

Investigation of Binary and Ternary Systems of Ionic Liquids with Water and/or Supercritical CO₂ by in Situ Attenuated Total Reflection Infrared Spectroscopy

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Two commonly used ionic liquids (ILs), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), as well as binary and ternary mixtures of them with water and/or supercritical CO₂ (scCO₂) were investigated by means of infrared spectroscopy at high pressure. The experiments were performed using attenuated total reflection (ATR) infrared spectroscopy on dry and wet ILs at 40 °C and pressures up to 150 bar of scCO₂. The studies indicate that the content of water does not change significantly the solubility of CO₂ in the ionic liquids tested. Furthermore, the presence of water does not change significantly the interaction between the IL anion and CO₂, which explains why the presence of water in IL does not modify the solubility of CO₂ in the system, even in the case of an initial molar ratio of ~50/50 of water in [bmim][BF₄]. We show that despite the limited solubility of water in supercritical CO₂ an ionic liquid can be efficiently dried using scCO₂ extraction even in the case of a hydrophilic ionic liquid (e.g., [bmim][BF₄]). During the scCO₂ extraction, the concentration of water was followed in situ using attenuated total reflection (ATR) infrared spectroscopy. After extraction, no residual water could be detected by this technique, which corresponds approximately to a water concentration of below 320 ppm.

1. Introduction

Ionic liquids (ILs) have gained remarkable attention during the past decade particularly because of their potential utility as green solvents. Negligible vapor pressure, high thermal stability, and the possibility of tuning their physical properties by changing anion and cation are some of the reasons which spurred the interest in ILs. Supercritical carbon dioxide (scCO₂) is very soluble in ILs, while most of the ILs show negligible solubility in scCO₂. This particular phenomenon makes such systems especially attractive which is reflected by the increasing interest for applying ILs for extraction and in catalytic reactions. Recent reviews provide a broad overview of the opportunities ILs can provide and highlight the potential of IL–scCO₂ systems for various applications.^{1,2} Brennecke and co-workers investigated thermodynamic properties of IL–scCO₂ systems^{3–5} as well as their application in extraction.^{6,7} Other groups used IL–scCO₂ systems to improve catalytic processes.^{8–10} We showed recently a repeatable green pathway for hydrogenations, using transition metal nanoparticles stabilized in IL as a catalyst, followed by scCO₂ extraction.¹¹ One of the problems encountered with ILs is the sensitivity of their physical properties toward the amount of impurities.¹² Some ILs are very hygroscopic, and the amount of water, even in small quantity, can for example substantially decrease the activity of a catalyst in an IL.¹³

Aki et al. showed that a small amount of water has no effect on the solubility of CO₂ in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N]. The authors explained this behavior by suggesting that any hydrogen bonding of water with the IL anion does not eliminate anion–CO₂ interactions.⁵ Later, Zhang et al. studied the 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄])–water–CO₂ ternary system below the critical temperature of CO₂ and at

pressures up to 160 bar where the concentration of water is much bigger than the concentration of IL.¹⁴ In that case, CO₂ induces two liquid phases with the IL-rich phase at the bottom and a water-rich phase on top. Ventura et al. focused on another IL–water–CO₂ system at temperatures ranging from 3 to 97 °C where the concentration of IL was not higher than 12 mol %.¹⁵ Under these conditions, the presence of IL enhances the solubility of CO₂ in the (water + IL) system, and the authors attributed this to a salting effect of the IL on the solubility of CO₂. Fu et al. analyzed the effect of water in a 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆])–water–CO₂ system at temperatures ranging from 40 to 60 °C with a water concentration between 0.0067 and 1.6 mass %, and in some of these cases, water had a small influence on the CO₂ solubility.¹⁶

IR spectroscopy has the advantage to be able to quantify the amount of several compounds in a complex sample and also to observe in situ molecular interactions. As an example of a quantification study, the solubility of CO₂ in [bmim][PF₆] at 40 °C under high pressure was published recently.¹⁷ The early work of Cammarata et al. used accurately the infrared spectra of wet ILs (with 8 different anions) to describe the hydrogen bond network as anion···H–O–H···anion.¹⁸ Afterward, molecular organization of a small concentration of water in ILs using IR and Raman spectroscopy was also meticulously analyzed and compared to density functional theory (DFT) calculations to validate this structure of wet ILs.^{19,20} When increasing the concentration of water in ionic liquid (from 10 to 34 mol %), IR spectroscopy was also used to observe the state of agglomeration of water molecules.²¹ For even higher concentrations of water, IL–water systems were investigated by analyzing the CH and OH stretching modes²² and also the BF₄[–] symmetric stretching using Raman spectroscopy.²³ IR spectroscopy demonstrates a great potential to investigate precisely molecular interactions in both IL–water and IL–CO₂

