

# Functionalized dicationic ionic liquids: Green and efficient alternatives for catalysts in phthalate plasticizers preparation

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MS received 9 January 2016; revised 22 April 2016; accepted 14 June 2016

**Abstract.** Two highly acidic, imidazolium-based, functionalized dicationic ionic liquids (FDCILs) were synthesized and characterized by FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The synthesized FDCILs were used as efficient and green catalysts in the synthesis of phthalate plasticizers through esterification of phthalic anhydride (PhA) with ethanol, n-propanol and n-butanol. Among these two FDCILs, (dimethyl-4-sulfobutyl-ammonium) 1,2-ethan-1-methyl-imidazolium-sulfonic acid hydrogen sulfate performed better. The catalytic activity of FDCIL is related to the density of acidic groups on it and the length of the carbon chain in the cationic part. The influences of the reaction temperature, catalyst dosage, and molar ratio of phthalic anhydride to alcohol on the esterification reaction were investigated. The reusability of the catalyst in these reactions was studied too. The diester phthalates were obtained up to 98.8% yield. The products can be separated easily by decantation from the reaction mixture.

**Keywords.** Acidic dicationic ionic liquids; highly acidic catalysts; esterification; phthalate plasticizers.

## 1. Introduction

Phthalate plasticizers are the main plasticizers used as softening agents in various industrial applications.<sup>1</sup> These compounds are mainly used as plasticizers for cellulosic resins and some vinyl ester resins, PVC and nitrocellulose lacquers.<sup>2</sup> Diethyl, dibutyl and dioctyl phthalates are the most common plasticizers used in the formulation of double-based solid propellants.<sup>3,4</sup> Phthalates are manufactured by esterification reaction between corresponding acids/ anhydrides and alcohols in the presence of acidic catalysts.<sup>5</sup> Various catalysts have been reported for this reaction. Sulfuric acid has been mainly used in traditional and industrial esterification of phthalates.<sup>2</sup> Many heterogeneous catalysts such as heteropoly acids,<sup>6</sup> zirconium titanium phosphate,<sup>7</sup> and zeolites<sup>8</sup> are used as catalysts for esterification of phthalic anhydride. However, the use of sulfuric acid causes some problems such as formation of by-products, corrosion, loss of catalyst, toxicity, tedious work-up and environmental problems.<sup>9</sup> Heterogeneous catalysts can give some benefits; for example, easy work-up, catalyst reusability and avoidance of corrosion.<sup>10</sup> Despite of the benefits of these catalysts,

some suffer from disadvantages such as limited accessibility of the matrix-bound catalyst, rapid deactivation and high molecular weight/active-site ratios.<sup>9</sup> Therefore, development of an efficient, highly selective, environmentally benign and easy method using novel catalysts for preparation of phthalate esters will be interesting.

Among the variety of catalysts, ionic liquids (ILs) have the advantages of liquid and solid phase together.<sup>11</sup> Task-specific ionic liquids (TSILs) have received great attention over the past few decades performing as catalyst and solvent in organic chemistry due to their unique properties such as environmentally friendly nature, non-volatility, high polarity, and good thermal and chemical stabilities.<sup>12–16</sup> TSIL can be defined as association of cation and anion, to which a functional group is covalently bonded that confers the assembly a specific task. In general, TSILs have been used as substitutes for conventional homogenous and heterogeneous acid catalysts.<sup>17</sup>

A new approach using alkyl sulfonated functionalized ILs has drawn more efforts due to their acidic properties and water solubility. Recently some imidazolium and pyridinium based acidic ILs were used as catalyst to prepare phthalate plasticizers.<sup>9,18</sup> Meanwhile, multifunctional ILs especially dicationic ILs (DCILs) are attracting more attention as alternative reaction media in green chemistry than conventional mono-cationic ILs.<sup>19,20</sup> The DCIL contains two head groups and aliphatic chain

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linked by either a rigid or flexible spacer.<sup>21</sup> Functionalization ability of DCILs were explored to design their structures with respect to cations, anions and length of their linker chains in between cations.<sup>22</sup>

