VIP Ionic Liquids Very Important Paper

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Charge-Scaling Effect in Ionic Liquids from the Charge-Density Analysis of *N*,*N*′-Dimethylimidazolium Methylsulfate**

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Abstract: *The charge scaling effect in ionic liquids was explored on the basis of experimental and theoretical charge-density analyses of $[C_1MIM][C_1SO_4]$ employing the quantum theory of atoms in molecules (QTAIM) approach. Integrated QTAIM charges of the experimental (calculated) charge density of the cation and anion resulted in non-integer values of ± 0.90 (± 0.87) e. Efficient charge transfer along the bond paths of the hydrogen bonds between the imidazolium ring and the anion was considered as the origin of these reduced charges. In addition, a detailed QTAIM analysis of the bonding situation in the $[C_1SO_4]^-$ anion revealed the presence of negative $\pi_O \rightarrow \sigma^*_{S\text{-}O}$ hyperconjugation.*

Ionic liquids (ILs)—ionic compounds with melting points below 100 °C—are interesting for many applications.[1] As many ion combinations yield an IL,[2] reliable models for the description, prediction, and control of fundamental physical IL properties are needed, for example, by static quantum chemical (QC) calculations,[3] molecular dynamics (MD) simulations,[3,4] quantitative structure–property relationships (QSPR),[5] group contribution,[6] and semi-empirical schemes.[3,7]

Within the MD simulations of ILs based on non-polarizable force fields, a meaningful assignment of individual atomic partial charges provides the key for a successful modeling of their individual physical and chemical properties.[8] Intuitively, one would suggest that the sum of the partial charges of the cationic and anionic IL moieties yield a formal charge of ± 1 e for $[A]^+[B]^-$ salts. However, a reduction of the ionic net charge of ILs is necessary[9–12] for the proper description of their dynamic properties by MD simulations employing non-polarizable force fields. According to this charge scaling (CS) effect for ILs, the total charge of univalent ions should range between 0.6 and 0.8 e.[11–13] The CS was also used in MD simulations of IL–water interfaces (scaling by 0.9),[14] polymer electrolytes (scaling by an effective dielectric constant),[15] high- and low-dielectric media, ion-solvent systems and ionic groups in proteins (scaling by $(\varepsilon_{el})^{-0.5}$, where ε_{el} is the electronic component or high-frequency limit of the relative permittivity).[16] In support of these findings, the sum of calculated partial charges of an ion within gas-phase ion pairs, charged clusters, or in the bulk phase do not sum up to unity in QC calculations and ab initio molecular dynamics of ILs.[9,10,17–20] For *N*-alkyl,*N*′-methylimidazolium chlorides this CS was explained by charge transfer.[17]

Non-integer charges were also found for NaCl or MgO crystals[21] by applying the QTAIM[22] approach to calculated electron densities, or were revealed by ab initio calculations of potential energy surfaces for a NaCl ion pair.[23] Experimental charge-density studies combined with the QTAIM approach revealed the CS effect in the crystalline phase of simple salts such as $[NH_3OH][Cl]$, $[Na][ClO_3]$, or $[K]_2[SO_4]$.[24–27] Indirect experimental evidence for the CS caused by charge transfer in ILs was inferred from X-ray photoelectron spectroscopy (XPS) combined with QC calculations,[18] supported by studies on a broader range of ILs.[29] However, a direct experimental evidence for such an (at first sight) "unphysical" treatment for the study of IL systems seems to be lacking.

Herein, direct experimental insight into the CS effect, on the basis of high resolution X-ray diffraction (XRD) studies of the prototype IL *N*,*N*′-dimethylimidazolium methylsulfate ($[C_1MIM][C_1SO_4]$), is reported. The crystal structure of $[C_1MIM][C_1SO_4]$ was already reported by Holbrey et al.[30] The ions $[C_1MIM]^+$ and $[C_1SO_4]^-$, and their local environment within the crystal structure of $[C_1MIM][C_1SO_4]$ are shown in Figure 1 a,b. Bond lengths and angles of our study at 100 K agree nicely with literature values[30] (173 K), and shall thus not be further discussed.

