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## Investigation of the New Room Temperature Ionic Liquid of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with Urea $\text{CO}(\text{NH}_2)_2$

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### Abstract:

Mixing aluminum nitrate nonahydrate with urea produced room temperatures clear colorless ionic liquid with lowest freezing temperature at (1: 1.2) mole ratio respectively. Freezing point phase diagram was determined and density, viscosity and conductivity were measured at room temperature. It showed physical properties similar to other ionic liquids. FT-IR, UV-Vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were used to study the interaction between its species where - CO — Al- bond was suggested and basic ion  $[\text{Al}(\text{NO}_3)_4]^-$  and acidic ions  $[\text{Al}(\text{NO}_3)_2 \cdot x\text{U}]^+$  were proposed. Water molecule believed to interact with both ions. Redox potential was determined to be about 2 Volt from - 0.6 to + 1.4 Volt with thermal stability up to 326 °C.

**Key words:** Room Temperature Ionic liquids (ILs), Green solvent, Physicochemical properties.

### Introduction:

Ionic liquids can be defined as a new class of solvents, or as salts with the melting point arbitrarily determined to be below 100°C. They are composed of ions and, thus, each IL possesses unique properties that are due to cation and an anion nature[1-4]. However, Room-Temperature Ionic Liquids (RTILs) have been developed to be the basic alternative to the volatile organic compounds(VOC) for being stable chemically and electrochemical, non-flammable, a high ionic density and conductivity, non-volatile, etc.[5]. So there are several reasons that ionic liquids are considered as “green solvents” and therefore, the ‘designer

solvent’ can be created for many applications, including biotransformation, chemical reactions (e.g. catalysis and hydrogenation), biorefinery concept, extraction and separation, and others[6,7].

A type of ionic liquids is the eutectic solvents, which have interesting solvent properties. The eutectic solvent of a mixture of choline chloride and urea melt at 12°C [8,9]. A series of ternary deep eutectic solvents made from sugar-urea- salt mixtures were also reported as solvents for organic synthesis[10]. One of other reported ionic liquids by Abood and co workers, involves the addition of a simple amide to  $\text{AlCl}_3$  resulting in the

formation of ionic liquids of the type  $[AlCl_2.nAmid]^+[AlCl_4]^-$  [11].

### Materials and Methods

All chemicals were supplied without any further purification. Aluminum nitrate nonahydrate  $Al(NO_3)_3.9H_2O$  98.5% BDH and Urea  $CO(NH_2)_2$  99.5% BDH both materials were used.

The Infrared spectra in the range (4000-400 $cm^{-1}$ ) were recorded on Fourier Transform Infrared Spectrophotometer, 2006, IR-Prestige 21, Shimadzu 8000. The HANNA instruments HI 9811 in mS/cm using to carry out conductivity measurement, and viscosity measurement were carried out manually, the density measurement was by using bottle size 25 ml. The Instrument for Cyclic voltammogram (CV) recorded using Digi-lvy-Dy2300 Bipotentiostat with Three-electrode system comprising of a platinum plate as working electrode (WE), a platinum disc of 2 mm as the counter electrode (CE) and a silver wire used as a reference electrode (RE). Using CECEL CE7200. Ultraviolet-visible spectrophotometer at room temperature using quartz cells of 1.0cm path length in the range of wavelength 190-900 nm to obtain electronic spectra.

Thermogravimetric analysis using (STA PT-1000) LINSEIS instrument, the heating rate of 10 $^{\circ}C/min$  in the range of 25-500 $^{\circ}C$ . NMR spectra were recorded on Burker 500M Hz instrument using DMSO- $d_6$  as solvent and TMS as an internal reference.

The elemental analysis (C.H.N) of urea nitrate were carried out by EM-017.mth instrument. The measurements of the XRD patterns of the combustion products were recorded using a Shimadzu XRD-6000 with Cu- $K\alpha$  radiations.

