

Molecular States of Water in Room Temperature Ionic Liquids

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Abstract: ATR and transmission IR spectroscopy have been used to investigate the state of water in room temperature ionic liquids (RTILs) based on the 1-alkyl-3-methylimidazolium cation with the different anions: [PF₆]⁻, [SbF₆]⁻, [BF₄]⁻, [ClO₄]⁻, [CF₃SO₃]⁻, [(CF₃SO₂)₂N]⁻, [NO₃]⁻ and [CF₃CO₂]⁻. It has been shown that in these RTILs water molecules absorbed from the air are present mostly in the “free” (not self-associated) state, bound *via* H-bonding with [PF₆]⁻, [BF₄]⁻, [SbF₆]⁻, [ClO₄]⁻, [CF₃SO₃]⁻, [(CF₃SO₂)₂N]⁻ with the concentrations of dissolved water in the range of 0.2-1.0 mol/dm³. It has been concluded that most of the water molecules at these concentrations exist in symmetric 1:2 type H-bonded complexes: anion...HOH...anion. Additional evidence that the preferred sites of interaction with water molecules are the anions in RTILs has been obtained from the experiments with RTILs of the 1-butyl-2,3-dimethylimidazolium and 1-butyl-2,3,4,5-tetramethylimidazolium cations. Water molecules can also form associated liquid-like formations in the RTILs, consisting of anions of stronger basicity such as [NO₃]⁻ and [CF₃CO₂]⁻. When these RTILs are exposed to air the water concentrations exceed 1.0 mol/dm³. The strength of H-bonding between water molecules and anions increases in the order [PF₆]⁻ < [SbF₆]⁻ < [BF₄]⁻ < [(CF₃SO₂)₂N]⁻ < [ClO₄]⁻ < [CF₃SO₃]⁻ < [NO₃]⁻ < [CF₃CO₂]⁻. The energies of this H-bonding were estimated from spectral shifts, with the resulting enthalpies in the range of 8-13 kJ/mol. ATR-IR spectroscopy has also been used to study H-bonding between methanol and RTILs.

Introduction

Room temperature ionic liquids (RTILs) are attracting significant attention as novel solvent systems for chemical reactions and separations.¹⁻⁷ The range of chemical reactions studied in RTILs used as solvents is continually expanding. The challenge of separation of the reaction products from RTILs can be overcome with the use of biphasic systems, for example *via* combining reactions in RTILs with the separations using supercritical fluids. The combination of ionic liquids with supercritical CO₂, for example, provides a new and promising method for catalyst separation and the design of novel synthetic routes.^{5,7-9}

The presence of water in RTILs may affect many of their solvent properties such as polarity, viscosity and conductivity. This may have an effect on reaction rates due to the coordinating ability with a catalyst and also on the solubility of other substances in RTILs. For example, the presence of water in an ionic liquid has resulted in the underestimation of the solubility of CO₂ in the ionic liquid.⁷ Water may also react with constituents of the RTIL; it has also been reported that water in RTILs based on the [PF₆]⁻ anion leads to a reaction producing HF.^{1a,4b} Seddon and co-workers have recently emphasized that efficient drying has to be ensured if RTILs are to be used as solvents for moisture sensitive substances.^{4a} It is also clear that the commonly called “hydrophobic” RTILs are actually hygroscopic and can absorb significant amounts of water from the atmosphere.^{4a,b} The water content of various RTILs may be strongly influenced by the nature of the cation and anion. However, the molecular state of water dissolved in various RTILs and the origins of water solubility in the RTILs have not yet been addressed. An insight at the molecular level into the state of water dissolved in RTILs is

needed for further understanding of RTILs as media for chemical synthesis and separation. In this study, in order to observe the behaviour under conditions in which the RTILs would find large-scale use, the RTILs were investigated with water contents in equilibrium with the air.

Infrared spectroscopy, arguably, is the most powerful method to probe the molecular state of water present in various solvents.¹⁰ Indeed, the molecular state of water dissolved in a variety of organic solvents and polymers has been elucidated using IR spectroscopy.¹¹⁻¹⁷ The vibrational modes of water that result in bands in the IR spectrum are very sensitive to the environment and intermolecular interactions.^{18,19} In particular, the stretching modes of water have been used to understand the type of bonding between water molecules in the liquid, solid and vapour phases, as well as interactions between water and many chemical substances.

In this work we applied ATR (Attenuated Total Reflectance) and transmission IR spectroscopy to study the molecular state of dissolved water in several ionic liquids based on the 1-butyl-3-methylimidazolium cation ($[\text{bmim}]^+$) with the $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{BF}_4]^-$, $[\text{ClO}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{NO}_3]^-$ and $[\text{CF}_3\text{CO}_2]^-$ anions (I)-(VII). We have also investigated both 1-butyl-2,3-dimethylimidazolium ($[\text{bm}_2\text{im}]^+$) and 1-butyl-2,3,4,5-teramethylimidazolium ($[\text{bm}_4\text{im}]^+$) based salts.

Experimental.

An ATR-IR accessory (“Golden Gate”, Specac, Ltd., UK) that utilises a diamond as the ATR crystal was used to obtain IR spectra, which were measured on an Equinox-55 FTIR spectrometer (Bruker, Germany) with MCT detector and a resolution of 2 cm^{-1} . A small droplet of ionic liquid was placed on the top of the diamond crystal as shown in Figure 1.

Single reflection ATR (incident angle 45°) ensures that the IR bands of vibrational modes of water dissolved in ionic liquids are not off-scale due to very short effective path length. This also has the advantage of minimising usage of the sample since very small amounts of RTILs were required to cover the 4 mm^2 surface of the diamond. The evanescent wave that forms in ATR (as schematically shown by the exponential line in Figure 1) probes a very shallow layer of the sample. Thus, the depth of penetration of the IR beam in this ATR arrangement is *ca.* $0.5 \text{ }\mu\text{m}$ in the region of the $\nu(\text{O-H})$ stretching modes of water. It is difficult to achieve such a small and constant path length in transmission spectroscopic cells. This advantage of ATR-IR spectroscopy has been widely utilised to analyse aqueous solutions. High-pressure *in situ* ATR-IR spectroscopy has recently been applied to measure spectra of CO_2 dissolved in ionic liquids⁸ and measure spectra of high-pressure gases, supercritical fluids and near-critical water.²⁰ An additional advantage of the ATR-IR approach is the ease of heating the diamond ATR element, which allowed us to measure the temperature dependence of IR spectra of RTILs and to monitor drying of RTILs upon heating. Karl-Fischer titrations were conducted using a Metrohm 737 KF Coulometer. $^1\text{H-NMR}$ data was recorded on a Jeol GSX-270 MHz spectrometer. The resonance frequency of deuterium in the solvents was used as an internal reference, which had a purity of $> 95 \%$.

