Synthesis and characterization of a new hydroxyl functionalized diacidic ionic liquid as catalyst for the preparation of diester plasticizers

Reza Fareghi-Alamdari [a,*], Mehri Nadiri Niri [a], Hassan Hazarkhani [b]

[a] Faculty of Chemistry and Chemical Engineering, Malek-Ashtar University of Technology, Tehran, Iran
[b] Center for Research and Science Education, Organization for Educational Research and Planning, Tehran, Iran

ARTICLE INFO

ABSTRACT

Two new functionalized diacidic ionic liquids (FDAILs) including hydroxyl functionalized diacidic ionic liquid (HFDAIL) and sulfonated diacidic ionic liquid (SFDAIL) were synthesized and characterized by ^{1}HNMR, ^{13}CNMR and FT-IR. The catalytic activities of these FDAILs were examined in esterification reaction of anhydrides with some alcohols to give corresponding dialkyl plasticizers under solvent-free conditions. The results indicate that HFDAIL, as hydroxyl-bearing catalyst, show better catalytic performance. Under the optimum conditions, using HFDAIL, the conversion of phthalic anhydride was high and diester plasticizers were obtained with good to excellent yields in the presence of only 10 mol% of ionic liquid. All the produced diesters could be easily recovered due to their immiscibility with the ionic liquid. Recycling experiments suggests that these ionic liquids can be reused several times without remarkable loss in their catalytic activity.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Plasticizers are almost a class of oligomers which are used in formulation of explosive fuels and leads to improvement in mechanical properties, softening polymeric tissue and flexibility [1–5]. One of the most popular plasticizers in double-based propellants are ester plasticizers such as diethyl, dibutyl and dioctyl phthalates, which are a class of the neutral plasticizers. Ester plasticizers are widely used in non-military industries, e.g. in formulation of PVC and cellulosic resins to manufacture of plastic products such as tube, blood bag and etc. [6–8]. The catalysts used in ester plasticizers synthesis process can be both homogeneous and heterogeneous. Most commonly used catalysts in traditional methods include sulfuric acid and solid acids [9–12]. The sulfuric acid cannot be reused and also has other disadvantages such as equipment corrosion, more byproducts production, tedious workup process and environmental problems. Furthermore, it is very difficult to separate and reuse the mineral acidic catalysts from the reaction mixture [13–16]. Solid acid catalysts [17–19] have capability to overcome many of the above mentioned defects. However, the use of solid acids in this reaction has many disadvantages including easy deactivation and high mass transfer resistance, which limit their efficiency [20]. Along this line, there is a need to expand an environmentally friendly and economic method for synthesis of ester plasticizers using esterification process.

On the other hand, the room temperature ionic liquids due to their tunable physical and chemical properties have attracted the attention of scientists in various fields such as synthesis, catalysis, separation and electrochemistry [21]. In the recent years, researchers are focused on synthesis of functionalized ionic liquids (FILs), in order to obtain better characteristics. Cole et al. [22] reported a pioneering work on sulfonic FIL with strong Brønsted acidity. Many progress have been achieved in this field and divers FIL for special applications have been reported [23,24]. Among them there are many studies on the use of FIL in different esterification processes [25,26]. However, to the best of our knowledge, there is no report on the synthesis of plasticizers using ionic liquids of this study.

In continuation of our works on synthesis and application of ionic liquids in the organic synthesis [27–30], herein, we would like to introduce two novel functionalized diacidic ionic liquids to be used in synthesis of diester plasticizers (Scheme 1). We have chosen ILs with these functional groups as catalysts for esterification reactions because: (1) they are immiscible with a number of organic solvents, (2) they are soluble in a wide range of inorganic and organic materials, (3) high hydrophilicity and acidity of the hydroxyl functionalized catalyst and (4) They can be recycled for several times. The structures of ionic liquids used in this study are shown in Fig. 1.

2. Experimental

2.1. Material and methods

All solvents and chemicals were commercially available and used without further purification and purchased from Merck and Fluka chemical companies. NMR spectra were recorded on a Bruker DRX - 500 spectrometer in DMSO or D_2O and calibrated with tetramethylsilane (TMS) as the internal reference. IR measurements were performed on a Nicolet 800

