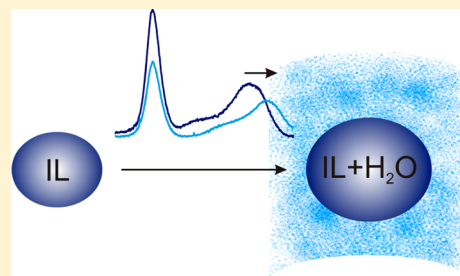


Interaction of Levitated Ionic Liquid Droplets with Water

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S Supporting Information

ABSTRACT: The influence of a humid or dry atmosphere on acoustically levitated ionic liquid droplets was studied by volumetric analysis and vibrational spectroscopy. Imidazolium-based ionic liquids with two types of anions, fluorinated (BF_4^- and PF_6^-) and alkylsulfate anions, were investigated. The amount of absorbed water was correlated with structural differences of the ionic liquids and analyzed in terms of equilibrium mole fraction as well as absorption rate. The type of anion had the most significant influence on the amount of adsorbed water from the atmosphere. Furthermore, spectral changes in the in situ Raman spectra due to absorbed water were studied for all investigated ionic liquids. For 1-ethyl-3-methylimidazolium ethylsulfate, an exemplary detailed analysis of the intermolecular interactions between cations, anions and water was carried out based on the spectroscopic data. The observed band shifts were explained with a hydrogen bond between the anion and water.



■ INTRODUCTION

Acoustic levitation is a droplet-based microfluidic technique, which allows a contact-free handling of solid or liquid samples. Levitated droplets can serve as microreactors for small sample volumes in the microliter range and support the design and development of miniaturized techniques in analytical sciences. Contamination and analyte adsorption at container walls are eliminated and the sample is easily accessible for in situ and online analysis.¹ However, evaporation of the solvent and interactions with the surrounding atmosphere have to be taken into account.

In this study, the interaction of five different levitated ionic liquids with the surrounding atmosphere was investigated. Ionic liquids have a low melting point and are liquid at room temperature in contrast to typical ionic compounds such as sodium chloride.² Ionic liquids are very versatile solvents as the properties such as viscosity, polarity, and conductivity can be modulated through the choice of the cation and the anion.³ These tailor-made solvents find applications in the fields of analytical sciences as MALDI matrices or in organic reactions and as catalysts.⁴ Ionic liquids have a negligible vapor pressure due to the strong ionic interactions between cation and anion. Therefore, ionic liquids appear to be ideal solvents for levitated droplet experiments. A constant volume of the droplet is important for reliable analytical studies and reaction monitoring.⁵ Hence, interactions with the surrounding atmosphere have to be considered.^{6,7}

The investigated ionic liquids contain two different cations: 1-butyl-3-methylimidazolium (BMIM) and 1-ethyl-3-methylimidazolium (EMIM). As anions the fluorinated anions hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-) and the sulfate anions methyl sulfate (MeSO_4^-) and ethyl sulfate (EtSO_4^-) were studied. All investigated ionic liquids are commercially available, and their properties such as density

and viscosity are described in the literature.⁸ The fluorinated anions are frequently used but can decompose in aqueous solutions.⁹ Methyl and ethyl sulfate anions are an alternative to fluorine-based anions and are used for the synthesis of low cost ionic liquids.¹⁰ The amount of water in ionic liquids has a pronounced influence on the properties of the solvent, especially regarding the viscosity and density.^{7,11}

To study the interaction between ionic liquid droplets and the water from the surrounding atmosphere, vibrational spectroscopy provided insights into the interaction between the cation and anion of ionic liquids¹² and on the interactions in mixtures of ionic liquids with cosolvents such as water.^{13,14} The vibrational spectra of $[\text{EMIM}][\text{EtSO}_4]$ have been recently studied^{15,16} as well as the interaction of this ionic liquid with water.^{17–19} Studies of ionic liquids based on fluorinated anions such as $[\text{BMIM}][\text{BF}_4]$ ^{20,21} and its mixtures with water^{22–25} were not only concentrated on the ionic liquid vibrations but also on the spectral region of the OH stretching vibration of water.^{26,27} Further investigations of pure ionic liquids and mixtures with cosolvents were performed based on quantum chemical calculations,^{28,29} fluorescence spectroscopy,³⁰ NMR,³¹ sum frequency generation spectroscopy,³² and X-ray diffraction.¹⁰

The infrared spectroscopic studies suffer from spectral interferences with water and often D_2O is used instead of water.¹⁷ In contrast, Raman spectroscopy can be easily interfaced to an acoustic levitator.³³ The present study applies in situ Raman spectroscopy of different levitated ionic liquid droplets in a dry and high humidity atmosphere to monitor

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changes in the molecular interactions upon water uptake from the atmosphere.

