

Molecular features contributing to the lower viscosity of
phosphonium ionic liquids compared to their ammonium
analogues

Supporting Information

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1 Comparison of force field parameters to reference potential

A force field was developed without any contribution of Coulomb forces and of Lennard-Jones potentials on dihedral potentials. Figure 1 and 2 show a comparison of the reference energy potential surface (TPSS-D3(RI)/6-31++G**) and the potential of the final force field.

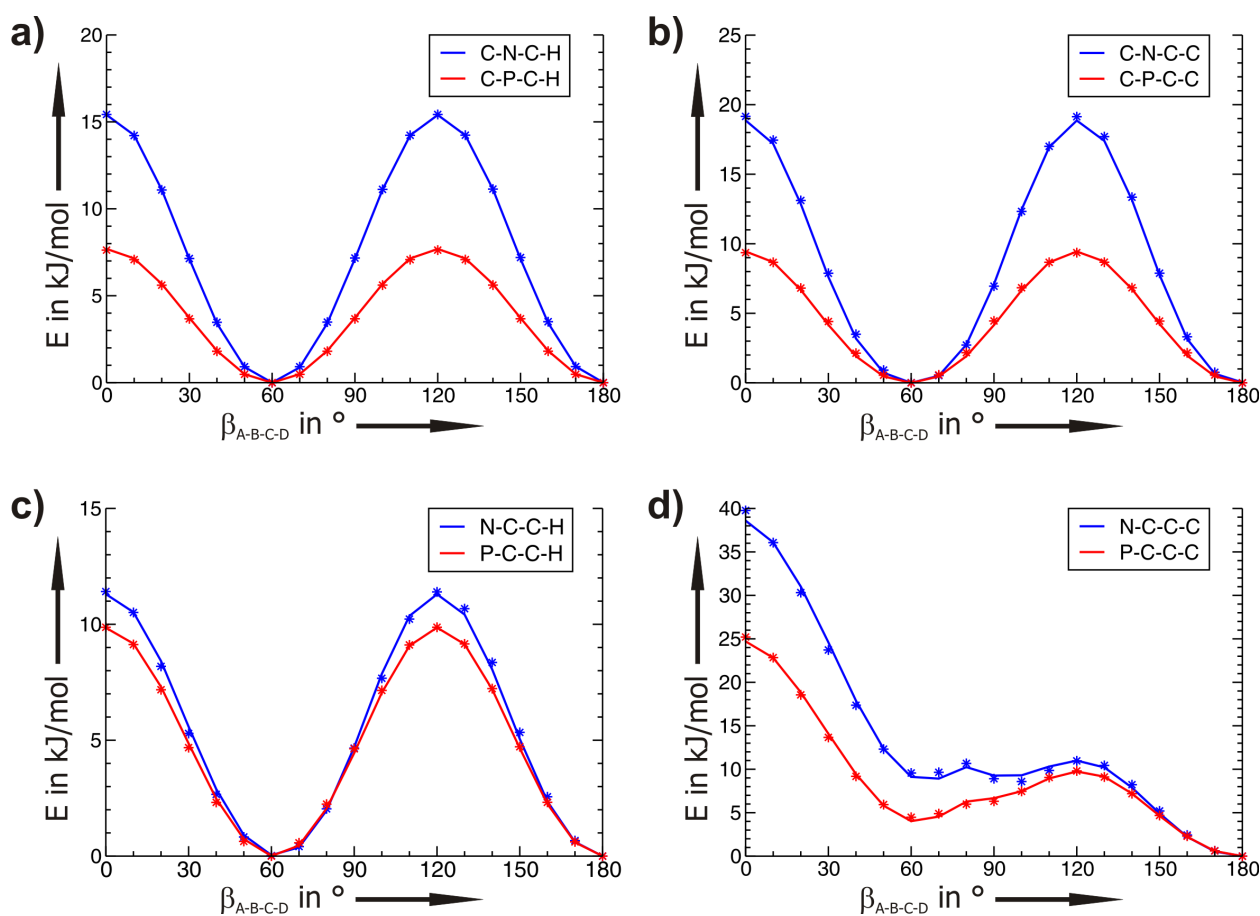


Figure 1: Comparison of the TPSS-D3(RI)/6-31++G** dihedral energy potential surface (solid line) and the force field with the final force constants $K_{m,d}$ (star symbols).

