A EUROPEAN JOURNAL
CHEMPHYSCHEM
OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

Accepted Article

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To be cited as: *ChemPhysChem* 10.1002/cphc.201801206

Link to VoR: http://dx.doi.org/10.1002/cphc.201801206

A Journal of ChemPubSoc Europe

WILEY-VCH www.chemphyschem.org

10.1002/cphc.201801206

Cluster formation through hydrogen bond bridges across chloride anions in a hydroxyl-functionalized ionic liquid

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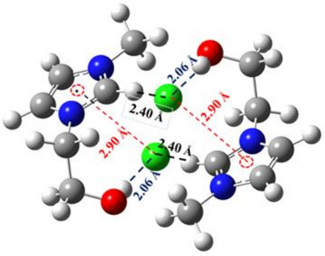
ABSTRACT

Several recent studies of hydroxyl-functionalized ionic liquids (ILs) have shown that cation-cation interactions can be dominating these materials at the molecular level when the anion involved is weakly interacting. The hydrogen bonds between the like ions led to the formation of interesting chain-like, ring-like, or distinct dimeric (i.e. two ion pairs) supermolecular clusters. In the present work, vibrational spectroscopy (ATR-IR and Raman) and quantum chemical theory (DFT) of the hydroxyl-functionalized imidazolium ionic liquid $C_2OHmimCl$ indicate that anion-cation hydrogen bonding interactions are dominating and lead to the formation of distinct dimeric ion pair clusters. In this arrangement the Cl^- anions function as a bridge between the cations by establishing bifurcated hydrogen bonds with the OH group of one cation and the C(2)-H of another cation. Cation-cation interactions, on the other hand, do not play a significant role in the observed clusters.

TOC GRAPHICS & TEXT



Peculiar ion pair dimers: A combined theoretical and experimental study of a hydroxyl-functionalized ionic liquid provides strong evidence for the formation of distinct ion-pair dimers in the condensed-phase material. The strongly-interacting chloride anions act as a hydrogen bonding bridge between the cations, and cation-cation interactions are negligible.

KEYWORDS: Ionic liquid; H-bonding Interaction; Ion pair; Cluster formation; Density Functional Theory (DFT)

Introduction

Ionic liquids (ILs) are fascinating materials and have received considerable attention in academia as well as industry over the past 20 years. The tunability of their properties via combining suitable cations and anions makes them attractive for applications in a variety of fields including organic synthesis, catalysis, electrochemistry, and separation.[1-4] These designable properties (e.g. viscosity, electrical conductivity, and non-volatility) are determined by the molecular interactions between the ions. Therefore, unravelling the structure-property relationships and finding universal correlations that can be utilized for a rational design, i.e. without the need for extensive trial-and-error testing, is an important goal.[5, 6] In fact, a full understanding of how the chemical structure of the ions and the interionic forces effect the macroscopic properties of an IL will be a game changer.

The molecular interactions inside ILs are rather complicated compared to other classes of materials. There are long-range coulombic forces due to the charges of the ions, dispersion forces between aliphatic chains, as well as hydrogen bonding. The interplay of these interactions yields a local structure and produces micro/mesoscopic local domains. Studying how these phenomena affect the macroscopic properties has been and still is a hot topic in chemistry and chemical engineering. A common approach is to investigate series of ILs with a systematically changing structure in one ion while keeping the other ion constant. For example, varying the alkyl chain length in 1,3-dialkylimidazolium ILs or changing the anion was performed in many studies.[7-14]

Studying ILs with functionalized side chains is another highly active area of research that aims at understanding the structure-property relationships. In particular, substituting alkyl chains by hydroxyl-functionalized moieties is currently very popular as this adds a further group that can potentially form hydrogen bonds. These hydroxyl-functionalized ILs were developed for a number of interesting applications. For example, they exhibit a remarkable capability of reversibly capturing green-house gases.[15-17] Moreover, the introduction of the hydroxyl group was found to enhance the hydrophilicity and enzyme activity,[18] to improve the solubility of inorganic salts,[19] and to make suitable reaction media for metal oxide powders with specified size.[20, 21]

