Ion-Pair Binding Energies of Ionic Liquids: Can DFT Compete with Ab Initio-Based Methods?

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In this work, we examine the performance of a range of local and hybrid DFT functionals (including BLYP, PBE, PW91, B3P86, B3LYP, and TPSS), new generation DFT functionals (including KMLYP, BMK, M05, and M05−2X), and DFT functionals with the explicit empirical correction for dispersion interactions (including BLYP-D, PBE-D, and B3P86-D) in calculating ion-pair binding energies of pyrrolidinium-based ionic liquids, $[C_n\text{mpyr}][X]$ (n = Me, Et, n-Pr and n-Bu and X = Cl, BF_4, PF_6, CH_3SO_3 (mesylate), CH_3PhSO_3 (tosylate), $N(CN)_2$, and NTf_2). Calculated IPBEs were compared to the results of the selected benchmark method, MP2/6-311+G(3df,2p). Modified MP2 methods such as SCS-MP2 and SOS-MP2 were also considered in the study. Errors of the DFT-based and ab initio-based methods in calculations of IPBEs of ionic liquids, trends in relative IPBEs, and basis-set superposition errors are discussed in depth. DFT functionals that can potentially be used to study binding energies of ionic liquids are identified.

Introduction

Ionic liquids have become a subject of extensive computational studies, especially using the molecular dynamics approach. Because of continuing increases in computer power, the use of ab initio-based and DFT-based quantum chemical methods have become attractive over the past decade in studying energetics of ionic liquids (ILs) from first principles. Ionic liquids − liquids that consist entirely of ions − are an interesting class of organic salts that exhibit a nonspecific type of interactions, that is Coulombic (electrostatic) interactions: both long-range attraction between positively and negatively charged ions and repulsion between ions of the same charge. Hence, ionic liquids form a network of long-range interactions, of which the interaction of each ion and its closest counterion represents the essential building blocks. Although ion pairs as long-lived individual species are less likely to exist (with exception for some cases[1]), an understanding of what intermolecular interactions contribute to the ion-pair binding energies, even at very short time scales, and what quantum chemical methods can be reliably used to describe them, is an essential first step toward understanding the energetics of ionic liquids as a bulk phase. Such an understanding will in turn provide guidance to two developing theoretical approaches in understanding the bulk properties of ionic liquids: large-scale calculations containing multiple ion pairs on one hand and ab initio MD simulations on the other (in the latter, DFT functionals are typically used as an ab initio method of choice). One of the goals of the present work is to investigate which ab initio methods provide the best picture of interactions at the ion-pair level, such that these large scale and MD calculations can be best supported.

Although ionic liquids consist entirely of ions, additional specific noncovalent interactions are still present, that is dispersion interactions due to electron correlation like van der Waals interactions between alkyl chains on cations, $\pi-\pi$ stacking interactions between cations/anions (depending on their chemical structure), and hydrogen bonding between polar groups. Although in hydrogen bonding the contribution from the Coulombic attraction dominates the binding energy in ionic systems, the energy contribution due to electron correlation cannot be neglected.[2] Further in the text, when we refer to hydrogen bonding as a dispersion interaction, we mean the energy component to the overall binding energy arising from electron correlation effects. The accurate description of weak noncovalent interactions requires a correlated level of theory (at least a second-order perturbation theory method, MP2), and, therefore, the choice of the computational method is very crucial in the accurate prediction of energetics in these organic ionic liquids.

DFT is always a cheaper (i.e., computationally inexpensive) alternative to ab initio-based methods because it has the same scaling with molecular system size as the Hartree−Fock method. Here, we refer to ab initio methods as those that are based on the wave function notation. Although DFT has been well accepted as an excellent computational approach for geometry optimizations, it is still an open question whether DFT can fare well when it comes to calculating thermodynamic properties such as binding energies, reaction enthalpies, kinetics, and bond dissociation energies. There have been a number of studies in which various DFT functionals were put to the test in studying noncovalent interactions occurring in aromatic systems, DNA base pairs, carboxylic acids, water clusters, and so forth.[3–10] Although local and hybrid DFT functionals failed to produce reasonable accuracy, with errors over 20 kJ mol^{-1} for some molecular interactions,[4,9] a new generation of DFT functionals like BMK, the M05/M06 family, functionals with explicit inclusion of dispersion forces (DFT-D), and double-hybrid functionals showed substantially improved accuracy,[4,8,11,12] especially for weak noncovalent interactions.

The use of DFT methods for studying ion-pair binding energies in ionic liquids has never been explored in depth. Because of the molecular size of ionic liquid ions, low-level ab initio methods in combination with relatively small basis sets[13] are typically used to study the intermolecular interactions occurring in ionic liquids. Tsuzuki et al.[14,15] applied the MP2 method in combination with a variety of basis sets to understand

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the magnitude and directionality of intermolecular interactions and the importance of hydrogen bonding in imidazolium-based ionic liquids. The authors showed that MP2/6-311G* produced interactions energies within 1 kcal mol^{-1} accuracy as compared to those of CCSD(T)/6-311G* for the minimum energy ion pair of 1-ethyl-3-methyl imidazolium BF$_4$. Although the electrostatic contribution was found to dominate the interaction energies, the contribution of induction is not negligible (from 34 to 50 kJ mol^{-1} for imidazolium-based ILs). Turner et al.[16] used HF and MP2 methods in combination with double-ζ quality basis sets to explore possible ion-pair conformations in 1-alkyl-3-methyl-imidazolium halides and calculate corresponding ion-pair interaction energies. In this study, the authors showed that the inability of the HF method to account for electron correlation effects results in a failure to reliably predict trends in interactions energies as compared to MP2/6-31+G*. A widely used hybrid functional, B3LYP, is generally used on its own to understand trends in thermodynamic properties of ionic liquids.[17,18] Publications where a comparison between DFT-based and ab initio-based methods as pursued are scarce. For example, in the paper by Hunt et al.[19] a comparison between the results of the hybrid B3LYP functional and standard MP2 using the TZVPP basis set was performed for four possible conformations of the dimethyl−imidazolium chloride ion pair. Compared to MP2, B3LYP showed an opposite trend in the stability of these conformations. Obviously, some precautions must be taken when applying DFT functionals to studying intermolecular interactions in ionic liquids. Hence, a more systematic study on the comparison of DFT-based and ab initio-based methods is needed to identify the best methods.

