



## Tuning the acidity of sulfonic functionalized ionic liquids for highly efficient and selective synthesis of terpene esters



Duan-Jian Tao<sup>a,\*</sup>, Yan Dong<sup>a</sup>, Zhi-Jun Cao<sup>a</sup>, Feng-Feng Chen<sup>a</sup>, Xiang-Shu Chen<sup>a,\*</sup>, Kuan Huang<sup>b</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Jiangxi Inorganic Membrane Materials Engineering Research Center, Jiangxi Normal University, Nanchang 330022, China

<sup>b</sup> Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

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### ABSTRACT

A series of sulfonic functionalized ionic liquids (SFILs) with different acidity were designed and prepared for the synthesis of terpene esters (e.g. geranyl acetate). The effect of acidity of SFILs on their performance was investigated systematically. It is found that tuning the acidity of SFILs to an appropriate value results in not only high conversion of geraniol but also superior selectivity of geranyl acetate. The SFILs can be easily separated from products by filtration under room temperature, thus showing good reusability. Furthermore, the kinetics for SFILs in the esterification of geraniol were determined as the basis for future process design.

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### Introduction

Turpentine is an important renewable biomass resource. It is the starting raw material for the synthesis of terpenols (e.g., geraniol, nerol, citronellol, dihydromyrcenol and terpinol) and their ester derivatives, which have widespread applications in food, perfume, cosmetic and pharmaceutical industries [1–4]. In comparison with terpenols, terpene esters are with more pleasant floral and fruity fragrance. The demand of terpene esters in industry keeps growing significantly over the past decades.

Terpene esters are synthesized from the esterification of terpenols with carboxylic acids or anhydrides, which is traditionally catalyzed by strong inorganic acids such as H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> [5]. Unfortunately, these acids are highly corrosive and contaminative, and they are difficult to recycle. Solid acid catalysts such as resins, heteropolyacids and molecular sieves can overcome the above-mentioned issues [6,7], however, they suffer from high mass transfer resistance, complex preparation process, and easy carbon deposition. Recently, enzymes start to attract extensive attentions due to their high specific selectivity, as well as biocompatibility [8–12]. Nevertheless, the application of enzymes is still very

limited because a long period of time is required to cultivate them and they are easily deactivated. Therefore, the exploration of new catalysts for the synthesis of terpene esters is highly valued for industrial applications.

Ionic liquids (ILs) are a class of *state-of-the-art* solvent for synthesis and catalysis. They have many unique properties including negligible volatility, high thermal stability, molecular designability and excellent reusability [13–16]. These characteristics enable ILs great potential applications in alkylation [17,18], esterification [19–21], hydration [22], Fischer indole synthesis [23], Mannich reaction [24], ketalization [25,26], etc.

On the basis of tailoring technology, a number of functionalized ILs tethered with acidic group have been constructed as catalysts for esterifications and transesterifications [27–30]. As for the synthesis of terpene esters, Liu et al. [31] investigated acidic ILs for the catalytic esterification of  $\alpha$ -terpineol, and found that 1-methyl-3-(3-sulfopropyl)-imidazolium dihydrogen phosphate ([HSO<sub>3</sub>-pmim][H<sub>2</sub>PO<sub>4</sub>]) exhibited terpeneol conversion of 99% and terpinyl acetate selectivity of 87%; after that, they [32,33] reported the synthesis of terpinyl acetate by esterification of  $\alpha$ -pinene with acetic acid using acidic ILs as catalysts, and found that 1-(3-sulfonic acid)propyl-3-poly(ethylene glycol) octadecylamine polyoxyethylene ethertetrafluoroborate ([PAC1815][BF<sub>4</sub>]) was an excellent catalyst.

A significant progress has been achieved in the performance of acidic ILs for the catalytic synthesis of terpene esters (e.g.,

\* Corresponding authors.

E-mail addresses: [djtao@jxnu.edu.cn](mailto:djtao@jxnu.edu.cn) (D.-J. Tao), [cxsg66cn@jxnu.edu.cn](mailto:cxsg66cn@jxnu.edu.cn) (X.-S. Chen).

conversion and selectivity), which is believed to be mainly determined by the acidity of ILs. However, the relationship between acidity and catalytic performance of acidic ILs has not been studied yet. In this work, we designed and synthesized a series of sulfonic functionalized ionic liquids (SFILs) with different acidity. Through investigating the effect of acidity of SFILs on their performance for catalyzing the esterification of terpenols, we demonstrated how to obtain the optimized conversion of terpenols and selectivity of terpene esters by tuning the acidity of SFILs.

## Experimental

### Materials

Tetramethylethylenediamine (99 wt.%), triethylamine (99 wt.%), acetic anhydride ( $\geq 98$  wt.%), sulfuric acid (98 wt.%), methanesulfonic acid (99 wt.%), 1,3-propyl sultone (99 wt.%) and 1,4-butyl sultone (99 wt.%), geraniol (98 wt.%), nerol (98 wt.%), citronellol (95 wt.%), terpineol (95 wt.%), dihydromyrcenol (99.5 wt.%), tetrafluoroboric acid (40 wt.% aqueous solution), hydrochloric acid (20 wt.% aqueous solution), and phosphoric acid (85 wt.% aqueous solution) were purchased from Aladdin Chemical Reagent Co. Ltd., Shanghai, China. Amberlyst-15 was obtained from Rohm and Haas Co. Ltd., Shanghai, China. All the chemicals were used as received without further purification.

