# Supporting Information for: 

# Structural Features of the $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ Ionic Liquid and Its Mixtures with Water: Insight from a ${ }^{1} \mathrm{H}$ NMR Experimental and QM/MD Study 

by
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## 1 Structural analysis

The $\mathrm{H} 4-\mathrm{Cl}^{-}$and $\mathrm{H} 5-\mathrm{Cl}^{-}$RDFs shown in Figures S 1 and S 2 , respectively, exhibit similar structure as that of $\mathrm{H}_{2}-\mathrm{Cl}^{-} \mathrm{RDF}$ in Figure 2a of the article. The most probable $\mathrm{H} 4 / 5 \cdots \mathrm{Cl}^{-}$hydrogen bond lengths are also equal to $2.67 \AA$, and spherical integration of $\mathrm{H} 4-\mathrm{Cl}^{-}$and $\mathrm{H} 5-\mathrm{Cl}^{-}$RDFs up to $4.0 \AA$ gives the coordination numbers of 1.28 and 1.22 , respectively, thus somewhat lower than the coordination number of chloride anions around the C2-H2 moiety.

The distribution of the $\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{Cl}^{-}$and $\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cl}^{-}$angles in neat $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ IL shown in Figures S3 and S4, respectively, exhibit similar shapes as that seen for the distribution of the $\mathrm{C} 2-\mathrm{H} 2 \cdots \mathrm{Cl}^{-}$angle shown in Figure 3a of the article. However, the most probable $\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{Cl}^{-}$and $\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cl}^{-}$angles are found to be around 140 deg in both cases, thus somewhat larger as compared to the most probable angle of the C2$\mathrm{H} 2 \cdots \mathrm{Cl}^{-}$hydrogen bond. Part of the anions are found to be situated on top of the $\mathrm{C} 4-\mathrm{H} 4$ and $\mathrm{C} 5-\mathrm{H} 5$ bonds, and linear hydrogen bonds are rare. The distribution of the $\mathrm{C} 5-\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{Cl}^{-}$and $\mathrm{C} 4-\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cl}^{-}$dihedral angles illustrated in Figures S 5 and S 6 , respectively, show pronounced maxima at $\pm 120$ deg just as seen for the distribution of the N1-C2-H2 $\cdots \mathrm{Cl}^{-}$dihedral angle in Figure 3b of the article, thus the preference for the chlorides to be located either on the butyl or the methyl side with equal probabilities. In addition, the probability for the anions to be located in the plane of the imidazolium ring are higher in these cases as compared to the corresponding case where anions are found in the vicinity of the C2-H2 bond. The distributions seen in Figures S5 and S6 are rather different in the range of -90 to +90 deg as compared to that shown in Figure 3b. They suggest that chloride anions are also often found in the area in-between $\mathrm{C} 4-\mathrm{H} 4$ and $\mathrm{C} 5-\mathrm{H} 5$ bonds, and they prefer to be located roughly in the plane of the imidazolium ring in this case.

Unlike for the case of distribution of chloride around the C2-H2 moiety, the angular distributions of chloride anions around the C4-H4 and C5-H5 bonds shown in Figures S3 and S 4 , respectively, are less sensitive to the amount of water in the mixture. However, the dihedral angle distributions shown in Figures S5 and S6 indicate the increasing preference for the chloride anions to stay in the region in-between the C4-H4 and C5-H5 moieties with the rising content of water in the mixture. The populations of anions on the methyl and butyl sides are thus seen to diminish, especially in the system with $\chi_{\mathrm{IL}}=0.25$.


Figure S1: Radial distribution functions between H 4 atom and $\mathrm{Cl}^{-}$ion in neat [C4mim][Cl] IL and its mixtures with water, scaled by the number density of the chloride anions, $n_{\mathrm{Cl}}$, for each specific system.


Figure S2: Radial distribution functions between H 5 atom and $\mathrm{Cl}^{-}$ion in neat [C4mim][Cl] IL and its mixtures with water, scaled by the number density of the chloride anions, $n_{\mathrm{Cl}}$, for each specific system.


