand exchange :

One important indicator of reactivity is the rate of degenerate exchange of ligands, for example, the rate of interchange of coordinate water in $[M(H_2O)_6]^{n+}$, complexes varies over 20 orders of magnitude. Complexes where the ligands are released and rebound rapidly are classified as labile, such labile complexes can be quite stable thermodynamically. Typical labile metal complexes either have low-charge (Na^+), electrons in d-orbitals that are antibonding with respect to the ligands (Zn^{2+}), or lack covalency (Ln^{3+}, where Ln is any lanthanide). The lability of a metal complex also depends on the high-spin vs. low-spin configurations when such is possible. Thus, high-spin Fe(II) and Co(III) form labile complexes, whereas low-spin analogues are inert. Cr(III) can exists only in the low-spin state (quartet), which is inert because of its high formal oxidation state, absence of electrons in orbitals that are M-L antibonding, plus some "ligand field stabilization" associated with the d^3 configuration.

3- Associative processes :

Complexes that have unfilled or half-filled orbitals often show the capability to react with substrates. Most substrates have a singlet ground-state; that is, they have lone electron pairs (e.g., water, amines, ethers), so these substrates need an empty orbital to be able to react with a metal centre. Some substrates (e.g., molecular oxygen) have a triplet ground state, which results that metals with half-filled orbitals have a tendency to react with such substrates (it must be said that the dioxygen-molecule also has lone pairs, so it is also capable to react as a 'normal' Lewis base).

1.7. Chemistry of some first transition metal elements:-

1.7.1. Chromium (III), (d^3):-

Chromium (III) forms stable salt with all the common anions and its complexes with virtually any species capable of donating an electron-pair. These complexes may be anionic, cationic, or neutral and, with hardly any exceptions are octahedral. [41] There is also a multitude of complexes with two or more different ligands such as pentammines $[Cr(NH_3)_5X]^{n+1}$ which have been extensively used in kinetic. These various complexes are notable for their kinetic inertness, which is compatible with the half-filled T_{2g} level arising from an octahedral d^3 configuration, ligand displacement or rearrangement reaction of Cr (III) complexes are only about 10 times faster than those of Co (III), with half-times in the range of several hours.

This is the reason why many thermodynamically unstable complexes of Cr (III) can be isolated as solid and that they persist for relatively long time in solution, even under conditions of marked thermodynamic instability.

$[CrX_6]^{3-}$ (X=halide, CN^-, SCN^-, N_3, H_2O, NH_3).

$[Cr(L\text{-}L)_3]$ (L-L= amino acid anions).

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$, which is regular octahedral, occurs in aqueous solution and in numerous solid salts such as the green $[Cr(H_2O)_6]Cl_3$. Chromium (III) is the arch type d^3 ion and the electronic spectra and magnetic properties of its complexes have been exhaustively studied .[42]

Chromium (III) chloride type d^3 formed deep green colored solution in choline chloride/tartaric acid ionic liquid and gave octahedral coordination complex with 4 Cl^- and 1 tartarate ion. [43]

The magnetic properties of the octahedral Cr (III) complexes are uncomplicated. All such complexes must have three unpaired electrons irrespective of the strength of the ligand field, and this has been confirmed for all known mononuclear complexes. The spectra of Cr (III) complexes are also well understood in their main features, in an octahedral field, the splitting of free ion ground ^{4}F term, along with the presence of the excited ^{4}P term of the same multiplicity, provides or indicates the possibility of three spin-allowed d-d transition, and these have been observed in a considerable number of complexes, the spectorchemical series was originally established by using data for Cr (III) and Co (III) complexes .[42] In molten salt anhydrous chromium (III) chloride dissolved only slowly forming pale green solutions after more than 15h for 10^{-3} mol dm^{-3} concentrations at 90 °C in acetamide-potassium nitrate and 8h at 140 °C in butyramide-sodium nitrate melts.[44]

1.7.2. Iron (III), (d^5) and iron (II), (d^6):-

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron (II) compounds are called ferrous, and iron (III) compounds ferric. [45][46] There are also many mixed valence compounds that contain both iron(II) and iron(III) centers, such as magnetite and Prussian blue ($Fe_4(Fe[CN]_6)_3$). The iron compounds produced on the largest scale in industry are iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron (III) chloride ($FeCl_3$). Iron (II) sulfate or ferrous sulfate is the chemical compound with the formula $FeSO_4$, known since ancient times as copperas and as green vitriol, the blue-green heptahydrate is the most common form of this material. All iron sulfates dissolve in water to give the same aqua complex $[Fe(H_2O)_6]^{2+}$, which has octahedral molecular geometry and is paramagnetic. On heating, iron (II) sulfate first loses its water of crystallization and the original green crystals are converted into a dirty-yellow anhydrous solid, when further heated the anhydrous material releases sulfur dioxide and white fumes of sulfur trioxide, leaving a reddish-brown iron (III) oxide. Decomposition of iron (II) sulfate begins at about 480 °C. Like all iron (II) salts, iron (II) sulfate is a reducing agent. For example, it reduces nitric acid to nitrogen oxide and chlorine to chloride. [46]

Iron (III) occurs in salts with most anions, except those that are incompatible with it because of their character as reducing agent. In aqueous solution Fe (III) is one of the most conspicuous features of ferric ion in aqueous solution. It has a tendency to hydrolyze and/ or form complexes. It has been established that the hydrolysis (equivalent in the first stage to acid dissociation of the aqua ion) is governed in its initial stage. The various hydroxo species, such as $[Fe(OH)(H_2O)_5]^{2+}$, are yellow because of charge transfer band in the ultraviolet region, which has tails coming into the visible region. Thus aqueous solutions of ferric salts even with non complexing anion are yellow unless strongly acid. [42,47]

Iron (III) chloride was found to be soluble in the acetamide-potassium nitrate eutectic at 90 °C giving initially a pale yellow solution which darkened rapidly to a strong brown color within 15 min. The pale yellow solution gave one absorption band at $\upsilon = 16900\ cm^{-1}$ ($\varepsilon = 35\ mol^{-1}\ dm^{3}\ cm^{-1}$) close to an absorption edge at $\upsilon = 21000\ cm^{-1}$, while the dark brown solution showed only the absorption edge. The pale yellow solution may be due to a tetrahedral complex perhaps containing some chloride ($FeCl_4^-$ in $LiNO_3$-KNO_3 eutectic at 160 °C, the band at $\upsilon = 16000\ cm^{-1}$, $\varepsilon = 32\ mol^{-1}\ dm^{3}\ cm^{-1}$) which was replaced over 15 min by more stable simple complexes containing acetamide and/or nitrate, or perhaps by more polymerized solvolyzed iron specie. [44]

1.7.3. Cobalt (II), (d^7):-

There is a very marked contrast in this oxidation state between cobalt (II) on the one hand and the two heavier member of the group on the other hand, for cobalt (II) it is one of the two most stable oxidation state. Complexes of configuration comparable to stability with the T_{2g}^{6} E_g^{1} of Co(II) **,** show a greater diversity of types and are more labile. [41]

The aqua ion $[Co(H_2O)_6]^{2+}$ is the simplest complex of cobalt (II). In aqueous solution containing no complexing agents, the oxidation to Co (III) is very unfavorable. Cobalt (II) forms numerous complexes, mostly either octahedral or tetrahedral but five-coordination and square species are also known. [47]

There are tetrahedral complexes of cobalt (II) more than other transition metal ions. This is in accord with the fact that for a d^7 ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other d^n $(1\leq n \leq 9)$ configuration. Because of the small stability difference between octahedral and tetrahedral Co(II) complexes, there are several cases in which the two types with the same ligand are both known and may be in equilibrium.

In ionic liquid such as choline chloride / tartaric acid cobalt (II) chloride formed tetrahedral coordination complex $[CoCl_4]^{2-}$. [43]

As already noted, cobalt (II) occurs in a great variety of structural environments. Because of this the electronic structures, hence the spectral and magnetic properties of the ion, are extremely varied. In each case of high-spin octahedral and tetrahedral complexes, there is a quartet ground state (^4F) and three spin-allowed electronic transitions to the excited quartet state (^4P). [41,47]

1.7.4. Nickel (II), (d^8):-

The stereochemistry of Ni (II) has been a topic of continuing interest, and kinetic and mechanistic studies on complexes of Ni (II). The absence of any other oxidation state of comparable stability for nickel implies compounds of Ni (II) which are largely immune to normal redox reactions. [41]

Ni (II) forms salts with virtually every anion and has extensive aqueous solutions chemistry based on the green hexaaquanickel (II), $[Ni(H_2O)_6]^{2+}$ ion which is always present in the absence of strongly complexing ligands.

The coordination number of Ni (II) rarely exceeds 6 and its principal stereo chemistries are octahedral and square planer, tetrahedral (4-coordinate) with rather fewer examples of trigonal bipyramidal, square pyramidal (5-coordinate), octahedral complexes of Ni (II) are obtained often from aqueous solution by replacement of coordinating water, especially with neutral N-donner ligands such as NH_3, en, bipy, and phen, but also with NCS^-, NO_2^-, and O-donner such as DMSO (Me_2SO).[42,47]

When Ni (II) chloride react with choline chloride / tartaric acid ionic liquid its formed tetrahedral complex, the presence of this type of ionic liquid effect of the Ni (II) and make coordination with it. [43]

Nickel (II) forms a large number of complexes encompassing coordination numbers 4, 5, and 6 in structural types of neutral ligands. It is characteristic of Ni (II) complexes that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent.[44]

1.7.5. Copper (II), (d^9):-

Simple salts are formed with most anions, except CN^- and I^- instead of forming covalent Cu (I) compounds which are insoluble in water. Most Cu (I) compounds are fairly readily oxidized to Cu (II) compounds. There is a well-defined aqueous chemistry of Cu^{2+}, and large number of salts of various anions, many of which are water soluble. The blue color of their solution arises from the $[Cu(H_2O)_6]^{2+}$ ion, and they frequently crystallize as hydrates. The aqueous solutions are prone to slight hydrolysis and, unless stabilized by a small amount of acid, are liable to deposit basic salts. The most common coordination numbers of Copper (II) are 4,5, and 6, but regular geometries are rare and the distinction between square-planer and tetragonally distorted octahedral coordination is generally not easily made. The reason for this is ascribed to the Jahn-Teller effect arising from the unequal occupation of the E_g pair of orbitals (dz^2 and dx^2-y^2) when a d^9 ion is subjected to an octahedral crystal field. The d^9 configuration makes Cu(II) subject to Jahn-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 d^9 configuration can be thought of as an inversion of d_1, relatively simple spectra might be expected, and it is indeed true that the great majority of Cu (II) compounds are blue or green because of a single broad absorption band in the region 11000-16000 cm^{-1}, however as already noted, the d^9 ion is characterized by large distortion from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions which are by no means easy to assign unambiguously.[41]

In d^9 ion the free-ion ground ${}^2D$ term is expected to split in a crystal field in the same way as the ${}^5D$ term of the d^4 ion, (${}^2E_g \rightarrow {}^2T_{2g}$) and a similar interpretation of spectra is like wise expected in octahedral system.

Unfortunately this is now more difficult because of the greater overlapping of bands which occurs in the case of Cu (II). The *T* ground term of the tetrahedrally coordinated ion implies an orbital contribution to the magnetic moment, but the *E* ground term of the octahedrally coordinated ion is caused by 'mixing' of the excited *T* term into the *E* ground term with compounds whose geometry approaches octahedral having moments at the lower end, and those with geometries approaching tetrahedral having moments at the higher end, but their measurements can not be used diagnostically with safety unless supported by other evidence.[41,47]

1.8. Interaction of the ligands with the metal ions:-

The tendency of a metal ion to form a stable complex with ligands depends on many rules such as the hard and soft acids and bases (HSAB) principal of Pearson [42] which imply that metal ion tend to coordinate with certain functional groups of the ligand to form 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).[41,47] 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 .[47]

The Irving Williams series,[48] 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:[42,47]

Tendency of ligands to complex Class (a) metal ions	Tendency of ligands to complex Class (b) metal ions
N>>P> As >Ab	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 .[42]

One of the important aspects of CFT is that all ligands are not identical when it comes to a causing separation of the d-orbitals. 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 (E_g 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:

$I^- < Br^- < SCN^- \sim Cl^- < F^- < OH^- \sim ONO^- < C_2O_4{}^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 \sim pyr \sim en < bipy < phen < CN^- \sim CO$

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

The CFT method has provided a quantitative measure of the d-splitting. The T_{2g} / E_g 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 SML 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 SML 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

$Cl^- < F^- < OH_2 < CN^-$ $\quad\quad$ $Cl^- < OH_2 < NH_3 < CN^-$

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

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

Weak field strength (small Δ_0) $\quad\quad$ Strong field strength (largeΔ_0)

π-donors $\quad\quad$ 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. [41,47]

Aim of present work:

The aim of the work is to synthesized a new ionic liquid for green chemical applications and studied the interaction with particularly transition metal cations, e.g. : chromium (III) chloride, iron (III) chloride, iron (II) sulfate, cobalt (II) sulfate, nickel (II) sulfate and copper (II) sulfate, were investigated for their dissolution in ionic liquid and reaction with selected ligands of potassium thiocyanate, sodium nitrite, oxalic acid and EDTA and followed by electronic spectroscopic investigations to establish their behavior and stability in the liquid.

Chapter **2**

Experimental Part

2.1. Chemicals:-

All chemicals were used with highest purity available and without further purification. Table (2-1) shows the reagents, their purities and suppliers:

Table (2.1):- The used chemicals with their purities and suppliers.

Chemical compounds	Purity %	Company
Hydrated ammonium aluminum sulfate	99	BDH
Urea	99.5	THOMAS BAKER
Chromium(III) chloride hexahydrate	99	BDH
Iron(III) chloride hexahydrate	98	BDH
Iron(II) sulfate heptahydrate	99	BDH
Cobalt(II) sulfate heptahydrate	98	BDH
Nickel(II) sulfate hexahydrate	99	BDH
Copper(II) sulfate pentahydrate	99	BDH
Potassium thiocyanate	98	Merck
Sodium nitrite	95.5	Fluka
Oxalic acid	99.5	BDH
EDTA	98.7	THOMAS BAKER

2.2. Practical Methods:-

2.2.1. Preparation of hydrated ammonium aluminum sulfate/ urea room temperature ionic liquid:-

Solid salts of hydrated ammonium aluminum sulfate [$NH_4Al(SO_4)_2.12H_2O$] which has m.p. 93.5°C,[49] and urea [NH_2CONH_2] with m.p. 132°C,[50] will mixed in ratio (1:5) mole respectively,[8] then it heated gradually to 85°C, with continuous gentle stirring until both hydrated ammonium aluminum sulfate and urea melted together producing a colorless liquid. The resulted melt was gradually cooled to room temperature and remained as a liquid. The melt was kept sealed in a dry desiccators for further use.

2.2.2. Preparation of some transition metal ions in ionic liquid and water:-

A known weight of solid transition metal salts was added to appropriate volume of ionic liquid at room temperature, the mixture was left for 15 minutes in case of Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} and two hours for Ni^{2+} with stirring and heating up to 40°C, while Co^{2+} dissolved immediately, Table (2.2). Accordingly the color of the solution was changed indicating dissolution of the salt in ionic liquid. No precipitation or gaseous evaporation were noticed through out the dissolution process. While in water all the transition metal salts dissolved immediately. The resulted mixtures investigated by Ultraviolet Visible Spectroscopy then the obtained spectra were analyzed.

Table (2-2):- Concentrations and weights of transition metal salts in aqueous solution and in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

Transition metal salts	**Weight(g) in 50 ml water**	**Concentration(M) in water**	**Weight(g)in 10 ml ionic liquid**	**Concentration(M) in ionic liquid**
$CrCl_3.6H_2O$	0.13	0.01	0.026	0.01
$FeCl_3.6H_2O$	0.13	0.01	0.027	0.01
$FeSO_4.7H_2O$	0.13	0.01	0.08	0.03
$CoSO_4.7H_2O$	0.14	0.01	0.14	0.05
$NiSO_4.6H_2O$	0.13	0.01	0.05	0.02
$CuSO_4.5H_2O$	0.12	0.01	0.12	0.05

2.2.3. Substitution reaction studies:-

For substitution reaction studies, the transition metal salts in ionic liquid was mixed with appropriate amount of alkali metal salts KSCN, $NaNO_2$, EDTA and oxalic acid. The dissolution of the added ligands varied in their nature of reaction, in some cases they required gentle heating while others reacted without heating. However, time was also varied and stated throughout this work.

2.3. Instruments:-

2.3.1. Electronic absorption measurements:-

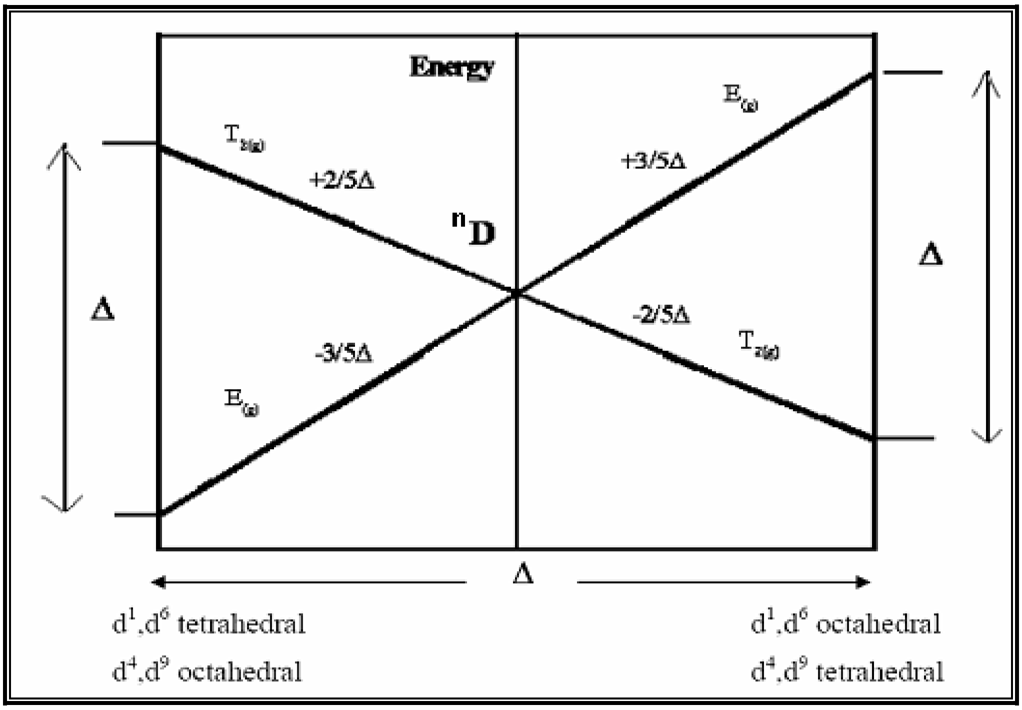
The electronic spectra of complex solutions were obtained by using CECEL CE7200, UV-Vis, Ultraviolet Visible spectrophotometer at room temperature using quartz cells of 1.0 cm path length and water reference in the range of wavelength 190-900 nm. Ionic liquid solvent was not used as reference because it was not possible to obtain a base line with ionic liquid and the water reference was not interfered with the absorption of ionic liquid and did not show any absorption in the visible region except a low absorbance band at 276 nm in the ultraviolet region.

2.4. Assignment of spectra:-

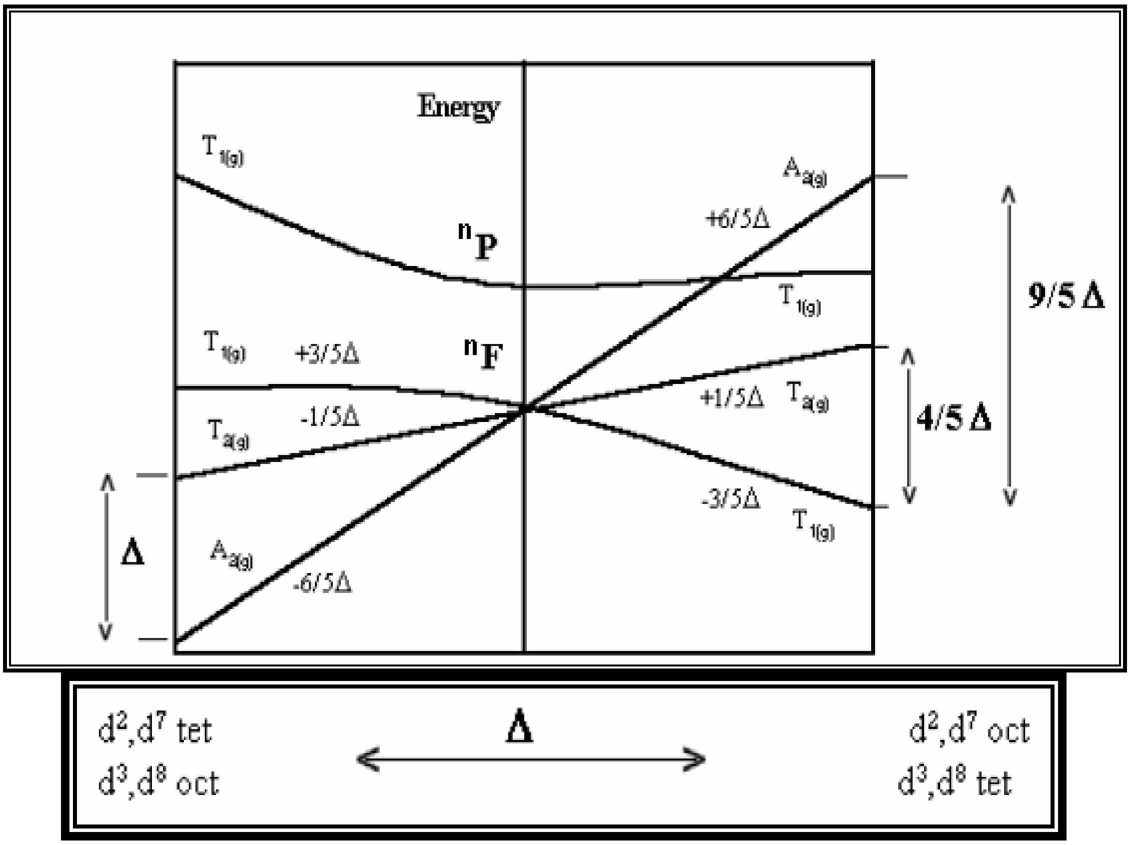
2.4.1. Orgel diagrams:-

Orgel diagrams are useful 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 $d^{1, 4, 6, 9}$ the other for $d^{2, 3, 7, 8}$) pack a lot of information in very little space, as shown in scheme (2.1) and (2.2). Nevertheless, there are three major limitations to using Orgel diagrams:

1- They are restricted to weak field/high spin conditions and offer no information for $d^{4, 5, 6, 7}$ strong fields/ low spin cases.
2- They only show symmetry states of same highest spin multiplicity.
3- They are qualitative, and therefore energy values cannot be obtained or calculated from them. [51,52]



Scheme (2.1):-The splitting of free-ion D terms in octahedral and tetrahedral fields.[52]



Scheme (2.2):-The splitting of free-ion F and P term in octahedral and tetrahedral fields. [52]

2.4.2. Tanabe-Sugano diagrams:-

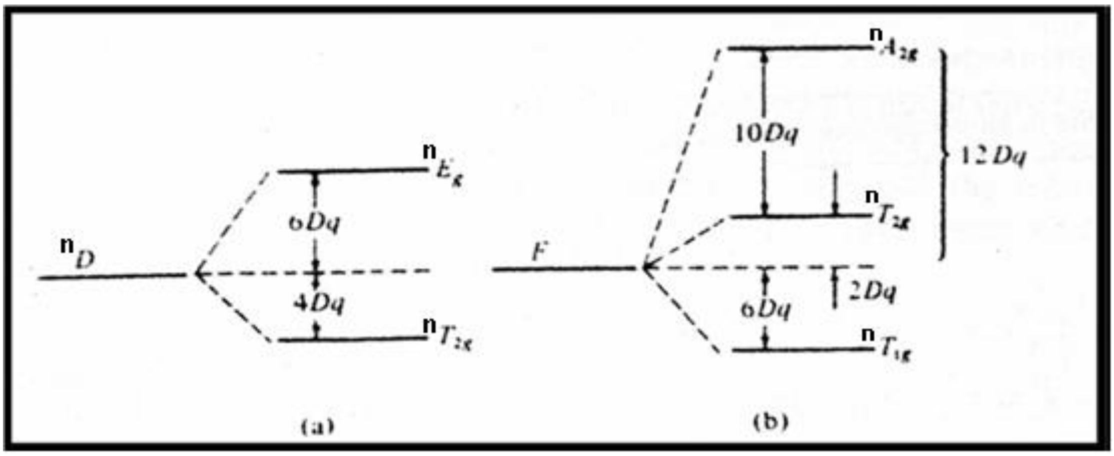
Tanabe-Sugano diagram use the ground symmetry state as a straight-line horizontal base, whereas Orgel diagrams place the parent term in a central location and direct ground symmetry states below it. Appear "split" for d^4, d^5, d^6, d^7, cases because both low and high spin symmetry states are included. 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 information 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}, E_g, or E, T_2 symmetry states. 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). [51,52]

2.4.3. Equations:-

The equations that have been used in the discussion of spectra of each complex were different from metal to another according to the splitting of terms for d^n configurations as shown in scheme (2.3).



