Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids

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The effect of water content on room-temperature ionic liquids (RTILs) was studied by Karl Fischer titration and cyclic voltammetry in the following ionic liquids: tris(P-hexyl)tetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate $[P_{14,6,6,6}][NTf_2]$, *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_4mpyrr][NTf_2]$, 1-hexyl-3-methylimidazolium tris(perfluoroethyl)trifluorophosphate $[C_6mim][FAP]$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_4mim][NTf_2]$, 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide $[C_4dmim][NTf_2]$, *N*-hexyltriethylammonium bis(trifluoromethylsolfonyl)imide $[N_{6,2,2,2}][NTf_2]$, 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2mim][NTf_2]$, 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$, 1-hexyl-3-methylimidazolium iodide $[C_4mim][I]$, 1-butyl-3-methylimidazolium trifluoromethylsulfonate $[C_4mim][OTf]$, and 1-hexyl-3-methylimidazolium chloride $[C_6mim][Cl]$. In addition, electrochemically relevant properties such as viscosity, conductivity, density, and melting point of RTILs are summarized from previous literature and are discussed. Karl Fisher titrations were carried out to determine the water content of RTILs for vacuum-dried, atmospheric, and wet samples. The anion in particular was found to affect the level of water uptake. The hydrophobicity of the anions adhered to the following trend: $[FAP]^- > [NTf_2]^- > [PF_6]^- > [BF_4]^- >$ halides. Cyclic voltammetry shows that an increase in water content significantly narrows the electrochemical window of each ionic liquid. The electrochemical window decreases in the following order: vacuum-dried > atmospheric > wet at 298 K > 318 K > 338 K. The anodic and cathodic potentials vs ferrocene internal reference are also listed under vacuum-dried and atmospheric conditions. The data obtained may aid the selection of a RTIL for use as a solvent in electrochemical applications.

1. Introduction

1.1. Introduction to RTILs. Room-temperature ionic liquids (RTILs) are composed entirely of ions and exist in the liquid state at 298 K.[1] RTILs as a class typically contain a bulky organic cation that is weakly coordinated to an organic or inorganic anion.[2] Weak coordination results in a reduction in the lattice energies and crystalline structure of the salt and, hence, lowers the melting point.[3] RTILs have attracted much attention recently as a replacement for traditional organic solvents as they possess many attractive properties. Among these properties are intrinsic ion conductivity, low volatility, high chemical and thermal stability, low combustibility, and wide electrochemical windows.[2,4−10] The presence of an abundance of charge carriers means that when RTILs are used as solvents no supporting electrolyte is required for electrochemical experiments, and this minimizes waste. One would expect that intrinsic conductivity would allow faster mass transport of the analyte to the electrode surface, but the high viscosity of RTILs (ca. 1 to 2 orders of magnitude higher than conventional solvents) results in conductivities approximately similar to traditional organic solvents with added supporting electrolyte (e.g., MeCN with 0.1 M TBAP).[2] The low volatility of RTILs makes them

more environmentally attractive than volatile organic solvents, and thus they have been termed "green solvents".[9] The reduction and oxidation of the cations and anions accounts for the wide electrochemical window so that a window of (5 to 6) V or more is not unusual for an ionic liquid.[7] The ability to vary the nature of the cation and the anion allows one to tune the solvents for a specific purpose and has given them the name "designer solvents".[4,6] This paper is concerned with the use of RTILs for electrochemistry.

RTILs have been used in many electrochemical applications such as solar cells, electrochemical sensors, fuel cells, capacitors and in lithium batteries and are employed as solvents in electrochemical experiments.[11] Recently, electrodes modified with ionic liquids have been studied. It has been shown that it is possible to use ionic liquid formation on the electrode surface to form a liquid−liquid interface with an aqueous phase as an electroanlaytical tool for quantitative anion detection[12−14] and could possibly replace previously used volatile organic solvents. The low volatility and high thermal stability of RTILs is also advantageous for gas detection and the development of robust gas sensors. A gas sensor lifetime is determined by how quickly the electrolyte dries up, and most conventional electrolytes (e.g., H_2SO_4/H_2O) dry up quickly and thus cannot survive drastic temperature changes. Ionic liquids can sustain high temperature and pressure changes and remain physically and chemically unchanged.[15]

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Table 1. Physical Properties of RTILs

RTIL	η (T = 293 K) cP[a]	κ (T = 293 K) mS·cm^{-1}	ρ (T = 293 K) g·cm^{-1}	MP K	decomp[44] K
[P$_{14,6,6,6}$][NTf$_2$]	464	–	1.18[44]	223[6]	473
[C$_4$mpyrr][NTf$_2$]	89[21]	2.2[45]	1.40[44]	186[45]	583
[C$_6$mim][FAP]	74[19]	1.3[19]	1.56[44]	–	573
[C$_4$mim][NTf$_2$]	52[39]	3.9[39]	1.44[44]	219[6]	548
[C$_4$dmim][NTf$_2$]	105[21]	2.0[46]	1.42[44]	–	–
[N$_{6,2,2,2}$][NTf$_2$]	167[47]	0.7[26]	1.27[47]	219[6]	–
[C$_4$mim][PF$_6$]	371[48]	1.5[49]	1.37[48]	205[50]	573
[C$_2$mim][NTf$_2$]	34[39]	8.8[39]	1.53[44]	186[51]	553
[C$_4$mim][BF$_4$]	112[21]	1.7[49]	1.21[48]	191[6]	573
[C$_4$mim][I]	1110[18]	–	1.49[44]	201[6]	473
[C$_4$mim][OTf]	90[39]	3.7[39]	1.30[39]	191[52]	573
[C$_6$mim][Cl]	7456[19]	–	1.05[44]	188[6]	483

^{a} 1 cP = 1 mPa·s.

