Validation of Dispersion-Corrected Density Functional Theory Approaches for Ionic Liquid Systems

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The performance of several general gradient approximation, meta general gradient approximation, and hybrid functionals is tested against Møller−Plesset perturbation theory second-order for ionic liquid systems. Additionally, two dispersion-corrected approaches (addition of van der Waals forces by a $1/r^6$ term and employing a dispersion-corrected atom-center dispersion pseudopotential) were studied. For the 1-butyl-3-methylimidazolium cation neglecting dispersion results in different trends for structural stabilities. The two applied correction schemes for density functional theory improve the results tremendously. Investigating several 1-butyl-3-methylimidazolium dicianamide ion pairs shows a mean absolute deviation from Møller−Plesset perturbation theory of 35.7 kJ/mol for Hartree−Fock and up to 33.2 kJ/mol for the density functional theory methods. The dispersion-corrected methods reduce the mean absolute deviation to less than 10 kJ/mol. Comparing adducts of the 1-ethyl-3-methylimidazolium dicianamide ion pair with Diels−Alder educts (cyclopentadiene and methylacrylate) shows similar energetic differences as for the ion pairs. Furthermore large deviations in geometries for the intermolecular distances were found for the Hartree−Fock approach (mean absolute deviation: 190 pm) and density functional theory (mean absolute deviation up to 178 pm) while for the dispersion-corrected methods the mean absolute deviation is less than 50 pm.

1. Introduction

Ionic liquids (ILs) are salts with a melting temperature below 100 °C. Owing to their low vapor pressure and their tuneable properties, ILs have become a hot research area.[1−7] Most common ILs consist of inorganic anions and organic cations with alkyl side chains and aromatic systems. Thus, it can be expected that weak van der Waals interactions will play an important role. Recently, an investigation of our group has shown that weak London dispersion forces have an important impact on the equilibrium structure and the interaction energy of ionic liquids.[8] We found a flattening of the repulsive region of the interaction potential of ILs induced by dispersion and induction forces. Furthermore, the equilibrium distance is not exclusively determined by the most important attractive force, namely the electrostatic interaction. It is instead shifted to smaller distances, implying that the ions interact in the repulsive potential region regarding electrostatic forces only.[8] Ab initio correlated or so-called post-Hartree−Fock (HF) methods provide proper descriptions of dispersion forces but are computationally difficult for systems larger than tens of atoms. On the other hand, Kohn−Sham density functional theory (KS-DFT),[9,10] with computational cost much lower than that of conventional correlated methods, accounts for electrostatic, exchange, and induction forces very well but fails for the right description of dispersion forces.[11−13] Several possible solutions were proposed to correct this shortcoming of the KS-DFT approach.[14−31] The most simple introduction of van der Waals forces is by addition a $1/r^6$ term,[15,18,21,24,28,30] which was originally applied to correct the HF energy.[32] Furthermore, a dispersion correction can be included in a pseudopotential model.[19,23] Another approach named the weighted density approximation (WDA)[14] starts from the exact expression for the exchange correlation functional to obtain a WDA. An unknown pair-correlation function enters the expression which leads to an introduction of a weighted density parameter. It is also possible to include weak dispersion forces by making use of the correlation described by the MP2 methodology, as for example in the "range-separated-hybrid" scheme.[26,29]

Our investigations focus on the performance of the KS-DFT approach for ILs by common density functionals as well as two proposed approaches to improve the performance of KS-DFT without significantly increasing the computational effort. A low increased computational time seems to be necessary since a previous study has shown the importance of cooperativity and points out the importance of including a large number of ion pairs.[33] The first approach (DFT-D) includes the dispersion correction in the functional by a sum of damped interatomic potentials[28] while the second includes the correction in the electronic structure by a dispersion-corrected atom-center dispersion potential (DCACP).[23,34] Both approaches have shown an impressive performance for biomolecules compared to common functionals[35,36] and have been successfully employed in several investigations.[37−39]

After a short section describing the employed computational approaches, we present the results of the investigation for different conformers of the 1-butyl-3-methylimidazolium cation. This is followed by a discussion of cation−anion interaction. We proceed with an investigation of the IL-solute interaction for the educts of the Diels−Alder reaction. Finally, a short summary of the results end this article.

