Synthesis and physical study of new ionic liquids based imidazolium salts

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Abstract:

New ionic liquids have been synthesized in good yields. The synthesis approach was applied a synthesis of new alkylhildes and react them with both methyl and benzyl imidazole to get the target compounds. The new compounds were characteristic by 1HNMR, FT-IR and UV-Visible techniques. The conductivity measurements in different solvents was studied as well.

Keywords: Ionic liquids, imidazole, conductivity imidazolium salts.

Introduction:

Ionic liquids are represent the wonderful materials based on their unique properties[1]. These compounds" also called a salts "containing an organic positively charged core and an inorganic or organic counter ions with a negative charges. In particular, the ionic liquids can be defied as a semi-organic salt possess a melting points below 100 Celsius[2][3] . Furthermore, due to their low vapor pressure, high viscosity, high density, non-flammability and miscibility with other organic\water solvents, the ionic liquids are used as a green solvent instead of common solvent in several organic reactions [4]. In addition, the usage of ionic liquid have been extent in various applications such as extractions of certain component, super-molecular substances, catalysis, carbon dioxide capturing and lithium battery manufacturing[5][6][7]. Among them, the primary concerns of both academic and industrial research for replacing the organic solvents which is harmful to the environment by friendly recyclable solvent, i.e. ionic liquid containing 1,3-dialkylimidazolium and benzimiazolium cations which are attracted a large number of research groups in the last few decades[8]. The 1-alkyl-3-methylimidazolium based ionic liquids have been exhibit an unusual separation of polar compounds as stationary phase to isolate non-polar compounds due to their dual nature properties of these type of compounds[9][10]. Moreover, in the conductivity measurements is essential to determine the ability of ionic liquid to play as an electrolyte in electrochemistry applications[11][12][13]. Accordingly, the physicochemical properties of ionic liquids play a crucial role for the suitable application. In this context, we have been synthesize a new room temperature ionic liquids and study their conductivity and viscosity in advance[14][15].

2- Experimental:

2-1 General Considrations:

FT-IR spectra were recorded using Fourier transform infrared Shimadzu FT.IR-8400S infrared spectrophotometer by KBr disc, pharmacy collage , University of Kufa. UV –Visible spectrometer double beem Shimadzu UV 1650 PC/Japan . Measurements are made at the Faculty of pharmacy , University of Kufa., Thin layer chromatography was perform on TLC Merck F-256 aluminum coated silica gel 60 using variant solvent eluents. ^{1}H NMR were recorded on Fourier transformation Bruker spectrometer, operating at(400 MHz) with (D_2O). Measurements are made at the Department of Chemistry, Faculty of Science, and University of Mashhad.

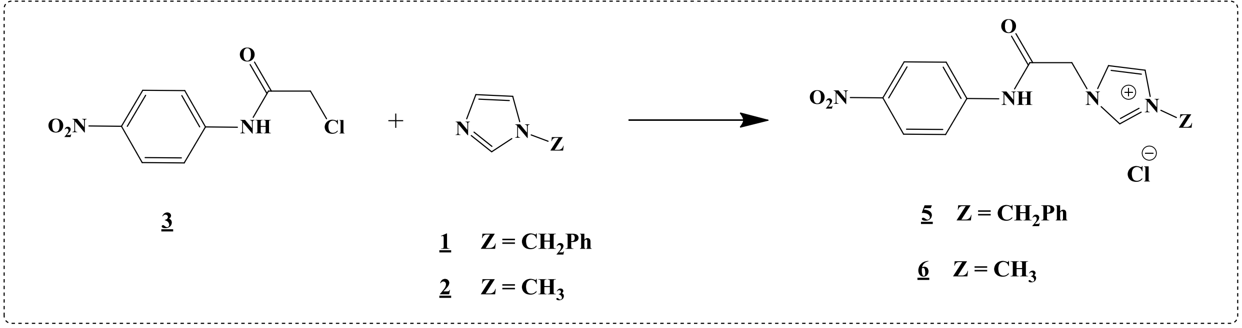
2-2 Syntheses

2-2-1 synthesis of 2-chloro-N-(4-nitrophenyl)-acetamide 3

4-nitroaniline 4 (1.5gm, 0.27 mmol) was dissolve in chloroform (20 mL), and pyridine (5 mL) was added. The mixture was stirred for 30 min at 0^{o}C, and the chloroacetyl chloride ((2gm, 0.27mmol) was added drop wise. The resulting mixture was stirred for 24 hours at room temperature. After complete the reaction by TLC, the mixture was extract with water (50 mL) several times, the organic layer was dried by adding of sodium sulfate, filtered and the chloroform was evaporated to obtain a brown gummy ,3 g (85 % yield).

