Water-in-Salt Electrolytes: An Interfacial Perspective

Ming Chen,[1] Guang Feng,[1,*] Rui Qiao[2,*]

[1]State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

[2]Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States

Abstract

Liquid electrolytes with high ionic conductivity, high transference number for the target ions, and excellent electrochemical, chemical, and thermal stability are essential for electrochemical energy storage devices. Water-in-salt (WIS) electrolytes, in which the salt-water ratio is larger than one, are gaining intensive attention in the electrochemical community. Here, we review the recent work on WIS and the closely-related water-in-ionic liquids electrolytes. We highlight the fact that many properties of these electrolytes, in bulk and at electrolyte-electrode interfaces, are underpinned by the physics and chemistry of the interfaces formed between water and ions (or aggregated water/ion clusters). Manipulating these interfaces by tailoring the selection of ions and water-ion ratio opens up new dimensions in the optimization of liquid electrolytes but also poses new challenges. We conclude the review by highlighting several directions for research on WIS electrolytes, in particular, the study of WIS electrolyte-electrode interfaces using surface force measurements.

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* To whom correspondence should be addressed (R.Q.: ruiqiao@vt.edu; G.F. gfeng@hust.edu.cn).

Introduction

Driven by diverse needs, including electrification of transportation and the grid-scale deployment of electricity generation from intermittent renewable sources, the development of electrochemical energy storage (EES) systems has been at the forefront of energy technologies for decades. Much advance has been made thus far, e.g., the development of Li-ion batteries has been recognized by the 2019 Nobel Prize in Chemistry. Nevertheless, developing EES systems with high energy density, high power density, high level of safety, and low cost remains a grand challenge.[1-4] A crucial component in these devices is the electrolyte, which completes the electrical circuit by conducting ions but not electrons. Often times, the electrolyte performance is the limiting factor governing the performance of EES systems.[4-9] In most existing EES systems, liquid electrolytes are adopted because the solid electrolytes cannot yet compete with liquid electrolytes in terms of the overall electrochemical, mechanical, and thermal performance and cost. Hence, exploration and optimization of liquid electrolytes have become a very active area in the EES field.[5]

The development of liquid electrolytes has traditionally focused on salt solutions with moderate ion concentration as the ionic conductivity typically decreases as electrolytes become highly concentrated. However, several waves of departure from this paradigm have emerged in recent years. The early one is perhaps due to the resurgence of room-temperature ionic liquids (ILs) as an electrolyte. The more recent one is related to the emergence of super-concentrated electrolytes. These electrolytes[10-16] include examples such as water-in-salt (WIS) solutions[10-14] and solvate ionic liquids.[15,16] They can be loosely termed as "solvent-in-salt" (SIS) electrolytes as the solvent-to-ion ratio is very small. Research on both ILs and SIS electrolytes has experienced explosive growth in recent years, and many reviews have been developed to them.[4-7,17-21] In this brief review, we shall focus on SIS electrolytes in which water is the solvent not only because these electrolytes exhibit some of the most spectacular performance but also because the insights on these electrolytes will likely be relevant to other SIS electrolytes as well.

The term of "Water-in-salt" electrolyte was probably coined by Suo et al.[10] They reported that a 21 m (mol/kg) lithium bis(trifluromethylsulfonyl)imide (LiTFSI)) solution has an electrochemical window of 3 V, which is far higher than that of conventional aqueous electrolytes (~ 1 V). When used with the conventional $LiMn_2O_4/Mo_6S_8$ electrochemical couple,

the resulting Li-ion battery achieves an open circuit voltage of 2.3 V, an energy density of 84 Wh/kg, and a nearly 100% Coulombic efficiency in the first 1000 cycles.[10] This work ushered intensive research on WIS. For example, the "water-in-salt" concept has been extended to many other cations such as Na^+, K^+, and Zn^{2+} ions, and different anions, as well as mixtures of different salts (e.g., LiTFSI combined with LiOTF).[11,22-25]

In the above WIS electrolytes, which are intended for usage in Li-batteries, salts are composed of Li^+ ions and organic anions (e.g., $TFSI^-$)[10] or inorganic anions (e.g., NO_3^-).[26] WIS with these types of salts can be considered as the "standard" WIS. These salts, however, are not the only choices. In fact, other salts with low melting points (e.g., ILs) can also be used. In fact, the work on water-in-ionic-liquids electrolytes has a longer history than that on the standard WIS. Research on water-in-ionic-liquids was initially driven by the need to understand the consequences of the contamination of ILs, which are highly hygroscopic,[27,28] by water, even for hydrophobic ILs. Later, studies were driven by the recognition that water can be used as an additive to manipulate the properties of ILs, but it can also potentially compromise the electrochemical window of ILs. These Investigationes have led to a growing body of knowledge that benefits the development of EES systems such as supercapacitors.[17-20]

Below we review the work on both standard WIS solutions and water-in-ionic-liquid electrolytes. These researches can be broadly divided into those targeting behavior in the bulk or behavior at electrified interfaces. An emerging picture from these researches is that both types of behaviors are intimately tied to the physics and chemistry of the interfaces formed between water molecules and ions (or aggregated clusters) and modification of these interfaces near electrified surfaces.

1. Standard water-in-salt electrolytes

1.1 Behavior in bulk

Much of the current research on bulk WIS electrolytes focuses on the ion transport process in these electrolytes and their underpinning in the molecular/mesoscale structure of the electrolytes. [29-34] An emerging picture is that bulk WIS electrolytes are highly heterogeneous, with ions and water molecules self-assembled into nanoscale domains. There are an enormous number of ion-

