

Lewis Acidity/Basicity Changes in Imidazolium Based Ionic Liquids Brought About by Impurities

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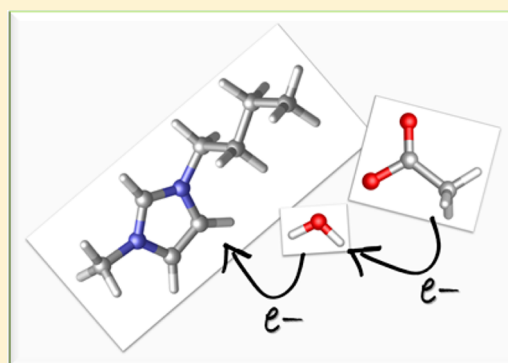
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S Supporting Information

ABSTRACT: We herein report on the effect that water molecules, present as impurities, in the vicinity of an ionic liquid model structure, may induce on the Lewis acidity/basicity patterns normally observed in these materials. Depending on the position and orientation of water, the Lewis acidity/basicity pattern changes from “normal distribution” (i.e., the basicity located at the anion moiety and the acidity located at the cation fragment) to “bifunctional distribution” (i.e., the acidity and basicity located at the cation moiety). In some specific cases, there appears a third Lewis acidity/basicity distribution, where water may bind both the cation and the anion of the ion pair; a response we tentatively call “amphoteric”. These effects are clearly traced to the hydrogen bond formation ability of water to coordinate different regions of pure ionic liquids taken as references.



INTRODUCTION

From the early 1990s, room temperature ionic liquids (RTILs) have gained renewed attention due to the increasing range of applications, including almost all fields of chemistry and chemical engineering.^{1–4} For instance, RTILs are currently being used in catalysis,^{5–10} organic synthesis,^{5,6,11–15} extractions,^{16–18} kinetics,^{19–23} electrochemistry,²⁴ and solar cells.^{25–28} Among the more appealing properties that these materials display, their combinatorial flexibility is by far the most interesting and powerful property for it allows RTILs to be designed for specific applications by varying the anion–cation combinations. This property went on to call them “design solvents” because their properties can be adjusted to suit the requirements of a particular reaction or process, including room temperature catalysis.^{5,6,29,30} The number of combinations considering the available anions and cations amounts to the huge figure of 10^{18} RTILs that can potentially be prepared. Currently, approximately 300 RTILs are commercially available, and about 1000 others have been prepared and reported in the literature.³¹ The choice and design of the suitable RTIL for each reaction is not an easy task because their microscopic chemical structures are still unknown.^{5,6,15} Furthermore, starting from the formidable number of combinations leading to new task specific RTILs, one can say that “probably the optimum RTIL for a specific reaction or process is included within this 10^{18} possible combinations”. Note however that now the problem becomes equivalent to finding a needle in a haystack. It is precisely at this point where theory may help.

To date, Lewis acidity and basicity are concepts that are exclusively associated with the ability of the cation to accept a hydrogen bond (HB) and to donate an HB in the case of anions forming the RTIL, respectively.^{14,24,32–35} Welton et al. investigated a series of RTILs using a linear solvation energy relationship (LSER) approach.³² They found that hydrogen bond acidity (HBA) values are largely determined by the nature of the cation, with a lower contribution of the anion. On the other hand, they predicted that hydrogen bonding to solutes would be significant even in the absence of strong HB accepting anions. Hydrogen bond basicity (HBB) on the other hand is dominated by the anion, mainly those that are the conjugate bases of strong acids. Chiappe et al. investigated the Stille cross-coupling reaction in 10 different RTILs to evaluate solvation effects on the transfer of vinyl and alkyl groups.¹⁴ They found that the introduction of a methyl group at position C2 in imidazolium derivatives suppresses the HB acidity of the solvent. This response emphasizes the anion effect: it enhances the rate of the cross-coupling in the hexafluorophosphate series, whereas it has no effect in the bis(trifluoromethylsulfonyl)imide derivatives. On the other hand, Cerda-Monje et al. introduced an index that provides a quantitative estimation of the HB acceptor basicity and HB donor acidity of RTIL.³³ These indexes use the specific solute–solvent interactions described in terms of the electronic chemical potential for proton migration

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between the anion or cation at the transition state structure of the cycloaddition of cyclopentadiene toward acrolein. Cerdá-Monje et al. concluded that solvation effects by RTIL are strongly solute-dependent, and therefore, it is no longer possible to think in a universal model of solvation for these reaction media.

