The interaction of ammonia with the protic ionic liquid ethylammonium nitrate: a simulation study

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Simulation Details

The ethylammonium molecule was parameterized by using the partial charges previously evaluated by Choe *et al.* [1] using the 6-31G** method, while the LJ parameters were reported by Umebayashi *et al.* [2]. On the other hand, the nitrate anion was modelled as a set of seven sites, three of them being heavy sites and the other four virtual. The heavy sites carry no charge, but each of them is associated with 1/3 of the total mass of the ion and placed in such a way they yield the right tensor of inertia. In contrast, virtual sites are massless but have partial charges of $q_N = +0.794$ for the nitrogen atom and $q_O = -0.598$ for the oxygen atoms [3], whose LJ parameters are, respectively, $\sigma_N = 3.496 \cdot 10^{-1}$ nm, $\varepsilon_N = 7.1128 \cdot 10^{-1}$ kJ/mol, $\sigma_O = 3.175 \cdot 10^{-1}$ nm and $\varepsilon_O = 8.7864 \cdot 10^{-1}$ kJ/mol; and were fitted in order to reproduce the experimental density of the pure IL.

Temperature is maintained constant by applying a V-rescale thermostat [4] with a coupling constant of 0.1 ps and 0.5 ps, for the bulk and confined sim-

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ulations, respectively. Pressure control in the bulk systems was performed by using the Parrinello-Rahman barostat [5] with a relaxation time of 1 ps. In these bulk simulations long-range electrostatic interactions were calculated by using the particle-mesh Ewald (PME) [6] method with a cutoff of 1.1 nm, and the same cutoff distance was considered for LJ interactions. In the confined systems, these cutoffs were varied to 1.3 nm and 1 nm, respectively. The linear constraint solver (LINCS) algorithm [7, 8] was used to hold the bonds rigid. We employed periodic boundary conditions along the three directions and Yeh-Berkowitz corrections were included for the slab geometry [9, 10].

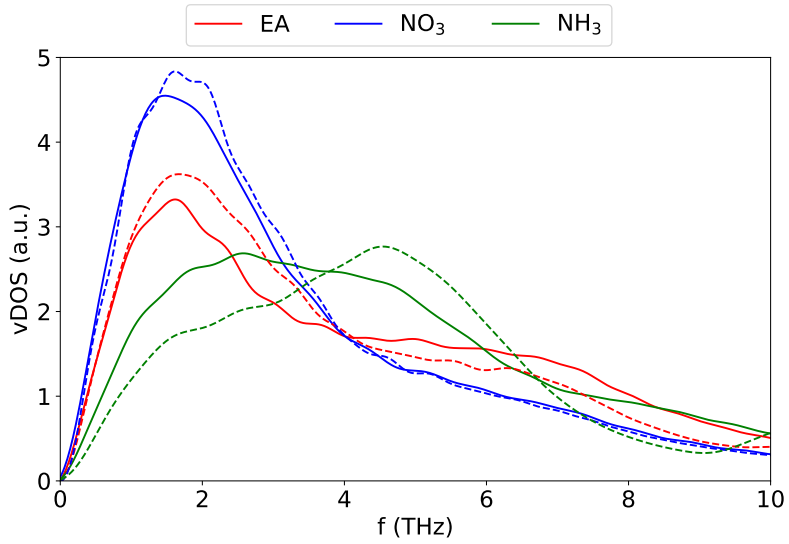

Figure S1: Vibrational density of states for both 4-site (solid lines) and 6-site (dashed lines) models at a 50% ammonia concentration.

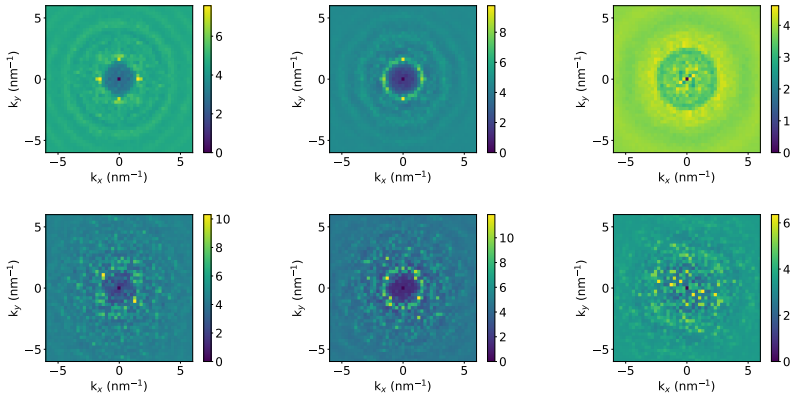

Figure S2: Time-averaged 2D Fourier transforms of the first layer positions in the neutral simulations for a 50% concentration. The upper row corresponds to the 4-site model systems, while the bottom row contains the results for the 6-site systems. The species represented are, from left to right, cation, anion and ammonia.

