Journal of Al-Nahrain University Vol.16 (3), September, 2013, pp.46-55 Science

The Electronic Transition Behavior Cr (III), Fe (III), Fe (II) and Ni (II), Transition Metal Cations In Ammonium Alum-Urea Room Temperature Ionic Liquid

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Abstract

Some transition metal cations, Cr (III), Fe (III), Fe (II) and Ni (II), were soluble in the new alum/urea ionic liquid and found to coordinate to it with weak coordination bond. This was reflected by the change of strength of the electronic spectra of the cations or the nature of these spectra as with Fe (II) when it showed high spin and low spin with nitrite and thiocyanate ions. It was also observed that water molecules of the solid composition of ionic liquid were not free in ionic liquid particularly when metal cations electronic behavior were compared to those in aqueous solution. Basic species of ionic liquid were suggested to have weak ionic strength.

Keyword: Ionic liquid, Transition metal, UV. Visible, Electronic transition.

Introduction

Green chemistry or sustainable chemistry, is the use of chemistry for pollution prevention the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.[1,2] Green solvents are environmentally friendly solvents or bio solvents, which may even be derived from the processing of agricultural crops. Ethyl lactate, for example is a green solvent derived from processing corn.[3]

The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment. The use of toxic solvents contributes to air emission of volatile organic compounds (VOCs), they are now considered as environmentally unacceptable.[4] Alternative promising areas of research in the replacement of the use of VOCs in industry include the application of supercritical carbon dioxide and ionic liquids as alternative solvents, both of which have proved to have valuable applications.[5]

An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salt whose melting point is below some arbitrary temperature, such as 100°C (212°F). IL is largely made of ions and short-lived ion pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts or liquid salts, the ionic bond is usually stronger than the Vander Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. One of the earliest truly room temperature ionic liquids was ethyl ammonium nitrate [$C_2H_5NH_3^+NO_3^-$] (m.p. 12°C), synthesized in 1914 by Paul Walden.[6] In the 1970s and 1980s ionic liquids based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, were initially developed for use as electrolytes in battery applications.[7,8] In 1992, Wilkes and Zaworotko obtained ionic liquids with 'neutral' weakly coordinating anions such as hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-), allowing a much wider range of applications.[9] Abbott et. al.[10] prepared a new class of air and moisture stable ionic liquids based on choline chloride, a green chemistry of such ionic liquids were demonstrated particularly in the metal process such as metal winding coating. Most recently a new ionic liquids based on aluminium chloride were prepared by Abood,[11] when the aluminium chloride combined with either urea, acetamide or trimethyl urea. These ionic liquids are much stable than chloroaluminate ionic liquids, offering solvent with relatively cheaper and easily prepared ionic liquids and promising similar properties in at least its catalytic properties for organic reactions and aluminum metal coating on metal substrate. Ammonium alum mixed with urea or acetamide offered a room temperature ionic liquid with highly moisture and air stable characterization.[12] As this is green ionic liquid therefore expected to be used in variable process such as metal coating and it offer good media to dissolve some water insoluble compounds such as silver sulfate.[12]

Ionic liquids are often moderate to poor conductors of electricity, non-ionizing (e.g. non-polar), highly viscous and frequently exhibit low vapor pressure, their other properties are diverse, many have low combustibility, excellent thermal stability, some ionic liquids (such as 1-butyl -3-methylimidazolium nitrate) generate flammable gases on thermal decomposition, thermal stability and melting point depend on the liquid's components.[13]

Renner[14] has summarized some applications of ionic liquids for both homogeneous and heterogeneous catalysts as selected ionic liquids can be immiscible with the reactants and products but dissolve the catalysts, synthesis of pharmaceuticals, treatment of high-level nuclear waste, removing of metal ions such as removal of cadmium and mercury from contaminated water. Ionic liquids can also selectively dissolve and remove gases and could be used for air purification on submarines and spaceships.[14]

The present work concentrated on investigating the interaction, coordination and reactivity of chromium (3+), Fe (2+ and 3+) and Ni (2+) in the new ionic liquid formed by mixing ammonium alum with urea.[12] electronic spectroscopy was used to follow their coordination with the ionic liquid ionic basic species and their substitution upon addition of thiocyanate, nitrite, EDTA or oxalic acid to establish their stability in the alum/urea ionic liquid.

Experimental

Ammonium alum, Chromium (III) chloride hexahydrate, Iron (III) chloride hexahydrate, Iron (II) sulfate heptahydrate, Oxalic acid and Sodium nitrite of BDH of not less than 99% and Urea and EDTA of THOMAS BAKER and Sodium nitrite of FLUKA of 99.5% purity were used without further purification.

