

# Validation of Structural Grounds for Anomalous Molecular Mobility in Ionic Liquid Glasses

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## 1. Chemicals

Chlorobutane, N-methyl imidazole, pyridine, sodium tetrafluoroborate and all standard chemicals were obtained from commercial sources. 1-Butanol-d<sub>10</sub> was purchased from Sigma Aldrich.

The ionic liquids [Bmim]Cl and [BuPy]Cl were obtained by analogy with the literature method<sup>S1</sup> from 1-methyl imidazole or pyridine and chlorobutane. The ionic liquids [Bmim]BF<sub>4</sub> and [BuPy]BF<sub>4</sub> were obtained by previously reported method.<sup>S2</sup>

## 2. Synthesis of deuterated ionic liquids

### *D*<sub>9</sub>-Bromobutane

A 25 ml round-bottomed flask fitted with magnetic stirrer bar and reflux condenser was charged by 6.35 g of 48 mas % HBr solution (37.7 mmol of HBr). 1.85 g (1.05 ml, 19.0 mmol) of 96% H<sub>2</sub>SO<sub>4</sub> was slowly added with stirring. After warming to the room temperature, 2.61 g (31.4 mmol) of 1-Butanol-d<sub>10</sub> was added with stirring and then 1.61 g (0.92 ml, 17.0 mmol) of 96% H<sub>2</sub>SO<sub>4</sub> was added dropwise. The mixture was refluxed for 3 h and then the product was distilled off in a slight vacuum (Bp. about 40°C at 140 torr). The product was washed with saturated NaHCO<sub>3</sub> solution and then with water, dried over MgSO<sub>4</sub> and distilled. 3.47 g (76%) of d<sub>9</sub>-brombutane as a colorless liquid was obtained. In the GCMS we observed one peak with molecular ion of mass 146.

#### *[D<sub>9</sub>-Bmim]Br and [d<sub>9</sub>-BuPy]Br*

A 25 ml two-neck round-bottomed flask fitted with magnetic stirrer bar, reflux condenser, dropping funnel and argon supply was charged by solution of 21.5 mmol of N-methylimidazole or pyridine in 5 ml of acetonitrile. The system was filled by argon and heated to 70°C. Then solution of 3.47 g (24.0 mmol) of d<sub>9</sub>-bromobutane in 5 ml of acetonitrile was added dropwise. The mixture was refluxed under argon atmosphere for 6 h. The volatile components were distilled off in vacuo. The residue was washed with diethyl ether and dried in high vacuum (10<sup>-3</sup> bar) at 60°C for 6 hours. The product yield was 55%

#### *[D<sub>12</sub>-Bmim]Br (by analogy with ref.<sup>53</sup>)*

In the glove box a 5 ml round-bottomed flask fitted with magnetic stirrer bar was charged by 2.0 g (8.8 mmol) of d<sub>9</sub>-BmimBr and catalytic amount of K<sub>2</sub>CO<sub>3</sub> (about 3 mg, 0.02 mmol). Outside the glove box 3 ml of D<sub>2</sub>O (150 mmol) was added by syringe. The system was supplied by reflux condenser and the mixture was refluxed under argon atmosphere for 3 h. Then water was distilled off in vacuo and the second portion of D<sub>2</sub>O (3 ml, 150 mmol) was added. The mixture was refluxed under argon atmosphere for 3 h. Then water was distilled off in vacuo and the residue was dissolved in dry dichloromethane and dried over MgSO<sub>4</sub>. Then MgSO<sub>4</sub> was filtered, solvent was evaporated and product was dried in high vacuum (10<sup>-3</sup> bar) at 60°C for 6 hours. 1.03 g (55%) of the product as colorless solid was obtained.

#### *BF<sub>4</sub>-containing ionic liquids (general procedure)*

A 5 ml round-bottomed flask fitted with magnetic stirrer bar and reflux condenser was charged by 5 mmol of corresponding bromide ionic liquid, 0.83 g (7.5 mmol) of NaBF<sub>4</sub> and 2 ml of water\*. The mixture was stirred for 2 hours. The product was extracted by 3x2 ml of CH<sub>2</sub>Cl<sub>2</sub> (organic layer is upper). The solvent was evaporated and then the second portion of NaBF<sub>4</sub> (0.83 g, 7.5 mmol) and 2 ml of water\* were added and the resulting mixture was stirred for 3 hours. The product was extracted by 3x2 ml of CH<sub>2</sub>Cl<sub>2</sub> (organic layer is upper). The extract was dried over MgSO<sub>4</sub> and evaporated in vacuum. The product was dried in high vacuum (10<sup>-3</sup> bar) at 60°C for 6 hours. Yield of products are 55-65 %. The reaction of sample of ionic liquid with AgNO<sub>3</sub> was negative, that demonstrates the absence of Br<sup>-</sup> ions in the ionic liquid media.

