New Brønsted-Acidic Ionic Liquids Based on 8-hydroxyquinoline Cation as Catalysts for the Esterification Reaction of n-hexylic acid

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Abstract—Five new acidic ionic liquids were firstly synthesized from 8-hydroxyquinoline and five kinds of acid such as H_2PO_4, H_2SO_4, CH_3SO_3H, T_SOH, HBF_4 by one-pot method. The structures of the synthesized compounds were characterized by ^1H NMR, IR and MS. Acidities of the ILs was determined by Hammett acidity with the method of UV-Vis spectroscopic measurement. Because of the combinational advantages of homogeneous and heterogeneous catalysis, these new catalysts showed good reactivity under mild conditions and recoverability by simple filtration after reaction. The yield of esterification reaction was measured by GC. The acidity order of the novel ILs is HSO_4^- > BF_4^-> $CH_3SO_3^-$>TSO^-> $H_2PO_4^-$. The order of acidity of ILs were shown in the result of acidities of the ILs and the yield related the ILs showed the same trend. Therefore, The ionic liquid with HSO_4^- as anion exhibited the best catalytic performance. The conversion yield of n-hexylic acid was up to 91.4% under the conditions.

Keywords-ionic liquid; 8-hydroxyquinoline; catalyst; esterification; long-chain fatty acid

I. INTRODUCTION

Esters are important class of organic solvents, essential chemicals and pharmaceutical intermediates which are widely used in the related industry [1,2]. The esterification of long-chain fatty acid has spurred a great deal of interest in the synthesis of biodesel [3,4]. But their esterification yields are much lower than those of short-chain fatty acid [5]. Thus, it is necessary to synthesize new catalysts to increase the yield of long-chain fatty acid alkyl eaters. Conventional organic solid acids and inorganic acids such as H2SO4, H3PO4, HCl could be used as catalysts for esterification [6-9]. However, their application is limited due to some drawbacks such as equipment corrosion, physical injury, tedious workup procedure, lower activity and ecological problems [10,11].

Ionic liquids (ILs), consisting of organic cations and inorganic or organic anions, are known as special salts with some characteristics [12]. Esterification catalyzed by ILs is more attractive in past years. Compared with non-functionalized ionic liquids, SO3H-functionalized ionic liquids had high catalytic activity and the highest yield of ester was 93% [9]. 4-sulfobenzyl imidazolium hydrogenulfate ionic liquid was synthesized for catalyzing the esterification of oleic acid with methanol [13]. Dicationic acidic ionic liquids (DAILs) containing double-SO_3H cations had excellent yield of the desired ester [14]. For improving ILs recovery and reuse, some significant attempts have been performed. A kind of unconventional heteropolyanion-based ionic liquid with temperature-controlled liquid-solid separation for esterification was developed and obtained higher yield of 95.4% for tributyl citrate [15]. Because of difficulty for the recovery of ILs, high reaction temperature and complex synthesis process, some results are not entirely satisfactory. Recently, the reports of benzothiazolium-based Ils [16] were rather few as self-separation catalysts for esterification.

As is mentioned above, the unconventional ionic liquids have been paid more attention because of the combining advantages of both homogeneous and heterogeneous catalysts. Therefore, development of new ILs catalysts for long-chain esterification with higher reaction efficiency and convenient recovery is necessary. In this research, five new highly Brønsted acidic ionic liquids characterized based on 8-hydroxyquinoline cation and a series of anions $H_2PO_4^-$, $H_SO_4^-$, $CH_3SO_3^-$, TsO^- and BF_4^- (see Fig. 1) were synthesized. Otherwise, the catalysis activity and self-separation in esterification reaction of n-hexylic acid were investigated.

