Electronic Supplementary Material for PCCP

Supporting Information

(What keeps ionic liquids in flow?)

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[2] This work was supported by the DFG, in particular by the projects KI-768/4-1 from the ERA-chemistry and KI-768/5-2 SPP-IL program. Computer time from the RZ Leipzig and NIC Jülich are gratefully acknowledged. The authors would like to thank Peter Wasserscheid for suggesting to look at the [C_1C_1mim][Cl] versus [C_1mim][Cl] problem with the SAPT method. JT thanks the Fonds der Chemischen Industrie for financial support.

A Additional comments to Fig. 3

The interaction energies obtained by the SAPT approach can be expressed as:

$$E_{tot} = E^1_{ele} + E^1_{ex} + E^2_{ind} + E^2_{ind-ex} + E^2_{disp} + E^2_{disp-ex} \tag{1}$$

E_{tot} is the total interaction energy, E^1_{ele} accounts for electrostatic interaction, E^1_{ex} results from exchange of electrons of unperturbed monomers, E^2_{ind} originates from the damped permanent and induced multipole moment interaction, E^2_{ind-ex} is the additional exchange repulsion due to induction interaction, E^2_{disp} originates from damped instantaneous electric multipole moment interaction and $E^2_{disp-ex}$ is the additional exchange repulsion due to dispersion interaction.[1] To obtain the induction forces we add up E^2_{ind} and E^2_{ind-ex}. The dispersion forces were calculated by adding up E^2_{disp} and $E^2_{disp-ex}$. The detailed comparison of [Na][Cl] to [C_1mim][Cl] can be found in our previous publication.[2]

B Cation-cation spatial distribution function

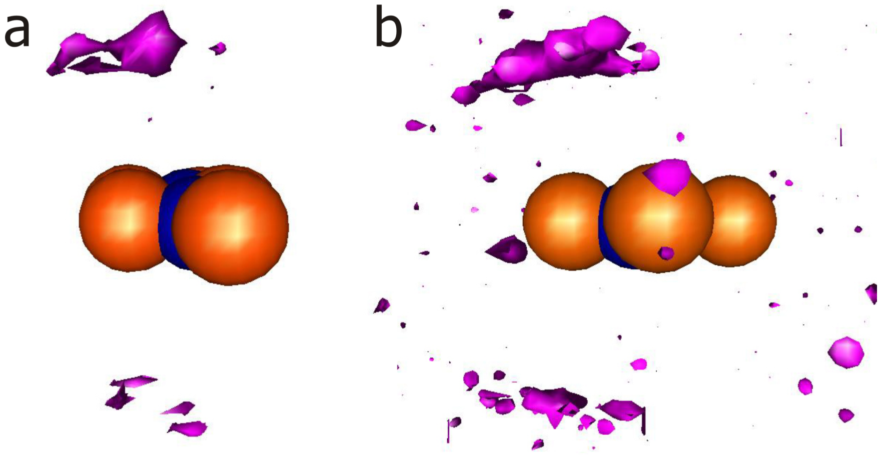

Figure A: Spatial distribution function (SDF) of the cation for [C_2mim][Cl] (a) and [C_2C_1mim][Cl] (b) around the imidazolium plane. The isosurface is plotted at 1.4 (magenta surface) times the corresponding average density.

C Values of SAPT-calculation for Fig. 3

Table A: Equilibrium distance Δd in pm; sum of electrostatic interaction E^1_{ele} and Pauli repulsion E^1_{ex} E_A; sum of electrostatic interaction E^1_{ele}, Pauli repulsion E^1_{ex} and contribution of induction (E^2_{ind} and E^2_{ind-ex}) E_B and total energy E_{tot} including dispersion forces (E^2_{disp} and $E^2_{disp-ex}$) in kJ/mol.

