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Microwave-accelerated esterification of salicylic acid using Brönsted acidic ionic liquids as catalysts

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ABSTRACT

A variety of Brönsted acidic ionic liquids were screened as catalysts for the esterification of salicylic acid. The experimental results indicated that SO_3H-functionalized ionic liquids with HSO_4^- performed high catalytic activity under microwave irradiation, and the yields can reach 91.9–93.6%. Furthermore, ionic liquids can be easily separated by simple decantation and have a fair reusability. The Brönsted acidity–catalytic activity relationships were also investigated and the results showed that the activity of the acidic ionic liquids is in excellent agreement with their acidity order.

1. Introduction

As fine chemicals, methyl salicylate (MS) has been widely used as flavor and fragrance agent, cosmetic and dye carrier, as well as ultraviolet (UV)-light stabilizer in acrylic resins [1]. Fisher esterification is one of the simplest methods to obtain this ester. However, these reactions usually employ mineral acids, such as H_2SO_4, HF and H_3PO_4. It is well-known that these catalysts suffer from inherent problems of corrosiveness, more byproducts, environmental hazards, difficulty in catalyst recovery and reuse, and high susceptibility to water. Additionally, solid acid catalysts such as mesoporous materials [2,3], zeolites [4,5], and anion-modified metal oxides [6] are also used as esterification catalysts. Although above-mentioned shortcomings can be overcome, these catalysts have their own disadvantages, for example, high mass transfer resistance, easy to deactivation, adsorption of products, which limit their applications.

Ionic liquids (ILs) have been revealed as green reaction media owing to their negligible volatility, excellent thermal stability, and the variety of structures available [7–9]. So applications of ILs have been extensively studied with high yields, among which esterification is hot topic. The majority of research has focused primarily on $[BMIM][PF_6]$ and $[BMIM][BF_4]$ as catalysts and reaction media for esterification [10,11]. However, these ILs contain halogen atom, which may cause serious concerns under certain conditions. Therefore, the development of halogen-free ILs is highly desirable. Imidazolium salts with HSO_4^- and $H_2PO_4^-$ as anion, and protic pyridinium ILs have been synthesized [12,13]. These ILs showed excellent catalytic activity. Furthermore, Cole et al. [14] first synthesized Brönsted acidic ILs that bear an alkane sulfonic acid group in the cation. These ILs can be used as dual solvent–catalysts in esterification. Since then, SO_3H-functionalized ILs were widely used in esterification, for instance, esterification of acetic acid [15], benzoic acid [16] and aliphatic acids [17]. So far, only one report regarding synthesis of salicylate using ILs has been published [18]. However, the reaction time is long.

Esterification under microwave irradiation, besides being environmentally friendly, is also marked by a considerable reduction in reaction time in comparison to conventional esterification [19,20]. Furthermore, to the best of our knowledge, esterification of salicylic acid in ILs has not yet been achieved under microwave irradiation. In this paper, several Brönsted acidic ILs were prepared and used in the microwave-accelerated synthesis of salicylate. Two SO_3H-functionalized ILs showed high catalytic activity in a very short period of time. Additionally, the stability and reuse performance of these ILs were also examined.

2. Experimental section

2.1. Chemicals and instruments

All the chemicals were commercially available and were used without further purification.

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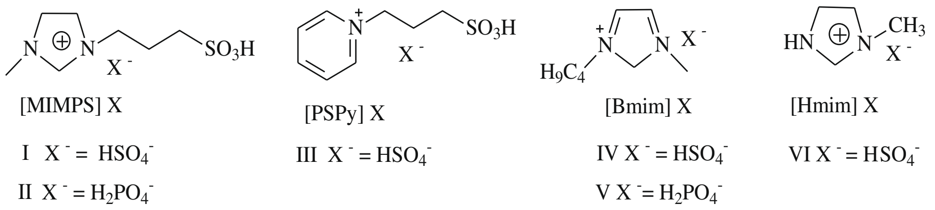

Fig. 1. Ionic liquids used in this paper.

UV–vis spectra were recorded on a UV-2450 spectrophotometer (Shimadzu Corporation, Japan) in H_2O. NMR spectra were recorded on an AV-400 spectrometer (Bruker Corporation, Germany) in D_2O. FT-IR spectra were performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr pellets at room temperature. TG/DSC was done on STA-449C Jupiter (NETZSCH Corporation, Germany).