Because it is well-known that many DFT functionals lack a proper descritption of dispersion interactions, the main goal of this work was to put several DFT functionals to the test. To understand what methods among a hierarchy of DFT-based methods can be used in calculations of interaction energies of ionic liquids, we conducted an extensive study of binding energies of single ion pairs consisting of the cations and anions routinely used in ionic liquids. Pyrrolidinium-based cations in combination with a number of ionic liquid anions of different size, symmetry, and shape such as Cl, BF$_4$, PF$_6$, CH$_3$SO$_3$ (mesylate), CH$_3$PhSO$_3$ (tosylate), N(CN)$_2$ (dca), and NTf$_2$ were chosen as a test set. In addition to structural differences, the selected anions exhibit a varying degree of charge delocalization according to the proton affinity criterion[20] and are likely to form multiple hydrogen bonds with the pyrrolidinium cations due to the presence of the electronegative atoms such as F, Cl, N, and O. Pyrrolidinium cations (C$_n$mpyr, n = Me, Et, n-Pr, and n-Bu) provide two possible sites for the formation of hydrogen bonds with the hydrogens of either the alkyl chain or the pyrrolidinium ring. Although the predominant contribution to the binding energy of ionic liquids is the Coulombic (electrostatic) interaction[14] that dominates the HF energy, the dispersion component of the binding energy originating from electron correlation effects in hydrogen bonding and van der Waals interactions cannot be neglected. In addition, inclusion of electron correlation in ab initio calculations may result in a slight reduction of Coulombic interactions in hydrogen-bonded systems due to improved treatment of the charge distribution.[2] Therefore, the designed test set serves as an excellent example for testing reliability of DFT-based methods with respect to hydrogen-bonding interactions occurring in ionic liquids between cations and anions. Other possible interactions such as $\pi-\pi$ stacking interactions between anions like tosylate (CH$_3$PhSO$_3$) and van

der Waals interactions between the alkyl chains on the cation are not considered here.

In this work, we examine the performance of a range of local and hybrid DFT functionals (including BLYP, PBE, PW91, B3P86, B3LYP, and TPSS), new generation DFT functionals (including KMLYP, BMK, M05, and M05−2X), and DFT functionals with the explicit empirical correction for dispersion interactions (including BLYP-D, PBE-D, and B3P86-D) in calculating ion-pair binding energies (IPBEs) of pyrrolidinium-based ionic liquids, [C$_n$mpyr][X] (n = Me, Et, n-Pr, and n-Bu and X = Cl, BF$_4$, PF$_6$, CH$_3$SO$_3$ (mesylate), CH$_3$PhSO$_3$ (tosylate), N(CN)$_2$, and NTf$_2$). Apart from the DFT-based methods, modified MP2 methods such as SCS-MP2 and SOS-MP2 were also included in the study. Theoretical IPBEs were compared to the results of the selected benchmark method, MP2/6-311+G(3df,2p) (for the choice of the benchmark method and the basis set, see Results and Discussion). In the article, we discuss errors of the DFT-based methods and modified MP2 methods in calculations of IPBEs of ionic liquids, trends in *relative* IPBEs, and basis-set superposition errors. We identify DFT functionals with the least deviation from the benchmark method that can potentially be employed to accurately calculate energetics of ionic liquids.

Theoretical Procedures

Standard ab initio molecular orbital theory and DFT calculations were carried out using the *Gaussian 03* and *ADF 2007* sets of programs. All geometry optimizations were performed at the B3LYP/6-31+G(d) level of theory. Individual cations and anions were fully conformationally screened at this level of theory to ensure that the global (rather than merely local) minima were obtained. The screening was achieved by exploring all conformations arising from the rotations around chemical bonds. The conformation of the lowest energy was selected as the global minimum. The screening of the pyrrolidinium cations, C$_n$mpyr, with the chain length increasing from Me to Bu showed that the alkyl chain preferred to adopt a linear arrangement in the case of the propyl and butyl chains. This finding is in good agreement with crystal structures resolved for some of the studied ionic liquids like [C$_4$mpyr][NTf$_2$][21,22] and [C$_3$mpyr][Cl].[23] Therefore, further in the text we refer to the C$_n$mpyr cations with n = Me, Et, n-Pr, and n-Bu.

For the optimizations of the ion pairs, the individual ions in their lowest-energy conformation were used as a starting point. Two configurations for ion pairs of pyrrolidinium-based salts were considered, abrreviated here as conf1 and conf2 as shown in Figure 1. In both conformations, the cation and anion interact with one another electrostatically as well as through hydrogen bonding that is expected to have a larger contribution to the binding energy for the side conformation, conf2. The conf1 configuration, in which the anion interacts with the cation from below of the pyrrolidinium ring, was found to be the global minimum for most of the anions studied, with one exception for the dca anion. In the latter, the side conformation was found to be of the lowest energy. The side position (conf2) of the anion interacting with the cation was intentionally selected to probe the performance of DFT-based methods for treating the dispersion component of the hydrogen bonding due to electron correlation between the anion and the hydrogen atoms of the pyrrolidinium ring and the alkyl chain. In the case of the NTf$_2$ anion for each position (conf1 and conf2), there are two possible interaciton modes: 1) monodentate, conf1-N, and conf2-N, in which NTf$_2$ interacitons with the cation through the nitrogen and 2) bidentate, conf1-O and conf2-O, in which two oxygens
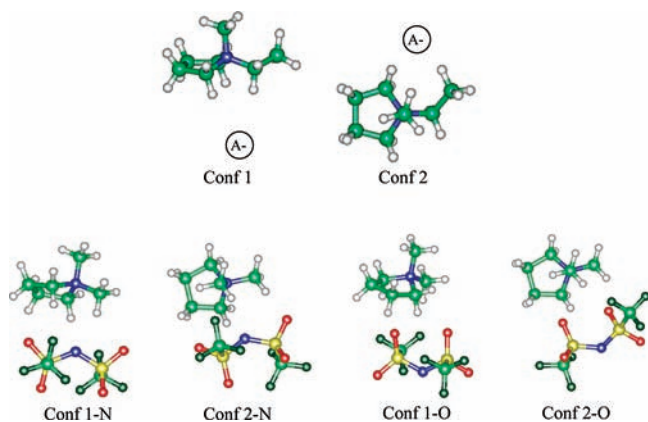
Figure 1. Ion-pair conformations of [$C_n$mpyr][X] considered in this work.

on NTf_2 form a noncovalent bond with the $C_n$mpyr caiton (for more detail see Figure 1). The optimized geometries of all of the species studied here are given in the Supporting Information in the form of the Gaussian archive files (Table S1 of the Supporting Information).

To avoid a basis-set superposition error (BSSE) ion-pair binding energies (IPBEs) were counter-poise corrected using a standard approach by Boys and Bernardi.[24] The final expression for the IPBE was as follows:

$$\text{IPBE} = E^{CP}(C\cdots A) - E_{min}(C) - E_{min}(A) + \Delta\text{ZPVE} \quad (1)$$

where $E^{CP}(CA)$ is the counter-poise corrected electronic energy of the ion pair and $E_{min}(C)$ and $E_{min}(A)$ are the electronic energies of the cation and the anion in their minimum-energy geometries. Zero-point vibrational energies were calculated using scaled B3LYP/6-31+G(d) vibrational frequencies.[25]

It is known in the literature that the counter-poise correction by Boys and Bernardi tends to overestimate the BSSE effect,[26] which is expected to be larger for ab initio-based methods compared to DFT-based ones. Because the IPBE calculations were carried out in the same manner in this work using both ab initio-based and DFT-based methods, the magnitude of the basis superposition error does not affect the trends in *relative* IPBEs found in this work.

