Acidity Tunable Ionic Liquids as Catalysts for Conversion of Agar into Mixed Sugars

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1-butyl-3-methylimidazolium bisulfate ([Bmim][HSO_4]). To a solution of silver sulfate (4.08 g) in 40% H_2SO_4 (20 mL) was added to 1-butyl-3-methylimidazolium bromide (4.05 g) dissolved in ethyl alcohol. The mixture was stirred for 2 h at 50 °C. The precipitate was filtered off. To the filtrate was added acetonitrile, the mixture was filtered again, and acetonitrile was distilled off. the procedure was repeated several times. The product is a liquid of amber color, which crystallized at storage. The product was recrystallized from a mixture of acetonitrile and ethyl acetate, 1:5. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (m, 3H), 1.22 (m, 2H), 1.66 (t, 22H), 2.95 (s, 1H), 3.92 (s, 2H), 4.18 (m, 3H), 7.55 (s, 1H), 8.99 (s, 1H), 10.70 (s, 2H). IR (KBr, cm^{-1}): 3101, 2964, 1577, 1456, 1158, 1030, 838. Anal. Calcd. for $C_8H_{16}N_2O_4S$: C, 40.66; H, 6.83; N, 11.86; O, 27.08; S, 13.57. Found: C, 38.11; H, 6.73; N, 11.26; O, 31.74; S, 15.73. MS (EI) *m*/*z*: 236.08 (M^+).

1-methylimidazolium bisulfate ([Hmim][HSO_4]). 1-Methylimidazole (1.59 mL, 20 mmol) and acetonitrile (5 mL) were charge into a 25 mL round-bottom flask. Then, the mixtures were stirred at 0 °C for 1 min. Then, a stoichiometric amount of concentrated sulfuric acid (97%, 1.03 mL) was added drop wise and the mixture was stirred for 1 h at 0 °C and then stirred for 2 h at room temperature. The acidic ionic liquid was washed repeatedly with ether to remove non-ionic residues and dried in vacumm. ^{1}H NMR (200 MHz, D_2O) δ 2.65 (s, 1H), 3.02 (s, 3H), 3.41 (s, 1H), 3.58 (t, 2H), 4.35 (t, 2H). IR (KBr, cm^{-1}): 3147, 1592, 1547, 1158, 1030, 830. Anal. Calcd. for $C_4H_8N_2O_4S$: C, 26.66; H, 4.48; N, 15.55; O, 35.52; S, 17.80. Found: C, 26.83; H, 4.70; N, 15.60; O, 35.03; S, 19.84. MS (EI) *m*/*z*: 180.02 (M^+).

Choline bisulfate ([Chol][HSO_4]). Choline chloride (50 g) were charge into a 500 mL round-bottom flask. Then, a stoichiometric amount of concentrated sulfuric acid (50%, 35.93 mL) was added drop wise and the mixture stirred for 24 h at room temperature. The acidic ionic liquid was washed repeatedly with ethyl acetate to remove non-ionic residues and dried in vacuum. ^{1}H NMR (200 MHz, D_2O) δ 1.78 (s, 1H), 3.61 (d, 3H), 7.12 (d, 2H), 8.38 (d, 2H). IR (KBr, cm^{-1}): 3040, 1220, 1036. Anal. Calcd. for $C_5H_{15}NO_5S$: C, 29.84; H, 7.51; N, 6.96; O, 39.75; S, 15.93. Found: C, 32.72; H, 7.33; N, 7.60; O, 28.95; S, 19.17. MS (EI) *m*/*z*: 201.07 (M^+).

Tetra-*n*-butylphosphonium bisulfate ([Bu_4P][HSO_4]). Tetrabutylphosphonium chloride (10 g) were charge into a 250 mL round-bottom flask. Then, a stoichiometric amount of concentrated sulfuric acid (50%, 3.4 mL) was added drop wise and the mixture stirred for 24 h at room temperature. The acidic ionic liquid was washed repeatedly with hexane to remove non-ionic residues and dried in vacuum. ^{1}H NMR (200 MHz, D_2O) δ 0.61 (m, 3H), 1.12 (t, 2H), 1.91 (d, 2H). IR (KBr, cm^{-1}): 2964, 1455, 1379, 1150. Anal. Calcd. for $C_{16}H_{37}O_4PS$: C, 53.90; H, 10.46; O, 17.95; P, 8.69; S, 8.99. Found: C, 53.36; H, 10.44; O, 15.97; S, 7.77. MS (EI) *m*/*z*: 356.22 (M^+).

Tetra-*n*-butylammonium bisulfate ([Bu_4N][HSO_4]). Tetrabutylammonium chloride (10 g) were charge into a 250 mL round-bottom flask. Then, a stoichiometric amount of concentrated sulfuric acid (50%, 3.61 mL) was added drop wise and the mixture stirred for 24 h at room temperature. The acidic ionic liquid was washed repeatedly with hexane to remove non-ionic residues and dried in vacuum. ^{1}H NMR (200 MHz, D_2O) δ 0.63 (t, 3H), 1.12 (s, 2H), 1.41 (s, 2H), 2.96 (d, 2H). IR (KBr, cm^{-1}): 2964, 1234, 1455, 1379, 1150. Anal. Calcd. for $C_{16}H_{37}NO_4S$: C, 56.60; H, 10.98; N, 4.13; O, 18.85; S, 9.44. Found: C, 56.54; H, 11.20; N, 4.18; O, 18.58; S, 8.24. MS (EI) *m*/*z*: 339.24 (M^+).

Morpholium bisulfate ([Morph][HSO4]). Morpholine (10 mL, 123 mmol) and ethyl acetate (50 mL) were charge into a 500 mL round-bottom flask. Then, the mixtures were stirred at 0 °C for 1 min. Then, a stoichiometric amount of concentrated sulfuric acid (97%, 6.36 mL) was added drop wise and the mixture stirred for 2 h at 0 °C and then stirred for 22 h at room temperature. The acidic ionic liquid was washed repeatedly with ethanol and acetone to remove non-ionic residues and dried in vacuum. ^{1}H NMR (200 MHz, D_2O) δ 1.85 (s, 1H), 3.09 (s, 2H), 3.78 (s, 2H). IR (KBr, cm^{-1}): 3032, 2872, 1424, 1310, 1150, 846. Anal. Calcd. for $C_4H_{11}NO_5S$: C, 25.94; H, 5.99; N, 7.56; O, 43.19; S, 17.31. Found: C, 29.73; H, 6.80; N, 8.36; O, 38.92; S, 16.32. MS (EI) *m*/*z*: 185.04 (M^+).