Summary
The inevitable presence of water at the interfaces of ionic liquids and solid surfaces can either be a nuisance or a delight, depending on the applications. Here, researches on the adsorption of water at these interfaces, its effects on the interfaces' molecular structure and dynamics, and its practical implications are reviewed.

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Introduction
Room-temperature ionic liquids (RTILs) consist solely of ions but remain in the liquid state at ambient temperature. Pure RTILs often have remarkable properties including extraordinarily low vapor pressure, excellent thermal stability, and wide electrochemical windows, which make them appealing working liquids in many applications [1,2]. However, the early application of RTILs was hampered by their instability in presence of water. The development of 1-ethyl-3-methylimidazolium-based RTILs in 1992 represents a significant step toward resolving this issue [3] (for a historical perspective, see Ref. 1). This progress, along with the emergence of concepts such as task-specific RTILs [4,5], helped initiate the rapid growth of the RTIL field. Since then, numerous applications have been demonstrated, e.g., as solvents for synthesis, absorbent for CO2 capture, electrolytes in energy storage devices, and lubricants or lubricant additives, to name just a few [6–11]. In many of these applications, the system performance is governed by the structure and dynamics of the RTIL-solid interfaces. Consequently, research on these interfaces grew significantly and has become one of the frontiers in interfacial science. Many of the essential understanding and exciting discoveries have been reviewed recently [12–14].

Perhaps because the water stability issue has largely been mitigated in many RTILs, few work on RTIL-solid interfaces considered the issue of water at these interfaces. However, water is readily absorbed by many RTILs from the ambient environment [15] and water can modify the liquid structure and ion-ion interactions in bulk RTILs [16]. Therefore, many fundamental questions arise, e.g., to what extent water molecules accumulate at RTIL-solid interfaces, how they modify these interfaces, and what is the macroscopic consequence of the water adsorption. In the last 5 years, these questions have attracted much attention from researchers in diverse fields. Here, we review the key understanding on these questions so far and offer our perspective on future research in this area. We distinguish two types of solid surfaces: electrode surfaces whose charge is controlled by external potentials and dielectric surfaces whose charge is controlled by the interactions/reactions of their atoms with the surrounding media. This distinction is not rigorous as electrodes may have surface groups that can be electrified and dielectric surfaces can be electrified by external voltages. Nevertheless, the electrode and dielectric surfaces considered here are useful models as they represent two limits of real solid surfaces, each leading to unique physics at RTIL-solid interfaces.

Water at RTIL-electrode interfaces
The issue of water at RTIL-electrode interfaces was examined systematically using molecular dynamics (MD) simulations in 2014 [17**]. Humid RTILs were enclosed between two oppositely charged graphene electrodes and the adsorption of water on the electrode surfaces was measured. For both RTILs examined, [Bmim][PF6] and [Bmim][TFSI], water is depleted from the electrode at low surface charge but greatly enriched at elevated surface charge densities, more so near the positive electrodes (Figure 1a). At the water loading considered, the adsorbed water molecules are far away from each other. Although they barely affect the ion distribution near the electrode, they enhance the capacitance of the double layer by up to 10%. Later MD simulations using [Bmim][BF4] produced similar results in terms of water adsorption [18**]. A new observation is that, because of the more humid RTILs used, the adsorbed water molecules form clusters on the...
electrodes and lead to a transition of the lateral ordering of the counterions on the electrodes (see Figure 1c).