METHODS

Five ionic liquids were investigated based on two imidazolium-based cations, 1-butyl-3-methylimidazolium (BMIM) and 1-ethyl-3-methylimidazolium (EMIM) and four anions hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), methyl sulfate (MeSO_4), and ethyl sulfate (EtSO_4). 1-Butyl-3-methylimidazolium hexafluorophosphate (for synthesis, Merck, Darmstadt, Germany), 1-butyl-3-methylimidazolium tetrafluoroborate (for synthesis, Merck), 1-butyl-3-methylimidazolium methyl sulfate (for synthesis, Merck), 1-ethyl-3-methylimidazolium ethyl sulfate ($\geq 98\%$, Merck), and 1-ethyl-3-methylimidazolium methylsulfate ($\geq 98\%$, Sigma-Aldrich, Taufkirchen, Germany) were used without further purification.

The experimental setup is described in ref 33. In brief, ionic liquid droplets with typical volumes of $4\ \mu\text{L}$ were levitated using an acoustic levitator (58 kHz, Tec 5, Oberursel, Germany). The droplets were manually injected into the acoustic levitator with an Eppendorf pipet ($0.5\text{--}10\ \mu\text{L}$). For the observation of the droplet volume, an IR flash lamp and camera (programmable IR camera, Vision & Control, Jena, Germany) were used with an in-house-written program to operate the IR camera and to determine the droplet size.

The variation of the surrounding atmosphere of the droplet was realized by a gas stream around the reflector³⁴ which was either nitrogen (Air Liquide, Düsseldorf, Germany) or nitrogen bubbled through a gas-washing bottle filled with water (deionized, $18.2\ \text{M}\Omega\ \text{cm}$). Similar approaches with a gas stream for atmosphere control around acoustically levitated droplets are described in the literature.^{35–37} The gas stream was adjusted to a flow rate of $3\ \text{L/min}$ using a flow sensor (Sensirion, CMOSens Mass Flow Meter EM1, Staefa, Switzerland). The temperature and relative humidity were measured using a Lab Jack U12 with an EI-1050 sensor (Meilhaus Electronic, Puchheim, Germany) and a Sensirion EK-H5 with a SHT-21 sensor (Sensirion, Staefa, Switzerland). All experiments were carried out at room temperature ($22\text{--}24\ ^\circ\text{C}$). For the experiments under dry conditions, the relative humidity ranged from 7 to 14% RH, the experiments under high humidity conditions were carried out with 61 to 74% RH.

For Raman spectroscopy, a HeNe laser (633 nm, 35 mW, $\sim 1800\ \text{W/cm}^2$, Melles Griot, Bensheim, Germany) was used as excitation source. The spectra were recorded using a spectrometer (SR-303i, Andor, Belfast, Northern Ireland) with either a 300 lines/mm, 1800 lines/mm or 2400 lines/mm grating and a CCD camera (Andor iDus DU420-BV). The spectra were recorded with 1 s (300 lines/mm), 10 s (1800 lines/mm) or 60 s (2400 lines/mm) integration time.

FTIR spectra of ionic liquid films were recorded using a Bruker Equinox 55 (Ettlingen, Germany) with a KBr beamsplitter and a DTGS detector in the MIR region from 400 to $4000\ \text{cm}^{-1}$ (32 scans, $2\ \text{cm}^{-1}$ resolution). The ionic liquid films were prepared between two KBr slides and measured immediately thereafter. Spectra of ionic liquid water mixtures were recorded after exposure of the ionic liquid film to the atmosphere by removal of one KBr slide for 60 s.

RESULTS AND DISCUSSION

Volumetric Analysis. To explore the water uptake from the atmosphere, the droplet volume of levitated ionic liquid

droplets exposed to a high humidity atmosphere (61% RH) was monitored over time. The volume increase for the five different ionic liquids is displayed in Figure 1. The most pronounced

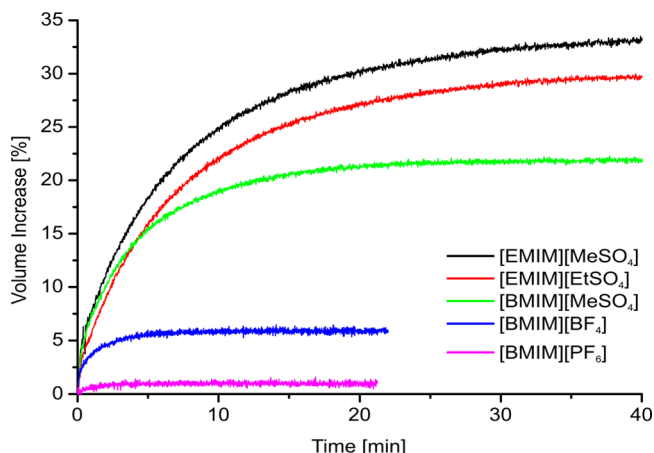


Figure 1. Volume increase due to water uptake from the humid atmosphere (61% RH) for the five investigated ionic liquids.