2.2. General preparation of Brönsted acidic ionic liquids

The ionic liquids (ILs) used in this paper (Fig. 1) were synthesized according to previous literatures [12,16,21]. The ILs were analyzed by ^1H, ^{13}C NMR spectroscopies, and the spectral data agreed with their structures.

Spectral data for [PSPy][HSO_4]: ^1H NMR (400 MHz, D_2O): δ 2.28 (m, 2H), 2.80 (t, 2H), 4.59 (t, 2H), 7.90 (t, 2H), 8.38 (t, 1H), 8.70 (s, 1H); ^{13}C NMR (100 MHz, D_2O): δ 26.06, 47.00, 59.84, 128.37, 144.32, 145.89.

2.3. Esterification under microwave irradiation

The reactions were carried out in Microwave Synthesis System (MAS-I, Sineo Microwave Chemical Technology Co. Ltd., Shanghai, China) equipped with a magnetic stirrer and a water-cooled condenser. Temperature was controlled by automatic adjusting of an infrared temperature sensor. In a typical procedure, a solution of the substrates consisting of 0.02 mol salicylic acid, 0.05–0.08 mol methanol, and 4–12 mmol ILs were prepared and irradiated for 10–30 min. After the reaction, the mixture became biphasic, and diethyl ether was added to dissolve the unreacted salicylic acid (SA). The upper layer consisting of the produced ester and some unreacted SA was isolated by simple decantation, while the lower layer, viscous ILs, could be used in next reaction after removal of water at 90 °C for 6 h. Produced methyl salicylate was analyzed by ^1H NMR (^1H NMR (400 MHz, acetone-d 6): δ 3.95 (s, 3H), 6.91 (t, 1H), 6.97 (d, 1H), 7.50 (t, 1H), 7.81 (d, 1H), 10.79 (s, 1H)).

The composition of the products was analyzed by GC-FID (Agilent 7890A, HP-5 column, 30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC process started at 70 °C and the temperature was raised to 170 °C at 15 °C/min. The products were identified by comparing with the standards, and GC results showed that the major product was methyl salicylate and the minor side product was phenol. The conversion and selectivity were calculated according to the area of chromatograph peak [4].

$$\text{Conversion of salicylic acid (SA)}/\% = 100 - \frac{[\text{salicylic acid}]}{[\text{salicylic acid}] + [\text{methyl salicylate}] + [\text{phenol}]} * 100 \tag{1}$$

$$\text{Selectivity for methyl salicylate (MS)}/\% = \frac{[\text{methyl salicylate}]}{[\text{methyl salicylate}] + [\text{phenol}]} * 100 \tag{2}$$

$$\text{Yield of methyl salicylate (MS)}/\% = \text{conversion of SA} * \text{selectivity for MS} \tag{3}$$

2.4. UV–vis acidity determination

According to previous work [17], the Brönsted acidity was evaluated from the determination of the Hammett acidity function, using UV–vis spectroscopy. In the present case, ILs and the indicator 4-nitroaniline were dissolved in H_2O at concentrations of 3.2×10^{-2} mol/L and 2.9×10^{-3} mol/L, respectively.

3. Results and discussion

3.1. The effect of conventional and microwave heating on the synthesis in ILs

For the purpose of comparison, methyl salicylate was synthesized under conventional conditions and under microwave irradiation. Some data under conventional conditions (entries 5–7) are not given here by reason that it cannot be determined for its low catalytic activity. Other results are listed in Table 1.

According to the obtained data under microwave irradiation, the catalytic activity of SO_3H-functionalized ILs [PSPy][HSO_4] and [MIMPS][HSO_4] (Table 1, entries 1 and 2) was better than that of non-functionalized ILs (entries 3, 4 and 6). The yields can reach 91.9–93.6%. Under conventional conditions, the yields ranged from 2.2% to 36.6%, respectively, thereby, highlighting the role of microwave irradiation in promoting the esterification. Additionally, blank experiment (without catalyst) under the same microwave irradiation manifested that the application of SO_3H-functionalized ILs could effectively promote the reaction.

3.2. Optimization of reaction conditions

[PSPy][HSO_4] was used as catalyst to define the optimal reaction parameters of the synthesis under microwave irradiation. The effect of varying the concentration of the [PSPy][HSO_4] was explored (Table 2, entries 2, 8 and 9). The maximum yield was obtained when 10 mmol of ILs was added. An excess of ILs resulted in a decrease of yield. The optimal molar ratio of methanol to salicylic

Table 1
The effect of conventional and microwave heating on the synthesis in ILs.