The unpredictable way in which the RTILs operate as solvents encourages further experimental and theoretical studies including design, properties, and applications. In a previous work we introduced a new concept to classify Lewis acidity/basicity (LAB) patterns in RTILs.³⁴ They were defined as “normal distribution” of HBA and HBB, for those RTILs where the Lewis molecular acidity is mainly centered at the cation fragment, whereas the Lewis molecular basicity is centered at the corresponding anion. “Bifunctional distribution” was used to label those RTILs where both the Lewis acidity and basicity are located at the same region of the RTIL. These concepts are based on the regional ionization potential (IP_R) index.³⁶ This quantity describes the effect induced by the anion in interaction with a cation of general structure 1-butyl-3-methylimidazolium ($[C_4C_1]Im$).³⁴ The IP_R is given by eq 1 below:³⁴

$$IP_R = (E_L^c - E_H^a) \times f_{\Omega}^- \quad (1)$$

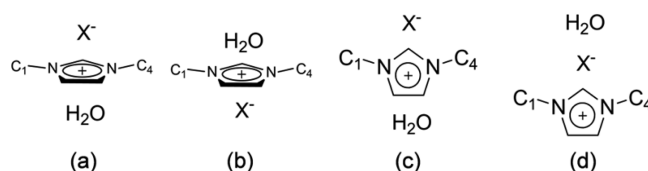
In eq 1, E_L^c and E_H^a correspond to the one electron energies of the frontier molecular orbital LUMO and HOMO, of the isolated cation and anion, respectively, and f_{Ω}^- is the nucleophilic Fukui function condensed over the anion.^{37–41} For IP_R values higher than 1.5 eV, the RTIL is considered to have a normal LAB distribution. For IP_R values lesser than 1.5 eV, the RTIL is considered as bifunctional. However, the bifunctionality of the cation is a strong anion-dependent property through polarization effects.³⁴

The main issue we shall address in this work is about the effect that any impurity could have over the Lewis acidity/basicity of ionic liquids. The problem is pertinent because these properties generally attributed to “pure ionic liquids” in the form of “anion effect” or “cation effect” may be wrongly assigned because of the presence of a third body in the system. The choice of water as a model impurity is also pertinent because RTILs are highly hygroscopic materials, and because of the amphoteric character of water to bind molecules via electrophilic or nucleophilic hydrogen bonding modes. We analyze the effect that a water molecule may have on the LAB patterns for 15 $[C_4C_1]Im$ based RTILs. During the review processes, two referees called our attention to the reliability of our results to anticipate if in condensed liquid phase the distribution of water ions will be similar to those in the studied cases. Certainly the model used cannot be considered as a real picture of a condensed phase. However, the model certainly assesses via three different and independent approaches that water can affect the hydrogen bonding properties of the cation and anion forming an ionic liquid.

MODELS AND COMPUTATIONAL DETAILS

In order to obtain relevant information about the interaction of RTIL with water, we chose four arbitrary different initial guesses in a set of 15 different RTILs based on the 1-butyl-3-methylimidazolium $[C_4C_1]Im$ cation. This choice was made on the basis of chemical intuition. The resulting arrangements are depicted in Scheme 1.

Scheme 1. Initial Guesses for the Location of a Water Molecule: (a) Behind, (b) Front-Side, (c) Below, and (d) Above



The set of 15 RTILs in the arrangements depicted in Scheme 1 were optimized using Truhlar’s M06HF together with the 6-311++G(d,p) basis set. The M06HF method has been successfully tested to quantitatively reproduce the noncovalent interactions of several ternary systems consisting of an ion pair with a water molecule.⁴² In order to discard the basis set effect on the results obtained, the calculations were also performed using the Dunning–Huzinaga AUG-cc-pVTZ basis set as described elsewhere.³⁸ The Lewis acidity and basicity contributions were calculated using the electrophilic (f^+) and nucleophilic (f^-) Fukui functions using a procedure described elsewhere.^{37–41} The regional Lewis acidity (+) or basicity (−) may readily be obtained using eq 2, below:^{34,38}

