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## Synthesis of triacetin by protic ionic liquids as catalysts

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### Abstract

Triacetin (glycerol triacetate) is one of the important derivatives of glycerol and can be applied into many industrial fields. Usually, it is prepared industrially in the presence of strong mineral acidic catalysts. The main shortcomings include serious environmental issues, complicated technique of synthesis and no recyclability of the used catalyst. In this work, the results of application of a collection of protic ionic liquids as homogeneous catalysts for triacetin esterification is reported. The study analyzed a wide spectrum of ionic structures, the proposed protic ionic liquids comprising aliphatic, aromatic or polyvalent structures as anions and mono or disubstitutions into the cations. The protic ionic liquids catalysts were used without apparent loss of efficiency in repeated cycles, with excellent performance and conversion into triacetin yield remained above 90%.

**Keywords:** glycerol, catalysis, protic ionic liquids, triacetin

### Introduction

With the rapid development of the biodiesel industry, there is now urgency to make full use of glycerol, a byproduct of biodiesel production, avoiding the high costs of storage and non-sustainable applications such as burning glycerol to produce electricity. Triacetin, an important derivative of glycerol, is the simplest fat after triformate glycerol. It is an artificial chemical compound and can be used in many areas of industrial interest. Commonly, it is used as food additive, solvent flavorings, and wetting solvent (E1518), as well as, excipient in pharmaceutical products where is applied as plasticizer and solvent. It can also be used as a fuel additive and as anti-knock agent to improve the properties of viscosity in biodiesel. It is usually prepared in the presence of mineral acid catalysts (Figure 1), but the shortcomings of such processes include environmental issues, and no recycling of the catalyst synthesis and complex techniques of separation of product.

In recent years, significant progress has been made in the study and application of room temperature ionic liquids [1]. These substances have received, over the last decade, wide attention as environmentally-benign alternatives to conventional organic solvents [2-3]. Although these ionic liquids are too "organic solvents," they exhibit a variety of useful properties which have not been achieved in conventional liquids, until now. Ionic liquids are typically consisted of small anions and bulky cations which, for example, are imidazolium, pyridinium, quaternary ammonium, and phosphonium structures. Against the strong electrostatic interaction among ions, the steric effect of large size of cations prevents ionic liquids from getting solidified at room temperature as occurs in common salts. The coulombic interaction between ions is so strong compared to intermolecular interaction between dipolar molecules that microscopic behavior of ionic liquids is different from that of conventional dipolar liquids. In fact, strong aggregates and cholate behaviour has been observed, as well as not homogenous distribution of cations and anions at microscopic scale. The same behaviour has been observed for those ionic liquids so-called Brønsted salts (or protic ionic liquids) [4, 5] where steric hindrance has been distributed among anions and cations.

In this paper, the studied protic ionic liquid belong to a new family based on substituted amines as cations and deprotonated organic acids as anions. The main merit of this kind of compounds is to obtain sufficient steric hindrance with a reduced number of atoms without complex structures or potential hazard molecular groups (halogens, heterocycles etc),

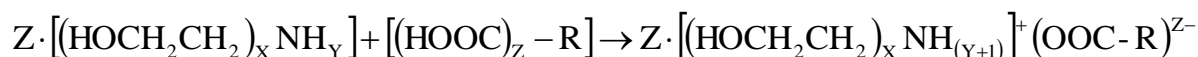
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showing the same capabilities that traditional ionic liquids and additional advantages as their low cost, simple chemical preparation and biodegradability into natural environment<sup>[6-9]</sup>. In what is referred to reaction media, ionic liquids have been the subject of considerable interest in the context of green synthesis because they have been found to act as selective catalysts for different reactions.

