The sulfonic acid-functionalized ionic liquids with pyridinium cations: Acidities and their acidity–catalytic activity relationships

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Abstract

The Brønsted acidities of sulfonic acid-functionalized ionic liquids (SFILs) with pyridinium cations were investigated. The Hammett function values of SFILs are between -1.5 and -3.6 at $110\,^\circ$C. The acidities of SFILs depend on the anions, and have the order as follows: [PSPy][BF$_4$] > [PSPy][HSO$_4$] > [PSPy][pTSA] > [PSPy][H$_2$PO$_4$] ([PSPy] = N-propane–sulfonic acid pyridinium). The acidity order of SFILs is consistent with their activity order observed in some acid-catalyzed reactions. The minimum-energy geometries of SFILs manifest that anions have strong interactions with the sulfonic acid proton. It is considered that in addition to the alkyl sulfonic acid group, the anion is likely to serve as available acid sites. Hence the acidities and catalytic activities of SFILs depend on the kinds of anions.
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Keywords: Sulfonic acid-functionalized ionic liquid; Pyridinium cation; Brønsted acidity; Ab initio calculation

1. Introduction

Ionic liquids, when used for replacing classical organic solvents, offer a new and environmentally benign approach toward modern chemical processes [1–4]. The implementation of task-specific ionic liquids further enhances the versatility of ionic liquids for the cases where both reagent and medium are coupled [5–8].

One of the increasing interests about task-specific ionic liquids focuses on designing acidic ionic liquids to replace traditional homogenous and heterogeneous acids in chemical processes. Such acidic ionic liquids have the potential as dual solvent-catalysts for the organic reactions. It is well known that the ionic liquids with metal halide anions manifest Lewis acidity, especially those based upon chloroaluminate anions. However, these ionic liquids are sensitive to moisture and unstable in water [1,2,9]. So, the preparation and application of such types of ionic liquids often needs extreme operational conditions. Therefore, the development of water-stable acidic ionic liquid is highly desirable.

One approach to designing water-stable acidic ionic liquids was to introduce the acidity in the anions. Keim and Wasserscheid prepared imidazolium salts with [HSO$_4{}^-$] as anion [10]. The ionic liquids were used as Brønsted acidic catalysts for the esterifications [11,12] and alkylation reaction [13]. Furthermore, some acids could react directly with N-alkylimidazole or N-alkylpyridine to form acidic ionic liquids, which bear an acidic proton on nitrogen atom of imidazolium or pyridinium [14,15]. The acidic ionic liquids have been used as acid catalysts for the alkylation reaction [15], esterification [14,15], Mannich reaction [16], Biginelli condensation [17] and Friedlander annulation [18].

Another efficient approach to designing water-stable acidic ionic liquids was to introduce the functional acidic group on the cation. Fei et al. [19] prepared imidazolium salts with one or two carboxylic acid substituent groups. However, the acidities of all the salts are weak, and pK_a values of all the salts lie between 1.33 and 4.59 at $25\,^\circ$C [19]. Recently, a new Brønsted acidic ionic liquid emerged, which bears an alkyl sulfonic acid group in cations. Cole et al. [20] firstly synthesized Brønsted acidic ionic liquids that bear an alkyl sulfonic acid group in imidazolium cations or triphenylphosphine cations. In a previous work, we synthesized Brønsted acidic ionic liquids that bear an alkyl sulfonic acid group in pyridinium cations with different
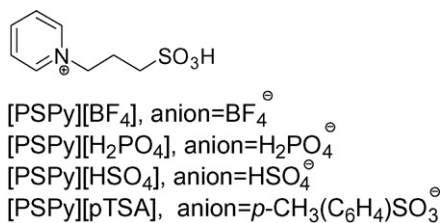

Fig. 1. The structures of sulfonic acid-functionalized ionic liquids with pyridinium cations.

Table 1
H_0 values of the SFILs with different anions at 110 °C

SFILs	Water content of SFILs (%)	[I] (%)	[HI] (%)	H_0
[PSPy][BF$_4$]	5.7	33	67	-3.6[a]
[PSPy][HSO$_4$]	5.0	51	49	-3.3[a]
[PSPy][pTSA]	6.1	36	64	-2.1[b]
[PSPy][H$_2$PO$_4$]	6.0	81	19	-1.2[b]
[PSPy][H$_2$PO$_4$]	2.0	65	35	-1.5[b]

[a] Indicator: 2,4-dichloro-6-nitroaniline.
[b] Indicator: 2,5-dichloro-4-nitroaniline.

anions [21]. The structures of the sulfonic acid-functionalized ionic liquids (SFILs) with pyridinium cations are shown in Fig. 1, where [PSPy] was *N*-propane sulfonic acid pyridinium. The SFILs are water-stable, nonvolatile, noncorrosive and immiscible with many organic solvents.