A few DCILs were used as catalysts in the esterification reaction. Basic binuclear functional ILs were synthesized and used as catalyst in the preparation of biodiesel through transesterification from cottonseed oil,<sup>23</sup> and esterification of organic acids with ethanol was carried out in the presence of a dicationic ionic liquid.<sup>24</sup> A group of imidazolium-based DCILs have been used for esterification of alcohols by carboxylic acids.<sup>25</sup> In these reactions, researchers have focused on the synthesis and application of geminal DCILs (same cationic counterparts). Recently, we synthesized dual dicyanamide-based ionic liquids consisting of coupled ammonium-imidazolium cationic structures and also unsymmetrical dicationic azide functionalized ionic liquids and studied their physical and thermal properties.<sup>26,27</sup> Continuing our research activities in the field of synthesis, characterization and application of ionic liquids,<sup>26-32</sup> we decided to synthesize the geminal and unsymmetrical (different cationic counterparts) DCILs with traditional counter anion,  $\text{HSO}_4^-$ . The catalytic activities of the synthesized FDCILs were tested for esterification of phthalic anhydride with ethanol, n-propanol and n-butanol (Scheme 1). The structures of FDCILs used in this study are shown in Figure 1.

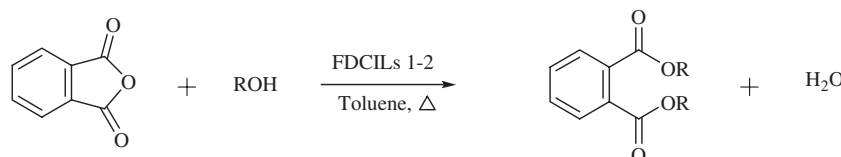
## 2. Experimental

### 2.1 Materials and apparatus

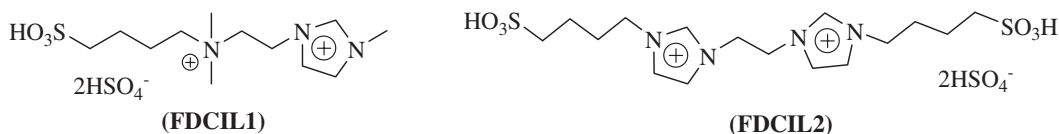
All reagents and solvents were purchased from Merck and Fluka chemical companies. The newly synthesized FDCILs were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR on a Bruker DRX - 300 spectrometer. Chemical shifts are reported relative to TMS as an internal standard. The solvents used were DMSO and  $\text{D}_2\text{O}$ . FT-IR spectra were obtained on a Nicolet 800 instrument. Elemental analyses were obtained using a Heraeus CHN analyzer. Melting points were determined using melting point IA 8103 apparatus. Quantitative product analysis was conducted by gas chromatography on Hewlett Packard HP-5890 instrument equipped with HP-1 column (30 m long, 0.5 mm diameter), and flame ionization detector (FDI), using  $\text{N}_2$  as carrier gas at a flow rate of  $2 \text{ mL} \cdot \text{min}^{-1}$ .

### 2.2 Preparation of functionalized dicationic ionic liquids (FDCILs)

**2.2a Synthesis of 4-((2-Hydroxyethyl) dimethyl azanyl) butan-1-sulfate (I):** 2-(Dimethyl amino)-ethanol (10.1 mL, 100 mmol) was dissolved in toluene under vigorous stirring. 10.2 mL (100 mmol) of 1,4-butane sulfonate was poured slowly in an ice bath. After the pouring was finished, the



**Scheme 1.** Esterification of phthalic anhydride with alcohols using **FDCIL1** and **2**.



**FDCIL1:** [(Dimethyl-4-sulfobutyl-ammonium)-1,2-ethane-1H-imidazolium sulfonic acid] hydrogen sulfate.

**FDCIL2:** 3,3'-(1,2-Ethanediylium)bis[1-(4-sulfobutyl)-1H-imidazolium sulfonic acid] hydrogen sulfate.

**Figure 1.** Structures of FDCILs used in this study. **FDCIL1:** [(Dimethyl-4-sulfobutyl-ammonium)-1,2-ethane-1H-imidazolium sulfonic acid] hydrogen sulfate. **FDCIL2:** 3,3'-(1,2-Ethanediylium)bis[1-(4-sulfobutyl)-1H-imidazolium sulfonic acid] hydrogen sulfate.

mixture was slowly heated up to 111°C and refluxed for 12 h. Then, the reaction mixture was filtered to get the white precipitate. The precipitate was washed thrice with diethyl ether and dried at 80°C for 5 h, giving **(1)** as a white powder (M.p. 74°C, yield 93.8%).