$$f_{\Omega}^{\pm} = \int_{\Omega^{\pm}} f^{\pm}(\vec{r}) d\vec{r} \quad (2)$$

Here, f^+ or f^- stands for the site showing the higher ability to accept or donate electronic charge or, equivalently, with those sites displaying the higher abilities to donate or accept hydrogen bonds. Hereafter, Ω^{\pm} represents molecular regions where the electrophilic Fukui function (Ω^+) and nucleophilic Fukui function (Ω^-) have a maximum, respectively.^{34,38} To complement the theoretical study based on electronic descriptor of the Lewis acidity/basicity, topological analyses of the electron density in the framework of Bader’s quantum theory of atoms in molecules (QTAIM) were carried out using the AIMAll software,^{43,44} together with a natural bond orbital analysis (NBO).⁴⁵ This population analysis is normally complemented with second order perturbation energies. This perturbation theory analysis, which is a tool that allows understanding molecular interactions from a localized non-bonding orbital of an idealized Lewis structure with an empty non-Lewis orbital. For each donor and acceptor orbital i and j , say, the energy of stabilization is denoted by $E^{(2)}$, and it is evaluated following eq 3

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_j - \epsilon_i} \quad (3)$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements, and $F(i, j)$ are the off-diagonal elements of the Fock matrix. All the calculations were carried out with Gaussian 09 software.⁴⁶ QTAIM analyses were performed using the AIMAll software.⁴⁴

RESULTS AND DISCUSSION

The main question in the present work is whether or not the presence of one water molecule can affect the electronic structure of RTIL based on the $[C_4C_1]Im$ cation. This question may first be answered using the IP_R index using eq 1. Because the cation is the same for the whole series, the regional IP_R values are integrated over the anion. Note that the effect of the cation is self-contained in the IP_R values, because the f^-

Table 1. Regional Ionization Potential (IP_R) and Predicted LAB Distributions for Different Anions Interacting with $[C_4C_1Im]^+$ Cation in the Presence of a Water Molecule^a

anion	M06HF/6-311++G(d,p)				M06HF/AUG-cc-pVTZ				LAB distribution
	a	b	C	d	a	B	c	d	
Al ₂ Cl ₇ ⁻	0.48	0.45	0.47	0.49	0.49	0.46	0.48	0.49	bifunctional
AlCl ₄ ⁻	0.39	0.39	0.39	0.37	0.40	0.40	0.40	0.38	bifunctional
BF ₄ ⁻	0.14	0.15	0.12	0.13	0.15	0.15	0.12	0.13	bifunctional
Br ⁻	2.53	2.35	2.43	2.40	2.57	2.39	2.46	2.43	normal
CF ₃ CO ₂ ⁻	2.44	0.86	0.74	0.89	2.48	0.88	0.75	0.90	amphoteric
CH ₃ SO ₃ ⁻	0.31	1.09	0.30	0.29	0.31	1.10	0.30	0.29	bifunctional
Cl ⁻	2.40	2.28	2.14	2.27	2.43	2.31	2.17	2.30	normal
ClO ₄ ⁻	0.25	0.25	0.22	0.25	0.25	0.26	0.22	0.25	bifunctional
DCA ^b	2.51	2.52	2.56	2.51	2.54	2.55	2.59	2.55	normal
H ₂ PO ₄ ⁻	0.25	0.28	0.27	0.25	0.25	0.29	0.27	0.25	bifunctional
HSO ₄ ⁻	0.27	0.23	0.25	0.26	0.27	0.24	0.26	0.27	bifunctional
NTf ₂ ^c	0.43	0.42	2.42	0.42	0.43	0.43	2.45	0.43	amphoteric
OAc ^d	0.48	2.47	0.36	2.49	0.48	2.50	0.36	2.53	amphoteric
OTf ^e	0.28	0.25	0.27	0.26	0.29	0.25	0.28	0.26	bifunctional
PF ₆ ⁻	0.16	0.16	0.12	0.15	0.14	0.16	0.13	0.16	bifunctional

^aThe configurations are those depicted in Scheme 1. All values were obtained at the M06HF/AUG-cc-pVTZ level of theory, and they are expressed in eV units. ^bDicyanamide. ^cBis(trifluoromethanesulfonimide). ^dAcetate. ^eTrifluoromethanesulfonate.

index is normalized to unity. The results are summarized in Table 1.