The applications of the Brønsted acidic ionic liquids with alkyl sulfonic acid group in cations as replacement of conventional homogenous and heterogeneous acids have received great attention. Recently, these kind of Brønsted acidic ionic liquid have been used as acid catalysts for the esterification [21–23], alkylation reaction [24,25], Pechmann reactions [26], acetalization and oligomerization of branched olefins [27], cyclization of 1-dodecene [28], and the synthesis of tetraarylporphyrins [29] and D,L-α-tocopherol [30].

The acidity of ionic liquid is the important property relevant to its catalytic activity for acid-catalyzed reactions. So far,
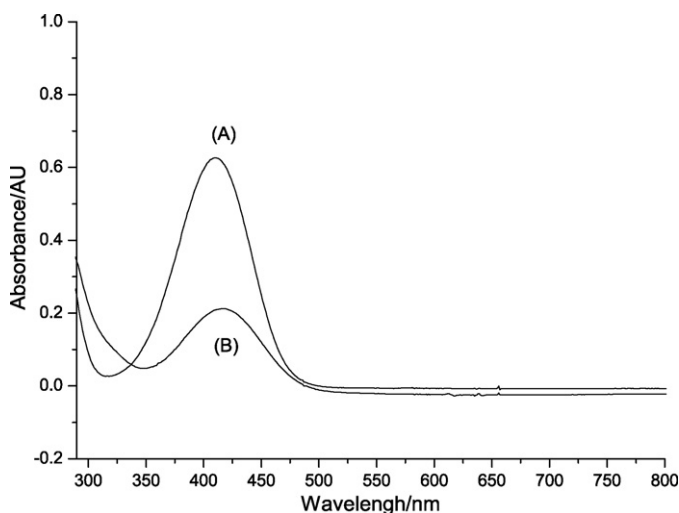

Fig. 2. Absorption spectra of 0.025 mg/ml 2,4-dichloro-6-nitroaniline in ethanol (A) and [PSPy][BF$_4$] (B).

the fundamental studies on the acidities of the Brønsted acidic ionic liquids and their acidity–catalytic activity relationships are relatively rare. In our previous work of using the SFILs with different anions in the esterification reactions [21] and the synthesis of D,L-α-tocopherol [30], we found that the catalytic activities of the SFILs were dependent on the kinds of anions. SFILs with [BF$_4^-$] and [HSO$_4^-$] as anions showed the best catalytic activity, and the catalytic activities of SFILs with [pTSA$^-$] and [H$_2$PO$_4^-$] as anions were poor. The phenomena imply that the kinds of anions maybe have important impact on the acidities of SFILs. In order to understand the catalytic activities of SFILs, it is necessary to study their acidities, especially the effect of anions to their acidities.

In this work, the acidities of SFILs were determined using the Hammett method with UV–vis spectroscopy, and their acidity–catalytic activity relationships were discussed. Furthermore, the acidities of SFILs were discussed at the molecular level according to their minimum-energy geometries determined by ab initio calculations.

2. Experimental

2.1. Materials and reagents

The 3-propane sulfonate pyridinium (PSPy) (97%) were purchased from WUHAN FENGFAN CHEMICAL CO. LTD., China. 2,4-Dichloro-6-nitroaniline (97%) was purchased from Aldrich. 2,5-Dichloro-4-nitroaniline (97%) was purchased from Acros. All other chemicals (analytical grade) were obtained commercially and used without further purification unless otherwise stated.

Table 2
Catalytic activities of SFILs with different anions to the esterification and the synthesis of D,L-α-tocopherol [21,30]

SFILs	The yield of tocopherol (%)[a]	The yield of ethyl benzoate (%)[b]
[PSPy][BF$_4$]	62.6	84
[PSPy][HSO$_4$]	52.6	91.5[c]
[PSPy][pTSA]	9.5	69.7
[PSPy][H$_2$PO$_4$]	<1	<1

[a] The synthesis of tocopherol were carried at 110 °C, 3 h, and the molar ratio of trimethylhydroquinone:isophytol:SFIL is 1:1:1.6; the water content of SFILs at the beginning of the reaction: [PSPy][BF$_4$] (6.8%), [PSPy][HSO$_4$] (4.5%), [PSPy][pTSA] (3.1%), [PSPy][H$_2$PO$_4$] (2.6%). The reaction systems exihibited good biphasic behaviors when reactions completed. The produced tocopherol in the light phase was isolated by decantation, and the tocopherol dissolved in the SFIL phase was extracted with ethyl acetate. The concentration of tocopherol in crude product was analyzed by HPLC (C$_{18}$ column), and the yield of tocopherol was based on the crude product.
[b] The esterifications of benzoic acid with ethanol were carried at 85 °C, 3 h, and the molar ratio of acid:ethanol:SFIL is 1:2:1. The water content of SFILs at the beginning of the reaction: [PSPy][BF$_4$] (6.0%), [PSPy][HSO$_4$] (5.3%), [PSPy][pTSA] (4.6%), [PSPy][H$_2$PO$_4$] (2.3%). The reaction systems exihibited good biphasic behaviors when reactions completed. The produced ethyl benzoate in the light phase was isolated by decantation, and the ethyl benzoate dissolved in the SFIL phase was extracted with ethyl acetate. The concentration of ethyl benzoate in the crude product was analyzed by GC (HP-FFAP), and the yield of ethyl benzoate was based on the crude product.
[c] In the experiment, 13.1% ethanol transformed into diethyl oxide.

