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On the Origin of Ionicity in Ionic liquids. Ion Pairing versus Charge Transfer

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Abstract

In this paper we show by using static DFT calculations and classical molecular dynamics simulations that the charge transfer between ionic liquid ions plays a major role in the observed discrepancies between the overall mobility of the ions and the observed conductivities of the corresponding ionic liquids, while it also directly suppresses the association of oppositely charged ions, thus the ion pairing. Accordingly, in electrochemical applications of these materials it is important to consider this reduction of the total charges on the ions, which can greatly affect the performance of the given process or device in which the ionic liquid is used. By slightly shifting from the salt-like to a molecular liquid-like system via the decreased charges, the charge transfer also fluidizes the ionic liquid. We believe that this vital information on the molecular level structure of ionic liquids offers a better understanding of these materials, and allows us to improve the *a priori* design of ionic liquids for any given purpose.

Introduction

Association of oppositely charged ions, thus ion pairing,[1] is a fundamental concept for electrolyte systems, that governs many of their physicochemical properties such as viscosity, conductivity and osmotic pressure; therefore affecting greatly the design and application of batteries, solar cells, and fuel cells. Ion pairing, however, can also have a considerable, albeit more complex role in synthetic approaches, since via selectively oriented associations of ionic reactants/catalysts control over regio- or stereoselectivity can be achieved,[2,3] increasing the effectivness of the corresponding applications, or even enabling reaction paths that are otherwise not favored.[1,2,4] Due to these very diverse effects of this very basic elementary behavior, it has been in the focus of physical chemical research for many decades.[1–3,5–9]

Ion pairing is an especially intriguing issue in ionic liquids (ILs),[10–14] where the solvent itself is composed of ions. ILs are used in an extremely wide variety of applications, as e.g. electrolytes for electrochemical purposes,[15–27] or tunable media for synthesis.[12–14,28] Due to the aforementioned connection between the physicochemical properties of the electrolytes and ion pairing, and since many of the potential beneficial properties of ILs are related to their ionic nature,[10–15,29] there is a substantial overlap between the fields ion pairing and ionic liquids, and the possible formation of ion pairs[29–34] and other neutral subunits[35–40] in these materials is of great current interest.

Somewhat related to the electrochemical and synthetic points of views in the applications of ILs in general, there have been different ways of approaching ion pairing in these materials. On one hand, the pure IL can be investigated in terms of ion pairing, while on the other hand ionic solutes in ILs, or mixtures of ILs with ionic or molecular solvents can also be considered. In pure IL systems however, not only observing, but also defining an ion pair is difficult, since one cation is surrounded by many anions and *vice versa*,[34,40–45] and unless there is a distinct interaction with one of the neighbouring particles, choosing any specific "pair" seems rather unwarranted.[44] From the microscopic point of view a possible way to look at ion pairing in pure ILs is to define it via a distance and time scale; thus, how far and for how long do the oppositely charged, neighbouring ions travel together in the liquid.[32]

By applying this definition it has been shown by molecular dynamics simulations that ion pairs are very short lived in ionic liquids and that the ions are generally diffusing rather independently from one another,[32] inferring a lack of ion pairing. In good agreement, the separation of ion pairs has also been found to have low energy demand in a later study, which agrees with the charge screening effect of the ionic media.[46]

From certain macroscopic studies, however, a somewhat different picture was obtained. Watanabe and coworkers have compared[30,31] the mobility of the ILs' ions to the conductivity of the IL itself for a wide variety of ILs according to

$$\Lambda_{\mathrm{NMR}} = \frac{N_A e^2}{kT}(D^+ + D^-) \tag{1}$$

and

$$\mathrm{I} = \frac{\Lambda_{\mathrm{imp}}}{\Lambda_{\mathrm{NMR}}}\ , \tag{2}$$

where N_A is the Avogadro number, e is the charge of the electron, k is the Boltzmann factor, T is the temperature, D^+ and D^- are the diffusion constants of the cation and the anion, Λ_{NMR} is the ion mobility from the NMR measurements, Λ_{imp} is the ion mobility from the conductivity measurements, while I is defined as the very helpful ionicity scale. It was shown by Watanabe and coworkers[30,31]—in agreement with the deviations from ideality in the Walden plot[24,47–49]—that for all ILs the actual mobilities of the IL ions (measured by NMR) are significantly larger than those that one can obtain from the conductivity measurements; thus, the ionicity values (eq. 2) are lower than one. In other words, ILs conduct less than expected according to the diffusion coefficients of the IL particles. Assuming that eq. 1 holds, this discrepancy could only be rationalized by considering a correlated motion[50] of the oppositely charged ions, hence—in contrast to the molecular dynamics results above—the presence of ion pairs to some extent,[30,31] or other, low-charge aggregates was concluded. This point of view dates back to the very early investigations of ILs by Walden.[47] Accordingly, the ionicity value was interpreted as the ratio of the "effective concentration of charged species" and the total concentration of the ionic liquid.[31]

Unlike in the case of neat ILs, ionic solutes can clearly be distinguished from the IL solvent, therefore their ion pairing can be observed directly. Although in a strict meaning these measurements concern only the behaviour of the solute in the IL, and not the solvent itself, IL-like solutes can also be considered as probes, which are incorporated into the IL in a way that they are not distinguishable from the solvent, and therefore they nevertheless hold some information on the association processes of the IL solvent. As a pioneering study in this field, the kinetics of the S_N2 reaction shown in Figure 1 was investigated,[29] and a different reaction mechanism was suggested in ILs compared to molecular solvents, identifying a real ionic liquid effect. Instead of a two-step mechanism, involving an intermediate step of a contact ion pair formation, a direct, one-step mechanism could be observed,[29] and later confirmed by theoretical calculations.[51–53] Similar conclusions could be deduced from spectroscopic measurements for Kosower's salt in different ILs,[33] that no preferential ion pairing is present in IL solutions. Thus, these results—in agreement with molecular dynamics simulations, and in contrast to the conductivity measurements—suggest the lack of ion pairing in ionic liquids.

