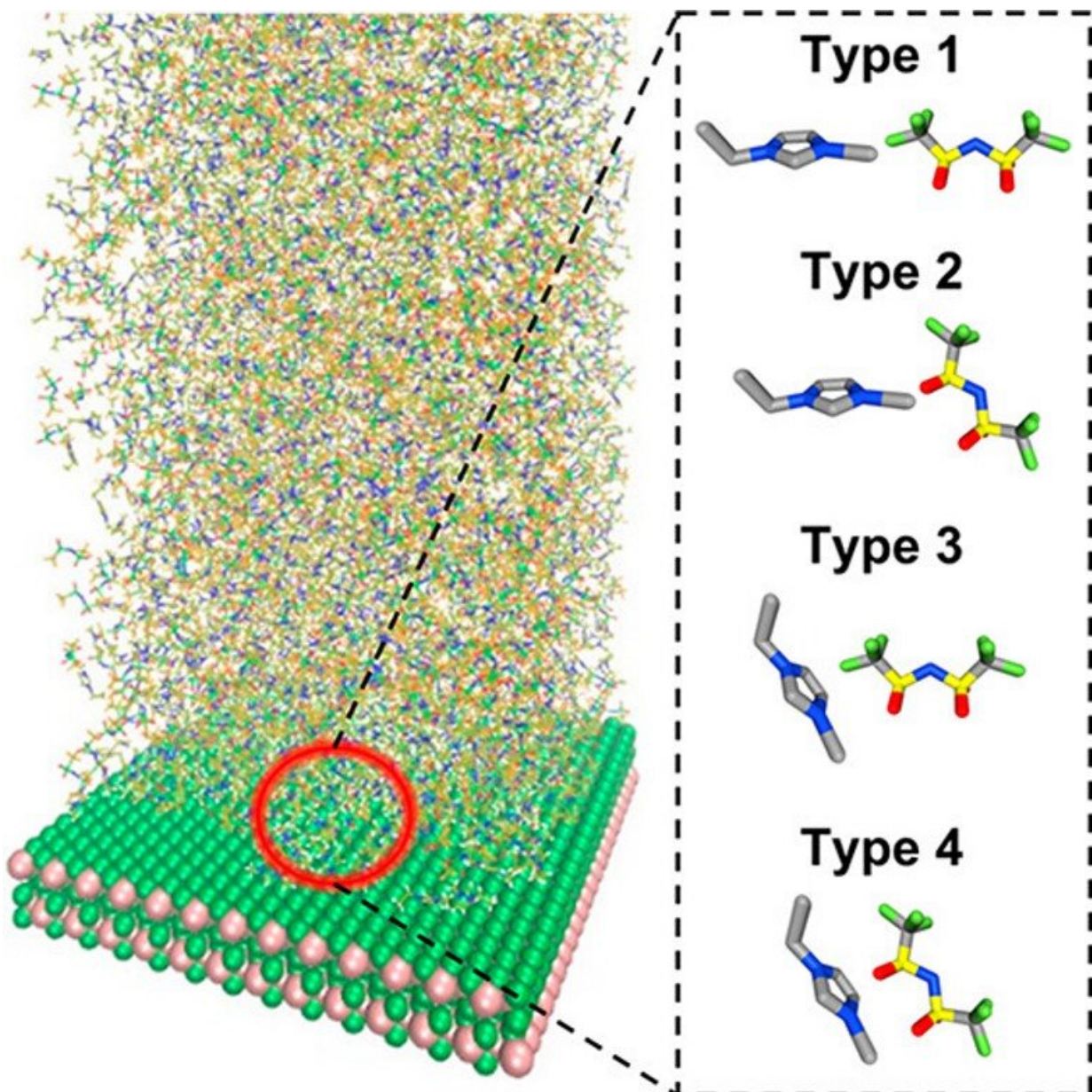


# Generality vs. specificity: Unraveling the electric double layer structure of highly ionic liquid electrolytes

November 17 2022



Electric double layers. Credit: The Grainger College of Engineering at the University of Illinois Urbana-Champaign

Using a combination of simulation and experimental techniques, University of Illinois Urbana-Champaign Material Science and Engineering researchers have been able to identify the electric double layer structure of an ionic liquid on a series of crystalline electrodes.

The research, published October 5 in *Journal of Physical Chemistry Letters*, combined [molecular dynamics](#) (MD) simulations and electrochemical 3D [atomic force microscopy](#) (EC-3D-AFM) to get a more complete understanding of the solid-liquid interface.

