Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Water Distribution at the Electrified Interface of Deep Eutectic Solvents

Mesfin Haile Mamme,*[a,c] Samuel L.C. Moors,[c,] El Amine Mernissi Cherigui,[a] Herman Terryn[a], Johan Deconinck[b], Jon Ustarroz*[a,d,†], Frank De Proft[c,†]

[a]*Vrije Universiteit Brussel (VUB), Research Group Electrochemical and Surface Engineering (SURF), Pleinlaan 2, 1050 Brussels, Belgium.*

[b] *Vrije Universiteit Brussel (VUB), Department of Electrical Engineering and Power Electronics, Pleinlaan 2, 1050 Brussels, Belgium.*

[c]*Vrije Universiteit Brussel (VUB), Eenheid Algemene Chemie (ALGC), Pleinlaan 2, 1050 Brussels, Belgium.*

[d]*Universite Libre de Bruxelles (ULB),Chemistry of Surface, Interface and Nanomaterials (ChemSIN), Boulevard du Triomphe 2, CP 255, 1050, Brussels, Belgium.*

*Corresponding authors: mmamme@vub.be, jon.ustarroz@vub.be

† These co-last authors contributed equally to this work

S1. Influence of surface charge density on adsorption of ions and molecules of mixed water-reline system (choline chloride-urea +3 wt% water) on graphene.

Figure S1 shows the evolution of the normalized number density of choline (Ch^+) and urea (URE) as a function of distance from the negatively charged (first column) and positively charged (second column) electrode for different surface polarization.

