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Brönsted Acidic Ionic Liquids as Efficient and Recyclable Catalysts for the Carbonylation of Formaldehyde

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Abstract Methyl glycolate (MG), as a precursor to ethylene glycol (EG), was synthesized by an efficient and eco-friendly procedure of one-pot, two-step, sequential reaction, including carbonylation and esterification from HCHO with Brönsted acidic ionic liquids (BAILs) as catalysts. MG was obtained in high yield under mild conditions. In addition, the catalyst could be recycled eight times after separating the unreacted materials and products from the reaction system by distillation under vacuum and no significant decrease in catalytic activity was observed.

Keywords Formaldehyde · Carbonylation · Methyl glycolate · Ethylene glycol · Ionic liquids

1 Introduction

Ethylene glycol (EG) is an important industrial chemical used in the manufacture of polyester resins and fibers and antifreeze. The conventional process for producing EG includes the partial oxidation of ethylene and the hydration of ethylene oxide [1]. However, this procedure is associated with disadvantages such as harsh reaction conditions, poor chemoselectivity and yield. A number of routes have been explored to synthesize EG from syngas or its derivatives in place of petroleum-derived ethylene as a starting material [2–5]. Of these, carbonylation of HCHO with CO via methyl glycolate (MG) using sulphuric acid as a catalyst was practiced commercially by Du Pont company [4, 6–9], the drawback of very rigorous reaction conditions and serious corrosion limited the development of this method. To overcome the disadvantages caused by liquid acids, the more environmentally friendly solid acids, such as resins, zeolite and heteropolyacids, have been employed in the carbonylation of HCHO [5, 10–13]. MG yield up to 78% could be obtained at a high initial CO pressure of 24 MPa using Amberlyst 15 as catalyst. Nevertheless, the rapid deactivation of solid acids might be the major drawbacks from the viewpoint of industrial application. Up to now, although much progress has been made in the alternative catalysts for the carbonylation of HCHO, the search for the new type of convenient and green catalysts is still being actively pursued.

Ionic liquids (ILs) have attracted interest as environmentally benign media for catalytic processes because of their favorable properties. Brönsted acidic ILs (BAILs), which possess the advantageous characteristics of solid acids and liquid acids, have been designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid [14]. More recently, ILs as solvents or catalysts in the carbonylation of HCHO have been reported [15], affording a new approach in the production of EG. In view of developing an efficient and green procedure for synthesizing of MG derived from HCHO and CO, we report here for the first time the application of SO_3H-functionalized BAILs for the carbonylation of HCHO (Scheme 1).

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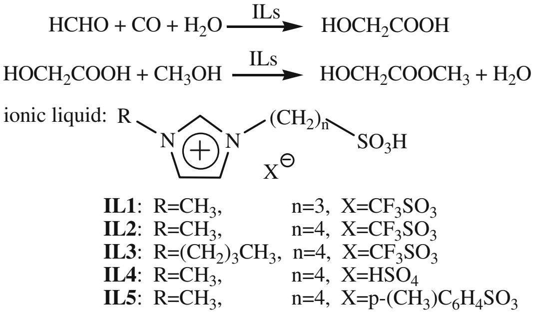


$HCHO + CO + H_2O \xrightarrow{ILs} HOCH_2COOH$

$HOCH_2COOH + CH_3OH \xrightarrow{ILs} HOCH_2COOCH_3 + H_2O$

IL1: R=CH_3, n=3, X=CF_3SO_3
IL2: R=CH_3, n=4, X=CF_3SO_3
IL3: R=$(CH_2)_3CH_3$, n=4, X=CF_3SO_3
IL4: R=CH_3, n=4, X=HSO_4
IL5: R=CH_3, n=4, X=p-$(CH_3)C_6H_4SO_3$

Scheme 1 Carbonylation of HCHO with CO catalyzed by acidic ionic liquids

2 Experimental

2.1 Ionic Liquids Preparation

The BAILs were prepared according to the similar procedure [16]. A stoichiometric amount of 1,4-butane or 1,3-propane sultone was added dropwise to a solution of *N*-alkyl imidazole in toluene, and then the mixture was stirred at 60 °C for 8 h. The obtained white powdery solid was filtered, washed with toluene and dried in vacuo to afford pure 1-alkyl-3-(alkyl-4 or 3-sulfonate) imidazolium betaine. Then the zwitterion and corresponding acid were mixed in a molar ratio of 1:1 in anhydrous toluene, and stirred magnetically at 60 °C for 8 h, followed by washing with toluene and drying in vacuo to obtain the final ILs. ^{1}H NMR spectra and ^{13}C NMR spectra in D_2O were recorded on an Inova-400 MHz instrument using tetramethylsilane (TMS) as internal standard. Elementary analyses were obtained with an elementar Vario EL cube instrument.