Scheme (2.3):- Splitting of terms for d^n configurations in to (a) and (b). [42]

Jorgenson rule has been used to measure the tendency of metal ion to form a complex, 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:

$$10Dq = f_{\text{ligand}} \times g_{\text{ion}} \times 1000 \text{ --------------------------------------- } (2\text{-}1)$$

Table (2.3):- Values of *(g)* and (*f*) factors for metal ions and various ligands. [42]

Transition metal ion	**Value of (g) factor**	**Various ligands**	**Value of (f) factor**
Cr(III)	17.4	Cl^-	0.78
Fe(III)	14.0	H_2O	1.00
Fe(II)	15.2	SCN^-	0.73
Co(II)	9.00	Urea	0.92
Ni(II)	8.70		
Cu(II)	12.5		

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

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

The nephelauxetic ratio β is given by:

$\beta = B`/B^{\circ}$ --- (2-3)

Where (B`) is Racah parameter. And (B°) is for free ion.

2.4.4. Example of calculations:-

Consider an example application of a Tanabe-Sugano diagram for d^8 octahedral case. The absorption spectral data of a Ni^{2+} solution is shown below in Table (2.4). For example, the mathematical calculation of spectra of $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

Table (2.4):- Peak position of nickel (II) ions in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

Ion	ν_2 cm^{-1}	ν_3 cm^{-1}	ν_1 cm^{-1}	ν_3/ν_2	$\Delta o/B`$	Ref.
Ni^{2+}	14914	24906	?	1.67	9	This work

Two bands are observed within the range of measurement. They have maxima at 14914 cm^{-1} and 24906 cm^{-1}. Nickel is in the +2 oxidation state, so this is a d^8 system. Reference to Orgel diagram informs that (3 d-d) bands are expected and they can be assigned as:

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

Δo is taken to equal the absorption energy of ν_1, and the intersect on the x-axis of Tanabe-Sugano diagram equal $\Delta_o/B^`$. And by drawing a vertical line from this point it will intersect with other allowing electronic state of Tanabe-Sugano diagram for d^8.

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

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.

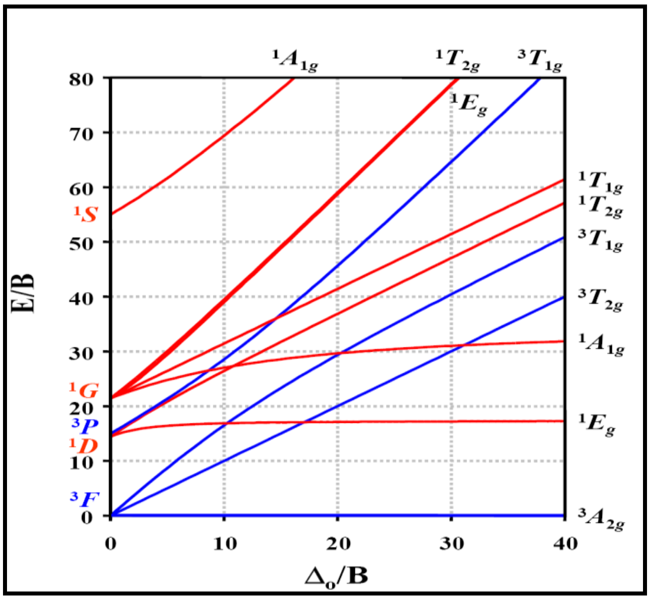
2- To determine the magnitude of the ligand field splitting parameter, Δ**o**.

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

Assumes bands are the second and third (so first 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 $\Delta o/B^`$ (i.e., ligand field splitting parameter / e-e repulsion parameter). [51,53]

Step (1): The calculated ratio of experimental band energies is: E (υ_3) / E (υ_2) = 1.67

Find chart lines for second and third symmetry states by Tanabe-Sugano diagram, and record their values at each abscissa mark.



Scheme (2.4):- Tanabe-Sugano diagram for d^8 ion configuration.

Δo/B`	**9**	**10**
E (ν_2) /B`	16	17
E (ν_3) /B`	27	28

Then find ratio of T-S chart values [(E (ν_3)/B̀)/(E (ν_2)/B̀)]= E (ν_3) / E (ν_2).

E (ν_3) / E (ν_2)	1.68	1.64

Step (2): Find the specific value for Δo/B̀**,** having a chart value for ν_3/ν_2 that matches or close to the experimental ratio of 1.67 .

When Δo/B` = 9, the chart ν_3/ν_2 **=** 1.68 so it will be used in the analysis.

Step(3): Use experimental values of E(ν_2) and E(ν_3) to obtain values for Racah B`:

E(ν_2) via B̀ = 16 → 14914 cm^{-1} / 16 = 932.1 cm^{-1}

E(ν_3) via B̀ **=** 27 → 24906 cm^{-1} / 27 = 922.4 cm^{-1}

Then find the average of B̀ = 927.2 cm^{-1}

Step(4): To determine ν_1 , $\Delta o/\grave{B}$ intersection with $^3T_{2g}$ at $E(\nu_1)/\grave{B} = 9$

So: $E(\nu_1)/\grave{B} = 9$, and $\grave{B} = 927.2\ cm^{-1}$,then $E(\nu_1)= 8345\ cm^{-1}$.

Step(5): To determine the nephelauxetic ratio β :

$\beta = \grave{B} / B_{\text{(free ion)}}$ then $\beta = 927.2 / 1030 = 0.9$.

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

$10Dq = f_{\text{ligand}} \times g_{\text{ion}} \times 1000$

$10Dq= \nu_1 = 8345\ cm^{-1}$

Then $8345 = f_{\text{ligand}} \times 8.7 \times 1000$

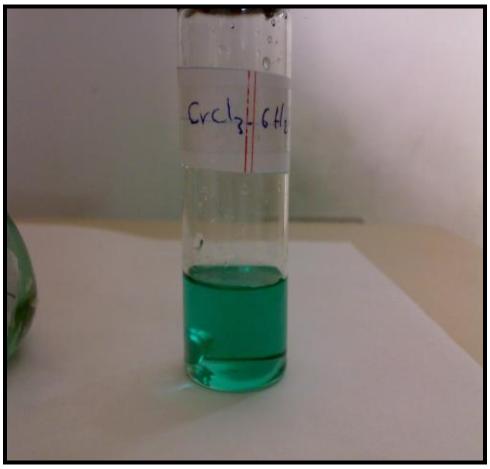
$f_{\text{ligand}} = 0.96\ cm^{-1}$

Chapter **3**

Results
&
Discussion

3.1. Chromium (III) chloride hexahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Chromium (III) chloride hexahydrate was not found to be easily soluble in ionic liquid at room temperature until the temperature was raised to 40°C, the 0.01 M of the metal chloride solution in the ionic liquid was achieved after 15 minutes with magnetic stirring. The resulted solution was clear deep green as shown in picture (3.1).



Picture (3.1):- 0.01 M of $CrCl_3.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at 40°C.

This solubility was found to be much better than those reported for the same compound in other ionic liquids or molten salts, for example the salt was found to be much less soluble 0.001 M after 15 hours at 90°C in acetamide/potassium nitrate melt or 8 hours at 140°C in butyramide/sodium nitrate.[44] In room temperature ionic liquid chromium (III) chloride was reported to have solubility of 0.1 M after 72 hours in choline chloride/urea with continuous stirring.[54] This may indicate that hydrated ammonium aluminum sulfate/urea ionic liquid is stronger solvent than those reported before with better solvation energy to interact with chromium chloride.

The electronic UV-Visible test of the deep green solution was carried out to investigate the electronic behavior of the resulted coordinated chromium (III) ion in the ionic liquid. Therefore the test showed two absorption bands in the visible region at 435.5 nm and 615 nm, the latter band showed two shoulders at the lower energy region 658.9 nm and 689.5 nm, Fig. (3.1.A).

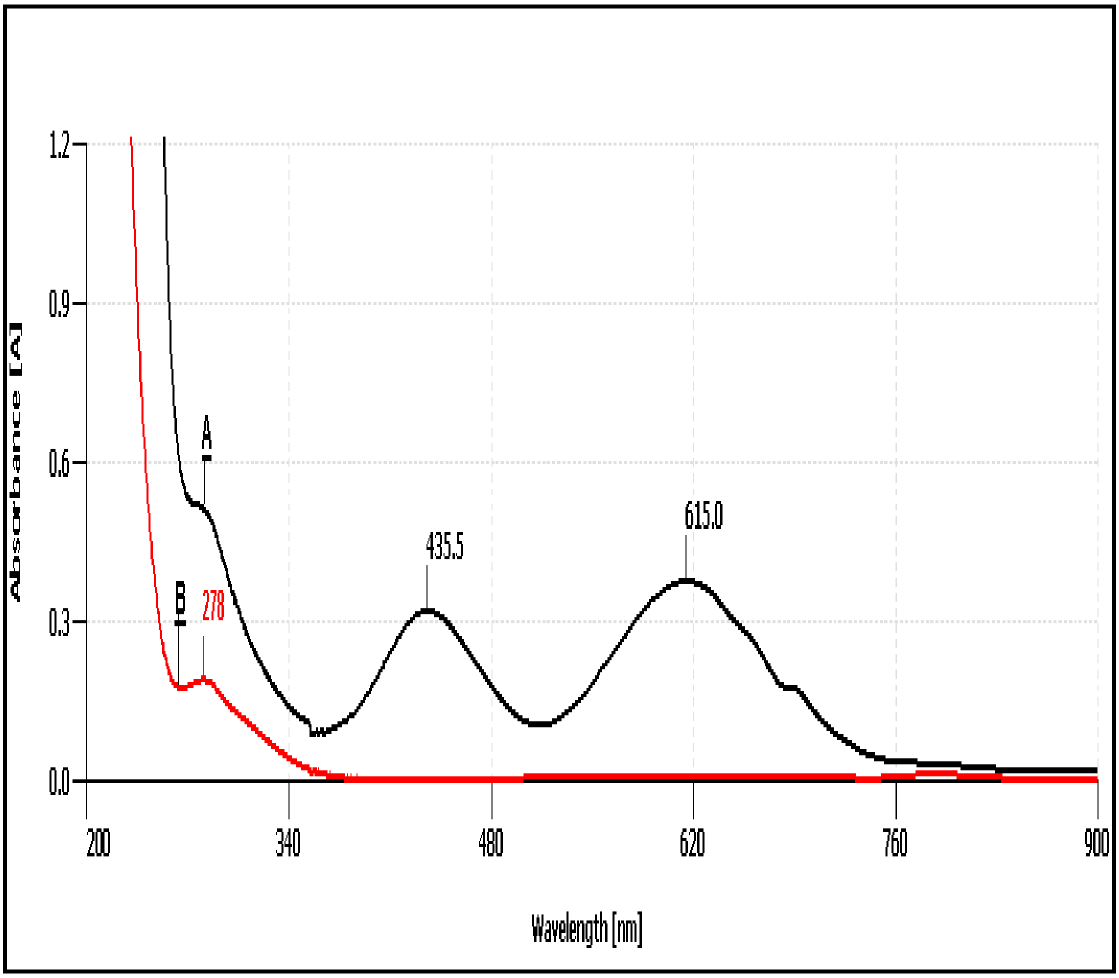


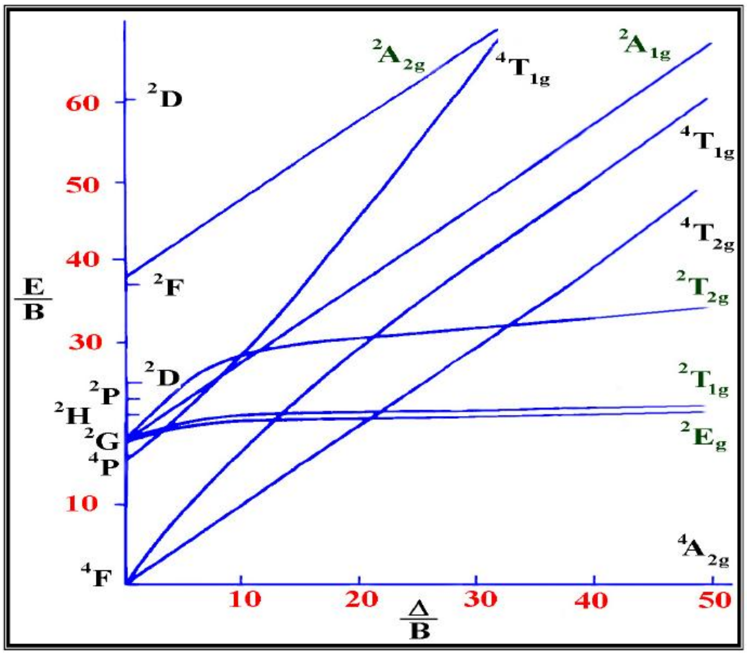
Fig. (3.1):- The UV-Visible spectra of [A]: $CrCl_3.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Hydrated ammonium aluminum sulfate/urea ionic liquid 1:5 mole ratio respectively.

In the ultraviolet region the deep green solution showed a charge transfer band started around 350 nm with a very large absorbance. However distinct band at 278 nm with absorbance 0.5 comparable to that of the first two bands, appeared as a shoulder on the charge transfer band and in the same position of that shown by ionic liquid itself, Fig. (3.1.B).

The term symbol for the ground state of chromium ion ^4F and ^4P in d^3 would split in octahedral crystal field as follows:

$\upsilon_1 = {}^4A_{2g}(F) \rightarrow {}^4T_{2g}\ (F)$
$\upsilon_2 = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}\ (F)$
$\upsilon_3 = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}\ (P)$

When the third band was calculated for Cr (III) using Tanabe-Sugano diagram, Scheme (3.1), and the first two bands were considered as transition one and two υ_1, υ_2, it was found that its value 273.8 nm, Table (3.1) in the ultraviolet region that coninside with that of the ionic liquid at 278 nm Fig. (3.1.B), the calculated υ_3 band has higher absorbance that overshade the lower absorbance band of ionic liquid. Therefore the band at 278 nm is considered to be the third electronic transition band of Cr (III) in ionic liquid.



Scheme (3.1):- Tanabe-Sugano diagram for d^3 octahedral ion configuration.

It was found that the band energies of the coordinated Cr (III) ion in hydrated ammonium aluminum sulfate/urea ionic liquid were close to those reported in other ionic liquids, Table (3.1) such as Cr (III) chloride in choline chloride/urea 608 nm and 440 nm that the Cr (III) reported to have octahedral coordination with six urea ligand.[54] In addition spectra of Cr (III) ion in acetamide/potassium nitrate 596.6 nm and 445.4 nm where Cr (III) ions also assigned to have octahedral coordination with six acetamide or six nitrate ligands.[44]

Therefore the observed bands in hydrated ammonium aluminum sulfate/urea ionic liquid would also expected to have octahedral geometry. Yet the energy splitting of the electronic states (term symbol) is relatively at lower energy from those reported values in other medium or solid alum reflecting the weaker field strength of ionic species of this ionic liquid.

In LiCl/KCl melt, the band energies reported at 800 nm and 540.5 nm and Cr (III) ions also assigned to have octahedral coordination with six chloride ions.[55] Therefore the relatively higher energy observed in this work would explain the stronger nature of ionic species of hydrated ammonium aluminum sulfate/urea ionic liquid than chloride in LiCl/KCl melt.

The octahedral geometry also supported by small molar absorption value 37 $Lmol^{-1}cm^{-1}$.

To compare the behavior of chromium (III) ions in hydrated ammonium aluminum sulfate/urea ionic liquid and in aqueous solution, a similar 0.01 M solution of the chromium (III) chloride salts in aqueous solution showed two bands in the visible region 420 nm and 587 nm, Fig. (3.2.A). The wavelength observed in aqueous solution were at lower energy than those obtained in hydrated ammonium aluminum sulfate/urea ionic liquid, gives a support to the weaker nature of the ionic liquid species coordinated to chromium (III) ions than water molecule. Additionally it could also be noticed that the molar absorptivity in ionic liquid is higher than in aqueous solution, Table (3.1) which indicates the less symmetrical coordinated geometry of Cr (III) ions in ionic liquid. This would indicates a complex ionic liquid species coordinated to Cr (III).

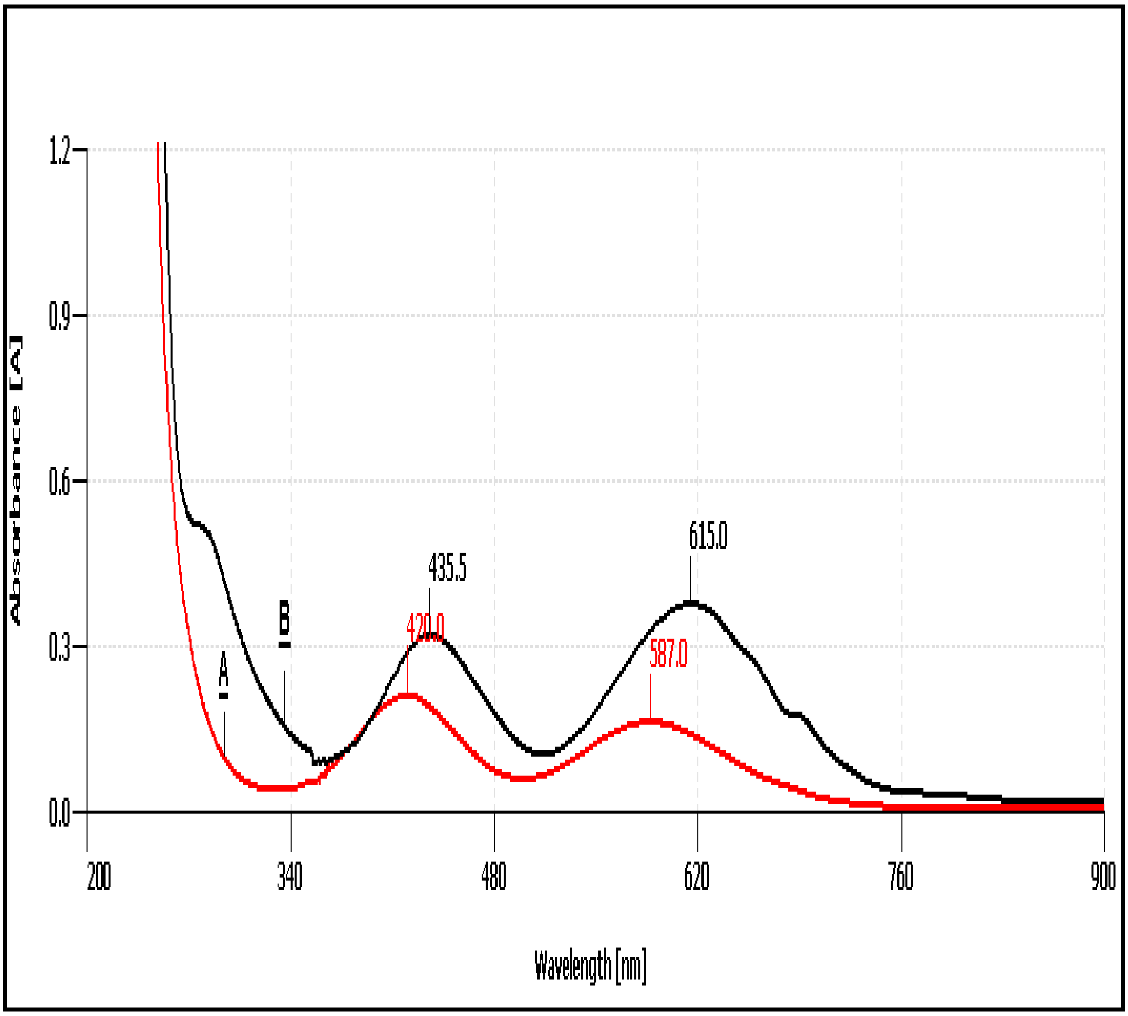


Fig. (3.2):- The UV-Visible spectra of 0.01 M $CrCl_3.6H_2O$ [A]: In aqueous solution. [B]: In hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

The shoulder bands of Cr (III) ions in hydrated ammonium aluminum sulfate/urea ionic liquid Fig. (3.1.A) were assigned to electronic transition from $^4A_{2g}$ ground state to spin non allowed of doublet states ^2E_g and $^2T_{1g}$ of the ^2G state of free ion, Scheme (3.1).

$^4A_{2g} \rightarrow {}^2E_g$

$^4A_{2g} \rightarrow {}^2T_{1g}$

Based on the values obtained in ionic liquid for the (g) metal value, the calculated value of the ligand factor (f) was found to have value of 0.93 which is smaller than the water field factor ($f_{\mathbf{H2O}}$ =1).[42] This might be also explain the lower energy bands observed in ionic liquid than in aqueous solution.

The higher energy differences between the spectra of Cr (III) in aqueous media compared to those in ionic liquid and the calculated different values of Racah parameter in both media strongly suggested that the interaction in ionic liquid is not with water molecule that are initially present in the lattice of starting material ($NH_4Al(SO_4)_2.12H_2O$). This indicated that the presence of water molecule in ionic liquid is not as free molecules but still retaining their original interaction with the metals of the alum Al^{3+} or K^+ there by allowing the negatively ionic species with weaker strength to bound with chromium (III) metal in a coordination interaction.

3.1.1. Reaction with potassium thiocyanate:-

In an attempt to study the possible substitution reaction of ionic liquid species by added biphilic anionic species, thiocyanate was added to ionic liquid containing chromium (III) chloride in a 1:1 mole ratio. The original deep green solution did not change color and the UV-Visible spectroscopic measurement revealed no change to the original spectra obtained for initial deep green solution, Fig. (3.3.B). The one exceptions to the above finding is the charge transfer which started at 350 nm, but with much higher absorbance in case of addition potassium thiocyanate. The charge transfer might be related to interaction of chromium (III) ion with one or more KSCN and hence the charge transfer is from ligand to metal [Thiocyanate - Cr (III)]. This suggestion is supported by the fact that thiocyanate ligand has a field factor of 0.73,[42] which is much smaller than those calculated for the ionic species of the ionic liquid coordinated to chromium (III) cation. The absence of clear evidence of the coordination nature around chromium cations would not reject the possibility of interaction of one or more thiocyanate ligand to chromium (III) cation.

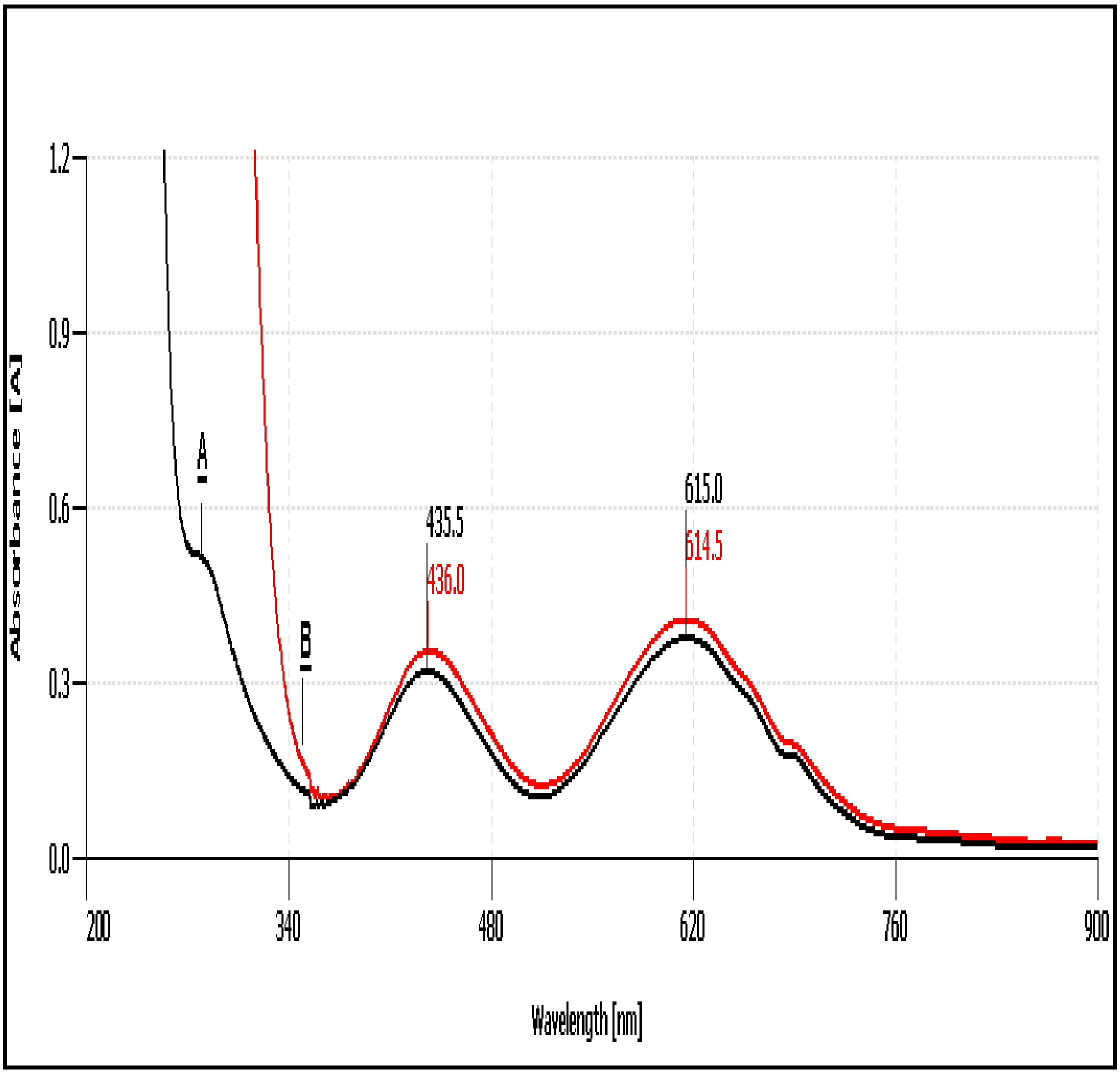


Fig. (3.3):- The UV-Visible spectra for $CrCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Addition one equivalent mole of potassium thiocyanate to $CrCl_3.6H_2O$.