Various DFT functionals were employed to test their applicability to studying binding energies of ionic liquids. The selected functionals included: 1) local functionals, BLYP, PW91,[27] and PBE;[28] 2) hybrid functionals, B3P86, B3LYP, TPSS,[7] and KMLYP;[29] and 3) hybrid meta-GGA functionals, BMK,[11] M05, and M05−2X[8] (for more detail on the exchange and correlation components of these functionals, see a recent review by Sousa et al.[30]). The recent M05 family of functionals is of particular interest, as they appear to overcome certain limitations inherent to other DFT functionals, especially for interaction energies in molecular systems with the noncovalent type of bonding (for more detail see refs 8, 9) DFT ion-pair binding energies were calculated using the 6-311+G(3df,2p) basis set.

In addition to the mentioned set of functionals, DFT-D functionals like BLYP-D, PBE-D, and B3LYP-D were used to probe the effect of the direct inclusion of the empirical dispersion interaction term into the total Kohn−Sham electronic energy:[5]

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} =$$
$$E_{KS-DFT} - S_6 \sum_i \sum_j \frac{C_6^{ij}}{R_{ij}^6} f_{dump}(R_{ij}) \quad (2)$$

The inclusion of dispersion forces (the last term in equation) was shown to improve results for $\pi-\pi$ stacking interactions[5,31] and hydrogen-bonded DNA base pairs.[3,6,32] No counter-poise correction was considered in these calculations (for more detail, see the text below). Because the ADF package utilizes exclusively Slater-type basis functions, a built-in triple-ζ quality doubly polarized basis set, TZ2P, was used instead of 6-311+G(3df,2p).

In this study, we decided to avoid the use of double-hybrid DFT functionals that contain the PT2 correction based on the MP2-like perturbative correlation energy:[4,12,33]

$$E_C^{PT2} = \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} \frac{|(ij||ab)|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (3)$$

Although the originally proposed double-hybrid functional was used HF orbitals in eq 3, recent modifications[4,12,33] of the double-hybrid approach employ self-consistent Kohn−Sham orbitals and the corresponding eigenvalues to compute the E^{PT2} correction, thus presenting an issue of omission of singly excited configurations that no longer obey Brillouin's theorem in the case of the Kohn−Sham formalism. Although double-hybrid DFT functionals seem to produce results of good accuracy for noncovalent bonding, they are not yet readily available in the *Gaussian* package. For this reason, double-hybrid DFT functionals were not employed in this work.

Modified versions of MP2 such as spin-component scaled MP2 (SCS-MP2)[34] and scaled opposite spin (SOS-MP2)[35] containing empirical scaling factors in the MP2 correlation energy showed improved accuracy for a number of molecular properties, including molecular interaction energies. For a number of molecular systems exhibiting different type of noncovalent bonding the standard MP2 method seems to outperform SCS-MP2 and SOS-MP2.[4] In this work, both SCS-MP2 and SOS-MP2 were used to explore their performance for studying binding energies of ionic liquid ion pairs and to identify any outstanding cases, for which the deviations from the standard MP2 are outside the expected range of 1−3 kcal mol^{-1}.

Methods of coupled cluster theory like CCSD(T) require at least a triple-ζ quality basis set to produce accurate results for interaction energies and are considered benchmark methods in combination with a complete basis set.[36] Application of coupled cluster theory is limited to only small- and medium-sized molecular systems because of their scaling as N^7 where N is the number of basis functions reflecting the molecular size (also known as the bottle neck of correlated methods). Most of the ionic liquids studied here contain over 12 non-hydrogen atoms, which makes the application of CCSD(T) computationally very demanding and less feasible. Linear scaling local coupled cluster theory introduced by Werner et al.[37,38] could potentially be used instead of conventional computationally demanding coupled cluster methods for studying short-range interactions of ionic liquids. Up to now, MP2 is still a cheaper alternative to high-level correlated methods and is the best ab initio method (optimal ratio of computational cost vs accuracy) to study noncovalent bonding interactions, outperforming many DFT-based methods.[4,9,12] Tsuzuki et al.[14] showed that, in fact, MP2

TABLE 1: IPBEs (in kJ mol^{-1}) Calculated at HF and MP2 with the aug-cc-pVTZ Basis Set, Deviations of IPBEs (ΔIPBE, kJ mol^{-1}) Calculated Using the 6-311+G(3df,2p) Basis Set with Respect to the aug-cc-pVTZ Basis Set at Two Levels of Theory, HF and MP2; Basis Set Superposition Errors (BSSE, kJ mol^{-1}) of IPBEs Calculated at MP2 Level of Theory Using Two Basis Sets, 6-311+G(3df,2p) and aug-cc-pVTZ

ion pair	IPBE (HF)	IPBE (MP2)	ΔIPBE		BSSE	
			HF	MP2	aug-cc-pVTZ	6-311+G(3df,2p)
[C$_1$mpyr][Cl], conf1	-359.2	-398.4	1.2	5.6	7.1	8.2
[C$_2$mpyr][Cl], conf1	-354.4	-394.2	1.1	5.4	7.2	8.7
[C$_3$mpyr][Cl], conf1	-352.6	-392.8	1.1	5.2	7.6	9.0
[C$_1$mpyr][BF$_4$], conf1	-330.4	-359.4	-0.8	1.7	9.8	11.5
[C$_2$mpyr][BF$_4$], conf1	-326.8	-356.4	-0.7	1.8	10.4	12.1
[C$_1$mpyr][PF$_6$], conf1	-304.9	-334.1	-1.4	1.2	11.8	11.3
[C$_2$mpyr][PF$_6$], conf1	-299.1	-329.1	-1.1	1.5	12.1	12.0
[C$_1$mpyr][mes], conf1	-356.8	-392.8	0.3	3.5	10.3	12.1
[C$_2$mpyr][mes], conf1	-352.1	-389.4	0.3	3.8	11.0	12.8
[C$_1$mpyr][dca], conf1	-306.5	-346.2	0.1	3.1	6.4	6.0
[C$_2$mpyr][dca], conf1	-302.0	-341.8	0.1	3.1	6.8	6.3
[C$_1$mpyr][NTf$_2$], conf1-N	-283.3	-326.6	0.2	2.6	14.6	14.5
[C$_1$mpyr][NTf$_2$], conf1-O	-288.7	-319.6	0.0	2.0	12.9	13.6
[C$_1$mpyr][Cl], conf2	-354.9	-393.1	1.0	5.3	6.8	7.8
[C$_2$mpyr][Cl], conf2	-339.6	-378.4	0.9	5.0	7.2	8.3
[C$_3$mpyr][Cl], conf2	-336.6	-375.6	0.9	4.9	7.2	8.7
[C$_1$mpyr][BF$_4$], conf2	-325.7	-352.6	-1.0	1.2	9.3	10.4
[C$_2$mpyr][BF$_4$], conf2	-314.5	-343.3	-0.5	1.8	9.6	11.2
[C$_1$mpyr][PF$_6$], conf2	-300.7	-328.0	-1.7	0.7	11.0	10.2
[C$_2$mpyr][PF$_6$], conf2	-290.5	-319.1	-1.1	1.3	11.4	11.0
[C$_1$mpyr][mes], conf2	-349.0	-381.0	0.4	3.4	9.4	10.8
[C$_2$mpyr][mes], conf2	-339.4	-375.1	0.4	3.5	10.2	11.7
[C$_1$mpyr][dca], conf2	-307.9	-351.2	0.3	3.5	6.7	6.3
[C$_2$mpyr][dca], conf2	-300.9	-343.8	0.2	3.4	6.8	6.1
[C$_1$mpyr][NTf$_2$], conf2-N	-280.7	-322.6	0.4	2.8	14.3	14.3
[C$_1$mpyr][NTf$_2$], conf2-O	-289.0	-321.6	-0.1	2.0	12.9	13.6
MAD			**0.7**	**3.1**	**9.6**	**10.3**