In this work, a collection of new protic ionic liquids have been synthesized and characterized to be applied as homogeneous catalysts. The application of these solvents for triacetin synthesis shows excellent catalytic activity and selectivity in the esterification of glycerol. The catalytic performance of this kind of solvent and the easy reuse of protic ionic liquids can contribute to the development of environmentally friendly strategies for the synthesis of triacetin and the use of glycerol stock for the generation of products of value in high demand on the international market.



where X is the number of ethanol substitutions into the amine compound, Y the protons directly bonded to N atom into amine (Y+1=3) and Z the number of carboxyl groups into acid (3 for citric acid, 2 oxalic acid and adipic acid and 1 for the other ones). R means the residual structure into the organic acid. For example, when X=1, Y=2, and Z=1 this equation shows the chemical reaction for the reactants monoethanolamine + formic acid, and 2-hydroxy ethylammonium formate (2-HEAF) as neutralization product. If X=2, Y=1, and Z=3 this equation shows the chemical reaction for the reactants diethanolamine + citric acid, and 2-hydroxy diethylammonium citrate (2-HDEACi) as neutralization product. The corresponding protic ionic liquids were prepared: 2-hydroxy ethanolammonium formate (2-HEAF), 2-hydroxy diethanolammonium formate (2-HDEAF), 2-hydroxy ethanolammonium acetate (2-HEAA), 2-hydroxy diethanolammonium acetate (2-HDEAA), 2-hydroxy ethanolammonium propionate (2-HEAPr), 2-hydroxy diethanolammonium propionate (2-HDEAPr), 2-hydroxy ethanolammonium butyrate (2-HEAB), 2-hydroxy ethanolammonium ftalate (2-HEAFt), 2-hydroxy diethanolammonium oxalate (2-HDEAOx), 2-hydroxy diethanolammonium adipate (2-HDEAAAd), 2-hydroxy ethanolammonium citrate (2-HEACi) and 2-hydroxy diethanolammonium citrate (2-HDEACi). Spectroscopic and thermodynamic analyses should be gathered in earlier published works<sup>[10-12]</sup>. Figure 2 shows a collection of protic ionic liquids used in this work.

### Spectroscopy test

FT-IR spectrum was taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk. The broad band in the 3500-2400 cm<sup>-1</sup> range exhibits characteristic ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centered at 1600 cm<sup>-1</sup> is a combined band of the carbonyl stretching and N-H plane bending vibrations, as well as two characteristic band are showed 3500-2400 cm<sup>-1</sup> for NH<sub>3</sub><sup>+</sup> + OH<sup>-</sup> and other wide band at 1600 cm<sup>-1</sup> for

### Materials and methods

#### Preparation of the ionic liquids

The amine compounds (monoethanolamine and diethanolamine were Merck Synthesis, better than 99%) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor and a dropping funnel. The flask was mounted in a thermal bath. A slight heating and strong agitation are necessary to increase miscibility between reactants and then, allow reaction. The organic acid (formic, acetic, propionic, butyric, ftalic, oxalic, adipic or citric acids, Merck Synthesis, better than 99%) was added dropwise or by means an appropriate solvent to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. No solid crystals or precipitation was noticed when the liquid sample was purified or was stored at freeze temperature for a few months after synthesis. The reaction is a acid-base neutralization creating a salt of mono or di ethanolamine, that in a general form should be expressed as follows for the protic ionic liquids:

COO<sup>-</sup> + N-H plane bend.

All the NMR experiments were performed at 298 K in a 17.6 T Varian Inova-750 spectrometer (operating at 750 MHz proton frequency). The spectra were processed with Mestre-C software. As observed into Table 2, there were observed the following chemical shifts for 2-HEAB: NMR-<sup>1</sup>H spectrum (δ: 3.14 and δ: 3.82 (m, 2H; H-2' and H-3', alfa to amine group and alfa to hydroxyl group), δ: 2.16 (t, 2H, alfa to carboxilate group), δ: 1.56 (st, 2H, beta to carboxilate group), δ: 0.90 (t, 3H, gamma to carboxilate group). HSQC (δ: 41.2 for C-2' and δ 57.3 for C-3'. Alfa, beta and gamma carbons to carboxile group, δ: 39.2 (C-2), δ: 19.2 (C-3) and δ: 12.9 (C-4). In HMBC, the correlation of hydrogens H-2 (δ: 2.16) with C-1 (δ: 183.5) and C-3 (δ: 19.2) with 2J and C-4 (δ: 12.9) with 3J, confirms the chemical shift of the groups and the ionic structure of 2-HEAB.

