Assessment of the Performance of Commonly Used DFT Functionals vs. MP2 in the Study of IL-Water, IL-Ethanol and IL-$(H_2O)_3$ Clusters.

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Abstract

We present a comparative study of the accuracy of different DFT approaches *vs*. MP2 for evaluating Ionic Liquids (ILs) + cosolvent. Namely, we are interested in [XBmim] + cosolvent (X being Cl^-, BF_4^-, PF_6^-, and $CH_3SO_3^-$ anions and cosolvent being water or ethanol) and [XBmim] +$(H_2O)_3$ clusters. In this study the B3LYP, B3LYP-D3, M06, M06-2X and M06-HF functionals with Pople and Dunning basis sets are considered. We find that the influence of the basis sets is a factor to take into consideration. As already seen for weakly bonded systems when the basis set quality is low the uncorrected counterpoise (unCP) or averaging counterpoise (averCP) energies must be used due to cancellation errors. Besides, the inclusion of extra diffuse functions and polarization is also required specially in the case of ILs interacting with water clusters. The B3LYP functional does not reproduce either the structure or the interaction energies for ILs+H_2O and ILs+EtOH aggregates, the energetic discrepancies being more significant than the structural ones. Among the dispersive corrected functionals, M06-2X results resemble to a great extent the reference data when the unCP interaction energies are considered for both water and ethanol. In turn, M06 and B3LYP-D3 functionals are the best option for ILs containing polar and non polar anions, respectively, whether the averCP interactions energies are taking into consideration. From the structural point of view, B3LYP and M06 functionals describe more open structures whereas B3LYP-D3, M06-2X and M06-HF structures resemble quite well MP2 results. When the number of water molecules increases the H bonding motif gains importance and the effect depends on the underlying functional. Only M06-2X and M06-HF behaviour is similar to

that observed for one water molecule. This is important because to describe ILs-cosolvent solutions is not only necessary to take into account the ILs-cosolvent interactions but also the cosolvent-cosolvent ones in the ensemble of the system.

1. Introduction.

Over the last few years the versatile nature of the ionic liquids (ILs) has increased their interest in both academia and industry.[1, 2, 3, 4, 5, 6, 7] Their double featuring as solvents and templates allow them to play a significant role in the synthesis of inorganic materials. Several examples are available describing their use in the preparation of ordered mesoporous materials[8, 9, 10, 11, 12] or zeolites.[12, 13, 14, 15, 16, 17] Recently, the use of imidazolium ILs based for the synthesis of zeolites has been published.[18] It is found that the silicon source determines the formation of BEA (Beta Polymorph A) or MFI (Mordenite Framework Inverted) zeolites. Depending on this source, different preorganized complexes are obtained that result in the formation of a given zeolite structure. In the presence of ethanol, the ionic liquid forms preorganized complexes that drive the formation of MFI. In its absence, BEA is obtained. In addition, the anion nature is revealed as a determinant factor. This way, [ClBmim] and [CH_3SO_3Bmim] (where Bmim means 1-butyl-3-methylimidazolium) ILs succeed in their role of structure directing agents while [BF_4Bmim] and [PF_6Bmim] ILs failed in this task and an amorphous material is obtained.[19] On the basis of these results it is interesting to get insight into the microscopic nature of water/IL and ethanol/IL mixtures. The local structural organization and physicochemical properties of these ILs-cosolvent aggregates can provide an explanation of their templating function in the zeolite structure formation. However, it must be concerned that the study of ILs is a challenge for computational chemistry. Although ILs consist entirely of ions and, consequently, are dominated by coulombic forces, additional specific non covalent interactions are also present. Dispersion interactions due to electron correlation like van der Waals interactions among alkyl chains on the cations, π-π stacking interactions between cations and cation-anion, and the H bonding between polar groups play a significant role in a good description of these systems. When a protic cosolvent like water or ethanol is considered H bondings gain importance. The proper

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treatment of ILs-cosolvent aggregates necessitates the use of methods that can account for all the interactions present in these systems.

As previously mentioned, the description of the π-π cation stacking is essential in the context of ILs. Nevertheless, in the case of water and ethanol-ILs mixtures the extension of the IL network widely depends on the cosolvent concentration. This way when the $x_{H_2O} > 0.8$ a reduction of the cohesions between anions and cations is observed.[20, 21, 22, 23, 24, 25, 26, 27, 28, 29] At these conditions, the original ion networks are no longer available and new water-cation/water-anion networks appear.[20, 22, 23, 24, 25, 26, 27, 28, 29, 30] This process induces changes in several structural and dynamic properties of the liquid[21, 31] and it can end up with the mere interaction of water molecules with an ion pair. When the cosolvent is ethanol, the extension of the IL network disruption is less dramatic and larger ionic clusters appear in the IL-alcohol mixture due to the fact that ethanol molecules are much more homogeneously placed in the structure of the IL even at high ethanol concentrations.[32, 33] Regarding the tertiary ILs/water/ethanol mixture, Wu et al.[34] concluded that ethanol molecules are capable of breaking the complexes cation$\cdots$HOH$\cdots$anion via cation-water and anion-water interactions. As a result, the addition of ethanol weakens the interaction of ILs with water. In these situations π-π stacking interactions between cations disappear and the interactions with the cosolvent gain importance.

Traditionally, small clusters and their interactions with cosolvents have been studied on the basis of quantum chemistry. Bearing in mind the size of these species ab initio post HF methods are very expensive from the computational point of view. For this reason DFT methods have been widely used, the most popular functional being B3LYP. However, it is well-known that DFT fails when describing bonded systems where dispersions forces are significant.[35, 36, 37] A general procedure to overcome this DFT limitation is advisable. The solution for this problem have different strategies. One popular strategy, known as DFT-D3, is to augment conventional functionals with pairwise addition of C^n/r^n (n being 6 and 8) correction terms to the internuclear energy expression.[38] These terms are smoothly cut off in the short range, where they are not relevant, but explicitly enforce the desired long-range asymptotic behavior. A different strategy is to use semilocal or hybrid functionals that contain a large number of free parameters in the functional form. These parameters are semiempirically fit using diverse data sets that include data not only from thermochemistry but also from kinetics, noncovalent interactions, etc. In this way, many deficiencies of traditional

semilocal and hybrid functionals, including the treatment of dispersion, can be minimized. This philosophy is best illustrated by the meta-GGA M06 suite of functionals.[39, 40, 41, 42] The M06 functionals differ in the data sets used in their parametrization and the fraction of exact exchange being used 0%, 27%, 54% and 100% for M06-L, M06, M06 2X and M06-HF, respectively. On this context, some studies have evaluated how the inclusion of dispersion improves the performance of DFT on ILs and ILs + one water molecule.[43, 44, 45, 46, 47]

The evaluation of the performance of DFT dispersion corrected functionals for the description of ILs-cosolvent aggregates implies the comparison with reference data. As a rule, DFT results have been compared with post HF methods methods. The use of CCSD(T)/CBS is desirable but on many occasions not affordable from the computational point of view. Previous studies show that the MP2 level of computation has been proven to properly describe ILs clusters in comparison with CCSD(T)/CBS.[48, 35, 44, 49] The influence of the basis sets is important but negligible discrepancies can be obtained when the results are properly treated. It is well-known that counterpoise[50] correction (CP) is employed in the estimation of interaction energies to reduce the basis set superposition error (BSSE). Frequently, complexes are overbound in uncorrected (unCP) calculations and underbound in CP computations. The basis set incompleteness gives rise to underbound estimations. Following this argument if the basis set used is fairly close to basis set limits CP results will yield answers very close to the true basis set limit. However, if the basis set used is far away from the converged complete basis set limit the underestimation of the interaction energy can cancel out the BSSE and unCP results compare rather well with the correct result.[51, 52, 53, 54, 55, 56] Halkier and co-workers[57, 58] found that for small basis sets unCP was often closer to the CBS limit that other CP or averCP, that is, averaging (CP+unCP)/2 quantities. Sherrill *et al.*[59] conclude that the merits of CP corrections in studies of van der Waals clusters depend on the theoretical method, basis sets and binding motifs. These authors suggest that for MP2 computations averCP and unCP results are more adequate than CP-corrected results provided the basis set is a quadruple-zeta quality or below. The unCP results being more accurate for hydrogen bonded systems.[59]

Here, we compare both strategies (correction terms on B3LYP functional and the inclusion of weakly bonded systems in the parametration data set) to include dispersion corrections by studying systematically their performance

on ILs-cosolvent aggregates. It is significant to assess the level of accuracy that can be expected from both. In particular, we examine ILs-water and ILs-ethanol cluster using DFT (dispersion corrected and uncorrected) and MP2 methods with Pople and Dunning basis sets. We also study the importance of dispersion corrections and basis sets when water clusters interacting with ILs are taking into account, that is, when H bonding gains importance in these systems.