2. Computational Details

The programs provided by the Turbomole-suite[40] were applied for the non dispersion-corrected KS-DFT, Hartree−Fock (HF),

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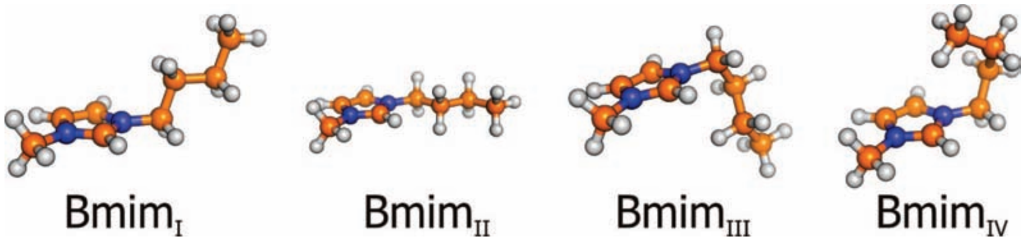

Figure 1. Investigated conformers of **Bmim**.

TABLE 1: Angular Momentum *l* and Pseudization Radii *r* in atomic units of the Local Potential for the Corresponding Elements and Functionals

	l_{BP86}	r_{BP86}	l_{PBE}	r_{PBE}	l_{BLYP}	r_{BLYP}
H	p	0.5000	p	0.3828	p	0.5000
C	d	0.7159	d	0.7159	d	0.7159
N	d	0.6031	d	0.6031	d	1.1200
O	d	1.1200	d	1.1200	p	see ref 34

and Møller−Plesset perturbation theory second-order (MP2) calculations while the ORCA program[41] was applied for calculations employing the dispersion correction proposed by Grimme (DFT-D[28]). To provide comparability the VWN-V LDA correlation, part of the functional was selected in both program packages. The TZVPP[42] basis set was used throughout and all energies were counterpoise corrected with the procedure of Boys and Bernardi[43] 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 calculations were applied in combination with the RI-technique[44,45] and the frozen core approximation. The frozen core orbitals were attributed by default settings of the rimp2prep tool which means all orbitals with an energy below 3.0 au were considered as core orbitals. Please note that HF does not consider van der Waals forces by definition, while MP2 describes dispersion forces very well. However, in some cases, MP2 fails to give the correct description of van der Waals forces; for example, it overestimates $\pi-\pi$ stacking. Nevertheless, the difference of the HF and the MP2 approach provides an estimation of the dispersion forces. Calculations employing the PBE,[46,47] PBE-D,[28,46,47] BLYP,[48,49] BLYP-D,[28,48,49] BP86,[48,50] BP86-D,[28,48,50] TPSS,[51] and TPSS-D[48,51] functionals were carried out with the resolution of identity approximation.[52−54] Furthermore, the performance of the B3LYP[48,49,55] and the PBE0[46,47,56] hybrid functional was investigated to determine the role of the exact Hartree−Fock exchange.

Calculations employing the dispersion-corrected approach proposed by Lilienfeld et. al[23] were carried out with the CPMD-program.[57] Kohn−Sham orbitals were expanded in a plane wave basis with a kinetic energy cutoff of 70 Ry. Norm conserving pseudopotentials of the Troullier−Martin type were taken with pseudization radii shown in Table 1.[34,58] Core−valence interaction of all atoms were treated by s-, p-, d, and f-potentials. The pseudopotentials were applied in the Kleinman−Bylander representation[59] with the angular momentum as a local potential shown in Table 1. The box length was set to 35.0 bohr in each calculation.