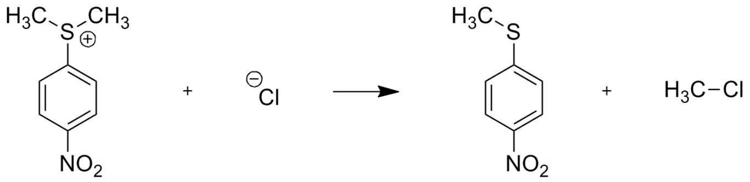

Figure 1: Reaction between charged species in ionic liquids, which—unlike in molecular solvents—was shown to occur in one step, without the initial ion pair formation of the substrates.

Again in contrast to these observations, a theoretical study on the NaCl ion pair in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_4C_1Im][NTf_2]$) ionic liquids by classical molecular dynamics simulations showed[54] that separating the Na^+ and the Cl^- ions is *endothermic* with a reaction free energy of 38 kJ/mol, thus, the ion pair formation is that much favoured over dissociation. It is important to note here that NaCl is rather poorly soluble in ionic liquids[55] due to the very stable ionic lattice of this salt, which hence forms larger aggregates in the form of precipitation, as was also shown by the authors of this study.[54] Nevertheless, these two extreme cases of different behaviours for this classical salt-like structure or the IL-like solutes, together with the contradicting findings described above show, that the problem of ion pairing in ionic liquids is a very complex matter and still further efforts are needed to understand this aspect of the ILs' microscopic structures.

In order to establish a bridge between the dissonant results from these thorough measurements performed by very different experimental[29–31, 33] and theoretical[32] techniques on the association processes of the ions in ionic liquids, it is worth starting from the molecular structure of ionic liquid ions within the IL. Although the total charges of independent, isolated ions or molecules clearly must be integers, in ionic liquids these ions are not isolated from each other at all, they form an extensive network of interactions, including hydrogen bonding.[41, 44, 56–64] Since these interactions involve orbital interactions[41, 56, 59] that can result in a partial charge transfer,[59] it is, in principle, possible to have fractional charges on each ion. Indeed, in 2002 it was noticed that the partial charges in a gas phase ion pair of 1-butyl-3-methylimidazolium hexafluorophosphate add up to a non-integer value of ± 0.904,[65] and later it was shown by ab initio molecular dynamics simulations[41] that in the liquid 1,3-dimethylimidazolium chloride charges at the ions are ca. ± 0.75, while static calculations on clusters of the same compound also resulted in a similar value of ca. ± 0.8.[66] Beside the plenty of computational results, it has to be mentioned that the charge transfer has also been observed experimentally.[67]

This issue becomes particularly important from a more technical point of view. To set up force fields for classical molecular dynamics simulations the charges have been generally estimated (with some exeptions[68–70]) by a population analysis of a single, isolated ion in the gas phase, where the total charge is an integer value. This simplified picture results in an overbinding of the ions,[61, 71] making the liquid structure slightly more stiff, providing erroneous dynamic properties including viscosity and diffusion constants.[61, 71, 72] To correct this slight overestimation of the intermolecular Coulombic forces, two approaches have been shown to be applicable. The first possibility is to apply a polarizable force field,[73–77] where the electrons can slightly be shifted off the nuclei, adjusting the electrostatic interactions to the surroundings, which can counteract the overbinding of the ions in the liquid. However, polarizability is meant as the measure for the ability to shift electrons and nuclei *within* a molecule under the influence of an external electric field, and therefore the polarization is taken into account in polarizable models within the initially defined ions of the IL. Due to the presence of the aforementioned network of interactions, in ILs such polarization occurs intermolecularly, shifting electrons, or in case of extremely strong hydrogen bonds even protons from one ion to another.[35–37,39] Thus, polarizable models that do not account for the polarization through the intermolecular interaction network are not necessarily representing a physically correct description of the system. The other possible way to deal with the decrease of the ions' charges in ionic liquids is simply scaling down all atomic charges that are obtained for the atoms of single gas phase ions,[61,70,71,74,78–80] thus the provided total charges are lower than the unity values. This model is clearly less flexible than a polarizable force field, and it also assumes that all atomic charges are decreased the same extent, and stay constant for the entire simulation time. On the other hand, this approach explicitly accounts for the charge transfer *between* the anions and cations (viz. "intermolecular polarization"), which is shown to be a real physical effect (see above).[67,81] Thus, the charge scaling approach provides a simple, and well applicable method to describe both proper structure and dynamics in ILs[70] if treated with care.[70,74] In general, the scaled total charges of the ions that are fitting best to describe dynamic properties were fluctuating around $\pm 0.7 - 0.9$,[61,70,78–80,82] matching qualitatively the charges obtained in the quantum chemical calculations as mentioned above. It is also noteworthy in this respect that the strength of the interactions in the IL is highly dependent on the specific cation-anion combination, which presumably results in different charge transfer in each solvent, requiring varying scaling factors. In such a sense the transferability is affected, and the charges at the ions should be determined individually for any given IL,[68,69] and thus huge efforts have to be made to obtain such force fields with more accurate charges.

In terms of ion pairing the charge transfer has a very important potential consequence: if the charges are lower than one less charge is carried by the transport of a particle, and accordingly a drop of the conductivity can be expected, as it would with the aggregation of ions (see eq. 1) In the light of these considerations, all theoretical and experimental results based on charge transport and the assumption that the charge at the ions is $\pm e$ should be revisited; and since Coulombic interactions are of high importance in ILs, how much the presence of charge transfer influences our general picture of both microscopic and macroscopic structures of ionic liquids with respect to ion pairing should be evaluated in each case.

In this study we evaluate the extent of charge transfer for single ion pairs of several commonly used ionic liquids, and consider its possible contribution to the previously defined ionicity values. Via artificially induced charge transfer within a probe ion pair we also evaluate the structural effects of the obtained lower charges on the ionic liquid itself, including ion pairing.

Applied methods

To estimate the extent of charge transfer in general, a variety of ionic liquids were chosen. The labelling of the ions is shown in Figure 2. To calculate the charges on the ionic liquid ions, two conformations of a single ion pair (see Supp. Inf.) of each investigated IL have been optimized in a COSMO[83,84] ensemble ($\epsilon = 15$; distance between the solvent and the atomic van der Waals radii was 2.5 Å), using the TPSS-D3 meta-GGA type density functional that contains Grimme's dispersion correction D3,[85,86] with a def2-TZVP basis set, by the Turbomole 6.5 program package.[87] The COSMO continuum model allows to obtain a more realistic picture on the IL itself from the single ion pair calculations, which, on the other hand, makes it significantly simpler to treat the ILs computationally.

