

Atomistic Insight into the Electrochemical Double Layer of Choline Chloride-Urea Deep Eutectic Solvents: A Clustered Interfacial Structuring[†]

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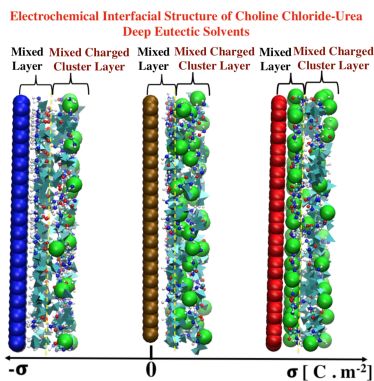
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Abstract

Green, stable and wide electrochemical window deep eutectic solvents (DESS) are ideal candidates for electrochemical systems. However, despite several studies of their bulk properties, their structure and properties under electrified confinement are barely investigated, which hinders the widespread use of these solvents in electrochemical applications. In this letter, we explore the electrical double layer structure of 1:2 choline chloride-urea (Reline), with a particular focus on the electrosorption of the hydrogen

bond donor on a graphene electrode using atomistic molecular dynamics simulations. We discovered that the interface is composed of a mixed layer of urea and counterions followed by a mixed charged clustered structure of all the Reline components. This interfacial structuring is strongly dependent on the balance between intermolecular interactions and surface polarization. These results provide new insights into the electrical double layer structure of a new generation of electrolytes whose interfacial structure can be tuned at the molecular level.

TOC Graphics



A fundamental understanding of the electrical double layer structure (EDLS) is crucial for every electrochemical process, ranging from electroplating to energy conversion. The understanding of the EDLS of aqueous and conventional solvents (dilute electrolytes) has advanced enormously since the first report of the Helmholtz double layer.¹ In this framework (dilute solutions), ions are considered as well-separated point charges in the electrolyte. This is valid for the electrochemistry of aqueous and some organic solvents at moderate electrode polarizations. In this model, the EDLS is described by one compact layer close to the electrode followed by a diffuse layer.^{1,2} However, for many applications, water or organic based solvents are increasingly replaced by room temperature ionic liquids (RTILs) and/or deep eutectic solvents (DESs). This is especially the case for electrodeposition, energy conversion and storage and bioscience³⁻⁷. RTILs are only composed of large and asymmetric ions whereas DESs feature neutral hydrogen bond donors (HBD) as well. In both cases, these solvents are very different from aqueous solutions of typical ions (Na^+ , K^+ , Cl^- , ...), which are small ions with uniform charge density. Therefore, it is expected that their EDLS would be very different than this of conventional aqueous solutions. The electrochemical interface of RTILs has been thoroughly studied for several decades.⁸ It can be summarized as follows: at moderate surface polarization, the surface charge is overscreened by a single layer of counterions (either cations or anions), which is compensated by an excess of coions in the following layer; at high surface polarization, the crowding of counterions (anions/cations) overtake the overscreening and extends over two or more layers, which results into an excess of coions in the following layer.^{8,9}

Although RTILs are used in various contexts,^{3,6,10} their use in many applications is limited due to their high cost and tedious synthetic routes.^{4,11-13} In this context, DESs have generated a great interest as alternatives to both conventional solvents and RTILs.^{5,11,12,14,15} Although the potential window of these solvents is not as wide as this of RTILs, it is wider than this of water and allows, for example, the electrochemical deposition of non-noble met-

als with fairly low reduction potential such as nickel,^{16–20} copper²¹ or zinc²² without the loss of efficiency arising from water electrolysis in aqueous solvents. Other properties that make these solvents technologically interesting are their ease of synthesis, low price, great stability at moderate to high temperatures and non-toxicity.^{5,12,23} These desirable properties lead to the improvement of the efficiency and the safety of vast number of electrochemical applications such as batteries,^{24,25} supercapacitors,²⁶ solar cells,²⁷ catalysis,²⁸ and electroplating^{16–22} and among others.^{4,5,11,19}

As a result, a number of fundamental studies have been carried out to rationalize the relationship between the structural organization of DESs (with emphasis on complexation) and melting point depression.^{11,15,29–34} In this regard, studies have shown that the strong intermolecular interaction between HBD and anions of hydrogen bond acceptor (HBA), i.e, the hydrogen bond network, is responsible for the disruption of long-range order anions-cations electrostatic interaction and low melting temperature at the compositions close to this of the eutectic mixture.^{11,15,30,33–36}