[C$_1$mim][Cl]				[C$_1$Py][Cl]			
Δd	E_A	E_B	E_{tot}	Δd	E_A	E_B	E_{tot}
-50	-153.07	-299.04	-378.68	-30	-176.75	-300.89	-361.10
-30	-244.22	-330.13	-390.08	-20	-213.24	-310.02	-361.77
-10	-293.65	-352.51	-397.94	-10	-240.32	-318.39	-362.93
0	-308.19	-359.27	-398.89	0	-259.99	-324.98	-363.40
10	-317.95	-363.32	-397.90	10	-273.91	-329.50	-362.68
20	-324.03	-365.00	-395.23	20	-283.34	-331.94	-360.65
30	-327.29	-364.73	-391.17	30	-289.31	-332.53	-357.40
40	-328.38	-362.88	-386.02	40	-292.63	-331.52	-353.10
50	-327.85	-359.79	-380.04	50	-293.93	-329.24	-347.98
60	-326.07	-355.73	-373.48	60	-293.70	-325.96	-342.23
70	-323.37	-350.98	-366.53	70	-292.32	-321.91	-336.06
90	-316.1	-340.08	-352.01	80	-290.07	-317.29	-329.61
110	-307.35	-328.19	-337.37			–	

Table B: Equilibrium distance Δd in pm; sum of electrostatic interaction E^1_{ele} and Pauli repulsion E^1_{ex} E_A; sum of electrostatic interaction E^1_{ele}, Pauli repulsion E^1_{ex} and contribution of induction (E^2_{ind} and E^2_{ind-ex}) E_B and total energy E_{tot} including dispersion forces (E^2_{disp} and $E^2_{disp-ex}$) in kJ/mol.

[N_{2111}][Cl]				[Na][Cl]			
Δd	E_A	E_B	E_{tot}	Δd	E_A	E_B	E_{tot}
–50	–155.96	–256.91	–332.28	–50	–281.84	–420.06	–422.25
–30	–233.30	–305.41	–361.60	–20	–459.86	–537.48	–538.63
–10	–278.00	–333.62	–375.66	0	–488.69	–550.68	–551.40
0	–291.65	–341.56	–377.97	10	–490.17	–546.89	–547.47
10	–300.98	–346.21	–377.78	20	–486.96	–538.85	–539.33
20	–306.87	–348.16	–375.56	30	–480.45	–528.08	–528.47
30	–310.04	–347.94	–371.72	40	–471.79	–515.54	–515.87
40	–311.08	–345.99	–366.65	50	–461.82	–501.96	–502.24
50	–310.49	–342.73	–360.67	60	–451.10	–487.83	–488.08
60	–308.64	–338.46	–354.05	70	–440.02	–473.54	–473.76
70	–305.86	–333.47	–347.01	80	–428.86	–459.37	–459.56
		–		90	–417.79	–445.5	–445.65

D SAPT for [C_1mim][Cl] vs. [C_1C_1mim][Cl]

The SAPT approach was also applied to [C_1C_1mim][Cl], see Fig. B. We found a higher contribution of dispersion and a lower contribution of electrostatic forces for [C_1C_1mim][Cl] than for [C_1mim][Cl]. However, the total potentials are very similar. Please note, that the plotted potentials are depicted only in one dimension. Movements of the anion around the imidazolium plane are not considered. Unfortunately, only a small cc-pVDZ basis set could be employed due to the size of the system.