### Synthesis and characterization of SFILs

Six sulfonic functionalized ionic liquids (SFILs), namely *N,N,N',N'*-tetramethyl-*N,N'*-dipropanesulfonic ethylenediammonium hydrogensulfate ( $[\text{Ps}_2\text{TMEDA}][\text{HSO}_4]_2$ ), *N,N,N',N'*-tetramethyl-*N,N'*-dipropanesulfonic ethylenediammonium tetrafluoroborate ( $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$ ), *N,N,N',N'*-tetramethyl-*N,N'*-dipropanesulfonic ethylenediammonium dihydrogenphosphate ( $[\text{Ps}_2\text{TMEDA}][\text{H}_2\text{PO}_4]_2$ ), *N*-butanesulfonic triethylammonium hydrogensulfate ( $[\text{BsEt}_3\text{N}][\text{HSO}_4]$ ), *N*-propanesulfonic triethylammonium chloride ( $[\text{PsEt}_3\text{N}][\text{Cl}]$ ) and *N*-propanesulfonic triethylammonium nitrate ( $[\text{PsEt}_3\text{N}][\text{NO}_3]$ ), were designed in this work, and their chemical structures are shown in Scheme 1. They were synthesized according to our previous work [20]. Taking  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  as an example: ethanol (20 mL) and tetramethylethylenediamine (6.96 g, 0.06 mol) were charged into a 100 mL round bottom

flask. After that, 1,3-propyl sultone (14.64 g, 0.12 mol) was added dropwise with stirring at 343.15 K and the reaction was kept for 12 h; the intermediate product (*N,N,N',N'*-tetramethyl-*N,N'*-diproplylsultone) was washed repeatedly with diethyl ether to remove non-ionic residues and further dried under vacuum at 353.15 K for 8 h; *N,N,N',N'*-tetramethyl-*N,N'*-diproplylsultone (10.8 g, 0.03 mol) was loaded into a 250 mL round bottom flask, then an aqueous solution of tetrafluoroboric acid (5.27 g, 0.06 mol) was added dropwise with stirring at 343.15 K and the reaction was kept for 8 h; resulted product was washed repeatedly with acetone to remove unreacted inner salts and dried under vacuum at 353.15 K for 12 h to afford  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  with a yield of 92%.

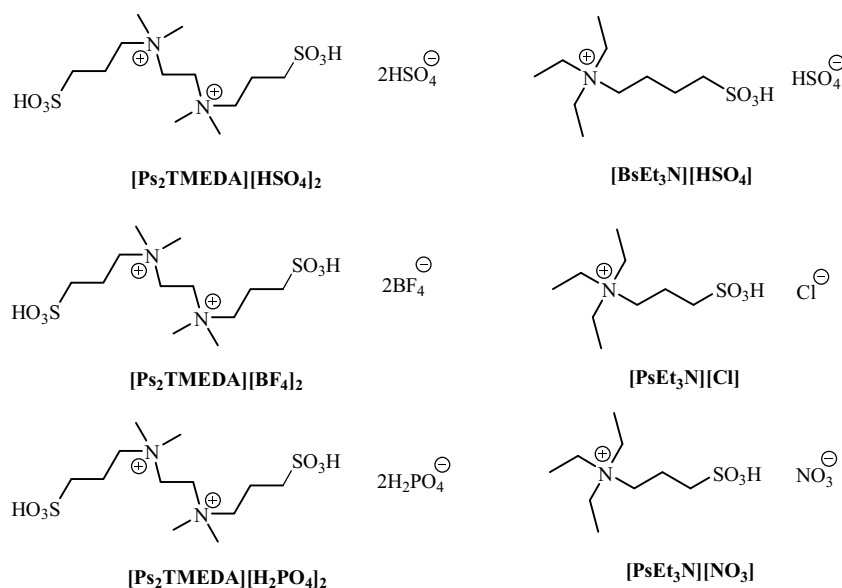
The preparation procedures of  $[\text{Ps}_2\text{TMEDA}][\text{HSO}_4]_2$ ,  $[\text{Ps}_2\text{TMEDA}][\text{H}_2\text{PO}_4]_2$ ,  $[\text{BsEt}_3\text{N}][\text{HSO}_4]$ ,  $[\text{PsEt}_3\text{N}][\text{Cl}]$ , and  $[\text{PsEt}_3\text{N}][\text{NO}_3]$  are similar to that in the case of  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$ . Then the chemical structures of SFILs were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (Bruker Ascend 400), FTIR spectra (Thermo Nicolet 870), elemental analysis (Elementar Vario E1 III) and thermal analysis (Netzsch STA 449C). Characterization results are presented in the Supporting information.

### Measurement of acidity

The acidity of SFILs was measured by both IR spectra (Thermo Nicolet 870) and pH-meter (PHS-3F). The IR spectra was collected for mixtures of SFIL and pyridine with the volume ratio of 1:5. For Brønsted acids, a new absorption peak will appear at around  $1540\text{ cm}^{-1}$  in the IR spectra of SFIL + pyridine mixtures in relation to that of pure pyridine, which indicates the formation of protonated pyridine cation. For Lewis acids, a new absorption peak will appear at around  $1450\text{ cm}^{-1}$ , which indicates the coordination of pyridine to the Lewis acidic center. The intensity of this peak can be used to characterize the Brønsted acidity of SFILs [34,35]. On the other hand, the pH values of aqueous solutions of SFILs (0.025 mol/L) were also determined to evaluate the acidity of SFILs.