2. Computational Methods.

Quantum mechanics optimizations of [XBmim] + H_2O, [XBmim] + EtOH and [XBmim] + $(H_2O)_3$ aggregates (X being Cl^-, BF_4^-, PF_6^-, and $CH_3SO_3^-$ anions) are carried out. The initial structures for the [XBmim] + H_2O and [XBmim] + EtOH clusters were taken from previous gas-phase structure optimizations in our group.[19] The [XBmim] + $(H_2O)_3$ aggregates are generated as indicated in the next section. As density functionals, the hybrid B3LYP[60, 61], B3LYP-D3 that includes Grimme's third version of an empirical correction[38], and a number of functionals of the Minnesota M06 family: M06, M06-2X and M06-HF are tested.[40, 41, 42] These functionals are chosen because previous studies[43] conclude 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 ILs. MP2 level of computation is selected as reference data for future comparisons with the DFT results. Pople basis sets are used, namely, the 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets. This election is motivated by the common use of these basis sets in the description of these systems, the goodness of two latter in previous results[44, 49] and as a compromise between computational cost and reasonable accuracy. Due to the slight variations in geometry when going from 6-311+G(d) to 6-311++G(d,p) basis sets, MP2 optimizations at 6-311++G(d,p) basis sets are avoided and only single point calculations on the 6-311+G(d) structures are carried out. It is well known that MP2 results with Pople basis sets present larger BSSE than DFT methods. For this reason, single point calculations using aug-cc-pVDZ and aug-cc-pVTZ basis set are also carried out to evaluate the effect on our conclusions. The CP correction using the procedure of Boys and Bernardi[50] is computed. In all cases, fully optimized structures are characterized by computing second energy derivatives. Computations are carried out by the Gaussian09 program.[62]

3. Results and Discussion.

3.1. ILs-ethanol and ILs-water clusters.

The structures for ILs-ethanol and ILs-water clusters optimized at the MP2/6-311+G(d) level are collected in Fig. 1. There are not essential deviations in the global arrangement of the clusters for the DFT optimizations and the two other basis sets. The former figure will be used as a basis for the discussion of the similarities and discrepancies among the different methods. (The cartesian coordinates for all the minima can be found in the Supporting Information). The analysis of Fig. 1 indicates that there are not noticeable differences in the aggregate arrangement when ILs-ethanol and ILs-water clusters are compared. The different topology of the cosolvent is not a determining factor for the cluster structure. As expected, in all the structures the hydrogen bond between the anion and the cosolvent molecule is observed. The cosolvent molecule interacts with both partners of the anion/cation couple even if on some occasions its interaction with the imidazolium ring does not present a specific hydrogen bond nature. The cosolvent or the anion is located somehow on the top of the ring interacting with acidic H of the ring, labelled from now on as H_a, the alkyl chains and π cloud of the ring.

The interaction energy of each cluster is computed as usual as the difference among the whole cluster and the monomers,

$$\Delta E_{\text{int}} = E(X_1, X_2, ..., X_n) - \sum_{i}^{n} E(1)(X_i) \tag{1}$$

Fig. 2 shows the comparison of the unCP DFT interaction energies *vs.* the unCP MP2 values for the ILs-ethanol and ILs-water clusters optimized using 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets. Several conclusions can be immediately drawn from the analysis of Fig. 2. The interaction energies of the ILs containing Cl^- and $CH_3SO_3^-$ anions are more negative than those for BF_4^- and PF_6^- ones no matter the level of computation. Besides, for each method these energies depend on the nature of the anion but barely on the cosolvent (water or ethanol). There is a different trend of the most stable aggregate for a given anion. B3LYP results indicate that the clusters with water as a cosolvent are more stable than those with ethanol. The reference data, *i.e.* MP2 estimations, predict a higher stability for ethanol clusters. This trend is in agreement with experimental evidences that show how ethanol molecules can displaced water molecules interacting

[BF$_4$Bmim]+EtOH

[BF$_4$Bmim]+H$_2$O

[ClBmim]+EtOH

[ClBmim]+H$_2$O

[CH$_3$SO$_3$Bmim]+EtOH

[CH$_3$SO$_3$Bmim]+H$_2$O
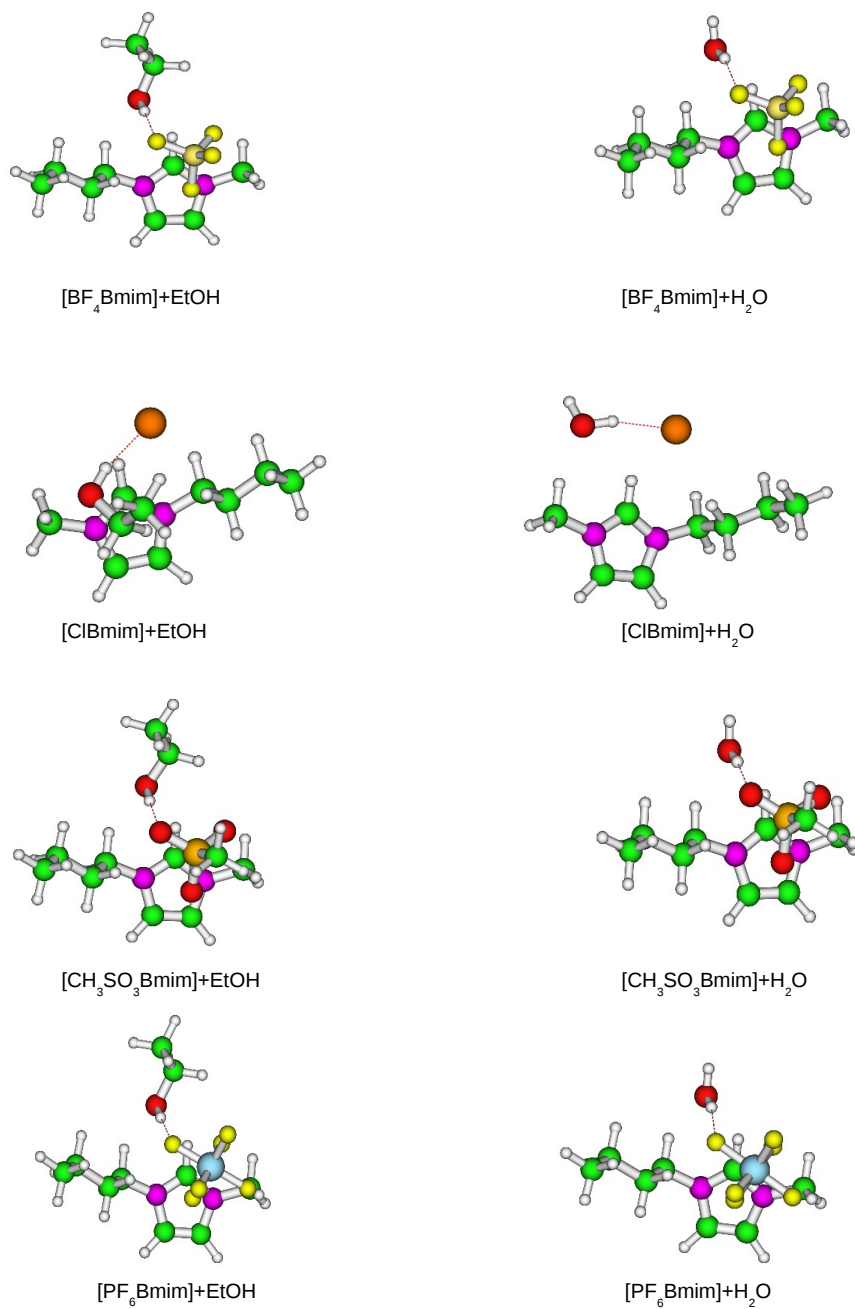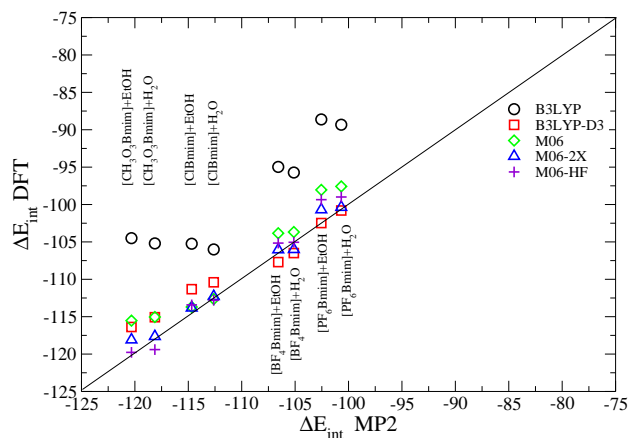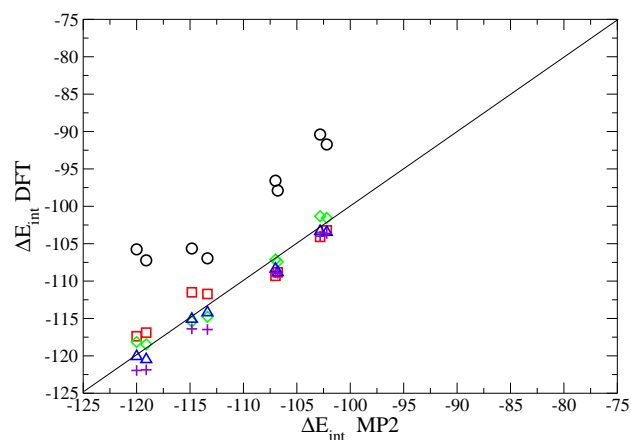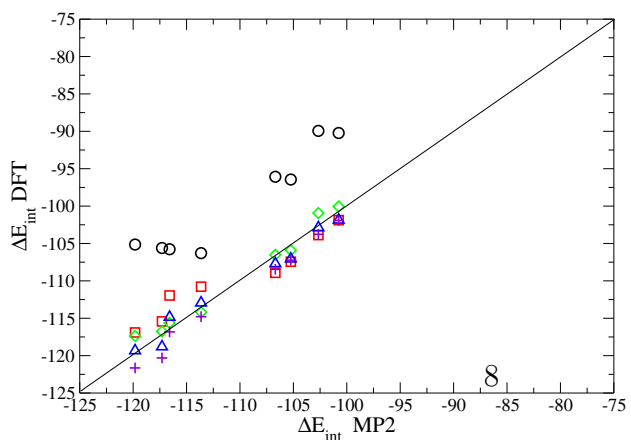
[PF$_6$Bmim]+EtOH

