

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

Mikhail Yu. Ivanov,^{†,*} Sergey A. Prikhod'ko,[§] Olga D. Bakulina,^{†,‡} Alexey S. Kiryutin,[†] Nicolay Yu. Adonin,[§] Matvey V. Fedin^{†,*}

[†]International Tomography Center SB RAS, Institutskaya Street 3a, 630090 Novosibirsk, Russia

[‡]Novosibirsk State University, Pirogova Street 2, 630090 Novosibirsk, Russia

[§]Boreskov Institute of Catalysis SB RAS, Lavrentiev Avenue 5, 630090 Novosibirsk, Russia

Table of Contents

1. Chemicals.....	S1
2. Synthesis of deuterated ionic liquids.....	S1
3. The NMR spectral data of ionic liquids.....	S2
4. Spin-echo decay simulation	S4
5. References.....	S5

1. Chemicals

Chlorobutane, N-methyl imidazole, pyridine, sodium tetrafluoroborate and all standard chemicals were obtained from commercial sources. 1-Butanol-d₁₀ was purchased from Sigma Aldrich.

The ionic liquids [Bmim]Cl and [BuPy]Cl were obtained by analogy with the literature method^{S1} from 1-methyl imidazole or pyridine and chlorobutane. The ionic liquids [Bmim]BF₄ and [BuPy]BF₄ were obtained by previously reported method.^{S2}

2. Synthesis of deuterated ionic liquids

D₉-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% H₂SO₄ was slowly added with stirring. After warming to the room temperature, 2.61 g (31.4 mmol) of 1-Butanol-d₁₀ was added with stirring and then 1.61 g (0.92 ml, 17.0 mmol) of 96% H₂SO₄ 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 NaHCO₃ solution and then with water, dried over MgSO₄ and distilled. 3.47 g (76%) of d₉-brombutane as a colorless liquid was obtained. In the GCMS we observed one peak with molecular ion of mass 146.

[D₉-Bmim]Br and [d₉-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 d₉-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 (10⁻³ bar) at 60°C for 6 hours. The product yield was 55%

[D₁₂-Bmim]Br (by analogy with ref.^{S3})

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 d₉-BmimBr and catalytic amount of K₂CO₃ (about 3 mg, 0.02 mmol). Outside the glove box 3 ml of D₂O (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 D₂O (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 MgSO₄. Then MgSO₄ was filtered, solvent was evaporated and product was dried in high vacuum (10⁻³ bar) at 60°C for 6 hours. 1.03 g (55%) of the product as colorless solid was obtained.

BF₄-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 NaBF₄ and 2 ml of water*. The mixture was stirred for 2 hours. The product was extracted by 3x2 ml of CH₂Cl₂ (organic layer is upper). The solvent was evaporated and then the second portion of NaBF₄ (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 CH₂Cl₂ (organic layer is upper). The extract was dried over MgSO₄ and evaporated in vacuum. The product was dried in high vacuum (10⁻³ bar) at 60°C for 6 hours. Yield of products are 55-65 %. The reaction of sample of ionic liquid with AgNO₃ was negative, that demonstrates the absence of Br⁻ ions in the ionic liquid media.

*For synthesis of [d₁₂-Bmim]BF₄ D₂O 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 ¹H and ²D NMR spectra were obtained at room temperature. The ¹H NMR spectra were obtained for protonated ionic liquids dissolved in deuterated acetonitrile, while for deuterated substances ¹H and ²D spectra were obtained in protonated acetonitrile. ¹H NMR spectra in protonated solvents were recorded using efficient solvent suppression technique "excitation sculpting" (zgpg30 pulse program).^{S4} Proton chemical shifts were referenced to residual signal of acetonitrile (δ=1.94 ppm).^{S5} Chemical shifts in ²D NMR spectra were adjusted manually for the best correlation with ¹H NMR spectra.

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

¹H NMR: δ 9.25 (s, 1H, H-2); 7.51 (s, 1H, H-4); 7.47 (s, 1H, H-5); 4.23 (t, 2H, ³J_{HH} 7.3 Hz, N-CH₂); 3.91 (s, 3H, NCH₃); 1.85 (tt, 2H, ³J_{HH} 7.4 Hz, ³J_{HH} 7.4 Hz, 2-CH₂); 1.35 (qt, 2H, ³J_{HH} 7.5 Hz, ³J_{HH} 7.5 Hz, 3-CH₂); 0.96 (t, 3H, ³J_{HH} 7.4 Hz, 4-CH₃).

1-(d₉-Butyl)-3-methylimidazolium bromide ([d9-Bmim]Br)

¹H 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-CH₃).

²D NMR: δ 4.25 (s, 2D, N-CD₂); 1.84 (s, 2D, 2-CD₂); 1.33 (s, 2D, 3-CD₂); 0.94 (s, 3D, 4-CD₃).

1-(d₉-Butyl)-3-methyl(2,4,5-deutero)imidazolium bromide ([d12-Bmim]Br)

¹H NMR: δ 3.99 (s, 3H, NCH₃).

²D 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-CD₂); 1.85 (s, 2D, 2-CD₂); 1.34 (s, 2D, 3-CD₂); 0.96 (s, 3D, 4-CD₃).

1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄)

¹H NMR: δ 8.51 (s, 1H, H-2); 7.42 (s, 1H, H-4); 7.39 (s, 1H, H-5); 4.16 (t, 2H, ³J_{HH} 7.3 Hz, N-CH₂); 3.85 (s, 3H, N-CH₃); 1.83 (tt, 2H, ³J_{HH} 7.4 Hz, ³J_{HH} 7.5 Hz, 2-CH₂); 1.34 (qt, 2H, ³J_{HH} 7.5 Hz, ³J_{HH} 7.5 Hz, 3-CH₂); 0.95 (t, 3H, ³J_{HH} 7.4 Hz, 4-CH₃).

