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The Charge Neutral Species in the Electrical Double Layer: No Longer a Background

by Yue Qi, Xi Tan, and Chaoxuan Gu

The electrical double layer (EDL) is central to electrochemistry and has long been defined by charged species, with charge-neutral solvents treated as passive dielectric media in macroscopic models. Decades of advancements in molecular simulations and characterizations have revealed that solvent molecules are structurally and functionally active components of the EDL. Water, in particular, exhibits layering, potential-dependent orientation, and strong coupling with ions. Together, they determine ion distributions, interfacial potential drop, and capacitance. In organic electrolytes, mixed charge-neutral species further introduce complex and tunable interfacial environments that govern electrochemical reactivity and selectivity. Here, we highlight the evolving understanding of charge-neutral species in the EDL and discuss emerging opportunities to design the interfacial structures for energy storage and electrosynthesis.

Charged interfaces are the foundation of electrochemistry. The term "electrical double layer" (EDL) suggests two layers of charge, one on the solid electrode and the other in the salt solution (electrolyte) with opposite signs, situated at the electrode/electrolyte interface. This nanoscale feature gives rise to interfacial capacitances. In his seminal work, David C. Grahame reviewed the theory of EDL and the measured capacitance.[1] The theory assumed ideal polarized interfaces, which means the concentrations of all the species no longer change with time. Most of the experimental results discussed in Grahame's paper are based on mercury (Hg) electrodes, water as the solvent, and salt concentrations less than 1.0 M. Through the comparison of theoretically calculated and experimentally observed capacitances, including both agreements and disagreements, ion distributions in the EDL are illustrated (Fig. 1a). In these pictures, Grahame drew the adsorbed ions and the solvated ions in the inner and outer Helmholtz planes.

Over the last four-score years, the close interaction between experiments and theory has been enhanced by more accurate molecular simulation methods and precise characterization methods which probe nanoscale interfaces. The iteration of agreements and disagreements among theory, simulations, and experiments continues to improve our fundamental understanding of EDL and our ability to predict its impact in electrochemical systems.

In this article, we discuss the behavior of charge-neutral species, including solvents and other additives or reactants, in the EDL. Rather than serving merely as a dielectric medium, solvent molecules such as water reorient in response to surface charge and self-organize into layered structures at the inner Helmholtz plane, thus strongly influencing the capacitance and the potential drop within the EDL. In mixed-solvent systems, solvent concentrations in the EDL can deviate dramatically from their bulk concentrations, impacting interface electrochemical reactions. Thus, solvents play a critical role in shaping the EDL structure and electrochemical reactions.

Water as a Unique Solvent in the EDL

In Grahame's model, the solvent (water) was treated as a uniform material with a dielectric constant of 78.49. The high dielectric constant reflects the large dipole moment and strong polarity of water molecules, which will reorient under an electric field. While Grahame did not explicitly include the role of the water dipole in the EDL, Watts-Tobin pointed out, in 1961, that the reorientation of water molecules under an electrical field occurs much faster than ion transport, contributing to the large potential drop.[2] On the metal electrode side, the electron density on the surface will be influenced by the electrical field developed at the interface. The intricate interactions among ions, solvent dipoles, and electrons from the electrode surface were described in the ion-dipole-jellium model by Schmickler and Henderson.[3] This theoretical model gave predictions for the mercury electrodes used in Grahame's experiments, as well as other metal electrodes. These theories envisioned the physical mechanisms within the nanoscale EDL and provided the mathematical framework to connect the nanoscale phenomena with system-level measurements (e.g., capacitance).

With the development of computers, molecular simulations have quickly helped to paint the molecular behavior of EDL. The Watts-Tobin model could be viewed as the first molecular model, in which a monolayer of water was represented as dipoles reorienting on the electrode surface.[2] Lee et al.[4] used molecular dynamics (MD)[5] with a classical force field (ST2)[6] to simulate water (216 water molecules) sandwiched between two hydrophobic plates (not charged) and reported layering of water near the surface due to hydrogen bonds (H-bonds). The water molecules in the first layer (in direct contact with the electrode surface) prefer to form H-bonds with water molecules in the second layer by sharing their hydrogens and leaving the lone pair lobe toward the electrode surface. This arrangement is also called "ice-like" structures and the "bi-layer" structures. The electrode surface charge and ions in the inner Helmholtz layer will inevitably disturb the water layers. More simulations on the EDL structures of water, both pure and salt-containing, at electrified interfaces can be found in reviews on the topic.[7] One important assumption in the MD simulations is the interaction between the charged electrode surface and water. The simple Lennard-Jones 9-3 potentials used by Lee[4] were replaced by Shelley et al.[8] with a jellium model, along with water orientation-dependent terms to describe the mercury/water interface. Density functional theory (DFT)–based ab initio MD (AIMD) simulations were first performed on a copper/water interface by Price and Halley.[9] Both MD and AIMD showed that the layering of water is because the water-water interactions due to H-bonds are more significant than the metal-water interactions in determining the EDL structure, at least at the voltage near the potential of zero charge (PZC).