2.2. Preparation of SFILs with pyridinium cations

The SFILs with pyridinium cations, [PSPy][BF$_4$], [PSPy][HSO$_4$], [PSPy][pTSA] and [PSPy][H$_2$PO$_4$] were prepared in a procedure similar to that reported in our previous paper [21].

The equimolar PSPy with H$_2$SO$_4$ (98% aqueous), H$_3$PO$_4$ (85% aqueous) or p-toluenesulfonic acid hydrate (pTSA·H$_2$O) were mixed and stirred for 72 h at 80 °C to form SFILs aqueous solution.

The equimolar PSPy with HBF$_4$ (40% aqueous) were mixed and stirred for 40 days at room temperature to form [PSPy][BF$_4$] aqueous solution.

The SFILs aqueous solution was dried in vacuum (<0.01 Torr) at 80 °C to remove water. However, the SFILs could not be absolutely dried. The residual water content of SFILs was 2–6% (determined by the Karl Fisher titration with a Mitsubishi moisture meter, model CA-05). It is likely that the residual water has a very strong interaction with SFILs. Then, the produced SFILs were washed repeatedly with ethyl acetate to remove the non-ionic residues, including possible unreacted acid (the four acids were all soluble in ethyl acetate). Finally, the SFILs were dried in vacuum (<0.01 Torr) at 80 °C again to remove ethyl acetate. The yields of SFILs were consistent with the theoretic values. There is no detectable extraction of free acid in the produced SFIL.

The high purity of SFILs was evaluated by NMR and MS spectrum, which were shown as follows:

[PSPy][BF$_4$]: ESI-MS m/z: [M-H]$^-$ Calcd. 288.11, found 288.06. ^{1}H NMR (300 MHz, D$_2$O), δ 8.72 (d × d, $^3J_{HH}$ = 6.6, $^4J_{HH}$ ≈ 1.3, 2H), 8.42 (t × t, $^3J_{HH}$ = 7.7, $^4J_{HH}$ ≈ 1.3, 1H), 7.94 (t, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 6.6, 2H), 4.73 (s, 1H), 4.63 (t, $^3J_{HH}$ ≈ 7.3, 2H), 2.84 (t, $^3J_{HH}$ ≈ 7.3, 2H), 2.29–2.35 (m, 2H). ^{13}C NMR (75.5 MHz, D$_2$O), δ 145.95, 144.40, 128.42, 59.91, 47.06, 26.15. ^{19}F (300 MHz, D$_2$O), −150.25, −150.30.

[PSPy][pTSA]: ESI-MS m/z: [M-H]$^-$ Calcd. 372.5, found 372.05. ^{1}H NMR (300 MHz, D$_2$O), δ 8.46 (d × d, $^3J_{HH}$ = 6.6, $^4J_{HH}$ ≈ 1.3, 2H), 8.16 (t × t, $^3J_{HH}$ = 7.7, $^4J_{HH}$ ≈ 1.3, 1H), 7.68 (t, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 6.6, 2H), 7.31 (d, $^3J_{HH}$ ≈ 8.1, 2H), 6.95 (d, $^3J_{HH}$ ≈ 8.1, 2H), 4.74 (s, 1H), 4.38 (t, $^3J_{HH}$ ≈ 7.4, 2H), 2.66 (t, $^3J_{HH}$ ≈ 7.4, 2H), 2.09–2.14 (m, 2H), 2.00 (s, 3H). ^{13}C NMR (75.5 MHz, D$_2$O), δ 145.70, 144.06, 142.15, 139.51, 129.33, 128.24, 125.22, 59.72, 46.95, 26.09, 20.40.

[PSPy][HSO$_4$]: ESI-MS m/z: [M-H]$^-$ Calcd. 298.38, found 297.99.

[PSPy][H$_2$PO$_4$]: ESI-MS m/z: [M-H]$^-$ Calcd. 298.30, found 297.97.