The charges were calculated with different localization techniques (Blöchl,[88] Mulliken,[89] AIM, RESP[90]) for both considered conformers, and then were averaged. Blöchl and RESP charges were calculated by the CP2K program package[91] at the BLYP-D3/TZVP-MOLOPT-GTH level with type GTH-PBE pseudopotentials, while the AIM charges in the BLYP-D3/def2-TZVP geometries were produced by the AIMAll program package using the electron density of the same method.[92] Here only the Blöchl and RESP charges are shown, for the rest of the data, see the Supp. Inf. A more thorough investigation of these charges is currently conducted in our group. It should be stressed here that due to the fact that partial atomic charges are not observable properties, their calculation is very dependent on the method. On the other hand, although there are reasons and examples for and against the different localization techniques for certain problems, there is, nevertheless, no clear hierarchy among them, and therefore, by such calculations only a qualitative picture[93] can be obtained.

The most sophisticated protocolls to derive charges for setting up force fields were published lately, based on bulk AIMD simulations,[70,81,82,94,95] or extensive cluster analysis.[68,69] However, these approaches are rather demanding computationally to be used for the more time-efficient generation of force fields, and therefore it will be very intersting to see in future studies whether our simple scheme can provide comparable results to these very thorough calculations above, while being only marginally more expensive than the previously applied single ion approach.

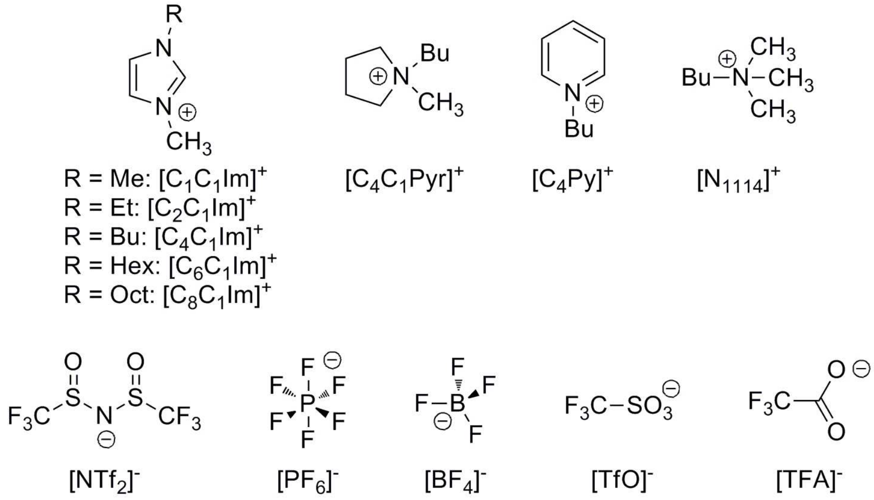

Figure 2: The IL ions considered in this study, and their abbreviations.

Classical molecular dynamics simulations were performed by using the LAMMPS program package,[96,97] applying the usual Lorentz–Berthelot mixing rules with previously fitted potentials for the ionic liquid,[98,99] for the Na^+,[100] and for the Cl^-.[99] The total charges of the ionic liquid ions were set to ±0.8, which was obtained by scaling the RESP fitted charges of the single ions, as described previously.[101] The charge of the sodium and chloride ions was

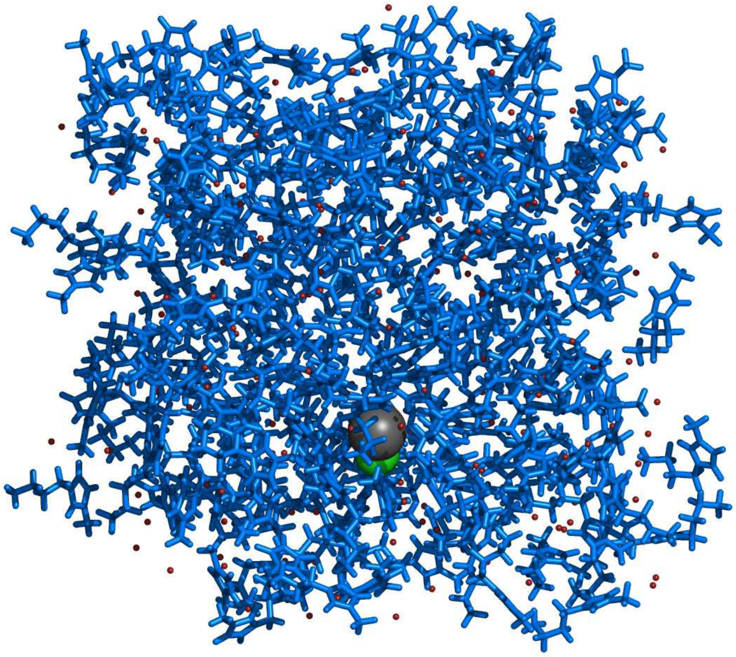

Figure 3: Example for the simulation boxes of [C_4C_1Im]Br with an ion pair of NaCl. [C_4C_1Im]$^+$: blue; Br$^-$: red; Na$^+$: grey; Cl$^-$: green.

set to ±0.5, ±0.8, ±1.0, ±1.5, ±2.0, ±3.0 in a series of different simulations. For the ±0.8 charge setup, the effect of the sodium ion's size was also investigated, which was varied by different σ values in the Lennard–Jones potential (for the potential form, see Supp. Inf.), being 1.5 and 2 times larger than the originally fitted parameter. The cut-off for non-bonding interactions was chosen as somewhat larger than 2.5 times the biggest σ value present in the force field (for details, see Supp. Inf.). The simulation box (for a representative snapshot see Figure 3) contained 200 1-butyl-3-methylimidazolium bromide ion pairs, and a single sodium chloride contact ion pair. Each initial box had a density of 1 g cm^{-3}, which was simulated in an NPT ensemble for 1 ns, in order to achieve the equilibrium density. The average cell vector of the last 0.5 ns was used in the further simulations. 1 ns of equilibration of the obtained box in the NVT ensemble was followed by the production run of 10 ns, again in the NVT ensemble. The timestep of 1 fs was chosen, and the trajectory was saved throughout the whole 10 ns in every 1000 steps (in every 1 ps).

