Journal of Molecular Liquids303 : (2020) // Article ID 112588, which has beenpublished in final form at https://doi.org/10.1016/j.molliq.2020.112588.

Lignin solvation by ionic liquids: the role of cation-Supplementary Material

Jon Zubeltzu[b,c], Elena Formoso[b,d], Elixabete Rezabal[a,b]

[a] *Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), 20018 Donostia, Euskadi (Spain)*
[b] *Donostia International Physics Center (DIPC) 20018 Donostia, Euskadi (Spain)*
[c] *Ingenieritza Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), 20018 Donostia, Euskadi (Spain)*
[d] *Farmazia Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), 01006 Vitoria-Gasteiz, Euskaldi (Spain)*

Email address: elixabete.rezabal@ehu.eus (Elixabete Rezabal)

Supplementary material list

- Figure S1: Evolution of ^{lig}H11-Cl^- RDFs trough 100ps and 1 ns statistical sampling.
- Figure S2: ^{lig}O12-^{imi}HX and (b)^{lig}O7-^{imi}HX RDFs in classical MD simulations.
- Figure S3: Scans of the different lignin-IL interactions considered in the study, based on the force-field-based calculations.
- Figure S4: Evolution of ^{lig}ring-^{imi}ring RDF in AIMD trajectory 1
- Figure S5: RDF analysis of the AIMD2 trajectory
- Figure S6: Topological analysis of the AIMD2 trajectory
- Figure S7: Choline-based IL-lignin local minima characterized.
- Figure S8: Et_3NH-based IL-lignin local minima characterized.

S1. Classical MD trajectory analysis

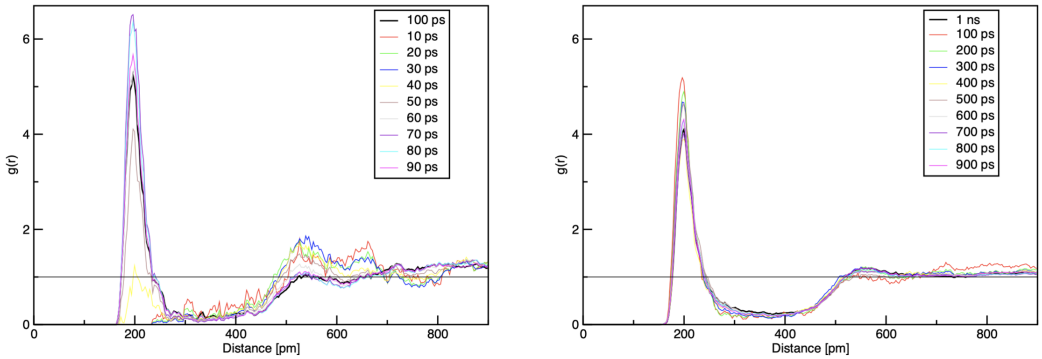

Figure S1: Evolution of ^{lig}H11-Cl^{-} RDFs trough 100ps (left) and 1 ns (right) statistical sampling by means of classical MD simulations on a box of 20 IL pairs and a time step of 0.5 fs.

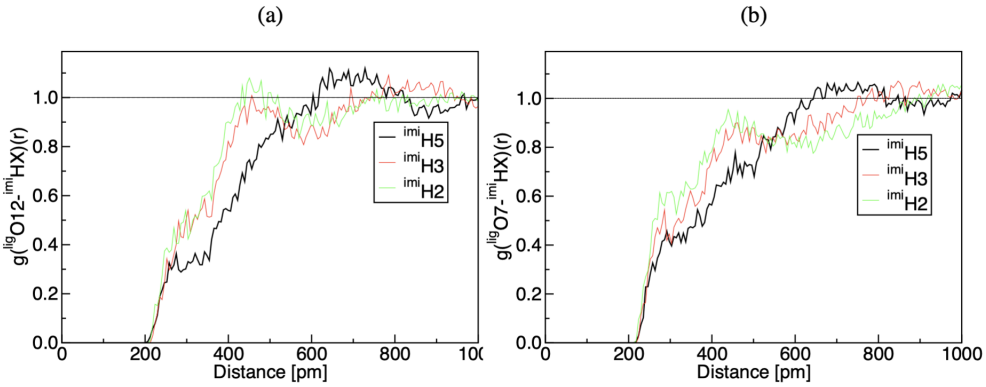

Figure S2: Radial distribution functions obtained from the classical MD simulations between (a)^{lig}O12-^{imi}HX and (b)^{lig}O7-^{imi}HX.