differences in water uptake from the atmosphere were observed depending on the anion of the ionic liquid. The two ionic liquids with a fluorinated anion took up only a minor amount of water from the atmosphere compared to the sulfate anions, which is in agreement with earlier work.³⁸ [BMIM][BF_4] showed a droplet volume increase of about 6% whereas [BMIM][PF_6] took up almost no water from the atmosphere. For the ionic liquids with a sulfate anion, a large volume increase between 20–35% was observed. Hydrogen bonds play a significant role in the interaction between water and the anion of the ionic liquids. The investigated alkylsulfate anions are better hydrogen bond acceptors than BF_4 and PF_6 ³⁹ what explains the larger amount of absorbed water.

The change of the alkyl group chain length of the cation (EMIM compared to BMIM) has obviously a larger influence on the water uptake from the atmosphere than the difference of the alkyl chain length of the anion (MeSO_4 compared to EtSO_4). The data reveal that in general the water uptake is the smaller the longer the alkyl side chain of the imidazolium cation or the sulfate anion, as it was previously observed for sulfate based ionic liquids.³⁸ This can be explained by the increasing unpolar domains in ionic liquids with long alkyl chains⁴⁰ where the interaction sites for water are more limited than in ionic liquids with short alkyl chains. In the present study, the amount of water uptake from the atmosphere is therefore largest for the smallest anion and cation ([EMIM][MeSO_4]). The volume increase in percent is shown in Figure 1 for an initial droplet volume of $4\ \mu\text{L}$ of ionic liquid, but the same percentage increase was observed for initial volumes between 2.5 and $5\ \mu\text{L}$.

To correlate the volume increase with the mole fraction of water in the ionic liquid, mole fractions for mixtures of water and [BMIM][BF_4] or [EMIM][EtSO_4] were calculated taking into account the excess volumes.^{41,42} The calculations show that the influence of the excess volume is not negligible but small and that the mole fraction has an error of about 1% when the excess volume is not taken into account. The excess volume was therefore disregarded in the further calculations to allow an easy correlation between the volume observation and immediate interpretation of the data for online monitoring. The mole fraction of water calculated from the volume of the

Table 1. Kinetic Parameters, Including Uncertainties and Adjusted Coefficient of Determination (R^2), Obtained by Curve Fitting (Molar Ratio $M = n_{\text{H}_2\text{O}}/n_{\text{IL}}$ vs Time), Volume Increase, and Molar Fraction $x_{\text{H}_2\text{O}}$ after Equilibrium of Water Uptake for 61% RH

	k/min^{-1}	$M_{\infty}/\%$	$k M_{\infty}/\text{min}^{-1}$	R^2	volume increase/%	$x_{\text{H}_2\text{O}}(\text{eq})$
[BMIM][PF ₆]	1.45 ± 0.08	12.6 ± 0.1	18	0.264	1	0.11
[BMIM][BF ₄]	0.89 ± 0.01	60.2 ± 0.1	54	0.870	6	0.37
[BMIM][MeSO ₄]	0.261 ± 0.001	255.5 ± 0.2	67	0.965	24	0.72
[EMIM][EtSO ₄]	0.1403 ± 0.0004	312.3 ± 0.2	44	0.989	30	0.76
[EMIM][MeSO ₄]	0.1571 ± 0.0007	307.7 ± 0.3	48	0.980	33	0.76

droplet at the equilibrium of water uptake from the atmosphere is $x_{\text{H}_2\text{O}} = 0.11$ for [BMIM][PF₆], $x_{\text{H}_2\text{O}} = 0.37$ for [BMIM][BF₄], $x_{\text{H}_2\text{O}} = 0.72$ for [BMIM][MeSO₄], $x_{\text{H}_2\text{O}} = 0.76$ for [EMIM][EtSO₄] and [EMIM][MeSO₄] (see Table 1).