Ammonium alum, $[NH_4Al(SO_4)_2.12H_2O]$ and urea $[NH_2CoNH_2]$ in mole ratio of (1:5) were milled, mixed and heated gradually to (85°C) with continuous gentle stirring until both melted together producing colorless liquid. The resulted melt was gradually cooled to room temperature and remained liquid[12] and stored in sealed container.

The electronic spectra of complex solutions were obtained by using CECEL CE7200, UV-Vis, Ultraviolet Visible spectrophotometer at room temperature using quartz cells of 1.0 cm path length and water reference in the range of wavelength 190-900 nm. While no absorption was recorded in the visible region a low absorbance band at 276 nm in the ultraviolet region was observed and related to the ionic liquid.

Results and Discussion

1. Chromium (III) chloride hexahydrate in ionic liquid:

Chromium (III) chloride hexahydrate ($CrCl_3.6H_2O$) dissolved in ammonium alum–urea ionic liquid with agitation at 40°C and the resulted solution of 0.1 M after 15 minutes was deep green in color, Scheme (1.A). This solubility was found to be much better than those reported for the same compound in other ionic liquids or molten salts.[15,16] For example the salt was found to be much less soluble (0.001 M) after 15 hours at (90°C) in acetamide/potassium nitrate melt or also 0.001M after 8 hours at (140°C) in butyramide/sodium nitrate.[15] In addition this compound was reported to have solubility of (0.1 M) after 72 hours in choline chloride/urea with continuous stirring.[16] This may indicate that hydrated ammonium alum/urea ionic liquid is stronger solvent than those reported above with having larger solvation energy to interact with chromium chloride ions.

The electronic ultraviolet-visible test of the deep green solution was carried out to investigate the electronic behavior of the resulted coordinated chromium (III) ion in the ionic liquid. Therefore the test showed two absorption bands in the visible region at (435 nm) and (615 nm), the latter band showed two shoulders at the lower energy region (689 nm) and (658 nm) Fig. (1.B).

In the ultraviolet region the deep green solution showed a charge transfer band started around (350 nm) with very large absorbance and a distinct band at (278 nm) appeared as a shoulder on the charge transfer band and in the same position of that shown by ionic liquid alone Fig. (1.A). It is known that electronic ground state, ^4F, of d^3 ionic configuration of Cr (III) would split in octahedral crystal field into three electronic transitions and thus the observed spectra were assigned to the first two bands while the third spectra was calculated using Tanabe-Sugano diagram and found to have a value of 273 nm, almost in the same position of that of the ionic liquid alone (278 nm) but with higher absorbance which covered that of the ionic liquid.

It was found that the band energies of the coordinated Cr (III) ion in hydrated ammonium aluminum sulfate ($NH_4Al(SO_4)_2$)/urea ionic liquid were close to those reported in other ionic liquids, Table (1), such as Cr (III) chloride in choline chloride/urea (608 nm and 440 nm) where the Cr (III) reported to have octahedral coordination with six urea ligands.[16] In addition spectra of Cr (III) ion in acetamide/potassium nitrate (596 nm and 445 nm) where Cr (III) ions also assigned to have octahedral coordination with six acetamide or six nitrate ligands.[15] In its solid state, chromium alum, showed two bands in the visible region at (574 nm and 408 nm), also assigned to an octahedral geometry.[17]

Therefore the observed bands in hydrated ammonium aluminum sulfate/urea ionic liquid would also expected to have octahedral geometry, yet the energy splitting of the electronic states (term symbol) is relatively at lower energy from those reported values in other medium or solid alum reflecting the weaker field strength of ionic species of this ionic liquid. However, chloride molten salts which have solely chloride ions showed weaker interaction of chloride with Cr (III) ions as reported in LiCl/KCl melt where band energies reported at 800 nm and 540 nm [18] compared to those of the present ionic liquids.

Chromium (III) was also re-tested in aqueous medium by uv-visible spectroscopy to establish whether the cations interacted solely with water molecules of the hydrated alum salt or with other species present in the ionic liquid such as urea, sulfate or a complex ions arise from the formation of the ionic liquid. Therefore the electronic behavior of chromium (III) in both ionic liquid and water are presented in Fig. (1.C).