3.1.2. Reaction with Ethylene Diamine Tetra Acetic Acid (EDTA):-

When (EDTA) Ethylene Diamine Tetra Acetic Acid was added to chromium (III) chloride in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in the mole ratio 1:1, there isn't any change in color of solution or in its spectrum, Fig. (3.4.B). The expected interaction of the hexadentate EDTA ligand was increased to 1:4 mole ratio which showed an increase in molar absorptivity, Table (3.1) and in the absorbance of the third electronic transition band of chromium cation, Fig. (3.4.C).

The third transition band seems to start at lower energy than the charge transfer of the chromium (III) cation in hydrated ammonium aluminum sulfate/urea ionic liquid alone. This increase was obvious with the addition of EDTA which increased to 1:10 mole ratio, the change observed in the spectra of chromium (III) with the latter mole ratio with EDTA, Fig. (3.4.D), also showed an increase in the molar absorptivity of the first and second transition bands, Table (3.1).

These changes may suggest an interaction of the usually inert chromium (III) cation with highly concentration of EDTA ligand, that changed the ligand sphere around the metal cation.

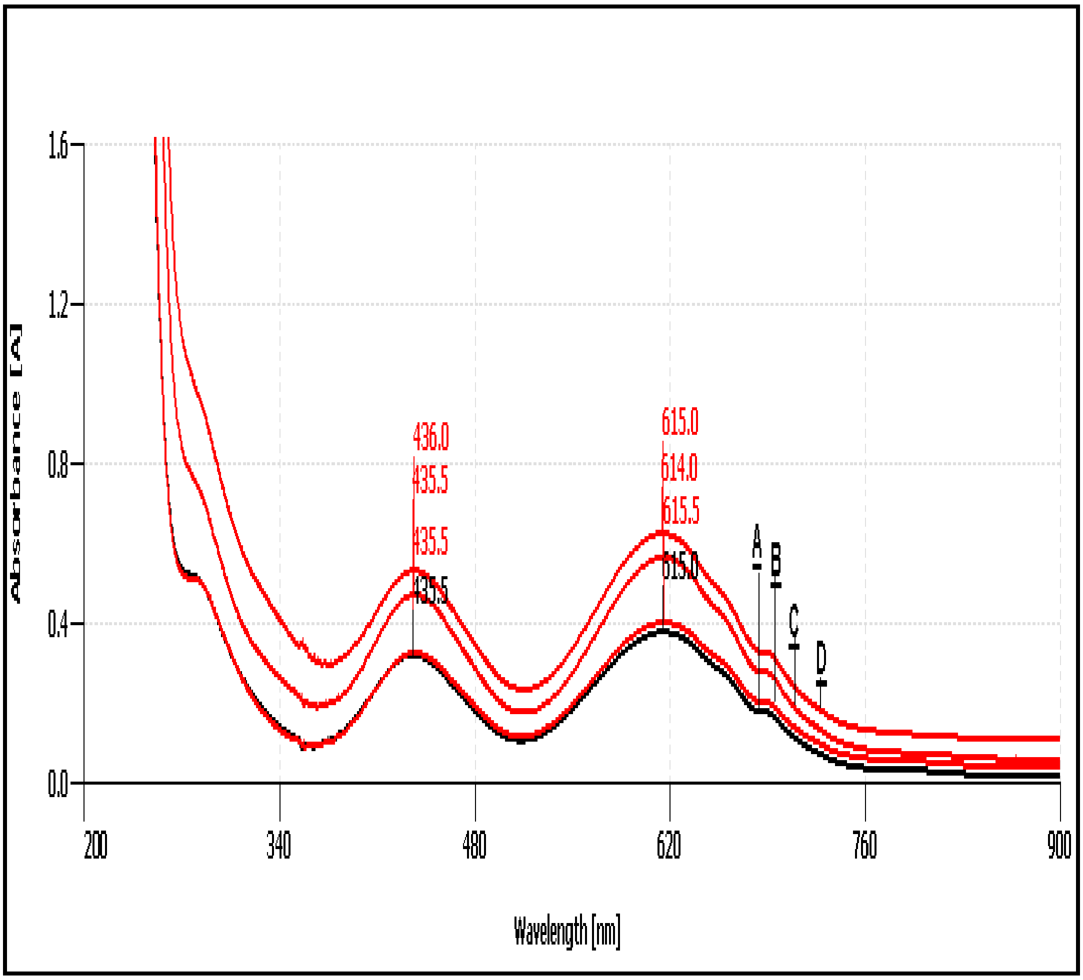


Fig. (3.4):- The UV-Visible spectra for $CrCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea ionic liquid. [B]: Addition one equivalent mole of EDTA to $CrCl_3.6H_2O$. [C]: Addition 4 moles of EDTA to $CrCl_3.6H_2O$. [D]: Addition 10 moles of EDTA to $CrCl_3.6H_2O$.

3.1.3. Reaction with sodium nitrite and oxalic acid:-

When another biphilic ligand, sodium nitrite ($NaNO_2$) was added as monodentate ligand to chromium (III) chloride hexahydrate solution in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in a mole ratio of 1:1, the original color green solution did not change. When the mixture was examined by UV-Visible spectroscopic there is no change in bands compared with the original spectrum obtained for initial green solution, Fig. (3.5.B), Table (3.1), even when increase the moles for sodium nitrite there is no change in bands or color. This may indicate the stronger interaction of chromium (III) ions as inert element with hydrated ammonium aluminum sulfate/urea ionic liquid.

When oxalic acid was added as bidentate ligand to chromium (III) chloride hexahydrate solution in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in mole ratio of 1:1, it showed no change in color and revealed no change in the value of the bands for the deep green solution Fig. (3.5.C).

The charge transfer obtained from the added oxalic acid to chromium (III) solution that also started at 350 nm but jumped up with a very high absorbance and overshade the υ_3 of chromium (III) usually appeared in this ionic liquid or with added ligands. This charge transfer also might be taken as interaction of oxalate ion with chromium (III).

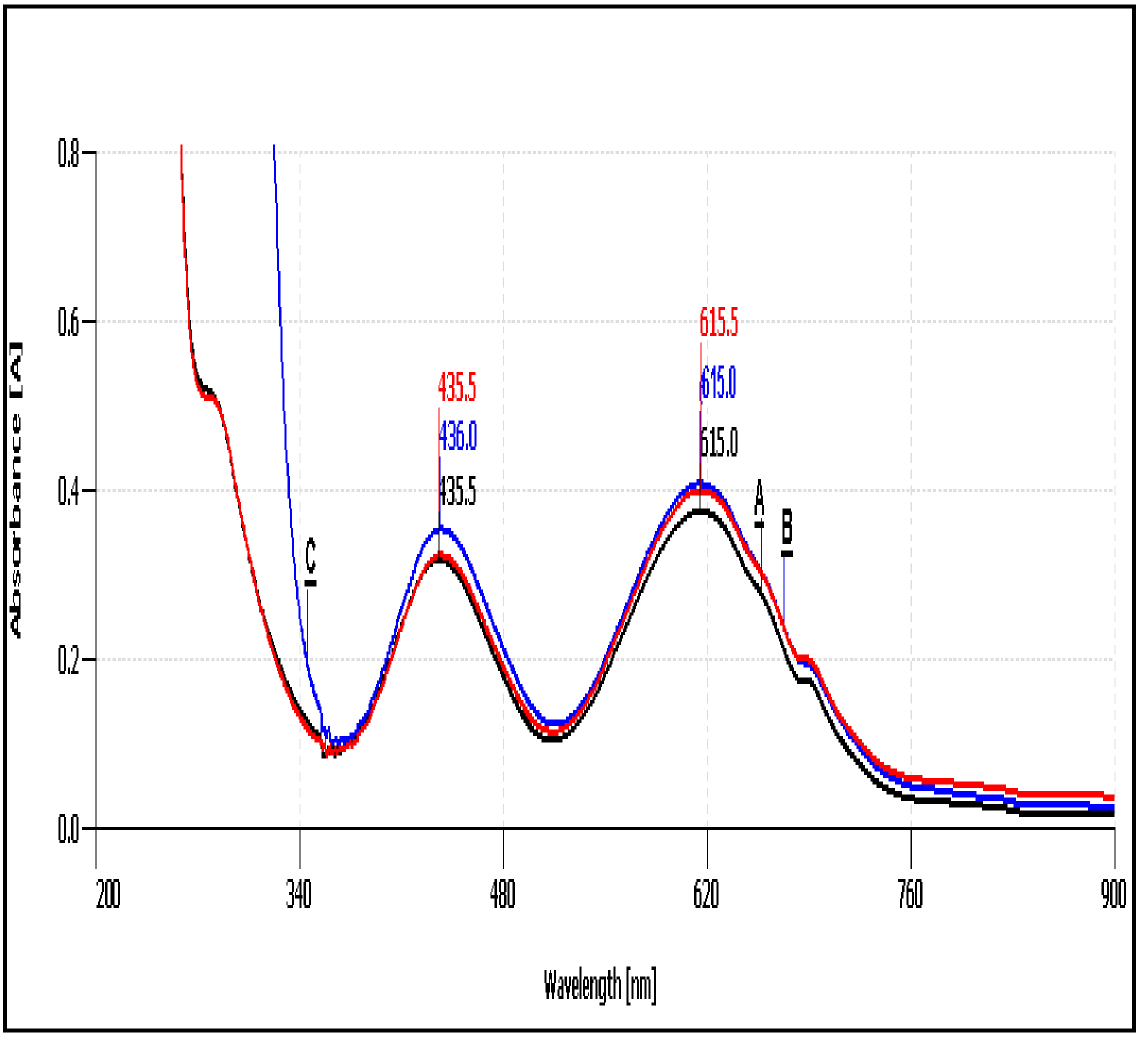


Fig. (3.5):- The ultraviolet visible spectra for $CrCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea ionic liquid. [B]: Addition one mole of sodium nitrite to $CrCl_3.6H_2O$. [C]: Addition one equivalent mole of oxalic acid to $CrCl_3.6H_2O$.

Table (3.1):- Electronic spectra for complexes of $CrCl_3.6H_2O$ in various room temperature ionic liquids.

Chromium (III) chloride	**Absorption bands (nm)**	**B\` (cm^{-1})**	**Cal. B**	**10 Dq (cm^{-1})**	**Suggested Structure**	**ε ($Lmol^{-1} cm^{-1}$)**	**Ref.**
Aqueous solution	υ_1= 587 υ_2= 420 $\upsilon_{3(cal.)}$= 262.3	680.8	0.74	17035	Oh $[Cr(H_2O)_6]^{3+}$	16 21	This work
$NH_4Al(SO_4)_2$ $.12H_2O$/urea	υ_1= 615 υ_2= 435.5 $\upsilon_{3(cal.)}$= 273.8	676.4	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	37 32	This work
$NH_4Al(SO_4)_2$ $.12H_2O$/urea + KSCN(1:1) mole	υ_1= 614.5 υ_2= 436 $\upsilon_{3(cal.)}$= 273.8	676.3	0.73	16273	Distorted Oh $[Cr(IL)_6]^{3+}$	41 35	This work
$NH_4Al(SO_4)_2$ $.12H_2O$/urea +$NaNO_2$(1:1) mole	υ_1= 615.5 υ_2= 435.5 $\upsilon_{3(cal.)}$= 273.9	676.1	0.73	16246	Distorted Oh $[Cr(IL)_6]^{3+}$	40 32	This work
$NH_4Al(SO_4)_2$ $.12H_2O$/urea+ Oxalic acid (1:1) mole	υ_1= 615 υ_2= 436 $\upsilon_{3cal.}$= 273.9	676	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	41 35	This work
$NH_4Al(SO_4)_2$ $.12H_2O$/urea+ EDTA(1:4) mole	υ_1= 615 υ_2= 436 $\upsilon_{3cal.}$= 273.9	676	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	56 47	This work

$NH_4Al(SO_4)_2$ $.12H_2O$/urea+ EDTA(1:10) mole	υ_1= 614 υ_2= 435.5 $\upsilon_{3cal.}$= 273.5	676.9	0.73	16286	Distorted Oh $[Cr(IL)_6]^{3+}$	62 53	This work
Choline chloride/ Urea	υ_1= 608 υ_2= 440	632	0.87	16447	Oh $[Cr(urea)_6]^{3+}$	4.06	54
Butyramide/ $NaNO_3$ at 140°C	υ_1= 602.4 υ_2= 444	-	-	-	Oh (6 butyramide)	-	44
Acetamide/ KNO_3 at 90°C	υ_1= 596.6 υ_2= 445.4	-	-	-	Oh (6 acetamide)	-	44
LiCl/KCl at 400°C	υ_1= 800 υ_2= 540.5	-	-	-	Oh (6 Cl^-) $[CrCl_6]^{3-}$	-	55

3.2. Iron (III) chloride hexahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Iron (III) chloride hexahydrate was also not found to be easily soluble in hydrated ammonium aluminum sulfate/urea at room temperature until the temperature was raised to 40°C, when 0.01 M of iron chloride solution in ionic liquid was achieved after 15 minutes with magnetic stirring. The resulted solution was clear pale yellow as shown in picture (3.2).

Picture (3.2):- 0.01 M pale yellow solution for $FeCl_3.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at 40°C.

The solubility of iron (III) chloride in hydrated ammonium aluminum sulfate/urea ionic liquid was found to be at lower temperature 40°C than those reported for the same compound in other ionic liquids or molten salts. For example, iron (III) chloride after 15 minutes was reported to be soluble in acetamide-potassium nitrate at 90°C, and in $LiNO_3/KNO_3$ the Fe (III) ions soluble after 15 minutes at 160°C.[44] In another room temperature ionic liquid iron (III) chloride was reported to have a solubility in choline chloride/urea of 0.1 M after 72 hours with continuous stirring longer time than in ionic liquid of present work.[54] This may indicate that the hydrated ammonium aluminum sulfate/urea ionic liquid is stronger solvent than those reported above.

The pale yellow solution was examined by UV-Visible test and showed three bands with small absorbance in the visible region at 556 nm, 782 nm, and 876 nm as shown in Fig. (3.6.A), this bands were assigned to non allowed transition of d^5 configuration ^6S state. Also in visible region iron (III) chloride showed charge transfer around 500 nm that cover some of the blue end of the visible region and could be the reason for its pale yellow color.

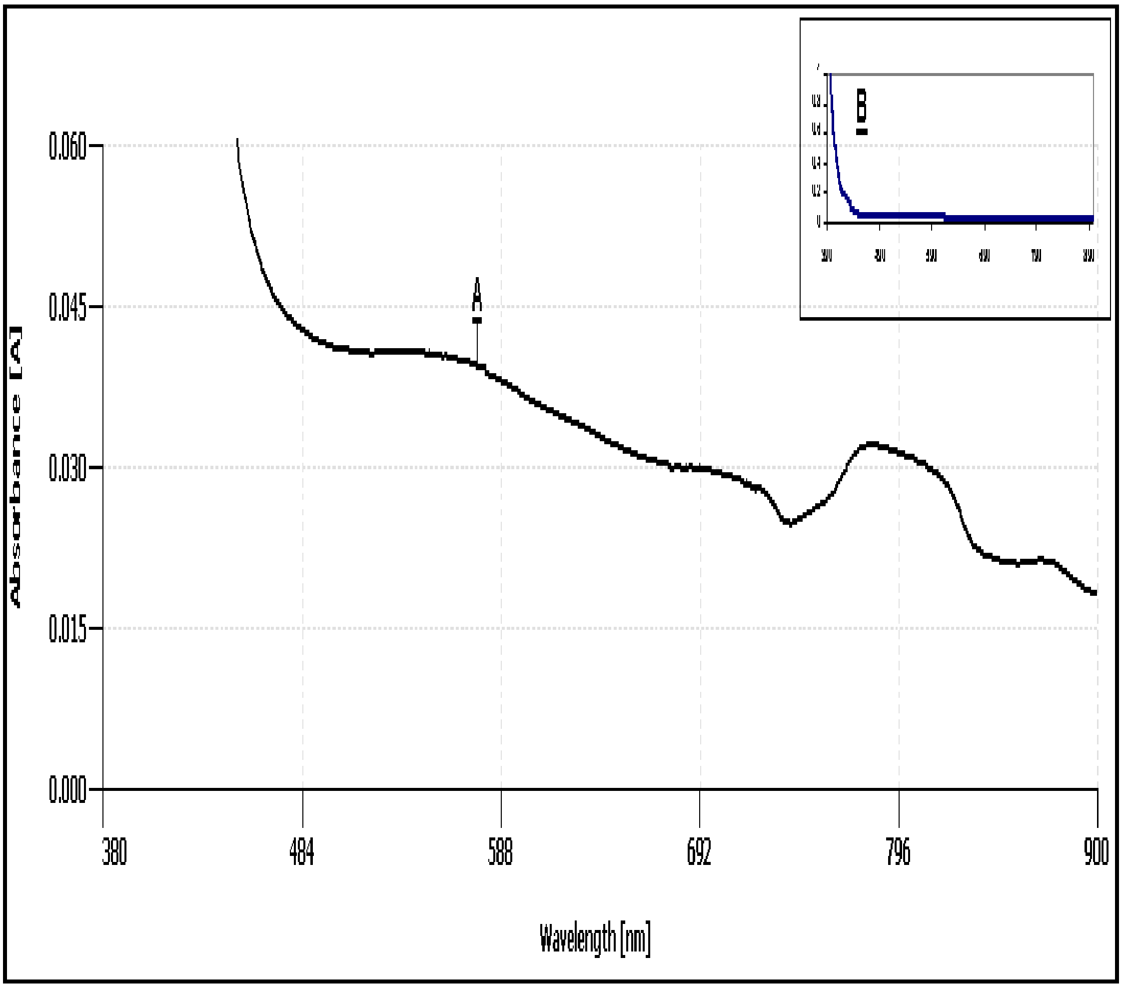
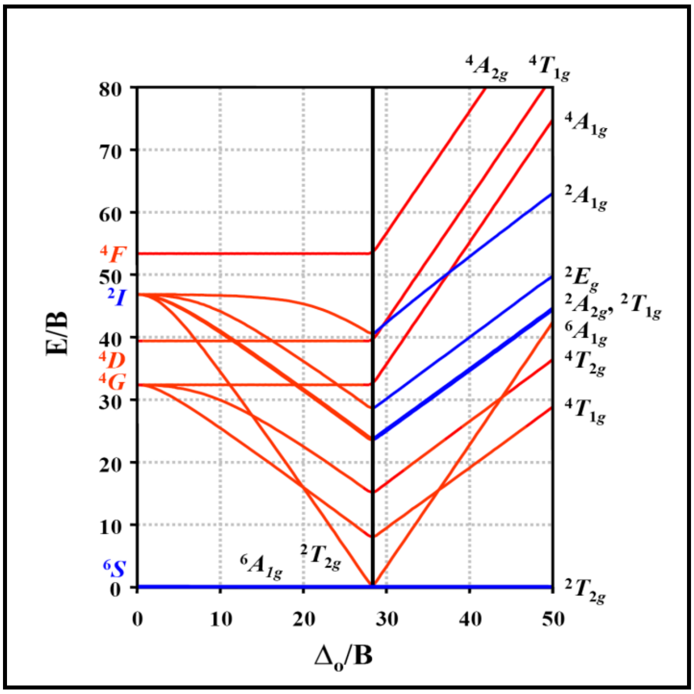


Fig. (3.6):- The UV-Visible spectrum for $FeCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with small absorbance. [B]: Inset $FeCl_3.6H_2O$ in ionic liquid full range.

It was found that the band energies for Fe (III) chloride close to those reported in other ionic liquids such as, in room temperature ionic liquid choline chloride/tartaric acid which have 878 nm, 698 nm, and 447 nm absorptions and assigned to have tetrahedral coordination.[43] Similar geometry was also assigned in choline chloride/malonic acid where its bands was 888.5 nm, 677 nm, and 532.9 nm.[54] Therefore the closely similar observed bands of iron (III) ions in hydrated ammonium aluminum sulfate/urea ionic liquid would also expected to have tetrahedral coordination geometry.

The term symbol for the ground state of Fe (III) ions in d^5 configuration of ^6S, Scheme (3.2), for tetrahedral crystal field can be assigned to represent the observed bands as follow:

$^6A_1 \rightarrow {}^4T_1$
$^6A_1 \rightarrow {}^4T_2$
$^6A_1 \rightarrow {}^4A_1 + {}^4E$



Scheme (3.2):- Tanabe-Sugano diagram for d^5 tetrahedral and octahedral ion configuration.

Iron (III) chloride in aqueous solution gave yellow colored solution with clear band at 482.7 nm Fig. (3.7.B) and expected to be responsible for the yellow color as it cover the blue end of the visible region, the charge transfer shifted to lower energy in aqueous solution than in ionic liquid of this work. This indicate that Fe (III) cation is not coordinated to the water molecule of the ionic liquid but to its ionic species as was observed previously with Cr (III) (C.F. 3.2.A).

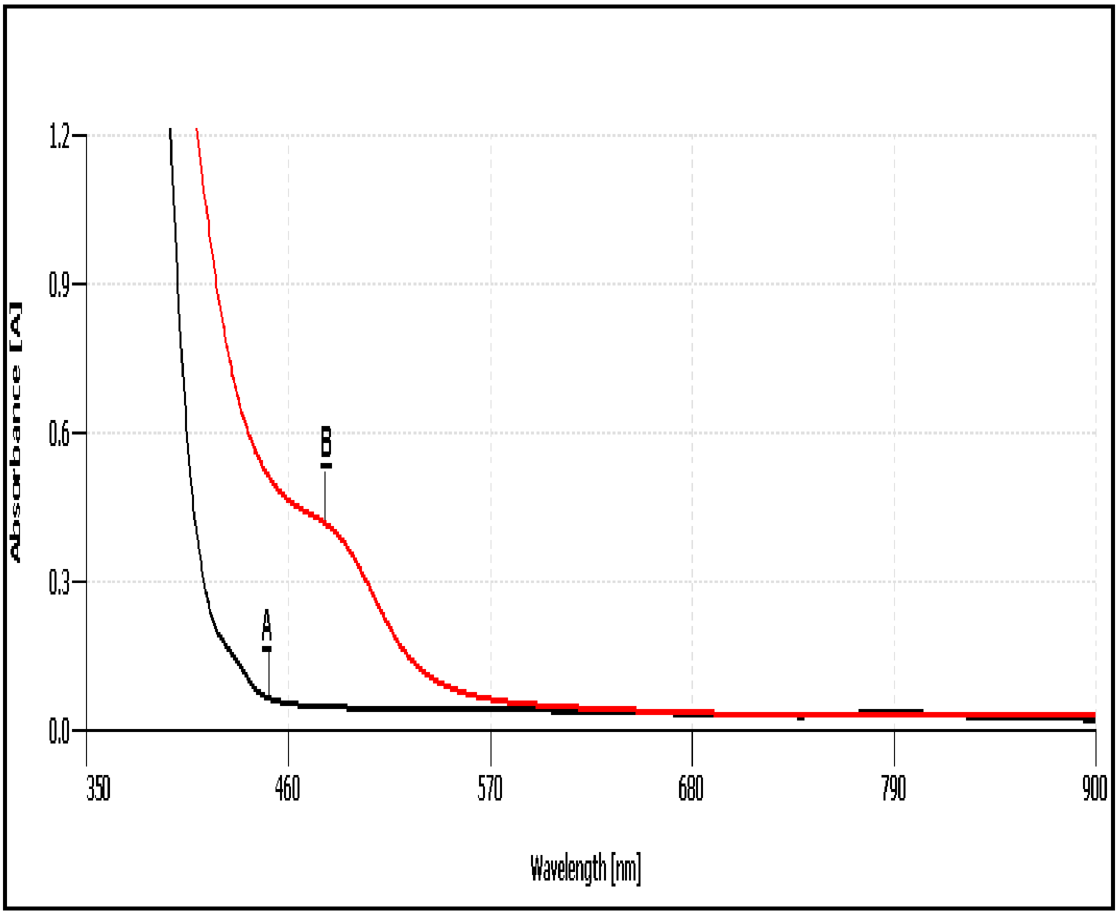
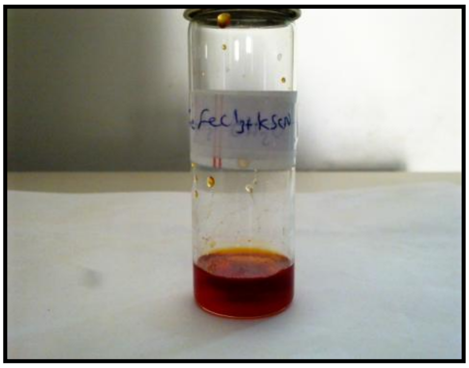


Fig. (3.7):- The UV-Visible spectroscopy for 0.01 M $FeCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Aqueous solution.

3.2.1. Reaction with potassium thiocyanate:-

The addition of potassium thiocyanate (KSCN) to Fe (III) ion in hydrated ammonium aluminum sulfate/urea ionic liquid solution at room temperature in ratio of 1:1 mole, showed color change from pale yellow to blood-red solution, as shown in picture (3.3).



Picture (3.3):- Blood-red colored solution for $FeCl_3.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with addition KSCN 1:1 mole ratio respectively.