The equilibrium of water uptake is reached after about 40 min for all ionic liquids with sulfate anions, for the fluorinated anions it is reached much faster. Comparison with kinetic results from the literature⁶ for [BMIM][BF₄] and [BMIM][PF₆] show an agreement for the amount of water which is absorbed by the ionic liquids when the equilibrium is reached. For the observed volume increase shown in Figure 1, the molar ratio M ($M = n_{\text{H}_2\text{O}}/n_{\text{IL}}$) was calculated for the five investigated substances with densities of the dry ionic liquids from the literature^{43–45} and plotted vs time. The resulting curves were fitted to the equation $M = M_{\infty}(1 - e^{-kt})$ with t (time) and two kinetic parameters M_{∞} (molar ratio at equilibrium) and k (absorption rate constant)⁶ using Origin 8.1G software. The values obtained by nonlinear curve fitting are listed in Table 1. The product $k \times M_{\infty}$ represents the speed of the absorption of water by the ionic liquid.⁶

The values for [BMIM][BF₄] and [BMIM][PF₆] observed for M_{∞} in this study with a humidity of the surrounding atmosphere of 61% RH lie between the values for 43% RH and 81% RH from the literature.⁶ The values for the absorption rate constant k differ significantly from the literature data as the equilibrium is reached much faster in the levitated droplet experiments, because the surface to volume ratio is much larger in this experiment compared to the cylindrical vessel used in the literature study. The effect of a much shorter time needed to reach the equilibrium was also observed for ionic liquid nanoparticles.⁴⁶

The values for k in relation to the surface to volume ratio are approximately hundred times larger for the levitated droplet experiments ($286 \times 10^{-6} \text{ min}^{-1} \text{ m}$ for [BMIM][BF₄]) compared to the bulk experiments ($3.1 \times 10^{-6} \text{ min}^{-1} \text{ m}$ for [BMIM][BF₄], 43%RH).⁶ The larger values can be explained by the movement of the levitated droplet due to acoustic streaming and the gas stream around the droplet compared to the stagnant liquid in the vessel. The tendency that the absorption rate constant is larger for [BMIM][PF₆] than for [BMIM][BF₄] is in agreement with the literature.⁶ In comparison to the ionic liquids with fluorinated anions, the investigated ionic liquids based on sulfate anions show a smaller absorption rate constant.

The amount of water uptake from the atmosphere depends on the surface of the ionic liquid which is exposed to the atmosphere.³⁸ A levitated droplet of [BMIM][BF₄] absorbed an amount of water per surface of about $2 \text{ mg}/\text{cm}^2$ after 20 min. This is a significantly smaller amount than described in the literature for a larger volume of ionic liquid but a similar surface to volume ratio compared to the levitated droplet.³⁸ However,

apart from the surface to volume ratio of the droplet also the contactless handling, i.e., the absence of solid–liquid surface boundaries and the mixing effect induced by internal circulation of the liquid in the levitated droplet due to acoustic streaming have to be considered as potential reasons for the lower amount of absorbed water.

Spectroscopic Investigation. For a more detailed investigation of the interaction of the ionic liquids with water, Raman spectra of the ionic liquids were recorded under dry conditions and during the levitation in a high humidity atmosphere. Intermolecular interactions in pure ionic liquids comprise contributions of electrostatic, inductive, and dispersive interactions.⁴⁷ The impact of hydrogen bonding on the interaction between anions and cations in neat ionic liquids is still under discussion.⁴⁸ For ionic liquid water mixtures, the interaction between water and the ions is described mainly as interaction through hydrogen bonds between water as donor and the anion of the ionic liquid as acceptor.^{17,18,49} For higher water concentrations, hydrogen bonds between the C2–H group of the imidazolium cation and water are also described.¹⁷ The interactions between water and the ionic liquid ions cause changes in the interaction between the two ions and therefore lead to differences in the vibrational band positions between the neat ionic liquid and mixtures with water.

The spectra of the five ionic liquids under dry conditions and after equilibrium of water uptake from the atmosphere are shown in Figure 2. For the two ionic liquids with fluorinated anions no shifts of the ionic liquid vibrational bands upon water uptake were observed. In the literature, a blue shift of about 6 cm^{-1} is reported for the BF₄ stretching vibration at 765 cm^{-1} with increasing water concentration.²² We observe no shift of this band, but the water concentration in [BMIM][BF₄] after water uptake from the atmosphere is much lower ($x_{\text{H}_2\text{O}} = 0.37$) in this study compared to the study of Jeon et al. where effects were observed starting at a water concentration of $\sim 7.5 \text{ mol/L}$ ($x_{\text{H}_2\text{O}} = 0.62$).²² The conformation of the alkyl group in ionic liquids with BMIM cation was investigated in the region $590\text{--}630 \text{ cm}^{-1}$, where gauche/trans specific bands of the alkyl side group of the cation were observed.^{22,50} For all BMIM-based ionic liquids investigated in this study, both bands were observed: the band around 600 cm^{-1} for the gauche conformer and the band at 625 cm^{-1} for the trans conformer.⁵¹ In our experiments, the amount of absorbed water from the atmosphere for [BMIM][BF₄] and [BMIM][PF₆] is too low to observe the conformational changes of the alkyl group of the cation reported in the study of Jeon et al.²² The spectra of [BMIM][MeSO₄] are overlaid by a fluorescence background and therefore the interpretation of the intensities of the conformation specific bands is not possible.

