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Proton Transfer and Polarity Changes in Ionic Liquid/water mixtures

A perspective on hydrogen bonds from *ab initio* molecular dynamics at the example of 1-ethyl-3-methylimidazolium acetate/water mixtures - Part 1

Supporting Information

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Table S1. Statistical data on bond lengths/angles in the simulated molecules. ”Mono” refers to an isolated monomer calculation of the specified molecule in vacuum at 0 K. σ is the standard deviation.

System	Bond/Angle	Mean value	σ	Min	Max
A	$[C_2C_1Im]^+$ C2-H2	109.7 pm	3.4	97.0	130.7
B		109.0 pm	3.1	96.1	126.9
C		108.7 pm	3.2	97.8	121.7
Mono		108.2 pm			
A	$[C_2C_1Im]^+$ C4-H4	109.1 pm	3.2	96.1	127.6
B		108.7 pm	3.0	96.3	125.4
C		108.5 pm	2.9	97.5	121.1
Mono		108.2 pm			
A	$[C_2C_1Im]^+$ C5-H5	109.1 pm	3.2	96.0	127.7
B		108.7 pm	2.9	96.7	124.8
C		108.5 pm	2.9	96.0	123.6
Mono		108.2 pm			
A	$[OAc]^-$ C1’-C2’	155.4 pm	4.1	140.0	179.7
B		154.4 pm	4.0	139.1	175.6
C		153.2 pm	3.7	140.4	169.0
Mono		158.4 pm			
A	$[OAc]^-$ C1’-O’	128.2 pm	2.6	116.6	143.8
B		128.4 pm	2.7	116.8	144.3
C		128.7 pm	2.7	118.1	140.5
Mono		127.3 pm			
A	$[OAc]^-$ O’-C1’-O’	125.5º	3.0	112.3	138.8
B		124.3º	3.0	111.6	137.9
C		123.1º	3.0	111.0	135.2
Mono		129.5º			
A	H_2O Ow-Hw	99.6 pm	3.1	86.6	124.6
B		99.8 pm	3.2	85.9	126.9
C		99.7 pm	3.1	87.1	124.3
Mono		97.4 pm			
B	H_2O Hw-Ow-Hw	105.3º	5.6	79.6	144.7
C		105.9º	5.5	79.9	140.2
D		105.8º	5.5	79.5	139.8
Mono		104.3º			

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Table S2. Statistical data on the dipole moments of the simulated molecules. Ref. indicates the reference center for dipole calculation of charged particles: CoG=center of geometry, CoR=geometric center of ring. All values are in Debye.

System	Molecule	Ref.	Mean	σ	Min	Max
A	$[C_2C_1Im]^+$	CoG	2.73	0.61	0.82	5.13
B			2.70	0.62	0.34	4.85
C			2.73	0.51	0.92	4.46
Mono			2.15			
A	$[C_2C_1Im]^+$	CoM	2.21	0.64	0.29	4.79
B			2.21	0.59	0.21	4.49
C			2.19	0.55	0.41	4.01
Mono			1.51			
A	$[C_2C_1Im]^+$	CoR	2.84	0.68	0.27	5.11
B			2.87	0.62	0.62	5.11
C			2.80	0.56	1.01	4.61
Mono			2.38			
A	$[OAc]^-$	CoG	8.85	0.46	7.37	10.92
B			9.29	0.48	7.17	11.31
C			10.05	0.51	8.43	11.82
Mono			6.69			
B	H_2O		2.80	0.32	1.78	4.36
C			3.05	0.31	1.53	4.91
D			3.00	0.30	1.79	4.80
Mono			1.83			