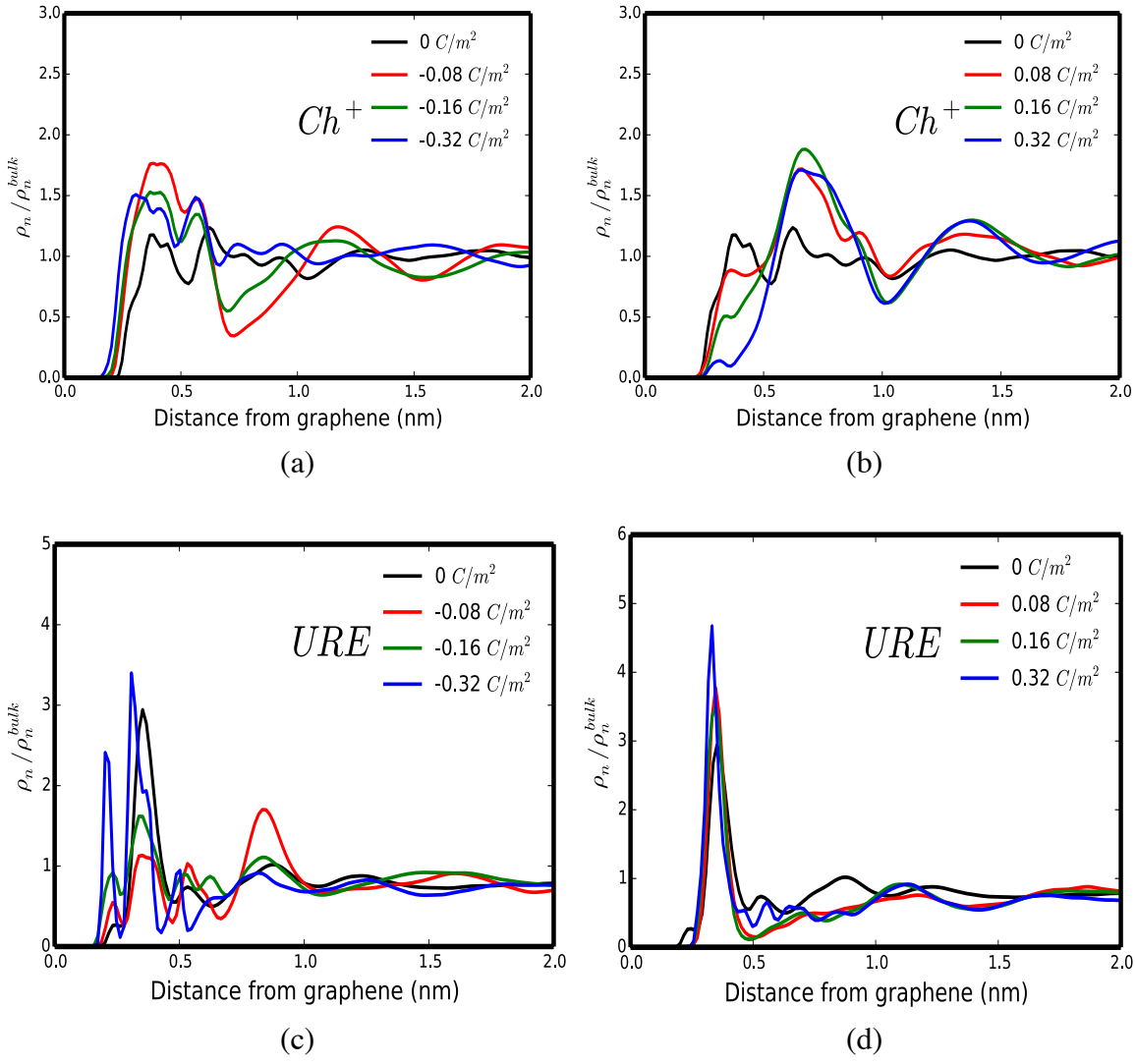

Figure S1. Normalized number denisty profile of choline cation (Ch^{+}) (a and b) and urea molecule (URE) (c and d) as a function of distance from the graphene electrode for different surface polarization.

S2. Influence of surface polarization on the electrosorption of chloride anions and water molecules of mixed water-reline system (choline chloride-urea +3 wt% water) on graphene.

Figure S2 shows the evolution of the normalized number density of water (H_2O) and chloride (Cl^-) as a function of distance from the negatively charged (first column) and positively charged (second column) electrode for different surface polarization.