For the three investigated ionic liquids with sulfate anions, spectral changes were observed during the uptake of water from

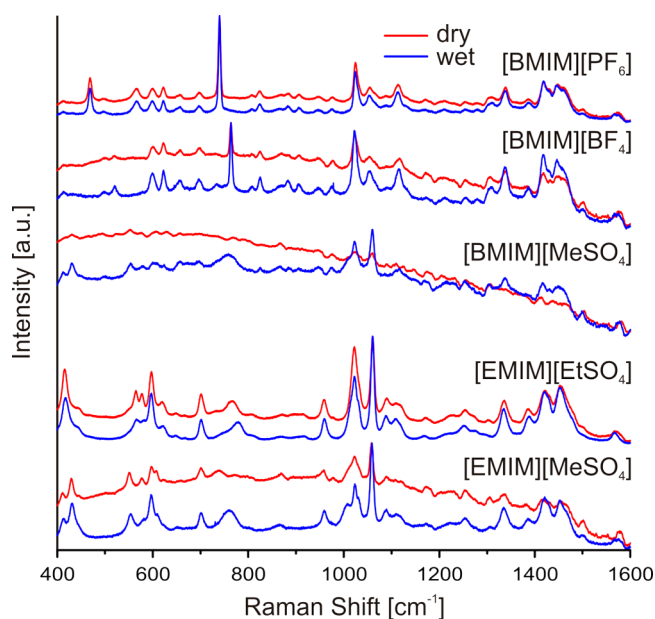


Figure 2. Raman spectra of levitated ionic liquid droplets under dry (7% RH) and humid (61% RH) conditions.

the atmosphere for the bands around 560, 580, and 760 cm^{-1} . The observed band shifts will be described in detail using the example of [EMIM][EtSO₄] because this ionic liquid shows the least fluorescence. The Raman spectra of [EMIM][EtSO₄] show several band shifts upon an increasing amount of water which are listed in Table 2 and shown in Figure 3. For

Table 2. Band Positions in Raman and IR Spectra of [EMIM][EtSO₄] under Dry Atmosphere Conditions and Wavenumber Differences between the Spectra Recorded under Humid and Dry Conditions

Raman shift(dry)/ cm^{-1}	Δ Raman shift(humid-dry)/ cm^{-1}	$\tilde{\nu}(\text{IR, dry})/\text{cm}^{-1}$	$\Delta\tilde{\nu}(\text{humid-dry})/\text{cm}^{-1}$
565	3	567	^a
578	4	578	0 ^b
765	15	768	7
1022	0	1020	−4
1225	−6	1227	−8
2905	2	2901	5
2968	0	2982	5
3106	8	3105	6
3158	8	3151	2

^aThe band at 567 cm^{-1} overlaps in the spectrum recorded under humid conditions with the band at 578 cm^{-1} , a value for the wavenumber shift can therefore not be determined. ^bA substantial broadening of the band but no shift of the band position was observed.

facilitation of the band assignment and comparison with the Raman spectra, FTIR spectra of ionic liquid films were measured: one spectrum directly after preparation, where the water content is low and one spectrum with increased water content due to water uptake from the atmosphere (Figure 3, bottom). The observed band shifts in the IR spectra upon water uptake are comparable to the observed effects in the Raman spectra (Table 2). Blue shifted as well as red-shifted bands were observed in both Raman and IR spectra. The regions, where the most prominent band shifts occur, are between 500–1250 cm^{-1} and in the region of 2900–3160 cm^{-1} .