**2.2b Synthesis of 4-((2-chloroethyl)dimethylazanyl)butan-1-sulfate (2):** 16.1 g (70 mmol) of **(1)** was dissolved in chloroform under vigorous stirring and thionyl chloride (5 mL, 70 mmol) was poured slowly to the reaction mixture in an ice bath. The mixture was slowly heated up to 62°C and refluxed for 12 h. Then it was washed with chloroform thrice and heated at 50°C for 2 h, giving **(2)** as a light yellow viscous liquid (yield 94.7%).

**2.2c Synthesis of (dimethyl-4-sulfobutyl-ammonium)1,2-ethan-1-methyl-imidazolium sulfate (3):** 3.0 g (12 mmol) of **(2)** and 1-methyl imidazole (1.0 g, 12 mmol) were dissolved in acetonitrile under vigorous stirring and refluxed for 12 h. Then, the reaction mixture was filtered to get the white precipitate. The precipitate was washed thrice with diethyl ether and dried at 80°C for 5 h, giving **(3)** as a white powder (M.p. 109°C, yield 94.5%).

**2.2d Synthesis of (dimethyl-4-sulfobutyl-ammonium)1,2-ethan-1-methyl-imidazolium-sulfonic acid hydrogen sulfate (FDCIL1):** 2.56 g (10 mmol) of **(3)** was dissolved in methanol and sulfuric acid 98% (10.6 mL, 20 mmol) was poured slowly. The mixture was heated up to 60°C and stirred for 12 h. Then, the reaction mixture was washed thrice with diethyl ether and heated at 70°C for 1 h, giving **FDCIL1**. Compound **FDCIL1**: Light yellow viscous liquid; yield 96.3%; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C, TMS, δ ppm) 1.07-1.13 (m, 2H, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.24-1.26 (m, 2H, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.29 (t, *J* = 7.48 Hz, 2H, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.47 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.66 (s, 3H, Im-CH<sub>3</sub>), 2.70-2.76 (m, 2H, HSO<sub>3</sub>CH<sub>2</sub>), 3.04 (t, *J* = 6.0 Hz, 2H, N(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Im), 3.30 (t, *J* = 6.0 Hz, 2H, N(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Im), 6.75 (s, 1H, H<sub>Im</sub>), 6.76 (s, 1H, H<sub>Im</sub>), 7.94 (s, 1H, H<sub>Im</sub>). <sup>13</sup>CNMR (75 MHz, D<sub>2</sub>O, 25°C, TMS, δ ppm) 20.10, 20.21, 34.69, 49.24, 50.40, 54.55, 63.61, 64.12, 118.72, 118.76, 122.33; FT-IR (KBr) ν/cm<sup>-1</sup>: 2953, 1636, 1474, 1230, 1166, 1150, 881, 591; Anal. Calcd. for C<sub>12</sub>H<sub>27</sub>O<sub>11</sub>N<sub>3</sub>S<sub>3</sub> Calcd. C, 29.69; H, 5.56; N, 8.65% Found C, 29.64; H, 5.63; N, 8.81%.

**2.2e Synthesis of 1, 1'-(1, 2-ethanediyl) bis-1H-imidazolium (4):** Imidazole (1.36 g, 20 mmol), sodium hydroxide (0.4 g, 10 mmol) and dimethyl sulfoxide 20 mL

were mixed and stirred magnetically at 60°C until imidazole was dissolved. Subsequently, 0.8 mL (10 mmol) of 1,2-dibromoethane was added dropwise into the mixture at 60°C and stirred continuously for 2 h. After that, the reaction mixture was dumped into cold water, and settled for 3 h to form **(4)** as a white solid product (M.p. 84°C, yield 94.8%).

