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TOPICAL REVIEW — Water at molecular level

Effects of water on the structure and transport properties of room temperature ionic liquids and concentrated electrolyte solutions*

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Transport properties and the associated structural heterogeneity of room temperature aqueous ionic liquids and especially of super-concentrated electrolyte aqueous solutions have received increasing attention, due to their potential application in ionic battery. This paper briefly reviews the results reported mainly since 2010 about the liquid–liquid separation, aggregation of polar and apolar domains in neat RTILs, and solvent clusters and 3D networks chiefly constructed by anions in super-concentrated electrolyte solutions. At the same time, the dominating effect of desolvation process of metal ions at electrode/electrolyte interface upon the transport of metal ions is stressed. This paper also presents the current understanding of how water affects the anion–cation interaction, structural heterogeneities, the structure of primary coordination sheath of metal ions and consequently their transport properties in free water-poor electrolytes.

Keywords: super-concentrated electrolyte solutions, room temperature ionic liquids, water effect, structural heterogeneity, transport property

PACS: 78.30.cd, 66.10.−x, 66.30.jj, 47.57.eb **DOI:** 10.1088/1674-1056/ab9c07

1. Introduction

Room-temperature ionic liquids (RTILs), a novel class of low melting point salts consisting entirely of ions, have received increasing attention in the past few decades due to their low volatility, good thermal stability, and wide electrochemical windows. RTILs have been widely applied in the fields of catalysis,[1] chemical synthesis,[2] liquid–liquid extraction,[3] molecular gas capture,[4] biomass conversion,[5] biotransformation,[6] fuel production,[7] ionic battery,[8] and many other fields. To further understand the dynamic and thermodynamic properties of RTILs, their structures have been studied extensively.[9–18] Among them, the mesoscale structure of ionic liquids, especially whether there are nanometer-sized aggregates, local liquid–liquid separation, and percolation network in the bulk and/or interfacial RTILs, have been studied experimentally and theoretically. These structure models have also been adopted or proposed to qualitatively explain the abnormal physiochemical properties, particularly the self-diffusion and conductivity of RTILs.

Pure ionic liquids were first reported by Walden[19] in 1914, while their implementation has been strongly limited by their strict water-free preparation and working conditions. In 1992, Wilkes and Zaworotko synthesized the first air and moisture insensitive RTILs.[20] This aqueous RTIL can be regarded as a kind of super-concentrated aqueous solutions. Of course, some concentrated electrolyte solutions can also be viewed as quasi-ionic liquids because of their low volatility and stability. Both of these two kinds of liquids have been adopted as electrolytes in ionic battery. Hence, the comparison between them can highlight the effect of metal ions on the structures and physical properties of the solutions. In addition, a key issue is to reveal how water molecules affect the structures and physical properties of such liquids. Among all of the physicochemical properties, the transport of ions and water plays a key role in the implementation of these concentrated solutions notably in the field of electrochemistry.

For water-rich solutions, Stokes–Einstein (SE) relation can successfully describe the diffusion behavior of solvated ions, based on the averaged macroscopic viscosity and the hydrodynamic radius of the hydrated ions.[21,22] In water-rich solutions, hydrated ions can be nearly completely separated by free water, i.e., the fraction of ionic pairs and solute aggregations can be neglected.[23] In contrast, for concentrated electrolytes solutions and aqueous ionic liquids, free water is almost unavailable and the motion of each component correlates with its surroundings more strongly, therefore SE relation cannot be applied anymore.[24] Interestingly, contrary to expectation, trace amounts of water molecules in RTILs

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or concentrated electrolytes diffuse faster by about one order of magnitude than predicted by SE relation.[25] Moreover, trace amounts of water can obviously accelerate the diffusion of charged species in super-concentrated solutions.[26] Generally, these abnormal diffusion behaviors of water and charged species have been understood on the basis of mesoscopic structural heterogeneities.

In this review, the transport property and structure of RTILs, super-concentrated electrolyte solutions, and their water content dependences are reviewed. In Section 2, the mesoscopic structural heterogeneity of some neat ionic liquids is introduced and then the effect of water is highlighted. Section 3 focuses on the effect of water on the diffusion properties of RTILs and super-concentrated electrolytes, the characteristics of diffusion of water itself, and the transport behavior of ions through interface between liquid electrolyte and solid electrode. Section 4 provides a brief summary.