Experimental charge-density distributions were obtained by fitting a Hansen–Coppens multipolar model[22,31] to high-resolution XRD data obtained at 100 K.[32] The static charge-density maps derived from the experimental diffraction data compare well with the respective computed maps.[33] Table 1, Figure 1 c,d, and Sections S10 and S11 in the Supporting Infomation contain detailed QTAIM analyses[22] of the

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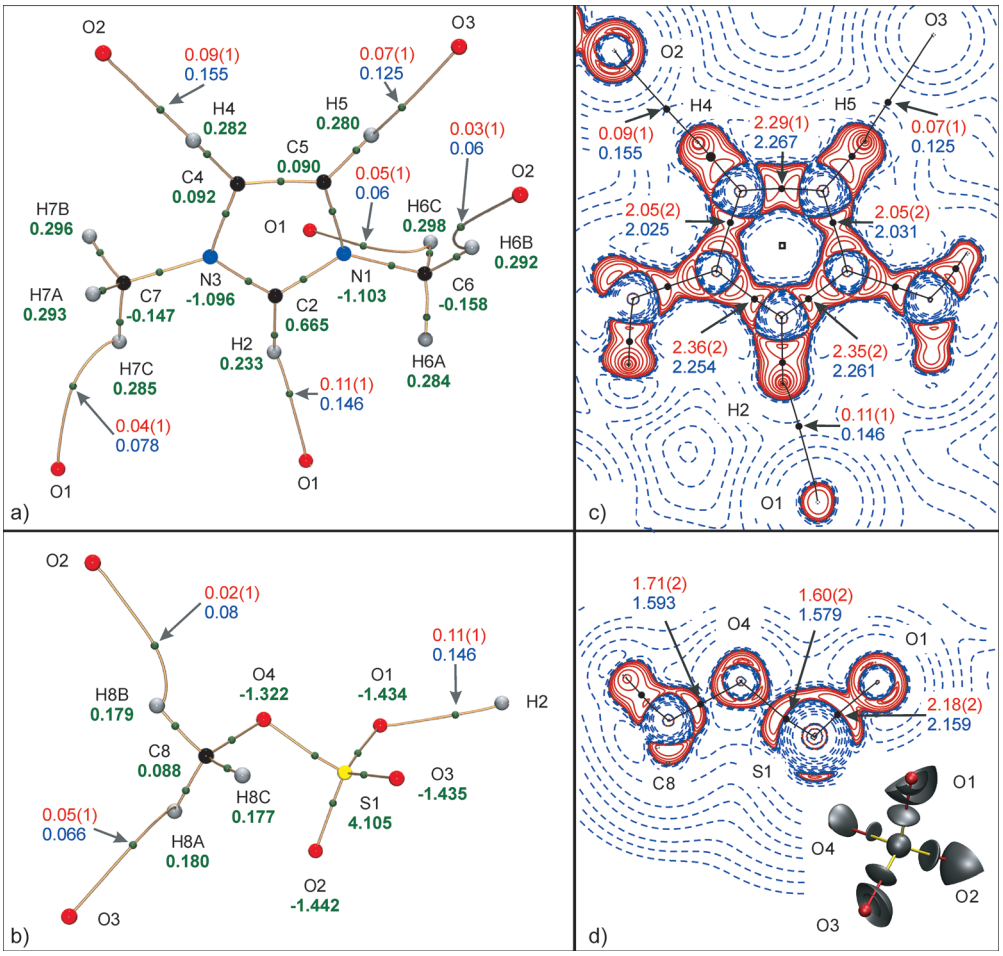

