

SUPPORTING INFORMATION

Understanding Structure-Property Relationship of SO₃H-Functionalized Ionic Liquids together with Sulfuric Acid in Catalyzing Isobutane Alkylation with C4 Olefin

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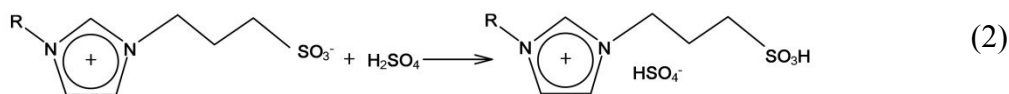
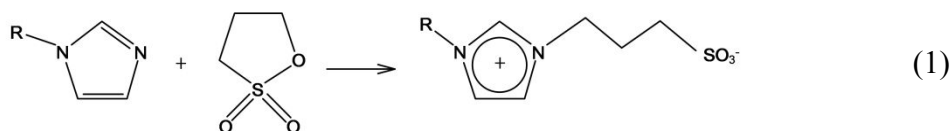
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1. Synthesis and characterization of SO₃H-functionalized ionic liquids

A certain amount of 1,3-propyl sultone was dissolved in ethyl acetate, and then equimolar amounts of N-alkylimidazolium were added dropwise under the condition of ice water bathing. The mixtures were heated up to 353 K and stirred for 6 hours when finishing dropping. MPSIm, EPSIm, and BPSIm (precursor of [MPSIm][HSO₄], [EPSIm][HSO₄] and [BPSIm][HSO₄], respectively), are white powder, and were washed by ethyl acetate for three times and dried by vacuum drying oven. HPSIm, OPSIm (precursor of [HPSIm][HSO₄] and [OPSIm][HSO₄], respectively), are viscous liquids, and were washed by ethyl acetate for three times, separated by liquid separation funnel and then dried by rotary evaporator. The reaction equation of this step was described in

Eq.1. Subsequently, equimolar amounts of H_2SO_4 were added dropwise to 1-alkyl-3-(propyl -3-sulfonate) imidazolium betaines (MPSIm, EPSIm and BPSIm were firstly dissolved in water) in the ice water bath conditions and stirred for 6 hours at 353 K when finishing dropping. The resultant was washed by water for three times and dried by rotary evaporator. The moisture content of ionic liquids was analyzed by automatic Karl Fischer moisture analyzer, to ensure that the moisture content was less than 0.5 wt % to avoid equipment corrosion by dilute sulfuric acid. The reaction equation of this step was described as Eq.2.



[MPSIm][HSO₄]: ¹H-NMR (400 MHz, D₂O, δ ppm): 2.15 (m, 2H), 2.76 (t, 2H), 3.74 (s, 3H), 4.21 (t, 2H), 7.29 (s, H), 7.37 (s, H), 8.59 (s, H). ¹³C-NMR (400 MHz, D₂O, δ ppm): 24.99, 35.61, 47.10, 47.62, 122.07, 123.66, 136.07.

[EPSIm][HSO₄]: ¹H-NMR (400 MHz, D₂O, δ ppm): 1.33 (t, 3H), 2.15 (m, 2H), 2.75 (m, 2H), 4.18 (m, 4H), 7.34(s, H), 7.40 (s, H), 8.62 (s, H). ¹³C-NMR (400 MHz, D₂O, δ ppm): 14.21, 24.93, 44.75, 47.12, 47.60, 122.10, 122.56, 134.95.

[BPSIm][HSO₄]: ¹H-NMR (400 MHz, D₂O, δ ppm): 0.59 (t, 3H), 1.01 (m, 2H), 1.54 (m, 2H), 2.01 (m, 2H), 3.90 (t, 2H), 4.06 (t, 2H), 7.24 (d, 2H), 8.50 (s, H). ¹³C-NMR (400 MHz, D₂O, δ ppm): 12.23, 19.67, 24.94, 31.08, 47.12, 47.64, 49.32, 122.20, 122.51, 135.32.

[HPSIm][HSO₄]: ¹H-NMR (400 MHz, D₂O, δ ppm): 0.66 (t, 3H), 1.10 (s, 6H), 1.69 (t, 2H), 2.16 (m, 2H), 2.73 (m, 2H), 4.02 (m, 2H), 4.20 (t, 2H), 7.34 (s, H), 7.37 (s, H), 8.65 (s, H). ¹³C-NMR (400 MHz, D₂O, δ ppm): 13.10, 21.63, 24.96, 25.00, 29.94, 30.17,

47.11, 47.64, 49.60, 122.20, 122.52, 135.27.

[OPSIIm][HSO₄]: ¹H-NMR (400 MHz, D₂O, TMS, δ ppm): 0.68 (t, 3H), 1.12 (m, 10H), 1.70 (t, 2H), 2.16 (m, 2H), 2.75 (t, 2H), 4.04 (t, 2H), 4.21 (t, 2H), 7.36 (s, H), 7.39 (s, H), 8.67 (s, H). ¹³C-NMR (400 MHz, D₂O, δ ppm): 13.36, 21.94, 25.07, 25.28, 27.80, 28.29, 29.05, 30.96, 47.12, 47.68, 49.60, 122.27, 122.51, 135.33.