gives intermolecular interactions in ionic liquids of CCSD(T) accuracy. Because quadruple-ζ quality basis sets are exceptionally expensive to use in studying energetics of ionic liquids consisting of more than 25 non-hydrogen atoms, in this work ion-pair binding energies were calculated at the MP2 level of theory using two triple-ζ basis sets: 6-311+G(3df,2p) and aug-cc-pVTZ with a view to examining the effect of basis set and basis-set superposition error. Because of a small deviation between the two basis sets within the 1 kcal mol^{-1} accuracy, the MP2/6-311+G(3df,2p) method (computationally less demanding than MP2/aug-cc-pVTZ) was chosen as the benchmark method, to which all DFT, SCS-MP2, and SOS-MP2 results on IPBEs were compared.

Results and Discussion

Ion-Pair Binding Energies: Basis Set Effect. A comparison of IPBEs calculated using the Pople 6-311+G(3d,2p) basis set with respect to the correlated consistent aug-cc-pVTZ basis set at two levels of theory, HF and MP2, is given in Table 1. Basis-set superposition errors calculated for both basis sets at the MP2 level are also presented in Table 1. Because the aug-cc-pVTZ basis set contains a large number of basis functions, only C$_1$mpyr- and C$_2$mpyr-based ion pairs were considered in these calculations, with the only exception being the [C$_3$mpyr][Cl] ion pair. For the same reason, tosylate-based ion pairs and [C$_2$mpyr][NTf$_2$] were omitted in this part of the study.

Analysis of the results in Table 1 shows that for all ion pairs the HF method converges already with the 6-311+G(3df,2p), with a slight deviation from HF/aug-cc-pVTZ by 0.7 kJ mol^{-1} on average. At the MP2 level of theory, the deviation between the two basis sets is slightly larger but still rather small, only 3.1 kJ mol^{-1} on average, which is within chemical accuracy of

1 kcal mol^{-1}. Certainly, the basis set is of importance for ionic liquids due to the presence of hydrogen bonding.[15,18] The findings so far indicate that already the 6-311+G(3df,2p) basis set is enough to capture the effect of dispersion interactions in ionic liquids. For most of the anions studied here, 6-311+G(3df,2p) gives results of better than 3.5 kJ mol^{-1} accuracy. The only exception is the Cl-based ion pairs, for which the error rises to about 5.5 kJ mol^{-1}, still close to chemical accuracy. To this end, MP2/6-311+G(3df,2p) can be considered to be a reliable method for studying interactions in ionic liquids, quantitatively as well as qualitatively. Therefore, this method was chosen as the benchmark method in the rest of the study.

The BSSE corrections are comparable for both basis sets, with a maximum deviation of 1.5 kJ mol^{-1} between the two. The magnitude of the BSSE correction is not negligible, 9.6 kJ mol^{-1} and 10.3 kJ mol^{-1} on average for aug-cc-pVTZ and 6-311+G(3df,2p), respectively. It is not surprising that this correction increases with increasing size of the anion, that is the number of electrons. Hence, BSSE is smallest for Cl- and dca-type ion pairs (around 7 kJ mol^{-1}) and largest for the NTf$_2$-type ion pairs (around 13 to 15 kJ mol^{-1} depending on the configuration). Although the BSSE correction represents only a small fraction (2−5%) of the total binding energy, the implications on calculations of ionic clusters or aggregates can be far more important, especially for ionic liquids containing bulky ions with a few functional groups. Therefore, BSSE should be taken into consideration when a comparison of the binding energies for different-sized anions and cations is made. There is a suggestion in the literature that the Boys and Bernardi approach overestimates the effect of BSSE.[26] Finding a solution to this problem was not within the scope of the article.

TABLE 2: Mean Average Deviations of DFT-Based and Ab Initio-Based Methods of the Binding Energies of the [$C_n$mpyr][X] Ion Pairs in Two Conformations, conf1 and conf2 with Respect to the Benchmark Method, MP2/6-311+G(3df,2p)