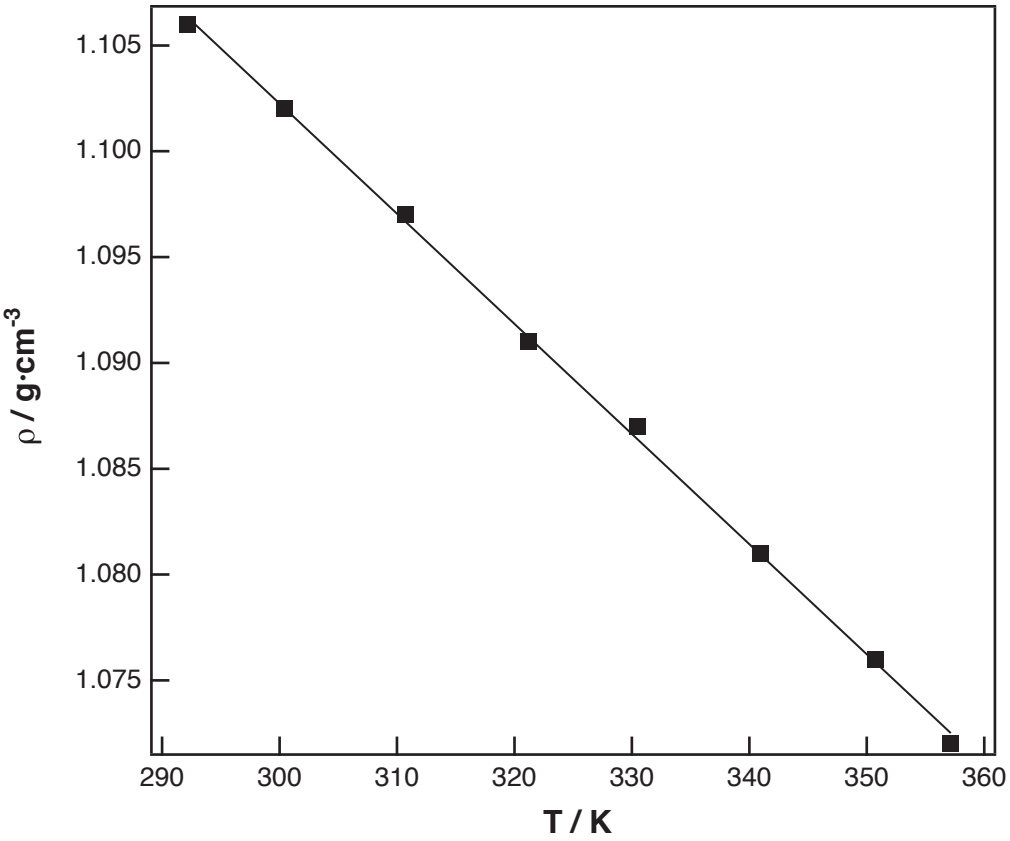

Figure S1. Dependence of the experimental density with the temperature. The density of $[C_2C_1Im][OAc]$ (IoLiTec, Lot G001101.4) has been determined using a sand bath (T±0.2 K) in a BYK midget density cup.