water interfaces in these electrolytes, and the structure and dynamics of these interfaces govern the ion transport.
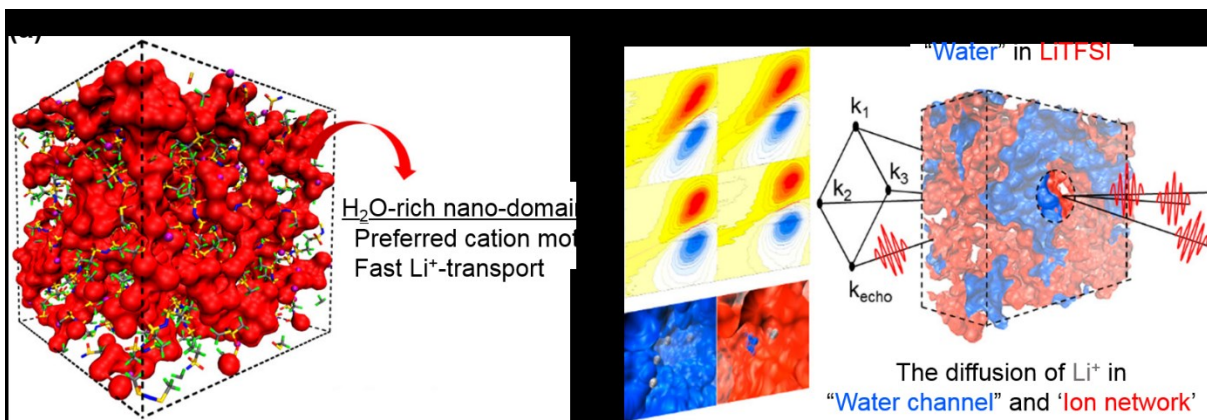

Figure 1. Bulk water-in-salt electrolytes are interface-rich materials. (a) A snapshot of the molecular model of a 21 m LiTFSI−H_2O.[29] An interconnected H_2O region (red) and TFSI$^-$ anions are visible. (b) A snapshot of the "water channel" (blue) and ion networks (red) in a 21 m LiTFSI obtained from molecular dynamics simulations.[30] Figures are adapted from Refs 29 and 30 with the permission of ACS.

Molecular dynamics (MD) simulations indicated that in 21 m LiTFSI WIS electrolyte, owing to the disproportion of cation solvation, a heterogeneous liquid structure with a characteristic length of 1 - 2 nm occurs, leading to the effective decoupling of cations from the traps of anions, which provides a three-dimensional (3D) $Li^+(H_2O)_4$ network (**Figure 1a**).[29] The formation of this 3D heterogeneous domain provides an effective channel for the fast transport of hydrated Li^+ ions with a high transference number (0.73), which is a key to guarantee the high-rate performance of lithium batteries. With femtosecond Infrared (IR) spectroscopy and MD simulations, a somewhat different picture was obtained.[30] It was suggested, at very high concentrations, the chaotropic TFSI$^-$ anions form a porous ion network rather than clusters, and this network is spontaneously entwined by nanometric water channels (**Figure 1b**). Two types of water molecules, bulk-like and interfacial water molecules, exist: the bulk-like water molecules in the ion transport channels are tangled within ion networks and serve as a medium for Li^+ ion transport; the interfacial water molecules are interspersed in the porous ion networks and serve as a lubricant.[30] Thus, acting like conducting wire, the hydrated Li^+ ions travel through bulk-like water channels, while simultaneously being lubricated by the surface water.[30]

While the results of these studies differ in the specifics of the heterogeneous structure of ions and water, they both highlight the formation of rich interfaces between the ions and water domains in

WIS electrolytes and the importance of these domains and interfaces in determining the ion transport. One way to engineer these domains and interfaces is to tailor the type of anions in the electrolytes. Using MD simulations, several anions have been adopted to investigate the effects of anions on the structure in WIS electrolytes keeping Li^+ as the cation.[31] It was found that the structure of water depends strongly on the type of anions. Specifically, the hydrogen bond networks among water molecules were fully broken among LiTFSI, LiFSI, and LiOTF in the high concentration. For NO_3^-, however, water molecules can still be hydrogen-bonded with each other. This comparative study laid the groundwork for future studies on a comprehensive understanding of the formation of ion/water domains in WIS electrolytes and its impact on ion transport.

1.2 Behavior at electrified interfaces

One of the pressing questions for WIS electrolytes is why they can operate stably on electrodes in far higher potential windows than water. It appears that the significant expansion of the electrochemical window (e.g., from 1.23 V to ~3 V)[10] has both thermodynamic and kinetic origins (**Figure 2a**), and both origins are tied strongly to the structure of WIS electrolytes near the electrodes.[12,26]

From the thermodynamic perspective, Yamada *et al.*[12] discovered that the Raman spectra of water exhibit only a sharp peak near a very high wavenumber, in contrast to the observation of broad band for water in dilute electrolytes. The sharp peak suggests that the conventional water clusters in dilute electrolytes are largely eliminated, and water in WIS exists in an environment where O-H bond of water is reinforced, which lowers the reactivity of water molecules.[35] In addition, it has been suggested that the electrons of the oxygen atom of a Li-coordinated water molecule are donated to the associated Li^+ ion, leading to a lower highest occupied molecular orbital (HOMO) level and thus increasing the oxidation potential of water.[12] While these studies are largely based on analysis bulk WIS electrolytes, interfacial effects have also been implicated in recent work. For example, the exclusion of "free" water molecules from the positive electrode has been suggested to contribute to the suppressed water decomposition.[14]

From the kinetic perspective, a variety of mechanisms related to the formation of dense solid-electrolyte interphase (SEI) have been suggested to explain the suppressed gas evolution on the electrodes. The formation mechanism of SEI films and their chemical composition, as well as