However, despite a number of studies on the bulk structure and the dynamics and molecular interactions of DESs, the structure and behavior of their electrified interface is not yet clearly understood. So far, although crucial for many technological applications, only a limited number of studies have focused on the electrochemical interface of DESs with polarized surfaces, being contradictory with regard to the composition of the interfacial layers.^{37–42} Figueiredo et al³⁷ investigated the interfacial behavior of the choline chloride- glycerol (Glyceline) eutectic mixture on glassy carbon, platinum and gold electrodes using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). This study showed that the Glyceline interfacial structure is weakly dependent on the potential but strongly affected by the electrode material. It was stated that, whereas increasing the negative potential causes an increase of the differential capacitance because of increased cation adsorption, the differential capac-

itance remains unaffected by an increase in positive potential, due to the complexation of chloride ions with glycerol molecules. A follow-up study from the same group³⁸ for different DESs on the mercury electrode suggested that, at negative potential, the interfacial structure is similar to that of the aqueous electrolyte, which is a layer of cations (i.e. choline) separated from the mercury electrode surface by a layer of HBD molecules. On the contrary, at the positive electrode, anion adsorption increases with increasing potential. Furthermore, by using sample-rotated small angle X-ray scattering (SR-SAXS) and EIS, the interfacial properties of choline chloride-urea (Reline) on lead nanoparticles have also been studied.⁴² This study showed that the differential capacitance is not constant neither in the anode nor in the cathode region, unlike previous studies.^{37,38} Besides, Chen et al studied the EDLS for three different DESs on a highly ordered pyrolytic graphite (HOPG) electrode as a function of the applied potential using atomic force microscopy (AFM), contact angle measurements and density functional theory (DFT).³⁹ Their results revealed that the DESs interfacial structure can be described as a multilayer, where the number of layers is dependent on the surface polarization and the hydrogen bonding capacity of the HBD molecule. In addition, the DFT simulations indicated that in all cases the HBD (i.e., urea, ethylene glycol and glycerol) is away from the graphite interface at all potentials. This is however not in accordance with the experimental results previously reported.^{37,38} In addition, Atilhan et al. explored the interfacial properties of choline chloride-levulinic acid on uncharged silver, aluminum and platinum electrodes using classical molecular dynamics.⁴⁰ This study revealed that ions and molecules are strongly adsorbed in the vicinity of the electrode: parallel alignment of levulinic acid molecules and choline cations. Recently, when the present study was already completed, Kaur et al reported that the electrode surface charge screening is done not only by the ions (cations/anions), but also by the HBD (i.e., urea) in Reline using a molecular dynamics simulation.⁴¹

The literature survey points out that, although experimental techniques are continuously

improving, there are still some limitations preventing the rationalization of the nanoscale electrochemical interfacial behaviour of DESs, among which signal-to-noise ratio, lack of spatial or surface sensitivity and time resolution. On the other hand, since the choline chloride-urea eutectic mixture is highly dense, and only composed of large asymmetric ionic (Ch^+ and Cl^-) and molecular components (URE), short-range ion-ion and ion-molecule interactions play a dominant role both in the bulk as well as at the interface properties. This results in the breakdown of the standard mean-field approximation, which is the basis of the dilute solution theory.

Alternatively, in this work we use atomistic molecular dynamics to explore the interfacial behaviour of Reline DES on a graphene electrode at a molecular scale. Such atomistic-molecular approach allows investigating all the possible bulk and interfacial interactions and, consequently, helps to shed light on the nanoscale electrochemical interfacial structure of DESs. Using such an approach, we show a previously unrecognized phenomenon: the electrochemical interface is composed by a mixed layer structure of two components (urea and either choline or chloride) followed by a mixed charged clustered layer of the three components (clusters of either urea with more choline than chloride or urea with more chloride than choline) regardless of the surface polarization. In addition, we explain the intrinsic molecular mechanism and physics behind hydrogen bond donor (urea) electrosorption from choline chloride-urea DES. Hence, we believe that this work sets the bases for a systematic experimental investigation of the electrochemical interfacial structure of DESs.

Benchmark: In order to ensure that our approach is valid to determine appropriately the EDLS, we first calculated the interface for a conventional sodium chloride aqueous solvent (10 wt% NaCl) confined within two graphene electrodes at a constant surface charge density ($\sigma = \pm 0.32 \text{ C/m}^2$). Figure 1(a – b) shows the simulated EDLS of this solution close to the negatively charged (a) and positively charged (b) graphene electrode as a function of distance.

Near both charged electrode surfaces, counterions are adsorbed behind the first water layer (outer Helmholtz layer) followed by a diffuse layer.⁴³ These results are perfectly in line with the well established dilute solution model, the Gouy-chapman-stern (GCS) model.^{1,43} In addition, to validate the force field parameters of Reline, we compared the simulated density of Reline with literature results (both experimental and computational)^{30,44,45} (see Figure 1(c)) at different temperatures. Interestingly, we found an excellent agreement between our simulated data and the experimental data reported by Shah et al.³⁰ Here it is important to mention that the force field parameters used in this study for Reline were the same than these used by Shah et al.³⁰ However, our simulated data agree better with the experimental results, with a deviation between experimental and simulated density being close to zero for high temperatures. The reason is that the length of our simulation time was 300 ns, more than 150 times longer than this reported previously.³⁰ This emphasizes, that even by employing the most appropriate force field parameters, a certain simulation time needs to be guaranteed for an appropriate description of the physico-chemical properties of DESs, mainly due to their high viscosity.