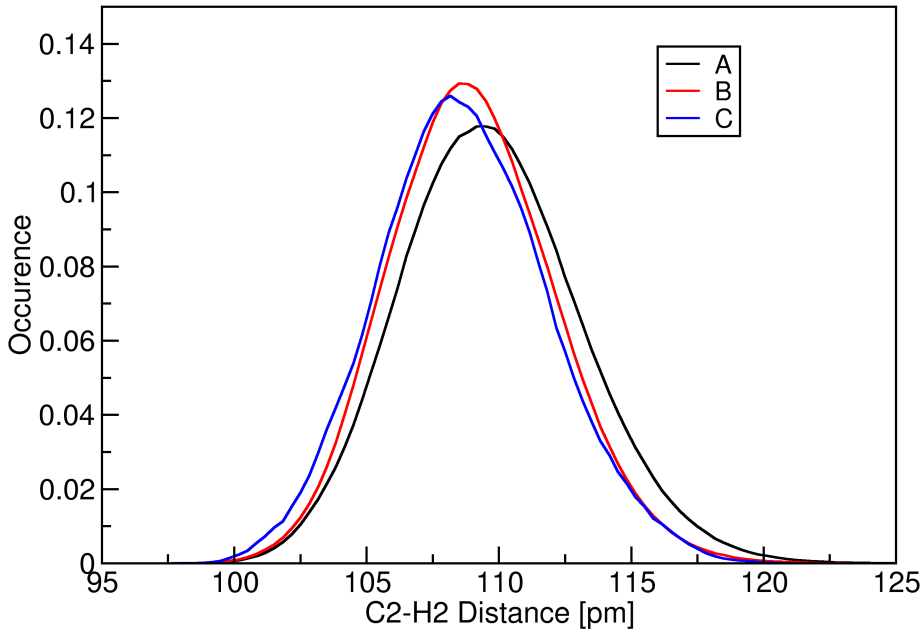

Figure S2. Distribution of the bond length between the carbon atom C2 of the imidazolium ring and the hydrogen atom H2 obtained along the simulations. The black curve represents the system with pure ionic liquid, the red curve corresponds to the system with x_{water}=0.75 and the green curve represents the system with x_{water}=0.99.

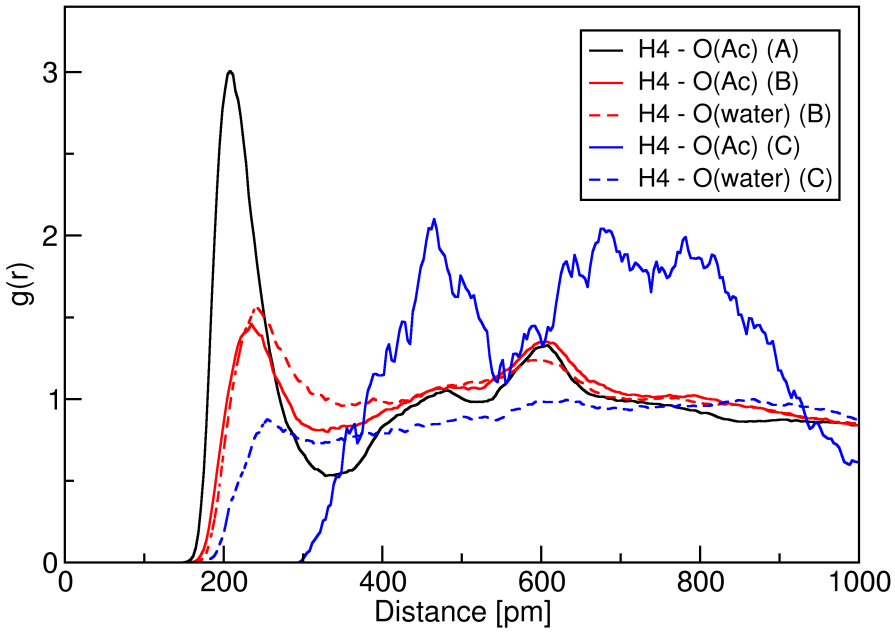

Figure S3. Cation-anion and cation-water site-site radial distribution functions (RDFs). Solid lines: hydrogen atom H4 of the $[C_2C_1Im]^+$ around the oxygen atoms of the $[OAc]^-$ anion, dashed lines: hydrogen atom H4 of the $[C_2C_1Im]^+$ around the oxygen atoms water.