To investigate the free energy profile of the NaCl ion pair's dissociation process, thermodynamic integration was performed for all systems along increasing Na-Cl distance. In these simulations the box was prepared analogously to the equilibrium simulations described above, but during the production run an extra harmonic potential with a force constant of 2000 kcal mol^{-1} Å^{-1} was applied at the Na-Cl distance, and the corresponding forces were collected in each step. The system was equilibrated in an NVT ensemble for an extra 0.1 ns at each distance, which was followed by a 0.25 ns production run in the same NVT ensemble.

For the analysis of the classical molecular dynamics results the TRAVIS program[102] was applied. The labeling of the $[C_4C_1Im]^+$ cation is shown in Figure 4 as used throughout the article.

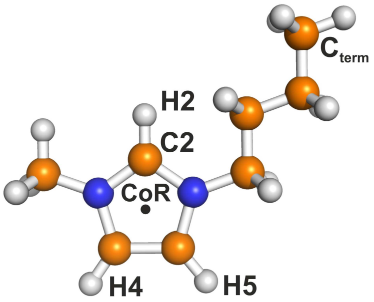

Figure 4: Labelling of the $[C_4C_1Im]^+$ cation used throughout the paper. CoR = Center of Ring; H: white; C: brown; N: blue.

1 Results and Discussion

1.1 Charge transfer in ionic liquid ions, and its effect on ionicity

First we performed static quantum chemical calculations on a series of ILs to acquire a rough estimate of the charge transfer, and to evaluate its effect on the ionicity values. Thus, we selected a set of highly investigated ionic liquids (Table 1), and calculated the charges on the ions in an ion pair of each kind within a continuum solvent model. The obtained charges, together with the originally published[30,31] and the hereby recalculated ionicities are shown in Table 1.

IL	I	$\lvert q_{Bl}\rvert$	I'_{Bl}	$\lvert q_{RESP}\rvert$	I'_{RESP}
$[C_4C_1Im][NTf_2]$	0.61^a	0.82	0.90	0.74	1.11
$[C_4C_1Im][PF_6]$	0.68^a	0.91	0.82	0.88	0.88
$[C_4C_1Im][BF_4]$	0.64^a	0.88	0.83	0.87	0.85
$[C_4C_1Im][TfO]$	0.57^a	0.84	0.80	0.88	0.74
$[C_4C_1Im][TFA]$	0.52^a	0.84	0.73	0.84	0.75
$[C_1C_1Im][NTf_2]$	0.76^a	0.83	1.09	0.81	1.16
$[C_2C_1Im][NTf_2]$	0.75^a	0.85	1.04	0.78	1.23
$[C_4C_1Im][NTf_2]$	0.61^a	0.82	0.90	0.74	1.11
$[C_6C_1Im][NTf_2]$	0.57^a	0.78	0.93	0.77	0.97
$[C_8C_1Im][NTf_2]$	0.54^a	0.72	1.04	0.66	1.26
$[C_4C_1Im][NTf_2]$	0.61^a	0.82	0.90	0.74	1.11
$[C_4C_1Pyr][NTf_2]$	0.70^a	0.75	1.26	0.77	1.18
$[C_4Py][NTf_2]$	0.63^a	0.75	1.12	0.78	1.04
$[N_{1114}][NTf_2]$	0.65^a	0.79	1.04	0.79	1.04

[a] values taken from literature[30,31]

Table 1: Calculated absolute charges on the ions within a single ion pair. For the Lewis structural formula of the considered ions, see Figure 2. I: ionicity (see eq. 2); $\lvert q_{Bl}\rvert$: absolute charges at the ions, based on the Blöchl partial charges; I'_{Bl}: ionicities recalculated by using $\lvert q_{Bl}\rvert$; $\lvert q_{RESP}\rvert$: absolute charges at the ions, based on the RESP fitted charges; I'_{RESP}: ionicities recalculated by using $\lvert q_{RESP}\rvert$.

As can be seen from the data (Table 1), the absolute values of the charges at the ions are indeed significantly lower than unity, which shows the presence of a large charge transfer between the anion and the cation within all the ion pairs. The charge transfer varies by altering the anion (upper third of Table 1), the length of the side chain (middle third of Table 1), and the cationic head group as well (lower third of Table 1), but also by the localization method that is used for the calculation of the charges (see Supp. Inf.). Generally, the more spherical inorganic anions (PF_6^- and BF_4^-) have the smallest deviation from unit charges, while the large and flexible NTf_2^- anion exhibits the largest charge transfer. The increasing length of the cation's side chain induces an increase of the deviation from the unit charges, while the cationic head groups also show different charge transfers, although the order depends on the localization technique.

According to the large charge transfer values obtained, and to eqs. 1-2 (note that the square of the charge is used in eq. 1!), the reduction of mobile charge can originate both from ion pairing and from the charge transfer; thus, the latter effect is also reflected in the ionicity values. It is, however, possible to use these charges as the charge of the ions instead of the originally applied unit charges in eq. 1, and hence eliminate the effect of the charge transfer from the ionicity values reported[30,31] previously. As can be seen in Table 1, the recalculated ionicity values (I') are remarkably higher, demonstrating that the original values are indeed significantly influenced by the charge transfer between the ions and that the long-term association of ions into neutral subunits plays a smaller role than previously inferred from the corresponding conductivity measurements.[30,31] It is important to point out that there are some cases, in which the obtained I' values are larger than one. This is in clear contrast to chemical intuition, since it would mean that the ions carry more charge than expected from their total charges (calculated here), and their measured mobilities (published previously[30,31]). This might be explained by the limitations of the simple model applied, such as considering two conformations of one single ion pair with an implicit solvent without temperature effects and fluctuations. Accordingly, we are planning to perform a subsequent study with a more systematic approach to this specific matter, but the difficulties of the electron localization during the charge calculations makes this issue very complicated, especially considering that the square of the charge is applied in eq. 1, which enlarges any slight error. It is, however, clear already according to these crude values that considering the observed slight changes in the total charges at the ions is important when analyzing ILs' ionicities, since these can alter the physical picture of IL systems.