Very recently, a number of spectroscopic and theoretical studies focused on the molecular interactions of hydroxyl-functionalized ILs.[22-26] In these papers, a large variety of cations, e.g. imidazolium-, ammonium-, piperidinium-, pyrrolidinium-, and pyridinium-based ones, was functionalized with an OH-containing group. The counterions included bis(trifluoromethylsulfonyl)imide (NTf_2), tetrafluoroborate (BF_4), and picrate. Interestingly, in all these studies the experimental and theoretical results led to the conclusion that the OH-functionalized ILs share strong cation-cation interactions. The hydrogen bonding between the OH groups of one cation and either the OH group of another one or the C(2)-H proton of the imidazolium ring of a second cation was found to overcome the coloumbic repulsion of the like ions. However, experimentally, only the OH…OH hydrogen bonds could be observed unambiguously. In some ILs, a hydrogen bonding network with chain or ring-like structures was found,[24] which is very similar to the observations in simple aliphatic alkyl alcohols.[27, 28] Due to all these studies pointing into the same direction, it was reasonable to speculate/conclude that cation-cation interactions are a universal phenomenon in OH-functionalized ILs.[26] However, a comparative study of the Ludwig group[29] showed that the cation-cation interactions are only dominating in the case of weakly interacting anions. In ILs with strongly interacting anions, on the other hand, cation-anion interactions via the hydroxyl group were observed as an important mechanism.

In this study we show an example of an OH-functionalized IL, which forms distinct dimeric clusters through cation-anion interactions. For this purpose, 1-(hydroxyethyl)-3-methylimidazolium chloride (C_2OHmimCl) was studied theoretically and experimentally. The schematic structure of the cation and anion is depicted in Chart 1 together with the atom numbering scheme.

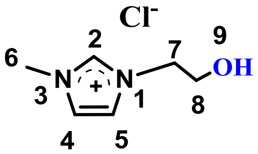


Chart 1. Structure and atom numbering scheme of title compound.

Materials and Methods

Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium chloride(C_2OHmimCl). All materials were of analytical grade and procured from Sigma Aldrich. This includes solvents for the synthesis (ultrapure water, acetonitrile, dichloromethane, ethanol) and D_2O and $CDCl_3$ for the NMR experiments. The detailed synthesis procedure is described in a previous paper.[30] In brief, a mixture of 2-chloroethanol (0.67 mL, 10 mmol) and 1- methylimidazole (1.1 g, 10 mmol) was heated for 24 h at 120 °C. The crude product, which crystallized upon cooling, was finely crushed, washed with Et_2O (3x80 mL), and dried under reduced pressure for 10 h. In order to remove volatile components and water, the IL was dried under constant stirring at a temperature of 298 K for about 24 h at a reduced pressure of 2 Pa; there was no detectable mass loss of a 2 g sample during this period of time. Finally, the water content was below 100 ppm as proved by Karl Fischer titration. After drying, the samples were handled under argon atmosphere.

C_2OHmimCl: State: Pale yellow powder; mp 56 °C; Yield: 1.8 g (94.5%); ^{1}H-NMR:(600 MHz, D_2O): δ (ppm) 8.78 (s, ^{1}H), 7.54 (s, ^{1}H), 7.49 (s, ^{1}H), 4.34 (t, ^{2}H, J = 4.9 Hz), 3.96 (t,^{2}H, J = 4.9 Hz), 3.93 (s, ^{3}H);^{13}C-NMR (150.93 MHz, D_2O): δ (ppm) 136.4,123.6, 122.4, 59.8, 51.5, 35.7.

Instrumentation. Infrared Spectroscopy. For the study of the vibrational properties, attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectra were acquired on a Vertex 70-RAM II Bruker spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate TM diamond ATR accessory (Specac Ltd., Slough, UK). FTIR/ATR spectra (600-3500 cm^{-1}) were collected with a nominal resolution of 1 cm^{-1} by co-adding 64 scans for each spectrum.

