Adventitious Water Sorption in a Hydrophilic and a Hydrophobic Ionic Liquid: Analysis and Implications

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Supporting Information

ABSTRACT: The sorption of water in ionic liquids (ILs) is nearly impossible to prevent, and its presence is known to have a significant effect on the resulting mixtures’ bulk and interfacial properties. The so-called “saturation” water concentrations have been reported, but water sorption rates and mixing behaviors in ILs are often overlooked as variables that can significantly change the resulting mixtures’ physical properties over experimental time frames of several minutes to hours. The purpose of this work is to establish a range of these effects over similar time frames for two model ILs, protic ethylammonium nitrate (EAN) and aprotic butyltrimethylammonium bis(trifluoromethanesulfonyl)imide (N1114 TFSI), as they are exposed to controlled dry and humid environments. We report the water sorption rates for these liquids (270 ± 30 ppm/min for EAN and 30 ± 3 ppm/min for N1114 TFSI), examine the accuracy and precision associated with common methods for reporting water content, and discuss implications of changing water concentrations on experimental data and results.

INTRODUCTION

Ionic liquids (ILs) are fluids composed entirely of ions. Unlike molten salts, for example, NaCl which melts at 800 °C, ILs commonly have melting temperatures below or near room temperature. This is a direct result of pairing sterically bulky, low symmetry, organic cations with similarly bulky organic or inorganic anions. ILs have widespread applications in the fields of electrochemistry, lubrication, catalysis, and as general solvents by virtue of their low vapor pressure, high thermal and chemical stability, wide electrochemical windows, and low flammability. ILs also offer avenues for tuning their properties via addition or removal of key functional groups, or by creating mixtures of varying cations and anions. As ILs enter use in new areas of chemistry, a learning curve associated with defining and reporting important metrics of IL cleanliness or purity might be expected. Many experimental results are confounded by significant variations in IL batch-to-batch purity, largely due to current IL syntheses that occur in relatively small volumes via varying protocols. Water is a common and important impurity in ILs, and a few reports now exist that describe methods for removing water from and quantifying water in IL samples. Additional papers have reported water sorption rates and self-limiting water concentrations for a few IL species. The effects of water are significantly different for protic and aprotic ILs. Most protic ILs are fully miscible with water, whereas aprotic ILs are typically more hydrophobic and often display upper water solubility limits in the range of several hundreds to thousands of ppm before forming separate aqueous and IL domains. Sorption of water gives rise to varying physicochemical properties of the IL/water mixtures, for example, smaller electrochemical window, altered conductivity, viscosity, density, and reactivity. These changes can be beneficial or detrimental depending on the application. One such application is the dissolution of biomass in IL + water mixtures. They suggest that moderate water may promote biomass dissolution by lowering the viscosity through weakening the hydrogen bond between the IL cation and anion. However, too much water may inhibit biomass dissolution by inhibiting the interaction of the biomass with the IL. In either case, knowledge of the concentration of water in the IL, as well as the mixture’s sorption properties, is vital to connect the properties of the IL solution to the composition of the mixture. The difficulty associated with producing truly dry ILs (quantitative water removal) makes it reasonable to presume that many, if not most, experimental researchers will be conducting experiments in ILs that contain significant amounts of water. Hence, it is important to properly understand and manage water’s effects to advance the utility of ILs.

Protic ILs are formed by a simple proton transfer between neat Bronsted acids and bases where there is an acidic proton remaining on the cation species, whereas aprotic ILs involve more complex syntheses and do not contain a labile hydrogen. Although all ILs are hygroscopic, the upper limit of water sorption and the ILs’ hydrophobicity/hydrophilicity vary over a wide range. For example, ILs can be composed of

Received: June 30, 2016  
Accepted: September 5, 2016  
Published: September 16, 2016
hydrophilic, polar anions, such as halides, nitrate, methyl sulfates, or formate, which encourage miscibility with water. However, hydrophobic, nonpolar anions, such as hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, or tris-(perfluoroalkyl)trifluorophosphate, are more resilient to sorbing adventitious water. Similarly for cations, the addition of n-alkyl side chains can regulate water solubility; longer, more hydrophobic alkyl chains impede water solubility but can also significantly affect other properties such as viscosity or conductivity. It has also been suggested that imidazolium cations favor water sorption more than pyrrolidinium or pyridinium ILs, based on the more hydrophilic nature of imidazolium.\(^{18}\) Recently introduced triphlic ILs consisting of three different nanometer-sized domains, polar, apolar, and fluorophilic, can have important implications on analytical separations, extraction, and catalysis.\(^{19,20}\) Intermolecular structures of ILs can be affected by the presence of water thereby affecting their performance in applications.