Syntheses

Unless otherwise stated ALL reactions were conducted in an anaerobic atmosphere of nitrogen. Solvents were distilled from the relevant drying agents prior to use. Toluene was stored over Na and distilled (benzophenone used as a moisture indicator). Ethylacetate and dichloromethane were distilled from CaH_2 . 1-methylimidazole and 1,2-dimethylimidazole were distilled from KOH. 1,2,4,5-tetramethylimidazole was sublimed

under vacuum prior to use. 1-chlorobutane and 1-iodobutane were washed with concentrated H₂SO₄ then distilled from P₂O₅. Chloride content of the ionic liquids was determined by a AgNO₃ test. AgCl has a solubility of 1.4 mg l⁻¹ in water, hence all of the ionic liquids synthesised will have a chloride content below this value. Full experimental details for all ionic liquids have been deposited as supplementary materials.[†]

1-Butyl-3-methylimidazolium Chlorides - [bmim]Cl & [bmmim]Cl

To a vigorously stirred solution of 1-methylimidazole or 1,2-dimethylimidazole (1.25 mol) in toluene (125 cm³) at 0°C 1-chlorobutane (144 cm³, 1.38 mol) was added. The solutions were heated to reflux at *ca.* 110°C for 24 hours, after which there were placed in a freezer at *ca.* -20°C for 12 hours. The toluene was decanted from the remaining viscous oils/semi-solids and re-crystallized from acetonitrile and then repeatedly re-crystallized from ethylacetate to yield white crystalline solids, which were dried *in vacuo* to give [bmim]Cl and [bmmim]Cl in approximately 86 to 90 % yield and were characterised by ¹H-NMR and mass spectrometry.

1-Butyl-3-methylimidazolium

[Anion] = PF₆, BF₄, ClO₄, CF₃CO₂, CF₃SO₃, (CF₃SO₂)₂N, SbF₆, NO₃

and 1-butyl-2,3-dimethylimidazolium ionic liquids

[Anion] = PF₆, BF₄, ClO₄, CF₃CO₂, CF₃SO₃, (CF₃SO₂)₂N, SbF₆, NO₃

The respective metal salt (0.32 mol), required to give the desired ionic liquid, was added to a solution of either [bmim]Cl or [bmmim]Cl (0.29 mol) in dichloromethane and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the organic phase repeatedly washed with small volumes of water (*ca.* 30 cm³) until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated

AgNO₃ solution. The organic phase was then washed a further two times with water to ensure complete removal of the chloride salt. The solvent was removed *in vacuo* and the resulting ionic liquid stirred with activated charcoal for 12 hours, after which the ionic liquid was passed through a short alumina column(s) (acidic and/or neutral) to give a colourless ionic liquid, which was dried at *ca.* 100°C *in vacuo* for *ca.* 24 hours or until no visible signs of water were present in the IR spectrum (CaF₂ plates). Yields generally 70 to 80 %. The ionic liquids were characterised by ¹H-NMR and mass spectrometry.

1-Butyl-2,3,4,5-tetramethylimidazolium Iodide - [bm₄im][I]

To a vigorously stirred solution of 1,2,4,5-tetramethylimidazole (25 g, 0.201 mol) in toluene (100 cm³) 1-iodobutane (27.5 cm³, 0.242 mol) was added. The solution was heated and refluxed at *ca.* 110°C for 24 hours, after which it was placed in a freezer at *ca.* -20°C for 12 hours. The toluene was decanted and the remaining viscous oil/semi-solid repeatedly re-crystallized from ethylacetate to yield an off-white semi-crystalline solid, which was dried *in vacuo* to give [bm₄im]I in approximately 85 % yield, which was stored in the dark and characterised by ¹H-NMR and mass spectrometry.

1-Butyl-2,3,4,5-tetramethylimidazolium [bm₄im] Salts

[Anion] = PF₆, BF₄, (CF₃SO₂)₂N

The respective metal salt (53.5 mmol), required to give the desired ionic salt/liquid, was added to a solution of [bm₄im]I (15g, 48.6 mmol) in dichloromethane and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the organic phase reduced *in vacuo*. This was then re-dissolved in diethylether and repeatedly washed with small volumes of water (*ca.* 30 cm³) until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated AgNO₃ solution. The organic phase

was then washed a further two times with water to ensure complete removal of the chloride salt. Removal of the organic solvent *in vacuo* gave either solids (with [PF₆]⁻ and BF₄) or a viscous tar (with [(CF₃SO₂)₂N]⁻). Yields generally 70 to 80 %. The ionic liquid/solids were characterised by ¹H-NMR and mass spectrometry.

Results and discussions

The IR spectrum of water is one of the most studied among the spectra of the polyatomic molecules. The water molecule has C_{2v} symmetry with three IR active vibrations. One can, however, observe more than three bands in the IR spectrum of water due to the appearance of combination, librational and overtone bands. The IR band corresponding to the bending mode (ν_2) of water (either pure or dissolved in solvents) usually absorbs in the region 1595-1650 cm⁻¹. However, this band alone is seldom used to elucidate the molecular state of water. By contrast, stretching vibrational modes of water have been extensively used to study the molecular state of water dissolved in various solvents and absorbed in many materials, such as polymers.^{11,14,21} The IR bands corresponding to antisymmetric (ν_3) and symmetric (ν_1) stretching modes of water usually lie in the region 3000-3800 cm⁻¹. The position and intensity of these bands are very sensitive to the water environment and to the state of water association *via* H-bonding. The ν_3 and ν_1 bands in water vapour absorb at 3756 and 3657 cm⁻¹ respectively;^{22,23} these bands shift to lower wavenumber when water interacts with the environment (e.g. water dissolved in a solvent or sorbed into a polymer). The difference in the maximum positions of these bands is *ca.* 100 cm⁻¹ in the case of water bound in symmetric complexes, with both protons of water participating in H-bonding. In the IR spectrum of liquid water the ν_3 and ν_1 bands appear to merge, producing a broad band with the peak maximum at *ca.* 3300 cm⁻¹ (the dashed

line in Figure 2). In fact, this band is comprised of the ν_3 and ν_1 bands that broaden considerably due to the effect of H-bonding. Fermi resonance between ν_1 and $2\nu_2$ further complicates the structure of the broad band at *ca.* 3300 cm^{-1} . As mentioned, it is rather difficult to deduce information on the molecular state of water dissolved in various solvents based on the shifts of the stretching bands of water. The reason for this is that there is a strong coupling between the ν_3 and ν_1 bands. The use of HDO molecules provides a possibility to overcome this problem and has been successfully used to study the state of water dissolved in organic solvents. The presence of HDO molecules is usually easy to achieve by adding small amounts of D_2O into H_2O . However, the danger of isotope exchange with solvent molecules, especially when the solvent possesses acidic protons, as in the case of the cations in ionic liquids is present. Moreover, it is the presence of H_2O in RTILs absorbed from the atmosphere or as a byproduct from synthetic routes that affects the properties of RTILs, which is of major interest. Therefore, our analysis of the molecular state of water will be based mostly on H_2O , supported by additional measurements of HDO in RTILs.