The wavelength observed in aqueous solution were at higher energy than those obtained in hydrated ammonium aluminum sulfate/urea ionic liquid (420 nm and 587 nm) Fig. (1.C) compared to (435 nm and 615 nm) Fig. (1.B) of aqueous and ionic liquid respectively, gives a support to the weaker nature of the ionic liquid species coordinated to chromium (III) ions than water molecule and thus water molecule presented in the initial alum salt are not free in ionic liquid, otherwise it would coordinate to chromium cations and give similar spectra to those shown in aqueous solution. An additional support to this conclusion is the higher molar absorptivity Table (1) of the metal cations in ionic liquid (37 and 32 L $mol^{-1}cm^{-1}$) than in aqueous solution (16 and 21 L $mol^{-1}cm^{-1}$) reflecting most probably the less symmetrical geometrical structure in ionic liquid where complex ionic species coordinated to the metal cations than in aqueous solution where only water molecules are present. Furthermore the ligand factor (f_{ligand}) obtained from the following equation , (g_{ion}) represent the metal strength, normally applied for aqueous metal solutions:[19]

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

was found to have a value of (0.93) which is smaller than the water field factor ($f = 1$). This might also gives additional support to the lower energy bands observed in ionic liquid than in aqueous solution.

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

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

In general it could be concluded that the higher energy differences between the spectra of Cr (III) in aqueous media compared to those in ionic liquid, f_{ligand} and the calculated different values of molar absorptivities in both media strongly suggested that the interaction in ionic liquid is not with water molecule that are initially present in the lattice of starting ammonium alum salt ($NH_4Al(SO_4)_2.12H_2O$). This also indicated that the presence of water molecule in ionic liquid is not as free molecules but still retaining their original interaction with the cations of the alum (Al^{3+} or NH_4^+) there by allowing ionic species with weaker strength to bound with chromium (III) metal in an octahedral coordination interaction.

In an attempt to study the possible substitution reaction of ionic liquid species by added anionic species, biphilic thiocyanate or sodium nitrite, EDTA and oxalate were added to ionic liquid solution containing chromium (III) chloride in a (1:1) mole ratio. The original deep green solution did not change color and the UV-Visible spectroscopic measurement revealed no change to the original spectra of chromium solution even when the concentration increased to 10:1 (ligand : metal). The only change was observed at the third transition band when the intramolecular transition of the ligands started at lower energy thereby covered the metal (υ_3) transition. The spectra and their absorptivity are presented in Table (1).

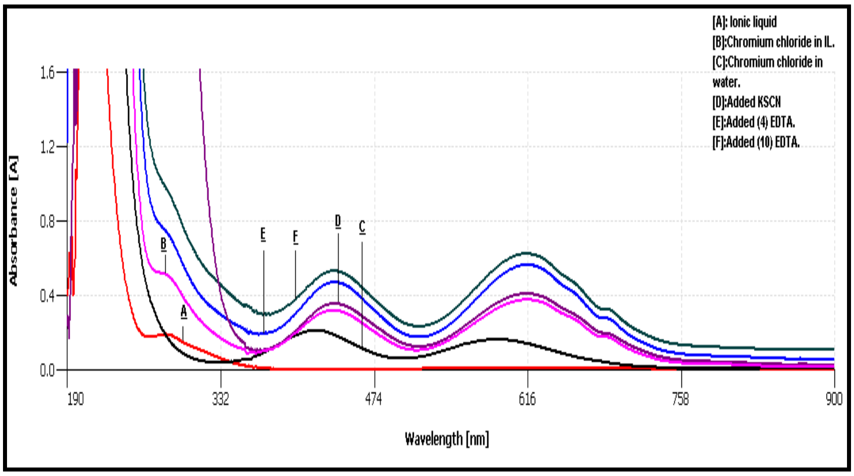


Fig. (1) [A] Ammonium alum/urea ionic liquid alone. [B]: Chromium (III) chloride in ammonium alum/urea ionic liquid. [C]: Chromium (III) chloride in water. [D]: Added (1) mole KSCN. [E]: Added (4) moles of EDTA. [F]: Added (10) moles of EDTA.

Table (1)

Electronic spectra for complexes of $CrCl_3.6H_2O$ in various room temperature ionic liquids.