Entry	Ionic liquid	Yield (%)		Selectivity(%)[b]	
		MH[c]	CH[d]	MH[c]	CH[d]
1	[PSPy][HSO_4]	93.6	36.6	99.9	99.9
2[a]	[MIMPS][HSO_4]	91.9	33.1	99	99.9
3	[Bmim][HSO_4]	17.6	4.5	99.9	99.9
4	[Hmim][HSO_4]	7.4	2.2	99.9	99.9
5	[MIMPS][H_2PO_4]	4.2	–	99.9	–
6	[Bmim][H_2PO_4]	1.7	–	99.9	–
7	Blank	1.0	–	99.9	–

Reaction conditions: ratio of methanol to salicylic acid = 3:1; ILs 10 mmol; refluxed for 20 min at 105 °C.

[a] Refluxed at 95 °C.

[b] Selectivity for methyl salicylate (base on salicylic acid).

[c] MH: microwave heating.

[d] CH: conventional heating.

Table 2
Results of esterification of salicylic acid with methanol in different microwave irradiation conditions.[a]

Entry	n ([PSPy][HSO_4]) (mmol)	t (min)	T (°C)	n_A:n_B	Yield (%)
1	10	15	105	3:1	87.1
2	10	20	105	3:1	93.6
3	10	25	105	3:1	92.2
4	10	30	105	3:1	89.3
5	10	20	85	3:1	80.8
6	10	20	95	3:1	87.6
7	10	20	115	3:1	94.2
8	8	20	105	3:1	82
9	12	20	105	3:1	89.4
10	10	20	105	2.5:1	84.1
11	10	20	105	4:1	66.4

[a] Selectivity for methyl salicylate (base on salicylic acid) were higher than 99%.

acid was found to be 3:1. The effect of varying reaction time (entries 1–4) and reaction temperature (entries 2, 5–7) were also studied. The high yield (93.6%) was achieved at 105 °C in 20 min.

3.3. Esterification of alcohols catalyzed by [PSPy][HSO_4] under microwave irradiation

After optimizing the conditions, we examined the generality of these conditions to other substrates. Thus in homogeneous conditions, a series of experiments were tested (Table 3). It is observed that activities of primary alcohols increased as the carbon chain of the alcohol grew longer (entries 2–6), however, selectivity for esters decreased. The results also show that the esterification with secondary alcohols gave lower conversion compared with primary alcohols (entries 7–8).

3.4. Recycling of ionic liquid [PSPy][HSO_4]

To make this method more suitable, we examined the reusability of [PSPy][HSO_4] under microwave irradiation. The data listed in Fig. 2 show that [PSPy][HSO_4] can be reused six times without significant loss of activity, which indicates that as the catalyst for esterification, [PSPy][HSO_4] has excellent reusability. Furthermore, [PSPy][HSO_4] was readily separated and directly used for the next cycle after removal of water at 90 °C for 6 h.

3.5. Acidities of the ILs–catalytic activity relationships

The Brönsted acidities of the ILs were determined using the Hammett method, and measured by evaluating the protonation extent of indicator base in the ILs. The Hammett function (H_0) is written as: $H_0 = pK(\mathrm{In})_{aq} + \log([\mathrm{In}]/[\mathrm{In\,H^+}])$. In represents indicator, pK(In)aq is the pK_a value of the indicator referred to an aqueous solution. [In] and [In H^+] are the molar concentrations of the unprotonated and protonated forms of the indicator, respectively.

Table 3
Esterification of different alcohols catalyzed by [PSPy][HSO_4] under microwave irradiation.

Entry	Alcohol	Conversion (%)	Selectivity (%)[a]
1	Methanol	93.7	99.9
2	Ethanol	67.1	99.9
3	Butanol	74.4	81.9
4	Amyl alcohol	91.2	79.7
5	Hexanol	95.4	68.6
6	Octanol	97.9	60
7	Isopropyl alcohol	30.1	96.7
8	sec-Butyl alcohol	29.3	82.1

Reaction conditions: ratio of methanol to salicylic acid = 3:1; [PSPy][HSO_4] 10 mmol; refluxed for 20 min at 105 °C.

[a] Selectivity for esters (base on salicylic acid).