**2.2f Synthesis of 3, 3'-(1, 2-ethanediyl) bis [1-(4-sulfobutyl)-1H-imidazoliumdisulfate (5):** 2.64 g (0.02 mol) of **(6)** was mixed with 4.09 mL (0.04 mol) 1, 4-butane sulfonate under stirring at room temperature for 72 h. After solidification of the mass, the product was washed three times with diethyl ether and dried at 120°C for 2 h, giving **(5)** as a white powder (M.p. 124°C, yield 96.3%).

**2.2g Synthesis of 3,3'-(1,2-ethanediyl)bis[1-(4-sulfobutyl)-1H-imidazolium hydrogen sulfate (FDCIL2):** 2 g (5 mmol) of **(5)** was dissolved in methanol and 0.5 mL (10 mmol) of sulfuric acid 98% was added slowly. The mixture was heated up to 60°C and stirred for 6 h. The reaction mixture was washed with diethyl ether and toluene three times and heated at 120°C for 1 h, giving **FDCIL2**. Compound **FDCIL2**: Light yellow viscous liquid; yield 95.3%; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C, TMS, δ ppm) 1.39-1.456 (m, 4H, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.63-1.95 (m, 4H, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.11 (t, *J* = 5.8 Hz, 4H, HSO<sub>3</sub>CH<sub>2</sub>), 3.33 (s, 4H, Im(CH<sub>2</sub>)<sub>2</sub>Im), 4.33 (t, 4H, *J* = 5.4 Hz, HSO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 7.68 (d, *J* = 6.9 Hz, 4H, H<sub>Im</sub>), 8.36 (s, 2H, H<sub>Im</sub>); <sup>13</sup>CNMR (75 MHz, D<sub>2</sub>O, 25°C, TMS, δ ppm) 23.69, 24.08, 49.06, 49.87, 54.63, 121.07, 121.17, 123.69; FT-IR (KBr) ν/cm<sup>-1</sup>: 3422, 3140, 2939, 1638, 1448, 1350, 1302, 1188, 1066, 784, 603; Anal. Calcd. for C<sub>16</sub>H<sub>30</sub>O<sub>14</sub>N<sub>4</sub>S<sub>4</sub> Calcd. C, 30.48; H, 4.76; N, 8.89% Found C, 30.36; H, 4.80; N, 8.92%.

### 2.3 General procedure for the synthesis of phthalate plasticizers with **FDCIL1,2**

Weighed amounts of phthalic anhydride, alcohol (ethanol, n-propanol or n-butanol), ionic liquid and toluene (as solvent) were mixed in a flask equipped with a reflux condenser, dean-stark and magnetic stirring apparatus. The reaction mixture was refluxed until completion of the reaction. Completion of the reaction was monitored by TLC (EtOAc/n-hexane 2:5). After completion of the reaction, the mixture was washed with ethyl acetate to separate the catalyst. Then, solvents were removed under reduced pressure at 90°C and the residue

was purified by column chromatography to afford pure products.

### 3. Results and discussion

In this study, highly acidic FDCILs were synthesized with high yields using multistep synthetic route as shown in Scheme 2. The structure of these ionic liquids were elucidated by NMR and FT-IR spectroscopy as well as elemental analysis. The acidity of FDCILs was determined in ethanol (Table 1). Two kinds of FDCILs of this study showed strong acidity. This is the main reason why they could efficiently promote the esterification reaction.

In order to optimize the esterification reaction conditions, effect of some parameters such as reaction temperature, catalyst dosage and molar ratio of phthalic anhydride to alcohol on the synthesis of phthalate diesters were studied. After that, phthalate diesters were synthesized using phthalic anhydride and various

