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Department of Chemistry

SPECTROSCOPIC INVESTIGATION FOR SOME TRANSITION METAL SALTS IN IONIC LIQUID

A Thesis
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Supervisor Certification

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Committee certification

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

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2013

الاهداء

بسم الله الرحمن الرحيم

(وقُلْ إعْمَلوا فَسَيرى اللهُ عَمَلَكُمْ وَ رَسولُهُ و المُؤمِنونْ)

صدق الله العظيم

إلى من بلغ الرسالة وأدى الأمانة ونصح الأمة، إلى نور العالمين نبي الرحمة سيدنا محمد (صلى الله عليه واله وصحبه اجمعين)

إلى من أضاء بعلمه عقل غيره و هدى بالجواب الصحيح حيرة سائليه، فأظهر بسماحته تواضع العلماء وبرحابته سماحة العارفين، الى استاذي الجليل المشرف على رسالتي (الدكتور هادي محمد علي عبود) المحترم ادامه الله منهلاً للعلم والمعرفة.

الى من علمني ان اصمد امام امواج البحر الثائرة ، إلى من علمني العطاء بدون انتظار، إلى من أحمل أسمه بكل افتخار..... الى (ابي الحنون).

إلى معنى الحب و الحنان والتفاني ، إلى بسمة الحياة وسر الوجود، إلى من كان دعائها سر نجاحي وحنانها بلسم جراحي ..... الى (امي الحبيبة).

الى من بهم أكبر وعليهم أعتمد، إلى توائم روحي ورفقاء دربي، الى من بوجودهم اكتسب قوة لا حدود لها ..... الى (اخواتي الحبيبات واخي الحبيب).

إلى الأخوات اللواتي لم تلدهن أمي، إلى من كانوا معي على طريق النجاح والخير، إلى من عرفت كيف أجدهم وعلموني أن لا أضيعهم ..... الى (صديقاتي العزيزات).

مروة حميد فاضل

٢٠١٣

Abstract:

Aluminum chloride-urea ionic liquid was investigated by Lewis acid-base titration with chloride ions for its active species concentration with the aide of electronic spectroscopy. A coordination bonds between aluminum cationic species of the ionic liquid and the aromatic ring of toluene or benzene was assumed to be responsible for new bands formed in visible and ultraviolet regions.

Upon Lewis acid-base titration these bands was found to disappear and the concentration of the acidic species therefore was elucidated to be around 75 mole % of the initial aluminum chloride used to prepare a 1.5 mole aluminum chloride to 1 mole urea ionic liquid. The product of this reaction was assumed to be between mole acidic species to mole chloride ion according to the mole fraction elucidated graph.

The behavior of some transition metal compounds (chlorides and sulfates) of (Cu(II), Co(II) and Ni(II)) coordination in the ionic liquid was also investigated in this ionic liquid by electronic spectroscopy. Cobalt chloride showed a different behavior than the distorted octahedral geometry of copper chloride as it reacted with the anionic species to precipitate as form of a tetrahedral complex containing urea, aluminum and chloride ions.

The behavior of nickel sulfate in the ionic liquid also showed an acid-base reaction with the acidic species of ionic liquid as the bands at 334 nm and 474 nm decreased with increasing the salt concentration. The coordination of Ni(II) cation was found to be an octahedral geometry with stronger ligand field effect. Similar strong ligand field was also observed with copper sulfate which showed four bands resulted from separating metal d-orbitals more obviously than the tetragonal John-Teller effect found with copper chloride in same ionic liquid.

List of Abbreviations

Abbreviations	**Name**
RTIL	Room temperature ionic liquid
$[EtNH_3]\ NO_3$	Ethylammonium nitrate or ethylamine nitrate
BMIM	1-Butyl-3-Methyl Imidazolium
$[BMP]Tf_2N$	1-butyl-1-methyl pyrrolidinium bis (tri fluoro methyl sulfonyl) imide
$[(CF_3\ SO_2)_2\ N]^-$	Bis (tri fluoro methyl) sulphomide anion
PF_6	Hexa fluoro phosphate
BF_4	Tetra fluoro borate
$[RhCl(PPh_3)_3]$	tris(tri phenyl phosphine) rhodium chloride
$[CF_3CO_2]$	Tri fluoro acetate

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Chapter One

Introduction

1.1 General Concept of ionic liquid:

For two millennia, most of our understanding in chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Most chemical reactions have been carried out in molecular solvents recently, however, a new class of solvents have emerged—ionic liquids [1]. These solvents are often fluids at room temperature, and consist entirely of ionic species. They have many fascinating properties which make them of fundamental interest to all chemists, since both the thermodynamics and kinetics of reactions carried out in ionic liquids are different to those in conventional molecular solvents, thus the chemistry is different and unpredictable at the current state of knowledge[1].

Classical organic solvents as toluene, diethyl ether or methanol are bound in their application by e.g. their boiling point; ionic liquids do not encounter this problem. Their vapor pressure is negligible under most reaction conditions used [2,3]. As they are made up of at least two components which can be varied (the anion and cation), the solvents can be designed with a particular end use in mind, or to possess a particular set of properties [1]. Furthermore, their potential as green solvents due to lack of volatility attracted a lot of interest as they have been successfully employed in various technical processes [4], but arguably the most outstanding quality after all is their modularity to which they owe their name 'designer solvent'.

At first, the prospect of carrying out chemical reactions in ionic liquids may seem daunting to a chemist who has not worked with them before, but it turns out that carrying reactions out in ionic liquids can be exceptionally easy. The first room-temperature ionic liquid ethyl ammonium nitrate $[EtNH_3]$ $[NO_3]$ (m.p. 12 °C) was discovered in 1914 [2]. This organic salt already was a room temperature ionic liquid, but didn't prompt any significant interest at that time. This was surprising as this discovery brought out a new class of solvents. It took about two decades (1934) [5] before the next ionic liquid was presented to the public in a patent. In this patent it was claimed that certain organic salt have the ability to dissolve cellulose and alter its reactivity [5], later on, in 1948 this ionic liquid was followed by chloroaluminate base ionic liquids [6], but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum (III) chloride and *N*-alkyl pyridinium chloride [7] or 1, 3-dialkylimidazolium chloride [8].

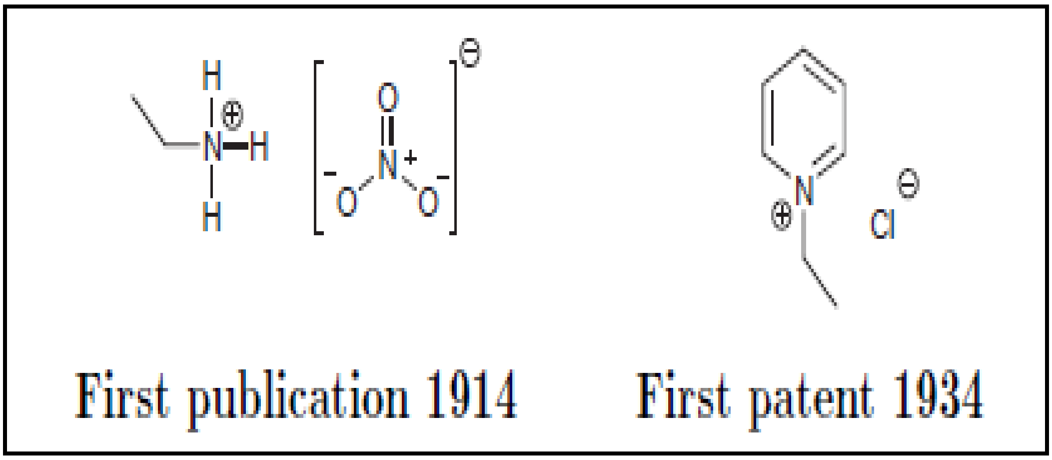

Fig. (1.1): First ionic liquids reported [2, 5].

At this point ionic liquid were still more interesting to electrochemists rather than to organic or catalytic chemists. Just one paper about a homogenous reaction, the hydroformylation, in an ionic liquid was published by Parshall in 1972 [9]. But other scientists had chosen to focus more on their electrochemical properties like e.g. Swain et al. [10]. He used tetraalkylammonium ionic liquid to describe kinetic and electrochemical effects. In 1975 the Osteryoung [7] group and Gilbert et al.[11] studied the physical properties of pyridinium-based chloroaluminate ionic liquid, an ionic liquid that raised hope to be applicable in batteries, especially by the United Sstates air force. This hope had to be abandoned duo to the easy reducibility of the pyridinium moiety, a real constraint for application in batteries. Thus, seven years later in 1982 Wilkes and Hussey [12] tried to look for a less reducible cation by MNDO (modified neglect of differential overlap) calculations [13].

In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point [14]. Ionic liquids come in two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved).

For example, $[EtNH_3][NO_3]$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present. Examples of ionic liquids consisting of a simple salt are given in (Fig. 1.2), and these show room temperature melting behavior.

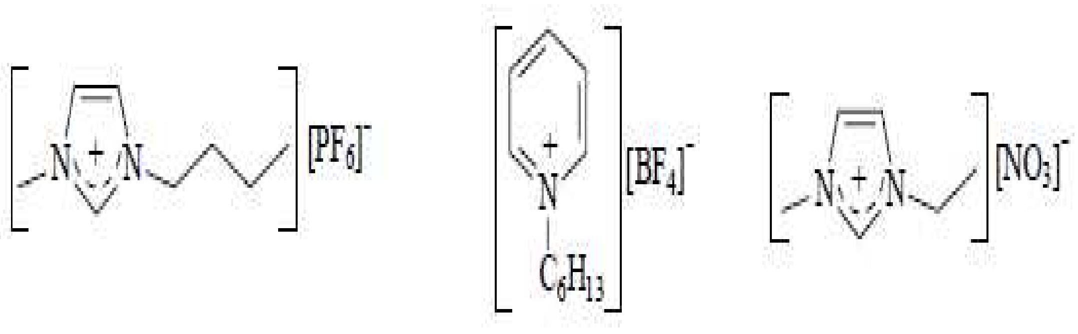

Fig. (1.2): Examples of simple room-temperature ionic liquid[1].

For the binary systems, the melting point depends upon composition, and this complex behavior has been studied extensively for the archetypal system, [emim] Cl-$AlCl_3$ ([emim] $^+$ = 1-ethyl-3-methylimidazolium) [15]. Ionic liquids have been described as designer solvents [16], and this means that their properties can be adjusted to suit the requirements of a particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions. For example, the melting points of 1-alkyl-3-methylimidazolium tetrafluoroborates [17] and hexafluorophosphates [18] are a function of the length of the 1-alkyl group, and form liquid crystalline phases for alkyl chain lengths over 12 carbon atoms. Another important property that changes with structure is the miscibility of water in these ionic liquids. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but at or above 6 carbon atoms, they form a separate phase when mixed with water [1]. This behavior can be of substantial benefit when carrying out solvent extractions or product separations, as the relative solubility of the ionic and extraction phase can be adjusted to make the separation as easy as possible.

1.2 Characterization of Ionic Liquid:

Ionic liquids are one kind of molten salts with melting points of below 100 ° C, and sometimes as low as -96 ° C giving a liquid with ionic properties at least to some extent, most of these liquids have organic cations and inorganic anions. They possess a wide liquid rang, in some cases in excess of 400 ° C which represent a new class of solvent with non-molecular, ionic character. The apparently somewhat arbitrary line drowns between molten salt and ionic liquids at a melt temperature of 100 ° C can be justified by the abrupt improvement in the range of applications for liquid salts below this temperature [19].

Ionic liquids are attractive solvents as they are non-volatile, non-flammable, have a high thermal stability and are relatively inexpensive to manufacture. They usually exist as liquids well below room temperature up to a temperature as high as 200 ° C [20, 21].

Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstandingly good solvents for a variety of compounds, and their lack of a measurable vapor pressure makes them a desirable substitute for Volatile Organic Compounds (VOCs).

The key-point about ionic liquids is that they are liquid salts, which means that they consist of a salt exists in the liquid phase and have to be manufactured, they are not simply salts dissolved in liquid. Usually one or both of the ions is particularly large and the cation has a low degree of symmetry, these factors result in ionic liquids having a reduced lattice energy and hence lower melting points [1].

Ionic liquids are interesting for the special properties unique to fluids of chareged particals and for applications of ionic liquids as environmentally friendly as solvent [22] .

1.2.1 Advantages and Disadvantages of Ionic Liquids:

RTILs possess a unique array of physicochemical properties that make them suitable numerous task-specific applications in which conventional solvents are non-applicable or insufficiently effective. Such properties include:

1. Density: Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g cm^{-3} and their densities decrease with increase in the length of the alkyl chain in the cation. The densities of ionic liquids are also affected by the identity of anions [23, 24].

2. Viscosity: Generally, ionic liquids are more viscous than common molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature [25, 23]. The viscosity of ionic liquids is determined by Van der Waals (VDW) [27] forces and hydrogen bonding. Electrostatic forces may also play an important role. Alkyl chain lengthening in the cation leads to an increase in viscosity. This is due to stronger Van der Waals forces between cations leading to increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced effect on viscosity [28].

3. Melting Point: Ionic liquids have been defined to have melting point below 100 ° C and most of them are liquid at room temperature. Both cations and anions contribute to the low melting points of ionic liquids. The increase in anion size leads to decrease in melting point [3]. Cations size and symmetry make an important impact on the melting point of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction [24].

4. Conductivity: Ionic liquids have reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to 10 mS cm-1) [27]. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on the fact that ionic liquids are composed solely of ions, it would be expected that ionic liquids have high conductivities. This is not the case since the conductivity of any solution depends not only on the number of charge carriers but also on their mobility. The large constituent ions of ionic liquids reduce the ion mobility which in turn leads to lower conductivities. Furthermore, ion pair formation and/or ion aggregation lead to reduced conductivity. The conductivity of ionic liquids of higher viscosity exhibit lower conductivity. Increasing the temperature increases conductivity and lowers viscosity [29].

5. **Stability and Thermal Stability:** In most of these applications, 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 incorporated 1, 3-dialkyl imidazolium cations are generally more resistant than traditional solvent under certain harsh process conditions, such as those occur in oxidation, photolysis and radiation processes [32]. Ionic liquids can be thermally stable up to

temperatures of 450 ° C. The thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively [3].

6. **Electrochemical window:** By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. As known in aqueous solution, the electro-deposition of elements and compounds is limited by the low electrochemical window of water (about 1.2 V). On the contrary, ionic liquids have significantly larger electrochemical windows, e.g. 4.15 V for [bmim] BF_6 at a platinum electrode, 4.10 V for [bmim] BF_4 and 5.5 V for [BMP] Tf_2N at a glassy carbon electrode [30].

7. Low nucleophilicity and capability of providing weakly coordinating or non-coordinating environment [31].

8. Color: High quality ionic liquid incorporating $[bmim]^+$ cation and a variety of anions such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3CO_2]^-$ 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 yellow to orange. The formation of the color has been attributed to the use of row materials with color or excessive heating during the synthesis of imidazolium salt [32, 33].

9. Hygroscopicity: The water content has an influence on the viscosity of ionic liquids. Viscosity measurements indicate that ionic liquids become less viscous with increasing the water content. Hydrolysis problems can also occur. Most of the ionic liquids have extremely low vapor pressure, which allows removing water by simple heating under vacuum.

10. Hydrophopicity: The degree of polarity can be varied by adapting the length of the 1-alkyl chain (in 1, 3-substituted imidazolium cations). The anion chemistry has a large influence on the properties of ILs, though little variation in properties might be expected between same-cation salts of these species, the actual differences can be dramatic, for example, $[bmim]PF_6^-$ is immiscible with water, whereas $[bmim]BF_4^-$ is water soluble [32].

1.3 Synthesis of Ionic Liquids:

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

1- Metathesis reactions: are good candidates for those new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials [34(b)].

$$[EMIM]I + Ag[BF_4] \rightarrow [EMIM][BF_4] + AgI\downarrow \quad \text{at } (12°C)$$

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 in vacuum [34(b)].

$$\text{Solfonic acid} + [R_4N][OH] \rightarrow [R_4N][RSO_3] + H_2O$$

3- Direct combination of salts: direct combination of a halide salt with a metal halide [34(b)], such as:

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

When a large amount of $AlCl_3$ was used it gave $[Al_2Cl_7]^-$ this considered (acidic part), and the addition of excess from $AlCl_3$ gave $[Al_3Cl_{10}]^-$, this reaction must prepare in dry and high purity conditions.

4. Eutectic method: Another method for ionic liquid preparation:

Choline chloride + urea → [choline chloride] [urea]

The imidazolium-based ionic liquids can be derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide, in general the chloride[25]. This precursor is prepared by alkylation of 1-methylimidazole. The alkylation is carried out in an autoclave, at 6 atmosphere of nitrogen and 90 ° C without addition of solvent, if the chloroalkane is gaseous at room temperature(e.g.,chloroethane). Higher homologues can be prepared under atmospheric pressure [25].

This precursor is then either used in a metathetic reaction, where the 1-alkyl-3-methylimidazolium halide is reacted with a Group 1 metal salt, in particular a sodium salt, or a silver salt of the desired anion, or in an acid-base neutralization reaction [25]. This reaction is stoichiometric and, therefore, equimolar amounts of waste MX or HX are produced. This could be circumvented by the direct alkylation of 1-methylimidazole with, for example, alkyl trifluoromethanesulfonate or alkyl bis(trifluoromethanesulfonyl) amide [26].

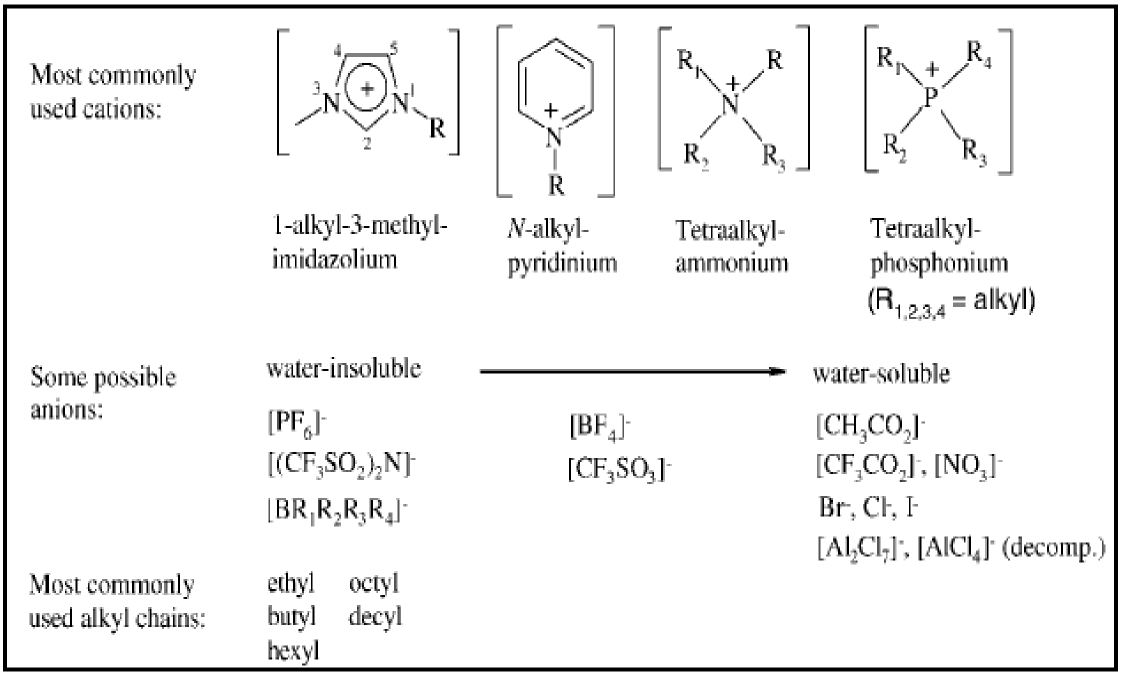

Fig. (1.3): The building blocks of ionic liquids.

1.4 The Aluminum Chloride-Based Ionic Liquid:

Chloroaluminate ionic liquids are one of the most widely studied topics in the condensed phase at present. They were initially of interest for the reduction of aluminum for both battery and plating applications [36, 37].

Hurley and Weir [38] stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. Ionic liquids were in some period discovered by US scientists Hurley and Weir [38] at the Rice Institute in Texas in 1951while looking for a cheaper and easier way to electroplate aluminum. The ionic liquid they produced was an alkylpyridinium chloroaluminate. The imidazolium cations were discovered by Hussey and Wilkes at the US Air Force Academy while looking for a replacement for the alkylpyridinium cations since they were relatively easy to reduce, both chemically and electrochemically. Their particular favorite, [ethyl methyl imidazolium] [$AlCl_4$] had a melting point below room temperature [8]. The chloroaluminate ionic liquids act as both catalyst and solvent in many processes, chemical reactions in the chloroaluminate ionic liquids, including Friedel-Crafts[39] and oligomerisation reactions [40] have been tested successfully.