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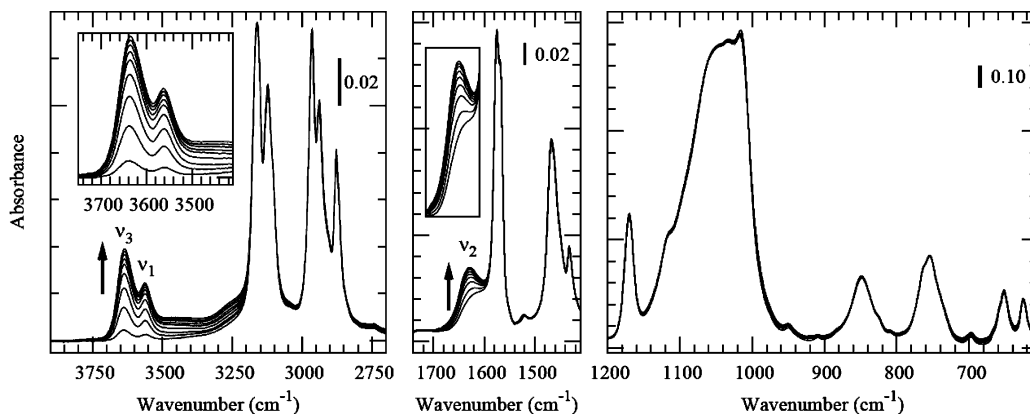


Figure 1. ATR-FTIR spectra of a 1–2 mm layer of slightly wet [bmim][BF₄] at 25 °C after exposure to air (40–50% humidity). Spectra were recorded every 30 min during 4 h. Arrows in the upward direction indicate the water bands increasing with time.

binary systems. Nevertheless, to our knowledge, the case of an IL–water–CO₂ ternary system has not been studied yet using vibrational spectroscopy. Both water and CO₂ molecules were found to be located next to the anion in ILs; however, the few studies^{5,14,16} on these ternary systems do not investigate the effect of a large amount of water on the solubility of CO₂ in ILs.

In the present study, we elucidate the properties of a hydrophilic ([bmim][BF₄]) and a hydrophobic ([bmim][PF₆]) IL under dry and wet conditions at 40 °C and up to 150 bar of scCO₂. The binary systems of IL–water will be compared to the ternary systems under similar conditions. The case of water in CO₂ is not discussed in the present work because it is well-known and described already.^{24,25} Water is soluble in CO₂, and when CO₂ is added to ILs, water is also extracted from the ILs. The extraction of water from ILs using scCO₂ is described in detail in the last part of this study.

2. Experimental Details

The especially constructed high-pressure stainless steel (316 L) cell used in this study with an internal volume of 10 mL is equipped with an attenuated total reflection (ATR) crystal (ZnSe; angle of incidence 60°; 6 active reflections) on the bottom to analyze the liquid phase. The cell has been described in detail elsewhere.²⁶ A PTFE ring was used as sealing between the multiple reflection ZnSe ATR crystal and the cell to avoid any leaking. Spectra were recorded using an EQUINOX-55 Fourier transform infrared (FT-IR) spectrometer (Bruker Optics). ATR spectra were recorded on the range of 4000–600 cm^{−1} with a resolution of 2 cm^{−1} using a liquid N₂-cooled mercury cadmium telluride (MCT) detector. High-pressure CO₂ was fed into the cell using a PM-101 compressor (NWA).

Liquid CO₂ (PanGas; purity 99.9995%) was used as received. [bmim][BF₄] and [bmim][PF₆] (with an initial purity of 99%) were purchased from Acros Organics and ABCR, respectively. Both ILs were dried and cleaned using scCO₂ extraction as described elsewhere.²⁷ The amount of water in the “dry” ionic liquids was below 320 ppm, and the final concentration of Cl[−] was decreased by at least an order of magnitude below 10 ppm.

A typical experiment was realized using 0.3–2 g of IL, which created a thin liquid film of a few millimeters. In the kinetic studies, a spectrum of 128 coadditions was recorded every 5 min to obtain a noise below 0.001 in absorbance. In the other cases, the system was considered to be in equilibrium when the temperature, pressure, and spectrum of the sample were unchanged for at least 30 min. High-pressure experiments were realized at 40 (±1) °C and pressure up to 150 (±1) bar.

Warning. These experiments involve high pressures and should only be carried out with equipment with the appropriate pressure rating.