If we take a look at Table 1, the anions Br⁻, Cl⁻, and DCA⁻ display values of $IP_R > 1.5$, thereby suggesting that their LAB is normally distributed, independent of the position of the water molecule. On the other hand, for RTIL bearing anions Al₂Cl₇⁻, AlCl₄⁻, BF₄⁻, CH₃SO₃⁻, ClO₄⁻, H₂PO₄⁻, HSO₄⁻, OTf⁻, and PF₆⁻ for which $IP_R < 1.5$, a bifunctional distribution of the LAB is predicted, independent of the position of the water molecule.

It is important to note that, for CF₃CO₂⁻, NTf₂⁻, and OAc⁻ containing RTILs, different IP_R responses are obtained (see Table 1). Note that this time the LAB distribution is dependent on the position of water relative to the isolated ion pair model structure. The net result is that, for these RTILs, there is the possibility of having an amphoteric response. For instance, for the CF₃CO₂⁻ derivative in the “above” configuration (see Figure 1) the RTIL is predicted to display a normal LAB distribution. Similar responses are obtained for the RTIL bearing NTf₂⁻ and OAc⁻ anions. This result is relevant for it suggests that the “cation effect” or “anion effect” defined in the

literature may be modified by the presence of any species, present as solutes or any impurity in the RTIL phase. This model may be extensive to mixtures of RTIL/RTIL or mixtures of RTIL with any conventional organic solvents. It is important to emphasize at this point that M06HF together with the 6-311++G(d,p) basis set and AUG-cc-pVTZ lead almost to the same results, thereby suggesting that the IP_R index is basis set independent. The results described at this point are much too qualitative. Beyond the numerical results, it is more important to assess the origin of them. In this sense, and in order to rationalize the observed responses for CF₃CO₂⁻, NTf₂⁻, and OAc⁻ based RTILs, a Fukui function analysis was performed. Figure 1 shows the nucleophilic Fukui Function for two different and relevant positions.

All the RTILs considered in this study establish hydrogen bonding between water and the anion in all configurations explored, except for $[C_4C_1Im]CF_3CO_2$. In this case, the molecule of water “below” is the unique configuration where water does not establish an HB to the anion (see $[C_4C_1Im]-CF_3CO_2$ configuration “below” in Figure 1). This result is relevant because the change in the initial position of water in this case could change the LAB distribution from bifunctional to normal if water does not interact with the anion.

Another abnormal case is the $[C_4C_1Im]NTf_2$ ion pair, where the molecule of water in the “above” configuration only establishes HB to the anion (see $[C_4C_1Im]NTf_2$ “above” in Figure 1). In the other three configurations water establishes an HB to the RTIL using the acidic hydrogen atoms of the imidazolium moiety (see for instance $[C_4C_1Im]NTf_2$ “behind” in Figure 1). In this case, when a configuration has more than one HB, a change is generated in the LAB distribution from normal to bifunctional, when water interacts with the anion and the cation at the same time. We shall call this situation the “amphoteric” distribution. For $[C_4C_1Im]OAc$, the situation is opposite with respect to $[C_4C_1Im]NTf_2$. In this case, the “below” and “above” configurations only establish an HB to the anion whereas the “front-side” and “behind” configurations establish HB to the anion, with the acidic hydrogen atoms of the imidazolium cation. Here the LAB distribution changes

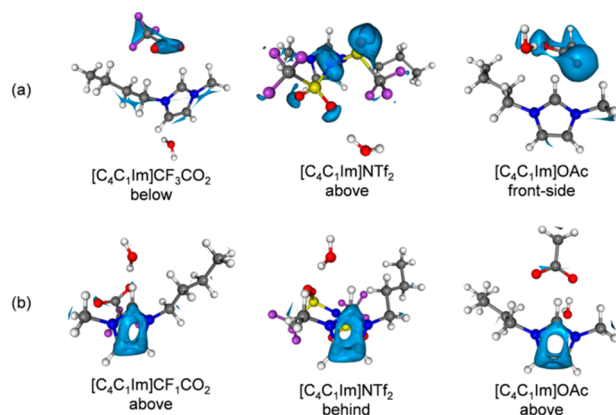


Figure 1. Surfaces in blue represent nucleophilic Fukui function for $[C_4C_1Im]CF_3CO_2$, $[C_4C_1Im]NTf_2$, and $[C_4C_1Im]OAc$ condensed at (a) anion and (b) cation for the interaction with water in two different positions.

from bifunctional to normal when water interacts with both the anion and the cation.