R = Methyl, Ethyl, n- Propyl, n-Butyl, 2- Ethylhexyl, 2- Methoxyethyl, Allyl
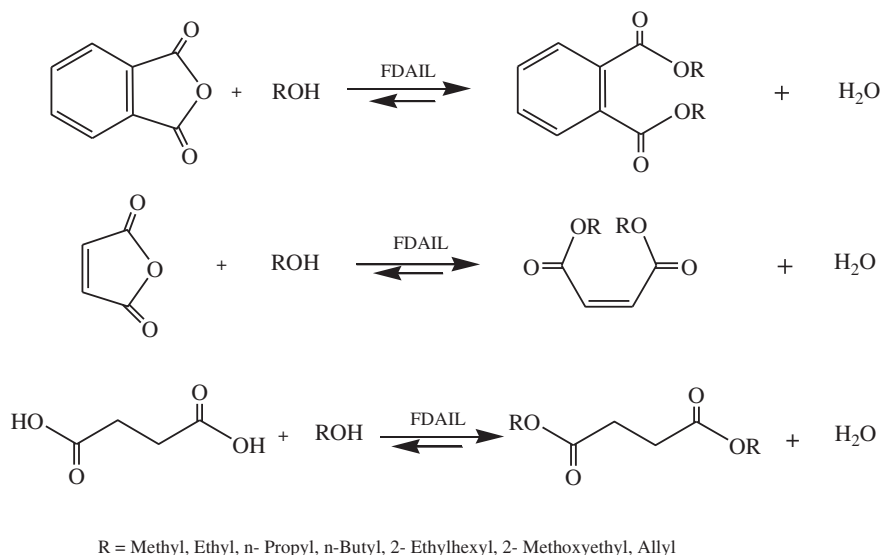
Scheme 1. Esterification of phthalic and maleic anhydrides and succinic acid with alcohols using synthesized FDAILs.

instrument using KBr or liquid film. 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 N_2 as carrier gas at a flow rate of 2 mL·min^{-1}.

2.2. Preparation of hydroxyl and sulfonic acid functionalized diacidic ionic liquids

2.2.1. Preparation of 2,2-bis ((3-methylimidazolidin-1-yl) methyl) propane-1,3-diol bromide salt (IL-Br)

A mixture of 0.52 g 1-methylimidazole (6.25 mmol, 0.5 mL) and 0.65 g 2,2-bis (bromomethyl)-1,3-propanediol (2.5 mmol) was heated at 150 °C for 8 h under magnetic stirring. After cooling to room temperature, the obtained solid was washed three times with acetonitrile and the residue was dried in an oven at 100 °C for 2 h, giving IL-Br as a white powder (yield: 95.25%, melting point = 150 °C). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 3.24 (s, 4H; C$\underline{H}_2$N), 3.84 (s, 6H; C$\underline{H}_3$), 4.31 (s, 4H; C$\underline{H}_2$OH), 4.72 (s, 2H; O$\underline{H}$), 7.42 (dd, J = 10 Hz, J = 5 Hz, 4H; C$\underline{H}$ ═C$\underline{H}$), 8.72 (s, 2H; NC$\underline{H}$N). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 35.94, 45.21, 48.58, 58.48, 123.72, 123.86, 137.38. FT-IR (KBr, ν/cm^{-1}): 620.8, 770.7, 829.8, 1060.5, 1164.9, 1450.8, 1573.1, 1760.4, 1655.9, 2935.4, 3260.7.

2.2.2. Preparation of 3,3′-(2,2-bis ((sulfoxy) methyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) bromide (SFDAIL)

The sulfonic acid functionalized ionic liquid, was prepared by nucleophilic substitution reaction of IL-Br salt with chlorosulphonic acid. To do this, 0.8 g IL-Br salt (2 mmol) was solved in acetonitrile. Then 0.5 mL chlorosulphonic acid (8 mmol) was dropped slowly at room temperature. After the dropping was finished, the mixture was stirred for 4 h at the same temperature. The reaction mixture was filtered to get the yellow precipitate. It was washed with toluene three times and dried under vacuum at 100 °C for 1 h, giving SFDAIL as a yellow solid (yield: 97.5%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 3.33 (s, 4H; C$\underline{H}_2$N), 3.47 (s, 6H; C$\underline{H}_3$), 4.04 (s, 4H; C$\underline{H}_2$OH), 5.33 (s, 2H; SO$_3\underline{H}$), 7.06 (d, J = 5 Hz, 4H; C$\underline{H}$ ═C$\underline{H}$), 8.30 (s, 2H; NC$\underline{H}$N). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 36.19, 43.83, 48.27, 63.89, 123.88, 124.26, 137.79. FT-IR (KBr, ν/cm^{-1}): 587.3, 782.5, 1019.1, 1251.7, 1458.7, 1584.9, 1709.1, 3160.1.

2.2.3. Preparation of 3,3′-(2,2-bis (hydroxymethyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) hydrogen sulfate (HFDAIL)