To the best of our knowledge, only three CCSD(T) calculations of ILs are reported in the literature.[60−62] Izgorodina et al. studied proton affinities of common IL anions and found a worse performance for common DFT functionals compared to the CCSD(T) reference.[61] Hunt and Gould used a double-ζ basis set for the interaction of 1-butyl-3-methylimidazolium chloride,[60] while Zhao et al. investigated 1,3-dimethylimidazolium chloride (MmimCl) with a sufficiently large basis set.[62] Zhao et al. found only small differences between MP2 and CCSD(T) energies. Furthermore, they stated that a triple-ζ basis set is sufficient to obtain equilibrium structures with MP2. CCSD(T) reference values can not be obtained for much larger systems than those investigated by Zhao et al. where only small deviations between MP2 and CCSD(T) were found. Thus we employed MP2(RI)/TZVPP as reference.

TABLE 2: Comparison of Different Approaches for the Relative Energy of Conformers of Bmim compared to $Bmim_I$[a]

	$Bmim_{II}$	**$Bmim_{III}$**	**$Bmim_{IV}$**	MAD
HF	3.4	1.7	13.2	5.7
BP86	2.6	1.1	10.6	4.4
PBE	2.3	0.6	9.4	3.9
BLYP	3.6	1.7	11.5	5.2
TPSS	2.3	1.4	10.9	4.7
B3LYP	3.0	1.3	11.1	4.8
PBE0	2.0	1.7	13.2	5.7
BP86-D	0.6	−2.7	1.4	0.9
PBE-D	1.1	−2.0	3.1	1.4
BLYP-D	1.5	−2.2	2.1	0.8
TPSS-D	0.4	−2.3	2.3	1.2
$BP86_{DCACP}$	2.4	−1.8	3.4	1.1
PBE_{DCACP}	2.4	−1.0	5.2	2.0
$BLYP_{DCACP}$	3.2	−1.1	4.2	1.7
MP2	2.6	−3.2	1.7	

[a] MAD is the mean absolute deviation. All values are given in kilojoules per mole.

TABLE 3: Comparison of the Dissociation Energy for Different Approaches of [Bmim][DCA][a]

	IL_I	IL_{II}	IL_{III}	IL_{IV}	IL_V	MAD
HF	321.1	317.8	315.2	313.5	317.4	35.7
BP86	331.0	329.2	323.9	321.1	327.2	26.2
PBE	340.8	339.3	331.9	331.3	338.3	16.4
BLYP	324.4	322.0	317.4	314.3	319.5	33.2
TPSS	332.0	330.0	326.4	321.4	328.1	25.1
B3LYP	329.8	327.4	323.2	319.8	325.5	27.6
PBE0	341.0	339.6	334.4	333.8	338.4	15.3
BP86-D	354.7	354.4	357.5	356.7	360.5	4.1
PBE-D	357.5	356.9	356.8	356.3	361.0	5.0
BLYP-D	350.5	350.1	353.4	351.6	357.0	1.6
TPSS-D	356.5	355.3	358.0	357.1	361.3	4.9
$BP86_{DCACP}$	353.2	355.5	350.6	349.6	355.8	4.4
PBE_{DCACP}	347.2	347.8	344.8	343.3	346.8	6.7
$BLYP_{DCACP}$	343.5	344.7	341.6	340.1	345.9	9.5
MP2	348.1	349.1	353.2	354.3	358.8	

[a] MAD is the mean absolute deviation. All values are in kilojoules per mole.

3. Results and Discussion

3.1. Conformers of the Cation. A recent study by Hunt attributed the increased melting temperature and viscosity of 1-butyl-2,3-dimethylimidazolium based ILs compared to 1-bu-