For example, spectra of 2-HDEAF (FTIR) and 2-HEAB (NMR-<sup>1</sup>H, HSQC and HMBC) are enclosed (Figures 3a and 3b-d, respectively).

### Physical properties equipment

Usual manipulation and purification of protic ionic liquids in our experimental works was applied<sup>[13]</sup>. The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of 10<sup>-5</sup> gcm<sup>-3</sup> and 1 ms<sup>-1</sup>. Apparatus calibration was performed periodically in accordance with vendor instructions using a double reference (Millipore quality water and ambient air at each temperature). Accuracy in the temperature of measurement was better than ±10<sup>-2</sup> K by means a device that applies the Peltier principle to maintain isothermal conditions during the measurements. The samples were thermostatted in a closed vessel before measurements to prevent evaporation.

### Stability at room temperature

The potential exists for many of these fused ammonium salts to undergo a condensation reaction to form an amide

compound. An adequate control of temperature is essential throughout the chemical reaction of salt formation, otherwise heat evolution may produce the dehydration of the salt to give the corresponding amide. Dehydration commences around 150 °C, for those lightest ionic liquids in this family. The colour varies at each case from transparent to dark brown when reaction process and purification (strong agitation and slight heating for vaporization of residual non-reacted acid at least for 72 h) was completed. There was no detectable decomposition for the ionic liquids studied here when left for over 12 months at laboratory temperature.

### Triacetin process

General esterification procedure: Alcohol (25 mmol), acetic acid (27.5 mmol) and protic ionic liquid (12.5 mmol) as catalyst were added into a laboratory reactor with gas condenser and stirred at isothermal condition (90 °C for 6 h). After that period of reaction, the collection of samples taken at fixed times during the process, were analysed by titration. For recycling use of the protic ionic liquid, the ester was separated by a liquid-liquid extraction solvent (n-hexane), washed with saturated sodium hydrogen carbonate and water, and dried as made after synthesis (strong agitation, moderate heat and low pressure, at least 72 h). Figure 4 showed the general process for protic ionic liquid catalysis of esterification.

### Results and discussion

In this work, a collection of protic ionic liquids have been synthesized, characterized and applied as catalysts for triacetin synthesis. The application of these solvents for triacetin esterification shows excellent catalytic activity and selectivity in the esterification of glycerol. Twelve water-stable ionic liquids (2-hydroxy ethanolammonium formate (2-HEAF), 2-hydroxy diethanolammonium formate (2-HDEAF), 2-hydroxy ethanolammonium acetate (2-HEAA), 2-hydroxy diethanolammonium acetate (2-HDEAA), 2-hydroxy ethanolammonium propionate (2-HEAPr), 2-hydroxy diethanolammonium propionate (2-HDEAPr), 2-hydroxy ethanolammonium butyrate (2-HEAB), 2-hydroxy ethanolammonium itate (2-HEAFt), 2-hydroxy diethanolammonium oxalate (2-HDEAOx), 2-hydroxy diethanolammonium adipate (2-HDEAAd), 2-hydroxy ethanolammonium citrate (2-HEACi) and 2-hydroxy

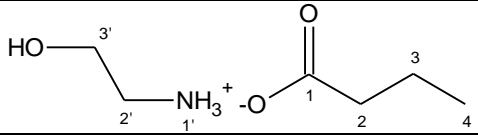
diethanolammonium citrate (2-HDEACi)) were applied as solvents and acid catalysts for Fischer reactions of glycerol and acetic acid to obtain triacetin as main esterification product.