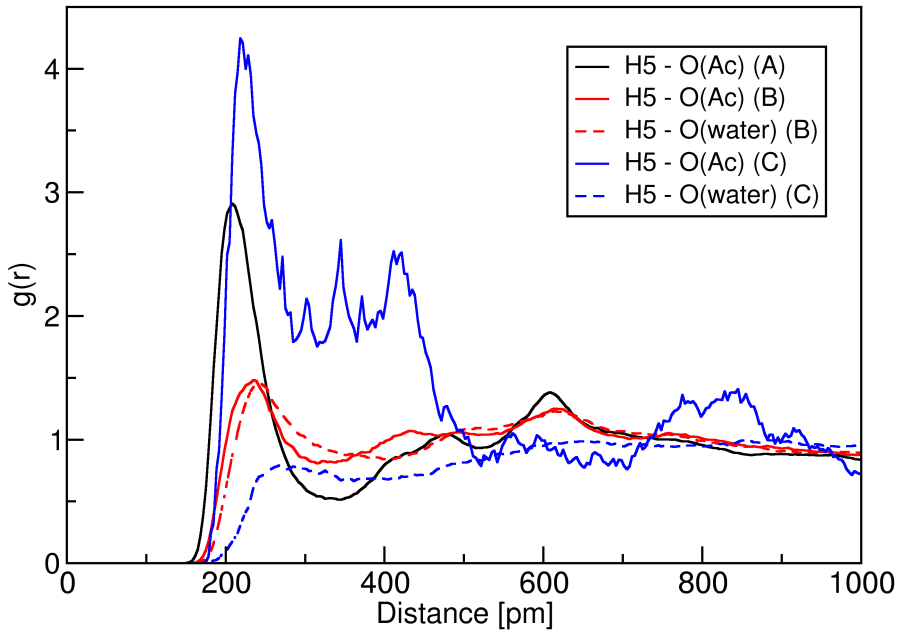

Figure S4. Cation-anion and cation-water site-site radial distribution functions (RDFs). Solid lines: hydrogen atom H5 of the $[C_2C_1Im]^+$ around the oxygen atoms of the $[OAc]^-$ anion, dashed lines: hydrogen atom H5 of the $[C_2C_1Im]^+$ around the oxygen atoms water.

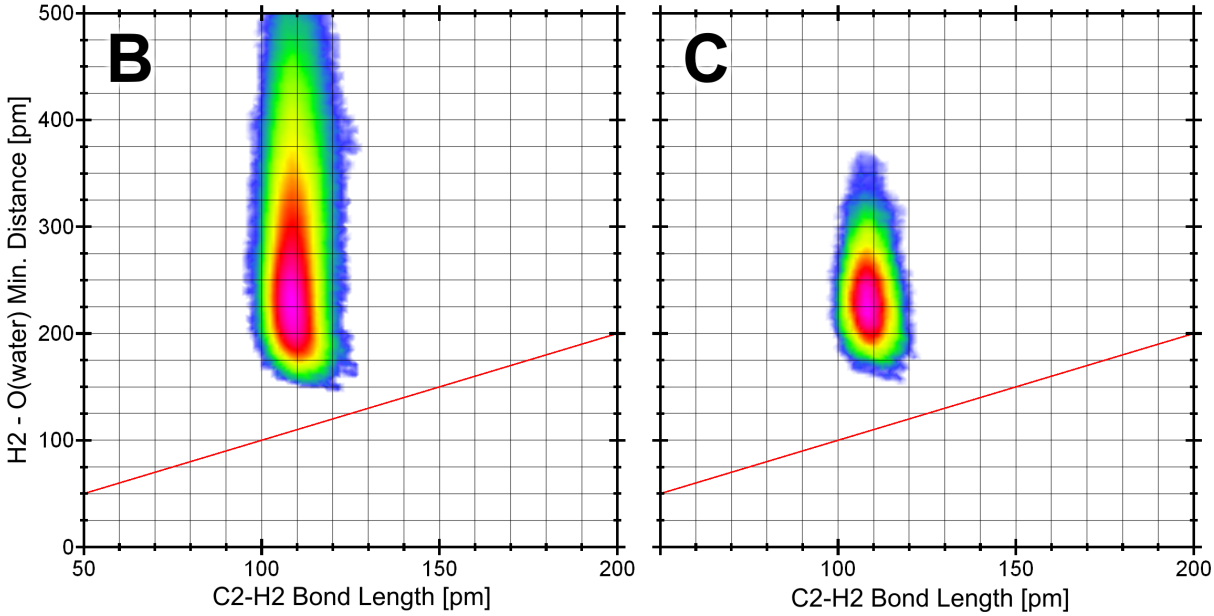

Figure S5. Combined Distribution Function showing the abstraction of the hydrogen atom H2 of the $[C_2C_1Im]^+$ cation by the oxygen atom Ow of water. The red line indicates the configurations where $r_1 = r_2$.