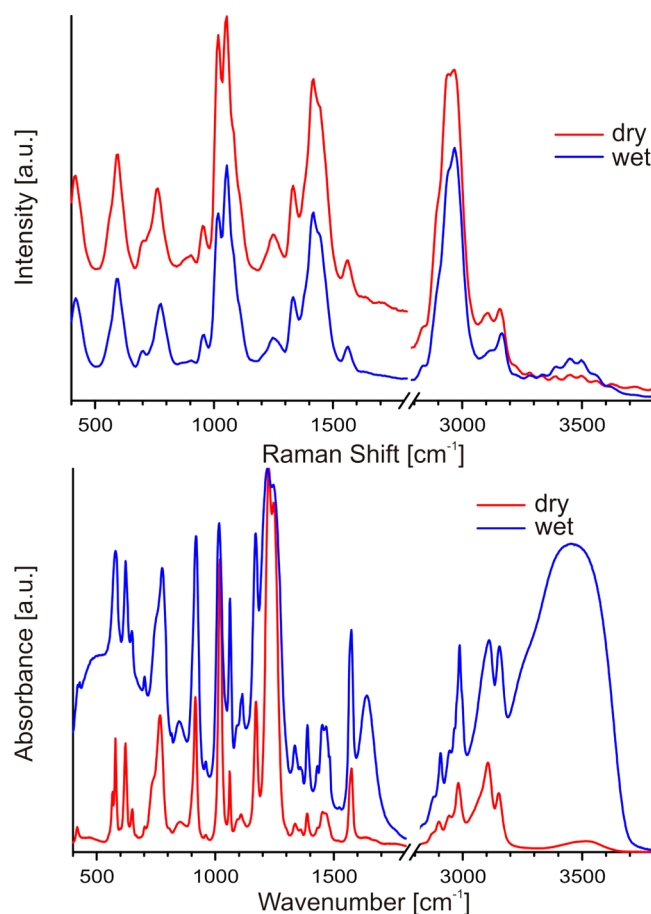


Figure 3. Top: Raman spectra of levitated [EMIM][EtSO₄] droplets under dry and humid conditions. Bottom: FTIR spectra of [EMIM][EtSO₄] films directly after preparation and after exposure to air.

For the bands in the Raman spectra of dry [EMIM][EtSO₄] at 565, 578, and 765 cm^{-1} , a blue shift was observed upon water uptake from the atmosphere (Figure 4). According to the vibrational band assignment based on DFT calculations,¹⁵ the bands at 565 and 578 cm^{-1} can be assigned to O–S–O bending and wagging vibrations of the anion. The blue shift of the bending vibrations in the humid ionic liquid can be explained with the interaction between anion and water as supported by DFT calculations depicted in the Supporting Information (Figure S1 and Tables S1 and S2). A strengthening of the interaction with water compared to the pure ionic liquid leads to a blue shift of the O–S–O bending vibrations⁵² and a red shift of the SO₃ stretching vibrations (e.g., 1225 cm^{-1}) which will be discussed and explained below.

The most pronounced blue shift between dry and humid [EMIM][EtSO₄] of 15 cm^{-1} was observed for the band at 765 cm^{-1} . In contrast to the recent study by Noack et al.,¹⁹ where this band is assigned mainly to cationic bending vibrations of the ring C–H groups, we assign this band to the S–O stretching vibration of the S–O–C₂H₅ group (Tables S1 and S2 of the Supporting Information). Our assignment is supported by a study of the conformational equilibrium of the EMIM cation,⁵³ where no cation bands were observed between 705 and 800 cm^{-1} and by the study of Grondin et al.,¹³ where the intensity of the cation band of [EMIM][Br] at 758 cm^{-1} was very weak. Furthermore, comparison of the Raman spectra of the five investigated ionic liquids in this study

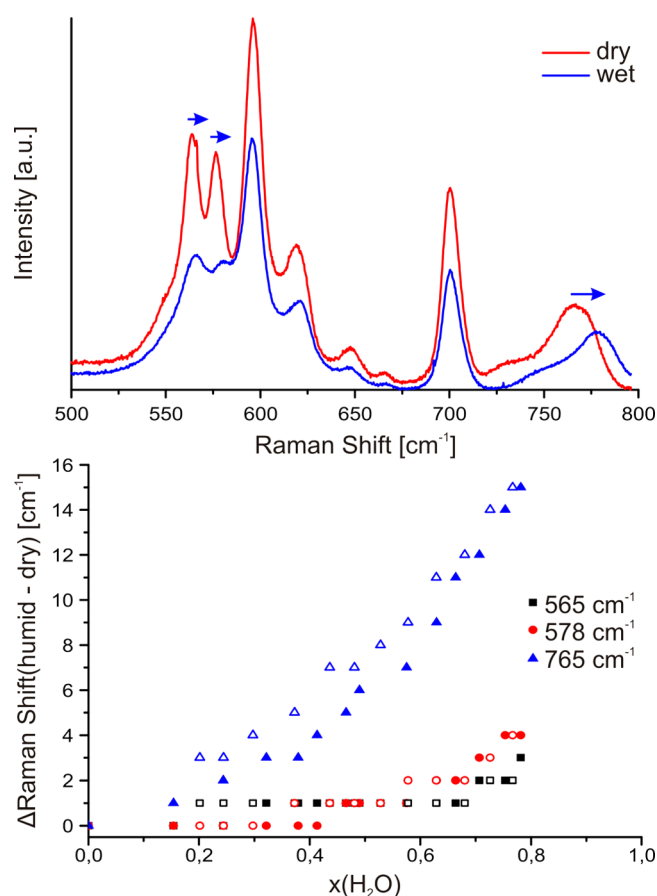


Figure 4. Top: Raman spectra of [EMIM][EtSO₄] in the range of 500–800 cm^{-1} under dry and humid conditions. Bottom: Correlation between the mole fraction of water in [EMIM][EtSO₄] and the band shift in the Raman spectra (filled symbols, Raman shift during water uptake from the atmosphere under high humidity conditions; open symbols, Raman shift during water release from [EMIM][EtSO₄] under dry conditions).