2-3 General Procedure for Syntheses of Ionic Liquid:

Compound 3 (1.0 mmol) was dissolved in acetonitrile (30 mL) and stirred until dissolved, then methyl 1 or benzyl imidazole 2 (1.0 mmol) was added. The mixture was stirred at 50 oC for 24 hrs. The acetonitrile was evaporated under reduced pressure to left the product in reasonable yield.



Scheme 1: Synthesis of ionic liquids 5 and 6

2-3-11-benzyl-3-(2-((4-nitrophenyl) amino)-2-oxoethyl) imidazol-3-ium chloride 5

Compound 3 (0.59gm, 0.27mmol) and benzylimidazole 1 (0.22gm, 0.27mmol) were reacted in the same manner of the general procedure (2-3), to left the product as a gummy white ((0.57g) in 71 % yield.

^{1}H NMR (400 MHz, Deuterium Oxide) δ 8.76 (s, 1H), 8.43 (d, *J* = 7.1 Hz, 1H), 7.93 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.12 (d, *J* = 8.4 Hz , 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 2H), 5.01 (s, 3H).

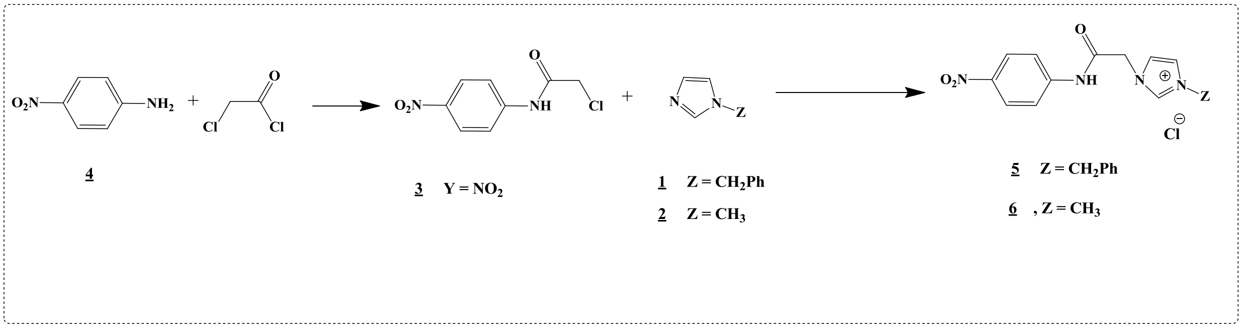
2-3-21-methyl-3-(2-((4-nitrophenyl) amino)-2-oxoethyl) imidazol- 3- ium chloride 6

Compound 3 ((0.58gm, 0.22mmol) and methyllimidazole 2 (0.22gm, 0.27mmol) were were reacted in the same manner of the general procedure (2-3), to left the product as a white semi-powder ((0.61g) in 76 % yield.

3- Results and Discussion:

3-1 Synthesis of ionic liquids

The synthetic route was outlined in such away to be simple, reproducible and relatively access. (Scheme 2)



Scheme 2: Synthesis of target compouns 3-6

The irst step in the preparation is the reaction of 4-nitroaniline with chloroacetyl chloride in presence of pyridine as a scavenger for by-product hydrochloric acid. However, the product was good enough for further synthesis without purification. The IR spectrum of compound **3** was shown the characteristic peaks represented by 3263 cm^{-1} for NH group of amide, 3128 cm^{-1} for aromatic C-H , while the peaks on 1672 cm^{-1} for C=O stretching vibration and the peaks on 1600-1480 cm^{-1} could be attributed for aromatic C=C stretching. Moreover, the peak around 1186 cm^{-1} was represented the C-O stretching. In addition, compound **3** was showed strong peaks at 1571 and1344 cm^{-1} could be assigned for NO_2 group. (Figure 1).