In 1970s and 1980s, Osteryoung[7] and Hussey[34] carried out extensive research on organic aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by Hussey[35]. The ionic liquids based on $AlCl_3$ can be regarded as the first generation of ionic liquids.

Eutectics between $AlCl_3$ and quaternary ammonium salts were studied and they were found to contain complex anions such as $AlCl_4^-$ and $Al_2Cl_7^-$. In the last 10 years many papers has appeared where the complex anions have been replaced by discrete, closed-shell anions such as BF_4^-, PF_6^- and $(CF_3SO_2)_2N^-$ and a number of good reviews have been published in this area[41–42]. These salts have tended to have lower viscosities, higher conductivities and wider potential windows.

These liquids have been proffered as suitable for a wide variety of applications ranging from fuel desulphurization[43] to metal processing[44]. However, very few have come to practical fruition as yet although several are at pilot scale. This is partly due to the complexity of synthesis and purification. In an endeavor to produce simpler liquids with applications in metal finishing that is, large volume applications, several groups[45–46] have revisited the eutectic based ionic liquids and shown that the ideas used for aluminium eutectics are valid for other metals for example, zinc and tin. The ideas can be expanded to use hydrated metal salts [47] and even hydrogen-bond donors[48, 49] (HBD) to complex the halide ion of the quaternary ammonium salt.

The widely spread application of ionic liquids are evidenced through their use in catalysis[50], electrochemistry[51], biotechnology[52] and material processing[53]. One of the only factors linking all of these ionic liquids is the use of organic cations, most of which are nitrogen based with the vast majority containing imidazolium moieties. Metal containing ionic liquids have primarily incorporated the active metal center as a chlorometllate anion. Aluminum-based ionic liquids are well known and exemplars using imidazolium and pyridinium chlorides are amongst the first studied ionic liquids[8, 36]. In all cases aluminum forms anionic species including $AlCl_4^-$ and $Al_2Cl_7^-$[54]. One issue associated with this is the Lewis acidity and general reactivity of the metal center which is largely affected by the relative content of the Lewis base in the liquid. Cationic aluminum complexes are less common than their anionic counterparts and are certainly unknown in ionic liquids.

The majority of ionic liquids are based on quaternary ammonium or phosphonium cations[55], however it was recently shown that room temperature eutectics should also be formed between $ZnCl_2$ and simple amides and dioles. It was shown that $AlCl_3$ can also undergo disproportionation by forming a complex with acetamide or urea and the complex is liquid at ambient temperature with a 3 to 4 fold higher conductivity than the corresponding zinc chloride eutectics[57].

By varying the molar ratio of the organic salt to $AlCl_3$, basic, neutral and acidic melts can be formed. System with a molar ratio of $AlCl_3$:RCl less than 1 was reported to be basic, consist of R^+, Cl^- and $AlCl_4^-$ ions; A molar ratio of $AlCl_3$:RCl greater than 1 is acidic, which contains R^+, $Al_2Cl_7^-$ and $AlCl_4^-$ ions. The acidity of the system changes sharply about the 1:1 molar ratio. The addition of $AlCl_3$ to RCl initially leads to the formation of $AlCl_4^-$; beyond the 1:1 molar ratio composition, the $AlCl_3$ reacts with the $AlCl_4^-$ to form $Al_2Cl_7^-$. Aluminum electrodeposition is feasible in acidic melts in which polymeric forms of $[AlCl_4]^-$, $[Al_2Cl_7]^-$, and $[Al_3Cl_{10}]^-$ occur [56].

The dominant equilibrium that describes this system can be expressed as:

$$Al_2Cl_7^- + Cl^- \longrightarrow 2AlCl_4^-$$

The hepta chloroaluminate ion is a strong Lewis acid and chloride ion is the conjugate Lewis base.

To characterize the $AlCl_3$-amide complexes; Abood et. al. [57] used a variety of analytical techniques were applied to the liquids. FAB-MS showed several aluminum containing species which were $[AlCl_2.(Acet)_2]^+$ and $[AlCl_2(Acet)]^+$, slight traces of aluminum containing cations which could be $[AlCl(Aect)_5]^{2+}$.

There was primary aluminum containing anionic specie which was $AlCl_4^-$ with only small traces of $Al_2Cl_7^-$. Analogous complexes were found when using Urea as the amide although the signal for $[AlCl_2.U]^+$ was comparatively small compared with the acetamide case [57]. Jacobs and Nöcker showed that the complex $[AlCl_2 (NH_3)_4]^+ [AlCl_4]^-$ could be formed but this was a solid with a melting point of 150 ° C [58]. Similar studies with pyridine and tetrahydrofuran yielded analogous complexes with 4 neutral ligands surrounding the aluminum center and 2 additional axial chloride ligands *i.e.* an octahedral geometry [59, 60]. The speciation observed from FAB-MS suggested that the lower melting points of these complexes are due to their coordination geometry.

^{27}Al NMR spectroscopy of the $AlCl_3$-amide liquid showed the presence of 3 main peaks at $\delta_=$ 101.1, 88.6, and 73.6 ppm. The peak at 88.6 is thought to correspond to $AlCl_4^-$ since it integrates to the other two peaks. It was assumed that the peaks at δ= 101.1 and 73.6 ppm corresponded to the complexes $[AlCl_2\ (Acet)_2]^+$ and $[AlCl_2\ (Acet)]^+$ respectively [57].

The method of complexation can be determined through analysis of the IR spectra of the liquid and pure amide. Significant shifts in the stretching frequencies of the N-H were shifted from 3300 and 3151 cm^{-1} in pure acetamide to 3435 and 3361 cm^{-1} in the eutectic liquid. The C=O stretching frequencies were shifted from 1673 and 1631 cm^{-1} to 1662 and 1557 cm^{-1}. Similar shifts were also observed for the $AlCl_3$-urea liquid and these suggested that the complexation to the aluminum occurs through the oxygen on the amide. The liquid only forms in the compositional range 1:1 < amide: $AlCl_3$ < 1:2. Outside these limits a suspension of either $AlCl_3$ or amide in the eutectic forms [57].

This is clearly related to the stoichiometry of the amide: $AlCl_3$ complex, once the $AlCl_2^+$ is saturated with amide no further material will dissolve in the liquid. Therefore it can be concluded that the reaction occurring to produce the aluminum-based ionic liquid is: [57]

$$2AlCl_3 + nAmide \leftrightarrow [AlCl_2.nAmide]^+\ AlCl_4^- \qquad (3)$$

This liquid was found to be optically transparent, highly fluid and have a density of 1.4 g cm^{-3}, a conductivity of 0.804 mS cm^{-1} and a viscosity of 60 cP at 25 ° C [57]. 1:1 $AlCl_3$: acetamide and 1:1 $AlCl_3$: urea systems were found to have similar but lower conductivity and higher viscosity than the 1:1 3-butyl-1-methyl imidazolium chloride: $AlCl_3$ system (which has a conductivity of 10 mS cm^{-1} and a viscosity of 27 cP). The properties of these liquids are similar to those of other ionic liquids based on quaternary ammonium cations, and they are easy to prepare and less water sensitive than other aluminum containing liquids [57].

An inert organic solvent can be used to prepare chloroaluminate (III)-based ionic liquid; the inert solvent would in such cases provide cooling media to the thermodynamically exothermic reaction of aluminum chloride with amide (for example urea). If not prepared in inert organic solvent, the solid reaction of $AlCl_3$-Urea would require cooling the reactants to prevent the formation of hot spots that might burn some of the organic components. If this occurred, these impurities would be difficult to separate and the ionic liquid would be less pure media.

Cooling should not be extreme as the reaction needs to be warmed at least to room temperature with physical mixing to initiate the reaction, thus appeared the assistant of preparation of this type of ionic liquid in organic media.

Additional benefit can be obtained from the in situe preparation of ionic liquid in inert organic solvent is that the produced ionic liquid would have less sensitive to atmospheric moisture as the ionic liquid would be diluted in organic solvent, particularly aluminum chloride- urea ionic liquid reported to be less moisture sensitive than other types of aluminum chloride ionic liquid such as with imidazolium or pyridine.

There is a disadvantage of the ionic liquid being prepared in inert organic solvent that is the unavoidable presence of the organic solvent, which would also be easily evaporated. Therefore; a tight sealing of ionic liquids containers is necessary. An additional advantage is the reported era of electrodeposition of aluminum metal from the diluted ionic liquids in (for example) toluene.

1.4.1 Reactions in Aluminum Chloride Based Ionic Liquids:

The chemical behavior of Franklin acidic chloroaluminate (III) ionic liquids (where X ($AlCl_3$) > 0.50) is that of a powerful Lewis acid. As might be expected, it promotes reactions that are conventionally promoted by aluminum (III) chloride, without suffering the disadvantage of the low solubility of aluminum (III) chloride in many solvents. Indeed, chloroaluminate (III) ionic liquids are exceptionally powerful solvents, being able to dissolve kerogen [61], C60 and many polymers [62]. The preparation of these ionic liquids is straight forward. Simply by mixing the appropriate organic halide salt with aluminum (III) chloride results in the two solids melt together to form the ionic liquid. However, this synthesis must be performed in an inert atmosphere [1].

A classical reaction promoted by Lewis acids is the Friedel-Crafts reaction, which was found to work efficiently in chloroaluminate (III) ionic liquids[39]. A number of commercially important fragrance molecules have been synthesized by Friedel-Crafts acylation reactions in these ionic liquids[63]. Traseolide® (5-acetyl-1,1,2,6-tetramethyl-3-

isopropylindane) and Tonalid® (6-acetyl-1,1,2,4,4,7-hexamethyltetralin) have been made in high yield in the ionic liquid [emim]Cl-$AlCl_3$ (X = 0.67) (Fig.(1.4)). In the acylation of naphthalene, the ionic liquid gives the highest known selectivity for the 1-position [63].

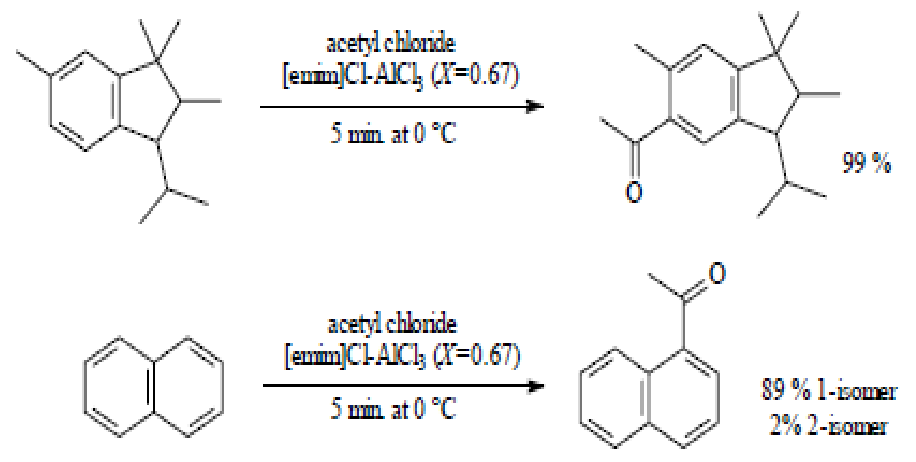

Fig. (1.4): The acetylation of 1, 1, 2, 6-tetramethyl-3-isopropylindane (upper) and naphthalene (lower) in [emim]Cl-$AlCl_3$ (x= 0.67).

Cracking and isomerization reactions occur readily in acidic chloroaluminate (III) ionic liquids. A remarkable example of this is the reaction of polyethylene, which is converted to a mixture of gaseous alkanes with the formula (C_nH_{2n+2}, where n = 3–5) and cyclic alkanes with a hydrogen to carbon ratio of less than two (Fig. (1.5))[64]. The distribution of the products obtained from this reaction depends upon the reaction temperature and differs from other polyethylene recycling reactions in that aromatics and alkenes are not formed in significant concentrations [64].

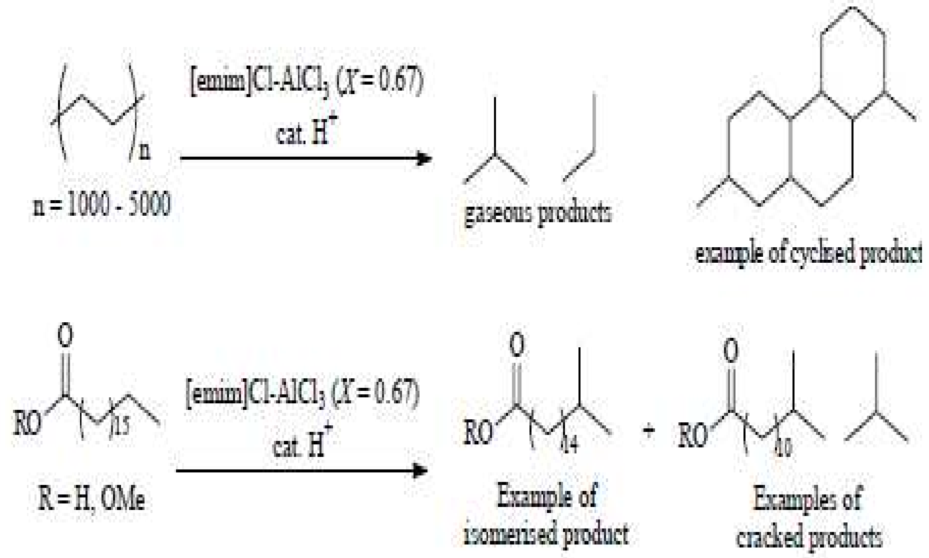

Fig. (1.5): Isomerization and cracking reactions of alkanes and alkyl chains in chloroaluminate (III) ionic liquids.

Another significant difference is that this ionic liquid reaction occurs at temperatures as low as 90 °C, whereas conventional catalytic reactions require much higher temperatures, typically 300–1000 ° C [65]. A similar reaction occurs with fatty acids such as stearic acid or methyl stearate, which undergo isomerization, cracking, and dimerization reactions. This has been used to convert solid stearic acid into the more valuable liquid, iso-stearic acid [66]. The isomerization and dimerization of oleic acid and methyl oleate has also been found to occur in chloroaluminate (III) ionic liquids [67].

The dimerization and oligomerization of olefins in the presence of homogeneous nickel (II) catalyst has been studied extensively in chloroaluminate (III) and alkylchloroaluminate (III) ionic liquids [68, 69]. Few catalysts are known that catalyze the linear dimerization and oligomerization of C4-olefins. Linear C8-olefin dimers are highly desirable intermediates for the production of C9-plasticizers, exhibiting better thermal properties than those produced from highly branched C8-olefin dimer feedstock[1].

The products of these reactions are insoluble in the ionic liquid and can be separated by decantation, leaving the ionic liquid and catalyst behind, from where the catalyst and solvent can be reused. Polycyclic aromatic hydrocarbons dissolve in chloroaluminate (III) ionic liquids to form highly colored paramagnetic solutions [70].

The addition of a reducing agent, such as an electropositive metal, and a proton source results in the selective hydrogenation of the aromatic compounds. For example, pyrene and anthracene can be reduced to perhydropyrene and perhydroanthracene at ambient temperatures and pressures; only the thermodynamically most stable isomer of the product is obtained [71].

This contrasts with catalytic hydrogenation reactions, which require high temperatures and pressures, an expensive platinum oxide catalyst and give rise to an isomeric mixture of products [72].

By careful monitoring of the reduction in the ionic liquid, a number of intermediate products can be isolated, and the sequence of the chemical reduction process can be determined (Fig. (1.6)).

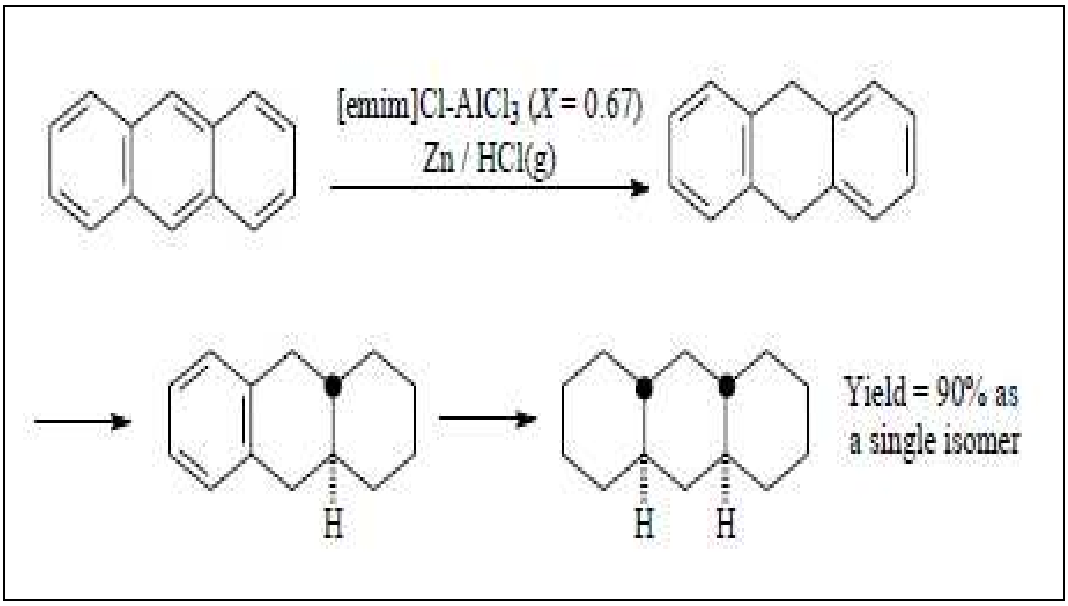

Fig.(1.6): The sequence in the reduction of anthracene to perhydroanthracene [71].

It is also possible to carry out catalytic hydrogenation reactions of cyclohexene using Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, in basic chloroaluminate(III) ionic liquids [73], but neutral ionic liquids are preferred for this type of reaction, for ease of handling and lower moisture sensitivity.

$AlCl_3$ is a Lewis acid and has been used in ionic liquids for a range of catalytic reactions [55]. To demonstrate the efficiency of the $AlCl_3$: amide (urea and acetamide) systems the acetylation of ferrocene was carried out in an analogous method to that using 1 emimI: $2AlCl_3$ [74]. The reactions were carried out in a Schlenk flask under N_2 at 0 ° C for 2 hours with subsequent work up by quenching with 2 M HCl solution and extraction with dichloromethane [57]. Interestingly, the two amide-based liquids show differing reactivity. The urea liquid gave moderate yield of each of the compounds (acetylferrocene and diacetylferrocene) whereas the acetamide liquid gave a yield of 56% of the diacetylated product with low quantities of the monoacetylated intermediate [57]. This later result is an improvement on that reported for the emim $AlCl_3I$ liquid despite the fact that there is significantly less $AlCl_3$. The fact that no product was obtained using 1:1 emimI: $AlCl_3$ suggests that $AlCl_3I^-$ is not very Lewis acidic. It also suggests that the cationic aluminum containing species is more Lewis acidic than $Al_2Cl_7^-$ [57].

Other technological applications of aluminum-based ionic liquids have been for batteries or metal deposition [75, 76].

1.4.2 Electrodeposition of Aluminum:

Electrodeposition in ionic liquids would have many advantages. The low working temperature (120 ° C and higher) compared with the hot plating process suppresses the formation of brittle intermetallic compounds in the under layer. The higher electrical conductivity of the electrolyte (by 1 to 2 orders) makes it possible to carry out the electrolysis at higher current densities. There is less toxicity, no danger of explosion and control of the thickness of the Al layer make it potentially attractive for wider application.

Aluminium can be electrodeposited in molten salts (chloroaluminate molten salts), mainly chlorides, where Al can be deposited either by using a soluble aluminium anode or the electrochemical decomposition of the electroactive species, $Al_2Cl_7^-$, which formed in the Lewis acidic molten $AlCl_3$: Alkali metal chloride mixture of molar ratio 2:1[77].

The electrochemical reduction of the electroactive species occurs as the following [78]:

$$4\,Al_2Cl_7^- + 3e^- \rightarrow Al + 7\,AlCl_4^-$$

Extensive work has been reported on the electrodeposition of aluminium from such type. The first paper on the electrolytic aluminium deposition from a molten $AlCl_3$-NaCl mixture was published at the mid of nineteenth century [79].

