

# Lewis Molecular Acidity of Ionic Liquids from Empirical Energy–Density Models

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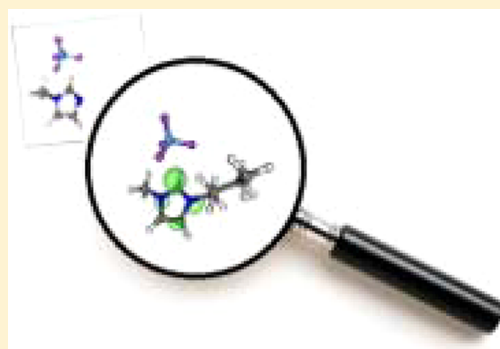
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## S Supporting Information

**ABSTRACT:** Two complementary models of Lewis molecular acidity are introduced and tested in a wide series of 45 room temperature ionic liquids (RTIL). They are defined in the context of the conceptual density functional theory. The first one, which we tentatively call the excess electronic chemical potential, assesses the electron accepting power of the RTIL by relating the H-bond donor acidity with the charge transfer associated to the acidic H-atom migration at the cation of the RTIL considered as a HB-donor species. This global index accounts for the molecular acidity of the cation moiety of the ionic liquid that takes into account the perturbation of the anionic partner. The second index is defined in terms of the local charge capacity modeled through the maximum electronic charge that the cation, in its valence state, may accept from an unspecified environment. Each model is compared with the experimental HB-donor acidity parameter of the Kamlet Taft model. The best comparison is obtained for a combination of both the excess electronic chemical potential and the local charge capacity. As expected, the correlations with the Kamlet Taft  $\alpha$  parameter do not lead to a universal model of HB-donor acidity. Reduced correlations for limited series of structurally related RTIL are obtained instead. Finally, we illustrate the reliability and usefulness of the proposed model of RTIL molecular acidity to explain the cation-dependent solvent effects on the reactivity trends for cycloaddition, Kemp elimination, and Menshutkin reactions, for which experimental rate coefficients are available from literature.



## INTRODUCTION

Room-temperature ionic liquids (RTILs) have been the focus of increasing interest in almost all the field of chemistry in the last decades – apart from their remarkable physicochemical properties that have made them green solvents in regard to reducing environmental levels of volatile organic compounds (VOCs). Their major strength relies on its high combinatorial flexibility that provides a huge number of combinations that has led to the idea that reaction media can be designed to suit particular reaction conditions including catalysis at room temperature (task specific RTILs).<sup>1,2</sup> Most ionic liquids display similar polarities, yet their solvent properties can differ considerably from one another as well as from traditional molecular solvents. As in the past, solvation effects modeled from their electrical properties would greatly help in our understanding of the solute–solvent interactions that drive a chemical process in solution at microscopic level. However, electrostatic contribution is only one of the relevant components of solvation phenomena, and some specific nonelectrostatic contribution must be considered.

Solvation effects by RTILs have been treated using several procedures. Experimentally, the development of empirical

solvent polarity scales have been used to explain the differences in solvent-mediated reaction pathways, reaction yields, synthesis product ratios, and even rate coefficients and selectivity.<sup>3–6</sup> However, two different ionic liquids that have essentially identical polarity ratings or descriptors can produce very different results when used as solvents for organic reactions. Among the most used solvent polarity scales, the Kamlet Taft is one of the most popular. For instance, any XYZ property in solution is normally expressed as a linear solvation free energy relationship (LSER) as follows:

$$XYZ = (XYZ)_o + a\alpha + b\beta + s\pi^* \quad (1)$$

where  $(XYZ)_o$  is the intrinsic property of the isolated solute and  $a$ ,  $b$ , and  $s$ , are coefficients accompanying the contribution of the solvent hydrogen bond donor acidity ( $\alpha$ ); the hydrogen bond acceptor basicity ( $\beta$ ), and the solvent dipolarity–polarizability ( $\pi^*$ ), respectively. Complete sets of Kamlet–Taft parameters have been measured for a wide series of

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RTILs.<sup>7</sup> Other scales include other sets of macroscopic properties of the solvent as viscosity, molar volumes, and so forth.

The usefulness and the limits of validity of LSER models of solvation have been recently reviewed by Hallet and Welton.<sup>8</sup> These authors made a critical analysis on the reliability of the proposed solvent polarity scales: the first one involves the transferability of the response of a particular probe solute, or solutes, from some known molecular solvent to ionic liquids. This transferability would warrant that the polarities of the ionic liquid and the molecular solvent are the same and that the appropriate value of the parameter can then safely be assigned to the ionic liquid. The second implicit assumption is that the effect of transferring from a molecular solvent to an ionic liquid is the same for all probes. They conclude that it is important to consider the nature of the solute as well as the solvent when establishing reliable solvent polarity parameters mainly, when this solute is transferred from a neutral molecular solvent to an ionic liquid. The main message, however, is that it cannot be a priori established if one solvent polarity scale respect to another one is right or wrong: "each scale will turn useful in a given set of circumstances and in other ones they will not".<sup>8</sup> This problem can turn dramatic if one tries to use these polarity scales to validate theoretical scales that are useful to model solute solvent interactions in terms of fundamental descriptors of the electronic structure of matter. In this sense, the LSER-based scales of solvent polarity bears the caveat emptor warning to the would-be users of these data.

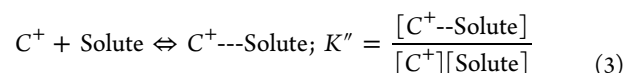
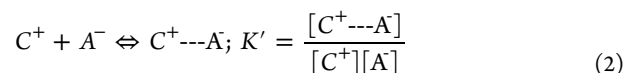
The theoretical modeling of solvation effects in ionic liquids present additional problems that can be outlined as follows: because in general ionic liquids are not ion pairs (albeit they can associate to different extents<sup>9</sup>), it becomes impossible to associate cations and anions forming a RTIL an effective dipole, from which a reaction field potential can be unequivocally defined. In this sense, continuum models based on a unique bulk dielectric constant are no longer applicable, albeit macroscopic dielectric constants for several RTIL have been experimentally determined.<sup>10,11</sup> Polarizable continuum models (PCM)<sup>12,13</sup> proposed to describe solvent effects in conventional media, where effective dipoles can be defined, are based on the idea that, according to the reaction field theory, the effective Hamiltonian of the solute may be defined for a perturbing reaction field potential created by an ensemble of dipoles in interaction with neutral and charged solutes. The variational treatment of the isolated solute Hamiltonian corrected with a proper reaction field potential leads to the ground state electrostatic free energy of solvation and the ground state density.<sup>14</sup> The electrostatic contribution may be further improved by adding empirical parameters describing HB-acidity and basicity parameters as well as other macroscopic parameters of the solvent.<sup>15,16</sup> However, even though reliable numerical values of the solvation free energy can be obtained, there still remain the descriptions of the specific solute–solvent interactions that influence a chemical process in solution.