While the most important aspect of these findings is to show that ILs are, in general, less prone to ion pairing than was previously conculded based on conductivity measurements, there are some interesting details that should also be pointed out. Although it is tempting to explain the amount of charge transfer in the different ion pairs simply by the strength of the interactions, comparing our charge transfer results to experimental data[62] on the hydrogen bond strengths did not provide any clear correlation. Nevertheless, with these estimated values the trends in the ionicities are altered at some points, to reflect a ranking that corresponds more to the general chemical picture of the considered materials. The more salt-like, small and spherical PF_6^- and BF_4^- derivatives seem oddly less associated in the original data set than those with the more flexible, less hydrogen-bonding NTf_2^-, which is completely corrected by considering the effect of charge transfer. Similarly, as has been pointed out,[103] for longer side chains one can anticipate that the contribution of the stronger, associative Coulombic interactions decreases, leading to less ion pairing. On the other hand, longer sidechains are known to induce a mesoscale ordering of the polar and non-polar domains of the IL molecules.[103–108] In case of this high degree of separation the cationic head groups and anions are closer in space, and therefore while the overall contribution of Coulombic interactions may become lower, it can even be increased locally between the charge carrying moieties, possibly inducing higher ion pairing and charge transfer between the ions. Accordingly, it is difficult to predict the effect of longer side chains on ion pairing, but it is interesting to observe that taking the charge transfer into consideration, the original trends in ionicities change, and the corrected values scatter around $\mathrm{I}' = 1 - 1.2$.

1.2 Structural Effects of the Charge Transfer: Ion Paring and More

After having seen that the charge transfer plays a major role in the deviations between the conductivities and particle mobilities, it is also important to discuss the structural changes that it induces. To observe such differences, we placed a single probe ion pair of sodium chloride in 1-butyl-3-methylimidazolium bromide and performed a series of molecular dynamics simulations with artificially varying charges on the sodium and the chloride anions. With these manually varied charges we represent the different states of charge transfer within the ion pair, showing how it influences the interactions between these two ions, or with the solvent. While the simplicity of the solute ion pair makes it easier to interpret the changes in intermolecular interactions, the relatively small bromide anion of the ionic liquid avoids artifacts of size differences between the solute and solvent anions [cf. chloride and bis(trifluoromethylsulfonyl)imide]. Moreover, due to the similar sizes of the bromide and chloride anions, the dissociation-association processes of the ion pair can be spontaneous according to the very simple hypothetical $NaCl + Br^- \rightarrow NaBr + Cl^-$ substitution reaction, which also holds valuable information on the system.

The observable attractive interactions within these systems are Na^+-Cl^-, Na^+-Br^-, and Cl^--$[C_4C_1Im]^+$, where the latter generally takes effect via the ring hydrogen atoms, especially via the H2 (for labelling see Figure 4).[41, 44, 56–61] The characteristic distances that we focused on were those between Na^+ and Cl^-, Na^+ and Br^-, Cl^- and the Center of Ring in the $[C_4C_1Im]^+$ cation, Cl^- and H2 of the $[C_4C_1Im]^+$ cation, and finally between the Na^+ and the C_{term} of $[C_4C_1Im]^+$. In Table 2 the location of the first peak in each corresponding radial distribution function is presented. While with $|q| = 0.5$ the NaCl ion pair spontaneously, and irreversibly dissociates, for $|q| = 0.8$ such dissociation occurs for a few ps period of time, and then the solute ion pair is regenerated (Figure 5). For the even higher charges no dissociation is observed at all. The Na-Cl distance exhibits high dependency on the charge, as it drops from 270.2 pm ($|q| = 0.8$) to 195.2 pm ($|q| = 3$), showing that the ion pair formation is more probable in the cases of the high charges, while decreasing the charge—via e.g. charge

$\lvert\mathbf{q}\rvert$ e	$\mathbf{d}_{\text{Na-Cl}}$ pm	$\mathbf{d}_{\text{Na-Br}}$ pm	$\mathbf{d}_{\text{Cl-H2}}$ pm	$\mathbf{d}_{\text{Na-C}_{\text{term}}}$ pm	$\mathbf{N}_{\text{Br}}^{\text{Na}}$ -	$\mathbf{N}_{[\text{C}_4\text{C}_1\text{Im}]}^{\text{Cl}}$ -	$\text{Ex}_{\text{Br}}^{\text{Na}}$ -	$\tau_{[\text{C}_4\text{C}_1\text{Im}]}^{\text{Cl}}$ ps
0.5	$-^{a}$	281.8	294.5	478.2	2.99	4.38	55^{b}	45
0.8	270.7±56.9	275.4	275.5	642.2	2.64	4.62	11^{b}	79
1.0	249.8±9.5	269.2	269.2	661.8	3.00	4.67	0^{b}	124
1.5	226.0±4.4	256.5	262.9	655.7	3.00	4.58	0^{b}	240
2.0	212.3±2.8	250.2	256.5	661.8	3.00	4.67	0^{b}	534
3.0	195.2±1.6	243.8	250.2	611.3	3.00	4.63	0^{b}	913

[a] spontaneous dissociation occurs

[b] due to the rarity of the exchange event, mean lifetimes cannot be given

Table 2: Characteristic distances (in pm units) in the simulations of a single NaCl ion pair in $[\text{C}_4\text{C}_1\text{Im}]\text{Br}$ ionic liquid, with different charges on the Na^+ and Cl^- ions. For the numbering of the atoms in the $[\text{C}_4\text{C}_1\text{Im}]^+$ cation, see Figure 4. $\text{N}_{\text{Br}}^{\text{Na}}$: average number of coordinating Br^- anions around the sodium ion within the first solvation shell; $\text{N}_{[\text{C}_4\text{C}_1\text{Im}]}^{\text{Cl}}$: average number of $[\text{C}_4\text{C}_1\text{Im}]^+$ cations around the Cl^- anion; $\text{Ex}_{\text{Br}}^{\text{Na}}$: observed number of exchanges of Br^- anions between the bulk and the first solvent shell of the Na^+ cation throughout the simulation; $\tau_{[\text{C}_4\text{C}_1\text{Im}]}^{\text{Cl}}$: mean lifetime of $[\text{C}_4\text{C}_1\text{Im}]^+$–$\text{Cl}^-$ interactions (for description of lifetime calculations, see: ref[80]).

transfer—makes ion pair formation less probable.