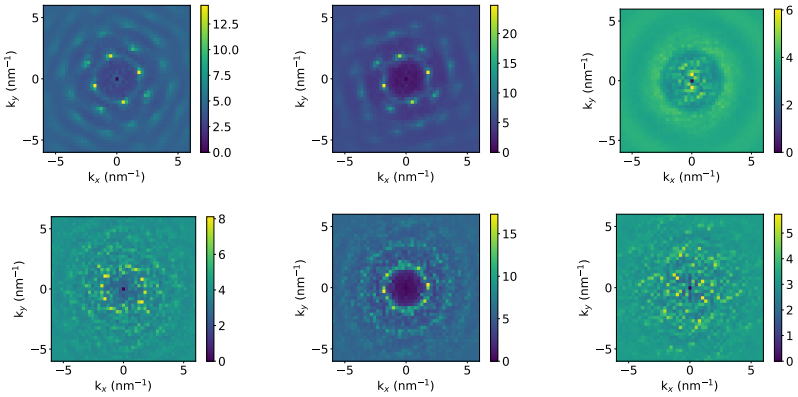

Figure S3: Time-averaged 2D Fourier transforms of the first layer positions near the positively charged wall for a 50% concentration. The upper row corresponds to the 4-site model systems, while the bottom row contains the results for the 6-site systems. The species represented are, from left to right, cation, anion and ammonia.

References

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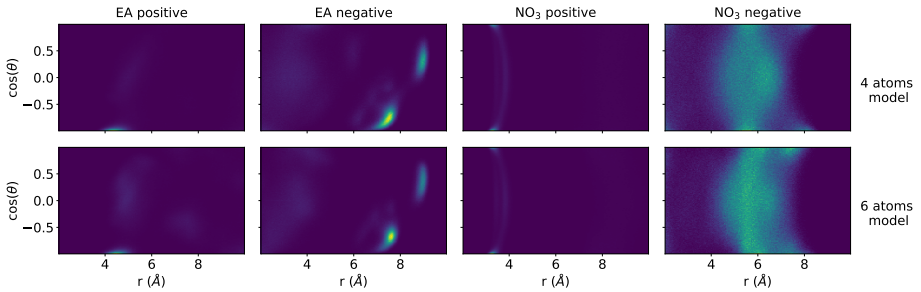

Figure S4: 2D-histogram of the orientations by distance of the molecules from the charged walls. The first two columns corresponds to the cation orientations, near the positively charged wall (first column) and the negatively charged wall (second column). The anion results are plotted in the third (positively charged wall) and fourth (negatively charged wall) columns. The upper row corresponds to the 4-site model systems, while the bottom row contains the results for the 6-site systems.

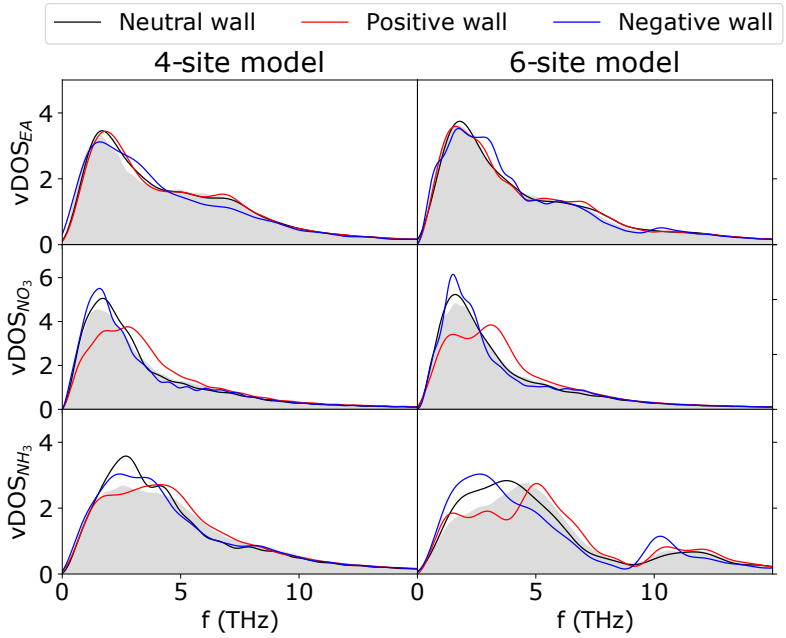

Figure S5: Vibrational densities of states of the three species in both mixtures confined between neutral and charged walls, for a 50% concentration of NH_3. The grey coloured area corresponds to the bulk results.

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