indicates that this band is mainly from anion vibrations, because no comparable intensity in this region is observed in the [BMIM][BF₄] and [BMIM][PF₆] spectra apart from the very intensive bands of the BF₄ and PF₆ anions. A comparable blue shift of $\sim 20 \text{ cm}^{-1}$ to the one we detect, was observed for the S–OH stretching vibration in [EMIM][HSO₄] (at 850 cm^{-1}) for a sample exposed to moisture.⁵⁴ An explanation for the blue shift is given in a study of the microsolvation behavior of the bisulfate anion,⁵⁵ where the authors suggest that solvation increases the strength of the S–O bond as evidenced by a calculated increase of the polarization of the $\text{O}\delta^- - \text{H}\delta^+$ bond with increased hydrogen bonding. The opposite effect is observed in temperature dependent Raman spectra where hydrogen bonds are broken upon increasing temperature and the S–OH stretching vibration is red-shifted.⁵⁶ The blue shift of this band is therefore in line with the observations for the O–S–O bending and wagging vibrations of the anion, which indicate a strong hydrogen bond between water and the ionic liquid anion.

The blue shifts of the above-described anion bands are correlated to the mole fraction of water in the ionic liquid obtained from the droplet volume in Figure 4. The correlation between band shift and mole fraction is not linear due to different solvation steps as described by Zhang for [EMIM]-

[EtSO₄]¹⁷ and by Takamuku for [EMIM][BF₄].⁵⁷ To investigate the reversibility of the band shift upon water uptake and release the humidity of the surrounding air was first set to high humidity conditions as in the above-described experiments and after the equilibrium of water uptake has been reached the humidity was decreased to about 10% RH by applying a dry nitrogen gas stream around the droplet. The monitored volume decreased to the initial volume of the ionic liquid and the Raman band position shifted back to the initially observed positions for the dry ionic liquid as shown in Figure 4. The water uptake and release from the atmosphere was therefore reversible for [EMIM][EtSO₄] levitated droplets.

A red shift of the band 1225 cm^{-1} is observed in the Raman spectra of levitated [EMIM][EtSO₄] droplets upon water uptake from the atmosphere (Table 2) in agreement with literature data¹⁷ and DFT calculations (Table S2, Supporting Information). This band can be assigned to the antisymmetric SO₃ stretching vibration of the anion. The red shift of the SO₃ stretching vibrational band indicates that the hydrogen bond interaction between water and the anion is stronger than the interaction between anion and cation in the pure ionic liquid. The magnitude of the red shift of the antisymmetric SO₃ stretching vibration is in agreement with the observed wavenumber shift in the IR spectra of Zhang et al.¹⁷ Additional to the band shift of the asymmetric SO₃ stretching vibration at 1227 cm^{-1} also a red shift of the symmetric SO₃ stretching vibration at 1020 cm^{-1} was observed in the IR spectra, which was not visible in the Raman spectra of the levitated droplet.

The C–H stretching spectral region is also sensitive to cation–anion interactions.¹⁴ In this spectral region only small band shifts were observed for the alkyl stretching vibrations at 2905 and 2968 cm^{-1} in the Raman spectra depending on the water concentration in the ionic liquid. Stronger effects were observed for these bands in IR spectra of ionic liquid films, where a blue shift of the bands at 2901 and 2982 cm^{-1} was observed (see Figure 3 and Table 2). The observed blue shift of the C–H stretching bands of [EMIM][EtSO₄] is in agreement with similar observations for [BMIM][BF₄].²² The bands at 3106 and 3158 cm^{-1} show a blue shift upon increasing water concentration in both Raman and IR spectra. However, upon increasing water content, the bands in the C–H stretching region are overlaid by the intensive water band in the IR spectra. The band at 3106 cm^{-1} can be assigned to the C2–H stretching vibration of the imidazolium ring and the band at 3158 cm^{-1} to the symmetric and antisymmetric stretching vibrations of the C4,5–H of the imidazolium ring.¹⁷ The blue shift of the band is due to a weakened interaction between cation and anion because of the hydrogen bond interaction between water and the anion. The observed magnitude of the blue shift is less pronounced for water concentrations of up to a mole fraction of water of $x_{\text{H}_2\text{O}} = 0.76$ in [EMIM][EtSO₄] than described in the literature, especially for the C2–H stretching vibration.¹⁷ In summary, all observed band shifts in the spectra of [EMIM][EtSO₄] with increasing water content can be interpreted with a hydrogen bond interaction between anion and water, which influences and weakens the anion cation interaction.