In section 1.2, specific electrochemically relevant properties of RTILs are discussed with respect to the cations and anions that make up the ionic liquid, in particular, viscosity, conductivity, density, and melting point. The purpose is to review data already presented by other authors which will complement the data presented in this work. Overall, we seek to give insight into which RTILs are suitable for specific electrochemical applications. The remainder of the paper is concerned with new data relating the effect of trace water on RTILs as electrochemical solvents.

1.2. Physical Properties of RTILs and Their Electrochemical Significance. In Table 1, we report the physical and chemical properties of 12 RTILs from various authors. The table shows the 12 RTILs and their reported viscosity, conductivity, density, melting point, and decomposition temperature values. These are pertinent to the choice of electrochemical solvents.

1.2.1. Viscosity. The viscosity of a solvent is an important electrochemical property since high viscosities limit some applications and slow down the rate of diffusion-controlled chemical reactions.[16] Also, the diffusion coefficients of electrochemical species often reflect the different viscosities of RTILs where for sufficiently large molecules such as ferrocene or cobaltocene the diffusion coefficient is inversely proportional to the viscosity as implied by the Stokes–Einstein equation.[2] Ionic liquids have viscosities comparable to that of oils, i.e., 1 to 2 orders of magnitude higher than conventional solvents. The viscosity of RTILs is affected by the nature of both the cations and anions. The alkyl chain length of the imidazolium cations increases the liquids' viscosity due to a corresponding increase in van der Waals forces.[17] This result may seem counterintuitive as the associated electrostatic forces decrease as the side-chain length increases. However, the increasing contribution of weaker, nonassociating dispersion forces dominates the trend.[8] Therefore, longer alkyl substituents tend to give rise to more viscous RTILs.[18] The nature of the anion also affects the viscosity of the ionic liquid, particularly through relative basicity and the ability to participate in hydrogen bonding. It is shown in Table 1 that the perfluorinated [PF$_6$]$^-$ and [BF$_4$]$^-$ anions form much more viscous ionic liquids due to strong H···F interactions than those ionic liquids formed with the weakly basic [NTf$_2$]$^-$ anion, in which the negative charge is quite delocalized over the two sulfoxide groups.[1] Differences in viscosities may also be caused by the size, shape, and molar mass of the anion, with smaller, lighter, and more symmetric anions leading to more viscous ionic liquids. For example, the increase in symmetry of anions such as [PF$_6$]$^-$ or [BF$_4$]$^-$ as compared to the anion [NTf$_2$]$^-$, as well as increased H-bonding, may contribute to the higher viscosity of RTILs incorporating these

anions.[17,18] Table 1 shows that [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$] have viscosities of (371 and 112) cP at 293 K, respectively, compared to [C$_4$mim][NTf$_2$] which has a more bulky anion and a viscosity of 52 cP at 293 K. It is shown that the replacement of three fluorine atoms in the [PF$_6$]$^-$ anion by pentafluoroethyl groups hugely decreases the viscosity of imidazolium ionic liquids, as can be seen when comparing [C$_4$mim][PF$_6$] and [C$_6$mim][FAP].[19] It has also been suggested that the addition of fluorine atoms to the imide anion increases viscosity due to an increase in van der Waals forces.[17] The viscosities of ionic liquids are highly temperature dependent, with a 20 % change over 5 K not uncommon around room temperature.[20] Okoturo and VanderNoot[21] report the viscosities of 23 RTILs over a temperature range of (283 to 343) K and found that although some ionic liquids fit an Arrhenius relationship well over the whole temperature range those with symmetric cations or cations with functional groups fit better to the Vogel–Tammann–Fulcher (VFT) relationship.[22-24] Some ionic liquids did not fit well to either equation.[21]

1.2.2. Conductivity. In electrochemical experiments, the conductivity of a solvent is of vital importance. As discussed in section 1.1, RTILs have conductivities similar to those of organic solvents with added inorganic electrolytes (e.g., DMSO + 0.1 M TBAP has a conductivity of 27 mS·cm^{-1}).[1] Ionic liquids have advantages over traditional organic solvents as their conductivity is intrinsic, and they do not require the addition of a supporting electrolyte. The conductivity of a pure ionic liquid should depend on the mobility of the ions, which is influenced by the ion size, ion association, and particularly the viscosity.[19] In fact, the change in conductivity with composition in ionic liquids can be attributed almost directly to changes in the viscosity.[17] The high viscosity and large size of constituent ions result in reduced ion mobility and average conductivities. Conductivity generally decreases in the order of 1-alkyl-3-methylimidazolium > *N,N*-dialkylpyrrolidinium > tetraalkylammonium, attributed to the decrease in the planarity of the cationic core. The flatness of the imidazolium ring seems to allow a higher conductivity than does the tetrahedral nature of the ammonium salts, with the pyrrolidinium cation having an intermediate geometry.[1] This is apparent in Table 1, wherein the conductivities of [C$_4$mim][NTf$_2$], [C$_4$mpyrr][NTf$_2$], and [N$_{6,2,2,2}$][NTf$_2$] decrease according to the order listed above (3.9, 2.2, and 0.7) mS·cm^{-1}, respectively. At increased temperatures, the conductivity increases due to increased mobility resulting from a decrease in viscosity.[25,26] The variation of ionic liquid conductivity with temperature follows the Vogel–Tammann–Fulcher (VTF) relationship[20,26-28] (given below)

$$\kappa = A\sqrt{T}e^{-B}(T - T_0) \tag{1}$$

where κ is conductivity; A and B are empirically derived constants; and T_0 is the ideal glass temperature at which the conductivity drops to zero.