IL1: ^{1}H-NMR (400 MHz, D_2O): δ 2.231 (h, $J = 7.3$ Hz, 2H), 2.837 (t, $J = 7.6$ Hz, 2H), 3.806 (s, 3H), 4.277 (t, $J = 7.0$ Hz, 2H), 7.358 (d, $J = 3.6$ Hz, 1H), 7.434 (d, $J = 3.6$ Hz, 1H), 8.667 (s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ 24.991, 35.601, 47.099, 47.630, 117.970 ($J_{C\text{–}F} = 315.1$ Hz), 122.097, 123.673, 136.090. Anal. calcd for $C_8H_{13}N_2O_6S_2F_3$: C, 27.12; H, 3.70; N, 7.91. Found: C, 27.46; H, 3.08; N, 7.92.

IL2: ^{1}H-NMR (400 MHz, D_2O): δ 1.293 (h, $J = 7.8$ Hz, 2H), 1.564 (h, $J = 7.5$ Hz, 2H), 2.482 (t, $J = 7.6$ Hz, 2H), 3.433 (s, 3H), 3.781 (t, $J = 7.2$ Hz, 2H), 6.980 (d, $J = 3.6$ Hz, 1H), 7.032 (d, $J = 4.0$ Hz, 1H), 8.255 (s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ 20.912, 28.077, 35.616, 48.847, 50.060, 118.046 ($J_{C\text{–}F} = 315.1$ Hz), 122.113, 123.608, 135.825. Anal. calcd for $C_9H_{15}N_2O_6S_2F_3$: C, 29.35; H, 4.10; N, 7.61. Found: C, 29.32; H, 4.21; N, 7.56.

IL3: ^{1}H-NMR (400 MHz, D_2O): δ 0.797 (t, $J = 7.4$ Hz, 3H), 1.180 (m, $J = 7.4$ Hz, 2H), 1.640 (h, $J = 7.8$, 2H), 1.733 (h, $J = 7.3$, 2H), 1.909 (h, $J = 7.4$, 2H), 2.822 (t, $J = 7.8$, 2H), 4.079 (t, $J = 7.0$, 2H), 4.128 (t, $J = 7.0$, 2H), 7.387 (d, $J = 4.4$, 2H), 8.691 (s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ 12.497, 18.657, 20.846, 27.997, 31.088, 48.771, 49.270, 49.943, 117.964 ($J_{C\text{–}F} =$ 315.1 Hz), 122.177, 122.396, 135.093. Anal. calcd for $C_{12}H_{21}N_2O_6S_2F_3$: C, 35.12; H, 5.16; N, 6.83. Found: C, 35.32; H, 5.33; N, 6.81.

IL4: ^{1}H-NMR (400 MHz, D_2O): δ 1.577 (h, $J = 4.8$ Hz, 2H), 1.852 (h, $J = 7.8$ Hz, 2H), 2.775 (t, $J = 7.6$ Hz, 2H), 3.718 (s, 3H), 4.076 (t, $J = 7.0$ Hz, 2H), 7.264 (d, $J = 3.6$ Hz, 1H), 7.324 (d, $J = 3.6$ Hz, 1H), 8.573 (s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ 20.858, 28.041, 35.615, 48.846, 55.357, 122.079, 123.671, 135.940. Anal. calcd for $C_8H_{16}N_2O_7S_2$: C, 30.37; H, 5.10; N, 8.86. Found: C, 29.53; H, 5.20; N, 8.78.

IL5: ^{1}H-NMR (400 MHz, D_2O): δ 1.561 (h, $J = 7.7$ Hz, 2H), 1.835 (h, $J = 7.5$ Hz, 2H), 2.227 (s, 3H), 2.774 (t, J = 7.6 Hz, 2H), 3.703 (s, 3H), 4.050 (t, $J = 7.0$ Hz, 2H), 7.192 (d, $J = 6.4$ Hz, 2H), 7.244 (d, $J = 3.6$ Hz, 1H), 7.304 (d, $J = 3.6$ Hz, 1H), 7.508 (d, $J = 8.4$ Hz, 2H), 8.543 (s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ 20.386, 20.823, 27.991, 35.534, 48.790, 49.952, 122.031, 123.528, 125.232, 129.341, 135.787, 139.342, 142.353. Anal. calcd for $C_{15}H_{22}N_2O_6S_2$: C, 46.02; H, 5.66; N, 7.16. Found: C, 45.96; H, 5.72; N, 7.15.