Figure S3: Distribution of the $\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{Cl}^{-}$angle, $\Phi$, in neat $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}] \mathrm{IL}$ and its mixtures with water for $R\left(\mathrm{H} 4 \cdots \mathrm{Cl}^{-}\right) \leq 4.0 \AA$.


Figure S4: Distribution of the $\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cl}^{-}$angle, $\Phi$, in neat [C4mim][Cl] IL and its mixtures with water for $R\left(\mathrm{H} 5 \cdots \mathrm{Cl}^{-}\right) \leq 4.0 \AA$.


Figure S5: Distribution of the $\mathrm{C} 5-\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{Cl}^{-}$dihedral angle, $\Theta$, in neat [C4mim][Cl] IL and its mixtures with water for $R\left(\mathrm{H} 4 \cdots \mathrm{Cl}^{-}\right) \leq 4.0 \AA$.


Figure S6: Distribution of the $\mathrm{C} 4-\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cl}^{-}$dihedral angle, $\Theta$, in neat $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ IL and its mixtures with water for $R\left(\mathrm{H} 5 \cdots \mathrm{Cl}^{-}\right) \leq 4.0 \AA$.


Figure S7: The ${ }^{1} \mathrm{H}$ NMR spectrum of a sample of $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ with $\chi_{\mathrm{IL}}=0.98$ recorded at the temperature of 298 K . Atom numbering in C4mim ${ }^{+}$cation is included as an insert.


Figure S8: Radial distribution functions between H 4 and oxygen atoms of water in mixtures of $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ and water, scaled by the number density of the water molecules, $n_{\mathrm{w}}$, for each specific system.


Figure S9: Radial distribution functions between H 5 and oxygen atoms of water in mixtures of $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ and water, scaled by the number density of the water molecules, $n_{\mathrm{w}}$, for each specific system.


Figure S10: Radial distribution functions between C10 atoms of C4mim ${ }^{+}$cations in neat $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}] \mathrm{IL}$ and its mixtures with water, scaled by the number density of the imidazolium cations, $n_{\text {BMI }}$, for each specific system.


Figure S11: Visualization of a QM region in the QM/MM calculations for systems A to $\mathbf{F}$, see main text of the article for details. Central water molecule is represented by the ball-and-stick model. Additional species included to the QM region around the central water molecule are represented by the stick model, except for the chloride anions which are represented as green balls. Ions and water molecules described by the point charges in the QM/MM calculations are not shown. Note that the geometry of each system is taken from a single randomly selected configuration; the structure of the quantum mechanically treated region changes from configuration to configuration in each specific system.


Figure S12: Visualization of a QM region in the $\mathrm{QM} / \mathrm{MM}$ calculations for systems G to M, see main text of the article for details. Central C4mim ${ }^{+}$cation is represented by the ball-and-stick model. Additional species included to the QM region around the central cation are represented by the stick model, except for chloride anions which are represented as green balls. Ions and water molecules described by the point charges in the QM/MM calculations are not shown. Note that the geometry of each system is taken from a single randomly selected configuration; the structure and composition of the quantum mechanically treated region changes from configuration to configuration in each specific system. See Table 2 in the article for statistical information concerning the nature and amount of different species included to the QM region in these systems.
Table S1: The QM/MM based ${ }^{1} \mathrm{H}$ NMR isotropic shielding constants (in ppm ) of $\mathrm{C} 4 \mathrm{mim}^{+}$cation in pure $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}] \mathrm{IL}$ simulated at the temperature of 298 K . The KT3 functional and def2-TZVP basis set were used in the QM/MM calculation unless stated otherwise. All entries for shielding constants are arithemtic averages over 100 molecular configurations with central cation selected randomly in each configuration. Statistical errors calculated as sample standard deviations are given in paranthesis. The first column indicates the number of ions included to the QM region along with the central cation. Here, the three integers given in parentheses indicate the numbers of ions promoted to the QM region closest to $\mathrm{H} 2, \mathrm{H} 4$, and H 5 atoms, respectively. Second column indicates point-charge potential used for classical C4mim ${ }^{+}$cations. Refer to Figure 3 in the main text of the article for atom labeling in C4mim ${ }^{+}$cation. Experimental data for ${ }^{1} \mathrm{H}$ NMR chemical shifts of neat [C4mim][Cl] IL are listed in the last two lines of the table.