\*For synthesis of [d<sub>12</sub>-Bmim]BF<sub>4</sub> D<sub>2</sub>O was used as solvent.

### **3. The NMR spectral data of ionic liquids**

All NMR spectra were obtained using the Bruker AVANCE III HD spectrometer at 16.7 T and frequencies 700 MHz for protons and 107.5 MHz for deuterons. For each ionic liquid, a set of complementary <sup>1</sup>H and <sup>2</sup>D NMR spectra were obtained at room temperature. The <sup>1</sup>H NMR spectra were obtained for protonated ionic liquids dissolved in deuterated acetonitrile, while for deuterated substances <sup>1</sup>H and <sup>2</sup>D spectra were obtained in protonated acetonitrile. <sup>1</sup>H NMR spectra in protonated solvents were recorded using efficient solvent suppression technique "excitation sculpting" (zgesgp pulse program).<sup>54</sup> Proton chemical shifts were referenced to residual signal of acetonitrile (δ=1.94 ppm).<sup>55</sup> Chemical shifts in <sup>2</sup>D NMR spectra were adjusted manually for the best correlation with <sup>1</sup>H NMR spectra.

#### *1-Butyl-3-methylimidazolium bromide ([Bmim]Br)*

<sup>1</sup>H NMR: δ 9.25 (s, 1H, H-2); 7.51 (s, 1H, H-4); 7.47 (s, 1H, H-5); 4.23 (t, 2H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, N-CH<sub>2</sub>); 3.91 (s, 3H, NCH<sub>3</sub>); 1.85 (tt, 2H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, 2-CH<sub>2</sub>); 1.35 (qt, 2H, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, 3-CH<sub>2</sub>); 0.96 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, 4-CH<sub>3</sub>).

*1-(d<sub>9</sub>-Butyl)-3-methylimidazolium bromide ([d<sub>9</sub>-Bmim]Br)*

<sup>1</sup>H NMR: δ 9.42 (s, 1H, H-2); 7.62 (s, 1H, H-4); 7.58 (s, 1H, H-5); 3.99 (s, 3H, N-CH<sub>3</sub>).

<sup>2</sup>D NMR: δ 4.25 (s, 2D, N-CD<sub>2</sub>); 1.84 (s, 2D, 2-CD<sub>2</sub>); 1.33 (s, 2D, 3-CD<sub>2</sub>); 0.94 (s, 3D, 4-CD<sub>3</sub>).

*1-(d<sub>9</sub>-Butyl)-3-methyl(2,4,5-deutero)imidazolium bromide ([d<sub>12</sub>-Bmim]Br)*

<sup>1</sup>H NMR: δ 3.99 (s, 3H, NCH<sub>3</sub>).

<sup>2</sup>D NMR: δ 9.28 (s, 1D, D-2); 7.59 (s, 1D, D-4); 7.56 (s, 1D, D-5); 4.25 (s, 2D, N-CD<sub>2</sub>); 1.85 (s, 2D, 2-CD<sub>2</sub>); 1.34 (s, 2D, 3-CD<sub>2</sub>); 0.96 (s, 3D, 4-CD<sub>3</sub>).

*1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF<sub>4</sub>)*

<sup>1</sup>H NMR: δ 8.51 (s, 1H, H-2); 7.42 (s, 1H, H-4); 7.39 (s, 1H, H-5); 4.16 (t, 2H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, N-CH<sub>2</sub>); 3.85 (s, 3H, N-CH<sub>3</sub>); 1.83 (tt, 2H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, 2-CH<sub>2</sub>); 1.34 (qt, 2H, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, 3-CH<sub>2</sub>); 0.95 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, 4-CH<sub>3</sub>).

<sup>19</sup>F NMR: δ -152.67 (s, 4F, BF<sub>4</sub>).

*1-(d<sub>9</sub>-Butyl)-3-methylimidazolium tetrafluoroborate ([d<sub>9</sub>-Bmim]BF<sub>4</sub>)*

<sup>1</sup>H NMR: δ 8.54 (s, 1H, H-2); 7.46 (s, 1H, H-4); 7.43 (s, 1H, H-5); 3.90 (s, 3H, N-CH<sub>3</sub>).

<sup>2</sup>H NMR: δ 4.14 (s, 2D, N-CD<sub>2</sub>); 1.80 (s, 2D, 2-CD<sub>2</sub>); 1.30 (s, 2D, 3-CD<sub>2</sub>); 0.92 (s, 3D, 4-CD<sub>3</sub>).