The UV-vis spectra coupled with Hammett indicator such as aromatic amines has been used to quantify the acid strength of Brønsted acidic ILs and the value of Hammett acidity function (H₀) can be calculated by the maximal absorbance of the indicator (Yanlou et al., 2009).

The measurement of the acid strength of the SO₃H-functionalized ILs was conducted by the CARY 500 UV-visible spectrophotometer with a basic indicator (4-nitroaniline, PK_a=0.99) at room temperature as described in the literatures (Liu et al., 2011; Yang et al., 2010). The accuracy of H₀ obtained by UV-vis spectra depends on the indicator chosen. In this work, the 4-nitroaniline was selected as Hammett indicator according to previous publications (Liu et al., 2011; Xiao et al., 2014; Xu et al., 2009). The indicator 4-nitroaniline and SO₃H-functionalized ILs were dissolved into ethanol to form the solution with the concentration of 10 mg/L and 5 mmol/L, respectively. The value of H₀ can be calculated by Eq. (3):

$$H_0 = PK_a + \log([I]/[IH^+]) \quad (3)$$

where [I] represents the molar concentrations of the unprotonated form of 4-nitroaniline in ethanol, while [IH⁺] represents the protonated one. Thus, the lower value of H₀ indicates the higher Brønsted acidity.

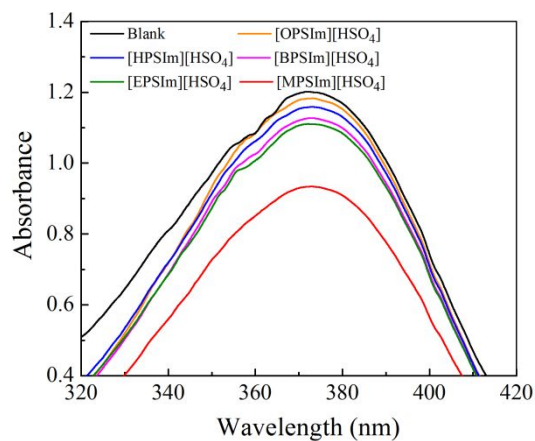


Figure S1. UV absorption spectra of SO₃H-functionalized ionic liquids in ethanol.

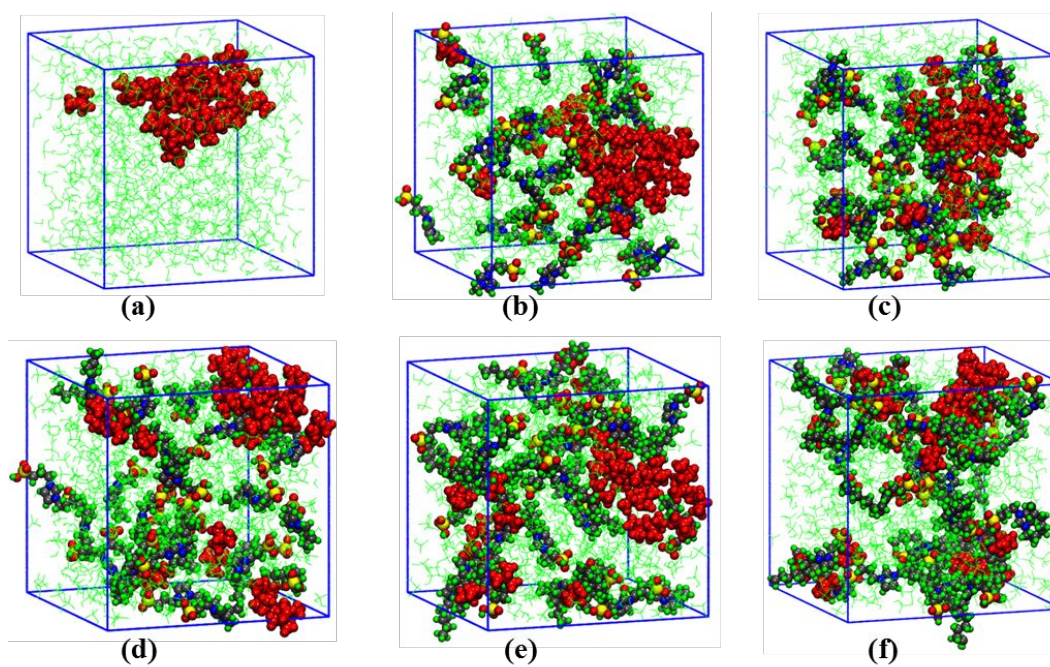


Figure S2. Snapshots of the isobutane dispersion behaviors in different simulation systems.

(a) Pure H₂SO₄ (b) [MPSIm][HSO₄] (c) [EPsIm][HSO₄] (d) [BPsIm][HSO₄] (e) [HPsIm][HSO₄] (f) [OPSIm][HSO₄]. Molecules in Red color represent isobutane, and molecules with the blue, grey, yellow, and red atoms stand for the cations of the SFILs. Molecules in Green represent H₂SO₄.