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Supporting Information

Physical Chemistry Chemical Physics (PCCP)

Comparative assessment of the performance of density functionals and dispersion correction on different properties of dicationic ionic liquids – An ab initio molecular dynamics (AIMD) study

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Fig. S1. RDFs between oxygen atoms of anion and hydrogen atoms of ring, linkage, and side alkyl chain of the cation based on the BLYP and PBE density functionals with and without D3-correction at 333.15 K and 1 atm.

S.1. Total and Partial Structure Factor

The X-ray scattering structure factors for $[C_3(\min)_2][NTF_2]_2$ DIL were calculated using the BLYP and PBE density functionals, both with and without D3-correction, to explore the effect of dispersion correction and density functional type on the structural heterogeneity of the studied DIL. This calculation was performed by employing the Fourier transform of the radial distribution function, $g_{ij}(r)$, indicating the probability of finding an atom of type *j* at a specific distance, *r*, from an atom of type *i*. Furthermore, this function is normalized so that the integral over all distances equals the total number of atoms of type *i* in the system. The structure factor *S(Q)* is then computed using the following formula:^{S1}

$$S(Q) = \frac{\sum_{ij} x_i x_j f_i(Q) f_j(Q) 4\pi \rho \int_0^{r_c} \left[g_{ij}(r) - 1 \right] r^2 \frac{\sin(Qr)}{Qr} dr}{\left[\sum_{ij} x_i f_i(Q) \right]^2}$$
(S1)

In this equation, x_i and x_j represent the mole fraction of type *i* and *j* atoms, respectively. *Q* stands for the scattering vector, f(Q) is the form factor of atom species, $g_{ij}(r)$ is the correlation function between atoms of type *i* and *j*, ρ indicates the number density of system, and r_c corresponds to the integration cutoff, set to one-half of the simulation box length.

The total and partial structure factors (i.e., cation-cation, anion-anion, and cation-anion) of the investigated DIL were calculated to explore the specific contributions of local organization, as illustrated in Fig. S2. It is known that the size of the system significantly influences the behavior of structure factors at low Q values. This influence arises from the fact that the simulation's structure factor is directly derived from the RDF.^{S2} In AIMD simulations, due to their high computational cost, only a limited number of molecules can be simulated. As a result, the radial distribution function may not effectively capture long-range interactions, which makes the structural features nearly invisible at low Q values. As depicted in this figure, total and partial structure factors are almost similar regarding the position of peaks in both PBE and BLYP functionals, with and without D3 correction. On the other hand, it can be seen that applying the dispersion corrections in both density functionals results in a reduction in peak intensities. Hence, we can conclude that the inclusion of dispersion correction decreases the structural heterogeneity of the investigated DIL. Furthermore, it is clear that, whether with or without dispersion

corrections, the BLYP functional demonstrates lower structural heterogeneity compared to the PBE functional and simulating $[C_3(mim)_2][NTF_2]_2$ DIL with BLYP-D3 results in the lowest structural heterogeneity.



Fig. S2. Total structure factors of the $[C_3(mim)_2][NTF_2]_2$ DIL, and partial static structure factors contributed by cation-cation, anion-anion, and cation-anion correlations based on the BLYP and PBE density functionals with and without D3-correction at 333.15 K and 1 atm.



Fig. S3. Distance distribution of the oxygen atoms of the first 5 neighboring anion from the H_R atom of the cation based on the BLYP and PBE density functionals with and without D3-correction at 333.15 K and 1 atm.

Methods	t ^{Cation}	t ^{Anion}
BLYP-D3	0.618	0.382
BLYP	0.598	0.403
PBE-D3	0.386	0.614
PBE	0.348	0.653
Experiment	0.550	0.451

Table S1. Transference numbers for the studied DIL in the BLYP and PBE density functionals with and without D3-correction compared to the experimental results at 333.15 K and 1 atm.



Fig. S4. Self-part of van Hove correlation functions of cations and anions based on the BLYP and PBE density functionals with and without D3-correction at 333.15 K and 1 atm.