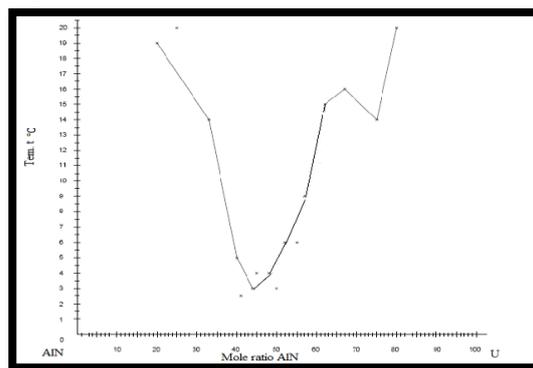
### Preparation of the Ionic Liquid

Aluminum nitrate nonahydrate and urea were used to prepare ionic liquid in

different proportions. Solid salts of aluminum nitrate nonahydrate which had a m.p. of 72 $^{\circ}C$  and urea with 132 $^{\circ}C$ . were mixed, then heated gradually to 85 $^{\circ}C$  for (2-3) hrs., with a continuous mechanical stirring until both melt together providing a colorless and homogeneous liquid. The produced ionic liquid then cooled to room temperature and stored in a sealed container. Samples from this ionic liquid were used for further identifications.

### Results and Discussion:

The prepared binary ionic liquid,  $[Al(NO_3)_3.9H_2O/urea]$  was found to have the lowest freezing point at 3 $^{\circ}C$  and can be used as an ambient temperature solvent. The molar ratio effect on freezing point is illustrated in Figure.(1).



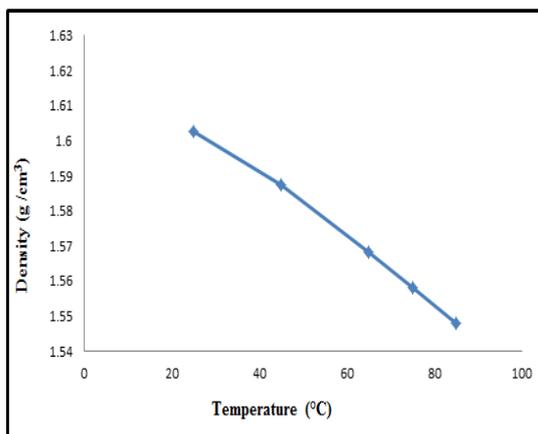
**Fig. (1):Phase diagram for (Aluminum nitrate with Urea) system plot for  $t^{\circ}C$  versus mole ratio of aluminum nitrate.**

This liquid was found to have a conductivity of 9.09 $mS\ cm^{-1}$ , density 1.6028  $g\ .cm^{-3}$  and viscosity of 20.579 pois at 25 $^{\circ}C$ , Table (1) shows a comparison at between three ionic liquids (ILs) on urea with three different aluminum salts 25 $^{\circ}C$ . The effects of temperatures on the density and viscosity of the new ionic liquid (IL) in this work has both density and the viscosity to be decreased with increasing temperature.

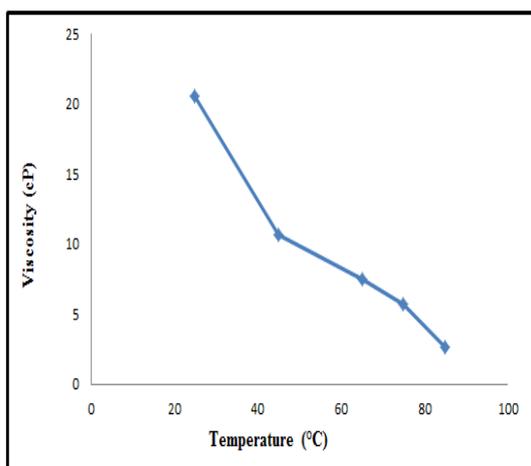
Arrhenius plot of viscosity against temperature was accepted by ionic liquid and showed that viscosity dependent on the temperature, this illustrated in Figures (2 to 4). Figure (5) shows a plot of conductivity and viscosity of  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} / \text{CO}(\text{NH}_2)_2]$  (1:1.2) mole ratio.

**Table(1):Density, viscosity, and conductivity for different Ionic Liquids.**

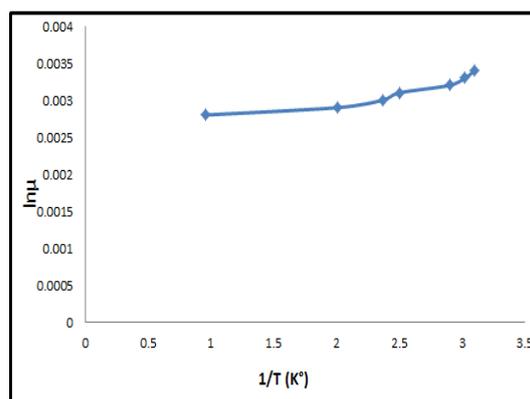
ILs	Density (g.cm <sup>-3</sup> )	Viscosity (cP)	Conductivity (mS.cm <sup>-1</sup> )	pH	Ref.
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}:\text{Urea}$	1.6028	20.579	9.09	1.1	In this work
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}:\text{Urea}$	1.5	-----	4.05	4.2	12
$\text{AlCl}_3:\text{Urea}$	1.4	60	0.804	---	11