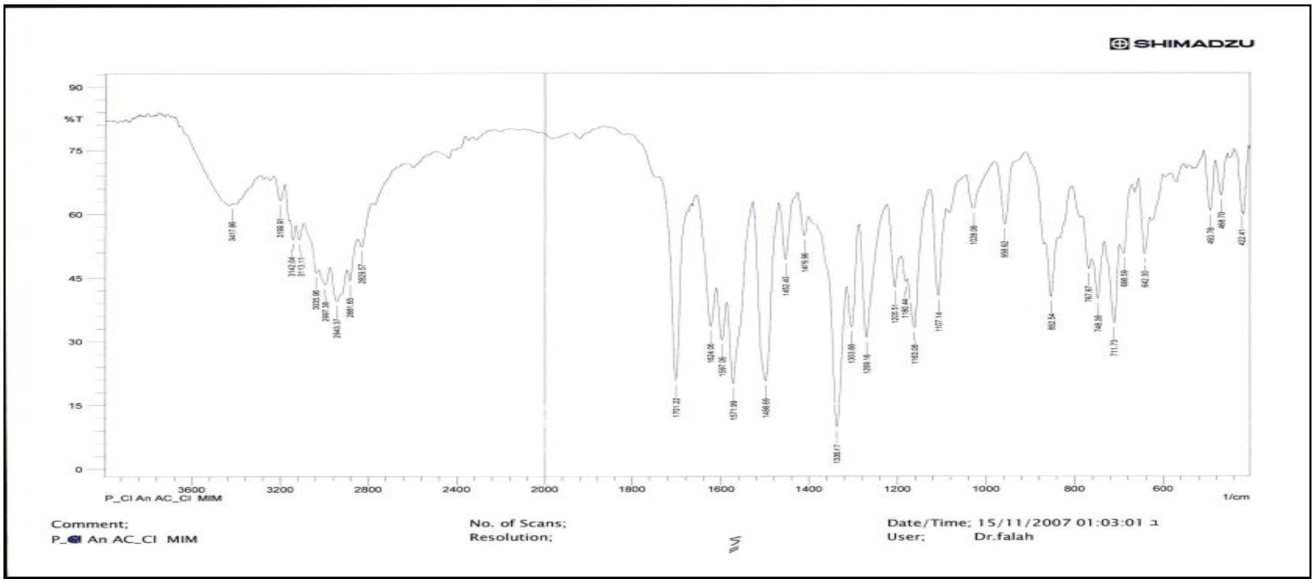


Figure 1: FT-IR spectrum of compound 3

The target compounds **5** and **6** have been synthesized from the reaction of compound **3** with either benzyl imidazole **1** or methyl imidazole **2** in acetonitrile of equimolar ratio respectively. Even though, compound **3** was relatively reactive due to the position of chloride atom in the alpha position to the carbonyl, the reaction was allowed to complete overnight to get the product with high purity which was proved by the sharp melting point.

The reaction was followed the $S_N2$mechanism when the pair of electrons on nitrogen group attach to the alpha-methylene carbonyl of compound **3**, at the same time the chloro- group was left to be the counter ion of the new positively charge cation (Scheme 3).

The FTIR spectrum (Figures 2 and 3) showed characterized peaks of certain product which were listed in (Table 1)

Table 1: FTIR peaks of compounds **5** and **6**

Compound	N-H	C-H ar	C-H al.	C=O	C=N	C=C	NO_2	C-H
5	**3431**	**3059**	**2918**	**1695**	**1618**	**1560, 1494**	**1500,1344**	**1369, 1286**
6	**3377**	**3099**	**2953**	**1672**	**1614**	**1560, 1485**	**1571,1498**	**1409, 1274**

