



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



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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 H₂SO₄ and H₃PO₄ [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 α -terpineol, and found that 1-methyl-3-(3-sulfopropyl)-imidazolium dihydrogen phosphate ([HSO₃-pmim][H₂PO₄]) 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 α -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][BF₄]) 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.,

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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 (≥ 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'*-dipropanesulfone) 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'*-dipropanesulfone (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%.

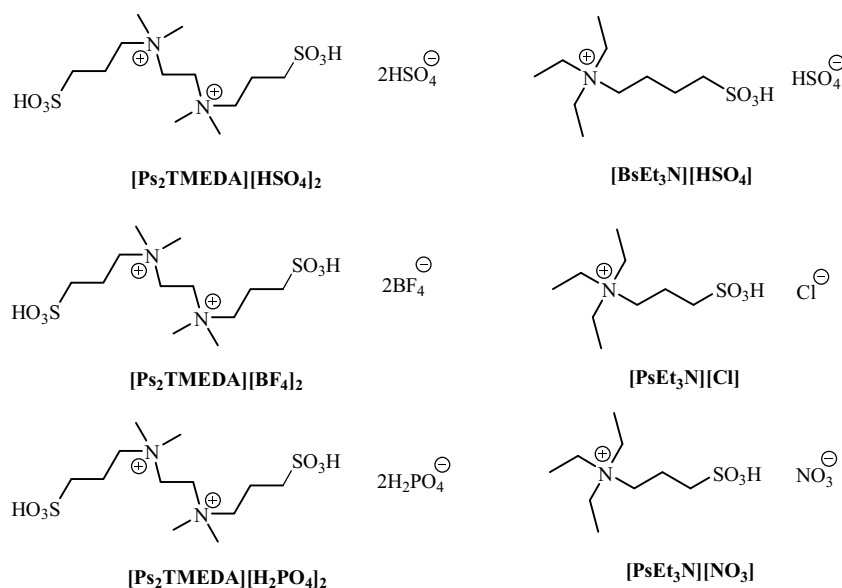
The preparation procedures of $[\text{Ps}_2\text{TMEDA}][\text{HSO}_4]_2$, $[\text{Ps}_2\text{TMEDA}][\text{H}_2\text{PO}_4]_2$, $[\text{BsEt}_3\text{N}][\text{HSO}_4]$, $[\text{PsEt}_3\text{N}][\text{Cl}]$, and $[\text{PsEt}_3\text{N}][\text{NO}_3]$ are similar to that in the case of $[\text{Ps}_2\text{TMEDA}][\text{BF}_4]_2$. Then the chemical structures of SFILs were characterized by ^1H NMR and ^{13}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 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 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).

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