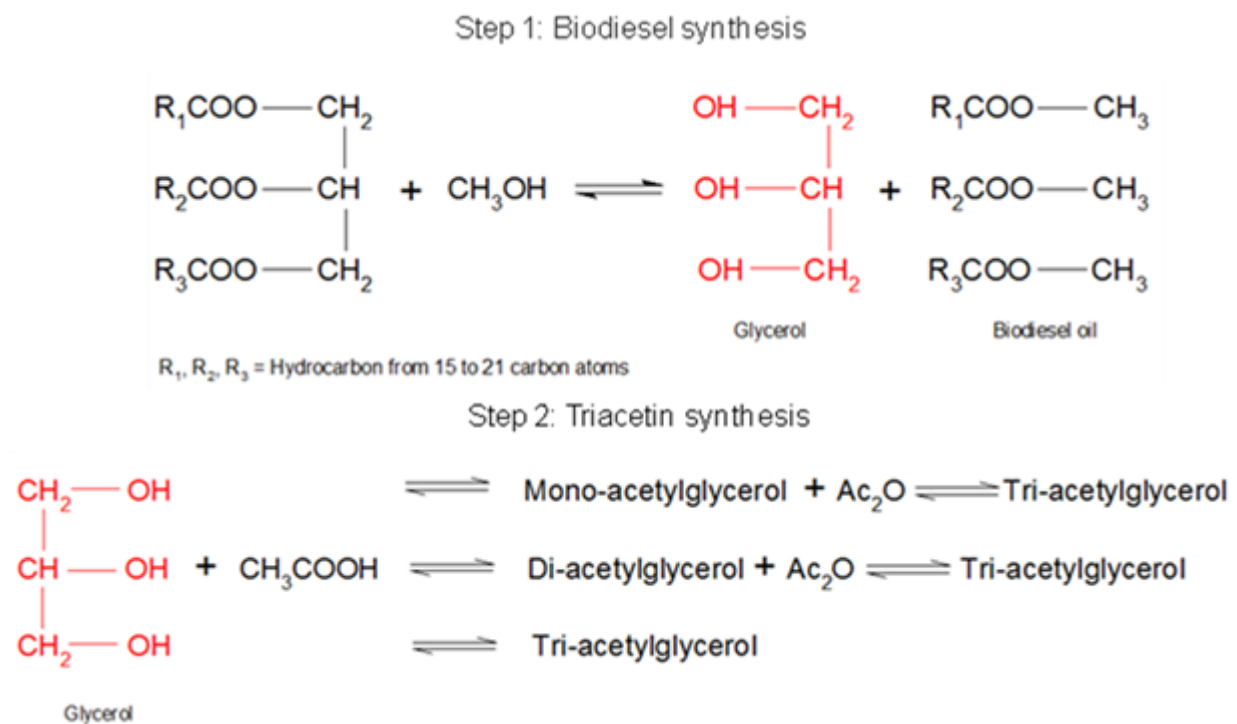
The catalytic activity of these ionic liquids was strongly dependent on the acidity of their anions and cations. The hydrophilicity of the ionic liquids and its affinity with the reactants affects its catalytic reactivity. The results indicated that the acidic strength determined the catalytic performance of the ionic liquids, showing good catalytic performance. For example, Figure 5 shows the catalysts trend at 80 °C for selected protic ionic liquids, compared with sulphuric acid catalyst and the process without catalyst (white). As observed, despite low process temperature, 2-HEAFt and 2-HEACi, achieve similar results to that of industrial catalysis. Figures 6 and 7 gather the obtained results of 2-HEACi as a function of temperature, showing comparative results with sulphuric acid at both temperatures.

### Conclusions

A collection of protic ionic liquids of low molar mass were synthesized, being spectroscopic (FTIR, NMR-<sup>1</sup>H, HSQC and HMBC) and thermodynamic characterized. They were applied as homogeneous catalysts for triacetin esterification, with excellent performance without drawbacks commonly associated as corrosion or saponification. The study analyzed a wide spectrum of ionic structures, the proposed compounds comprising aliphatic (formate, acetate, propionate and butyrate ions), aromatic (falic ion) or polivalent structures (oxalic, adipic or citric ions) as anions and mono or disubstitutions into the nitrogen-based cations (2-hydroxy ethyl ammonium and 2-hydroxy diethylammonium ions). Those structures of polyelectrolyte nature gathered a better capability of catalytic conversion. They were used without apparent lost of efficiency in repeated cycles, conversion into triacetin yields remained above 90% at different temperature conditions, without catalysts degradation. The use of these ionic compounds as catalysts, of low cost, biodegradable character, hydrophilic nature and simple chemical synthesis, is consistent with the principles of Green Chemistry, aiding in the development of sustainable and respectful processes with the environment.