When the blood-red solution was examined by UV-Visible spectroscopy it showed absorption bands in the visible region at 556, 876 nm and 782 nm with lower absorbance, the band at 556 nm was disappeared because the charge transfer shifted to lower energy region than in ionic liquid, Fig (3.8.B), the charge transfer transition band was started in the visible region around 700 nm absorbing much of the blue end of the visible region and appearing as blood-red colored solution. This changing in color and in charge transfer transition indicate interaction between the metal and SCN^- ligand in ionic liquid.

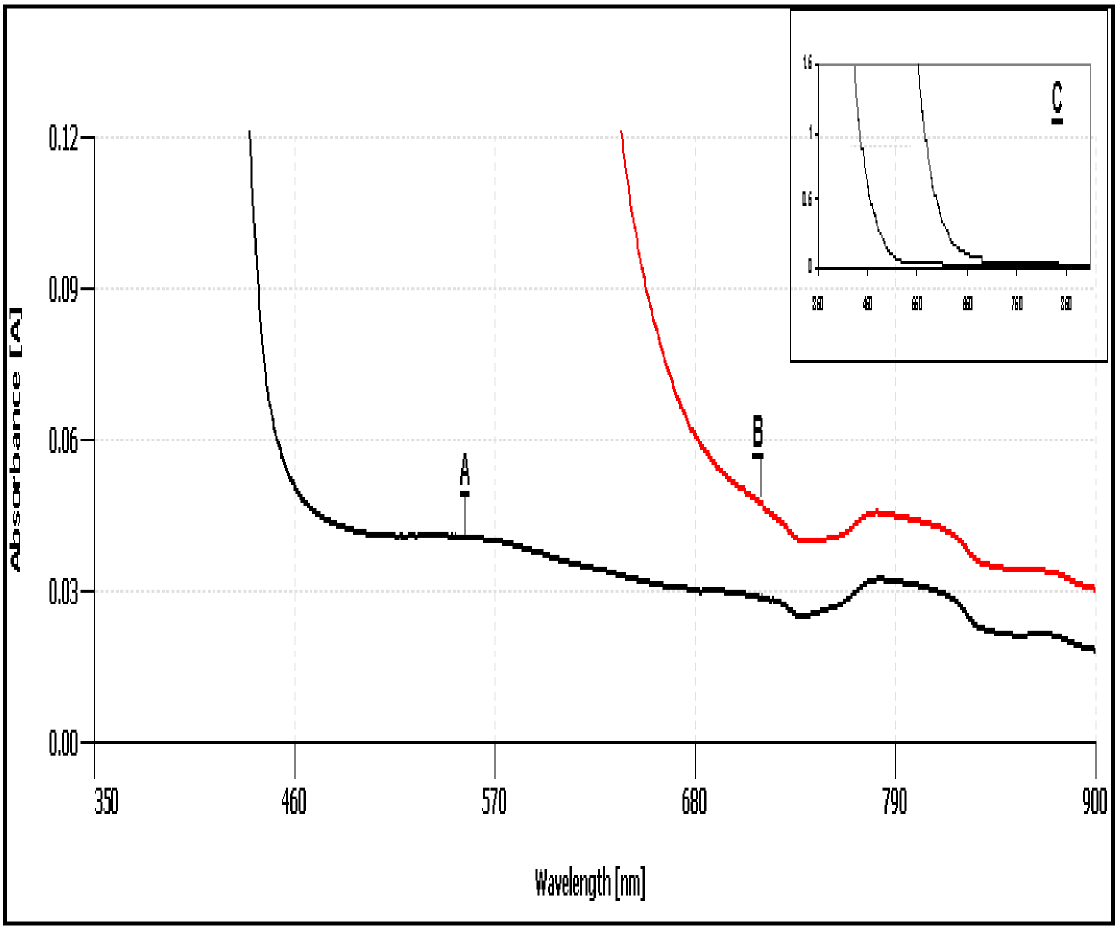


Fig. (3.8):- The UV-Visible spectra for $FeCl_3.6H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid [B]: Addition one equivalent mole of KSCN to $FeCl_3.6H_2O$. [C]:Inset $FeCl_3.6H_2O$ in ionic liquid and with added KSCN full range.

3.2.2. Reaction with sodium nitrite:-

Addition of biphilic ligand like sodium nitrite ($NaNO_2$) to the d^5 Fe (III) chloride in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in mole ratio of 1:1, did not show visual change in color of the original solution. However, when the resulted solution was examined by ultraviolet-visible spectroscopy it showed no change in previous bands without ligand $NaNO_2$, Fig. (3.9.B), and this could be indicate the weaker NO_2^- strength than that of the ionic species present in ionic liquid, similar finding was also observed with chromium (III) Fig. (3.5.B).

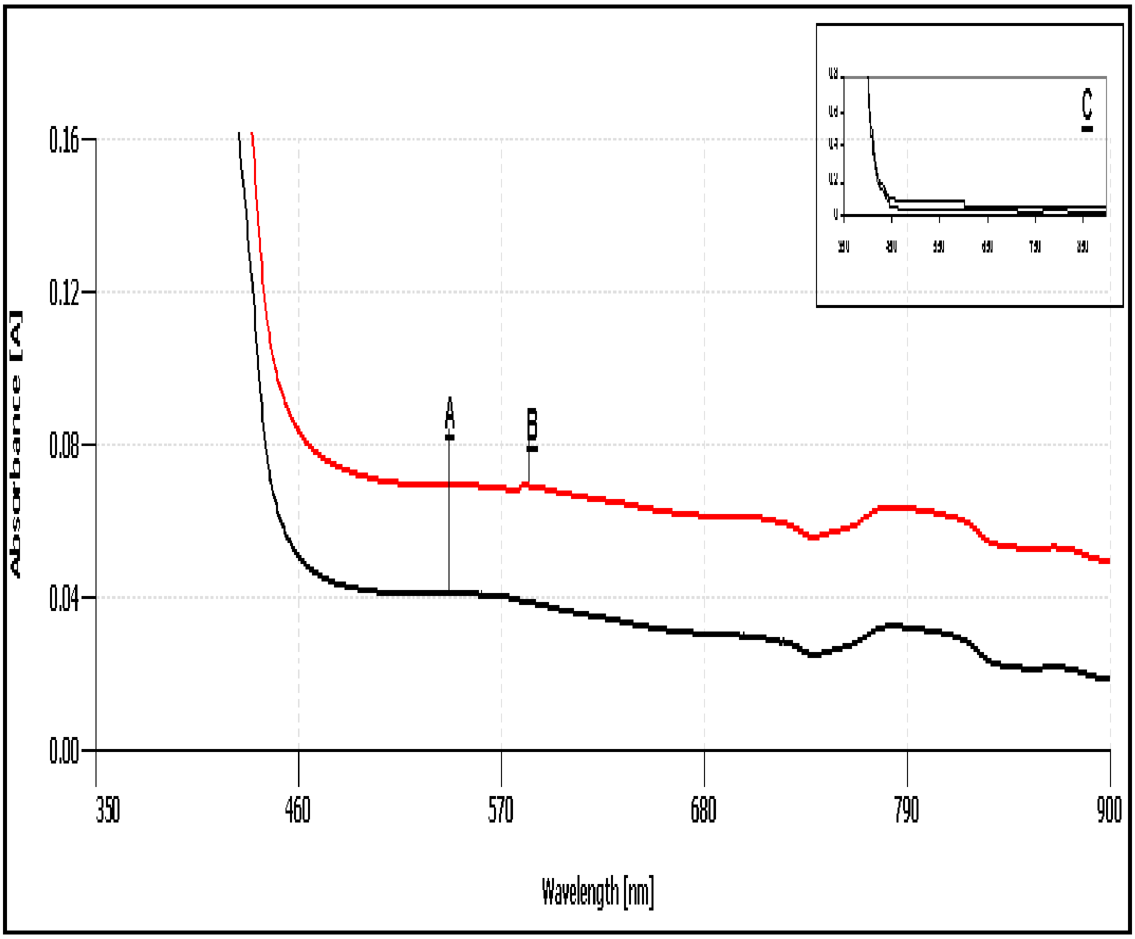


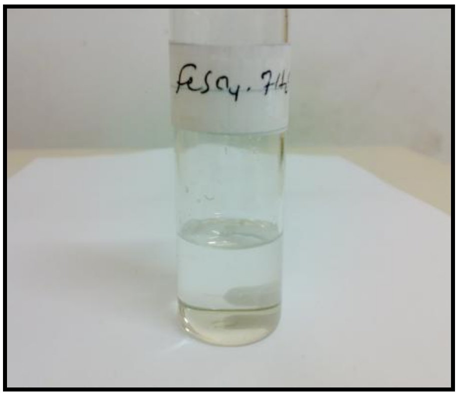
Fig. (3.9):- The UV-Visible spectra for $FeCl_3.6H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid [B]: Addition one equivalent mole of $NaNO_2$ to $FeCl_3.6H_2O$. [C]:Inset $FeCl_3.H_2O$ in ionic liquid and with added $NaNO_2$ full range.

Table (3.2):- The behavior of Fe (III) ion in ionic liquid and with added the ligands.

Iron (III) chloride	Absorption bands (nm)	Color	ε($Lmol^{-1}cm^{-1}$)	Suggested structure	Ref.
Aqueous solution	υ= 482.7	Yellow	40.6	Oh. $[Fe(H_2O)_6]^{3+}$	This work
Hydrated ammonium aluminum sulfate/urea	$υ_1$= 876 $υ_2$= 782 $υ_3$= 556	Pale yellow	2 3.2 4	Th. $[Fe(IL)_4]^{3+}$	This work
Hydrated ammonium aluminum sulfate/urea + KSCN (1:1) mole	$υ_1$= 876 $υ_2$= 782	Blood red	3.3 4.5	Th. Fe^{3+} interact with KSCN	This work
Hydrated ammonium aluminum sulfate/urea + $NaNO_2$ (1:1) mole	$υ_1$= 876 $υ_2$= 782 $υ_3$= 556	Pale yellow	5.2 6.3 6.7	Th. $[Fe(IL)_4]^{3+}$	This work
Choline chloride/ tartaric acid	$υ_1$= 878 $υ_2$= 698 $υ_3$= 447	Pale yellow	-	Th. one tartarate and two chloride	43
Choline chloride/ malonic acid	$υ_1$= 888.5 $υ_2$= 677 $υ_3$= 532.9	Pale yellow	-	Th. $[Fe(malonic\ acid)Cl_2]^{+}$	54

3.3. Iron (II) sulfate heptahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Iron (II) sulfate heptahydrate was not found to be easily soluble in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid at concentration 0.03 M until the temperature was raised to 40°C the metal sulfate complete dissolution after 15 minutes with magnetic stirring. The resulted solution was colorless as shown in picture (3.4).



Picture (3.4):- 0.03 M colorless solution for $FeSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at 40°C.

The electronic UV-Visible spectroscopy examination of the colorless solution showed one broad absorption band at 899 cm^{-1} near IR region Fig. (3.10). Iron (II) sulfate colorless solution also showed charge transfer started around 400 nm.

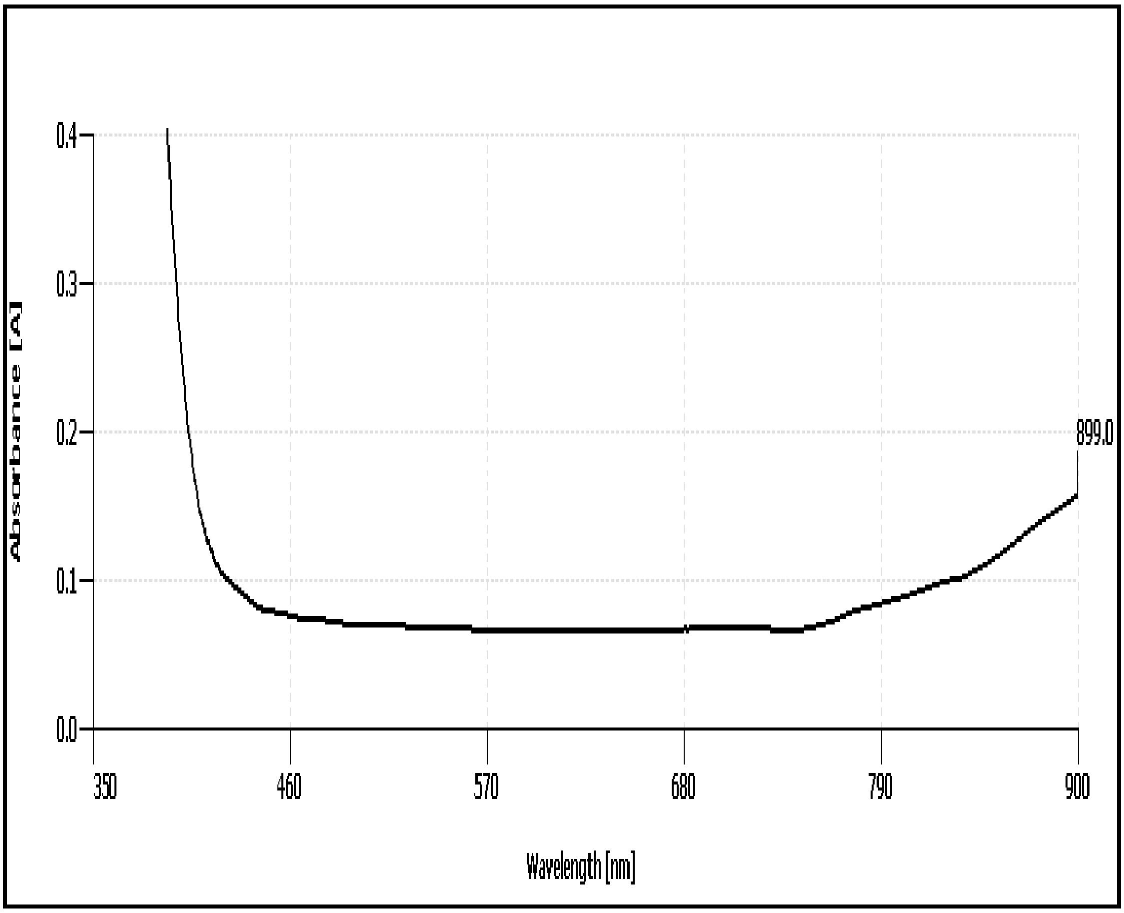
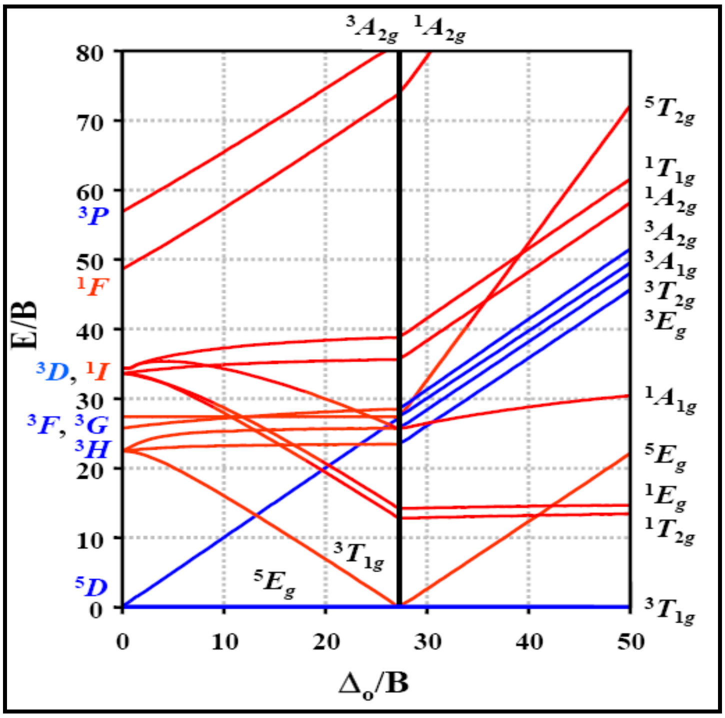


Fig. (3.10):- The UV-Visible spectrum of $FeSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

The term symbol for the ground state of Fe (II) ions in d^6, Scheme (3.3) is ^5D may be split in tetrahedral crystal field as follow: $^5E \rightarrow {}^5T_2$.



Scheme (3.3):- Tanabe-Sugano diagram for d^6 tetrahedral ion configuration.

Iron (II) sulfate considered to have tetrahedral coordination based on the band energy found in this work which were close to the band energies for iron (II) ion in other ionic liquids. For example, iron (II) chloride in LiCl/KCl at 400°C reported to have 1960 nm band and assigned to form tetrahedral coordination, and at 1000°C have 1666 nm and assigned to a distorted tetrahedral coordination,[55] so the iron (II) ion in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid would not differ in its weak cationic charge to form tetrahedral geometry.

To compare the behavior of iron (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid and in aqueous solution, the 0.01 M solution of iron (II) sulfate salt in aqueous solution showed a yellow color with a band at 360 nm, Fig. (3.11.A), the lower wavelength observed in aqueous solution than those obtained in hydrated ammonium aluminum sulfate/urea ionic liquid support the weaker nature of ionic liquid species resulted in a weaker strength interaction to iron (II) ion.

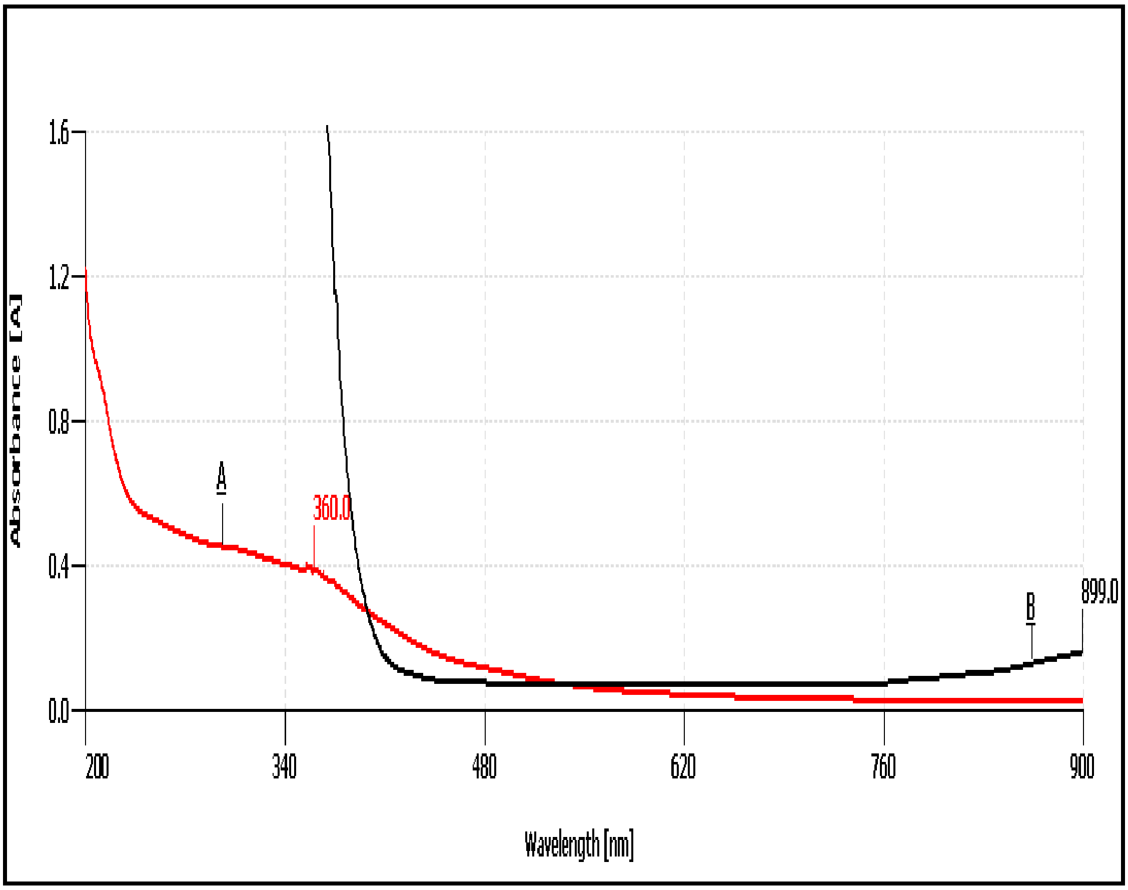


Fig. (3.11):- The UV-Visible spectra of $FeSO_4.7H_2O$ in [A]: Aqueous solution. [B]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

3.3.1. Reaction with potassium thiocyanate:-

In an attempt to study the possible substitution reaction of ionic liquid species by adding anionic biphilic species, thiocyanate was added to ionic liquid solution containing iron (II) sulfate in 1:1 mole ratio, the original colorless solution changed after heating to 40°C to orange as shown in picture (3.5).

Picture (3.5):- Orange colored solution for $FeSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea ionic liquid with addition KSCN 1:1 mole ratio dissolved at 40°C.

The resulted solution was examined by UV-Visible spectroscopy and found to have a distinctive high absorbance band at 436 nm followed by a very high charge transfer spectrum, Fig. (3.12.B), that indicate the occurrence of interaction when thiocyanate was added as a ligand to iron (II) sulfate in ionic liquid solution.

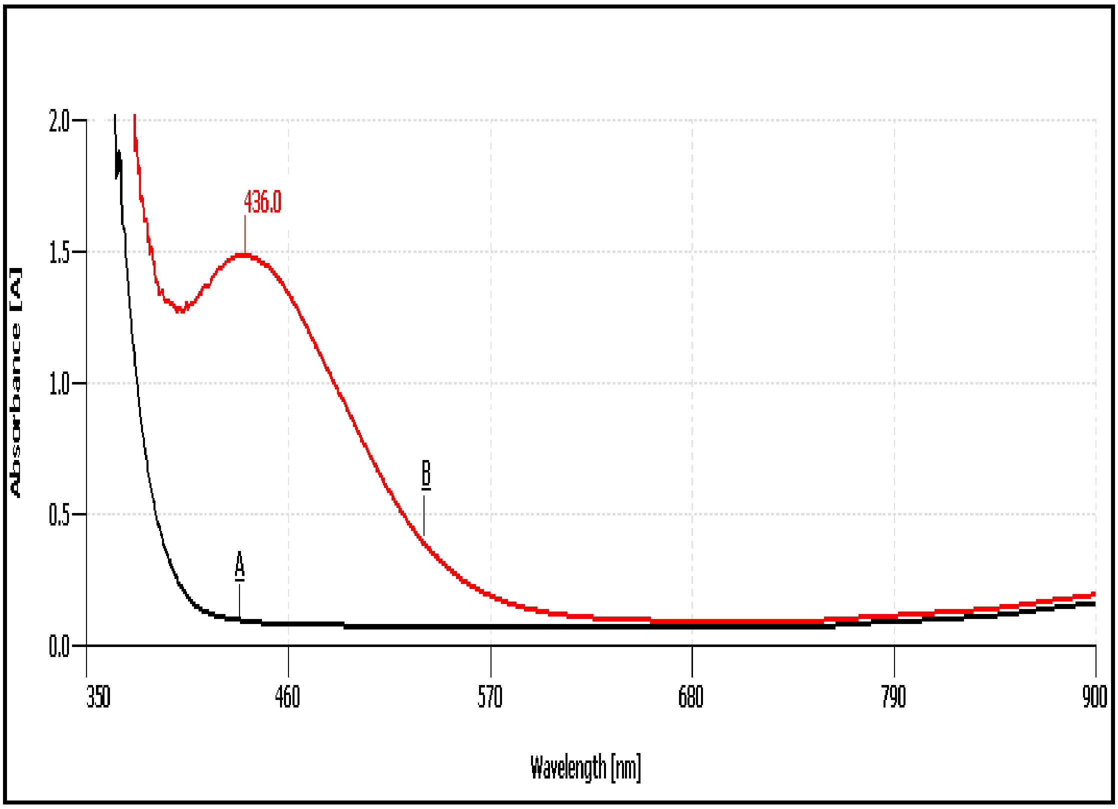
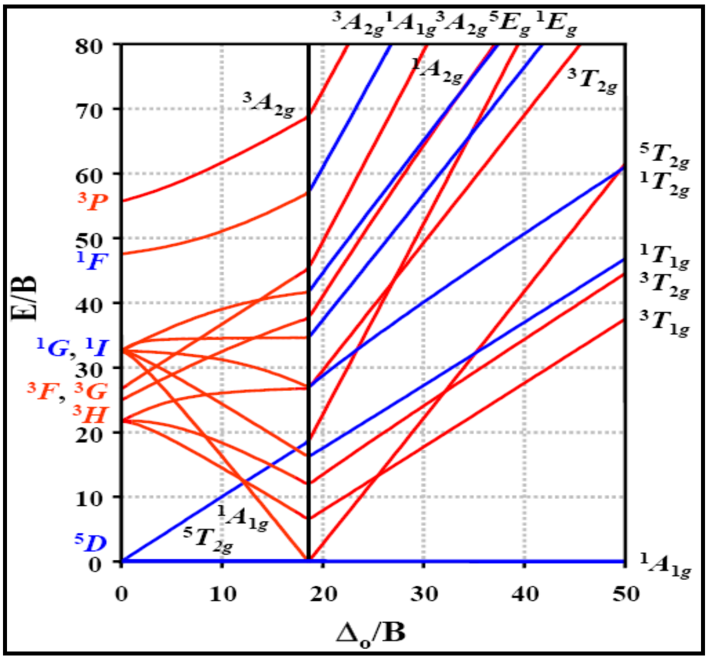


Fig. (3.12):- The UV-Visible spectra for $FeSO_4.7H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Addition one equivalent mole of KSCN to $FeSO_4.7H_2O$.