Because the EDL is extremely thin, typically only a few Ångstroms to a few nanometers thick, resolving its structure requires separating the weak interfacial signals from the much stronger signals from the bulk electrode and electrolyte. In 1994, Toney et al. used in situ X-ray scattering to measure the water density profile on single-crystalline Ag(111) surfaces.[10] The NaF salt concentration is low (0.002M to 0.1M) and only two voltages above and below the PZC were measured. The results confirmed that water molecules

(continued on next page)

are ordered up to three layers (Fig. 1b), consistent with theoretical prediction. However, they also found that the first layer of water has a higher density than bulk water, especially at +0.52 V above the PZC; this phenomenon has not been predicted by previous theory or simulations. Ataka et al. probed water structures on Au(111) surfaces with surface-enhanced infrared absorption spectroscopy in a wider range of electric potentials (-0.6~0.8 V with respect to the PZC) in 0.5 M perchloric acid.[11] A more complex picture emerged. Around the PZC, water lies flat. At potentials more negative than the PZC, water molecules are weakly H-bonded with two H-atoms closer to the surface than O-atoms. The previously discussed "ice-like" structures (Fig. 1c) appear at potentials slightly more positive than the PZC. The ice-like structure is broken at more positive potentials due to the adsorption of anions. The broken H-bonds due to anion adsorptions led to more closely packed water, consistent with the higher density measured from X-ray scattering. Therefore, some simulation results of EDL structures are only partially valid if ions are not present in the simulation.

Another advancement is the increasing collaboration of modeling and experiments. One example is the X-ray absorption spectroscopy (XAS) measurements of the dynamic structure of water at Au electrode flowing with a 10 μM NaCl aqueous electrolyte.[12] AIMD simulations were used to generate structural trajectories of the Au/water interface, from which XAS spectra were computed. The statistics of the first-layer water molecules were captured: about 50% lie flat on the surface, while the other 50%, which have broken hydrogen bonds, do not contribute to the XAS because of coupling with the Au surface. This example highlighted the importance of integrating simulations with experiments to avoid misinterpretation. Here, the model revealed a previously unknown physics arising from the strong coupling between the X-ray excited states and the surface electronic structure. Due to this effect, even more flat-lying water molecules with broken hydrogen bonds appear under negative bias. However, they produce a spectrum similar to that of bulk water. Without the direct structure-spectrum simulations, this could be misleading. Given the complexity of the EDL, multimodal characterization combined with accurate simulations is essential for a coherent picture.

How does layered water change our understanding of ion distributions in the EDL? The presence of cations in the EDL has received much attention recently, as they are critical for electrocatalytic reactions. Markovic et al. showed that for the hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), and methanol oxidation, the reaction rates follow the order of $Cs^+ > K^+ > Na^+ > Li^+$ at the potential range from 0.8 to 1.0 V vs the reversible hydrogen electrode (RHE). The cation size was generally used to explain this activity trend. A recent MD simulation by Moss and Doblhoff-Dier predicted that the distance of the alkali cations (Li^+, Na^+, Cs^+) to the Pt(111) surface not only scales with cation size, but also with how the solvation shell fits with the water layers.[13] For example, Li^+ will sit slightly below the first water layer, so the triangular face of its tetrahedral coordinated water shell will fit with the first water layer. On the other hand, Na^+ will sit directly in the first water layer to maintain its octahedral water solvation structure (Fig. 1d). Thus, the layering of water and layering of ions are coordinated. Higher ion concentrations will also break the water H-bond network.

From the iterations among theory, experiments, and simulations, the understanding evolves. It is clear that theory and simulations play complementary but distinct roles. There is an increasing number of AIMD simulations of the metal/electrolyte interface dedicated to electrocatalytic reactions, giving qualitative predictions, while quantitative connections with experimentally measured electrochemical data are rather limited.