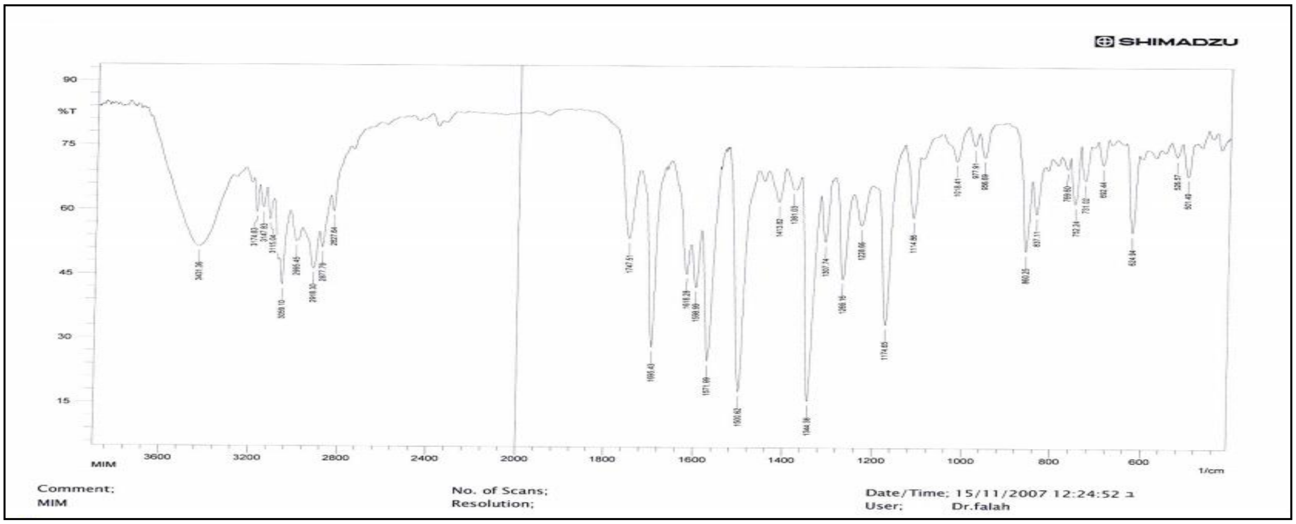


Figure 2: FT-IR spectrum of compound **5**

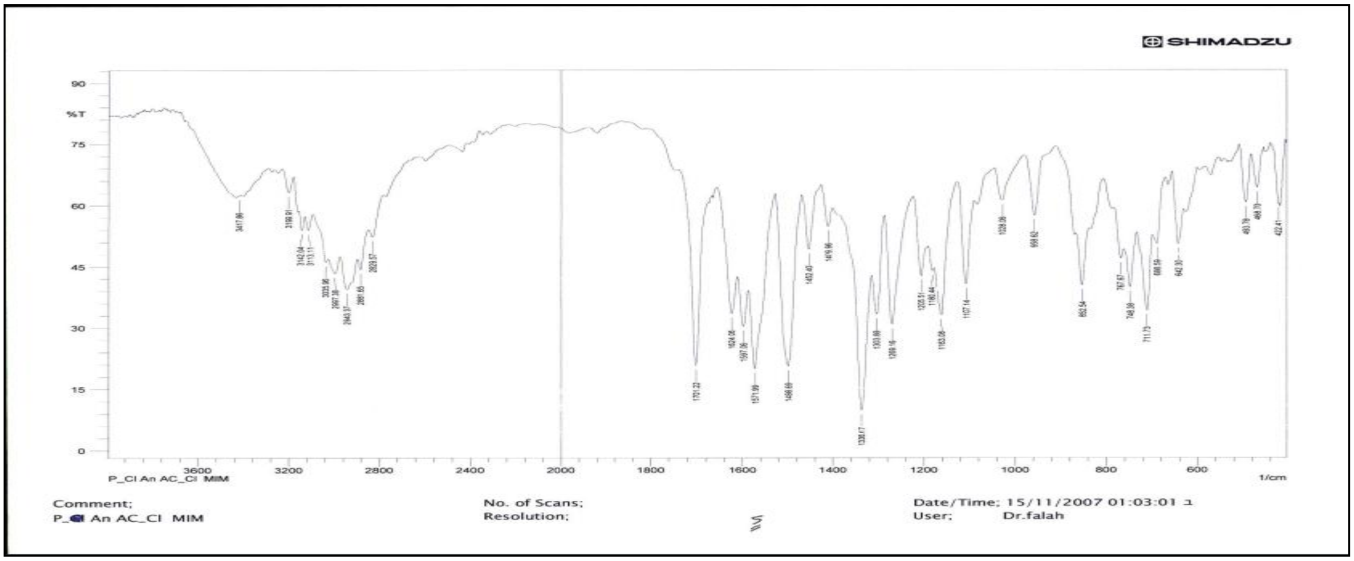


Figure 3: FT-IR spectrum of compound **6**

The ^{1}HNMR spectrum in D_2O of compound **6** shown characteristic peaks of the target compound, the singlet at 8.76 ppm for the middle proton of imidazolium. The two doublets at 8.43 and 7.93 ppm which assigned to the adjacent protons of imidazolium ring. In addition, the other two doublets at 7.40 and 6.97 ppm is assigned to four aromatic benzene protons on para-substituted. The singlet at 5.6 ppm is represented the two protons connected to the imidazole while the singlet at 4.5 ppm is represented the methyl protons of methyl imidazole.[17]