Figure 2 presents ATR-IR spectra of the RTIL, (III) and liquid water in the $\nu(\text{O-H})$ region. Two distinct bands corresponding to the ν_3 and ν_1 modes of water dissolved in (III) are shown to absorb at 3640 and 3560 cm^{-1} . The IR spectrum of liquid water is shown for comparison. The position of these two bands of water dissolved in (III) indicates that water molecules are *not* associated into clusters or pools of water, and can be assigned as “free” water molecules interacting *via* H-bonding with the $[\text{BF}_4]^-$ anion. This assignment is consistent with the literature data on the spectroscopic manifestation of the formation of symmetrical complexes of water molecules with weak bases. Two bands at 3640 and 3590 cm^{-1} in the Raman spectrum of water with added NaPF_6 have been previously observed.²⁴ However, the presence of the second band has been assigned

to “electrostatic interactions”, while Scherer²¹ has suggested that the appearance of these bands can be explained by the formation of two weak H-bonds of water molecules with the two anions of the added salt. An analogous spectral picture has been reported for the weakly interacting water involving both its protons in the case of water absorbed into polymers where the interaction with the basic sites of the opposite polymer chains was possible.^{12b}

If RTILs are left open to atmosphere they can easily absorb water. The amount of absorbed water depends on the nature of the RTILs, and would also, of course, depend on the relative humidity and temperature. However, here we are interested in the molecular state of water present in RTIL when they are open to the air at ambient conditions, rather than solubilities of water in RTILs for two-phase systems. The question arises whether the molecular state of water is strongly influenced by its concentration. Figure 3 shows the IR spectra of water in (III) as a function of time upon water absorption into (III) placed on the diamond ATR crystal from the atmosphere. It can be seen that the position of the bands and their shape do not essentially change as a function of concentration, indicating that there is no change in the state of water in the concentrations up to *ca.* 0.8 mol/dm³. The dashed line represents the spectrum of (III) showing the presence of the small but measurable amount of water. The growth of the water bands with time demonstrates that the amount of water in (III) increases due to absorption of water from the atmosphere. We are continuing to investigate the nature of water in RTILs at greater concentrations, which will be reported elsewhere. Another important observation is that heating of (III) at temperatures of 80 °C has resulted in the decrease of the water bands up to their disappearance (not illustrated). The disappearance of the IR bands of water in (III) upon heating indicates that RTILs can be dried by heating and simultaneously monitored *via* spectroscopy for the presence or absence of water.

To determine the effect of the anion on the interaction between water molecules and ionic liquid a range of RTILs with various anions was measured. In these experiments the droplet of ionic liquid was placed on the diamond ATR crystal to allow moisture from the air to be adsorbed at ambient conditions into the ionic liquid until saturation at a given humidity (*ca.* 60-70% at the conditions of our spectroscopic experiments). For quantitative comparison of the solubility of water in different ionic liquids the two-phase system, water/RTIL, has to be studied. However, it is important to stress that here we investigated the molecular state of water based on the positions of the IR bands of water rather than to compare their concentrations based on the intensities of these bands. Seddon and co-workers⁴ have measured water content in some RTILs using the Karl-Fischer titration method. Their results have also been based on the saturation of the ionic liquids by the moisture from the atmosphere. We have shown that the state of water in (III) in the concentration range changing from the dry (III) to the saturated with water when open to air (up to 1 mol/dm^3 for RTILs (I) - (V)) does not depend on the amount of water present. The concentration range of the water absorbed into these RTILs has been estimated using a molar absorptivity of the stretching bands of water²⁵ dissolved in CH_2Cl_2 . The molar absorptivity (ϵ) based on the peak intensity for the ν_3 band of water dissolved in CH_2Cl_2 is *ca.* $100\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. Then, following the Lambert-Beer law ($A = \epsilon cl$ where c is concentration, and l is the path length), the concentration of water can be calculated. The effective path length for the ν_3 band has been calculated accordingly to Harrick, (taking into account the refractive index of RTILs as 1.467^{1d} and the refractive index of diamond 2.4), which resulted in l being *ca.* $1.1\mu\text{m}$.

The measured ATR-IR absorbance (A) of the ν_3 band of water in [I] in equilibrium with water from the air is 0.004. This results in a concentration of water of *ca.* 0.36 mol/dm^3 . However, the absorbance of the ν_3 band used in our calculation is very small and well

below the typical absorbances used in quantitative calculations. Therefore, we have also measured the spectra of (I) saturated with water using a transmission cell with CaF_2 windows and path length of *ca.* 66 μm . This measurement resulted in the absorbance of the ν_3 band, $A = 0.3$ which is a very reasonable absorbance for quantitative calculations. Calculated concentration of water in (I) in this case is *ca.* 0.45 mol/dm^3 , which is in good agreement to the estimated concentration, based on ATR-IR data. It should be noted that in our calculations the assumption was made that the molar absorptivity of the IR bands of water are similar to the absorptivity of these bands of water dissolved in CH_2Cl_2 . The measured absorbance of the ν_3 band of water in (III) in equilibrium with air exceeds the absorbance of this band of water in (I) by a factor of two, thus resulting in the water content *ca.* 0.9 mol/dm^3 . This result is consistent with our (see below) measurements *via* Karl-Fischer titration of the water content sorbed into (I) and (III) from the air and are in agreement with those by Seddon and co-workers.⁴ Transmission spectroscopy has also been used to analyse the combination band $\nu_3 + \nu_2$ of water dissolved in (I). Additional evidence for H-bonding of water dissolved in (I) has been provided by the observation of the combination band of water ($\nu_3 + \nu_2$) in (I) using transmission cell with the path length of *ca.* 120 μm . The band has its peak maximum at 5273 cm^{-1} and the half-width of the band is *ca.* 60 cm^{-1} . The position of this band provides additional evidence that water in (I) is weakly H-bonded. This conclusion is based on the comparison with the literature data on the position of this combination band of water in various solvents,²² which places (I) between CCl_4 and polycarbonate in the strength of these bases to H-bond with water. Figure 4 shows the ATR-IR spectra in the region 3700-3000 cm^{-1} for $[\text{bmim}][\text{CF}_3\text{CO}_2]$, and shows that the state of water does not change as a function of its concentration within the range that is achieved by absorption of water from the atmosphere at ambient temperature. The shape of the band in $\nu(\text{O-H})$ region is remarkably different from the

absorption in this region in the case of (III), nevertheless, this shape remains essentially un-changed upon heating of this RTIL, indicative that although the state of water in this RTIL is different from that in (III) it does not change as a function of water concentration (however, the appearance of a weak band at *ca.* 3670 cm^{-1} will be discussed below). Additionally, heating this RTIL has resulted in the total removal of measurable amounts of water, indicated by the bottom line in the Figure 4.

Figure 5 shows the comparison of the IR spectra of the different RTILs in the $\nu(\text{O-H})$ region after each of the ionic liquids was placed on the diamond ATR crystal and exposed to the atmosphere. It is important to note that dry ionic liquids do not have absorptions in this region. This was confirmed by heating the ionic liquids placed on the diamond to temperatures of 80-100 $^{\circ}\text{C}$ to remove any residual water. The appearance and growth of the bands in the $\nu(\text{O-H})$ region was detected after the samples were cooled down to the room temperature. Two bands corresponding to the ν_3 and ν_1 can be identified in the nine studied ionic liquids and the maxima of the positions of these bands are summarised in the Table 1. By contrast, spectra of the two other ionic liquids (VI and VII) presented in Figure 5 do not show well-resolved structure in their spectra in this region and are dominated by strong broad bands. Molecules of water dissolved in six ionic liquids consisting of either $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{BF}_4]^-$, $[\text{ClO}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[(\text{CF}_3\text{SO}_2)\text{N}]^-$ anions are “free” water molecules, interacting *via* H-bonds with the anions in a symmetric complex (both protons of water bound to two discrete anions): $\text{A}^- \cdots \text{H-O-H} \cdots \text{A}^-$ (where A^- represents the anion in RTILs). Additional support for the assignment of the molecular state of water in RTILs (I)-(V), and (XIII) stems from the two following observations. Firstly, the difference in the positions of the ν_3 and ν_1 bands of water ($\nu_3 - \nu_1$) remains almost constant within the range of 70-80 cm^{-1} for the studied RTILs, indicating a similar type of bonding of water. It has been found earlier that such