¹⁹F NMR: δ -152.67 (s, 4F, BF₄).

1-(d₉-Butyl)-3-methylimidazolium tetrafluoroborate ([d9-Bmim]BF₄)

¹H 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-CH₃).

²H NMR: δ 4.14 (s, 2D, N-CD₂); 1.80 (s, 2D, 2-CD₂); 1.30 (s, 2D, 3-CD₂); 0.92 (s, 3D, 4-CD₃).

¹⁹F NMR: δ -151.83 (s, 4F, BF₄).

1-(d₉-Butyl)-3-methyl(2,4,5-deutero)imidazolium tetrafluoroborate ([d12-Bmim]BF₄)

¹H NMR: δ 3.91 (s, 3H, N-CH₃).

²H 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-CD₂); 1.80 (s, 2D, 2-CD₂); 1.30 (s, 2D, 3-CD₂); 0.92 (s, 3D, 4-CD₃).

¹⁹F NMR: δ -151.80 (s, 4F, BF₄).

N-Butylpyridinium tetrafluoroborate ([BuPy]BF₄)

¹H NMR: δ 8.75 (d, 2H, ³J_{HH} 5.6 Hz, o-H); 8.54 (tt, 1H, ³J_{HH} 7.8 Hz, ⁴J_{HH} 1.2 Hz, p-H); 8.06 (dd, 2H, ³J_{HH} 6.7 Hz, ³J_{HH} 6.7 Hz, m-H); 4.56 (t, 2H, ³J_{HH} 7.6 Hz, N-CH₂); 1.97 (tt, 2H, ³J_{HH} 7.4 Hz, ³J_{HH} 7.6 Hz, 2-CH₂); 1.39 (qt, 2H, ³J_{HH} 7.5 Hz, ³J_{HH} 7.5 Hz, 3-CH₂); 0.97 (t, 3H, ³J_{HH} 7.4 Hz, 4-CH₃).

¹⁹F NMR: δ -152.40 (s, 4F, BF₄).

N-(d₉-Butyl)pyridinium tetrafluoroborate ([d9-BuPy]BF₄)

¹H NMR: δ 8.79 (d, 2H, ³J_{HH} 6.2 Hz, o-H); 8.58 (t, 1H, ³J_{HH} 8.0 Hz, p-H); 8.11 (bs, 2H, m-H).

²H NMR: δ 4.54 (s, 2D, N-CD₂); 1.93 (s, 2D, 2-CD₂); 1.34 (s, 2D, 3-CD₂); 0.93 (s, 3D, 4-CD₃).

¹⁹F NMR: δ -152.11 (s, 4F, BF₄).

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 π 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.

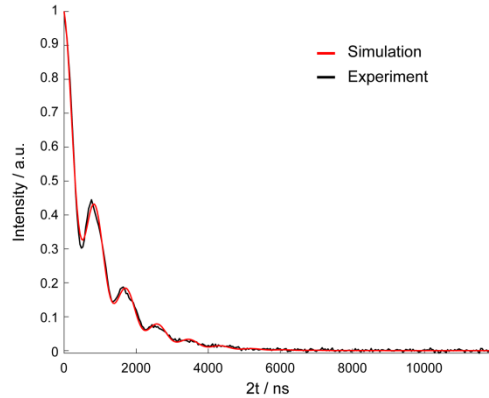


Figure S1. The example of spin-echo decay with ESEEM modulation. Black curve – experimental data, red curve – simulation.

This curve can be described by following expression^{S6}

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

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

5. References

- (S1) Dupont, J.; Consorti, C. S.; Suarez, P. a. Z.; De Souza, R. F. PREPARATION OF 1-BUTYL-3-METHYL IMIDAZOLIUM-BASED ROOM TEMPERATURE IONIC LIQUIDS. *Org. Synth.* **2002**, 79 (September), 236. <https://doi.org/10.15227/orgsyn.079.0236>.
- (S2) Bakulina, O. D.; Ivanov, M. Y.; Prikhod'ko, S. A.; Pylaeva, S.; Zaytseva, I. V; Surovtsev, N. V; Adonin, N. Y.; Fedin, M. V. Nanocage Formation and Structural Anomalies in Imidazolium Ionic Liquid Glasses Governed by Alkyl Chains of Cations. *Nanoscale* **2020**, 12 (38), 19982–19991. <https://doi.org/10.1039/D0NR06065H>.
- (S3) Bottini, G.; Moyna, G. Determining the Relative Strengths of Aromatic and Aliphatic C–H · · · X Hydrogen Bonds in Imidazolium Ionic Liquids through Measurement of H/D Isotope Effects on ¹⁹F Nuclear Shielding. *Magn. Reson. Chem.* **2018**, 56 (2), 103–107. <https://doi.org/10.1002/mrc.4615>.
- (S4) Hwang, T. L.; Shaka, A. J. Water Suppression That Works. Excitation Sculpting Using Arbitrary Wave-Forms and Pulsed-Field Gradients. *J. Magn. Reson. Ser. A* **1995**, 112 (2), 275–279. <https://doi.org/10.1006/jmra.1995.1047>.
- (S5) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, 29 (9), 2176–2179. <https://doi.org/10.1021/om100106e>.
- (S6) Schweiger, A.; Jeschke, G. *Principles of Pulse Electron Paramagnetic Resonance*, 1st ed.; Oxford University Press: Oxford, 2001.