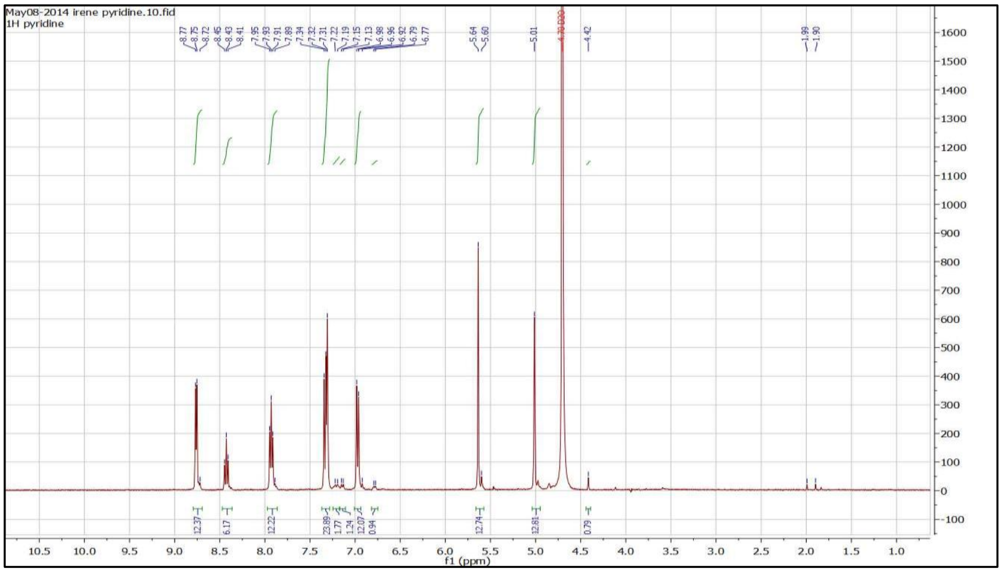
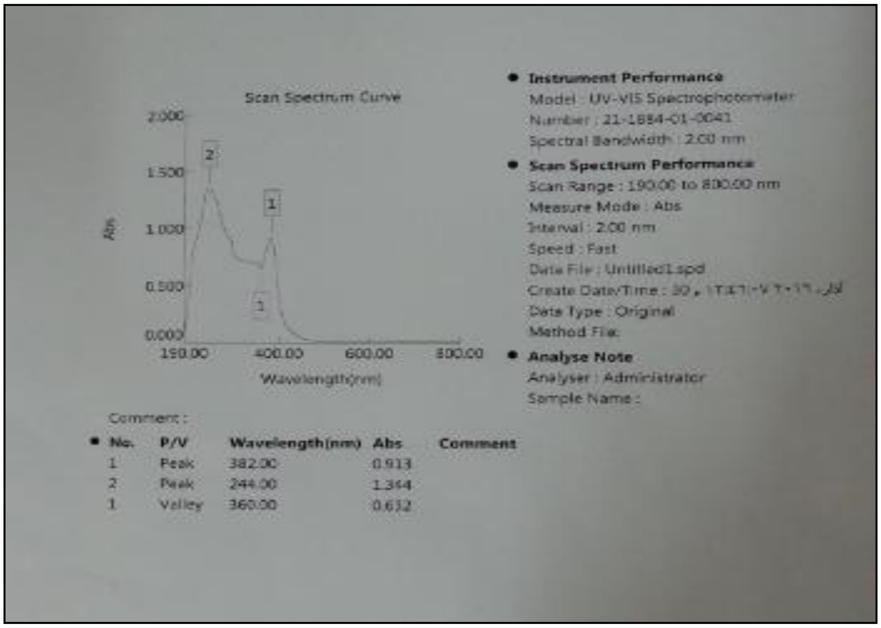


Figure 4: ^{1}HNMR spectrum of compound **6**

The UV-Vis spectra of compound **5** (figure 5) was shown an absorption peak at 244 nm which could assigned to the K-band in benzene ring (π to π*), while the absorption peak at 382 can be assigned to the conjugation of nitrogroup with the aromatic double bonds (n to π*)



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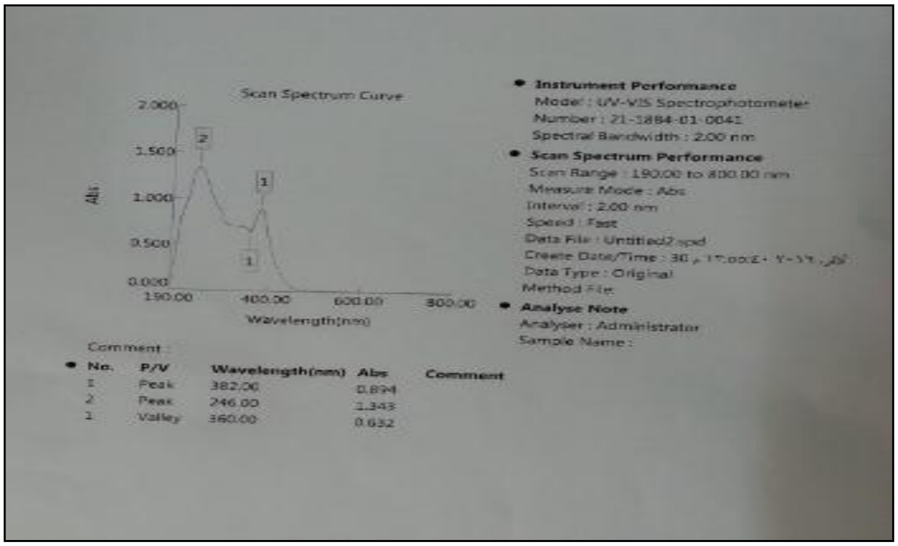
- **Analyse Note**
  Analyser : Administrator
  Sample Name :