1.2.3. Density. Density of solvents is an important consideration for the development of certain types of batteries where weight issues are a concern. The density of an ionic liquid generally decreases with increasing length of alkyl chains in cations or anions.[8] Adding CH$_2$ groups to the alkyl chain on the imidazolium cation decreases the density since CH$_2$ is less dense than the imidazolium ring.[18] The density of RTILs increases with the molar mass of the anion in the approximate order [BF$_4$]$^-$ < [OTf]$^-$ < [PF$_6$]$^-$ < [NTf$_2$]$^-$ < [FAP]$^-$. In the studies of Huddleston et al.,[18] it was noted that the densities of simple halide salts such as [C$_4$mim][Cl] were lower than that of [C$_4$mim][PF$_6$], which is reflected in Table 1 when

[C$_6$mim][Cl] is compared to [C$_4$mim][PF$_6$] (1.05 g·cm^{-1} compared to 1.37 g·cm^{-1}). However, [C$_4$mim][I] has a higher density than [C$_4$mim][PF$_6$] (1.49 g·cm^{-1} compared to 1.37 g·cm^{-1}). Several researchers have recorded densities as a function of temperature and have reported an approximately linear decrease of density with temperature.[29−31]

1.2.4. Melting and Decomposition Temperature. The workable liquid range is a significant factor in electrochemical sensors, e.g., for gases such as hydrogen sulfide.[15] Low melting points of RTILs are achieved by selectively combining cationic and anionic species to produce salts that have low lattice energies, largely due to the asymmetric cations. Thermal decomposition temperatures decrease as the anion hydrophilicity increases; therefore, one can conclude that drying improves the thermal stability of many RTILs. Halide anions reduce the thermal stability of ionic liquids, with decomposition occurring at least 373 K below corresponding RTILs with nonhalide anions. Relative anion stabilities have been suggested by Huddleston et al. as [PF$_6$]$^-$ > [NTf$_2$]$^-$ ≈ [BF$_4$]$^-$ > halides,[18] and Table 1 shows that this is indeed the case. The ionic liquids [C$_4$mim][PF$_6$], [C$_4$mim][NTf$_2$], and [C$_4$mim][BF$_4$] have decomposition temperatures of 373 K higher than the corresponding halide ionic liquid [C$_4$mim][I]. Kroon et al. suggest that [NTf$_2$]$^-$ is more thermally stable than both [PF$_6$]$^-$ and [BF$_4$]$^-$ but agree that all of these anions are far more thermally stable than halides. Ionic liquids with the FAP anion are also very thermally stable,[19] as can be seen from a decomposition temperature of 573 K for [C$_6$mim][FAP]. The decomposition temperature of RTILs also depends on the type of cation. The trend of thermal stability with respect to cation species appears to go as follows: phosphonium > imidazolium > tetraalkylammonium ≈ pyrrolidinium.[32]

1.3. Water as an Impurity in RTILs. Water is considered to be one of the most significant impurities in RTILs as it is ubiquitous, and even hydrophobic RTILs absorb some from the atmosphere.[10] The effect of water on RTILs has been studied regarding properties such as viscosity, conductivity, and electrochemical window. It has been shown that an increase in water content in an ionic liquid leads to a decrease in viscosity, accounting for many of the discrepancies in experimental viscosity measurements.[33,34] Viscosity values are related to conductivity values since a decrease in viscosity enhances the mass transport of analyte to the electrode surface. Therefore, a change in the water content of an ionic liquid will also affect conductivity: as water content increases, so does conductivity.[10] The relationship between water content and density of a RTIL has also been studied, and it has been shown that an increase in water content causes a decrease in the density of an ionic liquid. A decrease in viscosity and subsequent increase in conductivity may appear to be advantageous. However, an increase in water content results in a reduction in the electrochemical window of an ionic liquid.[35] The narrowing of the electrochemical window occurs at both the cathodic and anodic limits. The process responsible for this is likely water electrolysis.[36] It has been reported that ionic liquids containing the [PF$_6$]$^-$ and [BF$_4$]$^-$ anions can exhibit the largest electrochemical window, but such anions are susceptible to hydrolysis when in contact with water and can result in the undesirable evolution of hydrogen fluoride.[7] With this in mind, studies have been carried out to examine which RTILs have the greatest water uptake. In particular, Ignat'ev et al. have studied several ionic liquids containing the [FAP]$^-$ anion, a hydrophobic anion that is immiscible with water.[19] The water uptake for [FAP]$^-$ ILs

is much less than that for ILs containing other anions such as [NTf$_2$]$^-$ and [PF$_6$]$^-$.

