Effect of the Cation on the Interactions between Alkyl Methyl Imidazolium Chloride Ionic Liquids and Water

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ABSTRACT: A systematic study of the interactions between water and alkyl methyl imidazolium chloride ionic liquids at 298.2 K, based on activity coefficients estimated from water activity measurements in the entire solubility range, is presented. The results show that the activity coefficients of water in the studied ILs are controlled by the hydrophilicity of the cation and the cation—anion interaction. To achieve a deeper understanding on the interactions between water and the ILs, COSMO-RS and FTIR spectroscopy were also applied. COSMO-RS was used to predict the activity coefficient of water in the studied ionic liquids along with the excess enthalpies, suggesting the formation of complexes between three molecules of water and one IL molecule. On the basis of quantum-chemical calculations, it is found that cation—anion interaction plays an important role upon the ability of the IL anion to interact with water. The changes in the peak positions/band areas of OH vibrational modes of water as a function of IL concentration were investigated, and the impact of the cation on the hydrogen-bonding network of water is identified and discussed.

1. INTRODUCTION

Ionic liquids (ILs) are novel solvents with unique characteristics that make them attractive candidates for use in synthesis, catalysis, sensoristics, and electrochemistry processes and as alternative media for extractions and purifications.1−3 A detailed understanding of their behavior at molecular level is important to further explore the application of ILs.4 Comprehensive characterization of the molecular dynamics and organization of ILs as a function of cation and anion nature,5,6 concentration,7,8 and temperature9 is crucial to understand the molecular interaction in the bulk. The presence of water in ILs affects many of their properties such as polarity, viscosity, conductivity, reactivity and solvating ability.10−12 The role of water in ILs is complex and depends on the constituent ions and supramolecular structure of the ILs.13−16 Most ILs are hygroscopic and absorb water vapor from the atmosphere,8,17 and due to their high molecular weight even traces of water, on a mass per mass basis, turn out to be abundant water in these materials on a mole fraction scale, with important impact on their behavior. For that reason, Seddon and coworkers have early emphasized that efficient drying is necessary in studies of neat RTILs and for most of their applications as solvents.8 Application in capturing CO2 from flue gas using ILs has shown the presence of water in ILs to play an important role.18 Also, in membrane applications using ILs, it has been found that the presence of water significantly alters membrane performance.19 The same has been observed for cellulose processing, where the presence of water has a significant impact upon its solubility.20 Even for electronic applications, a very small amount of water may influence the electrochemical window.21 ILs—water binary systems have also recently attracted increased attention because of their potential for absorption cooling22−27 and their application in extraction processes with both hydrophobic ILs28−30 or with aqueous biphasic systems based on hydrophilic ILs, which are used in the purification of biomolecules and other added-value compounds.31−33

Mixtures of ILs and water were first investigated computationally by Hanke et al.,34 performing molecular dynamics (MD) simulations, where the coordination structure of water with ions was analyzed. The arrangement of water molecules in imidazolium-based ILs has been studied in various subsequent works by the same group and others.35,36 It has been observed that water molecules strongly associate with anions. Furthermore, water molecules in the IL were found to be isolated, while dimers and clusters of water were observed only at very high water concentrations in water miscible ILs.37−39 Mele et al.30 reported that tight ion pairs in ILs remain even after interactions with large amounts of water. Some other authors reported that water molecules interact with the IL clusters without forming a hydrogen-bond network among them.13,41,42 Other theoretical studies also shed light on how the water interaction in the bulk.
Figure 1. continued
molecules interact with the IL when the binary mixture is created, which shows the structural organization of ILs in dilute regime and percolating network of water molecules in the IL-rich region. Jiang et al. analyzed the effect of varying water concentrations on the nanostructural organization of IL–water mixtures using MD simulation. Feng and Voth investigated the effects of cation tail length and anion on dynamics and structure in imidazolium-based IL/water mixtures. Raabe and Köhler performed MD simulations and found that tail aggregation depends on alkyl side-chain length and temperature for imidazolium-based ILs.