Comment :

No.	P/V	Wavelength(nm)	Abs	Comment
1	Peak	382.00	0.913	
2	Peak	244.00	1.344	
1	Valley	360.00	0.632	

Figure 4: UV-Vis spectrum of compound **5**



- **Instrument Performance**
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- **Analyse Note**
  Analyser : Administrator
  Sample Name :

Comment :

No.	**P/V**	**Wavelength(nm)**	**Abs**	**Comment**
1	Peak	382.00	0.894	
2	Peak	246.00	1.343	
1	Valley	360.00	0.632	

Figure 5: UV-Vis spectrum of compound **6**

3.2 Conductivity study:

One of the important character is the ionic conductivity to judge if the material as suitable as electrolyte or not. However, the ionic liquids are consist entirely of charge possessing species, which probably, seem to be highly conductivity. In this context, the study of conductivity of these ionic liquids, i.e., 5 and 6 at 25 to 100 ^{o}C it was presented in figure 6. As expected, the conductivity is increased with rising of temperature, and there was non-linear increase could be extracted from the graph.

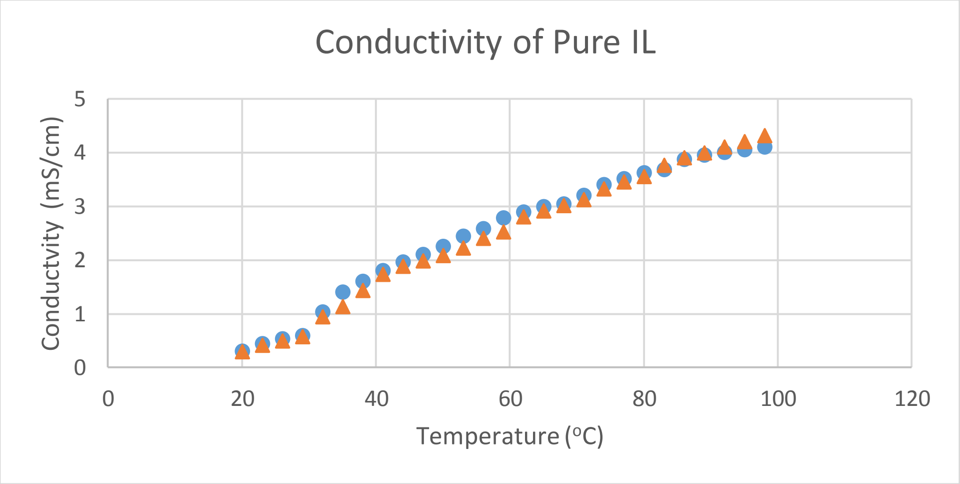

Figure 6: Theconductivity plot of synthesized Ionic liquids ● **5** and ▲ **6** as a temperature function.

The ionic liquids volumes and several binaries were kept without change. The binary mixtures of ionic liquids **5** and **6** with water and acetonitrile over a range of temperature are introduced. The conductivity of pure compounds **5** and **6** are affected by the addition of solvent.

Either increase or decrease in the conductivity rely upon the quantity of solvent added and the extent of the dissociation of ionic liquids to their ions. The addition of water or acetonitrile to the compounds **5** and **6** as a co-solvent are presented in figures 7-10. These measurements are mainly aimed to provide the results of transport coefficient modification when the co-solvent was added. Interestingly, conductivity of compound 5 is increased as a result of adding water. In addition, an increasing in conductivity was observed with increasing of temperature figure 7.