The first attempt to use this electrolyte for the deposition of aluminium on an iron base was made by Plotnikov and et. al. [80-81]. Chittum [82] proposed LiCl instead of NaCl. The quality of the Al layers deposited in molten electrolytes containing aluminium and alkali chlorides was examined by Orleva and Lainer [83]. Bromides as well as chlorides have been tested as possible electrolytes for the deposition of Al layers [84-85]. A systematic investigation of electrolytic aluminium-plating in molten chlorides was carried out by Delimarskii and et. al. [86-87]. From the different mixtures containing aluminium and alkali chlorides, the binary mixture with a composition corresponding to the compound $2AlCl_3.NaCl$ was found to be the most suitable electrolyte. As the electrolyte is hygroscopic, electrolysis is carried out in an inert atmosphere; furthermore dehydrating substances, such as silicagel and active coal should be added directly to the electrolyte. This increases the current efficiency of the electrolysis [88].

The results of the electrolysis of the binary aluminium chloride – alkali chloride ($AlCl_3$-MCl) mixtures, however, were disappointing as in all cases Al was deposited in the form of a dull, coarse-grained layer with low anticorrosion resistance. Therefore, numerous attempts were made to influence the process of electrocrystallization of aluminium, mainly by addition of different metals, either in the form of compounds (chlorides or oxides), or as auxiliary anodes of respective metals. The influence of Sn, Pb [86, 87], Zn, Sb, Bi [89], Mn [90], Cu, Ag, Cd, Ga, In, Tl, Ge [91] and V [92] have been studied. It was found that only Sn, Pb and Mn have a favourable influence on the properties of the deposited layer. In all cases, however, instead of pure aluminium the corresponding aluminium alloy was deposited.

Paucirova and Matiasovsky[93] in 1975 have succeeded to electroplate iron substrates by a fine-crystalline, silver-bright and non-porous aluminium layer from molten salts based on chlorides[77]. Also, they found that the optimum electrolyte for aluminium electroplating in molten salts was a quaternary mixture of 80 wt.% $AlCl_3$ + 10 wt.% KC1 + 5 wt.% NaCl + 5 wt.% NaI and in the temperature range 150 – 200 ° C with a cathodic current density of up to 7 A dm-2. G. R. Stafford reported that aluminium, aluminium–manganese and aluminium-titanium alloys can be electrodeposited from $AlCl_3$-NaCl molten salt at 150 ° C [78, 94].

The drawbacks of the $AlCl_3$-NaCl molten salt are its high $AlCl_3$ vapor pressure, which may result in explosions at elevated temperatures and the fact that the melt is very corrosive. Therefore ionic liquids might be an alternative [77].

1.4.3 Electrodeposition of Aluminium from Ionic liquids:

Electrodeposition of aluminium from ionic liquids can be performed at room temperature. The aluminium deposits obtained are usually of good quality, high purity, of low porosity and heat resistant [77]. Popular examples of ionic liquids include the chloroaluminate, which are prepared by mixing anhydrous $AlCl_3$ with a suitable organic halide. This kind of ionic liquids can be considered as the first generation of ionic liquids. Moreover, it is the simplest system from which aluminium can be easily electrodeposited. As the molar ratio of this mixture changes, the melt can be classified as basic, neutral or acidic in the sense of Lewis acidity. In the neutral 1: l melt Al is present almost entirely as $AlCl_4^-$ ions, whereas in the 2: l melt it is present as $Al_2Cl_7^-$ [77].

The melts having a molar ratio between 1: l and 2:1, both $Al_2Cl_7^-$ and $AlCl_4^-$ ions will be present. The acid-base properties of the melt at ambient temperature may be described by the following equilibrium [95]:

$$2\,AlCl_4^- \leftrightarrow Al_2Cl_7^- + Cl^-$$

In acidic melts, $Al_2Cl_7^-$ ion is the only species from which aluminium can be electrodeposited according to the following reaction [77]:

$$4\,Al_2Cl_7^- + 3e^- \rightarrow Al + 7\,AlCl_4^-$$

In presence of excess of AlCl3, the following reaction is virtually complete [77]:

$$AlCl_4^- + AlCl_3 \rightarrow Al_2Cl_7^-$$

A lot of work has been done using chloroaluminate ionic liquids to get high quality aluminium deposits by several authors. For example, $AlCl_3$ / 1-ethyl-3-methylimidazolium chloride ($AlCl_3$ / [EMIm] Cl) and the ionic liquids $AlCl_3$ / N-butylpyridinium chloride ($AlCl_3$ / N-BPC) have been widely used in electrodeposition of aluminium and its alloys [77].

Among six kinds of $AlCl_3$/ILs systems (ILs [bmim]Cl, [bmim]Br, [bmim]BF_4, [bmim]PF_6, [emim][$EtSO_4$] and [bmim][HSO_4]), which have been studied by YUE Gui-kuan, LU Xing-mei, ZHU Yan-li, WANG Hui, ZHANG Xiang-ping and ZHANG Suo-jiang [96], it was reported that $AlCl_3$/[bmim]Cl and $AlCl_3$/[bmim]Br are the most appropriate electrolytes for the electrodeposition of Al with the highest average conductivities (in the acid range where aluminum can be electrodeposited).

For ionic liquids with large halide concentrations the breakdown of metal oxides on electrode surfaces is prevalent, it is easier for ionic liquids with chloride ions which can act as good ligands for the dissolving metal ions [44].

Hussey and et. al. did intensive studies on the electrodeposition of aluminium and aluminium alloys in $AlCl_3$ / [emim] Cl ionic liquid. They succeeded to electrodeposit transition metal-aluminium alloys such as Al-Mo [97], Al-Ti [98], Al-Zr [99], Ag-Al [100], and ternary Al-Mo-Mn [101] alloys. These alloys are technologically important because of their corrosion resistance, especially pitting corrosion, and in some cases, their interesting magnetic properties.

Jiang et al.[102] have studied the electrodeposition, electrochemical nucleation and surface morphology of aluminum on both tungsten and aluminium electrodes from 2:1 molar ratio $AlCl_3$: [emim]Cl ionic liquid. The electrodeposits obtained on both tungsten and aluminium electrodes were dense, continuous and well adherent.

The $AlCl_3$ / [emim]Cl (60/40 mol.%) ionic liquid was used to electroplate mild steel by well adherent and highly resisted to scratches aluminium coatings [103] . However, the quality of the deposit can be greatly improved by utilizing pulse plating techniques [104,105] or by addition of some organic solvents such as benzene and methyl t-butyl ether that improve the deposit surface morphology. It is possible that the organic molecules[105] play the role of brighteners.

Endres et al. reported that nanocrystalline aluminium can be made electrochemically in Lewis acidic ionic liquids based on $AlCl_3$ and [emim]Cl under galvanostatic conditions by addition of nicotinic acid [106]. Also the $AlCl_3$ / 1-ethyl-3-methylimidazolium chloride ($AlCl_3$ /

[emim]Cl) melt is a viscous and transparent liquid at room temperature when the molar composition is in the range of 0.3:1 to 2:1 [107].

Lai [108] have electrodeposited aluminium in room temperature $AlCl_3$ /[emim]Cl ionic liquid on glassy carbon, platinum and tungsten. Moreover, he has studied the mechanism of the electrodeposition and dissolution processes in such ionic liquid. The obtained results indicated that the aluminium deposition process at the above-mentioned substrates is preceded by a nucleation step and is kinetically complicated. The deposited aluminium was found to be unstable and subject to a slow corrosion process. This is most likely due to impurities and organic cation present in the melt.

Also, aluminum deposition from $AlCl_3$ / [emim]Cl ionic liquid was studied employing an inverted optical microscope to perform in situ optical observations during the deposition process at tungsten electrode. Thin, continuous aluminum coatings with crystal sizes below optical microscopic resolution were produced from a 1.1:1 $AlCl_3$: [emim] Cl molten salt at potentials < -0.2 V vs. an Al (III)/Al reference electrode [77].

$AlCl_3$-based ionic liquid was reported to be colored when diluted with organic solvent (toluene), and this dilution was found to enhance the quality of the electrodeposition conducted in this type of ionic liquid. Hussey et al. studied the Lewis acidic $AlCl_3$-EMIMCl ionic liquid [> 50 mole % $AlCl_3$] and found that although aluminum could be electroplated from the neat ionic liquid, the quality of the electrodeposit is greatly improved and enhanced by the addition of benzene as a co-solvent (109). Abbott et al. studied the addition of 30% v/v of toluene to $AlCl_3$-EMIMCl ionic liquid, the addition of toluene was useful to accelerate the rate and modify the deposited aluminum particles [110].

$AlCl_3$-amide ionic liquid was found to have 3 peaks when tested by ^{27}Al NMR spectroscopy which corresponds to the presence of $AlCl_4^-$, $[AlCl_2\ (Acet.)_2]^+$ and $[AlCl_2\ (Acet.)]^+$, the size of the peak that corresponds to $AlCl_4^-$ was found to increase upon the addition of $MgCl_2$ while the other two peaks decreased [57]. Thus it was indicated that the addition of chloride ion caused the reaction of the chloride ion with the cationic parts as their peaks decreased and producing $AlCl_4^-$ as its peak increased.

This work intended to investigate the $AlCl_3$-Urea ionic liquid prepared in organic solvents (toluene and benzene) and the coordination of aluminum species in them. The ionic liquid produced was of deep red color in benzene and of dark green color in toluene. These liquids showed the presence of new bands (compared to the bands of the organic solvents) in the visible region when examined by UV/Vis. Spectroscopy. These new bands were used to detect the Lewis acid-base titration of the acidic active species $[AlCl_2\ (n.Urea)]^+$ [57] of the ionic liquid with chloride ion using potassium and calcium chloride and the determination of the concentration of these species in this ionic liquid. The coordination of some transition metals in $AlCl_3$-urea ionic liquid in toluene was investigated.

1.5 Aim of The Present Work:

Aluminum chloride is one of the widely used group three metal compounds. One of its major interests is to synthesis ionic liquids for their wide chemical applications. The new synthesized aluminum chloride-urea ionic liquid has proved to have comparable properties to these of chloroaluminate ionic liquid as catalyst for organic reactions and aluminum metal deposition at room temperature. However, the aluminum chloride-urea ionic liquid containing an active species of the type $[AlCl_2.nU]^+$ which are reported to be the major active species. And hence the aim was:-

1. Determination of the concentration and identification of the interaction of aluminum chloride-urea ionic liquid with organic diluent by investigation with spectroscopic methods.
2. In addition, studying their reactions with Lewis basic chloride ions of alkali, alkali metals and determination of the concentration of active species.
3. Moreover, elucidation of the reaction of some transition metal compounds in the diluted ionic liquid in toluene, coordination nature, and the possible complex formation in this new solvent.

2.1 Chemicals:

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

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

Chemical compounds	Purity %	Company
Aluminum chloride	98	Fluka
Urea	99.5	Thomas Baker
Toluene	99.5	Chem. Supply
Benzene	99.7	Thomas Baker
n-Hexane	99.9	Laboratory Chemical
Calcium chloride	98	Chem. Supply
Potassium chloride	99	CarloErBa
Cobalt chloride	98	Chem. supply
Cupric chloride	98	Riedel-de Haën
Cupric sulfate	99.5	Analar
Nickel sulfate	99	Riedel-de Haën

2.2 Practical Methods:-

2.2.1. Preparation of Aluminum chloride- Urea ionic Liquid:-

Aluminum chloride and urea were used to prepare the ionic liquid in different proportions which must be within 2:1 to 1:1 mole ratio to insure the formation of liquid state [57].

Two methods were adopted for this preparation:

1. Direct addition of milled urea to powder aluminum chloride when a vigorous reaction was started to form liquid. After a small portion

of ionic liquid was formed, further aluminum chloride followed by urea portions were added to this liquid and again the reaction took place to form another amount of liquid.

The increment additions of aluminum chloride and urea were continued until all the weights of both salts were consumed to form the ionic liquid.

2. The second procedure was made by reaction of the salts in an inert organic diluent solvent such as toluene, benzene and hexane. This was carried out by adding the proper portion of aluminum chloride to a reaction tube followed by the addition of organic solvent. After that the weighted out urea portion was added incrementally to the reaction tube where a reaction of urea with aluminum chloride has started indicated by the color change of the organic solvent from colorless to green color and the consuming of aluminum chloride as urea was added in each time. This was also carried out until no further urea or aluminum chloride was left in the reaction tube.

The final ionic liquids obtained from both procedures of ionic liquid preparation were kept in a sealed tube and stored in a desiccator filled with silica gel to prevent the contact of moisture with the ionic liquid.

All precipitates formed from the addition of various compounds to the ionic liquid diluted by toluene were separated by decantation and washed with toluene after words.

2.2.2. Preparation of Calcium and Potassium Chloride Mixtures with Ionic Liquid:-

Calcium chloride and potassium chloride was added to 1ml of (46.7% (1.5 $AlCl_3$: 1urea) + 53.3% toluene) ionic liquid in a series of percentage additions that calculated on the basis of the original aluminum chloride used in the preparation of the ionic liquid (10, 12.5, 14.3, 16.7, 20, 25, 33, 40, 50, 60, 75, 80, 90 and 100) mole %. Both calcium and potassium chlorides mixtures were left for 2 hours with stirring at room temperature.

The calcium chloride additions produced two layers which were composed of:-

1. Colorless upper layer liquid that was confirmed to be toluene when examined with the ultraviolet\visible spectroscopy.
2. Light green lower layer liquid which was examined by the UV\Vis. spectroscopy.

While potassium chloride additions produced three layers which were:-

1. Colorless upper layer liquid which was confirmed to be toluene by examining it with the UV\Vis. spectroscopy.
2. Light green lower layer liquid which also was examined by the UV\Vis. spectroscopy.
3. White precipitate layer was obtained after washing with toluene, and its amount increased with the sequent increment of potassium chloride additions.

The (80-100) mole % additions of potassium chloride produced the first and the third layers.

2.2.3. Preparation of Transition Metal Mixtures with Ionic Liquid:-

The transition metal compounds were added in a series of concentrations to 1ml of (46.7% (1.5 $AlCl_3$: 1urea) + 53.3% toluene) at room temperature with stirring, table (2.2), the mixtures was left for 1 hour for all additions in case of nickel and copper sulfate compounds, 20 minutes for the highest concentration of copper chloride and 3 hours in case of cobalt chloride.

Table (2.2):- Concentrations of the transition metal compounds in the ionic liquid.

Nickel and copper sulfate (M)	Copper and cobalt chloride (M)
0.2	0.1
0.5	0.2
1	0.4
1.2	0.5
1.5	0.8
1.8	1
2	

Qualitative tests were carried out using procedures outlined in "Vogel's Textbook of Macro and Semi-micro Qualitative Inorganic Analysis" [113(b)] as follows:

Chloride test was made by using silver nitrate giving white precipitate of silver chloride ion. Aluminum test was carried out using sodium hydroxide producing a white precipitate of aluminum hydroxide.

2.3 Instruments:-

The main instrument used throughout this study was the electronic spectroscopy of the resulted transition metal complexes in the ionic liquid.

2.3.1. Electronic absorption spectra:-

The electronic spectra of complex solutions were obtained by using CECEL CE7200, 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.

2.3.2. Fourier Transform Infrared spectroscopy (FTIR):-

FTIR spectra in the range (4000- 400) cm-1 were recorded using potassium bromide disc on FTIR instrument model 8000 Shimadzu, spectrophotometer, Japan.

2.4. Assignment of spectra:-

2.4.1. Orgel diagrams:-

Orgel diagrams were 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 Fig. (2.1) and (2.2). Nevertheless, there are three major limitations to use 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. [111,112]

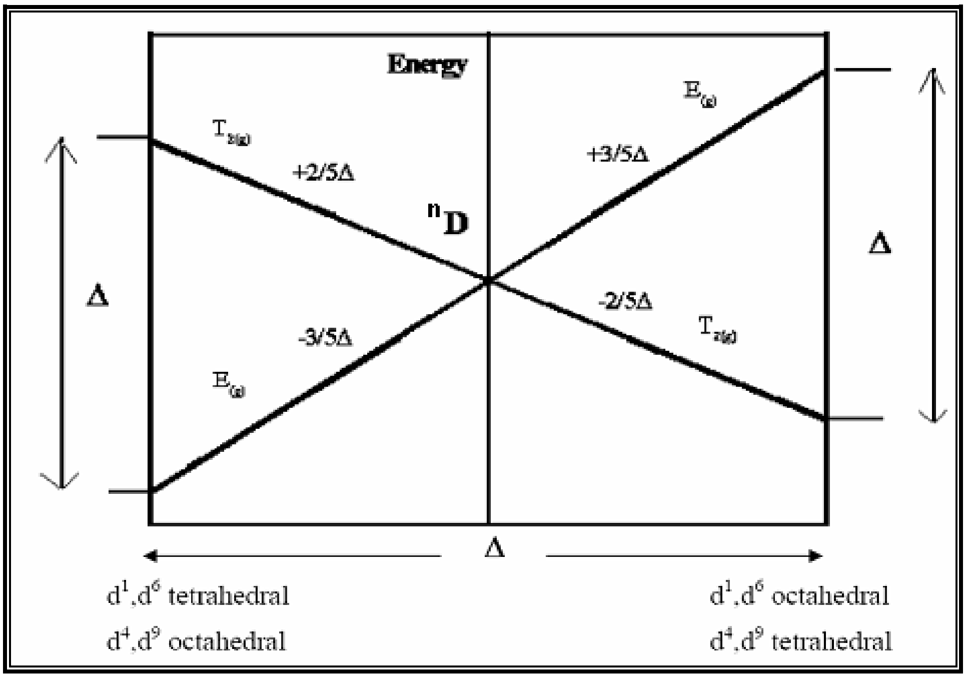

Fig.(2.1):-The splitting of free-ion D terms in octahedral and tetrahedral fields.[112]

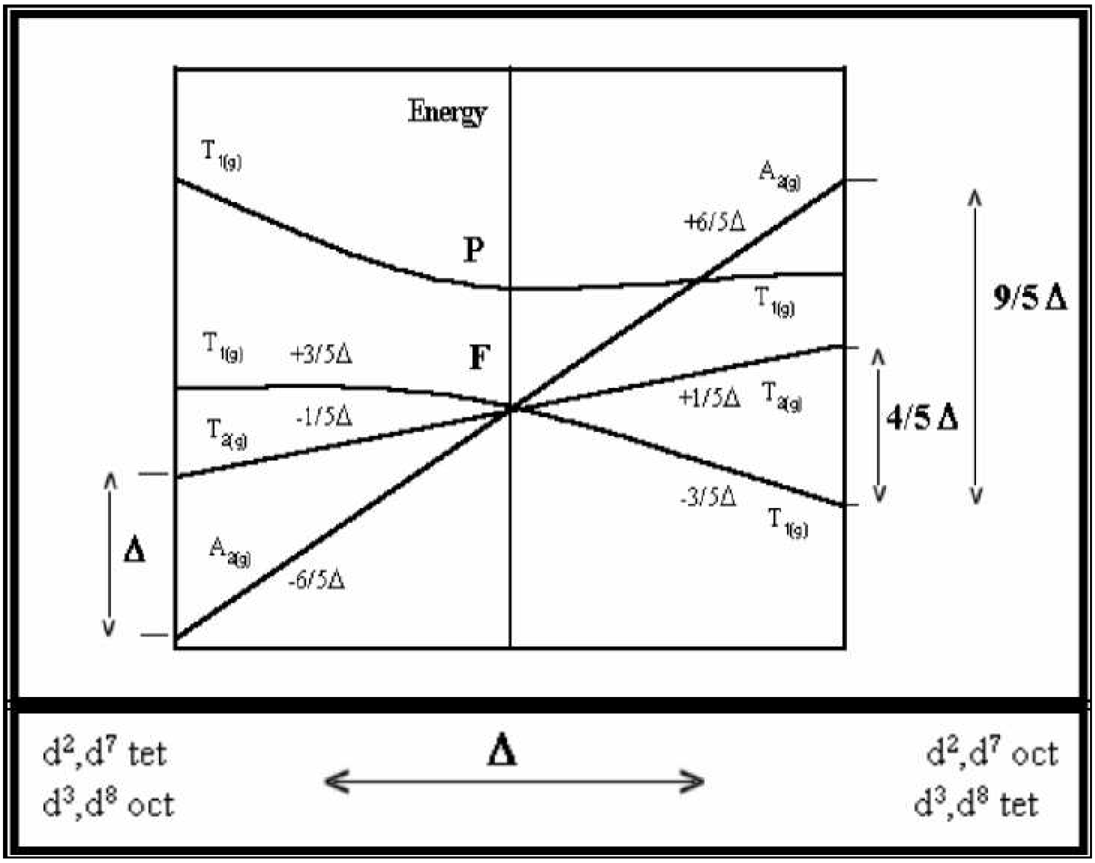

Fig. (2.2):-The splitting of free-ion F and P term in octahedral and tetrahedral fields. [112]

2.4.2. Tanabe-Sugano diagrams:-

Tanabe-Sugano diagram uses 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). [111, 112]

2.4.3. Equations:-

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

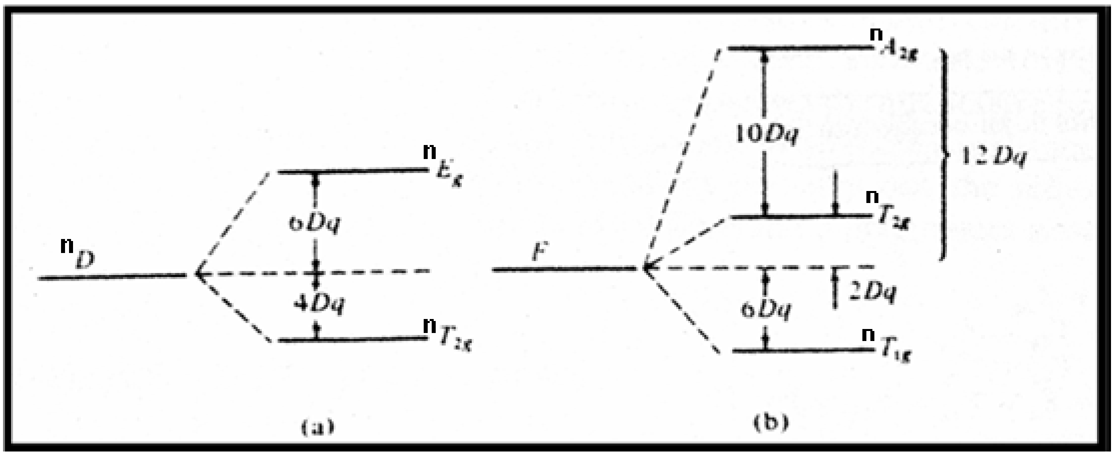

Fig. (2.3):- Splitting of terms for d^n configurations into (a) and (b). [113(a)]

Also Jorgenson rule [113(a)] have 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.[113(a)]

Transition metal ion	**Value of (g) factor**	**Various ligands**	**Value of (f) factor**
Co(II)	9.00	Cl^-	0.78
Ni(II)	8.70	H_2O	1.00
Cu(II)	12.5	Urea	0.92

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

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

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

The nephelauxetic ratio β is given by:

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

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

Chapter Three

Results &Discussion

3.1 Preparation of Aluminum Chloride-Urea Ionic Liquid in Solvents:

Aluminum chloride-urea ionic liquid can be prepared as a direct mixing of the two salts under inert atmosphere or such mixing can be carried out in an organic solvent like toluene, benzene and n-hexane. The resulted ionic liquids in these organic diluents showed similar behavior at least to the reduction-oxidation cyclic voltammogram of Al^{+3} active species [110].