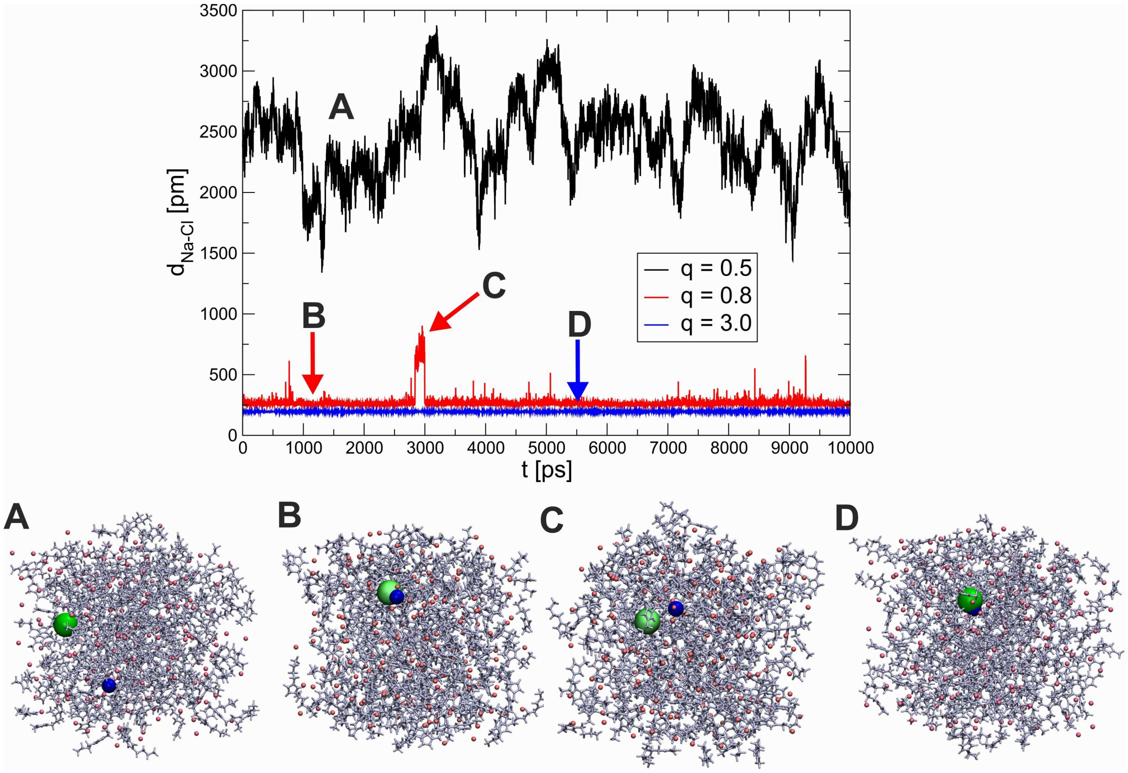

Figure 5: Development of the Na-Cl distances over time in three simulations, with 0.5, 0.8 and 3.0 e absolute charges on the ions. Below four snapshots are shown from these trajectories, taken from the points marked by arrows ($[C_4C_1Im]^+$: grey; Br^+: red; Cl^-: green; Na^+: blue).

Due to the aforementioned spontaneous dissociation, in the $|q| = 0.5$ case the whole of both surfaces of the solute ions are available for solvation, and therefore upon increasing the charge to $|q| = 0.8$ the average coordination number of bromide anions around the sodium cation decreases (Table 2). In the rest of the structural properties in Table 2 the increasing strength of solute-solvent interactions are clearly indicated throughout the whole range (Table 2). Interestingly, nevertheless, the average number of coordinating bromide anions does not exceed three, while the average number of $[C_4C_1Im]^+$ cations around the chloride also shows only a fluctuating trend between four and five. The lack of any clear increasing trend can be explained by the repulsive forces between the alike solvating IL ions, and also by the gradually increasing Na^+-$[C_4C_1Im]^+$ and Cl^--Br^- interactions.

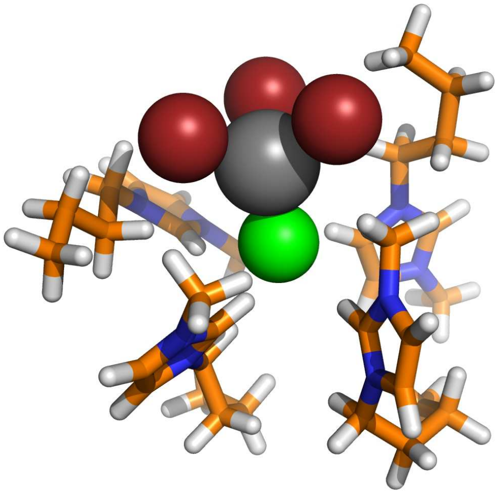

Figure 6: A representative snapshot of the NaCl (|q| = 2) ion pair's solvation shell in $[C_4C_1Im]^+$.