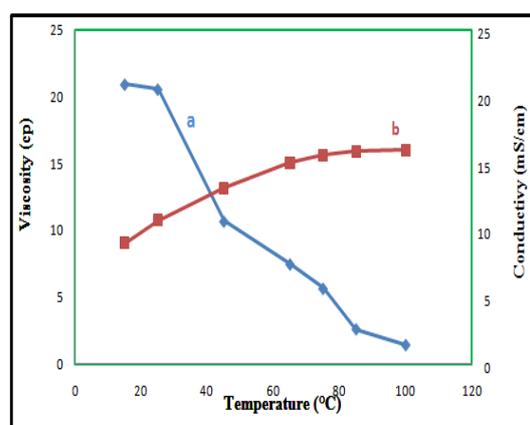
**Fig.(2):Density of ionic liquid at different temperatures.**



**Fig.(3):Viscosity of ionic liquid at different temperatures.**



**Fig. ( 4):Arrhenius plot of viscosity of ionic liquid vs temperature.**



**Fig.(5): a. Viscosity, b. Conductivity, at different temperature of ionic liquid**

Ionic liquid had the ability to dissolve in polar solvent such as water and ethanol, but did not dissolve in non polar solvents like toluene, ether, and DMSO. The pH of ionic liquid was unexpectedly high Table(1).

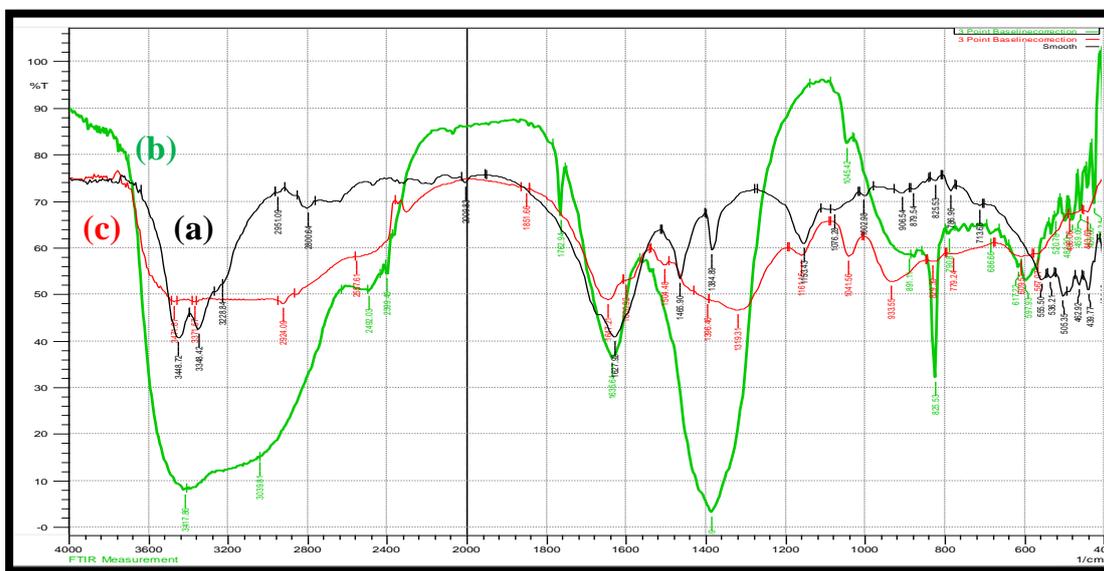
A variety of analytical techniques were used to identify by new ionic liquid FT-IR, electronic spectra, thermal analysis, electrochemical measurement and NMR which will be explained as below.