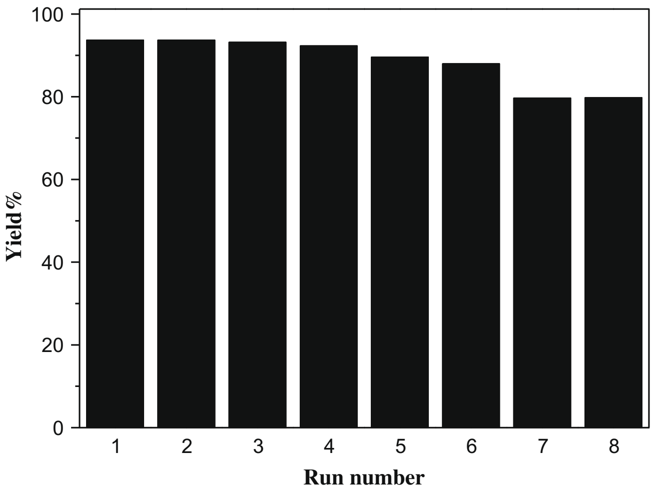

Fig. 2. Recycling of [PSPy][HSO_4] in the synthesis of methyl salicylate. Reaction conditions: ratio of methanol to salicylic acid = 3:1; [PSPy][HSO_4] 10 mmol; refluxed for 20 min at 105 °C.

Table 4
Hammett function values of various acidic ILs and their activity for esterification of salicylic acid with methanol.

Entry	Ionic liquids	A_{max}	[In](%)	[In H^+](%)	H_0[a]	Yield (%)
1	NA	1.5486	100	0	–	1.0
2	[PSPy][HSO_4]	1.0988	70.95	29.05	1.38	93.6
3	[MIMPS][HSO_4]	1.1045	71.32	28.68	1.39	91.9
4	[MIMPS][H_2PO_4]	1.3763	88.87	11.13	1.89	4.2
5	[Bmim][HSO_4]	1.2932	83.51	16.49	1.70	17.6
6	[Hmim][HSO_4]	1.3204	85.26	14.74	1.75	7.4
7	[Bmim][H_2PO_4]	1.4115	91.15	8.85	2.00	1.7

Reaction conditions: ratio of methanol to salicylic acid = 3:1; ILs 10 mmol; refluxed for 20 min at 105 °C.

[a] $H_0 = pK(\mathrm{In})\mathrm{aq} + \log([\mathrm{In}]/[\mathrm{In\,H^+}])$. In – indicator 4-nitroaniline (NA), $pK(\mathrm{NA})_{aq} = 0.99$; Solvent H_2O; $c(\mathrm{NA}) = 2.9 \times 10^{-3}$ mol/L, $c(\mathrm{IL}) = 3.2 \times 10^{-2}$ mol/L; temperature 25 °C.

In our experiment, 4-nitroaniline was chosen as basic indicator and H_2O as the solvent. The maximal absorbance of unprotonated form of 4-nitroaniline was observed at 380 nm in H_2O. The results are outlined in Table 4. It is clearly shown that SO_3H-functionalized ILs (entries 2 and 3) exhibited strong Brönsted acidity. However, when the anion is $H_2PO_4^-$ (entry 4) the acidity is remarkable weak, which may be due to the lower acidity of H_3PO_4. Three conventional non-functionalized ILs (entries 5–7) showed nearly no acidity. As a result, these ILs showed poor activity. In a word, the acidity order of various ILs is as follows: [PSPy][HSO_4] > [MIMPS][HSO_4] > [Bmim][HSO_4] > [Hmim][HSO_4] > [MIMPS][H_2PO_4] > [Bmim][H_2PO_4]. It is found that the activity of the acidic ILs is in excellent agreement with their acidity order.

4. Conclusion

From the detailed studies, the following conclusions can be derived:

(1) Microwave irradiation was found to have a beneficial effect on the esterification of salicylic acid.
(2) SO_3H-functionalized Brönsted acidic ILs with HSO_4^- showed good catalytic activity. The yield and selectivity for methyl salicylate can reach 93.6% and 99.9%, respectively.

(3) ILs are immiscible with the products, so they can be easily separated by simple decantation and reused repeatedly after removal of water without significant loss of activity.

(4) The Brönsted acidity–catalytic activity relationships were investigated. It is found that the activity of the acidic ILs is in excellent agreement with their acidity order.

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