The addition of a simple amide (in this case urea) to aluminum chloride caused the formation of a liquid containing cationic species $[AlCl_2.nAmide]^+$ and anionic species $AlCl_4^-$ as illustrated in the following equation [57]:

$$2AlCl_3 + n.\ Amide \rightleftarrows [AlCl_2.nAmide]^+ + AlCl_4^- \quad \ldots\ldots\ (3.1)$$

The aluminum chloride and urea reacted exothermically and immediately without external heating and the mixture reported to reach a temperature around 75 °C [57]. This ionic liquid is shown to be a suitable medium for the acetylation of ferrocene and the electrodeposition of aluminum and demonstrated that quaternary ammonium cations are not always needed to form ionic liquids [57].

3.1.1 Preparation of Aluminum Chloride-Urea Ionic Liquid in Toluene:

Toluene was not reacted with/or dissolved aluminum chloride or urea, this made the preparation of the aluminum chloride-urea ionic liquid safer, since toluene would work as a protector for the reactants and ionic liquid because the aluminum chloride and its ionic liquids known to be sensitive to moisture or water. In addition toluene would also work as a reaction medium and would help distributing the heat released from the aluminum chloride-urea exothermic reaction. This would prevent the formation of hot spots area which could lead to burn some of ionic liquid forming impurities from this side decomposition reaction.

At the same time it was found that toluene interacted with the ionic liquid changing it from faint yellow to dark green color (46.7 v/v% (1.5 $AlCl_3$:1Urea) ionic liquid and 53.3 v/v% toluene). Toluene is known to have two bands (E_2 and B) in the ultraviolet region where E_2 band has higher energy than B band and both are related to the π-π^* aromatic ring transition [115]. When toluene alone was examined by ultraviolet/visible spectroscopy in present work, these two bands were observed at 199.5nm (E_2) and 264nm (B) [Fig. 3.1] which were found to be close to those reported in literature [115].

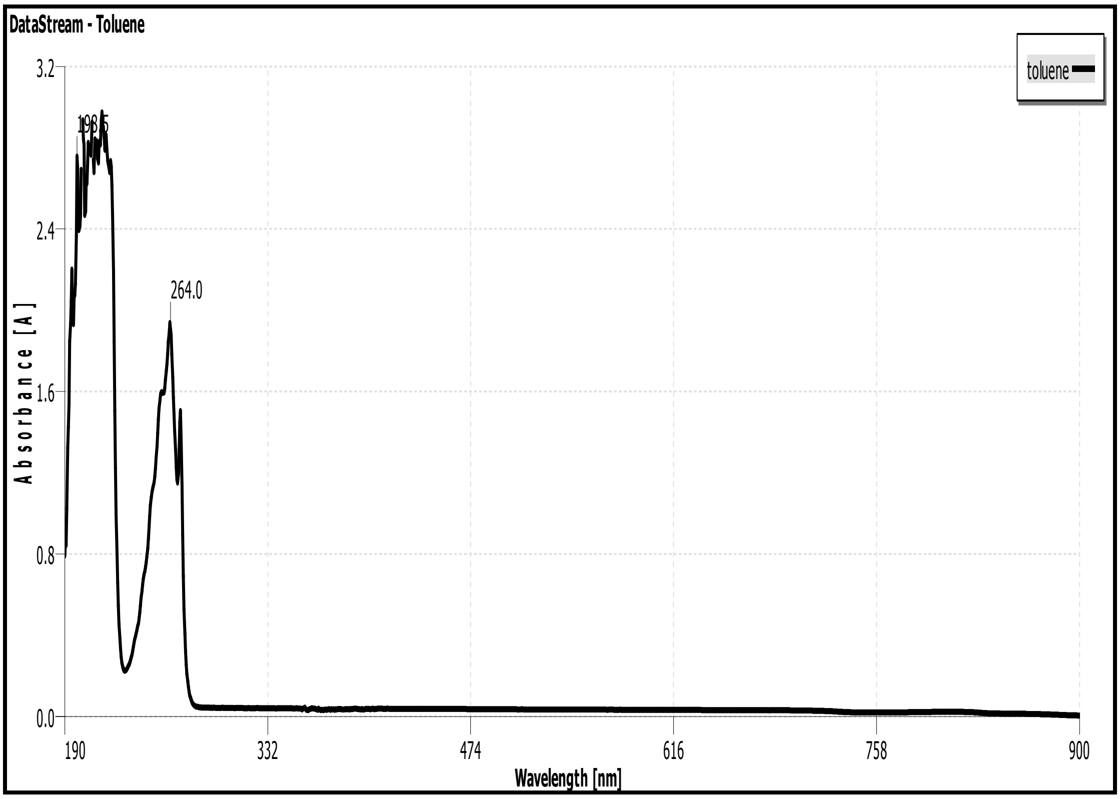

Fig. 3.1:- The ultraviolet\visible spectrum of toluene.

However, when ionic liquid was prepared in toluene, the color of the mixture was turned immediately to dark green. This dark green solution of diluted ionic liquid in toluene was examined by ultraviolet-visible spectroscopy and showed, on one hand, that the initial E_2 and B bands of toluene but observed at similar absorption wavelengths with increased absorption intensities (compare Fig.3.2,A and B).

On the other hand, two new bands at 334 and 474 nm were also recorded for ionic liquid in toluene. The latter two bands were related to an interaction of Lewis acidic species of the ionic liquid $[AlCl_2.nU]^+$ with the ring π-bond electrons of toluene causing the charge transfer between toluene and metal cationic species. This interaction may be considered as coordinated bond and electrons being donated from the π-ring bond of toluene to metal cationic species.

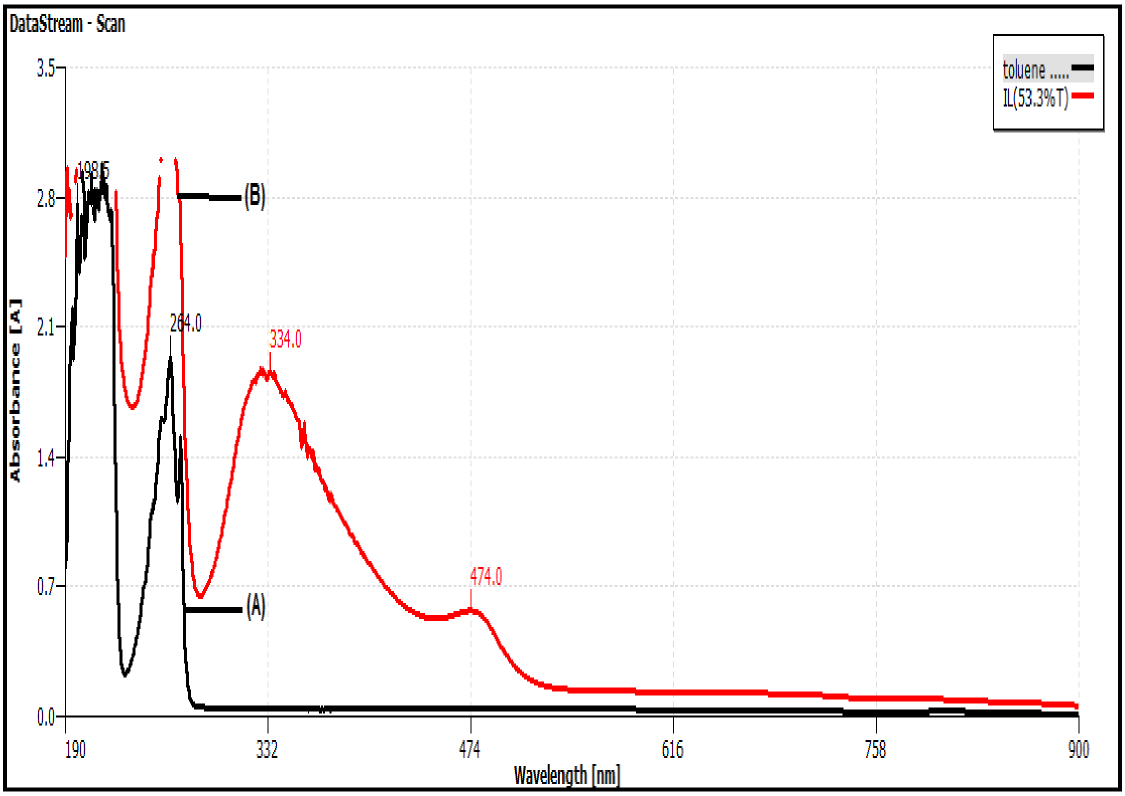

Fig. 3.2:- The ultraviolet\visible spectra of (A) toluene and (B) (1.5AlCl$_3$:1urea) ionic liquid in toluene.

This type of interaction would be analogous to those of transition metal-arene organometallic complexes which were first recognized in the 1950's [116]. Such interaction helps the addition of nucleophiles to the arene liquid causing de-protonation of acidic arene protons. η^6- metal complexes were also suggested for bi-metallic chromium carbonyl-arene complexes of chromium or tungsten as stated by Fischer [117]. In addition such interaction may enhance the reported catalytic reaction of ferrocene acylation [57]. On this basis, the original aromatic ring bands of toluene (E_2 and B) are also expected to be enhanced to higher absorbance (ε_{max}) than in toluene alone.

3.1.2 Preparation of Aluminum Chloride-Urea Ionic Liquid in Benzene:

The preparation of aluminum chloride -urea ionic liquid in benzene (80 v/v% (2AlCl3:1Urea) and 20 v/v% benzene) showed an immediate exothermic reaction between the reactants in which benzene helped to distribute the heat released from the reaction and protecting aluminum chloride -urea ionic liquid from moisture or air in similar attempts to those in toluene.

In the ultraviolet region benzene was reported to have three bands which were related to π-π* aromatic ring transitions and named E_1, E_2 and B where E_1 at higher energy than E_2 and B bands, and E_2 band at higher energy of B band [115]. The E_1 band could not be observed since it was reported to have a wavelength of 180nm [115] which was out of the instrument's range (190-900) nm. The other two bands (E_2 and B) were observed in present work in the ultraviolet region at 199.5nm and 257nm respectively [Fig. 3.3, B] similar to those reported in literature [115].

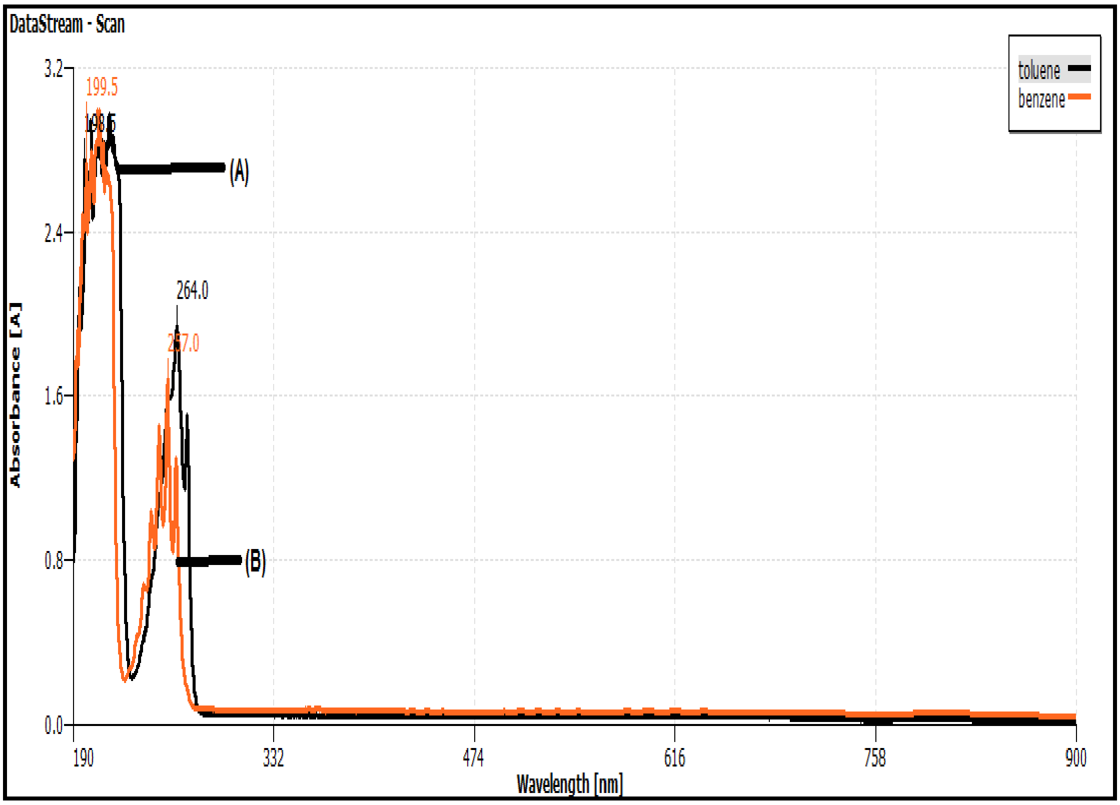

Fig. 3.3:- The ultraviolet\visible spectra of (A) toluene and (B) benzene.

The color of the prepared ionic liquid in benzene showed a deep red color which was examined by the ultraviolet-visible spectroscopy [Fig. 3.4B] which revealed an increase in the initial absorbance of benzene B and E_2 bands at same wavelengths, and the appearance of two new bands similar to those obtained in toluene. The new bands appeared at 320 nm and 420 nm which were also related to the interaction of the same acidic cationic species of the ionic liquid $[AlCl_2.nUrea]^+$ with the π-ring electrons of benzene ring in a similar mechanism of the interaction with toluene (see sec. 3.1.1).

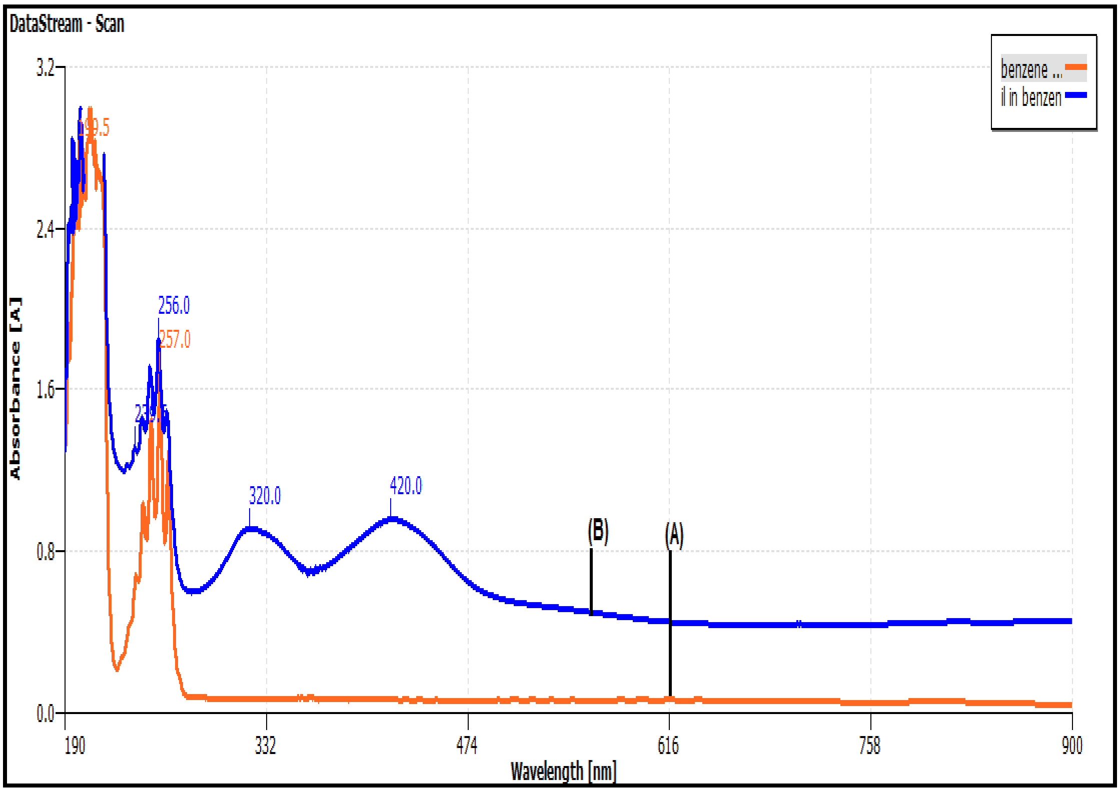

Fig. 3.4:- The ultraviolet\visible spectra of (A) benzene and (B) aluminum chloride-urea ionic liquid in benzene.

3.1.3 Preparation of Aluminum Chloride-Urea Ionic Liquid in n-Hexane:

n-Hexane is also used in the preparation of the aluminum chloride - urea ionic liquid, but it was found to form a protective colorless layer. The resulted mixture of ionic liquid in n-hexane (composed of 80 v/v% n-hexane and 20 v/v% (1.6$AlCl_3$:1Urea) ionic liquid) showed two separated layers; although it was mixed with continuous agitation at 30-50 °C for one hour, where the top colorless layer was n-hexane and the lower layer deep orange contain the ionic liquid. Unlike toluene and benzene, n-hexane layer did not show a color change when ionic liquid was prepared in this organic diluent and neither it mixed with ionic liquid. The deep orange color can be related to reaction of ionic liquid with some unknown impurities either present in n-hexane or resulted from decomposition of some ionic liquid due to hot spot formation which could not be avoided by heat diffusion in n-hexane.

Although it is not the task of the present work to identify the impurities present in n-hexane, ionic liquid formed in this mixture could indicate its catalytic activity to purify n-hexane from organic impurities. However, it was also noted that if pure n-hexane was used; it would play an important role in the preparation of ionic liquid as a protective layer, preventing ionic liquid from contacting with atmospheric air. The reason for not mixing ionic liquid with hexane would be related to the absence of lone pair in the organic solvent that may be interacted with the acidic species present in the ionic liquid. From the results obtained and ease of preparation of ionic liquid of aluminum chloride-urea, it may be said that toluene and benzene both are suitable for preparation of ionic liquid in situ, but not n-hexane. It is also expected that any organic liquid could be mixed with ionic liquid as long as it contains lone pair presented as free electrons on an atom or from double bond and π-ring bonds.

Therefore; toluene was chosen to undertake experimental work for the investigation of possible determination of acidic species in ionic liquid from their interaction with π-ring electrons.