Two key experimental parameters for water sorption studies for a given IL are the relative humidity of the surrounding environment and the flow rate of gas/vapor over or through the IL.\(^{11}\) However, a search of the current literature returns only one publication that discusses water sorption into ILs with a reported flow rate,\(^{12}\) and only a small handful of papers examine water sorption with respect to relative humidity.\(^{8,12,21,22}\) Using gravimetric analysis, Chiappe reports that water sorption is first order in bulk, aprotic ILs.\(^{13}\) However, using spectroscopy, Tran revealed that the anion is the key factor in determining water sorption kinetics that are complex, may sometimes follow first-order kinetics, but can also exhibit changes so as the sorption proceeds to higher water concentrations.\(^{9}\)

Because of water’s ubiquity and sometimes deleterious effects on IL performances, it can be argued to be one of the most important impurities in ILs. It can be incorporated into ILs as a residue from synthesis, as a reaction byproduct, or by sorption from the atmosphere (e.g., via handling during experimentation). Drying ILs is usually achieved by placing the IL under high vacuum at elevated temperatures for several hours (e.g., 10\(^{-5}\) mbar at 60 °C for 10 h).\(^{9}\) However, removing all water is challenging, and the extent of residual water’s role in the IL is largely unknown.

Given the propensity for impurities to concentrate at interfaces, the presence of even very low levels (<100 ppm) of water raises serious implications for heterogeneous processes in IL solvents.\(^{23}\) Previous studies on the effect of water on the interferential structure of ILs show that water prefers to interact with the bulk molecules in water-miscible ILs, whereas in the case of water-immiscible ILs, water tends to solvate ions at the interface, as indicated by the change in orientation of surface cation dipoles when exposed to water.\(^{24,25}\) A recent paper by Endres et al. using in situ atomic force microscopy and vibrational spectroscopy demonstrates that the structure of the innermost (Stern) layer in 1-ethyl-3-methylimidazolium trifluoromethylsulfonate + water on Au(111) depends on both the applied potential and quantity of water.\(^{26}\) Their work reveals a transition from a multilayer structure to a classical double layer structure at −1.0 V versus Pt quasireference electrode (QRE) upon changing the water concentration from 30 to 50 vol %.\(^{26}\)

Water will certainly be active within the electrochemical double layer (EDL), affecting RED/OX processes, altering electrochemical windows, and possibly degrading the electrode surface.\(^{27}\) Water sorption from the atmosphere has been studied in aprotic imidazolium-based ILs by gravimetric analysis,\(^{11}\) with near-infrared (IR) spectroscopy,\(^{3}\) by volumetric analysis from a levitated IL droplet,\(^{21}\) and in tandem with electrochemistry.\(^{5,12}\) Bond et al. further compared protic ammonium-based and aprotic imidazolium-based ILs and showed that the water concentration could accurately be determined in situ using cathodic stripping voltammetry, representing a novel approach for precise water determination in ILs (in some instances down to 10 ppm water) with water below ∼2500 ppm.\(^{8}\) ILs show larger (3–7 V) operating electrochemical windows than many aqueous (<2 V) and nonaqueous (3–4 V) molecular solvents.\(^{28}\) This opens the possibility of previously inaccessible reaction potentials, expanding the ability to address intriguing research problems such as electrochemical reduction of the radical O\(_2\)\(^{•+}\) anion,\(^{29}\) and the electrochemical separation of lanthanide and actinide metals.\(^{30}\) ILs have also proven effective as media for bioelectrochemistry\(^{31}\) and in studies of conducting polymers due to IL’s negligible volatility.\(^{32}\) ILs are becoming popular solvents in various fields of chemistry and materials science.\(^{33}\) Furthermore, it should be pointed out that any water in the IL will certainly play an important role at heterogeneous interfaces (e.g., electrode surfaces). In hydrophobic ILs, such as N1114 TFSI, there is an apparent propensity of water to segregate toward the hydrophilic metal electrode surface. This can impede observation of electrochemical processes, change adsorption of analyte species at the electrode surface, or alter the EDL morphology.\(^{27}\)