their microstructure, were meticulously examined by Suo *et al.*[36] They suggested that SEI films are contributed by the reduction of anion complexes (or clusters) and dissolved gases such as CO_2 and O_2 (**Figure 2b**): the former offers a source for LiF and the latter produces Li_2CO_3 and Li_2O. Furthermore, the high ion concentration is essential to ensure that the reaction products could deposit on anode surfaces without dissolution, so that a dense and stable SEI film is formed. Other pathways for SEI formation have also been suggested. For example, the hydroxide ions produced by water decomposition can catalyze the decomposition of fluorinated organic anions. This is followed by a nucleophilic attack, resulting in the growth of a passivating SEI layer (**Figure 2c**).[35] Another interesting result is the unique behavior of $LiNO_3$ WIS electrolytes (**Figure 2d**): instead of the growth of SEI interphase, the kinetic contribution to the suppression of water decomposition was suggested to come from the polymer-like chains of $(Li^+(H_2O)_2)_n$. Fundamentally, it is the energy barrier for water molecules to escape from these polymer-like chains that dominates the electrochemical stability improvements.[26]
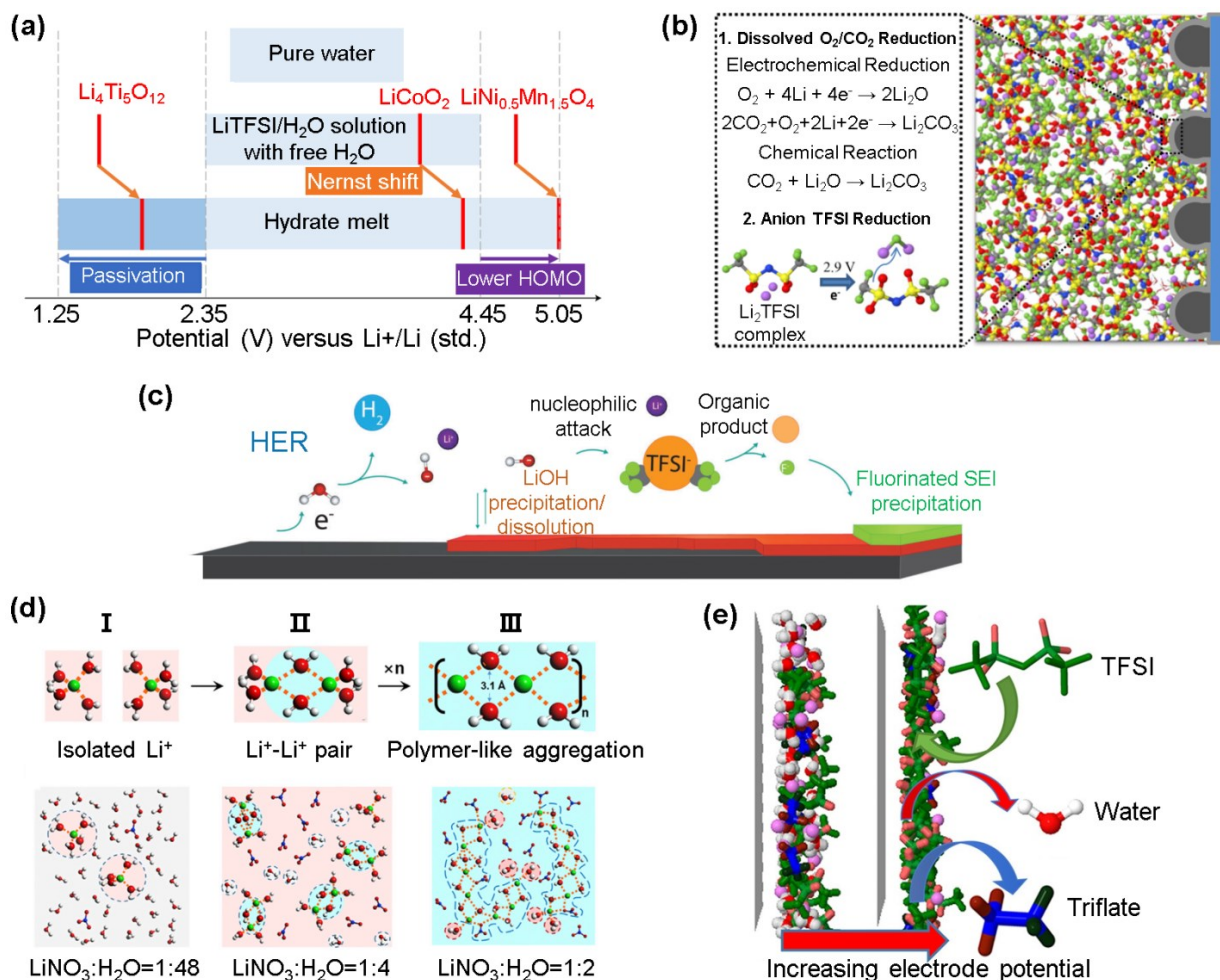

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Figure 2. Voltage expansion in the Water-in-Salt electrolytes. (a) Possible thermodynamic and kinetic factors responsible for the expansion of the electrochemical window.[12] (b) Plausible reactions of water-in-salt electrolyte at electrode surfaces.[36] (c) An illustration of the formation of the SEI film through the ''water reduction-mediated mechanism''.[35] (d) A depiction of the evolution of Li^+ hydration shell in diluted to super-concentrated $LiNO_3$ solution.[26] (e) A schematic evolution of the interfacial layer near positive electrodes in WIS electrolyte.[37] Panel (a) is adapted from Ref. 12 with the permission of Nature. Panels (b) and (e) are reproduced from Ref. 36 and Ref. 37, respectively, with the permission of ACS. Panel (c) is reproduced from Ref. 35 with the permission of RSC. Panel (d) is adapted from Ref. 26 with the permission of Cell.

The above experimental work provided key clues for the good stability of WIS electrolytes on electrodes. The stability of WIS electrolytes is further understood by molecular simulations, which present atomistic pictures of the processes envisioned in experimental works and details of the interfacial structure of water and ions.[37,38] The interfacial structure of 21 m LiTFSI and 7 m LiOTF electrolytes in contact with carbon electrodes was reported by Vatamanu and Borodin. It was found that the TFSI⁻ anions, preferable to the OTF⁻ anions, are adsorbed on the positive electrodes. This result highlights the selectivity of anions in the double layers. Meanwhile, water molecules are expelled from the positive electrodes (**Figure 2e**),[37] which helps improve the electrolyte's oxidation stability, in agreement with that found in prior experiments.[14]
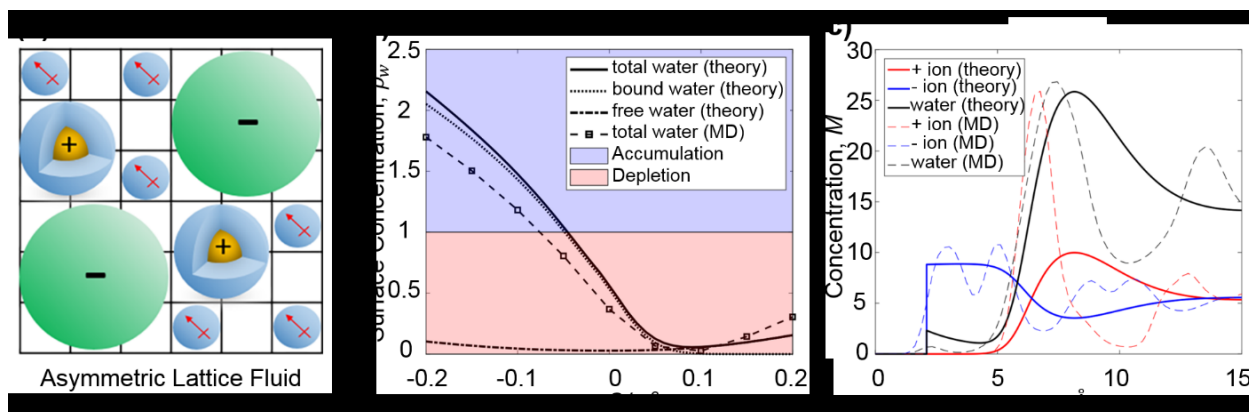