The hydroxyl functionalized ionic liquid was prepared by anion exchange of IL-Br salt. 0.5 g (1.2 mmol) of IL-Br salt, obtained in the first stage, was dissolved in methanol (30 mL) under stirring. After that the system was slowly heated up to 60 °C in an oil bath. Then 0.13 mL sulfuric acid (2.4 mmol) was dropped and stirred for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The resultant material was washed with dichloromethane (3 × 5 mL) and then dried under vacuum at 100 °C for 2 h to afford HFDAIL as yellow viscous oil liquid at 95% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 3.20 (s, 4H; C$\underline{H}_2$N), 3.81 (s, 6H; C$\underline{H}_3$), 4.27 (s, 4H; C$\underline{H}_2$OH), 4.74 (s, 2H; O$\underline{H}$), 7.39 (dd, J = 10 Hz, J = 5 Hz, 4H; C$\underline{H}$ ═C$\underline{H}$), 8.69 (s,
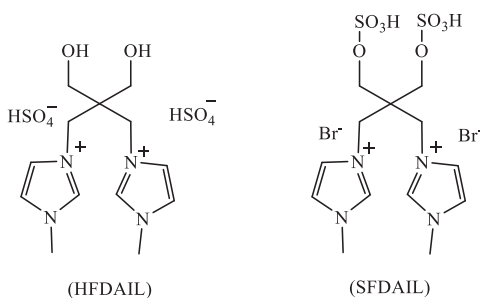
(SFDAIL): 3,3'- (2,2-Bis ((sulfoxy) methyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) bromide
(HFDAIL): 3,3'- (2,2-Bis (hydroxymethyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) hydrogen sulfate

Fig. 1. Structures of FDAILs used in this study.

2H; NCHN). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 36.73, 44.97, 49.63, 59.53, 124.31, 124.58, 138.73. FT-IR (KBr, ν/cm^{-1}): 589.8, 776.2, 879.9, 1053.6, 1222.7, 1458.4, 1572.1, 1641.8, 2509.7, 3095.5, 3328.5.

2.3. Acidity measurement of the catalyst

To measure the acidity of ionic liquids, first of all the NaOH solution was standardized. Dried potassium hydrogen phthalate (0.03 g) was dissolved in 25 mL distilled water and titrated the 0.05 N NaOH solution (the titrant, 50 mL) using 3 drops of phenolphthalein as the indicator. Then the acidity of the synthesized ionic liquids (0.03 g ionic liquid in 50 mL distilled water) were determined by acid-base titration against the standard NaOH solution.

2.4. Synthesis of dibutyl phthalate as a typical procedure for esterification reaction of phthalic anhydride with butanol

The typical procedure for esterification of phthalic anhydride with butanol is as follows: phthalic anhydride (1 mmol, 0.15 g), butanol (5 mmol, 0.46 mL, 0.37 g) and HFDAIL as catalyst (10 mol% to phthalic anhydride, 0.05 g) were charged into a 50 mL round bottom flask with a dean-stark apparatus, reflux condenser and a magnetic stirrer. Then the mixture was stirred at 125 °C for 7 h. The completion of reaction was monitored by TLC using (EtOAC/Hexane 2:8) as eluent. After completion of the reaction as indicated by TLC, the product (dibutyl phthalate) was separated simply by extraction with ethyl acetate (3 × 5 mL) and ethyl acetate was evaporated under vacuum to afford desired product as yellow oil liquid at 95% yield (0/26 g, boiling point = 340 °C). The obtained product dried under vacuum at 70 °C for 5 h. Viscous ionic liquid could be reused after removal of water under vacuum at 80 °C for 5 h without any disposal.

3. Results and discussion

In this study, ionic liquids were prepared by two-step synthetic protocol (Scheme 2). At the first step, IL-Br salt was prepared by nucleophilic substitution reaction of 1-methylimidazole and 2,2-bis(bromomethyl)-1,3-propanediol. Then the resulting ionic liquid (IL-Br) was transformed into the target compounds by using chlorosulphonic acid and concentrated sulphuric acid as sulfonating and anion exchange agents to afford SFDAIL and HFDAIL respectively.

The acidity of the synthesized ionic liquids was determined by acid-base titration against a standard NaOH solution with phenolphthalein as indicator. The results are shown in Table 1. As indicated in this Table, the synthesized ionic liquids especially HFDAIL, showed high acidity. Therefore we tested their catalytic activity in the esterification reactions. In order to optimize the reaction conditions, the esterification of phthalic anhydride with butanol was examined and the influence of reaction temperature, molar ratio of catalyst and molar ratio of phthalic anhydride to alcohol were studied. The results are shown in Figs. 2 and 3 and Table 2.

3.1. Optimizing the reaction conditions of synthesis of phthalate plasticizers by the novel synthesized ionic liquids
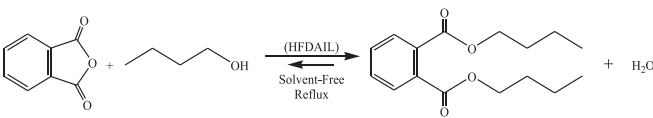
3.1.1. Investigation of the role of catalyst in the esterification reaction of phthalic anhydride with butanol
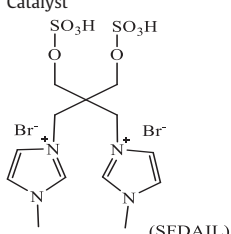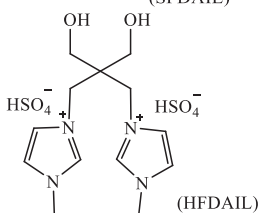
The results of our experiments showed that the catalytic activity of HFDAIL, for esterification of phthalic anhydride with butanol, was remarkably better than SFDAIL (Table 1). This may be attributed to the more acidity of HFDAIL and hydrophilic property of hydroxyl groups attached to the cation. Two hydroxyl groups of this catalyst, can absorb the produced water and thus enhance the reaction rate and product yield.

