

## Synthesis of Some Carboxylate Tetraethylammonium Salts as Ionic Liquids

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### Abstract

Some of organic ammonium salts, namely: 2-((4-carboxyphenyl) carbamoyl) benzoate tetraethylammonium, B1, 4-oxo-4-(pyridin-3-ylamino)-2-butenate tetraethylammonium, B2, 2-((4-carbamoylphenyl) carbamoyl) benzoate tetraethylammonium, B3, 4-((4-carbamoylphenyl)amino)-4-oxobutanoate tetraethylammonium, B4, are successfully synthesized as ionic liquids. By spectral techniques of FTIR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  the structures of organic salts are confirmed. The thermal analysis by differential scanning calorimetry (DSC) has shown the thermal stability of the organic ammonium salts (B1-B4). A high conductivity characteristic as compared with that of NaCl has been detected in the aqueous solution.

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### 1. Introduction

The ionic liquids (ILs) have been usually specified as chemical compounds. These (ILs) can be consisted only ions, and they have melting points lower than  $100^\circ\text{C}$ . Paul Walden in 1914 reported the first IL (ethylammonium nitrate). Never thought IL would do this after nearly a century, it has become a major scientific discipline [1]. ILs remain longer preferably as traditional volatile solvents as well as, catalysts in many chemical and physical processes. It often moderately equipped with "designer" and "green" characteristics [2]. ILs continue to be developed as chemical diversity increases. Ionic liquids are included many types (ILs room-temperature [3], ILs task-specific [4], poly ILs [5] and supported membranes ILs [6], that included ILs composites supported on organic-metal frameworks [7]. Many ILs are applied at high temperatures (chemical reactions, extraction, separation, lubrication, etc.) [8], indicated that the thermal stability of ILs is of particular importance. The structure, composition, and properties of ILs can change significantly after degradation [9, 10]. This conflicts green chemistry and green solvents goals. ILs in pure form, have ability to attitude electrical conductivity within the liquid phase via the charged ions movements. This recognizes them from usual ionic materials which should firstly dissolved in water as a solvent, in order to prepare

electrolytes, which solids. These adorable properties have led the researchers to expand the utility of ILs in a huge use of energy applications including conductions, like, electrolytes in certain batteries [11] and some kinds of fuel cells [12], electrochemical energy storage systems (supercapacitors) [13], and units of hydrogen storage [14]. In this work, we reported the synthesis and characterizations of organic salts (B1-B4) as shown in Figure 1.

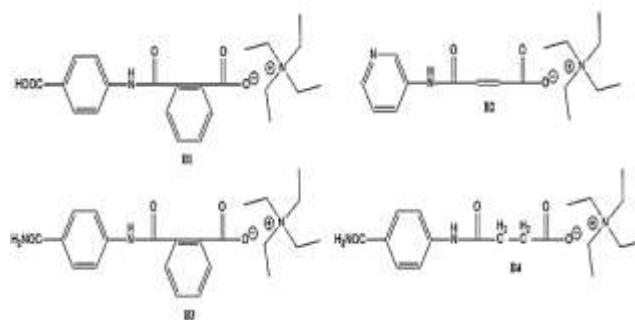


Figure 1. New organic ammonium salts

### 2. Materials and Methods

#### 2.1. Materials

Chemicals reagents and solvents were supplied from Sigma-Aldrich and they were used without further purification.

#### 2.2. Instrumentation

The synthesized organic compounds were identified by FTIR spectrophotometry (Bruker) with wave number (400-4000 $\text{cm}^{-1}$ ) and  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR (Bruker, 400 MHz) were used (DMSO- $d_6$ ) as a solvent. Laboratory Conductivity meter inoLab Cond 720 that used from Carl Stuart limited company, The scanning calorimetry (differential scanning calorimeter (Perkin Elmer DSC-7)) was used for the synthesized ionic liquids characterization, applying the ASTM E-794-06 method with DSC in a range at 25°C to 600°C at 5°C/min and Argon gas (Praxair Brand) 99.999% purity as a gas purge with a flow gas of 20 mL/min.

### 2.3. General procedure for synthesized tetraethyl ammonium salts (B1-B4)

A mixture of an amine (0.01 mol) with (0.01 mol) of an acid anhydride in THF (10 mL) were stirred at r.t. for four hours. The stirring stopped and the mixture was left 24 hrs at r.t. until the solid amic acid precipitated. The precipitate was filtered, and washed with THF (2 × 10 mL)[15]. After that, amic acid (0.01 mol) was mixed with 35% tetraethyl ammonium hydroxide in MeOH (10 mL) and stirred at r.t. for 3 hrs. Then, the mixture was left at 37 °C for 48 hrs. The final salt was washed with MeOH (2 × 10 mL) then dried.

