# Local Structure Evolution and its Connection to Thermodynamic and Transport Properties of 1-Buty-3-methylimidazolium Tetrafluoroborate and Water Mixtures by Molecular Dynamics Simulations

**Xiujuan Zhong, Zhen Fan, Zhiping Liu*, Dapeng Cao***

Division of Molecular and Materials Simulation, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

**Supporting information:** All the parameters of force field used in this work can be found in Table S1. Densities by simulations of different box sizes are compared in Table S2. Figure S1 provided the comparisons of the center-of-mass radial distribution function of water and anion calculated in different size simulations. Figure S2 showed the snapshots in mixtures of $x_2$=0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 0.95.

Table S1: Force field parameters for $[C_4mim][BF_4]$ and water in this work.

| atoms | Lennard-Jones | | Charges (e) |
|---|---|---|---|
| | σ/ Å | ε/ kcal.mol$^{-1}$ | |
| NA | 3.250 | 0.170 | 0.0150 |
| CR | 3.400 | 0.086 | 0.0000 |
| CW | 3.400 | 0.086 | -0.1600 |
| H5 | 1.247 | 0.030 | 0.1500 |
| H4 | 1.604 | 0.030 | 0.2000 |
| CN3 | 3.660 | 0.190 | 0.2600 |
| CN2 | 3.820 | 0.091 | 0.2300 |
| CT2 | 3.950 | 0.091 | 0.050* |
| CT3 | 3.750 | 0.190 | 0.000 |
| B | 3.580 | 0.096 | 0.428 |
| F | 3.118 | 0.062 | -0.307 |
| O | 3.164 | 0.163 | -1.048 |
| H | 0 | 0 | 0.524 |
| Bond | $k_r$ / kcal.mol$^{-1}$Å$^{-2}$ | | $r_0$ / Å |
| NA-CR | 411.1 | | 1.325 |
| CW-NA | 411.1 | | 1.378 |
| CW-CW | 478.4 | | 1.343 |
| CW-H4 | 344.3 | | 1.070 |
| CR-H5 | 344.3 | | 1.070 |
| NA-CN3 | 258.5 | | 1.500 |
| NA-CN2 | 258.5 | | 1.490 |
| CT2-CN2 | 194.6 | | 1.610 |
| CT2-CT2 | 194.6 | | 1.610 |
| CT2-CT3 | 261.0 | | 1.610 |
| B-F | 300.0 | | 1.390 |
| O-Hw | - | | 0.957 |
| angle | $k_\theta$ / kcal.mol$^{-1}$rad$^{-2}$ | | $\theta_0$ / rad |
| CW-NA-CR | 67.8 | | 108.0 |
| NA-CR-NA | 73.7 | | 109.9 |
| NA-CR-H5 | 51.2 | | 125.7 |
| H4-CW-NA | 51.2 | | 122.1 |
| H4-CW-CW | 50.0 | | 130.7 |
| NA-CW-CW | 69.8 | | 107.1 |
| NA-CN2-CT2 | 80.0 | | 112.2 |
| CW-NA-CN2 | 64.2 | | 125.7 |
| CR-NA-CN2 | 64.2 | | 126.3 |
| CN3-NA-CW | 64.2 | | 125.7 |
| CN3-NA-CR | 64.2 | | 126.3 |
| CT2-CT2-CN2 | 93.6 | | 102.2 |