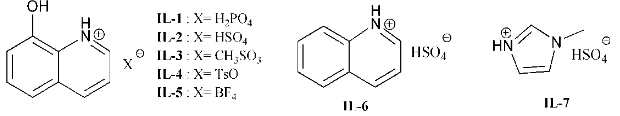

Figure 1. Structures of ionic liquids prepared and used in this paper

II. EXPERIMENT

A. Reagents and materials

8-hydroxyquinoline and long-chain fatty acids were purchased from Kelong Chemical reagents Factory (Chengdu, China). All chemicals were analytical reagent and commercially available. The melting points were determined on an XRC-1 melting point apparatus (Sichuan University Instrument Factory, P.R. China). The electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a ZQ 4000 mass spectrometer (Waters, USA). 1H NMR spectra were recorded on an AV-400 NMR spectrometer (Bruker, Germany) in CH3DO with TMS as internal standard. IR measurements were performed on a SPECTRUM 400 FT-IR（Perkin-Elmer, USA）absorption spectrometer using KBr disc. The concentrations of products were analyzed by a GC 7900 (Techcomp, China) equipped with a TM-1701 column (30m long, 1μm i.d, 0.32mm film thickness) and a flame ionization detector (FID).

B. Synthesis of ionic liquids

50 mL anhydrous ethanol was taken in the round bottom flask in an ice bath followed by adding 7.258 g (0.05 mol) 8-hydroxyquinoline. Then, 30% phosphoric acid was dropped slowly into the solution and the mixture was stirred for 4 h at room temperature. Subsequently, water and ethanol were removed under vacuum, and then yellow viscous crude product was obtained and washed with acetone (3 × 30 mL). Further purification of the ionic liquid was achieved by recrystallization from mixture of ethyl acetate and appropriate ethanol. The mixture was filtered and dried under vacuum to yield light yellow powder product IL-1. Other four ionic liquids were prepared by the similar procedure to IL-1 except that different acids were used. The yields of IL-1, 2, 3, 4 and 5 were respectively 83.7%, 79.6%, 78.5%, 86.2%, and 91.6%, respectively. IL-6 and IL-7 were synthesized according to the reported literatures [17].

spectral data for IL-1: m.p. 178-180^{o}C; IR (KBr, cm-1): 3358 (-OH stretching of hydroxyl), 1600, 1479 (C=C- stretching of aromatic ring), 1260 (-P=O stretching of H2PO4-); ^{1}HNMR (400 MHz, CH_3DO,δ / ppm): 9.14 (1H, m, -N=CH-CH=CH-), 9.05 (1H, m, -N=CH-CH=CH-), 8.09 (1H, t, J=8 Hz, OH-C=CH-CH=CH-), 7.78 (2H, m, -N=CH-CH=CH-, OH-C=CH-CH=CH-), 7.5 (1H, m, OH-C=CH-).

spectral data for IL-2: m.p. 166-168^{o}C; IR (KBr, cm-1): 3384 (-OH stretching of hydroxyl), 1600, 1543 (C=C- stretching of aromatic ring), 1202 (-S=O stretching of HSO4-); ^{1}HNMR (400 MHz, CH_3DO,δ / ppm): 9.18 (1H, m, -N=CH-), 9.09 (1H, q, -N=CH-CH=CH-), 8.11 (1H, t, J=8 Hz, OH-C=CH-CH=CH-), 7.78 (2H, m, -N=CH-CH=CH-, OH-C=CH-CH=CH-), 7.52 (1H, m, OH-C=CH-); MS (m/z): m/z (+) 146.06, m/z (–) 97.03.

spectral data for IL-3: m.p. 170-172^{o}C; IR (KBr, cm-1): 3354 (-OH stretching of hydroxyl), 2957 (-CH3 stretching of CH3SO3-), 1590, 1470 (C=C- stretching of aromatic ring), 1199 (-S=O stretching of CH3SO3-); ^{1}HNMR (400 MHz, CH_3DO,δ / ppm): 9.18 (1H, d, J=8 Hz, -N=CH-), 9.09 (1H, d, J=8 Hz, -N=CH-CH=CH-), 8.11 (1H, t, J=8 Hz, OH-C=CH-CH=CH-), 7.81 (2H, m, -N=CH-CH=CH-, OH-C=CH-CH=CH-), 7.52 (1H, d, OH-C=CH-), 2.73 (3H, s, CH_3-SO_3-).