- A1, 2-((4-carboxyphenyl)carbamoyl)benzoic acid, mp: 155-158°C, Yield %:77, FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3300, O-H carboxylic 3200-2500, C-H aromatic 3010, C=O carboxylic 1700, C=O amide 1644.

- A2, 4-oxo-4-(pyridin-3-ylamino)-2-butenic acid, mp: 163-165°C, Yield %:73, FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3366, O-H carboxylic 3200-2500, C-H aromatic 3052, C=O carboxylic 1703, C=O amide 1643.

-A3, 2-((4-carbamoylphenyl)carbamoyl)benzoic acid, mp: decomp. at 195°C, Yield %:74, FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3339, O-H carboxylic 3200-2500, C-H aromatic 3016, C=O carboxylic 1701, C=O amide 1651.

- A4, 4-((4-carbamoylphenyl)amino)-4-oxobutanoic acid, mp: 192-195°C, Yield %:73, FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3339, O-H carboxylic 3200-2500, C-H aromatic 3042, -C-H aliphatic at 2988 and 2850, -C=O carboxylic 1710, -C=O amide 1644, -N-H amide 3377.

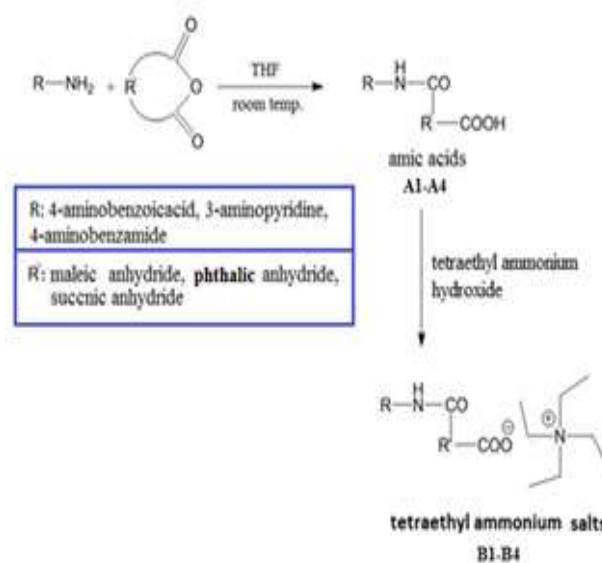
- B1, 2-((4-carboxyphenyl)carbamoyl)benzoate tetraethyl ammonium, bp: 230°C, Yield %:73, yellow thick liq., FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3336, C-H aromatic 3071, C-H aliphatic 2980, 2880, C=O carboxylic 1700, C=O carboxylate 1690, C=O amide 1650,  $^1\text{H}$ -NMR data (ppm): N+(12H, -

CH<sub>3</sub>, m, 1.12; 8H, -CH<sub>2</sub>, m, 3.11), aromatic ring (8H, m, 6.54-7.81), N-H amide (1H, s, 8.26), COOH (1H, s, 14.21)

- B2, 4-oxo-4-(pyridin-3-ylamino)-2-butenate tetraethyl ammonium, bp: 210°C, Yield %:70, black liq., FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3415, C-H aromatic 3100, -C-H aliphatic 2986, 2880, -C=O carboxylate 1705, -C=O amide 1641,  $^1\text{H}$ -NMR data (ppm): N+(12H, -CH<sub>3</sub>, m, 1.12; 8H, -CH<sub>2</sub>, m, 3.11), unsaturated alkane (2H, d, 5.75, 6.23), pyridine ring (4H, m, 6.71-8.91), N-H amide (1H, s, 11.42).

- B3, 2-((4-carbamoylphenyl)carbamoyl)benzoate tetraethyl ammonium, , bp: 218°C, Yield %:69, white thick liq., FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3419, 3360, 3300, C-H aromatic 3028, C-H aliphatic 2980, 2880, C=O carboxylate 1700, C=O amide 1665, 1652,  $^1\text{H}$ -NMR data (ppm): N+(12H, -CH<sub>3</sub>, m, 1.12; 8H, -CH<sub>2</sub>, m, 3.11), -CONH<sub>2</sub> (2H, s, 7.75), aromatic ring (8H, m, 7.17-8.23), N-H amide (1H, s, 10.3),  $^{13}\text{C}$ -NMR data (ppm): N+(-CH<sub>3</sub>, 7.5 ; -CH<sub>2</sub>, 51.8 ), aromatic ring (120-135), carbonyl amide (140, 166), carbonyl acetate (168)