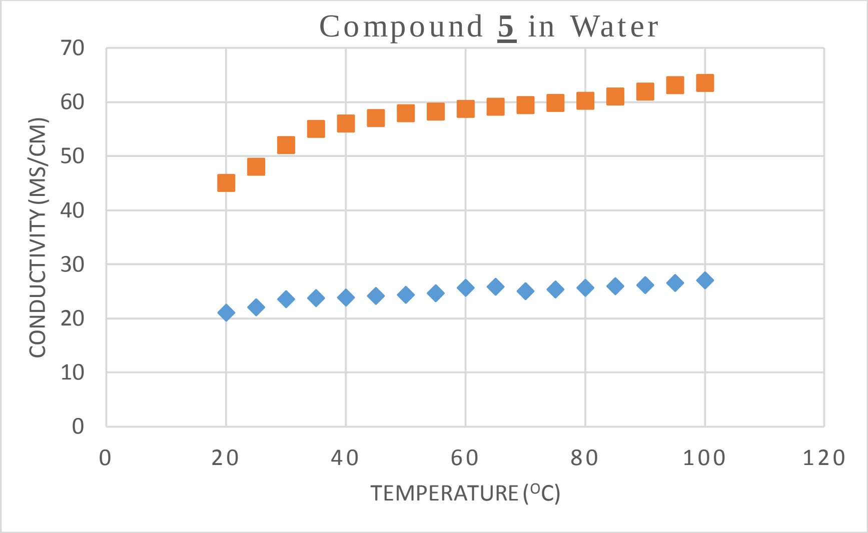

Figure 7: Plot of conductivity of pure Ionic liquid 5 in water as a temperature function. [blue = pure solvent, red = mixture with solvent]

Similar effect has been found when water was added to the ionic liquid 6 with slightly increments (figure 8). The conductivity increasing can be attributed to presence of water capability to form a rich-regions which are sorrowing the ionic liquids molecules. As the quantity of water increase the diffusion constant and interaction energies of interaction of water and the ionic liquid ions are less than the ion-ion interaction, and as a result the conductivity would increase.

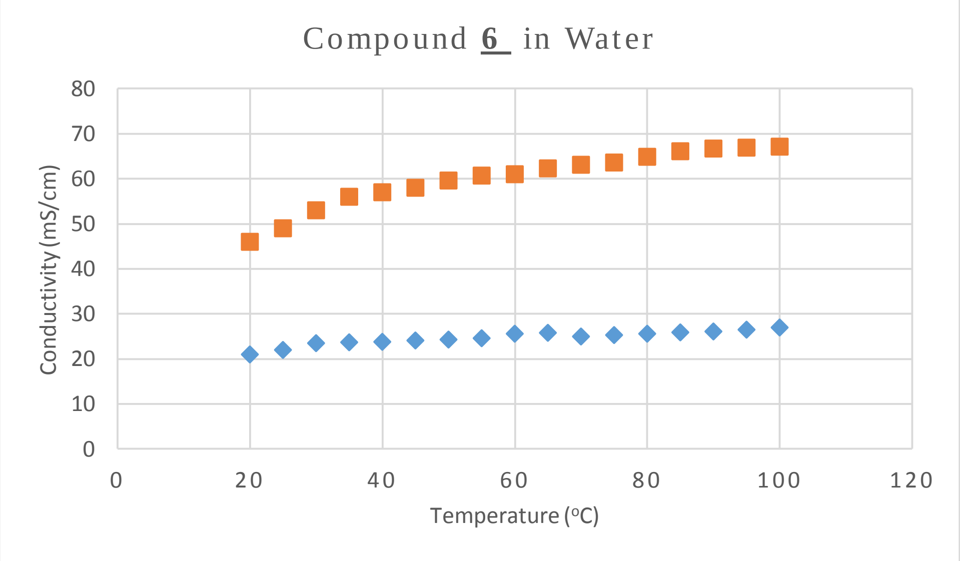

Figure 8: Plot of conductivity of pure Ionic liquid 6 in water as a temperature function. [blue = pure solvent, red = mixture with solvent]

The presence of methyl residue in compound **6** make it easier to move in solution than the benzyl residue in compound **5**, i.e. the bulky cation of compound **5** is move slowly in water upon conductivity measurements.

In contrast, the electrical conductivity is decreased upon addition of acetonitrile as a co-solvent to the ionic liquids **5** and **6**, figures 9 and 10. The pure acetonitrile showed itself a decreasing of conductivity with temperature. Obviously, the conductivity was decreased when the acetonitrile was added as a co-solvent with increasing of temperature in non-linear matter.