In this work, our focus is on the modeling of the Lewis molecular acidity of ionic liquids using two different but complementary approaches. The first one is obtained by introducing the excess electronic chemical potential of the cation, which describes the residual electronic charge capacity of the cation that results after subtracting the contribution arising from the interaction of the cation with the counterion forming the RTIL. The second model relates the Lewis molecular acidity of the RTIL with its local charge capacity. In

this sense, Lewis acidity is considered as a semilocal (regional) property of the RTIL instead of being a global property of the whole structure. The resulting models are compared with different series of 45 imidazolium-based ionic liquids including a set of 12 Bronsted acid ionic liquids (BAILS),<sup>17</sup> for which pK<sub>a</sub> values are available in the literature. A second comparison with Kamlet–Taft hydrogen bond donor acidity ( $\alpha$ ) parameter is also performed and the major difficulties to get coherent and stable correlations are discussed. Finally, a reduced regression analysis is performed to explain Lewis acidic solvent effects on the rate constants for three families of organic reactions.

## THEORETICAL BASIS

**Excess Electronic Chemical Potential Model.** Molecular acidity in ionic liquids is a property mainly associated with the cation forming the RTIL. In a previous work, we defined the HB acidity in ionic liquids by introducing a solute-dependent quantity expressed in terms of the electronic chemical potential of the isolated cation with reference to an interacting cation–substrate complex.<sup>16</sup> The complex was built up using the transition state structure of the substrate. This model, even useful to rationalize the rate coefficients for the cycloaddition reaction of cyclopentadiene (CP) and acrolein is strongly restricted and needs the potential energy surface to be fully explored. In the present approach, we intend to introduce a more general descriptor by simply evaluating the excess electronic chemical potential that results after subtracting the intrinsic electronic chemical potential of the cation, from its valence value evaluated at the minimum energy of the a virtual ion pair formed with its corresponding counterion in each RTIL. In this way, the perturbing effect of the anion is thereby considered. The model is based upon Welton et al. proposal that the effective HB acidity must be defined after considering the following equilibria:<sup>8</sup>



According to Welton et al.,<sup>8</sup> in the first equilibrium the cation may interact with the ionic liquid anion through hydrogen bonding. In the second competing equilibrium, the cation may also form a hydrogen bond with the solute. The overall result is that the potential hydrogen bond of the cation is reduced by the anion effect and the net result is that the cation hydrogen bond acidity of the isolated cation toward the solute is less than that of the isolated cation. In a previous work, we described the HB donor acidity as the variation in electronic chemical potential of the cation because, in the process of donating a HB, there is a partial electronic charge transfer toward the atom acting as HB donor (i.e., Lewis acidity).<sup>16</sup> From this argument, we may immediately define an effective electronic chemical potential, corrected by the interaction of the cation with the compensating negatively charged counterion, that we shall call excess electronic chemical potential  $\mu_+^E$ , which may be defined as:

$$\mu_+^E = \mu_+ @ (\text{ion pair}) - \mu_+^0 \quad (4)$$

Where  $\mu_+^0$  is the electronic chemical potential of the isolated cation and  $\mu_+ @ (\text{ion pair})$  is the valence electronic chemical potential of the cation forming part of the bound RTIL ion pair.

Note that the bound ion pair is just taken here as a hypothetical reference state, not as a minimum energy of a molecule. The calculation of  $\mu_{+@}$  (ion pair) is readily performed by projecting the global electronic chemical potential weighted by the corresponding electrophilic Fukui function.<sup>18</sup>

**Local Charge Capacity Model.** If we accept the hypothesis that molecular acidity is a semilocal (regional) intrinsic property of the cation forming the RTIL, there is a second possibility of defining a reliable index for molecular Lewis acidity. It is based on the same idea that, after partially releasing a hydrogen atom to form a HB complex, the Lewis acidic region of the RTIL may assess the propensity to donate a HB in the form of a charge capacity index at the site of the HB donor atom. There is a simple justification for this definition. We can just define the charge capacity at site  $j$ ,  $\kappa_j$  say, as the maximum electronic charge  $\Delta N_{\max}$  that the Lewis acid (the cation of the RTIL in the present case) may accept from the environment to stabilize its energy. This is exactly the definition of the electrophilicity index  $\omega$  as defined by Parr et al. The global electrophilicity has been given the following definition:<sup>19</sup>

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

in terms of the electronic chemical potential  $\mu$  and the chemical hardness  $\eta$ . The quantity  $\Delta N_{\max}$  is given by:

$$\Delta N_{\max} = -\frac{\mu}{\eta} \quad (6)$$

Because the global softness is the inverse of the chemical hardness, it follows immediately that the charge capacity at site  $j$  may be defined as:

$$\kappa_j = \Delta N_{\max}(j) = f_j^+ \Delta N_{\max} \quad (7)$$

where  $f_j^+$  is the condensed to atom electrophilic Fukui function.<sup>18</sup> Note that this definition is possible because the global softness of a molecule is an additive quantity.

The model of molecular acidity based on the charge capacity index is closely related to that based on the excess electronic chemical potential in the sense that it is expressed in terms of the electronic chemical potential of the cation but this time corrected by a hardness term describing the resistance of the system to exchange electronic charge with the environment.