3. Results and Discussion

3.1. Effect of Water on [bmim][BF₄]. In the case of [bmim][BF₄], water is fully miscible with the IL, and its concentration increases when [bmim][BF₄] is in contact with water. Figure 1 illustrates the water uptake observed with ATR-FTIR spectroscopy of wet [bmim][BF₄], and the amount of water increases due to the absorption from the humidity of air. The evolution of the water bands corresponds to the variation of the concentration of water on the bottom of the film that is in the interface region near the internal reflection element. The symmetric (ν_1) and asymmetric (ν_3) stretching modes of free water are at 3560 and 3640 cm^{−1}, respectively, while the bending mode (ν_2) is at 1635 cm^{−1} being in accordance with the literature.^{18–20,22} Apart from the signal of “free” water molecules (non-hydrogen-bonded with other water molecules), a signal at lower frequency 3500–3100 cm^{−1} also appears, corresponding to the water molecules hydrogen-bonded with other water molecules. While the concentration of water increased, the signal of IL decreased monotonically by 2–3% (corresponding to the small swelling of the IL) with the exception of the broad and very strong [BF₄] band situated at 1100–1000 cm^{−1} which changed slightly in shape. The effect of water on the [BF₄] vibration could be related to the presence of water close to the anion, as explained by Porter et al. using molecular dynamic simulations in the case of 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF₄]²⁸ and already observed by IR spectroscopy as reported in several papers.^{18–20}

3.2. Effect of scCO₂ on [bmim][BF₄]. The binary system [bmim][BF₄]–CO₂ under high pressure has already been studied in the past few years.^{5,29} Infrared spectra of the system at 120 bar and 50 °C were presented and explained in detail by our group recently.³⁰ The evolution of the ATR-FTIR spectra of the binary system up to 100 bar at 40 °C is depicted in Figure 2. The two infrared active vibrations of CO₂, ν_3 asymmetric stretching mode, and ν_2 bending mode are at 2340 and 660 cm^{−1}, respectively. The intensity of these bands increased rapidly with pressure, and they can be used to calculate accurately the concentration of CO₂ in ILs as shown in our previous work.¹⁷ Over these two strong CO₂ bands, some combinations can also be detected as well as a band at 2276 cm^{−1} which could be assigned to a hot band ($(\nu_3 + \nu_2) - \nu_2$)³¹ or more likely to the ¹³C isotope of the ν_3 asymmetric stretching mode.³² While the concentration of CO₂ increased with pressure, the intensity of

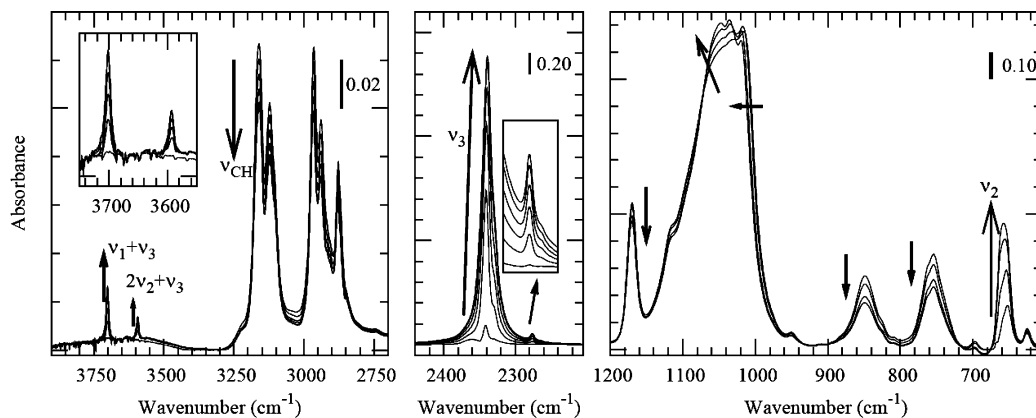


Figure 2. ATR-FTIR spectra of dry [bmim][BF₄] at 40 °C and under a CO₂ pressure of 0, 20, 40, 60, 80, and 100 bar. Arrows show the evolution of intensity of the corresponding bands with pressure.

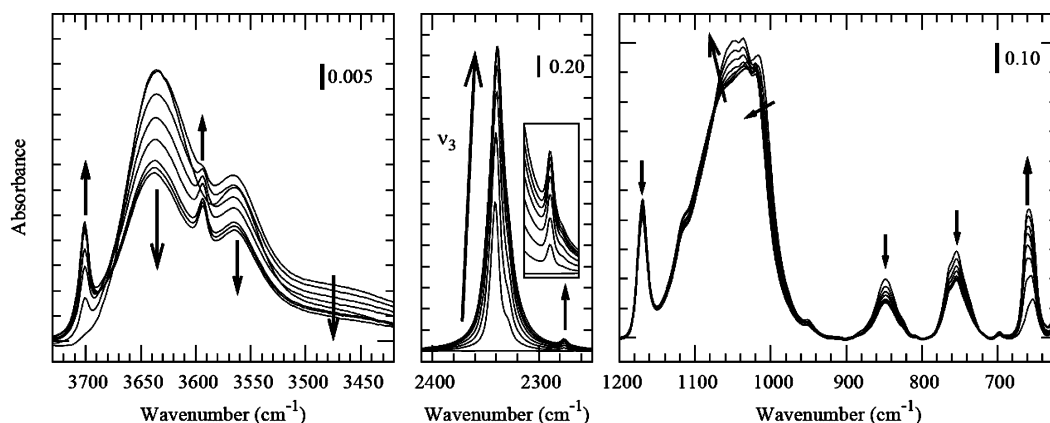


Figure 3. ATR-FTIR spectra of wet [bmim][BF₄] at 40 °C and under a CO₂ pressure of 0, 20, 40, 60, 80, 100, 125, and 150 bar. Arrows show the evolution of intensity of the corresponding bands with pressure.