| | | | |
|---|---|---|---|
| CT2-CT2-CT3 | 113.6 | | 104.8 |
| F-B-F | 50.0 | | 109.5 |
| H-O-H | - | | 104.5 |

| dihedral | n | $k_\chi$ / kcal.mol$^{-1}$ | δ / degree |
|---|---|---|---|
| H4-CW-NA-CN3 | 2 | 1.5 | 180 |
| H4-CW-NA-CR | 2 | 2 | 180 |
| CW-CW-NA-CR | 2 | 12 | 180 |
| NA-CW-CW-H4 | 2 | 1.5 | 180 |
| NA-CW-CW-NA | 2 | 12 | 180 |
| CN3-NA-CR-NA | 2 | 2 | 180 |
| CN3-NA-CR-H5 | 2 | 1.5 | 180 |
| CW-NA-CR-NA | 2 | 12 | 180 |
| CW-NA-CR-H5 | 2 | 1.5 | 180 |
| CW-CW-NA-CN2 | 2 | 2 | 180 |
| H4-CW-NA-CN2 | 2 | 1.5 | 180 |
| NA-CR-NA-CN2 | 2 | 2 | 180 |
| H5-CR-NA-CN2 | 2 | 1.5 | 180 |
| CN3-NA-CW-CW | 2 | 2 | 180 |
| H4-CW-CW-H4 | 2 | 1.5 | 180 |
| CW-NA-CN2-CT2 | 1 | 0.694 | 0 |
| | 2 | 0.554 | 180 |
| | 3 | -0.564 | 0 |
| CR-NA-CN2-CT2 | 1 | 0.518 | 0 |
| | 2 | 0.046 | 180 |
| | 3 | -0.782 | 0 |
| X-CT2-CT2-X | 1 | -3.5 | 0 |
| | 2 | 1.6 | 180 |
| | 3 | 1.6 | 0 |
| Improper torsions | | | |
| NA-NA-CR-H5 | 2 | 1.1 | 180 |
| CR-CW-NA-CN3 | 2 | 2 | 180 |
| CR-CW-NA-CN2 | 2 | 2 | 180 |
| NA-CW-CW-H4 | 2 | 1.1 | 180 |

*The charge value is for CT2 connected with CN2. For other CT2, the charges are set to zero.

Table S2. Comparisons of densities by molecular dynamics simulations in different sizes (at 298.15K)

| Molar fraction of water | Box size | Number of Ion pairs | Number of water molecules | Simulation size $L_{box}$ (Å) | densities |
|---|---|---|---|---|---|
| 0.2 | Small | 260 | 65 | 43.121±0.006 | 1.1962 |
| | Large | 2784 | 696 | 96.253±0.004 | 1.1960 |
| 0.4 | Small | 165 | 110 | 52.211±0.009 | 1.1883 |
| | Large | 2688 | 1792 | 96.348±0.004 | 1.1888 |
| 0.6 | Small | 110 | 165 | 38.013±0.005 | 1.1761 |
| | Large | 2520 | 3780 | 96.596+0.003 | 1.1757 |
| 0.8 | Small | 65 | 260 | 34.008±0.004 | 1.1441 |
| | Large | 1295 | 5180 | 82.433±0.004 | 1.1447 |

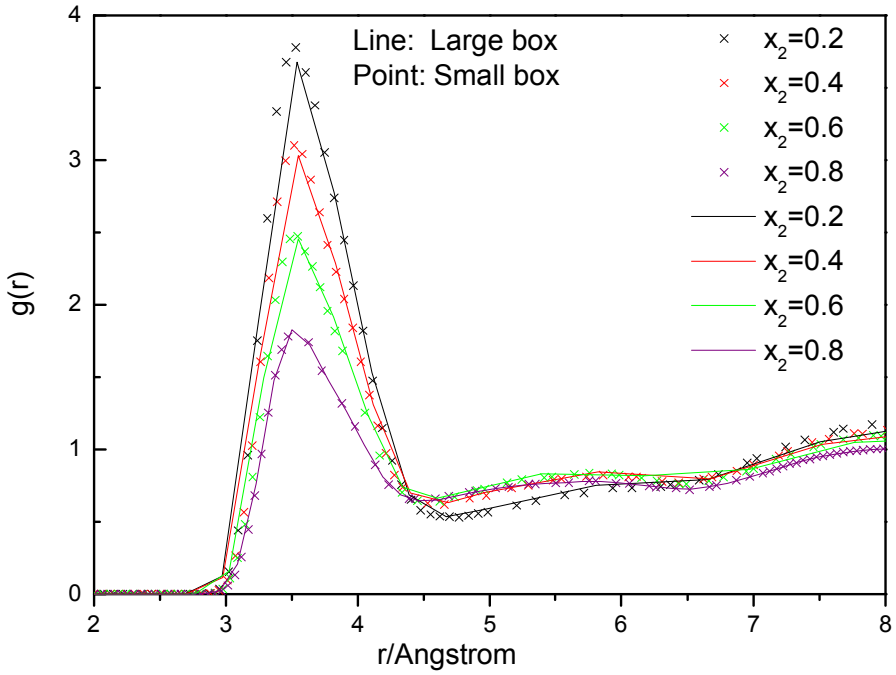
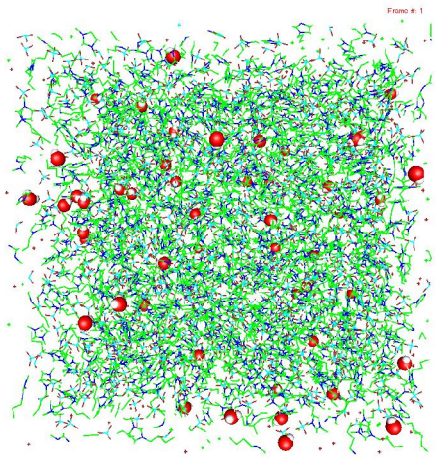
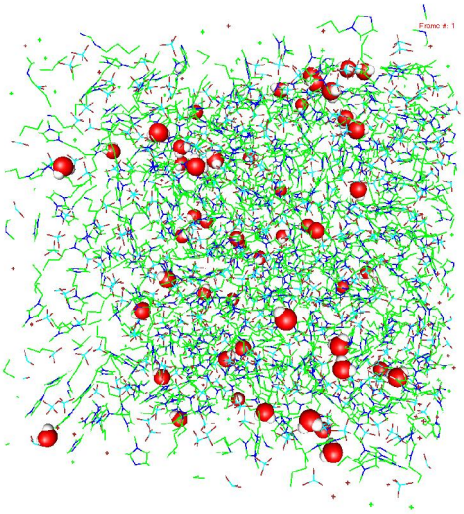