3.2 Determination of The Active Acidic Species in Aluminum Chloride-urea Ionic Liquid using chloride ion:

The cationic species [57] as were found in this work to be the major species responsible for the interaction of ionic liquid with solvent used as diluent (cf. sec. 3.1). This influence was used to determine the concentration of the active species present in this ionic liquid by reacting them with metal chloride (e.g. calcium chloride and potassium chloride) in a Lewis acid-base reaction where ionic liquid positive species would act as Lewis acid and the added chloride as Lewis base. It was found that when an excess portion of metal chloride was added to the dark green ionic liquid solution in toluene, this caused the separation of two liquid layers, an upper colorless layer and lower layer of light green color.

The slow reaction of calcium chloride and potassium chloride with ionic liquid was found to be less exothermic than the preparation of ionic liquid (estimated by touching the reaction tube) and left for two hours with mechanical stirring at room temperature to reach equilibrium.

When incremental portions of chloride were added to the dark green mixture of ionic liquid in toluene, it showed an increase of colorless upper layer, increased in volume with increasing chloride concentration. This layer showed similar absorption band to these of pure toluene [Fig. 3.5]. However, the lower layer that changed color from dark green to light green showed a suspension of added excess calcium chloride when it exceeded a 75 mole% of the original aluminum chloride used in the preparation of the ionic liquid.

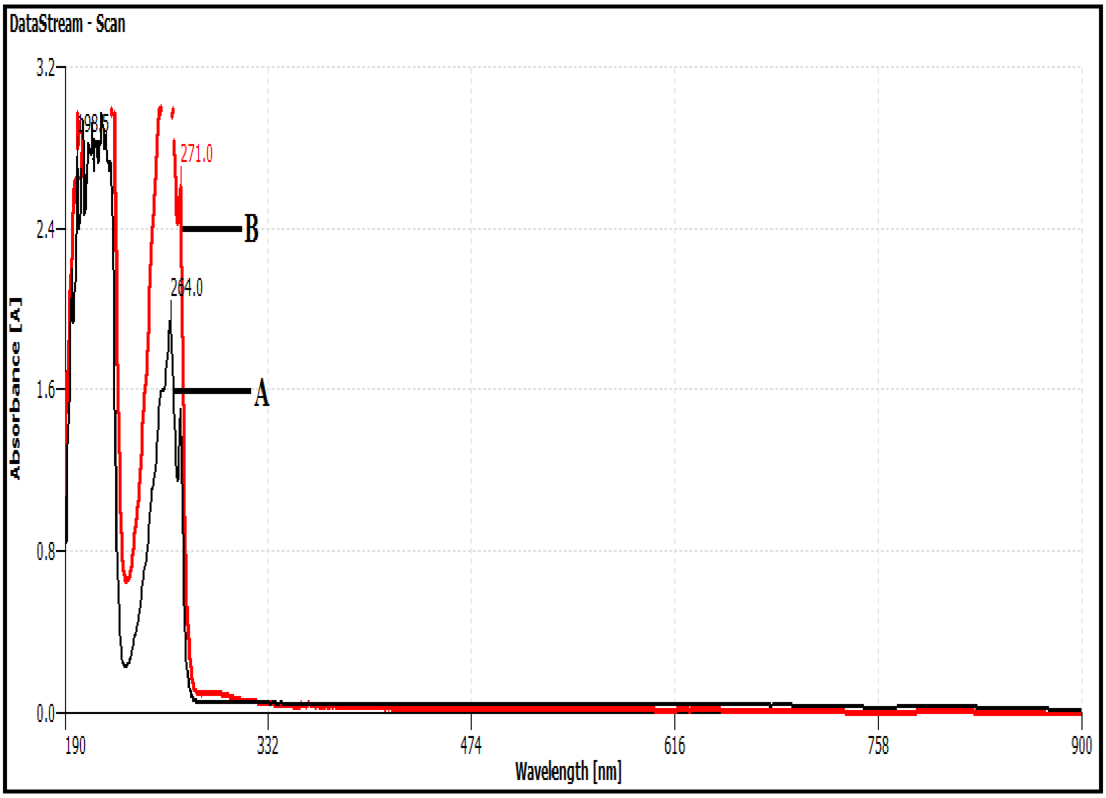

Fig. 3.5:- The ultraviolet\visible spectrum of (A) pure toluene and (B) colorless upper layer.

When potassium chloride was added to the mixture it was noticed that in addition to the two layers noticed with calcium chloride, a precipitate was settled at the bottom of the reaction tube and increased with increasing the amount of potassium chloride. This precipitate was found to be white in color when separated from the mixture and washed with excess toluene, and showed the vibrational bands similar to those of urea when examined by FTIR [Fig. 3.6].

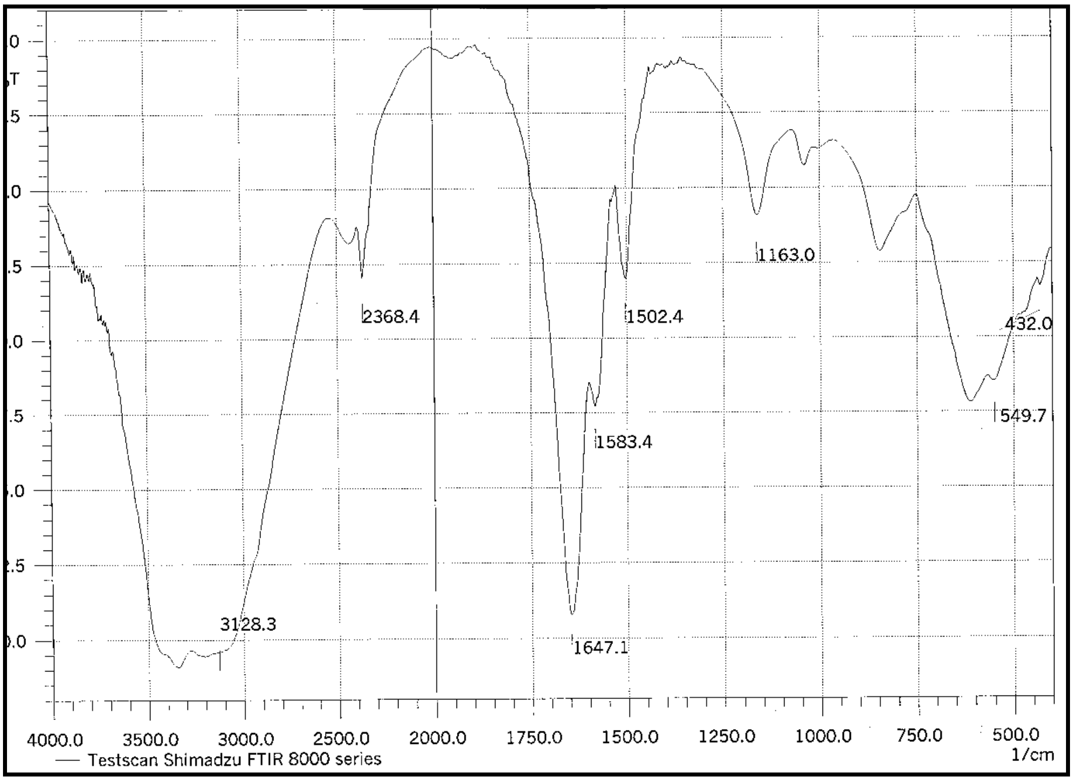

Fig. 3.6:- The FTIR spectrum of the precipitate produced by potassium chloride addition to (1.5$AlCl_3$:1urea) ionic liquid in toluene.

This Lewis acid-base reaction was followed by ultraviolet/visible examination of the light green solution Fig. 3.6 and 3.8.

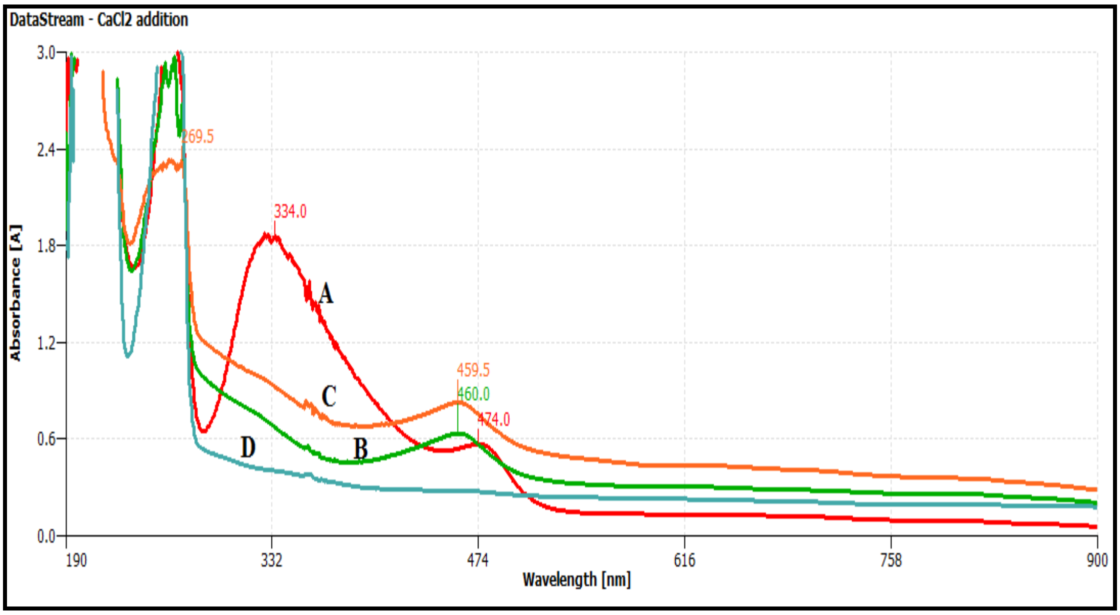

Fig. 3.7: Ultraviolet\visible spectra of (A) 1.5$AlCl_3$:1urea ionic liquid in toluene, (B) 12.5 mole %, (C) 14.3 mole %, (D) 75 mole % of calcium chloride additions.

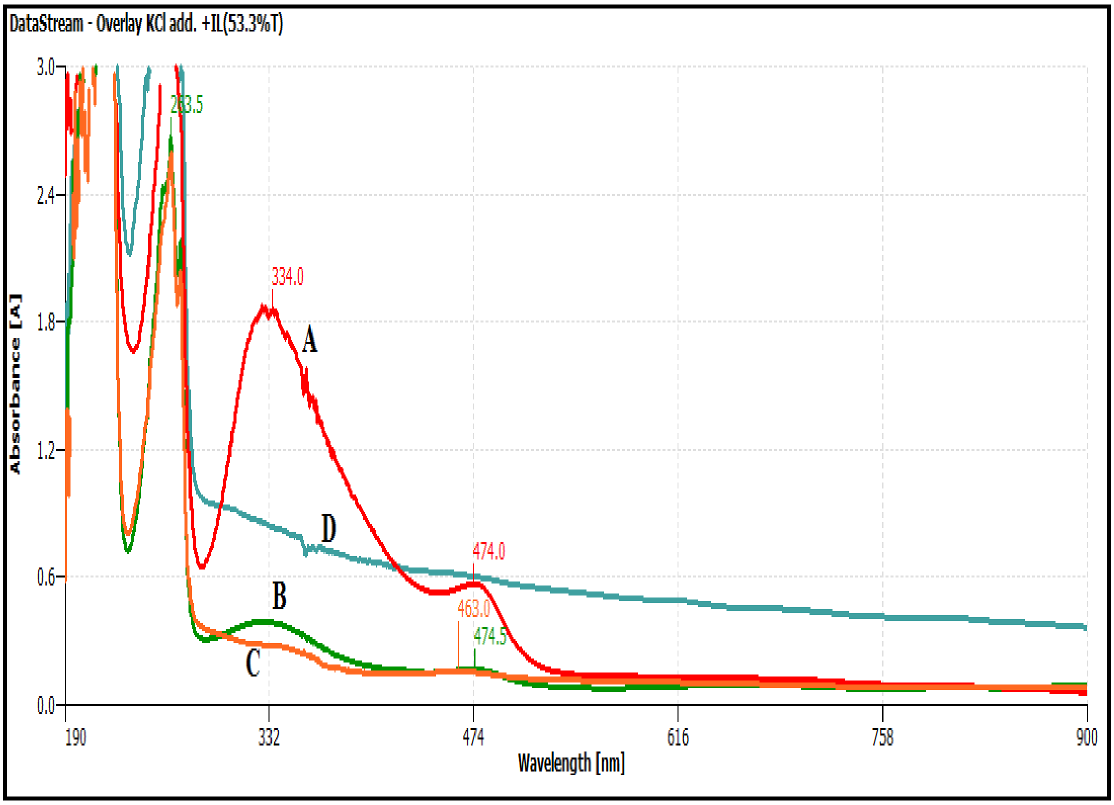

Fig. 3.8: Ultraviolet\visible spectra of (A) 1.5AlCl3:1urea in toluene, (B) 12.5 mole %, (C) 14.3 mole %, (D) 75 mole % of potassium chloride additions.

When potassium or calcium chloride was incrementally added it was observed that the toluene bands (E_2 and B) decreased in their intensities (ε_{max}) and the other two bands (334 nm and 474 nm) were clearly affected by the sequence of additions of calcium or potassium chloride. The band at 334 nm was sharply decreased from the first addition corresponded to 10 mole% addition of potassium or calcium chlorides (calculated on the basis of total $AlCl_3$), and it continued to decrease until it disappeared completely at 75 mole% addition. The lower less intense absorbance band at 474nm was also decreased when chloride was added but to less extent until it was entirely disappeared at the 75 mole% addition of calcium chloride compare [Fig. 3.7] and [Fig. 3.8].

The bands at 474 nm and at 334 nm represent new bands of the toluene interaction with the active acidic species $[AlCl_2.nU]^+$ of the ionic liquid; the presence of these two bands can be considered as a guiding sign for the concentration of the active acidic $[AlCl_2.nU]^+$ species. The sudden decrease and the gradual decrease in the at 334 nm and at 474 nm bands respectively with the gradual increase in the calcium or potassium chloride addition can be explained as follows;

The calcium or potassium chloride addition to the ionic liquid provides the medium with Lewis basic chloride anion and since the ionic liquid already possessed an active Lewis acidic species $[AlCl_2.nU]^+$ [57], the basic chloride ion reacted with the active acidic species thought to produce ionic species of $AlCl_4^-$. Thus as the concentration of the chloride ion increase the reaction with the acidic species would also increase, and the concentration of these acidic species in the ionic liquid would decrease. Thus the bands at 474 nm and at 334 nm (which correspond to the interaction of acidic species with toluene) were decreased as the amount of the acidic species reacted with the chloride ion. Thus acidic species lose their interaction with toluene causing the separation of toluene from the mixture as an upper colorless layer.

Therefore; it is possible to represent the overall reaction between one mole acidic species of ionic liquid with the two moles of Lewis base (chloride ions) as follow;

$$[AlCl_2.nU]^+ + 2Cl^- \rightarrow AlCl_4^- + n.\ Urea \ldots\ldots\ldots\ldots (3.2)$$

This reaction is analogous, as Lewis acid base reaction, to that reported for chloroaluminate acidic species reaction [118] but with different molar concentration;

$Al_2Cl_7^- + Cl^- \rightarrow 2\ AlCl_4^-$ ……..…… (3.3)

Thus it can be said that the Lewis acid-base titration and concentration elucidation of the acidic species of aluminum chloride-amide ionic liquids was around 75 mole% of the initial $AlCl_3$ used in the preparation of 1.5:1 mole ratio of $AlCl_3$: Urea.

It should be noticed that addition of potassium chloride resulted in formation of solid material insoluble in the liquid state of the system, in contrast to calcium chloride addition where only liquid system was observed and no solid material was obtained. The FTIR examination of the solid material in the first case revealed only the existence of urea vibrational bands [Fig. 3.6]. This could be related to the changing in the mole ratio of ionic liquid state as some aluminum chloride was consumed in the Lewis acid-base reaction and forming a system out of the limitation of liquid state reported for this type of ionic liquid as being between 2:1 and 1:1 ($AlCl_3$:amide) [57]. However in the second case, this was not observed properly due to dissolution of calcium complex formed with urea making a new liquid system mixture with other species present. This needs to be confirmed by further work which was out of the scope of the present research.

When the obtained absorbance was represented with mole ratio as in [Fig. 3.9] it clearly represents two reactions.

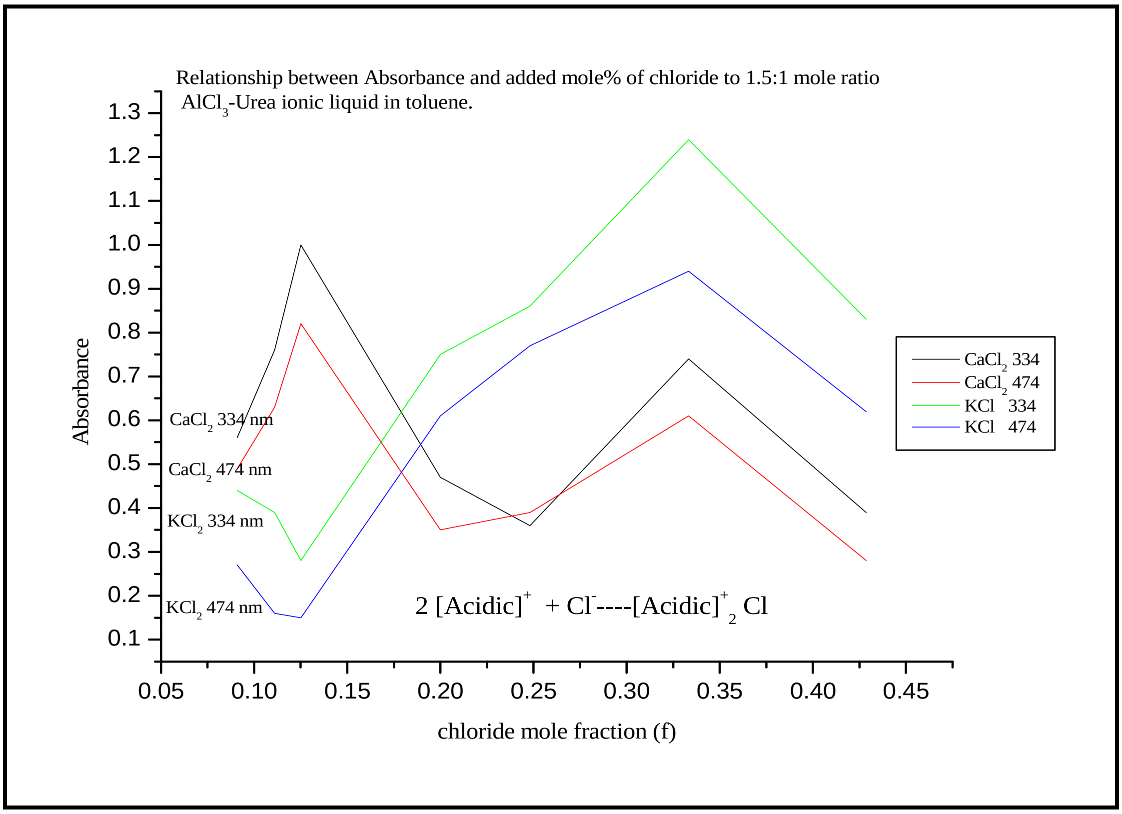

Fig. 3.9: Mole fraction representation of added calcium chloride (A1 at 334 nm and A2 at 474 nm) and potassium chloride (B1 at 334 nm and B2 at 474 nm) to ionic liquid in toluene.

The first at the low mole fraction of added chloride mole fraction of (0.125) in similar mechanism, if potassium or calcium salt were used in the neutralization reactions, until a mole fraction of 0.2 of chloride, where a second reaction between the formed product and added chloride was commenced. The latter reaction revealed the formation of 2 to 1 mole reaction of acidic species to chloride ions as the maximum absorbance was obtained at 0.33 mole fraction of chloride ions (cf. reaction 3.2).

Although the first reaction differ if chlorides were added as potassium salt or calcium salt probably due to cationic charge effect of single and double charges respectively, but they both showed similar trend in the second reaction. The latter reaction may be assumed as commenced between the products of the first reaction (being of similar nature) with added additional chloride salts regardless of the nature of the cationic presents.

Further observation was the nature of both absorption bands at 334 nm and at 474 nm which they showed identical behaviors in both cases of chloride salts, indicating their similar origin, as stated above, stemmed from the interaction between cationic acidic species and aromatic ring system.

3.3Chloride Containing Transition Metal compounds in Aluminum Chloride-Urea Ionic Liquid in Toluene:

Transition metal chlorides cupric chloride and cobalt chloride were added to the ionic liquid composing of 46.7% (1.5aluminum chloride-1urea) and 53.3% toluene to investigate the transition metal coordination in the presence of Lewis acid base reaction and also to follow their reaction with the acidic species:

3.3.1Cupric Chloride in Aluminum Chloride-Urea Ionic Liquid in Toluene:

It was found that cupric chloride reaction with ionic liquid in toluene was an immediate, exothermic and faster than that of calcium and potassium chloride as it required shorter time (20 minutes at maximum) for the largest concentration of cupric chloride to complete its reaction with acidic species with mechanical stirring at room temperature.