2. Mesoscopic inhomogeneity of RTILs and its dependence on water content

2.1. Neat RTILs

In 2005, Watanabe *et al.* and Voth *et al.* discussed the spatial inhomogeneity of some neat RTILs almost at the same time.[27,28] Watanabe *et al.*[27] measured the alkyl chain length-dependent diffusion coefficient (D), conductivity (σ), viscosity (η) of 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide ([*R*mim] [TFSI], R = methyl (m), ethyl (e), etc.). The results suggested that aside from ionic size and shape, ionic aggregate-induced structural inhomogeneity must also be considered to explain the transport properties of this system. Voth and coworkers[28] discussed the spatial inhomogeneity in pure ionic liquids [Emim$^+$][NO_3^-] (Emim: 1-Ethyl-3-methylimidazolium Tetrafluoroborate) by simulation using the multi-scale coarse-graining method. They proposed that, different from the nearly homogeneously distributed charged anions and headgroups of Emim$^+$, the neutral alkyl chain of the cation tends to aggregate due to the collective short-range interaction. Moreover, this aggregation was suggested to significantly depend on the alkyl length. Also in 2005, Raman spectroscopic measurement was performed by Ozawa and Hamaguchi to study the local structure of Bmim$X$ (Bmim: 1-butyl-3-methylimidazolium; X = Cl, Br, I, BF_4, PF_6).[29] A slow transformation between trans- and gauche-conformers for Bmim$^+$ suggested that this transfer process takes place not at the single-molecular level but through a collective behavior of the ensembles of Bmim$^+$. Based on the previous measurements of Raman spectroscopy[30–32] and wide-angle x-ray scattering[33] of [Bmim]Cl, Ozawa and coworkers proposed that some specific local structures with crystal-like order exist in liquid [Bmim]X. Moreover, by coherent anti-Stokes Raman scattering (CARS) measurements of $C_n$mim[PF_6] (n = 4, 6, 8), they also found that the spatial distribution patterns of the CARS signals become narrower as n increases from 4 to 8, suggesting the formation of specific local structures with several tens of nanometers in these ionic liquids (see Fig. 1).[34] One year later, Russina *et al.* provided the first experimental evidence about the existence of well-defined nanoscale heterogeneities in neat liquid and supercooled [$C_n$mim]Cl by means of x-ray diffraction.[10] Thereafter, they keep paying attention to the concentration and temperature-dependent mesoscopic structures of different RTILs mainly based on the measurements of the prepeak of x-ray scattering spectroscopy.[12,14,15] However, the structural origin of low-Q prepeak of small angle x-ray/neutron scattering (SAXS, SANS) of RTILs is still subject to debate. For example, in 2010, Hardacre and coworkers suggested that, for [$C_n$mim][PF_6], the low-Q prepeak arises from the second coordination shells of the ions along the vector of alkyl-chain, but not from a long-range correlated mesoscopic structure.[36] Margulis *et al.* also gave the similar advice.[37] According to this advice, the low-Q prepeak of SAXS of [$C_n$mim][PF_6] exists only because of the intrinsic anisotropy of the cation.

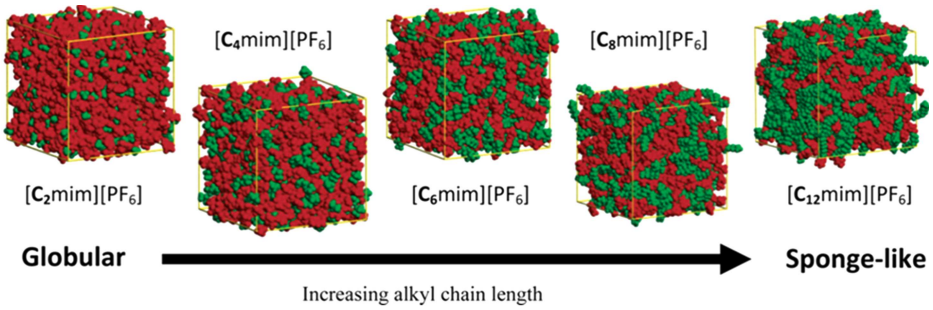


Fig. 1. Snapshots of the structure of [$C_n$mim][PF_6] for n = 2−12 (from left to right). Polar domains: anion + cation imidazolium ring (red); nonpolar domains: cation alkyl chain (green). When n = 2, small and globular apolar "islands" form within the continuous polar network. An increase of the alkyl chain length (n = 6, 8, 12) enables hydrocarbon domains to interconnect in a bicontinuous, sponge-like nanostructure. [C_4mim][PF_6] marks the transition between the two solvent morphologies. Reprinted with permission from Ref. [35]. Copyright 2006, American Chemical Society.

Although there is controversy in the interpretation of the spectra of SAXS/SANS, more obvious progress has still been made in revealing the meso-structure of ionic liquids. Readers interested in further details on this topic are referred to several recent reviews.[18,38,39] Several key viewpoints can be highlighted here briefly. First, larger volume ratio of charged groups to uncharged ones enforces a stronger segregation of polar and apolar domains in RTILs. Second, protic RTILs mesoscopic structure is sensitive not to anion type but to cation alkyl chain length. Third, the distribution of the alkyl chain of the cation influences the connectivity of the polar domains.[35]