Chromium (III) chloride	***Absorption bands (nm)***	***B` (cm^{-1})***	***Cal. B***	***10Dq (cm^{-1})***	***Suggested Structure***	***ε ($Lmol^{-1}$ cm^{-1})***
Aqueous solution	υ_1= 587 υ_2= 420 $\upsilon_{3(cal.)}$= 262	680.8	0.74	17035	Oh$[Cr(H_2O)_6]^{3+}$	16 21
$NH_4Al(SO_4)_2.12H_2O$/ urea	υ_1= 615 υ_2= 435 $\upsilon_{3(cal.)}$= 273	676.4	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	37 32
$NH_4Al(SO_4)_2.12H_2O$/ urea+KSCN (1:1) mole	υ_1= 614 υ_2= 436 $\upsilon_{3(cal.)}$= 273	676.3	0.73	16273	Distorted Oh $[Cr(IL)_6]^{3+}$	41 35
$NH_4Al(SO_4)_2.12H_2O$/ urea+$NaNO_2$ (1:1) mole	υ_1= 615 υ_2= 435 $\upsilon_{3(cal.)}$= 273	676.1	0.73	16246	Distorted Oh $[Cr(IL)_6]^{3+}$	40 32
$NH_4Al(SO_4)_2.12H_2O$/ urea+Oxalic acid (1:1) mole	υ_1= 615 υ_2= 436 $\upsilon_{3cal.}$= 273	676	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	41 35
$NH_4Al(SO_4)_2.12H_2O$/ urea+EDTA (1:4) mole	υ_1= 615 υ_2= 436 $\upsilon_{3cal.}$= 273	676	0.73	16260	Distorted Oh $[Cr(IL)_6]^{3+}$	56 47
$NH_4Al(SO_4)_2.12H_2O$/ urea+EDTA (1:10) mole	υ_1= 614 υ_2= 435 $\upsilon_{3cal.}$= 273	676.9	0.73	16286	Distorted Oh $[Cr(IL)_6]^{3+}$	62 53

2. Iron salts:

Iron (III) chloride hexahydrate showed a very faint yellow solution (0.01M at 40°C for 15 minute) Scheme (1.B), in the ammonium alum/urea ionic liquid reflecting the very weak transition of the forbidden by Laporte rule d^5 electronic transition (556 nm, 782 nm, and 876 nm), Fig. (2.A).

The metal salt was found to be more soluble than in acetamide-potassium nitrate or in in $LiNO_3/KNO_3$ when the salt dissolved at 90°C and 160°C [15] or required longer time in choline chloride/urea of (0.1 M) after 72 hours.[16]

Although when sodium nitrite was added to this solution in a 1:1 mole ratio did not show any changes to the color or the transition states of the metal, potassium thiocynate in the same ratio changed the solution to deep red Scheme (1.C) which arise from the ligand to metal charge transfer transition which absorbed most of the blue end of the visible region. The similar absorption and molar absorptivities in different ionic liquids are summarized in Table (2) and thus iron (III) chloride was assigned a tetrahedral structure similar to those suggested in other ionic liquids.[15,16]

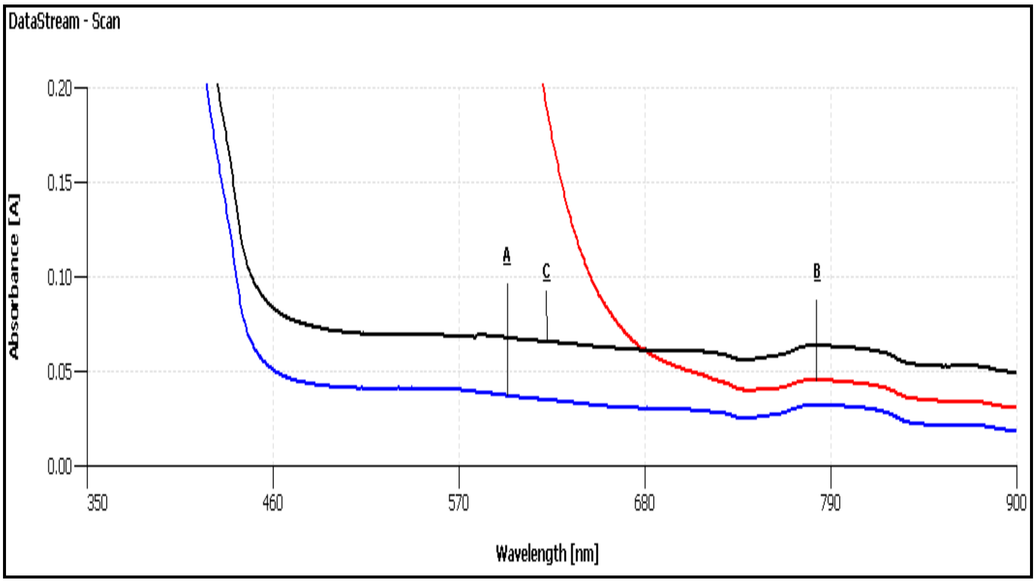


Fig. (2) [A] Iron (III) chloride in ammonium alum/urea ionic liquid. [B]: Added (1) mole KSCN. [C]: Added (1) mole sodium nitrite.