- B4, 4-((4-carbamoylphenyl)amino)-4-oxobutanoate tetraethyl ammonium, bp: 218°C, Yield %:71, white thick liq., FTIR data ( $\text{cm}^{-1}$ ): N-H amide 3422, 3339, 3300, C-H aromatic 3047, -C-H aliphatic 2989, 2880, -C=O carboxylate 1700, -C=O amide 1641,  $^1\text{H}$ -NMR data (ppm): N+(12H, -CH<sub>3</sub>, m, 1.12; 8H, -CH<sub>2</sub>, m, 3.11), saturated alkane (4H, m, 2.02-2.34), -CONH<sub>2</sub> (2H, s, 7.61), aromatic ring (4H, m, 7.04-7.81), N-H amide (1H, s, 10.33) ,  $^{13}\text{C}$ -NMR data (ppm): N+(-CH<sub>3</sub>, 7.5 ; -CH<sub>2</sub>, 51.8 ), alkane (131, 133), aromatic ring (120-135), carbonyl amide (140, 166), carbonyl acetate (176).



Scheme 1. Synthesis of ammonium salts B1-B4.

### 3. Results and Discussion

**3.1. Experimental Investigation,** The synthesis of tetraethylammonium salts (B1-B4) of this work was included preparation of the amic acids (A1-A4, see Scheme 1) by using different amines to reacting with the acid anhydrides. The next step of the reaction is the acid-base reactions between tetraethylammonium hydroxide and amic acids to yield tetraethylammonium salts (B1-B4, see Scheme 1). The FT-IR spectral data are shown appearing stretching bands of amide at 3300-3380  $\text{cm}^{-1}$  and 1640-1650  $\text{cm}^{-1}$ , (N-H, C=O), respectively, of (A1-A4) and stretching bands of carboxylate (C=O) 1690-1700  $\text{cm}^{-1}$  of (B1-B4). As well as, the peaks of tetraethylammonium are clearly shown by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  at  $\delta$  1.12, 3.11 & 7.7, 51.8 ppm spectral data for tetraethylammonium salts (B1-B4).

### 3.2. Ionic liquid characterization

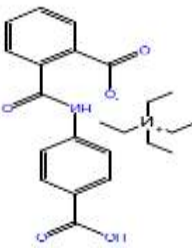

The scanning calorimetry was used to determine the thermal stability of the prepared organic ammonium salts (B1-B4) as ionic liquids, using the ASTM (E-794-06) measurement in the calorimeter of differential scanning (DSC-7 Perkin Elmer) in the range ( 25°C to 600°C) at 5°C/min, with surrounding Argon gas as a gas purge by 20 mL/min flow rate. The thermal characteristics of

original organic ammonium salts (B1-B4) were obtained and reported.

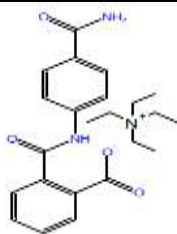
As shown by DSC Figures (2-5) and data of Table 1, the original organic ammonium salts (B1-B4) exhibit characterization of ionic liquids with a few endo-thermic peaks with the temperature degree was increased. For the ammonium salt (B1), the first peak is obtained due to lose of water molecules at 90° C as showed in Figure 2, while, the temperature is increased that make to appear others endothermic peaks, these peaks are belonged to 257 and 367°C for decomposition. By depending on boiling points in Table 1 for ammonium salts (B1-B4) and what are shown in DSC Figures (3-6) of endothermic peaks, we concluded that ammonium salts (B1-B4) exhibit characterization of ionic liquids with thermal stability [16].

We used data measurements of lab conductivity for comparing the conductivity of aqueous solution (0.1%) of prepared organic ammonium salts (B1-B4) with (0.1%) aqueous solution of NaCl at room temperature. Table 1 is showing that ammonium salts (B1-B4) exhibit characterization of ionic liquids with high conductivity with comparing by aqueous solution of NaCl [17].

**Table 1:** DSC and conductivity data for compounds (B1-B4)..

Comp. No.	Compound Structure	Conductivity ( $\mu\text{s}/\text{cm}$ )	DSC (°C)	Boiling point (°C)
Blank	NaCl	2.8		
B1		136.5	178, 257, 367	230
B2		305.0	175, 350	210