Figure S1. Center-of-mass based radial distribution function of water and anion calculated from small and large sizes of simulation at water molar fraction of $x_2$=0.2, 0.4, 0.6 and 0.8.



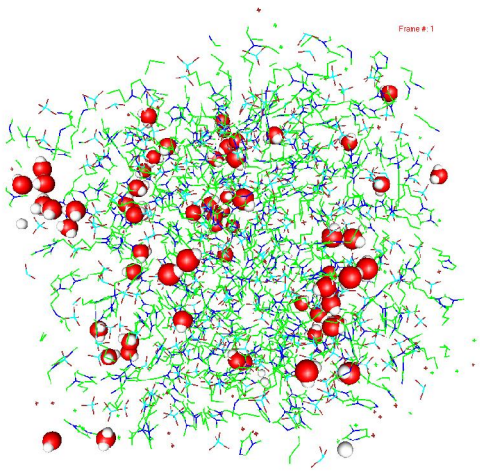
$x_2$=0.05

82% monomer, 15% dimer



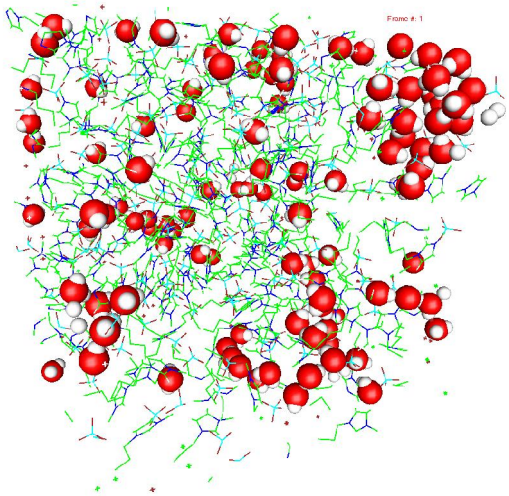
$x_2$=0.1

67% monomer, 22% dimer, ..., 8% 3-mer



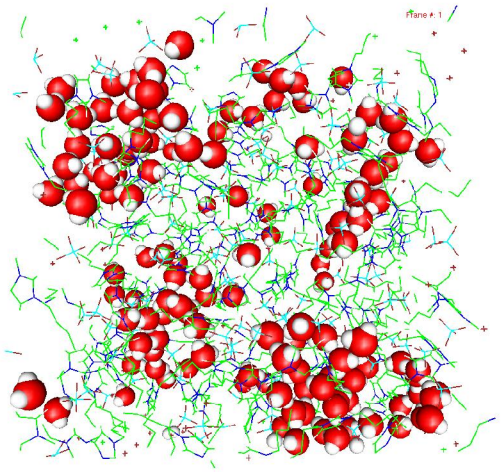
$x_2$=0.2

44% monomer, 19% dimer, 11% 3-mer



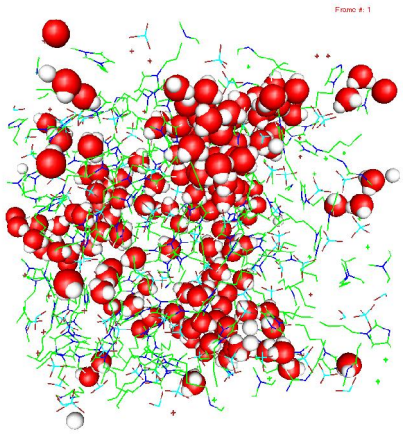
$x_2$=0.4

20% monomer, 12% dimer, ..., 6% 5-mer



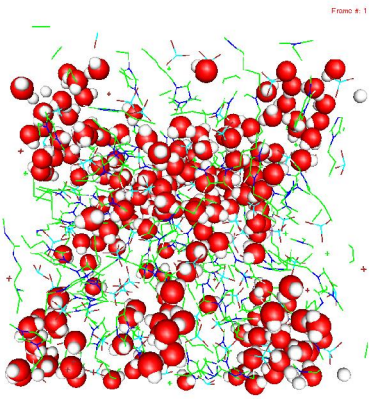