IR-spectra showed an interaction between the components of ionic liquid. The comparison in vibration frequencies of ionic liquid and aluminum nitrate and urea salts are showed in Table (2). The vibration frequency of carbonyl group ( $\nu_{\text{CO}}$ ) shifted about  $34 \text{ cm}^{-1}$  lower than the frequency in free solid urea. The

stretching frequencies of ( $\nu$ N-H) of urea also changed with blue shifts (about  $30\text{ cm}^{-1}$ ) for the symmetrical vibration and to red shift for asymmetric vibration the frequency of  $\nu$ N-H about  $6\text{ cm}^{-1}$  in IL. Other frequencies of stretching vibration bands of  $\nu$ N-O resulted from  $\text{NO}_3^-$  group at  $1384\text{ cm}^{-1}$  shifted to higher frequency while the stretching vibration bands of  $\nu$ Al-O were shifted to lower frequencies in ionic liquid[12,13], Figure.(6).

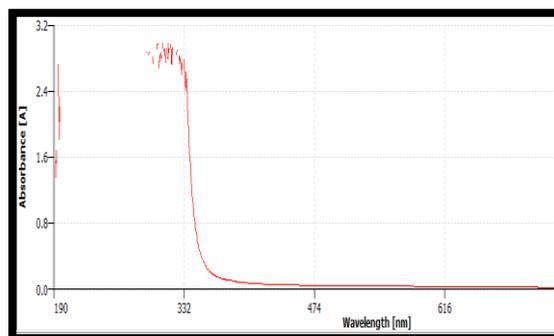
**Table (2): FT-IR absorption bands of starting materials and ionic liquid.**

Functional group	Urea	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	IL at ratio (1:1.2)
$\nu$ (N - H)	3448, 3348	-----	3471, 3371
$\nu$ (C = O)	1624,1681	-----	1647
$\nu$ s(C-N) $\nu$ as(C-N)	1153 1465	-----	1165, 1049 1504
$\delta$ (N-H)	1624,1604	-----	1585
N-O in $\text{NO}_3^-$	-----	1384	1380, 1338
Al-O	-----	825,779 ,594	825, 729, 567
(O-H)	-----	3039, 3417, 2492	2492, 1600w



**Fig.(6): IR- spectra of (a)urea,(b) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and (c)IL.**

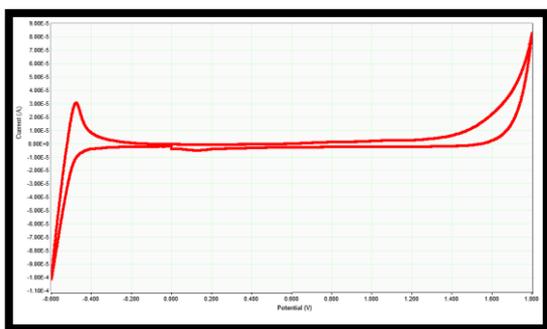
The electronic spectrum of colorless ionic liquid showed absorption bands in the ultraviolet region at (190 – 338 nm), suggested the transition of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  of amine and carbonyl groups, Figure (7).



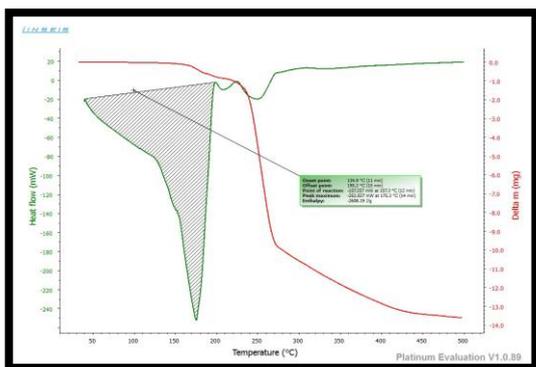
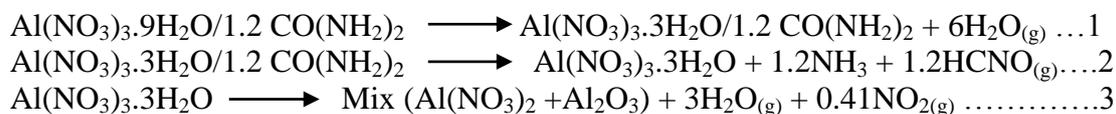
**Fig.(7): Electronic spectrum of the Ionic Liquid**

The electrochemical potential window of ionic liquids of  $-0.6$  to  $+1.4$  represented the difference between the

reduction potential limit and oxidation potential limit of its species. Figure(8) showed the scale of electrochemical window for the 1:1.2 Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O/ Urea, a scale of potential with total electrochemical potential of 2V. In comparison with other ionic liquids, e.g. ChCl/ urea with a potential window of (-1.2 to +1.2), while aqueous systems possessed about 1.23V. It is clear that ionic liquid has higher potential than water.