Table (2)
The behavior of Fe (III) ion in ionic liquid and with added the ligands.

Iron (III) chloride	***Absorption bands (nm)***	***Color***	***ε(Lmol⁻¹cm⁻¹)***	***Suggested structure***
Aqueous solution	$\upsilon = 482$	Yellow	40.6	Oh.$[Fe(H_2O)_6]^{3+}$
ammonium alum/urea	$\upsilon_1 = 876$ $\upsilon_2 = 782$ $\upsilon_3 = 556$	Pale yellow	2 3.2 4	Th.$[Fe(IL)_4]^{3+}$
Ammonium alum/urea + KSCN(1:1) mole	$\upsilon_1 = 876$ $\upsilon_2 = 782$	Blood red	3.3 4.5	Th.Fe^{3+} interact with KSCN
Ammonium alum/urea + $NaNO_2$(1:1) mole	$\upsilon_1 = 876$ $\upsilon_2 = 782$ $\upsilon_3 = 556$	Pale yellow	5.2 6.3 6.7	Th.$[Fe(IL)_4]^{3+}$

The electronic ultraviolet-visible spectroscopy examination of the colorless solution of 0.03 M Fe (II) sulfate heptahydrate showed one broad absorption band at (899 cm^{-1}) with charge transfer started around (400 nm) Fig. (3.A). The term symbol for the ground state of Fe (II) ions in (d^6), configuration is (^5D) that split in tetrahedral crystal field with a transition from ^5E to $^5T_2$. Similar coordination of Fe (II) in LiCl/KCl at (400°C) reported to have band at (1960 nm) and assigned to form tetrahedral coordination, and at (1000°C) to have band at (1666 nm) and assigned to a distorted tetrahedral coordination.[18]

Added anionic biphilic species, thiocyanate to ionic liquid solution containing Fe (II) sulfate in a (1:1) mole ratio, changed after heating to (40°C) to the original colorless solution to orange Scheme (1.D), and found to have a distinctive high absorbance band at (436 nm) with molar absorptivity of (49.3 $Lmol^{-1}cm^{-1}$) followed by a very high charge transfer spectrum, Fig. (3.B).

This was related to (^5D) term symbol for Fe (II) ion in (d^6) configuration that may split in octahedral crystal field at high spin as from $^5T_{2g}$ to ^5E_g.

$NaNO_2$ was reacted with the colorless Fe (II) solution in a 2:1 mole ratio giving olive green solution Scheme (1.E) with absorption bands at (457 nm and 588 nm υ_2 and υ_3) Fig. (3.C). These spectra were considered to be due to low spin d^6 configuration which would expected to show three transition bands arising from a singlet ground state of $^1A_{1g}$ to $^1T_{1g}$, $^1T_{2g}$ and ^1E_g as stated in Tanabe-Sugano diagram from which υ_1 was calculated to have a value of (966 nm). It is interesting to note that Fe (II) showed tetrahedral coordination in ionic liquid alone either in this work or LiCl/KCl molten salt[18], but the metal changed its coordination to octahedral either high spin incase of added thiocyanate or low spin with nitrite.

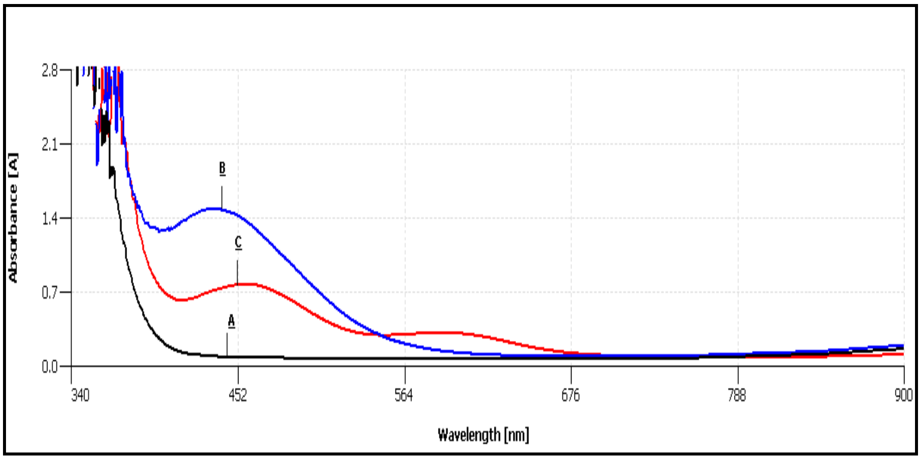


Fig. (3) [A] Iron (II) sulfate in ammonium alum/urea ionic liquid. [B]: Added (1) mole KSCN. [D]: Added (2) moles of sodium nitrite.