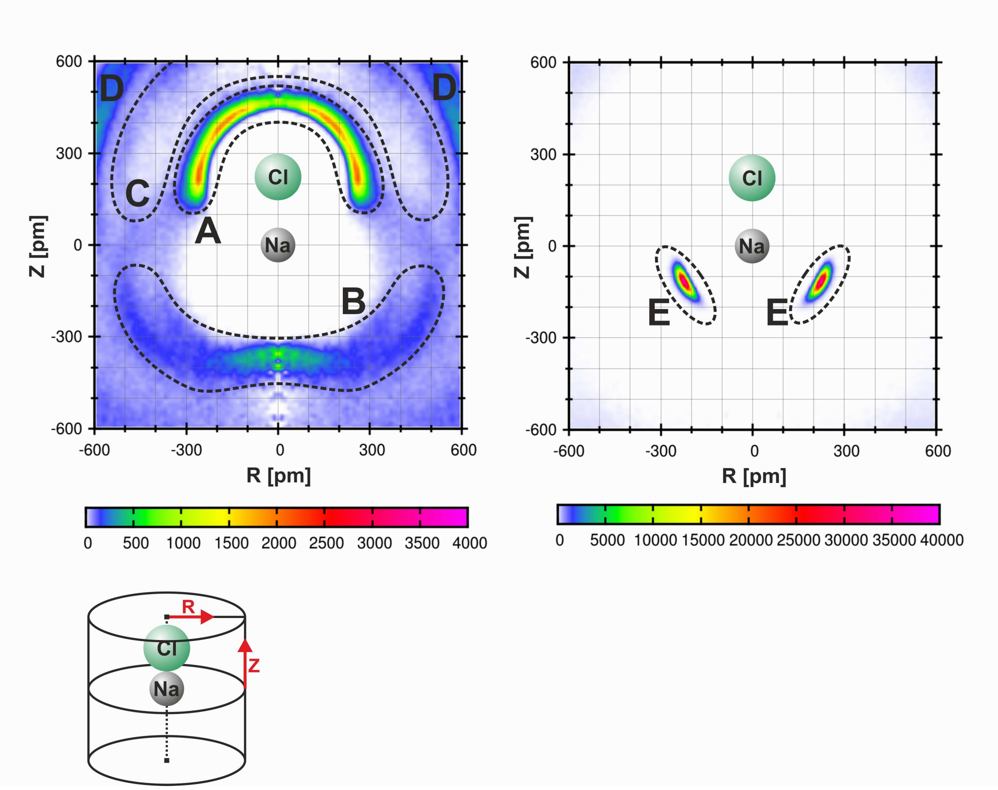

Figure 7: Pseudo-spatial distribution of the $[C_4C_1Im]^+$ cation's ring hydrogen atoms (left), and the bromide anions (right) around the NaCl ion pair (|q| = 2).

In the |q| = 0.5 case—keep the previously discussed dissociation in mind—the three coordinating bromide anions are arranged in a loose, often distorted planar triangular shape around the sodium ion. In the rest of the cases where the NaCl does not dissociate, however, the IL anions around the sodium cation are generally arranged in a fashion, so that they form a tetrahedron together with the chloride (Figure 6). Interestingly, this not only allows the longest possible Br^--Br^- and Cl^--Br^- distances, but also creates Br^--$[C_4C_1Im]^+$ interactions within the solvent shell, around the midpoint of the Na-Cl axis (cf. regions A and E in Figure 7). The exchange of IL ions between the bulk and the first solvent shell dramatically decreases by increasing charge (cf. $\mathrm{Ex}_{\mathrm{Br}}^{\mathrm{Na}}$ or $\tau_{[C_4C_1Im]}^{Cl}$ data for different |q| values in Table 2), which means that the solvent ions spend more time around the solute ion pair. Accordingly, the Br^--$[C_4C_1Im]^+$ interaction within the first solvent shell becomes more static, thus, it is apparent that the presence of highly charged ion pairs in the solution induces the formation of further, static ion pair-like structures in the surrounding ions. This is consistent with previous experimental data regarding the conductivity and glass formation of ILs, which showed that the decrease of the Coulombic interactions between the ions by (intramolecular) charge delocalisation results in an increase of the ion mobilities.[109] Furthermore, it is also worth mentioning that in the pseudo-spatial distribution of the $[C_4C_1Im]^+$ cation around the NaCl ion pair (Figure 7, left) also shows a structure inducing effect in the longer range: approaching the bulk from the chloride anion, after the first solvate shell with high occurrences of the IL cation (regions A, Figure 7) there is a region where the charged moieties are rare (region C, Figure 7), followed by a second solvate shell (region D, Figure 7). Also, some cations are apparently interacting with the bromide anions around the sodium ion, providing some occurrences in the lower half of Figure 7 (region B). After this second solvate ionshell, however, the effect of the increased ion-ion interactions are screened by the ion network of the IL, as has been shown before.[46]

Although some of these results represent extreme cases, the observed trends by the changes in charge are gradual, therefore they are very helpful in describing and understanding the effects of smaller fluctuations in the charges, such as the charge transfer described in the previous section. Accordingly, if there is a charge transfer between two neighbouring ions in the solution, which decreases the total charge of each ion involved, it helps the dissociation

|q|	**0.5**	**0.8**	**1.0**	**1.5**	**2.0**	**3.0**
$\Delta A^{\ddagger}$	13	29	84	247	573	1588
ΔA	-8	8	50	205	518	1547

Table 3: Free energy barrier and free energy of dissociation (in kJ mol^{-1} units) of the NaCl ion pair with different charges at the Na$^+$ and Cl$^-$ ions.

of the two species and breaks the static aggregation of the surrounding ions as well, thus, locally fluidizing the liquid. This can also be described as the charge transfer changes the IL into a more molecular liquid-like assembly, influencing its physicochemical properties to a great extent.

The energetics of the dissociation process is in agreement with all the trends in the interactions established above, viz. the dissociation free energies and the corresponding free energy barriers (Table 3) are gradually, and steeply increasing. For the $|q| = 0.5$ case the free energy is a low negative value, indicating a favored dissociation, in clear accordance with the spontaneous dissociation observed in this system, as described above; while for the $|q| = 3.0$ value it is almost 1600 kJ mol^{-1}. The barriers are generally by ca. 20-40 kJ mol^{-1} higher, than the dissociation free energies, thus, the barrier of the reverse process is, interestingly, hardly changing at all.

Since the disparity in ion size has also been reported to have an impact on the structure of ionic liquids,[110,111] while the size itself has been shown to have an effect on the association behavior,[50] the Lennard–Jones parameters of the sodium ion have also been varied at $|q| = 0.8$ charges, shifting the location of the potential minimum closer to or farther away from the sodium ion, thus practically changing the size of this ion. As it is shown in Table 4, the Na$^+$-Cl$^-$ and Na$^+$-Br$^-$ distances are, as expected, significantly increased by the change of the sodium ion's size, while those distances involving only the chloride anion remain mostly in the same range. The increased size of the sodium cation reduces the charge density at its surface, and therefore the attractive Coulombic interactions with the chloride and bromide anions are decreased. Accordingly, with increased sizes (150% and 200%) similar spontaneous dissociation of the NaCl ion pair occurs, as it has been shown for the $|q| = 0.5$ case above,

size$_{\mathrm{Na}}$	**d**$_{\mathrm{Na-Cl}}$	**d**$_{\mathrm{Na-Br}}$	**d**$_{\mathrm{Cl-H2}}$	**d**$_{\mathrm{Na-C_{term}}}$	**N**$^{\mathrm{Na}}_{\mathrm{Br}}$	**N**$^{\mathrm{Cl}}_{\mathrm{[C_4C_1Im]}}$	$\mathrm{Ex}^{\mathrm{Na}}_{\mathrm{Br}}$	$\tau^{\mathrm{Cl}}_{\mathrm{[C_4C_1Im]}}$
%	pm	pm	pm	pm	-	-	-	ps
100	270.7±56.9	275.4	275.5	642.2	2.64	4.62	11[b]	79
150	–[a]	338.8	275.5	503.1	4.01	5.07	35[b]	136
200	–[a]	408.5	269.2	490.5	4.72	5.20	99[b]	126