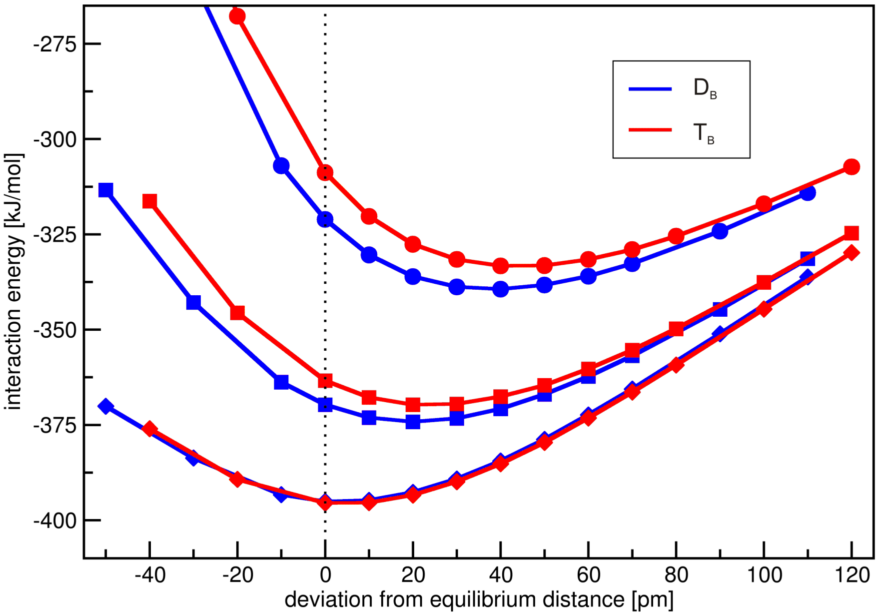

Figure B: Interaction energies versus distance for [C$_1$mim][Cl] (D$_B$) and [C$_1$C$_1$mim][Cl] (T$_B$) obtained by SAPT-calculations. *circles:* electrostatic E^1_{ele} and Pauli repulsion E^1_{ex}; *squares:* electrostatic E^1_{ele}, Pauli repulsion E^1_{ex} and induction (E^2_{ind} and E^2_{ind-ex}); *diamonds:* total energy including dispersion (E^2_{disp} and $E^2_{disp-ex}$). Basis set: cc-pVDZ

E Computational details

E.1 Static quantum chemistry

The programs provided by the TURBOMOLE[3]-suite were applied except for the symmetry-adapted perturbation theory calculations. Minimum structures were obtained employing the second-order Møller-Plesset perturbation theory (MP2) with the cc-pVTZ[4,5] basis set. Spin-component-scaled-MP2[6] (SCS-MP2) single point calculations were carried out on the optimized structures with the larger aug-cc-pVTZ[4,5] basis set. All given single point energies were counterpoise corrected with the procedure of Boys and Bernardi[7] in order to account for the basis set superposition errors (BSSEs). Additionally the convergency criterion was increased to 10^{-8} Hartree for all calculations. MP2 as well as SCS-MP2 calculations were applied in combination with the RI-technique[8,9] and the frozen core approximation. The symmetry-adapted perturbation theory[1] (SAPT) calculations were carried out with the aug-cc-pVDZ[4,5] basis set employing the MOLPRO[10]-program package.

E.2 Molecular dynamics simulations

Molecular dynamics simulations were performed using the program package GROMACS 3.3.1.[11–13] The simulated systems consisted of a cubic box with an edge length of 4520 pm ([C_2C_1mim][Cl]) or 4350 pm ([C_2mim][Cl]) enclosing 343 ion pairs. The systems was equilibrated for 1 nanosecond in the NPT ensemble, using the Parrinello-Rahman coupling scheme.[14,15] Simulations were performed in the NVT ensemble for 10 ns with a timestep of 1 fs and were kept at an average temperature of 460 K, employing a Nose–Hoover thermostat[16] with a relaxation time of 1 ps. If available, force field parameters were taken from the work of Liu.[17] Missing parameters were complemented by the AMBER all atom force field.[18] Explicit electrostatic interactions were considered up to a cut-off radius of 1.2 nm, and thereafter approximated by the particle mesh Ewald (PME) method.[19,20] In order to obtain atomic point charges, structures were optimized using Ahlrich's TZVP basis set and the general-gradient-corrected PBE functional by the TURBOMOLE program suite. The resolution of identity approximation[21,22] was employed for DFT calculations. Molecular RESP charges were derived from a Hartree–Fock 6-31G(d) single point calculation at the optimized structures using the GAUSSIAN code.[23] Resp charges were scaled by a factor of 0.85. The scaling of partial charges in classical molecular dynamics simulations with nonpolarizable force fields was proposed in several previous work, see for example Ref.[24] Scaled charges and geometries are listed in table C and D. We obtained a density of 1013.76 kg/m^3 for [C$_2$mim][Cl] at 460 K. Fannin and coworkers reported a density of 1137.8 kg/m^3 for [C$_2$mim][Cl] at 333 K and an extrapolation method for the density at different temperatures.[25] The extrapolated density is 1037 kg/m^3, which is only 2% above the value of our simulation. Furthermore, the qualitative shape of the spatial distribution function of the chloride anion of [C$_2$mim][Cl] is in very good agreement with *first–principles* molecular dynamics simulations. The density of [C$_2$C$_1$mim][Cl] is 924.52 kg/m^3 at 460 K. To the best of our knowledge, no density data or *first–principles* molecular dynamics simulations have been published for [C$_2$C$_1$mim][Cl].