<sup>19</sup>F NMR: δ -151.83 (s, 4F, BF<sub>4</sub>).

*1-(d<sub>9</sub>-Butyl)-3-methyl(2,4,5-deutero)imidazolium tetrafluoroborate ([d<sub>12</sub>-Bmim]BF<sub>4</sub>)*

<sup>1</sup>H NMR: δ 3.91 (s, 3H, N-CH<sub>3</sub>).

<sup>2</sup>H NMR: δ 8.53 (s, 1D, D-2); 7.46 (s, 1D, D-4); 7.43 (s, 1D, D-5); 4.14 (s, 2D, N-CD<sub>2</sub>); 1.80 (s, 2D, 2-CD<sub>2</sub>); 1.30 (s, 2D, 3-CD<sub>2</sub>); 0.92 (s, 3D, 4-CD<sub>3</sub>).

<sup>19</sup>F NMR: δ -151.80 (s, 4F, BF<sub>4</sub>).

*N-Butylpyridinium tetrafluoroborate ([BuPy]BF<sub>4</sub>)*

<sup>1</sup>H NMR: δ 8.75 (d, 2H, <sup>3</sup>J<sub>HH</sub> 5.6 Hz, o-H); 8.54 (tt, 1H, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, <sup>4</sup>J<sub>HH</sub> 1.2 Hz, p-H); 8.06 (dd, 2H, <sup>3</sup>J<sub>HH</sub> 6.7 Hz, <sup>3</sup>J<sub>HH</sub> 6.7 Hz, m-H); 4.56 (t, 2H, <sup>3</sup>J<sub>HH</sub> 7.6 Hz, N-CH<sub>2</sub>); 1.97 (tt, 2H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, <sup>3</sup>J<sub>HH</sub> 7.6 Hz, 2-CH<sub>2</sub>); 1.39 (qt, 2H, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, 3-CH<sub>2</sub>); 0.97 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, 4-CH<sub>3</sub>).

<sup>19</sup>F NMR: δ -152.40 (s, 4F, BF<sub>4</sub>).

*N-(d<sub>9</sub>-Butyl)pyridinium tetrafluoroborate ([d<sub>9</sub>-BuPy]BF<sub>4</sub>)*

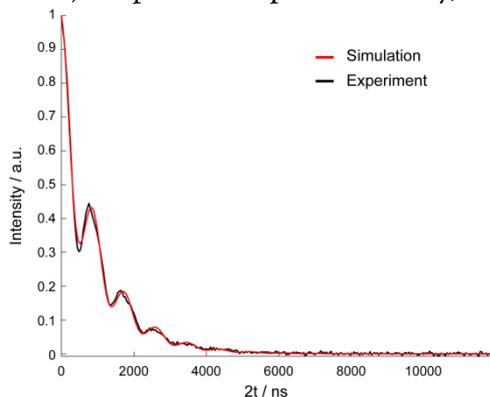
<sup>1</sup>H NMR: δ 8.79 (d, 2H, <sup>3</sup>J<sub>HH</sub> 6.2 Hz, o-H); 8.58 (t, 1H, <sup>3</sup>J<sub>HH</sub> 8.0 Hz, p-H); 8.11 (bs, 2H, m-H).

<sup>2</sup>H NMR: δ 4.54 (s, 2D, N-CD<sub>2</sub>); 1.93 (s, 2D, 2-CD<sub>2</sub>); 1.34 (s, 2D, 3-CD<sub>2</sub>); 0.93 (s, 3D, 4-CD<sub>3</sub>).

<sup>19</sup>F NMR: δ -152.11 (s, 4F, BF<sub>4</sub>).

#### 4. Spin-echo decay simulation

The echo-detected EPR spectra and phase memory times were recorded using the standard two-pulse echo sequence with pulse lengths being typically 100 ns for  $\pi$  and 50 ns for  $\pi/2$  pulses. The electron spin echo envelope modulations (ESEEM) are present in spin-echo decay, as is illustrated in Figure S1.



**Figure S1.** The example of spin-echo decay with ESEEM modulation. Black curve – experimental data, red curve – simulation.

This curve can be described by following expression<sup>S6</sup>

$$V(t) = A[\sin(\omega t + \varphi) + c]e^{-\frac{2t}{T_2}},$$

where  $\omega$  corresponds to deuterium ESEEM frequency at 9.6 GHz ( $\sim 2.29$  MHz),  $T_2$  – transverse relaxation time,  $A, c, \varphi$  – adjusted constants. As a result,  $T_2$  for corresponding field position at certain temperature had been obtained.

## 5. References

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