An additional analysis was performed in order to understand the role of water in the distribution of the electron density. In this sense, Bader's QTAIM analysis is a useful tool to understand bond formation processes and even interactions in RTIL using the electron density, ρ , and the Laplacian of the electron density, $\nabla^2\rho$.^{47–52} Table 2 displays the values of ρ and $\nabla^2\rho$ in the $(3, -1)$ critical points (bond critical points, BCPs) between water and the ion pair in the amphoteric distribution

Table 2. QTAIM Analysis of Amphoteric RTILs and a Representative Conformation of $[\text{C}_4\text{C}_1\text{Im}]\text{DCA}$ and $[\text{C}_4\text{C}_1\text{Im}]\text{BF}_4$ ^a

initial guess	LAB distribution	BCP	$\rho \times 10^{-2}$	$\nabla^2\rho \times 10^{-2}$	illustration
CF ₃ CO ₂ Anion					
below	normal	1	1.03	4.13	Figure 2a
		2	1.03	4.12	
front-side	bifunctional	1	1.18	4.02	Figure 2b
		2	2.30	9.53	
		3	5.88	14.3	
above	bifunctional	1	4.51	14.6	Figure 2c
		2	1.90	7.44	
behind	bifunctional	1	1.53	5.81	Figure 2d
		2	5.85	14.2	
		3	1.89	7.46	
NTf ₂ Anion					
below	bifunctional	1	2.06	8.72	Figure 3a
		2	3.39	13.6	
		3	0.850	2.94	
front-side	bifunctional	1	0.900	3.08	Figure 3b
		2	3.42	13.5	
		3	2.05	8.64	
above	normal	1	0.570	2.62	Figure 3c
		2	0.530	2.34	
		3	2.01	8.91	
behind	bifunctional	1	2.07	8.71	Figure 3d
		2	3.27	12.7	
		3	0.760	2.70	
OAc Above					
below	normal	1	1.51	6.03	Figure 4a
		2	6.23	14.0	
		3	0.390	1.30	
front-side	bifunctional	1	7.86	13.0	Figure 4b
		2	2.30	9.53	
		3	0.810	3.24	
		4	1.28	4.47	
above	normal	1	6.50	15.1	Figure 4c
		2	1.99	7.73	
behind	bifunctional	1	1.82	6.95	Figure 4d
		2	8.29	13.2	
		3	2.07	8.16	
BF ₄ Anion					
below	bifunctional	1	3.36	14.5	Figure 5a
		2	0.410	1.51	
		3	1.47	5.47	
		4	1.63	6.18	
DCA Anion					
below	normal	1	1.39	5.68	Figure 5b
		2	3.43	9.43	

^aThe values of ρ and $\nabla^2\rho$ are in atomic units.

cases. Additionally, the same BCPs were obtained for $[\text{C}_4\text{C}_1\text{Im}]\text{DCA}$ and $[\text{C}_4\text{C}_1\text{Im}]\text{BF}_4$ as representative cases of normal and bifunctional distributions for the sake of comparisons.

Let us start the QTAIM discussion by considering the $[\text{C}_4\text{C}_1\text{Im}]\text{CF}_3\text{CO}_2$ system (see Figure 2 for BCP visualization).

