Celal Bayar University Journal of Science
Volume 16, Issue 1, 2020, p 75-80
Doi: 10.18466/cbayarfbe.649172

Celal Bayar University Journal of Science

Synthesis of Some Novel Alkoxysilyl-functionalized Ionic Liquids

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Received: 20 November 2019
Accepted: 17 March 2020
DOI: 10.18466/cbayarfbe.649172

Abstract

The field of ionic liquid (IL) compounds has recently become one of the popular topics because of its green chemistry potential and superior properties. A series of some novel alkoxysilyl-functionalized ionic liquids that containing different hydrophobic chains have been synthesized and their structures were identified by an infrared spectrometer (FT-IR), nuclear magnetic resonance spectrometer (NMR). Thermal stabilities of synthesized ionic liquids were investigated. The new ionic liquid compounds are good candidates for different application areas due to their functional group which involves easy attachment of them on the surface of supporting materials.

Keywords: Alkoxysilyl-functionalized ionic liquid, dihydro imidazolium, ionic liquid.

1. Introduction

Ionic liquids (ILs) are salts which are created by combination of different type of cations, e.g., imidazolium, pyrrolidine pyridiniums, phosphonium, sulfonium, ammonium and anions e.g., halides (chloride, bromide, iodide), hexafluorophosphate, tetrafluoroborate, tosylated alkyl sulfates derivatives, thiocyanate, etc. They have good physical (melting point, boiling point, density, and viscosity…etc) and also chemical properties. ILs are thermally stable, non-volatile, non-flammable and have low toxicity solvents. Their melting points are generally below 100ºC. Their physical and chemical properties and behaviors can be changeable according to selected cation and anion and these flexible features make them most preferred materials for scientific and industrial fields [1-7].

ILs have wide application areas for different purposes. In geology, they have been used for extraction of some materials [8], In the textile industry, IL's have been preferable materials for some important textile processes and have been used successfully because of ecologically and industrial importance [9]. They are also important compounds for many fields of chemistry, such as biochemistry, electrochemistry, synthetic chemistry. The electrochemical deposition has been carried out successfully in IL's [10, 11]. They have been used in different types of batteries as electrolytes (solar cells, Li-Ion batteries, etc.) [12, 13], in biological systems for enzyme extractions and biocatalytic reactions as solvents [14]. In the other study, ILs have been used as an additive for the preparation of oxygen sensing solid matrix [15].

Ionic liquids have found attractive interest in the reactions as both solvent and also catalyst [16, 17, 18]. When IL's are used in reactions, the product isolation and setting up reactions are very easy and they take advantage in terms of recycling. They have perfect solubility for organic and inorganic materials. Laali's research group achieved great development by the use of ILs in synthetic chemistry. They used IL's as a solvent in different types of reactions (arylation, acylation, nitration, halogenation reactions …etc) and catalyst in metal-mediated bond-forming reactions. The progress was summarized in Laali's review study [19]. In the Welton's review study, it was also mentioned that ionic liquids were used for many synthesis and catalysis and green catalyst studies such as transition-Metal-Mediated Catalysis, substitution reactions, diels-alder, alkylation reactions, etc.) [20].

IL's are promising materials and synthesis of new derivatives and investigations on their properties is not enough yet. For this reason, synthesis and searching of properties of new IL's are crucial notably for their applications in different studies. In this study, some novel ionic liquids compounds (Figure1) containing alkoxysilyl functional group with different aliphatic and aromatic groups have been synthesized and their structures were determined by FTIR and ^{1}H and ^{13}C NMR techniques and also their thermal properties were investigated. We preferred to study the synthesis of

Celal Bayar University Journal of Science
Volume 16, Issue 1, 2020, p 75-80
Doi: 10.18466/cbayarfbe.649172

alkoxysilyl-functionalized ionic liquids because functionalized ionic liquids are important materials. IL compounds can be designed for specific purposes through functional groups. For example alkoxysilyl groups provide easy binding of ionic liquids to the supporting materials. There are some examples of analogous of synthesized compounds [21-24], but these ionic liquid compounds will be presented for the first time in the literature.