1.4. Aims. This work provides numerical data on the water contents and effect of water on the electrochemical windows of several RTILs. RTILs, whether they are hydrophobic or hydrophilic in nature, can absorb considerable amounts of water, which changes their physical and chemical properties.[36] This is of particular interest where electrochemical sensing is concerned. RTILs have been particularly well documented as solvents for gas sensing for gases such as O$_2$,[37] NO$_2$,[4] H$_2$,[11] SO$_2$,[38] and H$_2$S.[15] The uptake of water from any source reduces the wide electrochemical windows of RTILs and can limit their use as sensing solvents. RTIL-modified electrodes at a liquid−liquid interface with aqueous solution have also been studied over the last number of years[12−14] to substitute volatile organic solvents with more thermally stable RTILs. The effects of water on RTILs would be of particular interest in this field. In this work, we will show the extent of water uptake of several RTILs, as well as its effect on the electrochemical window of ionic liquids. This provides information to aid the selection of RTILs as solvents for electrochemical experiments.

2. Experimental

2.1. Chemical Reagents. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$mim][NTf$_2$]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_4$mim]-[NTf$_2$]), 1-hexyl-3-methylimidazolium chloride ([C$_6$mim][Cl]), and N-butyl-N-ethylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C$_4$mpyrr][NTf$_2$]) were prepared by standard literature procedures.[39] N-Hexyltriethylammonium bromide (Aldrich, 99 %) was used as purchased for metathesis with lithium bis(trifluoromethyl)sulfonylimide and purified by standard literature procedures[39] to yield [N$_{6,2,2,2}$][NTf$_2$]. 1-Butyl-3-methylimidazolium tetrafluoroborate ([C$_4$mim][BF$_4$], high purity), 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim]-[PF$_6$], high purity), 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([C$_4$mim][OTf], high purity), and tris(P-hexyl)-tetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate ([P$_{14,6,6,6}$][FAP], high purity) were kindly donated by Merck KGaA. [C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$], and [P$_{14,6,6,6}$][FAP] were used as received. [C$_4$mim][OTf] was first diluted with CH$_2$Cl$_2$ and passed through a column consisting of alternating layers of neutral aluminum oxide and silica gel to remove residual acidic impurities. 1-Hexyl-3-methylimidazolium tris(perfluoroethyl) trifluorophosphate ([C$_6$mim][FAP]) was synthesized as described in the literature.[19] Ferrocene (Fe(C$_5$H$_5$)$_2$, Fc, Aldrich, 98 %), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, < 99 %), and acetonitrile (Fischer Scientific, dried and distilled, < 99.99 %) were used as received, without further purification.

2.2. Instrumental. All electrochemical experiments were performed using a computer-controlled μ-Autolab potentiostat (Eco-Chemie, Netherlands). The electrochemical analysis of each RTIL was performed in a T-cell (reported previously)[11,36] using a Pt microdisk (10 μm diameter) as the working electrode and a platinum wire as a quasi-reference electrode. The working electrode was modified with a section of disposable micropipette tip, into which 20 μL of the RTIL was placed. The liquid was purged under vacuum for ca. 90 min for experiments performed under dried conditions. For wet experiments conducted at increasing temperatures, ultrapure water was placed in the T-cell around the base of the working electrode to create a highly moist atmosphere. Temperature-controlled experiments were performed in a thermostatted box (previously described by Evans

et al.)[40] which also functioned as a Faraday cage. The temperature was accurate to ± 0.5 K.[40] The microdisk working electrode was polished on soft lapping pads (Buehler, Illinois) with an alumina slurry of size (1 and 0.3) μm, respectively. The steady-state voltammetry of a 2 mM solution of Fc in acetonitrile containing 0.1 M TBAP was used to calculate the electrode diameter, adopting a value for the diffusion coefficient of $2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$ at 298 K.[41]

All Karl Fischer titrations were performed using a Cou-Lo Aquamax KF Moisture meter in conjuction with Cou-Lo Formula A Coloumetric Anode solution and Cou-Lo Formula C Coulometric Cathode solution (GRScientific, U.K.). Each RTIL sample was injected into the titrator using a 100 μL glass syringe with a 7 cm needle (SGE, U.K.). The syringe was flushed with methanol several times and then flushed with the ionic liquid to be titrated. The RTIL was then injected into the titrator, and a reading of water content was obtained. The Cou-Lo Aquamax uses the coulometric principle, whereby the water present in the sample is coulometrically titrated to a predefined end point at which there is a minute excess of free iodine present. Stoichiometrically, one mole of water will react with one mole of iodine, so that 1 mg of water is equivalent to 10.71 C of electricity. Combining the coulometric technique with Karl Fischer titration, the Aquamax titrator detemines the water content of the sample by measuring the amount of electrolysis current necessary to produce the required iodine. This is an absolute technique which does not require calibration of the reagents. Water content is given by Aquamax KF standard *W/w* calcutaion mode.

$$\text{result (ppm)} = \frac{\text{Microgram count}}{W - w}$$

where W = total weight of sampler + sample (mg) and w = tare weight of empty sampler (mg).

2.3. Sample Preparation. The data reported in section 3.1 were obtained from RTILs tested for water content. The RTILs were subject to the following pretreatments: vacuum-dried, wet, or used straight from the benchtop under atmospheric conditions. The atmospheric samples were used without any attempt at drying or purification. The vacuum-dried samples were purged under vacuum for 24 h while stirring continuously at a temperature of 333 K. The wet samples were prepared as follows: 1 mL of ionic liquid and 1 mL of deionized water were added to a small glass tube, shaken, and allowed to stand for approximately 24 h. Any water that did not mix with the RTILs was removed and the layer of ionic liquid titrated. For each measurement, the ionic liquids were kept at a temperature of 298 K. The data reported in section 3.2 were obtained from RTILs used to determine the effect of water on their electrochemical window. They were subject to the following conditions: atmospheric, vacuum-dried, and wet. The vacuum-dried and wet samples were prepared as per section 2.2.