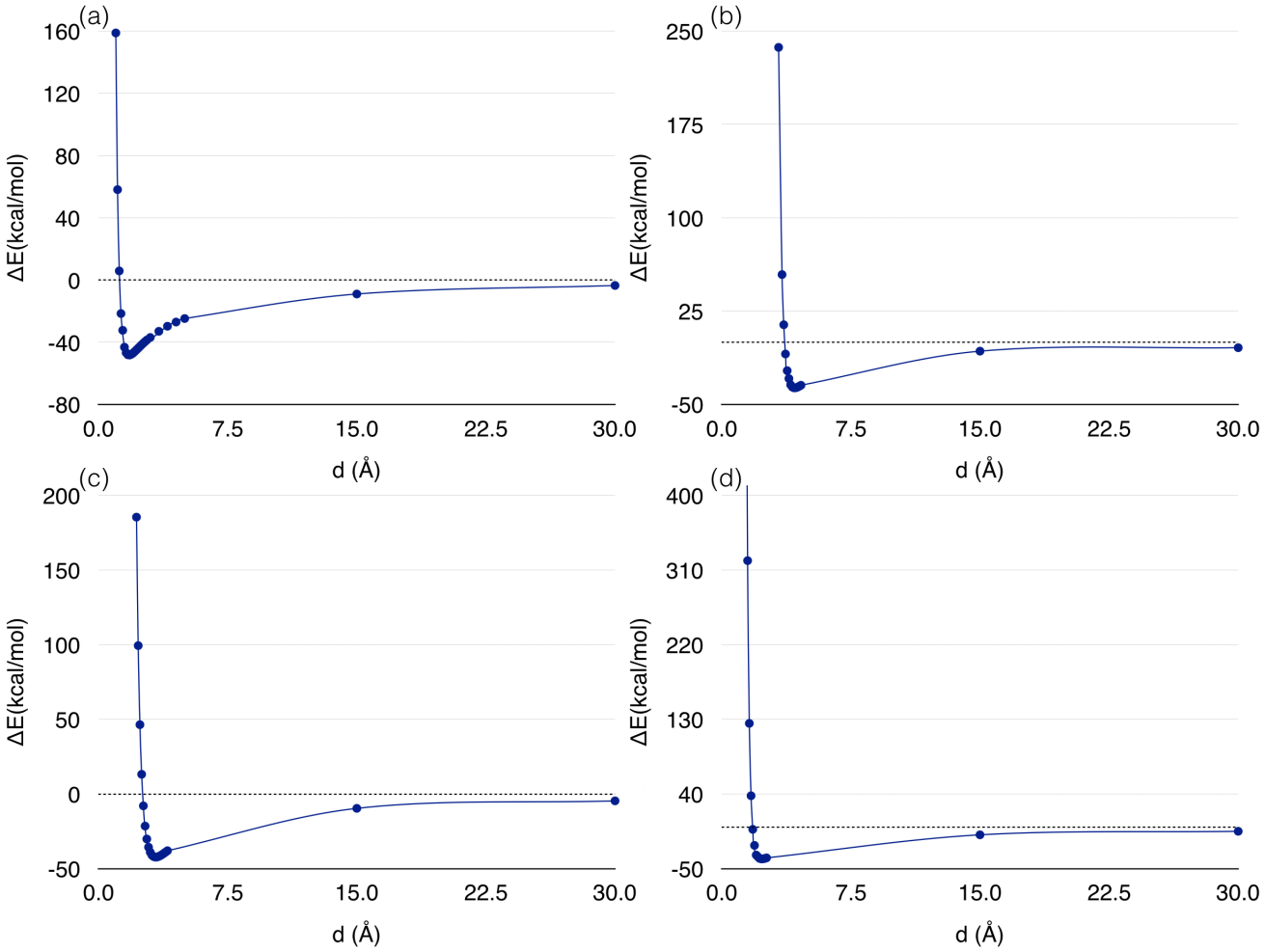

Figure S3: Scans of the different lignin-IL interactions considered in the study: (a) ^{lig}H11-Cl^{-} bond (b) ^{lig}ring -^{imi}alkyl side chain (c) ^{lig}ring -^{imi}ring (d) ^{lig}O11-^{imi}H5 interaction, based on the force-field-based calculations.