The term symbol for Fe (II) ion in d^6, Scheme (3.4) is ^5D may split in octahedral crystal field at high spin as follow : $^5T_{2g} \rightarrow {}^5E_g$.



Scheme (3.4):- Tanabe-Sugano diagram for d^6 octahedral ion configuration.

3.3.2. <u>Reaction with sodium nitrite:-</u>

When sodium nitrite ($NaNO_2$) was added to iron (II) sulfate heptahydrate in hydrated ammonium aluminum sulfate/urea ionic liquid solution in 1:1 mole ratio, the color of the original colorless solution and its absorption spectrum did not change, but when the moles of $NaNO_2$ increased to be 2:1 mole ratio the color changed to olive green solution as shown in the picture (3.6).

Picture (3.6):- Olive green colored solution for $FeSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea ionic liquid with addition $NaNO_2$ 1:2 mole ratio respectively.

By using UV-Visible test, the olive green solution showed two absorption bands at 457.5 nm and 588.5 nm Fig. (3.13.B), this spectra were considered to be due to low spin d^6 configuration. Low spin d^6 would expected to show three transition bands arising from a singlet ground state of $^1A_{1g}$ to $^1T_{1g}$, $^1T_{2g}$ and ^1E_g of Tanabe-Sugano diagram, Scheme (3.4). Considering these bands to be υ_2 and υ_3, the υ_1 would have a value of 966 nm. In comparison, the coordination of iron (II) sulfate in alum/urea at room temperature ionic liquid did not differ from those reported for example, in chloride ionic liquid at much higher temperature of 400°C in LiCl/KCl molten salt when a tetrahedral coordination also accepted as it absorption band was stated to be at lower energy 1960 nm than that obtained in alum/urea room temperature ionic liquid. This tetrahedral coordination was distorted when the temperature raised further to 1000°C, in the same chloride molten salt.[55] However, in presence of anionic ligands (thiocyanate and nitrite), the coordination changed to octahedral geometry with high and low spin depending on the ligand strength.

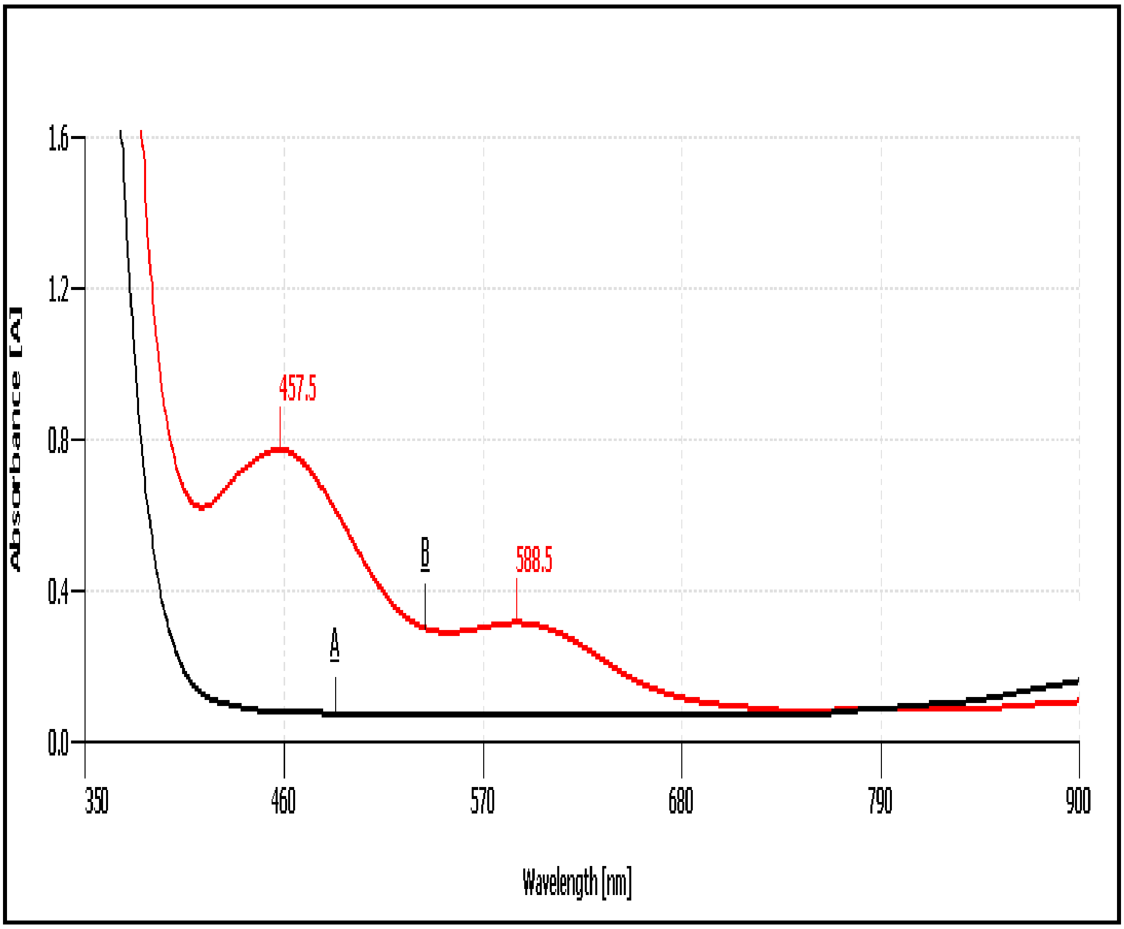


Fig. (3.13):- The UV-Visible spectra for $FeSO_4.7H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Addition 2 moles of $NaNO_2$ to one mole of $FeSO_4.7H_2O$.

Table (3.3):- The electronic spectra for Fe (II) ion in ionic liquid and with various ligands.

Iron (II) ion	Absorption bands(nm)	Color	Transitions	ε(Lmol^{-1}cm^{-1})	Suggested structure	Ref.
Aqueous solution	υ= 360	Yellow	$^5T_2g \rightarrow {}^5Eg$	39	Oh. $[Fe(H_2O)_6]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea	υ= 899	Color less	$^5E \rightarrow {}^5T_2$	5	Th. $[Fe(IL)_4]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea+ KSCN(1:1) mole	υ= 436	Orange	$^5T_2g \rightarrow {}^5Eg$	-	Distorted Oh. Fe^{2+} interact with KSCN	This work
Hydrated ammonium aluminum sulfate/urea+ $NaNO_2$(1:2) mole	$\upsilon_{1Cal.}$= 966 υ_2= 588.5 υ_3= 457.5	Olive green	$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$ $^1A_{1g} \rightarrow {}^1Eg$	10.3 25.6	Distorted Oh. Fe^{2+} interact with one or more $NaNO_2$	This work
LiCl/KCl at 400°C	υ= 1960	-	-	-	Th.	55
LiCl/KCl at 1000°C	υ= 1666	-	-	-	Distorted Th.	55

3.4. Cobalt (II) sulfate heptahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Cobalt (II) sulfate heptahydrate was found to be easily soluble in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in a concentration 0.05 M forming a clear pink solution as shown in picture (3.7).

Picture (3.7):- 0.05 M of pink colored solution for $CoSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at room temperature.

The solubility of cobalt (II) sulfate was found to be at lower temperature than those reported for cobalt (II) chloride in different ionic liquids or molten salts. For example, cobalt (II) ions was found to be much soluble 0.1 M after 72 hours in choline chloride/urea at room temperature, [54] at 40–70°C in $Ca(NO_3)_2.4H_2O$ / $CaCl_2$, [56] or in acetamide/$Ca(NO_3)_2.4H_2O$ was soluble at 40-90 °C. [57] In molten salt Co (II) ions melt at 447-480°C in LiCl/KCl. [55] This may indicate that hydrated ammonium aluminum sulfate/urea ionic liquid is stronger solvent than those reported above with better interaction between the solvent and ionic species of cobalt sulfate.

The electronic UV-Visible examination of the pink solution was carried out to investigate the electronic behavior of the resulted coordination for cobalt (II) ion in the ionic liquid, this examination showed two absorption bands in UV-Visible region at 276.5 nm and 522.5 nm in the visible region, the latter band showed a shoulder in a higher energy region at 474.7 nm, Fig. (3.14).

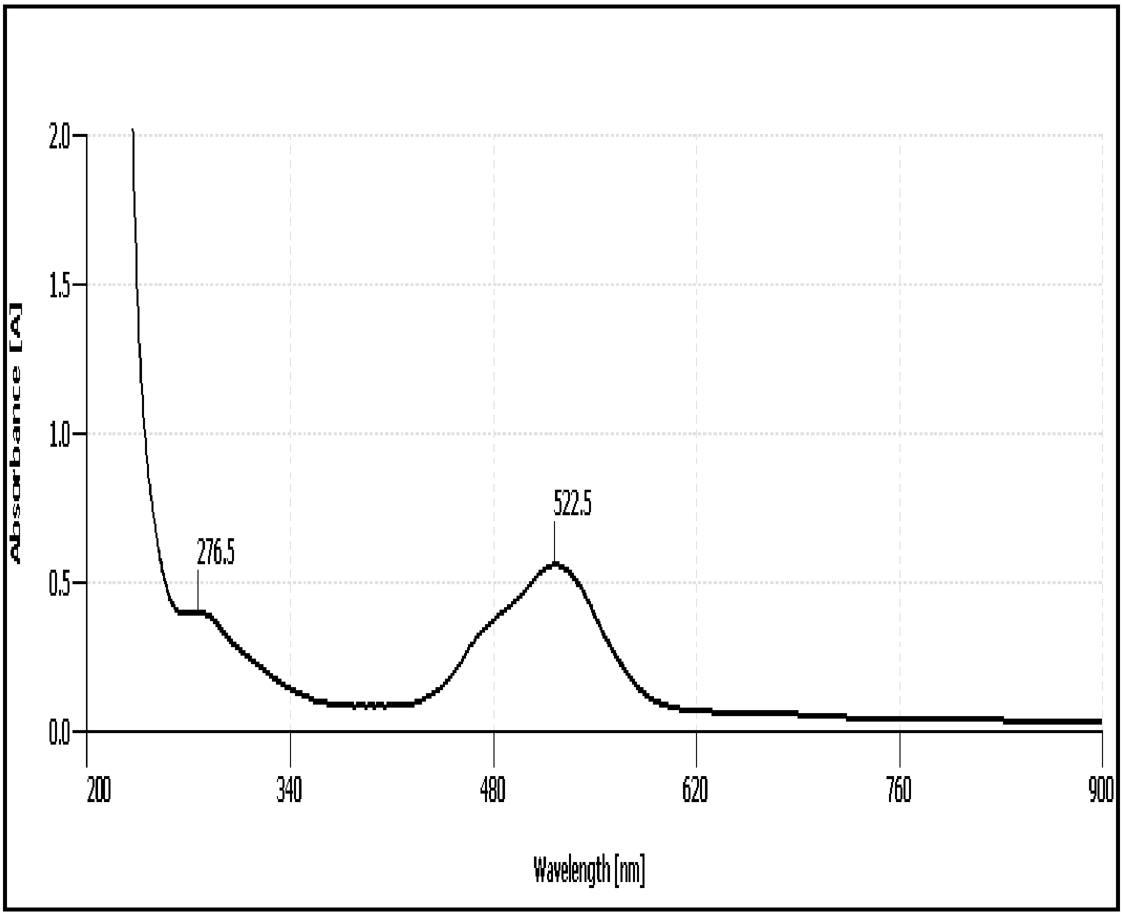
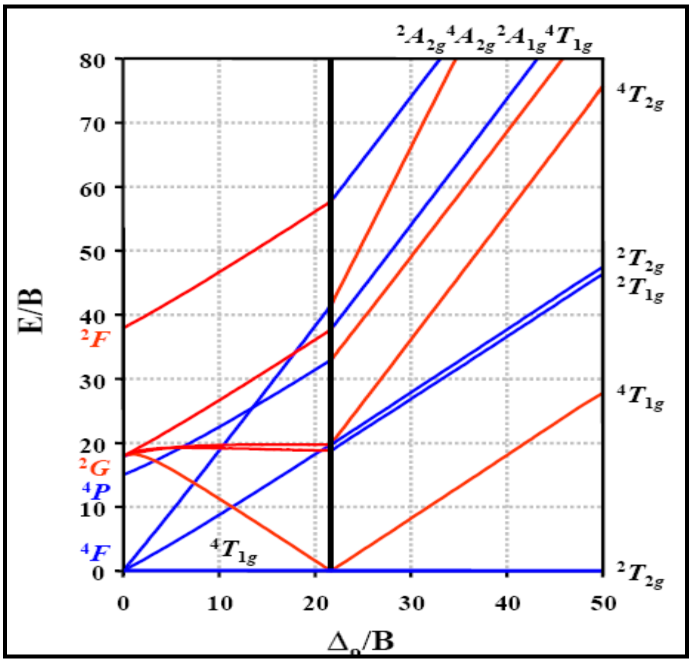


Fig. (3.14):- The UV-Visible spectrum for $CoSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

The term symbol for the ground state for Co (II) ion ^4F of d^7, Scheme (3.5) may split in octahedral crystal field as follows:

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



Scheme (3.5):- Tanabe-Sugano diagram for d^7 octahedral ion configuration.

When the first band was calculated for cobalt (II) using Tanabe-Sugano diagram and the first two bands were considered as transition two and three υ_2, υ_3, its value 1309 nm, Table (3.4).

It was found that the band energies of the coordinated Co (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid have close band energy to those reported for Co (II) chloride in other ionic liquids such as, in $Ca(NO_3)_2.4H_2O/CaCl_2$ 515 nm which formed an octahedral coordination,[56] and the spectrum in acetamide/$Ca(NO_3)_2.4H_2O$ with absorption band at 514.6 nm also assigned to form octahedral coordination.[57] However, cobalt (II) was assigned to have a tetrahedral geometry in other room temperature ionic liquid. For example, in choline chloride/urea when it showed bands at 671 nm and 641 nm and also in choline chloride/malonic acid when it showed bands at 672 nm, 642 nm and 619 nm. [54] Three bands were also reported at much higher temperature in LiCl/KCl molten salt 680 nm, 660 nm and 598.8 nm, and also assigned a tetrahedral coordination.[55] According to the similarities of the spectroscopic behavior of Co (II) sulfate observed in this work with those reported in other media, it was accepted to have an octahedral geometry with the ionic species of ionic liquid of this work and not with the molecules of water initially present in the lattice of the alum (hydrated ammonium aluminum sulfate).

For comparison, a prepared 0.01 M of Co (II) sulfate in aqueous solution was also examined by UV-Visible spectroscopy and showed one absorption band at 512 nm, Fig. (3.15.A), the lower wavelength observed in aqueous solution than that obtained in hydrated ammonium aluminum sulfate/urea ionic liquid gave additional support to the weaker nature of ionic liquid species coordinated to Co (II) ions. Additionally it could also be noticed that the molar absorptivity in ionic liquid is higher than in aqueous solution, Table (3.4), which indicates the relatively less symmetrical coordinated geometry of Co (II) ions in ionic liquid.

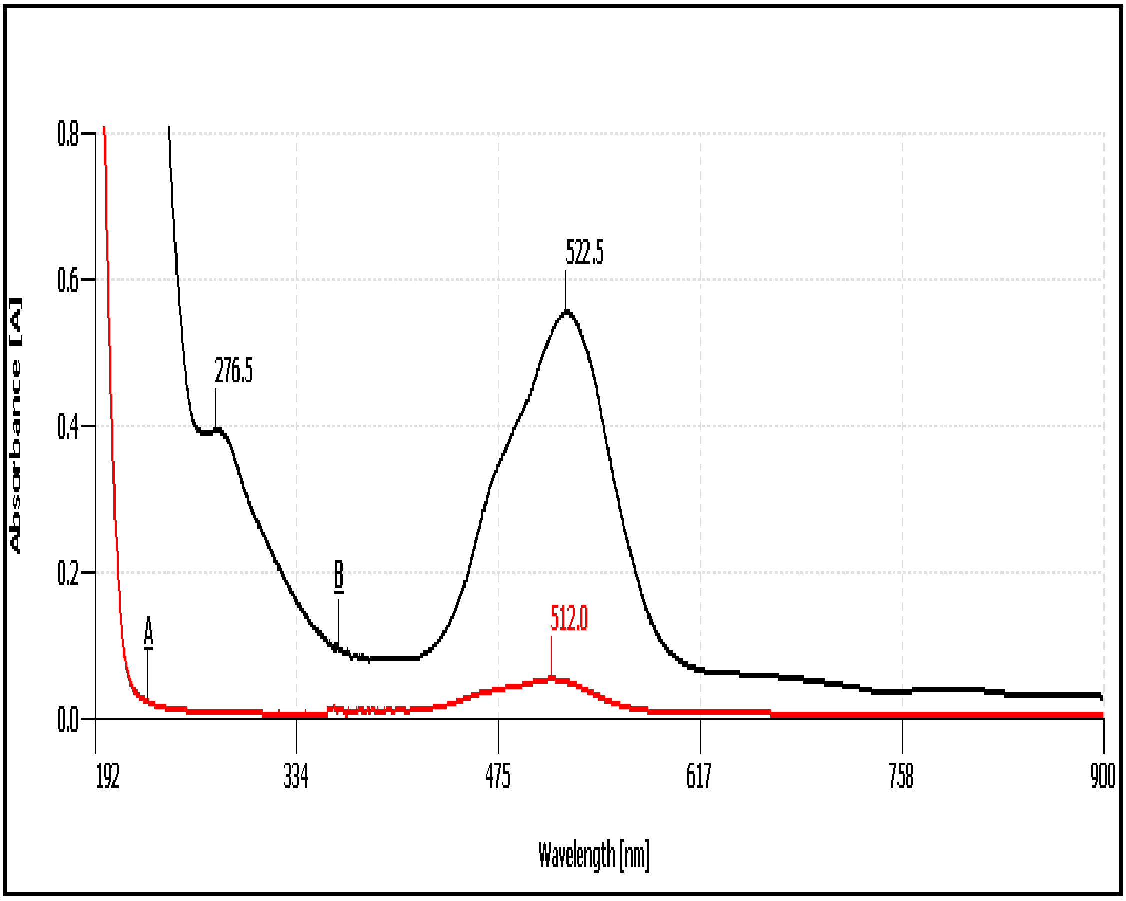


Fig. (3.15):- The UV-Visible spectra of $CoSO_4.7H_2O$ in [A]: 0.01 M aqueous solution. [B]: 0.05 M hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

3.4.1. Reaction with potassium thiocyanate:-

It was known that cobalt (II) cation present in variable media in different geometries depending on the concentration of the ligands, particularly of chloride anion.[58] Thus it was intended to study the behavior of this cation in alum ionic liquid as the present anionic species which are not simple as those studied earlier. Meanwhile, the expected behavior would reveal either similar geometrical configuration or different from those reported, to predicate the strength of the present anionic species of alum ionic liquid and their relative electrostatic repulsion characterization.

The easily soluble cobalt sulfate in ionic liquid at room temperature was mixed with different mole ratios of potassium thiocyanate from 1:1 to 1:35 mole of cobalt cation to thiocyanate in hydrated ammonium aluminum sulfate/urea ionic liquid. All these added ratios of thiocyanate required relatively higher temperature to be dissolved 40°C. This indicates the kinetically slower reaction of the cyanate ions with the cobalt cation in a substitution reaction to replace the coordinated ionic liquid anions by the thiocyanate anions. On going from 1:1 the clear pink color of the cobalt solution stated to change through clear violet at about 1:5 and final to the obvious blue color at 1:15 mole, picture 3.8. These solutions were investigated spectroscopicall by UV-Visible and showed different absorption behavior as shown in Fig. (3.16). The clear octahedral geometrical coordination of cobalt in pure ionic liquid, which is also found in a rich or pure $AlCl_3$ melts, [58,59] as stated to be due to the less electrostatic chloride ions present in those melts. This might also be proper explanation to the weaker ionic species of the present ionic liquid which are coordinated in a complex form to aluminum cation (probably $[Al(SO_4)_2.nH_2O]$.

The substitution reaction was spectroscopically noticeable when the ratios of added thiocyanate reached 1:10 when a band at 611.5 nm appeared on the octahedral band at 529 nm Fig. (3.16.D). The 611.5 nm band increased in intensity with addition thiocyanate until a more obvious tetrahedral peaks are revealed at 1:35 mole ratio Fig. (3.16.G). The latter are also reported for the tetrahedral geometry of cobalt cations in different media. [41,47,54,55] The mixed geometry or distorted octahedral geometry reported in variable media, were related to coordination of cobalt to complexing agent, more specifically mixed ligands.[60] This is in agreement in its general sense to the formation of mixed ligand complexes between original cobalt complex in ionic liquid with different substituted thiocyanate on going from 1:1 mole ratio to 1:35 mole ratio. Thus it can hardly explain the nature of Fig. (3.16 D, E and F) on a discrete cation-anion formation between cobalt either thiocyanate of ionic liquid anions. The nature of these complexes required more elaborated studies to investigate their nature, but it might be given a suggested nature based on the reported complexes in different media.[58,60] Therefore if the anionic species of ionic liquid given the letter (B) and thiocyanate letter (T), then the formed species on addition of thiocyanate might be proposed to have the following formula, $[CoB_6]^{2-}$, $[CoB_4T_2]^{2-}$, $[CoB_3T_2]^{2-}$ ….$[CoT_4]^{2-}$.

The changing of the coordination of Co^{2+} from octahedral in ionic liquid to tetrahedral with added thiocyanate would indicate the weaker electrostatic repulsion energy exhibited by the ionic liquid anion complex species allowing (6) ligand to be coordinated with cobalt. However, the changing in geometry to tetrahedral with thiocyanate also indicated high electrostatic repulsion of thiocyanate anion not allowing an octahedral geometrical coordination with Co^{2+} but rather more relaxed less repulsive tetrahedral geometry.

It was also noticed that the charge transfer spectral in presence of thiocyanate started at much lower energy than that observed with out thiocyanate (Compare Fig. 3.16 curve A with curve B-G).

This also could be taken as an evidence to the coordination of Co^{2+} with thiocyanate and therefore this charge transfer was related to electron transfer from ligand to metal which covered the spectra at 276.5 nm related to d-d electronic spectra of $^4T_{1g}(F)$ to $^4T_{1g}(P)$ of Co^{2+}.

The calculated molar absorptivity was taken to indicate the purity of geometrical coordination of cobalt to the anion in ionic liquid or with added ligands. Therefore molar absorptivity values which are presented in Table (3.4), reveal the increased distortion in the pure octahedral geometry of the coordinated metal in ionic liquid when adding thiocyanate. The changing in the coordination of the ligands around the metal from octahedral to tetrahedral may also be expected to go through the trigonal bipyramid or severally distorted octahedral, thus giving higher molar absorptivity.

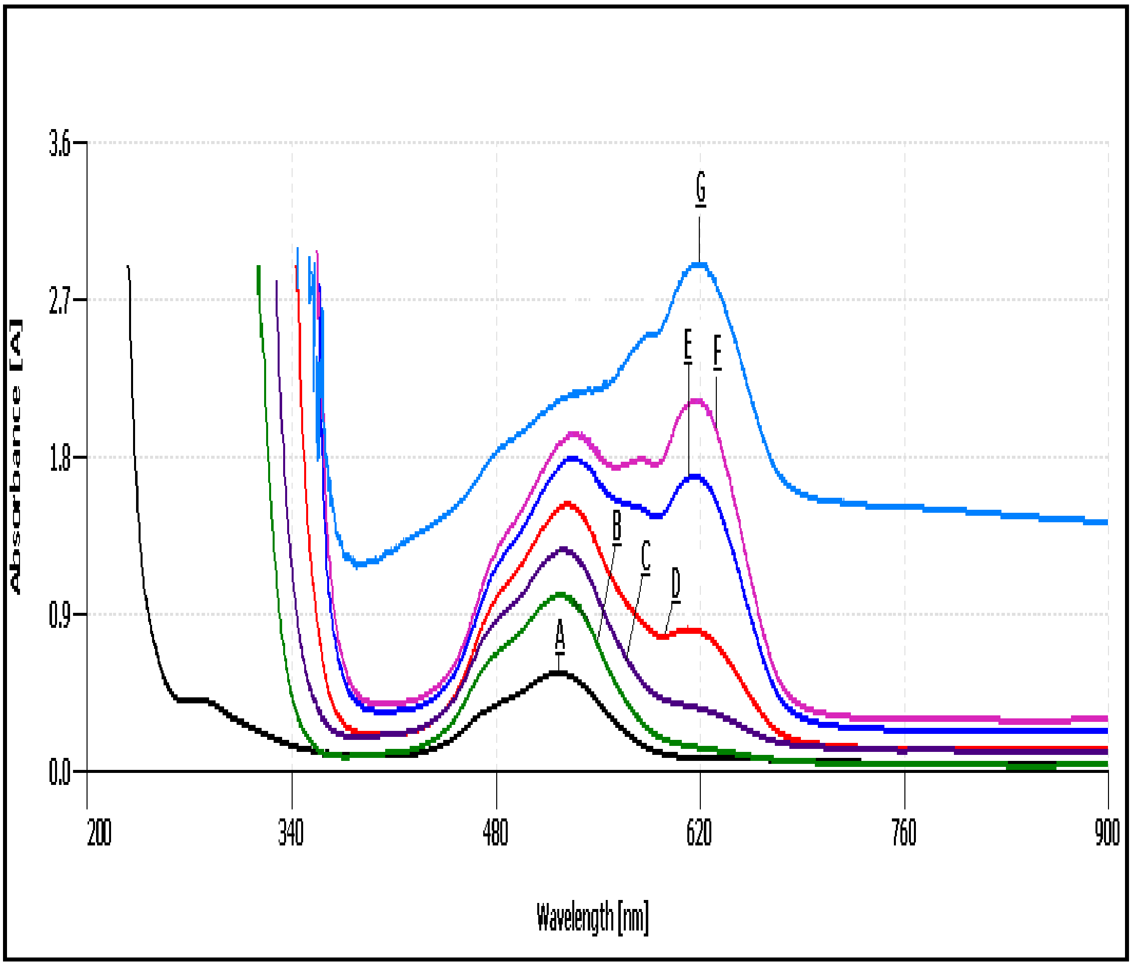
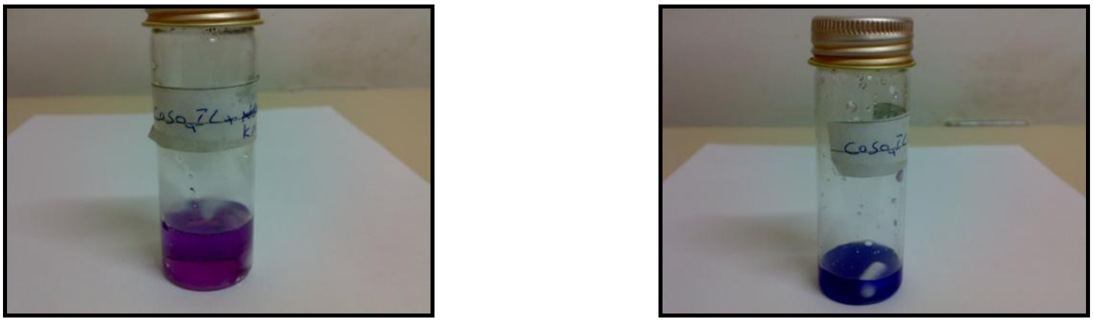


Fig. (3.16):- The UV-Visible spectra for $CoSO_4.7H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea ionic liquid. [B]:Addition 5 moles of KSCN to one mole of $CoSO_4.7H_2O$. [C]: Addition 7 moles of KSCN to one mole of $CoSO_4.7H_2O$. [D]: Addition 10 moles of KSCN to one mole of $CoSO_4.7H_2O$. [E]: Addition 13 moles of KSCN to one mole of $CoSO_4.7H_2O$. [F]: Addition 15 moles of KSCN to one mole of $CoSO_4.7H_2O$. [G]: Addition 35 moles of KSCN to one mole of $CoSO_4.7H_2O$.