[PF$_6$Bmim]+H$_2$O

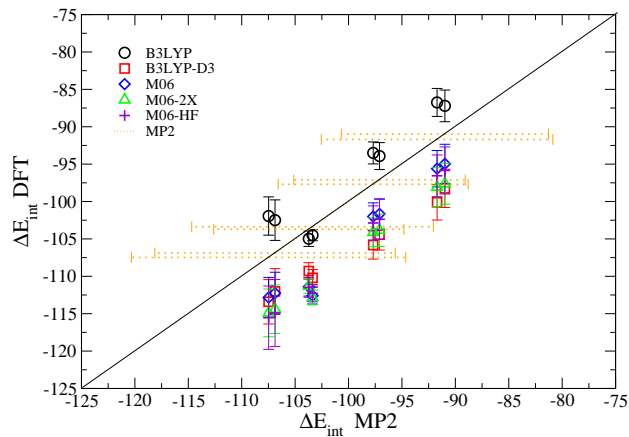Figure 1: Optimized structures obtained at MP2/6-311+G(d) for the ILs-cosolvent clusters.

a)

b)

c)

Figure 2: Plot of unCP ΔE_{int}DFT $vs.$ unCP ΔE_{int}MP2 for the optimized ILs-ethanol and ILs-water clusters using a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets.

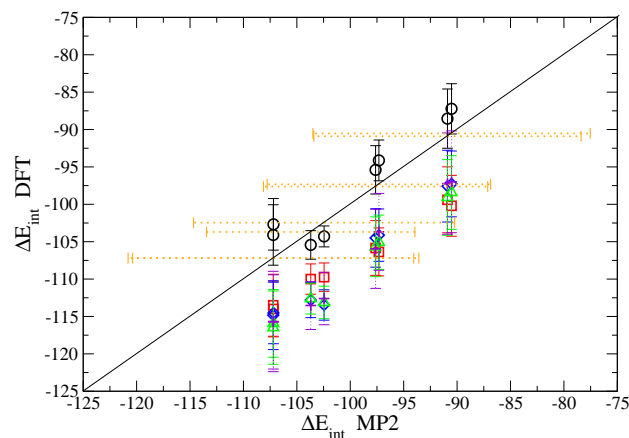with ILs in ILs/water/ethanol mixtures.[34, 63]. The results for the remaining functionals depend on the basis sets. The interaction energies with extra diffuse and polarization basis sets (6-31++G(d,p) and 6-311++G(d,p)) follow the MP2 trend whereas those with 6-311+G(d) basis sets are between B3LYP and MP2. It is well-known[64, 65] the importance of the diffuse functions in the description of the H bonding, specially when anionic species are involved. This fact can be an issue in the differences between 6-31++G(d,p) and 6-311++G(d,p), and 6-311+G(d) results. This topic will be treated in more detailed in the next section.

Fig. 3 shows the CP DFT interaction energies *vs*. the CP MP2 values for the ILs-ethanol and ILs-water clusters optimized at 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets. For the sake of comparison, BSSE has been included as a bar error. The analysis of Fig. 3 shows that BSSE correction represents only a small fraction (±1-5%) of the interaction energy for B3LYP, B3LYP-D3, M06 and M06-2X. Although still small, BSSE is a bit larger for M06-HF (±1-7%). However, it is far more important for MP2 results (±8-13%). As a rule, BSSE increases with increasing number of electrons, *i.e.* size of the anion.[43] This way, BSSE contribution is the smallest for ILs containing the Cl$^-$ anion and the largest for those with the CH$_3$SO$_3$$^-$ one. Finally, Fig. 4 plots the averCP DFT interaction energies *vs*. the averCP MP2 values for the ILs-ethanol and ILs-water clusters optimized at 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets. Certainly, the inclusion of BSSE correction changes the interpretation of the results.
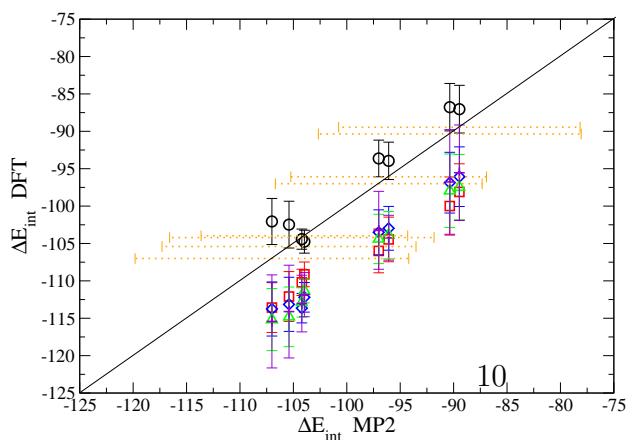
When BSSE is neglected, Fig. 2 shows that M06-2X results present the best resemblance to the MP2 interaction energies using 6-31++G(d,p), the largest deviation is 2.23 kcal/mol for the [CH$_3$SO$_3$Bmim]+EtOH aggregate. M06-HF interaction energies also present a small divergence from MP2 results followed by B3LYP-D3 and M06 functionals. With no doubt, B3LYP functional underestimates MP2 interactions energies giving the worst results. The analysis of Fig. 2 considering 6-311+G(d) and 6-311++G(d,p) basis sets produces similar conclusions but now M06-2X and M06 can be considered the most accurate functionals in comparison with the MP2 reference data. Although still close, M06-HF and B3LYP-D3 interaction energies present higher mean absolute errors, specially in the case of polar anions. Again, the B3LYP functional disagrees more than 10 kcal/mol with the MP2 results. No matter the basis sets, the B3LYP functional does quite poorly for the resemblance with MP2 results. The behaviour of the rest of functionals depends on the the cluster and basis sets but, in general, B3LYP-D3 func-
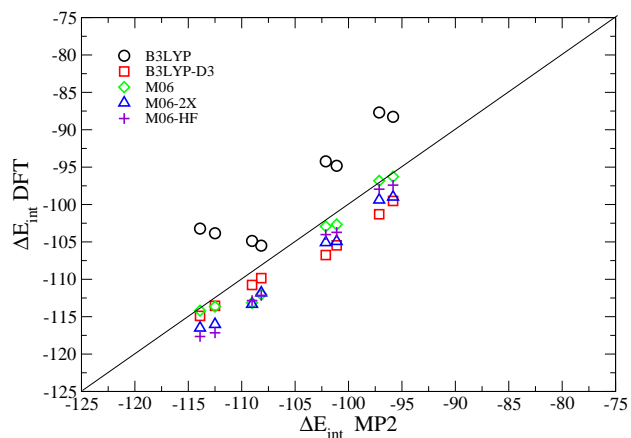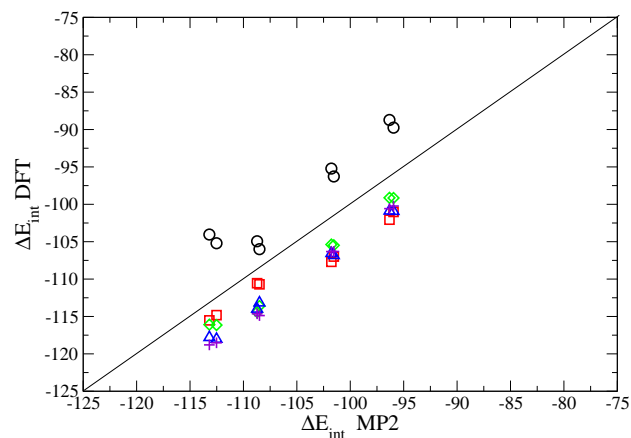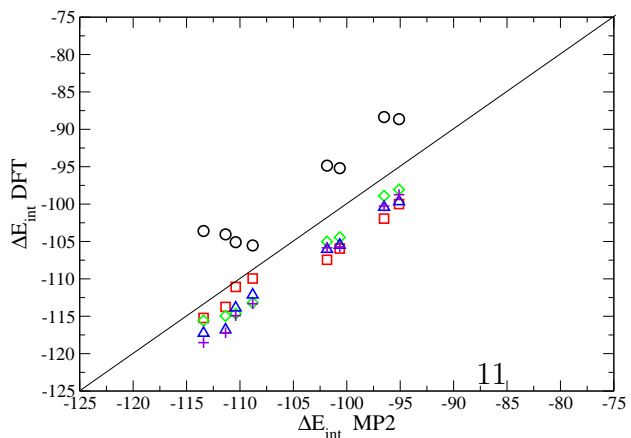
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a)

b)

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c)

Figure 3: Plot of CP ΔE_{int}DFT $vs.$ CP ΔE_{int}MP2 for the optimized ILs-ethanol and ILs-water clusters using a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets. BSSE has been included as a bar error.

a)

b)

c)

Figure 4: Plot of averCP ΔE_{int}DFT *vs.* averCPΔE_{int}MP2 for the ILs-ethanol and ILs-water clusters using a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets.