2.2. Aqueous RTILs

Water is probably the most common impurity in RTILs. A trace amount of water can dramatically affect the electrochemical and dynamic properties of RTILs. This behavior has currently been attributed to the water-accelerated formation of polar and apolar domain aggregations in RTILs. This acceleration effect of water was first proposed by Schröder and Dupont in 2000 to explain the observed stronger acceleration effect of water on the diffusion of the charged species than those of neutral ones dissolved in $Bmim^+BF_4^-$, $Bmim^+BF_6^-$, and $MDIM^+BF_4^-$, respectively.[26] Later, Rollet and Jouvensal observed that the diffusion coefficient of water rises about 25 times larger than those of ions with increasing water content for [Bmim][TFSI]–water system.[25] The emergence of water clusters at low water content and 3D porous networks at high water fraction were consequently proposed to explain this abnormal concentration-dependent diffusion behavior of water. In 2013, a mesoscopic structural heterogeneity was also adopted to explain a fraction SE relation between viscosity and diffusion coefficient for [Bmim][BF_4] aqueous solutions.[17] Two years later, MD simulation indicated that, for [Bmim]I–H_2O system, within nanosecond scale, ions localize in multi-coordinated ion cage structures wherein some water molecules are also confined.[40] In 2019, by means of PFG-NMR measurements, Chizhik and coworkers[41] also discussed the viscosity–diffusion decoupling behavior observed in aqueous solution of [Bmim]A (A = BF_4^-, NO_3^-, TfO^-, I^-, Br^-, and Cl^-). MD simulation helped them to provide a 'thin stream' structural distribution of unbound water. In other words, some water molecules spread along the hydrophilic parts of cations and anions but do not form the generally proposed nanometric clusters or water-pools. These authors pointed out that water cluster-like structure model does explain the observed splitting behavior of proton chemical shifts; however, this model cannot interpret the extra-slow exchange of hydrogen atoms between different kinds of water, e.g., between bound water and confined or free water. In contrary, these authors believed that their proposed thin-stream-like distribution of unbound water can interpret both these two behaviors reasonably well.

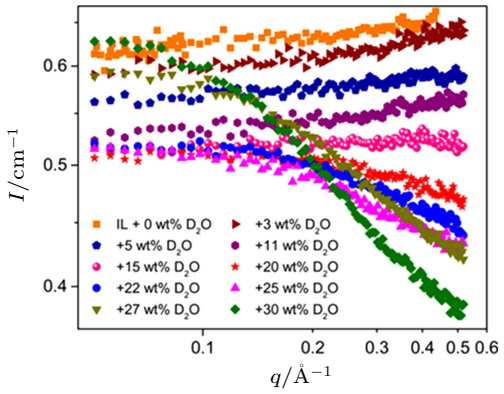


Fig. 2. SANS profiles for mixtures of [C_4mim][BF_4] and D_2O at 25 °C (Molecular weight of [C_4mim][BF_4]: 226 g/mol). (Reprinted with permission from Ref. [42]. Copyright 2016, American Chemical Society).

Water molecules exist in different states at different concentrations in RTILs. Four distinct water states and concentration regions were identified by MD simulation for aqueous solutions of 1-ethyl-3-methylimidazolium ethylsulfate ([C_2C_1im][$EtSO_4$]). They are isolated water molecules (molar fraction of water $x_{H2O} < 0.5$); chain-like water aggregates ($0.5 < x_{H2O} < 0.8$), a bicontinuous system ($0.8 < x_{H2O} < 0.95$), and isolated ions or small ion clusters ($x_{H2O} > 0.95$).[16] An analogous classification of concentration regions can also be observed in understanding the concentration-dependent structure of aqueous [C_6C_1im][NTf_2] solution. This classification was to some extent confirmed by several independent experimental structural measurements. As SANS measurements indicated, for [C_4mim][BF_4]–D_2O system of $x_{D2O} < 0.70$,[42] water molecules are isolated and accommodated in the polar network. The original characteristic nanostructure of RTILs is relatively unperturbed. Clusters of water become detectable only when increasing the water/ionic liquid molar ratio beyond $\sim 2:1$ (see Fig. 2). For another aqueous RTIL, i.e., ethylammonium nitrate (EAN)–D_2O mixture, a bicontinuous structure was confirmed to appear at $x_{D2O} = 0.86$.[43] Additionally, about 3 nm water pockets were proved to be present in [C_4min][NO_3]·3.5D_2O system.[44] Of course, this behavior depends on the cation type. For instance, a replacement of C_4 min^+ by $DEME^+$ can successfully suppress the formation of water pocket in [DEME][NO_3]·3.9D_2O.[44]

Aside from spectroscopic analysis, electron microscopy was also applied to directly reveal the self-organized water-containing structures in aqueous RTILs. By means of scanning electron microscopy, benefitting from the low volatility of RTILs, Kashin and coworkers directly observed water content-dependent macroscopic structure heterogeneity in aqueous [Bmim][BF_4] solutions (see Fig. 3).[45]

As above-mentioned, the structure of neat and aqueous RTILs is sensitive to the type and size of cations, e.g., the length of the alkyl chain. For instance, mesoscopic spatial

heterogeneity in neat [$C_n$mim][PF_6] and [$C_n$mim][Gly] can be observed only when n is no less than 4 and 6, respectively. To further understand the structure of RTILs and especially its cationic and/or anionic type dependence, typical cations of RTILs can be replaced by simple metal ions, e.g., Li^+, Na^+, and Zn^{2+}. A representative example is the super-concentrated electrolyte aqueous solution recently used as the electrolyte for ion battery.