## RESULTS AND DISCUSSION

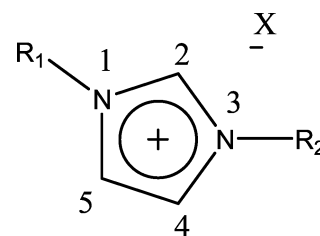
**Acidity Scales.** The Kamlet–Taft parameters have been determined for a wide variety of molecular solvents and RTILs by several authors.<sup>7,20</sup> Among the several parameters that describe the somehow elusive concept of solvent polarity,<sup>8</sup> there is the so-called hydrogen bond donor acidity parameter,  $\alpha$ , which is thought to assess the ability of the solvent to donate a hydrogen bond to another molecule in the system. The methodology to measure this parameter is based on the spectral shift that an arbitrary probe undergoes when dissolved in the solvent whose HB-donor acidity is being measured. Following Welton et al.,<sup>8</sup> this is the main source of instability in the reported  $\alpha$  value, especially for ionic solvents: the probes used are normally neutral not ionic molecules. We focus on this parameter because we intend to discuss the Lewis molecular acidity. Table 1 collects  $\alpha$  values for a series of 27 imidazolium-based ionic liquids, together with the corresponding values of electronic indices described in the preceding sections, namely, the excess electronic chemical potential,  $\mu_{+}^E$  and the regional

**Table 1.** Kamlet–Taft HB Acidity Parameter  $\alpha$  (Unit Less), Excess Electronic Chemical Potential (In eV Units) and the Charge Capacity at C2 Site (In e Units) of the Imidazolium Moiety of the RTIL

N°	RTILs	$\alpha^7$	$\mu_{+}^E$ (eV)	$\kappa_j$ (e)
1	Bmim BF <sub>4</sub>	0.63	4.192	0.100
2	Bmim CF <sub>3</sub> CO <sub>2</sub>	0.56	4.532	0.120
3	Bmim Cl	0.47	5.384	0.081
4	Bmim DCA	0.54	5.117	0.143
5	Bmim CH <sub>3</sub> SO <sub>3</sub>	0.44	4.645	0.101
6	Bmim NTf <sub>2</sub>	0.62	4.275	0.152
7	Bmim Otf	0.63	4.010	0.144
8	Bmim PF <sub>6</sub>	0.63	4.000	0.125
9	Bmmim NTf <sub>2</sub>	0.38	4.185	0.132
10	Emim BF <sub>4</sub>		4.223	0.095
11	Emim ClO <sub>4</sub>	0.56	4.086	0.119
12	Emim DCA	0.53	5.311	0.141
13	Emim NO <sub>3</sub>	0.48	4.622	0.084
14	Emim NTf <sub>2</sub>	0.66	4.159	0.131
15	Emim PF <sub>6</sub>	0.66	4.028	0.115
16	Emmim NTf <sub>2</sub>	0.42	4.212	0.131
17	Hmim BF <sub>4</sub>		4.183	0.118
18	Hmim Br	0.45	5.691	0.093
19	Hmim Cl	0.48	5.362	0.081
20	Hmim DCA	0.51	5.095	0.142
21	Hmim NO <sub>3</sub>		4.542	0.120
22	Hmim Otf	0.67	3.990	0.145
23	Hmim PF <sub>6</sub>	0.57	3.983	0.126
24	Omim BF <sub>4</sub>	0.62	3.824	0.155
25	Omim NO <sub>3</sub>		4.433	0.120
26	Omim PF <sub>6</sub>	0.58	4.138	0.152
27	Bzmim NTf <sub>2</sub>		3.508	0.063

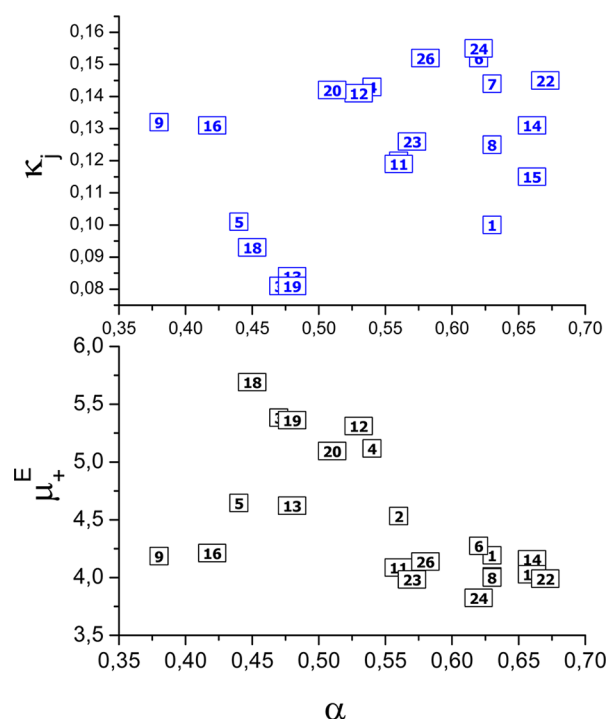
charge capacity  $\kappa_j$ . Our calculation based on the electrophilic Fukui function as a distribution function<sup>18</sup> consistently shows that the acidic sites for this series is the C2 center of the imidazolium ring of the RTIL (Scheme 1 for atom numbering).

### Scheme 1. General Structure of Imidazolium-Based RTIL



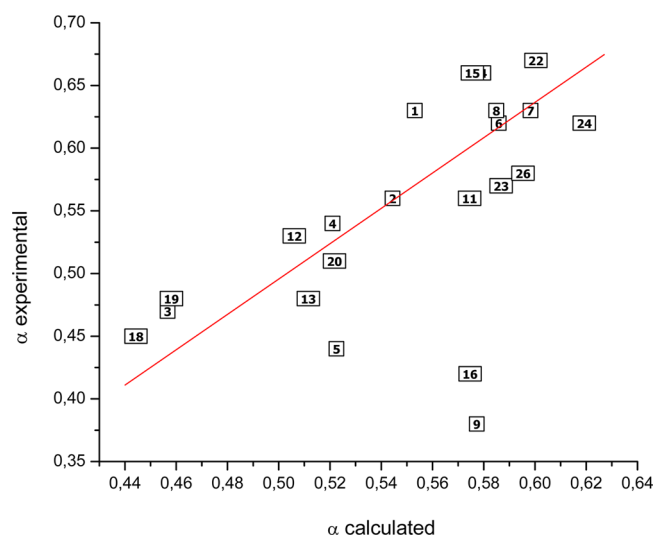
We first note that groups of RTILs of quite different structure display similar values of  $\alpha$ .<sup>7,8</sup> The implication of this result has a deeper meaning since several of them have been reported to display different solvating an even catalytic activities. Therefore, it is not surprising to find very loose correlations between the experimental HB acidity and the theoretical Lewis acidity descriptors. The comparisons are depicted in Figure 1.