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tional overestimates the interaction energies of the non polar anions, BF_4^- and PF_6^-, and underestimates the interaction energies of the polar ones, Cl^- and $CH_3SO_3^-$.

The scenario changes dramatically when BSSE is included (Fig. 3). In this case all the functionals considerably differ from MP2 results, The B3LYP functional being now the most accurate ($< 5\%$ of discrepancy). The CP results for all the functionals but B3LYP present a common behaviour, that is, they overestimate the reference data in a no negligible amount (6-10%) for all the basis sets here studied.

The inclusion of averCP also varies the results (Fig. 4). As it happens for the unCP interaction energies, the B3LYP functional does not reproduce the MP2 results but in this case it improves its accuracy specially for the Cl^- ion. The resemblance for the rest of functionals depends on the polar character of the anion but not on the cosolvent. This way, when polar anions are involved B3LYP-D3 functional gives the best results. However, in the case of non polar anions, BF_4^- and PF_6^-, the M06 interaction energies are the most accurate. Again, the goodness of the results is rather independent on the basis sets.

Differences between CP, averCP and unCP interaction energies agree well with previous results[59] describing weakly bound systems. They conclude that averCP and unCP corrected values have merit in avoiding the worst error for van der Waals clusters including H bonded motif provided the basis set is below quadruple zeta quality. Although ILs-cosolvent aggregate can not be considered as van der Waals clusters due to the importance of electrostatic interactions present a similar behaviour for the methods and basis set here tested. Bearing in mind the quality of the basis sets here used, the unCP and averCP results will be used in the discussion.

Discrepancies in the interaction energies among the different methods and basis sets have a twofold origin. On one hand, the inherent features of each method. On the other hand, the geometry of the cluster according to the resulting minima in each potential energy surface (PES). In order to know how the interaction energies of the MP2 structures are reproduced by the DFT methods single point calculations on these structures are carried out. The results are shown in Fig. 5.

The analysis of Fig. 5 indicates that the behaviour is not exactly the same as that obtained in optimized clusters. The order from better to worse reproduction of the unCP MP2 results is the following: M06-2X $\sim$ M06-HF $>$ M06 $>$ B3LYP-D3 $>$ B3LYP (but in the case of 6-31++G(d,p) where the order
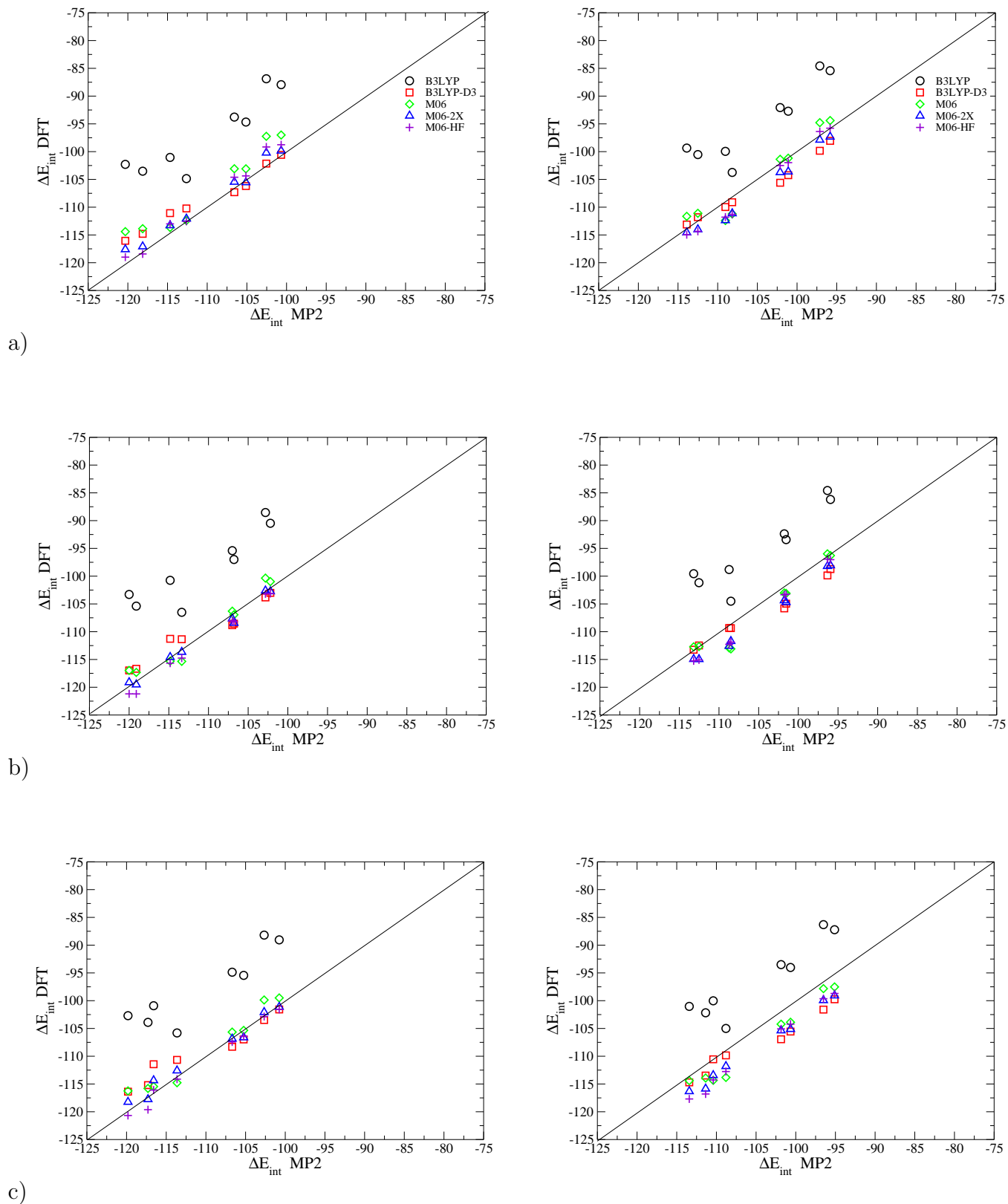
Figure 5: Plot of unCP ΔE_{int}DFT $vs.$ unCP ΔE_{int}MP2 (left) and averCP ΔE_{int}DFT $vs.$ averCP ΔE_{int}MP2 (right) for the ILs-ethanol and ILs-water clusters optimized at MP2 level with a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets.

between M06 and B3LYP-D3 is exchanged). Again, B3LYP energies differ from MP2 results in an important amount but now M06-HF improves its accuracy. As occurred in the case of the optimized clusters when the averCP results are analyzed, B3LYP-D3 functional reproduces better the aggregates with polar anions whereas M06 functional does the same with the non polar ones. Nevertheless, discrepancies are more important than in the case of the optimized clusters. This shows how in spite of most studies pay more attention to the energy discrepancies, due to the lack of dispersion contributions, their effects on structure are also relevant and must be considered.

In order to avoid any artifact due to basis set influence, an analogous comparison using Dunning basis sets has been studied, namely, aug-cc-pVDZ and aug-cc-pVTZ basis sets. As previously noted, DFT functionals are less affected by the basis sets selections than MP2 method. MP2 BSSE with Pople basis sets was in the order of 8-13% while it is 6-11% and 3-6% for aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. An analysis of the results collected in the Supporting Informations indicates that MP2 results are better reproduced when Dunnig basis sets are used. However, the conclusions derived from the previous comparisons are not altered.