2.3. UV–vis acidity determination

The fresh [PSPy][BF$_4$], [PSPy][pTSA], and [PSPy][HSO$_4$] are viscous colorless liquids at room temperature. They slowly solidify at room temperature after long times (e.g., several weeks). [PSPy][H$_2$PO$_4$] is a stiff solid at room temperature, and it melts at 90 °C. Due to the relatively high melting point of [PSPy][H$_2$PO$_4$] and the poor fluidities of the SFILs, it is difficult to determinate the acidity of SFILs by the Hammett method at room temperature. So the experiments were carried out at 110 °C. For comparing the acidities of SFILs with different anions, the temperature, the indicator concentration and the water content of SFILs were almost identical in all experiments. Typical experiment procedure was as follows: pure SFILs were heated to 110 °C to form liquid with good fluidity. The weighted indicator was added into the SFIL, and the mixture was stirred for 15 min to form the solution at 110 °C (indicator concentration: 0.025 mg/ml). The concentration of the indicator in the SFIL was located within the scale of the calibration curve. The UV spectra were recorded on an Agilent 8453 UV–vis spectrophotometer at room temperature. The calibration curves with the linearity higher than 0.999 for four indicators in the unprotonated form were constructed using their ethanol solutions.

2.4. Computational methods

The minimum-energy geometries of SFILs and isolated [PSPy$^+$] cation were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level using the Gaussian98 program [31]. A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum.

3. Results and discussion

3.1. Acidities of the SFILs

The Hammett method is an effective way to evaluate the acidities of acids, and Thomazeau [32] have determined the acidities of soluble HNTf$_2$ in non-chloroaluminate ionic liquids

Table 3
The geometry parameters of SFILs calculated at RHF/6-31(d,p) level[a]

	[PSPy]	[PSPy][BF$_4$]	[PSPy][HSO$_4$]	[PSPy][pTSA]	[PSPy][H$_2$PO$_4$]
H–O bond distance of sulfonic acid (Å)	H$_{25}$–O$_{13}$ = 0.952	H$_{25}$–O$_{13}$ = 0.965	H$_{25}$–O$_{13}$ = 0.973	H$_{25}$–O$_{13}$ = 0.989	H$_{32}$–O$_{20}$ = 0.993
The distance of anion to the sulfonic acid proton (Å)		H$_{25}$···F$_{30}$ = 1.723	H$_{25}$···O$_{28}$ = 1.714	H$_{25}$···O$_{36}$ = 1.613	H$_{32}$···O$_2$ = 1.564
Other hydrogen bonds in SFILs (Å)		H$_{16}$···F$_{27}$ = 2.117, H$_{19}$···F$_{29}$ = 2.321, H$_{22}$···F$_{29}$ = 2.550, H$_{22}$···F$_{30}$ = 2.332	H$_{19}$···O$_{27}$ = 2.416, H$_{22}$···O$_{27}$ = 2.667, H$_{22}$···O$_{28}$ = 2.612, H$_{15}$···O$_{27}$ = 2.209, H$_{19}$···O$_{27}$ = 2.417	H$_{15}$···O$_{34}$ = 2.366, H$_{19}$···O$_{34}$ = 2.338, H$_{23}$···O$_{34}$ = 2.356, H$_{15}$···O$_{35}$ = 2.375	H$_{22}$···O$_4$ = 1.897, H$_{30}$···O$_2$ = 2.579, H$_{26}$···O$_4$ = 2.249

[a] Subscript is the serial number of correspondence atom in Figs. 3–6.

using this method. In the article, the Brønsted acidities of the SFILs with different anions were determined using the Hammett method with UV–vis spectroscopy at 110 °C. The Brønsted acidities were measured by evaluating the protonation extent of uncharged indicator bases (named I) in the SFILs, in terms of the measurable ratio [I]/[IH$^+$]. The Hammett function (H_0) is defined as:

$$H_0 = pK(I)_{aq} + \log\left(\frac{[I]}{[IH^+]}\right)$$

where $pK(I)_{aq}$ is the pK_a value of the indicator referred to an aqueous solution, IH$^+$ is the protonated form of indicators, and [I] and [IH$^+$] are the molar concentrations of unprotonated and protonated form of indicators in the SFILs, respectively.

The Brønsted acidities of [PSPy][H$_2$PO$_4$] and [PSPy][pTSA] were determined with 2,5-dichloro-4-nitroaniline ($pK(I)_{aq} = -1.82$) as indicator. However, 2,5-dichloro-4-nitroaniline was fully protonated in [PSPy][BF$_4$] and [PSPy][HSO$_4$], which indicated that the acidities level of [PSPy][BF$_4$] and [PSPy][HSO$_4$] were too high for this indicator. Hence, 2,4-dichloro-6-nitroaniline ($pK(I)_{aq} = -3.31$) was chosen for [PSPy][BF$_4$] and [PSPy][HSO$_4$].

In the UV–vis spectra, the unprotonated forms of both indicators have specific absorption peaks. However, the protonated forms of the indicators cannot be seen due to their peak loca-

tion, probably below 300 nm, which is masked by the spectrum of the SFILs. In a typical spectra shown in Fig. 2, the absorbance of the unprotonated form of the indicator in [PSPy][BF$_4$] was weak compared to the sample of the indicator in ethanol, which indicated that the indicator was partially in the form as [IH$^+$]. We could determined the [I]/[IH$^+$] ratio from the measured absorbances, and then the H_0 value of SFIL was calculated.