3. Results and Discussion

In this work, we present numerical data on the water content of 12 RTILs calculated using the Karl Fisher titration method. These data give an indication of the hydrophobicity or hydrophilicity of each RTIL. We also present data showing the effect of water on the electrochemical window of 12 RTILs. The electrochemical window is calculated vs a ferrocene (fc) internal redox couple.[2] The limits of the electrochemical window are at current densities of 1 mA·cm^{-2} and 5 mA·cm^{-2}. These current densities are small to give a realistic indication of a suitable electrochemical window of RTILs for use as solvents for sensing at low concentrations of analyte.

**Table 2. Water Content^a of 12 RTILs in Atmospheric, Vacuum-Dried, and Wet Conditions at 298 K^b**

RTIL	atmospheric ppm	vacuum-dried ppm	wet ppm
$[P_{14,6,6,6}][NTf_2]$	328	–	–
$[C_4mpyrr][NTf_2]$	406	133	11407
$[C_6mim][FAP]$	417	203	3068
$[C_4mim][NTf_2]$	491	144	5680
$[C_4dmim][NTf_2]$	504	295	9868
$[N_{6,2,2,2}][NTf_2]$	1150	167	8200
$[C_4mim][PF_6]$	2119	268	24194
$[C_2mim][NTf_2]$	3385	105	19940
$[C_4mim][BF_4]$	5083	119	miscible
$[C_4mim][I]$	11349	1050	miscible
$[C_4mim][OTf]$	15227	250	miscible
$[C_6mim][Cl]$	61049	2231	miscible

^{a} Water content given by Aquamax KF standard *W/w* calcutaion mode. Result (ppm) = (microgram count)/(W − w), where W = total weight of sampler + sample (mg) and w = tare weight of empty sampler (mg). ^{b} Atmospheric: used straight from the bench without any attempt at drying or purification. Vacuum-dried: dried under vacuum for 24 h at 333 K while continuously stirring. Wet: mixed with equal parts of water for 24 h; immiscible water layer was decanted off.

3.1. Karl Fisher Titrations. We examined the water content of 12 RTILs with different cations and anions. The water content of each ionic liquid was obtained using a Karl Fisher titrator, discussed in section 2. Each RTIL was tested for water under three types of conditions: atmospheric, vacuum-dried, and wet. The atmospheric samples were those used straight from the bench without any attempt at drying or purification. The vacuum-dried samples were purged under vacuum for 24 h while stirring continuously at a temperature of 333 K. The wet RTILs were mixed with water in a glass tube and allowed to stand for 24 h. The measured water contents are presented in Table 2 and are organized in order of increasing hydrophilicity of air-equilibrated samples.

The miscibility of RTILs with water is determined to a large extent by the anion. The [FAP]$^-$ RTILs appear to be quite hydrophobic and immiscible with water. The water uptake of [FAP]$^-$ RTILs is generally less than those containing the [NTf$_2$]$^-$ anion and much less than those containing the [PF$_6$]$^-$.[19] This is shown in Table 2, where [P$_{14,6,6,6}$][FAP] and [C$_6$mim]-[FAP] have two of the three lowest water content values in atmospheric conditions. ILs containing anions such as [NTf$_2$]$^-$ and [PF$_6$]$^-$ are also immiscible and present a phase split in water at room temperature.[3,42] The water uptake of ILs containing the [NTf$_2$]$^-$ anion are also relatively low (compared to other anions) in atmospheric conditions. Each IL containing the [NTf$_2$]$^-$ cation (with the exception of [C$_2$mim][NTf$_2$]) has lower water content levels than the [PF$_6$]$^-$ ionic liquid, and some have water content levels comparable to the very hydrophobic [FAP]$^-$ ILs. Halide, [BF$_4$]$^-$, and [OTf]$^-$ ionic liquids are miscible with water, and this trend is evident in Table 2. The halide, [BF$_4$]$^-$, and [OTf]$^-$ RTILs have the highest water content in atmospheric conditions. [OTf]$^-$ likely hydrogen bonds strongly to water due to the presence of the [SO$_3$]$^-$ group and therefore has a high water content.