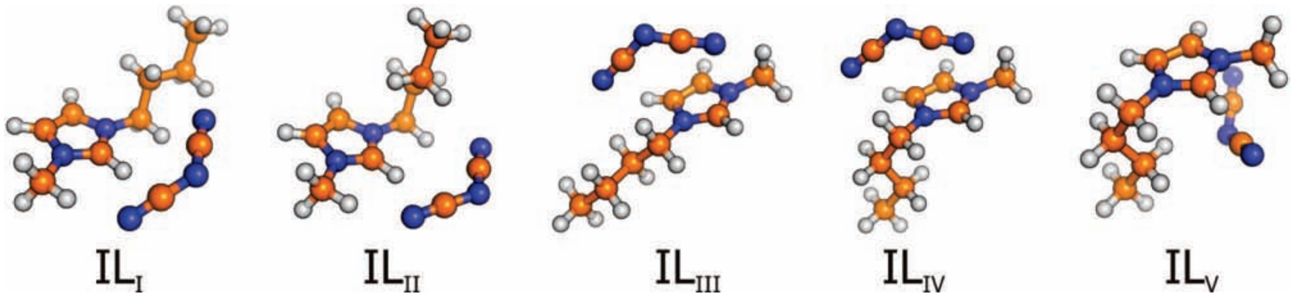

Figure 2. Investigated structures of the [**Bmim**][**DCA**] ion pair.

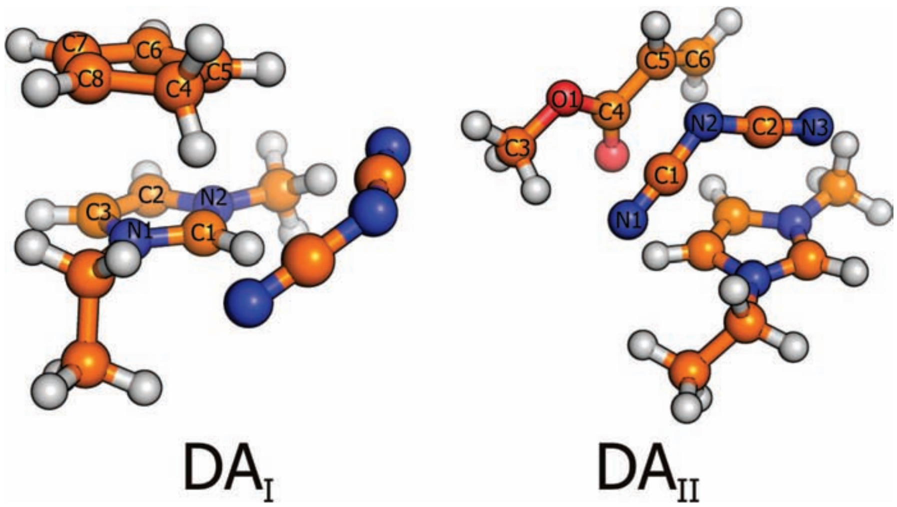

Figure 3. Investigated structures of the [Emim][DCA] ion pair with cyclopentadiene (**DA**$_I$) and methylacrylate (**DA**$_{II}$).

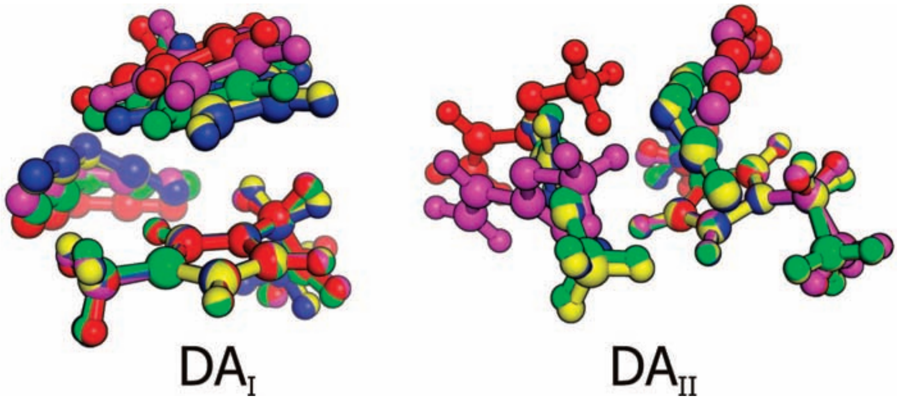

Figure 4. Comparison of the obtained geometries for **DA**$_I$ and **DA**$_{II}$ employing the HF (red), MP2 (blue), B3LYP (magenta), BLYP-D (yellow), and BP86$_{DCACP}$ (green) approaches.

tyl-3-methylimidazolium based ILs to the enhanced free rotation of the butyl-side-chain at the 1-butyl-3-methylimidazolium cation (**Bmim**).[63] The question arises how the consideration of weak dispersion forces affects the energy gap of different conformers. This was the starting point of our investigation.