### General procedure for catalytic esterification of terpenol

Specific amount of terpenol and carboxylic anhydride were loaded into a 50 mL three-necked round bottom flask equipped with a reflux condenser. The mixture was vigorously stirred and preheated to the target temperature. After the SFIL catalyst was



**Scheme 1.** The chemical structures of sulfonic functionalized ionic liquids (SFILs).

added to the flask, the reaction was kept for specific time. During the reaction, about 0.1 mL of sample was withdrawn from the flask at regular intervals. Qualitative analyses of the sample were examined by a Thermo Trace 1300 GC-ISQ, and quantitative analyses were carried out by an Agilent HP7890B gas chromatography, which is equipped with a hydrogen flame ionization detector (FID) and a capillary column HP-5 (methyl polysiloxane, 30 m × 0.32 mm × 1 μm), using nitrogen as the carrier gas at a flow rate of 3 mL/min. The temperatures of injector and detector were both kept at 523.15 K. After the completion of reaction, the mixture was cooled down to room temperature to form a solid–liquid biphasic, which can be easily separated by filtration. The liquid phase mainly contains terpene ester product and unreacted reactants, while the solid phase mainly contains SFIL catalyst and was recycled by drying under vacuum at 363.15 K for 12 h.

## Results and discussion

### Acidity of SFILs

Fig. 1 shows the IR spectra of pure pyridine and SFIL + pyridine mixtures. A new absorption peak appeared at around 1540 cm<sup>-1</sup> in the IR spectra of SFIL + pyridine mixtures relative to that of pure pyridine, indicating the Brønsted acidic nature of SFILs. According to the intensity of this peak, the sequence of acidity of the six SFILs designed and synthesized in this work is: [Ps<sub>2</sub>TMEDA][HSO<sub>4</sub>]<sub>2</sub> > [BsEt<sub>3</sub>N][HSO<sub>4</sub>] > [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> > [Ps<sub>2</sub>TMEDA][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub> > [PsEt<sub>3</sub>N][NO<sub>3</sub>] > [PsEt<sub>3</sub>N][Cl]. This is in consistency with the pH values of aqueous solutions of SFILs, as presented in Table 1.

It is validated from the acidity order and the pH values that tuning the cationic and anionic structures of SFILs can smoothly affect on their Brønsted acidities. The acid strength of these six SFILs could be divided into three ranges. [Ps<sub>2</sub>TMEDA][HSO<sub>4</sub>]<sub>2</sub> and [BsEt<sub>3</sub>N][HSO<sub>4</sub>] show the strongest acidities because of both of them including two kinds of acidic group—alkyl sulfonic acid and hydrogensulfate, implying that they may be similar to the nature of H<sub>2</sub>SO<sub>4</sub>. [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> and [Ps<sub>2</sub>TMEDA][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub> exhibit the less acidities than [BsEt<sub>3</sub>N][HSO<sub>4</sub>] and [Ps<sub>2</sub>TMEDA][HSO<sub>4</sub>]<sub>2</sub>, due to their relatively weak acidities of anions. In addition, the anions of [NO<sub>3</sub>] and [Cl] are demonstrated to be fairly neutral, resulting in the lowest acidities of [PsEt<sub>3</sub>N][NO<sub>3</sub>] and [PsEt<sub>3</sub>N][Cl].

### Effect of acidity of SFILs on their catalytic performance

The performance of SFILs for catalytic synthesis of terpene esters was screened first, taking the reaction of geraniol with acetic

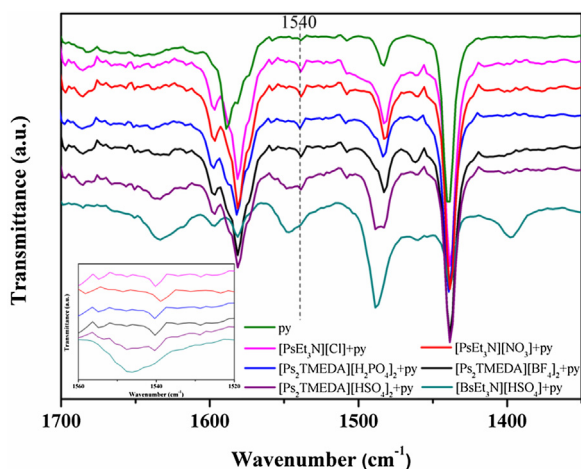


Fig. 1. IR spectra of pure pyridine and SFIL + pyridine mixtures.

Table 1

The pH values of aqueous solutions of SFILs.<sup>a</sup>

SFILs	pH values
[Ps <sub>2</sub> TMEDA][HSO <sub>4</sub> ] <sub>2</sub>	1.42
[BsEt <sub>3</sub> N][HSO <sub>4</sub> ]	1.54
[Ps <sub>2</sub> TMEDA][BF <sub>4</sub> ] <sub>2</sub>	1.64
[Ps <sub>2</sub> TMEDA][H <sub>2</sub> PO <sub>4</sub> ] <sub>2</sub>	1.83
[PsEt <sub>3</sub> N][NO <sub>3</sub> ]	3.46
[PsEt <sub>3</sub> N][Cl]	5.05

<sup>a</sup> The concentration of SFILs was 0.025 mol/L and the pH values were determined at 25 °C.

anhydride as an example. The reaction was conducted at 313.15 K for 0.5 h, with the geraniol/acetic anhydride molar ratio of 1:2 and the catalyst loading of 0.5 mol% (based on the amount of geraniol). Results are summarized in Table 2. In addition, the conversion of geraniol and selectivity of geranyl acetate are plotted against the acidity of SFILs to better illustrate the effect of acidity of SFILs on their catalytic performance, as shown in Fig. 2. It can be seen that [BsEt<sub>3</sub>N][HSO<sub>4</sub>], [Ps<sub>2</sub>TMEDA][HSO<sub>4</sub>]<sub>2</sub> and [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> have the highest conversions of geraniol (96–98%) among the six SFILs investigated. This is in consistency with their strong acidity. Generally speaking, SFILs with stronger acidity exhibit higher conversions of geraniol. However, the variation of selectivity of geranyl acetate with the acidity of SFILs is totally different. For example, [Ps<sub>2</sub>TMEDA][HSO<sub>4</sub>]<sub>2</sub> has the lowest selectivity of 79%, even though its acidity is the strongest.