Because polarity concept embodies several factors, it may be that the comparisons between  $\alpha$  and each of the theoretical descriptors of HB acidity separately may not assess the effective molecular interactions completely. To prove this prognosis, we performed a reduced linear regression analysis to get a comparison between the experimental HB acidity and a



**Figure 1.** Comparison between Kamlet–Taft HB acidity parameter and (a) the charge capacity index at the C2 center of the imidazolium cation and (b) the excess electronic chemical potential of some RTILs.

combination of  $\mu_+^E$  and  $\kappa_j$  descriptors. The comparison is plotted in Figure 2.



**Figure 2.** Comparison between Kamlet–Taft HB acidity parameter and a lineal combination of the excess electronic chemical potential and the charge capacity at C2 site of the imidazolium moiety of the RTIL.

Note that now the comparison even though not ideal is clearly better than that shown in Figure 1. Figure 2 shows that the RTILs: Bmmim NTf<sub>2</sub> and Emmim NTf<sub>2</sub> are clearly out of trend. It is interesting however to note that both RTIL bear a methyl group at the position C2, which is thought to be the Lewis acidic center. If we accept that this slight modification in the cationic moiety in the sense of the Hammett  $\sigma$  substituent parameter, which for H and –CH<sub>3</sub> ligands are very close to

each other, in this case become highly sensitive, because replacement of an H atom with a CH<sub>3</sub> group eliminate the probability of having a significant H-bond at that place (C2).

Up to now, we have confirmed that, for the set of RTIL 1–27, the Lewis acidic site is the C2 atom of the imidazolium ring. The question now is the following: is this the intrinsic acidic site for any imidazolium-based RTIL independent of the counterion? To answer this question, we considered the subset of 6 RTILs compiled in Table 2. It includes five Bmim and one

**Table 2.** Kamlet–Taft HB Acidity, Excess Electronic Chemical Potential, and the Charge Capacity at H6 Site of the Imidazolium Moiety of the RTIL

N°	RTILs	$\alpha^7$	$\mu_+^E$ (eV)	$\kappa_j$ (e)
28	Bmim HCOO	0.56	5.091	0.110
29	Bmim EtCO <sub>2</sub>	0.48	5.092	0.111
30	Bmim PrCO <sub>2</sub>	0.51	5.091	0.111
31	Bmim CH <sub>3</sub> COO	0.43	5.116	0.110
32	Bmim HOCH <sub>2</sub> CO <sub>2</sub>	0.44	5.088	0.093
33	Emim CH <sub>3</sub> COO	0.4	5.166	0.114

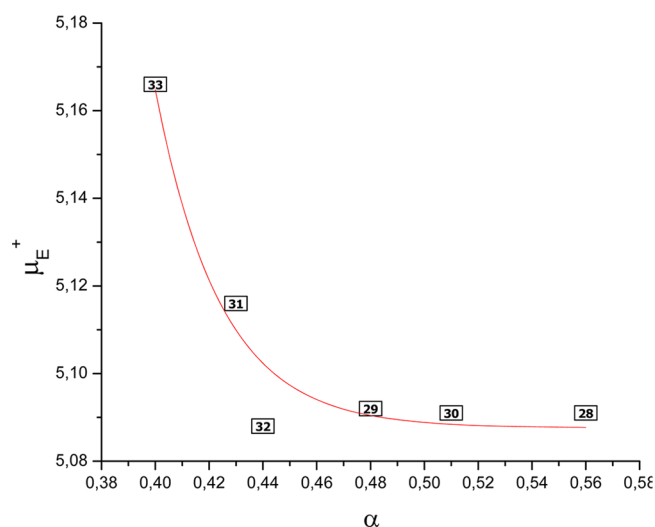
Emim-based RTIL with different formiate anion derivatives, for which experimental  $\alpha$  values are available.<sup>7</sup> The local analysis performed with the Fukui function formalism revealed an interesting result: the molecular acidity does not reside any more at the C2 site but at the hydrogen atom attached to C5 of the imidazolium ring. In other words, it seems that the presence of formiate derivative counterions activates a different Lewis acidic site. The origin of this electrophilic activation may be associated with an electronic effect that can be monitored by following the excess electronic chemical potential that drives the charge transfer. It is interesting to note further that the anion effect on the RTIL polarity, recently discussed by Chiappe et al.,<sup>21</sup> is in line with our regional activation model of Lewis molecular acidity of these ionic solvents.

Remember that H-bond acidity in the present model is related to electronic charge acceptance and that the local response is probed by the charge capacity index. We then compared the excess electronic chemical potential of the cation with the experimental  $\alpha$  values, and the resulting comparison is shown in Figure 3. Note that interestingly the fit of experimental and theoretical quantities is exponentially decaying, a result which is in line with the concept of mean electronic chemical potential model of Bartolotti and Parr,<sup>22</sup> who proposed that the electronic chemical potential displays an exponential decaying behavior with charge transfer. Note that the average fall off parameter is ca. 4.4 compared to that proposed by Bartolotti and Parr: 2.68 for diatomic neutral molecules.<sup>22</sup>

The small deviation shown by RTIL 32 may be traced to the functionalization of the anion by an hydroxilic group. This result is not really surprising, because it has been reported that RTILs are highly sensitive to functionalization.<sup>23,24</sup> The resulting exponential decaying fitting equation is:

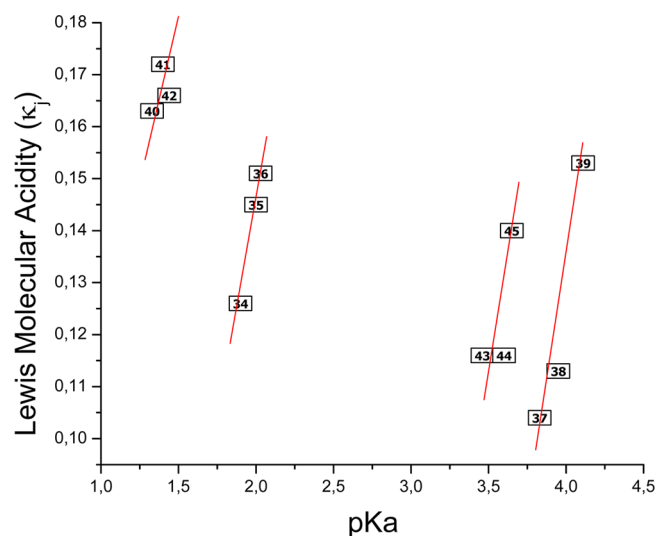
$$\alpha = 5,08762 + 1,18966 \times 10^6 e^{(-\kappa_j/0,02417)}; R^2 = 0,94323 \quad (8)$$