S2. AIMD trajectory analysis

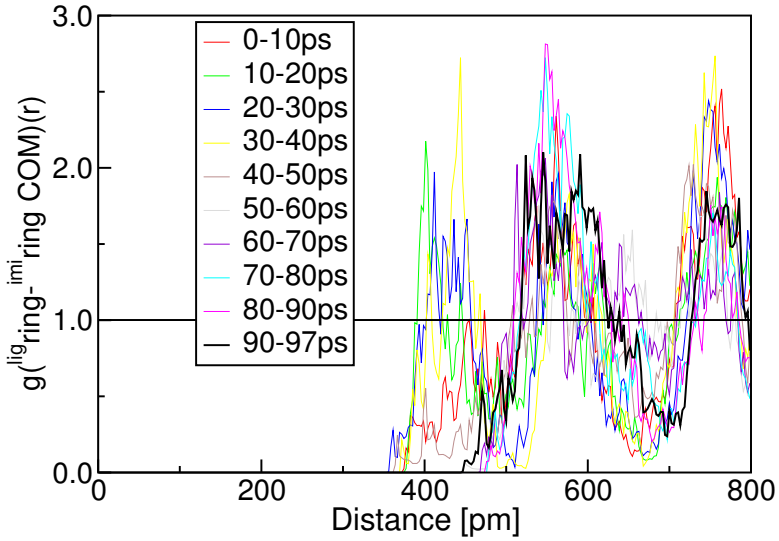

Figure S4: Lignin ring-imidazolium ring RDFs at 10 ps intervals in AIMD1 trajectory

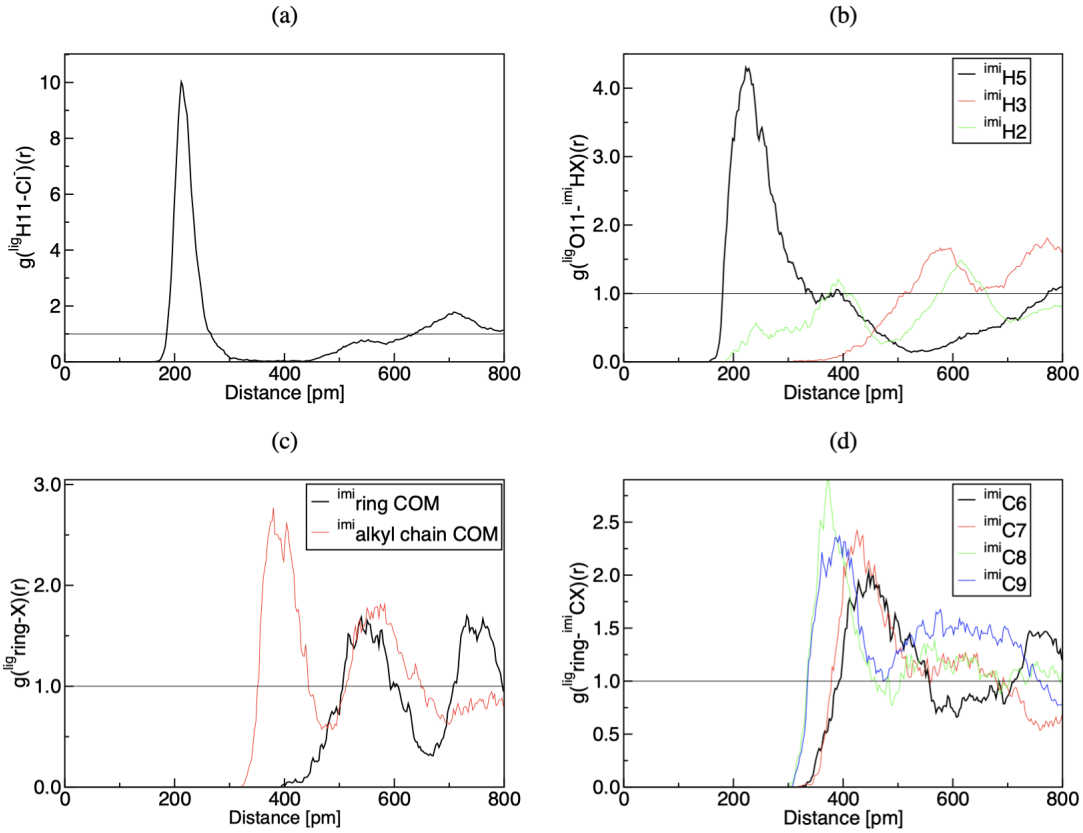

Figure S5: (a)^{lig}H11-anion interaction (b)^{lig}O11-imidazole ring Hs (c) and (d) lignin ring interactions in AIMD2 trajectory.