difference is characteristic for 2:1 complexes of water.^{14,21} Moreover, Ford and co-workers¹⁷ have analysed a very broad range of binary water-solvent mixtures, and found that for 2:1 complexes between solvent and water molecules the following relationship takes place between the shifts of the ν_3 and the ν_1 bands of water molecules: $\Delta\nu_3 = 1.17\Delta\nu_1 - 0.66$. It can be seen from Table 2 that shifts of the ν_3 and the ν_1 bands of water molecules in the six of the RTILs studied roughly follow the above relationship for 2:1 complexes of water. Thus, taking into account all spectral information we conclude that most of the water molecules absorbed from the atmosphere into the eight RTILs presented in Tables 1 and Table 2 are H-bonded *via* both hydrogen atoms of water to the two anions of RTILs. Table 1 also includes data from the literature on the wavenumbers of the stretching modes of water dissolved in some selected organic solvents for 2:1 complexes of water. This shows that the state of water in the concentration range 0.2 – 2.0 mol/dm³ absorbed from the air compares well with the state of water in these selected organic solvents.

The broad $\nu(\text{O-H})$ bands of water in the ionic liquids with $[\text{NO}_3]^-$ and $[\text{CF}_3\text{CO}_2]^-$ anions indicates the presence of water aggregates or other types of water association. The shape of the $\nu(\text{O-H})$ band in the $[\text{NO}_3]^-$ based RTIL has a visible shoulder at *ca.* 3530 cm⁻¹, which could represent the antisymmetric stretching mode of water H-bonded with an anion. Nevertheless, the overall broad structure of the band indicates that water clusters or water aggregates may be present. There is also the possibility that several water molecules are interacting with the $[\text{NO}_3]^-$ anions in a slightly different way, with the broad distribution of the water-anion distances resulting in the broad band. This may occur because of the planar symmetry of the nitrate anion. This possibility has been mentioned in related work on the hydration of this anion in aqueous solutions.²⁶ In the case of $[\text{bmim}][\text{CF}_3\text{CO}_2]$ the IR band of water strongly resembles the band of liquid-like

water. At higher water concentrations in this RTIL it was possible to detect a weak band at *ca.* 3670 cm^{-1} (see Figure 4) which can be assigned as the band of water bound weakly to the CF_3 end of the anion, rather than that of most of the water molecules that absorb at *ca.* 3400 cm^{-1} . This is consistent with the previous studies on the interaction of water with anions in aqueous solutions. Thus, Bergsrom and co-workers²⁶ have noted the presence of a high-wavenumber OD stretching band when studying the hydration of the $[\text{CF}_3\text{COO}]^-$ anion with HDO. The molecules of water that produce a broad band in the region around 3400 cm^{-1} represent water interacting strongly with the COO^- end of the anion and water forming aggregates around this anion. The support for the strong interaction between water molecules and the COO^- end of the anions comes from the observation of the shoulder with the low frequency shift (*ca.* 10 cm^{-1}) of the carboxyl band of this anion in the presence of water (Figure 6). This shift provides direct evidence that water molecules are bound to the COO^- end of the anion since the $\nu(\text{COO}^-)$ band shifts down in wavenumber. It was also possible to bind all COO^- moieties with water, when water was deliberately added into (VII), which was evident by the disappearance of the initial band at 1680 cm^{-1} . Assignment of the resultant spectrum is somewhat complicated due to the presence of the bending mode of water in the proximity of the shifted $\nu(\text{COO}^-)$ band. Therefore, these measurements were repeated by adding D_2O (since its bending band absorbs at lower wavenumbers, and thus does not interfere with the $\nu(\text{COO}^-)$ band), which has allowed observation of the $\nu(\text{COO}^-)$ as a single band at 1670 cm^{-1} indicative that all anions are bound to water *via* the COO^- group (Figure 7).

The important implications of these findings is that H_2O dissolved in some ionic liquids with a stronger anion basicity (such as $[\text{CF}_3\text{CO}_2]^-$) can form aggregates or, perhaps, even droplets of the bulk liquid-like water in ionic liquids, which is evidenced by a broad band at *ca.* 3400 cm^{-1} . Strong interactions of water with the anions and the

formation of associated water could be a precursor of the water miscibility with nitrate- and trifluoroacetate-based (VI and VII) ionic liquids.

The strength of H-bonding between H₂O molecules and anions can be estimated from the wavenumber shift ($\Delta\nu$) between ν_3 of the water in the vapour phase and ν_3 of the water dissolved in RTILs (for RTILs where separated bands due to the ν_3 and ν_1 bands are observed), by using the relationship:

$$\Delta H = -80(\nu_3^{\text{vapour}} - \nu_3^{\text{IL}}) / \nu_3^{\text{vapour}}$$

(where ΔH is an enthalpy of H-bonding in kcal/mol, ν_3^{vapour} is the wavenumber of the ν_3 of water in vapour, and ν_3^{IL} is the wavenumber of the ν_3 band of water in a RTIL). The corresponding enthalpies for the interaction of water with different anions in ionic liquids are summarised in Table 2. The calculated energies based on the spectral shifts of the ν_3 band places the anions of the corresponding IL in the strength of the interaction with water in the order: $[\text{PF}_6]^- < [\text{SbF}_6]^- < [\text{BF}_4]^- < [(\text{CF}_3\text{SO}_2)_2\text{N}]^- < [\text{ClO}_4]^- < [\text{CF}_3\text{SO}_3]^- < [\text{NO}_3]^-$. Additional support for this correlation stems from the investigation of the position of the bending mode of water (ν_2) dissolved in the studied RTILs (Table 1). It is known that the maximum of the IR band of the bending mode of water shifts to the higher wavenumber compared to the free water in gaseous state as a result of hydrogen bonding. Indeed, the data presented in Table 1 show that the frequency of the bending mode increases in the order $[\text{PF}_6]^- < [\text{BF}_4]^- < [\text{CF}_3\text{SO}_3]^- < [\text{NO}_3]^-$ reflecting the same order of the strength of interaction between water molecules and anions in RTILs as was revealed from the bands corresponding to the stretching mode region.

The comparison of our spectroscopic results with the studies of water/salt/CH₂Cl₂ systems²⁷ and with studies of isotopically dilute HDO molecules of water²⁸ shows that