the bands corresponding to [bmim][BF₄] decreased by 10–20% (except the broad BF₄[−] stretching band at 1100–1000 cm^{−1}), which corresponds to the swelling of the IL. These observations fit well to the evolution of CO₂ solubility in IL and volume expansivity of the IL with pressure reported in the literature.⁵ Apart from these expected evolutions, the broad and strong band of BF₄[−] at 1100–1000 cm^{−1} was shifted to higher frequency, and the intensity of this band increased with pressure. The difference in the evolution of the BF₄[−] vibration band observed in [bmim][BF₄]-water and [bmim][BF₄]-CO₂ binary systems led to the conclusion that the interactions between water and CO₂ with anions are fairly dissimilar. Kazarian et al. explained the organization of CO₂-[bmim][BF₄] under high pressure by the main axis of the O=C=O molecule being perpendicular to the B-F bond of the closest fluorine atom; in that case, the strong interaction was explained to exhibit strong Lewis acid-base interactions,³³ while the organization of water molecules in [bmim][BF₄] is BF₄⋯H-O-H⋯F₄B¹⁸ with a strong electrostatic character of the hydrogen bond of water with anions.²⁰ The BF₄[−] vibrational band in the 1100–1000 cm^{−1} region corresponds to a degenerate antisymmetric stretching mode ($\nu_3 \sim 1100$ cm^{−1}), plus the first overtone of the bending mode ($\nu_4 \sim 530$ cm^{−1}) and a Fermi-resonance between ν_3 and $2\nu_4$.³⁴ Moreover, natural isotopes with an abundance ratio of ¹⁰B and ¹¹B ($\sim 4:1$) also increase the convolution of this band. This makes any explanation for the change of the shape of the BF₄[−] band fairly complicated and highly speculative. Nevertheless, we believe that the modification of this BF₄[−] band is most likely related to the strong Lewis acid-base interaction of CO₂ with the anion. Another possible explanation is the change of

geometry of the cation. DFT calculations of several conformers show that the rotation of the alkyl group of the cation also has an effect on intensities and position of the BF₄[−] vibration bands,³⁵ and as shown by Raman spectroscopy, the addition of CO₂ to ILs has an effect on the geometry (distribution of the dihedral angle) of the butyl group of bmim⁺.¹⁷ The change of distance between the cation and anion could also give a similar change in the band, as explained later for the [bmim][PF₆].

3.3. Effect of Water and scCO₂ on [bmim][BF₄]. The ternary system of [bmim][BF₄]-water-CO₂ was also investigated at different pressures of CO₂ using an initial molar ratio of $\sim 60/40$ for [bmim][BF₄]/water. The evolution of the spectra with increasing pressure up to 150 bar at 40 °C is shown in Figure 3. In this ternary system, the bands of CO₂ were similar (positions and intensities) to those in the CO₂-IL binary system. IL bands were also decreasing in a similar way as in the binary system (except the BF₄[−] band at 1100–1000 cm^{−1}). Water bands ν_3 (3640 cm^{−1}) and ν_1 (3560 cm^{−1}) also decreased when the pressure increased, but the decrease was more prominent than for the IL band. At lower temperature (below the critical temperature of CO₂) similar pressures lead to a three-phase system, liquid-liquid-gas, where the bottom liquid is the IL-rich phase and the top liquid phase is the water-rich phase.¹⁴ We did not observe similar liquid-liquid equilibria at 40 °C. The bending mode of water also decreased, but the quantification was more difficult as the band overlapped with the IL band. The decrease in the intensity of the stretching mode bands of water can be associated to a decrease of the water concentration in the IL due to the solubility of water in scCO₂ (mol fraction 0.42 mol % H₂O in CO₂ at 40 °C and 100 bar in the binary

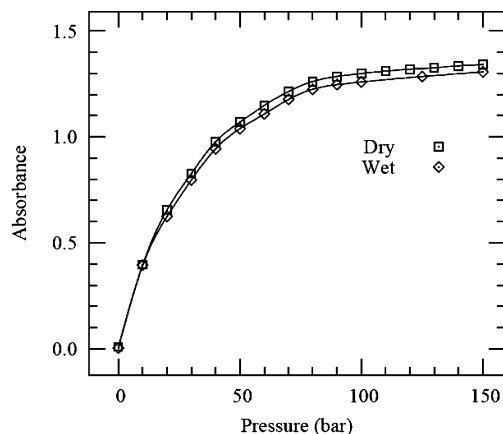


Figure 4. Evolution of the absorbance of the asymmetric stretching band of CO_2 at 2340 cm^{-1} in dry (<500 ppm of water) and in wet ($\sim 40\%$ water in IL (or $\sim 50\text{ mg}$ of water per gram of IL)) [bmim][BF_4].

system³⁶). Another possible explanation is the decrease of the molar absorptivity of the stretching mode of water with the increase of CO_2 concentration in the IL. The first hypothesis appears to be more probable, as we measured a water signal in the supercritical CO_2 phase in the IL–water–sc CO_2 ternary system.²⁷ More details are given in the sc CO_2 extraction section (3.6).