**Table 1:** Nuclear magnetic resonance parameters for 2-hydroxyethanolammonium butyrate (2-HEAB)

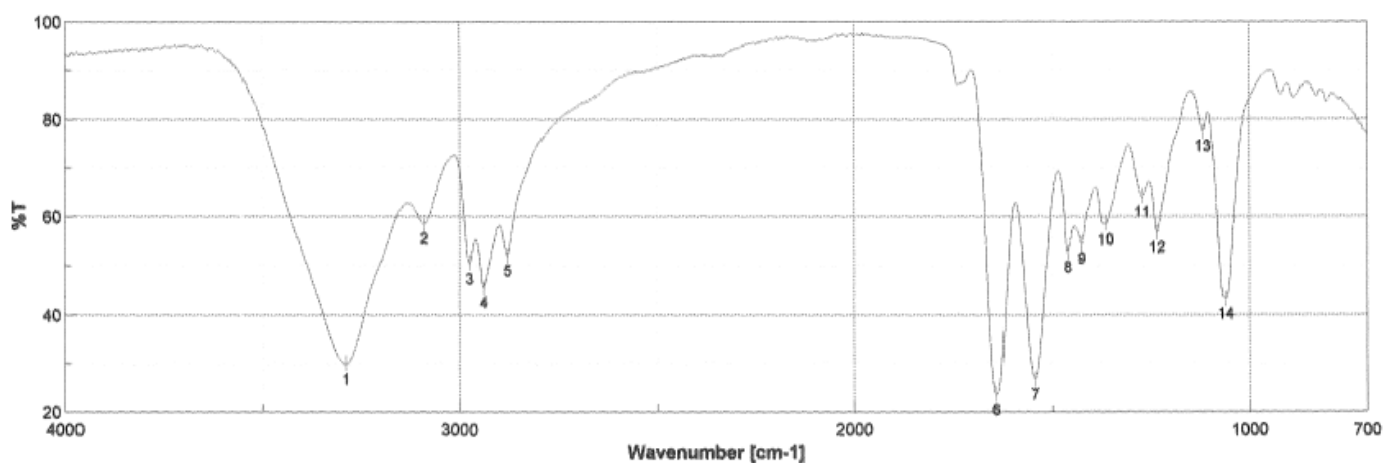
				
2-HEAB (500/125 MHz, D <sub>2</sub> O)				
H/C	<sup>1</sup> H δ (ppm), multiplicity, J(Hz)	<sup>13</sup> C δ (ppm)	HMBC - δ (ppm)	
			<sub>2</sub> J	<sub>3</sub> J
1	-	183.5	-	-
2	2.16 (t, J=7.35)	39.2	183.5 (C-1) 19.2 (C-3)	12.9 (C-4)
3	1.56 (st, J=7.35)	19.2	12.9 (C-4) 39.2 (C-2)	183.5 (C-1)
4	0.90 (t, J=7.35)	12.9	19.2 (C-3)	39.2 (C-2)
2'	3.14 (m)	41.2	57.3 (C-3')	-
3'	3.82 (m)	57.3	41.2 (C-2')	-