Interfacial structure of the Reline deep eutectic solvent: In order to shed light on the interfacial structure of Reline, a series of molecular dynamics simulations were performed at different surface charge polarizations ($-0.32 \text{ C/m}^2 - 0.32 \text{ C/m}^2$). Graphene was chosen as the electrode material due to its high specific surface area, light weight, good thermal stability and good conductivity.^{46,47} The normalized number density of cations, anions and neutral molecules (top) and the local space charge density contributed by choline cations (Ch^+) and chloride anions (Cl^-) (bottom) as a function of distance from the graphene electrode with different surface charge polarizations are shown in Figure 2. In all cases, the normalized number density and the local charge density show strong oscillations in the vicinity of the graphene electrode. These oscillations decay progressively until the bulk concentration is recovered at about 2 nm. This is similar to prior studies of RTILs close to the electrode

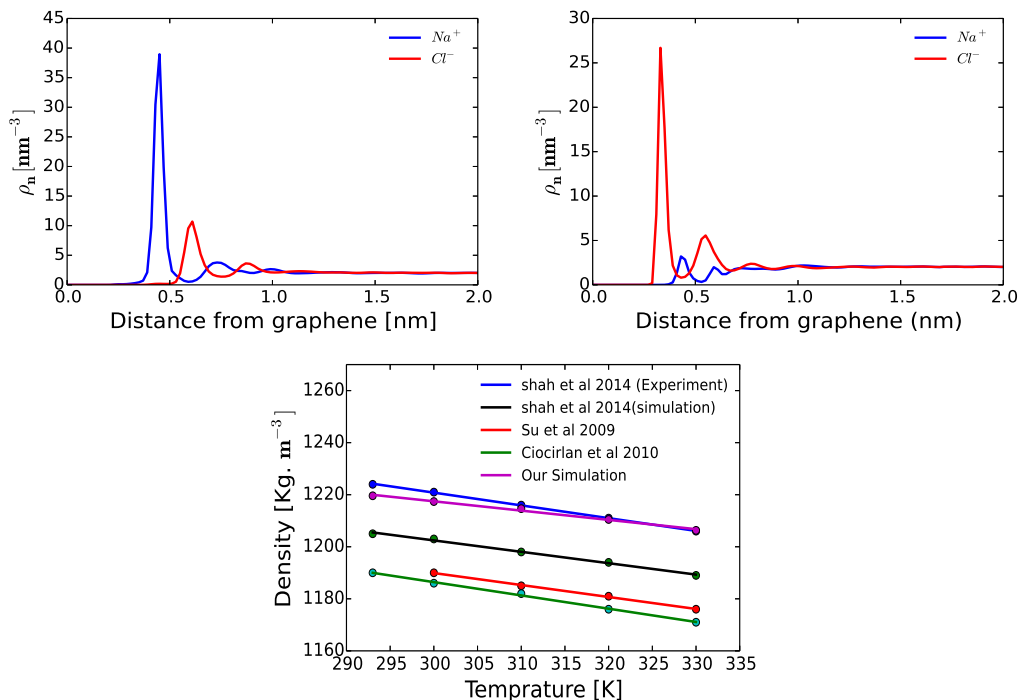


Figure 1: **Model validation.** The number density of Na^+ and Cl^- as function of distance from a graphene electrode with a charge of -0.32 C/m^2 (a) and 0.32 C/m^2 (b). Comparison of the evolution of the density of the Reline eutectic solvent (ChCl:Urea, 1:2) as a function of temperature (c).

surface^{8,9} in which anions and cations form alternating layers (multilayer adsorption). For explaining the interfacial structure of Reline we used the following definitions: a **mixed layer** is a layer that is composed of two of the Reline species (either urea and choline or urea and chloride) in the same region. A **mixed charged clustered layer** is a layer composed of the three Reline components (clusters of either urea with more choline than chloride or urea with more chloride than choline) in the same region. From Figure 2 it is clearly seen that the interfacial structure of Reline varies as a function of surface polarization. In the absence of surface charge, Figure 2(b), the first layer ($< 0.5 \text{ nm}$) is composed of choline cations (Ch^+ , red line) and urea molecules (URE, black line) with a ratio of about 1:1.73, which is a mixed layer, followed by a second layer (0.5 to 1 nm) of chloride anions (Cl^- , green line) dominated mixed charged clustered structure (Cl^- , Ch^+ and URE).