Using electrochemistry, Compton demonstrated that the IL potential window shrinks as the amount of water increases. He assigned this to the hydrogen evolution reaction (HER) occurring at lower overpotentials.\(^{12}\) Compton also showed that water can accelerate the diffusion of ionic components compared to neutral species in ILs and that “wet” ILs cannot be presumed to be homogeneous solvents. Rather, ILs form nanostructures with polar and nonpolar domains, which could contain pockets of higher or lower concentrations of water, respectively.\(^{12}\) This has been supported by other studies, which show that water molecules are present in the cation–anion-charged polar domain where water molecules form hydrogen bonds with anions and cations.\(^{34}\) Water has been shown to form clusters at water/IL ratios of 2:1, and microphase separation and micelle formation occur at higher concentrations.\(^{35}\) Welton et al. studied the molecular states of water in imidazolium-based ILs with different anions using Fourier transform infrared (FTIR) spectroscopy and attenuated total reflection (water concentration of 0.2–1.0 mol/L). They report that the anions’ basicity plays a very important role in the interaction with water molecules with more basic anions (i.e., NO\(_3\)\(^−\) and CF\(_3\)CO\(_2\)\(^−\)), showing stronger interactions with water. The IR peak profiles for water dissolved in ILs differs with anions but is not strongly affected by the total concentration of water dissolved.\(^{36}\)

The work we present here examines the water sorption in two ILs chosen to model the protic and aprotic classes, which are ethylammonium nitrate (EAN) and butylimethylammonium bis(trifluoromethylsulfonyl)imide (N1114 TFSI), respectively. Their structures are shown for reference in Figure 1 along with selected chemical properties. The protic EAN and aprotic N1114 TFSI display significantly different hydrophilic/hydrophobic characters. We examine their behavior when exposed to well-controlled humid environments and report
water uptake from Karl Fischer (KF), electrochemical, and IR spectroscopy analyses. Finally, we discuss the accuracy of standard KF measurements for water analyses and discuss the physicochemical properties of water for effects on IL solvents in electrochemistry and IR experiments.

## METHODS

### Materials.** IL samples EAN (>97%) and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide (N1114 TFSI, 99%) are obtained from Iolitec. The IL samples are dried under vacuum on a Schlenk line at 500 mTorr at 50 °C for a minimum of 48 h before use. Ferrocene (Fc/Fc+ , 99%) was purchased from Alfa Aesar and used to calibrate the potential axis by setting the E1/2 of this reversible wave to 0.0 V. UV grade CaF2 windows for IR studies were purchased from Casix, U.K., and used as received.

**Instrumentation.** KF. Water content is determined using a Metrohm 831 KF titrator with a two-reagent diaphragm cell. The outer cell consisted of Hydralan Coulomat AG anolyte (Fluka Analytical) or Aqualine Electrolyte AG (Fisher Scientific). Hydralan Water Standard 1.0 (Fluka Analytical) or Aqualine Electrolyte AG (Fisher Scientific) is used to calibrate the instrument after changing the KF reagents and periodically during the course of the experiment. The humidity and temperature of the KF reagents and periodically during the course of the experiment. The sample is stirred vigorously after each KF measurement to ensure homogeneity. An IL sample (2 mL total volume glass cell and a custom-sealed Teflon cap. The entire electrochemical cell (glass cell and cap) is cleaned by soaking in Nochromix acid, followed by rinsing with ample amounts of Milli-Q water. When not in use, the electrode is kept in Milli-Q water after polishing to preserve the electrode surface.

**Electrochemistry.** All electrochemistry experiments are carried out at room temperature and ambient pressure using a CH Instruments 660D potentiostat. All of the electrochemical measurements carried out here use ca. 300 μL of the sample.

**FTIR.** Thermo-Nicolet iS50 Fourier transform spectrometer with a liquid N2 cooled MCT-A detector is used to acquire FTIR spectra. A 12 μL aliquot of the sample is pressed between two CaF2 plates, and spectra are averaged over 128 scans (2 min) at 4 cm⁻¹ resolution. Duplicate spectra are obtained for each sample. The CaF2 plates are cleaned using copious acetone rinses followed by drying under dry nitrogen stream between measurements.

**Methods.** The IL–water samples are prepared by flowing water-saturated N2 gas (Praxair, high purity 99.998%) over quiescent IL (~4.5 mL) in a sealed 20 mL vial. A T-type fitting attached to the gas outlet is used to monitor the relative humidity using a traceable hygrometer (Fisher Scientific) over the course of the water uptake. The humidity and temperature are maintained at 61.5 ± 0.5% and 18.9 ± 0.1 °C, respectively, with a flow rate of 300 mL/min. After introducing water into the IL for a stipulated period of time, aliquots of the IL are withdrawn from the vial to perform KF, electrochemistry, and IR.