spectral data for IL-4: m.p. 154-156 oC; IR (KBr, cm-1): 3344 (-OH stretching of hydroxyl), 1591, 1482(C=C- stretching of aromatic ring), 1383(-CH3 bending of TsO-), 1204(-S=O stretching of TsO-); ^{1}HNMR (400 MHz, CH_3DO,δ / ppm): 9.14 (1H, t, J=12 Hz, -N=CH-), 9.03 (1H, t, J=24 Hz, -N=CH-CH=CH-), 8.06 (1H, t, J=8 Hz, OH-C=CH-CH=CH-), 7.70 (4H, s, benzene), 7.44 (1H, s, -N=CH-CH=CH-), 7.18 (2H, s, OH-C=CH-CH=CH-, OH-C=CH-), 2.33 (3H, s, J=8 Hz, CH_3-Ph).

spectral data for IL-5: m.p. 120-122^{o}C; IR (KBr, cm-1): 3389(-OH stretching of hydroxyl), 1543, 1479(C=C- stretching of aromatic ring), 1038(-BF stretching of BF4-); ^{1}HNMR (400 MHz, CH_3DO,δ / ppm): 9.18 (1H, m, -N=CH-), 9.09 (m,1H, -N=CH-CH=CH-), 8.11 (1H, t, J=8 Hz, OH-C=CH-CH=CH-), 7.80 (2H, m, -N=CH-CH=CH-, OH-C=CH-CH=CH-), 7.52 (1H, m, OH-C=CH-).

C. Acidity of new ionic liquids determination

To approximate the Brønsted acidity of the ILs, UV–Vis spectroscopic measurement was used to determine the Hammett acidity [18]. Hammett acidity function (H_0) is determined by UV–Vis spectrophotometry, wherein an indicator is trapped the dissociated proton. In a typical series, 4-nitroaniline as indicator was dissolved in methanol at concentrations of 0.1 mmol L-1, then 2 mmol L-1 solution of ILs were obtained with the solution of indicator. Based on the measurement, the ratio that was the ratio of protonated indicator to deprotonated [I]/[IH+] could be determined from the measured absorbance differences after addition of ILs. The Hammett acidity function could be calculated with (1) [19, 20]:

$$H_0 = \mathrm{pK(I)} + \log([I] / [IH^+]) \qquad (1)$$

where pK(I) is the pKa value of the indicator.

D. Procedure for synthesis of fatty acid ethyl esters

The required amounts of fatty acid, alcohol and IL were added to a round-bottom flask fitted with a reflux condenser. The esterification reaction was carried out for 1-6 h at the desired temperature with magnetic stirring. Then, when the mixture was cooled to 0^oC to form a liquid-solid system, the ionic liquids precipitated and collected by filtration and reused after evaporation of water. After water and unreacted alcohol were removed under vacuum, the product was washed with saturated salt water and isolated by separating funnel (see Fig. 2). For the analysis of the product, it was determined with gas chromatograph (GC), where 1 μL of sample was injected into the GC for each run. The injector temperature was 220^oC and the detector temperature was 220^oC, the oven temperature was kept at 60^oC for 1 min, and then increased to 220^oC in 10 min as the final oven temperature. Nitrogen was used as the carrier gas for the GC. The yield of fatty acid ethyl ether was calculated by (2) [21]:

$$\text{Yield of ether} = A \times \frac{\text{Weight of product (g)}}{\text{Weight of fatty acid (g)}} \times 100\% \qquad (2)$$

Where A is a relative percentage of the total peak area for fatty acid ethyl ether, and the ethyl ester was identified by comparing its retention time to the retention time of ethyl ether standard.