The identity of the anion appears to be a main factor in controlling the extent to which RTILs can be dried. The third column of Table 2 shows the water content of each IL under vacuum-dried conditions. The general trend of hydrophobicity of ionic liquids containing the [FAP]$^-$, [NTf$_2$]$^-$, and [PF$_6$]$^-$ anions is observed. However, it is interesting to note that the water content of [C$_4$mim][OTf] and [C$_4$mim][BF$_4$] after vacuum drying is comparable with the more hydrophobic ionic liquids,
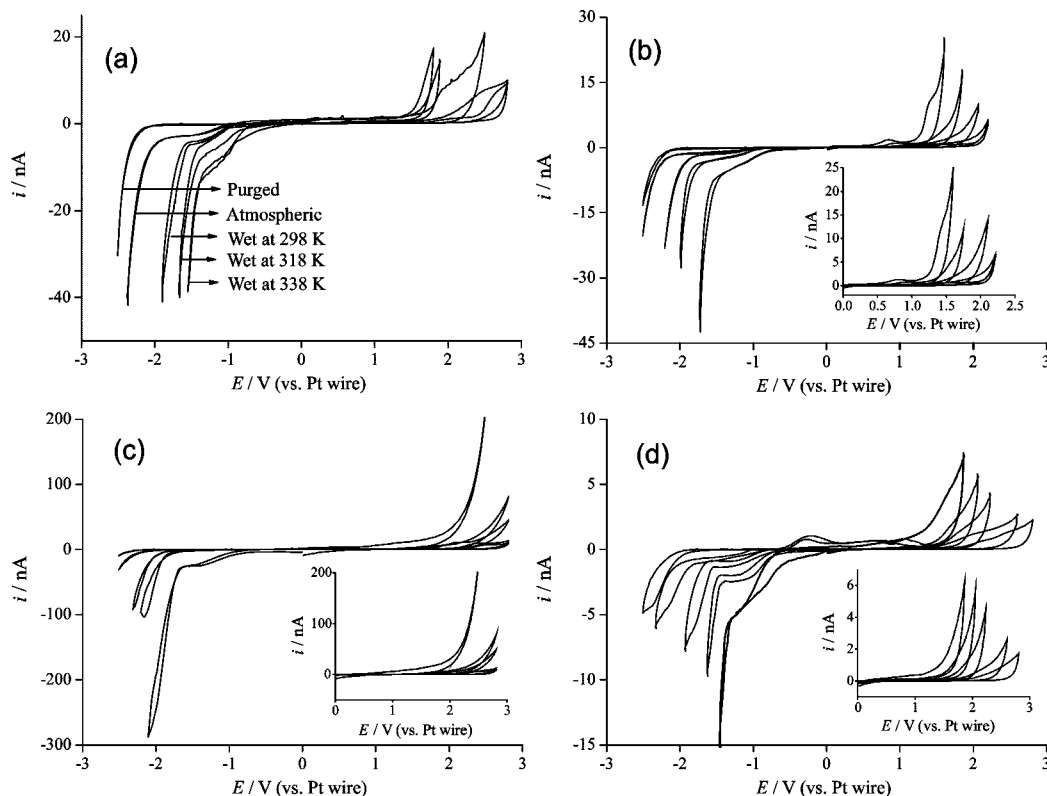
Figure 1. Effect of water on the electrochemical window of (a) [C$_2$mim][NTf$_2$], (b) [C$_4$mim][OTf], (c) [C$_4$mim][BF$_4$], and (d) [C$_4$mim][PF$_6$] with increasing water content for vacuum-dried, atmospheric, and wet conditions. Wet conditions were measured at temperatures (298, 318, and 338) K. CV was carried out on 10 μm Pt electrode vs Pt wire (0.3 mm). No fc/fc$^+$ internal reference is present in the scans below (fc/fc$^+$ internal reference is present for numerical data). Each scan was taken at 100 mV·s^{-1}.

while the RTILs containing halide anions still contain over 1000 ppm of water after drying. The fourth column of Table 2 shows the water content of wet RTILs. As before, a general trend of hydrophobicity of ILs containing [FAP]$^-$ and [NTf$_2$]$^-$ anions is observed. There is an exception to this trend: [C$_4$mpyrr][NTf$_2$] has a water content level higher than expected from its atmospheric water content. It is also noteworthy that even though [C$_4$mim][OTf] and [C$_4$mim][BF$_4$] were seen to have a lower water content than anticipated after vaccum drying, they are miscible with water under saturated conditions, which is expected. Therefore, hydrophobicity of anions here follows the general trend: [FAP]$^-$ > [NTf$_2$]$^-$ > [PF$_6$]$^-$ > [BF$_4$]$^-$ > halides, as previously suggested in the literature.[9,18,43]

The cation of an ionic liquid also affects its hydrophobicity and hydrophilicity. Hydrophobicity of an ionic liquid increases with increasing alkyl chain length.[3] This trend is observed in atmospheric conditions for [C$_4$mim][NTf$_2$] and [C$_2$mim][NTf$_2$] which have water content values of 491 ppm and 3385 ppm, respectively, at 298 K. This trend has also been observed with respect to [BF$_4$]$^-$ imidazolium RTILs, where the alkyl chain of [C$_n$mim]$^+$ with n < 6 is water soluble.[18]

The experimentally obtained values in Table 2 are not in perfect agreement with literature values for water content of dried or saturated RTILs.[18] However, the miscibility of halide and [BF$_4$]$^-$ RTILs with water is in agreement with the literature.

3.2. Cyclic Voltammetry of RTILs Exposed to Atmospheric Moisture at Different Temperatures. The effect of water on the electrochemical window of 12 RTILs was examined using cyclic voltammetry on a Pt microelectrode (diameter 10 μm) vs Pt quasi-reference electrode at scan rate of 100 mV·s^{-1}. Figure 1 shows the full electrochemical windows on platinum for four RTILs ([C$_2$mim][NTf$_2$], [C$_4$mim][OTf], [C$_4$mim][BF$_4$], and

[C$_4$mim][PF$_6$]) under vacuum-dried and atmospheric, wet conditions at increasing temperatures (see section 2.2 for definitions). In vacuum-dried conditions, little or no atmospheric moisture was present resulting in a redox window free of voltammetric features. In atmospheric conditions, the electrochemical windows were found to decrease, and the reduction of atmospheric oxygen was seen at a potential between (−1.0 and −1.5) V. Finally, water was added into the cell to create a wet atmosphere around the RTIL. With the addition of water into the cell, the amount of moisture uptake of the RTILs increased significantly as seen by the narrowing of the electrochemical windows in Figure 1. This behavior is known and has been observed previously by Silvester et al. They presented the voltammetry of [C$_4$mim][OTf] and showed a decrease in the electrochemical window from vacuum-dried conditions to atmospheric conditions.[35] In this work, in all 12 RTILs, a reduction in the electrochemical window was observed with increasing temperature.

