

## Investigation of Lewis Acid-Base Reaction of Acidic Species Present in Aluminum Chloride-Urea Ionic Liquid $[AlCl_2.nUrea]^+$

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### Abstract

Aluminum chloride-urea ionic liquid was investigated for its active species concentration with the aid of electronic spectroscopy by Lewis acid-base titration with chloride ions. 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 formed bands in visible and ultraviolet regions. Upon Lewis acid-base titration these bands disappeared and the concentration of the acidic species were 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 assumed to be between 1 acidic species to 1 chloride ion according to the mole fraction elucidated graph.

Keywords: Ionic liquid, aluminum chloride, urea, acetamide, toluene, Potassium chloride, Calcium chloride, UV/Vis.

### Introduction

Ionic liquids received more attention as alternative reaction media for their distinguished properties which obviously differentiate them from water or classical molecular organic solvents. They can be tailored in contrast to other solvent and thus considered unique [1]. Ionic liquids have attracted increasing interest for their promising role as alternative media in synthesis, separation, and electrochemistry as a result of their unique chemical and physical properties. They can dissolve a wide spectrum of organic, organometallic, and inorganic compounds [2]. Also, they have no detectable vapor pressure and are relatively thermally stable. Aluminum chloride-based ionic liquids with imidazolium or pyridinium chlorides (chloroaluminate ionic liquids) were the first studied ionic liquids. Chloroaluminate ionic liquid was reported to form basic, neutral and acidic melts by varying the molar ratio of the organic salt to  $AlCl_3$ . Basic ionic liquids with a molar ratio of  $AlCl_3$  of less than 1 consist of  $R^+$ ,  $Cl^-$  and  $AlCl_4^-$  ions. A molar ratio of  $AlCl_3:RCl$  greater than 1 form acidic ionic liquid which contains  $R^+$ ,  $Al_2Cl_7^-$  and  $AlCl_4^-$  ions [3, 4]. Aluminum chloride with simple amide (urea or acetamide) forms acidic ionic liquid consisted of positive acidic species  $[AlCl_2.nAmide]^+$  and ionic species  $[AlCl_4]^-$  having comparable properties to those of chloroaluminate ionic liquid [3].

The ionic liquids produced when aluminum chloride was combined with either urea or acetamide were much stable than chloroaluminate ionic liquid of i.e. imidazolium chloride but with promising similar properties in at least to its catalytic behavior for organic reactions and aluminum metal coating on metal substrate [3].  $AlCl_3$ -amide ionic liquids reported to become colored upon dilution with some organic solvents and the color was attributed to charge transfer between solvents and aluminum cations. The dilution with organic solvents was useful to accelerate the rate and modifying the deposited aluminum particles [8].

The aim of this work is to investigate the coordination of aluminum species upon dilution with organic solvent (particularly those having aromatic  $\pi$ -ring electrons such as toluene and benzene). The visible colors of ionic liquid with organic solvents could be used as indicator for Lewis acid-base titration of acidic active ionic liquid species and concentration determination in this type of ionic liquids. Aluminum chloride-urea was chosen to be diluted with aromatic solvents (toluene and benzene). While for their Lewis acid-base titration chloride salts of potassium and calcium were used.

## Experimental

Aluminum chloride of Fluka, urea and benzene of Thomas Baker, toluene and calcium chloride and potassium chloride of Chem. Supply of no less than 98% purity were used with no further purification.

The weighted amount of aluminum chloride was added to the reaction tube followed by the proper amount of the organic solvent. The weighted of urea portion was added incrementally to the reaction tube where a reaction between urea and aluminum chloride had commenced indicated by the color change of the organic solvent from colorless to green color in toluene and to deep red in benzene.

The deep red liquid composed of 80 vol.% (2AlCl<sub>3</sub>:1Urea) ionic liquid and 20 vol.% benzene. While the dark green liquid composed of 53.3 vol.% toluene and 46.7 vol.% ionic liquid (1.5AlCl<sub>3</sub>:1Urea). To 1ml of the dark green liquid, potassium or calcium chloride were added in an increment portions. The mole % of the chlorides were at 10, 12.5, 14.3, 16.7, 20, 25, 33, 40, 50, 60, 75, 80, 90 and 100 calculated on the bases of original aluminum chloride used to prepare ionic liquid.