2. Materials and Methods

1,4-Bis(bromomethyl)-2,3,5,6-tetramethyl benzene and pentamethylbenzyl bromide were synthesized according to the presented procedure in the literature [25-26], N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol was purchased from abcr. 1- Bromononane, diiodomethane, toluene were purchased from Sigma Aldrich.

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Mercury AS 400 instrument at 400 MHz (^{1}H) and 100.56 MHz (^{13}C) respectively. IR spectra were recorded on a Perkin Elmer-Spectrum 100 series spectrophotometer preparing KBr pellets. Thermal stability tests of compounds were performed by using Perkin Elmer Pyris 6 analyzer in the range 50-950 ºC under nitrogen (flow rate: 20 cm^3 / min) at a heating rate 20 ºC / min.

2.1. Synthesis of Ionic Liquid Compounds
2.1.1. Compound IL1

1-Nonyl-3-(3-triethoxysilylpropyl)-4,5-dihydro imidazolium bromide
Equal mole numbers of N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol and 1-bromononane were stirred in toluene at room temperature overnight. After that solvent and volatiles were evaporated from the resulting mixture under reduced pressure. Compound **IL1** was purified by washing with hexane. The solid compound was recrystallized in ether and dichloromethane solution.

Pale yellow solid; yield: (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) : 0.68 (m, 2H, CH_2-CH_2-Si), 0.82 (t, 3H, *J* = 6.8 Hz, -CH_2-CH_3,), 1.15-1.25 (m, 9H, CH_3-CH_2-O + 8H, 4CH_2), 1.60 (m, 2H, Si-CH_2-CH_2), 1.83 (m, 2H, CH_2), 2.22 (m, 2H, CH_2), 3.13 (m, 2H, CH_2), 3.50 (m, 4H, Si-CH_2-CH_2-CH_2-N, N-CH_2-CH_2-N-nonyl), 3.61 (q, 6H, *J* = 6.8 Hz, CH_3-CH_2-O,), 4.01 (m, 4H, N-CH_2-CH_2---CH_3, N-CH_2-CH_2--- CH_3), 8.95 (s, 1H, NC*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 10.5, 14.0, 18.4, 21.2, 22.6, 26.5, 27.5, 29.2, 29.4, 31.8, 48.4, 48.7, 50.2, 58.1, 157.6. FT-IR (KBr), (cm^{-1}): 3301, 2927, 2863, 1659, 1522, 1457, 1379, 1308, 1252, 1199, 1134, 1030, 914, 790, 589.

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2.1.2. Compound IL2

1-(Pentamethybenzyl)-3-(triethoxysilylpropyl)-4,5-dihydroimidazolium bromide
Commercial N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol and pentamethylbenzyl bromide compound, synthesized according to the presented procedure [25-26], were refluxed in toluene for six hours. At the end of the reaction, mixture was cooled and solvent and volatiles were evaporated under reduced pressure. Synthesized solid compound was purified by washing with ether and recrystallized in ether and dichloromethane solution.

White solid; yield: 99% ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.52 (t, 2H, *J* = 8.0 Hz, CH_2-CH_2-Si), 1.15 (m, 9H, *J* = 8.0 Hz, CH_3-CH_2-O), 1.70 (m, 2H, Si-CH_2-CH_2), 2.14-2.24 (6H, $CH_3C_6H_2$, 6H, m- $CH_3C_6H_2$, 3H, *p*-$CH_3C_6H_2$), 3.57 (t, 2H, *J* = 6.8 Hz, Si-CH_2-CH_2-CH_2-N), 3.73 (q, 6H, CH_3-CH_2-O), 3.93-3.97 (m, 4H N-CH_2-CH_2-N), 4.85 (s, 2H, $CH_2C_6H_2Me_3$), 8.84 (s, 1H, NC*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) : 7.2, 17.0, 17.2, 17.3, 18.5, 18.6, 21.2, 47.7, 48.6, 48.8, 50.5, 58.8, 125.8, 133.6, 133.8, 136.8, 157.2. FT-IR (KBr), (cm-1) 3412, 2973, 2927, 2883, 1651, 1514, 1473, 1445, 1378, 1298, 1248, 1194, 1165, 1103, 1077, 1014, 958, 902, 870, 788, 686, 620, 493, 467.