$x_2$=0.5

11% monomer, 10% dimer, …, 40% n-mer (n>20)



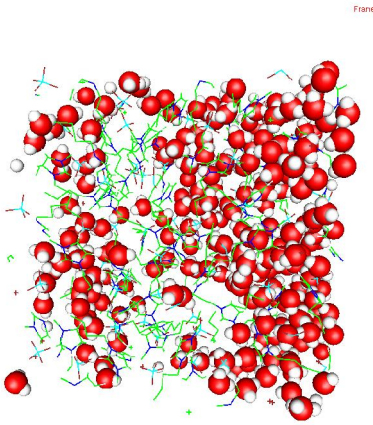
$x_2$=0.6

5.5% monomer, 4.5% dimer, …, 72% n-mer (n>20)



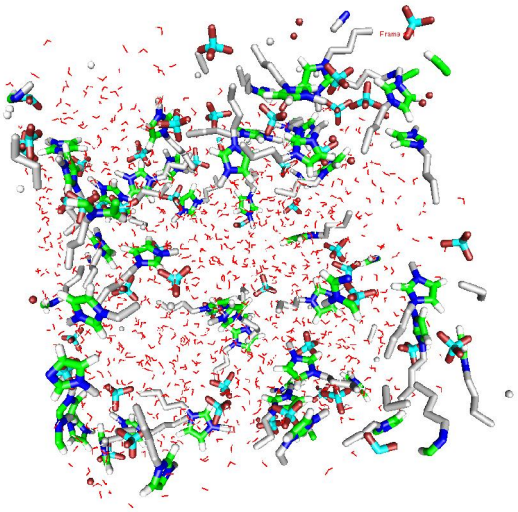
$x_2$=0.7

3% monomer, …, 80% n-mer (n>140)

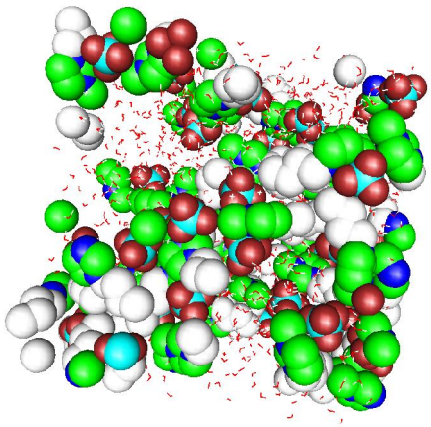


$x_2$=0.8

1.4% monomer, …, 96% n-mer (n>240)



$x_2$=0.95



$x_2$=0.95

Figure S2 Snapshots of mixtures for water mole fraction of $x_2$=0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 0.95. Color code: O atom, red: C atom, green; N atom, blue; B atom, cyan; F atom, pink.