X, conf	BLYP	PBE	B3P86	TPSS	PW91	B3LYP	BMK	KMLYP	M05	M05−2X	HF	SCS-MP2	SOS-MP2
Cl, conf1	17.2	1.0	3.6	5.2	2.7	13.6	9.6	7.7	2.9	0.6	35.6	9.1	13.6
Cl, conf2	15.0	2.2	2.1	3.8	4.6	12.0	8.8	8.4	2.0	0.5	34.8	8.7	13.1
BF$_4$, conf1	24.2	9.8	12.5	16.7	7.7	17.0	6.7	10.6	5.3	3.6	27.2	7.2	10.7
BF$_4$, conf2	21.8	7.8	10.7	14.7	5.9	15.2	6.6	10.8	4.3	2.7	26.0	6.8	10.2
PF$_6$, conf1	25.5	12.5	15.7	19.2	10.3	18.6	11.1	7.3	8.0	1.1	27.5	7.2	10.8
PF$_6$, conf2	22.9	10.4	13.6	17.0	8.3	16.6	10.8	7.8	6.7	0.9	25.9	6.7	10.1
mes, conf1	33.1	15.6	16.1	22.3	13.1	24.2	12.2	8.3	12.1	2.0	34.1	9.7	14.6
mes, conf2	29.6	12.7	13.4	19.5	10.5	21.4	11.1	9.2	10.2	1.2	31.9	9.1	13.7
tos, conf1	33.2	17.2	17.1	23.7	14.6	23.9	12.6	8.1	12.0	1.7	32.7	9.6	14.4
tos, conf2	30.2	14.8	14.7	21.2	12.3	21.5	12.0	8.7	10.6	0.9	30.9	9.0	13.5
dca, conf1	30.6	13.4	17.1	21.0	11.2	24.3	16.6	2.1	8.8	3.9	37.4	9.9	14.8
dca, conf2	34.0	15.8	19.1	23.9	13.8	27.1	16.5	1.0	10.8	3.4	39.8	10.0	15.0
NTf$_2$, conf1-N	36.5	21.5	23.2	28.3	18.7	27.2	19.9	3.0	12.6	5.1	43.2	10.7	16.0
NTf$_2$, conf2-N	37.4	21.9	23.7	29.5	19.3	27.9	18.4	3.4	12.0	4.6	41.2	10.3	15.5
NTf$_2$, conf1-O	43.2	25.0	29.5	33.3	22.4	35.0	25.4	4.4	18.2	9.5	30.5	8.9	13.4
NTf$_2$, conf2-O	38.2	21.1	26.0	30.2	18.6	30.9	24.3	2.6	14.9	9.6	32.1	9.2	13.8
MAD Total[a]	**29.5**	**13.9**	**16.1**	**20.6**	**12.1**	**22.3**	**13.9**	**6.5**	**9.5**	**3.2**	**33.2**	**8.9**	**13.3**
MAD %[b]	**8.7**	**4.1**	**4.8**	**6.1**	**3.6**	**6.5**	**4.1**	**1.8**	**2.8**	**1.0**	**9.6**	**2.6**	**3.9**
Stdev Total[a]	**1.0**	**2.0**	**1.7**	**1.6**	**1.7**	**1.8**	**1.9**	**1.6**	**1.0**	**0.6**	**1.0**	**0.2**	**0.3**

[a] Total MADs were calculated as an average of individual MADs for each ion pair. Total standard deviations (Stdev) were also calculated in the same manner. [b] Percent errors were calculated the same way as the total MAD with respect to the binding energies calculated at the MP2/6-311+G(3df,2p).

Performance of DFT-Based and Ab Initio-Based Methods for IPBEs of Pyrrolidinium-Based Ion Pairs. Mean average deviations (MADs), total MADs, and standard deviations (Stdev) for DFT, HF, SCS-MP2, and SOS-MP2 with respect to the benchmark method, MP2/6-311+G(3df,2p), are given in Table 2. MADs for each series, [$C_n$mpyr][X] (with n = Me, Et, n-Pr, and n-Bu and the same anion, X), were calculated. Total MADs for each of the quantum chemical methods used were then taken as an average of the MADs for each series. The same strategy was applied to the calculations of standard deviations. The values of the DFT, HF, SCS-MP2, SOS-MP2, and MP2 ion-pair binding energies of ion pairs under study the together with the individual errors for all of the methods with respect to MP2/6-311+G(3df,2p) are given in the Supporting Information (Tables S2 and S3 of the Supporting Information).

The deviation of the HF binding energies from those of MP2 is a good indication of the magnitude of dispersion interactions, that is hydrogen bonding in cation−anion pairs of pyrrolidinium-based ionic liquids. This effect is not negligible for ionic liquids, with the hydrogen bonding spanning the range from 26 to 43 kJ mol⁻¹ that corresponds to the contribution of 7% (BF$_4$) to 14% (NTf$_2$) in the total IPBE.

The DFT functionals used show standard deviations between 0.6 and 2.0 kJ mol⁻¹ indicating that the absolute errors within each series, [$C_n$mpyr][X] (with n = Me, Et, n-Pr, and n-Bu and the same anion, X) do not change significantly with increasing chain length on the caiton, and, hence, the MADs for each series in Table 2 are indicative of the magnitude of the maximum deviation for a particular anion. Below in the text, we refer to the MADs for each series as maximum errors/deviations.

The functionals that perform best for pyrrolidinium-based ionic liquids are KMLYP and M05−2X with total MADs of 6.5 and 3.2 kJ mol⁻¹, respectively. Although this is an improvement compared to other functionals, the maximum deviations are still above chemical accuracy, that is 10.8 kJ mol⁻¹ for KMLYP and 9.6 kJ mol⁻¹ for M05−2X. The KMLYP functional produces smaller errors for the N(CN)$_2$ and NTf$_2$-containing ion pairs despite dispersion-rich interactions in these ionic systems, whereas the M05−2X functional favors anions with a lesser contribution from hydrogen bonding, such as Cl,

BF$_4$, PF$_6$, mesylate, and tosylate. Both functionals include 56% of the exact HF exchange (55.7% for KMLYP to be exact) that seems to be one of the important components in capturing the effect of short-range interactions like hydrogen bonding in ionic liquids. In addition, the Minnessota functional, M05−2X, offers an improved treatment of the medium-range exchange and correlation, thus producing the best MADs for ionic liquids studied. For the other two functionals from the new generation functionals, BMK and M05, the errors in IPBEs seem to increase with increasing dispersion component, which correlates with increasing size of the anion in the ion pair. BMK does not fare well in describing the intermolecular interactions in ionic liquids, especially for more complex anions, giving a rather large maximum deviation of 25 kJ mol⁻¹. M05 performs slightly better with the total MAD of 9.5 kJ mol⁻¹, which is three times as much than that of M05−2X with still unacceptable maximum error of 18.2 kJ mol⁻¹. The most likely reason for reduced accuracy could lie in a lesser contribution from the exact HF exchange that equates to 42% for BMK and only 28% for M05. A new functional M06−2X with 54% of the HF exchange and improved accuracy for weak noncovalent interactions (about 0.5 kcal mol⁻¹)[10] could potentially improve results for binding energies of ionic liquids. A further study to test if the maximum error can be brought below chemical accuracy when using M06−2X needs to be performed before this functional can be applied to accurately predict energetics in ILs.

For the rest of the local and hybrid DFT functionals, the total MADs are over 12 kJ mol⁻¹, with errors increasing with increasing dispersion component in the ion pair. In most cases, the DFT functionals produce slightly smaller errors for the side conformations, which is in accord with the dispersion interactions prevailing in the global configuration, conf1 (with exception for the dca anion).