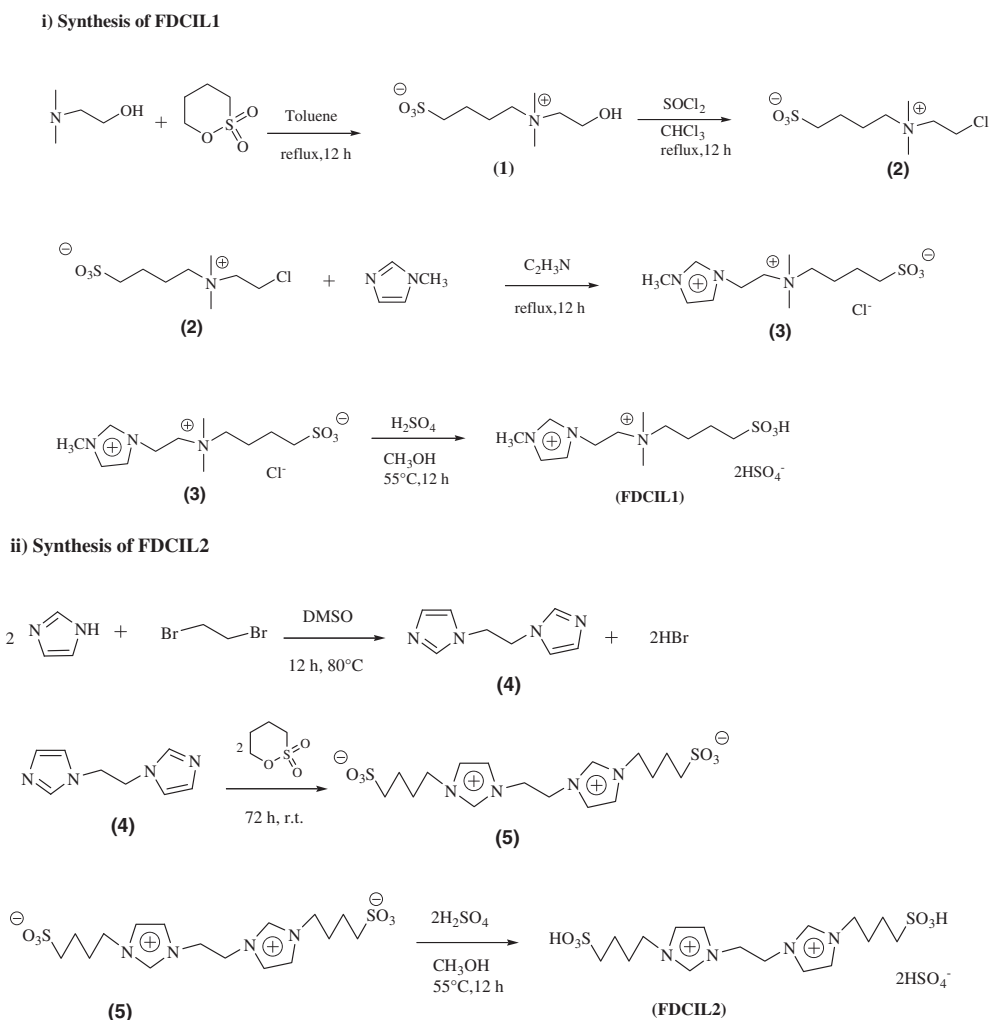
**Table 1.** The pH value of FDCILs in ethanol at concentration of 1 mmol.L<sup>-1</sup> at 298 K.

Ionic Liquid	FDCIL1	FDCIL2
pH value	1.09	1.22

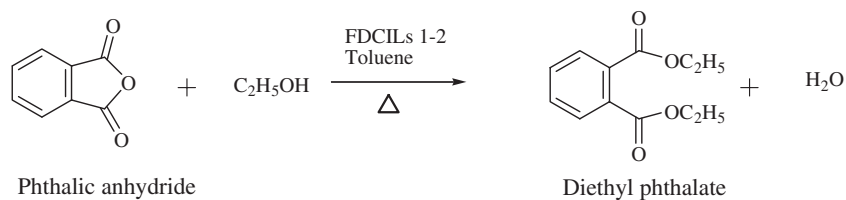
alcohols with FDCILs1-2 as catalyst under optimized conditions.

#### 3.1 Comparison the efficiency of the newly synthesized **FDCIL1-2** in the esterification reaction of phthalic anhydride with ethanol

Evaluation of the efficiency of synthesized FDCILs in the esterification of phthalic anhydride with ethanol (Scheme 3) revealed that **FDCIL1** is an effective catalyst for the esterification reaction. Table 2, entries 1-2 give the yield values of the esterification of phthalic anhydride with ethanol in the presence of **FDCIL1-2**. These results suggested that the performance of