Scheme 2 shows the possible mechanism for the reaction of geraniol with acetic anhydride in presence of acid catalysts [32,33]. A carbonium intermediate forms in the first step due to the dihydroxylation reaction. However, the carbonium is likely to rearrange if the acidity of catalyst is too strong, which results in various side reactions. Obviously, the acidity of catalysts plays an important role in determining the reaction pathway. It can be observed from Fig. 2 that SFILs with too weak acidity are accompanied with low conversion of geraniol, while SFILs with too strong acidity are accompanied with low selectivity of geranyl acetate. As a result, the acidity of SFIL should be tuned to a proper value to achieve a balance between conversion and selectivity. To this end, [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> is the best candidate, which displays not only high conversion of geraniol (96%) but also superior selectivity of geranyl acetate (97%) in comparison with other SFILs.

For comparison, we investigated the esterification of geraniol in the presence of other acid catalysts such as general acidic ILS [36,37], mineral acids (H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>), and acidic cation-exchange resin (Amberlyst-15). Results are presented in Table 2. It can be seen that the SFIL [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> with optimized acidity have a comparable conversion of geraniol but higher

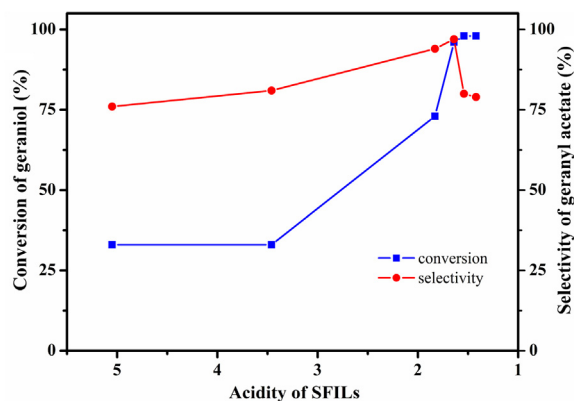
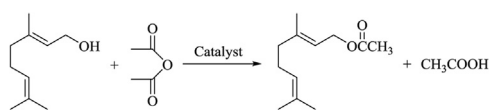


Fig. 2. Effect of acidity of SFILs (denoted as the pH values of 0.025 mol/L aqueous solutions) on the conversion of geraniol and selectivity of geranyl acetate.

**Table 2**Performance of different catalysts for the esterification of geraniol with acetic anhydride.<sup>a</sup>

Entry	Catalyst	Conversion of geraniol (%)	Selectivity of geranyl acetate (%)
1	[BSEt <sub>3</sub> N][HSO <sub>4</sub> ]	98	80
2	[Ps <sub>2</sub> TMEDA][HSO <sub>4</sub> ] <sub>2</sub>	98	79
3	[Ps <sub>2</sub> TMEDA][BF <sub>4</sub> ] <sub>2</sub>	96	97
4	[Ps <sub>2</sub> TMEDA][H <sub>2</sub> PO <sub>4</sub> ] <sub>2</sub>	73	94
5	[PSEt <sub>3</sub> N][NO <sub>3</sub> ]	32	81
6	[PSEt <sub>3</sub> N][Cl]	33	76
7	[BsMim][HSO <sub>4</sub> ]	99	84
8	[Hmpy][HSO <sub>4</sub> ]	75	62
9	[Bmim][HSO <sub>4</sub> ]	31	61
10	H <sub>2</sub> SO <sub>4</sub>	99	81
11	H <sub>3</sub> PO <sub>4</sub>	47	86
12	Amberlyst-15	45	90

<sup>a</sup> Reaction temperature 313.15 K, reaction time 0.5 h, molar ratio of geraniol to acetic anhydride 1:2, and catalyst loading 0.5 mol%.

selectivity of geranyl acetate in relation to [BsMim][HSO<sub>4</sub>] and H<sub>2</sub>SO<sub>4</sub>. Compared with [Hmpy][HSO<sub>4</sub>], [Bmim][HSO<sub>4</sub>], H<sub>3</sub>PO<sub>4</sub>, and Amberlyst-15, [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> is significantly superior in both conversion and selectivity. From this comparison, it can be concluded that SFILs with tunable acidity are a class of promising catalysts for the production of terpene esters due to their controllable activity.