**Fig.(8):Cyclic voltammogram for Pt electrode in nonahydrate aluminum nitrate/ urea mixture (1:1.2) at room temperature**



**Fig. (9): (TGA) and (DSC) analysis of aluminum nitrate /urea ionic liquid**

The <sup>1</sup>H NMR spectrum data of ionic liquid showed only one peak at δ = 5.28 ppm, similarly the free urea gave one peak at 5.6 ppm which can be assigned to (4H; 2NH<sub>2</sub>) four protons of two symmetric amino groups. The <sup>13</sup>C NMR spectra for free urea and ionic liquid

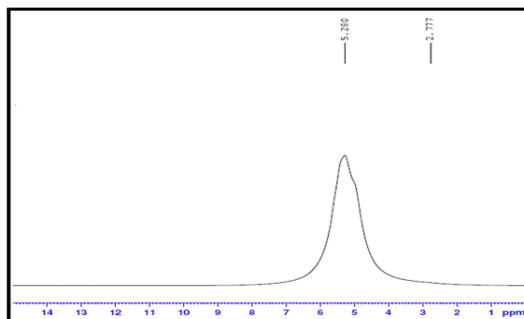
TGA and DSC analysis data were presented in Fig. (9) indicating a high thermal stability up to a temperature of 326°C associated with an endothermic peaks referred to an enthalpy value of -3319.94 KJ/Kg, followed by three decomposition stages started from 326 °C until 500°C with a total weight loss of 56.59% and changes in heat through two decomposition curves as illustrated in Figure (9) at 236 to 271 °C.

First decomposition stage indicated loss of a small non- interacted water molecules and the second stage suggested urea decomposition, while the third decomposition stage is due to gaseous evaporation of water and nitrogen dioxide.

showed a signal band at approximately the same value of C=O, as shown in Fig. (10 and11), the data are listed in Table( 3).

**Table (3): <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts (δ in ppm) of urea and Ionic Liquid.**

Compound	δ( <sup>1</sup> H)	δ( <sup>13</sup> C)	Ref.
CO(NH <sub>2</sub> ) <sub>2</sub>	5.6(s, br, NH <sub>2</sub> )	160.70(s, CO)	14
IL	5.2(s, br, NH <sub>2</sub> )	159.46(s, CO)	In this work



**Fig.(10):<sup>1</sup>H– NMR spectrum of Ionic liquid**

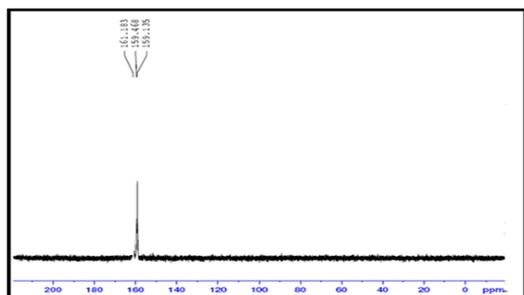
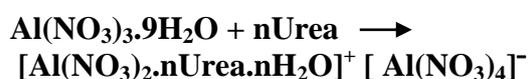


Fig. (11):  $^{13}\text{C}$  – NMR spectrum of Ionic liquid.

All the previous examination of ionic liquid helped to suggest an equation of ionic liquid formation as follow:



water molecules believed to interact with both ion.

The crystalline solid separated from IL were used taken for further identifications and analysis by X-ray diffraction, FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and CHN. The crystalline identified by X- ray diffraction measurement showed the lattice  $d$ -spacing of 3.088 with a maximum intensity for  $2\theta = 28.775^\circ$ . This result agrees with stander  $d$ -spacing of urea nitrate of 3.10[14].The spectrum and data of X-ray analysis are shown in Figure(12) and Table(4).

Table(4): X- ray diffraction of urea nitrate.