Although the IL was not stirred during water uptake, the sample was stirred vigorously before each KF measurement and before taking aliquots for analysis. The upper limit for the N1114 TFSI water solubility is achieved by placing 1 mL of IL and 1 mL of Milli-Q water in a sealed vial, which is vigorously shaken, and then allowed to stand for >24 h at room temperature. Any water not mixed with the IL is decanted, and the IL layer was analyzed using KF.

The electrochemical cell is composed of a three-electrode arrangement with 2 mL total volume glass cell and a custom-sealed Teflon cap. The entire electrochemical cell (glass cell and cap) is cleaned by soaking in Nochromix acid, followed by rinsing with ample amounts of Milli-Q water. The humidity and temperature of the KF reagents and periodically during the course of the experiment. The 2 mm diameter polycrystalline disk, and its effective surface area was calculated to be 0.033 cm² from the Randles–Sevcik equation, obtained from the current response of 10 mM Ru(NH3)6 3+/2+ (Strem Chemicals 99%) in 0.1 M NaF (Alfa Aesar, 99.99% metals basis).

Equation 1 is the Randles–Sevcik equation used to calculate the effective surface area (A) of the working electrode.

\[
f_p = (2.69 \times 10^5)n^{1/2}A^{1/2}D^{1/2}C^{1/2}
\]

The silver working electrode is polished successively with 1.0 and 0.3 μm MicroPolish II aluminum oxide powder (Buehler) on microcloth PSA (Buehler) pads, sonicated in Milli-Q water for 5 min, and rinsed with ample amounts of Milli-Q water. When not in use, the electrode is kept in Milli-Q water after polishing to preserve the electrode surface.

The counter electrode and QRE are made of Pt wire (Alfa Aesar, 99.997% metals basis) and cleaned by passing through a hydrogen flame (Praxair, UHP H2, 99.999%) before introduction into the electrochemical cell.

All electrochemical measurements are carried out on the laboratory benchtop in a grounded Faraday cage. To maintain the integrity of the water content, no purging of the IL or IL–water solutions is done before electrochemical measurements because routine purging of the solution and/or headspace with dry, inert gas has been shown to drastically alter the concentration of water. Instead an airtight Teflon cap is used with tightly sealed ports for the three electrodes.

Capacitance measurements are done in tandem with cyclic voltammetry measurements in the same solution. Impedance versus potential measurements taken at a frequency of f = 10 Hz and an amplitude of 5 mV are used to calculate the capacitance versus potential curves. To minimize hysteresis, these data are always acquired from negative to positive (i.e., cathodic potentials to anodic potentials). Capacitance (C) in farads is related to impedance (Zj) in ohms via

Equation 2 is the capacitance equation used to calculate the effective capacitance from the measured imaginary impedance (Zj).
where $\omega = 2\pi f$.\(^3^9\)

**RESULTS AND DISCUSSION**

Our work focuses on ILs with low concentrations of water (ca. 0.005–0.60%, or 50–6000 ppm water), which is where a majority of experimentalists operate. We report water uptake in these liquids from a metered, humidified nitrogen gas flow across the headspace of an IL sample enclosed in a scintillation vial. This provides quantifiable levels of water exposure and for mitigation of dissolved oxygen that can hinder electrochemical analyses. We will present and discuss data and results for EAN, followed by N1114 TFSI.

**EAN.** Water sorption data for EAN can be seen in Figure 2, plotted as a function of time. Data points represent an average of three independent trials conducted under the same experimental conditions. A table of all independent measurements is provided for reference in Table S1. The trend in capacitance values is inversely related to the current density.