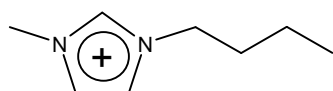
the relative order of the interaction of water with anions in the systems containing the same anions as in the RTILs studied here is identical. Our findings are also consistent with the work on the interaction between methanol and various anions,²⁹ where exactly the same trend of basicity of the anions was shown, based on the shifts of the $\nu(\text{O-H})$ band of methanol dissolved in solutions of salts in CH_2Cl_2 . The $\nu(\text{O-H})$ band of methanol dissolved in (I) appeared at *ca.* 3618 cm^{-1} , which coincides with the position of the $\nu(\text{O-H})$ band of methanol in a solution of containing $[\text{PF}_6]^-$ in CH_2Cl_2 , which has been reported.²⁹ This also indicates that the relative basicity of anions in dilute solutions and in ionic liquids is similar. It is important to note that in the latter case methanol was dissolved in RTILs in the absence of any other solvent. In both cases the corresponding spectral shifts of the $\nu(\text{O-H})$ bands (for water and methanol weakly bound to the anions) appeared similar. This implies that, as suggested by Seddon and co-workers,^{4a} anions play a major role in solubility and the miscibility of water with RTILs, while cations probably play a secondary role. Support for the last statement also comes from the measurements of the two RTILs (I and III), in which one of the hydrogen atoms was substituted by a CH_3 group. As Figure 8 shows, the positions of water bands in such ionic liquids based on the $[\text{PF}_6]^-$ anion are almost exactly the same. Seddon and co-workers^{4a} have studied the water content of several RTILs in which the absorption of water from the atmosphere at ambient temperature was measured as a function of time. Their trend in water content is consistent with our scale of the strength of the interaction between water molecules and the anion in RTILs. Brennecke has reported preliminary results on the measurements of water solubilities³⁰ in two phase system of water/(I). Our spectroscopic study provides an additional insight into the state of water dissolved in RTILs open to the air at ambient conditions and shows that “molecularly dispersed”, H-bonded to anions water is a major state of water molecules dissolved in RTILs *via*

absorption from the atmosphere at concentrations in the range 0.2 – 2.0 mol/dm³. Nevertheless, we cannot exclude the presence of water-water aggregates in these RTILs at higher water concentrations when water is added into these RTILs. Indeed, addition of water into (I) to achieve saturation conditions (*ca.* 2 w/w % at room temperature) of water, and transmission spectroscopy with a longer path length (60 μm) was used, and we were able to detect a weak, broad band, with the maximum at 3473 cm⁻¹, along with the strong bands at 3672 and 3595 cm⁻¹. The latter two bands correspond to the water interacting with anions in RTILs, as discussed before, whilst the former corresponds to the water aggregates, probably forming around those molecules of water that have already H-bonded to the anions. This demonstrates the power of IR spectroscopy in studying water content in RTILs, while the gravimetric measurements of water in RTILs³¹ do not provide information on the state of water in RTILs when water is added deliberately. In such cases the molecular state of water can change as a function of water concentration, thus complicating any type of modelling of the quantitative results for water absorption. The quantitative measurement of water/RTIL two-phase systems deserves a separate study via IR spectroscopy.

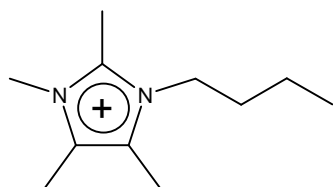
We have also investigated the imidazolium $\nu(\text{C-H})$ stretching region of the RTILs spectra (3200-3000 cm⁻¹). One would expect a shift in the position of that $\nu(\text{C-H})$ bands, if significant hydrogen bonding between the acidic protons of the imidazolium ring and water were present. However, our spectra show negligible changes in this region in going from dry to wet ionic liquids. The $\nu(\text{C-H})$ bands are sensitive to the nature of the *anion* of the dry ionic liquid. Analysis of the spectra in this region clearly indicate a cation-anion interaction that increases in the order [PF₆]⁻, [BF₄]⁻, [(CF₃SO₂)₂N]⁻, [ClO₄]⁻, [CF₃SO₃]⁻, [NO₃]⁻ and [CF₃CO₂]⁻. This is consistent with a possible formation of a

cation-anion hydrogen bond. We are continuing to investigate these phenomena and will report our results elsewhere.

In addition, the possible effect of the acidic ring protons of the imidazolium ring cation on the molecular state of water has also been studied. Although spectroscopic evidence reported above strongly supports that water molecules preferably interact with anions, there is, in principal, a possibility that water may interact *via* H-bonding between the oxygen atom and acidic protons in the imidazolium ring. Therefore, it is important to study the molecular state of water in RTILs, where all or some of the hydrogen atoms on the imidazolium ring have been substituted with CH₃ groups (chemical structures of such cations presented schematically below).



1-butyl-3-methylimidazolium cation



1-butyl-2,3,4,5-tetramethylimidazolium cation

RTILs comprising of the 1-butyl-2,3-dimethylimidazolium cation with [PF₆]⁻, [BF₄]⁻ and [(CF₃SO₂)₂N]⁻ anions (VIII, IX and X correspondingly) along with 1-butyl-2,3,4,5-tetramethylimidazolium [bm₄im] [BF₄]⁻ and [(CF₃SO₂)₂N]⁻ have been investigated and their ATR-IR spectra have been recorded. Analysis of the ν(O-H) region of VIII and IX has demonstrated that there is no effect substituting a proton for a methyl group at the C2 position of the imidazolium ring of VIII and IX. Figure 8 shows the ν(O-H) bands of water in the ATR-IR spectra of (I) and (VIII). The positions and shapes of the ν₁ and ν₃ bands of water absorbed from the air into these two RTILs are very similar, indicating

that substitution of the C2 proton in the imidazolium ring with a CH₃ group has no effect on the molecular state of water. Nevertheless, the substitution of one of the hydrogen atoms in the imidazolium ring (even the most acidic one), does not exclude the possibility of interactions between water molecules and the remaining acidic protons of the imidazolium ring. To this end, we have studied the IR spectra of RTILs with all of the H atoms of the imidazolium ring substituted by CH₃ groups. Perhaps surprisingly, the 1-butyl-2,3,4,5-tetramethylimidazolium-based salt with the [BF₄]⁻ anion (XI) is a solid at room temperature. It is surprising as one would expect that with the absence of the acidic protons of the imidazolium ring the interaction of the cation with the anion would be weaker, therefore favouring a liquid state. The ATR-IR spectrum of (XI) has been recorded, which showed no evidence of water (up to the limit of the detection *via* single reflection ATR-IR spectroscopy). Nevertheless, a small amount of water was deliberately added to (XI) and the ATR-IR spectra recorded. The weak bands corresponding to the ν_1 and ν_3 bands of water in (XI) have been detected. The wavenumbers at the maximum of each band being almost exactly the same as the wavenumbers at the maximum of the ν_1 and ν_3 bands of water dissolved in (III). This observation suggests that the water molecules dissolved in (XI) interact in similar way with its surrounding as water molecules dissolved in (III).

Although (III) and (XI) comprise of the same anions, these RTILs exist in different physical states. In order to prove the concept that the acidic protons in the imidazolium ring have no effect on the molecular state of water analogous imidazolium salts (with and without acidic protons) need to be measured in the same physical state. To this end, the ATR-IR spectrum of [bmim][CF₃SO₂]₂N⁻ (XIII), was compared with the ATR-IR spectrum of (XII), where all of the ring hydrogen atoms have been substituted by CH₃ groups. Figure 9 shows the $\nu(\text{O-H})$ region of the IR spectra of (XII) and (XIII). The

absence of the imidazolium ring hydrogen atoms is clearly seen in the spectrum of (XII), by the absence of the bands in the region around 3100 cm^{-1} . There is a strong doublet, which can be attributed to water. Indeed, two overlapping bands at 3605 and 3544 cm^{-1} indicate that water molecules have been absorbed into (XII) from the air. The similarity of the spectra of the water molecules absorbed into (IV) and (XII) (based on the wavenumbers at the maximum of the bands) suggests that water molecules are H-bonded to the anions in (XII). In the region of the bending mode of water there is a relatively strong band at 1633 cm^{-1} (not illustrated) that also supports weak H-bonding between water molecules and (XII). Most importantly, Figure 9 demonstrates that the absence of acidic protons in the imidazolium ring *increases* the amount of absorbed water since there were relatively weak bands due to water being absorbed into (XIII), compared with water absorbed into (XII). As the hydrogen bond donor ability of the cation decreases {XIII >XII} the strength of the hydrogen bond between water and the anion increases. This can be interpreted as arising from a competition between the imidazolium ring and water for the hydrogen bond acceptor sites of the anions. We can also tentatively explain the difference in the amount of absorbed water from the air into these analogous RTILs by the suggestion that introducing CH_3 groups into the imidazolium ring creates more free volume in (XII) compared to (XIII), thus allowing water molecules to reach their preferred sites of interaction more easily. Nevertheless, this is very strong evidence that the preferred sites of interaction with water molecules are the anions in RTILs as has been demonstrated above for other RTILs discussed in this paper.