The insets to Figure 1 show the anodic scan only of [C$_4$mim][OTf], [C$_4$mim][BF$_4$], and [C$_4$mim][PF$_6$]. The voltammograms were typically scanned from (0.0 to +2.8) V versus a Pt quasi-reference electrode under the same conditions as the redox scans above. These anodic scans show little difference from the redox scans in the same electrochemical window; however, it is apparent from Figure 1d that the reverse of the redox scans (particularly for higher temperatures) at 1.0 V has some features that are not present on the oxidative scans, probably due to the oxidation of a product formed during the reduction of water/oxygen. The anodic window also decreases significantly with increasing water content.

The quantitative effect of water impurities on the electrochemical window of 12 RTILs is given in Table 3. Ferrocene was added to the system as an internal standard to determine

Table 3. Effect of Atmospheric Moisture on the Electrochemical Window of 12 RTILs[a]

RTIL	E(vacuum-dried)/V		E(atmospheric)/V		E(wet at 298 K)/V		E(wet at 318 K)/V		E(wet at 338 K)/V	
	$j = 1$	$j = 5$	$j = 1$	$j = 5$	$j = 1$	$j = 5$	$j = 1$	$j = 5$	$j = 1$	$j = 5$
$[P_{14,6,6,6}][NTf_2]$	5.2	5.4	3.2	4.0	1.8	2.6	1.6	2.1	0.8	2.0
$[C_4mpyrr][NTf_2]$	4.2	5.2	3.0	4.6	2.0	2.8	2.0	2.9	1.2	1.4
$[C_6mim][FAP]$	4.6	4.8	3.0	3.7	2.5	3.3	2.4	2.7	1.6	2.6
$[C_4mim][NTf_2]$	4.3	5.0	2.9	3.5	2.8	3.7	2.4	2.9	1.4	2.5
$[C_4dmim][NTf_2]$	4.7	5.2	3.3	4.4	2.9	3.8	2.4	3.1	1.4	2.5
$[N_{6,2,2,2}][NTf_2]$	4.7	5.4	2.3	4.6	2.2	3.4	1.9	2.5	1.7	1.7
$[C_4mim][PF_6]$	4.8	5.0	3.9	4.5	2.6	3.1	1.7	239	1.6	1.9
$[C_2mim][NTf_2]$	4.2	4.6	2.8	2.7	2.6	3.2	1.4	2.5	0.7	1.6
$[C_4mim][BF_4]$	4.6	5.1	2.4	4.0	2.0	3.6	2.4	3.2	2.3	2.8
$[C_4mim][I]$	2.0	2.2	1.9	2.2	1.6	1.8	0.0	0.5	0.0	0.0
$[C_4mim][OTf]$	4.2	5.1	3.3	4.8	2.7	4.2	1.5	2.7	1.3	2.8
$[C_6mim][Cl]$	3.0	3.3	2.9	3.3	2.4	2.8	2.4	2.3	1.4	1.4

[a] Electrochemical window limits vs fc/fc[+] at current densities (j) of 1 mA·cm^{-2} ($j = 1$) and 5 mA·cm^{-2} ($j = 5$). Vacuum-dried: dried under vacuum for 90 min. Atmospheric: used straight from the bench without any attempt at drying or purification. Wet: in a water-sat. atmosphere at temperatures (298, 318, and 338) K.

Table 4. Anodic and Cathodic Potentials vs fc/fc[+] for the Electrochemical Window of 12 RTILs at Current Density 1 mA·cm^{-2}[a]

RTIL	vacuum-dried			atmospheric		
	E(cathodic)/V	E(anodic)/V	E(total)/V	E(cathodic)/V	E(anodic)/V	E(total)/V
$[P_{14,6,6,6}][NTf_2]$	−2.7	+2.5	5.2	−1.5	+1.7	3.2
$[C_4mpyrr][NTf_2]$	−2.8	+1.4	4.2	−1.4	+1.6	3.0
$[C_6mim][FAP]$	−2.6	+2.0	4.6	−1.3	+1.7	3.0
$[C_4mim][NTf_2]$	−2.5	+1.8	4.3	−1.3	+1.6	2.9
$[C_4dmim][NTf_2]$	−2.5	+2.2	4.7	−1.5	+1.8	3.3
$[N_{6,2,2,2}][NTf_2]$	−2.6	+2.1	4.7	−1.4	+1.9	2.3
$[C_4mim][PF_6]$	−2.7	+2.1	4.8	−1.7	+2.2	3.9
$[C_2mim][NTf_2]$	−2.2	+2.0	4.2	−1.2	+1.6	2.8
$[C_4mim][BF_4]$	−2.6	+2.0	4.6	−1.1	+1.3	2.4
$[C_4mim][I]$	−2.0	+0.0	2.0	−1.9	+0.0	1.9
$[C_4mim][OTf]$	−2.6	+1.6	4.2	−1.6	+1.7	3.3
$[C_6mim][Cl]$	−2.6	+0.4	3.0	−2.4	+0.5	2.9

[a] Vacuum-dried: dried under vacuum for 90 min. Atmospheric: used straight from the bench without any attempt at drying or purification.