Interactions of water dissolved in various ILs have been extensively studied using spectroscopy. The vibrational modes of water that result in the OH-stretching region (3000–3800 cm⁻¹) of the bulk water represent the inhomogeneous environment of water molecules due to hydrogen bonding, which are relevant to the intermolecular interactions, to study the structural change of water due to anion and cation of ILs. The most widely used spectroscopic technique for probing the interaction of ILs–water is infrared (IR). The water content of various ILs is strongly influenced by the nature of the anion and, to a lesser extent, the cation. Most of these studies are related to the interaction of water and the anion, while interactions of the proton on the cation with water are much less evaluated. Jeon et al. studied binary mixtures of [C₅mim][BF₄] with water to explain the relative position of the anion with respect to the imidazolium cation, and the same authors investigated the binary mixtures of [C₅mim][BF₄] with water, over the whole composition range, using attenuated total reflectance infrared (ATR-IR) and studied the effect of the IL on the water structure by analyzing the OH stretching vibrations of liquid water. Cammarata et al. studied the interaction strength of various anions with water and additionally showed the minor cation influences on the molecular states of water in the OH stretching region. Recently, Singh and Kumar studied the structure of imidazolium-based ILs in terms of conformational change in alkyl chain and positioning of anions with respect to cations as a function of water concentration using Fourier transform infrared (FTIR) spectroscopy.

The activity coefficients measure the degree of nonideality of a compound in solution and provide relevant information on the thermodynamic behavior of a solvent. In the present work, 11 hydrophilic ILs with methylimidazolium-based cations and chloride as common anion were chosen to investigate the effect of the number and size of the alkyl side chains on the imidazolium cation upon the interaction between water and the chloride anion at 298.2 K in the entire solubility range of ILs with water. The activity coefficients were assessed by measuring the water activities. Contributing to deepening of the understanding of these important binary mixtures, further information about the water–IL interactions was obtained using FTIR spectroscopy, and density functional theory (DFT) calculations were used to evaluate the strength of the cation–anion interaction. Finally, COSMO-RS is applied to support the information obtained from experimental data and gather further knowledge on the water–IL interactions.

2. EXPERIMENTAL SECTION

2.1. Materials. The studied ILs 1-methylimidazolium chloride, [C₅mim]Cl (98 wt %); 1,3-dimethyl-imidazolium chloride, [C₃mim]Cl (99 wt %); 1-ethyl-3-methylimidazolium chloride, [C₄mim]Cl (98 wt %); 1-butyl-3-methylimidazolium chloride, [C₅mim]Cl; 1-butyl-2,3-dimethylimidazolium chloride, [C₄C₅mim]Cl (99 wt %); 1-pentyl-3-methylimidazolium chloride, [C₅mim]Cl (98 wt %); 1-heptyl-3-methylimidazolium chloride, [C₇mim]Cl (98 wt %); 1-methyl-3-octylimidazolium chloride, [C₈mim]Cl (98 wt %); 1-butyl-3-methylimidazolium chloride, [C₂mim]Cl (98 wt %); 1-pentyl-3-methylimidazolium chloride, [C₅mim]Cl (98 wt %); 1-hexyl-3-methylimidazolium chloride, [C₆mim]Cl (98 wt %); 1-heptyl-3-methylimidazolium chloride, [C₇mim]Cl (98 wt %); 1-methyl-3-octylimidazolium...
chloride, [C8mim]Cl (99 wt %); 1-decyl-3-methylimidazolium chloride, [C10mim]Cl (98 wt %); and 1-allyl-3-methylimidazolium chloride, [α1C1mim]Cl (98 wt %) were obtained from IoLiTec (Germany). For calculation of mole fraction, actual weight mass of ILs has been considered, that is, treated as ion pairs. Figure 1 depicts the chemical structures of the studied methyl imidazolium ILs. Prior to the measurement of the activity coefficient, individual samples of each IL were dried at moderate temperature (~323 K) and at high vacuum (~10^{-3} Pa), under constant stirring, and for a minimum period of 48 h to remove traces of water and volatile compounds. The purities of these ILs were further checked by H and C NMR and were shown to be ≥99 wt %. The water content of each IL was determined by Karl Fischer titration (Mettler Toledo DL32 Karl Fischer coulometer using the Hydranal-Coulomat E from Riedel-de Haen as analyte) and found to be <30 × 10^{-6} mass fraction. Double-distilled water, passed through a reverse-osmosis system and further treated with a Milli-Q plus 185 water purification equipment, was used in all experiments.