![Figure 2](image)

*Figure 2. Average water concentration of EAN over 20 min of exposure to a humidified nitrogen stream. Data points are averages of at least three trials under identical experimental conditions. Some error bars are contained within the size of the data point.*

Figure S1a and the inset demonstrate a narrowing of the cathodic potential limit in EAN concomitant with increasing water concentration. Oxidation of the silver electrode in the anodic limit has an onset potential near 0 V versus Fc/Fc'. The potential window narrows by ca. 40 mV between the driest and wettest EAN samples (120–8900 ppm). A similar effect has been demonstrated previously on Pt electrodes in imidazolium-based IL and is attributed to HER occurring on silver at less negative overpotentials as the water concentration increases.\(^3^6\) Impedance–potential curves shown in Figure S1b demonstrate an increase in the overall capacitance of the system as the concentration of water increases. Dry ILs are known to have capacitance charging values on the order of 10 $\mu \text{F/cm}^2$, which is significantly less than those of dilute aqueous electrolytes and suggested to indicate a collapsed double-layer structure.\(^5^,\(^4^0\) The increase in capacitance values observed with increasing hydration of the IL suggests that water may be affecting the interface by solvating the IL, which would increasingly resemble an aqueous electrolyte interface and increase the capacitive response. Figure 3a shows the increase in the peak cathodic current, taken at the switching potential $−1.16$ V versus Fc/Fc', as a function of increasing water concentrations. The trend appears to level off at water concentrations of $\geq 3500$ ppm water. This could be indicative of water condensing at the electrode surface, exposing the cathode to a water film as the bulk concentration exceeds $3500$ ppm in EAN. Interestingly, water condensing on an Au electrode has been recently reported in BMIM TFSI at bulk concentrations as low as 700 ppm water.\(^2^7^,\(^4^1\) Figure 3b shows capacitive values taken at the local minimum (found at $−0.42$ V vs Fc/Fc' see Figure S1b) for the EAN system as a function of water concentration. The trend in capacitance values is inversely related to the current density.
phobicity,11 which support the idea that IL hydrophobicity is in imidazolium-based ILs of varying degrees of hydro-
nitrogen stream. A similar trend is reported for water sorption concentration with increasing exposure to the humidi
N1114 TFSI also show a clear increase in the water
region could be attributed to the interaction of water molecules with the ethylammonium cation through formation of hydro-
gons.46 The intensity increases with an increase in water content. At lower water concentrations (data not shown), the energy of IR absorption and width of this peak also indicate large water domains. No significant changes in absorption were observed elsewhere in the mid-IR region (see Figure S4). The data in Figure 5 show a linear trend between the IR absorbance and water concentrations as quantified by KF titration. The water peak’s IR absorption increases with water concentration, following an expected Beer–Lambert law relationship.

N1114 TFSI. N1114 TFSI is aprotic and considerably more hydrophobic than EAN, largely due to the alkyl substituents of the cation and perfluoromethyl terminal groups on the anion. It is not fully miscible with water, and sorption plateaus at ca. 13 600 ± 300 ppm water (∼1.4%), which defines the water solubility upper limit. The water sorption data in Figure 6 for N1114 TFSI also show a clear increase in the water concentration with increasing exposure to the humidified nitrogen stream. A similar trend is reported for water sorption in imidazolium-based ILs of varying degrees of hydrophobicity,13 which support the idea that IL hydrophobicity is a major factor of water sorption. The water sorption data obtained for N1114 TFSI show a roughly linear sorption behavior for the range examined. Individual values acquired from KF titration for N1114 TFSI water content over three independent trials are provided in Table S2 for reference.

The most prominent feature when comparing cyclic voltammograms in Figure S2a is an increase in the peak current at −1.1 V versus Fe/Fe⁺ as a function of increasing water concentration. This peak is assigned to the reduction of a surface oxide on the silver working electrode. The oxide is created at more positive potentials between −0.9 and −1.0 V and is attributed to the formation of Ag₂O on the electrode surface. Similar oxidation and reduction features have been reported on gold electrodes, and their intensities are a function of the IL water content.8 The anodic potential limit in these data decreases as the concentration of water increases. This is due to increasing current assigned to HER.12,36 It is important to note that, although the Pt QRE has become very commonly used in IL systems, it is subject to significant changes in behavior with respect to water concentration. We account for this in our work by incorporating the Fe/Fe⁺ redox couple, but a clear demonstration of this effect is shown in Figure S3.47 Electrochemical capacitance data that correspond to the cyclic voltammogram data for N1114 TFSI are shown in Figure S2b, and the potential axis has been corrected analogously to the cyclic voltammograms. These demonstrate an increase in the capacitive feature at −1.1 V versus Fe/Fe⁺. This is hypothesized to correlate with the large cathodic reduction feature in the cyclic voltammograms, as the concentration of water increases. Figure 7a plots the peak current for the oxide feature against
water concentration in the IL solution and shows that increasing water gives rise to larger peak current densities. Similar increases in current density have been reported for other aprotic ILs and attributed to increased HER current.8,9 Figure 7b illustrates the increase in capacitance response, also taken at −1.1 V versus Fc/Fc+ as the concentration of water increases. It is important to note that the large capacitance values obtained here are conflated with significant redox current from the Ag oxide feature at the same potential, but an identical, increasing trend is seen for capacitance values at other voltages within the potential window examined. The increase in capacitive response from the silver oxide is in qualitative agreement with previous reports for oxide formation on gold electrodes in the presence of water.8