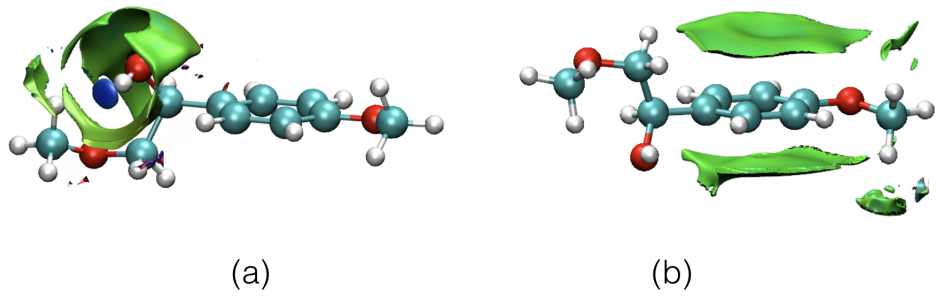

Figure S6: aNCI analysis of the interactions established by (a) ^{lig}H11 (localized, blue surface close to the hydrogen, sign(λ_2)ρ = -0.032) and ^{lig}O11 (wide green surface around the oxygen atom, $\rho \simeq 0.013$) and (b) ^{lig}ring (wide green surface above and below the ring, $\rho \simeq 0.013$) with the surrounding IL througout AIMD2 trajectory.

S3. Static DFT conformational research

In this section, three anions and three cations were combined and their affinity for lignin was calculated. Due to the computational cost of the calculations, the conformational research was differently done in each of them. Regarding the $BMIM^+$-based ILs, the first solvation shell of the lignin in [BMIM][Cl] was extracted from the AIMD simulations and the geometry optimized at the B3LYP-D/SVP (GIL-SMD) level. Posteriorly, the anion of this optimized geometry was substituted for acetate and methylsulfonate, and reoptimized. Regarding the choline-based ILs, the analysis and optimization of different coordination modes of the IL with the lignin led to six different low lying isomers for [Ch][Cl] (see Figure S7). In these six geometries, the Cl^- anion was substituted by acetate molecules, leading to four different geometries after optimization. In both [Ch][Cl] and [Ch][Acet] combinations, the same isomer was found to be the most stable one. Therefore, this geometry was modified into a $[Ch][CH_3SO_4]$ complex, and reoptimized.

Finally, in the case of Et_3NH-based IL-lignin complexes, the coordination possibilities are much more limited than in the case of choline-based ILs, and therefore less conformations were characterized among the low-lying isomers (see Figure S8).