2.2. Measurement of Water Activities and Water Activity Coefficients. The measurements of water activities (ςw) were performed using a Novasina hygrometer LabMaster-a, (Switzerland). The measuring principle of the instrument is based on the resistive-electrolytic method. The accuracy of the instrument is 0.001ςw, enabling measurements under controlled chamber temperature conditions (±0.15 K), and was calibrated with six saturated pure salt standard solutions (water activities ranging from 0.113 to 0.973), which were included in the instrument. However, to achieve the given accuracy, a calibration curve was built using either KCl or CaCl2 aqueous solutions at different salt molalities, depending on the magnitude of the water activity values to be measured. The obtained values were compared with those recommended in the extensive reviews by Archer70 for KCl or Rard and Clegg71 for CaCl2. For each measurement, samples of approximately 2 to 3 cm³ were prepared by weighing the appropriate amounts of each compound, presenting a water mole fraction uncertainty of ±0.0001, after being charged in the measuring dishes and finally placed in the airtight equilibrium chamber. The exchange of free water takes place until the partial pressure of water vapor reaches the equilibrium, which is confirmed following the aw variation with time. When a constant value is reached, the water activity is recorded. Diluted solutions reach equilibrium in <1 h, but solutions with high concentration of ILs could take up to 8 h. The water activity coefficient (γw) is then calculated from the water activities as

\[
\gamma_w = \frac{\alpha_w}{x_w}
\]

where \(\alpha_w\) is the water activity and \(x_w\) is the mole fraction of water.

2.3. FT-IR Measurements. ATR and FTIR spectra of water/ILs/water solutions were measured using ABB MB3000 FTIR spectrometer equipped with PIKE MIRacle and single-reflection diamond/ZnSe crystal plate. The spectral region was 400–4000 cm⁻¹ with resolution 4 cm⁻¹ and 100 scans. At least five repeated measurements were performed for each sample. Second-derivative spectra of the hydroxyl (~3250 cm⁻¹) region were used as peak position guides for the Gaussian curve-fitting analysis. The second-derivative and the curve fitting were done using PeakFit v4.0 (AISN Software).

2.4. COSMO-RS Modeling. COSMO-RS (conductor-like screening model for real solvents) is the extension of COSMO model to statistical thermodynamics used for predicting thermo-phsyco-chemico properties of fluids in its pure and mixture state. The detailed theory on COSMO-RS can be found at the original work of Klumt.72 The detailed calculation and procedure of estimating activity coefficient using COSMO-RS can be found elsewhere,73,74 and the procedure of estimating excess enthalpy can be found in the literature.75 The first step in the COSMO-RS prediction procedure is applying the continuum solvation model COSMO to simulate a virtual conductor environment for the molecule of interest. It is then followed by a screening charge density, \(\sigma_p\), on the nearby conductor, obtained through the standard quantum-chemical calculation. The 3D distribution of the screening charge density on the surface of each molecule is converted into a surface composition function, called by the sigma profile (\(\sigma\) profile), \(p(\sigma)\). In the second step, the statistical thermodynamics treatment of the molecular interactions is performed in the COSMOtherm software using the parameter file BP_TZVP_C30_1301 (COSMOLogic, Leverkusen, Germany).76