Due to the discrepancies found on the relative stabilities of the ILs-ethanol and ILs-water clusters as a function of the method, IL-cosolvent and cation-anion interactions in the geometry of the cluster are also evaluated. Fig. 6 shows the comparison of IL-cosolvent and cation-anion binding energies (BE) for the MP2 and DFT methods calculated as follows:

$$BE_{\text{IL}-\text{cosolvent}} = E(IL - cosolvent) - E(IL) - E(cosolvent) \qquad (2)$$

$$BE_{\text{cation}-\text{anion}} = E(IL) - E(cation) - E(anion) \qquad (3)$$

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B3LYP

B3LYP-D3

M06

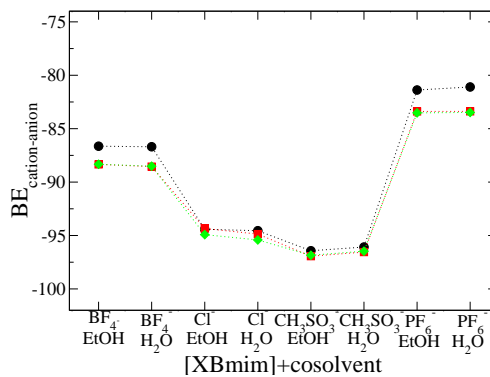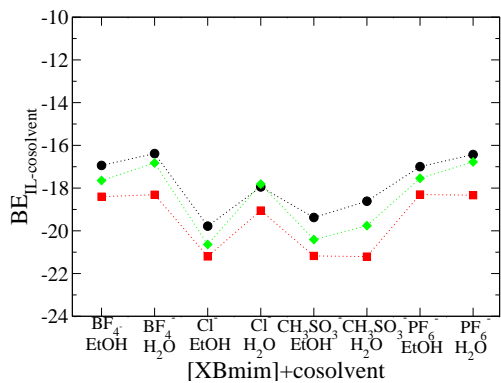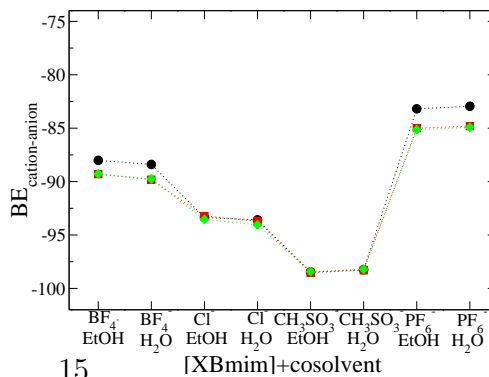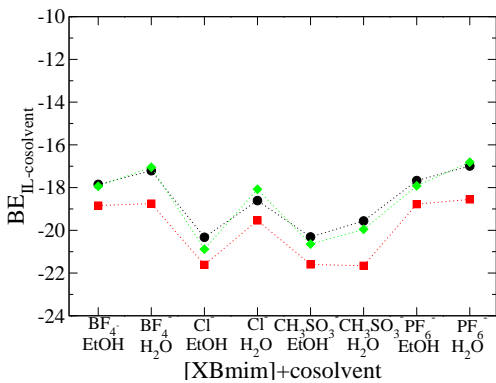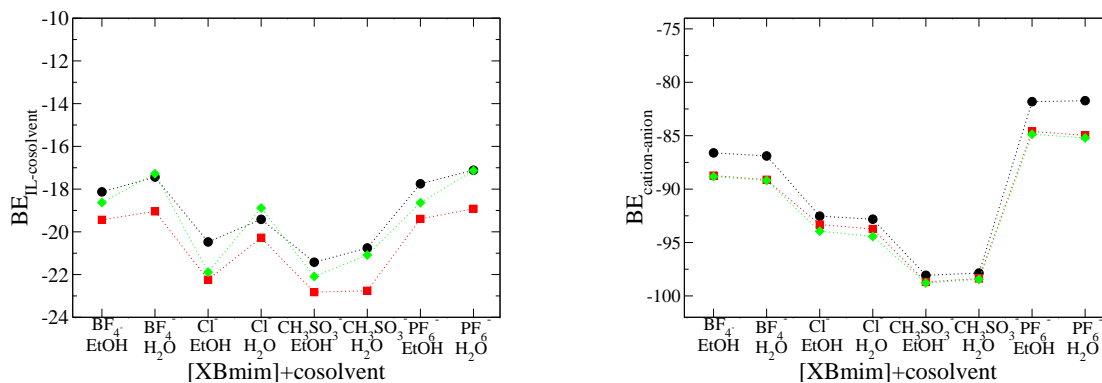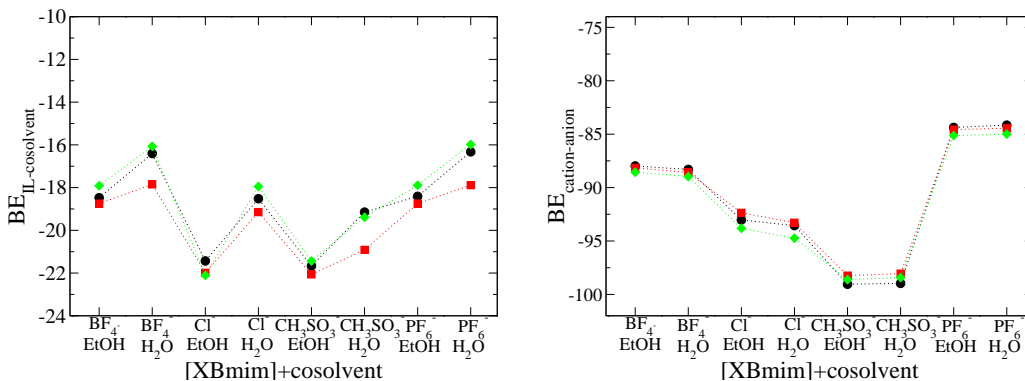M06-2x

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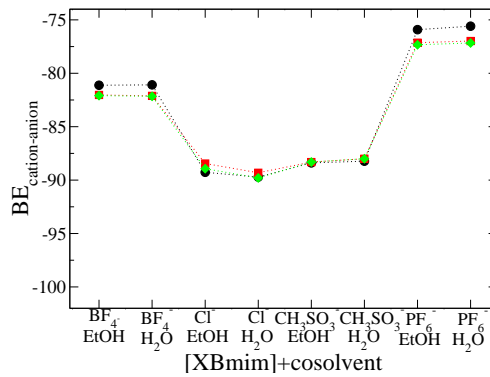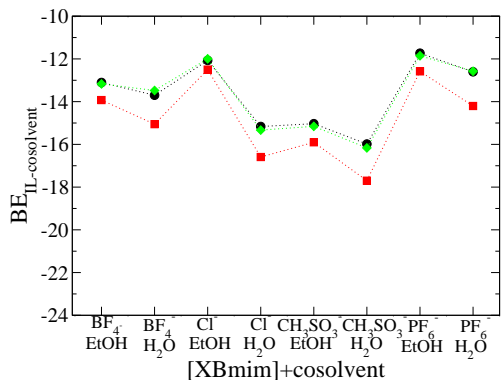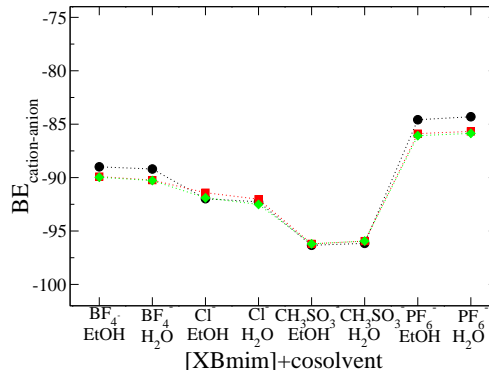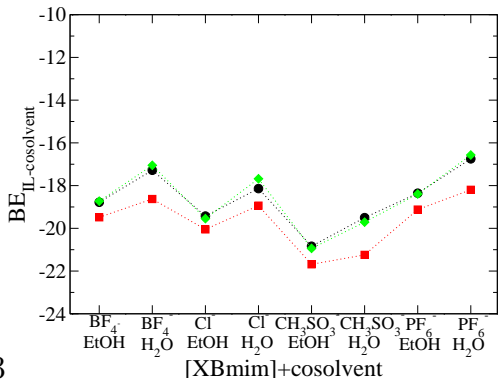
M06-HF

MP2

Figure 6: Plot of the DFT and MP2 IL-cosolvent (left) and cation-anion (right) binding energies for the ILs-cosolvent clusters optimized at MP2 level with 6-31++G(d,p) (black), 6-311+G(d) (red) and 6-3111++G(d,p) (green) basis sets.

1 The first conclusion that can be extracted from the analysis of Fig. 6
2 is the fact that 6-31++G(d,p) and 6-311++G(d,p) IL-cosolvent estimations
3 (on the left in the figure) run in parallel, specially for B3LYP and B3LYP-D3
4 methods, whereas 6-311+G(d) basis sets overestimate the former results. In
5 addition, the profile given by B3LYP is different from those described by the
6 rest of the methods what is the origin of the discrepancy in the relative sta-
7 bility of water and ethanol clusters. The analysis of the anion-cation interac-
8 tions (on the right in the figure) shows that DFT/6-311+G(d) and DFT/6-
9 311++G(d,p) results follow the same trend whereas DFT/6-31++G(d,p)
10 estimations underestimate the interaction, the discrepancies being more im-
11 portant for the non polar anions than for the polar ones. The MP2 profiles
12 are quite similar no matter the basis sets. The conclusions extracted from
13 Fig. 6 supply new aspects in the description of ILs-cosolvent clusters. This
14 way, although 6-31++G(d,p) and 6-311++G(d,p) basis sets proved similar
15 interaction energies when DFT method are employed, the former is not able
16 to evaluate cation-anion interactions specially when non polar anions are
17 considered.