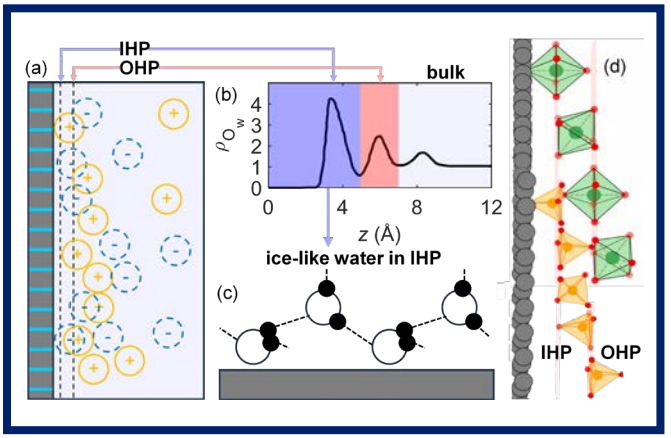


Fig 1. ***Evolving view of water in the electrical double layer (EDL).*** *(a) EDL structure replotted from Grahame with water as a background.[1] (b) Layering of water observed by X-ray agrees with (c) the ice-like water structure at potentials slightly more positive than the PZC.[10, 11] (d) The cation hydration shell (green and yellow for different ion sizes) fits into the layered hydrogen-bond network, reproduced from recent MD simulation results.[13] Reproduced with permission. Copyright 1947, ACS; 1994, Springer; 1996, ACS; 2026, Elsevier.*

Countless Combinations of Organic Solvents

Compared with water, which is uniquely important and complicated, the EDL structures in organic solvents appeared somewhat simpler in Grahame's experiments on methanol.[14] The capacitance of multiple salts in methanol was qualitatively similar to that observed in aqueous solutions at elevated temperatures, without the characteristic "hump" observed in water, indicating no strong methanol layering in the EDL. However, this apparent simplicity breaks down when Hou et al. tried to find solvent descriptors to correlate with EDL capacitance.[15] They found no simple relationship between EDL capacitance and the dielectric constant, viscosity, boiling temperature, or dipole moment of solvents. It becomes more complicated for mixed solvents. Early studies of binary organic solvents, such as methanol and acetone, already revealed selective adsorption of acetone on the mercury electrode surface, particularly on the cathodic branch of the capacity curve.[16]

With hundreds of commonly used organic solvents, 10^9 molecules in public databases, and countless possible mixtures, organic electrolytes create a vast design space for electrochemical applications, as shown in Fig 2. Here, the organic solvent broadly includes all the charge-neutral species in the liquid electrolyte, solvent, additives, reactants, and reaction mediators for a variety of applications.

Energy Storage Devices

For energy storage devices, such as capacitors and batteries, the cell voltage is limited by the electrolyte reduction and oxidation potentials. Thus, moving from aqueous to organic electrolytes increases the cell voltage from 0.9 V to 2.5~2.7 V for EDL capacitors (EDLC) and to 3.0~4.2 V for Li-ion batteries, proportionally increasing both energy and power. Yet, the need to understand the role of charge-neutral species in EDL structure is different.

Supercapacitors

Motivated by experiments on EDLC with organic solvents,[17] MD simulations have revealed that the EDL structure in tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile (ACN) exhibits solvent layering and alternating layers of cations/anions.[18] In some cases, organic solvents were shown to enhance the EDLC performance,[19] but other studies found little effect of solvent choice on the inner layer capacitance across a range of organic solvents,[20] likely reflecting different solvent and electrode surface interactions.

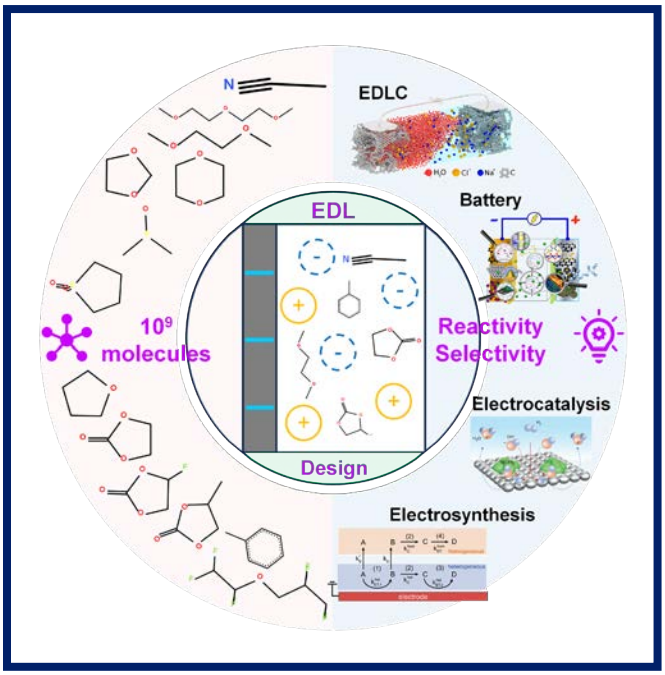


Fig 2. ***Direct design of the EDL in organic electrolytes for electrochemical applications.*** *Mixtures of solvent molecules organize at charged interfaces to tune local composition and interfacial structure, enabling applications in capacitors, batteries, electrocatalysis, and electrosynthesis. Reproduced with permission.[29-32] Copyright 2014, 2022, 2025, ACS; 2013, Springer.*

