Stability of the Zwitterionic Liquid Butyl-Methyl-Imidazol-2-ylidene Borane

Steffen Tröger-Müller, Markus Antonietti, Clemens Liedel*

Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14476 Potsdam, Germany, E-mail: Clemens.Liedel@mpikg.mpg.de

Supporting Information

Contents

NMR-Spectra ........................................................................................................................................... 2
  1-Butyl-3-methylimidazolium iodide (IL-H-I) ....................................................................................... 2
  1-Butyl-3-methylimidazol-2-ylidene borane (ZIL) ............................................................................... 3
  1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL-H-TFSI) .................................. 4
  1-Butyl-2,3-dimethylimidazolium iodide (IL-Me-I) .............................................................................. 5
  1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide  (IL-Me-TFSI) ......................... 6
Differential Scanning Calorimetry ........................................................................................................... 7
  1-Butyl-2-methylimidazolium iodide (IL-H-I) ....................................................................................... 7
  1-Butyl-3-methylimidazol-2-ylidene borane (ZIL) ............................................................................... 7
  1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL-H-TFSI) .................................. 8
  1-Butyl-2,3-dimethylimidazolium iodide (IL-Me-I) .............................................................................. 8
  1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide  (IL-Me-TFSI) ......................... 9
Viscosity measurements .......................................................................................................................... 9
  Shear stress–shear rate measurements ............................................................................................ 10
  Up and down sweeps and linear regressions of up sweeps .............................................................. 11
    1-Butyl-3-methylimidazolium iodide (IL-H-I) .................................................................................. 11
    1-Butyl-3-methylimidazol-2-ylidene borane (ZIL) ........................................................................ 12
    1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL-H-TFSI) ......................... 13
    1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide  (IL-Me-TFSI) ................... 14
Equilibration of the ZIL with ambient humidity ................................................................................ 15
  Thermal behavior and decomposition .............................................................................................. 15
NMR-Spectra

1-Butyl-3-methylimidazolium iodide (IL-H-I)
1-Butyl-3-methylimidazol-2-ylidene borane (ZIL)
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyle)imide (IL-H-TFSI)
1-Butyl-2,3-dimethylimidazolium iodide (IL-Me-I)
1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (IL-Me-TFSI)
Differential Scanning Calorimetry
Graphs display the third heating phase. The irregular behavior below -120 °C results from instrumentalization.

1-Butyl-2-methylimidazolium iodide (IL-H-I)

Glass transition: -68.3 °C, 0.243 J g⁻¹ K⁻¹

1-Butyl-3-methylimidazol-2-ylidene borane (ZIL)

Glass transition: -64.9 °C, 0.305 J g⁻¹ K⁻¹
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL-H-TFSI)

Glass transition: -85.5 °C, 0.255 J g⁻¹ K⁻¹.
Cold crystallization: -41.5 °C; -20.1 °C; -40.68 J g⁻¹ (both together)
Melting: 1.3 °C, 40.86 J g⁻¹

1-Butyl-2,3-dimethylimidazolium iodide (IL-Me-I)

Melting could not be determined due to the measurement interval ending at 100 °C.
1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (IL-Me-TFSI)

Glass transition: -75.4 °C, 0.195 J g⁻¹ K⁻¹

**Viscosity measurements**
Dynamic viscosity was determined from the slope of a linear fit of shear rate – shear stress curves. All tested (zwitter)ionic liquids show Newtonian behavior. All tested liquid systems were dried extensively before measurement, however, measurements could not be performed under dry conditions, so ILs take up water from the atmosphere during measurement causing viscosity to decrease over time. The displayed measurements represent the first measurement cycle of a shear rate sweep from 500 to 3000 s⁻¹. In the case of the ZIL, additional measurements were performed after equilibration of the water content with the environment to illuminate the influence of water content.
Shear stress–shear rate measurements
Up and down sweeps and linear regressions of up sweeps

1-Butyl-3-methylimidazolium iodide (IL-H-I)
1-Butyl-3-methylimidazol-2-ylidene borane (ZIL)

![Graph showing the viscosity of ZIL as a function of shear rate.](image)

![Graph showing the shear stress as a function of shear rate with a linear fit.](image)
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyle)imide (IL-H-TFSI)
1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyle)imide (IL-Me-TFSI)
Equilibration of the ZIL with ambient humidity

Thermal behavior and decomposition
Masses are rounded to the closest integer.

m/z 2
m/z 14

![Graph](image)

m/z 16

![Graph](image)
m/z 1; 44

m/z 56; 58
m/z 68; 80; 82; 94; 96; 124; 139

m/z 138; 154