Figure 8 shows the FTIR absorption profile of dry (80 ppm water) and wet (8900 ppm water) N1114 TFSI. The spectra are normalized to the C=H stretching mode at 3050 cm⁻¹ to correct for small variations in the FTIR transmission cell path length. The peaks in these two spectra overlap well except in the region between 3500 and 3700 cm⁻¹ where water peaks are observed. Two water absorption features at 3640 and 3560 cm⁻¹ correspond to the lowest and highest water concentrations. These correspond to the lowest and highest water concentrations in a particular sorption trial. The inset highlights data for these water modes are plotted as a function of water concentration in Figure 9. The absorbance values of both water peaks increase linearly with the water concentration in all trials.

Discussion. EAN is a protic, hydrophilic IL, and a linear fit to the water uptake data in Figure 2 yields a water sorption rate of 270 ± 30 ppm/min. N1114 TFSI is an aprotic, hydrophobic IL that shows a lower water sorption rate of 30 ± 3 ppm/min, based on a linear fit to data in Figure 6. We attribute the difference in sorption rates primarily to the significant variation of hydrophobic character of the ILs and capability of both cation and anion in the case of EAN to form hydrogen bonds with water. We find here that the water uptake rate of 1-butyl-3-methylimidazolium TFSI (η = 54.5 cP at 25 °C) is lower (21 ± 1 ppm/min) than that of N1114 TFSI (η = 116 cP at 25 °C), indicating that the bulk IL viscosity is not the major factor in water sorption for these IL mixtures. The peak profile corresponding to the C–H stretching of the imidazolium ring varies with the anion, indicating that anions interact with the hydrogens on the ring.8 In the presence of water, the hydrogens on the imidazolium ring compete with water to interact with the anion. In the case of N1114 TFSI, no such hydrogens are present to compete with water. Hence, sorption of water is higher in N1114 TFSI. It should be noted that the rates of water sorption are likely to change as the sorption process continues beyond the range examined here. Indeed, some reports show that the rate of water sorption reaches a plateau as the IL + water solution becomes saturated with water.8,9,11,12,21,22 Changing rates of sorption suggest that the sorption curves similar to those shown in Figures 2 and 6 could show one or more inflection points if followed to longer times (higher water concentrations), but it is reasonable to expect linear sorption behaviors within the fairly narrow window of water concentrations observed here.

At the gas–liquid interface, an impinging gas molecule has three possible fates; it can bounce off the surface, reside briefly at the surface before dissolving into the IL, or reside briefly and again desorb back into the gas phase.11 The favorability of the water molecule–surface interaction depends on many factors. These include the surface area of the IL,10 stirring which might alter the interfacial structure, the gas flow rate and its angle of incidence, the presence of small impurities (including other water molecules) within the IL which may enhance water sorption,50,51 and the chemical nature52 of the chosen IL. In our
gas phase molecules, and subsequent solvation with IL ions or region, which has been reported to be a slow process for other ultimate water miscibility. Clusters, which may work to enhance water dissolution into the manufacturer (Metrohm) recommends using 1.0 sample volume lost to KF analysis is not trivial. The KF research is done using small volumes to minimize costs, and the sample is often achieved using KF titration. However, most ILs likely contain equal contributions from cations and anions. It is also suggested that the anion plays a key role in solubilizing water in bulk ILs. Water interacts with IL through formation of hydrogen bonds with the anion where water acts as a Bronsted acid and the anion acts as the Bronsted base. The strength of the hydrogen bond depends on the anion basicity. Tailoring the IL to have a larger surface contribution from the anion could increase the probability of an impinging water molecule to stick to the IL surface, rather than bounce off a neutral or positive site. The second step is diffusion of gas molecules through the gas–liquid interfacial region, which has been reported to be a slow process for other gas phase molecules, and subsequent solvation with IL ions or other water molecules. In the absence of stirring, this will likely be driven by concentration gradients and governed by chemical interaction forces (e.g., hydrogen bonding and van der Waals forces) between the water and the IL. In the ILs studied here, NO$_3^−$ (pK$_a$ of HNO$_3$ = 1.7) ion is a stronger Bronsted base than TFSI (pK$_a$ of HTFSI = −11.9), which makes its interaction with water stronger, in addition to the interaction of the ammonium head group with water. This promotes a water solvating effect and leads to water clusters around the anion in EAN more readily than the weaker base TFSI ion. The broad IR water peak in Figure 4 supports the possibility of water clusters, which may work to enhance water dissolution into the IL bulk phase, increasing the overall rate of water sorption and ultimate water miscibility.