Observed $2\theta$ value	$d$ , Å	Int. I(C/Sec.)	Muller indices (h k l)
20.54	4.32	7	0 2 0
22.90	4.05	5	2 0 0
23.5	3.7	4	2 <sup>-</sup> 2 1
24.80	3.58	9	3 1 2
25.05	3.55	15	0 2 1
26.21	3.39	9	2 <sup>-</sup> 2 2
27.42	3.30	6	1 <sup>-</sup> 3 1
28.88	3.088	100	3 <sup>-</sup> 2 1
29.144	3.061	72	3 <sup>-</sup> 2 2
29.618	3.013	4	2 <sup>-</sup> 3 0
30.40	2.93	8	2 <sup>-</sup> 3 2
31.27	2.85	4	2 <sup>-</sup> 4 1
35.03	1.54	4	5 <sup>-</sup> 1 2
45.83	1.97	3	1 <sup>-</sup> 0 4
59.571	1.55	7	5 <sup>-</sup> 2 4

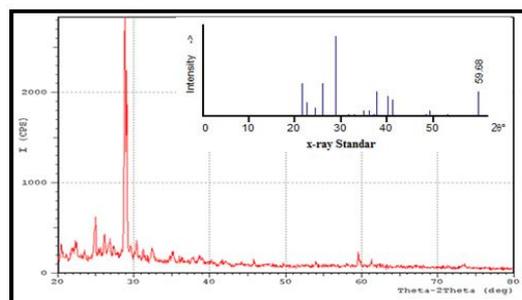


Fig. (12): X- ray diffraction of Urea nitrate

Another indication of this urea nitrate salt determined by elemental analysis (C. H. N.) which gave, C = 8.861(9.756), H = 3.433(4.065) and N=29.567(32.146). These results values agreed with the theoretical values of urea nitrate except the value of nitrogen element which was higher due to ionic liquid remained in the crystalline salt. This may be attributed to presence of very small amount of ionic liquid adhered to urea nitrate due to difficult separation.

IR spectrum showed, the stretching vibration of the carbonyl group at the  $1647.21\text{cm}^{-1}$  which can be presented in both ionic liquid and urea nitrate other frequency appeared at  $1384.89\text{cm}^{-1}$  was assigned to  $\text{NO}_3^-$  group which was less broad than the peak in ionic liquid, but when comparing the band of  $\nu\text{N-H}$  with that appeared  $3460.30\text{cm}^{-1}$  and  $3360.00\text{cm}^{-1}$  in urea nitrate, had small blue shift about  $15\text{cm}^{-1}$  and red shift about  $19\text{cm}^{-1}$  in IL respectively. The stretching vibration band of  $\nu\text{C-N}$  which appeared as a sharp and medium band at  $1161\text{cm}^{-1}$  which were shifted in urea nitrate(UN) to about  $5\text{cm}^{-1}$ . Fig.(13) and Table(5) shows FT-IR spectrum and the data of urea nitrate.

**Table (5) : Comparison of the main absorption bands of FT-IR for IL and UN**

Compounds	$\nu_{\text{asy}}^{\text{N-Hcm}^{-1}}$ $\nu_{\text{sy}}^{\text{N-H}}$	$\nu_{\text{C=O cm}^{-1}}$	$\delta_{\text{N-Hcm}^{-1}}$	$\nu_{\text{asy}}^{\text{C-Ncm}^{-1}}$ $\nu_{\text{as}}^{\text{C-N}}$	$\nu_{\text{asy}}^{\text{C-Ncm}^{-1}}$
IL	3444.87 3379.29	1647.21 1762.94	1585	1504 1166	1384.89
UN in this work	3460.30 3360.00	1647.21 1762.94	1585	1161 1049.2	1400
UN Reported	3443 3340 3210	1665 1710	1170	1060	1390