Figure 3. A continuum model for a water-in-salt electrolyte near an electrode.[39] (a) The electrolyte is modeled as a mixture of free water, hydrated cation, and anions. (b) Comparison of the sorption of water within 0.5 nm from the surface of an electrode in contact with a 21m LiTFSI WIS electrolyte predicted by the model and MD simulations. (c) Comparison of the distribution of water and ions across the double layer near in the same electrolyte near an electrode with a surface charge density of +0.1 C/m^2. Figures are reproduced from Ref. 39 with permission from ACS.

While molecular simulations can reveal details of the interfaces between WIS electrolytes and electrodes, the interpretation of the underlying physics can be complicated. Theories with explicitly defined physics (often can be easily turned on and off) can be powerful tools for a

thorough understanding of these interfaces. In this regard, an elegant mode[39] based on the Poisson-Fermi theory has been developed to predict the structure of these interfaces. This model leverages the understanding from MD simulations (e.g., the existence of free and Li-bounded water molecules and the strong correlations between ions) and treats a WIS electrolyte as a three-component asymmetric lattice fluid consisting of anions, hydrated cations, and free water (**Figure 3a**). By introducing a grand canonical chemical potential that considers electro-sorption, ion hydration, and ion-ion correlations (achieved through the Bazant-Storey-Kornyshev model originally formulated for ILs[40]), a model with seven parameters was constructed. Importantly, these parameters (e.g., ion size, effective dipole moment, and the fraction of free/bound water) have clear physical meaning and can mostly be extracted from independent MD simulations. The parameterized model can predict the electrosorption of water in the interfacial zone and the distribution of ions across the double layers near the electrode quite well (**Figure 3b** and **3c**). In particular, the significant depletion of water near positive electrodes, which is thought to help expand the electrochemical windows of WIS electrolytes, is captured. Moreover, the model was able to characterize the specificity of water sorption as a function of the choice of salt. For example, the model reproduces the stronger sorption of water in LiTFSI WIS than in LiOTF WIS on negative electrodes. Given that these two salts are quite similar, the performance of the model is impressive.

In part due to the understanding of the thermodynamics and kinetics behind the stability of WIS electrolytes at electrodes, notable progress has been made to enhance the performance of WIS electrolytes. For example, the $LiCoO_2/Mo_6S_8$ couple delivered an output voltage of 2.5 V with an energy density of 120 Wh/kg for 1000 cycles with an extremely low capacity decay rate.[41] Adding fluoride to the $LiTFSI/LiOTF/H_2O$ WIS electrolytes has led to a 4.0 V aqueous Li-ion battery with high reversibility and efficiency.[13]

2. Water-in-ionic-liquid electrolytes

2.1 Behavior in bulk

Research on water-in-ionic-liquid electrolytes, which precedes that on standard WIS electrolyte, has been partly driven by an idea of using water as an additive to improve their dynamic properties (e.g., to increase their conductivity and lower their viscosity). Many of these researches revealed that the dynamic properties of binary IL-water mixtures deviate strongly

from the ideal mixing results and attributed the nonidealities to the evolving microstructure of ILs and water in the electrolytes as water's mole fraction is varied.[42-44]

Small-angle neutron scattering measurements on [Bmim][BF$_4$]/D$_2$O system revealed interesting transitions of the microstructures in these electrolytes as water is introduced.[45] In the IL-rich regime, with the addition of trace water to ILs, water molecules remain isolated and interspersed in the cation-anion polar network, and the electrolyte is quasi-homogeneous. A microphase transition, in which nanometer-sized water clusters appear, occurs when the water-IL ratio exceeds ~2:1. Upon further addition of water, water molecules start to percolate the IL network (**Figure 4a**). These structural evolutions seem to be general for water-in-ionic-liquid electrolytes, as similar trends have been reported in other studies.[46] These structural evolutions are considered to lead to the non-ideal decrease of the electrolyte viscosity with water loading. They are also in line with the hypothesized water transport mechanisms in some water loading windows. Specifically, pulsed-field gradient-NMR and wide-angle X-ray scattering measurements on [C$_6$mim]X/water (X = Cl$^-$ and I$^-$) mixtures suggested a hopping mechanism for the water diffusion: water molecules often "bind" to ions and hop between binding polar ionic species rapidly during their random walk (**Figure 4b**).[47] It is worth to note that the H-bonding between water molecules and ions plays a key role in the microstructure evolution and the transport of water and ion.[53,54] The strength of H-bonds with the cation's acidic protons is enhanced as the electronegativity of anion increases but is weakened with very high water loading.