KCl or CaCl<sub>2</sub> additions were followed by CECEL CE7200UV-Vis, Ultraviolet Visible spectrophotometer at room temperature using quartz cells of 1.0 cm path length and water as reference in the range of (190-900) nm. FTIR of SHIMADZU 8300 Fourier Transform Infrared Spectrophotometer (F.T.IR), Japan, using the (KBr) disk in the wave number range (4000-400) cm<sup>-1</sup> was also used to investigate ionic liquid solid materials.

## Results and Discussion

### a. Ionic Liquid in Toluene:

Toluene is known to have two bands (E<sub>2</sub> and B) in the ultraviolet region. E<sub>2</sub> band has higher energy than B band which both are related to the  $\pi$ - $\pi^*$  aromatic ring transition [5]. These two bands were observed at 199.5nm (E<sub>2</sub>) and 264nm (B) Fig.(2, B) when toluene alone was examined by ultraviolet/visible spectroscopy in present work.

However, when ionic liquid was prepared in toluene, the color changed to deep green. This green mixture of diluted ionic liquid in toluene was examined by ultraviolet-visible

spectroscopy and showed, on one hand, an increase in the initial B and E<sub>2</sub> bands of toluene at similar absorption wavelengths and an increase in their absorption intensities (compare Fig. (2, A and B).

On the other hand, two new bands at 334nm and 474nm were recorded for ionic liquid in toluene. The latter two bands were believed to be caused by an interaction of Lewis acidic species of the ionic liquid [AlCl<sub>2</sub>.nU]<sup>+</sup> with the ring  $\pi$ -bond electrons of toluene causing the charge transfer between toluene and metal cationic species. This bond may be considered as coordinated bond and electrons being donated from the  $\pi$ -ring bond of toluene to metal cationic species.

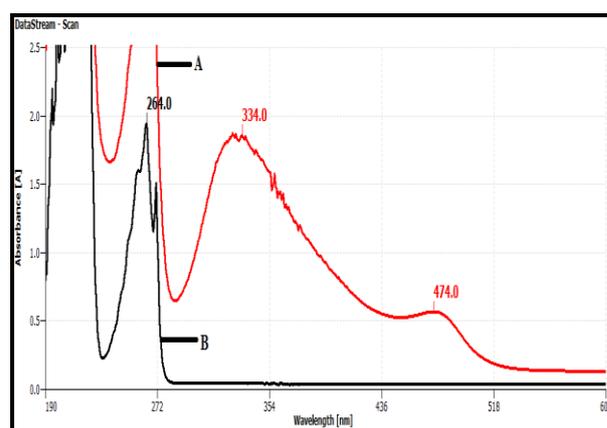


Fig.(1) UV/Vis.spectrum of (A) ionic liquid in toluene and (B) toluene alone.

This type of interaction would be analogous to those of transition metal-arene organometallic complexes which were first recognized in the 1950's [9]. Such interaction helps the addition of nucleophiles to the arene liquid causing de-protonation of acidic arene protons.  $\eta^6$ - metal complexes were also suggested for bi-metallic chromium carbonyl-arene complexes of chromium or tungsten as stated by Fischer [10].

On this basis, the original aromatic ring bands of toluene (B and E<sub>2</sub>) are also expected to be affected by this new interaction with the ring- $\pi$  electrons and seem to be enhanced as illustrated by the higher absorbance ( $\epsilon_{\max}$ ) than in toluene alone.