#### Recycle of SFILs

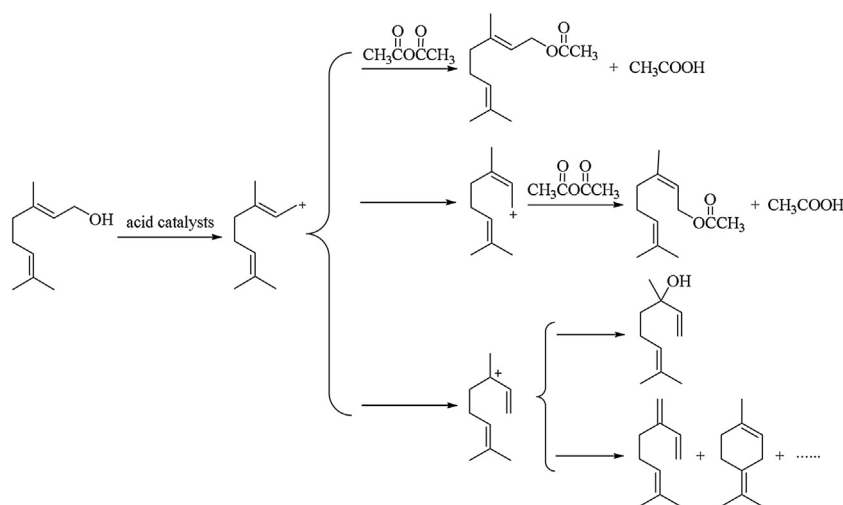
The reusability of catalysts is very important for their industrial applications. A significant issue with traditional inorganic and organic strong acids (e.g., H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CH<sub>3</sub>SO<sub>3</sub>H) is that they are difficult to recycle [38]. This leads to the production of large amount of waste acids, which is a huge threat to the environment. To test the reusability of SFILs in the catalytic esterification of geraniol, [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> was selected as an example due to its highest performance. The reaction system with [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> as the catalyst was cooled down to room temperature after the completion of esterification. It is surprisingly found that the mixture splits into a solid–liquid biphase, as shown in Scheme 3. The liquid phase mainly contains geranyl acetate and unreacted

reactants, while the solid phase mainly contains [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub>. The phase split is caused by the limit solubility of [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> in esters under room temperature. Thus [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> can be easily separated from products by filtration. Then [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> was dried under vacuum at 363.15 K for 12 h and used for the catalytic esterification of geraniol again. [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> was reused for 5 times and results are shown in Fig. 3. As can be seen, the reusability of [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> is fairly good with only a slight decrease in the conversion of geraniol, which may be caused by the loss of partial catalyst during handling.

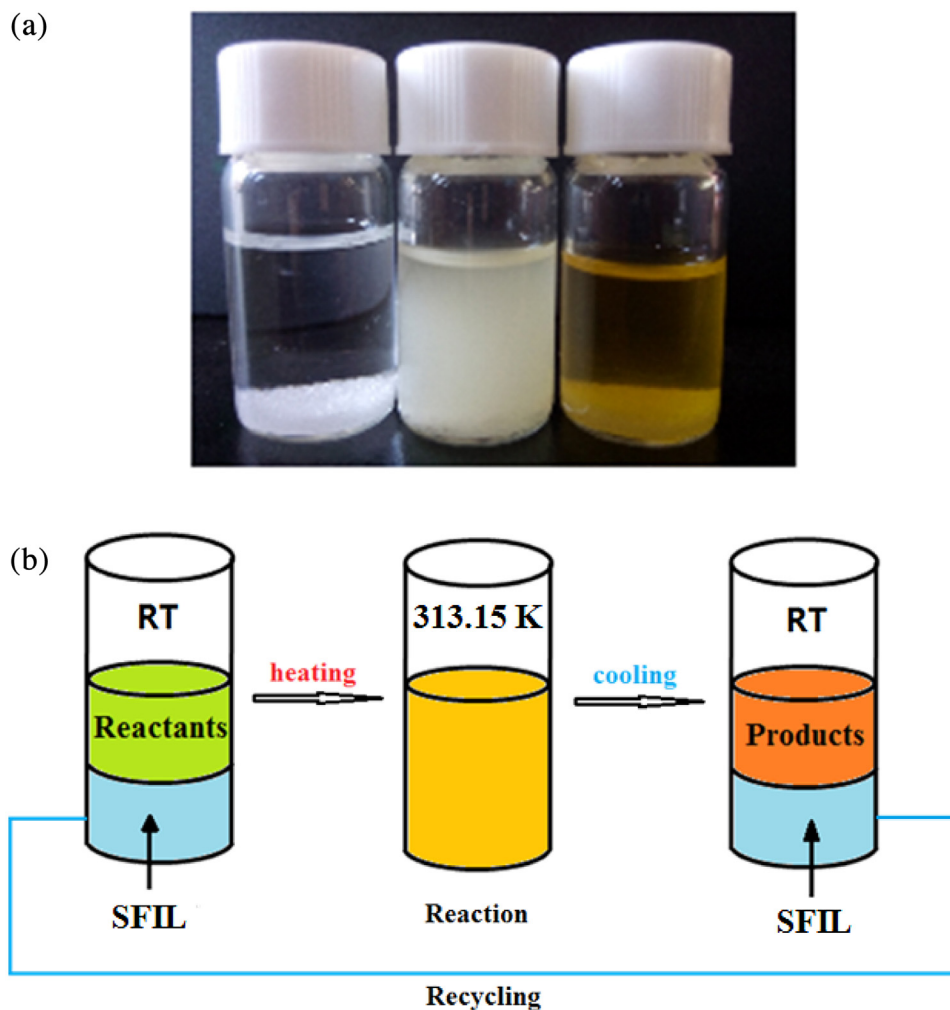
#### Optimization of reaction conditions

To find the best conditions for [Ps<sub>2</sub>TMEDA][BF<sub>4</sub>]<sub>2</sub> in the catalytic esterification of geraniol, we investigated the effect of reaction temperature, reaction time, catalyst loading and reactants ratio on the conversion of geraniol and selectivity of geranyl acetate.

The effect of reaction temperature was examined in the range of 298.15–333.15 K with reaction time of 0.5 h, geraniol/acetic anhydride molar ratio of 1:2 and catalyst loading of 0.5 mol%. Results are illustrated in Fig. 4a. As the reaction temperature



**Scheme 2.** The possible mechanism for the reaction of geraniol with acetic anhydride in the presence of acid catalysts.