Interestingly, for the charged graphene electrode, the first layer is not only composed of counter ions, but it is a mixed structure instead, regardless of the magnitude of the surface charge imposed. Near the negatively charged electrode, the mixed layer is composed of choline cations (Ch^+ , red line) and urea molecules (URE, black line) with the ratios of 1:1, 1:1.44 and 1:1.35 for a surface polarization of -0.08 C/m^2 , -0.16 C/m^2 and -0.32 C/m^2 , respectively. Alternatively, near the positively charged electrode, it is mainly composed of chloride anions (Cl^- , green line) and urea molecules (URE, black line) (i.e, with Ch:Cl:URE ratios of 1:2.25:3.75 for 0.08 C/m^2 , 1:3.27:4.82 for 0.16 C/m^2 and 1:5.44:5.77 for 0.32 C/m^2), regardless of the magnitude of the surface charge density (see supporting information Figure S2). Here it is important to mention that increasing the negative surface polarization (from 0 to -0.32 C/m^2) also has only a minor effect on the number density of choline (small increase) in the vicinity of the electrode. This is mainly explained by the strong coordination of choline with other Reline species at higher negative surface polarization (see supporting information Figure S2). This effect is similar to what has been reported for Reline-mercury interfacial structure using EIS and CV.³⁸ Additionally, it is interesting to note that, in contrast to the positively charged electrode, increasing the surface polarization on the negatively charged electrode from 0 to -0.32 C/m^2 results in the number density of the hydrogen bond donor molecule (URE) displaying two peaks within the interfacial layer (see also Supporting Information Figure S2). It must be noted however that the peak position of the second maximum (further away from the interface) remains the same than in the uncharged or positively charged electrode. The fact that the urea number density displays two maxima for negatively charged electrodes is related to two different orientations of the urea molecule. To describe the orientation of the urea molecule near the surface, we used the terms "perpendicular", "parallel" and "flat", where perpendicular and parallel refer to the directions of the \vec{CO} vector (a vector from the carbon to the oxygen atom) of the urea molecule with respect to the electrode surface; whereas flat refers to the conformation in which all the atoms of the urea molecule are nearly at the same distance from the electrode surface. The first peak, that

only develops when the surface is negatively charged, corresponds to a perpendicular configuration (i.e, the \vec{CO} vector of urea molecule points toward the bulk), which is clearly shown in Figure5(e). Alternatively, the second peak represents parallel orientation to the graphene surface (see Figure5(e)) . The first peak (urea perpendicular to the graphene surface) only appears in the negatively charged electrode. This is due to the fact that, when the electrode is negatively charged, there is a strong electrostatic repulsion between the negative electrode and the negative pole of the urea molecule, which is the Oxygen atom. Alternatively, on the positively charged electrode (Figure2(c)), increasing the surface polarization promotes the adsorption of chloride anions and enhances the electrostatic attraction between the negative pole of urea molecule and positively charged surface. The two synergistic interactions, the electrostatic interaction and a strong hydrogen bonding URE - Cl⁻ explains the presence of urea molecules in the following layer, oriented flat to the electrode surface (see Figure5(e)).

Electrochemical Fingerprints of Urea: The presence of counter anions/cations in the vicinity of the positively/negatively charged graphene electrode is not surprising. This is due to electrostatic interaction and occurs in a similar way in aqueous solvents and RTILs.^{1,2,8,9,43} However, the presence of a substantial amount of urea molecules on both electrodes needs to be further studied. This has been shown previously in experiments conducted by Figueiredo et al³⁷ and Costa et al³⁸ and by simulations of Kaur et al.⁴¹ Practically, enrichment of urea molecules in the vicinity of the electrode surface has both positive and negative impacts on the electrochemical processes. For instance, in the case of electrodeposition, urea enriched surfaces will help to obtain uniform film/nanoparticles by slowing down/capping the surface electrochemical reactions.^{18,19} On the other hand, in other electrochemical systems such as batteries and supercapacitors, on the contrary, the enrichment of urea at the surface of the electrode will lead to slower charging and discharging and a smaller capacitance.^{37,38}

To acquire a deeper understanding of the electrosorption of urea molecules, we first investigated the correlation between the electric field and preferential adsorption of urea molecules