Table (3)
The electronic spectra for Fe (II) ion in ionic liquid and with various ligands.

Iron (II) ion	***Absorption bands(nm)***	***Color***	***Transitions***	***ε($Lmol^{-1}cm^{-1}$)***	***Suggested structure***
Aqueous solution	υ= 360	Yellow	$^5T_{2g} \rightarrow {}^5E_g$	39	Oh.$[Fe(H_2O)_6]^{2+}$
Ammonium aluminum /urea	υ= 899	Color less	$^5E \rightarrow {}^5T_2$	5	Th.$[Fe(IL)_4]^{2+}$
Ammonium alum/urea+KSCN(1:1) mole	υ= 436	Orange	$^5T_{2g} \rightarrow {}^5E_g$	49.3	Distorted Oh. Fe^{2+} interact with KSCN
Ammonium alum/urea+$NaNO_2$(1:2) mole	$\upsilon_{1Cal.}$= 966 υ_2= 588 υ_3= 457	Olive green	$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$ $^1A_{1g} \rightarrow {}^1E_g$	10.3 25.6	Distorted Oh. Fe^{2+} interact with one or more $NaNO_2$

3.Nickel sulfate hexahydrate:

Nickel (II) sulfate hexahydrate, (0.02 M), was achieved after 2 hours at 40 ˚C, 2 hours giving pale green Scheme (1.F). Similarly in choline chloride/urea ionic liquid nickel chloride dissolved with difficulty as it required 72 hours at room temperature.[16] The chloride solubility was also reported in LiCl/KCl molten salt at (700-1000°C) and in CsCl melt at (864°C).[18] Therefore the sulfate being faily soluble in ammonium alum/urea ionic liquid.

The electronic transition of the pale green solution of nickel sulfate in ammonium alum/urea ionic liquid was investigated by ultraviolet-visible and revealed two bands at 401 nm of $\upsilon_3 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and a split band in the visible region at (670 nm $\upsilon_2 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ Fig. (4.B). These are known range for octahedral coordination of nickel complexes, yet the third band which normally existed at lower frequency was not detected due to the limit of the spectrophotometer. While $\upsilon_1={}^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ was calculated from Tanabe-Sugano diagram for d^8 configuration which indicated that its value equal to (1198 nm). The relatively broad band at 670 nm could be related to two bands resulted from the d-d spin allowed electron state of ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and spin forbidden ${}^3A_{2g}\rightarrow {}^1E_g$ electronic state which appeared due to orbital coupling.[20] The similarity in its behavior, nickel (II) sulfate hexahydrate also showed octahedral configuration in aqueous solution Table (4) but with relatively higher transition energies, reflecting the stronger water molecules as a ligand in comparison to ionic liquid species, and also support the previous behavior found with Cr (III), Fe (III) and Fe (II) which also suggested weaker ionic liquid than water molecules interaction. These added observation strongly suggest the non free nature of the originally present water.

Spectroscopic investigation of the successful addition of thiocyanate Fig. (5.B) reveal an obvious change in the charge transfer spectra which stated with very high absorbance at around (333 nm) overshadow the ionic liquid transition at (277 nm). This might be taken as an indication to the interaction between thiocyanate with Ni (II) although the metal did not change its octahedral configuration when substituted its ionic liquid interaction with thiocyanate anion. Another indication to the interacted thiocyanate with Ni (II) although it showed similar band energies Table (4), the molar absorptivity increased by four times on addition of (10:1) thiocyanate to Ni (II) cation indicating a less symmetrical coordination of ligands to the metal there by reducing the octahedral symmetry. However, the further increased in molar absorptivity at (30:1) mole ratio could be explained also to the increased concentration of the complex. The octahedral coordination of Ni (II) in different ionic liquids was also reported in butyramide/$NaNO_3$ and acetamide/KNO_3,[15] and in choline chloride/urea.[16] However in highly ionic chloride melt CsCl Ni (II) showed tetrahedral coordination and distorted tetrahedral in LiCl/KCl molten salts.[18] This would revealed the less electrostatic nature of interaction of Ni (II) in present ionic liquid. In contras to its behaivior to the monodentate ligands in choline chloride/malonic acid room temperature ionic liquid, nickel (II) showed a tetrahedral coordination.[16] Equivalent concentration of sodium nitrite added to nickel sulfate solution did not change the position of the electronic transition bands of nickel (II) in ionic liquid, revealing no strong direct interaction of the metal with nitrite. However this does not means that there was no interacted effect due to presence of nitrite in solution. This might be seen from the higher molar absorptivity in presence of nitrite ligand compared to without adding nitrite (compared 4.1 $Lmol^{-1}cm^{-1}$ to 15.5 $Lmol^{-1}cm^{-1}$ respectively).