Figure 1. Molecular graphs of the cationic (a) and the anionic (b) moieties in $[C_1MIM][C_1SO_4]$, showing the individual bond paths (golden lines). The bond critical points (BCPs) are marked with dark green dots; $\rho(\mathbf{r}_c)$ values at the C–H···O BCPs in e Å^{-3} (experimental values in red, theoretical values in blue); experimental atomic charges are given in dark green color). The experimental (theoretical) C–H···O distances (Å) are as follows: C2–H2···O1: 2.081 (2.049), C4–H4···O2: 2.036 (1.989), C5–H5···O3: 2.156 (2.123), C6–H6B···O2: 2.532 (2.484), C6–H6C···O1: 2.541 (2.526), C7–H7C···O1: 2.391 (2.350), C8–H8A···O3: 2.449 (2.404), C8–H8B···O2: 2.398 (2.315). Contour map of $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ in the molecular plane of the cation (c) and in the S1-O4-C8 plane of the anion (d); bond paths are drawn as black lines, and the experimental (red color) and theoretical (blue color) $\rho(\mathbf{r}_c)$ values (black circles) are specified in e Å^{-3}. Positive (solid red) and negative (dashed blue) contour lines are drawn at 0, $\pm1\times10^n$, $\pm2\times10^n$, $\pm4\times10^n$, and $\pm8\times10^n$ e Å^{-5}, with $n = 0, \pm1$, and ±2. The insert shows a 3D map of $L(\mathbf{r})$ (at 12 e Å^{-5}) around S1.

theoretical and experimental charge-density distributions.[27] Figure 1 c,d shows the experimental contour maps of the negative Laplacian, $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$, the bond paths, and the salient critical points, in the molecular plane of the imidazolium cation and in the S1-O4-C8 plane of the anion, respectively. Both display the expected topological features of imidazolium salts.[34]

QTAIM partial charges were obtained by integration of the experimentally derived (exp.) and calculated (calc.) electron densities within the zero-flux-surfaces of the atomic subsystems. The corresponding ionic net charges ($Q^{+/-}$) amount to $Q^{+/-}(\text{exp.}) = 0.90$ e and $Q^{+/-}(\text{calc.}) = 0.87$ e (Figure 1 a,b). These reduced ion charges signal the presence of charge transfer in $[C_1MIM][C_1SO_4]$. In this respect, the network of intermolecular hydrogen bonds between cation and anion in $[C_1MIM][C_1SO_4]$ might provide efficient channels for charge transfer.[28,35] The complex hydrogen-bonding scenario has therefore been elucidated by a detailed bond path analysis (Figure 1 a,b). We note the good agreement between the theoretical and experimental density accumulations at the individual O···H bond critical points (BCPs), and point out that the strongest hydrogen bonds are established between the C–H groups of the imidazolium ring and the three S–O oxo groups of the anion: C2–H2···O1, C4–H4···O2 and C5–H5···O3 (Figure 1), which are characterized by rather short H···O contacts and rather linear bond paths. These findings support the viewpoint that the hydrogen bonds might operate as bridges for charge transfer.[28,35] Further support is given by gas-phase calculations of an ion pair and ionic clusters with subsequent QTAIM analyses (Figure S7). The $Q^{+/-}$ values are reduced from 0.95 e in the ion pair (lacking a 3D network of intermolecular O···H bonds) to 0.91 e in an ion cluster formed by one ion surrounded by four counterions and finally to 0.90 e in a cation centered cluster consisting of nine cations and eight anions. The strongest hydrogen bonds in the latter cluster are formed by the same H···O entities as in the experimental and theoretical $[C_1MIM][C_1SO_4]$ model.[27]

In the related $[C_1MIM][Cl]$, a charge of -0.82 e upon extrapolation to infinite cluster size was reported for the chloride ion.[19] Schmidt et al. calculated, however, an even smaller $Q^{+/-} = 0.63$ e charge for the ions in $[C_1MIM][Cl]$ in the bulk phase using the Blöchl method.[9] Simulations of the crystalline state of [RMIM][x] (X = BF_4, PF_6) salts resulted in $Q^{+/-} = 0.80$–0.81 e.[20] The reduced ionic charges of our benchmark model $[C_1MIM][C_1SO_4]$ are somewhat higher, but within the same order of magnitude. Nevertheless, the present charge-density study provides strong experimental support for the presence of CS in crystalline ILs and the important role of intermolecular hydrogen bonds to facilitate an efficient charge transfer between the ionic entities. Thus,

Table 1: Selected bond distances (d) and topological parameters ($\rho(\mathbf{r}_c)$ [eÅ^{-3}], $\nabla^2\rho(\mathbf{r}_c)$ [eÅ^{-5}], ε) at salient bond critical points in [C_1MIM]-[C_1SO_4].