For four of the DFT functionals, B3P86, PBE, TPSS, and PW91, the errors span a wide range, for example from 1.0 kJ mol⁻¹ for Cl to 25 kJ mol⁻¹ for NTf$_2$ in the case of the PBE functional, which makes their application to studying ionic liquids very unreliable. These four functionals produce IPBEs within chemical accuracy only for the Cl-type ion pairs, with
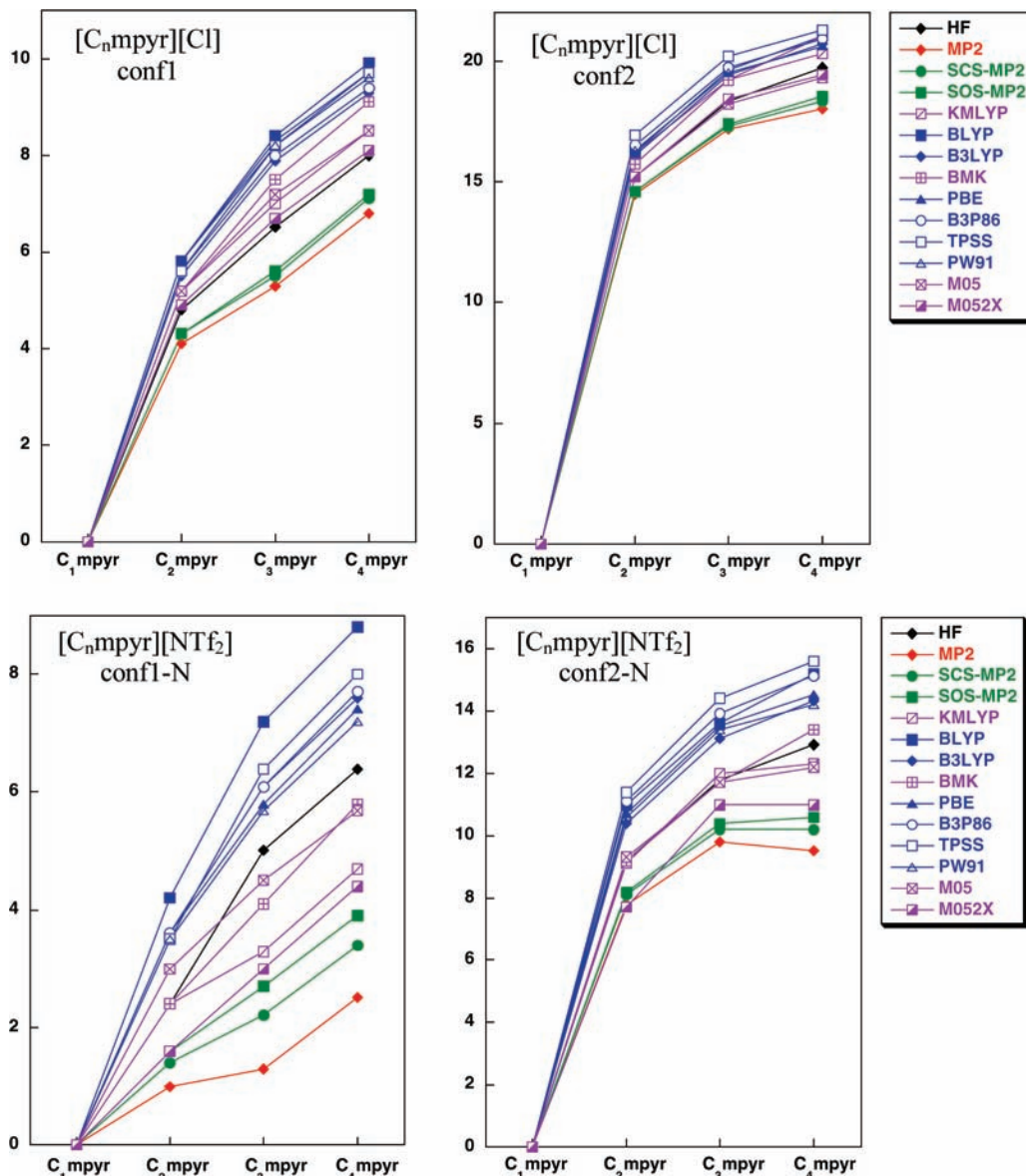
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Figure 2. Relative ion-pair binding energies of the [$C_n$mpyr][X] ion pairs (with n = Me, Et, n-Pr, and n-Bu and X = Cl and NTf$_2$) calculated using DFT-based and ab initio-based methods.

MADs exceeding 20 kJ mol^{-1} for the ion pairs containing anions with dispersion-rich intermolecular interactions.

With respect to their errors, the DFT functionals used in this study are ranked as follows (from good to poor): M05−2X < KMLYP < M05 < PW91 < PBE < BMK < B3P86 < TPSS < B3LYP < BLYP. Not surprisingly, BLYP has the largest total MAD of 29.5 kJ mol^{-1}. What is surprising is that B3LYP does not fare well for all of the ion pairs studied having the second largest MAD among the DFT functionals. Because the B3LYP errors appear to systematically increase with increasing dispersion contribution in the ion pair, the B3LYP functional should not be used to probe energetics in ionic liquids.

As expected, modified MP2 methods, SCS-MP2 and SOS-MP2, produce IPBEs that are lower than those of MP2 by 7 to 9 kJ mol^{-1} and 10 to 16 kJ mol^{-1}, respectively. It was previously established that modified MP2 methods usually give lower binding energies that are closer to CCSD(T) or QCSD(T) results (for example, see refs 35, 39, 40). The ranges are within chemical accuracy and no outstanding deviations from MP2 were found thus indicating that the standard MP2 method already captures the trends in dispersion interactions between the cation and anion in ionic liquids.

Relative Ion-Pair Binding Energies of Pyrrolidinium-Based Ion Pairs. The relative IPBEs were calculated relative to the ion-pair binding energy of [C_1mpyr][X] for each series, [$C_n$mpyr][X] (with n = Me, Et, n-Pr, and n-Bu and the same anion, X). Here, the results for both global (conf1) and side (conf2) configurations of ion pairs containing Cl and NTf$_2$ as the anion are presented in Figure 2 (in the case of the NTf$_2$ anion, the results for the N-type coordinated configurations, conf1-N and conf2-N, are given). The graphs for the other ion pairs are included in Figure S1 in the Supporting Information.