Molecular simulations also provided useful insights into the microstructure and dynamics of bulk water-in-ionic-liquids electrolytes. Sha *et al.* studied the relationship of the ion association and the dynamic properties of [Bmim][I]/water mixtures in dilute to pure ILs (**Figure 4c**).[48] By analyzing the potential energy of each species as a function of the IL mole fraction (x_{IL}), they showed that the ion hydration greatly affects the bulk properties of these electrolytes. Specifically, ions are localized in multi-coordinated ion "cages" in pure or concentrated IL solutions. However, the cage structure breaks down and is replaced by ion-hydration if x_{IL} becomes lower than 0.25. Such ion association has a significant impact on ion dynamics, e.g., the mole conductivity in concentrated IL electrolytes scales linearly with the ion association lifetime. By using MD simulations and the Kirkwood–Buff theory,[49-51] the evolution of the microstructure in these electrolytes was also found to be in line with the conclusion inferred from experiments

that the microstructure was shown to be water content-dependent.[45] Furthermore, water molecules tend to self-associate and form clusters in a more hydrophobic IL environment at moderately low water content.[49] Generally, the presence of water helps to enhance the ion diffusivity greatly.[50] Nevertheless, a somewhat different behavior was reported for [Emim]$^+$-based ILs with three different anions.[52] Specifically, in the [Emim][OAc]/water system, "anion-water-anion" wires forms spontaneously, leading to the significant anion nanostructuring. Similar wires and anion structuring, however, do not exist in [Emim][Tfa]- and [Emim][BF$_4$]-water mixtures, consistent with the experimental observation in [Bmim][BF$_4$]/D$_2$O electrolytes.[45] The more structured [Emim][OAc]/H$_2$O mixtures thus have slower H-bond dynamics and ion diffusion, and the ion diffusivity does not increase much till the water content is very high, in sharp contrast with the situation in the other two IL-water mixtures (**Figure 4d**).
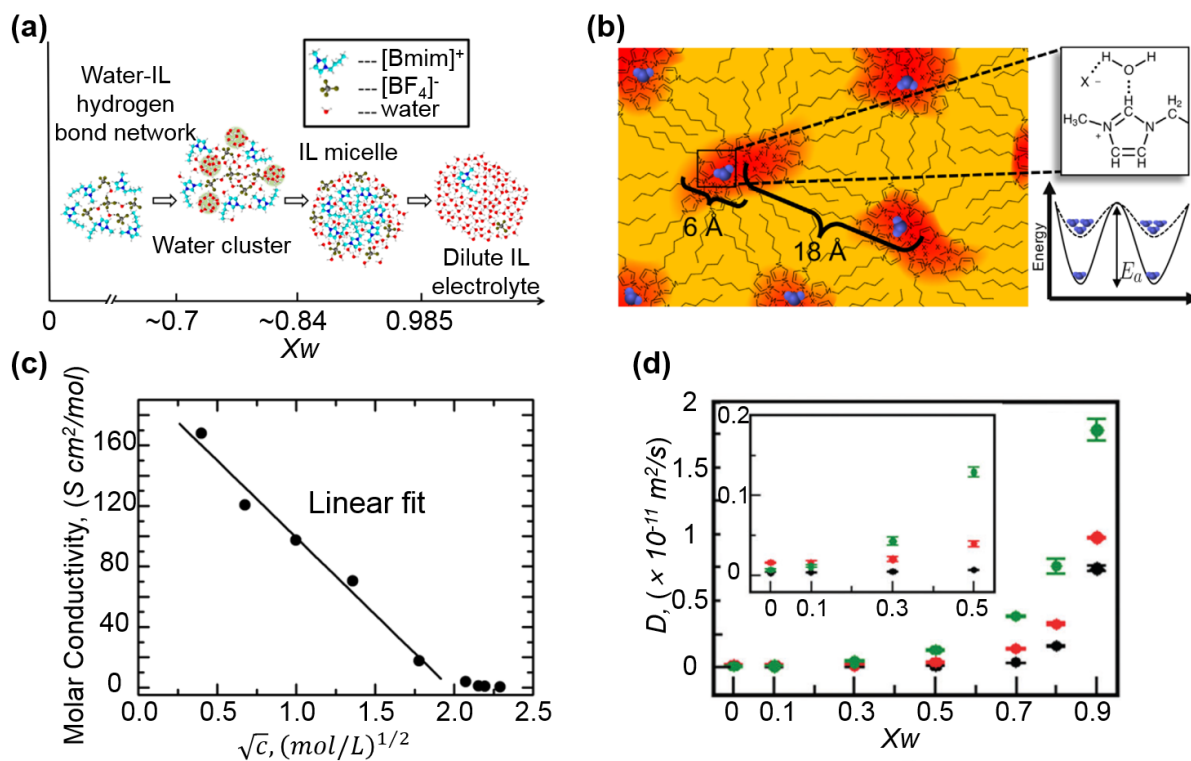

Figure 4. The microstructure and dynamic properties of bulk water-in-ionic-liquid systems. (a) The evolution of the microstructures in [Bmim][BF$_4$]-D$_2$O mixtures as a function of the mole fraction of the water.[45] (b) A schematic illustration of the water molecules intercalating within the polar hopping sites.[47] (c) The mole conductivities of [Bmim][I]+H$_2$O as a function of the square root of the IL mole concentrations.[48] (d) The self-diffusion coefficients of anions in binary electrolytes of [Emim][OAc] (black), [Emim][Tfa] (red) and [Emim][BF$_4$] (green) at different water mole fraction.[52] Figures (a) and (c) are adapted from Ref. 45 and Ref. 48, respectively, with the permission of ACS. Figures (b) is reproduced from Ref. 47 with the permission of APS. Figure (d) is reproduced from Ref. 52 with the permission of RSC.

2.2 Behavior at electrified interfaces

The behavior of water-in-ionic-liquid electrolytes at electrified interfaces has been studied using theoretical modeling,[53-55] molecular simulations,[56-58] and experiments.[59-63] The studies published before the middle of 2018, especially on the theoretical and simulation fronts, have been summarized in a recent review article.[17] The key findings of these works are that (1) water is often (though not always) enriched near charged electrodes, with stronger adsorption near positive electrodes, (2) water tends to reduce the electrochemical window of ILs,[55,60-65] and (3) the electro-adsorbed water molecules can markedly modify the structure and dynamics of ILs both in the out-of-plane direction (normal to the electrode surface) and in the in-plane direction. These findings have been enriched since then. For example, molecular simulations confirmed that water molecules could overcome the energy barriers in double layers to become adsorbed on the electrodes, and the stripe-like structure formed by pure ILs on anodes tended to become hexagonal-like with the addition of polar cosolvents (e.g., water).[66] Furthermore, as revealed by X-ray scattering, quasi-elastic neutron scattering, and MD simulations, water molecules adsorbed at [Emim][TFSI]-MXene electrode interfaces can enhance the mobility of *confined* ions.[67]

Surface force studies played a critical role in developing the aforementioned insight for water-in-ionic liquids elecrolytes at electrified interfaces. Similar studies, however, have yet to appear for standard WIS electrolytes. Therefore, in hope to stimulate similar lines of studies for standard WIS electrolytes, below we will first highlight a few surface force studies on the water-in-ionic liquids elecrolytes. We will then highlight a few surprising new simulation and experimental results that appeared after the middle of 2018.