Table C: Scaled RESP charges [e] used in the MD simulations for [C_2mim][Cl]. Furthermore, coordinates of the molecule providing the RESP charges are given in Å.

atom	x [Å]	y [Å]	z [Å]	q [e]
C	-0.000497603	-0.253195314	-2.424663879	-0.156573
N	1.240322969	-0.415568599	-1.837261370	0.0839094
C	1.137736643	-0.097452398	-0.534411288	-0.0900244
N	-0.130738815	0.263295585	-0.277083545	0.2087511
C	-0.860240262	0.170626613	-1.447141509	-0.214997
C	2.505214827	-0.848092752	-2.498396786	0.0978452
C	-0.659214778	0.652850932	1.036256995	-0.334110
H	-1.916444094	0.410498631	-1.489251000	0.2284411
H	-0.175173480	-0.445461832	-3.475776560	0.214846
H	1.945343004	-0.125493056	0.189415577	0.203265
H	0.177253106	0.847652158	1.715709998	0.1556903
H	-1.255197375	1.566201497	0.928986397	0.1556904
H	-1.281995166	-0.154876182	1.440645074	0.1556903
H	2.883441215	-1.706736713	-1.926091611	0.0560311
H	3.220399671	-0.020126935	-2.391626711	0.0560311
C	2.321749792	-1.215025227	-3.960069940	-0.246399
H	3.295142215	-1.533863268	-4.355441377	0.0919708
H	1.624012942	-2.053031412	-4.094057476	0.0919708
H	1.990054889	-0.359951860	-4.565261924	0.0919708

Table D: RESP charges [e] used in the MD simulations for [C_2C_1mim][Cl]. Furthermore, coordinates of the molecule providing the RESP charges are given in Å.

atom	x [Å]	y [Å]	z [Å]	q [e]
C	0.032655247	-0.313818178	-2.396520132	-0.166104
N	1.298974625	-0.371045947	-1.840159735	0.011055
C	1.230586169	0.002131502	-0.539601293	0.212477
N	-0.063783823	0.297339044	-0.274427705	0.124477
C	-0.820177210	0.103322019	-1.416155376	-0.244928
C	2.551496137	-0.763170509	-2.538511056	0.094082
C	-0.586521448	0.729743213	1.025806630	-0.234897
H	-1.889788155	0.276158589	-1.434571036	0.234232
H	-0.159374430	-0.568723261	-3.430497191	0.220398
C	2.359681898	0.107461585	0.414433576	-0.358094
H	0.023838919	1.548488690	1.424878794	0.127465
H	-1.610514063	1.089276472	0.883856486	0.127465
H	-0.594899437	-0.110164837	1.733078283	0.127465
H	2.986713450	-1.602747084	-1.977154033	0.064037
H	3.243375989	0.088645905	-2.469565544	0.064037
C	2.333628218	-1.156705367	-3.989388950	-0.291212
H	3.306179541	-1.432269532	-4.417915683	0.103353
H	1.673578894	-2.029243352	-4.088286913	0.103353
H	1.936037883	-0.327022333	-4.589892054	0.103353
H	3.194602356	-0.533661232	0.108244207	0.142662
H	2.735368865	1.141968450	0.474859784	0.142662
H	2.051806735	-0.198002826	1.423207488	0.142662

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