The results previously discussed prompted us to perform a detailed analysis for a series of 12 Bronsted acid ionic liquids (BAILs) recently reported.<sup>17</sup> For this series compiled in Table 3, the authors reported pK<sub>a</sub> values.<sup>17</sup> The pK<sub>a</sub> of a molecule describes its acidity/basicity in an acid–base equilibrium, where



**Figure 3.** Comparison between the experimental HB donor acidity parameter and the excess electronic chemical potential of the RTIL.

the hydrogen atom (a proton) is completely transferred. However, we are interested on the Lewis acidic center, not the Brønsted acidic one. We will show that, within this framework, the functionalized imidazolium cation of these RTILs respond again as a Lewis local acidic activation at site C2. The results of the comparison between experimental  $pK_a$  and the Lewis molecular acidity described by the  $\kappa_i$  descriptor are depicted in Figure 4. The comparison between both quantities split the series of BAILs into four groups; a result which at this stage is not really surprising. However, it is interesting to note that each group consistently classifies RTILs that bear structurally related cations; independent of the anions. This result probably means that substituent effects at the cation moiety outweigh the counterion effects. This comparison can be viewed as a no local problem: a perturbation is made at the Brønsted acidic fragment of the cation that in turn elicits a response at the Lewis acidic center. Note that at lower  $pK_a$  regions, the carboxylic fragment will have an anionic (carboxylate) structure, and it is the electron withdrawing substituent effect of the carboxylate fragment that activates the Lewis C2 acidic



**Figure 4.** Comparison between experimental  $pK_a$  and molecular Lewis acidity described by the  $\kappa_i$  index.

center: the lower the  $pK_a$  value results in a more efficient activation of Lewis acidity at C2 (Figure 4).

For instance, a first group corresponding to the more Lewis acidic RTILs (compounds 40–42) shares the same strong activating group. Because the  $-\text{CH}_2\text{COOH}$  ligand promotes electron withdrawing effects on the ring, the C2 site may become electrophilically activated. Note that the other subgroups follow a similar pattern, which appears to be driven by the methylenic chain length.

**Solvent Effects on Rate Coefficients.** A final test about the usefulness and reliability of the model of Lewis molecular acidity can be done using experimental data independent of the elusive LSER model of solvation. A good candidate is the rate coefficients for some organic reactions that have been run in RTILs. We must emphasize, however, that we will be dealing only with the HB donor acidity effects on the rate coefficients, because both the global and the local electron donating power of molecules cannot be described within a common framework similar to that leading to eqs 5–7. However, the definition of

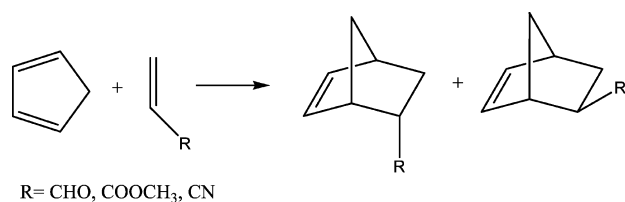
**Table 3.** Brønsted Acid Ionic Liquids (BAILs);  $pK_a$  Values and Electronic Descriptors of Lewis Acidity

BAILs	R1	R2	X <sup>-</sup>	$pK_a^{17}$	$\mu_E^+$ (eV)	$\kappa_i$ (e)
34	CH <sub>3</sub>	CH <sub>2</sub> COOH	Cl	1.9	5.383	0.126
35	CH <sub>3</sub>	CH <sub>2</sub> COOH	BF <sub>4</sub>	2	4.209	0.145
36	CH <sub>3</sub>	CH <sub>2</sub> COOH	SO <sub>3</sub> CF <sub>3</sub>	2.03	4.117	0.151
37	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> COOH	Cl	3.83	5.259	0.104
38	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> COOH	BF <sub>4</sub>	3.95	4.103	0.113
39	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> COOH	SO <sub>3</sub> CF <sub>3</sub>	4.11	3.914	0.153
40	CH <sub>2</sub> COOH	CH <sub>2</sub> COOH	Cl	1.33	4.624	0.163
41	CH <sub>2</sub> COOH	CH <sub>2</sub> COOH	BF <sub>4</sub>	1.4	3.731	0.172
42	CH <sub>2</sub> COOH	CH <sub>2</sub> COOH	SO <sub>3</sub> CF <sub>3</sub>	1.44	3.766	0.166
43	(CH <sub>2</sub> ) <sub>3</sub> COOH	(CH <sub>2</sub> ) <sub>3</sub> COOH	Cl	3.46	4.925	0.116
44	(CH <sub>2</sub> ) <sub>3</sub> COOH	(CH <sub>2</sub> ) <sub>3</sub> COOH	BF <sub>4</sub>	3.6	3.822	0.116
45	(CH <sub>2</sub> ) <sub>3</sub> COOH	(CH <sub>2</sub> ) <sub>3</sub> COOH	SO <sub>3</sub> CF <sub>3</sub>	3.65	4.167	0.140

the excess electronic chemical potential for electron donating species (i.e., Lewis basicity) may be safely achieved using an expression similar to that expressed in eq 4 and opens an interesting alternative to define an HB-acceptor basicity, which is under development in our group. Three classical organic reactions, namely, Diels–Alder, Kemp elimination, and Menschutkin reaction will be examined. For these systems, rate coefficients have been reported.

**Diels–Alder reactions.** Diels–Alder reactions were among the first to be kinetically studied in RTIL. The reaction between cyclopentadiene and acrolein, methyl acrylate, and acrylonitrile has been studied in several ionic liquids and molecular solvent.<sup>25–27</sup>