The position of the ν_3 CO_2 band does not shift with the presence of water, while the ν_2 CO_2 bending mode seems to undergo changes when adding CO_2 to IL in the presence of water. In fact, in the case of dry IL– CO_2 , with interaction between a fluorine atom of the anion and the carbon atom of CO_2 , the bending mode of CO_2 is split in two components.³³ The bending mode of CO_2 was also used previously to probe CO_2 interactions, in particular inside polymers.³¹ In the case of ILs, the CO_2 bending mode intensity of the highest wavenumber ($\sim 664\text{ cm}^{-1}$) component increased compared to the intensity of the other component ($\sim 654\text{ cm}^{-1}$). The variation of intensity could be induced by a rearrangement between BF_4^- , H_2O , and CO_2 molecules. The intensity and strong overlapping with other bands do not allow us to observe any small change in the bending mode of water. In this case, the perturbation of water molecules in the IL– CO_2 system can only be seen by the change of the CO_2 bending mode. The strong Lewis acid–base interaction of CO_2 with the anion induces the split of the bending mode, and the shape of this mode is perturbed by the presence of adjacent water. As explained by Kazarian et al.,³¹ the shift and the splitting of the ν_2 bending mode of CO_2 depend on the intensity of the Lewis acid–base interaction. In our case, the addition of water does decrease slightly the broadness of the band (the detailed spectra of the CO_2 bending mode in dry and wet [bmim][BF_4] are given in the Supporting Information). Water molecules do not decrease significantly the intensity of the interaction between CO_2 and [bmim][BF_4].

3.4. Solubility of CO_2 in Dry and Wet [bmim][BF_4]. Even if both H_2O and CO_2 molecules are interacting directly with the anions in IL, no obvious interactions between them could be observed. In Figure 4, the evolution of the absorbance of the CO_2 bending mode in dry and wet [bmim][BF_4] at 40°C up to 150 bar is presented. The absorbance is directly correlated to the concentration, the beam path length, and the molar absorptivity (Beer–Lambert law). In the case of ATR, the path length is replaced by the effective thickness which depends on the wavelength of the incident beam, the incident angle, the refractive indexes of the ATR crystal and the sample, the number

of reflections, and the polarization of the light. ATR theory is properly explained in detail elsewhere.³⁷ To compare dry and wet ILs, the variation of the refractive index should be taken into account, while other parameters remain constant. The refractive index decreases from 1.422³⁸ for a dry IL at 25°C to 1.412³⁸ with 50 mol % of water, which would induce a decrease of the effective thickness by 2%. Apart from that, to compare the results with identical quantity of IL, the variation of the volume between dry and wet IL also needs to be taken into account. The wet [bmim][BF_4] (with 50 mol % water) is 2% less dense than the dry IL,³⁸ while the mass of water is 7.4%. Therefore, the dissolution of 1 mol of water in 1 mol of [bmim][BF_4] results in an increase of the volume of the liquid by 8.4%. To be able to compare the concentration of CO_2 in dry and wet [bmim][BF_4] corrected by both effects, the absorbance of the wet IL given in Figure 4 needs to be increased by 10%. In that case, the solubility of CO_2 is a few percent higher in wet IL than in dry IL, but water does not change significantly the concentration of CO_2 in [bmim][BF_4], even when water is present in non-negligible concentration for a pressure up to 150 bar at 40°C . This result is consistent with the literature where small amounts of water dissolved in ILs have been investigated. Aki et al. did not observe any difference in the solubility of CO_2 between dry [bmim][Tf_2N] and IL saturated water (1.35 wt %) at 25°C .⁵ Similarly, in the case of [bmim][PF_6] at 40 and 60°C up to 90 bar, the variation in the solubility of CO_2 (considering water as an impurity in the calculation of the concentration) was measured, concluding that the effect of water in IL is generally quite small.¹⁶

3.5. Effect of Water and/or sc CO_2 on [bmim][PF_6]. As in the case of [bmim][BF_4], ATR-FTIR spectra of water trapped from air (40–50% humidity) in [bmim][PF_6] are presented in Figure 5. The main difference between these spectra and the ones presented earlier is inevitably connected to the bands of the anion. The PF_6^- band at 800 cm^{-1} is even stronger than the BF_4^- band at $1100\text{--}1000\text{ cm}^{-1}$. The amount of water diffusing into the IL is small compared to [bmim][BF_4]. The three vibrational modes of water were detectable and did not increase much after exposure during a few hours to air. Water molecules were not hydrogen bonded to each other, as in this IL no band was detectable in the range of $3550\text{--}3250\text{ cm}^{-1}$. All these findings are comparable to the existing literature.^{16,19,20,39,40} The intensities of the IL bands did not decrease by more than 1 or 2%. Therefore it was not possible to quantify the probable small swelling of [bmim][PF_6] caused by the diffusion of water into the IL.