B3 63.7 150, 289 218



B4 23.8 121, 350 218

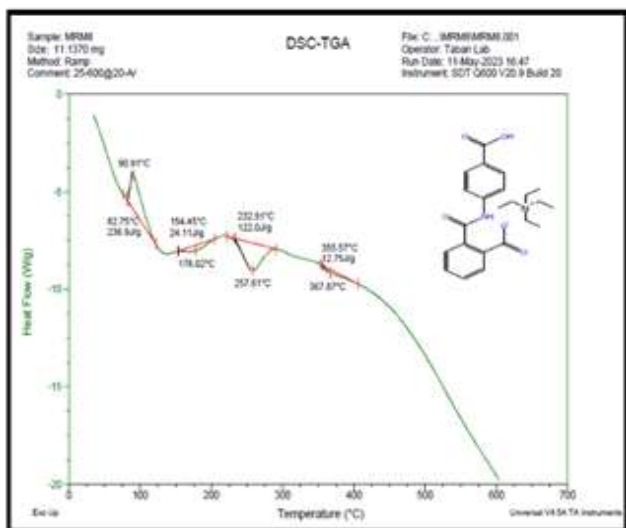
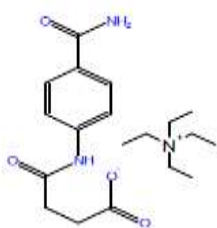


Figure 2: DSC for compound B1

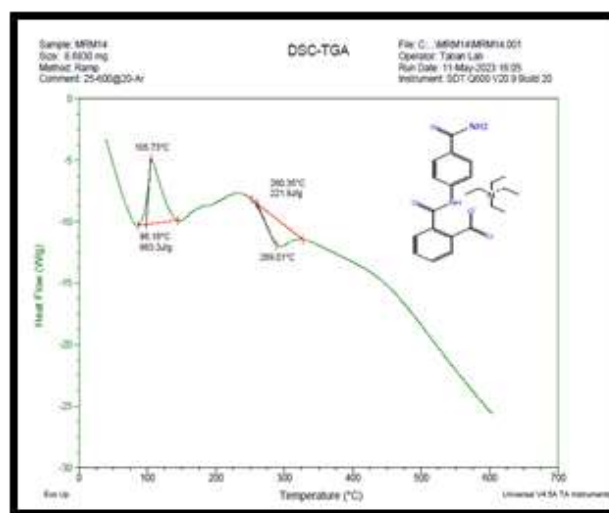


Figure 4: DSC for compound B3.

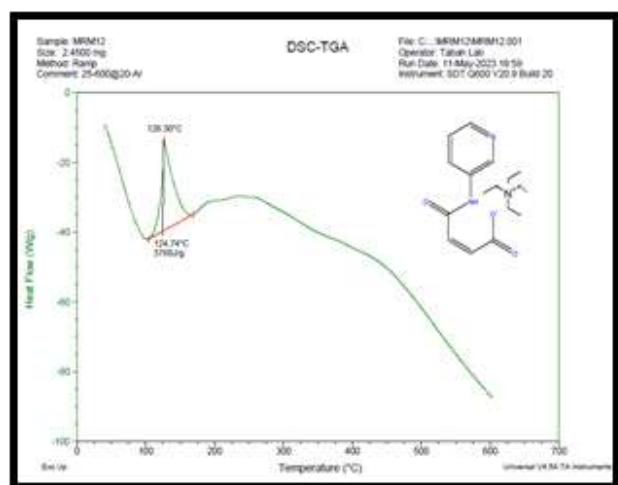


Figure 3: DSC for compound B2.

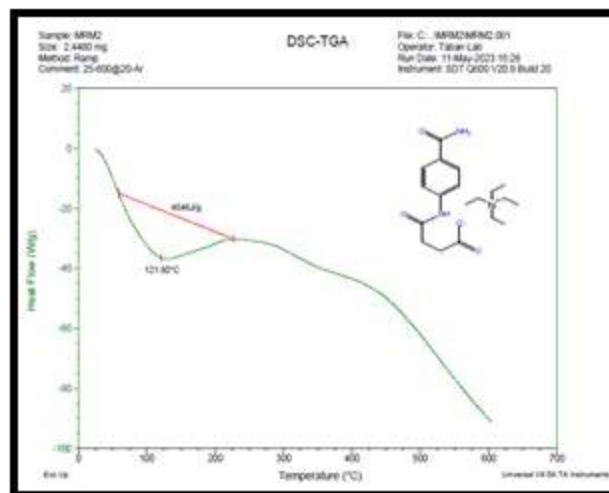


Figure 5: DSC for compound B4.

## 4. Conclusions

Tetraethyl ammonium organic salts (B1– B4) were successfully synthesized. Due to their thermal stability shown by using thermal analysis test such as DSC technique, characterizations of ionic liquids are revealed. Organic salts (B1– B4) have also shown high conductivity in an aqueous solution comparing to a reference of saline solution. These physical properties make them promising candidates for green solvents, catalysts and electrolytes.

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## Conflict of interest

There are no conflicts to declare

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