2.1.3. Compound IL3

1,1'-(Methylene)bis{3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium iodide
N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol (7.39 mmol) and diiodomethane (3.69 mmol) were stirred in toluene at reflux temperature for four hours. After cooling to room temperature solvent and volatiles were evaporated under reduced pressure. Further purification was done as mentioned before for **IL1** and **IL2**.

Yellow-orange solid; yield: 96% ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.65 (t, 4H, *J* = 8.8 Hz, CH_2-CH_2-Si), 1.23 (m, 18H, CH_3-CH_2-O), 1.86 (m, 4H, Si-CH_2-CH_2), 3.60 (t, 4H, *J* = 7.2 Hz, -CH_2), 3.83 (m, 12 H, CH_3-CH_2-O), 4.10 (t, 4H, *J* = 11.2 Hz, -CH_2) 4,45 (t, 4H, J = 9.6 Hz, CH_2), 5.90 (s, 2H, N-CH_2-N), 9.65 (s, 2H, N-C*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 7.8, 18.7, 21.2, 49.6, 49.8, 51.5, 58.8, 59.5, 96.4, 158.9. FT-IR (KBr), (cm-1) : 3520, 3440, 3308, 2937, 2882, 2054, 1651, 1526, 1449, 1378, 1304, 1249, 1195, 1102, 906, 636, 554, 453.

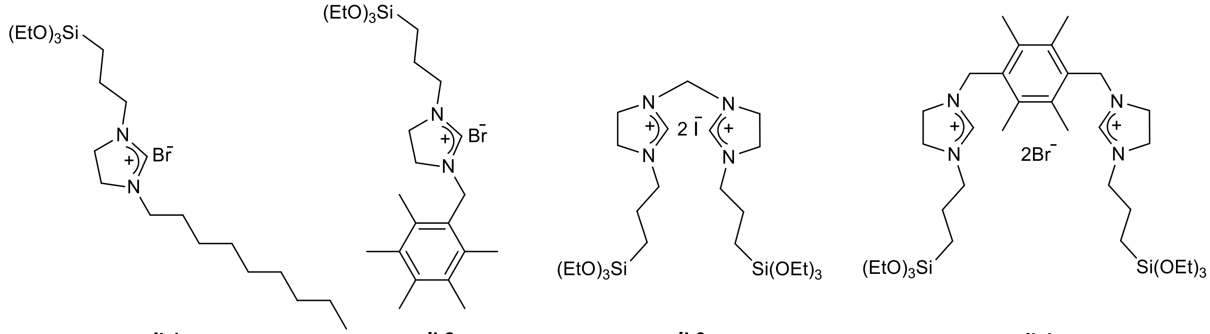
2.1.4. Compound IL4

1,1'-(2,3,5,6-Tetramethyl-1,4-phenylene) bis(methylene)bis{3-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazolium bromide
Commercial N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol and 1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene, synthesized according to published

Celal Bayar University Journal of Science
Volume 16, Issue 1, 2020, p 75-80
Doi: 10.18466/cbayarfbe.649172

procedure [25-26], were refluxed in toluene. Reaction mixture was cooled and solvent and volatiles were evaporated under reduced pressure. Synthesized yellow solid compound was purified by washing with ether and were recrystallized in ether and dichloromethane solution.

yellow solid; yield: 98% ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.47 (m, 4H, CH_2-CH_2-Si), 1.12 (t, 18H, J = 6.4 Hz, CH_3-CH_2-O), 1.55 (m, 4H, Si-CH_2-CH_2), 2.22 (s, 12H, 4 CH_3), 3.45 (t, 4H, J = 6.4 Hz, - CH_2), 3.72 (q, 12 H, J = 7.2 Hz CH_3-CH_2-O), 3.85 (m, 8H, -CH_2), 4.65 (s, 4H, 2N-CH_2-Ph), 8.45 (s, 2H, N-CH-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 7.2, 17.2, 18.4, 21.3, 47.9, 48.5, 50.3, 58.6, 129.7, 135.5, 157.2. FT-IR (KBr), (cm-1): 3579, 3440, 3180, 2936, 2881, 2055, 1652, 1627, 1449, 1377, 1305, 1250, 1195, 1100, 905, 693, 552, 461.