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Table 1: Root mean squared deviations from MP2 distances, angles and dihedral angles for the optimized DFT ILs-cosolvent clusters at 6-31++G(d,p), 6-31+++G(d), 6-31+++(d,p) basis sets. Distances and angles are given in Å and degrees, respectively.

[a] The distance parameters account for the distance between the H_a atom of the ring and the closest atom of the anion, the distance between the H_a atom of the ring and the O atom of the cosolvent molecule and the distance between the H atom of the cosolvent molecule and the central atom of the anion. [b] The angle parameter encompasses both the angle formed by the C-H_a bond with the central atom of the anion and with the O atom of the cosolvent molecule. [c] The dihedral parameter includes the dihedral angles between the ring and the plane containing the C-H_a bond and the central angle of the anion or the O atom of the cosolvent molecule.

	6-31++G(d,p)					6-31+++G(d)					6-31+++G(d,p)				
Distance[a]	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X
BF$_4$Bmim-cosolvent	0.15	0.07	0.14	0.13	0.16	0.12	0.24	0.18	0.14	0.20	0.13	0.14	0.16	0.17	0.18
ClBmim-cosolvent	0.09	0.07	0.07	0.11	0.15	0.28	0.10	0.27	0.22	0.28	0.13	0.19	0.13	0.19	0.23
CH$_3$SO$_3$Bmim-cosolvent	0.06	0.09	0.17	0.17	0.13	0.17	0.09	0.18	0.15	0.13	0.16	0.11	0.16	0.16	0.18
PF$_6$Bmim-cosolvent	0.07	0.08	0.07	0.08	0.11	0.14	0.14	0.14	0.14	0.22	0.13	0.14	0.16	0.15	0.17
Angle[b]	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X
BF$_4$Bmim-cosolvent	14.17	3.39	7.50	4.77	5.12	10.83	3.43	7.70	6.06	5.61	11.82	4.42	7.65	5.94	6.12
ClBmim-cosolvent	22.53	11.69	22.90	5.68	19.86	25.29	9.27	25.09	35.04	35.85	26.05	12.19	17.96	25.19	25.32
CH$_3$SO$_3$Bmim-cosolvent	12.39	7.71	10.20	7.25	5.34	13.21	5.61	8.53	12.22	4.09	13.50	6.16	8.86	12.37	4.77
PF$_6$Bmim-cosolvent	12.07	3.00	4.87	3.67	3.81	10.76	2.06	5.07	3.24	1.66	12.11	3.24	4.66	2.60	1.22
Dihedral[c]	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X
BF$_4$Bmim-cosolvent	20.80	4.15	7.18	5.70	4.12	18.91	3.12	7.65	6.06	4.50	17.62	4.53	7.53	5.79	11.09
ClBmim-cosolvent	59.10	9.67	19.77	29.16	44.42	52.16	12.92	51.13	66.72	48.10	59.18	23.24	26.13	40.53	34.11
CH$_3$SO$_3$Bmim-cosolvent	16.30	8.79	12.30	4.61	4.74	18.86	6.54	10.85	5.45	2.96	19.58	8.31	11.30	5.52	3.12
PF$_6$Bmim-cosolvent	18.87	4.92	7.04	1.87	5.27	18.67	4.00	7.07	1.58	1.58	18.15	3.00	6.56	3.12	1.41

Now it is time to analyze the differences in the structure of the minima among the computational levels here studied.

MP2 aggregates, as shown in Fig. 1, present the anion or the cosolvent over the aromatic ring in a kind of stacking arrangement. In order to globally compare the performance of the DFT methods respect to the MP2 structures, the root squared deviations of a given set of geometrical parameters are given in Table 1. (The specific values of the geometrical parameters chosen for the comparison are collected in the Supplementary Information.) The distance parameter accounts for the main interaction sites between the monomers forming the cluster, that is, the H bonding between the anion and the cosolvent, and their interaction with the H_a atom of the ring. Additionally to the primary stabilizing factors, the interaction of the H atoms of the alkyl chains and the ring with the anion and cosolvent molecule are also responsible for the relative orientation to each order. This is illustrated in the angle parameter that encompasses both the angle between the C-H_a bond with the central atom of the anion and with the O atom of the cosolvent molecule. It is also relevant describing the relative orientation of the anion and cosolvent respect to the imidazolium ring. This is revealed by the dihedral angles described in Table 1 and outlined in the Supplementary Information.

Small variations of the distance parameters can be observed depending on the method and basis sets. Angles and dihedral angles described by B3LYP functional present the most important deviations giving rise to more open structures, that is, either the anion or the cosolvent or both are on the top the ring mainly interacting with the H_a atom. Likely, this is a consequence of the lack of dispersion contributions in this functional. After the B3LYP functional, M06 angles differ more from MP2 estimations, specially in the case of the polar anions. The similarities of B3LYP-D3, M06-2X and M06-HF with MP2 geometrical parameters depend on the cluster but in general, except for ILs containing Cl^- anion, roughly reproduce MP2 geometries. Although some discrepancies are found according to the basis sets, these are less significant than those derived from the underlying functional.

It is necessary to comment that the aggregates involving the Cl^- anion have the most important differences in structure depending on the method and the basis sets used, specially for the [ClBmim]+H_2O cluster. Clearly, the potential energy surface when the Cl^- anion is involved is more complex than that for the rest of ILs here studied. At the MP2 level, the minimum at 6-31++G(d,p) implies the Cl^- anion and water molecule out of the ring plane (dihedral angles of 19° and 77°, respectively) whereas for the 6-311+G(d) basis sets the water molecule is in plane with imidazolium ring. Although only single point calculations at MP2 level are performed at MP2 level with the 6-311++G(d,p) basis sets, an exception is carried out for the [ClBmim]+H_2O aggregate in order to evaluate if the inclusion of more diffuse and polarization functions gives rise to a different minimum. The

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resulting dihedral angles are 18° and 62° for Cl^- and O, respectively. This means that the minimum at 6-311++G(d,p) is alike the one at 6-31++G(d,p). Thus, the comparison of [ClBmim]-H_2O cluster structures among different methods should be evaluated carefully.

Bearing in mind the energetic and geometrical results for ILs-cosolvent aggregates it seems that B3LYP results are wrong for both energy and structure. M06-2X and B3LYP-D3 functionals reproduce quite well MP2 results although M06-HF can not be discarded. M06 functional gives rise to appropriate energetic estimations but their structures resemble the B3LYP ones.

3.2. ILs-$(H_2O)_3$ clusters.

As mentioned before, IL network in the presence of water mainly depends on the water concentration. When the content of water is high ($x_{H_2O} > 0.8$) clusters of water molecules interact with isolated ionic pairs. In order to know how this situation where H bonding gains importance is described by DFT and different basis sets the analysis of ILs-$(H_2O)_3$ aggregates is carried out. Three water molecules can interact among them and with ILs in different ways. To sample their potential energy surface (PES) the following procedure is followed: starting from the previous ILs-water clusters, the water molecule is substituted by a) a $(H_2O)_3$ cluster where the H bonding among the water molecules is maximized, that is, the three molecules interacting altogether forming a trimer. (see Fig. 7) This arrangement allows the three water molecules can interact with the anion and the cation simultaneously; b) a $(H_2O)_3$ cluster in which the first and third water molecules do not interact. This situation favours the interaction of two water molecules with the anion and the cation at the same time; c) a $(H_2O)_3$ cluster similar to case b) but where only one water molecule interacts with the IL via hydrogen bond. Empirical evidences preclude the consideration of individual water molecules interacting with the IL, thus these initial configurations have not been taking into consideration. The structures obtained by substitution are optimized at B3LYP/6-31+G(d) level of computation. These resulting minimum structures were in turn used as starting points for the prospection of the ILs-$(H_2O)_3$ PES by changing the angle and dihedral angle of the water clusters respect to the IL. It is needed to point out that although the identity of water clusters is preserved when the angles and dihedral angles are changed, no restrictions are imposed in the subsequent optimizations and water-water and water-IL arrangement can evolve freely.

