

High CO₂ Solubility and Permeability in Ionic Liquids with Tetracyanoborate Anion

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1. Viscosity

Viscosity measurements were acquired from 20 °C to 60 °C. Values are given in the following table.

Ionic Liquid	Viscosity (cP)					
	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C
[emim]	19.5	15.5	13.2	9.4	7.17	5.36
[bmim]	44.9	29.1	23.6	15.6	11.2	8.34
[emmim]	36.0	27.3	22.2	15.5	11.1	8.45
[C ₄ MPyrr]	58.9	45.0	35.4	24.2	17.3	13.3
[C ₄ mpip]	111	81.2	61.0	37.8	25.4	18.3

2. Synthesis of RTILs

All compounds were synthesized and purified using standard literature procedures for the synthesis of ionic liquids. The ionic liquids were washed with water until addition of silver nitrate to the aqueous wash produced no visible precipitation. The ionic liquids were dried under high vacuum using a Labconco Freezone 2.5 lyophilizer. Water content was measure using an Aquapal III Karl-Fischer titrator. All ionic liquid were dried until there was less than 100ppm water.

1-butyl-1-methylpiperidin-1-ium tetracyanoborate (1)

A 3.45g (0.14 mol) aliquot of 1-butyl-1-methylpiperidin-1-ium bromide was dissolved in 15ml of dry methanol and added to a solution of 2.01g (0.14 mol) of Sodium Tetracyanoborate in 10ml of dry methanol. An immediate white precipitate formed, and the mixture was stirred under N₂ overnight. The reaction was cooled to -10°C and filtered quickly. The solvent was evaporated and the residue was dissolved in dichloromethane and washed with water (6 x 50ml). The solvent was evaporated yielding a clear liquid which was dried under high vacuum for 3 days. Yield: 3.43g (87%) ¹H NMR (Acetone-d₆,400MHz): δ = 3.51 - 3.60 (m, 6 H), 3.26 (s, 3 H), 1.96 - 2.08 (m, 4 H), 1.83 - 1.94 (m, 2 H), 1.67 - 1.80 (m, 2 H), 1.45 (sxt, J=7.4 Hz, 2 H), 1.00 ppm (t, J=7.4 Hz, 3 H) ¹³C NMR (Acetone-d₆,101MHz): δ = 124.2, 123.5, 122.8, 122.1, 64.3, 62.0, 48.5, 24.4, 21.8, 20.6, 20.4, 13.9 ppm. ESI-MS: (+ve) 156.19 *m/z* [C₁₀H₂₂N₁]⁺; ESI-MS: (-ve) 115.03 *m/z* [BC₄N₄]⁻.

1-butyl-1-methylpyrrolidin-1-ium tetracyanoborate (2)

Compound **2** was synthesized in the same manner as **1**, using 1-butyl-1-methylpyrrolidin-1-ium bromide and sodium tetracyanoborate yielding a clear liquid. Yield: 3.11g (83%) ¹H NMR

(Acetone- d_6 , 400MHz): δ = 3.61 - 3.76 (m, 4 H), 3.47 - 3.56 (m, 2 H), 3.23 (s, 3 H), 2.31 (br. s., 4 H), 1.83 - 1.96 (m, 2 H), 1.43 (sxt, J =7.4 Hz, 2 H), 0.98 ppm (t, J =7.3 Hz, 3 H) ^{13}C NMR (Acetone- d_6 , 101MHz): δ = 124.1, 123.4, 122.7, 122.0, 65.2, 65.0, 49.0, 26.2, 22.3, 20.4, 20.4, 13.8 ppm. ESI-MS: (+ve) 142.16 m/z [$\text{C}_9\text{H}_{20}\text{N}_1$] $^+$; ESI-MS: (-ve) 115.03 m/z [BC_4N_4] $^-$.

3-butyl-1-methyl-1H-imidazol-3-ium tetracyanoborate (3)

Compound **3** was synthesized in the same manner as **1**, using 3-butyl-1-methyl-1H-imidazol-3-ium bromide and potassium tetracyanoborate yielding a light yellow liquid. Yield: 3.02g (92%). ^1H NMR (Acetone- d_6 , 400MHz): δ = 9.03 (s, 1 H), 7.75 (s, 1 H), 7.70 (s, 1 H), 4.36 (t, J =7.3 Hz, 2 H), 4.06 (s, 3 H), 1.93 (quin, J =7.5 Hz, 2 H), 1.39 (dq, J =15.1, 7.4 Hz, 2 H), 0.95 ppm (t, J =7.3 Hz, 3 H) ^{13}C NMR (Acetone- d_6 , 101MHz): δ = 136.5, 124.0, 123.3, 122.6, 121.9, 121.2, 49.4, 35.9, 31.9, 19.1, 12.8 ppm. ESI-MS: (+ve) 139.12 m/z [$\text{C}_8\text{H}_{15}\text{N}_2$] $^+$; ESI-MS: (-ve) 115.03 m/z [BC_4N_4] $^-$.

3-ethyl-1,2-dimethyl-1H-imidazol-3-ium tetracyanoborate (4)

Compound **4** was synthesized in the same manner as **1**, using 3-ethyl-1,2-dimethyl-1H-imidazol-3-ium bromide and potassium tetracyanoborate yielding a light yellow liquid. Yield: 2.71g (87%). ^1H NMR (Acetone- d_6 , 400MHz): δ = 7.62 (d, J =2.0 Hz, 1 H), 7.58 (d, J =2.0 Hz, 1 H), 4.33 (q, J =7.3 Hz, 2 H), 3.95 (s, 3 H), 2.78 (s, 3 H), 1.51 ppm (t, J =7.3 Hz, 3 H) ^{13}C NMR (Acetone- d_6 , 101MHz): δ = 145.4, 124.1, 123.4, 122.7, 122.0, 121.3, 44.3, 35.5, 15.3, 9.6 ppm. ESI-MS: (+ve) 125.11 m/z [$\text{C}_7\text{H}_{13}\text{N}_2$] $^+$; ESI-MS: (-ve) 115.03 m/z [BC_4N_4] $^-$.