The cupric chloride behavior in aluminum chloride-urea ionic liquid in toluene differed from that in other ionic liquids or molten salts media. In choline chloride-urea ionic liquid, 0.1M cupric chloride was found to be only soluble after 72 hours similar concentration was found to be soluble in choline chloride- malonic acid ionic liquid after similar time [119] although it contains acidic organic salt. In LiCl\KCl molten salt ionic liquid cupric chloride was found to be soluble at (400 °C) [120].

Thus it can be said that cupric chloride was much more soluble in aluminum chloride-urea ionic liquid (1M) than in choline chloride-urea or malonic acid ionic liquids or in LiCl\KCl molten salt ionic liquid, due to, most expectedly, its reaction with acidic species of $AlCl_3$-urea ionic liquid as stated in Table (3.1) which shows the concentration of cupric chloride and its reaction time in ionic liquid.

Table (3.1):- Concentrations of cupric chloride added to aluminum chloride-urea ionic liquid in toluene at room temperature.

Cupric chloride Concentration(M)	Reaction Time (minutes)
0.1	10
0.2	11
0.4	12
0.5	14
0.8	18
1	20

As with calcium or potassium chloride, addition of cupric chloride also caused separation of two layers. The upper colorless layer was examined by ultraviolet/visible spectroscopy which showed similar bands to those of toluene. And the lower deep green layer which was examined by ultraviolet/visible spectroscopy before and after the chloride addition and found to be experience some changes. The color of the mixture was also changed from dark green to deep green when the cupric chloride was added.

The amount of separated toluene as an upper layer increased with increasing the concentration of cupric chloride, which indicated consuming of ionic liquid through the Lewis acid-base reaction between the Lewis base chloride anion and the Lewis acid species of the aluminum chloride-urea $[AlCl_2.nU]^+$. As it was found in qualitative experiment that ionic liquid limited dilution toluene do not exceed 20 v/v% of ionic liquid and 80 v/v% of toluene. This also indicated the reduction in the acidic species coordinated with toluene there by releasing toluene in excess than the required dilution with acidic species of original ionic liquid.

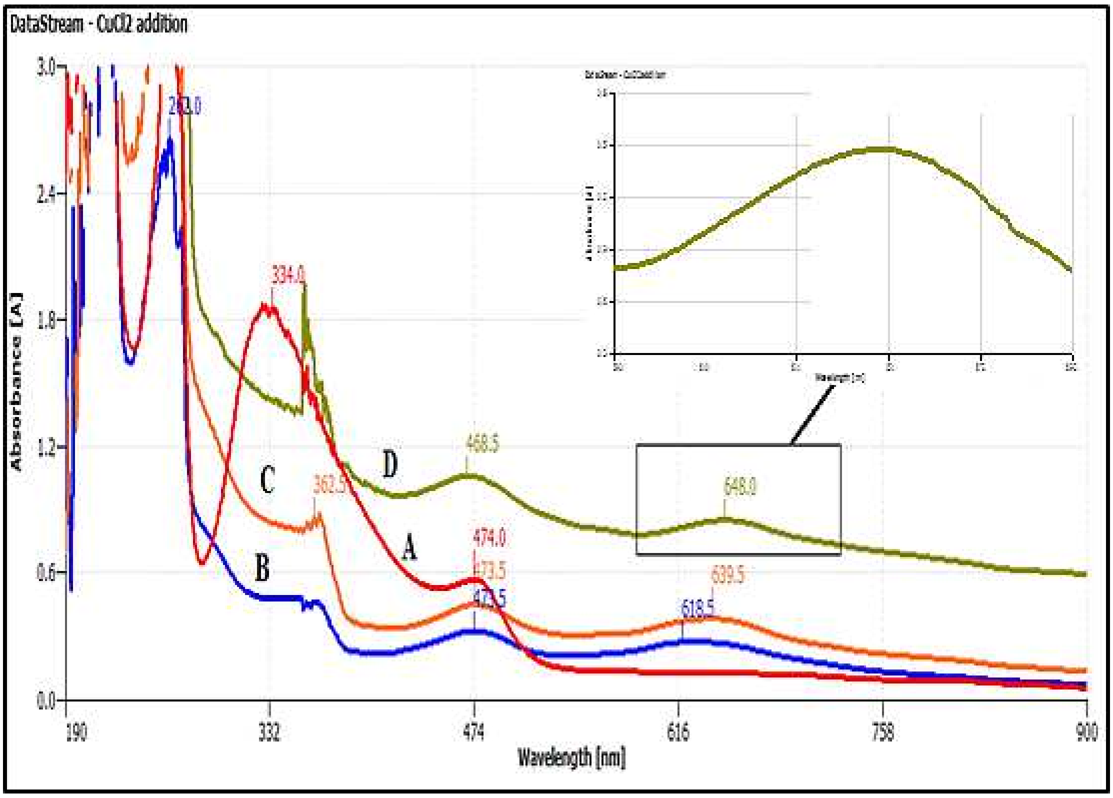

Fig. 3.10: Ultraviolet\visible spectra of (A)1.5 aluminum chloride-1urea ionic liquid in toluene, (B)0.1M, (C)0.4M and (D)1M cupric chloride in the (1.5 aluminum chloride-1urea) ionic liquid in toluene and the inset of 1M cupric chloride in ionic liquid (590 – 692) nm.

Spectroscopic investigation of above acid-base reaction and cupric chloride coordination in ionic liquid revealed several findings in supporting of the occurrence of such reaction and type of coordination present in ionic liquid. This can be illustrated as shown in [Fig. 3.10] where different concentrations of cupric chloride caused the decrease of the bands of acidic species coordination to toluene due to neutralization with chloride ions reducing their concentration and thereby, band intensities (334 nm and 474 nm). However, the band of octahedral coordinated copper (II) cation remained so as indicated by the presence of its absorption at 639.5 nm [Fig. 3.10, C]. However, it was noticed that the toluene interaction with acidic species of ionic liquid, where reduced as indicated by the reduction of bands intensities (334 nm and 474 nm) and particularly the obvious disappearance of the band at 334 nm; while it was again appeared and increased their intensities with increasing the concentration of cupric chloride. This was related to a new interaction of Cu (II) complex with the π-ring bonds producing a new coordination of toluene and showing absorption similar to that of aluminum active species present originally in ionic liquid.

It is known that cupric chloride gave blue aqueous solution and it has a term symbol of Cu (II) ion (d^9) is (^2D) with one broad absorption band due to distorted Cu (II) octahedral structure. Cu (II) subjected to (John-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. [121]

In a comparison between the behaviors of Cu (II) chloride in aqueous solution and in aluminum chloride-urea ionic liquid in toluene [Fig. 3.12] cupric chloride was found to give one broad band at 819.5 nm in aqueous and 639.5 in ionic liquid.

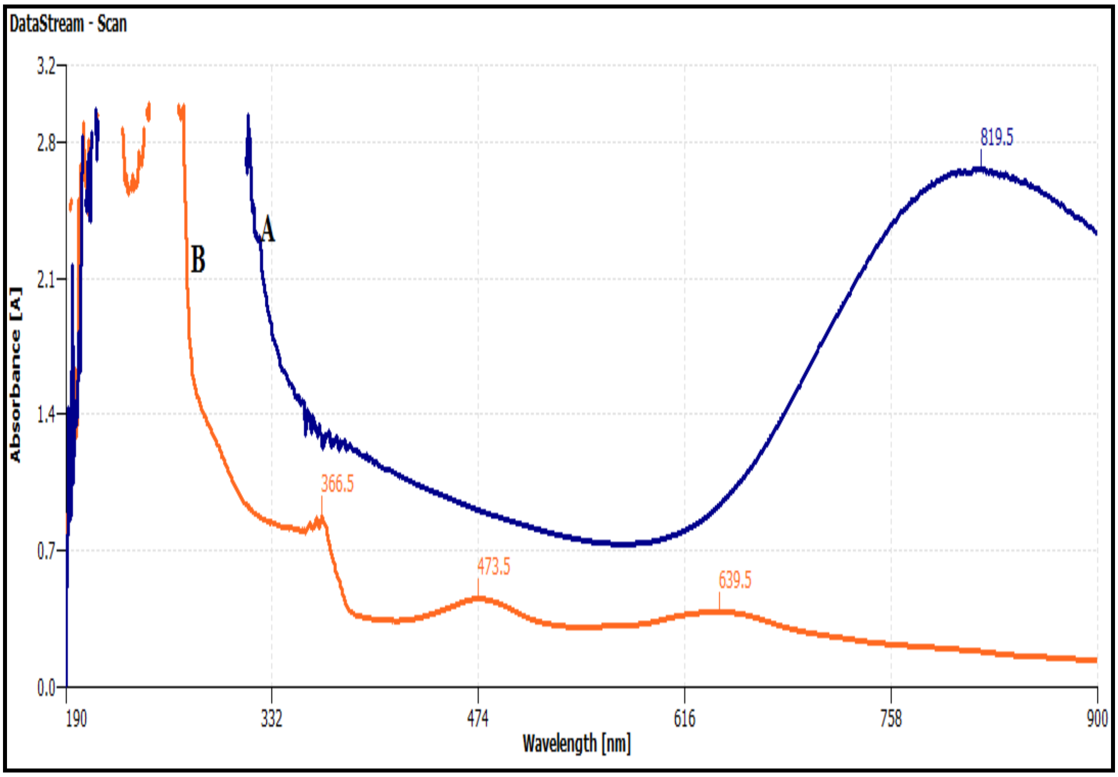

Fig. 3.11: Ultraviolet\visible spectra of cupric chloride (A) in water (B) in ionic liquid in toluene.

This would reflect that Cu (II) cation had interacted in ionic liquid with stronger ligand field than water. In addition, the molar absorptivity in ionic liquid was found to be larger than that in water (compare 36 with 13.3 L mol^{-1} cm^{-1} respectively), which indicate a less symmetrical arrangement of the already distorted octahedral structure of copper (II) as revealed from the broad band in both media.

Although Cu (II) cation showed different coordination nature in variable solvents (Table 3.2), yet in this ionic liquid showed a stronger field than any of the other solvents (639.5 nm). This is not the normal finding of weak ionic liquids coordination nature with copper or other transition metal cations [122, 120, 119, and 123] which might be caused by the production of complex anion a part from the original anion of ionic liquid, with stronger field. This anion expected to be produced from the acid-base reaction of acidic species neutralization of ionic liquid.

Table (3.2):- The behavior of Cu (II) ion in various solvents.

Solution of Cu (II) ions	**Color**	**Absorption bands (nm)**	**Transition**	**ε(Lmol^{-1} cm^{-1})**	**Suggested structure**	**Ref.**
Aqueous solution	Blue	υ =819.5	$^2Eg \rightarrow {}^2T_2g$	13.3	Oh. $[Cu(H_2O)_6]^{2+}$	This work
Aluminum chloride\urea in toluene	Deep green	υ =630	$^2Eg \rightarrow {}^2T_2g$	36	Oh. $[Cu(IL)_6]^{2+}$	This work
Hydrated Ammonium Aluminum sulfate/urea	Blue	υ= 802.5	$^2Eg \rightarrow {}^2T_2g$	29.8	Distorted Oh. $[Cu(IL)_6]^{2+}$	122
LiCl/KCl	Pale blue	υ= 1052	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	-	Distorted Oh. Or Td.	120
Choline chloride/tartaric acid	Yellow	υ= 1089	$^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	10.6	Td. two chloride and one tartarate ions	123
Choline chloride/urea	Blue	υ= 766	$^2Eg \rightarrow {}^2T_2g$	17.02	Oh. $[Cu(urea)_6]^{2+}$	119

3.3.2 Cobalt Chloride in Aluminum Chloride-Urea Ionic Liquid in Toluene:

Anhydrous cobalt chloride was incrementally added in a series of concentration (0.1, 0.2, 0.4, 0.5, 0.8 and 1) M to aluminum chloride-urea ionic liquid diluted with toluene. It was found that the color of the ionic liquid changed from dark green color to olive color after 3 hours of mechanical agitation at room temperature, but when the mixture was left to settle it separated into two layers, the first was upper green layer liquid and the other was olive colored precipitate. The cobalt chloride behavior in aluminum chloride-urea ionic liquid diluted with toluene differed from that in other ionic liquids or molten salts media. In choline chloride-urea ionic liquid (0.1 M) was found to be only soluble after 72 hours at room temperature [119], and at (40-70 ° C) in $Ca(NO_3)_2.4H_2O/CaCl_2$ [124]. In acetamide/$Ca(NO_3)_2.4H_2O$ it was soluble at (40-90 ° C)[125]. In molten salt Co (II) ions dissolved at (447-480 ° C) in LiCl/KCl [120].

When the upper layer was examined with the ultraviolet-visible spectroscopy [Fig. 3.12] at different concentrations of added cobalt chloride it showed the disappearance of the bands of coordinated acidic species to toluene because of neutralization of chloride ions reduced the concentration of acidic species and thereby there bands' intensities (334 nm and 474 nm). However, no cobalt bands were observed in this spectrum.

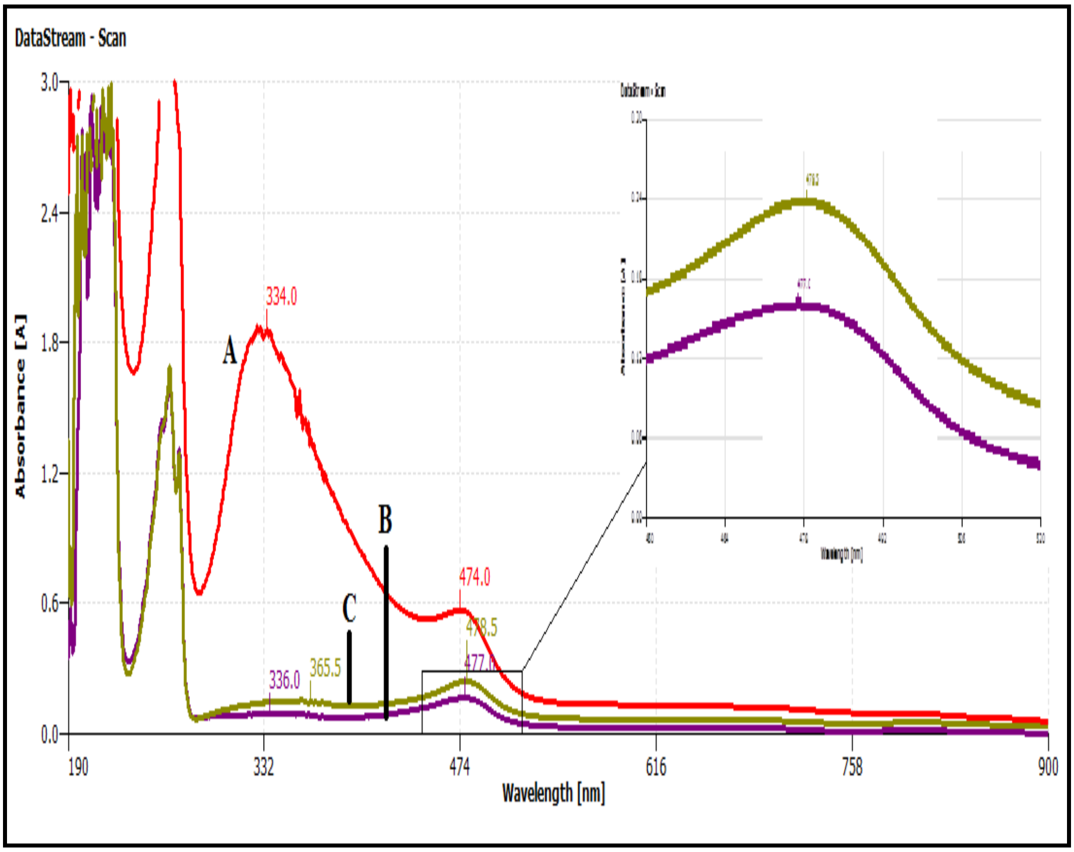

Fig. 3.12: Ultraviolet\visible spectra of (A) aluminum chloride-urea ionic liquid in toluene, (B) 0.5M and (C)1M cobalt chloride in ionic liquid, inset (C and B) cobalt chloride in ionic liquid (450-520) nm.

The lower layer olive precipitate was mixed with diethyl ether in an attempt to extract any cobalt complex produced from above reaction. After shaking with diethyl ether and left to settle, the mixture separated into two parts. The upper layer contained diethyl ether and a lower layer contained light sky blue precipitate. The precipitate was separated and washed with extra diethyl ether. The solid precipitate was found to be sensitive to air as it change color to pink indicting geometrical changes from blue tetrahedral into pink octahedral cobalt complex. However, the cobalt precipitate was found qualitatively to contain urea when tested by FTIR as it showed the major vibrational frequencies for carbonyl (C=O) and amide groups ($-NH_2$) at 1643 cm^{-1} and 1579 cm^{-1} and also qualitatively was tested for chloride ion with silver nitrate solution forming white precipitate indicating the presence of chloride ion.

Further investigation and chemical analysis is required to identify the cobalt complex nature and characterization, but this is out of the time required for the present work.

3.4 Sulfate containing Transition metal Compounds in Aluminum Chloride-Urea Ionic Liquid diluted with Toluene:

Sulfate containing compounds (nickel sulfate and cupric sulfate) were added to ionic liquid composed of 46.7% (1.5aluminum chloride-1urea) and 53.3% toluene to investigate the reaction of acidic species with sulfate anions instead of chloride ions and the coordination effect where sulfate anions are present.

3.4.1 Nickel Sulfate in Aluminum Chloride-Urea Ionic Liquid in Toluene:

Upon addition of nickel sulfate to the ionic liquid, it reacted immediately with an exothermic nature due to warming the reaction tube.

Dissolution of nickel salts in other molten salts or ionic liquid were reported without acid-base reaction. For example; nickel chloride was found to be soluble in choline chloride-urea room temperature ionic liquid slowly and required 72 hours to dissolve completely (0.1M nickel chloride) [119]. However, nickel sulfate required worming up to 40 °C to dissolve in hydrated ammonium aluminum sulfate/urea ionic liquid[122] much less concentration than nickel chloride in choline chloride-urea ionic liquid (compare 0.1 M with 0.02 M). In addition salt nickel chloride in LiCl/KCl was found to be soluble at 700-1000 °C and in CsCl melt at 864 ° C [120].

Nickel sulfate portions were incrementally added to ionic liquid (0.2 M, 0.5 M, 1 M, 1.2 M, 1.5 M, 1.8 M and 2 M), and these additions produced three layers which were:

1. Colorless upper layer liquid which was found to be toluene only when examined by ultraviolet\ visible spectroscopy.

2. Deep green lower layer liquid, this layer was tested by the ultraviolet\visible spectroscopy [Fig. 3.13] containing nickel cation and ionic liquid as will be discussed later.
3. Light green precipitate layer which was found to contain only nickel, sulfates, chloride anion and aluminum when tested qualitatively with the absence of urea.

The amount of the upper layer described above differs with respect to the added amount of the nickel sulfate, as the nickel sulfate addition increased the separation of toluene also increased which clearly indicated the Lewis acid-base reaction between the Lewis base sulfate anion and the Lewis acidic cationic species $[AlCl_2.nU]^+$ of the ionic liquid.

So the reaction between nickel sulfate and the acidic species $[AlCl_2.nU]^+$ break up the interaction between toluene and original acidic aluminum species, and thereby the toluene was separated as an upper layer since its density is less than the ionic liquid's.

Nickel sulfate addition also changed the dark green color of the aluminum chloride-urea (53.3% toluene) ionic liquid which had bands at 474 nm and 334 nm in the visible and ultraviolet regions to liquid of deep green color [Fig. 3.13] that has bands at 644 nm and 431 nm (0.2 M nickel sulfate).