(A): Violet color

(**1**($CoSO_4.7H_2O$ in ionic liquid):**5**(KSCN))

(B): Blue color

(**1**($CoSO_4.7H_2O$ in ionic liquid):**15**(KSCN))

Picture (3.8):- Different colored solution for $CoSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with addition KSCN in different ratio.

3.4.2. Reaction with sodium nitrite:-

Addition of nitrite anions as sodium nitrite to Co (II) sulfate in ionic liquid, that dissolved easily at room temperature, in contrast to the thiocyanate salt. When completely dissolved nitrite interacted with cobalt cation changing the original pink color solution in to orange color picture (3.9).

Picture (3.9):- Orange colored solution for $CoSO_4.7H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with added $NaNO_2$ in ratio 1:5 mole respectively.

Spectroscopic test of the resulted orange solution and those obtained from successive addition of nitrite to cobalt (II) revealed an increase in the intensity of the bands at 520.5 nm and 276.5 nm indicating an increase in concentration of coordinated cobalt (II) with added nitrite, Table (3.4) and Fig. (3.17). These two bands considered as transition two and three, by using Tanabe-Sugano diagram for d^7 configuration can be calculated the first transition band for each addition ratio.

From the Table (3.4), its also indicated that the molar absorptivity increased from 11 $Lmol^{-1}cm^{-1}$ to 13.8 $Lmol^{-1}cm^{-1}$ on first added nitrite at 1:1 mole ratio. This indicate a stronger added ligand to the weaker ionic liquid anions. In addition, the increased in molar absorptivity also indicate symmetrical coordinated Co^{2+} to the anions present in ionic liquid either with NO_2^- or both ionic liquid and NO_2^- as mixed ligands.

In contrast to the investigated of concentration effect of added thiocyanate to ionic liquid, the limited solubility of nitrite in this ionic liquid prevent more added concentration of nitrite to ionic liquid as it was observed to be suspended in the ionic liquid preventing the observation of spectroscopic measurement.

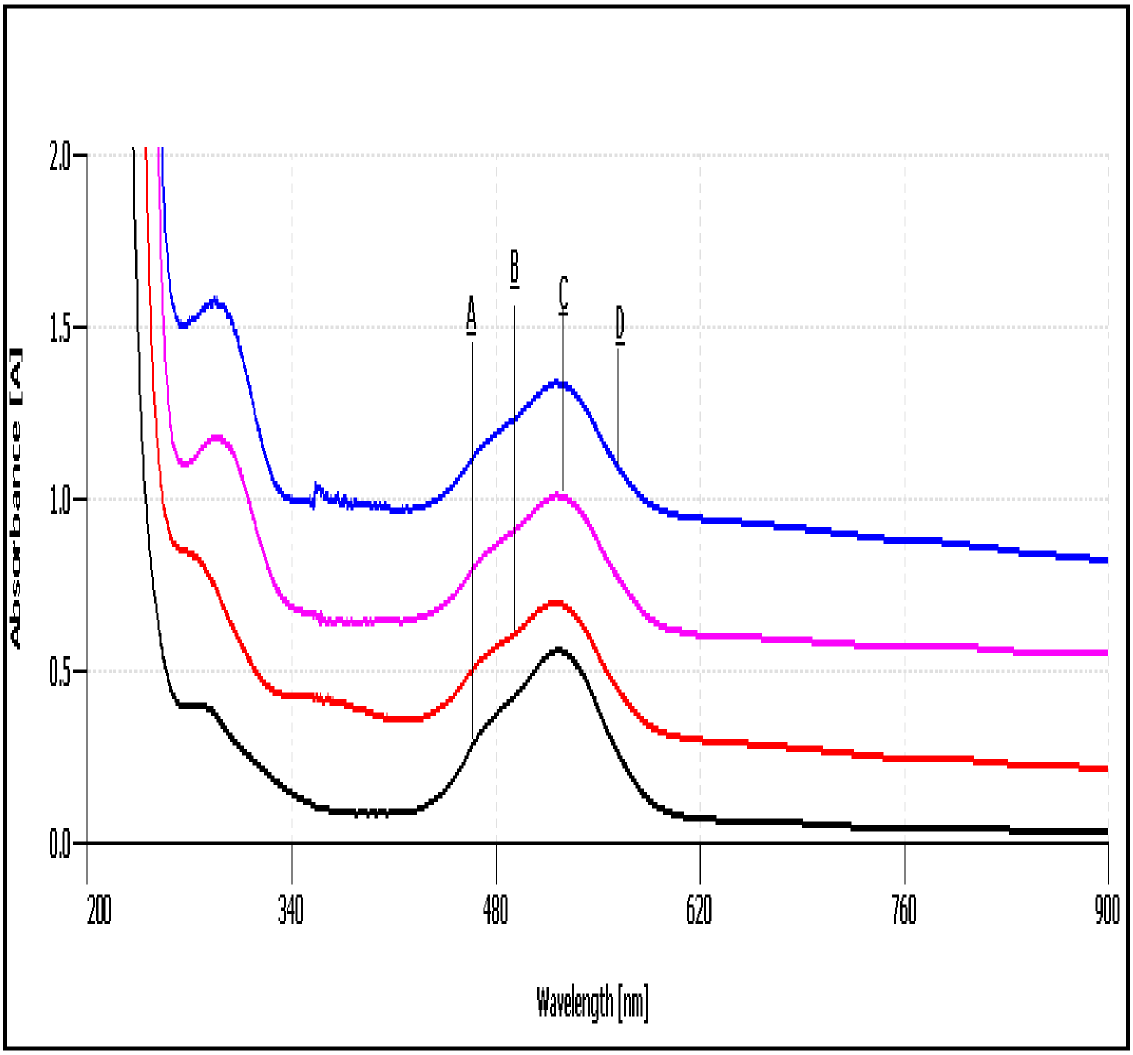


Fig. (3.17):- The UV-Visible spectra of $CoSO_4.7H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]:Addition equivalent mole of $NaNO_2$ to $CoSO_4.7H_2O$. [C]:Addition 3 moles of $NaNO_2$ to $CoSO_4.7H_2O$. [D]:Addition 5 moles of $NaNO_2$ to $CoSO_4.7H_2O$.

Table (3.4):- The electronic spectra for Co (II) ion in ionic liquid and with various ligands.

Co (II) ion	Absorption bands(nm)	Color	ε ($Lmol^{-1}cm^{-1}$)	Cal. B	Suggested structure	Ref.
Aqueous solution	$\upsilon = 512$	Pink	5	-	Octahedral $[Co(H_2O)_6]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea	$\upsilon_1 = 1309$ $\upsilon_2 = 522.5$ $\upsilon_3 = 276.5$	Pink	11 7.8	1.96	Octahedral $[Co(IL)_6]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea+ KSCN (1:5)mole	$\upsilon = 523.5$	Violet	20	-	Distorted octahedral Co^{2+} interact with one or more KSCN	This work
Hydrated ammonium aluminum sulfate/urea+ KSCN (1:7)mole	$\upsilon = 526.5$ $\upsilon = 625$	Violet	25.2 6.6	-	Distorted octahedral Co^{2+} interact with one or more KSCN	This work
Hydrated ammonium aluminum sulfate/urea+ KSCN (1:10)mole	$\upsilon = 529$ $\upsilon = 611.5$	Violet	30.2 16	-	Distorted octahedral Co^{2+} interact with one or more KSCN	This work
Hydrated ammonium aluminum sulfate/urea+KSCN (1:13)mole	$\upsilon = 532$ $\upsilon = 578$ $\upsilon = 616$	Deep Violet	-	-	Th. or distorted Oh. Co^{2+} interact with one or more KSCN	This work

Hydrated ammonium aluminum sulfate/urea+ KSCN(1:15)mole	υ= 532.5 υ= 579.5 υ= 616.5	Blue	-	-	Th. or trigonal bipyramid Co^{2+} interact with KSCN	This work
Hydrated ammonium aluminum sulfate/urea+ KSCN(1:35)mole	υ= 538 υ= 584 υ= 622	Blue	-	-	Th. Co^{2+} interact with KSCN	This work
Hydrated ammonium aluminum sulfate/urea+ $NaNO_2$(1:1)mole	$\upsilon_{1(Cal.)}$=1296 υ_2= 520.5 υ_3= 272	Light pink	13.8 16.8	1.98	Octahedral $[Co(IL)_6]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea+ $NaNO_2$(1:3)mole	$\upsilon_{1(Cal.)}$=1151 υ_2= 522 υ_3= 288.5	Light pink	20 23.6	1.79	Distorted octahedral Co^{2+} interact with one or more $NaNO_2$	This work
Hydrated ammonium aluminum sulfate/urea+ $NaNO_2$(1:5)mole	$\upsilon_{1(Cal.)}$=1146 υ_2= 521 υ_3= 286.5	Orange	26.6 31.6	1.79	Distorted octahedral Co^{2+} interact with one or more $NaNO_2$	This work
$Ca(NO_3)_2.4H_2O$/ $CaCl_2$	υ= 515	-	-	-	Octahedral	56
Acetamide/ $Ca(NO_3)_2.4H_2O$	υ= 514.6	-	-	-	Octahedral	57
Choline chloride/urea	υ= 641 υ= 671	-	-	-	Tetrahedral	54

Choline chloride/malonic acid	υ= 619 υ= 642 υ= 672	-	-	-	Tetrahedral	54
LiCl/KCl	υ= 598.8 υ= 660 υ= 680	-	-	-	Tetrahedral $[CoCl_4]^{2-}$	55

3.5. Nickel (II) sulfate hexahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Nickel (II) sulfate hexahydrate was found to be not easily soluble at room temperature in hydrated ammonium aluminum sulfate/urea ionic liquid until the temperature was elevated to 40°C with mechanical stirring, a 0.02 M of Ni (II) sulfate in ionic liquid was achieved after 2 hours giving pale green solution as shown in picture (3.10).

Picture (3.10):- 0.02 M pale green colored solution of $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at 40°C.

Similar behavior was found for nickel chloride in choline chloride/urea ionic liquid when 0.1 M was dissolved after 72 hours at room temperature,[54] compared to 0.02 M at 40°C for Ni (II) sulfate in ionic liquid of the present work. The nickel chloride solubility was also reported in LiCl/KCl molten salt at 700-1000°C and in CsCl melt at 864°C.[55] These high temperature would reflected the ease of solubility of Ni (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid at much lower temperature 40°C.

The electronic transition of the pale green solution of nickel sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid was investigated by UV-Visible and revealed two bands at 401.5 nm and split band in the visible region at 670.5 nm Fig. (3.18.B). These are the known ranges for octahedral coordination of nickel complexes, yet the third band which was normally existed at lower frequency was not detected due to the lower limit of the spectrophotometer.

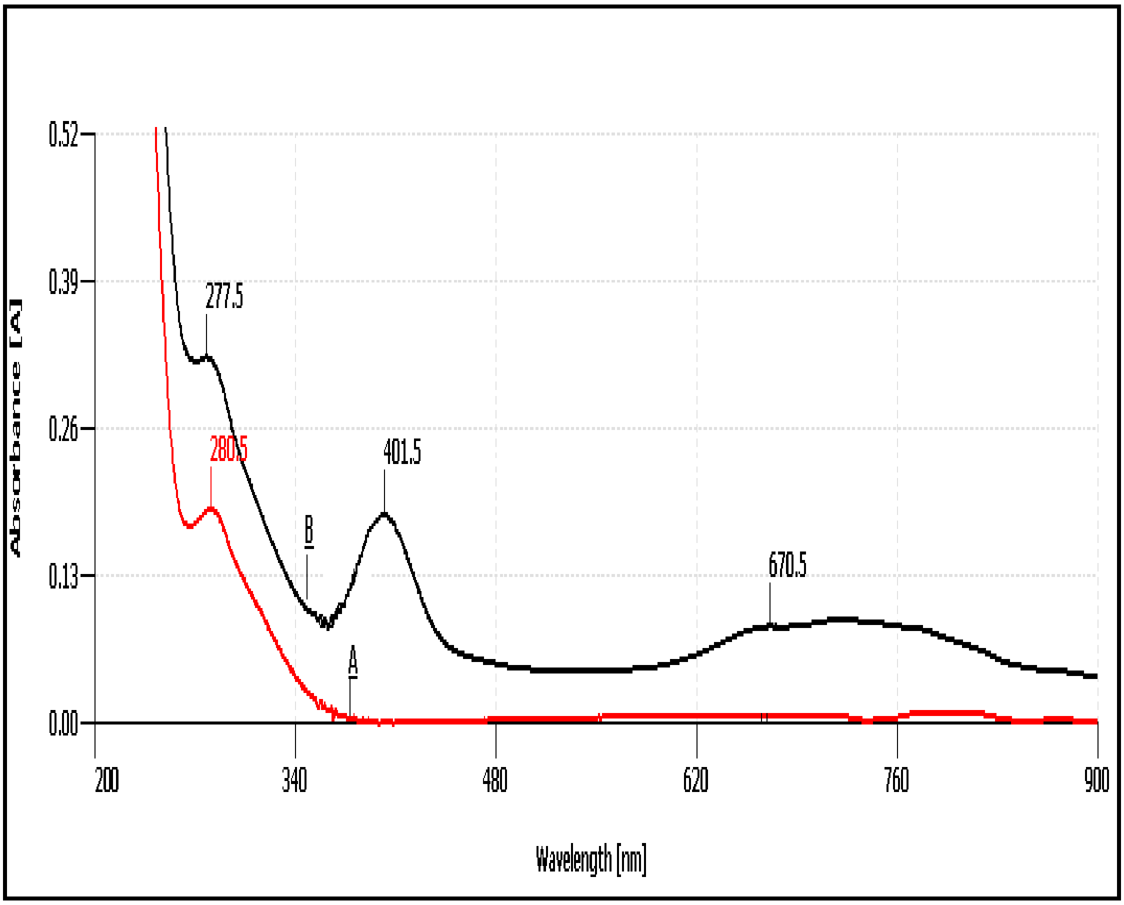


Fig. (3.18):- The UV-Visible spectrum for [A]: Hydrated ammonium aluminum sulfate/urea ionic liquid. [B]: $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

Orgel diagram, Scheme (2.2) refers to the d^8 octahedral electronic transition and can split as follows:

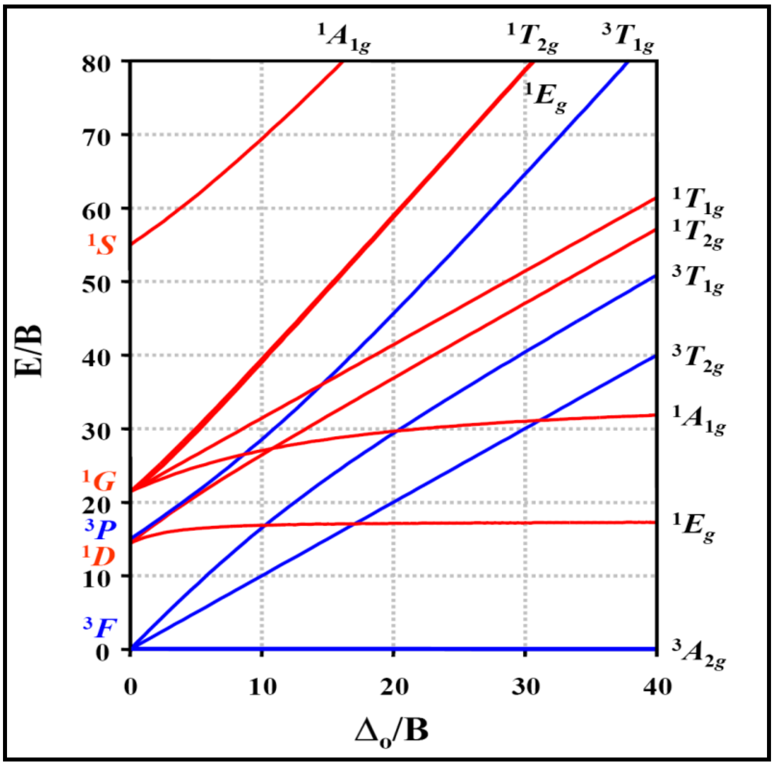
$\upsilon_1 = {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$

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

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

The observed bands of 401.5 nm and 670.5 nm, were related to υ_3 and υ_2 respectively, while υ_1 was calculated from Tanabe-Sugano diagram for d^8 configuration, Scheme (3.6), which indicated that its value equal to 1198 nm.

The relatively broad band at 670.5 nm in comparison to the other band at 401.5 nm could be related to two bands resulted from the d-d spin allowed electron state of ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and spin forbidden ${}^3A_{2g} \rightarrow {}^1E_g$ electronic state which appeared due to orbital coupling. In this case both bands would have close energy as when $\Delta_\circ/B$ was calculated found to have a value of (9). When straight line was drawn to mark the other transition states, indicated very close values of both above mentioned electronic states.



Scheme (3.6):- Tanabe-Sugano diagram for d^8 octahedral ion configuration.

Fig. (3.18) also showed the same position shoulder of the ionic liquid at 277.5 nm, now appeared with higher absorbance at the charge transfer transition of the ligands with nickel.

To compare the electronic transition behavior, nickel sulfate solution in water 0.01 M also showed two main electronic transition at 396.5 nm and split band at 656.5 nm, Fig. (3.19.A). The third band was calculated from Tanabe-Sugano diagram for d^8 configuration and was found to be 1113 nm, Table (3.5). The similarity in its behavior, nickel (II) sulfate hexahydrate also showed octahedral configuration in aqueous solution but with relatively higher transition energies, reflecting the stronger water molecules as a ligand in comparison to ionic liquid species, and also support the previous metal (Cr, Co, Fe) which also suggested weaker ionic liquid than water molecules interaction. These added observation strongly suggest the non free nature of the originally present water molecules in the crystal structure of the alum, and that water still interacted to aluminum and NH_4^+ cation in the liquid state in the ionic liquid. The small and close molar absorptivity value of nickel (II) cation in ionic liquid of present work and water Table (3.5), reveal the symmetrical coordination of ligands around the nickel cation. The octahedral coordination of nickel (II) in present ionic liquid was found similar to those obtained in different ionic liquid, yet showing varied band energies. For example, it showed bands at 410 nm, 669-746 nm and 1050 nm in choline chloride/urea room temperature ionic liquid.[54] while in acetamide/KNO_3 it showed 431 nm, 800 nm and 1333 nm, but at 429 nm, 793 nm and 1234 nm in butyramide-$NaNO_3$.[44]

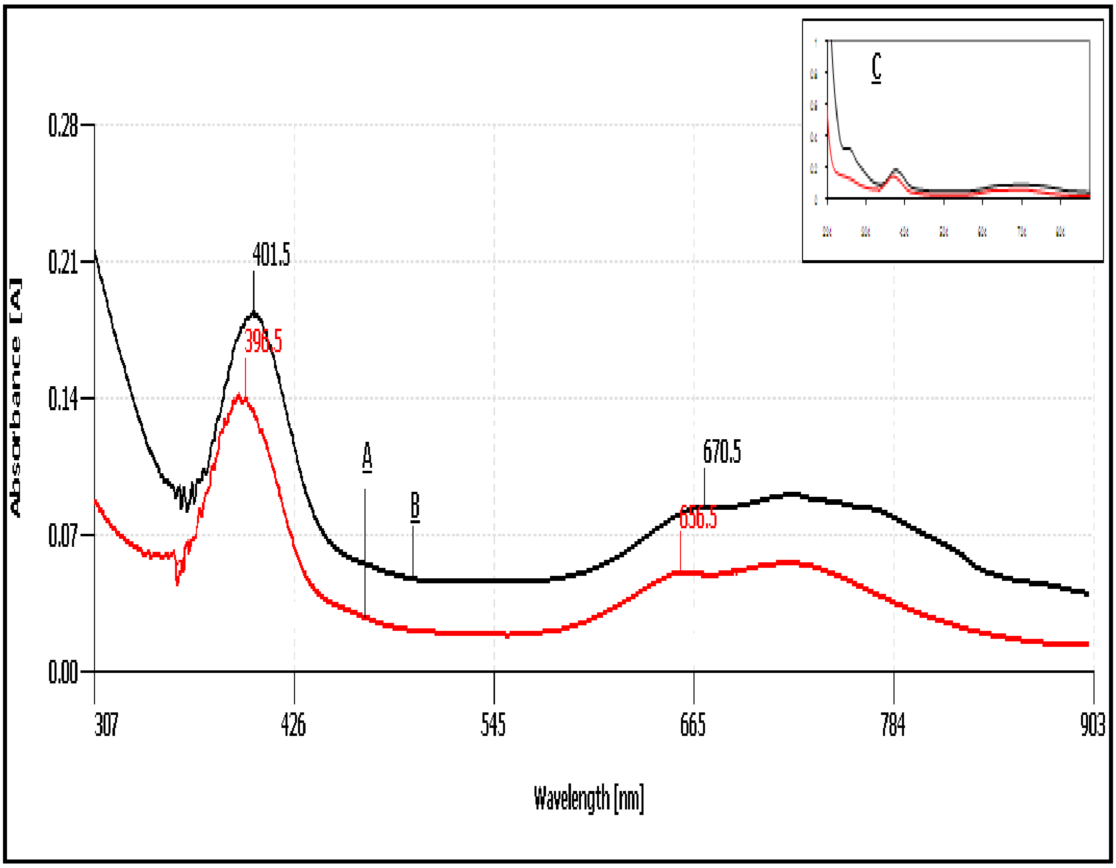


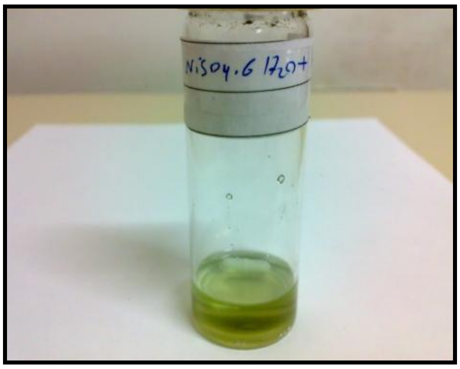
Fig. (3.19):- The UV-Visible spectra for $NiSO_4.6H_2O$ in [A]: 0.01M aqueous solution.[B]: 0.02M hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.[C]: Inset $NiSO_4.6H_2O$ in water and in hydrated ammonium aluminum sulfate/urea ionic liquid.

3.5.1. Reaction with potassium thiocyanate:-

To elaborate the behavior of Ni (II) in presence of a biphilic ligand, thiocyanat, as with cobalt (II) (section 3.4.1), the addition of potassium thiocyanate didn't show a dramatic changes as was observed with cobalt. The 1:1 mole ratio of added thiocyanate to Ni (II) didn't ever showed a color changes or deviation in the electronic band of Ni (II) in ionic liquid. However, the color changes appeared only when thiocyanate present in high concentration, therefore the color changed from pale green of Ni (II) in ionic liquid to green at 10:1 mole ratio picture (3.11), and to olive green at 30:1 mole ratio, picture (3.12).