Surface force studies. Surface force studies of water-in-ionic liquids at electrified interfaces have been motivated by applications such as lubrications.[68-70] On a more fundamental side, since surface forces are sensitive to interfacial structures and their modification by confinement, they are ideal tools for studying the structure of electrolytes at electrified interfaces.[71-79] Indeed, there has been a rich history of using surface force measurements to study the structure of interfacial electrolytes including ILs. While the interfacial structure of water-EAN mixture was studied as early as in 1988 by Horn and co-workers,[80] the study of water-in-ionic liquids at electrified interfaces with water-ion ratios relevant to WIS electrolytes appeared recently. Specifically, using surface force balance (SFB) and colloidal-probe lateral force microscopy, it has been

discovered that the availability of water from environment greatly affects the lubrication performance of ILs.[81,82] These dynamic measurements were also complemented by extended surface forces apparatus (eSFA), which provides information on how the structure of the nanometer-thin IL films confined between charged solid (mica) surfaces is affected by water (**Figure 5**). The findings from these studies have been confirmed and greatly expanded since then.[70,72-75,78,79,81,83-86]
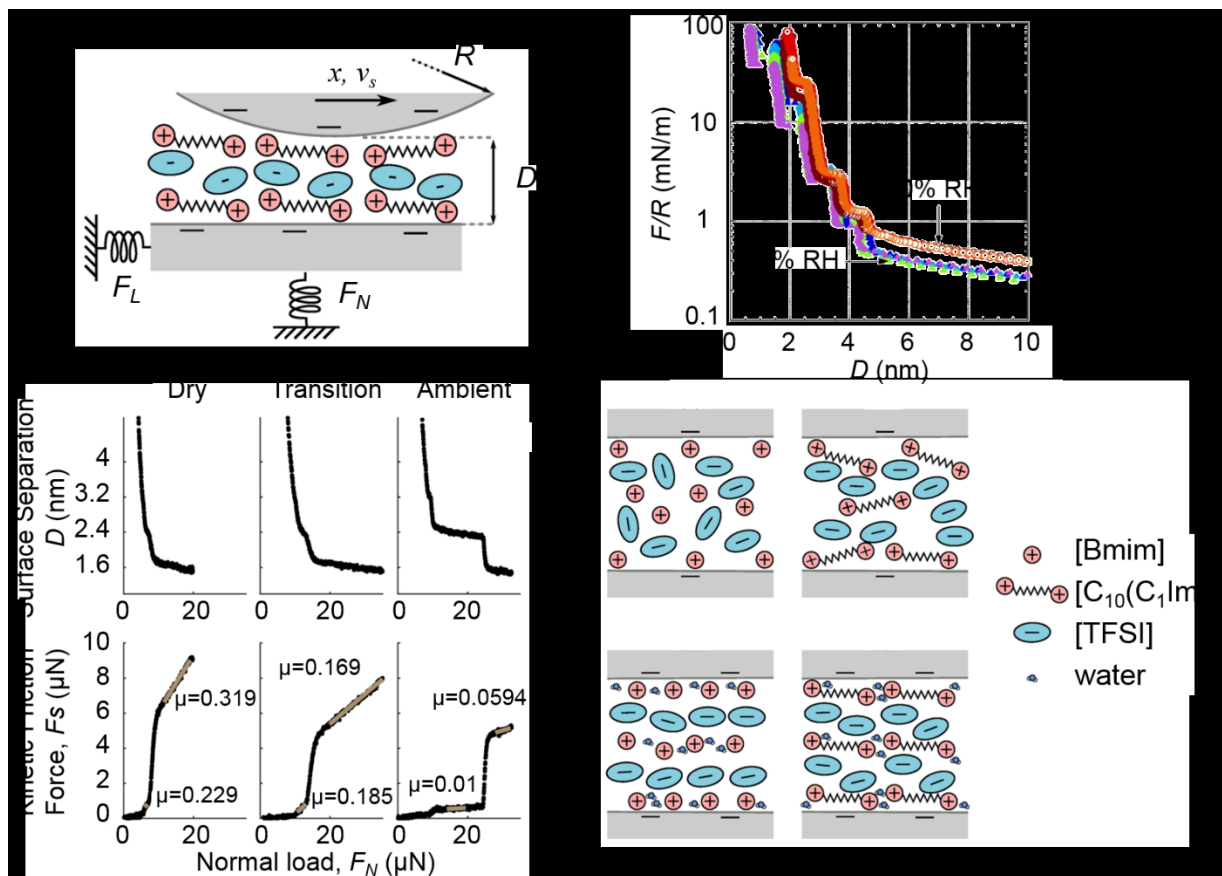

Figure 5. Surface force studies of water-in-ionic liquids at electrified interfaces. (a) A schematic of the surface force balance (SFB).[72] (b) The force profiles of [Emim][FAP] at 0 and 37% RH between mica surfaces.[83] (c) Surface separation D and the kinetic friction force F_S as a function of total normal load F_N, for the dry, transition, and ambient-equilibrated dicationic ionic liquid.[72] (d) A possible depiction of the effect of water on the configuration of monocationic and dicationic ionic liquids confined between mica surfaces.[72] Figures (a) and (c-d) are reproduced from Ref. 72 with the permission of ACS. The figure (b) is adapted from Ref. 83 with the permission of ACS.

An essential finding from these surface force studies is that water from the environment readily finds its way to electrified interfaces. The incorporation of water to these interfaces was unveiled to change the orientation of ion pairs at the interfaces and facilitate the squeeze-out of ILs between mica surfaces, leading to an increase of the ion layer thickness.[73,74,81,83] Thus, interfacial

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water can increase friction (**Figure 5b**)[83] and make the lubricating property of ILs worse.[73,74,81,83] This trend has been recovered in MD simulations.[86] Besides, the existence of water can even switch the shape of the friction response curve, so that adding water in [Emim][FAP] can generate a transition from the stick-slip mode to the continuous sliding mode.[83] However, an opposite trend occurs when using the dicationic IL ([$C_{10}(Im)_2$][TFSI]$_2$) with small fractions of water.[72] It was suggested that higher humidity causes a higher barrier for the squeeze-out of dicationic IL layers, and consequently, the friction coefficient is reduced by more than one order of magnitude than that for dry ILs under the same condition (**Figure 5c,d**).[72] When applied to the silica/silicon surfaces, the tribological performance of ILs was also improved due to the presence of water.[84] Combined with X-ray photoelectron spectroscopy and optical microscopy, the water is thought to react to help form a ductile surface film under tribological stresses, which smoothens the silica/silicon surfaces.[84] These results suggest that water plays multi-faceted roles at electrified interfaces that merit further investigations.