For each IL the three most stable IL-$(H_2O)_3$ aggregates resulted from the PES prospection were reoptimized at MP2 level of computation using 6-31++G(d,p) and 6-311+G(d) basis sets. Single point energy calculations using 6-311++G(d) basis sets on the latter geometries are also carried out. For a comparison with other
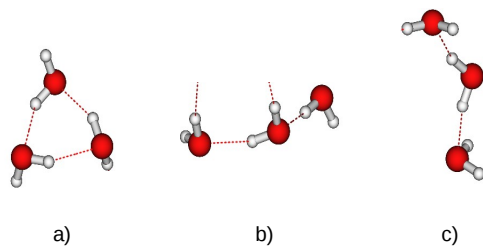
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Figure 7: Water clusters used in the prospection of the ILs-$(H_2O)_3$ PES.

methods single point calculations on the MP2 geometries at B3LYP, B3LYP-D3, M06, M06-2X, M06-HF levels are carried out. Although it has been already seen that B3LYP functional do not perform properly, it was kept in this part of the study to see if the increase of the number of water molecules in the aggregate contributes to a better description in the case of the lack of dispersion corrections. At this point it is worth pointing out that the complexity of the multidimensional ILs-$(H_2O)_3$ PES does not preclude the existence of other minima. However, the exploration of all the minima is out of the scope of this study.
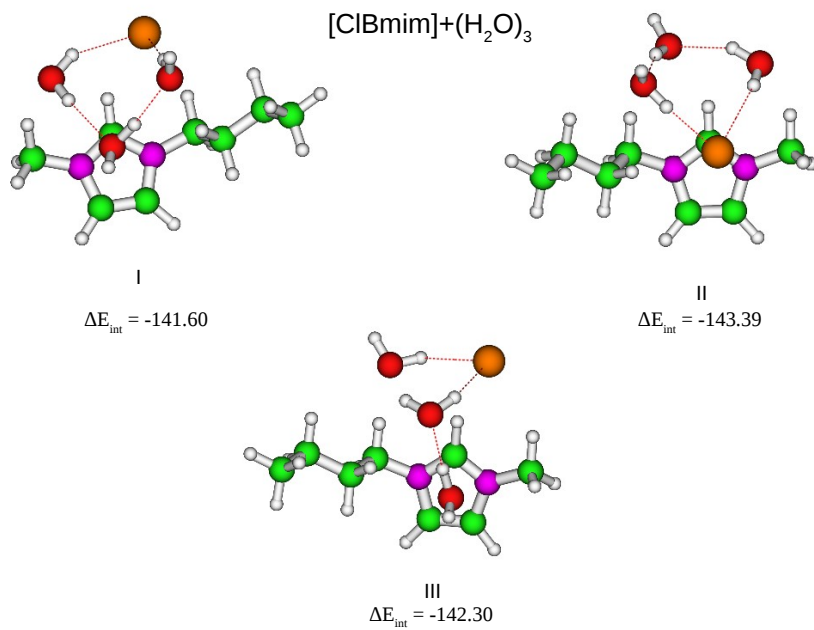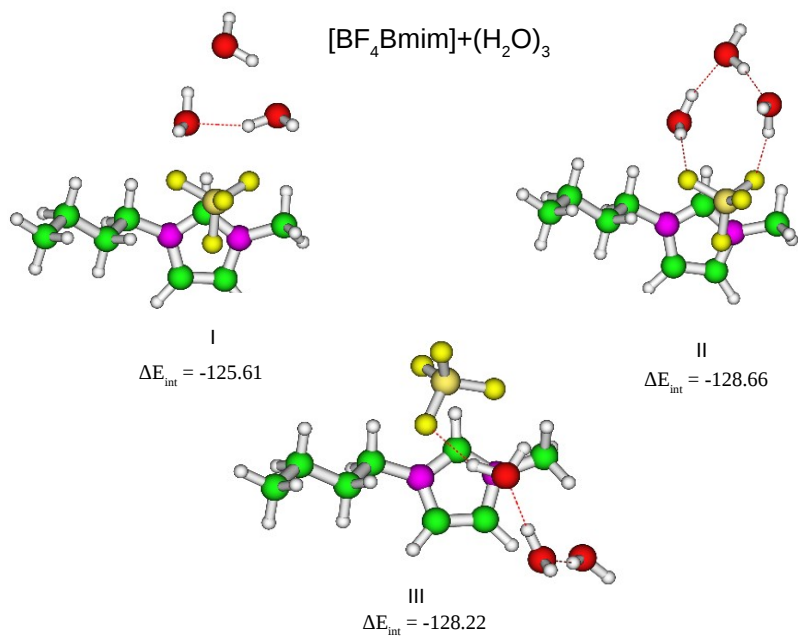
There are not important structural differences between the minima obtained with 6-31++G(d,p) and 6-311+G(d) basis sets. Fig. 8 collects the ILs-$(H_2O)_3$ clusters optimized at MP2/6-311+G(d). At the first moment it could be thought that the most stable structures would be those that maximize the interaction among the water molecules with the anion and the H_a atom of the ring. Nevertheless, the comparison of the three minima indicates that there is not a unique mode of interaction between water clusters and ILs. Besides, the position of the anion respect to the cation also differs being in the plane of the ring, over or in an intermediate situation. Again, and in spite of the importance of the H bonding among the water molecules it is necessary to take into consideration all the possible interactions including the less H acidic atoms, the π cloud of the ring and the alkyl chains to properly understand the ILs-$(H_2O)_3$ aggregates.

Fig. 9 contains the unCP and averCP interaction energies for the ILs-$(H_2O)_3$ clusters optimized at MP2 level and the single point DFT estimations.

The comparison of MP2 results using different basis sets indicates that the interaction energies are closer when extra diffuse and polarization basis sets are considered. Actually, the results for 6-311+G(d) and 6-311++G(d,p) are based on the same structures, the difference just being the basis sets. This is more relevant than in the case of the ILs-cosolvent aggregates due to the larger H bonding interaction when water clusters are present. A good election of basis sets gains importance in the case water-water interactions where the inclusion of extra diffuse and polarization basis set seems to be advisable.

The analysis of the profiles given by each method shows that the relative stability of the clusters barely changes when the unCP and averCP results are compared. The only exception is found for the $[PF_6Bmim]+(H_2O)_3$ clusters. In this case the unCP estimations indicate that the stability order of the clusters is II>I>III while the averCP results give rise to I>III>II.

The comparison of the results denotes that the trend followed by B3LYP regarding the ILs containing the Cl^- ions is different from that given by the remaining methods, in the sense that cluster II is the least stable whereas it is the most stable for the rest of the methods. In addition, a different tendency appears when the stability between cluster III for the Cl^- ion and cluster I for the $CH_3SO_3^-$ ion