### Scheme 2. General Scheme for the Cycloaddition of CP with Three Dienophiles

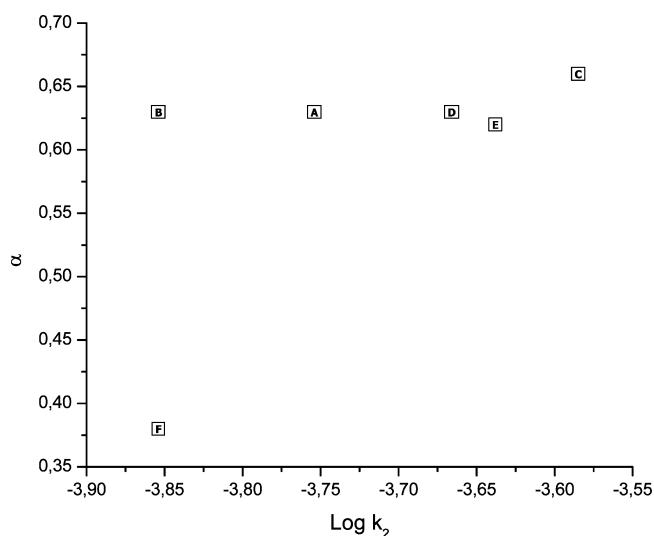


The solvent effects on these reactions have been examined using multiparameter linear solvation energy relationships.<sup>25</sup> The data recorded suggest that solvation effects are mainly determined by the RTIL hydrogen bond acidity in the reactions of acrolein and methyl acrylate but not for acrylonitrile. It is noteworthy that the number of parameters necessary to describe the kinetic and stereochemical response is generally higher than that required when the reaction is run in molecular solvents.<sup>25</sup> The LSER model in general yields poor correlations with the rate coefficients for reactions run in RTIL.<sup>25</sup> As discussed in previous sections, this methodology is strongly sensitive to the degree of transferability of the LSER set of parameters deduced from neutral probes to ionic species.<sup>8</sup> This reaction was previously studied by other authors and by us using multiparameter linear energy–density relationships.<sup>16,28</sup> For this reason, we decided to revisit this reaction using a more general approach that correct this weakness of the previous model. In addition, we have included the reaction of CP toward methyl acrylate and acrylonitrile to test the generality of the present model based on the excess electronic chemical potential and the regional charge capacity. The kinetic data are compiled in Table 4, and the electronic parameters are those compiled in Table 1.

**Table 4. Second-Order Rate Constants of the Diels–Alder Reaction between Cyclopentadiene and Three Dienophiles at 25 °C.<sup>25</sup>**

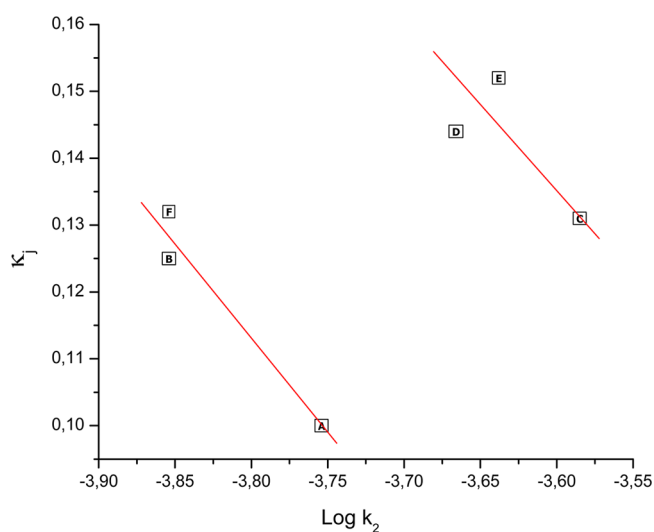
RTILs	Acrolein			Methyl Acrylate			Acrylonitrile		
	$k_2 \times 10^4 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^4 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$	$k_2 \times 10^5 / \text{M}^{-1} \text{s}^{-1}$
A Bmim BF <sub>4</sub>	1.76	1.40	4.69	4.31	4.48	2.63	2.53	1.06	3.64
B Bmim PF <sub>6</sub>	1.40	2.60	4.31	4.19	4.48	2.63	2.53	1.06	3.64
C Emim NTf <sub>2</sub>	2.60	2.16	4.19	4.30	4.48	2.63	2.53	1.06	3.64
D Bmim Otf	2.16	2.30	4.30	3.23	4.48	2.63	2.53	1.06	3.64
E Bmim NTf <sub>2</sub>	2.30	1.40	3.23	3.42	4.48	2.63	2.53	1.06	3.64
F Bmmim NTf <sub>2</sub>	1.40	3.42	3.42	4.00	4.48	2.63	2.53	1.06	3.64

To analyze solvation effects on the rate coefficients in these systems, we first compared the second-order rate constants with Kamlet–Taft HB acidity parameter ( $\alpha$ ). Figure 5 shows the result of this comparison.



**Figure 5.** Comparison between second-order rate constant of reaction between cyclopentadiene and acrolein with Kamlet–Taft HB acidity parameter.

It may be seen that the Kamlet–Taft model of HB-acidity predicts that five out of six RTILs will display approximately the same solvent effect, yet the RTIL structures are significantly different if we consider the counterion effects. This result may again be attributed to the quality of the  $\alpha$  parameter obtained from a neutral probe. To test the performance of the electronic descriptors of HB-acidity, we performed a comparable one parameter correlation between  $\log k_2$  and the electronic parameters introduced in this work. The best comparison is that obtained for the regional  $\kappa_j$  descriptor of Lewis acidity. This result may be an indication that the HB-donor acidity in this reaction is mainly regional in nature. The result of this comparison is shown in Figure 6. It may be seen that this



**Figure 6.** Comparison between  $\log k_2$  with the local charge capacity index.

comparison split the series of six RTILs into two groups: the first one includes Bmim BF<sub>4</sub>, Bmim PF<sub>6</sub>, and Bmmim NTf<sub>2</sub> and second one includes Emim NTf<sub>2</sub>, Bmim OTf, and Bmim NTf<sub>2</sub>. Because the response in both subgroups is clearly regional, we need additional information to explain the split. The first group is composed by the RTIL displaying the lower charge capacity and the lower rate coefficients. A NBO population analysis shows that for these RTILs the C2 site displays the higher electron population and therefore it consistently display a lower electrophilicity (0.459e, 0.459e, 0.641e, respectively). The second subgroup displays higher charge capacity and higher rate coefficients and the NBO analysis shows that the electronic population at C2 site are lower (0.441e, 0.435e, and 0.439e, respectively) and therefore they are expected to have a higher regional electrophilicity.

To make comparisons using a more general model, we performed a multiparameter regression procedure including both  $\mu^E_+$  and  $\kappa_j$  indices. For the reaction of CP and acrolein, the complete regression did not improved the description of  $\log k_2$  versus  $\kappa_j$  beyond that shown in Figure 7. However, for the reaction of CP with methyl acrylate and acrylonitrile the comparison between calculated and experimental  $\log k_2$  values were qualitatively acceptable. The plots of these comparisons are shown in parts a and b of Figure 7. A definitive analysis cannot be anticipated because in the present model there remain to include the effect of HB-acceptor basicity of the RTIL studied.