2.5. Binding Energy. The cation, anion, and ion-pair structures of the studied ILs were geometry-optimized at the density functional theory (DFT) and hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange–correlation functional level. The DGDZVP basis set and the integral equation formalism-polarizable continuum model (IEF-PCM) were employed. All DFT calculations were carried out using Gaussian 09 program,77 and the calculation results were visualized with Chemcraft 1.6 program [G. A. Zhurko, ChemCraft 1.6, (http://www.chemcraftprog.com)]. The ion-pair structures were constructed by combining the Cl anion in the proximity of the H atom attached to the 2-C atom of the imidazolium ring of the lowest energy conformation of the corresponding cations of [Cmim]Cl. In the case of [Cim]Cl, the Cl anion is also placed near the H atom attached to 1-N atom, and it is placed at the front of the methyl group attached to the 2-C atom of [Cmim]Cl. Vibrational frequencies were carried out to verify that the optimized structures were at the minimum energy structure, as no imaginary frequencies were found. The stable ion-pair structures and the H—Cl distances in angstroms are shown in Figure 1. The binding energies for the ion-pair formations were calculated as the differences between the total energies of the ion pairs and the separated ions.

3. RESULTS AND DISCUSSION

Table 1 presents the experimental results for the activity coefficient of water in the studied substituted methyl imidazolium chloride ILs at 298.2 K. To the best of our knowledge, no systematic study on the activity coefficient of water in such a large series of compounds was previously reported. However, a few sets were possible to find in the open literature used here for comparison purposes. In general, a good agreement was found between the experimental values measured in this work and scattered literature data using various techniques for dilute solutions of alkyl methyl imidazolium chloride ([Cmim]Cl,78–80 [Cmim]Cl81 [Cmim]Cl82 [Cmim]Cl83 in aqueous solution in the high range of water mole fractions at 298.2 K as shown in Figure S1 in the Supporting Information. Our choice of several substituted alkyl-methyl-imidazolium-based ILs as cation and chloride as common anion is aimed at studying the effect of the number and length of the cation alkyl chain in the interaction...
Table 1. Experimental Values of Activity Coefficient of Water in Imidazolium-Based Ionic Liquids at 298.2 K

<table>
<thead>
<tr>
<th>System</th>
<th>x_H2O</th>
<th>γ_H2O</th>
<th>x_H2O</th>
<th>γ_H2O</th>
<th>x_H2O</th>
<th>γ_H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O + [C4im]Cl</td>
<td>0.9836</td>
<td>0.981</td>
<td>0.9852</td>
<td>0.984</td>
<td>0.9876</td>
<td>0.989</td>
</tr>
<tr>
<td>H2O + [C4C1im]Cl</td>
<td>0.9633</td>
<td>0.974</td>
<td>0.9673</td>
<td>0.969</td>
<td>0.9643</td>
<td>0.964</td>
</tr>
<tr>
<td>H2O + [C5im]Cl</td>
<td>0.9365</td>
<td>0.945</td>
<td>0.9455</td>
<td>0.947</td>
<td>0.9397</td>
<td>0.931</td>
</tr>
<tr>
<td>H2O + [C5C1im]Cl</td>
<td>0.9075</td>
<td>0.916</td>
<td>0.9137</td>
<td>0.907</td>
<td>0.9086</td>
<td>0.875</td>
</tr>
<tr>
<td>H2O + [C6mim]Cl</td>
<td>0.8682</td>
<td>0.855</td>
<td>0.8802</td>
<td>0.808</td>
<td>0.8137</td>
<td>0.707</td>
</tr>
<tr>
<td>H2O + [C6C1im]Cl</td>
<td>0.8142</td>
<td>0.750</td>
<td>0.7741</td>
<td>0.571</td>
<td>0.7212</td>
<td>0.455</td>
</tr>
<tr>
<td>H2O + [C7mim]Cl</td>
<td>0.7316</td>
<td>0.592</td>
<td>0.7453</td>
<td>0.349</td>
<td>0.6533</td>
<td>0.349</td>
</tr>
<tr>
<td>H2O + [C7C1im]Cl</td>
<td>0.6233</td>
<td>0.483</td>
<td>0.7112</td>
<td>0.470</td>
<td>0.5822</td>
<td>0.273</td>
</tr>
</tbody>
</table>