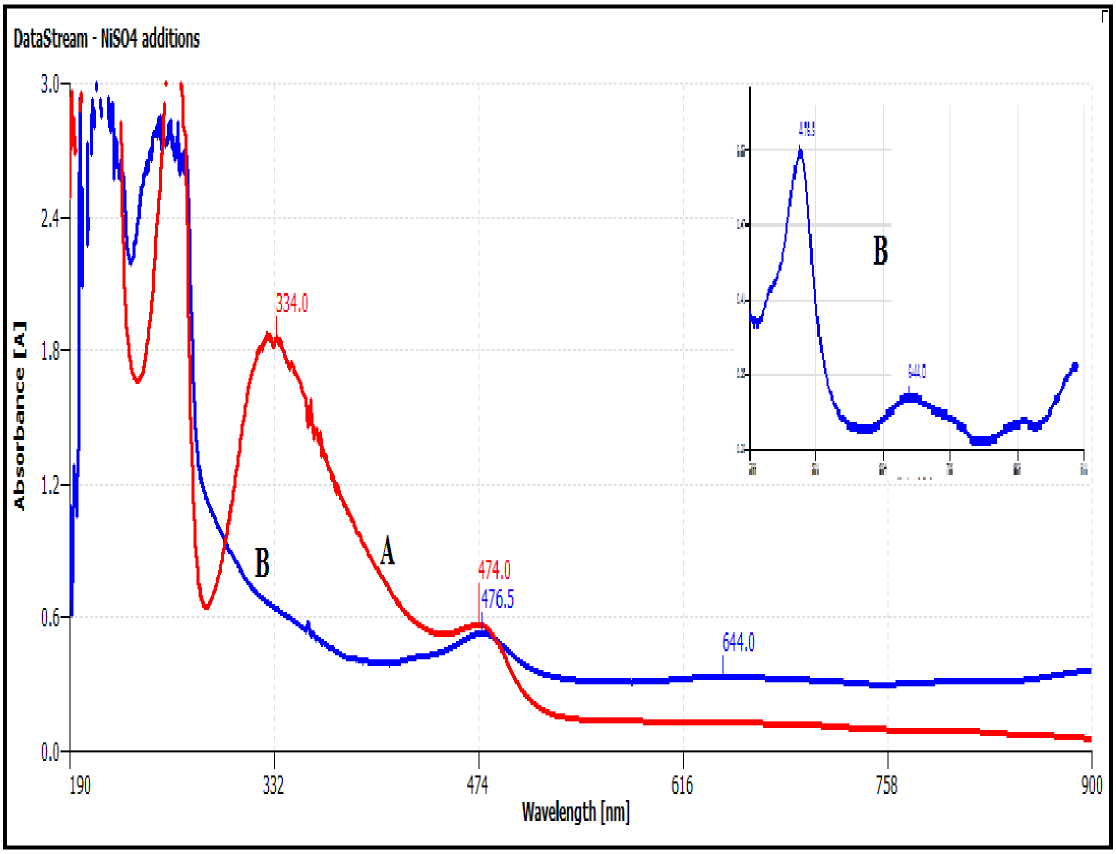

Fig. 3.13: Ultraviolet\visible spectra of (A) aluminum chloride-urea ionic liquid in toluene full range, (B) 0.2M nickel sulfate in the aluminum chloride-urea ionic liquid in toluene full range and the inset (B) the nickel sulfate band in ionic liquid (430-900) nm.

[Fig. 3.13] reveals the disappearance of the band at 334 nm when the smallest concentration of nickel sulfate was added (0.2 M), while the band at 474 nm experienced less change. However, the solution showed the appearance of new band at 644 nm, and a third band at 431 nm.

As with potassium chloride or calcium chloride, addition of nickel sulfate also believed to reduce the interaction of aluminum acidic species with toluene because both 474 nm and 334 nm bands reduced their intensities with increasing addition of sulfates referring to expected Lewis acid-base reaction.

Going back to nickel cation coordination interaction in this mixture showed bands with low intensities when compared to the allowed charge transition between aluminum acidic species and toluene. These bands were accepted to be at 644 nm representing the 2nd d-d Laborate forbidden transition of nickel octahedral coordination complex of the transition state of ^3A_2g (F) to ^3T_1g (F), while the third band was observed at 431 nm which could be due to ^3A_2g (F) → ^3T_1g (P) transition state.

The first band of nickel transition state of ^3A_2g (F) → ^3T_2g (F) would have a value of 905 nm when calculated from Tanabe-Sugano diagram [Fig. 3.14].

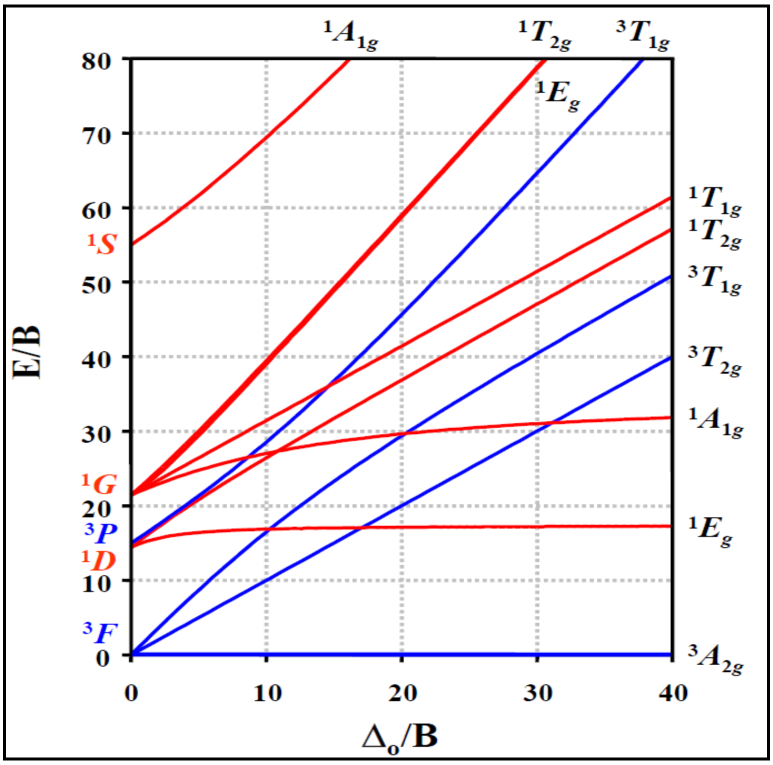

Fig. 3.14:- Tanabe-Sugano diagram for d^8 octahedral ion configuration.

The small and close molar absorptivity value of the bands of nickel (II) cation either in aluminum chloride-urea ionic liquid in toluene or water [Table (3.3)] revealed the symmetrical coordination of ligands around the nickel cation as it is reported that the value of ε in Oh geometry has a value ranged from 10 to 100 L $mol^{-1}.cm^{-1}$[R]. The octahedral coordination of nickel (II) in this ionic liquid was found to be similar to those obtained in different ionic liquid, yet showing different band energies. For example, it showed bands at (410 nm, 669-746 nm and

1050 nm) in choline chloride/urea room temperature ionic liquid.[119] while in acetamide/KNO_3 it showed bands at 431 nm, 800 nm and 1333 nm, but at 429 nm, 793 nm and 1234 nm in butyramide-$NaNO_3$.[126] These differences reflect the variable strength of these ionic liquid anionic species coordinated to nickel cation.

Table (3.3):- The electronic spectroscopic behavior of Ni (II) ion in various ionic liquids and molten salt ionic liquids and suggested structure.

Solutions of Ni (II) ion	**Absorption Bands (nm)**	**Color**	**B' (cm^{-1})**	**ε($Lmol^{-1}$ cm^{-1})**	**Cal. β**	**Suggested structure**	**Ref.**
Aqueous Solution	$\upsilon_{1cal.}$= 1075 υ_2= 658 υ_3= 395.5	green	775.03	31 85	0.75	Oh. $[Ni(H_2O)_6]^{2+}$	This Work
(Aluminum Chloride -urea) in toluene	$\upsilon_{1cal.}$ = 905 υ_2 = 644 υ_3 = 431	Deep green	356.25	36 33 42	0.346	Oh. distorted $[Ni(IL)_6]^{2+}$	This Work
LiCl\KCl	υ=1250 υ=704.2 υ=653.6	-	-	-	-	Distorted tetrahedral	120
CsCl	υ= 1333 υ=714.2 υ= 637	-	-	-	-	Tetrahedral	120
Butyramide/$NaNO_3$	υ=1234 υ=793 υ= 429	-	-	-	-	Octahedral	126
Acetamide/KNO_3	υ=1333 υ=800 υ= 431	-	-	-	-	Octahedral	126
Choline chloride/urea	υ= 1050 υ=(669-746) υ= 410	-	-	-	-	Oh. $[Ni(urea)_4Cl_2]$	119
$NH_4Al(SO_4)_2.12H_2O$ /urea	$\upsilon_{1cal.}$= 1198 υ_2= 670.5 υ_3= 401.5	Pale green	884.6	7 14.5	0.85	Oh. $[Ni(IL)_6]^{2+}$	122

3.4.2 Cupric Sulfate in Aluminum Chloride-Urea Ionic Liquid in Toluene:

The reaction of anhydrous copper sulfate with the ionic liquid was found to be exothermic as it was noticed, as with nickel sulfate, from the warm reaction tube. The reactions were left for an hour to complete its reaction which cooled to room temperature changing the dark green color ionic liquid to deep green liquid. This reaction of cupric sulfate was not observed in other ionic liquids probably due to the absence of similar species present in aluminum chloride-urea ionic liquid.

As Cu (II) salts were found to be soluble in a variety of ionic liquids and molten salts, for example; copper chloride was soluble after 72 hours in choline chloride-urea ionic liquid [119] and in LiCl\KCl copper (II) ion was soluble at 400 ° C [120]. While copper sulfate pentahydrate was 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 0.05 M of copper sulfate was soluble after 15 minutes producing clear blue solution[122].

As with nickel sulfate (see section 3.4.1), cupric sulfate was added in incremental concentrations of (0.2, 0.5, 1, 1.2, 1.5, 1.8 and 2) M and these additions were also found to separate the mixture into three layers which were:

1. Colorless upper layer liquid that found to be toluene when examined by ultraviolet\ visible spectroscopy [Fig. 3.5].
2. Deep green lower layer liquid tested by the ultraviolet\visible spectroscopy [Fig. 3.14].

3. Light green precipitate layer which was found to contain only copper, sulfates, chloride anion and aluminum when tested qualitatively with the absence of urea.

As the cupric sulfate addition increased the separation of toluene was noticed to be increased which indicated a Lewis acid-base reaction between the Lewis base cupric sulfate and the Lewis acidic species $[AlCl_2.nU]^+$ of the ionic liquid. So the interaction between the sulfate and the $[AlCl_2.nU]^+$ was suggested to be stronger than that between toluene and the acidic species $[AlCl_2.nU]^+$ and thus the toluene was separated and floated as an upper layer due to density differences in comparison with ionic liquid.

The electronic spectroscopic comparison [Fig. 3.14] between the behavior of aluminum chloride-urea ionic liquid in toluene alone and in presence of added cupric sulfate, it was observed that an immediate disappearance of the band at 334 nm along with the smallest added cupric sulfate concentration (0.2 M) while the band at 474 nm was decreased along with the continuous addition of cupric sulfate. However; new bands at 898 nm, at 820.5 nm, at 718.5 nm and at 675 nm were appeared in the visible region but with much lower absorbance than the 334 nm and 474 nm bands (noticed clearly when the chart was magnified as shown in [Fig. 3.14]. These new bands might be related to a geometrically distorted octahedral of copper (II) complex. The interaction of the ligands caused a large separation of d-orbitals which resulted in a separated four dzx or dzy orbitals to dz^2 and dx^2-y^2 and from dxy to dx^2-y^2 and dz^2 as illustrated in [Fig. 3.16].

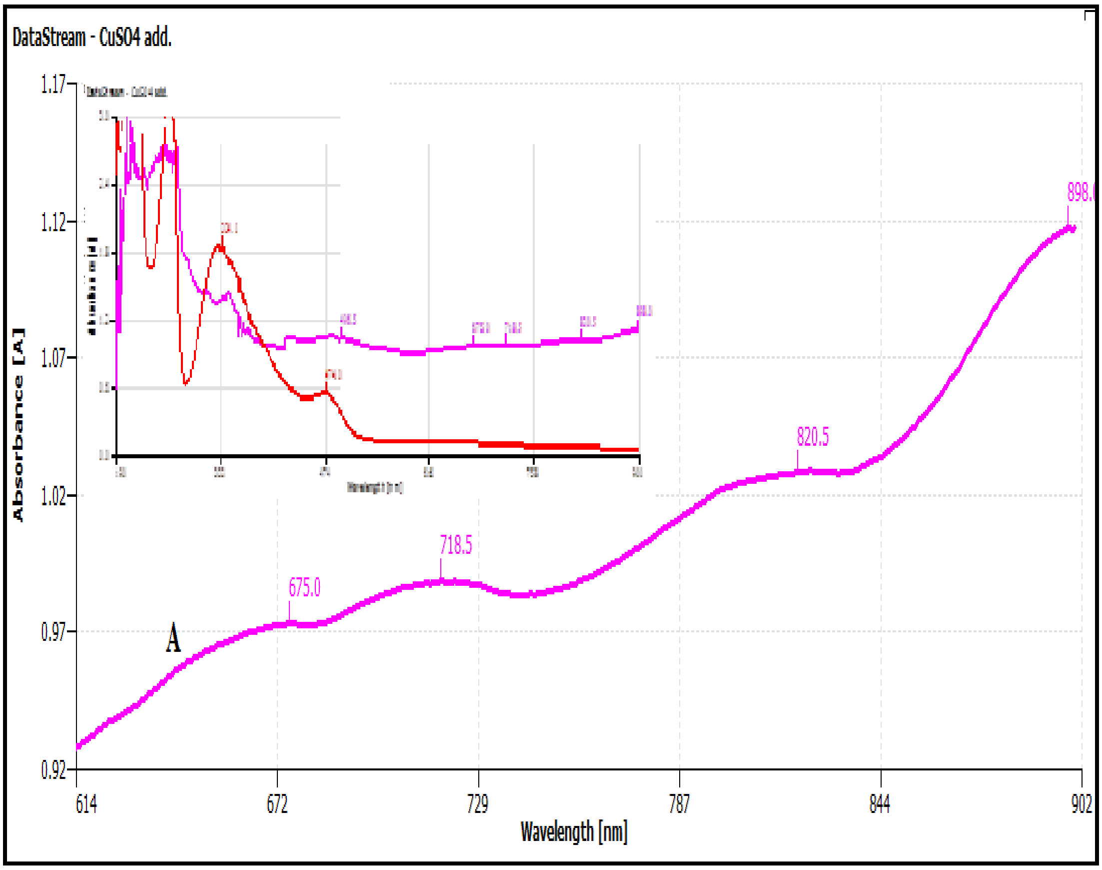

Fig. 3.15: Ultraviolet\visible spectra of (A) 1.5M cupric sulfate in the (aluminum chloride-urea) ionic liquid in toluene (614-902) nm, (B) inset: aluminum chloride-urea ionic liquid in toluene and cupric sulfate in the ionic liquid (full range).

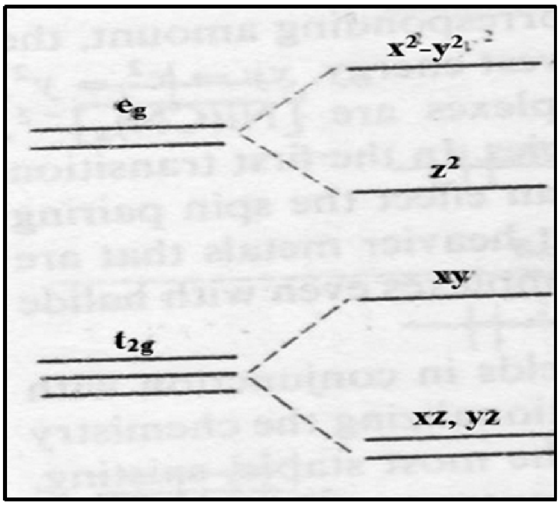

Fig. 3.16: Energy level diagram expected for distorted copper (II) resulted from copper sulfate in ionic liquid diluted with toluene [113(a)].

In a comparison between the behavior of Cu (II) sulfate in aqueous solution and in aluminum chloride-urea ionic liquid in toluene, a 0.2M aqueous solution of cupric chloride gave one broad band centered its maximum at 797.5 nm which represent a tetragonal structure of copper complex but with less separation of d-orbitals in comparison with those in ionic liquid as it appeared only in one broad band.

In comparison of the observation in present work with reported finding of the behavior of cupper (II) cation [Table 3.6] it was found that it had different coordination in different types of ionic liquid as Cu (II) ion had electronic transition band reported to be at (1089 nm) assigned to a tetrahedral geometry in choline chloride/tartaric acid ionic liquid [123], and at (1052 nm) assigned to form distorted octahedral or tetrahedral coordination in LiCl/KCl molten salt ionic liquid [120].

But in choline chloride/urea copper cation showed a band at (766 nm) which assigned to octahedral coordination [119]. Non electronic transition band was reported to separate as those obtained in the aluminum chloride-urea ionic liquid in toluene.

Table (3.4):- The electronic spectroscopic behavior of Cu (II) ion in various ionic liquids and molten salt ionic liquids.

Solution of Cu (II) ions	**Color**	**Absorption bands**	**Transition**	**ε(Lmol^{-1} cm^{-1})**	**Suggested structure**	**Ref.**
Aqueous solution	blue	υ =797.5 nm	$^{2}Eg \rightarrow {}^{2}T_{2}g$	10.8	Oh. $[Cu(H_2O)_6]^{2+}$	This work
Aluminum chloride\urea in toluene	Deep green	υ_1 =898 nm υ_2 =820.5 nm υ_3 =718.5 nm υ_4 =675 nm	$^{2}Eg \rightarrow {}^{2}A_{1}g$ $^{2}Eg \rightarrow {}^{2}B_{1}g$ $^{2}B_{2}g \rightarrow {}^{2}A_{1}g$ $^{2}B_{2}g \rightarrow {}^{2}B_{1}g$	14.9 13.7 13.2 12.97	Oh. distorted $[Cu(IL)_6]^{2+}$	This work
AlCl3- 1,methyl 3ethylimidazolium chloride	-	υ= 34139 cm^{-1} υ=24570 cm^{-1}	$^{2}B_{1} \rightarrow {}^{2}B_{2}$ $^{2}B_{1} \rightarrow {}^{2}E$	-	Tetrahedral CuCl4 $^{2-}$	128
LiCl/KCl	Pale blue	υ= 1052 nm	$^{2}B_{1}g \rightarrow {}^{2}B_{2}g$ $^{2}B_{1}g \rightarrow {}^{2}Eg$	-	Distorted Oh. Or Td.	120
Choline chloride/tartaric acid	Yellow	υ= 1089 nm	$^{2}B_{1} \rightarrow {}^{2}B_{2}$ $^{2}B_{1} \rightarrow {}^{2}E$	10.6	Td. two chloride and one tartrate ions	123
Choline chloride/urea	Blue	υ= 766 nm	$^{2}Eg \rightarrow {}^{2}T_{2}g$	17.02	Oh. $[Cu(urea)_6]^{2+}$	119

A general comparison can be drawn from the behavior of different type of metal salts used to neutralize the acidic species of ionic liquid. This can be referred to the chloride salts, as alkali metal potassium chloride and alkali earth metal chloride calcium chloride were straighter forward in their Lewis acid-base titration of the acidic species of ionic liquid. Both showed a 75 mole % neutralization of the original aluminum chloride in the (1.5:1) mole ionic liquid with urea. Yet as they showed two reactions of the neutralization Fig. 3.9, they only differ in the first reaction and assumed to be caused by the double charge of alkali metal cation. Their spectroscopic bands behave, however, showed similar trends.

Transition metal chlorides (cobalt and cupper) both showed similar acid-base reaction with ionic liquid acid specie, as indicated by similar reduction in the intensities of the bands of these acidic species with toluene indicating the concentration of metal chlorides. However, the coordination of cooper showed one broad band while in case of copper sulfate showed four bands. This was related to the strong field of the anionic ligands coordinated to copper cation separated its d-orbitals more obviously than the tetragonal John-Teller effect in the copper chloride case.

Cobalt showed a different behavior than copper chloride as it reacted with the anionic species to form a tetrahedral complex that was precipitated and the ligand showed no bands for cobalt. This complex showed the presence of urea, aluminum and chloride ions.

Nickel sulfate when used for neutralization of the acidic species of ionic liquid did not show a major differences, as the indicator bands 334 nm and 474 nm were also decreased with increasing the salt addition. The coordination of nickel cations were of octahedral geometry similar to ionic liquids but with stronger field effect in agreement with that found with cooper sulfate.

Conclusion:

Lewis acid-base reaction was found to be possible to estimate the concentration of the active species of aluminum chloride-urea type ionic liquid. This was found possible by reacting the ionic liquid with Lewis basic species such as chlorides or sulfates. The reaction was also found to be easily followed if aromatic organic diluent was used such as toluene or benzene. These two organic diluent interacted with the acidic species via its ring-π bonds forming a coordinated bond to the acidic species thereby induced a new electronic bonds to emerge at the ultraviolet and at visible region.