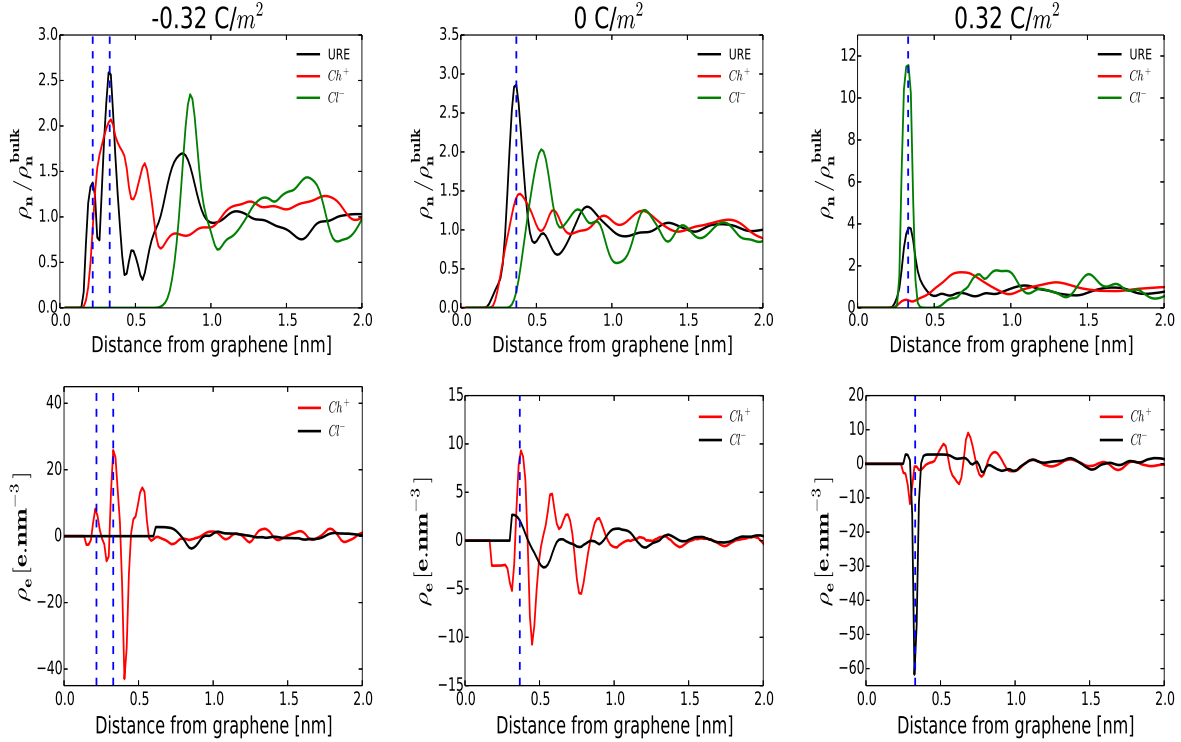


Figure 2: **Mixed and clustered EDLS.** The normalized number density profiles of all species (urea, URE; choline, Ch^+ and chloride, Cl^-) (a–c), and the local space charge density contributed by anions (Cl^-) and cations (Ch^+) (d–f) as a function of distance for different surface charge densities (-0.32 C/m^2 , first column; 0 C/m^2 , second column; and 0.32 C/m^2 , third column). The blue dashed lines show the positions of urea peaks in the interfacial region.

in the vicinity of the graphene electrode (Figure 3). Figure 3 shows the evolution of the electric field and the normalized number density of urea molecules for different surface polarization as a function of distance from the electrode surface. The electric field oscillates close to the electrode surface and gradually disappears as a function of distance. This is due to electric potential oscillation caused by the overscreening of the surface charge. In fact, since urea is a polar molecule, it will experience a net force due to the non-uniform electric field. If we approximate the urea molecule as a point dipole oriented in the direction of the electric field, then the net force (\vec{F}_x) is given by:

$$\vec{F}_x = P_x \cdot \frac{d\vec{E}_x}{dx} \quad (1)$$

Here P_x is the x-component of the dipole moment of urea molecule and \vec{E}_x is the average electric field perpendicular to the graphene electrode. Hence, in the interfacial region, urea molecules will move toward the direction where the magnitude of the electric field ($|\vec{E}_x|$) increases and accumulate at the position where the net force is zero, which implies that $\frac{d\vec{E}_x}{dx} = 0$. As a result, urea molecules are preferentially accumulated in a position that satisfies the maxima/minima of the electric field (the metastable positions, local minimum or maximum; and stable position, absolute minimum or maximum).

The results of the simulated electric field and normalized number density of urea molecules for three different surface charge densities (-0.32 C/m^2 (a), 0 C/m^2 (b) and 0.32 C/m^2 (c)) are shown in Figure 3. Even though this simple model does not take into account the finite size of the urea dipole, a good agreement between the positions of the extrema and the normalized number density peaks, especially at higher surface charge is found. However, for a moderately charged surface, the electric field alone cannot explain the preferential adsorption of urea molecules. For instance, in the case of the neutral electrode, Figure 3(b); based on the above argument the highest accumulation of urea molecules should be at around $x = 5.3 \text{ \AA}$ (i.e., a stable position). However, it appears at $x = 3.4 \text{ \AA}$. This is most probably due to the dominance of intermolecular interaction between urea and Reline species (Cl^- and Ch^+) over the dipole interaction of urea-graphene.

Further insight into urea–Reline intermolecular interactions can be gained by computing the local charge density as shown in Figure 2(d–f). The results show a strong correspondence between urea density peaks and the local excess charge density peaks, which is shown by the blue dashed line in Figure 2. This implies that there is a strong intermolecular interaction between Reline species (Cl^- (black line) and Ch^+ (red line)) and the urea molecules as it