Table 5. Anodic and Cathodic Potentials vs fc/fc[+] for the Electrochemical Window of 12 RTILs at Current Density 5 mA·cm^{-2}[a]

RTIL	vacuum-dried			atmospheric		
	E(cathodic)/V	E(anodic)/V	E(total)/V	E(cathodic)/V	E(anodic)/V	E(total)/V
$[P_{14,6,6,6}][NTf_2]$	−2.8	+2.6	5.4	−1.9	+2.1	4.0
$[C_4mpyrr][NTf_2]$	−3.2	+1.4	5.2	−2.0	+2.6	4.6
$[C_6mim][FAP]$	−2.4	+2.4	4.8	−1.7	+2.0	3.7
$[C_4mim][NTf_2]$	−2.7	+2.3	5.0	−1.5	+2.0	3.5
$[C_4dmim][NTf_2]$	−2.7	+2.5	5.2	−2.1	+2.3	4.4
$[N_{6,2,2,2}][NTf_2]$	−3.0	+2.4	5.4	−2.4	+2.2	4.6
$[C_4mim][PF_6]$	−2.9	+2.1	5.0	−2.1	+2.4	4.5
$[C_2mim][NTf_2]$	−2.4	+2.2	4.6	−2.0	+1.7	3.7
$[C_4mim][BF_4]$	−2.8	+2.3	5.1	−2.0	+2.0	4.0
$[C_4mim][I]$	−2.1	+0.1	2.2	−2.0	+0.1	2.1
$[C_4mim][OTf]$	−2.8	+2.3	5.1	−2.6	+2.2	4.8
$[C_6mim][Cl]$	−2.7	+0.6	3.3	−2.7	+0.6	3.3

[a] Vacuum-dried: dried under vacuum for 90 min. Atmospheric: used straight from the bench without any attempt at drying or purification.

the anodic and cathodic limits relative to the fc/fc[+] potential for the quantitative data.[2] The electrochemical window (in volts) vs fc/fc[+] is recorded in vacuum-dried conditions, atmospheric conditions, and wet conditions at (298, 318, and 338) K. The magnitudes of the electrochemical windows are defined by current densities (j) of 1 mA·cm^{-2} and 5 mA·cm^{-2}. These current densities are chosen to be quite low and should facilitate a realistic electrochemical window size, particularly for gas sensing at very low concentrations of analyte.

It can be seen that most of the RTILs have electrochemical windows of ca. (4.2 to 5.4) V in vacuum-dried conditions, with the widest seen in $[P_{14,6,6,6}][FAP]$. Increasing the amount of water impurities has the biggest effect on the electrochemical window of $[P_{14,6,6,6}][FAP]$, which has a window

that decreases from 5.2 V when purged to 0.8 V in wet conditions at 338 K. [FAP]$^-$ ionic liquids generally possess very wide electrochemical windows as the [FAP]$^-$ anion is believed to be the most stable to oxidation.[19] The water uptake for these ionic liquids is much less than that of the RTILs containing other anions as can be seen from Table 2. Slightly wider electrochemical windows are observed for [NTf$_2$]$^-$ anions compared to [BF$_4$]$^-$ and [PF$_6$]$^-$ in vacuum-dried conditions at current density 5 mA·cm^{-2}, although the difference is not significant, being only of the order of (0 to 400) mV. The electrochemical windows of these anions are comparable at current density 1 mA·cm^{-2}. The RTILs with the smallest electrochemical window are $[C_4mim][I]$ and $[C_6mim][Cl]$ due to the relatively low oxidation of the halide ion. The decrease

in electrochemical window of all 12 RTILs from vacuum-dried conditions to wet conditions at 338 K is significant and to the order of (1.6 to 4.4) V.

The anodic and cathodic potentials vs ferrocene internal reference are listed in Table 4 for current density 1 mA·cm^{-2} and Table 5 for current density 5 mA·cm^{-2}. Potential values are listed for vacuum-dried and atmospheric conditions. This is important when selecting an IL for an electrochemical experiment because the redox signals of an analyte must fall within the electrochemical window of the RTIL, and this can be conveniently quantified using an internal reference. This table is particularly useful for experiments employing RTILs as electrolyte sensors, as one can select a RTIL with a suitable electrochemical window vs ferrocene where the analytes' signals will be clearly visible.

4. Conclusions

The effect of water on the electrochemical windows of RTILs has been studied in 12 different ionic liquids. The water content of each ionic liquid in different conditions (vacuum-dried, atmospheric, and wet) was quantified, and a large variation in water uptake was observed. This variation in water content was mostly due to the identity of the anions in the ionic liquids and adhered to the following trend: [FAP]$^-$ > [NTf$_2$]$^-$ > [PF$_6$]$^-$ > [BF$_4$]$^-$ > [OTf]$^-$ > halides. A reduction in the electrochemical window at both the cathodic and anodic limits with increasing water content in each ionic liquid was observed. The decrease of the electrochemical windows has been measured against a standard internal reference couple, and the anodic and cathodic potentials vs ferrocene internal reference were presented under vacuum-purged and air-equilibrated conditions. This will aid the selection of RTILs for various electrochemical experiments and particularly as solvents in sensors for a variety of analytes.

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