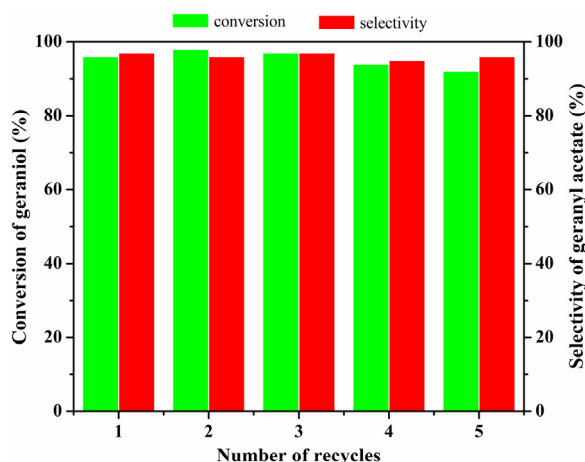
**Scheme 3.** Phase split of reaction system with  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  as catalyst.

increases from 298.15 to 313.15 K, the conversion of geraniol increases from 72% to 96%, while the selectivity of geranyl acetate almost remains unchanged ( $\sim 97\%$ ). The positive effect of reaction temperature on conversion in this range can be explained by the enhancement of reaction rate. However, as the reaction temperature further increases from 313.15 to 333.15 K, the conversion of

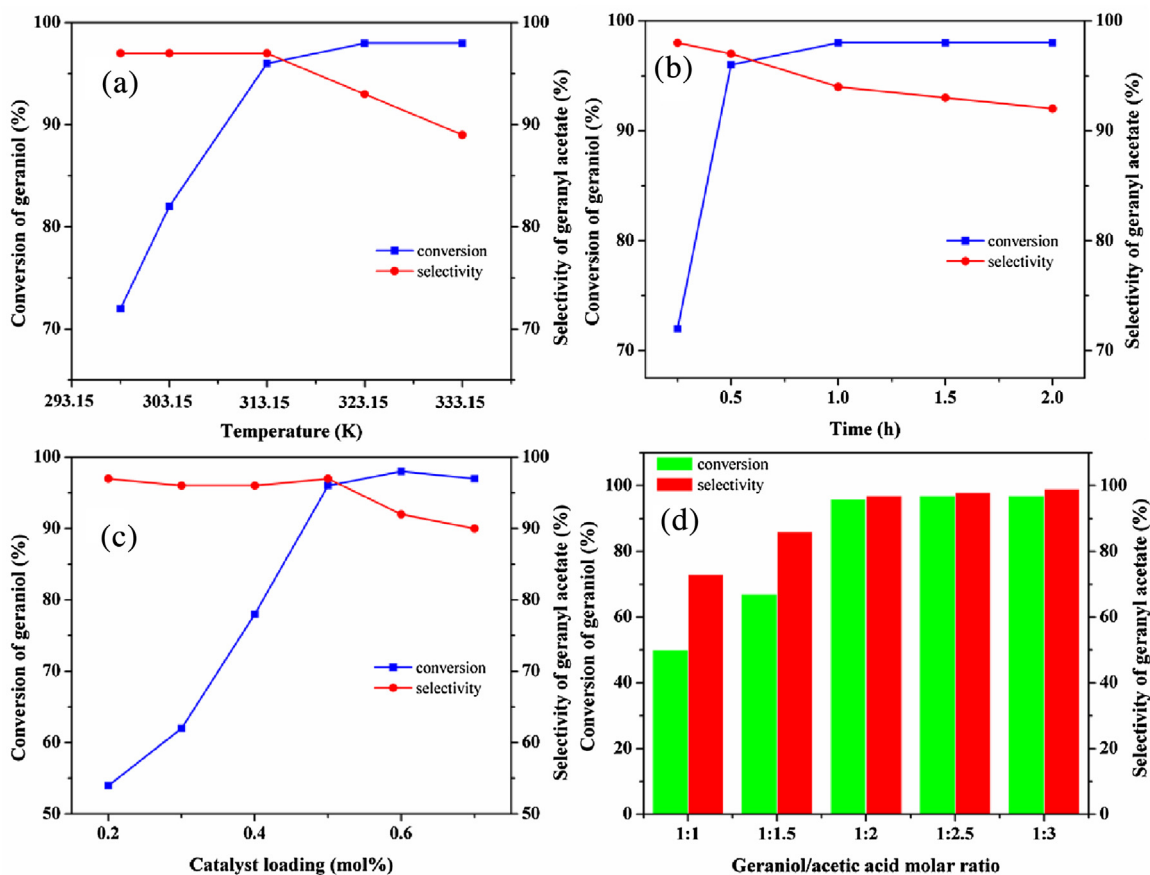
geraniol remains almost unchanged, while the selectivity of geranyl acetate starts to decrease. The negative effect of reaction temperature on selectivity in this range should be caused by the enhancement of side reactions. Therefore, an excessive reaction temperature is unfavorable for the esterification of geraniol and 313.15 K is regarded as the optimal reaction temperature.

The effect of reaction time was examined in the range of 0.25–2 h with reaction temperature of 313.15 K, geraniol/acetic anhydride molar ratio of 1:2 and catalyst loading of 0.5 mol%. Results are illustrated in Fig. 4b. The conversion of geraniol increases notably to 96% in the first 0.5 h but remains almost unchanged as reaction proceeds. In contrast, the selectivity of geranyl acetate gradually decreases as reaction proceeds, indicating the accumulation of byproducts with extended reaction time. As a result, 0.5 h is identified as the optimal reaction time.