Recent progress on electroadsorption of water. A central difference between the standard WIS and the water-in-ionic-liquids electrolytes is that the electrochemical window of the latter is reduced when water is introduced. For instance, the electrochemical window of [Pyr$_{14}$][TFSI] was distinctly decreased when water is introduced.[65] Therefore, a key task in water-in-ionic-liquid research is how to mitigate the issue of narrowed voltage window of water-in-ionic-liquids electrolytes. One approach is to minimize the electrosorption of water on the electrode surfaces for these electrolytes. Along this line, joint MD-experiment work has been reported on the electrosorption of water on electrodes in contact with humid ILs, with a focus on how the hydrophobicity/hydrophilicity of ILs affects water electrosorption.[87] A rather counterintuitive picture emerged from this work. Specifically, despite that hydrophilic ILs usually absorb much more water from environment than hydrophobic ones, hydrophilic ILs suppress the adsorption of water molecules on the negative electrodes, even at large potential, regardless of electrode material (**Figure 6a**).[87]

The peculiar dependence of water electrosorption was understood by analyzing the energetics of water molecules interacting with their surrounding ions and electrodes. The potential of mean force (PMF) curves of water exhibit negative free energy for water near electrode surfaces in contact with hydrophobic ILs, resulting in an accumulation of water; for electrodes in contact

with hydrophilic ILs, a positive PMF appears, resulting in the depletion of water. These different PMF curves (and thus, water adsorption behavior) were attributed to the interplay between the water-electrode and the water-ion interactions (**Figure 6c**). Water molecules could form more H-bonds with anions in hydrophilic ILs than in hydrophobic ILs, and the water-ion associations weaken the water-electrode interactions by changing the water molecules' orientation and position. Therefore, under negative polarization, as anions were driven away from the electrode surfaces, the water molecules in hydrophilic IL would have less tendency to be attracted to the electrode surface. This insight gained here may provide a guideline for maintaining the electrochemical window of humid ILs by suppressing the water electrosorption using hydrophilic ILs[87,88] and for applications such as electrochemical microsensor for oxygen.[89]
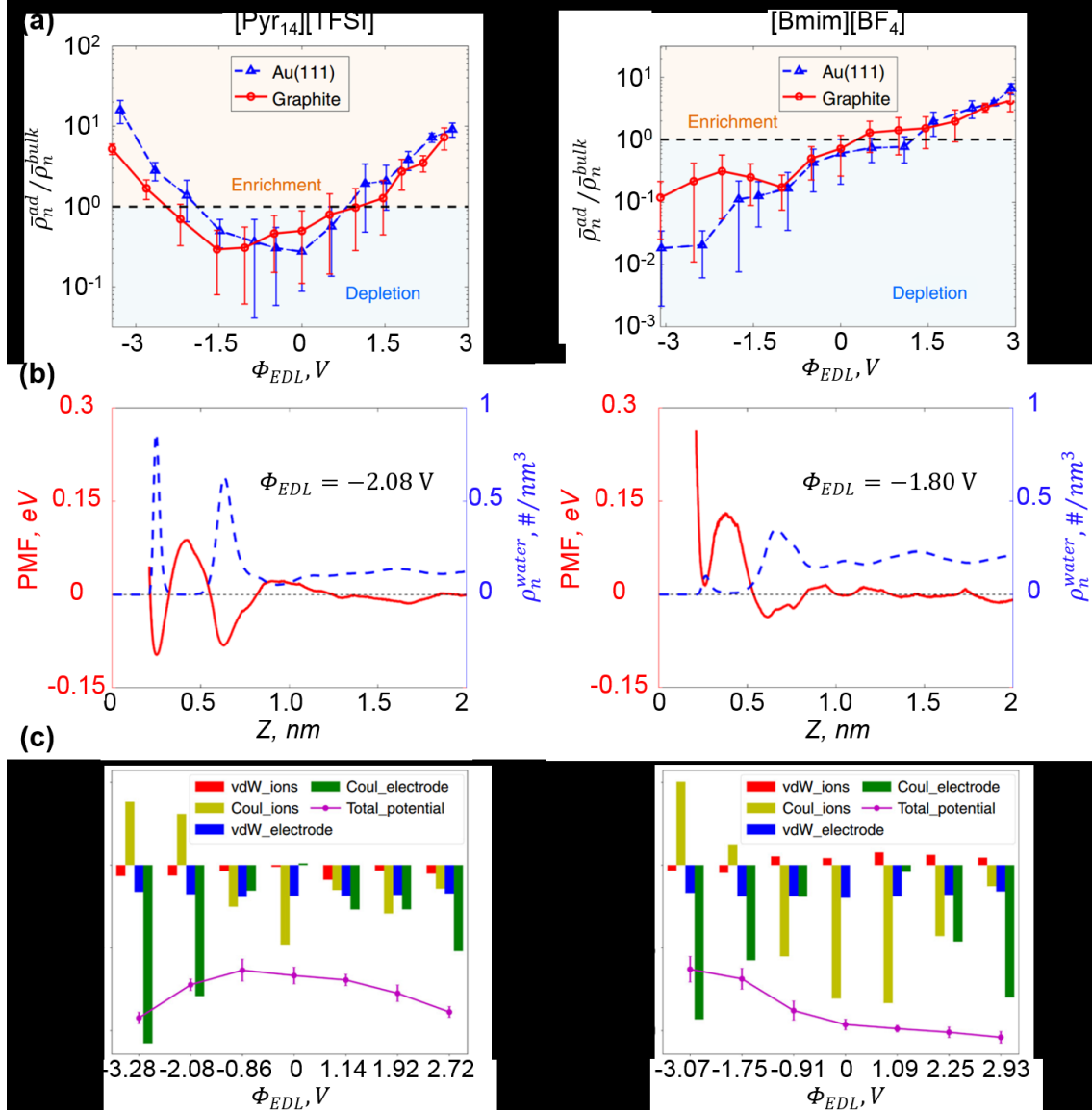
Figure 6. Water electrosorption on electrode surfaces and its origin. (a) Electrosorption of water from humid [Pyr$_{14}$][TFSI] and [Bmim][BF$_4$] on electrodes. (b) Correlation between the distributions of water density and the potential of mean force (PMF) for water near the negative electrodes. (c) Different components of the interaction energy of a water molecule adsorbed on an electrode surface. The figure is reproduced from Ref. 87 with the permission of Nature.