Spectroscopic investigation of the successful addition of thiocyanate, Fig. (3.20.B) reveal an obvious change in the charge transfer spectra which stated with very high absorbance at around 333 nm overshade the ionic liquid transition at 277.5 nm. This might be taken as indication to the interaction between thiocyanate with Ni (II) although the metal did not change its octahedral configuration when substituted its ionic liquid interaction with thiocyanate anion. Another indication to the interacted thiocyanate with Ni (II) although it showed similar band energies, Table (3.5), the molar absorptivity increased by four times on addition of 10:1 thiocyanate to Ni (II) cation indicating a less symmetrical coordination of ligands to the metal there by reducing the octahedral symmetry. However, the further increased in molar absorptivity at 30:1 mole ratio could be explained also to the increased concentration of the complex. The octahedral coordination of Ni (II) in different ionic liquids was also reported in butyramide/$NaNO_3$ and acetamide/KNO_3,[44] and in choline chloride/urea.[54] However in highly ionic chloride melt CsCl Ni (II) showed tetrahedral coordination and distorted tetrahedral in LiCl/KCl molten salts.[55] This would revealed the less electrostatic nature of interaction of Ni (II) in present ionic liquid. Incontras to its behaivior to the monodentate ligands in choline chloride/malonic acid room temperature ionic liquid, nickel (II) showed a tetrahedral coordination.[54]

Picture (3.11):- Green colored solution for $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with added KSCN 1:10 mole ratio respectively.



Picture (3.12):- Olive green colored solution for $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with added KSCN 1:30 mole ratio respectively.

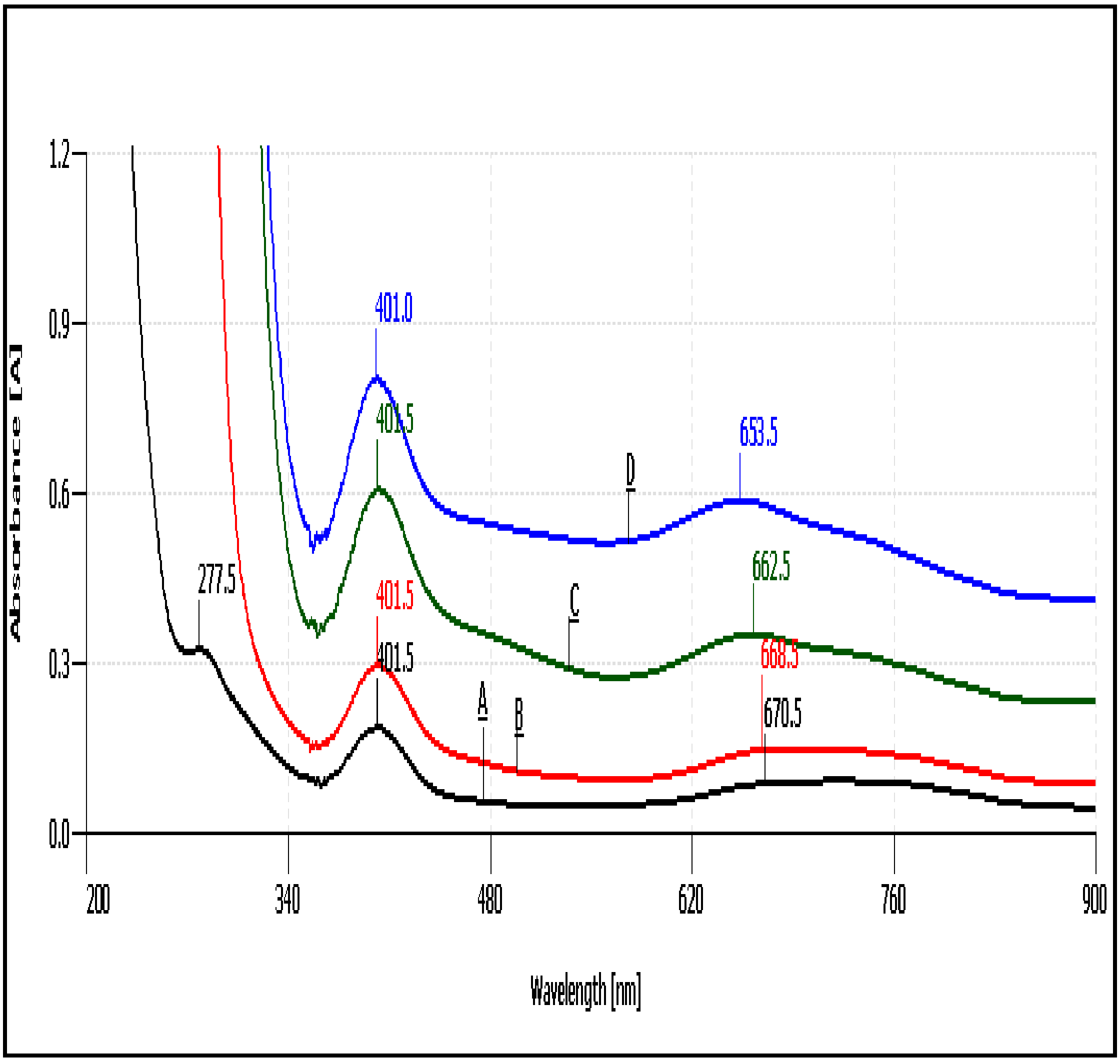
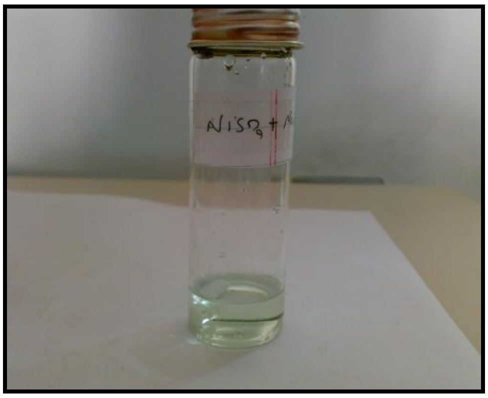


Fig. (3.20):-The UV-Visible spectra for $NiSO_4.6H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]:Addition 5 moles of KSCN to one mole of $NiSO_4.6H_2O$. [C]:addition 10 moles of KSCN to one mole of $NiSO_4.6H_2O$. [D]:addition 30 moles of KSCN to one mole of $NiSO_4.6H_2O$.

3.5.2. Reaction with sodium nitrite:-

When sodium nitrite ($NaNO_2$) was added to Ni (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in a ratio of 1:1, the color became fainted to almost colorless as shown in picture (3.13).



Picture (3.13):- Faint green solution for $NiSO_4.6H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with addition $NaNO_2$ 1:1 mole ratio respectively.

Sodium nitrite did not show a large changes in the position of the electronic transition bands of nickel (II) in ionic liquid, when the nitrite was added to nickel sulfate solution in a ratio of 1:1 the closely related electronic spectra and shape of the observed bands, Fig. (3.21.B) reveals no strong evidence to direct interaction of the metal with nitrite. However this does not means that there was no interacted effect due to presence of nitrite in solution. This might be seen from the higher molar absorptivity after adding nitrite ligand compared to before adding nitrite to nickel (II) solution in ionic liquid, Table (3.5). compared 4.1 $Lmol^{-1}cm^{-1}$ to 15.5 $Lmol^{-1}cm^{-1}$. By using Tanabe-Sugano diagram for d^8 configuration the third band was calculated and found to be 1187 nm.

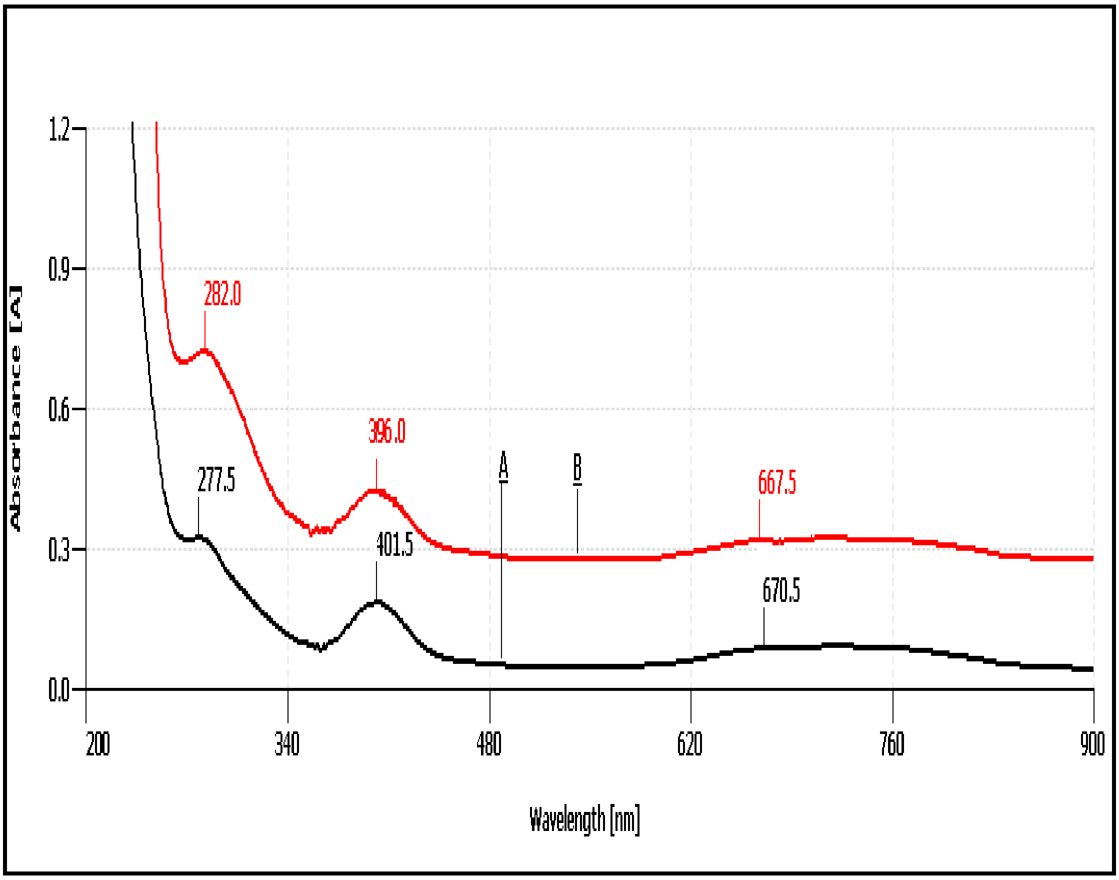


Fig. (3.21):- The UV-Visible spectra for $NiSO_4.6H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]:Addition equivalent mole of $NaNO_2$ to $NiSO_4.6H_2O$.

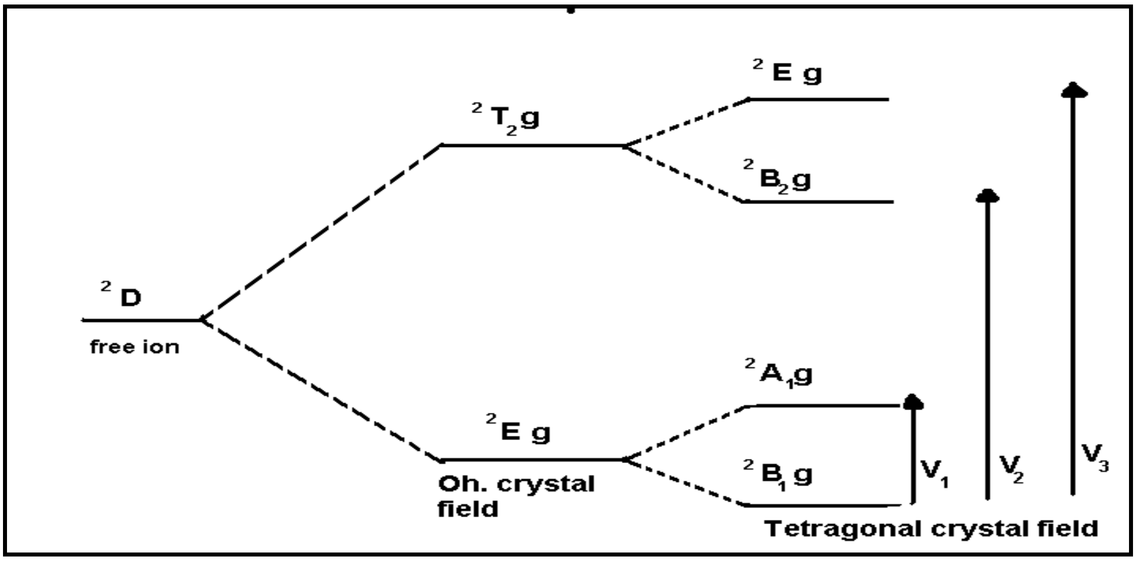
Table (3.5):- The electronic spectra for Ni (II) ion in ionic liquid and with various ligands.

Ni (II) ion	Absorption bands(nm)	Color	B\` (cm^{-1})	ε(Lmol^{-1}cm^{-1})	Cal. B	Suggested structure	Ref.
Aqueous solution	$\upsilon_{1cal.}$= 1113 υ_2= 656.5 υ_3= 396.5	Green	898.3	5 14	0.87	Oh. $[Ni(H_2O)_6]^{2+}$	This work
$NH_4Al(SO_4)_2.12H_2O$/urea	$\upsilon_{1cal.}$= 1198 υ_2= 670.5 υ_3= 401.5	Pale green	927.2	4.1 9.1	0.9	Oh. $[Ni(IL)_6]^{2+}$	This work
$NH_4Al(SO_4)_2.12H_2O$/urea + KSCN (1:5) mole	$\upsilon_{1cal.}$= 1130 υ_2= 668.5 υ_3= 401.5	Pale green	884.6	7 14.5	0.85	Oh. $[Ni(IL)_6]^{2+}$	This work
$NH_4Al(SO_4)_2.12H_2O$/urea + KSCN (1:10) mole	$\upsilon_{1cal.}$= 1125 υ_2= 662.5 υ_3= 401.5	Green	888.6	17.3 30.3	0.86	Oh. Ni^{2+} interact with one or more KSCN	This work
$NH_4Al(SO_4)_2.12H_2O$/urea + KSCN (1:30) mole	$\upsilon_{1cal.}$= 1116 υ_2= 653.5 υ_3= 401	Olive green	895.3	29 40	0.86	Distorted Oh. Ni^{2+} interact with one or more KSCN	This work
$NH_4Al(SO_4)_2.12H_2O$/urea + $NaNO_2$ (1:1) mole	$\upsilon_{1cal.}$= 1187 υ_2= 667.5 υ_3= 396	Faint green	935.7	15.5 21	0.9	Oh. Ni^{2+} interact with one or more $NaNO_2$	This work
LiCl/KCl	υ=1250 υ=704.2 υ=653.6	-	-	-	-	Distorted tetrahedral	55

CsCl	υ= 1333 υ= 714.2 υ= 637	-	-	-	-	Tetrahedral	55
Butyramide/$NaNO_3$	υ= 1234 υ= 793 υ= 429	-	-	-	-	Octahedral	44
Acetamide/KNO_3	υ= 1333 υ= 800 υ= 431	-	-	-	-	Octahedral	44
Choline chloride/urea	υ= 1050 υ=(669-746) υ= 410	-	-	-	-	Oh. $[Ni(urea)_4Cl_2]$	54

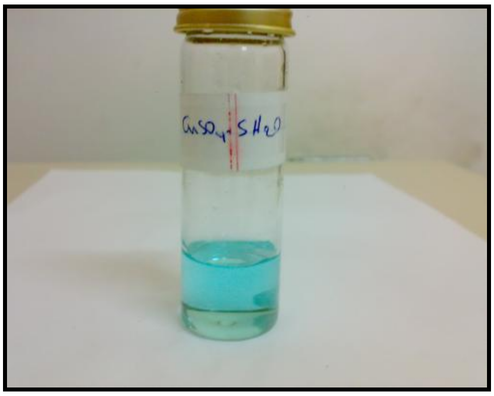
3.6. Copper (II) sulfate pentahydrate in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid:-

Copper (II) compounds in general form blue or green solutions, the d^9 ion is characterized by large distortion form octahedral symmetry and the bond is unsymmetrical, being the result of a number of transitions which are no means easy to assign unambiguously. The free ion ground ^2D term is expected to split in a crystal field in the same way as the term ^5D of the d^4 ion and a similar interpretation of the spectra is like wise expected. Unfortunately this is now more difficult because of the greater overlapping of bands which occurs in the case of Cu (II), as shown in Scheme (3.7). [41]



Scheme (3.7):- Crystal field splitting for ^2D configuration.

Copper (II) sulfate pentahydrate found not to be easily soluble in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature until the temperature was raised to 40°C, when a 0.05 M of metal sulfate was achieved after 15 minutes producing blue clear solution as shown in picture (3.14).



Picture (3.14):- 0.05 M blue colored solution for $CuSO_4.5H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid dissolved at 40°C.

It was found that the solubility for Cu (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid is different from Cu (II) chloride in other ionic liquids or molten salts. For example a 0.1 M of Cu (II) chloride in choline chloride/urea ionic liquid soluble after standing 72 hours, also in choline chloride/malonic acid a 0.1 M of metal chloride soluble after 72 hours.[54] In molten salt ionic liquid like LiCl/KCl the Cu (II) ions soluble at 400°C.[55] From that it could be suggested that Cu (II) sulfate in hydrated ammonium aluminum sulfate /urea ionic liquid more soluble than Cu chloride in chloride ionic liquids.

The ultraviolet-visible test for the blue solution showed one broad absorption with a maxima at 802.5 nm as shown in Fig. (3.22).

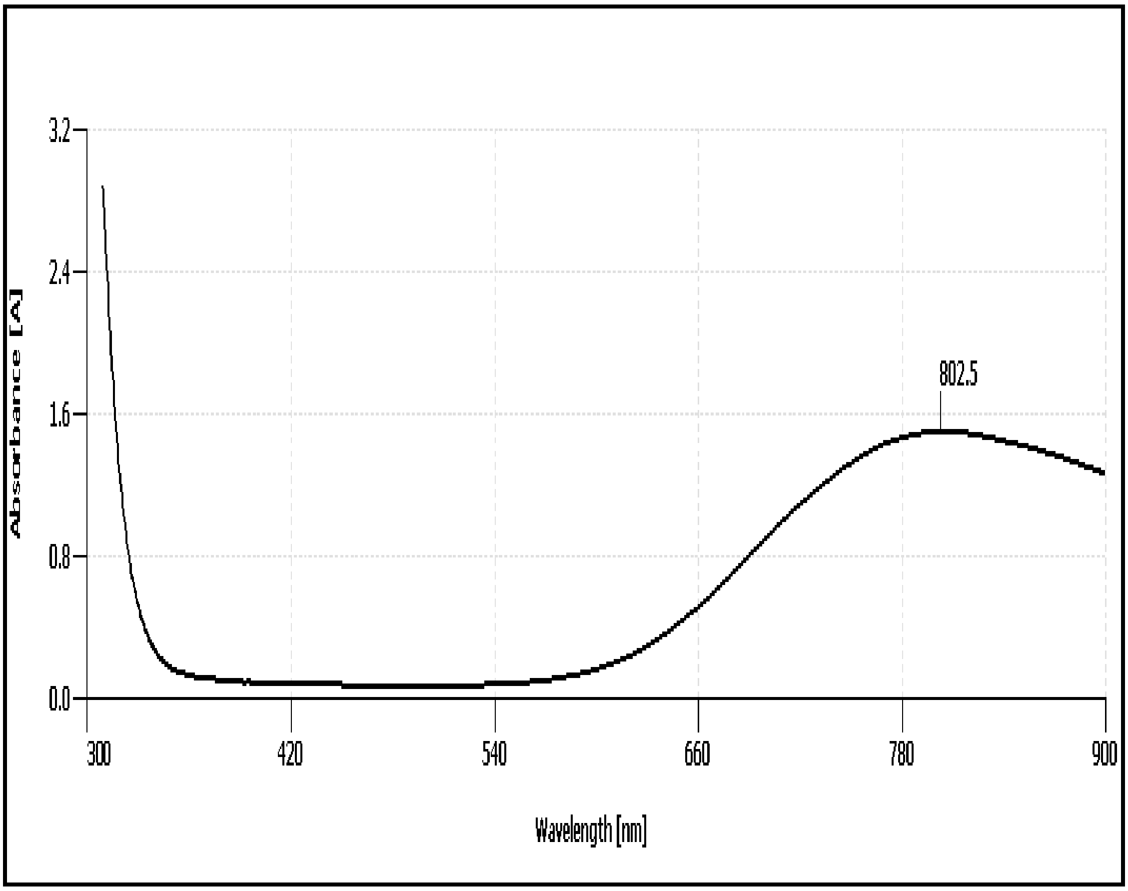


Fig. (3.22):- The UV-Visible spectrum for $CuSO_4.5H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

The term symbol for d^9 of Cu (II) ion its ^2D with one transition for broad absorption band due to distorted Cu (II) octahedral structure.

Cu (II) subjected to (Jahn-Teller) effect that any non-linear molecule with degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overlap energy of the complex. [61]

To compare the behavior of Cu (II) sulfate in aqueous solution and in hydrated ammonium aluminum sulfate/urea ionic liquid, a 0.01 M of Cu (II) sulfate was prepared in aqueous solution and gave one absorption band at 798.5 nm that shifted to higher energy than those obtained in hydrated ammonium aluminum sulfate/urea ionic liquid Fig. (3.23), that indicate Cu^{2+} would have a strong interaction with water molecules than with anionic species of ionic liquid, and this additional support to the weaker nature of ionic liquid. It could be noticed that the molar absorptivity in ionic liquid higher than in aqueous solution Table (3.6), which indicates the less symmetrical coordination geometry of Cu (II) ions in ionic liquid. These observation are in agreement to a similar behavior of the other cations studied in this project.

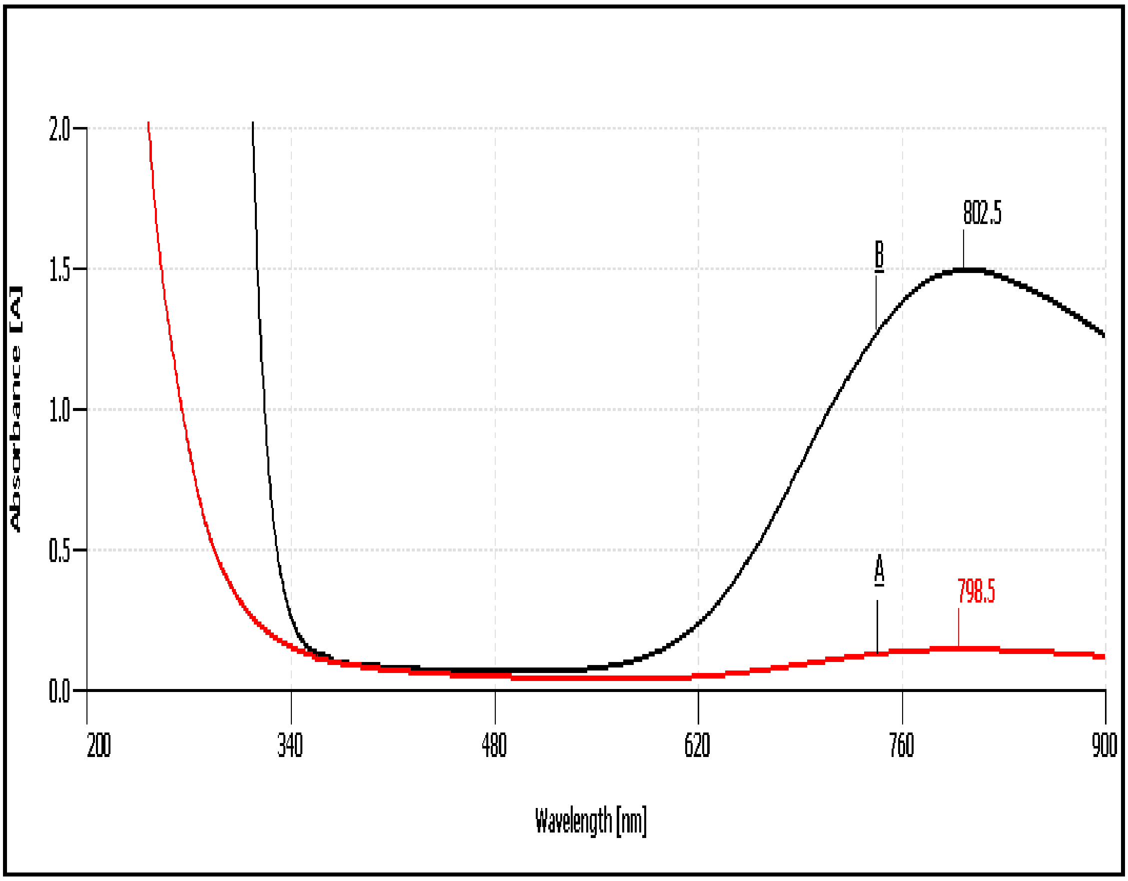


Fig. (3.23):- The UV-Visible spectra for $CuSO_4.5H_2O$ in [A]: 0.01 M aqueous solution.[B]: 0.05 M hydrated ammonium aluminum sulfate/urea room temperature ionic liquid.

Cu (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid have different coordination from Cu (II) chloride in other types of ionic liquids and molten salts such as, in LiCl/KCl when Cu (II) electronic transition band reported to have 1052 nm and assigned to form distorted octahedral or tetrahedral coordination.[55] In choline chloride/tartaric acid the band energy was 1089 nm and assigned to a tetrahedral geometry.[43]
But in choline chloride/urea the spectrum showed band energy at 766 nm reported to octahedral coordination,[54] a close electronic transition band was in the ionic liquid of this work 802.5 nm, and this could be related to octahedral coordination of Cu (II) cation.

Because there was no Tanabe-Sugano diagram for d^9 electronic configuration, using Orgel diagram to assign the value of 10 Dq, Cu (II) sulfate showed on broad band at 802.5 nm which can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions.