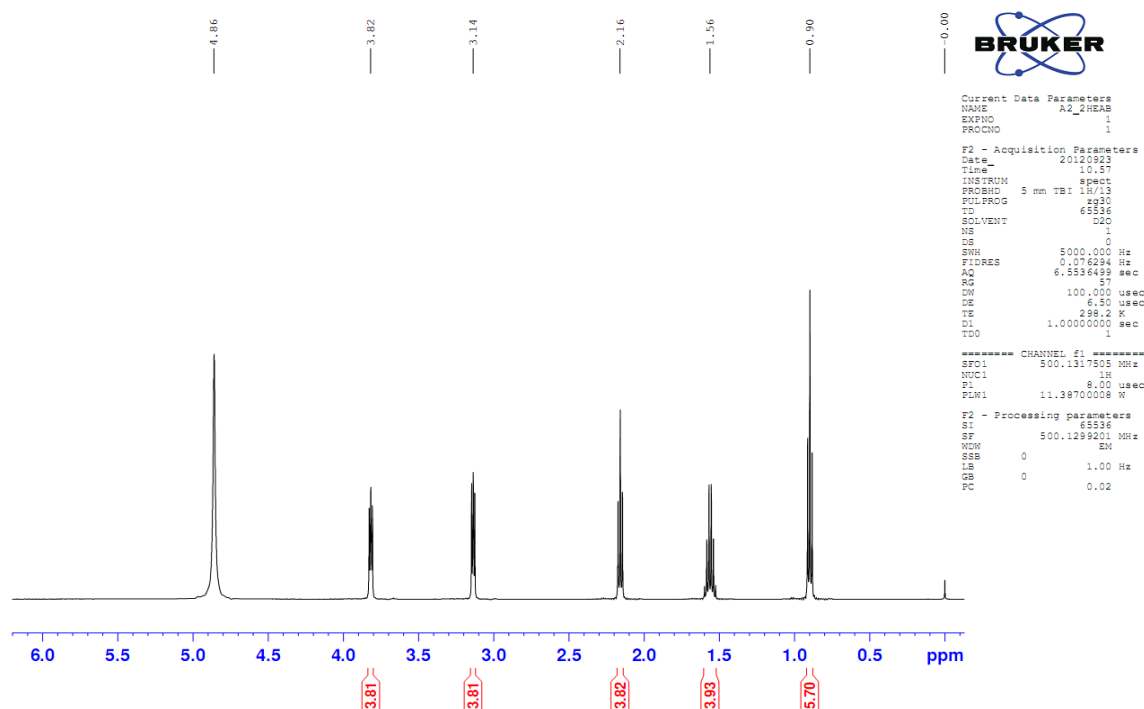
**Fig 1:** Scheme of glycerol esterification by acid catalyst to obtain triacetin



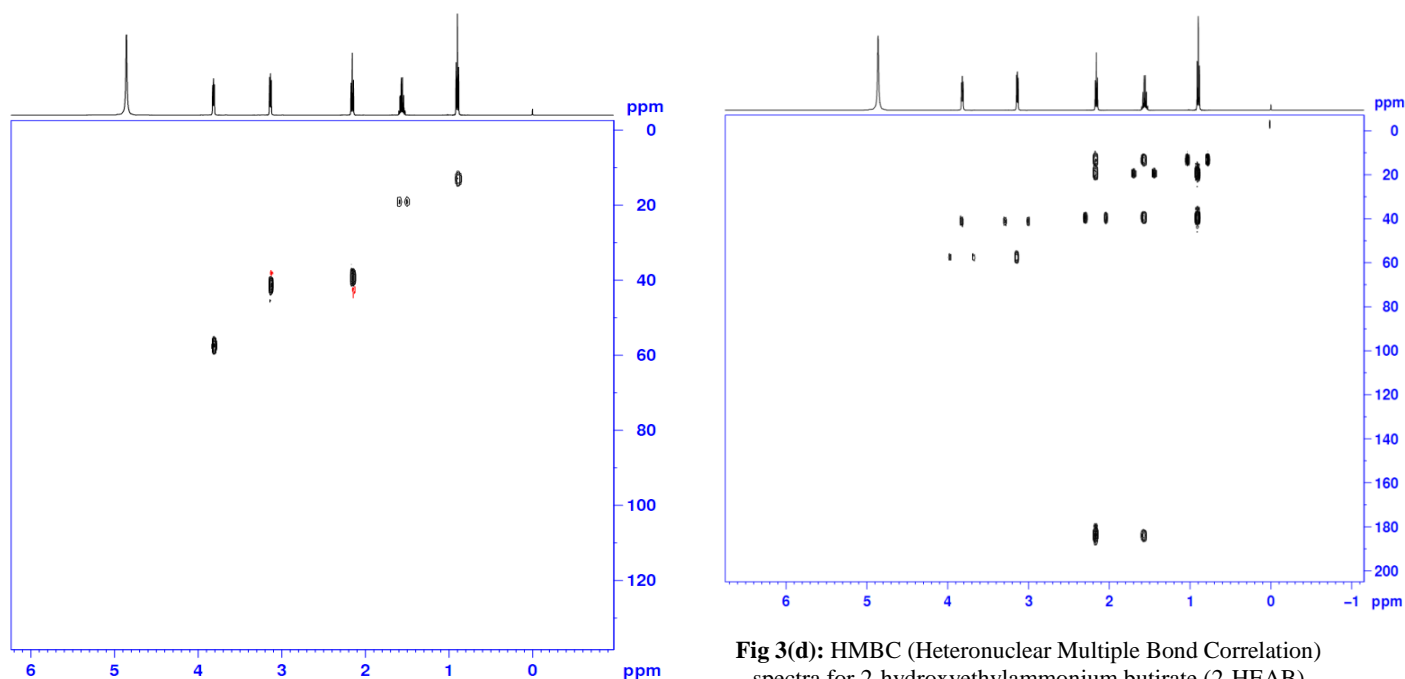
**Fig 2:** Different protic ionic liquids used in this work as catalysts for triacetin synthesis by esterification of glycerol