The absolute determination of water concentration in an IL sample is often achieved using KF titration. However, most IL research is done using small volumes to minimize costs, and the sample volume lost to KF analysis is not trivial. The KF manufacturer (Metrohm) recommends using 1.0–10.0 g of the sample (ca. 800–8000 μL for ILs) for water concentrations between 5000 and 10 ppm, respectively. This may not be cost-effective or even possible for some ILs, particularly those that come in limited quantities from custom syntheses, which can be resource intensive. For our KF measurements, we used an average sample size of 0.240 ± 0.02 g (≈200 μL). We find that this relatively small amount of IL gives KF results well above the threshold quantitation limits of the instrument. A literature search for water quantification in ILs returned only two other results that listed KF titration with a reported sample size (1 mL of 20% w/w solution of the IL in diluted anhydrous methanol or following ASTM Standard Test Method E 1064-00 with a sample size of 1.5 g of IL).

Because of the variability in sorption rates of water, several aliquots of the IL should be analyzed by KF to accurately quantify water concentrations (refer to Tables S1 and S2 for our compiled KF data). For example, replicate measurements on individual trials taken from the 20 min exposure (trial 2) sample of EAN gave water content values that range from 5707 to 5387 ppm; a difference of 320 ppm water or roughly an uncertainty of 6%. Other measurements of EAN taken directly from the Schlenk vacuum produce readings of water content that range from 133 to 104 ppm. Correspondingly, this difference represents an uncertainty of ca. 24%. Although all KF measurements did not produce variations of this magnitude, these deviations represent significant concern in experimental work and must be considered. A few reports have demonstrated similar uncertainties to those in our work here.

Proper maintenance and handling of the IL samples are also important. Samples in this study are dried and transferred using Schlenk techniques and stored in dry/glove boxes. In an effort to compare this careful handling to less stringent laboratory methods, we placed ~2 mL of N1114 TFSI in a capped 20 mL vial and kept it in a laboratory bench drawer for the duration of these experiments (18 days). We took an initial KF measurement and found that the IL contained ~100 ppm water, a relatively dry sample. We withdrew periodic aliquots for KF analysis, and after 2.5 weeks, the water content had increased to ~1100 ppm. The average humidity of our laboratory over this span is 20% (dry Iowa winter), and our laboratory temperature is around 20 °C. The hygroscopic nature of even this “hydrophobic” IL can result in an order of magnitude difference in the water content from storage in a sealed vial. For our experimentation, the ILs are constantly under vacuum on our Schlenk line for >2 days at 50 °C with vigorous stirring before use. Implementing a Schlenk line and dry/glove box is imperative to control or mitigate water sorption in ILs.

Viscosity is an important physicochemical parameter to understand and it varies from IL to IL. In general, ILs are more viscous (1–3 orders of magnitude) than aqueous and
nonaqueous solvents. Figure 1 lists the viscosities of the two ILs examined in this work. N1114 TFSI has a viscosity 4x higher than EAN. This has implications on several parameters, particularly in tribology and electrochemistry, but we do not believe that viscosity is a major factor in controlling the rate of water sorption in ILs, as indicated by the data acquired on BMIM TFSI, which is discussed above. In the presence of water, the IL–water mixture’s viscosity is lowered from that of the neat IL. This affects mass transport processes and is a major factor in the conductivity of the solvent. It is known that IL conductivity can be increased via water addition (with a concomitant lowering of the viscosity), but as we have seen, the presence of water has additional implications on the electrochemical system.