The effect of sc CO_2 in dry and wet [bmim][PF_6] is depicted in Figure 6. As in the case of [bmim][BF_4], the main effect of CO_2 at 40°C in IL was a swelling of the liquid phase. IL bands were decreasing with an increase of pressure (except the PF_6^- band at 800 cm^{-1} which increased and shifted to higher wavenumbers, similar to the BF_4^- bands when increasing the concentration of CO_2). Ab initio calculations have been used to analyze the shift of this asymmetric PF_6^- stretching band.⁴¹ Using these calculations, it was found that when Li^+ is added to PF_6^- the band is shifted to higher wavenumbers, and the intensity of the band is increased in the IR spectra. This behavior is in line with the observation made when adding sc CO_2 to [bmim][BF_4] and [bmim][PF_6] where the distance between the cation and anion is increased.⁴² The quantification of the swelling and the CO_2 solubility in dry IL using ATR-FTIR spectra has already been reported.¹⁷ Dry IL shown in Figure 6 was obtained by sc CO_2 extraction of water as explained in the next section. The spectra of the dry IL before adding CO_2 already showed a

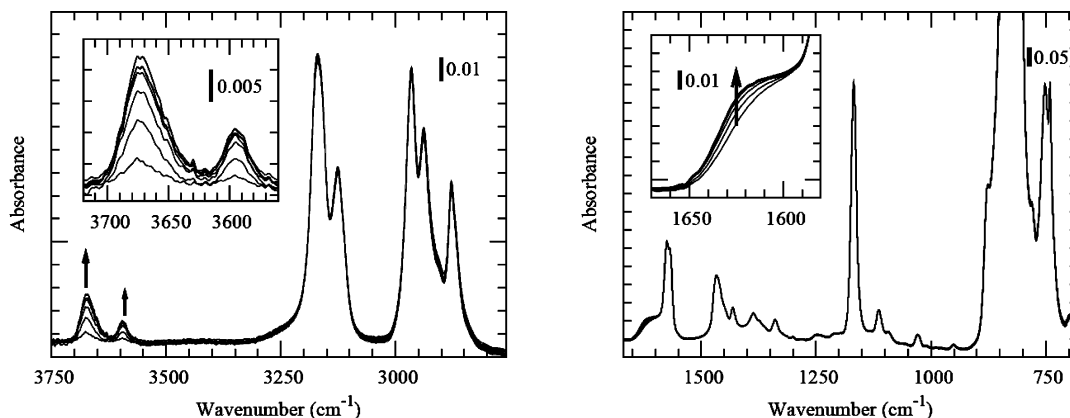


Figure 5. ATR-FTIR spectra of a ~ 2 mm layer of dry [bmim][PF₆] at 40 °C after exposure to air (40–50% humidity). Spectra were recorded every 30 min, and arrows show the evolution of intensity of the corresponding bands with time.