**Fig 3(a):** FTIR spectra for 2-hydroxydiethylammonium formate (2-HDEAF)

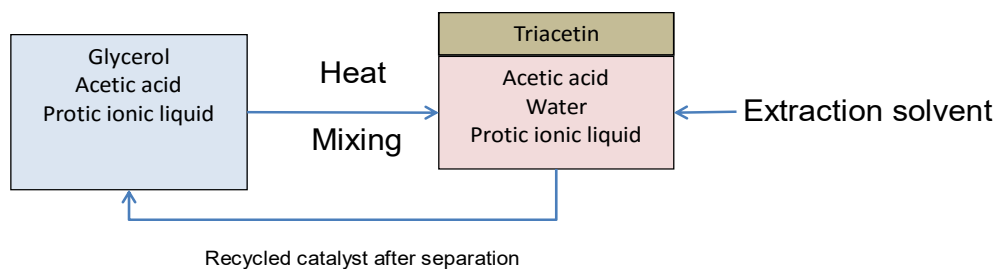


**Fig 3(b):** NMR- $H^1$  spectra for 2-hydroxyethylammonium butyrate (2-HEAB)



**Fig 3(c):** HSQC (Heteronuclear Single Quantum Coherence) spectra for 2-hydroxyethylammonium butyrate (2-HEAB)

**Fig 3(d):** HMBC (Heteronuclear Multiple Bond Correlation) spectra for 2-hydroxyethylammonium butyrate (2-HEAB)



Homogeneous system

Heterogeneous system