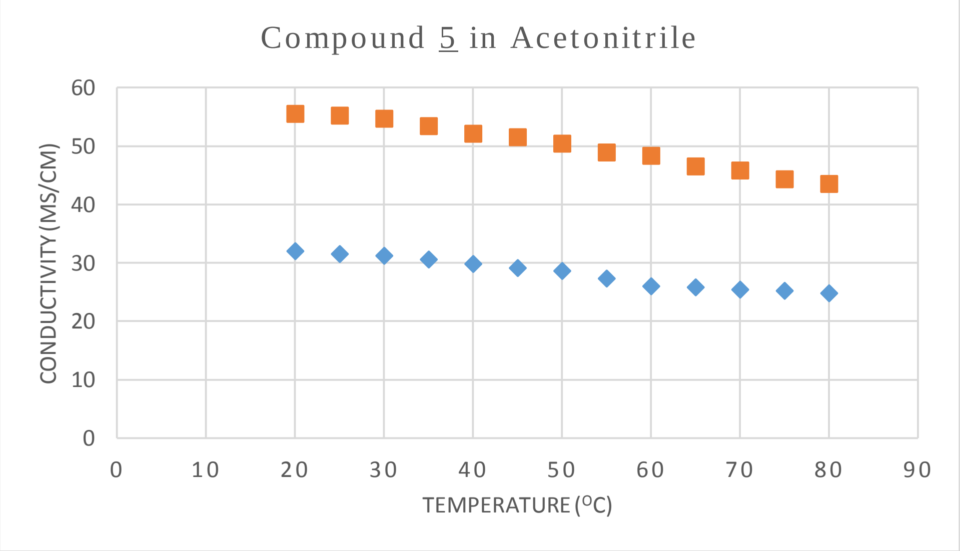

Figure 9: Plot of conductivity of pure Ionic liquid 5 in acetonitrile as a temperature function. [blue = pure solvent, red = mixture with solvent].

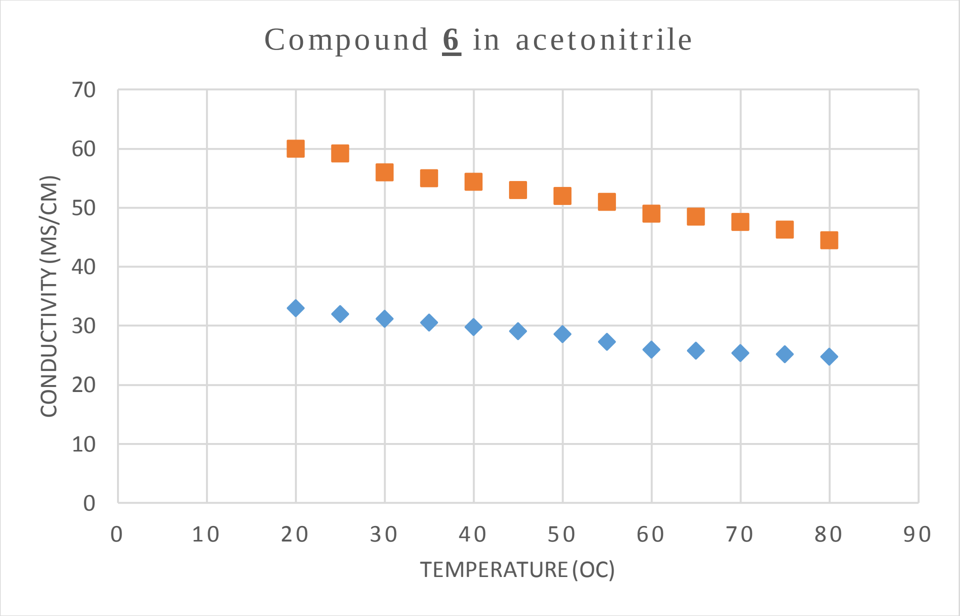

Figure 10: Plot of conductivity of pure Ionic liquid 6 in water as a temperature function [blue = pure solvent, red = mixture with solvent].

3.3 Conclusion

In summary, a successful synthesis of two new ionic liquids have been synthesized by the reaction of new alkyl halide with either methyl or benzyl imidazole, the conductivity measurements was shown there are different behavior in different solvent depends on polarity. The presence of water increase the conductivity with temperature, while the presence of acetonitrile as a co-solvent caused decrease in conductivity with increasing temperature.

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تحضير ودراسة فيزياوية لسوائل ايونية من املاح الاميدازوليوم

نهى سالم كريم
مدرس مساعد، قسم الكيمياء، كلية العلوم ، جامعة الكوفة، النجف ، العراق

الخلاصة:

تم تحضير سوائل ايونية بناتج وذلك بتحضير هاليد الكيل جديد من تفاعل بارا-نايتروانلين مع كلورواستيل كلورايد. ثم مفاعلة هاليد الالكيل الناتج مع كل من المثيل والبنزايل اميدازول للحصول على النواتج المطلوبة. شخصت جميع المركبات بالتقنيات الطيفية المتاحة مثل مطيافية الرنين النووي المغناطيسي ومطيافة الاشعة تحت الحمراء والاشعة فوق البنفسجية. كما تم دراسة قياس التوصيلة في مذيبات مختلفة للسوائل الايونية المحضرة.