Therefore, initial studies demonstrated that HFDAIL is more efficient catalytic system for this transformation. In this way, next optimization studies were performed using HFDAIL.
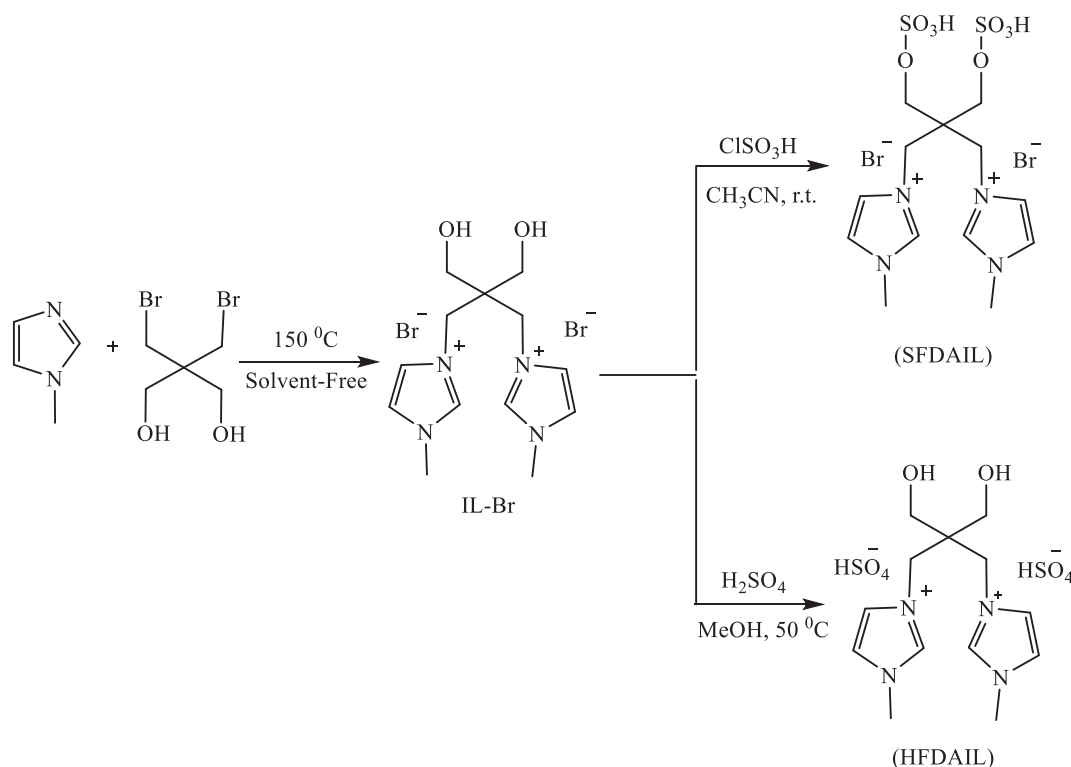
Scheme 2. Two-step synthetic route of hydroxyl and sulfonic acid functionalized diacidic ionic liquids.

Table 1
Comparison the acidity and performance of SFDAIL and HFDAIL in the esterification reaction of phthalic anhydride with butanol[a].

Entry	Catalyst	H$^+$ (mmol/g)[b]	Time (h)	Yield (%)
1	(SFDAIL)	1.0667	29	30
2	(HFDAIL)	2.266	7	60

[a] Reaction conditions: The molar ratio of butanol to phthalic anhydride to catalyst = 5:1:0.1, reaction temperature = 75 °C.
[b] The concentration of ILs is 1 mmol·L^{-1} in water.

3.1.2. Effect of the reaction temperature on esterification reaction

The effect of temperature was studied for the model reaction (phthalic anhydride with butanol) and results are summarized in Fig. 2. Based on these results, no reaction product occurs at 25 °C. The yield of product was enhanced by increasing the reaction temperature and at temperatures less than 100 °C water evaporation rate is low, so the equilibrium reaction returns to the reactants. It seems that by reaching the reaction temperature to the boiling point of water, the yield of product significantly improved.

It was observed that at higher temperatures, alcohol was quickly evaporated and hence rising temperature above 125 °C does not affect the reaction yield. The optimum reaction temperature for this synthesis process is selected as 125 °C.

Fig. 2. Results of esterification of phthalic anhydride with butanol at different temperatures with (HFDAIL) as catalyst. The molar ratio of butanol to phthalic anhydride to catalyst = 5:1:0.1.