Raman Spectroscopy. FT-RAMAN spectra were acquired by means of a Vertex 70-RAM II Bruker FT-RAMAN spectrometer with a Nd:YAG laser (yttrium aluminium garnet crystal doped with triply ionized neodymium) having a wavelength of 1064 nm and a maximum power of 1.5 W. The measurement accessory is pre-aligned; only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the focal point. The RAM II spectrometer is equipped with a liquid-nitrogen cooled Ge detector and FT-RAMAN spectra (200-3500 cm^{-1}) were collected with 1 cm^{-1} nominal resolution by co-adding 128 scans for each spectrum at room temperature.

Quantum Chemical Calculations. Structure Calculations. DFT (B3LYP and CAM-B3LYP method) calculations were employed to calculate the optimized energies and to compute the geometries for different possible conformers of the ion pair, and clusters of two ion pairs. The new hybrid exchange-correlation functional with long-range-corrected (LC) exchange functional CAM-B3LYP was chosen to obtain a better understanding of the intermolecular interactions as the standard B3LYP does not include a long-range correlation function. The high level basis set 6-311++G(d, p) was used in all the calculations, as it performed well in the prediction of molecular interactions.[31] The Gaussian 09 suite of programs[32] was used for all the computations, and the GaussView 5.1 program was used to visualize the structures.[33]

Wavenumber Calculations. The vibrational wavenumbers of all conformers of the cation, the anion, and the ion pair configurations of IL along with their IR and Raman intensities were also calculated using the Gaussian 09 program. All the calculations were performed without applying any constraints. In every case, the optimized structures finally converged into the minima of the potential surface, which was confirmed from the absence of negative (imaginary) wavenumbers for any normal mode.

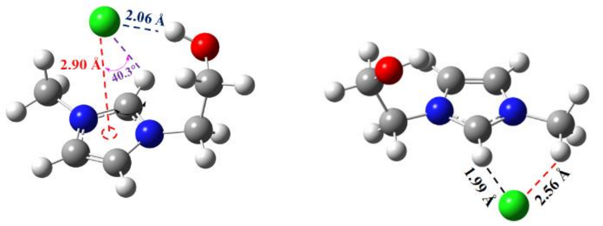
Binding Energy Calculation. Binding energy calculation of ion-pair was also performed using DFT calculations with the B3LYP/6-311++G(d,p) basis set using Gaussian 09 linked to the GaussView 5.1 program. The energy of the ion-pair formation (ΔE) was estimated using Eqn (1), according to Turner et al.[6]

$$\Delta \mathrm{E} = E_{AX} - E_{A^+}^{Min} - E_{X^-}^{Min} + E_{\mathrm{BSSE}} + \Delta \mathrm{ZPVE} \qquad (1)$$

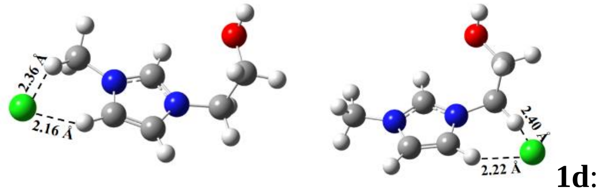
where ΔE is the energy of the ion-pair formation and EAX, EA+, EX- are the energy of ionic pair, the isolated cation, and anion, respectively. The interaction energies were corrected by the basis set super-position errors (BSSE) correction with the counterpoise procedure method advanced by Boys and Bernardi[34] at B3LYP/++G(d,p) level. Zero-point energy (ZPE) correction calculated using the unscaled B3LYP/6-311+G(d,p) frequencies was also taken into account for the calculated interaction energies.

Results and Discussion

In the first step, an isolated ion pair was considered in the theoretical analysis. Figure 1 illustrates four stable configurations establishing a number of different molecular interaction mechanisms. The lowest energy structure (Fig 1a) is characterized by the chloride anion forming interactions with the protons of the hydroxyl and the C(2)-H groups. In addition, a $\pi^+\cdots Cl^-$ interaction is observed. The other conformers show bifurcated $CH\cdots Cl^-$ interactions at the aromatic and aliphatic CH groups. A more detailed description and analysis of the isolated ion pair configurations is provided in the supplementary material.