2.2 Catalytic Reactions

The carbonylation of HCHO with CO was carried out using a 100 mL autoclave with a Teflon liner and a magnetic stirrer. 1,3,5-trioxone was used as a source of HCHO. In a typical experiment, 1,3,5-trioxane (22.3 mmol), BAILs (26.8 mmol), water (134.0 mmol) and solvent (20 mL) were charged into the reactor, and then CO (>99.95%) was introduced with initial pressure of 3.0–8.0 MPa at room temperature after flushed three times with CO. The reactions were performed at 100–180 °C for 2–10 h. After reaction, the autoclave was cooled to room temperature and depressurized. For the esterification, excess methanol (67 mmol) was added into the autoclave and refluxed for 2 h at 80 °C to esterify the glycolic acid into MG. The final products were identified and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS) (Agilent 7890A/5975C) and GC (Agilent 6890 equipped with a SE-54 capillary column), respectively. A known amount of *n*-hexane was added as an internal standard to the product mixture before the GC analysis. Unconverted HCHO was detected as dimethoxymethane. For the recycling of catalyst, dimethoxymethane, methanol and products were separated from the reaction system by distillation under vacuo of 10 mmHg at 90 °C after carbonylation and esterification, the IL and sulfolane was recovered and reused directly for a new batch reaction.

Table 1 Catalytic activities of different ILs on the carbonylation of HCHO

Entry[a]	ILs	HCHO conversion (%)	Yield (%)			Selectivity of MG (%)
			MG[b]	MMAc[b]	MF[b]	
1	IL1	98.9	96.4	1.5	0.02	97.4
2	IL2	99.3	97.6	1.0	0.6	98.3
3	IL3	97.9	82.3	15.3	0.3	84.1
4	IL4	90.2	85.2	2.6	0.01	92.6
5	IL5	76.3	73.6	0.1	2.6	92.8
6	p-TsOH	38.3	36.1	1.2	1.0	94.1

[a] Reaction conditions of carbonylation: IL/HCHO = 0.4 (molar ratio), H_2O/HCHO = 2 (molar ratio), 170 °C, 5.0 Mpa CO, 8 h

[b] MG methyl glycolate, MMAc methyl methoxy acetate, MF methyl formate

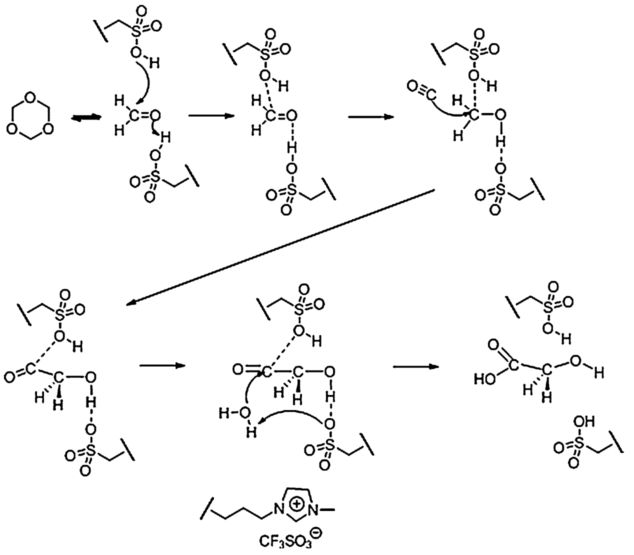
3 Results and Discussion

Firstly, we evaluated the activities of ILs catalysts in the one-pot, two steps sequential reaction of carbonylation HCHO with CO, then esterification with methanol (Table 1). We were pleased to find that each of the ILs tested promoted the reaction under 170 °C and 5.0 MPa of CO for 8 h.

It is clear that either the cations or the anions of the ILs influence the catalytic activity in any significant degree. High yield of 97.6% was obtained over IL2 (Table 1, entry 2), while for IL3, with butyl connected to the imidazolium cation, moderate yield of 82.3% was achieved (Table 1, entry 3). It might be attributed to high solubility of HCHO in IL2 because the hydrophile of IL increases with the decreasing of carbon number of *N*-alkyl substitution in imidazolium cation.