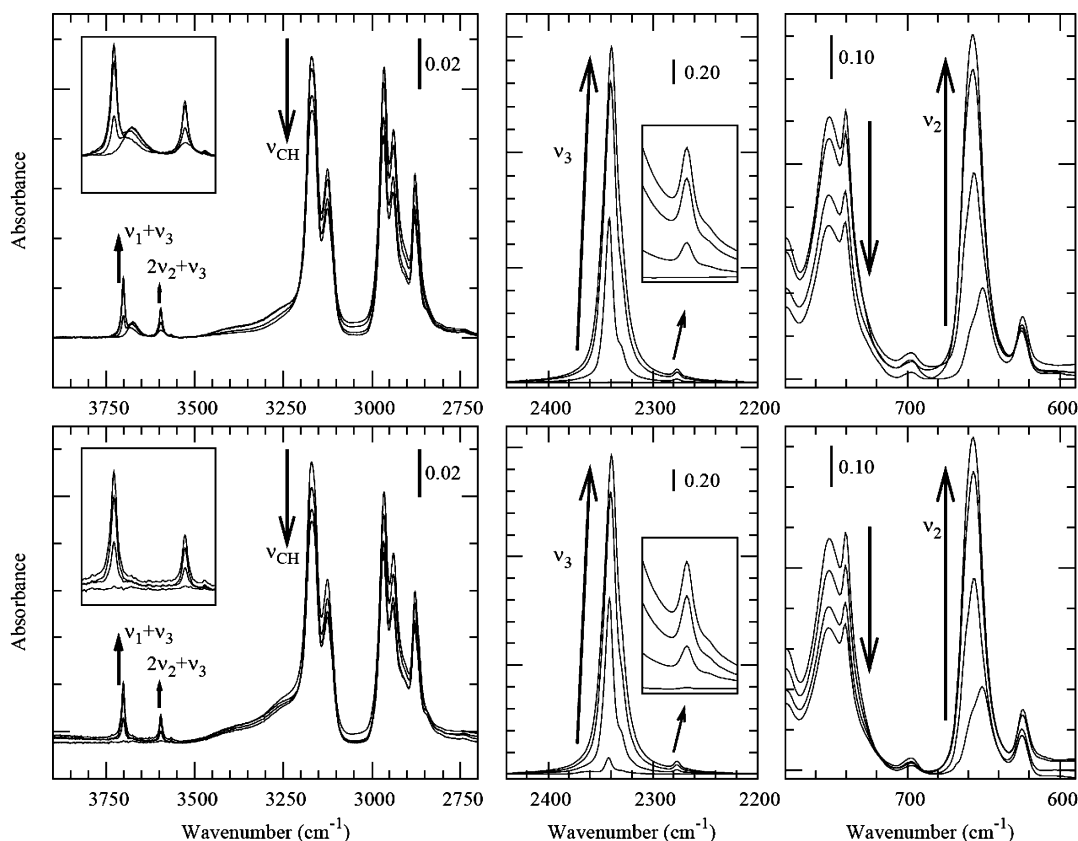


Figure 6. ATR-FTIR spectra of wet (top) and dry (bottom) [bmim][PF₆] at 40 °C and under a CO₂ pressure of 0, 20, 60, and 100 bar. Arrows show the evolution of intensity of the corresponding bands with pressure.

residual concentration of CO₂ in the IL (ν_2 bending mode at 2340 cm⁻¹) corresponding to the CO₂ left in the sample after extraction. Spectra of dry and wet ILs exposed to CO₂ were quite similar. Differences are found naturally in the presence of water bands at 3675, 3595, and ~ 1625 cm⁻¹ in the case of a wet sample. No difference between dry and wet IL was observed in the CO₂ bands. Nevertheless, the low concentration of water (<1%) and the overlapping of bending bands with the IL spectrum would probably not allow observing any minor changes due to an interaction between water with CO₂ or an anion when looking at the bending modes of water and CO₂. Stretching modes were not perturbed by the presence of water or by variation of the concentration of CO₂ in [bmim][PF₆].

Finally, as shown in Figure 6, the intensity of the absorption of the CO₂ bands at 2340 cm⁻¹ did not change significantly with the quantity of water, which is in good agreement with

the data found in the literature for water concentrations below 1 mol % in [bmim][PF₆].¹⁶

3.6. Purification of IL using scCO₂ Extraction. Water has shown a non-negligible solubility in scCO₂, and thus by contacting scCO₂ with ILs, water as well as other impurities can be extracted from ILs.²⁷ Figure 7 presents the evolution of the water stretching bands (ν_3 and ν_1) and CO₂ combination modes ($(\nu_1 + \nu_3)$ and $(2\nu_2 + \nu_3)$) in the range of 3740–3560 cm⁻¹ during the increase of pressure up to 100 bar as well as after flowing CO₂ for 60 min. The ν_3 water band decreased by $\sim 50\%$ when dissolving 100 bar of CO₂ in [bmim][PF₆]. The decrease corresponds to the swelling of the IL ($\sim 20\%$) plus the extraction from IL into the scCO₂ phase. In that case, the amount of water extracted could be estimated to be in the range of 0.1–1 mol % in IL. That would then represent a molar ratio of between 0.001 and 0.01 mol % of water in CO₂ after adding

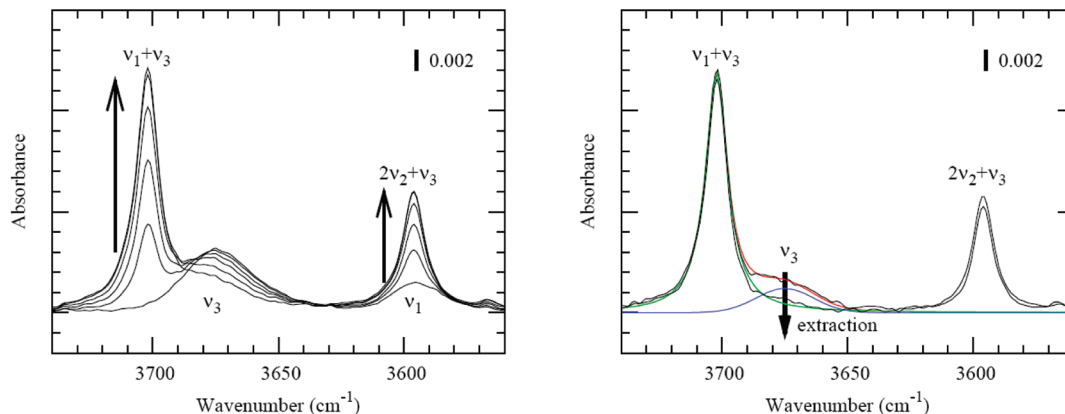


Figure 7. Evolution of the ATR-FTIR spectra at 40 °C while adding CO₂ at 0, 20, 40, 60, 80, and 100 bar (left). ATR-FTIR spectra of wet [bmim][PF₆] before and after 60 min of scCO₂ extraction at 100 bar and 40 °C (right). The spectra before extraction, in the range of 3750–3650 cm⁻¹, were deconvoluted using a Lorentzian function for the CO₂ combination band and a Gaussian function for the water ν_3 band.