| To QM | Pot. | H2 | H4 | H5 | H6 | H7 | H8 | H9 | H10 |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $(0,0,0)$ | - | $24.01(0.03)$ | $24.34(0.03)$ | $24.30(0.03)$ | $27.81(0.01)$ | $27.49(0.02)$ | $29.79(0.02)$ | $30.45(0.03)$ | $30.62(0.02)$ |
| $(0,0,0)$ | RESP | $23.59(0.04)$ | $23.98(0.04)$ | $23.99(0.04)$ | $27.77(0.02)$ | $27.35(0.03)$ | $29.83(0.04)$ | $30.46(0.03)$ | $30.84(0.03)$ |
| $(1,1,1)$ | RESP | $23.08(0.09)$ | $23.57(0.09)$ | $23.57(0.10)$ | $27.73(0.03)$ | $27.32(0.04)$ | $29.81(0.05)$ | $30.44(0.04)$ | $30.84(0.03)$ |
| $(1,1,1)^{a}$ | RESP | $23.04(0.10)$ | $23.53(0.10)$ | $23.54(0.10)$ | $27.74(0.04)$ | $27.33(0.04)$ | $29.82(0.05)$ | $30.45(0.04)$ | $30.86(0.03)$ |
| $(1,1,1)^{b}$ | RESP | $23.19(0.08)$ | $23.70(0.08)$ | $23.70(0.08)$ | $27.77(0.03)$ | $27.37(0.04)$ | $29.85(0.05)$ | $30.48(0.04)$ | $30.86(0.03)$ |
| $(3,2,2)^{a}$ | RESP | $22.44(0.08)$ | $23.22(0.10)$ | $23.23(0.08)$ | $27.63(0.05)$ | $27.20(0.06)$ | $29.79(0.05)$ | $30.45(0.05)$ | $30.93(0.03)$ |
| $R \leq 4.0 \AA^{a, c}$ | RESP | $22.53(0.09)$ | $23.21(0.10)$ | $23.11(0.08)$ | $27.41(0.05)$ | $27.10(0.06)$ | $29.73(0.06)$ | $30.54(0.06)$ | $30.90(0.05)$ |
| $R \leq 4.0 \AA^{a, c}$ | - | $22.61(0.09)$ | $23.02(0.10)$ | $23.08(0.10)$ | $27.39(0.06)$ | $27.14(0.08)$ | $29.84(0.07)$ | $30.60(0.06)$ | $31.03(0.06)$ |
| Exp. $\delta(\text { this work })^{d}$ | 10.23 | 8.33 | 8.47 | 4.05 | 4.34 | 1.61 | 0.94 | 0.50 |  |
| Exp. $\delta(\text { Cha } \text { et al. })^{e}$ | 10.22 | 8.34 | 8.47 | 4.08 | 4.36 | 1.63 | 0.96 | 0.53 |  |

${ }^{a}$ - def2-TZVP basis for central cation, 3-21G basis for all additional ions.
${ }^{c}$ - all ions that are within the $4 \AA$ distance from $\mathrm{H} 2, \mathrm{H} 4$ and H 5 as well as from carbons $6,8,9$ and 10 have been included to the QM region. ${ }^{1} \mathrm{H}$ NMR chemical shifts of $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]\left(\chi_{\mathrm{IL}}=0.98\right)$ measured at 298 K in this work. ${ }^{1} \mathrm{H}$ NMR chemical shifts of neat $[\mathrm{C} 4 \mathrm{mim}][\mathrm{Cl}]$ measured at 298 K in Phys. Chem. provided by Prof. D. Kim (Sogang University, Korea) through private communication.