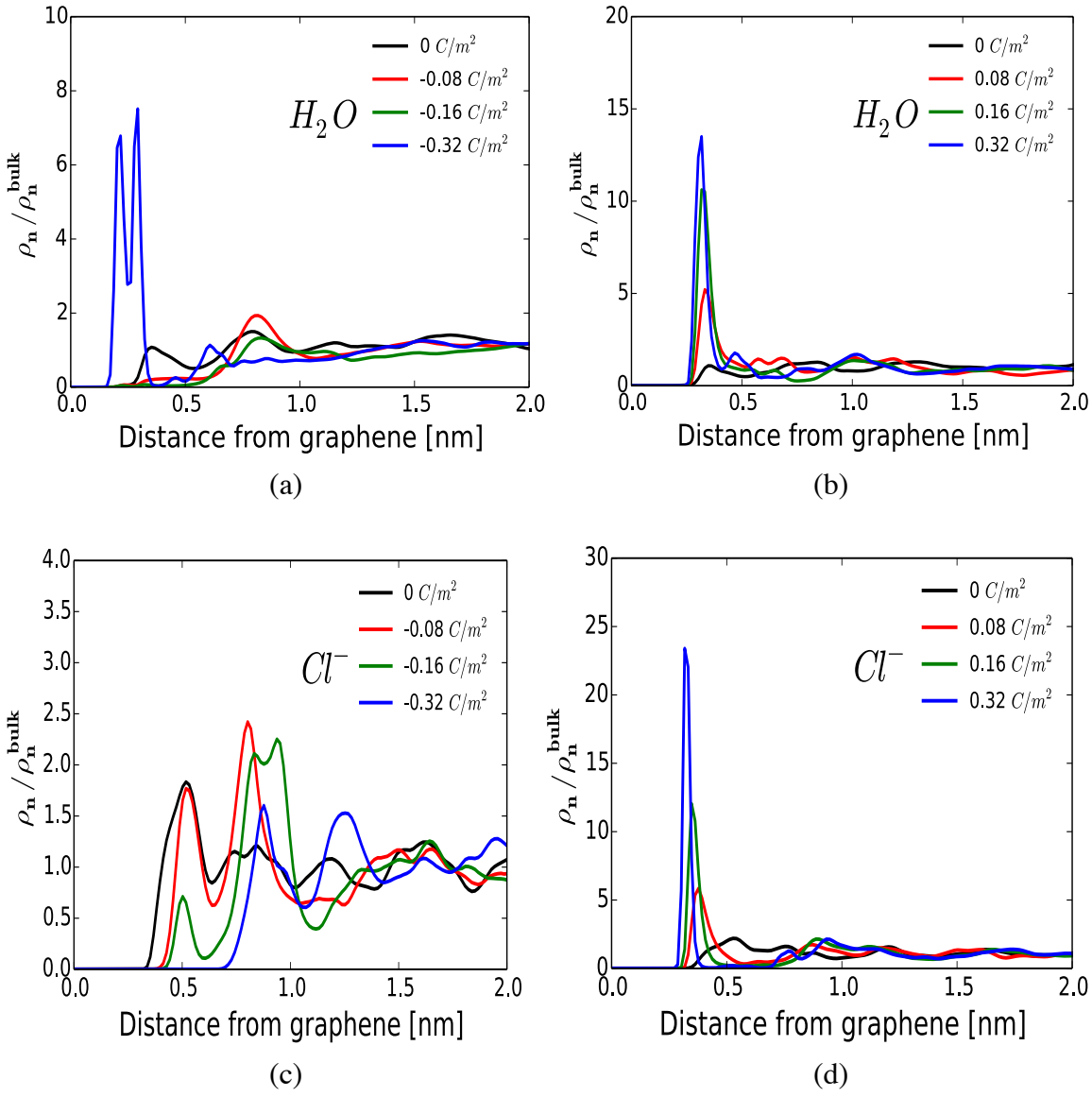

Figure S2. Influence of surface polarization on electrosorption of humid Reline species. The normalized number density of water molecules (a and b) and chloride (c and d) as a function of distance from the electrode surface.

S3. Intermolecular interactions in 1:2 molar ration of choline chloride-urea + 3 wt%.

Figure S3 shows the average strength of the intermolecular interactions between water molecules and Reline species (Urea-water, black bar; choline-water, red bar; chloride-water, green bar; and water-water, blue bar) at moderate surface polarizations.

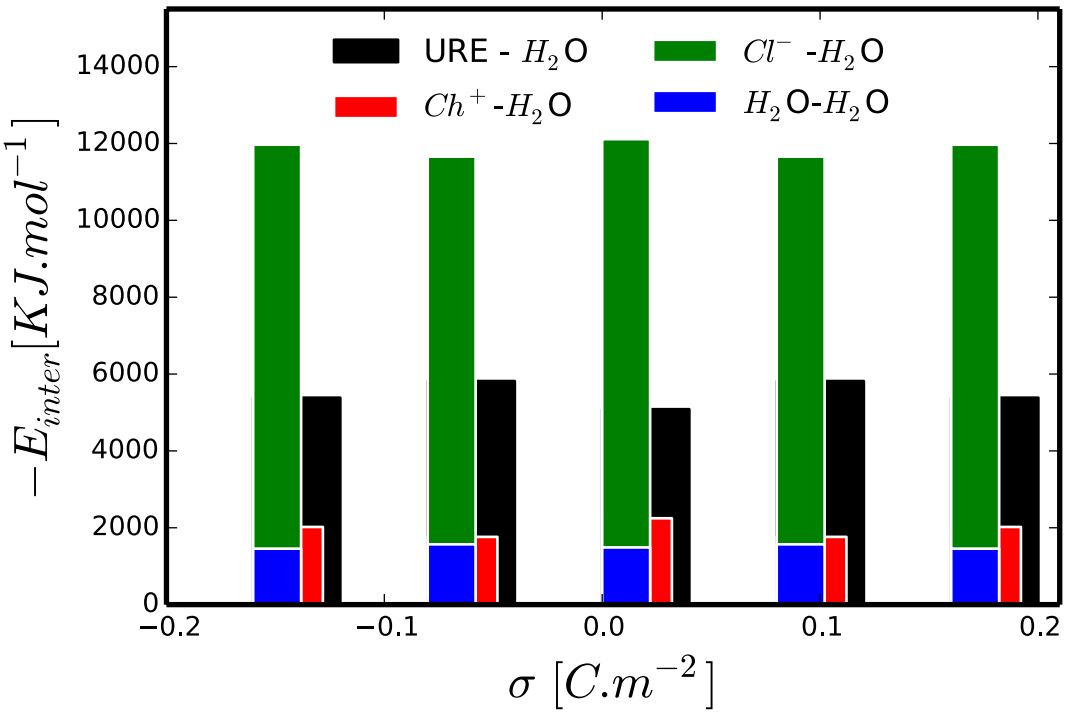

Figure S3. The intermolecular interactions between water and urea (URE-H_2O, black bar), water and choline (Ch^+-H_2O, red bar), water and chloride (Cl^--H_2O, green bar) and water and water (H_2O-H_2O, blue bar) at moderate polarizations.