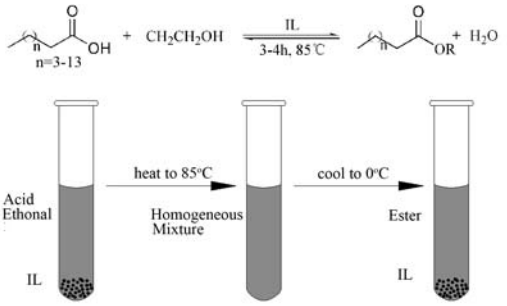

Figure 2. The process of esterification reaction

III. RESULTS AND DISCUSSION

A. Acidities of the ILs

With increasing acidity of the acidic ionic liquid, the concentration of the unprotonated form of the indicator decreases. The protonated form could not be observed because of its small absorbance. The Hammett function was calculated and the obtained values are listed in Table 1. The most acidic IL is IL-2, with an H0 value of 1.047. The H0 values of other ILs, IL-1, IL-3, IL-4, andIL-5, are 2.12, 1.401, 1.461, and 1.169, respectively. It is clearly shown that the acidity order of the novel ILs is IL-2 > IL-5> IL-3 > IL-4> IL-1.

TABLE I. HAMMETT ACIDITY FUNCTIONS (H_0) OF THE NOVEL ILs IN METHANOL

Ionic liquid	Absorbance	[I] / %	$[IH^+]$ / %	H_0
Blank	1.449	100	0	-
IL-1	1.349	93.10	6.90	2.120
IL-2	0.772	53.28	46.72	1.047
IL-3	1.044	72.05	27.95	1.401
IL-4	1.083	74.74	25.26	1.461
IL-5	0.872	60.18	39.82	1.169

B. Esterification of n-hexylic acid and ethanol with various ILs

The esterification of n-hexylic acid and ethanol was chosen as a model reaction for screening of acidic ILs. Fig.3 shows that the novel catalysts have good catalytic activity and the ester yield is up to 91.4% when IL-2 is used as a catalyst except for IL-1. The cations of ILs (IL-1, 2, 3, 4, 5) were the same, but various yields of products were obtained. It indicates the acidity and structure of the IL could play an important role in the improvement of esterification. It was found that IL-2 with HSO4- as anion exhibited a much better catalytic performance, which has the strongest acidity. The order of acidity of ILs were shown in the result of acidities of the ILs and the yield related the ILs showed the same trend as in Fig.3. The more acidic the anion, the stronger the acidity of IL and the better yield of ester.

Although IL-7 showed a little higher catalytic activity than IL-2, IL-7 was hardly recovered from the system due to their existence as liquid state. The yield of ester catalyzed by IL-6 was similar to IL-2, however, the new IL (IL-2) could be more precipitated readily when the reaction cooled to 0oC and was recycled easily by filtration. So, IL-2 was preferred for further studies.

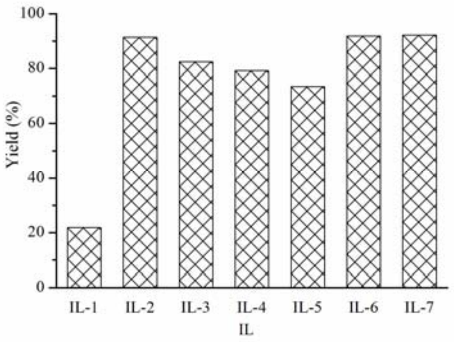

Figure 3. Effect of different ionic liquids catalysts on the esterification of n-hexylic acid (reaction conditions: n(ethanol): n(n-hexylic acid): n(ILs)= 4:1:0.8, 85oC, 3h).

IV. CONCLUSIONS

Five new Brønsted-acidic ionic liquids based on 8-hydroxyquinoline cation were synthesized and identified by spectral data. Then they were used as efficient catalysts for the esterification reaction of n-hexylic acids. Among the ionic liquids, IL with HSO_4^- as anion showed the best catalytic efficiency for esterification reaction. Especially, the IL with the advantages of both homogeneous catalysts and heterogeneous catalysts, it can be easily separated from product by simple filtration due to satisfactory precipitation in room temperature while high solubility in higher temperature. The IL exhibits satisfactory catalytic efficiency for the esterification of n-hexylic acids and has great potential for the industrial synthesis of biodiesel.

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