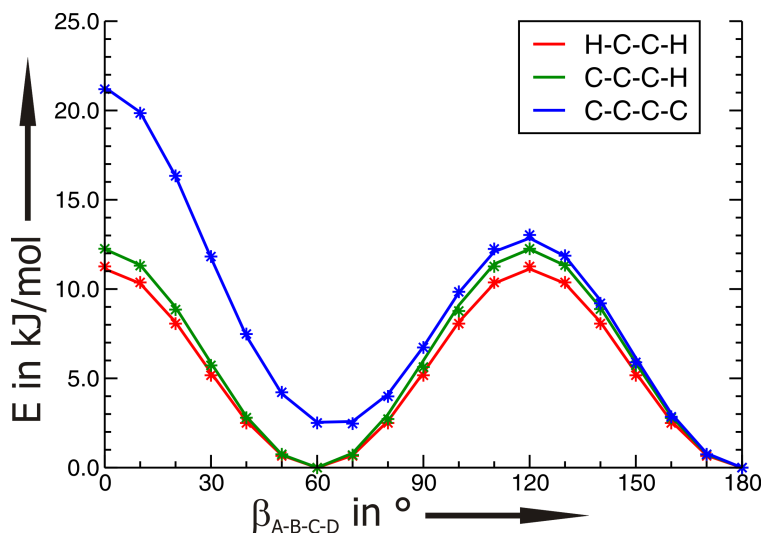


Figure 2: Comparison of the TPSS-D3(RI)/6-31++G** dihedral energy potential surface (solid line) and the force field with the final force constants $K_{m,d}$ (star symbols).

2 Calculation of counter ion association lifetime

An intermittent autocorrelation function with a time length of 15 ns was employed to calculate the counter ion association lifetime. The slope of the autocorrelation function is extrapolated to infinity by exponential fitting. In all cases, the coefficient of determination was larger than 0.99. The lifetime is obtained by the integral of the fitted function multiplied with two. The correlation functions can be seen in Fig. 3.

Additionally, the counter ion association displacement versus the counter ion association lifetime were calculated for **N-org** and **P-org**, see Fig. 4. Values are added to the plot as long as two counter ions fulfill the criterion of counter ion association. The center of mass of two associated ions was selected as center of movement. As can be seen, associated ions migrate only small distances significant below the diameter of the ions. Thus, the term ion pair does not seem suited for the investigated ILs because only long living ion cages are observed.

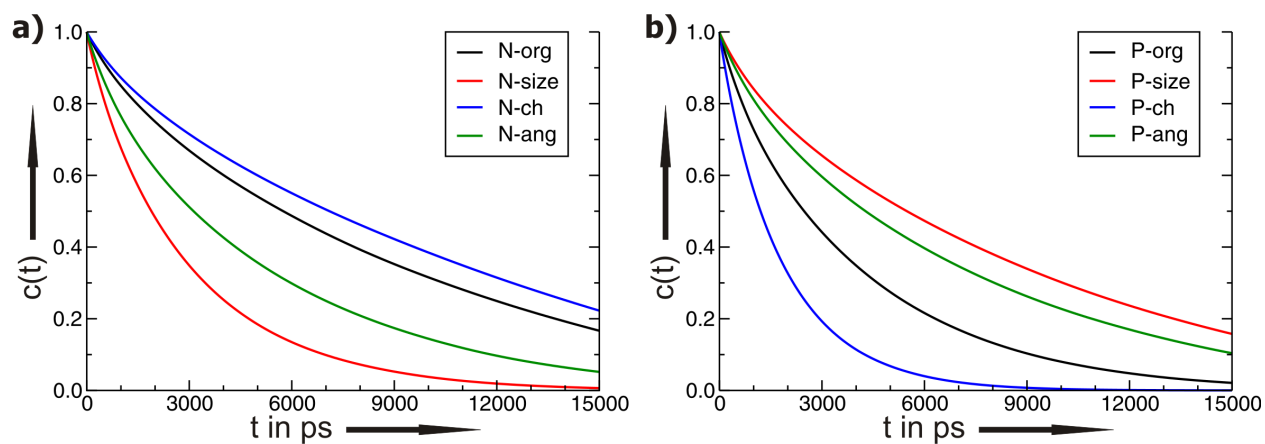


Figure 3: Plot of the counter ion association correlation function $c(t)$.