In general, the studied systems show activity coefficients lower than unity, indicating a favorable interaction between water and the studied imidazolium-based ILs, following the ranking presented here

\[
\gamma_{\text{C4im}Cl} \geq \gamma_{\text{C4C1im}Cl} \geq \gamma_{\text{C5im}Cl} > \gamma_{\text{C5C1im}Cl} > \gamma_{\text{C6mim}Cl} \geq \gamma_{\text{C6C1im}Cl} \geq \gamma_{\text{C7mim}Cl} > \gamma_{\text{C7C1im}Cl} > \gamma_{\text{C8mim}Cl} > \gamma_{\text{C10mim}Cl} = \gamma_{\text{alC1mim}Cl} = \gamma_{\text{C1mim}Cl} = \gamma_{\text{C2mim}Cl}
\]

It is known that the anion is dominant in the interactions that control the water miscibility, but the results here reported highlight the cation influence on the hydrophobicity and the hydrogen-bonding ability of the IL with water. The experimental activity coefficients are reported in Figure 2 along with the COSMO-RS predictions that are shown to provide a correct description of the trend observed.

Presently, predictive models for activity coefficients like those based on functional groups such as UNIFAC, are not simple to apply to ILs containing systems because an extensive and reliable parameter table is still missing. A more recent alternative is the COSMO-RS model for which only a small set of universal parameters must be calibrated. COSMO-RS is an efficient model alternative to structure-interpolating group contribution methods with the advantage that it provides information on the molecular interactions that can be obtained from the \( \sigma \) profiles, depicted in Figure 3. The \( \sigma \) profile of water displays a very broad peak on its negative side, water shows a broad peak at about −1.6 e\textsuperscript{−}\( \text{nm} \)\textsuperscript{2} resulting from the two polar hydrogen atoms, while on the positive side the same broad peak at 1.8 e\textsuperscript{−}\( \text{nm} \)\textsuperscript{2} results from the lone pairs of electrons of the oxygen atom. Both peaks lie beyond the threshold (\( \sigma E = ± 0.79 \text{ e}\textsuperscript{−}\( \text{nm} \)\textsuperscript{2})), which means large parts of the surface of water molecules are able to hydrogen bond. Both H-bond acceptors and donors can undergo efficient H bonding with water if they overcome that threshold. One of the other remarkable features of the water \( \sigma \) profile is the symmetry with respect to \( \sigma E \) that is, it shows the same amount of strongly positive and equally strong negative surface area, which energetically enables very favorable pairing of positive and negative surfaces and the formation of strong hydrogen bonding. The \( \sigma \) profiles of the pure substituted methyl imidazolium chloride ILs are shown in Figure 3 with the cationic imidazolium group lying somewhere in negative region and mostly in the nonpolar part (between −1 and 1). The \( \sigma \) potentials are depicted in Supporting Information (Figure S2).

As previously discussed by us, the COSMO-RS is not able to provide a quantitative description of the activity coefficients for the water-chloride-based IL systems, but as previously described in this work, the qualitative trend of the water activity coefficients is correctly predicted. Additionally, COSMO-RS has previously been shown to be a good tool for the prediction of excess enthalpies for water–IL systems, and thus the model is here used to foster the understanding of these systems. The \( H^E \) is the change in enthalpy upon mixture of the two components, and its estimation in the COSMO-RS method is the sum of three specific molecular interactions, that is, electrostatic/inductive, \( H^E_{\text{MF}} \); hydrogen bonds, \( H^E_{\text{HB}} \); and van der Waals forces, \( H^E_{\text{dVdW}} \), described here

\[
H^E = H^E_{\text{MF}} + H^E_{\text{HB}} + H^E_{\text{dVdW}}
\]

The mixing of water and the methyl-imidazolium-based ILs studied shows the negative excess enthalpy as predicted by using COSMO-RS at 298.2 K, which indicates favorable...
interactions. COSMO-RS is even able to predict the contribution of each specific intermolecular interaction individually for the studied systems throughout the whole composition, which is depicted in Figure S3 in the Supporting Information. From Figure 4, it can be clearly seen that in all studied binary mixtures, the dominant interaction is the hydrogen bonding, largely contributing to the exothermicity of the mixtures, which is in agreement with the literature, confirming that hydrogen bonding is the dominant interaction in water–IL system.37,89