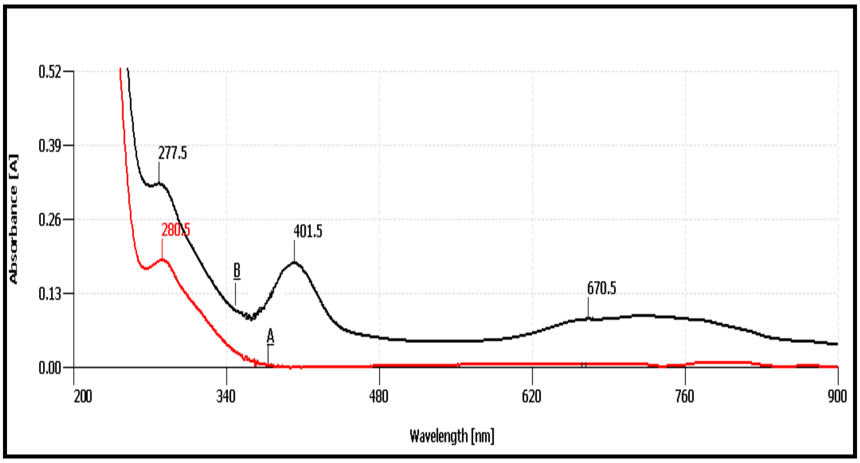


Fig. (4) The UV. Visible spectrum for [A]: ammonium aluminum alum /urea ionic liquid alone. [B]: $NiSO_4.6H_2O$ in ammonium aluminum alum / urea room temperature ionic liquid.

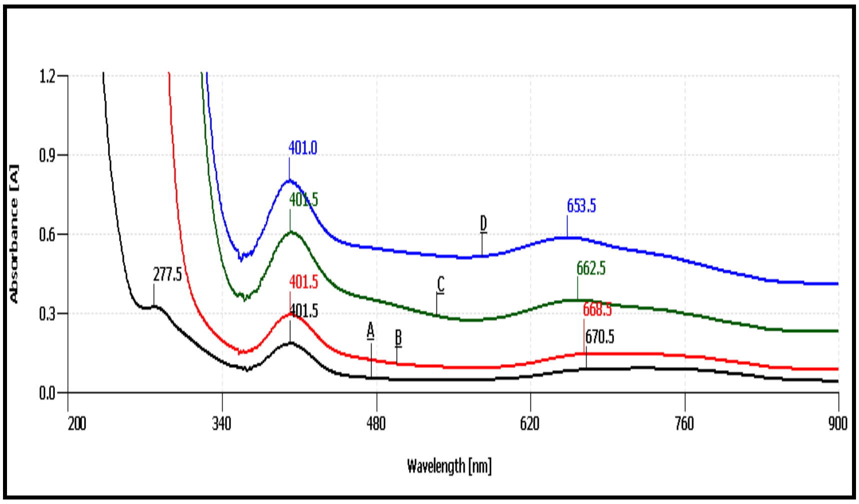


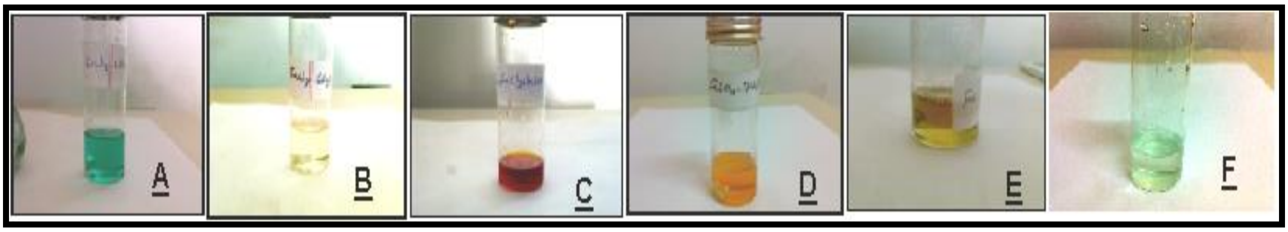
Fig. (5) The UV. Visible spectra for $NiSO_4.6H_2O$ in [A]: ammonium alum /urea room temperature ionic liquid. [B]: Added (5) moles of KSCN. [C]: Added (10) moles of KSCN. [D]: Added (30) moles of KSCN.