However simple metal chloride (potassium chloride or calcium chloride) reacted directly without further complication than the transition metal chloride (cobalt and copper chlorides). The reaction of the first two chlorides indicated a 75 mole % of the initial aluminum chloride used in the preparation of 1.5:1 mole ratio of aluminum chloride urea. Transition metal salts (chlorides or sulfates) also reacted as Lewis acid-base reaction with similar effect on the newly formed ultraviolet/visible bands at 334 nm and 474 nm, but transition metal cations showed different behaviors. Cobalt formed tetrahedral insoluble complex in ionic liquid while copper formed soluble octahedral complex. Sulfate anions showed stronger ligand field on both nickel and copper cation than the chloride on the copper cation geometries.

Future Work:

1. Separation of the resulted complexes.
2. Identification of the complexes produced in situ by different analytical methods.
3. Applying further methods to study the reaction processes, such as NMR, Mass spectroscopy, Atomic Absorption, etc.
4. Investigating different transition metal salts with stronger field to investigate the possibility of preparation of new complexes such as acetates.

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بسم الله الرحمن الرحيم

INVESTIGATION IN SOME GROUP THREE METAL COMPOUND IONIC LIQUIDS

General Concept of ionic liquid:

- Most chemical reactions have been carried out in molecular solvents recently, however, a new class of solvents have emerged called **ionic liquids** that are highly solvating ,non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve .
- They have many, fascinating properties which make them of fundamental interest to all chemists. As they are made up of at least two components **(cation and anion)** which can be varied ,these solvents can be designed with a particular end use in mind , or to possess a particular set of properties, hence ionic liquids are called **“DESIGNER SOLVENTS”**.
- Classical organic solvents are bound in their application by e.g. their boiling point; ionic liquids do not encounter this problem since their vapor pressure is negligible under most reaction conditions used.
- Their potential as green solvents due to lack of volatility attracted a lot of interests as they have been successfully employed in various technical processes.

- The first room-temperature ionic liquid ethyl ammonium nitrate $[EtNH_3]\ [NO_3]$ (m.pt. 12 °C) was discovered in 1914, the next ionic liquid was presented in a patent in 1934 which claimed that certain organic salt have the ability to dissolve cellulose and alter its reactivity, this ionic liquid was followed by chloroaluminate base ionic liquids, but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum (III) chloride and *N*-alkyl pyridinium chloride or 1, 3-dialkylimidazolium chloride.
- $[EtNH_3][NO_3]$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, their melting point and properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present.

Characterization of Ionic Liquid:

- Very low vapor pressure (do not evaporate at room temperature).
- Non-flammable.
- Dissolves many organic and inorganic materials.
- Highly polar.
- Liquid window of up to 400 °C .
- Excellent thermal stability up to 450 °C.
- Have moderate to poor conductivity.
- Large electrochemical window.
- Useful in many classes of chemical reactions, such as catalytic reactions, Friedel-Crafts reactions and gas purification.

Synthesis of Ionic Liquids:

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

1- Metathesis reactions: are good candidates for those preparing new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials.

$$\textbf{[EMIM]I + Ag[BF}_4\textbf{]} \rightarrow \textbf{[EMIM][BF}_4\textbf{] + Ag I}$$

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 in vacuum.

$$\textbf{Solfonic acid + [R}_4\textbf{N] [OH]} \rightarrow \textbf{[R}_4\textbf{N] [RSO}_3\textbf{] + H}_2\textbf{O}$$

3- Direct combination of salts: direct combination of a halide salt with a metal halide, such as:

$$AlCl_3 + [EMIM]Cl \rightarrow [EMIM]^+ + AlCl_4^-$$

The Aluminum Chloride-Based Ionic Liquid:

- Chloroaluminate ionic liquids are one of the most widely studied topics in the present. They were initially of interest for the reduction of aluminum for both battery and plating applications.
- In an attempt to find cheaper and easier way to electroplate aluminum, alkylpyridinium chloroaluminate ionic liquid was produced, but the alkylpyridinium cation was easy to be reduced and since [ethyl methyl imidazolium] $[AlCl_4]$ was preferred.
- Eutectics between AlCl3 and quaternary ammonium salts were studied and they were found to contain complex anions such as $AlCl_4^-$ and $Al_2Cl_7^-$. Then complex anions were replaced by discrete, closed-shell anions such as BF_4^-, PF_6^- and $(CF_3SO_2)_2N^-$.

- By varying the molar ratio of the organic salt to $AlCl_3$, basic, neutral and acidic melts can be formed. System with a molar ratio of $AlCl_3$:RCl less than 1 is basic, consist of R^+, Cl^- and $AlCl_4^-$ ions, a molar ratio of $AlCl_3$:RCl greater than 1 is acidic, which contains R^+, $Al_2Cl_7^-$ and $AlCl_4^-$ ions.

- The liquid of $AlCl_3$:amide only forms in the compositional range $1:1 < \text{amide}:AlCl_3 < 1:2$. Outside these limits a suspension of either $AlCl_3$ or amide forms in the liquid. This liquid was concluded to produce $[AlCl_2.nU]^+$ and $AlCl_4^-$.

- The size of the ^{27}Al NMR spectroscopy peak that corresponds to $AlCl_4^-$ was found to increase upon the addition of $MgCl_2$ while the $[AlCl_2.nU]^+$ peaks decreased indicating the reaction of the added chloride ion with the cationic part as its peak decreased and producing $AlCl_4^-$ as its peak increased.

- In this work the organic solvent was added to the aluminum chloride in reaction tube followed by urea and the final ionic liquid in case of toluene was composed of (46.7 v/v% (1.5 $AlCl_3$: 1urea) + 53.3 v/v% toluene), of (80 v/v% (2AlCl3:1Urea) and 20 v/v% benzene) in case of benzene and of (20 v/v% (1.6$AlCl_3$:1Urea) and 80 v/v% n-hexane) in case of hexane.

- Potassium and calcium chloride were added (to determine the active species concentration) to the liquid prepared in toluene in a series of percentage additions that calculated on the basis of the original aluminum chloride used in the preparation of the ionic liquid and were left for 2 hours of stirring at room temperature.

- A series of different concentrations of solid transition metal compounds were added to the liquid prepared in toluene at room temperature and were left for 1 hour in case of Ni^{2+} and Cu^{2+} sulfates, and 20 min. for the highest concentration of copper chloride and 3 hours in case of cobalt chloride.

Preparation of Aluminum Chloride-Urea Ionic Liquid in Toluene:

- When ionic liquid was prepared in toluene, the color of the mixture was turned immediately to dark green and the UV. Visible spectroscopy of this mixture showed the toluene bands with increased absorption intensities and two additional bands at 334 nm and 474 nm Fig. 1.

- The latter two bands were related to an interaction of Lewis acidic species of the ionic liquid $[AlCl_2.nU]^+$ with the ring π-bond electrons of toluene causing the charge transfer between toluene and metal cationic species.

Fig. 1:- The ultraviolet\visible spectra of (A) toluene and (B) (1.5$AlCl_3$:1urea) ionic liquid in toluene.

Preparation of Aluminum Chloride-Urea Ionic Liquid in Benzene:

- The color of the prepared ionic liquid in benzene showed a deep red color which showed by UV. Visible spectroscopy the presence of benzene bands and the appearance of two new bands similar to those obtained in toluene but at 320 nm and 420 nm Fig. 2.

- The new bands were also related to the interaction of the same acidic cationic species of the ionic liquid $[AlCl_2.nUrea]^+$ with the π-ring electrons of benzene ring in a similar mechanism of the interaction with toluene.

Fig. 2:- The ultraviolet\visible spectra of (A) benzene and (B) aluminum chloride-urea ionic liquid in benzene.

Preparation of Aluminum Chloride-Urea Ionic Liquid in n-Hexane:

- Hexane was found to form a protective colorless upper layer and the lower layer of deep orange color contained the ionic liquid.

- This color can be related to reaction of ionic liquid with some unknown impurities either present in n-hexane or resulted from decomposition of some ionic liquid due to hot spot formation which could not be avoided by heat diffusion in n-hexane.

- The reason for not mixing ionic liquid with hexane would be related to the absence of lone pair in the organic solvent that would interact with the acidic species present in the ionic liquid.

Determination of The Active Acidic Species:

- When incremental portions of chloride were added to the ionic liquid in toluene, it showed:
  - Colorless upper layer (toluene).
  - Light green lower layer in case of calcium and in addition to the two layers a third precipitate layer was produced and found to be urea by FTIR in case of potassium.
- UV. Visible spectroscopy showed in Fig.3 and 4 :
  - Decreased intensity of toluene bands.
  - The band at 334 nm was sharply decreased from the first addition.
  - The band at 474 nm also decreased.
- Then both bands continued to decrease along with additions until they disappeared completely at the 75 mole% addition.

Fig. 3: Ultraviolet\visible spectra of (A) 1.5$AlCl_3$:1urea ionic liquid in toluene, (B) 12.5 mole %, (C) 14.3 mole %, (D) 75 mole % of calcium chloride additions.

Fig. 4: Ultraviolet\visible spectra of (A) 1.5AlCl3:1urea in toluene, (B) 12.5 mole %, (C) 14.3 mole %, (D) 75 mole % of potassium chloride additions.

- Calcium and potassium chloride provided the medium with Lewis basic chloride anion which reacted with active Lewis acidic species $[AlCl_2.nU]^+$ present in the ionic liquid and thought to produce ionic species of $AlCl_4^-$ and urea.

- Thus it can be said that the concentration of the active acidic cationic species of aluminum chloride-amide ionic liquids was around 75 mole% of the initial $AlCl_3$ used in the preparation of 1.5:1 mole ratio of $AlCl_3$: Urea ionic liquid.

Cupric Chloride in Aluminum Chloride-Urea Ionic Liquid in Toluene:

- Copper chloride reaction with ionic liquid in toluene was an immediate, exothermic and faster than that of calcium and potassium chloride. The solution was of deep green color.

- The UV. Visible spectroscopy showed the Cu (II) absorption band in the visible region, indicating octahedral geometry Fig. 5.

- A new interaction of Cu (II) complex with the π-ring bonds producing a new coordination of toluene and showing absorption similar to that of aluminum active species present originally in ionic liquid.

Fig. 5: Ultraviolet\visible spectra of (A)1.5 aluminum chloride-1urea ionic liquid in toluene, (B)0.1M, (C)0.4M and (D)1M cupric chloride in the (1.5 aluminum chloride-1urea) ionic liquid in toluene and the inset of 1M cupric chloride in ionic liquid (590 – 692) nm.

Table (1):- The behavior of Cu (II) ion in various solvents.

Solution of Cu (II) ion	Color	Absorption bands (nm)	Transition	ε ($Lmol^{-1}$ cm^{-1})	Suggested structure
Aqueous solution	Blue	υ =819.5	$^2Eg \rightarrow {}^2T_2g$	13.3	Oh. $[Cu(H_2O)_6]^{2+}$
Aluminum chloride\urea in toluene	Deep green	υ =630	$^2Eg \rightarrow {}^2T_2g$	36	Oh. $[Cu(IL)_6]^{2+}$
Hydrated Ammonium Aluminum sulfate/urea	Blue	υ= 802.5	$^2Eg \rightarrow {}^2T_2g$	29.8	Distorted Oh. $[Cu(IL)_6]^{2+}$
LiCl/KCl	Pale blue	υ= 1052	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	-	Distorted Oh. or Td.
Choline chloride/ tartaric acid	Yellow	υ= 1089	$^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	10.6	Td. two chloride and one tartarate ions
Choline chloride/urea	Blue	υ= 766	$^2Eg \rightarrow {}^2T_2g$	17.02	Oh. $[Cu(urea)_6]^{2+}$

Cobalt Chloride in Aluminum Chloride-Urea Ionic Liquid in Toluene:

- The ionic liquid color changed from dark green color to olive color after 3 hours of mechanical agitation at room temperature, and when the mixture was left to settle two layers emerged green liquid layer and olive colored precipitate layer.

- The UV. Visible spectroscopy showed in Fig. 6:
    - Disappearance of the bands of coordinated acidic species to toluene due to neutralization with chloride ions.
    - No cobalt bands were observed in the spectrum.
- After extraction with diethyl ether the olive colored precipitate turned to light sky blue color and was found to be sensitive to air as it change color to pink indicting geometrical changes from blue tetrahedral into pink octahedral cobalt complex, and it was found to contain chloride ion and urea.

Fig. 6: Ultraviolet\visible spectra of (A) aluminum chloride-urea ionic liquid in toluene, (B) 0.5M and (C)1M cobalt chloride in ionic liquid, inset (C and B) cobalt chloride in ionic liquid (450-520) nm.

Nickel Sulfate in Aluminum Chloride-Urea Ionic Liquid in Toluene:

- Nickel sulfate reaction with the ionic liquid was of an exothermic nature, and produced three layers:
    - Upper colorless layer (toluene).
    - Deep green lower liquid layer.
    - Light green precipitate layer contain (nickel, sulfate, chloride, and aluminum ions) with the absence of urea.

- The UV. Visible spectroscopy showed in Fig. 7:
    - Disappearance of the band at 334 nm.
    - The band at 474 nm remained unchanged.
    - A new bands appeared at 431 nm, 644 nm and 905 nm which were related to the octahedral geometry.

Fig. 7: Ultraviolet\visible spectra of (A) aluminum chloride-urea ionic liquid in toluene full range, (B) 0.2M nickel sulfate in the aluminum chloride-urea ionic liquid in toluene full range and the inset (B) the nickel sulfate band in ionic liquid (430-900) nm.

Table (2):- The electronic spectroscopic behavior of Ni (II) ion in various ionic liquids and molten salt ionic liquids and suggested structure.

Solutions of Ni (II) ion	**Absorption Bands (nm)**	**Color**	**B' (cm^{-1})**	**ε($Lmol^{-1}$ cm^{-1})**	**Cal. β**	**Suggested structure**
Aqueous Solution	$\upsilon_{1cal.}$= 1075 υ_2= 658 υ_3= 395.5	Green	775.03	31 85	0.75	Oh. $[Ni(H_2O)_6]^{2+}$
(Aluminum Chloride -urea) in toluene	$\upsilon_{1cal.}$ = 905 υ_2 = 644 υ_3 = 431	Deep Green	356.25	36 33 42	0.346	Oh. distorted $[Ni(IL)_6]^{2+}$
LiCl\KCl	υ=1250 υ=704.2 υ=653.6	-	-	-	-	Distorted tetrahedral
CsCl	υ= 1333 υ=714.2 υ= 637	-	-	-	-	Tetrahedral

Butyramide/ $NaNO_3$	$\upsilon=1234$ $\upsilon=793$ $\upsilon= 429$	-	-	-	-	Octahedral
Acetamide/ KNO_3	$\upsilon=1333$ $\upsilon=800$ $\upsilon= 431$	-	-	-	-	Octahedral
Choline chloride/ urea	$\upsilon= 1050$ $\upsilon=(669-746)$ $\upsilon= 410$	-	-	-	-	Oh. $[Ni(urea)_4Cl_2]$
$NH_4Al(SO_4)_2 .12H_2O$/ urea	$\upsilon_{1cal.}= 1198$ $\upsilon_2= 670.5$ $\upsilon_3= 401.5$	Pale green	884.6	7 14.5	0.85	Oh. $[Ni(IL)_6]^{2+}$

Cupric Sulfate in Aluminum Chloride-Urea Ionic Liquid in Toluene:

- The reaction with the ionic liquid was exothermic and produced three layers:
  - Upper colorless toluene layer.
  - Deep green lower liquid layer.
  - Light green precipitate layer which was found to contain (copper, sulfate, chloride, and aluminum ions) with the absence of urea.
- The UV. Visible spectroscopy showed in Fig. 8 :
  - Immediate disappearance of the band at 334 nm
  - Decrease of the band at 474 nm along with the continuous addition of cupric sulfate.
  - New bands were appeared at 898 nm, at 820.5 nm, at 718.5 nm and 675 nm.
- The new four bands might be related to a geometrically distorted octahedral of copper (II) complex.

Fig. 8: Ultraviolet\visible spectra of (A) 1.5M cupric sulfate in the (aluminum chloride-urea) ionic liquid in toluene (614-902) nm, (B) inset: aluminum chloride-urea ionic liquid in toluene and cupric sulfate in the ionic liquid (full range).

Table (3):- The electronic spectroscopic behavior of Cu (II) ion in various ionic liquids and molten salt ionic liquids.

Solution of Cu (II) ions	**Color**	**Absorption bands (nm)**	**Transition**	**ε(Lmol^{-1} cm^{-1})**	**Suggested structure**
Aqueous solution	Blue	υ =797.5	$^2Eg \rightarrow {}^2T_2g$	10.8	Oh. $[Cu(H_2O)_6]^{2+}$
Aluminum chloride\urea in toluene	Deep green	υ_1 =898 υ_2 =820.5 υ_3 =718.5 υ_4 =675	$^2Eg \rightarrow {}^2A_1g$ $^2Eg \rightarrow {}^2B_1g$ $^2B_2g \rightarrow {}^2A_1g$ $^2B_2g \rightarrow {}^2B_1g$	14.9 13.7 13.2 12.97	Oh. distorted $[Cu(IL)_6]^{2+}$
AlCl3- 1,methyl 3ethylimidazolium chloride	-	υ= 34139(cm^{-1}) υ=24570 (cm^{-1})	$^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	-	Tetrahedral $CuCl4^{2-}$
LiCl/KCl	Pale blue	υ= 1052	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	-	Distorted Oh. Or Td.
Choline chloride/tartaric acid	Yellow	υ= 1089	$^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	10.6	Td. two chloride and one tartrate ions

الخلاصة:

تمت دراسة السائل الايوني المتكون من كلوريد الالمنيوم واليوريا لتحديد تركيز الاجزاء الفعالة بأستخدام التحليل الطيفي فوق البنفسجي المرئي لمتابعة تفاعل حامض وقاعدة لويس مع ايون الكلوريد. تكونت اصرة تناسقية بين اجزاء الالمنيوم الموجبة الموجودة في السائل الايوني وبين الحلقة الاروماتية للتولوين او البنزين ونتيجة لذلك تكونت حزم جديدة في المنطقة المرئية والفوق البنفسجية.

بأجراء تفاعل حامض وقاعدة لويس اختفت هذه الحزم الجديدة وتم عن طريق ذلك تحديد تركيز الاجزاء الموجبة الفعالة في السائل الايوني و كانت نسبتها المولية ٧٥% من كلوريد الالمنيوم الاصلي المستخدم في تحضير السائل الايوني بنسبة ١,٥ مول من كلوريد الالمنيوم الى ١ مول من اليوريا. وظهر من خلال الكسر المولي ان الناتج لهذا التفاعل كان بين ١مول من الاجزاء الموجبة الفعالة للسائل الايوني الى ١ مول من ايون الكلوريد المضاف.

تمت دراسة سلوك ايونات مركبات بعض العناصر الانتقالية (Cu (II)، Co (II) ، Ni (II)) في السائل الايوني بوجود تفاعل حامض و قاعدة لويس بيبن الاجزاء الحامضية الفعالية للسائل الايوني والجزء القاعدي من المواد المضافة (الكبريتات و الكلوريدات) بأستخدام التحليل الطيفي فوق البنفسجي المرئي. في اضافة كلوريد النحاس تناسق النحاس اظهر حزمة واحدة تابعة للشكل الهندسي ثماني السطوح. اما كلوريد الكوبلت اظهر سلوكاً مختلفاً عن كلوريد النحاس حيث انه تفاعل مع الاجزاء السالبة للسائل الايوني مكونا معقداً ذا شكل رباعي السطوح الذي كان قد تكون بشكل راسب اما السائل فلم يظهر اي حزم للكوبلت وهذا المعقد اظهر وجود اليوريا و ايونات الالمنيوم والكلوريد.

عند اضافة كبريتات النيكل للسائل الايوني سلوكها لم يظهر تغيرات كبيرة، حيث ان الحزم الدالة في ٣٣٤ نانومتر و ٤٧٤ نانومتر قد انخفضت مع زيادة اضافة الملح و تناسق ايون النيكل كان ذو شكل ثماني السطوح مشابه لذلك الذي ظهر في سوائل ايونية اخرى لكن بتأثير مجال اقوى كما ظهر في اضافة كبريتات النحاس.

اما في حالة اضافة كبريتات النحاس فأن تناسق النحاس اظهر وجود اربع حزم والتي تكون مرتبطة بالمجال القوي لليكندات السالبة المتناسقة مع ايون النحاس مما ادى الى فصل اوربيتالات-d بشكل اكثر وضوحا من تأثير John-Teller في حالة اضافة كلوريد النحاس.

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

دراسة طيفية لبعض املاح العناصر الانتقالية في السائل الايوني

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

من قبل

مروة حميد فاضل

بكلوريوس ٢٠١٠ (جامعة النهرين)

بأشراف

الدكتور هادي محمد علي عبود

CHAPTER ONE

INTRODUCTION

CHAPTER TWO

EXPERIMENTAL PATR

CHAPTER THREE

RESULTS AND DISCUSSION

REFERANCES