The computational predictions have largely been confirmed experimentally. Surface-enhanced infrared absorption spectroscopy of humid [Bmim][TFSA] near Au electrodes confirmed the strong adsorption of water on positive electrodes and the formation of hydrogen bonding between the water molecules [19]. Differential capacitance measurement at the interface of humid [Pyr][TFSI] and Au electrodes showed the enhanced capacitance at potential positive of the potential of zero charge (PZC) as the humidity of RTILs increases, which further implicates the adsorption of water on the electrodes [20]. The enrichment of water near electrodes is also found when RTILs are confined in some carbon pores [21], which helps improve supercapacitors’ power density and may also affect their capacitance [22,23]. Water adsorption is found to impact the double layers near planar electrodes greatly. In one study, when the water content in the bulk [BMP][TFSA] increases from 35 ppm to 137 ppm, the PZC of the Au electrodes in contact with the RTIL shows a negative shifts of 0.39 V [24]. Furthermore, Atomic force microscope (AFM) measurement shows that, while a 0.5 nm-thick cation layer exists on electrodes biased at −1.0 V, this charged inner layer is swelled to 1.04 nm when the water content in the bulk RTILs is increased to 90 ppm and the layer becomes less stiff. [24] A somewhat different picture was found in another AFM study: the first counterion layer on an Au electrode seems to become more ordered and more difficult to rupture when 10 vol% of water is introduced into the bulk [EMI][TfO] (see Figure 1d and e) [25]. Nevertheless, both studies suggest that the thickness of the ion layers further away from the electrode is little affected by the introduction of water [24]. These results suggest that the ions within molecular distance from the electrode will likely reorganize following significant water adsorption, though the extent of reorganization depends...
on the nature of RTILs and the strength of water adsorption.

The skeleton of the mechanisms underlying the water adsorption at RTIL-electrode interfaces and the ensuing change of interfacial structure, ion layer stiffness and double layer capacitance has been established to some extent. The water adsorption is governed mainly by the interplay of three factors: the dielectrophoretic force driving dipolar water molecules to positions with stronger electrical fields, the association of water molecules with their neighboring ions, and the availability of space near electrodes [17**]. In particular, the stronger affinity of water molecules to the anions dominating the ionic environment near positive electrodes [17**,18**] and their easier access to the interstitial spaces between the anion and the electrode surface (see Figure 1b) [17**] are responsible for the stronger water adsorption on positive electrodes found in some studies [17**–20]. The adsorbed water molecules not only can serve as a dielectric medium but can also interact preferentially with anions by forming hydrogen bonds with them. Therefore, they modulate the ion-ion interactions near electrode surfaces and thus can modify the organization of the interfacial ions.

Theories have been developed for the adsorption of water at RTIL-electrode interfaces [20,26**,27]. One theory takes into account both the long-range electrostatic ion-ion interactions and the short-ranged interactions between ions, water molecules, and the electrode (e.g., the different affinity of water molecules to anions and cations) [26**]. The latter allows the theory to capture the asymmetric dependence of water adsorption near positive and negative electrodes (see Figure 1f) as well as the emergence of satellite peaks in the differential capacitance curve. Another theory emphasizes the importance of the dielectric contrast between the ionic species and water [27]. This theory can explain the enrichment of water near electrodes and its significant impact on the double layer capacitance.

**Water at RTIL-dielectric interfaces**

The effect of water on RTIL-dielectric interfaces has been examined as early as in 1988, when diluting ethylammonium nitrate by water was found to convert the surface force curve between two mica walls from an oscillatory decay to the exponential decay [28]. However, systematic work of this topic only emerged recently. Many of these studies were motivated by the question of how ambient moisture may affect the lubrication performance of RTILs confined in the nanogaps between dielectric (e.g., mica) surfaces [29**–36]. An intriguing phenomenon discovered in these studies is that a small amount of water in the environment can markedly increase the friction [29**,30**]. A structural transition of the confined RTILs induced by water was implicated for this phenomenon [30**], and this was confirmed recently by MD simulations. Fajardo et al. studied and the structure and friction behavior of [Bmim][PF6] in the nanogap between two negatively charged mica surfaces in contact with a bath of dry or humid RTILs [37**]. They found that water mostly adsorb on the mica surface and the adsorption increases as water loading in the reservoir increases (see Figure 2a). As water molecules are adsorbed on the mica walls, the Bmim+ ions are displaced slightly away from the mica surface and increasingly orient their hydrophobic tails away from the mica surface; their distribution across the gap evolves from the non-overlapping to the interpenetrating mode (see Figure 2b and c). Meanwhile, under a fixed normal load, the mica gap width reduces till the bulk water loading increases beyond ~20% due to the dielectric screening by the adsorbed water, which is consistent with the “softening” of RTIL film.
by water inferred from the surface force data by Espinosa-Marzal et al. [30**] The departure of the Bmim\(^+\) distribution from the non-overlapping mode and its ultimate transition to the interpenetrating mode causes the sliding plane to move from the interface between the Bmim\(^+\) layers on opposing mica walls to the Bmim\(^+\)-mica interfaces, which leads to an increase of the friction (see Figure 2d) as observed experimentally [30**,37**].