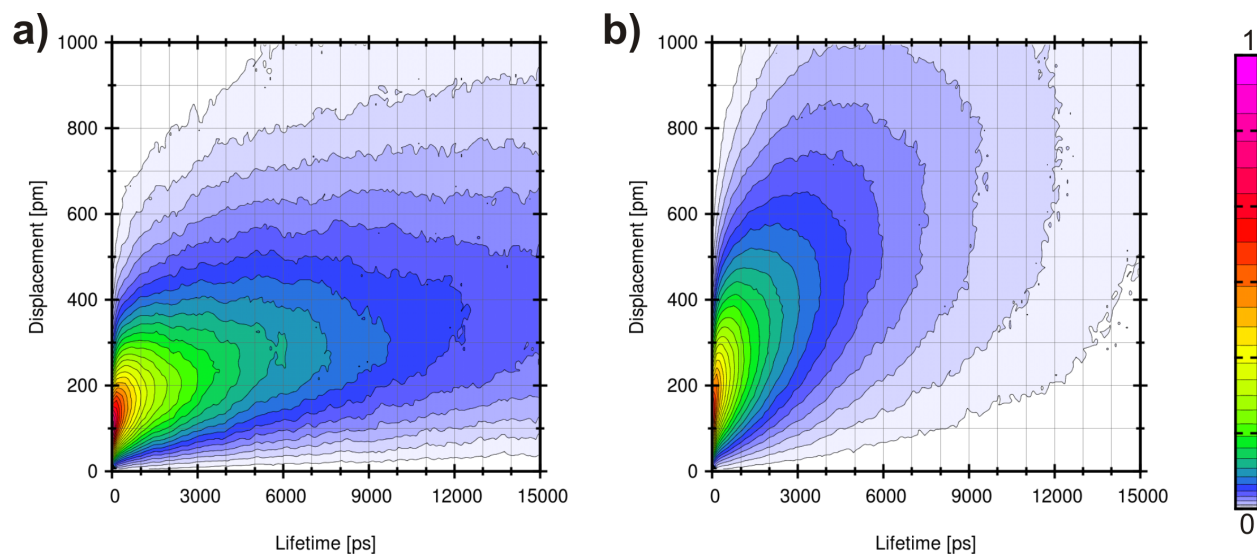


Figure 4: Plot of the counter ion association displacement versus the counter ion association lifetime for **N-org** (a) and **P-org** (b).

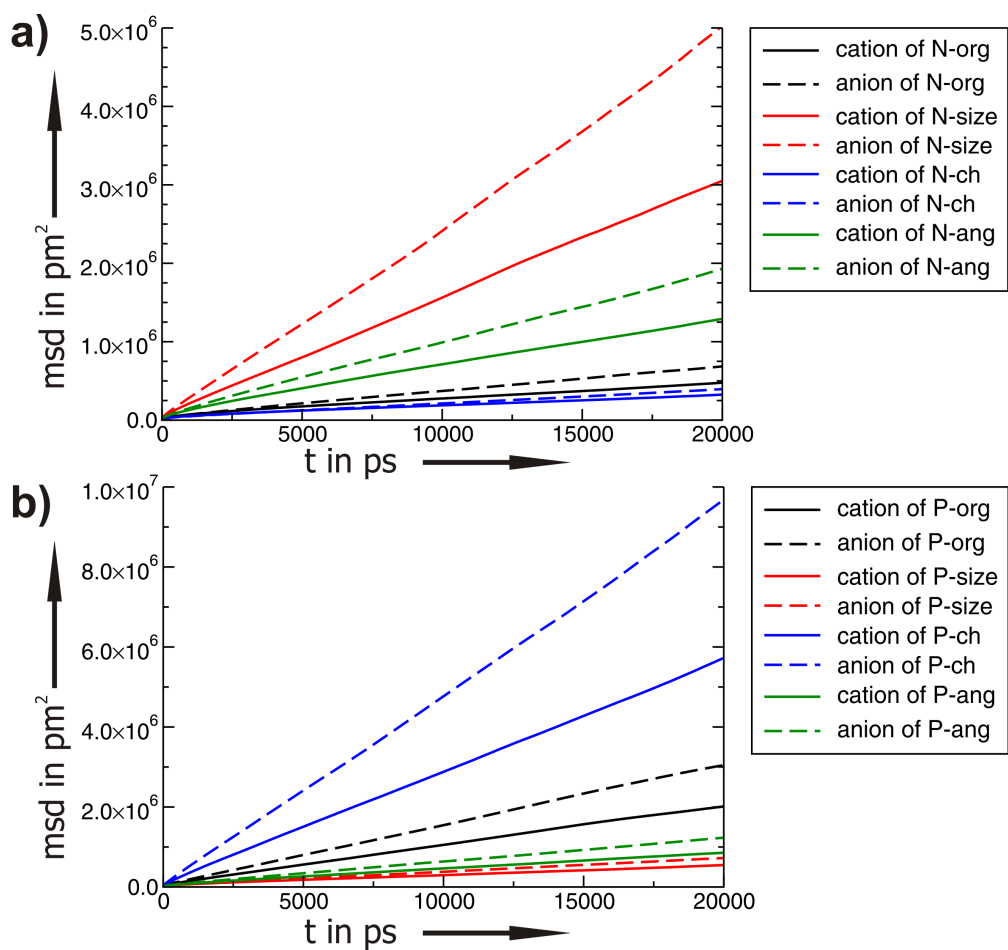


Figure 5: Plot of the mean square displacement versus time for all simulations. Diffusion coefficients were obtained by linear regression between 15 ns and 20 ns.