MatSE Professor Yingjie Zhang and grad student Kaustubh Panse, who collaborated with a group from The University of Texas at Austin to perform the MD simulations, recently adapted a well-known technique, AFM, to develop EC-3D-AFM, which performs AFM measurements in an electrochemical cell to study changes in surface morphology during electrochemical reactions.

Understanding the boundary between solids and liquids (the solid-liquid interface) is important to understanding how many materials systems, such as batteries and supercapacitors, work. The electric double layers (EDLs) at this interface, also called the solvation layer, refer to parallel layers of charges surrounding the solid. As Panse puts it, "EDLs are liquid molecule layers at the interface, and they occur because the underlying solid influences the liquid above due to the boundary effect and other interactions."

Understanding the EDL helps scientists determine how a system works, but it's tricky. Due to intermolecular (between molecules) and molecule-electrode interactions, it can be difficult to derive the EDL structure.

In this research, the team used [ionic liquids](#) (a salt in the liquid state), which are used in various electrochemical applications such as batteries, supercapacitors, and electrolyzers. However, ionic liquids haven't been as extensively studied as aqueous solutions. Panse says that the goal was to develop fundamental theory of how these ionic liquids are arranged on the interface. Furthermore, he explains that "the process that occurs at the interface determines the overall outcome: if molecules are lying flat along the interface, it is possible that can give much more capacitance than if the molecules are lying perpendicularly. Molecular orientation really affects the overall capacitance and the overall performance of the system."

The ionic liquid system used was 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI). EMIM-TFSI is a model system used in super capacitors and energy storage devices due to its high capacitive charging window. The team studied this ionic liquid on a series of crystalline electrodes: molybdenum disulfide ( $\text{MoS}_2$ ) flakes and highly oriented pyrolytic graphite (HOPG).

These crystalline electrodes are distinct in their [electronic properties](#), meaning that if the ion association is similar on both systems, then those results can be creditably attributed to the EDL rather than electrode interaction. The ionic liquid and electrodes were chosen because they are well-known and well-studied systems, allowing for a fundamental study of the EDL of an ionic liquid. During EC-3D-AFM experiments, how the system behaved at different potentials was measured and compiled to get a complete picture of the EDL.

The team observed strong association and intermolecular interaction

among [cations](#) ( $\text{EMIM}^+$ ) and [anions](#) ( $\text{TFSI}^-$ ) from the MD simulations. The simulation looked at all the possible pairs of species in the ionic liquid ( $\text{EMIM}^+$ - $\text{EMIM}^+$ ,  $\text{TFSI}^-$ - $\text{TFSI}^-$ ,  $\text{EMIM}^+$ - $\text{TFSI}^-$ ) in the first EDL of  $\text{EMIM-TFSI/MoS}_2$ . The results revealed a strong intermolecular interaction between cations ( $\text{EMIM}^+$ ) and anions ( $\text{TFSI}^-$ ), in contrast to the weaker  $\text{EMIM}^+$ - $\text{EMIM}^+$  and  $\text{TFSI}^-$ - $\text{TFSI}^-$  interactions.

Therefore, the team proposes that the cation-anion association structure of the innermost layer is the key descriptor of the EDL. The simulated EDL structure of  $\text{EMIM-TFSI}$  on both electrodes were "surprisingly similar," which indicates that electrode-specific interactions are much weaker than the effects of intermolecular interactions among the ionic species.

Those theoretical predictions were confirmed with EC-3D-AFM experiments. The researchers observed a similar response over a range of systems, so "it's highly likely that these descriptors can be widely applied to a large range of electrodes, electrolytes, and different electrochemical systems," Panse says. "We hope that they will serve as a good rational design guide for different electrochemical systems in the future."

**More information:** Kaustubh S. Panse et al, Innermost Ion Association Configuration Is a Key Structural Descriptor of Ionic Liquids at Electrified Interfaces, *The Journal of Physical Chemistry Letters* (2022). [DOI: 10.1021/acs.jpcllett.2c02768](https://doi.org/10.1021/acs.jpcllett.2c02768)

Provided by University of Illinois Grainger College of Engineering

Citation: Generality vs. specificity: Unraveling the electric double layer structure of highly ionic liquid electrolytes (2022, November 17) retrieved 24 June 2024 from

<https://phys.org/news/2022-11-generality-specificity-unraveling-electric-layer.html>

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