

Counting cations involved in cationic clusters of hydroxy-functionalized ionic liquids by means of infrared spectroscopy – Comparison to populations derived from neutron scattering and molecular dynamics simulations

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Synthesis of isotopically labelled ionic liquids [HOC₄Py][NTf₂]

Apart from the reactions in aqueous solutions all reactions were performed in a moisture guarded assembly and reflux condenser was used while heating. The used solvents were dried with molecular sieves to a water content less than 50 ppm and distilled freshly. All starting materials used in the synthesis were purchased from SIGMA ALDRICH. All starting materials were dried by conventional methods for the use in moisture-free reactions.

4-Bromo-1-trimethylsiloxybutane*

A mixture of equimolar amounts of dry tetrahydrofuran and bromotrimethylsilane was refluxed for 30 h and the crude product was then isolated by distillation in vacuum (78 °C; 17 mbar). The product was obtained as a colorless liquid. Yield 80 %.

4-Bromo-1-trimethylsiloxybutane: ¹H-NMR(298.2 K, DMSO-d₆, 300.13 MHz, [ppm]): δ = 0.05 (s, 9H, -Si(CH₃)); 1.52 (tt, 2H, CH₂-CH₂-O-); 1.84 (tt, 2H, Br-CH₂-CH₂-); 3.41 (t, 2H, CH₂-CH₂-O-); 3.53 (t, 2H, Br-CH₂-CH₂-). ¹³C-NMR(298 K, DMSO-d₆, 75.46 MHz, [ppm]): δ = 2.05 (s, -Si(CH₃); 29.24 (s, CH₂-CH₂-O-); 31.01 (s, Br-CH₂-CH₂-); 35.28 (s, Br-CH₂-CH₂-); 59.82 (s, CH₂-CH₂-O-).

* H. R. Kricheldorf, G. Mörber, W. Regel, *Synthesis* **1981**, 5, 383

1-(4-Trimethylsiloxybutyl)-pyridinium-bromide

Equimolar amounts of pyridine and 4-Bromo-1-trimethylsiloxybutane were mixed at room temperature and heated slowly up to round about 100 °C - 110 °C. When the reaction begins, the solution starts to cloud. After a few minutes two phases are formed, the lower one is yellow and the upper one is colorless. After about 5 h only one yellow phase is obtained. All volatiles were removed in vacuum. The crude product was cooled to room temperature whereby it starts to crystallize. Yield 75 %.

1-(4-Trimethylsiloxybutyl)-pyridinium-bromide: ¹H-NMR(298.2 K, DMSO-d₆, 300.13 MHz, [ppm]): δ = 0.05 (s, 9H, -Si(CH₃)); 1.41 (tt, 2H, CH₂-CH₂-O-); 1.96 (tt, 2H, N-CH₂-CH₂-); 3.41 (t, 2H, CH₂-CH₂-O-); 4.68 (t, 2H, N-CH₂-CH₂-); 8.14-8.21 (m, 2H, *m*-CH); 8.60-8.67 (m, 1H, *p*-CH); 9.03-9.09 (m, 2H, *o*-CH). ¹³C-NMR(298 K, DMSO-d₆, 75.46 MHz, [ppm]): δ = 2.05 (s, -Si(CH₃); 26.36 (s, CH₂-CH₂-O-); 27.34 (s, N-CH₂-CH₂-); 58.96 (s, N-CH₂-CH₂-); 60.19 (s, CH₂-CH₂-O-); 127.67 (s, *m*-CH); 144.65 (s, *p*-CH); 145.46 (s, *o*-CH).

1-(4-Hydroxybutyl)-pyridinium-bromide

1-(4-Trimethylsiloxybutyl)-pyridinium-bromide was dissolved in a tenfold excess of H₂O. The solution was stirred for 4 h at 80 °C. Two phases were formed. All volatiles were removed in vacuum. The procedure was repeated to remove all trimethylsilyl residuals. The crude product was cooled to room temperature whereby it starts to crystallize. The almost colorless crystalline crude product was recrystallized from a small amount of acetonitrile.

Yield 80 %.

1-(4-Hydroxybutyl)-pyridinium-bromide: $^1\text{H-NMR}$ (298.2 K, DMSO- d_6 , 300.13 MHz, [ppm]): δ = 1.41 (tt, 2H, $\text{CH}_2\text{-CH}_2\text{-O-}$); 1.96 (tt, 2H, $\text{N-CH}_2\text{-CH}_2\text{-}$); 3.41 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-O-}$); 4.13 (s, 1H, -OH); 4.68 (t, 2H, $\text{N-CH}_2\text{-CH}_2\text{-}$); 8.14-8.21 (m, 2H, *m-CH*); 8.60-8.67 (m, 1H, *p-CH*); 9.03-9.09 (m, 2H, *o-CH*). $^{13}\text{C-NMR}$ (298 K, DMSO- d_6 , 75.46 MHz, [ppm]): δ = 26.36 (s, $\text{CH}_2\text{-CH}_2\text{-O-}$); 27.34 (s, $\text{N-CH}_2\text{-CH}_2\text{-}$); 58.96 (s, $\text{N-CH}_2\text{-CH}_2\text{-}$); 60.19 (s, $\text{CH}_2\text{-CH}_2\text{-O-}$); 127.67 (s, *m-CH*); 144.65 (s, *p-CH*); 145.46 (s, *o-CH*).

1-(4-Hydroxybutyl)-pyridinium-bis(trifluoromethanesulfonyl)imide

1-(4-Hydroxybutyl)-pyridinium-bromide was solved in a few milliliters H_2O . This solution was added to an equimolar aqueous solution of LiNTf_2 . The mixture was stirred for 1h. During this time two phases were formed. The lower phase was washed several times with water until no residual bromine could be detected with silver nitrate solution. The thus obtained colorless liquid was dried for 6 h at 60 °C in vacuum ($< 1 \cdot 10^{-6}$ mbar). Yield: 90 %.

1-(4-Hydroxybutyl)-pyridinium-bis(trifluoromethanesulfonyl)imide: $^1\text{H-NMR}$ (298.2 K, DMSO- d_6 , 300.13 MHz, [ppm]): δ = 1.41 (tt, 2H, $\text{CH}_2\text{-CH}_2\text{-O-}$); 1.96 (tt, 2H, $\text{N-CH}_2\text{-CH}_2\text{-}$); 3.41 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-O-}$); 4.13 (s, 1H, -OH); 4.68 (t, 2H, $\text{N-CH}_2\text{-CH}_2\text{-}$); 8.14-8.21 (m, 2H, *m-CH*); 8.60-8.67 (m, 1H, *p-CH*); 9.03-9.09 (m, 2H, *o-CH*). $^{13}\text{C-NMR}$ (298 K, DMSO- d_6 , 75.46 MHz, [ppm]): δ = 26.36 (s, $\text{CH}_2\text{-CH}_2\text{-O-}$); 27.34 (s, $\text{N-CH}_2\text{-CH}_2\text{-}$); 58.96 (s, $\text{N-CH}_2\text{-CH}_2\text{-}$); 60.19 (s, $\text{CH}_2\text{-CH}_2\text{-O-}$); 119.43 (q, CF_3); 127.67 (s, *m-CH*); 144.65 (s, *p-CH*); 145.46 (s, *o-CH*).