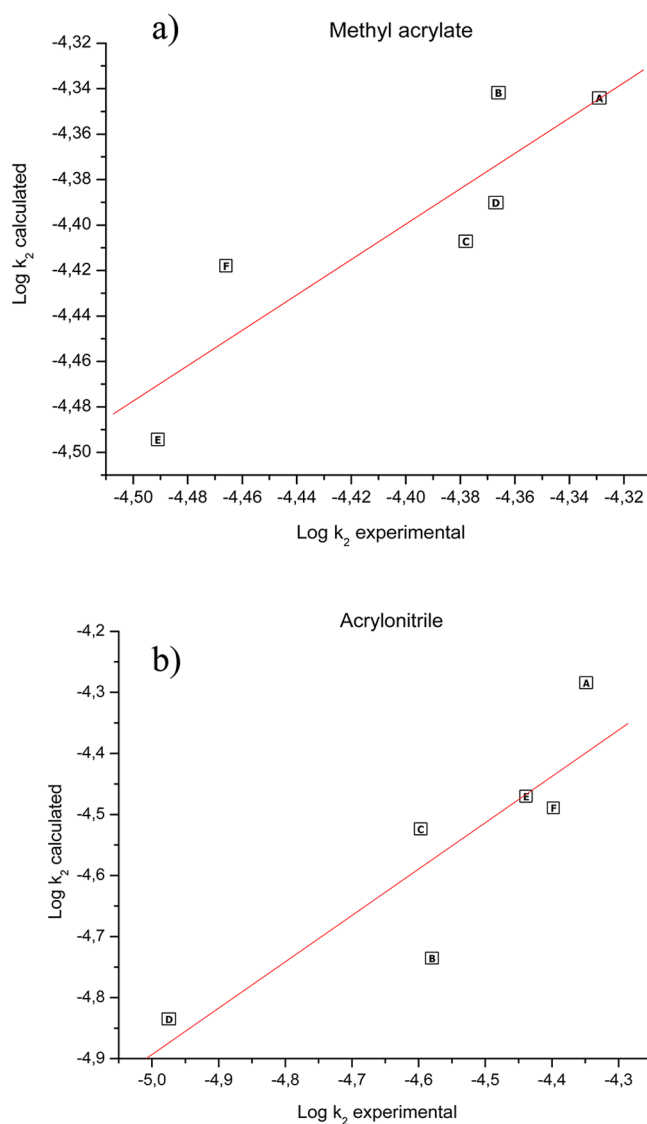
**Kemp Elimination.** The Kemp elimination reaction proceeds through a charge separated and ordered transition state, in which both C–H and N–O bonds are extensively cleaved, (see Scheme 3). For this reason, the pyrrolidine-induced elimination of 5-nitrobenzoxazole into the relevant 2-cyano-4-nitrophenolate has been used as a sample reaction by D' Anna et al.<sup>29,30</sup> to investigate molecular properties of some RTILs and their effect on the rate coefficients for this reaction. These authors proposed that an HB-donor acidity effects played against the reaction rate. They also went on to suggest that RTIL are able to establish  $\pi$ – $\pi$  and  $\pi$ -cation interactions that in some cases may significantly affect the reactivity in these solvent media.<sup>29</sup>

Because of the ionic nature of the transition state and the charged nature of products, we expect our model of Lewis acidity to be well suited to study this reaction because the electrostatic nature of both, the excess electronic chemical potential and the regional charge capacity. The kinetic data together with the values of both indices are compiled in Table 5 below:

We performed a multivariate regression procedure including both electronic indices, and the comparison between theoretical and experimental  $\log k_2$  values is shown in Figure 8.

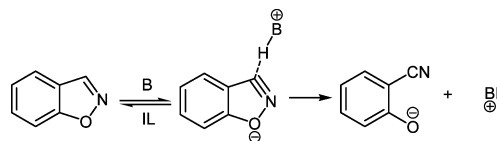
Note that the regression equation that combines the global effects of the excess electronic chemical potential with the regional charge capacity qualitatively improves the experimental ordering in rate coefficients. A more complete analysis incorporating orbital interactions, and the confirmation that specific  $\pi$ – $\pi$  and cation– $\pi$  interaction could be embedded in the information encompassed in the  $\mu^E_+$  and  $\kappa_j$  indices await further analysis.

**Menschutkin Reaction.** The rate constants for Menschutkin reaction of 1,2-dimethylimidazole with benzyl bromide have been determined in a number of RTILs and organic solvents by A. Skrzypczak et al.<sup>31</sup> (See Scheme 4).



**Figure 7.** (a) Comparison between calculated values and observed values of  $\log k_2$  of reaction the cyclopentadiene with methyl acrylate. (b) Comparison between calculated values and observed values of  $\log k_2$  of reaction the cyclopentadiene with acrylonitrile.

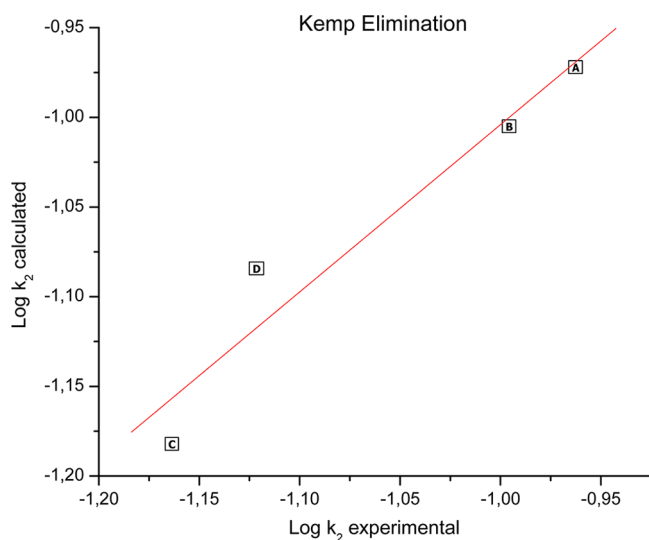
### Scheme 3. General Scheme for Kemp Elimination Reaction



**Table 5.** Second-Order Rate Constants at 298 K for Pyrrolidine-Catalyzed Elimination Reaction and Electronic Descriptors of Molecular Lewis Acidity<sup>27</sup>

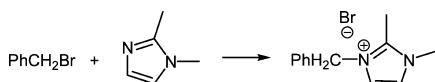
	RTILs	$k_2/M^{-1} s^{-1}$	$\mu^E_+$ (eV)	$\kappa_j$ (e)
A	Bmim BF <sub>4</sub>	0.109	4.192	0.100
B	Bmim PF <sub>6</sub>	0.101	4.000	0.125
C	Bmim NTf <sub>2</sub>	0.0686	4.275	0.152
D	Bmmim NTf <sub>2</sub>	0.0756	4.185	0.132

The authors performed additional correlations of the rate constants with solvatochromic parameters. The comparisons



**Figure 8.** Comparison between calculated values and observed values of  $\log k_2$  of reaction the pyrrolidine-induced elimination of 5-nitrobenzisoxazole into the relevant 2-cyano-4-nitrophenolate.