Table 3 shows the amount of water absorbed by ionic liquids after 24 hours exposure to the atmosphere at the relative humidity of 59%, using Karl Fischer titration methodology. The results for the trifluorosulphonimide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ based ionic liquids are consistent with the results obtained using ATR-IR spectroscopy (see e.g. Figure 9). As the protons

on the imidazolium ring are replaced with methyl groups the amount of absorbed water increases. This supports our proposal that acidic protons of the imidazolium ring do not play a direct role in water absorption and H-bonding with water molecules. Additional trends that can be deduced are that ionic liquids with analogous cations but differing anions show that the uptake of water is more pronounced for $[\text{BF}_4]^-$ based ionic liquids and follows the general trend: $[\text{PF}_6]^- < [(\text{CF}_3\text{SO}_2)_2\text{N}]^- < [\text{BF}_4]^-$.

Finally, experiments where small amounts of D_2O were added into the studied RTILs that had already been saturated by water from the atmosphere. This resulted in appearance of the bands of D_2O dissolved in these RTIL as well as HDO, due to the isotope exchange with H_2O . The results are summarised in Table 4. The positions of the ν_3 (D_2O), ν_1 (D_2O), ν (OH) in HDO and ν (OD) in HDO in RTIL (I)-(VI) confirm the same trend of the basicity for anions in RTIL. The positions for ν (OD) in HDO in RTIL (I)-(V) are very similar to the position of this band for the same anions in aqueous solution,^{26,28} and this provides an opportunity to study the hydration of anions in RTIL further. Previously it has been shown³² that the ν (OD) in the bulk, liquid HDO absorbs at 2509 cm^{-1} while the corresponding band affected by the cation (Bu_4N^+) absorbs at 2524 cm^{-1} , these values are much lower than the measured bands of the $\nu(\text{OD})$ for HDO in studied RTIL, thus supporting the assignment of these bands as affected by anions in RTIL.

Our findings on the interactions between water and ionic liquids are also consistent with our previous report on the Lewis acid-base interactions between CO_2 and two ionic liquids, where it has been shown that $[\text{BF}_4]^-$ was a stronger base than $[\text{PF}_6]^-$ in corresponding RTILs. In both these cases, H_2O and CO_2 , the anions appear to play a major role in interactions acting as a base towards these solutes. However, it was difficult to quantify the strength of the anions acting as a Lewis base towards CO_2 molecules. Fortunately, the IR bands corresponding to the stretching modes of water act

as a sensitive probe of the anion basicity in ionic liquids, and a quantitative estimation of the anions relative basicity was possible in this work.

Conclusions and implications

ATR-IR spectra of water absorbed into several ionic liquids from the air have been investigated. The presence of two bands corresponding to antisymmetric and symmetric stretching modes of water indicated that molecules of water are present in the “free” (not self-aggregated) state bound to the basic anion *via* H-bonding. The shift of the antisymmetric stretching band has been used to correlate the relative strength of the interaction between water and RTILs with different anions. The strength of H-bonding increases in the order $[\text{PF}_6]^- < [\text{SbF}_6]^- < [\text{BF}_4]^- < [\text{ClO}_4]^- < [\text{CF}_3\text{SO}_3]^- < [\text{NO}_3]^- < [\text{CF}_3\text{CO}_2]^-$. The hydration of anions in the first six RTILs from this row appears to be similar to hydration of these anions in the salts with different cations reported previously.²⁷ The energies of H-bonding between water and these RTILs were estimated from the spectral shifts, with enthalpies in the range of 8-13 kJ/mol. It has been shown that basicity of anions in RTILs measured *via* its ability to form H-bonding with water and methanol hardly differs from the corresponding basicities of these anions in dilute solutions of the salts in organic solvents. It has also been found that water can form liquid-like associated aggregates when it is absorbed from the air into RTILs with relatively strong anions such as $[\text{NO}_3]^-$ and $[\text{CF}_3\text{CO}_2]^-$. The presence of such water aggregates in these ionic liquids may have an affect on the reactivity of metal catalysts and other solutes. Water may also act as a co-solvent to dissolve substances that would otherwise not be soluble in RTILs.

The formation of H-bonding between water and anions in RTILs may have several other implications. Firstly, it demonstrates that the origins of water absorption from the air in the studied RTILs arises from the water interactions with anions. The water content in RTILs is also in direct correlation with the strength of these H-bonding interactions. The presence of water in ionic liquids may have important implications on the properties of RTILs as a solvent, such as conductivity, viscosity and diffusivity.³³ In addition, the molecular state of H-bonded water molecules may affect the reactivity of some solutes dissolved in RTILs. It has been shown, for example, that H-bonding of water molecules enhances the basicity of the oxygen atom³⁴ in the water molecules.

† Electronic supplementary information (ESI) available. See <http://www.rsc.org/>

Acknowledgements

We thank EPSRC for financial support, Specac, Ltd. Bruker optics, Ltd. for the loan of equipment, SACHEM for the loan of some ionic liquids ([I]); Prof. B. J. Briscoe, Dr. C., J. Lawrence, Mr. N. M. B. Flichy, Dr. G. G. Martirosyan and Dr. L. Lancaster and for their help and advice.

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Table 1. Wavenumbers (cm^{-1}) of vibrational modes of H_2O in vapour phase, dissolved in RTILs (with [bmim] cation) and organic solvents (for comparison from Refs.^{16,21}).

Anion	ν_3	ν_1	$\nu_3 - \nu_1$	ν_2
Vapour, no anion	3756	3657	99	1595
[PF ₆] ⁻ (I)	3672	3595	77	1610
1,2-Dichloroethane	3671	3592	79	
[SbF ₆] ⁻ (II)	3663	3580	83	
[BF ₄] ⁻ (III)	3640	3560	80	1625
Benzaldehyde	3639	3544	95	
[(CF ₃ SO ₂) ₂ N] ⁻ (XIII)	3637	3560	77	
[ClO ₄] ⁻ (IV)	3613	3540	73	
Acetophenone	3612	3535	77	
[(CF ₃ SO ₂) ₂ N] ⁻ * (XII)	3605	3544	61	1631
[CF ₃ SO ₃] ⁻ (V)	3575	3506	69	1630
Tetrahydrofuran	3572	3499	73	
[NO ₃] ⁻ (VI)	3520	3450	70	1640
[CF ₃ CO ₂] ⁻ (VII)	ν_3 and ν_1 bands merge into a broad band at ca. 3400 cm^{-1}			

* In this RTIL all of the hydrogen atoms on the imidazolium ring have been substituted with CH₃ groups.