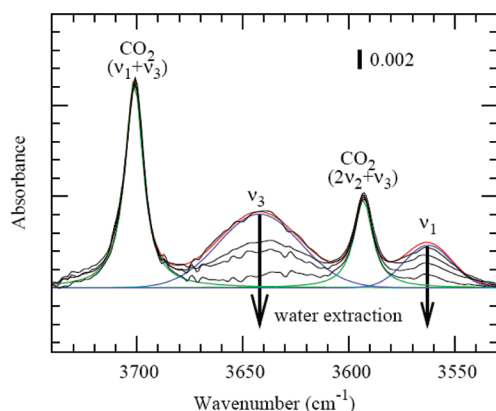


Figure 8. ATR-FTIR spectra of wet [bmim][BF₄] during scCO₂ extraction at 100 bar and 40 °C. The spectra before extraction, in the range of 3750–3530 cm⁻¹, were deconvoluted using two Lorentzian functions for the main CO₂ combination bands and two Gaussian functions for the water ν_3 and ν_1 bands.

100 bar of CO₂ (this experiment was performed with 0.6 g of IL in a total volume of 10 cm³). This value is 40–400 times lower than the maximum solubility of water in CO₂ under these thermodynamic conditions.²⁸ Then, CO₂ was passed over the IL, and after an hour of scCO₂ extraction the water bands were not detectable anymore. The deconvolution of the spectra of a wet IL in the range of 3740–3650 cm⁻¹ revealed that the spectra after extraction corresponded exactly to the CO₂ band, while the water stretching band disappeared. Figure 8 illustrates a similar water extraction from [bmim][BF₄]. Because the water bands are not overlapping with the two main combination bands of CO₂, as in the case of [bmim][PF₆], the deconvolution of the spectra is much easier. After extraction, a small signal was still visible at 3565 cm⁻¹. After comparison with the dry IL–CO₂ binary systems, it appears that this signal probably corresponds to CO₂ combination bands and not to traces of water. After depressurizing the cell and removing the CO₂, water bands did not reappear in the ILs.

Recently, Danten et al. measured precisely the molar absorptivity of ν_3 and ν_1 vibrations in IR of water diluted in several ILs including [bmim][BF₄] (ν_3 = 274.4 km/mol and ν_1 = 137.6 km/mol) and [bmim][PF₆] (ν_3 = 260.3 km/mol and ν_1 = 89.2 km/mol).²⁰ Using the molar absorptivity values of ν_3 of water in ILs, and an estimated limit of detection of our system (absorptivity of 0.001), the concentration of water in ILs was below 320 ppm for [bmim][BF₄] and 200 ppm for [bmim][PF₆] after scCO₂ extraction.

4. Conclusions

ATR-FTIR spectra of dry and wet ILs ([bmim][BF₄] and [bmim][PF₆]) at CO₂ pressures up to 150 bar at 40 °C were measured and analyzed. The molecular organization of water and CO₂ inside the ILs could be deduced by the changes (band shifts and change in intensities) in the infrared spectra. The addition of CO₂ altered the shape of the complex anion band but not the addition of water. In the ternary system, the presence of water changed slightly the bending mode vibration of CO₂ which indicated a small decrease of the interaction between CO₂ and anions, otherwise water and CO₂ did not seem to interact with each other. The addition of some water to [bmim][BF₄] did not change the solubility of CO₂ in that IL. Brennecke's group provided a possible explanation for the insensitivity of the CO₂ solubility on the presence of water, proposing that any hydrogen bonding of the water with the anion does not eliminate anion/CO₂ interactions.⁵ The results of our in situ infrared spectroscopy investigation of binary and ternary systems are in agreement with this hypothesis.

As water is soluble in scCO₂, it can be extracted from ILs, and therefore ILs can be efficiently dried by using scCO₂. After CO₂ extraction, the water concentration was below 320 ppm in [bmim][BF₄] and 200 ppm in [bmim][PF₆], as evidenced by ATR-FTIR spectroscopy.

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Supporting Information Available: CO₂ bands in dry (thin) and wet (bold) IL after subtraction of IL signal of ATR-FTIR spectra at 40 °C while adding CO₂ at 20, 40, 60, 80, and 100 bar. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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