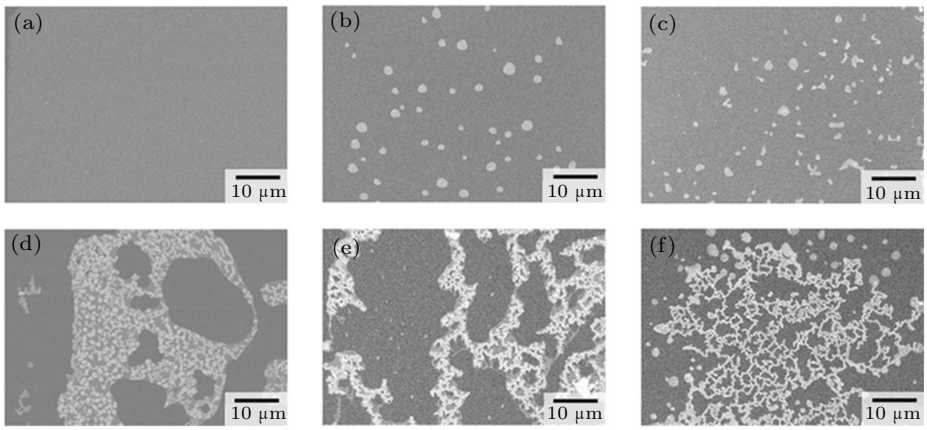


Fig. 3. Field-emission SEM images of [Bmim][BF_4] after addition of varying amounts of water: (a) dry sample; (b) ionic liquid with traces of water; (c)–(f) mixtures of ionic liquid with (c) 5 vol%, (d) 10 vol%, and (e), (f) 20 vol% added water. Reprinted with permission from Ref. [45]. Copyright 2016, John Wiley and Sons.

Super-concentrated electrolyte aqueous solutions, or 'water-in-salt' electrolytes, have recently drawn considerable interest primarily for their wider stable electrochemical windows, accelerated diffusion of ions, and an improving effect on the formation of stable solid electrode and liquid electrolyte interface (SEI).[46–57] A fact must be stressed that concentrated solutions deviate largely from the well-studied dilute solutions in structure and properties.[58–66] Here, we briefly introduce the mesoscopic heterogeneity of super-concentrated Li^+-based electrolyte solutions. The diffusion behaviors of ions and even water in concentrated solutions will be dealt with in the next section.

Combining MD simulation, SANS, and a variety of spectroscopic techniques, Xu and coworkers observed that, in aqueous LiTFSI solution at high salt concentrations (from 10 mol/kg to 21 mol/kg), a disproportion of cation solvation occurs, accompanied by the appearance of heterogeneous domains with a characteristic length scale of 1–2 nm, and the formation of $TFSI^-$ anionic 3D framework.[67] It was highlighted that, in 21 m LiTFSI aqueous solution, 40% of Li^+ is coordinated only by H_2O in its primary solvation sheath, while 25% of Li^+ is surrounded only by $TFSI^-$ locally. Whereas, this disproportion of cation solvation disappears when solvent water is replaced by N,N-dimethylformamide (DMF).[68] In 2018, IR pump–probe and 2D IR spectroscopy measurements led to a similar conclusion (Fig. 4).[69] Cho *et al.* confirmed that, in super-concentrated LiTFSI aqueous solution, ions form intricate 3D ionic networks intertwined with nanometer-sized water H-bonding networks or channels. In 2020, the measurements of linear Fourier transform infrared spectra, polarization-dependent 2D IR, IR transient absorption as well as MD simulations demonstrated the formation of highly interconnected networks of the $TFSI^-$ anions in super-concentrated aqueous LiTFSI solutions.[70] This result supports the suggestions of Cho *et al.*[69] and Xu *et al.*[67]

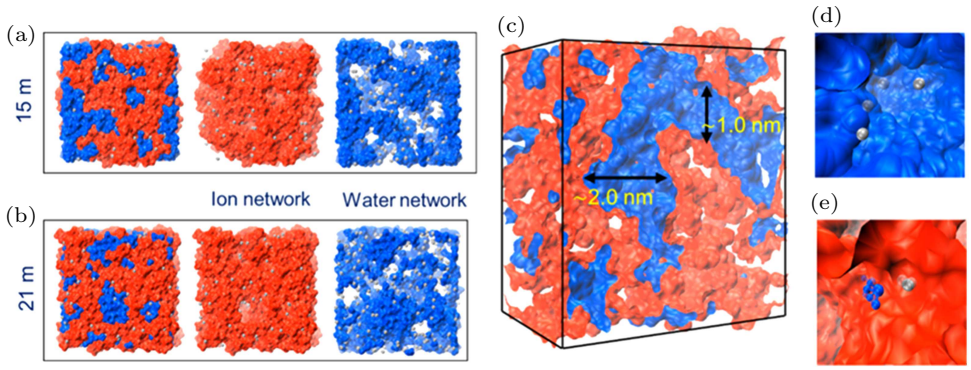


Fig. 4. MD-simulated structures of water H-bonding and ion networks in concentrated LiTFSI aqueous solutions. (a) and (b) MD snapshot structures of a LiTFSI solution (Fig. S7), ion aggregate (red), and water network (blue) at two different concentrations, 15 m and 21 m, respectively. (c) A slab of snapshot structure of a 21 m LiTFSI solution exhibits water channels and ion networks that serve as a porous framework providing open channels through which water can flow. (d) A mobile lithium (gray) ion at four sequential 1 ps steps through a bulk-like water channel, although one lithium ion in the ion network does not move (e). Reprinted with permission from Ref. [69]. Copyright 2018, American Chemical Society.