3.1.3. Effect of the molar ratio of reactants on esterification reaction

Increasing the amount of butanol promotes the reaction equilibrium toward the product and this is a suitable way to enhance the rate of esterification. As shown in Fig. 3, the reaction yield is enhanced by increasing the molar ratio of butanol to phthalic anhydride. No much improvement in reaction yield was observed for molar ratio of phthalic anhydride to butanol 1:7.5. This observation is attributed to the decrease in the concentration of the catalyst. The optimum molar ratio of phthalic anhydride to butanol is suggested to be 1:5.

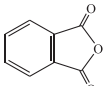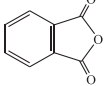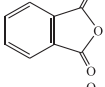### 3.1.4. Effect of amount of catalyst on esterification reaction
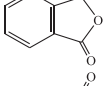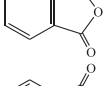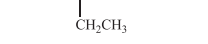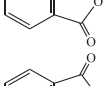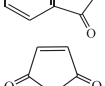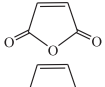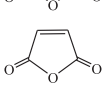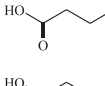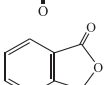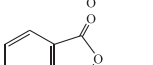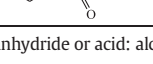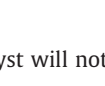
To investigate the optimum amount of HFDAIL, different quantities of the catalyst were tested. The yield of product was improved with increasing the catalyst loading (Table 2, entries 1, 2). The best result was obtained in the presence of 10 mol% of catalyst (Table 2, entry 2). Higher

Fig. 3. Results of esterification of phthalic anhydride with different amounts of butanol in the presence of HFDAIL as catalyst. The molar ratio of HFDAIL to phthalic anhydride = 1:10, reaction temperature = 125 °C.

Table 2
Results of esterification of phthalic anhydride with butanol in the presence of different ratios of HFDAIL to phthalic anhydride[a].

Entry	Catalyst (mol%)	Time (h)	Yield (%)
1	5	10	80
2	10	7	95
3	15	8	55
4	20	7	50

[a] Reaction coditions: The molar ratio of phthalic anhydride to butanol = 1:5 reaction temperature = 125 °C.

Table 3
Results of dialkyl phthalate, maleate and succinate diesters synthesis using different alcohols in presence of HFDAIL as catalyst[a].

Entry	Anhydride or Acid	Alcohol	Time (h)	Yield (%)
1		CH$_3$OH	24	40
2		HO⌒	24	50
3		HO⌒⌒	10	80
4		HO⌒⌒⌒	7	95
5		HO⌒⌒⌒⌒ (CH$_2$CH$_3$)	2	100
6		HO⌒=	6	60
7		HO⌒⌒O⌒	6	60
8		HO⌒⌒	9	95
9		HO⌒⌒⌒	4	98
10		HO⌒⌒⌒⌒ (CH$_2$CH$_3$)	2	100
11		HO⌒=	10	90
12		HO⌒⌒⌒	2	100
13		HO⌒=	3	100
14		HO⌒⌒⌒OH	4	–
15		HO⌒⌒⌒⌒(OH)⌒OH	4	–

[a] Reaction coditions: Reflux, anhydride or acid: alcohol: HFDAIL = 1:5:0.1.

molar ratios of the catalyst will not further improve in the reaction (Table 2, entries 3, 4).

3.2. Esterification reaction of succinic acid, phthalic and maleic anhydrides with various alcohols using HFDAIL

In order to study the generality of the protocol in esterification process for synthesis of diverse diester plasticizers, maleic, phthalic anhydride and succinic acid were reacted with different alcohols and results are summarized in the Table 3. Results show that in esterification reaction of phthalic and maleic anhydrides with alcohols, esterification of long alkyl chain alcohols are very satisfactory (Table 3, entries 1–5 and 8–10). However allyl alcohol and 2-methoxy ethanol did not act same as previous entries.

Succinic acid compared with phthalic and maleic anhydride has fewer steric hinderance in the reaction center (carbonyl carbon) and afforded better results in the presence of 1-butanol and allyl alcohol (Table 3, entries 12, 13). The produced esters were immiscible with HFDAIL and were separated by extraction with EtOAc. It should be mentioned that HFDAIL catalyst was reusable after removal of water.

3.3. Reusability of HFDAIL in esterification of phthalic anhydride

The reusability of HFDAIL was also evaluated in the esterification of phthalic anhydride with butanol (Fig. 4). As shown, HFDAIL could be recycled and reused for 7 runs without significant loss in its catalytic activity.
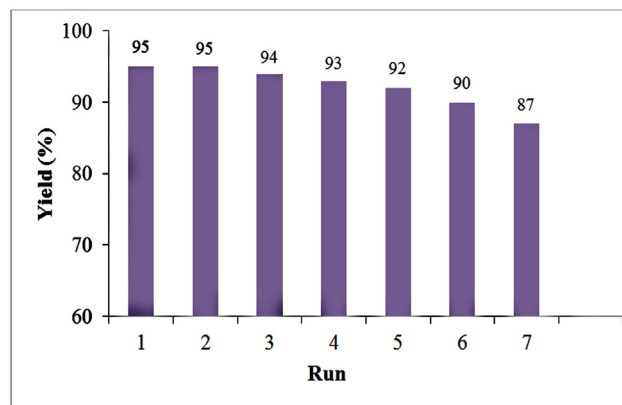
Fig. 4. Reusability of HFDAIL in the esterification reaction of phthalic anhydride with butanol under optimized reaction conditions.