Table 1 disclosed that [PSPy][BF$_4$] exhibits a stronger Brønsted acidity than the other three SFILs. The Brønsted acidity of [PSPy][HSO$_4$] is slightly weak as compared with [PSPy][BF$_4$], but is stronger than [PSPy][pTSA] and [PSPy][H$_2$PO$_4$]. In other words, the Brønsted acidities of the SFILs depend on the anions, and the acidity order is as follows: [PSPy][BF$_4$] > [PSPy][HSO$_4$] > [PSPy][pTSA] > [PSPy][H$_2$PO$_4$].

The acidity order is consistent with the activity order of the SFILs to catalyze the synthesis of D,L-α-tocopherol using trimethylhydroquinone and isophytol as reactants. As shown in Table 2, [PSPy][BF$_4$] showed the best catalytic activity for the synthesis of D,L-α-tocopherol. [PSPy][HSO$_4$] could also be used as the catalyst to promote the reaction, but its activity was slightly lower than that of [PSPy][BF$_4$]. The yield of D,L-α-tocopherol in [PSPy][pTSA] was poor, only 9.5%. The synthesis reaction cannot be catalyzed by [PSPy][H$_2$PO$_4$] [30].

In the esterification reactions of benzoic acid with ethanol, the catalytic activity order of the SFILs is [PSPy][HSO$_4$] >
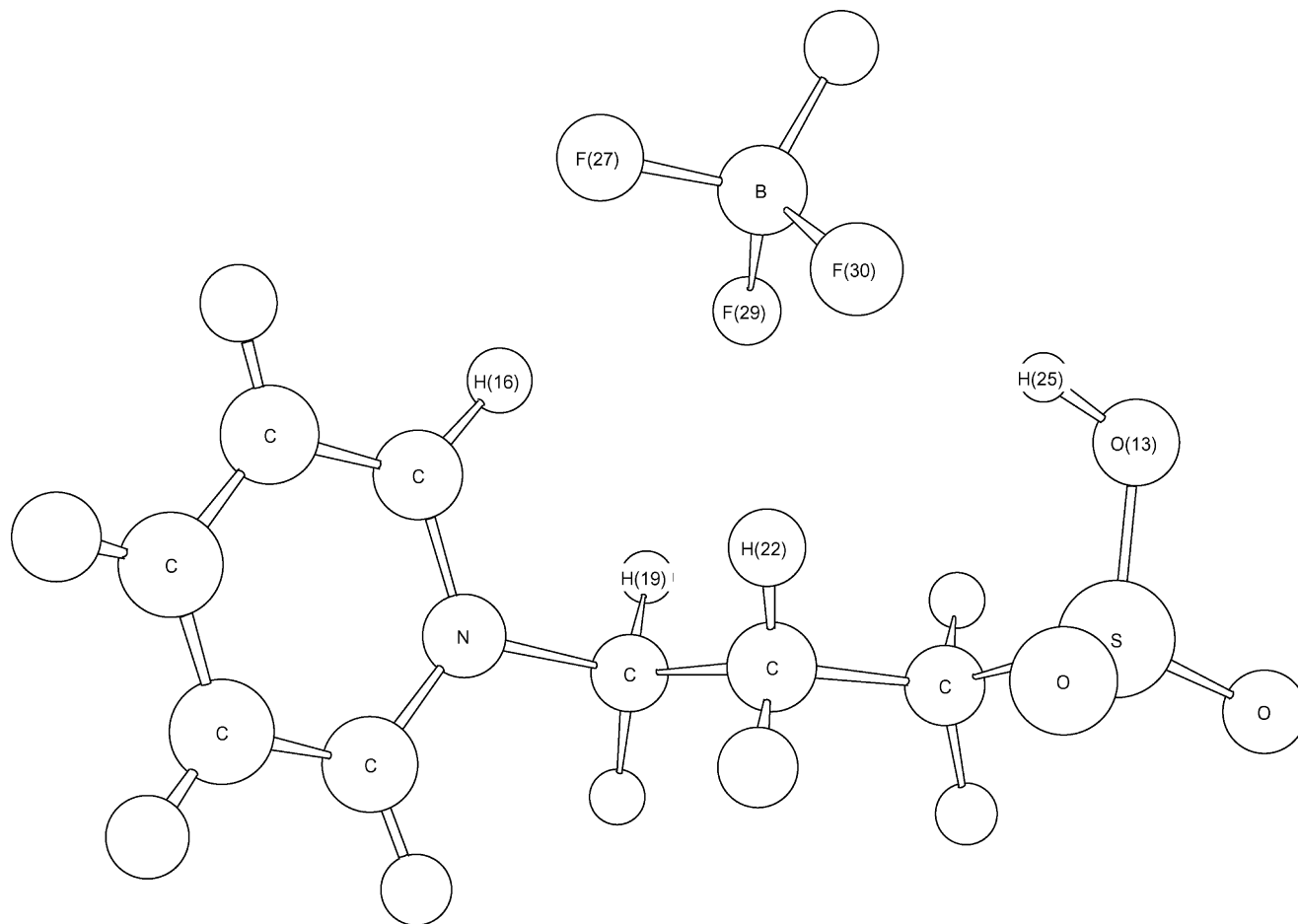