The electrostatic interactions are attractive, as indicated by its negative values, which slightly contribute to the total excess enthalpy of the mixture, whereas van der Waals interactions make a little contribution to the excess enthalpy values of these mixtures. Contribution of $H_{\text{mE}}^\text{el}$ is negative, as depicted in Figure S3 (see Supporting Information), which indicates that water reduces the electrostatics interaction between the cation and the anion of the ILs, which happens first by breaking hydrogen bond between $\text{H}_2\text{O}$–$\text{H}_2\text{O}$ molecule and [Cation]–[Anion] of the ILs, where the latter is followed by the formation of new hydrogen bonds between $\text{H}_2\text{O}$–[Anion] and for higher water concentrations between $\text{H}_2\text{O}$–[Cation] also.90 It has been reported that the hydrogen bonds between [Anion]–$\text{H}_2\text{O}$–[Cation] are stronger than [Cation]–[Anion].90,91 Figure S4 (see Supporting Information) for the binary system of water and ILs shows a minima at $x_{\text{H}_2\text{O}} = 0.75$ that seems to indicate the formation of the complex between three water molecules and one molecule of methyl-imidazolium-based ILs, which is also in accordance with the literature for methyl-imidazolium-based ILs–water systems.37,92 This value is considered the water percolation limit. As the water concentration changes in progressively more concentrated water-in-IL solutions, the water state changes from isolated water molecules, to string-like water clusters, to a percolated water continuous subphase. The percolation limit, first posited by Lynden-Bell et al.,34,37 was after confirmed by MD simulations at around $x_w = 0.75$,43 which corresponds to the minimum observed in the predicted $H_{\text{mE}}^\text{el}$ by COSMO-RS.

The results depicted in Figure 2 show that the hydrophobicity increases with the cation alkyl chain length, in agreement with previous literature results.6,93 However, a few compounds escape this general trend. Because $[\text{C}_{\text{i}}\text{im}]\text{Cl}$ has just one alkyl group attached to the imidazolium ring, it could be expected to present the strongest water interaction, yet, surprisingly, activity coefficients similar to those presented by...
[C6mim]Cl were observed, suggesting an unexpectedly poor interaction with water. The COSMO-RS validation of the peculiar behavior of the activity coefficient of water in [C1im]Cl prompted us to further attempt to explain this unexpected behavior. The predicted excess enthalpies for the system [C1im]Cl−water are significantly lower than those for the other [Cn mim]Cl systems, as shown in Figure 4, further supporting the vision of a poor interaction between [C1im]Cl and water. Binding energies between the Cl−anion and the cation were estimated by DFT. It was observed that the chloride anion has a much higher binding energy with the hydrogen atom attached to nitro group (−9.38 kcal/mol) than with the available free hydrogen atom attached to the C2 (−4.18 kcal/mol), which indicates that the Cl− anion prefers to bind with the hydrogen atom of nitro group rather than with that at the C2 position, which is the preferred interaction observed for the other ILs. This stronger structure decreases the dissociation of the IL and reduces the ability of the water to solvate the IL ions, thus increasing the hydrophobicity of the IL.

Another unexpected behavior was observed in the activity coefficients of [C6 mim]Cl and [C7 mim]Cl when compared with [C4 C1 mim]Cl. This is also validated by the COSMO-RS water activity coefficient predictions showing that the latter presents lower activity coefficients, indicating a slightly higher interaction with water when compared with its isomer [C4 mim] Cl and even with [C6 mim] Cl. This was unexpected because the acidic proton at C2 on the imidazolium ring confers the cation with a hydrogen-bonding donator ability, and its replacement by a methyl group should make it more hydrophobic, yet a more hygroscopic nature for methyl substituted imidazolium ILs has been previously reported.62,64 Again, this behavior could be attributed to ion-pair formation and could be explained on the basis of the excess enthalpies estimated from COSMO-RS and on the binding energies between cation and anion estimated by DFT. For [C4 C1 mim] Cl, the chloride anion has a lower binding energy (−1.94 kcal/mol) for the hydrogen atom of the methyl group attached at C2 position in comparison with [C4 mim] Cl (−3.98 kcal/mol) and [C5 mim] Cl (−3.98 kcal/mol), which in turn enhances the possibility of [C4 C1 mim] Cl to dissociate and interact with water, which is confirmed by the excess enthalpies that are clearly more negative than for the other compounds here compared. (See Figure 4.)