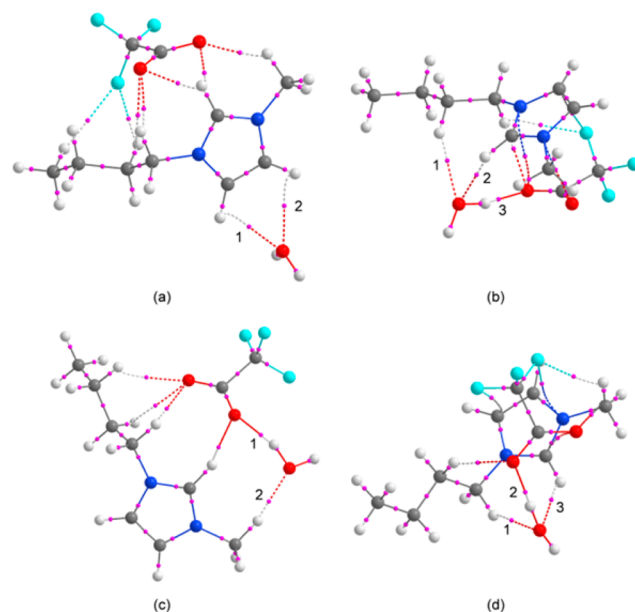


Figure 2. QTAIM analysis of $[\text{C}_4\text{C}_1\text{Im}]\text{CF}_3\text{CO}_2$ at four initial configurations: (a) below, (b) front-side, (c) above, and (d) behind. Pink spheres represent the $(3, -1)$ critical points. Other critical points were omitted to simplify the viewing.

In this case, the bifunctional distribution is characterized by enhanced ρ and $\nabla^2\rho$ values with respect to the normal distribution configuration. The values obtained show that, in the bifunctional conformations, the interaction between water and the ion pair is stronger. According to Bader's proposal, those BCPs with low and positive ρ and $\nabla^2\rho$ are commonly associated with HB. Those HBs with higher $\nabla^2\rho$ may be related to a strong interaction. For the whole set of configurations, except the one labeled "below", $\nabla^2\rho$ displays high values, thereby suggesting significant HB between the water molecule and the anion of the RTIL. In the "below" configuration, this descriptor has a marginal component associated uniquely with a weak interaction with the cation. In a previous work, we classified $[\text{C}_4\text{C}_1\text{Im}]\text{CF}_3\text{CO}_2$ as possessing a normal LAB distribution. The results obtained herein including a water molecule suggest that, if present, water could modify and control the electronic reorganization in this RTIL. In this sense, water may act as a bridge promoting a charge transfer from the anion to the cation.

Now, let us consider the interaction of $[\text{C}_4\text{C}_1\text{Im}]\text{NTf}_2$ ion pair with water (see Figure 3). In this case, the trend is quite similar with respect to that observed for the $[\text{C}_4\text{C}_1\text{Im}]\text{CF}_3\text{CO}_2$ ion pair. Previously, the NTf₂ derivative has been considered as possessing a bifunctional LAB distribution. However, in the initial guess configuration labeled "above", the results suggest that this ion pair could act as possessing a normal LAB distribution. In the remaining configurations, the result obtained is similar to that of the isolated ion pair. In Figure 3c, it may be seen that, in the "above" configuration, water weakly interacts with both the anion and cation. This response

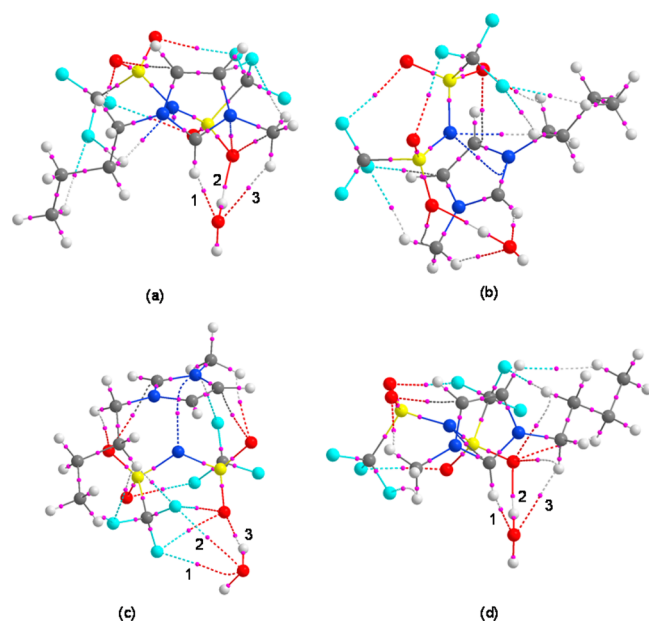


Figure 3. QTAIM analysis of $[\text{C}_4\text{C}_1\text{Im}]\text{NTf}_2$ at four initial configurations: (a) below, (b) front-side, (c) above, and (d) behind. Pink spheres represent the $(3, -1)$ critical points. Other critical points were omitted to simplify the viewing.

may be traced to a marginal effect of water on the reorganization of the electron density. In plain words, water could be acting simply as a spectator in this case.