**Scheme 2.** Multistep synthetic route of **FDCILs 1-2**.



**Scheme 3.** Esterification of phthalic anhydride with ethanol using **FDCILs 1-2**.

**Table 2.** Results of esterification of phthalic anhydride with different alcohols in the presence of FDCILs.

Entry	Catalyst	Alcohol	PhA: alcohol: <b>FDCIL</b> molar ratio	T (°C)	Time (h)	<sup>a</sup> Yield (%)
1	<b>FDCIL1</b>		1:2:0.2	110	6.5	57.3
2	<b>FDCIL2</b>		1:2:0.2	110	8	50.5
3	<b>FDCIL1</b>		1:2:0.2	r.t.	10	0
4	<b>FDCIL1</b>		1:2:0.2	40	10	0
5	<b>FDCIL1</b>		1:2:0.2	55	10	3.5
6	<b>FDCIL1</b>		1:2:0.2	70	10	12.7
7	<b>FDCIL1</b>		1:2:0.2	80	10	17.2
8	<b>FDCIL1</b>		1:2:0.2	90	8	28.3
9	<b>FDCIL1</b>		1:2:0.2	100	6.5	37.5
10	<b>FDCIL1</b>		1:2:0.2	115	4	72.3
11	<b>FDCIL1</b>		1:2:0.2	120	4	77.4
12	<b>FDCIL1</b>		1:2:0.2	130	4	77.4
13	<b>FDCIL1</b>		1:2.2:0.2	120	4	80.6
14	<b>FDCIL1</b>		1:2.5:0.2	120	3	96.4
15	<b>FDCIL1</b>		1:3:0.2	120	3	96.4
16	<b>FDCIL1</b>		1:2.5:0.05	120	3	41.3
17	<b>FDCIL1</b>		1:2.5:0.1	120	3	96.4
17	<b>FDCIL1</b>		1:2.5:0.4	120	3	96.4
18	<b>FDCIL1</b>		1:2.5:0.1	120	3	96.4
19	<b>FDCIL1</b>		1:2.5:0.1	120	3	98.1
20	<b>FDCIL1</b>		1:2.5:0.1	120	1.5	98.8
21	<b>FDCIL1</b>		1:2.5:0.1	120	2	- <sup>b</sup>
22	<b>FDCIL1</b>		1:2.5:0.1	120	2	- <sup>b</sup>
23	<b>FDCIL2</b>		1:2.5:0.1	120	3	91.6
24	<b>FDCIL2</b>		1:2.5:0.1	120	3	92.7
25	<b>FDCIL2</b>		1:2.5:0.1	120	1.5	95.1

<sup>a</sup>Yields estimated by GC.

<sup>b</sup>Polymer product.

FDCILs is dependent upon the character of the cation side chain (low lipophilic character of the **FDCIL1** cation). Moreover, the pH values of these catalysts showed that the acidity of **FDCIL1** is higher than **FDCIL2** (Table 1). So, as expected, **FDCIL1** performs better.

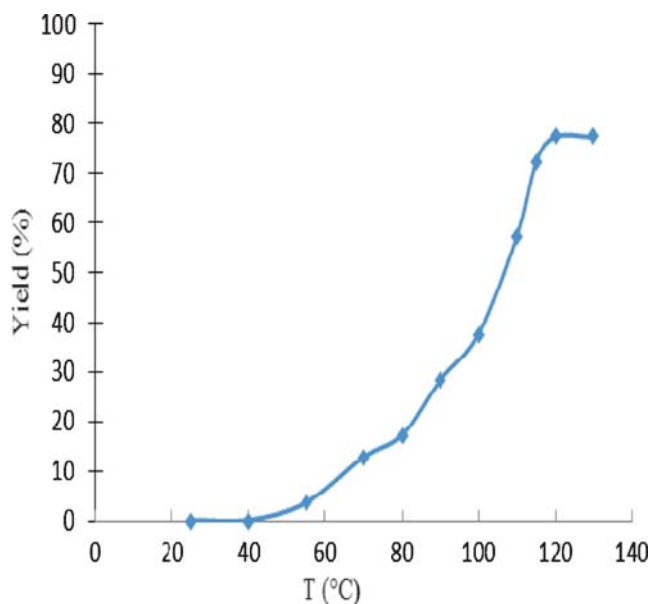
For optimization purpose, various reaction conditions for the synthesis of phthalate diesters were tested using **FDCIL1** as catalyst (Table 2, entries 1, 3–18).