A key parameter influencing catalyst efficacy in these systems proved to be the counteranion—$CF_3SO_3^-$ (Table 1, entries 1–3) salts are clearly superior to the other materials evaluated in this study. Of the ILs examined, IL2 showed the highest activity in terms of HCHO conversion, MG yield and selectivity (Table 1, entry 2). IL4 and IL5 could also used as catalysts to promote the reaction, but their activities seem to be slightly inferior as compared with that of IL2 (Table 1, entries 4 and 5). In view of the foregoing, IL2 should be a suitable catalyst for the carbonylation reaction.

The carbonylation of HCHO belongs to the known as Koch reaction which requires a strong acid to protonate formaldehyde because of its low proton affinity [7, 17]. In addition, esterification is also a typical acid-catalyzed reaction. Therefore, the catalytic performance depends very much on the Brönsted acidity of catalyst. In order to prove the consistency of the catalysts' activity with their acidity, the acidities of these three SO_3H-functionalized ILs have been examined using 4-nitroanline as indicator in H_2O according to the literature reported previously [18], and the order of ILs' acidity is IL2 > IL4 > IL5. This order is consistent with the sequence of catalytic activity observed in this reaction.



Scheme 2 Proposed reaction mechanism of the carbonylation of HCHO

For the purpose of comparison, the same reaction was also conducted using *p*-toluenesulfonic acid (*p*-TsOH), a typical Brönsted acid, as catalyst (Table 1, entry 6). The results show that the catalytic activity of *p*-TsOH is only half of the IL5′s under the same reaction conditions, even containing the same TsO^- anion. This phenomenon once again proved the important role of the IL's cation.

The carbonylation of HCHO takes place depending on how easily the formaldehyde is protonated. Based on the experimental results and discussion above, plausible pathways to the carbonylation reaction in the presence of IL2 are depicted in Scheme 2. The first step is the generation of HCHO in solution when 1,3,5-trioxane is used as a reactant. In the next step, protonation of monomeric HCHO yields a hydroxycarbocation. Then reaction of the hydroxycarbocation with CO leads to a resonance-stabilized acyl carbocation. Addition of water to the carbonylation product of the hydroxycarbocation leads to glycolic acid. In this process, IL2 was treated not only as a proton source, but also a stabilizer of the formed hydroxycarbocation through coordinative interaction [19].

With an active catalyst in hand, we next examined the effect of solvents on the carbonylation of HCHO and the results are shown in Table 2. Compared to the reaction with neat IL2 (Table 2, entry 1), reactions performed in polar solvents gave better results. 97.6% yield of MG could be achieved when the most polar solvent-sulfolane was

Table 2 Effect of solvent on the carbonylation of HCHO

Entry[a]	Solvent	HCHO conversion (%)	Yield (%)			Selectivity of MG (%)
			MG	MMAc	MF	
1	–	75.7	58.5	11.5	5.8	77.2
2	Sulfolane	99.3	97.6	1.0	0.6	98.3
4	1,4-Dioxane	83.5	68.3	10.4	4.8	81.8
5	Tetrahydrofuran	87.8	49.9	0	37.9	56.8
6	Toluene	57.3	15.4	18.1	23.9	26.7

[a] Reaction conditions of carbonylation: IL2/HCHO = 0.4 (molar ratio), $H_2O/HCHO = 2$ (molar ratio), 170 °C, 5.0 Mpa CO, 8 h

Table 3 Effect of the amount of IL2 on the carbonylation of HCHO

Entry	IL2/HCHO (molar ratio)	HCHO conversion (%)	Yield (%)			Selectivity of MG (%)
			MG	MMAc	MF	
1	0.2	49.4	48.2	0.3	0.9	97.6
2	0.3	69.1	68.7	0.3	0.1	99.4
3	0.4	88.3	87.2	0.5	0.7	98.3
4	0.6	88.2	85.9	0.5	1.3	97.5

Reaction conditions of carbonylation: $H_2O/HCHO = 2$ (molar ratio), 150 °C, 4.0 Mpa CO, 6 h