#### Scheme 4. General Scheme for Reaction between 1,2-Dimethylimidazole and Benzyl Bromide



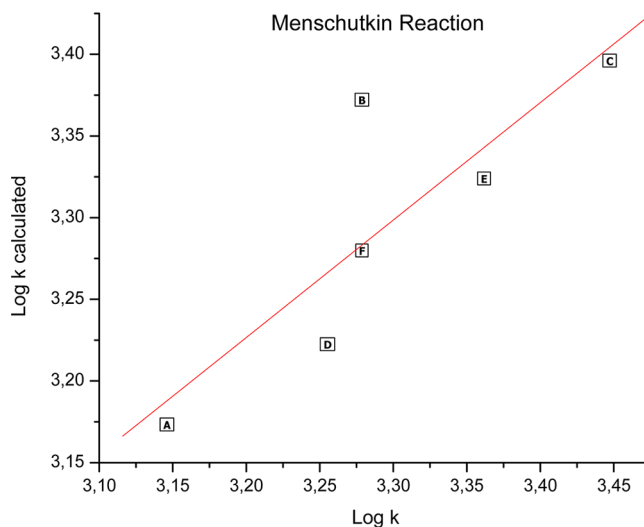
obtained for  $\log k$  with the Reichardt parameter  $E_T30$  for reactions run in molecular solvents were qualitatively significant. However, when data recorded in RTILs were added to these correlations the resulting comparison was clearly poor. This result agrees well with the idea proposed by Welton et al.<sup>8</sup> in the sense that solvatochromic parameters obtained for neutral probes are not transferable to ionic liquids and that only reduced comparisons among structurally related ionic solvents can be achieved. However, we feel that our theoretical parameters deduced from the electronic structure of molecules may recover a piece of universality in the relevant molecular interactions present in the solute–solvent interactions related to HB-donor acidity. We performed a multivariate regression procedure incorporating both the global and the regional descriptors. The experimental data and the values of the electronic descriptors are compiled in Table 6.

Menschutkin reaction involves a polar transition state and ionic products. Therefore, here again we expect our electronic indices that bear mostly electrostatic information to work qualitatively well, even in the absence of information about HB-acceptor basicity. On the basis of this idea, we performed a

**Table 6.** Rate Coefficients and Electronic Indices of Molecular Lewis Acidity for the Reaction between 1,2-Dimethylimidazole and Benzyl Bromide<sup>31</sup>

	RTILs	$k \times 10^{-3}/M^{-1} s^{-1}$	$\mu_{+}^E$ (eV)	$\kappa_j$ (e)
A	Bmim NTf <sub>2</sub>	1.4	4.275	0.152
B	Bmim PF <sub>6</sub>	1.90	4.000	0.125
C	Bmim BF <sub>4</sub>	2.80	4.192	0.100
D	Omim PF <sub>6</sub>	1.8	4.138	0.152
E	Omim BF <sub>4</sub>	2.30	3.824	0.155
F	Bmmim NTf <sub>2</sub>	1.90	4.185	0.132

multivariate regression procedure to compare the predicted and experimental rate coefficients for this reaction. The result of such comparison is shown in Figure 9.



**Figure 9.** Comparison between calculated values and observed values of  $\log k_2$  of reaction the pyrrolidine-induced elimination of 5-nitrobenzisoxazole into the relevant 2-cyano-4-nitrophenolate.

In the absence of HB-basicity factor, it is truly difficult again to make a deep analysis of the role that the energy-density-based descriptor of HB-donor acidity may have on the description of the rate coefficients for this polar process. However, as it has been shortly discussed here, it seems that kinetic data recorded in ionic liquids do respond better when the dissolved reagents are highly polar or even charged species. The definitive response to this conclusion cannot be deduced from this preliminary model, and the complete model including the basicity factors will certainly improve the picture drawn by incorporating the Lewis acidity contributions. Work along this line is under development in our group.

## CONCLUSIONS

In summary, the electronic structure indices provide a novel and promising approach to rationalize the electronic origin of molecular Lewis acidity for a wide series of 45 RTIL. The elusive character of the experimental model of HB-donor acidity is reflected in the present study when they are compared with models of Lewis molecular acidity in terms of electronic descriptor of molecular structure. The present contribution emphasizes the following promising results. It stresses the reliability of the electronic chemical potential as a descriptor of intramolecular charge transfer that is naturally associated with the H-bond formation process; second, molecular acidity appears as a regional property of molecules. This result has been already reported in different systems using the molecular electrostatic potential.<sup>32</sup> In this context, the present model of Lewis molecular acidity assesses first-order energy–density relationships through the electronic chemical potential; and second-order polarization contributions embodied in the charge capacity index, which is indirectly related to the regional softness at the cation fragments of the RTIL. Further studies incorporating nonelectrostatic contributions amenable to be described by reactivity indices are worth exploring. In this sense, the present contribution opens an alternative way in the



attempt to classify in general terms the HB-acidity using information from the electronic structure of matter.

## ■ COMPUTATIONAL DETAILS

All of the molecular species included in this study were fully optimized at the HF/6-311+G(d,p) level of theory, using the *Gaussian 03* package.<sup>33</sup> The Fukui function were evaluated at the HF/6-311G(d,p), because the presence of diffuse functions produce spurious negative values of FF. A detailed analysis of this problem has been reported previously.<sup>18</sup> With the energy and electronic density at hand, the electronic descriptors have been evaluated following the definitions given in the text.

## ■ ASSOCIATED CONTENT

### Supporting Information

Cartesian coordinates, energy and number of imaginary frequencies for the cations anions ion pair virtual structures, optimized at the HF/6-311+G(d,p) level of theory, complete ref 33. 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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