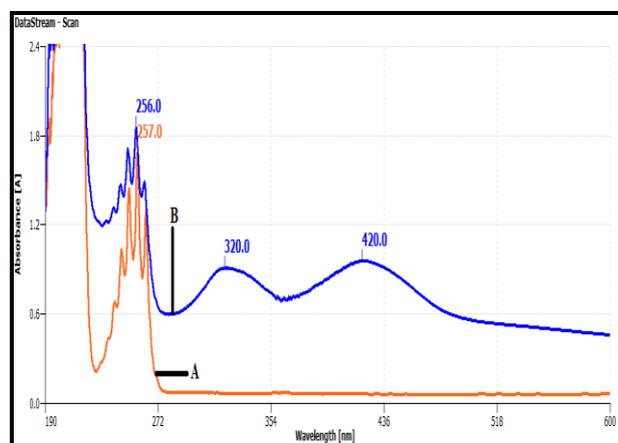
### b. Ionic Liquid in Benzene:

Benzene has three bands in the ultraviolet region which were related to  $\pi$ - $\pi^*$  aromatic ring transitions and named E<sub>1</sub>, E<sub>2</sub> and B where

$E_1$  at higher energy than  $E_2$  and B bands, and  $E_2$  band at higher energy of B band [5]. The  $E_1$  band could not be observed since it was reported to have a wavelength of 180 nm [5] which was out of the instrument's range (190-900) nm. The other bands  $E_2$  and B were observed in present work at 199.5nm and 257nm respectively Fig.(2A). Deep red color was formed by ionic liquid in benzene which was also examined by the ultraviolet-visible spectroscopy Fig.(2 B) and revealed an increase in the initial absorbance of benzene B and  $E_2$  bands at same wavelengths, as also observed in toluene, and the appearance of two new bands (also similar to the dilution in toluene) but at 320nm and 420nm which were similarly believed to be resulted from the interaction of the acidic cationic species of the ionic liquid  $[AlCl_2 \cdot nUrea]^+$  with the  $\pi$ -ring electrons in this case of benzene ring.

### c. Lewis acid-base neutralization with chloride:

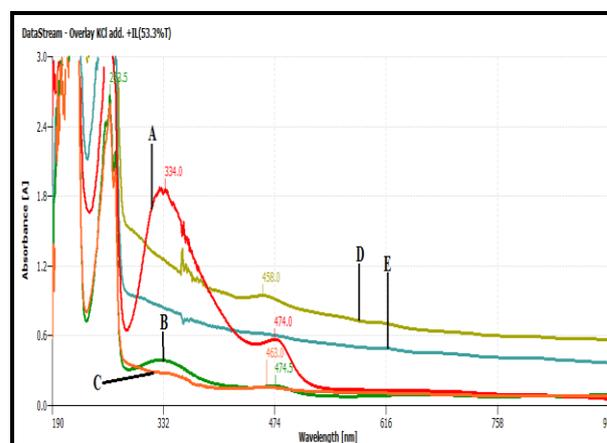
To confirm the interaction whether being caused by aluminum acidic species of the ionic liquid with ring  $\pi$ -electrons of toluene or benzene, a Lewis acid-base titration was conducted. This was carried out by reacting the Lewis acidic species with Lewis chloride anions added as either potassium or calcium chloride salts to ionic liquid prepared in toluene.



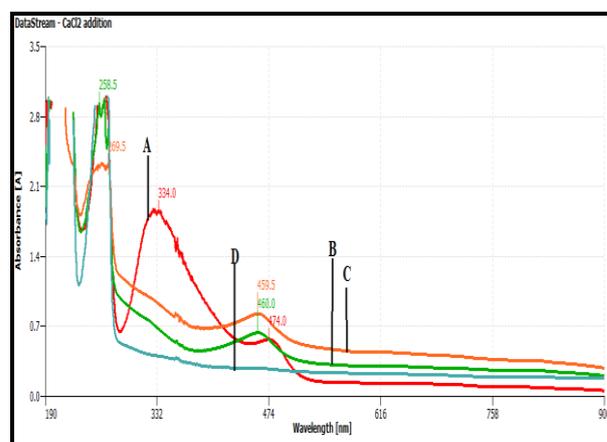
**Fig.(2) UV/Vis. Spectra of (A) benzene and (B) ionic liquid in benzene.**