The water adsorption-induced change of ion organization near dielectric surfaces revealed in lubrication studies is also corroborated by study of the interface of between RTILs and open surfaces [38*,39]. A new insight from these studies is that, while the adsorption of water often weakens the structural ordering of the interfacial RTILs, the opposite trend, which has been suggested in experimental studies [29**,40,41], can also occur. For example, the adsorption of water on the charged surface of a mica in contact with [Bmim][Tf₂N] strengthens the ordering of the contact-adsorbed Bmim\(^+\) ions and modestly enhances the self-assembly of the tails of the first and second Bmim\(^+\) layers [32,39]. The multifaceted effects of water have been shown to originate from the many roles water molecules play, which are already evident at RTIL-electrode interfaces: while they are molecular solvents that hydrate interfacial ions and compete with them for space, they are also dielectric medium screening ion-ion electrostatic interactions [39].

An important issue raised in the study of RTIL-dielectric interfaces is the electrification of the dielectric surfaces. Although it is generally assumed that many dielectric surfaces (e.g., mica and silica) immersed in RTILs are electrified, the underlying mechanisms are little understood. In two independent sets of studies, it was suggested that the adsorption of water at RTIL-mica interfaces prompts the dissociation of the K\(^+\) ions from mica surfaces and is crucial for their electrification [36,40–43*]. These ideas are supported by the measurement of the wetting and layering of RTILs on mica surfaces under different relative humidity [42*-44]. However, these opinions are challenged by a recent AFM study, which suggests that mica surfaces are readily electrified in dry protic RTILs such as PAN [45*]. The origin of this difference is unknown. However, given the wide variety of dielectric materials (whose surface atoms have different propensity to dissociate) and RTILs (whose ions have different ability to exchange with the atoms of dielectric surfaces), one may expect water to play a role in the electrification of at least some dielectric surfaces in RTILs.

**Perspectives**

Although research on water at RTIL-solid interfaces has a rather short history, much progress has been made in the last years. Based on these works, a general picture of RTIL-water-solid interfaces (see Figure 3) is emerging [39]. The three key aspects of these interfaces are the adsorption of water, the electrification of the solid...
surface, and the organization of ions in the interfacial zone. Because of the three-dimensional nature of the double layers in RTILs [13,46], the last aspect includes not only the ion organization in the normal and lateral directions, but also the aggregation of the polar and ionic motifs of the ions, which can span molecular to mesoscales [14]. Importantly, these three aspects are tightly coupled with each other near both electrode and dielectric surfaces, e.g., for an electrode biased by an applied potential, the adsorption of water changes the capacitance of the double layer, which in turn changes the electrode’s charge density, and thus the ion organization and water adsorption near the electrode. Although some aspects of the three-way coupling have been recognized, in general they remain underappreciated and poorly understood. Exploring these three aspects and their “messy” interplay will enable deeper understanding of RTIL-water-solid interfaces and their macroscopic properties. Among the many possible future directions, the following lines of studies worth particular attention:

**Exploring the specificity of solid surfaces and molecular ions**

Researchers have so far focused on a few solid surfaces (gold, graphene, mica, and to some extent silica) and RTILs. Even though some general trends are observed in many of these works (e.g., enrichment of water at solid-RTIL interfaces at high positive potentials), notable differences are also reported, e.g., at zero charge, water is thought to be enriched in the micropores of carbon-derived carbon electrodes but depleted in graphene nanopores [18**,21]; while water is enriched near negative electrodes in some RTILs, it is likely depleted when other RTILs are used [19,24*]. Understanding these differences and potentially harnessing them in applications require work on the specificities of the electrification of solid surfaces and ion organization and how they are coupled with the water adsorption at RTIL-solid interfaces.