The effect of catalyst loading was examined in the range of 0.2–0.7 mol% with reaction temperature of 313.15 K, reaction time of 0.5 h and geraniol/acetic anhydride molar ratio of 1:2. Results are illustrated in Fig. 4c. As the catalyst loading increases from 0.2 mol% to 0.5 mol%, the conversion of geraniol increases remarkably from 54% to 96%, while the selectivity of geranyl acetate almost remains unchanged ( $\sim 97\%$ ). The positive effect of catalyst loading on conversion in this range can be attributed to the enhancement of acidity in the reaction system, which is an important factor to promote the esterification reaction. However,



**Fig. 3.** Recycling of  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  for catalytic esterification of geraniol.



**Fig. 4.** Effect of (a) reaction temperature, (b) reaction time, (c) catalyst loading, and (d) geraniol/acetic anhydride molar ratio on the esterification of geraniol using  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  as catalyst.

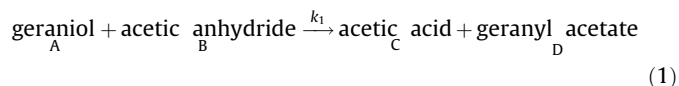
as the catalyst loading further increases from 0.5 mol% to 0.7 mol%, the conversion of geraniol remains almost unchanged, while the selectivity of geranyl acetate starts to decrease. The negative effect of catalyst loading on selectivity in this range should be caused by the enhancement of side reactions. Consequently, an excessive acidity is unfavorable for the esterification of geraniol and 0.5 mol% is regarded as the optimal catalyst loading.

The effect of geraniol/acetic anhydride molar ratio was examined in the range of 1:1–1:3, with reaction temperature of 313.15 K, reaction time of 0.5 h, catalyst loading of 0.5 mol%. Results are illustrated in Fig. 4d. As the geraniol/acetic anhydride molar ratio increases from 1:1 to 1:2, the conversion of geraniol increase significantly from 50–96%. The reason for this phenomenon is that excess amount of acetic anhydride can shift the reaction equilibrium toward products. As the geraniol/acetic anhydride molar ratio further increases from 1:2 to 1:3, the conversion of geraniol remains almost unchanged, which is limited by stoichiometrics. It should be noted that the geraniol/acetic anhydride molar ratio has no obvious effect on the selectivity of geranyl acetate. Thus, the optimal geraniol/acetic anhydride molar ratio for the production of geranyl acetate is 1:2.

#### Kinetics study

Since the reaction of geraniol with acetic anhydride proceeds very fast under the optimal conditions, the study of kinetics for  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  in the catalytic esterification of geraniol was carried out in the temperature range of 313.15–333.15 K with reaction time of 2 h, catalyst loading of 0.14 mol% and geraniol/acetic anhydride molar ratio of 1:1.

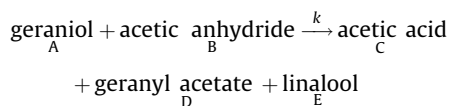
As shown in Scheme 2, the main reaction can be expressed as:



The secondary reaction is:



Then the total reaction can be expressed as:



The pseudohomogeneous (PH) model is widely used to describe the kinetics of liquid-phase reactions, in which reactants or solvents with high polarity are present [25,39,40]. Herein, the PH model was also used to describe the kinetics of esterification of geraniol catalyzed by  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$ . The rate equations for Reactions (1),(2) and the total Reaction (3) are:

$$\frac{dC_D}{dt} = k_1 C_A C_B \quad (4)$$

$$\frac{dC_E}{dt} = k_2 C_A \quad (5)$$

$$-\frac{dC_A}{dt} = k_1 C_A C_B + k_2 C_A \quad (6)$$

**Table 3**Calculated reaction rate constants at different temperatures.<sup>a</sup>

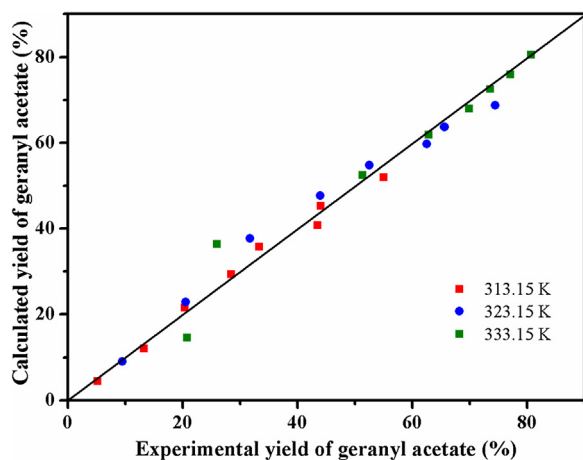
Temperature (K)	$k_1$ ( $\times 10^3$ L/mol/min)	$k_2$ ( $\times 10^4$ /min)
313.15	2.329	0.5450
323.15	5.049	1.365
333.15	9.696	2.583

<sup>a</sup> Reactions were carried out with reaction time of 2 h, catalyst loading of 0.14 mol % and geraniol/acetic acid molar ratio of 1:1.