The trends in relative IPBEs are similar for ion pairs containing the Cl, BF$_4$, and PF$_6$, whereas ions pairs incorporating the mesylate, tosylate, and dca anions exhibit trends typical for the NTf$_2$ anion. Analysis of the trends in Figure 2 shows that larger deviations from the MP2 trends are observed for the ion pairs with a larger contribution from dispersion interactions. Local and hybrid functionals (except for KMLYP) do not fare well in reproducing the trends in relative binding energies quantitatively, with deviations over 10 kJ mol^{-1}. Their trends normally fall above those of the new generation functionals (except for BMK), HF and MP2-based methods. As already seen from the discussion above, compared to the other func-

TABLE 3: Basis Set Superposition Errors (in kJ mol^{-1}) for DFT-Based Methods, Standard MP2 and Spin-Scaled MP2 Methods, SCS-MP2 and SOS-MP2 in Combination with the 6-311+G(3df,2p) Basis Set

X, conf	BLYP	PBE	B3P86	TPSS	PW91	B3LYP	BMK	KMLYP	M05	M05−2X	HF	MP2	SCS-MP2	SOS-MP2
Cl, conf1	2.6	3.4	3.0	2.3	3.4	2.8	3.8	3.9	3.6	2.5	2.5	8.7	9.1	9.2
Cl, conf2	2.5	3.4	2.9	2.3	3.4	2.8	3.8	3.8	3.5	2.4	2.4	8.4	8.7	8.9
BF$_4$, conf1	4.7	4.4	4.4	3.0	4.7	4.3	5.4	5.2	5.1	4.4	5.3	12.2	12.4	12.4
BF$_4$, conf2	4.5	4.3	4.2	2.8	4.5	4.1	5.2	5.1	5.0	4.2	5.4	11.8	12.0	12.1
PF$_6$, conf1	5.1	4.8	4.8	3.6	5.0	4.8	5.9	5.7	5.3	5.0	5.9	12.1	12.2	12.3
PF$_6$, conf2	4.8	4.6	4.6	3.4	4.8	4.5	5.6	5.4	5.0	4.7	5.6	11.1	11.2	11.3
mes, conf1	4.3	3.8	3.9	3.0	4.2	4.0	4.7	4.5	4.5	4.1	4.8	12.9	13.0	13.1
mes, conf2	4.0	3.6	3.6	2.7	3.9	3.7	4.3	4.2	4.1	3.8	4.5	11.6	11.8	11.9
tos, conf1	4.1	3.7	3.7	2.9	4.0	3.8	4.5	4.3	4.3	4.1	4.6	13.1	13.2	13.3
tos, conf2	3.8	3.3	3.4	2.6	3.6	3.5	4.1	3.9	3.9	3.8	4.2	11.7	11.8	11.9
dca, conf1	1.0	0.9	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.1	1.0	6.4	6.6	6.6
dca conf2	0.9	0.8	0.8	0.8	0.9	0.8	1.0	1.0	1.1	1.0	0.9	6.4	6.6	6.7
NTf$_2$, conf1-N	5.4	4.7	4.9	4.1	5.2	5.2	6.0	5.7	5.6	5.2	5.9	15.0	15.2	15.2
NTf$_2$, conf2-N	5.2	4.5	4.7	3.9	5.0	4.9	5.7	5.5	5.5	5.0	4.9	14.6	14.8	14.9
NTf$_2$, conf1-O	5.3	4.5	4.7	4.0	5.0	5.0	5.6	5.5	5.5	5.1	5.9	15.9	16.0	16.1
NTf$_2$, conf2-O	4.9	4.2	4.4	3.7	4.7	4.6	5.3	5.1	5.2	4.7	5.5	15.0	15.1	15.1
Total BSSE[a]	**3.9**	**3.7**	**3.7**	**2.9**	**3.9**	**3.7**	**4.5**	**4.4**	**4.3**	**3.8**	**4.3**	**11.8**	**11.9**	**11.7**

[a] Total BSSEs were calculated as an average of individual BSSEs for each ion pair.

tionals KMLYP and M05−2X produce trends that are closer to MP2. Surprisingly, BMK falls behind all other DFT functionals for simple ion pairs consisting of the PF$_6$ (side conformation) and BF$_4$ (global minimum conformation) anions as well as the side conformation of the dca ion pair. In the other cases, the BMK trends in IPBEs fall not far from those of the M05 family and KMLYP functionals. M05−2X performs by far the best compared to the DFT functionals used in this study (within 2 kJ mol^{-1} from the MP2 trends), although the functional still needs improvement to be more consistent across the anion range. For example, for side conformations of mesylate and tosylate ion pairs, it falls below the MP2 trend line (Figure S1 of the Supporting Information). For half of the ion pairs (including simpler anions like Cl and BF$_4$) considered, B3LYP produces the worst trends in relative binding energies, further confirming our previous conclusion that B3LYP can potentially lead to erroneous trends in binding energies. SCS-MP2 and SOS-MP2 trends are very close to those of MP2 (within 1 kJ mol^{-1}!), indicating the standard MP2 method performs well for ionic systems and can be reliably used for studying binding energies in ionic liquids.

Basis-Set Superposition Errors for DFT-Based and Ab Initio-Based Methods. Average basis-set superposition errors for each series, [C$_n$mpyr][X] (with n = Me, Et, n-Pr, and n-Bu and the same anion, X), are given in Table 3. Individual basis-set superposition errors are included in the Supporting Information (Table S4 of the Supporting Information).

Analysis of show that basis-set superposition errors for DFT functionals are rather small, below 6 kJ mol^{-1} (same as for HF), whereas all three MP2, SCS-MP2, and SOS-MP2 methods have BSSEs that are twice as much, that is 12 kJ mol^{-1} on average. These errors increase with increasing number of electrons, hence the number of basis functions in the systems. The same is observed for DFT, with the only difference that the deviations are smaller, within 2 kJ mol^{-1} as opposed to 6 kJ mol^{-1} for the MP2-based methods. It is also well understood that the counterpoise correction has an accumulative effect with increasing number of basis functions, hence increasing number of molecular species in the system. Although the BSSE error of 12 kJ mol^{-1} for MP2 can be considered to be not so significant for single ion pairs, it may represent an important issue for higher-order ionic systems consisting of a few ion pairs containing bulky organic functional groups and, hence, the effect of BSSE

TABLE 4: Deviations of the DFT-D Functionals, BLYP-D, PBE-D, and B3P86-D in the Binding Energies of the [C$_n$mpyr][X] Ion Pairs in Two Conformations, conf 1 and conf2, Calculated with Respect to the Benchmark Method, MP2/6-311+G(3df,2p)

X, conf	BLYP-D	PBE-D	B3P86-D
Cl, conf1	15.4	24.9	20.0
Cl, conf2	15.8	25.7	20.5
BF$_4$, conf1	18.0	17.3	16.6
BF$_4$, conf2	15.7	16.4	15.0
PF$_6$, conf1	13.3	11.3	10.6
PF$_6$, conf2	11.5	10.7	9.4
mes, conf1	5.3	8.8	7.7
mes, conf2	4.4	9.0	7.3
tos, conf1	5.3	7.1	6.5
tos, conf2	4.0	7.0	5.8
dca, conf1	3.9	8.2	5.4
dca conf2	4.7	8.3	6.3
NTf$_2$, conf1-N	4.0	5.4	3.9
NTf$_2$, conf2-N	5.9	7.6	5.5
NTf$_2$, conf1-O	0.3	1.0	1.4
NTf$_2$, conf2-O	0.1	1.5	0.9
MAD Total[a]	**8.0**	**10.6**	**8.9**
MAD %[b]	**2.3**	**3.0**	**2.5**
Stdev total[a]	**0.6**	**0.7**	**0.8**

[a] Total MADs were calculated as an average of individual MADs for each ion pair. Total standard deviations (Stdev) were also calculated in the same manner. [b] Percent errors were calculated the same way as the total MAD with respect to the binding energies calculated at the MP2/6-311+G(3df,2p).

needs to be taken into account in calculations of binding energies at correlated levels of theory.