Table (4)

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

Ni (II) ion	*Absorption bands(nm)*	*Color*	*B` (cm^{-1})*	*ε($Lmol^{-1}cm^{-1}$)*	*Suggested structure*
Aqueous solution	$\upsilon_{1cal.}$= 1113 υ_2= 656 υ_3= 396	Green	898.3	5 14	Oh. $[Ni(H_2O)_6]^{2+}$
$NH_4Al(SO_4)_2.12H_2O$/urea	$\upsilon_{1cal.}$= 1198 υ_2= 670 υ_3= 401	Pale green	927.2	4.1 9.1	Oh. $[Ni(IL)_6]^{2+}$
$NH_4Al(SO_4)_2.12H_2O$/urea+ KSCN (1:5) mole	$\upsilon_{1cal.}$= 1130 υ_2= 668 υ_3= 401	Pale green	884.6	7 14.5	Oh. $[Ni(IL)_6]^{2+}$
$NH_4Al(SO_4)_2.12H_2O$/urea + KSCN (1:10) mole	$\upsilon_{1cal.}$= 1125 υ_2= 662 υ_3= 401	Green	888.6	17.3 30.3	Oh. Ni^{2+} interact with one or more KSCN
$NH_4Al(SO_4)_2.12H_2O$/urea + KSCN (1:30) mole	$\upsilon_{1cal.}$= 1116 υ_2= 653 υ_3= 401	Olive green	895.3	29 40	Distorted Oh. Ni^{2+} interact with one or more KSCN
$NH_4Al(SO_4)_2.12H_2O$/urea + $NaNO_2$ (1:1) mole	$\upsilon_{1cal.}$= 1187 υ_2= 667 υ_3= 396	Faint green	935.7	15.5 21	Oh. Ni^{2+} interact with one or more $NaNO_2$

In conclusion, it was found that hydrated chromium chloride, iron (II) sulfate, Iron (III) chloride and nickel (II) sulfate fairly soluble in alum/urea ionic liquid and their coordination with the ionic species of ionic liquid was weak due to weak ionic strength of basic ionic liquid species. In addition the initially present water molecules of the ionic liquid composition were not free as they retained their interaction with the cations present in the initial solid lattice (Al^{3+} and NH_4^+). The metal cations showed interesting variable coordination in this liquid such as the octahedral stable Cr (III) and low and high spin octahedral Fe (II) when nitrite and thiocyanate ions are present respectively. Nickel however did not interact strongly with nitrite ions as did Fe (II) or in presence of thiocyanate. These in general would indicate that this ionic liquid could be used as medium for complex formation catalyst or gas purification which require coordination of different ligands with the cations.



Scheme (1) [A]: Chromium (III) chloride in ammonium alum/urea ionic liquid. [B]: Iron (III) chloride in ammonium alum/urea ionic liquid. [C]: Iron (III) chloride in IL with added KSCN (1:1) mole ratio. [D]: Iron (II) sulfate in IL with added KSCN (1:1) mole ratio. [E]: Iron (II) sulfate in IL with added sodium nitrite (1:2) mole ratio respectively. [F]: Nickel (II) sulfate in ammonium alum/urea ionic liquid.

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الخلاصة

بعض ايونات العناصر ألانتقاليه (Cr (II), Fe (III), Fe (II) و Ni (II)) تكون قابله للذوبان في السائل ألايوني الجديد (شب الامونيوم–يوريا) ووجد إنها قد ارتبطت مع السائل الأيوني باصره ضعيفة, وهذا ينعكس من خلال التغير في شده الأطياف الالكترونية من الايونات الموجبة و طبيعة هذه الأطياف كما في الحديد عندما اظهر دوران عالي البرم و واطئ البرم مع النترات و ايونات الثايوسيانايد، وأيضا كان واضح أن جزيئات الماء في السائل الأيوني للجزء الصلب لم تكن حره خصوصا عند مقارنه سلوك الايونات ألموجبه الالكترونية الموجوده في السائل الأيوني بتلك الموجوده في المحلول المائي.