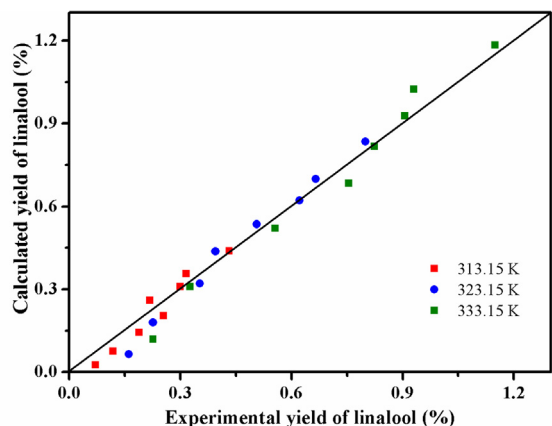
The reaction rate constants  $k_1$  and  $k_2$  can be estimated according to experimental data with Eqs. (4)–(6). And the values of  $k_1$  and  $k_2$  at different temperatures are given in Table 3. The PH model was used to describe the experimental kinetic data. A comparison was drawn (shown in Figs. 5 and 6) between the calculated and the experimental yields of the two products at different temperatures. It can be observed that the kinetic model is in good agreement with the experimental data, showing that the PH model is reliable enough for the study of the kinetics of esterification of geraniol in the presence of  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$ .

Moreover, with the reaction rate constants  $k_1$  and  $k_2$  at different temperatures, the activation energies and pre-exponential factors of Reactions (1) and (2) can be calculated according to the Arrhenius law by drawing a linear fit between  $\ln k$  and  $1/T$ :

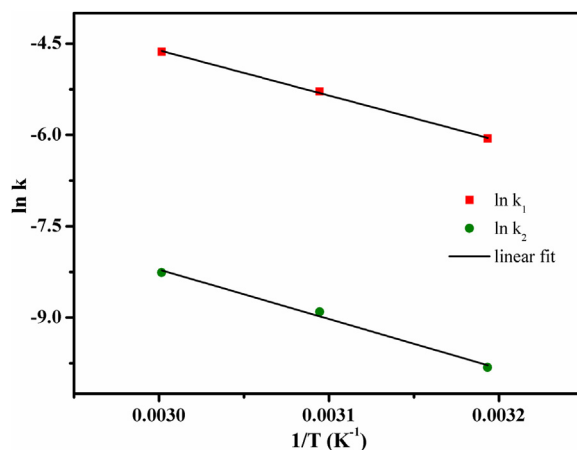
$$k = Ae^{\frac{E_a}{RT}} \quad (7)$$



**Fig. 5.** Comparison between the experimental and the calculated yield of geranyl acetate at different temperatures.



**Fig. 6.** Comparison between the experimental and the calculated yield of linalool at different temperatures.



**Fig. 7.** Arrhenius plots for the reaction of geraniol with acetic anhydride.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

The results of linear fit are presented in Fig. 7. The values of activation energies  $E_{a1}$  and  $E_{a2}$  are calculated to be 61.8 and 67.6 kJ/mol, respectively. And the values of pre-exponential factors  $A_1$  and  $A_2$  are calculated to be  $4.88 \times 10^7$  and  $1.06 \times 10^7$ , respectively. Therefore, the equation of the reaction rate constants can be written as:

$$k_1 = 4.88 \times 10^7 e^{-\frac{61.8 \times 10^3}{RT}} \quad (9)$$

$$k_2 = 1.06 \times 10^7 e^{-\frac{67.6 \times 10^3}{RT}} \quad (10)$$

It is obvious that the activation energy of Reaction (1) is lower than that of Reaction (2) ( $E_{a1} < E_{a2}$ ), implying that a relatively low temperature is beneficial for the main reaction while elevated temperature is beneficial for the secondary reaction. This is in consistency with the negative effect of reaction temperature on the selectivity of geranyl acetate demonstrated in Fig. 4a.

#### Esterification of other terpenols

To further investigate the wide applicability of acidity-tunable SFILs in the catalytic esterification of other terpenols,  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  was tested for catalyzing the reaction of nerol, citronellol, dihydromyrcenol and terpinol with acetic anhydride. The results are summarized in Table 4. As can be seen,  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$

**Table 4**Esterification of different terpenols with acetic anhydride using  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  as catalyst.<sup>a</sup>

Entry	Terpenols	Conversion of terpenols (%)	Selectivity of terpene acetate (%)
1	Geraniol <sup>b</sup>	96	97
2	Nerol <sup>c</sup>	97	97
3	Citronellol <sup>d</sup>	96	97
4	Dihydromyrcenol <sup>e</sup>	93	96
5	Terpinol <sup>e</sup>	96	87

<sup>a</sup> Reaction time: 0.5 h, catalyst loading: 0.5 mol%, terpenol/acetic anhydride molar ratio: 1:2.

<sup>b</sup> Reaction temperature: 313.15 K.

<sup>c</sup> Reaction temperature: 318.15 K.

<sup>d</sup> Reaction temperature: 323.15 K.

<sup>e</sup> Reaction temperature: 333.15 K.

displays excellent performance for the synthesis of terpene esters, with the conversion of terpenols of 93–97% and the selectivity of terpene esters of 87–97%. However, traditional acid catalysts  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and Amberlyst-15 were found to be significantly inferior in both conversion and selectivity (Table S1 in the Supporting information). The results imply the wide applicability of acidity-tunable SFILs in the production of various terpene esters.

## Conclusions

In summary, a new methodology based on tuning the acidity of ILs catalysts for enhancing the esterification of terpenols was developed in this work. Through investigating the effect of acidity of SFILs on the conversion of geraniol and selectivity of geranyl acetate, it is found the catalytic performance of SFILs can be optimized by adjusting their acidity to a moderate value. The best SFIL ( $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$ ) displays excellent activity in the catalytic synthesis of geranyl acetate, with the conversion of geraniol of 96% and selectivity of geranyl acetate of 97%, being superior to traditional acid catalysts.  $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$  is also featured with fairly good reusability and wide applicability in the esterification of other terpenols. The strategy introduced herein opens up a new opportunity to improve the efficiency of current industrial process for the production of terpene esters.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jiec.2016.07.014>.

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