[a] spontaneous dissociation occurs

[b] due to the rarity of the exchange event, mean lifetimes cannot be given

Table 4: Characteristic distances (in pm units) in the simulations of a single NaCl ion pair in $[\mathrm{C_4C_1Im}]\mathrm{Br}$ ionic liquid, with different sizes of the sodium anion (|q| = 0.8). The size is given as the percentage of that in the original force field, in terms of σ value in the corresponding Lennard–Jones potential. For the numbering of the atoms in the $[\mathrm{C_4C_1Im}]^+$ cation, see Figure 4. $\mathrm{N}^{\mathrm{Na}}_{\mathrm{Br}}$: average number of coordinating Br^- anions around the sodium ion within the first solvation shell during the simulations; $\mathrm{N}^{\mathrm{Cl}}_{\mathrm{[C_4C_1Im]}}$: average number of $[\mathrm{C_4C_1Im}]^+$ cations around the Cl^- anion; $\mathrm{Ex}^{\mathrm{Na}}_{\mathrm{Br}}$: observed number of exchanges of Br^- anions between the bulk and the first solvent shell of the Na^+ cation throughout the simulation; $\tau^{\mathrm{Cl}}_{\mathrm{[C_4C_1Im]}}$: mean lifetime of $[\mathrm{C_4C_1Im}]^+$–Cl^- interactions.

and also the dissociation free energies and free energy barriers show a generally decreasing, albeit somewhat scattering trend (Table 5). Similarly, the solute-solvent interactions are weakened by enlarging the sodium, as shown by the more frequent exchange of the Br^- anions in the solvent shell of the Na^+ cation.

However, while the strength of each Na^+-Br^- interplay is decreased by the increasing size of the Na^+, the number of interactions is also increased, and the average number of bromide anions around the sodium cation grows from 2.64 to 4.72 (Table 4), although the dissociation of the NaCl ion pair also takes a major role in this increase, as described above. Interestingly, not only the size and the composition of the solvent shell changes, but also the solute-solvent interaction modes: while in Table 2 it can be seen that by approaching higher charges the weaker, dispersion-like Na-butyl interplay becomes less significant (see $\mathrm{d}_{\mathrm{Na-C_{term}}}$ values), the larger size and the corresponding smaller charge density allows this interaction to take a

	50%	100%	150%	200%
$\Delta A^{\ddagger}$	54	29	33	12
ΔA	29	8	26	−4

Table 5: Free energy barrier and free energy of dissociation of the NaCl ion pair (in kJ mol^{-1} units) with different sizes of the Na^+ ion.

somewhat larger part in the solvation (Table 4). This is shown by the Na-C_{term} distances, which are decreasing with the increasing size of the ion, unlike any other distances involving the Na^+. This has some resemblance to the aforementioned microheterogeneity in ILs with long alkyl groups, where the non-polar side chains aggregate and form a microstructure within the IL.[103–108]

2 Summary and Conclusion

In the present paper we showed that considering the charge transfer has a dramatic effect on the ion pairing behaviour of ionic liquids, and resolves many discrepancies in earlier literature. We found large charge transfer values—viz. the decrease of the total charge on the ions—between the cation and the anion of a series of ionic liquid ion pairs, which is in agreement with previous *ab initio* data,[41,65,66] and also with the general behaviour of force fields for ionic liquids modified by charge alteration.[61,78–80] Since the comparison of the conductivity values and the ions' mobilities[30,31]—defining the term "ionicity"—must include the charge that is transported by the movement of the ions, the observed decrease of the charges affects greatly the interpretation of the observed ionicity values. Apparently, the originally published values involve not only the association processes, but also the charge transfer; in other words, while the neutralization of the mobile particles indeed occurs, it is not or not only via ion pair formation, but also via charge transfer. The charge-corrected values show, accordingly, a much more independent movement of the ions, and although the association of ions can be still surmised after the correction, ion pairing seems less important than thought before based on conductivity measurements. Thus, our data suggest a complex interplay of charge transfer and ion pairing behaviours, such that these cannot be entirely separated from each other, and they are likely to be two of the several significant factors that together will explain the lower than expected conductivities.

After having seen the importance of the charge transfer in ionic liquids, we focused on the structural effects of the differently separated charges within a probe ion pair in an ionic liquid, by using molecular dynamics simulations. The solvation of the NaCl probe ion pair showed large changes upon altering the charge on the sodium and on the chloride. By increasing the charge on the ions, the Na-Cl and the solute-solvent interactions become stronger, and the association of the ion pair is favoured, while the solvent shell becomes more static and concomitant ion pair formation in the IL itself is induced in the solvent shell. The decrease of the charge has the opposite effect, and one may assume that by the charge transfer the structure of the ionic liquid changes, and by becoming somewhat similar to a molecular liquid rather than a salt, it is becoming more fluid. This is in clear agreement with, and may explain the previous rule of thumb in molecular dynamics simulations of ionic liquids that the viscosities and other dynamic properties become more realistic, and more liquid-like if the charges are scaled by a factor of ca. 0.8.[61,78–80] From the technical point of view these results also point out the necessity for the scaling of charges to obtain a realistic physical picture of the IL, and this approach might be beneficial to consider in combination with polarizable force fields as well.

In summary, the importance of charge transfer is clearly indicated, which does not only explain, at least in part, the previously observed discrepancies between conductivity measurements and other approaches aiming to understand ion pairing in ionic liquids, but also that the structure is highly affected by it. The more molecular liquid-like structure of ILs, which is achieved by the charge transfer between the ions, may also serve as a significant contribution to answer the question, why are ionic liquids liquid?

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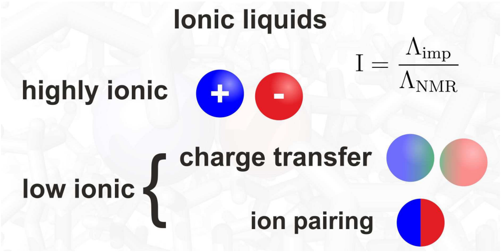

Charge transfer and ion pairing together are necessary to consider for explaining the ionicity and the structure of ionic liquids