3.4. Comparison of the efficiency of synthesized ionic liquids with reported catalysts in the esterification of phthalic anhydride.

Performance of the catalysts of this work in esterification reaction has been compared with other reported catalysts (Table 4). The data in Table 4 show that the catalytic activity of catalysts in this work, especially HFDAIL, was better than the other catalytic systems even H_2SO_4 (Table 4, entry 8) for the esterification reaction. Because these catalysts have high acidity and moreover, HFDAIL has two hydroxyl groups, which can absorb the produced water by hydrogen bonding (Scheme 4). So, the esterification reaction equilibrium will shift to the right and the product yield will increase.

3.5. Reaction mechanism

The proposed reaction mechanism of phthalic anhydride with alcohol is shown in Scheme 5. As shown, first, the carbonyl group is activated by adsorption of H^+ from the catalyst (HFDAIL). In the next step,

Table 4
Comparison of the efficiency of FDAILs of this work with other reported catalysts in the esterification of phthalic anhydride with butanol.

Entry	Catalyst	The molar ratio of PhA/BuOH	T (°C)	Time (h)	PhA conv. (%)	Yield (%)	Ref.
1		1:2.5	120–135	1.5	98	–	[31]
2	$H_6P_2W_{18}O_{62}$	1:2	110	4	91	–	[32]
3	$H_4Si\,MoO_{40}$	1:2	110	4	49	–	[32]
4		1:2.5	120–135	12	63	–	[31]
5	Phosphinite ionic liquids	1:2.1	100	3.5	78	–	[34]
6	Sulfamic acid	1:2.5	130–180	4	84	–	[33]
7	Amorphous zirconium titanium phosphate	1:2.5	115	10	–	62.4	[35]
8	H_2SO_4	1:5	125	4	93	84	This work
9		1:5	125	4	100	98	This work
10		1:5	125	8	100	70	This work
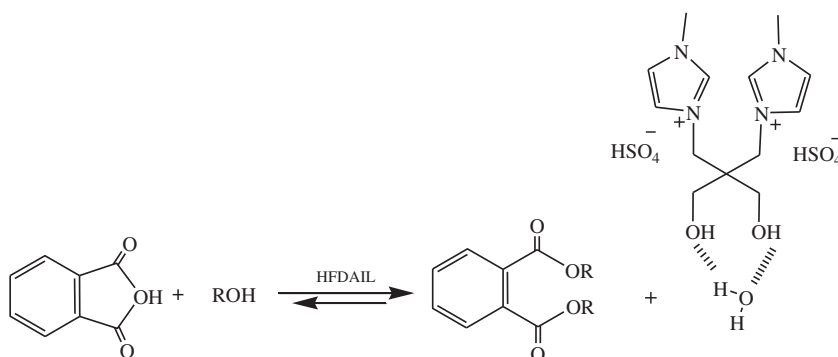
Scheme 3. Adsorption of water by HFDAIL in esterification reaction.
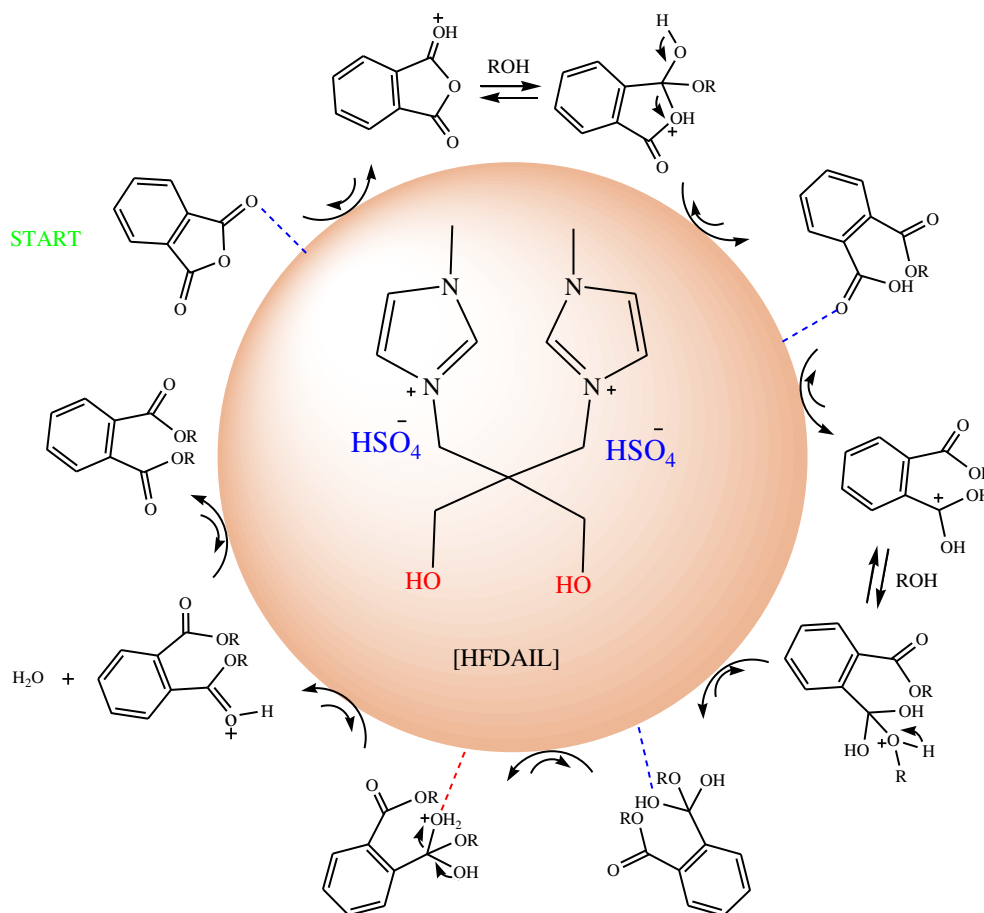
Scheme 4. The proposed reaction mechanism of the synthesis of phthalates from phethalic anhydride in the presence of HFDAIL.