The results concerning these two ILs (i.e., [C6 mim] Cl, [C4 C1 mim] Cl) suggest that an enhanced interaction of the cation with the water is not a guarantee of an enhanced interaction of the IL with water because this interaction results from a balance between the [Cation]−[Anion], [Cation]−H2O, and [Anion]−H2O interactions. An increase in the [Cation]−H2O interaction is often accompanied by a simultaneous increase in the [Cation]−[Anion] interaction.
that may actually reduce the ability of the final IL to interact with water and then lead to an increase in the IL hydrophobicity. A counterintuitive strategy for the design of ILs with a stronger interaction with water may actually be the decrease in the cation polarity or any other strategy that may contribute to decrease the [Cation]−[Anion] interaction, as observed for the [C6C1mim]Cl, where the introduction of a methyl group actually enhances the IL hydrophilicity, while the removal of one of the methyl groups, as in [C4mim]Cl, will actually enhance the hydrophobicity of the compound.

As previously mentioned, IR spectroscopy has been shown to be a tool for investigating molecular interactions between water and ILs.10−14 The normalized spectra in the OH stretching regions for the studied alkyl methyl imidazolium chloride—water systems are depicted in Figure 5 for xIL = 0.05 and 0.10. (For some other concentrations, see Supporting Information Figure S5.) FTIR-normalized absorbance spectra of water in the OH stretching for various studied water−ILs mixtures at different water (xH2O = 0.02, 0.05, 0.10, 0.25 and 0.4) mole fractions are depicted in the Supporting Information (Figure S6). As part of this study to understand the molecular interaction of water and ILs, we monitored the changes in the water spectrum in the presence of ILs species, that is, cation and anion. The mid-IR spectrum of liquid water has an intense and broad band envelope at ~3300 cm−1 that is assigned to the OH stretching modes.105−107 Curve fitting of water vibrational spectrum is often used to describe the structure of liquid water by the continuum model proposed by Walrafen108 and later advanced by Green et al.109 and Hare and Sorensen.110 A more thorough description of the fitting of the neat water spectrum can be found in the literature.105−107 Among the OH stretch band of water, the most prominent stretching is around 3250 and 3420 cm−1, which represent the strongly H-bonded patches of molecules with tetrahedral structure (ice like) and weakly H-bonded molecules (liquid like), respectively. The other component bands at 3550 and 3620 cm−1 are attributed to the coupling of OH antisymmetric stretching vibrational modes110 and the dangling OH stretching modes of water molecules, respectively. Although it is not possible to assign a defined frequency to the band resulting from the Cl−water hydrogen bonds, it is also within this broad band envelope. The normalized absorbance spectra of water in the OH stretching region clearly show a blue shift in all studied water−[C6mim]Cl, as depicted in Figure 5.

Figure 6 depicts the variation in peak position of the OH stretch band for the various mixtures as a function of IL concentration. A marked blue shift is observed, which increases with the increase in the alkyl chain length on the cation. These changes in the blue shift indicate a disruption in the water hydrogen-bonding network that results from a combined effect of the molar volume of the ions (the larger the disruption, the more important) and their ability to hydrogen bond with water (the larger the smaller is the disruption), as can be observed from the results reported by Singh and Kumar.111 Their results also show that small anions with a strong hydrogen-bond ability, such as chlorides, present a much reduced blue shift when compared with other larger or more hydrophobic anions, as observed in this work (Figure 6). The blue shift here observed seems to follow the increase in the cation hydrophobicity. The cation hydrophobicity is related to the alkyl chain length and thus the molar volume of the cation, following the order

**Figure 6.** Peak shift for OH stretching band of water for various studied water−ILs mixtures with increasing ILs mole fraction.