1a: $\Delta E_{rel} =$ 0 kcal mol^{-1} **1b**: $\Delta E_{rel} =$ 10.09 kcal mol^{-1}



1c: $\Delta E_{rel} =$ 15.28 kcal mol^{-1} **1d**: $\Delta E_{rel} =$ 11.98 kcal mol^{-1}

Figure 1 (a-d): Optimized structure of various ion pair configurations for $C_2OHmimCl$ in the gas phase.

In the next step, two ion pairs were considered at the same time. The optimized geometry of the resulting ion pair dimer is illustrated in Figure 2. Interestingly, in contrast to the previously studied OH-functionalized ILs,[26] where the cations formed a central unit stabilized by strong cation-cation hydrogen bonding, the current $C_2OHmimCl$ shows the opposite behavior. The two chloride anions take a central role acting a hydrogen bonding bridge between the cations. This yields a highly symmetric structure, in which each chloride ion establishes three different interactions: 1) an H-bond with the C(2)-H of one cation and 2) a $\pi^{+}\cdots Cl^{-}$ interaction plus 3) an H-bond with the OH group of the other cation. In other words, if at all cation-cation interactions play only a minor role here.

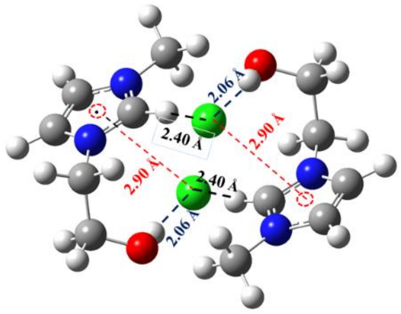
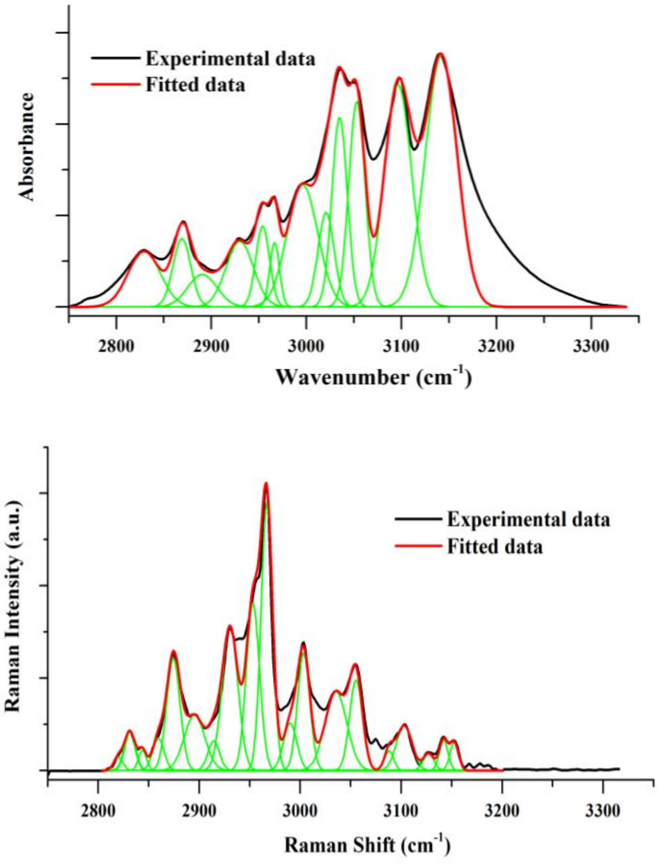


Figure 2. Optimized dimeric ion pair of $C_2OHmimCl$ in gas phase.