nucleophilic attack of alcohol on the activated carbonyl group is done. Finally, by nucleophilic attack of the second alcohol and releasing H_2O, diester is synthesized. As no monomer molecule is synthesized in this reaction; we can conclude that the first nucleophilic attack step is done very fast. It is noteworthy to mention that, the presence of OH groups in the structure of the catalyst, accelerate the esterification reaction due to the formation of hydrogen bonds and adsorption of the released water molecules.

4. Conclusions

In conclusion, we have synthesized two functionalized diacidic ionic liquids by a simple method in high yields, which served for the synthesis of phthalate, maleate and succinate esters by the reaction of phthalic and maleic anhydrides and succinic acid with alcohols. HFDAIL showed higher catalytic performance in comparison with other reported catalysts, suggesting its high acidity and hydrophilic property. This reaction system has several considerable properties; (1) the products yields are high; (2) the reaction times are short; (3) the catalysts show considerable acidity and therefore activity for these reactions; (4) the product can be separated by easy decantation with high yields and purity; (5) the catalysts can be recovered and reused for several times and (6) the catalysts are eco-friendly and safe.

References

[1] V.Y. Senichev, V.V. Tereshatov, Theories of compatibility, Chem. Acta 45 (2002) 123–134.
[2] J.P. Agrawal, High Energy Materials: Propellants, Explosives and Pyrotechnics, WILEY-VCH Verlag, Weinheim, 2010.
[3] A. Davenas, Solid Rocket Propulsion Technology, Oxford, Pergaman Press, New York, 1993.
[4] J.K. Sears, J.R. Darby, The Technology of Plasticizers, John Wiley & Sons, New York, 2003.
[5] A.T. Camp, H.S. Haiss, P.R. Mosher, Energetic plasticizers and improved gas producing charges, U.S. Pat (1993), 5205983. .
[6] S. Jobling, T. Reynolds, R. White, M. Parker, J. Sumpter, A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic, Environ. Health Perspect. 103 (1995) 582–587.
[7] R.D. Svoboda, Polymeric plasticizers for higher performance flexible PVC applications, J. Vinyl Add. Tech. 13 (1991) 130–133.
[8] P.M. Lorz, F.K. Towae, W. Enke, R. Jackh, N. Bhargava, W. Hillesheim, Phthalic acid and derivatives, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag, Weinheim 2007, pp. 441–465.
[9] M.P. Bernal, J. Coronas, M. Menendez, Coupling of reaction and separation at the microscopic level: esterification processes in a H-ZSM-5 membrane reactor, Chem. Eng. Sci. 57 (2002) 1557–1562.
[10] K.L. Yeung, X. Zhang, W.N. Lau, R. Martin-Aranda, Experiments and modeling of membrane microreactors, Catal. Today 110 (2005) 26–37.
[11] W.N. Lau, K.L. Yeung, R. Martin-Aranda, Knoevenagel condensation reaction between benzaldehyde and ethyl acetoacetate in microreactor and membrane microreactor, Microporous Mesoporous Mater. 115 (2008) 156–163.
[12] R. Tesser, M.D. Serio, L. Casale, L. Sannino, M. Ledda, E. Santacesaria, Acid exchange resins deactivation in the esterification of free fatty acids, Chem. Eng. J. 161 (2010) 212–222.
[13] P. Maki-Arvela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, Comparison of polyvinylbenzene and polyolefin supported sulphonic acid catalysts in the esterification of acetic acid, Appl. Catal., A 184 (1999) 25–32.