For the studied structures (see Figure 1), we found a different energetic order for the MP2 compared to the HF approach; see Table 2. While in the MP2 approach the energy gap to **Bmim**$_I$ is for all conformers below 5 kJ/mol, it is increased to more than 10 kJ/mol for the HF approach. Furthermore the most stable structure is **Bmim**$_I$ for the HF approach instead of the most stable structure for MP2 **Bmim**$_{III}$. Similar results can be found for the nondispersion-corrected KS-DFT where the PBE functional shows the best performance of all functionals. Please note that including the exact Hartree−Fock exchange does not improve the accuracy of KS-DFT.

In contrast to this, introducing a corrected description to account for van der Waals forces by the DFT-D or the DCACP approach improves the performance of KS-DFT remarkably; see Table 2. The mean absolute deviation (MAD) is decreased below 2 kJ/mol and **Bmim**$_{III}$ is determined as the most stable structure. The best performance of the two approaches provides the BLYD-D and the BP86$_{DCACP}$, respectively. Since dispersion forces have a significant impact upon the energy gap between different conformers, it can be recommended to include van der Waals forces by the DFT-D or the DCACP method in further theoretical investigations.

3.2. Cation−Anion Interaction. Experimental values of cation−anion interactions are nearly inaccessibly. Recently, Emel'yanenko et al. determined the enthalpy of formation for 1-butyl-3-methylimidazolium dicianamide ([**Bmim**][**DCA**]) and compared it to calculated values.[64] They found an excellent

TABLE 4: Comparison of Different Approaches for the Adiabatic Interaction Energy of a [Emim][DCA] Ion Pair with Cyclopentadiene (DA$_{\text{I}}$) and Methylacrylate (DA$_{\text{II}}$)[a]

	DA$_{\text{I}}$	**DA$_{\text{II}}$**	MAD
HF	−8.9	− 28.5	24.6
BP86	−6.6	−22.2	28.9
PBE	−16.6	−31.3	19.3
BLYP	−5.7	−23.0	28.9
TPSS	−10.2	−25.2	25.4
B3LYP	− 9.0	−23.7	26.9
PBE0	−16.4	−27.1	21.5
BP86-D	−46.6	−39.8	1.2
PBE-D	−42.9	−40.6	1.5
BLYP-D	−43.2	−40.1	1.6
TPSS-D	−47.0	−42.1	1.3
BP86$_{\text{DCACP}}$	−46.6	−47.2	3.7
PBE$_{\text{DCACP}}$	−34.3	−33.2	9.5
BLYP$_{\text{DCACP}}$	−40.3	−37.7	4.3
MP2	−45.5	−41.0	

[a] MAD is the mean absolute deviation. All values are in kilojoules per mole.

TABLE 5: Comparison of Different Approaches for Intermolecular Distances *r* of an [Emim][DCA] Ion Pair with an Educt of the Diels−Alder Reaction[a]

	BP86	PBE	BLYP	TPSS	B3LYP	PBE0	HF	MP2
				DA$_{\text{I}}$				
$r_{\text{C1−C4}}$	413	402	434	426	416	394	428	346
$r_{\text{N2−C5}}$	401	384	417	411	400	379	420	331
$r_{\text{C2−C6}}$	415	391	435	427	413	387	449	329
$r_{\text{C3−C7}}$	431	409	459	448	432	402	467	336
$r_{\text{N1−C8}}$	428	414	457	444	431	405	451	346
				DA$_{\text{II}}$				
$r_{\text{N1−C3}}$	353	351	359	353	354	351	361	338
$r_{\text{C1−O1}}$	492	492	504	480	515	504	511	321
$r_{\text{N2−C4}}$	597	578	608	581	630	618	607	319
$r_{\text{C2−C5}}$	701	683	715	672	748	730	758	335
$r_{\text{N3−C6}}$	779	742	791	746	828	810	844	397
MAD	161	145	178	159	177	158	190	

[a] MAD is the mean absolute deviation. All values are in picometers.