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[BF$_4$Bmim]+(H$_2$O)$_3$

I
ΔE_{int} = -125.61

II
ΔE_{int} = -128.66

III
ΔE_{int} = -128.22

[ClBmim]+(H$_2$O)$_3$

I
ΔE_{int} = -141.60

II
ΔE_{int} = -143.39

III
ΔE_{int} = -142.30

$[CH_3SO_3Bmim]+(H_2O)_3$

I
$\Delta E_{int} = -141.50$

II
$\Delta E_{int} = -145.94$

III
$\Delta E_{int} = -141.28$

$[PF_6Bmim]+(H_2O)_3$

I
$\Delta E_{int} = -125.62$

II
$\Delta E_{int} = -125.21$

III
$\Delta E_{int} = -124.20$
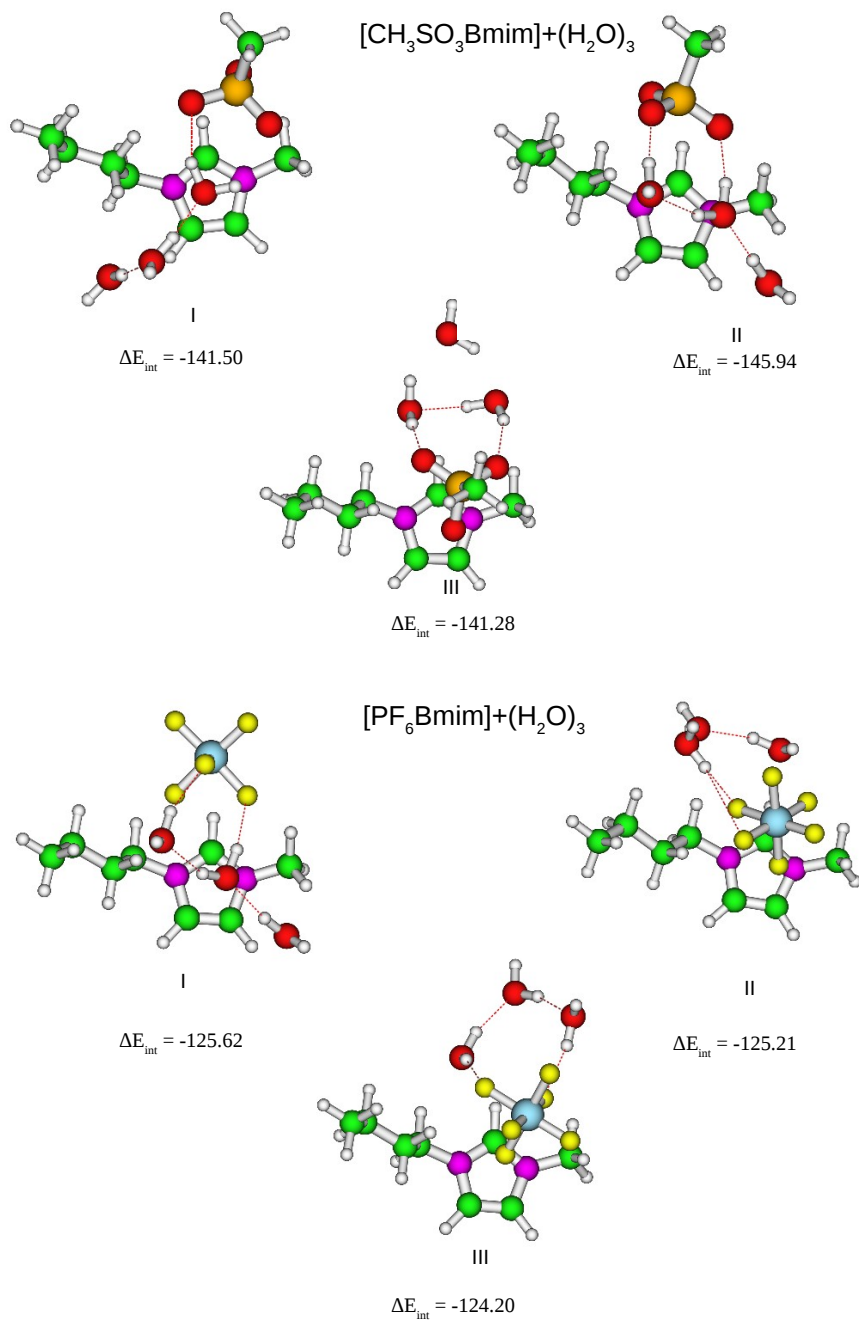
Figure 8: Optimized structures at MP2/6-311+G(d) level and interaction energies in kcal/mol obtained at MP2/6-311+G(d)//MP2/6-311++G(d,p) level for the ILs-$(H_2O)_3$ clusters.
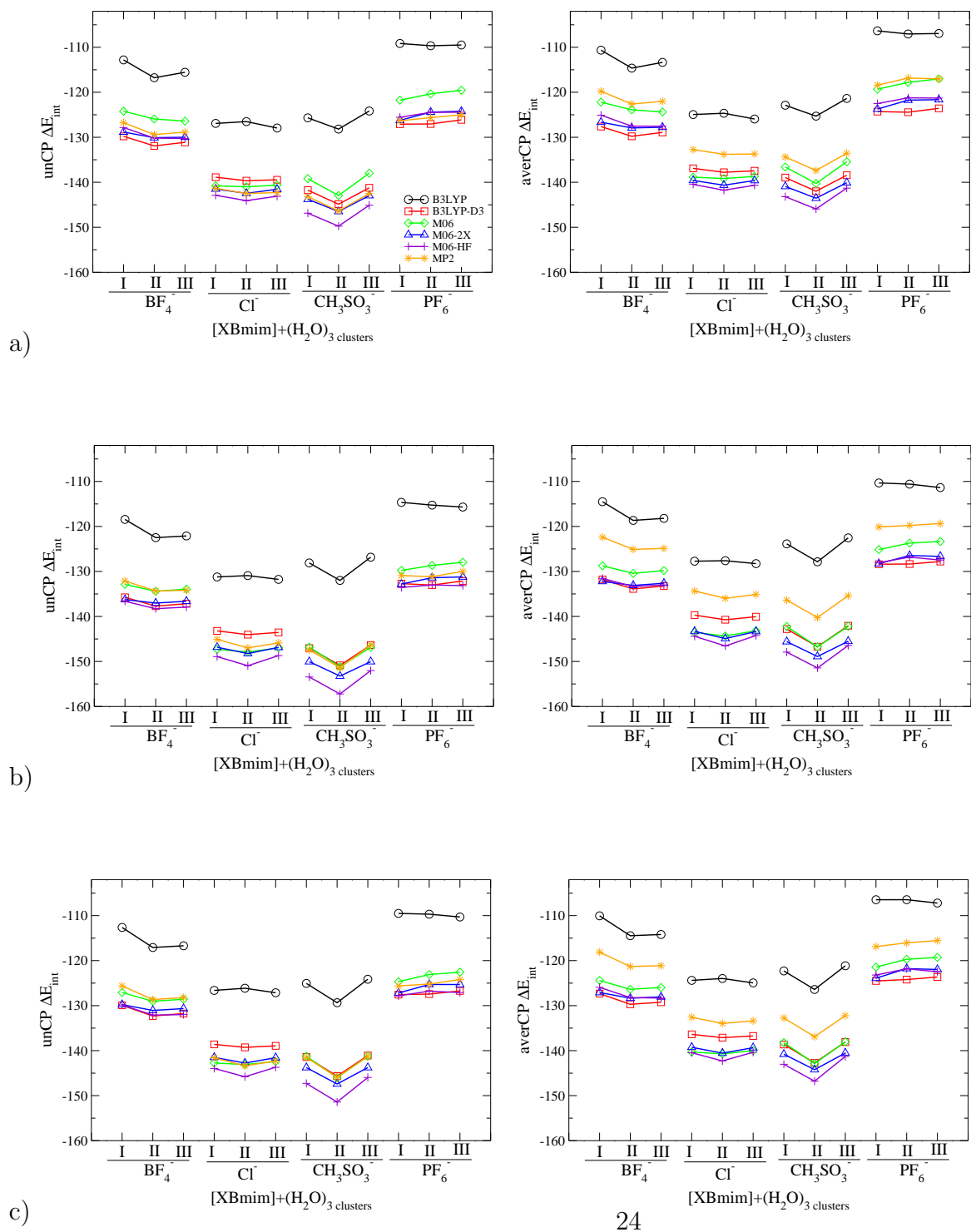
a)

b)

c)

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Figure 9: Plot of unCP ΔE_{int} (left) and averCP ΔE_{int} (right) for the ILs-$(H_2O)_3$ clusters optimized at MP2 level with a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets. The labels are related with the minima shown in Fig. 12.

are compared. unCP and averCP B3LYP and averCP M06 results indicate that the chloride cluster is more stable than the methanesulfonate one whereas the remaining methods, including MP2, give rise to the opposite results. Although this is not significant when only one anion is considerd could have important implications when the comparison among different ILs is performed.

Important discrepancies appear between DFT and MP2 results, partially due to the large BSSE affecting MP2 with Pople basis sets. As it occurred for the ILs-cosolvent clusters, B3LYP functional underestimates the interaction energies in a non negligible amount for both unCP and averCP results. Altough B3LYP offers some improvement of accuracy respect to the ILs-cosolvent clusters, it is too small to be of any practical significance. Contrary to the case of one cosolvent molecule, B3LYP-D3 functional overestimated the interaction energy of clusters containing polar ions and underestimeted those with non polar anions. M06 functional provides the best resemblance with MP2 estimations although not reproduced relative stabilities between Cl^- and $CH_3SO_3^-$ ILs. This can be due to the differences found in the geometry of the ILs-cosolvent clusters between MP2 and M06. The latter supplies more open structures and these variations can be the cause of different estimations of the PES. Although M06-2X and M06-HF functionals diverge from MP2 results are able to reproduce the averCP MP2 profiles in all cases, that is, for a given anion and among the ILs.

The trend followed by the functionals here analyzed depends on the anion nature and in the case of B3LYP-D3 and M06 functionals on the number of water molecules considered in the aggregates.

4. Concluding Remarks.

In this paper we carried out a systematic study of ILs-cosolvent clusters at different levels of computation using DFT and MP2 as a reference data.

We find that the inclusion of dispersion into the DFT approach is required in order to obtain reasonable results. The dispersion-corrected DFT methods here tested produce results of variable quality, as measured by deviation relative to the MP2 reference values.

B3LYP functional is not able to recover all the ingredients to describe properly these systems regardless the nature of the anion, cosolvent and the number of cosolvent molecules. The performance of DFT dispersive corrected methods is rather similar for water and ethanol as a cosolvent but it depends on anion nature. This way, M06-2X gives the best accuracy when the unCP energies are considered whereas the averCP energies suggest that M06 and B3LYP-D3 functionals performs better for polar and non polar anions, respectively. The reproduction of the MP2 structures follows the trend M06-2X > B3LYP-D3 ∼ M06-HF > M06 >

B3LYP. From the structural point of view, B3LYP and M06 functionals describe more open structures whereas the B3LYP-D3, M06-2X and M06-HF structures resemble to a great extent MP2 results.

The influence of the number of water molecules is not negligible for B3LYP-D3 and M06 functionals while M06-2X and M06-HF results maintain their behaviour although decrease their performance. This independence on the number of water molecules considered is important for describing ILs-cosolvent solutions with DFT because it is essential not only to reproduce well IL-cosolvent interactions but also cosolvent-cosolvent ones in the ensemble of the system.

The election of the basis sets is also crucial for a good description. As occurred for weakly bonded system when the quality of the basis set is low the unCP or averCP energies must be used due to cancellation errors. The inclusion of extra diffuse functions and polarization is also required specially in the case of ILs interacting with water clusters. Although 6-31++G(d,p) and 6-311++G(d,p) perform in similar way, the former overestimates the cation-anion binding energy what can have relevant implications due to the importance of this interactions in the global arrangement of ILs-cosolvent systems.

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