Of course, not all reported results support the cluster and/or percolating network structure model for water in super-concentrated electrolyte solutions. As an example, a first-principles MD study, performed by Yamada *et al.*, revealed that water in $Li(TFSI)_{0.7}(BETI)_{0.3}$–$H_2O$ system, ($BETI^-$: $N(SO_2C_2F_5)_2^-$) exists as isolated monomers or clusters but consisting only a few (at most five) water molecules even if the water/salt molar ratio is of 2 : 1,[71] close to that of 21 m LiTFSI aqueous solution. In 2020, another MD simulation was performed to extract information about the coordination structure of Li^+ in a super-concentrated aqueous hybrid-salt solution (WIHS), comprising 42 m LiTFSI and 21 m Me_3EtN·TFSI, wherein the salt/water molar ratio can reach up to 1.13 : 1.[50] As a result, the fraction of solvent separated ion pairs $Li^+(H_2O)$TFSI, being approximately the same for 21 m LiTFSI and 42 m WIHS, decreases significantly by a factor of about two with the adding of another 21 m LiTFSI into 42 m WIHS. At the same time, the clusters of $[Li^+(H_2O)_4]_n$ with the most probable size of 10–30 water molecules observed in 21 m LiTFSI are almost completely broken in 63 m WIHS.

Interestingly, until now, unlike for super-concentrated LiTFSI solution, there is no report about the formation of $TFSI^-$ networks in super-concentrated aqueous solutions of RTILs with the same anion. Complicated structures in RTILs result from various forces among their components, ranging from weak and isotropic force (van der Waals, dispersion), to strong (Columbic) and anisotropic ones (hydrogen bonding, dipole–dipole, and electron pair donor/acceptor interactions).[39] The addition of water together with small quantities of ions can cause a change in the type and strength of forces for each component with its surrounding environment, and therefore tunes the properties and structure of RTILs.[51,72,73] It is also the reason why RTILs are commonly described as a designer solvent.

3. Effect of water on the diffusion properties of RTILs or super-concentrated electrolytes

3.1. Effect of water on the transport behavior of ions

Transport properties are a critical aspect of all of physicochemical properties of RTILs. For simple liquids, e.g., dilute aqueous solutions, the hydrated ions or molecules, which are completely separated by free water, diffuse independently of each other via vehicular mechanism. The corresponding diffusion coefficient can be well described by the SE relation, i.e., $D = k_BT/C\pi\eta R$, where k_B is the Boltzmann constant, η the average macroscopic viscosity of solution, R the effective hydrodynamic radius of solute, c a constant between 6 and 4 depending on whether slip or stick conditions applied. The SE prediction tends to be more accurate when the diffusing solutes are much larger than or comparable with the solvent in size. Otherwise, the less solute/solvent size ratio, the more positive or negative deviation of D from the SE predication for uncharged or charged species, respectively.[74] For more complex system with high η, e.g., RTILs, SE relation becomes invalid. This invalidation is normally called 'breakdown of the SE relation' or 'decoupling of D from η'.[25,26,67,75–77] The breakdown of the SE relation has been partially attributed to the appearance of dynamic heterogeneities in RTILs. Dynamic and spatial structural heterogeneities correlate strongly.[78,79] Therefore, more and more researches focus on the structural heterogeneities of both dry and wet RTILs for comparison.

Up to now, two kinds of mechanisms have been frequently adopted to describe ion transport in neat RTILs. They are vehicular and structural mechanisms, respectively.[80–83] For the latter, ionic diffusion involves a collective process through the rearrangement of the local structure.[83,84] In other words, ion hops via a serial ion association–dissociation process.[84] In 2015, a MD simulation was performed to reveal the correlation between ion pair or ion cage lifetimes and transport properties of ionic liquids.[85] Intra- and intermolecular ion hoppings through the formation and breaking of ion-associations, involving four polymerized cationic monomers bonded to two different polymer chains, were also proposed to understand the diffusion mechanism of polymerized ionic liquids.[86] Recently, considering the Li^+-anion association state in contact ion pairs and aggregated cation–anion pairs in super-concentrated electrolyte solutions, Yamada *et al.* suggested that Li^+ should be expected to move in a hopping manner from one anion to another through Lewis basic sites (for example, O atoms on FSA^-), but this mechanism has yet to be demonstrated both experimentally and theoretically.[52] Moreover, a 'hole mechanism' was also proposed by Abbott to understand the viscosity and conductivity of ionic liquids based on an infinite dilution of holes.[87–89] In 2019, similar to the classification of free and bound (or hydrated) water in aqueous solutions, free and bound states of ions in RTILs are defined and quantified according to both kinetic and static criterions.[90] Next, a model of 'ionic semiconductor' with valence and conduction 'bands' with meV energy gap is proposed to discuss ionic interstate exchange. Importantly, the correlation of the kinetic of this interstates exchange with ionic transport is discussed by MD simulation.[90]