Table 4 Influence of H_2O addition on the carbonylation of HCHO

Entry	$H_2O/HCHO$ (mol/mol)	H_2O/Solvent (mL)	HCHO conversion (%)	Yield (%)			Selectivity of MG (%)
				MG	MMAc	MF	
1	0.5	0.6/20	86.2	85.2	0.9	0.1	98.8
2	1.0	1.2/20	87.2	86.1	0.4	0.6	98.8
3	2.0	2.4/20	88.3	87.0	0.4	0.8	98.5
4	3.0	3.6/20	82.7	80.1	0.5	2.1	96.8
5	4.0	4.8/20	74.8	73.6	0.3	1.0	98.3
6	6.0	7.2/20	70.3	68.9	0.4	1.0	98.1

Reaction conditions of carbonylation: IL2/HCHO = 0.4 (molar ratio), 150 °C, 4.0 Mpa CO, 6 h

used (Table 2, entry 2), and the yield decreased dramatically with decreasing polarity of the solvent. Sulfolane is an excellent medium for this carbonylation reaction, since it is not attacked readily by carbocationic species and its high dielectric constant (43.3) stabilizes ions relative to other species [20]. Moreover, IL2 shows a high solubility in sulfolane.

The influence of the molar ratio of IL2 to HCHO on the reaction was studied and the results are listed in Table 3. The HCHO conversion showed increases with the molar ratio of IL2 to HCHO increases, yet the yield and selectivity of MG showed a maximum. This type of behavior usually indicates the presence of other side reactions which produce a large number of byproducts. Hence, the optimum molar ratio of IL2 to HCHO is 0.4.

It was already known that water can significantly promote Koch carbonylation in the case of using catalyst such as heteropolyacids [11, 12]. Scheme 1 gives the reaction equation of carbonylation of HCHO with CO. It is evident that water participates in the reaction as reactant for formation of glycolic acid. To explore the rule of water in this process catalyzed by IL2, we conducted a study which focused on the effect of water on the carbonylation of HCHO. Table 4 is a summary of our results. The yield of MG increased with the addition of water into the reaction mixture, and reached its maximum at $H_2O/HCHO$ (molar ratio) = 2.0. Then the yield and the conversion gradually dropped as the amount of water continued to increase, which was probably caused by the dilution of the IL catalyst with the excess of water. Another reason is that water can compete with sulfolane, decreasing the stabilizing ability of the intermediates formed during the catalysis and then giving lower activities when a relative excess of water is present in the medium.

In order to optimize the reaction conditions, the effect of reaction pressure, reaction temperature, and reaction time were also investigated with catalyst IL2 and the results are summarized in Table 5. The increase of CO pressure is propitious for the carbonylation of HCHO (Table 5, entries 1–5). At 3.0 MPa of CO, the yield of MG is as low as

56.7%. With the increasing of the CO pressure, the reaction is significantly enhanced and reaches the good yield of MG as 91.3% at 5.0 MPa. A further increment of the CO pressure to 8.0 MPa, the yield of MG increases only a little to 92.7%. From the data of Table 5, we can see that temperature has a dramatic effect on the carbonylation of HCHO (Table 5, entries 3, 6–8). When the temperature increased from 120 °C to 170 °C, the yield of MG increased rapidly from 39.3% to 96.5%; further increase of the temperature, the yield of MG decreased due to the formation of byproducts which increase at higher temperature. The MG yield was also influenced by reaction time (Table 5, entries 7, 9–12). When the reactants were stirred for 2 h, the yield of MG could reach 84.7%, suggesting the high efficiency of the IL catalyst. After 8 h, the whole reaction tended to equilibrium with the conversion and the selective reaching 99.3 and 98.3%.

The possibility of reusability of IL2 under mild conditions was also studied. After removing unreacted HCHO, excess of methanol and products under vacuum, the IL2 dissolved in sulfolane was recovered and reused directly for a new batch reaction under the same conditions. As expected, IL2 exhibited nearly no any loss in activity after eight cycles, thus demonstrating that the SO_3H-functionalized IL was stable enough in the carbonylation process of HCHO, which is very favorable from a practical point of view (Fig. 1).