TABLE 6: Comparison of Different Approaches for Intermolecular Distances *r* of an [Emim][DCA] Ion Pair with an Educt of the Diels−Alder Reaction[a]

	BP86-D	PBE-D	BLYP-D	TPSS-D	BP86$_{\text{DCACP}}$	PBE$_{\text{DCACP}}$	BLYP$_{\text{DCACP}}$
				DA$_{\text{I}}$			
$r_{\text{C1−C4}}$	339	351	350	338	363	365	374
$r_{\text{N2−C5}}$	327	338	338	326	356	359	368
$r_{\text{C2−C6}}$	328	339	340	327	363	367	373
$r_{\text{C3−C7}}$	335	348	348	334	367	372	374
$r_{\text{N1−C8}}$	341	355	353	340	366	369	373
				DA$_{\text{II}}$			
$r_{\text{N1−C3}}$	334	337	339	334	337	344	338
$r_{\text{C1−O1}}$	319	327	325	322	328	335	333
$r_{\text{N2−C4}}$	326	339	330	335	349	335	357
$r_{\text{C2−C5}}$	332	345	342	337	350	351	388
$r_{\text{N3−C6}}$	381	395	398	389	405	409	478
MAD	5	8	7	5	19	21	36

[a] MAD is the mean absolute deviation. All values are in picometers.

agreement between experimental (363.4 ± 2.7 kJ/mol) and calculated results employing the G3MP2 method (359.6 kJ/mol), while the B3LYP functional (345.5 kJ/mol) underestimates the enthalpy of formation. These results indicate that dispersion forces should be treated in investigations of ILs. In a recent study of our group, we found a non-negligible impact of dispersion forces upon equilibrium structure and interaction energy for 1,3-dimethylimidazolium chloride.[8] In molecular dynamics simulations, a correct potential energy surface is necessary to obtain reliable results. Although, *first-principle* molecular dynamics (FPMD) simulations are necessary for ILs because induction forces should not be neglected, FPMD simulations are limited to the KS-DFT approach due to the size of the systems. Since KS-DFT suffers from a description of van der Waals forces, the dispersion correction of Grimme[28] or Lilienfeld[23] might be an efficient correction for this problem.

To investigate this, we determine the dissociation energy of [**Bmim**][**DCA**] for the structures shown in Figure 2. The HF approach underestimates the dissociation energy on average by more than 10% indicating out the importance of dispersion forces in ILs; see Table 3. Only a slight improvement is achieved in KS-DFT for the most common functionals. While the popular B3LYP-functional is nearly the worst case, a large improvement compared to the HF theory can be obtained employing the PBE or PBE0 functional. However, the mean absolute deviation for the PBE and PBE0 functional is still more than 15 kJ/mol. Furthermore for all functionals, **IL$_{\text{I}}$** is the most stable structure instead of the MP2 favored **IL$_{\text{V}}$**. The most stable structure is determined properly for all dispersion corrected approaches except for the PBE$_{\text{DCACP}}$ case. While BLYP-D outnumbers all other proven approaches with a MAD of only 1.6 kJ/mol, also the performance of BP86$_{\text{DCACP}}$ is remarkable. Both dispersion corrected approaches are therefore an option to consider dispersion forces in FPMD simulations of an IL with only slight increased computational time.