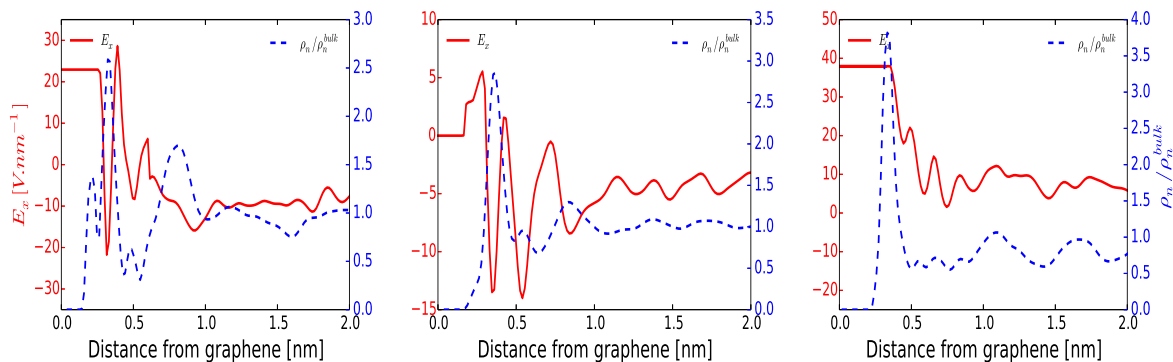


Figure 3: **Correlation between the electric field and preferential adsorption of urea.** The evolution of the electric field (E_x , left axis) and the normalized number density of urea (ρ_n/ρ_n^{bulk} , right axis) as a function of distance from the electrode surface for (a) -0.32 C/m^2 , (b) 0 C/m^2 and (c) 0.32 C/m^2 .

has been discussed previously by several authors.^{11,12,15,29,30,33–36}

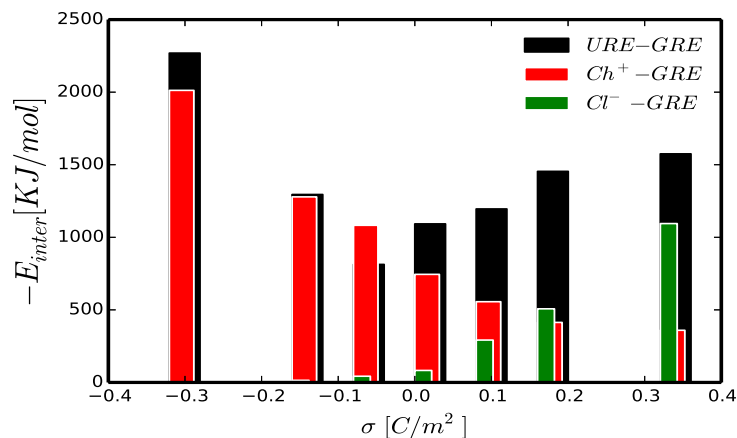


Figure 4: **Intermolecular interactions in electrified Reline eutectic solvent.** Intermolecular interactions between the Reline components (urea, choline and chloride) with the graphene electrode for different surface polarization.

Furthermore, since the preferential adsorption of urea molecules in the vicinity of the electrode surface is also linked to the intermolecular interaction, we have also performed intermolecular interaction calculations to rationalize the influence of surface polarization. Figure 4 shows the evolution of the intermolecular interactions between the Reline species (urea,

choline and chloride) and the graphene electrode as a function of surface polarization. From the results, one can see that the adsorption/accumulation of urea is not only dependent on the magnitude of the surface charge polarization, but also on the specific intermolecular interaction strength with the cations and anions of Reline. For instance, in the positive part, the urea-graphene (URE-GRE, black bar) interaction gets smaller for smaller charges, similar to the chloride-graphene (Cl^- -GRE, green bar) interaction. This trend slightly extends into the negative part. Alternatively, in the moderately and highly negatively charged part, the URE-GRE interaction follows the trend of the choline-graphene (Ch^+ -GRE, red bar) interaction. Here it is important to note that, from Figure 4, it can be seen that urea interactions with graphene at -0.32 C/m^2 are stronger than these at $+0.32\text{ C/m}^2$. This can be explained as follows. In the case of a positively charged surface, increasing of the surface charge up to $+0.16\text{ C/m}^2$ leads to an increase in both chloride anions and urea molecules in the vicinity of the electrode surface. However, a further increase in surface polarization to $+0.32\text{ C/m}^2$ results in a higher accumulation of chloride anions which causes the urea molecules to be pulled out from the interface to make space for chloride (see supporting information Figure S2). In other words, the interaction of urea and the positively charged graphene electrode depends on the competition between the available surface area and the electrostatic interaction between the chloride anion and the charged electrode surface. Alternatively, in the case of the negatively charged electrode, choline is less sensitive to an increase in surface charge density (the number density of choline cations increases only slightly when negative charges are applied). On top of this, increasing the negative surface charge density leads to rearrangement of urea molecule conformation (see Figure 5(e), perpendicular and parallel), which allows further space for a higher accumulation of the urea molecule next to the highly negatively charged surface. This is also shown in the Figure S4 of the Supporting Information: increasing the surface polarization results in a higher enhancement of the electrostatic interaction between urea and the negatively charged (-0.32 C/m^2) than that between urea and the positively charged electrode ($+0.32\text{ C/m}^2$).