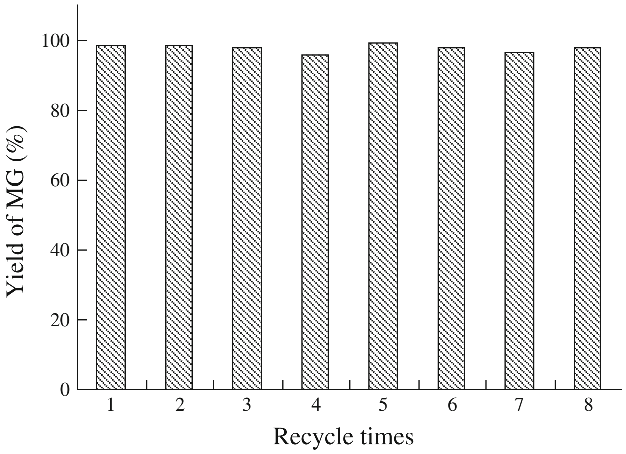


Fig. 1 Yield of MG after consecutive batches. Reaction conditions of carbonylation: IL2/HCHO = 0.4 (molar ratio), H_2O/HCHO=2(molar ratio), 170°C, 5.0 Mpa CO, 8 h

4 Conclusion

In conclusion, a highly effective catalytic carbonylation of HCHO with CO using BAILs as catalysts was successfully processed under mild reaction conditions. The conversion of HCHO and yield of MG gave up to 99.2% and 98.0%, respectively. The catalyst could be recycled eight times after removing unreacted HCHO, excess of methanol and products under vacuum. The activity did not change when it was recycled eight times. The present study shows that the SO_3H-functionalized BAILs has a potential application in the production of ethylene glycol.

5 Supporting Information Available

The acidities of these SO_3H-functionalized ILs have been examined using 4-nitroanline (Hammett constant is 0.99) as indicator in H_2O and the results are shown in Fig. 2. The Hammett acidity functions (H_0) is mathematically given by the following equation:

$$H_0 = \mathrm{p}K(\mathrm{A})_{\mathrm{aq}} + \lg\left([\mathrm{A}]_{\mathrm{s}}/[\mathrm{AH}^+]_{\mathrm{s}}\right)$$

Table 5 Effect of different reaction conditions using IL2 as catalyst

Entry	CO pressure (MPa)	Temperature (°C)	Time (h)	HCHO conversion (%)	Yield (%)			Selectivity of MG (%)
					MG	MMAc	MF	
1	3.0	150	6	58.7	56.7	0.5	1.5	96.6
2	4.0	150	6	88.3	87.0	0.5	0.8	98.5
3	5.0	150	6	92.7	91.3	0.8	0.6	98.5
4	6.0	150	6	92.4	91.0	0.9	0.5	98.6
5	8.0	150	6	94.1	92.7	0.5	0.8	98.6
6	5.0	120	6	40.8	39.3	0.1	1.4	96.4
7	5.0	170	6	98.5	96.5	0.7	1.3	97.9
8	5.0	180	6	99.2	96.1	2.2	0.9	96.9
9	5.0	170	2	87.0	84.7	0.4	1.9	97.3
10	5.0	170	4	93.1	90.3	0.9	1.9	97.0
11	5.0	170	8	99.3	97.6	1.0	0.6	98.3
12	5.0	170	10	99.2	98.0	0.8	0.4	98.7

Reaction conditions of carbonylation: IL2/HCHO = 0.4 (molar ratio), H_2O/HCHO = 2 (molar ratio)

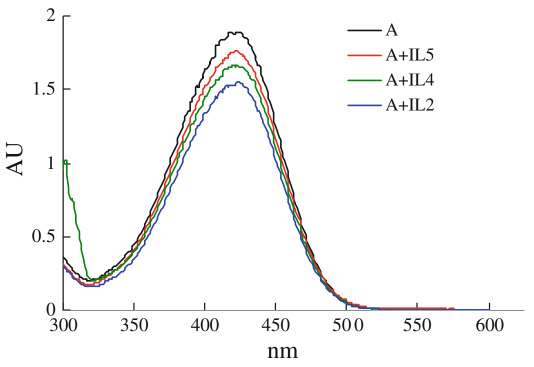


Fig. 2 Absorbance spectra of 4-nitroaniline (A) for various SO_3H-functionalized ILs in H_2O

Table 6 Calculation and comparison of H_0 values of different SO_3H-functionalized ILs in H_2O

Ionic liquids	Absorbance (AU)	[A] (%)	[HA^+] (%)	H_0
–	1.86	100	–	–
IL2	1.58	84.95	15.05	1.74
IL4	1.64	88.17	11.83	1.86
IL5	1.72	92.47	7.53	2.08

According to the calculated H_0 values listed in Table 6, it indicated that the order of ILs' acidity in water is IL2 > IL4 > IL5.

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