3.3. Ionic Liquid−Solute Interaction. The importance of ILs is highly reflected in their large applications for synthesis and catalysis.[5] A reliable study of the unique solvent−solute interactions needs a proper description of the participating forces. Diels−Alder reactions in ILs were investigated by several computational and experimental methods, because this reaction shows an unexpected high selectivity in ILs.[65−71] Hence, we studied the interaction of 1-ethyl-3-methylimidazolium dicianamide ([Emim][DCA]) with two educts of a Diels−Alder reaction, cyclopentadiene and methylacrylate. Furthermore both compounds represent typical organic reactants. While cyclopentadiene is a typical compound for π stacking, methylacrylate is able to form hydrogen bonds with the IL.

In our investigated structures, see Figure 3, the van der Waals forces have a high contribution to the relaxed interaction energy. The interaction energy is reduced by 80% for **DA$_{\text{I}}$** employing HF instead of MP2; see Table 4. For **DA$_{\text{II}}$**, the HF energy is decreased "only" by 30% compared to the MP2 value but the difference of the obtained equilibrium structures is impressive; see Table 5 and Figure 4. Please note that, for **DA$_{\text{II}}$**, the start structure for the optimization runs was always the structure obtained by the MP2 approach. A similar structural deviation to the MP2 geometry is obtained for all nondispersion corrected approaches. In opposite, the geometries of the dispersion corrected KS-DFT approaches agree very well with the MP2 reference; see Table 6 and Figure 4. Furthermore, the mean deviation of the obtained energies is quite small for the DFT-D method; see Table 4. BP86$_{\text{DCACP}}$ and BLYP$_{\text{DCACP}}$ are good alternatives, while PBE$_{\text{DCACP}}$ cannot be recommended. The large structural and energetic differences indicate that dispersion forces are much more important for the solute−solvent interaction of ILs than one might expect for a salt.

4. Summary and Conclusion

The focus of this work was the performance of common functionals, the DFT-D[28] and DCACP[23] approach for ionic liquids. The results for the energy gap of different **Bmim** conformers, the [**Bmim**][**DCA**] dissociation energy, and the IL−solute interaction emphasize the importance of weak dispersion forces in ILs. In all cases, the common general gradient approximation (GGA), meta general gradient approximation (mGGA), and hybrid functionals fail to correctly describe the interaction energies (MAD_{BP86} 20.2 kJ/mol; MAD_{PBE} 13.2 kJ/mol; MAD_{BLYP} 23.9 kJ/mol; MAD_{TPSS} 19.0 kJ/mol; MAD_{B3LYP} 20.6 kJ/mol; MAD_{PBE0} 13.2 kJ/mol). The improvement of the results by introducing the exact Hartree−Fock exchange in the hybrid functionals is marginal compared to the corresponding GGA functionals. We found that the popular B3LYP functional seems to be nearly the worst choice supporting the proposed "size inconsistency" of B3LYP by Grimme.[72] The PBE and PBE0 functional differ least from the reference values. However, only employing a dispersion correction reduces the deviations to the reference values to a passable amount ($MAD_{BP86\text{-}D}$ 2.6 kJ/mol; $MAD_{PBE\text{-}D}$ 3.2 kJ/mol; $MAD_{BLYP\text{-}D}$ 1.4 kJ/mol; $MAD_{TPSS\text{-}D}$ 3.1 kJ/mol; $MAD_{BP86_{DCACP}}$ 3.3 kJ/mol; $MAD_{PBE_{DCACP}}$ 5.9 kJ/mol; $MAD_{BLYP_{DCACP}}$ 6.1 kJ/mol). The BLYP-D and $BP86_{DCACP}$ method are the best choices for the improved KS-DFT approaches, respectively. Since HF theory does not consider dispersion forces by definition, the large structural (MAD_{HF} 190 pm) and energetic differences (MAD_{HF} 24.5 kJ/mol) compared to the MP2 values again indicate the importance of the dispersion forces in ILs. A recent investigation has already shown the role of these forces in the depression of the melting temperature.[8] The large impact of dispersion forces in our selected solute−solvent examples, the observed microheterogeneity[73−77] and $\pi-\pi$ stacking[78−80] of the cations in previous investigations imply that van der Waals forces might play an essential role in the unique solvent properties of ILs.

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