\[
\begin{align*}
[C_4mim]Cl &< [C_8mim]Cl < [C_6mim]Cl < [C_7mim]Cl \\
&< [C_9mim]Cl < [C_{10}mim]Cl \approx [C_{11}mim]Cl < [alC_{11}mim]Cl \\
&< [C_{12}mim]Cl < [C_{13}mim]Cl < [C_{14}mim]Cl
\end{align*}
\]

The only relevant exception observed is for [C6C1mim]Cl. Although its molar volume is identical to [C6mim]Cl, its IR spectra display a shift identical to [C9mim]Cl. In this case, for a similar molar volume of the cation, the effect of the higher anion solvability, that is, a higher capacity to establish hydrogen bonding with water, appears as a reduced disruption of the hydrogen bonding network of the water by this IL. The opposite effect observed for [C11mim]Cl in the activity coefficients is not observed here because the lower ability of the chloride anion to hydrogen bond with water in this IL is not compensated by the low molar volume effect upon the water hydrogen-bonding disruption.

For all water−ILs systems, the blue shifting observed is most prominent in the lower concentration of IL proofing to have a maximum impact upon the water hydrogen bonding for concentrations below xIL = 0.1, as the effect is much less important above this concentration. This is in agreement with the results by Singh and Kumar,111 and it seems to be related to a region of high water concentration where the water−ion clustering is very high, as described by Zhong et al.112 Above that value, the water network seems to be completely disrupted, and, as shown by different authors,113−115 other regions where smaller clusters of water, down to the limit of solitary water molecules, will be also present. The actual mole fraction for this transition seems to vary with the anion.112,116

4. CONCLUSIONS

The prospect of fine-tuning properties, through the combination of cations and anions, allows the design of task-specific ILs intended for a specific application. It is important to understand the behavior of water−ILs interaction quantitatively to design the process. The prediction based on COSMO-RS method was of great value to design applications based on ILs because they permit rationalization of the selection of the cation−ion pair for obtaining the type of interactions required to achieve a given behavior as a solvent. On the basis of new experimental water activity coefficient data, it was found that the interaction study of water−ILs is affected by increasing alkyl chain length on the imidazolium ring. COSMO-RS is found to be a reliable...
predictive method to estimate at least qualitatively the excess enthalpies and Gobbs free energy of binary mixtures of water and ILs, indicating that hydrogen bonding is the dominant interaction in the studied binary system. COSMO-RS also suggests the formation of complexes in the binary mixture of water and studied imidazolium-based ILs. Quantum-chemical calculation shows that cation-anion interaction plays an important role upon the ability of the IL to interact with water. IR spectroscopy shows a blue shift, which increases with the increase in the alkyl chain length on the cation, indicating a disruption in the water-hydrogen-bonding network that results from a combined effect of the molar volume of the ions and their ability to hydrogen bond with water.

**ASSOCIATED CONTENT**

Supporting Information

Comparison of experimental water activity ($\alpha_w$) and activity coefficient ($\gamma$) of some alkyl methyl imidazolium chloride ([C$_n$ mim]Cl, [C$_n$ mim]Br, [C$_n$ mim]I, and [C$_n$ mim]I) in aqueous solution at 298.2 K with reported values in literature; $\sigma$ potential of H$_2$O and studied alkyl methyl imidazolium chloride; concentration of specific interaction of each molecule to the excess enthalpy of binary mixture of H$_2$O and ILs at 298.2 K estimated by COSMO-RS; estimated total excess enthalpies and estimated excess Gobbs’s Free energy of binary mixture of ILs and water at 298.2 K predicted by COSMO-RS; FTIR-normalized absorbance spectra of water in the OH stretch region in the range 2800−3800 (cm$^{-1}$) at fixed concentrations of ILs for the various studied water−IL mixtures; and FTIR normalized absorbance spectra of water in the OH stretch region in the range 2800−3800 (cm$^{-1}$) for various studied water−IL mixtures at different water ($\chi_{$H_2O} = 0.02, 0.05, 0.10, 0.25, 0.40$) mole fractions. 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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