IL1 IL2 IL3 IL4

Figure 1. Structures of synthesized ionic liquid compounds.

3. Results and Discussion

In this study, some novel ionic liquids by combining dihydroimidazol containing ethoxysilyl functional group with bromoalkyl(aryl) units were designed. The combinations of aryl and alkyl groups with dihydroimidazole rings were differentiated to give ionic liquid compounds of different styles. In compounds **IL1** and **IL2**, unilateral alkyl and benzyl groups are attached to the dihydroimidazole ring respectively. In compounds **IL3** and **IL4**, the alkyl and xylyl groups are bridged between the two dihydroimidazole rings. These alkoxysilyl-functionalized ionic liquids are flexible to design materials for specific purposes. Four ionic liquid compounds were successfully synthesized, easily purified and obtained in high yields (96-99 %).
Purifications were made with evaporation, washing with solvents and crystallization techniques. The structures of synthesized compounds were confirmed by FTIR and ^{1}H NMR, ^{13}C NMR techniques. ^{1}H NMR spectrum of **IL2** ionic liquid compound is presented in figure 2.

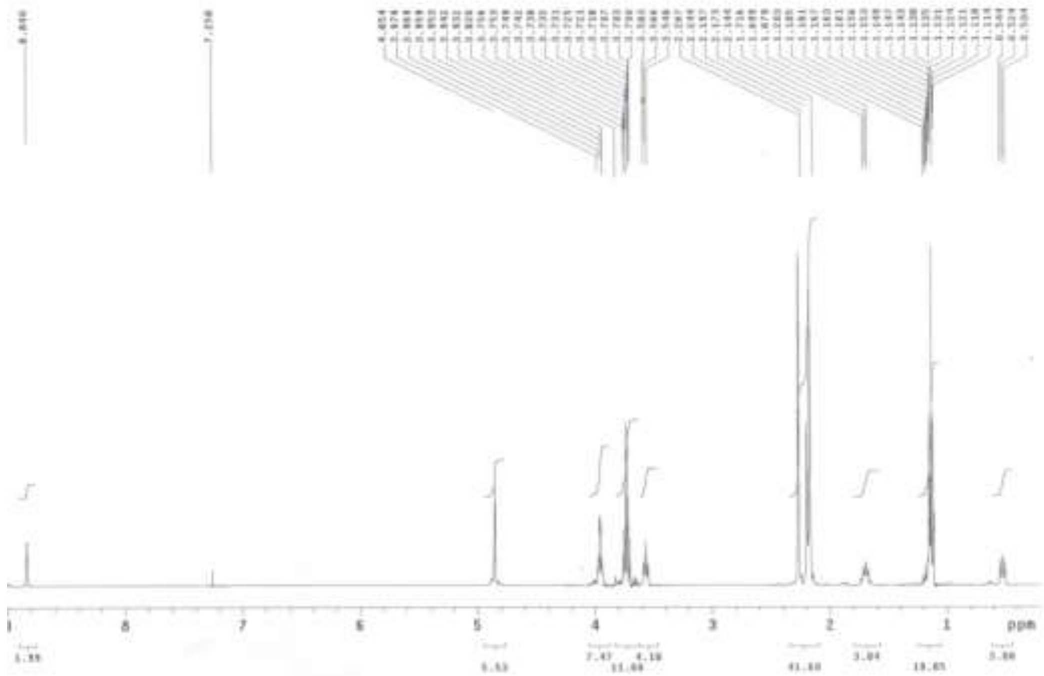


Figure 2. ^{1}H NMR spectrum of **IL2** ionic liquid compound.