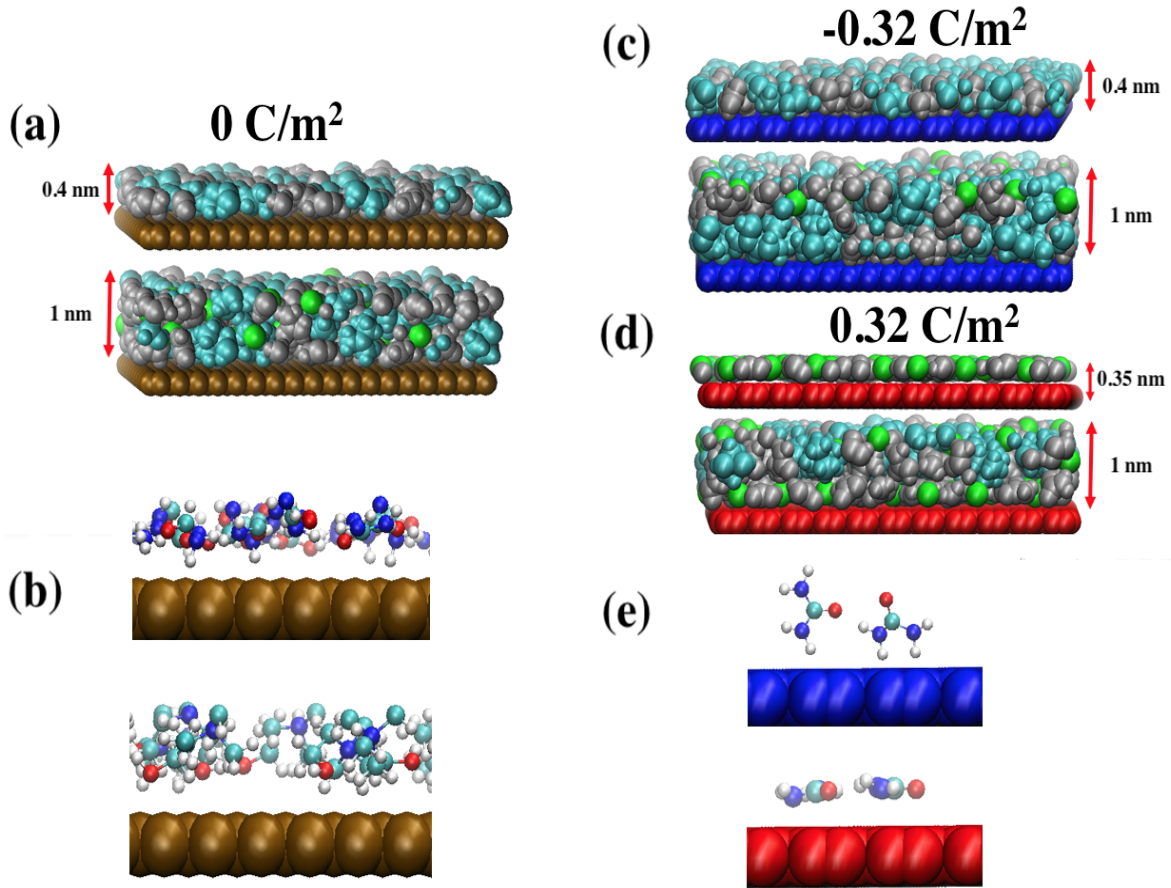


Figure 5: **The structural organization of the interfacial layers.** A snapshot of the distribution of the Reline components near the electrified interface for different surface polarization: 0 C/m^2 (a and b) and $\pm 0.32\text{ C/m}^2$ (c – e). The Reline species are represented with different colors (urea: silver; choline: cyan and chloride: green). The uncharged electrode is colored ochre, whereas the negatively and positively charged electrodes are colored blue and red respectively. Figures a, c and d show the composition of the first (top) layer and the first two (bottom) layers. Figure b shows the orientation of urea and choline in the first layer for the uncharged electrode. Figure e shows the orientations of urea molecules in the vicinity of $\pm 0.32\text{ C/m}^2$ charged graphene surface. The color coding of the atoms of urea and choline is: white: hydrogen; cyan: carbon; blue: nitrogen and red: oxygen.

From the results of Figure 2 – Figure 4, we clearly see that at a moderately charged surface, the local intermolecular interaction dominates the electrical double layer structure formation, whereas for a high electrification this dominance is overtaken by the external electrostatic interactions (GRE – URE, GRE – Cl^- and GRE – Ch^+). Nonetheless, in all cases, the