Table 2. The shifts of the ν_3 and ν_1 (cm^{-1}) of water in different ionic liquids (with [bmim] cation) compared with the corresponding water bands in vapour.

Anion	$\Delta\nu_3$	$\Delta\nu_1$	$-\Delta H/\text{kcal/mol}$, [kJ/mol]
[PF ₆] ⁻	84	62	1.8 [7.5]
[SbF ₆] ⁻	93	77	2.0 [8.3]
[BF ₄] ⁻	116	97	2.3 [9.6]
[(CF ₃ SO ₂) ₂ N] ⁻	119	97	2.5 [10.5]
[ClO ₄] ⁻	143	117	3.0 [12.5]
[(CF ₃ SO ₂) ₂ N] ⁻ *	151	113	3.2 [13.4]
[CF ₃ SO ₃] ⁻	181	151	3.8 [15.9]
[NO ₃] ⁻	236	207	5.0 [20.1]

* In this RTIL all of the hydrogen atoms on the imidazolium ring have been substituted with CH₃ groups.

Table 3. Water Content of Ionic Liquids exposed to air at relative humidity 59% (determined by Karl-Fischer titrations).

Ionic Liquid	Water Content / ppm
[bmim] [PF ₆]	2,640
[bm ₂ im] [PF ₆]	2,540
[bmim] [BF ₄]	19,500
[bm ₂ im] [BF ₄]	13,720
[bmim] [(CF ₃ SO ₂) ₂ N]	3,300
[bm ₂ im] [(CF ₃ SO ₂) ₂ N]	6,380
[bm ₄ im] [(CF ₃ SO ₂) ₂ N]	33,090

Table 4. Wavenumbers of the stretching vibrational modes (cm^{-1}) of D_2O and HDO dissolved in vapour phase, some ionic liquids and different media.

Anion	ν_3 (D_2O)	ν_1 (D_2O)	ν (OH) in HDO	ν (OD) in HDO
$[\text{PF}_6]^-$	2726	2626	3630	2673
$[\text{BF}_4]^-$	2694	2602	3600	2650
$[\text{ClO}_4]^-$	2665	2592	3570	2634
$[\text{CF}_3\text{SO}_3]^-$			3540	2600
$[\text{ClO}_4]^-$	2665	2592		2634
Vapour	2788	2671		2719
C_6H_6 Ref. ²³	2734	2630		
PMMA ³⁵	2700	2600		2650
PVDF ³⁶	2750	2646	3669	2696

PMMA - poly(methyl methacrylate)

PVDF - poly(vinylidene fluoride)

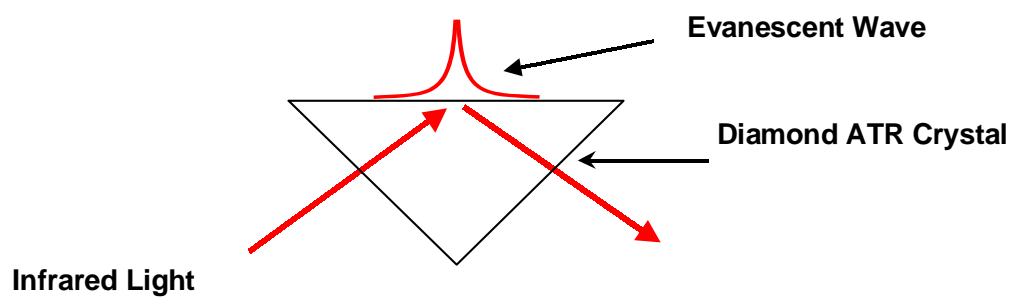


Figure 1. Schematic diagram of the ATR-IR spectroscopic measurement with a single reflection diamond ATR crystal showing formation of an evanescent wave.

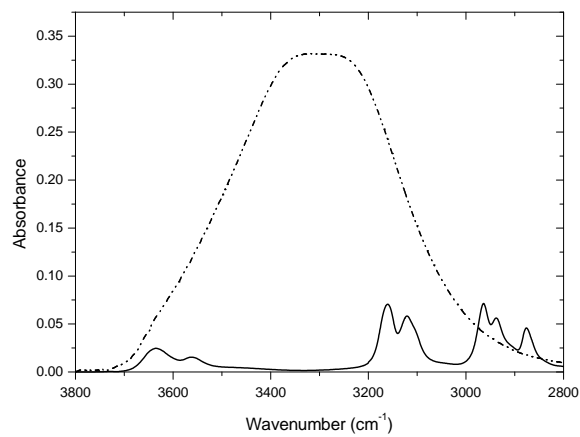


Figure 2. ATR-IR spectra in the $\nu(\text{O-H})$ region measured with a single reflection diamond ATR crystal: spectrum of liquid water (dashed-dotted line), spectrum of RTIL (III) (solid line) showing the bands of water dissolved in (III) at 3640 and 3560 cm^{-1} .

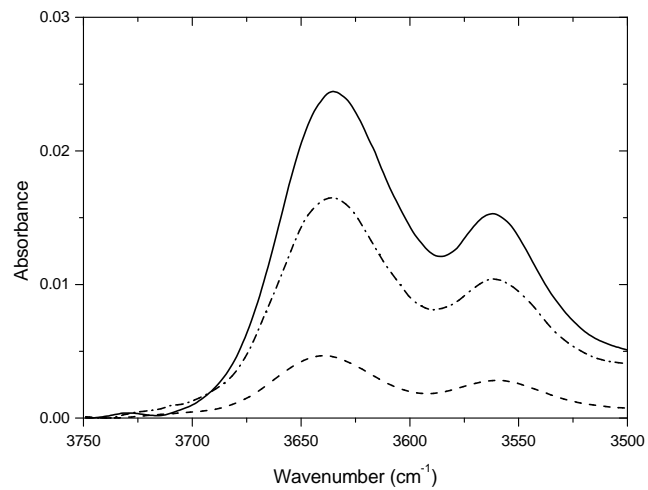


Figure 3. ATR-IR spectra of (III) in the $\nu(\text{O-H})$ region showing the uptake of water from air as a function of time: spectrum of (III) after it has been placed on the diamond ATR crystal

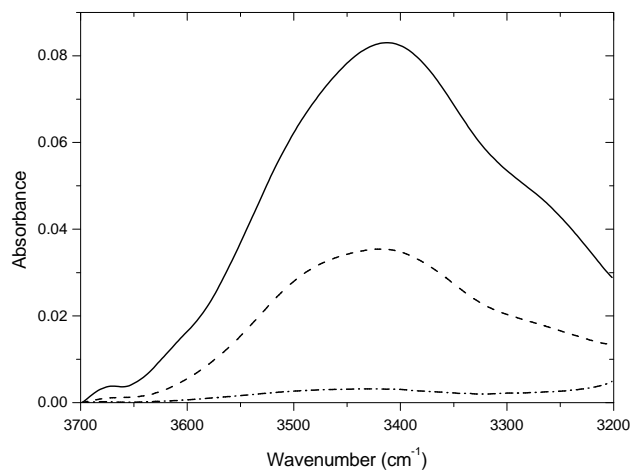


Figure 4. ATR-IR spectra of (VII) in the $\nu(\text{O-H})$ region showing the uptake of water from air as a function of time: spectrum of (VII) immediately after it has been placed on the diamond ATR crystal (dashed-dotted line), spectrum of (VII) after it has been exposed to atmosphere for 90 minutes (dashed line), spectrum of (VII) after it has been saturated by atmospheric water (solid line).