In order to verify these theoretical findings, the experimental vibrational spectra were analyzed. Figures 3a and 3b show the CH/OH stretching region of the FTIR and Raman spectra, respectively. The full spectra are shown in the supplementary material for completeness. The experimental data were decomposed by a spectral fitting routine in order to identify the individual vibrational contributions to the overall band. The band assignments are summarized in Table 1 together with the corresponding theoretically predicted wavenumbers for the lowest energy configurations.

10.1002/cphc.201801206

The previous studies of other OH-functionalized ILs indicated that hydrogen bonding between the OH groups of different cations and C(2)-H···OH hydrogen bonding are a dominating mechanisms. This resulted in OH vibrations similar to those found in alkyl alcohols.[26] The individual contributions to the OH stretching band in the normal aliphatic alkyl alcohols are commonly found at wavenumbers larger than 3200 cm^{-1}:[27] one peak at ~3250 cm^{-1} from the twofold H-bonded OH groups and one peak at ~3350 cm^{-1} single H-bonded groups. The vibrational spectra of C_2OHmimCl, however, do not show any characteristic signals in this range. Such signatures would be expected to appear as rather narrow peaks due to the highly defined hydrogen bonding state in the clusters. Instead the OH signatures are found at around 3100 cm^{-1}, which can be attributed to the strong interactions with the chloride ions. This supports the theoretical predictions. Another corroborating feature can be found in the fingerprint region (see supplementary material). The presence of a strong peak at 603 cm^{-1} plus the absence of a peak around 625 cm^{-1} suggests that the C_2OH chain more or less exclusively exists in its gauche form, which is a strong indicator of the predicted ion pair dimer configuration. Moreover, none of the spectral signatures suggests significant cation-cation interactions.



a)

b)

Figure 3: Experimental ATR-FTIR (a) and Raman (b) spectra of C_2OHmimCl.

Table 1: Selected Vibrational band assignments of C_2OHmimCl.

Band Assignment	Experimental: FTIR /Raman	Theory: Ion-pair	Theory:

			Dimeric IP
$\nu_{.}(C_{4,5} - H)$	3140/(3151, 3142)	3191/3173	3191/3173
$\nu_{.}(C_2 - H)$	-/3127	3205	3067
$\nu_{.}(O - H)$	3096/3101	3158	3221
$\nu_{AS}(N - CH_3)$	3051/3054	3051	3051
$\nu_{AS}(N - CH_2)$	3034/3035	3015	3008
$\nu_{.}(C = C)$	1570/1570	1597	1595

For the C-H region 3300-2700 cm^{-1}, the N-CH$_3$ stretching at 3051 cm^{-1} was selected as a reference peak for scaling the theoretical wavenumbers and the scaling factor is found to be 0.968.

Conclusions

This work presented a combined computational and experimental analysis of 1-(hydroxyethyl)-3-methylimidazolium chloride. The formation of distinct dimeric clusters from two ion pairs was found. Interestingly, these clusters are characterized by strong cation-anion interactions and a geometrical configuration, in which the chloride anions act as a hydrogen bonding bridge between the cations. Cation-cation interactions, which were found to be the dominating mechanism in hydroxyl-functionalized ionic liquids with weakly coordinating anions, do not play a significant role in the clusters observed herein. Our work shows that further theoretical and experimental effort is necessary to finally unravel the structure-property relationships of this fascinating class of materials. One specific point that should be addressed in future studies are temperature effects, which may cause significant changes to the observed interaction mechanisms.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

SKP thanks Prof. Puspendu K. Das for his suggestions and SERB for N-PDF post-doc fellowship (Scheme: N-PDF/2016/000041) at the Department of Inorganic and Physical Chemistry (IPC), Indian Institute of Science (IISc), Bangalore-560012, India. The authors gratefully acknowledge support (financial support and instrument facilities) from the Department of Chemistry at the Dr. Moulay Tahar University of Saida, Algeria and MESRS.

BH thanks Dr. Khonati for fruitful discussions and Q. Arnould for performing the FT-Raman measurements at the Walloon Agricultural Research Centre (CRA-W).

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