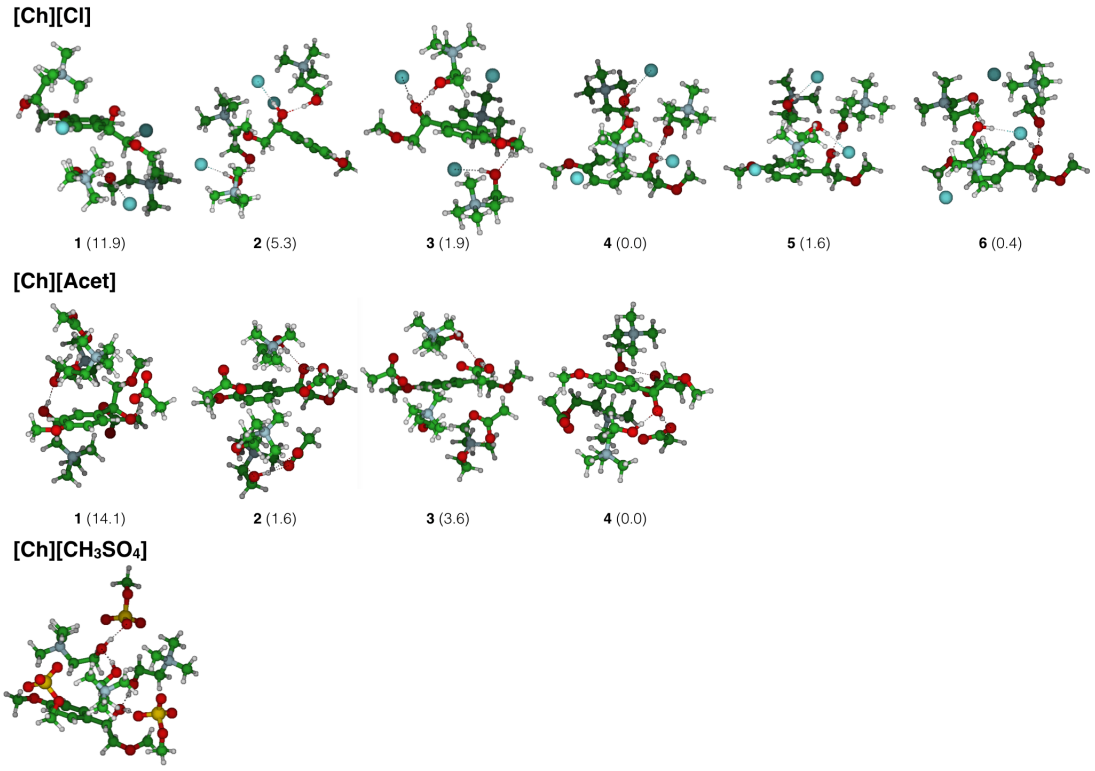

Figure S7: Choline-based IL-lignin complexes characterized, and the relative electronic energies in kcal/mol at the M062X/TZVP//B3LYP-D/SVP (GIL-SMD) level.

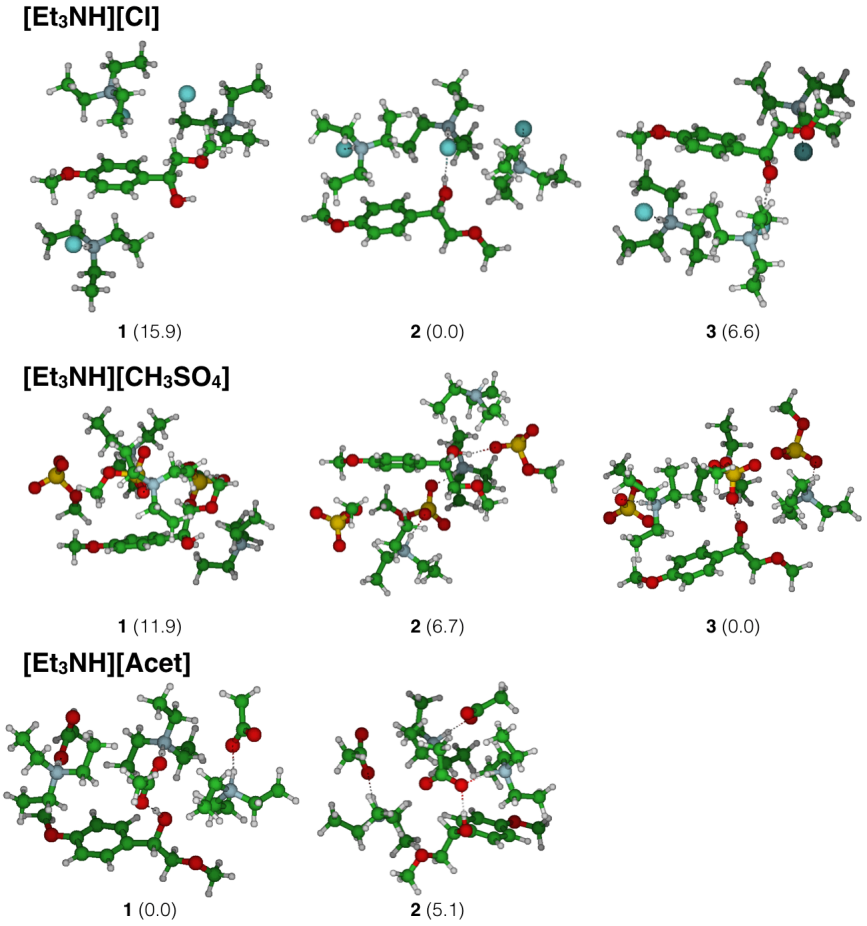

Figure S8: Et_3NH-based IL-lignin complexes characterized, and the relative electronic energies in kcal/mol at the M062X/TZVP//B3LYP-D/SVP (GIL-SMD) level.