Unit	Method	d [Å]	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	ε
Anion					
	Exp.	1.4431(2)	2.18(2)	24.7(1)	0.02
S1–O1	VASP[a]	1.4605	2.159	13.278	0.04
	C09[a]		1.957	26.238	0.12
	Exp.	1.5988(2)	1.60(2)	17.8(1)	0.10
S1–O4	VASP[a]	1.6318	1.579	−10.435	0.09
	C09[a]		1.476	−3.825	0.08
	Exp.	1.4347(4)	1.71(2)	−4.8(1)	0.01
O4–C8	VASP[a]	1.4478	1.593	−7.856	0.02
	C09[a]		1.562	−7.805	0.02
Cation					
	Exp.	1.3283(3)	2.36(2)	−22.6(1)	0.12
C2–N3	VASP[a]	1.3400	2.254	−13.399	0.23
	C09[a]		2.215	−19.864	0.24
	Exp.	1.3773(3)	2.05(2)	−14.4(1)	0.25
N3–C4	VASP[a]	1.3817	2.025	−12.266	0.12
	C09[a]		1.992	−14.995	0.14
	Exp.	1.3590(3)	2.29(1)	−19.1(1)	0.30
C4–C5	VASP[a]	1.3672	2.267	−23.014	0.45
	C09[a]		2.173	−21.602	0.32
	Exp.	1.4545(3)	1.72(2)	−11.4(1)	0.06
N3–C7	VASP[a]	1.4563	1.721	−13.664	0.01
	C09[a]		1.687	−13.310	0.03

[a] DFT calculations employing the VASP/CRYSTAL09 suite of programs (Ref. [33]).

the use of the CS model in non-polarizable force fields for ILs[9–12] was justified by a detailed experimental charge-density analysis.

In ongoing work to be published as a full paper, we concentrate on the bonding situation in the $[C_1SO_4]^-$ anion to clarify the extent of negative $\pi_O \rightarrow \sigma^*_{S\text{-}O}$ hyperconjugation,[36] which triggers back donation from the negatively charged oxygen atoms (−1.32 to −1.44 e) to the strongly positively charged (+4.11 e) sulfur atom. This process is less relevant in K_2SO_4,[26,37] but plays a significant role in the energetic stabilization of sulfones (O_2SR_2).[36] Indeed, the experimental and theoretical bond ellipticity values $\varepsilon_{S\text{-}O4}$ in the $[C_1SO_4]^-$ anion (ca. 0.1) are remarkably large and compare well with the corresponding values in sulfones which are characterized by S–O bond orders larger than unity.[38] Also, the large charge accumulation at the S–O BCPs in the $[C_1SO_4]^-$ anion (Figure 1 d), as well as an inspection of the crystal orbitals involved in the S–O bond formation (Figure S4–S6) strongly support the presence of negative $\pi_O \rightarrow \sigma^*_{S\text{-}O}$ hyperconjugation. This mechanism (besides the presence of intermolecular hydrogen bonding), might help to explain why the ionic net charge in $[C_1MIM][C_1SO_4]$ ($\pm 0.90/\pm 0.87$ e) is larger than that of [C_1MIM][Cl] (± 0.82 e). Future work shall therefore provide more insight for the π-character of S–O bonds in this and related anionic entities.[26] Furthermore, the derivation of various volume terms within the framework of volume-based thermodynamics[39] and their partitioning into ion volumes using the QTAIM approach will be presented.

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