For $[\text{C}_4\text{C}_1\text{Im}]\text{OAc}$ ion pair, the situation is a little different, after considering that the values of $\nabla^2\rho$ are quite similar in all cases. However, if we sum the individual contributions to $\nabla^2\rho$, the values obtained are 21.37×10^{-2} au, 25.77×10^{-2} au, 22.83×10^{-2} au, and 28.36×10^{-2} au, for the configurations “below”, “front-side”, “above”, and “behind”, respectively. This difference may be responsible for the different responses of this ion pair interacting with water. In those cases with higher $\nabla^2\rho$, HB is expected to be more effective, and consequently, the reorganization of the electron density with water in the middle changes the LAB distribution from normal in the isolated case, to bifunctional in the configurations “below” and “above” (see Figure 4).

Additionally, the QTAIM analysis was performed on the $[\text{C}_4\text{C}_1\text{Im}]\text{BF}_4$ and $[\text{C}_4\text{C}_1\text{Im}]\text{DCA}$ ion pairs (see Figure 5). This choice was made in order to summarize the results discussed up to this point. In the case of bifunctional RTIL, the probability of significant hydrogen bonding to water is expected for those systems presenting low and positive values of ρ and $\nabla^2\rho$ (see Table 2, entry for BF_4 anion).

Even though the QTAIM analysis seems to be sufficient to qualitatively explain the interaction of water with several RTILs, a final study was performed. Table 3 displays the second order perturbation theory energies, $E^{(2)}$'s, within the NBO framework. The $E^{(2)}$ energies were analyzed for the set of amphoteric ion pairs and for $[\text{C}_4\text{C}_1\text{Im}]\text{BF}_4$ and $[\text{C}_4\text{C}_1\text{Im}]\text{DCA}$ as representative cases of bifunctional and normal LAB distributions. The $E^{(2)}$ values displayed in Table 3 reveal a similar trend to those obtained with the QTAIM model in Table 2. In this sense, the energies observed for HB contributions may arbitrarily be separated into four contributions. These contributions are charge donation from water to the cation and the anion in RTIL, and the inverse processes, namely, from the cation and the anion to the water molecule. Let us first

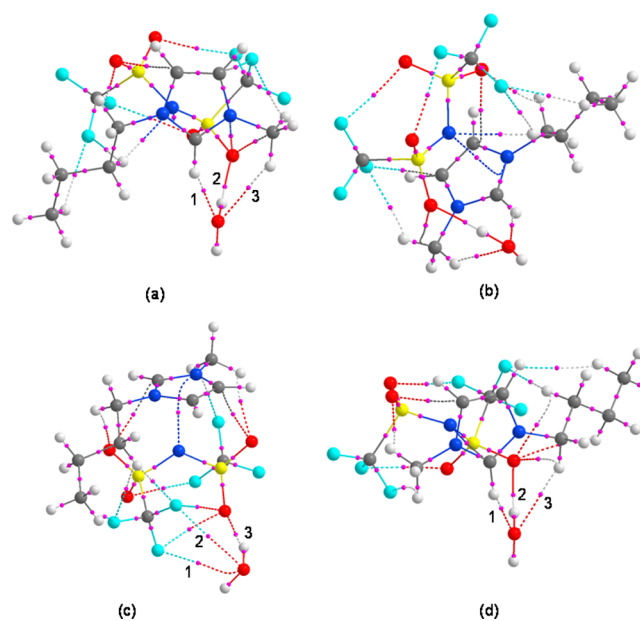


Figure 4. QTAIM analysis of $[\text{C}_4\text{C}_1\text{Im}]\text{OAc}$ at four initial configurations: (a) below, (b) front-side, (c) above, and (d) behind. Pink spheres represent the $(3, -1)$ critical points. Other critical points were omitted to simplify the viewing.