3. Perspectives

Water-in-salt electrolytes are emerging as one of the most exciting frontiers in the development of liquid electrolytes. The intensive researches thus far highlighted the essential role of water-ion and water-ion-electrode interfaces in determining their behavior in bulk and at electrode-electrolyte interfaces. Despite the rapid progress, many fundamental issues remain open. Among

many possible research topics and directions, we would suggest that the following three areas merit particular attention and research in the near future.

The bulk structure and dynamics of WIS electrolytes. The low water-to-ion ratio helps to ensure these electrolytes' electrochemical stability, but it also leads to a decrease of the bulk ion conductivity and, in some cases, a strong tendency for the electrolyte to crystallize. Therefore, understanding the structure and dynamics of bulk WIS electrolytes is crucial for their applications. Furthermore, delving deeply into the bulk behavior of WIS electrolytes is an essential step toward understanding their behavior at electrode-electrolyte interfaces. At present, even though it is generally accepted that there exist extensive 3D microstructures in WIS electrolytes, there are considerable debates on the specific arrangement of ions and waters in them, which greatly affect their bulk behavior. Therefore, clarifying the 3D microstructures of WIS electrolytes and linking these structures to their thermodynamic and transport properties (i.e., propensity to crystallize) should be a focus of research. Given that WIS electrolytes' behavior depends sensitively on the selection of anions, systematically varying the anions can be an effective way to tease out the essential physics and chemistry underlying the bulk behavior of these electrolytes. Because the bulk behavior of water-in-ionic-liquids systems is much better understood, research on that of the standard WIS electrolytes should leverage the techniques and insights from studies water-in-ionic-liquids systems whenever possible.

The reactivity of water/ions at electrode-WIS electrolyte interfaces. While such reactivity is critical to understand the superior performance of standard WIS electrolytes and the limited electrochemical stability of water-in-ionic-liquids at electrode interfaces, the understanding of such reactivity is very limited. In fact, much of the current knowledge of such reactivity is based on analysis of ion and water molecules in bulk electrolytes, even though it is known that the structure of electrolytes in bulk and at electrode surfaces can be very different. To resolve this issue, the analysis of the reactivity of water molecules and ions should be based on (or at least informed by) the electrochemical environment at the electrode-electrolyte interfaces. In this regard, a recent study on solvate ionic liquids at electrode interfaces is a useful reference. There, the coordination of Li^+ ions by triglyme bis(trifluoro-methanesulfonyl)imide (G3) was found to be considerably distorted as Li^+ ion moves toward the negative electrodes. Quantum calculations

based on the coordination structure computed in MD simulations revealed that structural distortion facilitates the electrochemical reduction of the Li^+ ions.[90]

Along with the research on the reactivity of water molecules and ions at electrified interfaces, the formation of SEI in WIS electrolytes should be investigated more thoroughly. The research on SEI formation is necessarily more difficult given the many reactions possible but will likely remain a focus of both fundamental and applied research in the years to come.

Surface forces mediated by standard WIS electrolytes. Surface force measurements have proven to be a powerful tool for understanding the interfacial behavior of water-in-ionic liquids. They have also led to some unexpected discoveries, e.g., the interactions mediated by ILs decays exponentially with a length scale orders of magnitude larger than the classical Debye length.[91-93] At present, we are not aware of any published work on surface forces mediated by the standard WIS electrolytes. Given that the interfacial structure of these electrolytes plays an essential role in their transport properties and electrochemical stability, by providing insights into such structure, surface force measurement can make a unique contribution to the emerging field of WIS electrolytes.

Conflict of interest statement

Nothing declared.

Acknowledgments

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

* of special interest

* * of outstanding interest

Ref. 10: ** The first work that proposed the concept of "water-in-salt" (WIS). The electrochemical window of the electrolytes exceeds 3 V.

Ref. 12: ** This work reported the enhanced stability of concentrated electrolytes and suggested that the extension of the potential window has both kinetic and thermodynamic origins.

Ref. 14: * This work presented a kinetic view that water molecules are excluded from positive electrodes.

Ref. 26: * A kinetic mechanism for the expansion of the electrochemical window was proposed.

Ref. 29: * The ion solvation and transport behaviors in water-in-salt electrolytes were delineated. A 3D network enabling fast ion transport was discovered.

Ref. 35: * This work proposed a catalytic process, in which water is involved, for producing the passivating SEI layer.

Ref. 36: * The chemical composition and the formation mechanism of the SEI films in water-in-salt electrolytes were systematically studied.

Ref. 39: ** A theory for the structure of the double layers in WIS electrolytes. The interaction between electrosorption, ion hydration, and ion-ion correlations were considered in this theory.

Ref. 47: ** A hopping mechanism for the anomalously fast diffusion of water molecules in ionic liquids was proposed.

Ref. 59:** The effects of water on the development of interfacial strcuture of ILs near mica surfaces was examined by surface force measurments.

Ref. 81: ** A surface force study of the effects of water on the boundary lubrication by RTILs. The adverse impact of moisture on the lubrication performance RTILs was reported and the underlying mechanism was proposed.

Ref 82: ** A surface force study of the lubrication properties and structure of nanoconfined RTIL films exposed to controlled humidity. The transition of lubrication mode and the structral basis were clarified.

Ref. 87: ** A counterintuitive picture of water adsorption was found: taking hydrophilic ionic liquids as electrolytes rather than hydrophobic ones suppresses water adsorption on negative electrodes.

Ref. 91:* The existence of long-range surface forces mediated by ionic liquids was discovered.