Celal Bayar University Journal of Science
Volume 16, Issue 1, 2020, p 75-80
Doi: 10.18466/cbayarfbe.649172

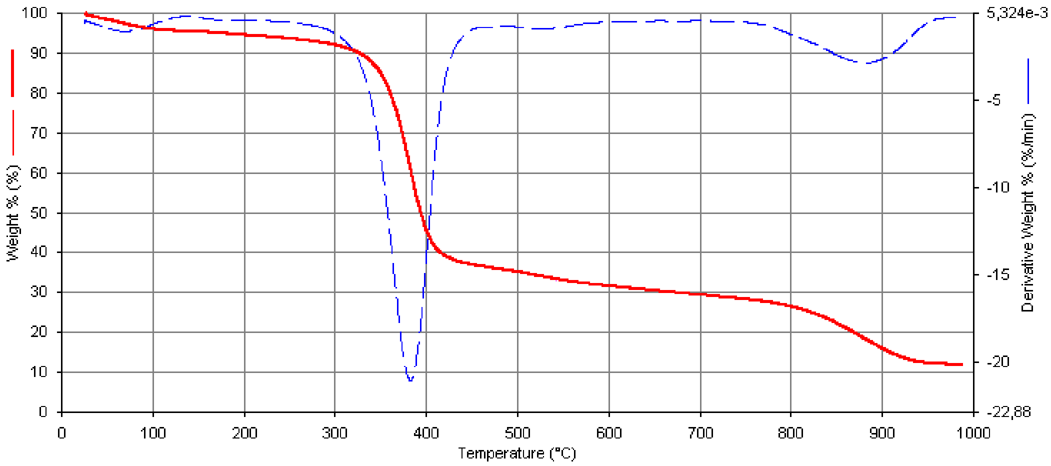


Figure 3. TGA curve of **IL1** compound.

Synthesized compounds are very valuable materials for applications. Ethoxysilyl functional groups allow them to bind some surfaces for different aims. Immobilization of catalysts or developing functionalized membrane systems can be provided easily [27-28]. They can be used as precursors of nanocomposites as well [29]. IL's are generally known to have high thermal stability in the literature [30-31]. In this study, thermal properties we investigated for IL1-4. Determination of thermal decomposition points are important for applications such as the use of substances as solvents or catalysts or etc. Thermal decomposition points of synthesized ionic liquids are shown in table 1 and TGA curve of **IL1** is also presented in figure 3.

When the TGA curves of the synthesized molecules are examined, mass loss before 100 ºC is thought to be caused by water. In other words, it is thought to be caused by the hygroscopic structure of ionic liquids. Hygroscopic behavior of IL's are known in the literature [32-33]. **IL1-4** are also thought to have hygroscopic properties. This can be specified that it can be understood from the OH peak in the IR spectrum and the loss of mass below 100 ºC in TGA measurement.

According to TGA curves, while **IL1** (figure 3) and **IL4** compounds were stable up to 380 ºC and 376 ºC respectively, disintegration of **IL2** and **IL3** compounds started at temperatures above 100 ºC and 20% mass losses were observed well before the onset of the main weight loss (main weight loss points: 358 ºC for **IL2**, 391 ºC for **IL3**), so Td values of **IL2** and **IL3** compounds were recorded at lower temperatures.

Table 1. Thermal decomposition points of IL's.

Ionic liquid	Td (ºC)	T (ºC) (for main weight loss)
IL1	**380**	**380**
IL2	**142**	**358**
IL3	**155**	**391**
IL4	**376**	**376**

Td: Degredation point (ºC)

4. Conclusion

In the study, triethoxy silyl attached ionic liquid compounds were synthesized successfully in different styles. The benzyl and alkyl groups were attached to a single imidazole (**IL1** and **IL2**) or used as the bridge between two imidazole rings (**IL3** and **IL4**). Their structures were verified by FTIR and ^{1}H NMR, ^{13}C NMR characterization techniques. It is important to identify the properties of the compounds to use the synthesized compounds in applications. In this sense, the thermal stability of the compounds was investigated in this study. The compounds **IL1** and **IL4** have also high thermal stability above 350 ºC and these ionic liquids suitable for use in high-temperature applications such as protection against high temperature corrosion of metals [34]. All new ionic liquids are very valuable for different applications because of ethoxysilyl functional group. Creating an immobilized catalyst systems with ILs can be one of the application area. Separation and recycling of catalyst can become easier in catalytic reactions. They can be used in solid-phase microextraction (SPME) systems as coating materials as well.

Acknowledgment

I would like to express my gratitude to Ege University, Faculty of Science, Chemistry Department for using its laboratories and facilities.

Ethics

There are no ethical issues after the publication of this manuscript.

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