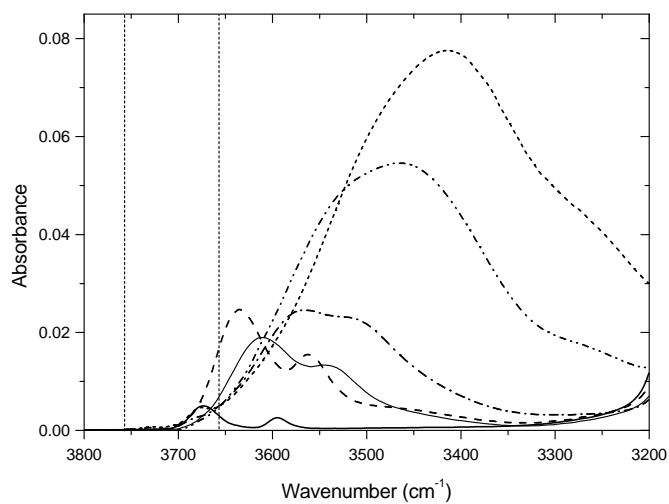


Figure 5. ATR-IR spectra of water in six RTILs: (I) - thick solid line (weak bands at 3672 and 3595 cm^{-1}), (III) – dashed line, (IV) thin solid line, (V) – dashed-dotted line, (VI) – dashed-double dotted line), (VII) – dotted line. Two vertical lines at 3756 and 3657 cm^{-1} indicating position of the ν_3 and ν_1 bands of water vapour are given for comparison.

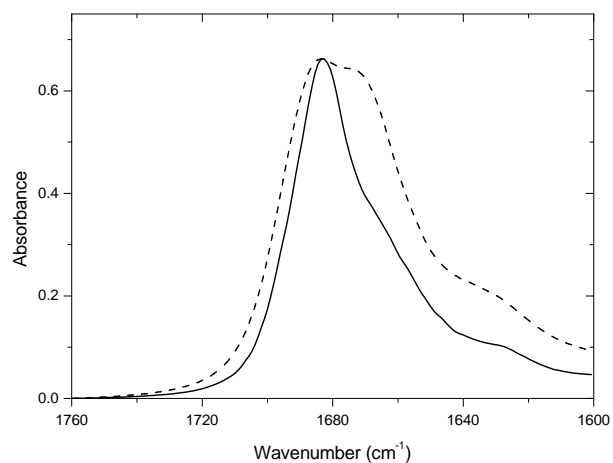


Figure 6. ATR-IR spectra in the $\nu(\text{COO}^-)$ band region for dry (VII) (solid line) and wet (VII) (dashed line), showing appearance of the bending band of water ν_2 at *ca.* 1640 cm^{-1} after (VII) has been saturated by atmospheric water and the appearance of the shifted $\nu(\text{COO}^-)$ band of (VII) at 1670 cm^{-1} .

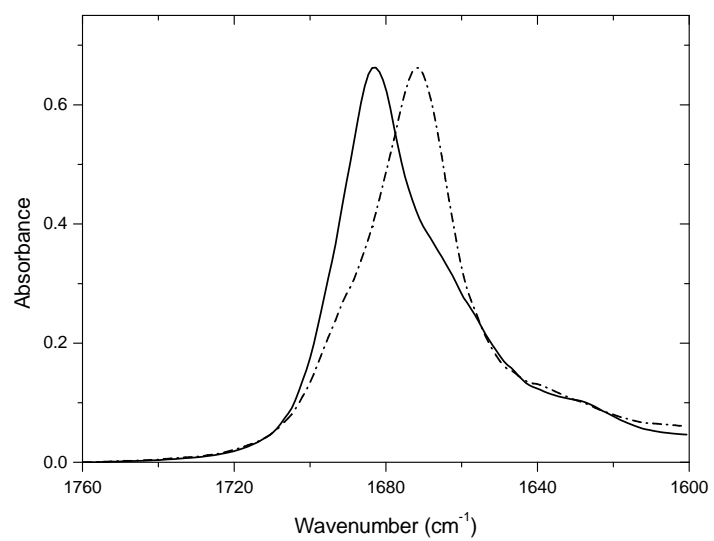


Figure 7. ATR-IR spectra of (VII) in the $\nu(\text{COO}^-)$ band region of showing disappearance of the $\nu(\text{COO}^-)$ band at 1680 cm^{-1} on addition of D_2O resulting in a shift of the $\nu(\text{COO}^-)$ band to 1670 cm^{-1} .

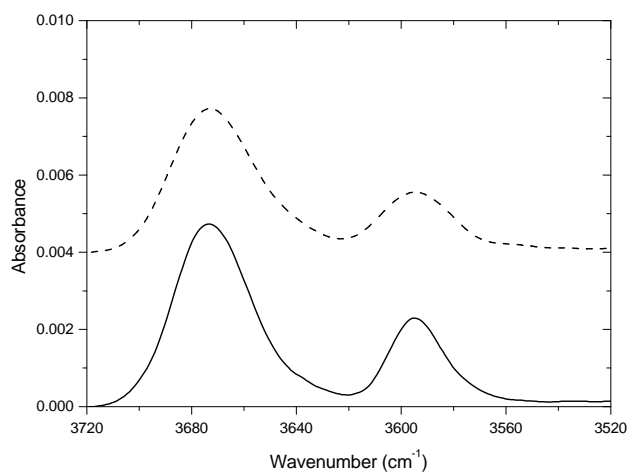


Figure 8. ATR-IR spectra of (I) (top spectrum) and (VIII) (bottom spectrum) in the region of the ν_3 and ν_1 bands of water adsorbed in these RTILs.

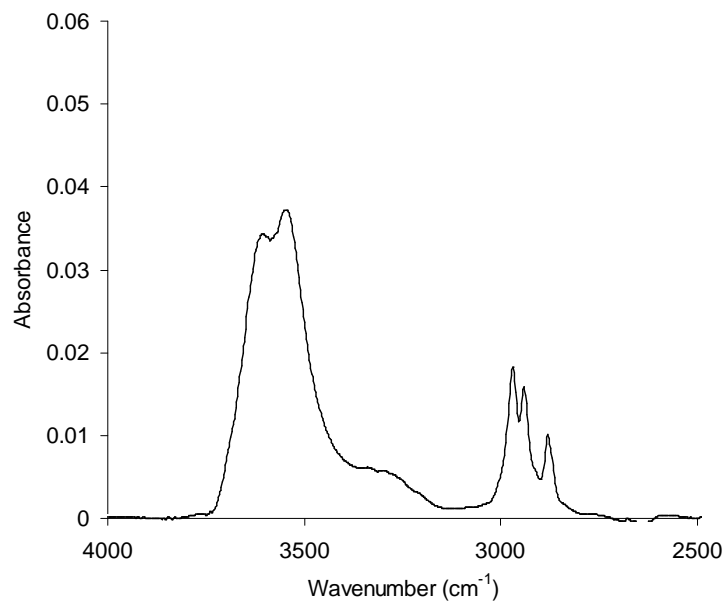


Figure 9. ATR-IR spectra of (XII) (solid line) and (XIII) (dotted line) in the region of the ν_3 and ν_1 bands of water adsorbed in these RTILs.