Diffusion properties of ions in RTILs remarkably depend on water content. In 2015, Araque *et al.* showed that, in neat $[Pyrr^+_{4,1}][TFSI^-]$ ($Pyrr^+_{4,1}$: 1-alkyl-1-methylpyrrolidinium), neutral molecule CH_4 and charged small molecule NH_4^+ diffuse faster and slower than the SE prediction, respectively.[91] The similar behavior can also be observed in $[Bmim^+][PF_6^-]$ and $[MDIM^+][BF_4^-]$ systems with dilute (mM level) MV^{2+} (methyl viologen), $Fe(CN)_6^{3-}$ (hexacyanoferrate(III)) and TMPD (N,N,N',N'-tetramethyl-p-

phenylenediamine).[26] Without water, TMPD diffuses faster than MV^{2+} and $Fe(CN)_6^{3-}$. However, when increasing the water molar fraction beyond 0.05 and 0.15, respectively, MV^{2+} and $Fe(CN)_6^{3-}$ diffuse faster than TMPD. A strong electrostatic interaction in RTILs can account for the slow diffusion of the charged solutes. With increasing water content, the charged solutes become surrounded by hydration sheath. The shielding effect of hydration sheath can effectively weaken the electrostatic interaction between the charged solutes with their environment. Consequently, this shielding effect can effectively accelerate the diffusion of the charged solutes. Nevertheless, even so, only a shielding effect cannot reasonably interpret the faster diffusion of the solvated charged solutes than the neutral one, because of the originally weak interaction between neutral solutes with their environment. Therefore, structural heterogeneity and especially the appearance of nanometer-sized 3D networks or percolation channel of water were then proposed to be the key factors for the accelerated effect of water. Now, this proposition is indirectly confirmed by MD simulation.[92,93] Moreno *et al.* and Higashi *et al.* reported that, at low water content, ions are selectively coordinated by individual water molecules, but their ionic network or channel is largely unperturbed.

Effect of water on ionic diffusion is cation/anion type-dependent. For [Emim]-[$EtSO_4$], the addition of water significantly reduces the magnitude of the difference between the diffusivities of the cations and anions especially when the concentration is slightly larger than one water molecule per two anion–cation pairs.[94] While, this trend is obviously suppressed with a further addition of water. As a comparison, diffusion coefficients of cations and anions of [Bmim]Cl, [Emim][Ac], and [dmim][DMP] (DMP: dimethylphosphate) remain almost unchanged with increasing water molar fraction up to about 0.8, and increase rapidly with a further increase of water content,[72] similar to that observed in [dmim][Cl] and [dmim][PF_6] systems.[95]

The acceleration effect of water on the diffusion of ions has been applied to the design of electrolyte of rechargeable ion batteries. Recently, more and more attention has been paid to the diffusion mechanism of water and ion in super-concentrated electrolyte solutions. For non-aqueous solvent solutions, the diffusion of ions can change from a vehicular type diffusion in a solvent-rich region to a so-called 'structural type' diffusion process in the solute-rich solutions, a result of the competition among the ion-solvent binding energy, solute or solvent aggregation behavior, and viscosity of solutions (see Fig. 5).[84] However, water is an exception. For aqueous LiTFSI solution, $Li^+(H_2O)_4$, a characteristic coordination structure of Li^+ in water-rich solutions, can also be detected even at 21 m (molar ratio of water to salt: 2.67), and its vehicular motion in a water-rich channel is suggested to be the main diffusion process of Li^+. The similar diffusion behavior is also claimed to be observed in an even more concentrated solution, i.e., 63 m water-in-hybrid-salt aqueous solution of 42 m LiTFSI +21 m Me_3EtN·TFSI, wherein the vehicular motion of $Li^+(H_2O)_n$ is still expected to be the dominated transport process of Li^+. This is the reason of the faster diffusion of Li^+ in 63 m aqueous solution than that in the neat RTIL (0.25LiTFSI + 0.75Pyr14·TFSI).[50] In 2019, Hu and coworkers also developed a new class of electrolytes for Na^+ ion battery, which has a total concentration of 31 mol·kg^{-1}, i.e., 22 mol·kg^{-1} tetraethylammonium triflate (TEAOTF) and 9 mol·kg^{-1} NaOTF. Interestingly, MD simulation results show that 55% of Na^+ exist as free cations (not coordinated by OTF^-), and most of these free Na^+ diffuse with water in a form of $Na^+(H_2O)_n$ within transient nanodomains with fast ion transport pathway appearing within the TEAOTF framework.[51]

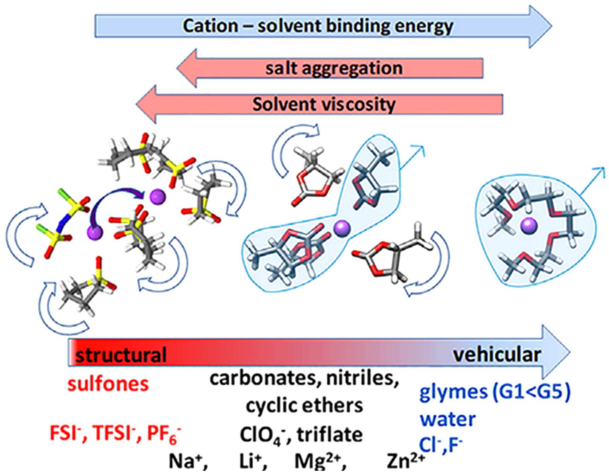


Fig. 5. Vehicular and structural diffusion contribution to the metal ion transport electrolyte solutions and corresponding influencing factors. Reprinted with permission from Ref. [84]. Copyright 2018, Elsevier.