S.2. Velocity autocorrelation function (VACF)

Another approach to investigate the influence of applying dispersion correction in BLYP and PBE density functionals on the dynamics behavior of [C₃(mim)₂][NTF₂]₂ DIL, is the velocity autocorrelation function (VACF). This function provides valuable insights into the effects of the formed cage in simple liquids with high densities, in which, an ion becomes surrounded by a shell of other ions, and during the initial collision, its velocity reverses, resulting in negative values of the correlation function.^{S3-S6} We can access several aspects of the VACF shape: (a) The time when an ion collides with its nearest neighbor (in a very rough approximation when VACF= $1/e\approx 0.3678$, (t_{coll}) ; (b) The time when the VACF change from 0 to negative values (t_{rev}) ; (c) The time of the largest negative correlation (t_{min}); (d) The corresponding value of VACF at t_{min} (VACF(t_{min})). The VACFs and their characteristic values for the ions of the studied DIL are presented in Fig. S5 and Table S2 based on the BLYP and PBE density functionals, with and without D3 correction. It can be observed that, before the collision occurred, in both density functionals, in the absence of D3 correction, the anion exhibited faster dynamics than cation. This behavior leads to faster collision times for the anions than the corresponding cations. However, when the dispersion correction is applied, this trend reverses, and the cations demonstrate smaller collision times compared to the anions. In contrast, after the collision occurs, based on both density functionals, with and without D3 correction, the dynamics of cations are faster than those of the anions. This is evident in the reversion time (i.e., when VACF=0) in which the cation experiencing a shorter reversion time compared to the anion. Also, it is shown that the time of minima of cation occurs at earlier than the anion, and the depth of negative correlation in cations is greater than the anions. These behaviors may be attributed to the lower molar mass of the cation (206.29 g.mol⁻¹) compared to the anion (280.15 g.mol⁻¹), in such a way that the cations appear to be rattling within the cage of anions as it has been observed also in some previous studies. As explained by Hansen and McDonald, a large mass difference between the ions causes the strongly oscillatory VACF of the lighter ion which is known as the frequent back scattering and thus 'rattling' motion of the ion in a cage of counter-ions.^{S6}

Furthermore, it is observed that applying the dispersion correction decreases the depth of negative correlation for cations in BLYP and PBE density functionals by approximately 16% and 8%, respectively. In contrast, the depth of negative correlation for anions in both density functionals decreases by about 7%.



Fig. S5. Velocity autocorrelation functions of cations and anions based on the BLYP and PBE density functionals with and without D3-correction at 333.15 K and 1 atm.

Table S2. Characteristic values of the velocity autocorrelation function for the cations and anions. t_{coll} , t_{rev} , t_{min} , and VACF(t_{min}) are the collision time, reverse time, the time of the largest negative correlation and its corresponding VACF value, respectively.

Ions	Methods	t_{coll} / ps	t_{rev} / ps	t_{min} / ps	VACF(tmin)
Cation	BLYP-D3	98.5	147.0	233.5	-0.2388
	BLYP	103.5	151.0	249.7	-0.2862
	PBE-D3	104.5	155.0	239.0	-0.2364
	PBE	105.5	155.5	253.2	-0.2570
Anion	BLYP-D3	99.5	202.5	399.5	-0.1502
	BLYP	97.5	186.0	275.8	-0.1187
	PBE-D3	105.5	204.0	417.0	-0.1266
	PBE	101.0	195.5	330.6	-0.1368



Fig. S6. Comparison between IR spectra of the studied DIL in the presence and absence of D3-correction obtained based on the PBE density functional at 333.15 K and 1 atm.



Fig. S7. Power spectra of studied DIL obtained based on the PBE density functional with and without D3-correction in the range of 0-900 cm⁻¹, 900-1700 cm⁻¹ and 2800-3350 cm⁻¹ at 333.15 K and 1 atm.

References

- S1. O. Borodin, W. Gorecki, G. D. Smith and M. Armand, J. Phys. Chem. B 2010, 114, 6786-6798.
- S2. E. Perlt, P. Ray, A. Hansen, F. Malberg, S. Grimme and B. Kirchner, *J. Chem. Phys.*, 2018, 148, 193835.
- S3. J. Dymond and B. Alder, J. Chem. Phys., 1966, 45, 2061-2068.
- S4. B. Alder and T. Wainwright, Phys. Rev. Lett., 1967, 18, 988.
- S5. B. Alder and T. Wainwright, Phys. Rev. A 1970, 1, 18.

S6. J.-P. Hansen and I. R. McDonald, Theory of simple liquids: with applications to soft matter. Academic Press, New York, 2013.