In the far-infrared spectral region intermolecular interactions between the cation and anion of the ionic liquid as well as between the ions and water can be observed.^{58,59} This spectral region is also accessible with Raman spectroscopy. In the Raman spectra between 50–200 cm^{-1} only one broad band

with a maximum at 86 cm^{-1} and a shoulder at 153 cm^{-1} was observed for $[\text{EMIM}][\text{EtSO}_4]$ (Supporting Information, Figure S2). No spectral differences were observed between the dry ionic liquid and the droplet under humid conditions after equilibrium of water uptake from the atmosphere. Spectral contributions of the water or interactions between water, anion and cation cannot be separated or identified in the broad band.

An advantage of Raman spectroscopy compared to IR spectroscopy is the lack of interference of water in Raman spectra. In this study, it would however be interesting to quantify the water content not only by the volume observation but also by the Raman intensity of the water band. The intensity of the OH stretching band of water has a very weak intensity for low water concentrations,^{23,60} nonetheless the band of the absorbed water in the ionic liquid was visible in the recorded Raman spectra (see Figure 3). For a correlation of Raman intensities with the mole fraction of water, a calibration curve was recorded by the measurement of Raman spectra of six $[\text{EMIM}][\text{EtSO}_4]$ /water mixtures with a mole fraction between zero and one. By integration of the spectral region of the CH stretching vibration of the ionic liquid and the OH stretching vibration of the water, the areas of the bands can be correlated with the water content in the ionic liquid (Supporting Information, Figure S3). The calculated mole fractions from the Raman band intensities based on the calibration curve are in agreement with the calculations from the droplet volume described in the beginning of this section.

CONCLUSION

The influence of a humid atmosphere on levitated ionic liquid droplets was investigated by means of volumetric analysis and vibrational spectroscopy. Included in this study were the hygroscopic ionic liquids $[\text{BMIM}][\text{MeSO}_4]$, $[\text{EMIM}][\text{MeSO}_4]$, and $[\text{EMIM}][\text{EtSO}_4]$ as well as the less hygroscopic ionic liquids $[\text{BMIM}][\text{BF}_4]$ and $[\text{BMIM}][\text{PF}_6]$.

The volumetric analysis showed that the nature of the anion has the most significant influence on the amount of water which is absorbed by an ionic liquid from the atmosphere. The ionic liquids with sulfate anions take up much more water than the ionic liquids with fluorinated anions. The investigation of different alkyl chain lengths of both cation and anion showed that the amount of absorbed water is the larger the shorter the alkyl side chains of the ionic liquid. The largest amount of absorbed water was observed for the ionic liquid $[\text{EMIM}][\text{MeSO}_4]$ with the shortest alkyl side chain lengths. The analysis of the volume increase was complemented by the calculation of the mole fraction of water after equilibrium of water uptake from the atmosphere, which was equal for $[\text{EMIM}][\text{MeSO}_4]$ and $[\text{EMIM}][\text{EtSO}_4]$. The absorption rate constant was determined by fitting the volume increase over time which resulted in higher absorption rate constants for the fluorinated anions than for the sulfate anions.

The process of water uptake from the atmosphere by the ionic liquids was also observed by Raman spectroscopy. $[\text{BMIM}][\text{PF}_6]$ and $[\text{BMIM}][\text{BF}_4]$ show no spectral changes due to the low amount of absorbed water. The ionic liquids containing a sulfate anion ($[\text{BMIM}][\text{MeSO}_4]$, $[\text{EMIM}][\text{MeSO}_4]$, and $[\text{EMIM}][\text{EtSO}_4]$) show several distinct band shifts in the Raman spectra upon increasing water concentration which were discussed on the example of $[\text{EMIM}][\text{EtSO}_4]$. The observed band shifts in the spectra of $[\text{EMIM}][\text{EtSO}_4]$ with increasing water content can be explained with a hydrogen bond interaction between anion

and water, which influences and weakens the anion cation interaction. In future experiments, the interactions between ionic liquids and the surrounding atmosphere will be further investigated using levitated ionic liquid droplets as micro-reactors for reaction monitoring. The present study shows that an exact adjustment of the atmospheric conditions is necessary when using ionic liquids as solvents for levitated droplet experiments.

ASSOCIATED CONTENT

Supporting Information

DFT calculations of $[\text{EMIM}][\text{EtSO}_4]$ and $[\text{EMIM}][\text{EtSO}_4] + \text{H}_2\text{O}$, Raman spectra in the region between 50 and 400 cm^{-1} , and correlation of Raman intensities of $[\text{EMIM}][\text{EtSO}_4]$ and water with the mole fraction of water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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