**Fig 4:** General process for laboratory triacetin synthesis by homogeneous catalysed process using protic ionic liquid

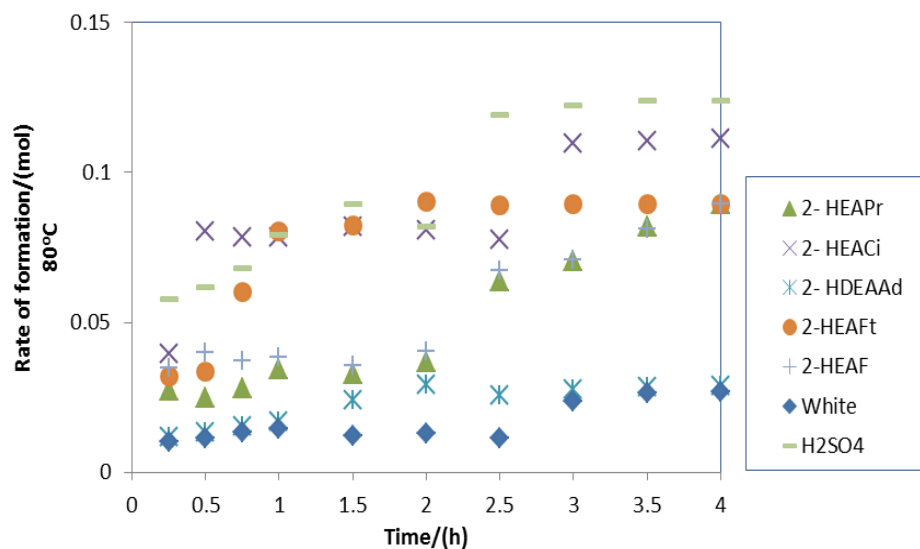


Fig 5: Triacetin production with different catalysts at 80 °C

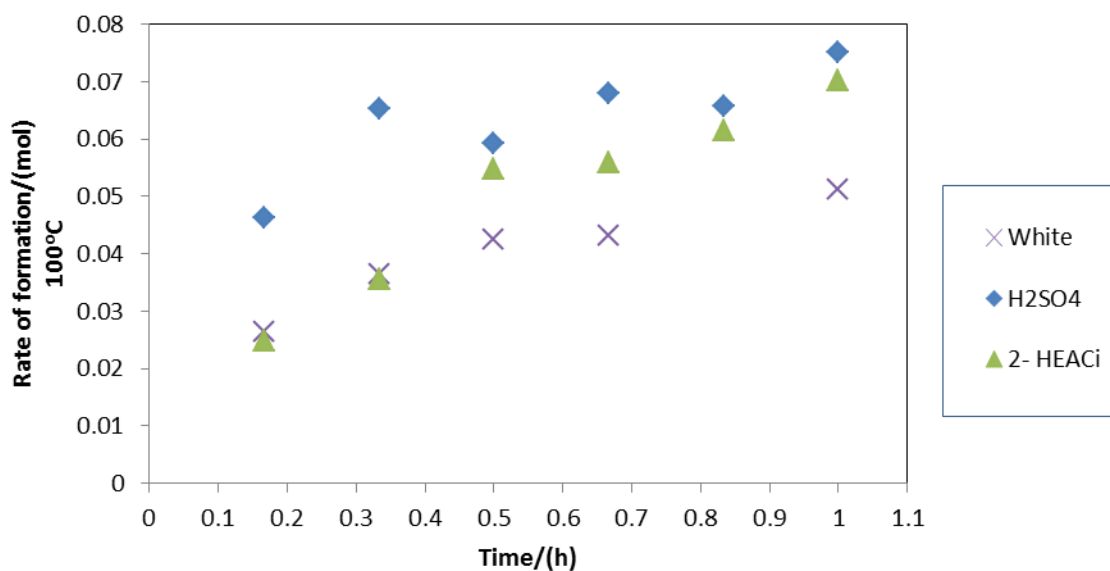


Fig 6: Production of triacetin using 2-HEACi as catalyst at 100 °C

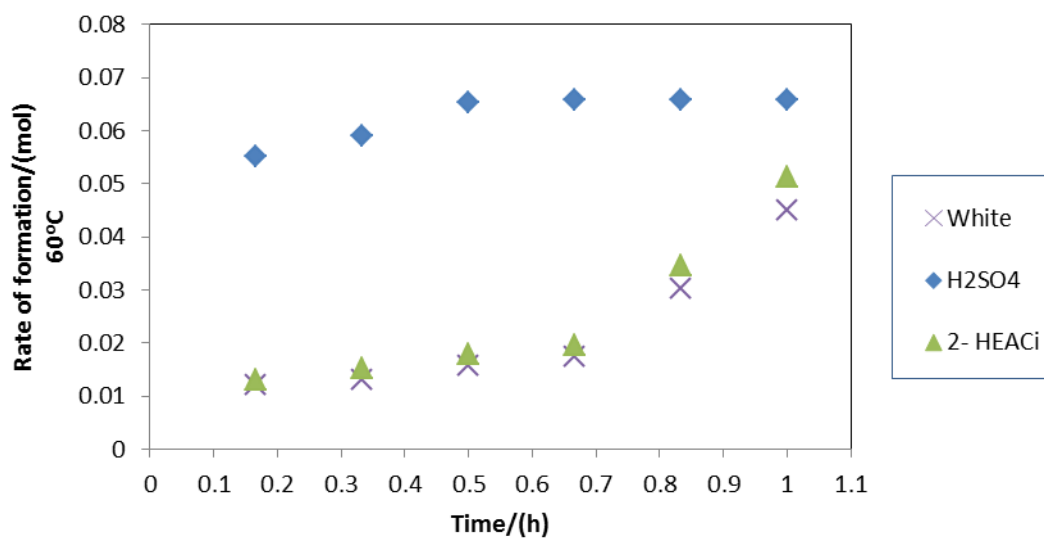


Fig 7: Production of triacetin using 2-HEACi as catalyst at 60 °C

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