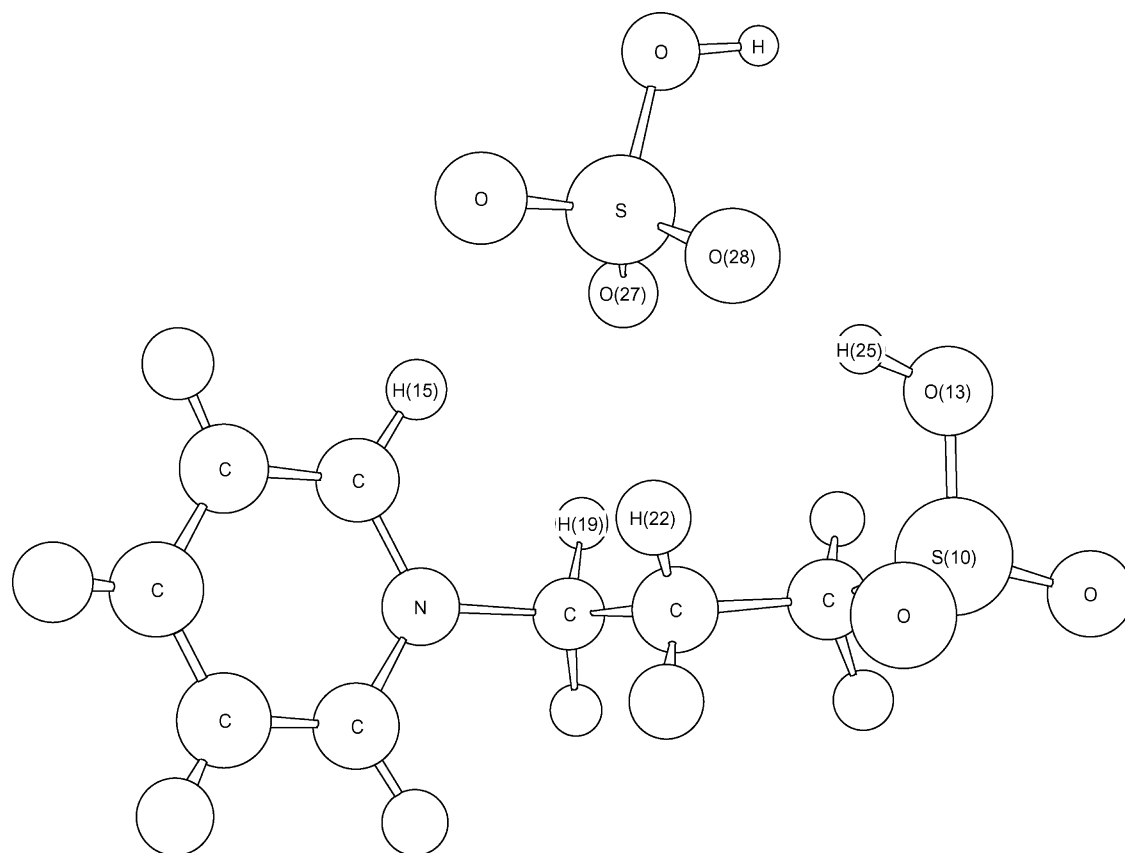Fig. 3. Molecular structure of [PSPy][BF$_4$] (RHF/6-31(d, p)).