3.2. Transport behavior of water

In RTILs–water mixtures, compared with ion diffusion, the diffusion properties of water are more specific, e.g., a high diffusion coefficient at low water content but an obvious water content dependence, and a more significant deviation from the prediction of SE relation. During the past two decades, these abnormal diffusion behaviors of water have been studied and discussed based on water aggregation and structural heterogeneity of RTILs.

In 2019, by means of a microfluidic Fabry–Perot interferometry device, and combining the measurements of PFG-NMR and WAXS, Bayles and coworkers studied composition-dependent molecular diffusivities in [$C_n$mim][X]–H_2O ($n = 4$, 6, X = Cl, Br, I), and proposed a hopping mechanism for the diffusion of water.[77] According to this mechanism, water molecules diffuse by hopping between polar ionic moieties that remain relatively immobile over timescales relevant for water hopping (see Fig. 6), akin to the diffusion along a lattice

in solids. Moreover, water diffuses between H-bonding sites over an energy barrier, which decreases with increasing water content.[77] Moreover, the corresponding hopping energy barrier relates to the strength of H-bonding between water and polar moieties in RTILs.

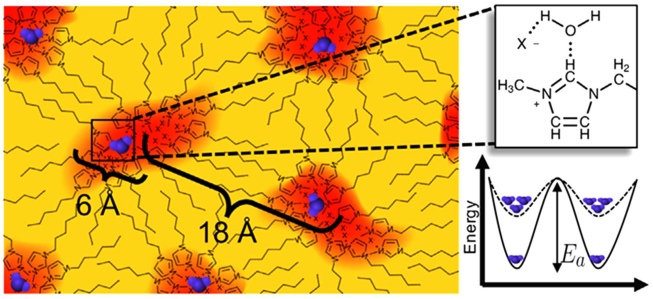


Fig. 6. Depiction of water (blue) intercalating within polar hopping sites. H_2O hops between sites at a rate dictated by an activation energy. H_2O diffusion occurring as a series of hops between relatively immobile, polar sites, akin to lattice diffusion in solids. Reprinted with permission from Ref. [77]. Copyright 2019, American Physical Society.

Compared with the research on the dynamic properties of water in RTILs, the study of water diffusion properties in super-concentrated electrolyte aqueous solutions is still in its infancy stage, although the diffusions of water and ions are correlated with each other.

3.3. Transport behavior of ions through solid electrolyte interface

Before ion intercalating into solid electrode, two subprocesses must be involved. They are the desolvation of ions and the subsequent diffusion of naked ion through interface between solid electrode and liquid electrolyte solution (SEI). The desolvation process has been regarded as the most sluggish and then the dominant step for ion transport during charging/discharging of an ion battery.

SEI forms during the initial full charging process. Before the formation of SEI, the electric double layer (EDL) already exists between solid electrode and liquid electrolyte with the so-called outer and inner Helmholtz layers.[96] The chemistry of EDL, the type of ion adsorbed on the surface of electrodes, and especially the component and the structure of solvation sheath of ions in EDL region determine the formation, chemistry, and structure of SEI.[96–101]

In 2004, Abe and coworkers first studied the activation energy for the transfer of desolvated Li^+ at SEI between graphite and electrolyte solutions, i.e., 1 mol/dm^3 $LiCF_3SO_3$ dissolved in 1,2-dimethoxyethane (DME) and DMSO, respectively.[102] The measured activation energies ranging from 53 kJ/mol to 59 kJ/mol are about twice as much as that of the solvated Li^+ transfer in a reference system without stable SEI film, i.e., graphite/$LiClO_4$ dissolved in mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Fig. 7). One year later, to further eliminate the potential influence of redox reaction, Abe and coworkers studied the ion transfer at the interface between a lithium-ion-conductive solid electrolyte and liquid electrolyte, i.e., $La_{0.55}Li_{0.35}TiO_3$/$LiCF_3SO_3$–PC system (PC: propylene carbonate). Almost similar activation energy for Li^+ transfer as that of graphite/$LiCF_3SO_3$–DMSO system was observed, and more importantly, which is consistent with the interaction between lithium ion and solvents in electrolyte, i.e., solvation energy of Li^+.[103] In 2010, to clarity whether the above-measured activation energy barriers arise from a 'desolvation/migration' complex, Xu and coworkers constructed an electrode/electrolyte system without SEI film, i.e., $Li_4Ti_5O_{12}$/$LiBF_4$–EC/EMC. It was observed that energy barrier for the Li^+ desolvation falls in the range of 52 ± 3 kJ/mol, consistent with the data reported by Abe *et al.* Therefore, Li^+ desolvation is indeed the most energy consuming step.[104–107]