### 3.2 Effect of the reaction temperature on esterification of phthalic anhydride

Effect of the reaction temperature on esterification of phthalic anhydride with ethanol was studied. The results of this study are shown in Table 2, entries 1, 3–12. It is clear from this Table that when the reaction was carried out at room temperature, phthalic anhydride was not converted into diethyl phthalate, even after 10 h. Esterification yield increased with a rise in temperature, reaching a maximum of 77.4% at 120°C (Table 2, entry 11). As can be seen from Table 2, entry 12, increasing the temperature above 120°C did not lead to any improvement. So, the optimum reaction temperature is 120°C (Figure 2).

### 3.3 Effect of the molar ratio of reactants on esterification of phthalic anhydride

Generally an excess amount of ethanol is necessary for esterification of phthalic anhydride; because, it can



**Figure 2.** Effect of the reaction temperature on the esterification of phthalic anhydride with ethanol. PA: Ethanol: **FDCIL1** molar ratios is 1: 2: 0.2 and the solvent is toluene.

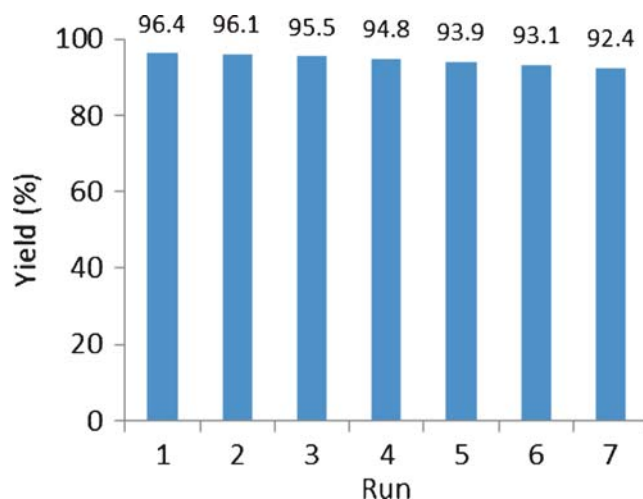
increase the rate of esterification. In addition, the optimized reaction temperature is higher than the boiling point of ethanol (78°C), therefore some of it vaporized during the reaction. The influence of reactants molar ratio was studied at 120°C, the reaction conditions and yields obtained are shown in Table 2, entries 11, 13–15. The results showed that increasing the molar ratio of phthalic anhydride to ethanol, increases the reaction yield. The highest achieved yield was 96.4% with phthalic anhydride to ethanol molar ratio of 1:2.5 (Table 2, entry 14). Further increase of this molar ratio did not increase the product yield probably because phthalic anhydride and **FDCIL1** became too diluted with excess ethanol.

### 3.4 Effect of catalyst concentration on esterification of phthalic anhydride

To determine the optimum concentration of the catalyst (**FDCIL1**) in the esterification reaction of phthalic anhydride with ethanol, the reaction was done at 120°C with phthalic anhydride: ethanol molar ratio of 1:2.5 and different amounts of **FDCIL1**. As shown in Table 2, entries 14, 16–18, by increasing the mole ratio of phthalic anhydride: **FDCIL1** from 0.05 to 0.1, the yield of diethyl phthalate increased. But further increase in amount of the catalyst did not improve the reaction yield.

### 3.5 Reusability of **FDCIL1** in esterification of phthalic anhydride

In order to examine the reusability of **FDCIL1** after completion of the reaction, ethyl acetate (2 × 5 mL) was added. The reaction mixture was divided into two



**Figure 3.** Reusability of **FDCIL1** in the esterification reaction of phthalic anhydride with ethanol.

layers. The upper phase contained the products and the lower phase the **FDCIL1**. After further extractions ( $3 \times 5$  mL ethyl acetate) and phase separation, the **FDCIL1** was dried under vacuum for 5 h at  $70^\circ\text{C}$ . The results of the reusability of **FDCIL1** are shown in Figure 3, indicating no major decrease in the product yield even after 7 runs.