3.6.1. Reaction with potassium thiocyanate:-

In an attempt to study the behavior of Cu (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid with addition the ligand, thiocyanate ligand was added to Cu (II) ions at room temperature in mole ratio (0.25:1) mole respectively, the original blue solution changed to turbid green, as shown in picture (3.15), which measured in UV-Visible instrument as 1mm film, the color change due to additional absorption of the solution.

Picture (3.15):- Green colored solution for $CuSO_4.5H_2O$ in hydrated ammonium aluminum sulfate/urea room temperature ionic liquid with addition KSCN (1:0.25) mole respectively.

The UV.Visible test showed one broad band at 806 nm that shifted to lower energy region and another band appeared at 361 nm, this absorption band related to added thiocyanate ligand to Cu (II) solution but it need further study to identified it, Fig. (3.24.B). In Cu (II) sulfate ionic liquid the distortion will be stronger than when added the ligand SCN^- because the absorbance higher in ionic liquid and the band more wider so its have more splitting. Molar absorptivity for Cu (II) sulfate when added the ligand 15.8 $Lmol^{-1}cm^{-1}$, Table (3.6), which is lower than the molar absorptivity in absence the ligand SCN^-, this is additional support that the distortion in Cu (II) sulfate ionic liquid is stronger than in presence the ligand SCN$^-$. Then when increase the moles of thiocyanate ligand the device could not detect it.

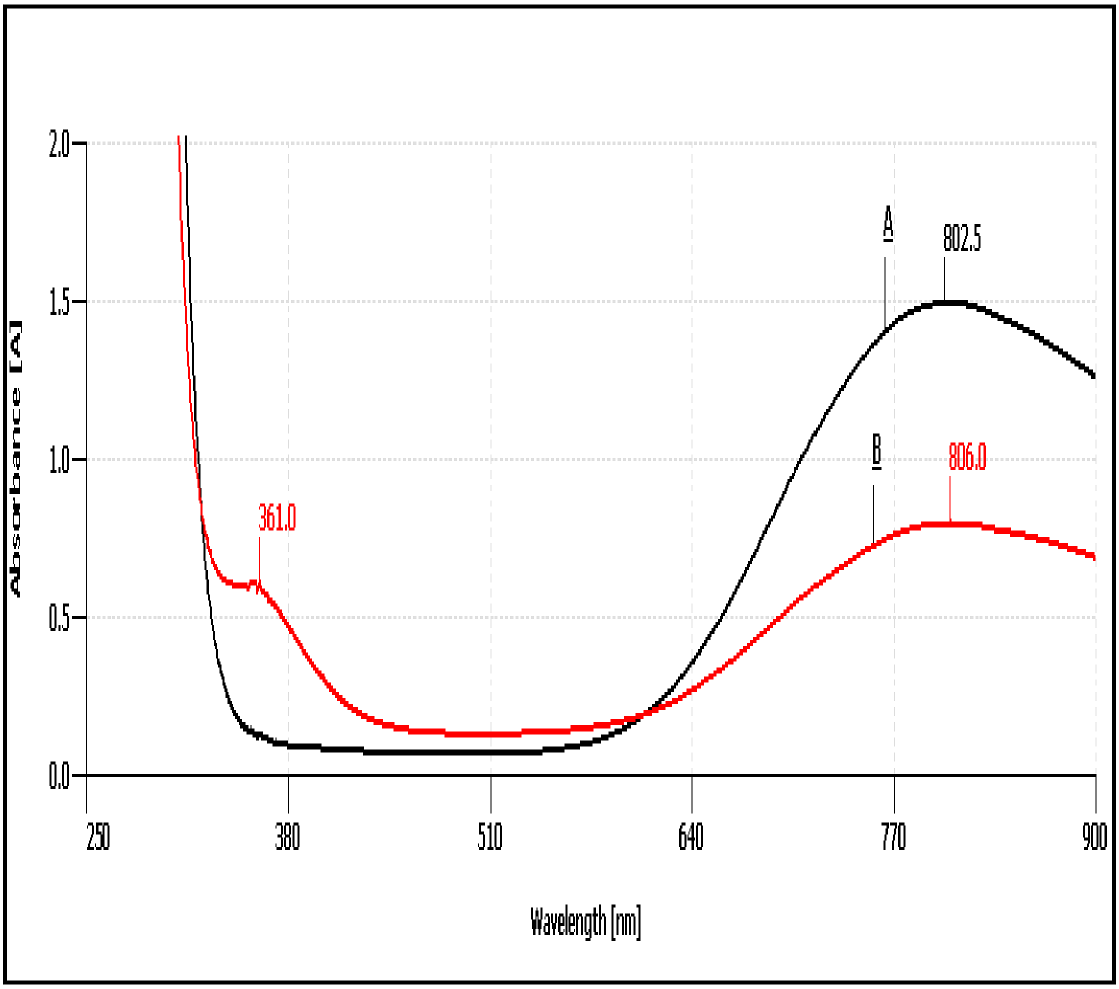


Fig. (3.24):- The UV-Visible spectra for $CuSO_4.5H_2O$ in [A]: Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]: Addition 0.25 mole of KSCN to one mole of $CuSO_4.5H_2O$.

3.6.2. Reaction with sodium nitrite:-

When sodium nitrite ($NaNO_2$) was added to Cu (II) sulfate in hydrated ammonium aluminum sulfate/urea ionic liquid at room temperature in a ratio of 1:1 mole, the original blue solution did not change. When the resulted solution was taken by UV-Visible test it showed a similar behavior to that solution without added sodium nitrite Fig. (3.25.B). It gave a very close absorption characterization in the position of the maximum absorbance and the shape of the absorbance. This might be indicate two possibilities to either the formation of very small concentration of copper nitrite coordinated to the original complex, or nitrite did not coordinated to copper at all. The latter possibility taken to explain the situation of the complex as it was observed that nitrite did not show obvious coordination in ionic liquid to other metal cations investigated in this work, even at 5:1 mole ratio of nitrite to cobalt sulfate (C.F. 3.4.2), the higher addition concentration of nitrite to metal cation would eliminate the first possibility.

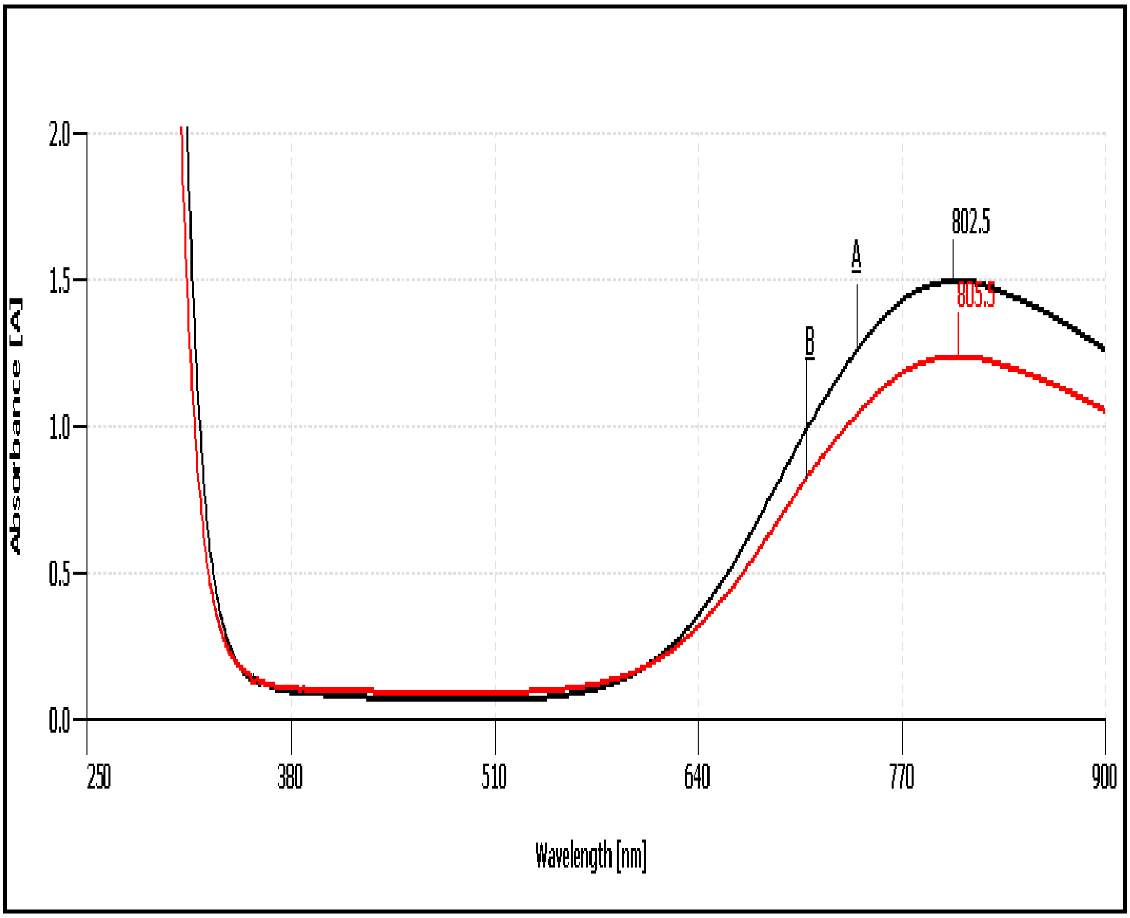


Fig. (3.25):- The UV-Visible spectra for $CuSO_4.5H_2O$ in [A]:Hydrated ammonium aluminum sulfate/urea room temperature ionic liquid. [B]:Addition equivalent mole of $NaNO_2$ to $CuSO_4.5H_2O$.

Table (3.6):- The behavior of Cu (II) ion in ionic liquid and with various solvents.

Solution of Cu (II) ions	Absorption bands (nm)	Transition	Color	ε(Lmol^{-1} cm^{-1})	Suggested structure	Ref.
Aqueous solution	υ= 798.5	$^2Eg\rightarrow {}^2T_2g$	Blue	14	Oh. $[Cu(H_2O)_6]^{2+}$	This work
Hydrated ammonium aluminum sulfate/urea	υ= 802.5	$^2Eg\rightarrow {}^2T_2g$	Blue	-	Distorted Oh. $[Cu(IL)_6]^{2+}$	This work
LiCl/KCl	υ= 1052	$^2B_1g\rightarrow {}^2B_2g$ $^2B_1g\rightarrow {}^2Eg$	Pale blue	-	Distorted Oh. or Th.	55
Choline chloride/tartaric acid	υ= 1089	$^2B_1\rightarrow {}^2B_2$ $^2B_1\rightarrow {}^2E$	Yellow	10.6	Th. two chloride and one tartarate ions	43
Choline chloride/urea	υ= 766	$^2Eg\rightarrow {}^2T_2g$	Blue	17.02	Oh. $[Cu(urea)_6]^{2+}$	54
Hydrated ammonium aluminum sulfate/urea + KSCN(1:0.25) mole	υ= 806 υ= 361	$^2Eg\rightarrow {}^2T_2g$	Green	15.8	Oh. Cu^{2+} interact with one or more KSCN	This work
Hydrated ammonium aluminum sulfate/urea + $NaNO_2$(1:1) mole	υ= 805.5	$^2Eg\rightarrow {}^2T_2g$	Blue	-	Distorted Oh. $[Cu(IL)_6]^{2+}$	This work

Conclusion:

It could be summarized that the some transition metal cations studied in present work behaved as follows:

1- They interacted to ionic species of the ammonium alum/urea ionic liquid regardless their oxidation state and their type of salts.
2- The water molecules originally present in the ammonium alum did not coordinated to the transition metal cations and hence not present in free state.
3- Some of the added ligands to metal cations substituted the weak coordinated ionic liquid species.
4- Coordination and concentration effects were obvious in case of cobalt cation in which the geometrical structure changed from octahedral to tetrahedral.

Future work:

1- Separation of the resulted substituted complexes and in case of turbid mixture [Cu (II) with KSCN] its preferable to filtrate it to get clear mixture.
2- Identification of complexes by different analytical method.
3- Applying different methods to further study of the reaction processes, such as NMR, Mass spectroscopy, ….. etc.

References

1. J. H. Davis and P. A. Fox; "From Curiosities to Commodities: Ionic liquids Begin the Transition", Chem.Comm., **11**, 1209-1212, **(2003)**.
2. M. H. Fang and L. S. Wang; "Hydrolysis and partial recycling of a chloroaluminate ionic liquid", International J. of Molecular Sciences, **8**, 470-477, **(2007)**.
3. M. C. Cann and M. E. Connelly; "Real World Cases in Green Chemistry", Chem. Soc., **10**, 212, **(2000)**.
4. J. Lunt; "Large-scale production, properties and commercial application of polylactic acid polymers", Polym. Degra. Stab., **59**, 145, **(1998)**.
5. Prepared by BCS incorporator, "Accelerating Ionic Liquid Commercialization", Research Needs to Advance New Technology**,** June, **(2004)**.
6. E. Lichtfouse, J. Schwarzbaure, and Didier; "Environmental Chemistry: green chemistry and pollutants in ecosystem", J. Springer, 542, **(2000)**.
7. S. Flanagan, E. Hall, W. Bowie, J. W. Fuhs, R. Logan, F. Maniei and A. Hunt; "A design of experiment approach to modeling activity coefficients in solvent mixtures", Green Chem., **7**, 333-338, **(2005)**.
8. H. M. A. Abood, "New ionic liquid made from hydrated aluminum sulfate with amide", Patent pending, Central Organization for Standardization and Quality, Property division, Application no. 336/2011, **(2011)**. IRAQ.
9. A. M. Weinberg; "The first Nuclear Era; the life and times of a technological fixer", J. Amazon, 198-200, **(1994)**.

10. B. N. Hoglund; "What is Molten Salts and Its Technolog?", J. Amazon, **(1997)**.
11. D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth and G. B. Deacon; "Low viscosity ionic liquids based on organic salts of the dicyanamide anion", Chem. Commun., **16**, 1430, **(2001)**.
12. E. F. Borra, O. Seddiki, R. Angel, D. Eisenstein, P. Hickson, K. R. Seddon and S. P. Worden; "Deposition of metal films on an ionic liquid as a basis for a lunar telescope", **447**, 979-981, **(2007)**.
13. S. Gabriel and J. Weiner; "Ueber einige Abkmmlinge des Propylamins", **21**, 2669-2679, **(1888)**.
14. P. Walden; "Molecular size and electrical conductivity of some salts", Bull. Acad. Imper. Sci. (St. Petersburg), 405-422, **(1914)**.
15. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung; "Electrochemical scrutiny of organometallic iron complexes and hexamethylbenzene in a room temperature molten salt", Chem. Soc., **97**, 3264, **(1975)**.
16. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey; "Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis", Inorg. Chem., **21**, 1263-1264, **(1982)**.
17. R. J. Gale and R. A. Osteryoung; "Potentiometric investigation of dialuminium heptachloride formation in aluminum chloride-1-butylpyridinium chloride mixtures", Inorganic Chemistry, **18**, 1603, **(1979)**.
18. J. S. Wilkes and M. J. Zaworotko; "Air and water stable 1-ethyl-3-methyl imidazolium based ionic liquids", Chem. Commun., 965-967, **(1992)**.

19. P. bonhŏtte, A. Dias, N. Papageoroiu, K. Kalyanasundraram and M. Grätzel; " Hydrophobic, highly conductive ambient-temperature molten salts", Inorg. Chem., **35**, 1168, **(1996).**
20. A. P. Abbott, G. Capper, D. L. Davies, H. Munro, R. Rasheed and V. Tambyrajah; "Preparation of novel, moisture-stable, lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains", Chem. Commun, 19, **(2010)**.
21. A. P. Abbott, C. A. Eardley, N. R. S. Farley and A. Pratt; "Novel room temperature molten salts for aluminum electrodeposition" Trans. Inst. Met. Finish, **77**, 26, **(1999)**.
22. V. Tambyrajah, P. R. Jenkins, R. C. Morales, D. L. Davies and A. P. Abbott; "The regiospecific fischer indole reaction in choline chloride and $ZnCl_2$ with product isolation by direct sublimation from the ionic liquid", Chem. Commun, 158, **(2004).**
23. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne, K. S. Ryder; " Hydrated aluminum salts-amide room temperature ionic liquids", Chem., Commun., **47**, 3523, **(2011)**.
24. T. Welton; "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis", Chem. Rev., **99**, 2071-2084, **(1999).**
25. C. Chiappe, D. Pieraccini; "Ionic liquids: solvent properties and organic reactivity", J. Phys. Org. Chem., **18**, 275-297, (2005).
26. J. S. Wilkes; " A short history of ionic liquids-from molten salts to neoteric solvents", **4**, 73-80, (2002).
27. A. J. Walker and N. C. Bruce; "Cofactor-dependent enzyme catalysis in functionalized ionic solvents", Chem. Commun., **22,** 2570-2571, **(2004).**
28. P. Wasserscheid and W. Keim; "Ionic liquids new solutions for transition metal catalysis", Angew Chem., Int. Ed., **39**, 3772, **(2000).**

29. C. Hardacre, K. Seddon and J. McGrath; "Room temperature ionic liquids", J. Chem. Eng. Data, **55**, 1390-1395, **(2004).**

30. N. Papaiconmou, N. yakelis, R. Bergman, and J. M. Prausntiz; "Synthesis and properties of seven ionic liquids containing 1-methyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations", J. Chem. Eng. Data, **51**, 1389-1393, **(2006).**

31. R. Renner; "Ionic Liquids: an Industrial Cleanup Solution", Enviro. Sci. & Tech., **35**, 410-413, **(2001).**

32. P. Wasserscheid and Thomas Welton; " Ionic liquid in synthesis: direct in organic and organometalic synthesis", 2nd edition, Wiley, Vol. **2**, 569-572, **(2007)**.

33. IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), Online corrected version: (2006) "complex", **(1997)**.

34. IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), Online corrected version: (2006) "coordination entity", **(1997)**.

35. Chemistry-dictionary.com - Definition of coordination sphere.

36. S. Steven and Zumdahl; Chemical Principles, Fifth Edition. New York: Houghton Mifflin. 943-946, 957, **(2005).**

37. N. N. Greenwood, N. Norman, Earnshaw and Alan; Chemistry of the Elements (2nd ed.), Oxford: Butterworth-Heinemann, **(1997).**

38. L. Gary, Miessler and D. A. Tarr; Inorganic Chemistry 2nd edition, 642, **(1999).**

39. F. Albert Cotton, G. Wilkinson and C. A. Murillo; Advanced Inorganic Chemistry, 6th edition, 1355, **(1999).**

40. D. Harris and M. Bertolucci; Symmetry and Spectroscopy. New York, Dover Publications, **(1989).**

41. F. Albert Cotton and G. Wilkinson; "Advanced Inorganic chemistry", 4th edition, A Wiley intercince publication, **(1981).**

42. J. E. Huheey; "Inorganic Chemistry, Principles and reactivity", 4th edition, Harper, New York, **(1993)**.

43. F. Awad; "Coordination of some transition metal ion complexes in choline chloride/tartaric acid room temperature ionic liquid", MSC. Thesis, Al-Nahrain University, Iraq, **(2008).**

44. E. I. Eweka and D.H. Kerridge; "Solution chemistry of molten amide-nitrate eutectic", Chem. Papers, **53**, l, 11-15, **(1999).**

45. H. Walter and Kohl; "Handbook of materials and techniques for vacuum devices", Springer, 164–167, **(1995).**

46. F. Arnold, Holleman, Egon, Wiberg and Nils; "Iron" (in German). Lehrbuch der Anorganischen Chemie (91–100 ed.). Walter de Gruyter, 1125–1146, **(1985).**

47. N. N. Greenwood and A. Earnshaw; "Chemistry of the elements", A Wiley intercince publication, 3rd edition, **(1986).**

48. H. M. Irving, R. J. Williams; "The stability of transition-metal complexes", J. Chem. Soc., 3192–3210, **(1953)**.

49. C. Robert and Weast; " Handbook of Chemistry and Physics (62nd ed.)", 74-75, **(1981)**.

50. M. Phyllis, Kurzer, Frederick and Sanderson; "Urea in the History of Organic Chemistry", J. Chemical Education (American Chemical Society), **33**, 452–459, **(1956)**.

51. Calculations using Orgel Diagram and Tanabe-Sugano diagram, From Wikipedia, the free encyclopedia.
52. R. J. Lancashire; "Chemistry of the first row transition metal complexes", Inorg. Chem., September, **(2005).**
53. CHEM 340, Lect-14, the using of Tanabe-Sugano diagram. (WWW.encyclopedia.org), **(2004)**.
54. M. Ali; "Ultraviolet Visible investigation of some transition metal compounds in room temperature ionic liquids molten salts", M.SC. Thesis, Al-Nahrain University, Iraq, **(2008).**
55. J. J. Lagowski; "The chemistry of non-aqueous solvents", 4th edition, Academic press, Vol. **5**, 1966-1978, New York, **(1978).**
56. I. J. Zsigrai, S. B. Gadzuric and R. Nikolic; "Cobalt (II) chloride complexes in calcium nitrate tetrahydrate melt", Institute of nuclear science, **80**, 1930-1933 **(2000).**
57. S. Jelena, N. Ruzica and V. Agan; "Cobalt (II) chloride complex formation in Acetamide-Calcium nitrate tetrahydrate melt", J. of solution chemistry, **33**, 287-300, **(2004).**
58. D. M. Gruen and R. L. McBeth; "The coordination chemistry of 3d transition metal ions in fused salt solutions", Pure Appl. Chem. , **6**, 23, **(1963).**
59. H. A. Qye and D. M. Gruen; "Densities of molten $AlCl_3$ and NaCl-$AlCl_3$ mixtures", Inorg. Chem., **4**, 8, 1173, **(1965).**
60. G. Stanescu and Ath. Trutia; "On absorption spectra of $CoCl_2$/aceton systems", J. optoelectronic and advance material", **7**, 1009, **(2005).**
61. H. Jahn and E. Teller; "Stability of Polyatomic Molecules in Degenerate Electronic States. I. Orbital Degeneracy", **161**, 220-235, **(1937).**

الخلاصة:

تم اكتشاف سلوك بعض الايونات ألموجبه للمعادن الانتقالية [Cr (III)، Fe (III)، Fe (II)، Co (II)، Ni (II)، Cu (II)] في السائل الأيوني لشب الأمونيوم – يوريا. والتحليل الطيفي لهذه العناصر والذي تبعه دراسات الأشعة فوق البنفسجية الإلكترونية كان لاقتراح الشكل الهندسي المنسق في السائل الأيوني وتقدير الشكل الأيوني الذي يرتبط بالايونات ألموجبه للعناصر الانتقالية .

أن فعاليه الايونات ألموجبه المعدنية تختلف عن بعضها البعض . ففي الايونات ألموجبه للكروم (III) كما هو متوقع أن يكون ذا شكل هندسي ثماني السطوح في أنواع السوائل ألايونيه، ويكون خاملا تجاه الأملاح المضافةله . وبالمثل الحديد (III) لا يظهر ميلا للتفاعل مع الأملاح التي تضاف له، ومع ذلك ساد عليه ظهور حزم انتقال الشحنة . أما الحديد (II) كانت له ظاهره مثيرة للاهتمام وهي البرم المرتفع للشكل ثماني السطوح الذي يرتبط مع الثايوسيانيد و ظهور البرم المنخفض للشكل ثماني السطوح عند إضافة النتريت .

وأظهر الكوبلت (II) سلوكا مثيرا للاهتمام في السائل الأيوني شب الامونيوم-اليوريا، لأنها متناسقة على شكل ثماني السطوح مع الأجزاء الأيونية. ومع ذلك عندما تمت دراسة هذا المحلول مع زيادة تركيز الثايوسيانيد، حيث وصل إلى ٣٥ ثايوسيانيد : ١ كوبلت مول ، ظهر تغير تدريجي في الشكل الهندسي على الأطياف و ربما تم تشكيل شكل رباعي السطوح في خليط المعقد مع وجود بعضا منه في شكل ثماني السطوح الأصلي.

أن حد قابلية الذوبان للنتريت في السوائل الأيونية قد توقف عندما وصلت النسبة إلى ١ للكوبلت (II) : ٥ للنتريت.

كما أظهر النيكل (II) السلوك ثماني السطوح في السائل الأيوني وتفاعل مع الأملاح المضافة له وتحديدا عند زيادة تركيز النيكل إلى ٣٠ حيث تغير اللون من الأخضر الشاحب إلى الأخضر الزيتوني.

وأظهرت الايونات ألموجبه للنحاس (II) لونا ازرقا واضحا ، و تشير أطيافه إلى تكون شكل ثماني السطوح ، في حين عند أضافه النتريت لا يظهر أي تغير في اللون ولكن تم تسجيل امتصاصية اقل. ومع ذلك، يبدو أن ثايوسيانيد يتفاعل مع النحاس الموجود في السائل الايوني وبذلك ينتج محلول اخضر حاوي على رواسب مع امتصاصية أقل بكثير مما مع السائل الأيوني وحده.

ومن المثير للاهتمام، لم يتم العثور على جزيئات الماء الموجودة في شب الأمونيوم الأصلي لترتبط مع الايونات ألموجبه المعدنية، كما تم العثور على أطياف تختلف بالمقارنة مع تلك التي تم الحصول عليها في المحلول المائي.

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تحليل الطيف الالكتروني لمركبات ايونات بعض العناصر ألانتقالية في سائل ايوني جديد

رسالة مقدمة إلى
كلية العلوم– جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير في الكيمياء

من قبل

زينة نذير رجب

بأشراف

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