The IR absorption profiles for water in the two reported ILs are significantly different, but data acquired for a single IL do not change the absorption profile shape even with significantly varying water concentrations. Water absorbed in EAN is represented by a single broad peak, corresponding to the symmetric stretching vibrational mode of water, whereas the water in N1114 TFSI is represented by two peaks, corresponding to the symmetric and asymmetric stretching modes. The presence of narrow O–H bands for the asymmetric and symmetric modes indicates the presence of water monomers that do not participate in a water–water hydrogen bonding network. This is a significant difference in the IR peak profile and is attributed to the different anions and the protic nature of EAN. In the case of EAN, the ethyl group forms the nonpolar domain and the charged groups form the polar domain in the bulk nanostructure. Water can form hydrogen bonds with the nitrate ion, which acts as a Bronsted base, as well as with the ammonium head group, which acts as a donor. In the presence of a Bronsted base like [NO$_3$]$^-$, several water molecules can interact with the anion through H-bonding. We predict that this can seed water clusters and lead to coalescing and red-shifting of OH asymmetric and symmetric stretching bands, as seen in Figure 4. The presence of two water peaks in the N1114 TFSI spectra is attributed to monomeric water molecules and agrees with the results reported by Welton et al. The IR absorption profiles for water in the two reported ILs are significantly different, but data acquired for a single IL do not change the absorption profile shape even with significantly varying water concentrations. Water absorbed in EAN is represented by a single broad peak, corresponding to the symmetric stretching vibrational mode of water, whereas the water in N1114 TFSI is represented by two peaks, corresponding to the symmetric and asymmetric stretching modes. The presence of narrow O–H bands for the asymmetric and symmetric modes indicates the presence of water monomers that do not participate in a water–water hydrogen bonding network. This is a significant difference in the IR peak profile and is attributed to the different anions and the protic nature of EAN. In the case of EAN, the ethyl group forms the nonpolar domain and the charged groups form the polar domain in the bulk nanostructure. Water can form hydrogen bonds with the nitrate ion, which acts as a Bronsted base, as well as with the ammonium head group, which acts as a donor. In the presence of a Bronsted base like [NO$_3$]$^-$, several water molecules can interact with the anion through H-bonding. We predict that this can seed water clusters and lead to coalescing and red-shifting of OH asymmetric and symmetric stretching bands, as seen in Figure 4. The presence of two water peaks in the N1114 TFSI spectra is attributed to monomeric water molecules and agrees with the results reported by Welton et al.

CONCLUSIONS

This work reports water sorption rates for one hydrophilic IL and one hydrophobic IL across a water concentration range from 50 to 6000 ppm. EAN is a protic IL that demonstrates a relatively fast water sorption rate (270 ± 30 ppm/min) over the first 20 min of exposure when compared to N1114 TFSI, a hydrophobic IL that sorbs water at a slower rate (30 ± 3 ppm/min) over the first 80 min of exposure. The interactions of water vary drastically in different ILs, as indicated by different IR peak profiles for the OH stretches of water. In these studies, EAN clearly shows a broad symmetric stretching peak indicative of water clusters able to form a hydrogen bonding network, whereas N1114 TFSI shows two well-resolved peaks corresponding to symmetric and asymmetric modes of water monomers. The behavior of water molecules in EAN or N1114 TFSI is not affected significantly by water concentration over the ranges examined here. Electrochemistry results show a systematic increase in HER currents at −1.16 V versus Fc/Fc$^+$ for EAN solutions that contained incrementally higher concentrations of water. This shows the expected increased current and lower overpotential expected for HER on silver cathodes as the concentration of water increases. Moreover, our data suggest that water may be “condensing” on the Ag electrode surface at concentrations ≥3500 ppm water. Furthermore, our data show the peak current due to Ag-oxide reduction at −1.1 V versus Fc/Fc$^+$ in N1114 TFSI correlated with the water concentration (i.e., a higher water concentration yielded a larger overall oxide reduction peak current). This confirms that water levels can be probed in situ, particularly at smaller concentrations (0.005–0.10%, or 50–1000 ppm water), where many experimentalists operate with ILs. All of the results presented in this study bring attention to key parameters that should be controlled to allow meaningful comparisons of data from IL experiments across the multiple fields in which they are now employed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00104.

Figure S1: electrochemical analysis of water in EAN, Figure S2: electrochemical analysis of water in N1114 TFSI, Figure S3: CVs to demonstrate the potential axis correction, Figure S4: full FTIR spectra of EAN and N1114 TFSI with varying concentration of water, Table S1: compiled results from KF analysis of EAN, and Table S2: compiled results from KF analysis of N1114 TFSI (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the Iowa Energy Center (OG-15-002) and the ACS-PRF (55279-DNJS).

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