system shows a mixed layer, followed by charged clustered structure, regardless of the electrification. Finally, to visualize the electrical double layer structures and the orientation of the urea molecules, a snapshot of the structural organization is shown in Figure 5. From these snapshots, it can be seen that, near both electrode surfaces, the first layer consists of counter ions that compensate the electrode charge and urea molecules with different orientations. The urea conformations are: a random orientation on the uncharged electrode (Figure 5b(i)), a mixture of perpendicular (CO dipole oriented towards the bulk solution) and parallel alignment (CO dipole perpendicular to the surface) on the negatively charged electrode (Figure 5e(i)), and a flat arrangement (all the atoms are nearly at the same distance from the electrode surface) on the positively charged graphene electrode (Figure 5e(ii)). Near the negatively charged electrode (blue electrode, Figure 5(c)), the first mixed layer is composed of a dense layer of urea molecules and choline cations that overcompensate the electrode surface charge. This layer is followed by a chloride anion dominated clustered layer, where the chloride anion compensates the overcompensation in the first layer. On the other hand, near the positively charged electrode (red electrode, Figure 5(d)), the first mixed layer (URE – Cl^-) is followed by a second choline dominated mixed charged clustered layer. Further, we also observe that, charging the graphene electrode results in a change in orientation of urea in the vicinity of the electrode (see Figures 5(b) and (e)). Changes in orientation and configuration of urea close to the interface are possibly caused by the competition between Van der Waals and electrostatic interactions of the atoms of urea and the charged/uncharged graphene carbons. At the positively charged electrode, urea molecules lie nearly flat on the surface of the graphene electrode, which results in a one atom thick mixed first layer. On the other hand, near the negatively charged electrode urea molecules are aligned perpendicular and parallel to the surface of the electrode. Similar observations on the orientational evolution of cations and anions of different RTILs close to the electrode surface have been reported both experimentally and computationally.^{8,48,49}

In summary, atomistic molecular dynamics have been used to simulate the electrical double layer structure of choline chloride-urea in 1:2 molar ratio (Reline) on a graphene electrode. The approach has been validated by benchmark calculations on a conventional sodium chloride solution on a graphene electrode. The simulations of the Reline-graphene interfacial structure show an unexpected and previously unrecognized interfacial structure: a mixed electrical double layer structure on both electrode surfaces. Unlike the interfacial structures observed and proposed for other electrolyte-solid interfaces (Compact-diffuse double layer for dilute solutions; overscreening or crowding for concentrated solutions), we find that the electrical double layer is actually a multilayer composed of a mixed layer of urea molecules and counterions (either Ch^+ or Cl^-) followed by a mixed charged clustered structure of all the Reline components (choline, chloride and urea), regardless of the magnitude of the surface polarization. For this, we identify two factors that govern and tune the interfacial structure: intermolecular interactions and the applied surface polarization. Our results reveal that for a moderately polarized electrode, the formation of the mixed structure is mainly dominated by the intermolecular interactions, whereas, for a highly polarized surface, the non-uniform electric field and the dipole moment are important. It must however be noted that, in this study, we considered a dry Reline eutectic mixture. However, in all practical applications, DESs always contain a small amount of water molecules due to their hygroscopic nature.^{18,29,30,50,51} This has been shown to have important implications on electrodeposition.^{18,19,50} Therefore, to properly compare experimental and simulated data on the polarized interface of DES, the effect of water needs to be taken into account for the simulations.⁵²

Methods

Classical atomistic molecular dynamics simulations were carried out to study the interfacial structure of the Reline DES on novel graphene electrode using the GROMACS 5.1.2 soft-

ware package. The system setup, is shown in the supporting information Figure S1. Periodic boundary conditions are applied in the Y and Z dimensions. There is no periodicity in the direction perpendicular to the graphene electrode. We adopt parallel graphene sheets (4.55 nm x 4.31 nm) as positive and negative electrodes, and the distance between them is fixed to 9.37 nm. The graphene atomic positions are frozen throughout the simulations. The system studied consists of 500 choline cations (Ch^+), 500 chloride anions (Cl^-) and 1000 urea (URE) molecules. The force field parameters for Reline species were taken from the swiss-param webserver,⁵³ which is derived from the Merck Molecular Force Field (MMFF) and which has been validated and used to predict the experimental physico-chemical properties of Reline with high accuracy.³⁰ The Lennard–Jones (LJ) parameters used for the graphene carbon atoms are $\sigma_c = 3.55 \times 10^{-1}$ nm and $\varepsilon_c = 2.9288 \times 10^{-1}$ kJ/mol.

To determine the domain size for the interfacial calculations, we first performed a dynamic energy minimization followed by an isothermal-isobaric (NPT) and canonical (NVT) equilibrations for 200 ns for bulk Reline solvent at a temperature of 300 K maintained with a V-rescale thermostat and a pressure of 1 bar maintained with the Parrinello-Rahman barostat. Once the density of the system is known, the resulting configuration is sandwiched between graphene electrodes and used for further NVT equilibration for 100 ns, followed by 300 ns production runs. For all simulations, we adopted 1 fs time steps. Here it is important to note that, since the Reline deep eutectic solvent is highly viscous, long simulation times are necessary to obtain reliable results.

The long range electrostatic interactions were computed by using the Particle Mesh Ewald summation (PME) method⁵⁴ with an FFT grid spacing of 0.16 nm with fourth order interpolation. A cutoff of 1.0 nm was used for the short–range, the Lennard–Jones and Coulomb interactions. The simulation results were analyzed by coupling GROMACS with Visual Molecular Dynamics (VMD) tools.⁵⁵

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Supporting Information Available

Supporting Information available:

- Simulation setup
- Influence of surface polarization on the number density of Reline species.
- Intermolecular interactions
- The electrostatic and non-electrostatic interactions.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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