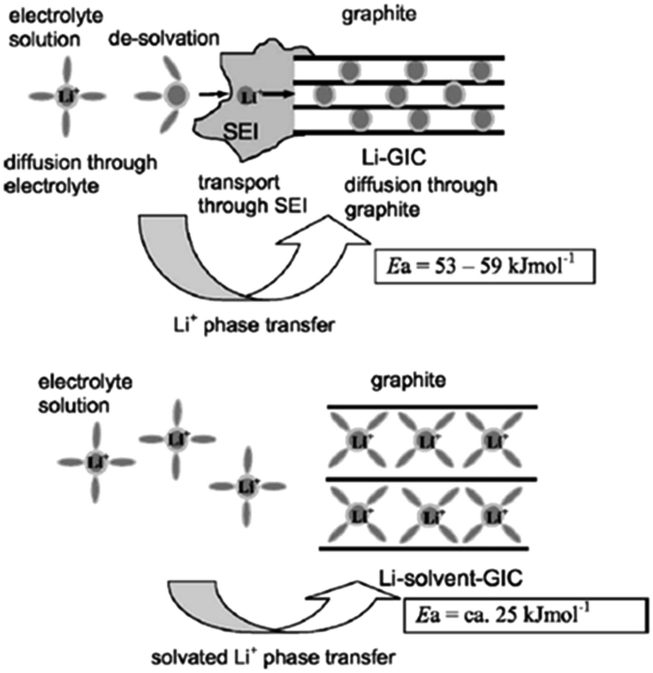


Fig. 7. Comparison of solvated lithium ion transfer and desolvated lithium ion transfer at graphite electrodes. Reprinted with permission from Ref. [103]. Copyright 2005, Electrochemical Society.

Considering the dominated effect of desolvation of ion on its diffusion in solid electrode and electrolyte solution system, as suggested by Xu and coworkers, the interfacial chemistry should be tuned to catalyze the desolvation of ions. This idea can be reflected in a recent study performed by Zhang and Huang.[96] They successfully modified the chemistry of SEI for $LiFePO_4$|Li-LiFSI/DME system by regulating the adsorbed species on electrode in inner Helmohotz plane, based on adding trace of CuF_2 and $LiNO_3$ in electrolyte. They subtly employed Cu^{2+} as targetable anion carriers to guide the NO_3^- to preferentially take part in the IHP. Under this regulation, the activation energy of the desolvation of Li^+ decreased down to 48.1 kJ/mol, about one-third of that for LiFSI/DME. The same

strategy was also applied to lower the charge transfer barrier of $LiMn_2O_4$ by controlling the surface chemistry, i.e., via nickel surface doping, to enhance Li^+ intercalation kinetics at sub-zero temperatures.

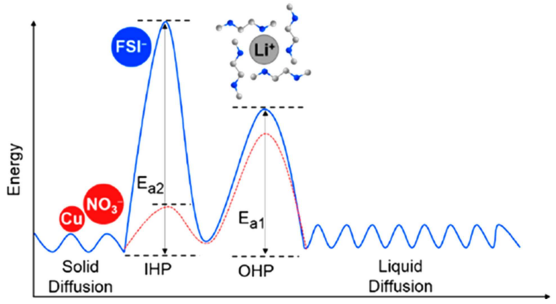


Fig. 8. Comparison of the energy barriers of desolvation of Li^+, E_{a2}, in the appearance and absence of the specific adsorption in the inner Helmholtz plane (IHP). OHP influences the energy barrier of the transport of solved Li^+, E_{a1}. Reprinted with permission from Ref. [96]. Copyright 2019, American Chemical Society.

4. Conclusion and perspectives

In this short review, we summarize the results reported mainly since 2010 about the mesoscopic structural heterogeneity and transport properties of ions for RTILs and super-concentrated electrolyte aqueous solutions. Here, the structural heterogeneities refer to the liquid–liquid separation, aggregation of polar and apolar domains in RTILs, solvent clusters, and 3D networks especially constructed by anions in super-concentrated electrolyte solutions. At the same time, the diffusion of ion through the interface between solid electrode and liquid electrolyte is also stressed. A fact has become clear that the process of desolvation (or de-coordination sheath) of ions determines their diffusion property in solid electrode–liquid electrolyte system.

Recently, aqueous RTILs and concentrated aqueous electrolyte solutions have received increasing attention especially towards developing salt-concentrated battery electrolytes. Comparatively speaking, our understanding of how water affects the structural heterogeneity, transport property, and electrochemical property of RTILs and especially super-concentrated electrolyte solutions is obviously insufficient. As briefly introduced above, the difficulty primarily comes from the original complex forces and then interactions among different components in these systems, which include Coulomb force, van der Waals interactions, and H-bonding. An open question is to what extent do H-bonding from water changes the initial interactions in these systems. Moreover, different from dilute solutions, wherein hydrated ions can be completely separated by free water, aqueous RTILs and super-concentrated aqueous electrolyte solutions comprise of almost no free water and hydration shell is shared by different solutes. As a result, crowded and confinement effects appear, which also play a key role in determining the structure and properties of both solvents and solutes. Importantly, the condition of this soft confinement is more complex than that of the hard confinement, e.g., liquid confined in nanometer-sized solid tube or hole.

To make up for such shortcomings, researches should be performed to reveal the effects of hydration water and water confined among ion pairs/clusters on cation–anion interaction, the structural heterogeneity of super-concentrated electrolyte solution and aqueous RTILs, and on the corresponding diffusion behavior of metal ions, water and the correlation among them. In other words, the favorite chemical and structural conditions for water to promote diffusion of metal ions should be clarified. Moreover, another challenging question is how traces amounts of water affect the composition and structure of coordination sheath of metal ions in bulk RTILs and super-concentrated electrolyte solutions, and especially in the interfacial film between these free water-free solutions and charged electrodes. These investigations can help to reveal the pathway for reducing the activation energy of desolvation or de-coordination of ions before their intercalating into electrodes.

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