Performance of DFT-D Functionals. Mean average deviations (MADs), total MADs, and standard deviations (Stdev) for the BYLP-D, PBE-D, and B3P86-D functionals with respect to the benchmark method, MP2/6-311+G(3df,2p), are given in Table 4. Individual errors for DFT-D functionals with respect to MP2/6-311+G(3df,2p) are given in the Supporting Information (Table S5 of the Supporting Information).

The BYLP-D, PBE-D, and B3P86-D functionals fail to achieve accurate predication of IPBEs for Cl, BF$_4$, and PF$_6$-based ion pairs. On the other hand, a significant improvement over the corresponding functionals, excluding the explicit dispersion term, is observed for ion pairs containing anions with dispersion-rich interactions such as mesylate, tosylate, dca, and

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NTf$_2$. For these four anions, DFT-D errors are under 9 kJ mol^{-1} and even under 5 kJ mol^{-1} for BLYP-D, which is a substantial improvement of 24 kJ mol^{-1} on average over the local BLYP functional. For comparison, the corresponding functionals without the dispersion term produce errors of over 13 kJ mol^{-1} for PBE and B3P86 and over 30 kJ mol^{-1} for BLYP.

The basis-set superposition errors were not included in calculations with DFT-D functionals. As was shown above, the BSSE corrections for DFT functionals are rather small for ion pairs of ionic liquids falling between 2.9 and 4.5 kJ mol^{-1} on average. The counter-poise corrected binding energies are expected to be smaller in magnitude than the uncorrected ones. Because the three DFT-D functionals overestimate the MP2 IPBEs (except for the O-coordinated conformations of the NTf$_2$ ion pair using BLYP-D), the errors might become even smaller for the complex anions like mesylate, tosylate, dca, and NTf$_2$, possibly falling below chemical accuracy. It seems that inclusion of the empirical dispersion term explicitly in the final electronic energy (eq 2) accounts for most of the dispersion interactions in ionic liquids. Surprisingly, BLYP-D performs best out of the three functionals, with B3P86-D not far behind. More research needs to be done to accurately assess reliability of DFT-D functionals to studying energetics of ionic liquids. Because the cation–anion interactions represent only a fraction of intermolecular interactions occurring in ionic liquids, other interactions like the alkyl–alkyl chain interactions on the cations and π–π stacking interactions between the cations and/or anions (depending on their chemical structure) need to be probed as well. For example, other cations like imidazolium that tend to be a subject to π–π stacking interactions need to be tested before drawing a conclusion. There is a possible limitation to this approach, as DFT-D functionals might not necessarily improve IPBEs for all ionic liquids cations/anions, which is obviously the case of Cl, BF$_4$, and PF$_6$-based ionic liquids. Hence, a necessary assessment study needs to be done for each ionic liquid separately.

Conclusion

In this work, we examine the performance of a range of local and hybrid DFT functionals, including BLYP, PBE, PW91, B3P86, B3LYP, and TPSS, new generation DFT functionals, including KMLYP, BMK, M05, and M05−2X, and DFT functionals with the explicit empirical correction for dispersion interactions, including BLYP-D, PBE-D, and B3P86-D, to study ion-pair binding energies of pyrrolidinium-based ionic liquids, [C$_n$mpyr][X] (n = Me, Et, n-Pr, and n-Bu and X = Cl, BF$_4$, PF$_6$, CH$_3$SO$_3$ (mesylate), CH$_3$PhSO$_3$ (tosylate), N(CN)$_2$, and NTf$_2$). Calculated IPBEs were compared to the results of the selected benchmark method, MP2/6-311+G(3df,2p).

With respect to their MADs, the DFT functionals used in this study are ranked as follows (from good to poor): M05−2X < KMLYP < M05 < PW91 < PBE < BMK < B3P86 < TPSS < B3LYP < BLYP. Except for the first three functionals in this sequence, the total MADs of DFT functionals: PW91, PBE, BMK, B3P86, TPSS, and B3LYP are over 12 kJ mol^{-1} and reaching 30 kJ mol^{-1} in the case of BLYP, with errors increasing with increasing dispersion component in the ion pair. The most widely used DFT functional, B3LYP, does not fare well for *all* of the ion pairs studied, having the second largest MAD of 22.3 kJ mol^{-1}. Many ionic liquid anions and cations are bulky and have multiple functional groups; hence, we do not recommend the use of these functionals to energetics in studying energetics of ionic liquids.

The functionals that perform best for pyrrolidinium-based ionic liquids are KMLYP and M05−2X with the total MADs

of 6.5 and 3.2 kJ mol^{-1}, respectively. Although this is an improvement compared to other functionals, the maximum deviations are still relatively large (over 10 kJ mol^{-1}) and are outside chemical accuracy. The M05−2X and KMLYP functionals with a large contribution (56%) of the exact HF exchange and an improved treatment of the medium-range exchange and medium-range correlation in the case of M05−2X appear to perform better for ionic liquids than the rest of the functionals employed. It seems that a large contribution from the HF exchange is one of the key components of any DFT functional to accurately account for the dispersion contribution of hydrogen bonding in ionic liquids. M06−2X, an improved version of M05−2X, needs to be tested to establish whether maximum deviations can be brought below chemical accuracy. M05−2X also produces best relative IPBEs (within 2 kJ mol^{-1} from MP2 trends), although its behavior is not consistent across the anions.

DFT functionals with inclusion of the explicit empirical dispersion term (BLYP-D, B3P86-D, and PBE-D) seem to significantly improve the description of ion-pair binding energies for complex anions like mesylate, tosylate, dca, and NTf2, whereas their performance is still poor for Cl, BF$_4$, and PF$_6$-based ion pairs. BLYP-D and B3P86-D could potentially be used but these functionals do not perform uniformly well for a range of anions. A more systematic study on the effect of the BSSE correction for these functionals is also needed.

Because the cation–anion interactions represent only a fraction of the intermolecular interactions occurring in ionic liquids, other interactions like the alkyl–alkyl chain interactions on the cations and π–π stacking interactions between the cations and/or anions (depending on their chemical structure) need to be probed for the DFT functionals such as M05−2X, M06−2X, KMLYP, BLYP-D, and B3P86-D to draw a conclusion on their reliability in studying energetics in ionic liquids.

Supporting Information Available: Tables of optimized geometries for ionic liquid ion pairs, binding energies of ion pairs, deviations of binding energies, and basis-set superposition errors. This material is available free of charge via the Internet at http://pubs.acs.org.

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