### 3.6 Esterification of phthalic anhydride with various alcohols using **FDCIL1-2**

Esterification of phthalic anhydride were carried out with ethanol, n-propanol and n-butanol in the presence of **FDCIL1-2**, and the diester product was isolated conveniently in high yield. Table 2 (entries 18–20, 23–25) shows the results of these reactions. As we explained above, **FDCIL1** showed higher efficiency in the synthesis of phthalate esters (Table 2, entries 18–20). It is noteworthy to mention that the immiscibility of the phthalate diester with the FDCIL facilitated the reaction equilibrium shifting to the product side. The same result was observed in another report.<sup>33</sup>

The esterification reaction that began as a homogeneous process, ended as biphasic mixture which facilitated the separation of phthalate esters from the reaction mixture.

We also tested the esterification reaction of phthalic anhydride with diols such as 1,4-butanediol and 1,5-pentanediol (Table 2, entries 21, 22). As we expected and as reported by other researchers,<sup>34,35</sup> related polyesters were produced.

### 3.7 Comparison the efficiency of FDCILs with other reported catalysts in the esterification of phthalic anhydride

Comparison of the efficiency of FDCILs with other catalytic systems in the esterification reaction of phthalic anhydride with n-butanol was studied too (Table 3). According to Table 3, the catalysts of this study, especially **FDCIL1**, are more effective than other reported catalysts for the esterification reaction.

### 3.8 Esterification of maleic and succinic anhydrides with ethanol in the presence of **FDCIL1**

To investigate the generality and scope of this method, the optimized reaction conditions was extended to other anhydrides such as maleic and succinic anhydrides (Table 4). Considering Table 4, it is clear that **FDCIL1** is an effective catalyst for the esterification reaction of these anhydrides too.

**Table 3.** Comparison of the activity of some catalysts in the esterification reaction of phthalic anhydride with n-butanol.

Entry	Catalyst	PhA: n-Butanol molar ratio	T ( $^\circ\text{C}$ )	Time (h)	PhA conv. (%)	Yield (%)	Ref.
1	Amberlyst-36	1:10	120	–	39	–	36
2	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	1:2	110	3	77	–	6
3	$\text{H}_{14}\text{NaP}_5\text{W}_{29}\text{MoO}_{110}$	1:2	110	3	100	–	6
4	[emim]BF <sub>4</sub>	1:2.5	120–130	7	62	–	9
5	Phosphinite ionic liquids	1:2.1	100	3.5	78	–	37
6	[HSO <sub>3</sub> -pmim] pTSA	1:2.5	120–130	7	98	–	9
7	Sulfamic acid	1:4	113–115	4	81.1	–	38
8	Amorphous zirconium titanium phosphate	1:2.5	115	10	–	62.4	39
9	<i>p</i> -Toluene sulfonic acid	1:2	110	4	35	–	6
10	<b>FDCIL1</b>	1:2.5	120	1.5	100	98.8	This work
11	<b>FDCIL2</b>	1:2.5	120	1.5	100	95.1	This work

**Table 4.** Results of esterification of maleic and succinic anhydrides with ethanol in the presence of **FDCIL1**<sup>a</sup>.

Entry	Anhydride	Time (h)	Conv. (%)	Yield (%)
1	Maleic anhydride	3	100	94.2
2	Succinic anhydride	3.5	100	91.5

<sup>a</sup> Reaction conditions: molar ratios of anhydride/ ethanol/ catalyst = 1: 2.5: 0.1, T =  $120^\circ\text{C}$ .

#### 4. Conclusions

Two novel, highly acidic imidazolium based FDCILs with  $\text{HSO}_4^-$  counter ion were synthesized, characterized and used as green and efficient catalysts for the esterification reaction of phthalic anhydride with various alcohols. The best results were obtained in the presence of **FDCIL1**, due to the higher acidity and low lipophilic character of the cationic side chain of this catalyst. Some valuable advantages of this method are high yields of the products, short reaction times, easy work up, not producing monoester by-product, reusability, non-toxicity, non-corrosive reagents, highly acidity of catalysts and less amounts of alcohol compared to some of the reported methods.

#### Supplementary Informaton (SI)

All additional information pertaining to characterization of the compounds using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are given in the supporting information. Supplementary information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

#### Acknowledgements

We gratefully acknowledge the financial support by Malek-Ashtar University of Technology.

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