[14] A. Heidekum, M.A. Harmer, W.F. Hoelderich, Addition of carboxylic acids to cyclic olefins catalyzed by strong acidic ion-exchange resins, J. Catal. 181 (1999) 217–222.

[15] I.J. Dijs, H.L.F. van Ochten, C.A. van Walree, J.W. Geus, L.W. Jenneskens, Alkyl sulphonic acid surface-functionalised silica as heterogeneous acid catalyst in the solvent-free liquid-phase addition of acetic acid to camphene, J. Mol. Catal. A Chem. 188 (2002) 209–224.

[16] R.A. Sheldon, R.S. Downing, Heteroneneous catalytic transformations for environmentally friendly production, Appl. Catal., A 189 (1999) 163–183.

[17] M. Yasunori, A. Masatomo, Manufacture method of ester, Jpn. Pat. (2001), JP 278840. .

[18] K. Saravanan, B. Tyagi, H.C. Bajaj, Catalytic activity of sulfated zirconia solid acid catalyst for esterification of myristic acid with methanol, Indian J. Chem. B 53 (2014) 799–805.

[19] P. Alpana, C. Uma, Metal (IV) tungstates as solid acid catalysts for the synthesis of phthalate diester-dioctyl phthalate (DOP), Indian J. Chem. B 10 (2003) 44–47.

[20] P. Tundo, P.T. Anastas (Eds.), Green Chemistry: Challenging Perspectives, Oxford University Press, USA, 2000.

[21] M. Vafaeezadeh, H. Alinezhad, Brønsted acidic ionic liquids: green catalysts for essential organic reactions, J. Mol. Liq. 218 (2016) 95–105.

[22] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis, Novel Brønsted acidic ionic liquids and their use as dual solvent-catalysts, J. Am. Chem. Soc. 124 (2002) 5962–5963.

[23] D.M. Li, F. Shi, J.J. Peng, S. Guo, Y.Q. Deng, Application of functional ionic liquids possessing two adjacent acid sites for acetalization of aldehydes, J. Organomet. Chem. 69 (2004) 3582–3585.

[24] Y.Q. Cai, Y.Q. Peng, G.H. Song, Amino-functionalized ionic liquid as an efficient and recyclable catalyst for knoevenagel reactions in water, Catal. Lett. 109 (2006) 61–64.

[25] H.B. Xing, T. Wang, Z.H. Zhou, Y.Y. Dai, Novel Brønsted-acidic ionic liquids for esterifications, Ind. Eng. Chem. Res. 44 (2005) 4147–4150.

[26] J.Z. Gui, X.H. Cong, D. Liu, X.T. Zhang, Z.D. Hu, Z.L. Sun, Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification, Catal. Commun. 5 (2004) 473–477.

[27] R. Fareghi-Alamdari, R. Hatefipour, Synthesis and thermophysical characterization of novel azide functionalized imidazolium based ionic liquids, Thermochim. Acta 617 (2015) 172–178.

[28] R. Fareghi-Alamdari, F. Ghorbani Zamani, M. Shekarriz, Synthesis and thermal characterization of new ammonium-imidazolium dual dicyanamide-based ionic liquids, J. Mol. Liq. 211 (2015) 831–838.

[29] R. Fareghi-Alamdari, F. Ghorbani Zamani, N. Zekri, An efficient and highly selective ortho-tert-butylation of p-cresol with tert-butyl methyl ether catalyzed by sulfonated ionic liquids, J. Serb. Chem. Soc. 79 (2014) 1337–1346.

[30] R. Fareghi-Alamdari, F. Ghorbani Zamani, M. Shekarriz, Synthesis and thermal characterization of mono and dicationic imidazolium pyridinium based ionic liquids, Orient. J. Chem. 31 (2015) 1127–1132.

[31] C. Xie, H. Li, L. Li, S. Yu, F. Liu, Synthesis of plasticizer ester using acid-functionalized ionic liquid as catalyst, J. Hazard. Mater. 151 (2008) 847–850.

[32] M. Arabi, M. Mohammadpour Amini, M. Abedini, A. Nemati, M. Alizadeh, Esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol catalyzed by heteropolyacids, J. Mol. Catal. A Chem. 200 (2003) 105–110.

[33] M.S. Patil, V.D. Gurudasani, G.A. Usmani, Esterification of phthalic anhydride with n-butanol using eco-friendly solid acid catalyst-sulfamic acid, Curr. World. Environ. 5 (2010) 107–109.

[34] H. Valizadeh, E. Khalili, Efficient synthesis of symmetrical phthalate and maleate diesters using phosphonite ionic liquids, J. Iran. Chem. Soc. 9 (2012) 529–534.

[35] R. Thakkar, U. Chudasama, Synthesis of mono and diesters eco-friendly solid acid catalyst-zirconium titanium phosphate, Green Chem. Lett. Rev. 2 (2009) 61–69.