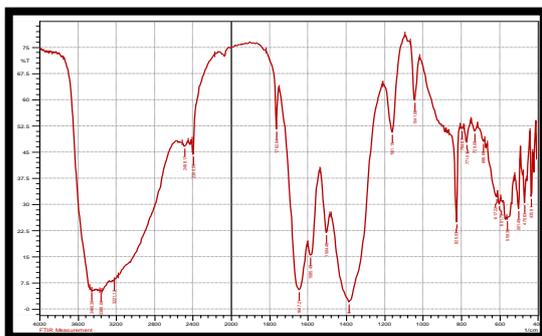
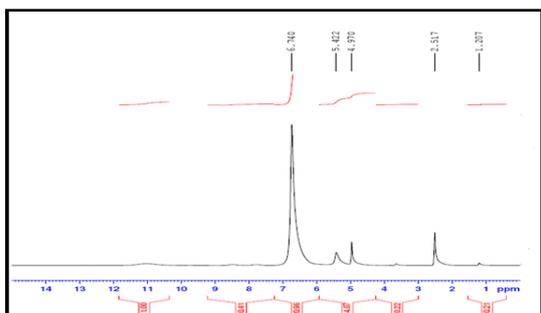
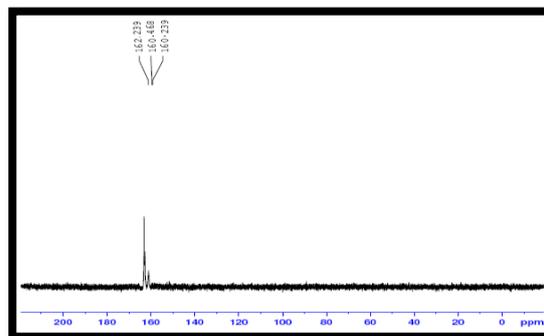
**Fig.(13):FT-IR spectrum of urea nitrate**

Figure (14) shows  $^1\text{H-NMR}$  of UN in which two peaks, one type of neutral  $-\text{NH}_2$  groups at  $\delta = 5.4$  ppm and the other one has a positively charged  $^+\text{NH}_2$ , which appeared at  $\delta = 6.7$  ppm. According to this result, it can be deduced that electronic environments of the urea protons changed with the formed urea nitrate[15]. Figure (15) shows  $^{13}\text{C-NMR}$  spectrum in which two peaks appeared due to the carbonyl group. The first one in the position 162 ppm belongs to urea nitrate (UN) in high intensity due to the proton bonding in the oxygen side of carbonyl group, while the second small peak is due to impurities[16].

**Fig. (14): $^1\text{H-NMR}$  spectrum of Urea nitrate.****Fig. (15): $^{13}\text{C-NMR}$  spectrum of Urea nitrate.**

### Conclusions:

Clear colorless room temperature ionic liquid was formed by mixing different molar ratio of aluminum nitrate nonahydrate and urea with lowest freezing temperature at  $3\text{ }^\circ\text{C}$  in (1 : 1.2) mole ratio. They formed acidic and basic species where aluminum cation interacted with the carbonyl group of urea in the acidic species in analogues to those formed in other aluminum salt / urea ionic liquid. This ionic liquid showed physical properties similar to other ionic liquids with stable redox potential over 2V (-0.6 to +1.4). Water content believed as in aluminum nitrate / urea ionic liquid is not present as free molecules giving an easy prepared water and atmospheric stable liquid for different chemical applications.

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## تشخيص السائل الايوني الجديد المتكون بدرجة حرارة الغرفة من نترات الالمنيوم المائية مع اليوريا

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### الخلاصة :

حضر سائل ايوني جديد عديم اللون وبدرجة حرارة الغرفة من مزج نترات الالمنيوم المائية مع اليوريا بنسبة مولية هي 1:2 على التوالي وبأدنى درجة انجماد تم التوصل اليها من دراسة مخطط الطور، ودراسة بعض الخواص مثل الكثافة و اللزوجة والتوصيلية الكهربائية عند درجة حرارة الغرفة فوجد ان السائل الايوني المحضر له خصائص فيزيائية مماثلة لسوائل ايونية اخرى. ولدراسة التداخل بين مكونات هذا السائل الايوني استخدمت التقنيات فيزيائية- طيفية طيف الاشعة تحت الحمراء و الاشعة فوق البنفسجية- المرئية و طيف الرنين النووي المغناطيسي حيث افترض تكون اصرة بين اوكسجين مجموعة الكربونيل والالمنيوم (-CO-Al-) مع اقتراح الايون السالب (القاعدي) هو  $[Al(NO_3)_4]^-$  والايون الموجب (الحامضي)  $[Al(NO_3)_2.XU]^+$  مع الافتراض حدوث تفاعل لجزيئات الماء مع كلا الايونيين. تم تحديد النافذة الكهربائية لهذا السائل الايوني وكانت حوالي 2V من 0.6- V الى 1.4 V + من معرفة جهد تأكسد- اختزال ويمتاز باستقرارية حرارية اعلى من 326 درجة مئوية.

**الكلمات المفتاحية:** السوائل الايونية بدرجة حرارة الغرفة، المذيبات الخضراء، الخواص الفيزيائية-الكيميائية.