Li-ion Batteries

In batteries, passivation layers on the two electrodes, referred to as the solid electrolyte interphase (SEI) on the negative electrode or the cathode-electrolyte interphase (CEI), enable the battery to operate outside of the electrolyte electrochemical stability window. Thus, multicomponent organic electrolytes are designed not only to ensure fast ion transport but also the interface stability.[21] MD simulations has shown that the local composition at the electrode can differ significantly from the bulk electrolyte. A representative example is the mixed ethylene carbonate (EC) and dimethyl carbonate (DMC) solvent with $LiPF_6$ salt EDL near a charged graphite electrode, where the more polar EC becomes enriched in the EDL near both positively and negatively charged electrodes.[22] Further, Wu et al. analyzed the MD-predicted representative structures in the EDL and fed them to DFT calculations to evaluate which species/clusters are most likely to be reduced and therefore contribute to SEI formation.[23] They showed that the appearance of same-charged ions in the EDL, such as anions on the negatively charged surfaces, is sensitive to solvents and temperature. Adding fluorinated additives (e.g., fluoroethylene carbonate, FEC) may not result in any increase in F-content in the SEI, due to compositional competition in the EDL. The results explain a series of experimental observations that cannot be interpreted by the bulk electrolyte alone. Therefore, what really gets reduced or oxidized at a battery electrode is not just determined by the bulk electrolyte composition, but also by which molecules and ions actually gather in the EDL next to the charged surface**.**

Therefore, in organic electrolytes, charge-neutral molecules are not only the dielectric medium in which ions move and redistribute, but also part of the EDL structure, which creates a local environment that determines potential drop, local composition, and reactivity. Instead of passively studying EDL structures, *can we actively design specific EDL structures to achieve desired electrochemical reactions?*

Design of EDL Structures for Electrochemical Synthesis and Catalysts

In electrosynthesis, electrolyte design is increasingly used to engineer the local microenvironment, not just to provide conductivity and stability. Solvents and supporting salts can influence yield and selectivity by controlling the near-electrode composition and interface structure. Once charge-neutral species enter the EDL, they are not distributed randomly. They can adsorb with preferred geometries, reorient under the local electric field, and form layered or heterogeneous interfacial structures. Two recent perspectives have highlighted that understanding the EDL structures will enable new reaction pathways for electrosynthesis and electrocatalysis.[24, 25] A direct example of the role of charge-neutral solvents comes from the electrohydrodimerization of acrylonitrile to adiponitrile.[26] This reaction is an important industrial electrosynthesis. In situ attenuated total reflectance-fourier transform infrared (ATR-FTIR) spectrum has shown that tetraalkylammonium ions accumulate in the EDL, creating a local environment that enhances neutral acrylonitrile while excluding water, thus preventing the hydrogen evolution reaction. This example provides direct evidence that EDL composition can regulate selectivity by controlling which neutral reactants are present near the electrode and by suppressing competing solvent reactions.

These dynamics of the EDL can also be used to tune electrochemical reactions,[27] because electrochemical processes occur with continuously evolving EDL rather than in a perfectly equilibrated interfacial structure. Recent MD studies have further highlighted the time-dependent redistribution of charge-neutral species in the EDL under both constant and alternating polarity conditions to mitigate side reactions.[28] A complete picture of neutral species in the EDL should therefore include their equilibrium, composition distribution, and arrangement, and how rapidly they respond to electrochemical driving forces. The temporal and spatial evolution of the species cascading from electrochemical reactions near the EDL region needs to be resolved.

Overall, charge-neutral molecules in organic electrolytes are not passive media. They contain rich chemistry for electrosynthesis. They are part of the EDL structure and help determine local composition and reactivity. Yet our understanding of EDLs in organic solvents remains far less developed than in water, leaving major opportunities to design interfacial environments for improved electrochemical synthesis and catalysis.

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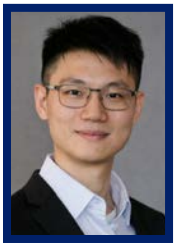


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