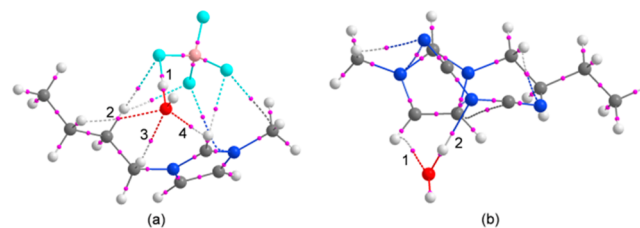


Figure 5. QTAIM analysis of (a) $[\text{C}_4\text{C}_1\text{Im}]\text{BF}_4$ and (b) $[\text{C}_4\text{C}_1\text{Im}]\text{DCA}$. Pink spheres represent the $(3, -1)$ critical points. Other critical points were omitted to simplify viewing.

consider columns two and three to discuss charge donation from water to the anion and from the cation to water. Both columns show low $E^{(2)}$ values.

These results are not surprising because water cannot donate additional charge to an already charged system nor can a cation donate charge to water. In the case of charge transfer from anion to water we observe, for CF_3CO_2 within the below configuration, that the $E^{(2)}$ value is marginal. The same response is obtained for charge transfer from water to the cation. The three remaining configurations have a similar trend: $E^{(2)} > 20$ kcal/mol in the interaction between the anion and water and $E^{(2)} = 7\text{--}10$ kcal/mol for the interaction between water and the cation. This result is relevant for it reveals a simple mechanism of electron density reorganization promoted by water: the anion interacts with water and redirects the electronic charge to the cation, in a similar way to that described within the reactivity indices and QTAIM analyses (Table 2).

CONCLUDING REMARKS

We have shown that water molecules present in the vicinity of a pure RTIL model structure can affect the LAB distribution of the liquid. Depending on the position of water molecules, LAB pattern changes from “normal distribution” to “bifunctional

Table 3. Second Order Perturbation Theory Energies, $E^{(2)}$ (in kcal/mol), for the Amphoteric Ion Pairs in Table 2^a

initial guess	water to anion	cation to water	anion to water	water to cation
CF ₃ CO ₂ Anion				
below	0.0	0.0	0.0	0.8
front-side	0.2	0.6	45.9	9.6
above	0.2	0.2	27.2	7.2
behind	0.2	0.5	45.2	9.7
NTf ₂ Anion				
below	0.4	0.5	16.1	9.4
front-side	0.4	0.5	16.9	8.7
above	0.3	0.0	5.4	0.0
behind	0.2	0.5	15.1	9.2
OAc Anion				
below	0.4	0.1	53.3	0.5
front-side	0.4	0.6	76.8	10.8
above	0.4	0.2	54.1	8.0
behind	1.2	0.5	82.4	11.9
BF ₄ Anion				
below	0.1	0.3	16.4	7.6
DCA Anion				
below	0.0	0.2	17.5	0.9

^aFor configuration references see Figures 3–5.

distribution” and vice versa. In some specific cases, there appears a third LAB distribution, where water may bind both the cation and the anion of the ion pair, a response we tentatively call “amphoteric”. These effects are clearly traced to the HB formation ability of water to coordinate different regions of the ion pair structure used to mimic the RTIL. These results have been obtained using three complementary approaches including electronic descriptors of reactivity (i.e., the regional ionization potential and the Fukui function basins), the topological analysis of the electron density, and second order perturbation theory. All three methods point to a simple mechanism of electron density reorganization promoted by water: the anion interacts with water and redirects the electronic charge to the cation, thereby modifying the LAB distribution of RTIL respect to the isolated ion pair. However, the presence of water in RTIL (for instance as moisture) alone does not guarantee changes in LAB distributions. The configuration in which water binds the RTIL is crucial, a result traced to the electrophilicity of the cation and the nucleophilicity of the anion. However, these conclusions await experimental verification in order to validate the qualitative responses predicted from this quantum chemistry model using an ion pair model for RTIL and one water molecule to mimic a dopant agent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b05305.

Cartesian coordinates, number of imaginary frequencies, and absolute energies for each calculated structure, and complete ref 43 (PDF)

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Notes

The authors declare no competing financial interest.

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