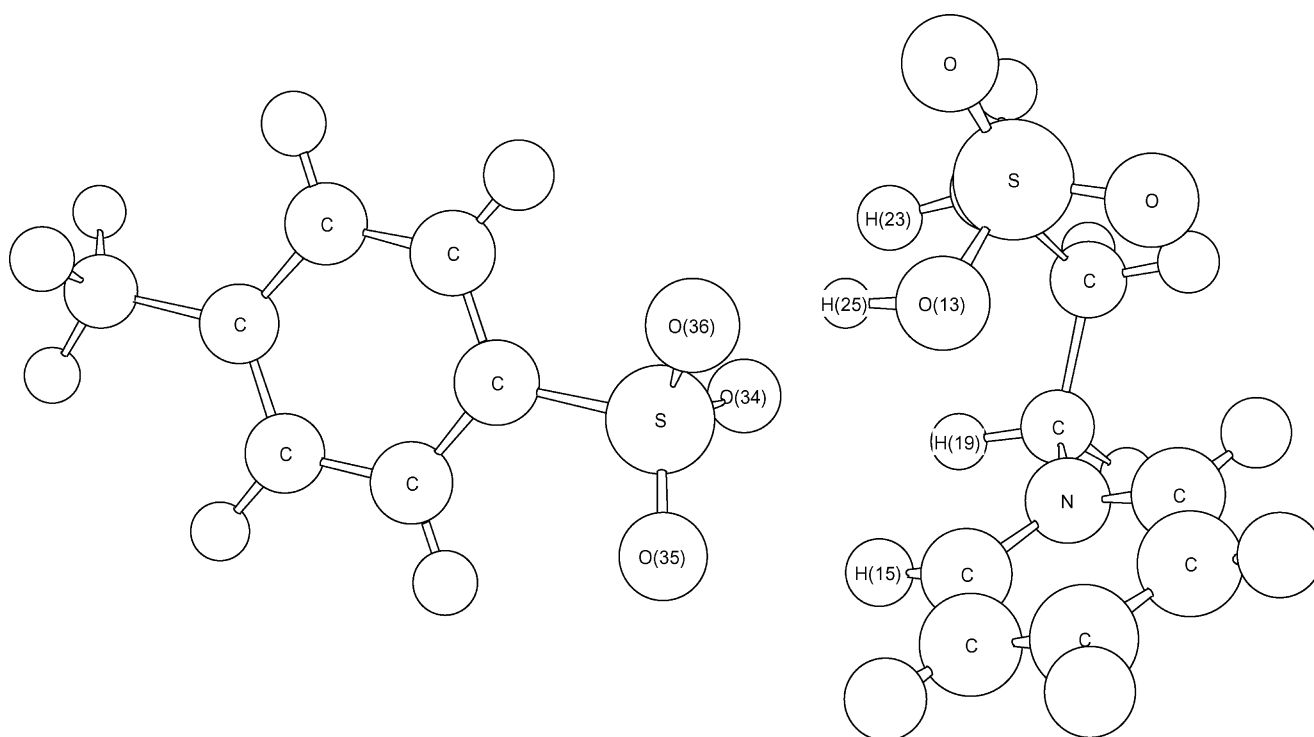Fig. 4. Molecular structure of [PSPy][HSO₄] (RHF/6-31(d, p)).

Fig. 5. Molecular structure of [PSPy][*p*TSA] (RHF/6-31(d, p)).

[PSPy][BF$_4$] > [PSPy][pTSA] > [PSPy][H$_2$PO$_4$] [21]. Except for [PSPy][BF$_4$] and [PSPy][HSO$_4$], the activity order of the SFILs was also consistent with their acidity order. The reverse order of [PSPy][BF$_4$] and [PSPy][HSO$_4$] was attributed to the biphasic behavior of the reaction system. The [PSPy][HSO$_4$] presented the better immisciblity with produced ester than [PSPy][BF$_4$] did, which facilitates the esterification reaction equilibrium shifting to the product side [21].

It is clear that the Brønsted acidities of SFILs depended on the anions, with the result that the catalytic activities of SFILs depended on the kinds of anions. In order to understand the role of anions in the Brønsted acidities of SFILs, the minimum-energy geometries of SFILs were determined using ab initio calculations.

3.2. The molecular geometries of SFILs

The minimum-energy geometries of SFILs and isolated [PSPy$^+$] cation were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level. The fully optimized geometries of the SFILs are presented in Figs. 3–6 and Table 3. It is obvious that a strong hydrogen bond network are present in the SFILs. The anions are located on the side of the propyl sulfonic acid group, and interact with the propyl alkyl sulfonic acid group and pyridinium ring in the form of C–H$\cdots$X (F, O) or O–H$\cdots$X type (hydrogen bonds).

For instance, [PSPy][BF$_4$] has five H$\cdots$F distances, which are shorter than the Van der Waals distance of 2.67 Å [33]. These include the anion to pyridinium ring C$_4$–H$_{16}\cdots$F$_{27}$ distances of 2.117 Å, an the anion to alkyl sulfonic acid chain C–H$_{19}\cdots$F$_{29}$, C–H$_{22}\cdots$F$_{22}$ and C–H$_{22}\cdots$F$_{30}$ distances of 2.321, 2.550 and 2.332 Å.

More importantly, [BF$_4{}^-$] strongly interacts with the sulfonic acid proton, with H$_{25}\cdots$F$_{30}$ distance of 1.723 Å. As listed in Table 3, other SFILs also exhibit the strong interaction between the anion and the sulfonic acid proton. The strongest interaction of the anion with the sulfonic acid proton exhibits in [PSPy][H$_2$PO$_4$], with H$_{32}$–O$_{20}$ distance of 1.564 Å. Due to these strong interactions between the anions with the sulfonic acid protons, the H–O bond of the sulfonic acid group has been lengthened with different levels compared with the one in the isolated cation. The H–O bond distance in SFILs is in the following ascending order: [PSPy][BF$_4$] < [PSPy][HSO$_4$] < [PSPy][pTSA] < [PSPy][H$_2$PO$_4$], which is reverse to their acidities.