Hence if this intended scheme of reaction was successful, then aluminum species would be neutralized forming  $AlCl_4^-$  anion, thereby two aims could be reached. The first is to determine the concentration of aluminum

acidic species present in ionic liquid and secondly this could be guided by the disappearance of the newly formed absorption bands observed in toluene or benzene diluted ionic liquids. Therefore, when potassium or calcium chloride was incrementally added, it was observed that the toluene bands ( $E_2$  and B) decreased in their intensities ( $\epsilon_{max}$ ) and the band at 334nm decreased sharply at 12.5 mole% addition of potassium or calcium chlorides (calculated on the basis of total  $AlCl_3$ ), and decreased more at 14.3 mole %. The lower less intense absorbance band at 474nm was also decreased when chloride was added but to less extent and completely disappeared at 75 mole% addition of potassium or calcium chloride to the dark green ionic liquid solution in toluene (compare Fig. (3) and Fig. (4)).



**Fig.(3) Ultraviolet/visible spectra of (A) 1.5AlCl<sub>3</sub>:lurea in toluene, (B) 12.5%, (C) 14.3%, (D) 50%, (E) 75% of potassium chloride additions.**

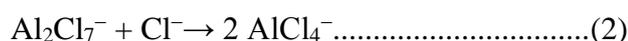


**Fig.(4) Ultraviolet/visible spectra of (A) 1.5AlCl<sub>3</sub>:lurea in toluene, (B) 12.5%, (C) 14.3%, (D) 75% of calcium chloride additions.**

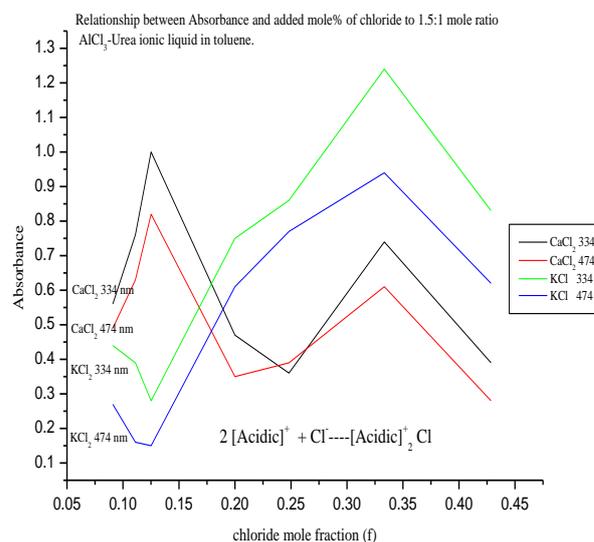
However, further addition of potassium or calcium chloride up to 100 mole% gave no additional observation except that the ionic liquid turned into suspension due to the limitation of potassium or calcium chloride solubility in the solution. Therefore; it is possible to represent the overall reaction between one mole acidic species of ionic liquid with the two moles of Lewis base (chloride ions) as follow;



This reaction is analogous, as Lewis acid base reaction, to that reported for chloroaluminate acidic species reaction [7] but with different molar concentration;



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. 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 ( $\text{AlCl}_3$ : amide) [3]. 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 were represented with mole ratio as in Fig.(5).



**Fig.(5) 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.**

It clearly represents two reactions. The first at the low mole fraction of added chloride (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 1). 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 334nm and 474 nm which they showed identical behaviors in both cases of chloride salts, indicating their similar origin stemmed from, as stated above, the interaction between cationic acidic species and aromatic ring system.

## Conclusions

Aromatic ring interaction with acidic cationic species of ionic liquid could be used by ultraviolet/visible spectroscopic method as indicator for the Lewis acid-base titration and concentration elucidation of the acidic species of aluminum chloride-amide ionic liquids which was around 75 mole% of the initial  $AlCl_3$  used in the preparation of 1.5:1 mole ratio of  $AlCl_3$ : Urea. This was resulted from two reactions and probably formation of complex product between acidic species and chloride ions.

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## الخلاصة

تمت دراسة السائل الايوني المتكون من كلوريد الالمنيوم واليوربا 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 و 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 اليوربا. وظهر من خلال الكسر المولي ان الناتج لهذا التفاعل كان بين ١ مول من الاجزاء الموجبة الفعالة للسائل الايوني الى ١ مول من ايون الكلوريد المضاف.