**Clarifying the reaction of isolated water molecules/clusters at RTIL-solid interfaces**

Although the reactions of water molecules at electrodes or dielectric surfaces are relatively well established when the electrolyte-solid interface contains abundant water molecules, the same cannot be said for single water molecules or small water clusters isolated in the ionic environment near electrode surfaces. There is evidence that the reaction of interfacial water in RTILs can lead to the adsorption of a myriad of other absorbates such as H^+ and OH^-, which can further complicate the RTIL-solid interfaces [47]. Clarifying these reactions are essential for understanding how water affects the practical operations of electrochemical systems employing RTILs.

**Exploring systems analogous to water-RTIL-solid interfaces**

The water-RTIL-solid interfaces are just one example of the composite electrolyte-solid interfaces where a solvent additive can greatly affect the interfaces. However, neither water has to be the solvent additive nor must RTILs be the electrolyte at such composite interfaces. In fact, the adsorption of organic solvents at RTIL-solid interfaces has been shown to benefit the dynamics of interfacial RTILs in micropores and has been investigated computationally and theoretically [48–51]. Likewise, at the interfaces between electrodes and water-in-salt electrolytes (e.g., a 21 molal LiTFSI-water solution), the adsorption of water at electrolyte-electrode interfaces critically affects electrolyte’s electrochemical window. Early computational work revealed that the electro-adsorption of water at these interfaces shows similarity with that at some RTIL-electrode interfaces (e.g., water is enriched at high negative potential) but also differences (e.g., water is depleted at >2 V vs. Li/Li^+ potential) [52]. Although the physics of the three-way coupling illustrated in Figure 3 in these systems has only begun to be explored, exciting progress is already emerging on the theoretical front [53*–54]. In particular, a modified Poisson-Fermi theory was developed for the water-in-salt electrolytes. By taking into account the subtle interplay between electro-sorption, ion hydration, and ion-ion correlations and parameterizing nearly all model inputs through independent MD simulations, the theory predicts the water electro-sorption and double layer structure near the electrodes with excellent accuracy [53**].

Further studies along the above directions will benefit from the interactions and collaborations between researchers working on experiments, simulations and theories. These studies will not only help the familiar applications such as electrochemical energy storage but also other emerging applications. For example, electrochemical synthesis of NH3 and CO in RTILs has been recently demonstrated [55–59]. Although the mechanisms are not fully understood, the water at the electrode-RTIL interfaces likely provides the needed proton and should be scrutinized. Likewise, the electrodeposition of Zn in RTILs has been found to exhibit different deposition microstructures when water is introduced [25]. The underlying mechanisms are as yet little understood but warrant further investigation. These and other applications call for fundamental research on water at RTIL-solid interfaces and we can expect exciting new discoveries to be made in the years to come.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest


The electro-adsorption of water at RTIL-gold interfaces and ensuing electrochemical changes (e.g., PZC and capacitance) and reorganization of interfacial ions were thoroughly examined.


The transition of interfacial ion organization induced by diluting RTILs with water was studied systematically using AFM under different electrode polarizations. The effect of water on the electrodeposition of Zn in RTILs was reported.


A theory for water adsorption at RTIL-electrode interfaces was proposed. The ion- and electrode-specificity of the water adsorption is taken into account in this theory.


The impact of environmental moisture on lubrication performance RTILs was reported and the underlying mechanism was proposed.


Water at ionic liquids-solid interfaces


The adsorption of water in RTILs confined in a nanogap between two mica surfaces was studied. The experimentally observed water-induce increase of friction was elucidated by examining how water adsorption modifies the ion organization and position of the sliding plane.


The first all-atom molecular simulation of water adsorption at mica-RTIL interfaces. The structure change of interfacial RTILs induced by water was detailed.


The effects of water on the ion organization near mica surfaces were quantified and the critical role of water in the electrification of mica surfaces was proposed.


The effects of environmental humidity on layering of RTILs near mica surfaces were demonstrated; the critical role of water in the electrification of mica surfaces was proposed.


The adsorption of various metal ions at RTIL-mica interface and the interfacial RTIL structure were studied. The electrification of mica in some protic RTILs in absence of water was suggested.


An elegant theory for the double layers in water-in-salt electrolytes that takes into account the subtle interplay between water electrosorption, ion hydration, and ion-ion correlations.