Based on the minimum-energy geometries of SFILs, it is considered that the SFILs have two adjacent acid sites. One is the alkyl sulfonate group, and the other is the anion. The acidities of SFILs depend both on the characteristics of the anions and on the sulfonate group. When the interaction between the anion and the sulfonic acid proton is stronger, the dependence of the acidity of the SFIL on the anion is more significant. When a conjugate
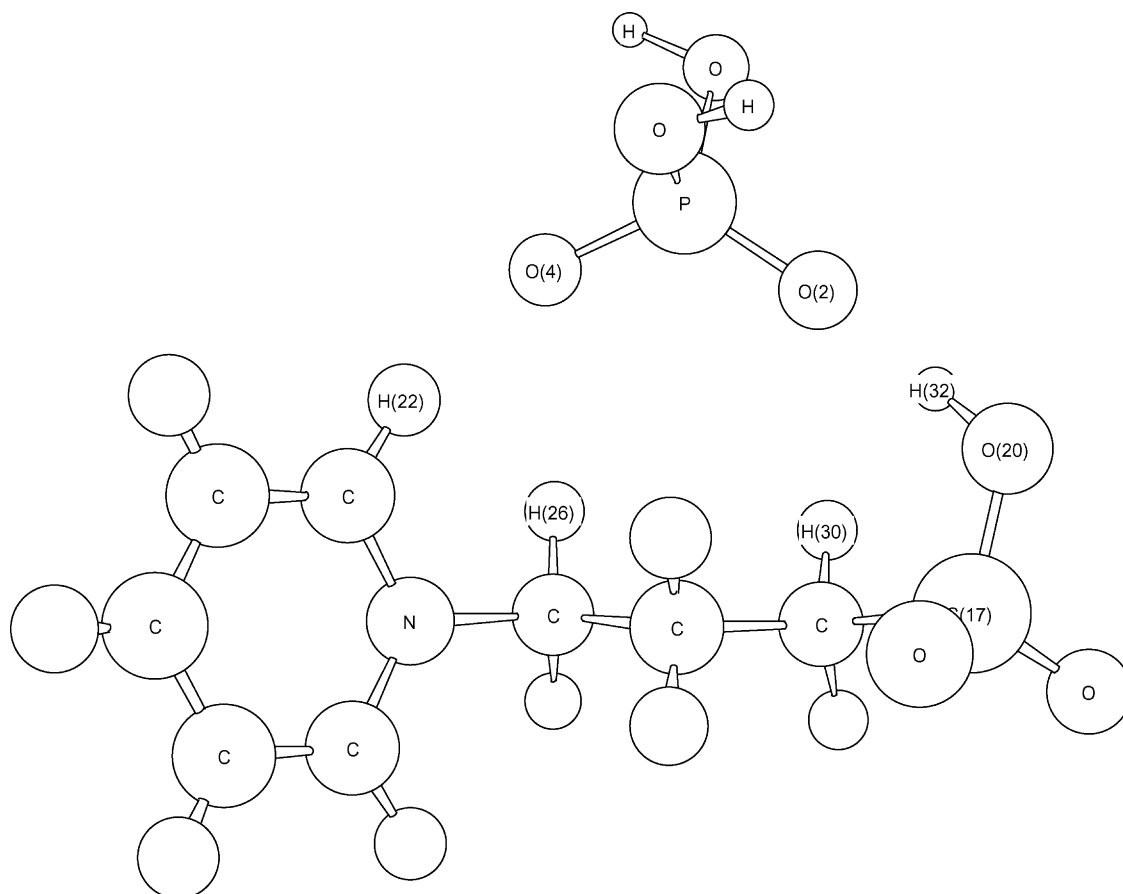

Fig. 6. Molecular structure of [PSPy][H$_2$PO$_4$] (RHF/6-31(d, p)).

base of a weak acid, such as [$H_2PO_4^-$], serves as the anion, the acidity of the SFIL is relatively weak. On the other hand, for the SFILs with the conjugate bases of strong acids as the anions, such as [PSPy][HSO₄] and [PSPy][BF₄], the acidities of the SFILs are relatively strong (Table 1).

4. Conclusions

The H_0 values of SFILs were determined using the Hammett method with UV–vis spectroscopy at 110 °C. The Brønsted acidities of SFILs depend on the anions, and obey the following order: [PSPy][BF₄] > [PSPy][HSO₄] > [PSPy][*p*TSA] > [PSPy][H₂PO₄]. The acidity order is consistent with the activity order of the SFILs in catalyzing the synthesis of D,L-α-tocopherol.

The minimum-energy geometries of SFILs reaveled that the anions have strong interaction with the sulfonic acid proton. It is considered that in addition to the alkyl sulfonic acid group, the anion is likely to serve as available acid sites. Hence the acidities and catalytic activities of SFILs depend on the kinds of anions.

Acknowledgements

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