

1 Assessment of the Performance of Commonly Used
2 DFT Functionals vs. MP2 in the Study of IL-Water,
3 IL-Ethanol and IL-(H₂O)₃ Clusters.

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7 **Abstract**

8 We present a comparative study of the accuracy of different DFT approaches
9 *vs.* MP2 for evaluating Ionic Liquids (ILs) + cosolvent. Namely, we are inter-
10 interested in [XBmim] + cosolvent (X being Cl⁻, BF₄⁻, PF₆⁻, and CH₃SO₃⁻
11 anions and cosolvent being water or ethanol) and [XBmim] +(H₂O)₃ clusters.
12 In this study the B3LYP, B3LYP-D3, M06, M06-2X and M06-HF functionals
13 with Pople and Dunning basis sets are considered. We find that the influ-
14 ence of the basis sets is a factor to take into consideration. As already seen
15 for weakly bonded systems when the basis set quality is low the uncorrected
16 counterpoise (unCP) or averaging counterpoise (averCP) energies must be
17 used due to cancellation errors. Besides, the inclusion of extra diffuse func-
18 tions and polarization is also required specially in the case of ILs interacting
19 with water clusters. The B3LYP functional does not reproduce either the
20 structure or the interaction energies for ILs+H₂O and ILs+EtOH aggregates,
21 the energetic discrepancies being more significant than the structural ones.
22 Among the dispersive corrected functionals, M06-2X results resemble to a
23 great extent the reference data when the unCP interaction energies are con-
24 sidered for both water and ethanol. In turn, M06 and B3LYP-D3 functionals
25 are the best option for ILs containing polar and non polar anions, respec-
26 tively, whether the averCP interactions energies are taking into considera-
27 tion. From the structural point of view, B3LYP and M06 functionals describe
28 more open structures whereas B3LYP-D3, M06-2X and M06-HF structures
29 resemble quite well MP2 results. When the number of water molecules in-
30 creases the H bonding motif gains importance and the effect depends on the
31 underlying functional. Only M06-2X and M06-HF behaviour is similar to

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

5 *Keywords:* Ionic Liquids; water; ethanol; DFT; MP2.

6 **1. Introduction.**

7 Over the last few years the versatile nature of the ionic liquids (ILs) has
8 increased their interest in both academia and industry.[1, 2, 3, 4, 5, 6, 7] Their
9 double featuring as solvents and templates allow them to play a significant
10 role in the synthesis of inorganic materials. Several examples are available
11 describing their use in the preparation of ordered mesoporous materials[8, 9,
12 10, 11, 12] or zeolites.[12, 13, 14, 15, 16, 17] Recently, the use of imidazolium
13 ILs based for the synthesis of zeolites has been published.[18] It is found that
14 the silicon source determines the formation of BEA (Beta Polymorph A) or
15 MFI (Mordenite Framework Inverted) zeolites. Depending on this source,
16 different preorganized complexes are obtained that result in the formation of
17 a given zeolite structure. In the presence of ethanol, the ionic liquid forms
18 preorganized complexes that drive the formation of MFI. In its absence,
19 BEA is obtained. In addition, the anion nature is revealed as a determi-
20 nant factor. This way, [ClBmim] and [CH₃SO₃Bmim] (where Bmim means
21 1-butyl-3-methylimidazolium) ILs succeed in their role of structure directing
22 agents while [BF₄Bmim] and [PF₆Bmim] ILs failed in this task and an amor-
23 phous material is obtained.[19] On the basis of these results it is interesting
24 to get insight into the microscopic nature of water/IL and ethanol/IL mix-
25 tures. The local structural organization and physicochemical properties of
26 these ILs-cosolvent aggregates can provide an explanation of their templating
27 function in the zeolite structure formation. However, it must be concerned
28 that the study of ILs is a challenge for computational chemistry. Although
29 ILs consist entirely of ions and, consequently, are dominated by coulombic
30 forces, additional specific non covalent interactions are also present. Disper-
31 sion interactions due to electron correlation like van der Waals interactions
32 among alkyl chains on the cations, π - π stacking interactions between cations
33 and cation-anion, and the H bonding between polar groups play a signifi-
34 cant role in a good description of these systems. When a protic cosolvent
35 like water or ethanol is considered H bondings gain importance. The proper

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

3 As previously mentioned, the description of the π - π cation stacking is es-
4 sential in the context of ILs. Nevertheless, in the case of water and ethanol-
5 ILs mixtures the extension of the IL network widely depends on the cosolvent
6 concentration. This way when the $x_{\text{H}_2\text{O}} > 0.8$ a reduction of the cohesions
7 between anions and cations is observed.[20, 21, 22, 23, 24, 25, 26, 27, 28, 29]
8 At these conditions, the original ion networks are no longer available and new
9 water-cation/water-anion networks appear.[20, 22, 23, 24, 25, 26, 27, 28, 29,
10 30] This process induces changes in several structural and dynamic proper-
11 ties of the liquid[21, 31] and it can end up with the mere interaction of water
12 molecules with an ion pair. When the cosolvent is ethanol, the extension of
13 the IL network disruption is less dramatic and larger ionic clusters appear
14 in the IL-alcohol mixture due to the fact that ethanol molecules are much
15 more homogeneously placed in the structure of the IL even at high ethanol
16 concentrations.[32, 33] Regarding the tertiary ILs/water/ethanol mixture,
17 Wu et al.[34] concluded that ethanol molecules are capable of breaking the
18 complexes cation \cdots HOH \cdots anion via cation-water and anion-water interac-
19 tions. As a result, the addition of ethanol weakens the interaction of ILs
20 with water. In these situations π - π stacking interactions between cations
21 disappear and the interactions with the cosolvent gain importance.

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

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

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

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

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

8 **2. Computational Methods.**

9 Quantum mechanics optimizations of [XBmim] + H₂O, [XBmim] + EtOH
10 and [XBmim] + (H₂O)₃ aggregates (X being Cl⁻, BF₄⁻, PF₆⁻, and CH₃SO₃⁻
11 anions) are carried out. The initial structures for the [XBmim] + H₂O and
12 [XBmim] + EtOH clusters were taken from previous gas-phase structure
13 optimizations in our group.[19] The [XBmim] + (H₂O)₃ aggregates are gener-
14 erated as indicated in the next section. As density functionals, the hybrid
15 B3LYP[60, 61], B3LYP-D3 that includes Grimme’s third version of an empir-
16 ical correction[38], and a number of functionals of the Minnesota M06 family:
17 M06, M06-2X and M06-HF are tested.[40, 41, 42] These functionals are cho-
18 sen because previous studies[43] conclude that a large contribution from the
19 HF exchange is one of the key components of any DFT functional to accu-
20 rately account for the dispersion contribution of hydrogen bonding in ILS.
21 MP2 level of computation is selected as reference data for future comparisons
22 with the DFT results. Pople basis sets are used, namely, the 6-31++G(d,p),
23 6-311+G(d) and 6-311++G(d,p) basis sets. This election is motivated by
24 the common use of these basis sets in the description of these systems, the
25 goodness of two latter in previous results[44, 49] and as a compromise be-
26 tween computational cost and reasonable accuracy. Due to the slight varia-
27 tions in geometry when going from 6-311+G(d) to 6-311++G(d,p) basis sets,
28 MP2 optimizations at 6-311++G(d,p) basis sets are avoided and only single
29 point calculations on the 6-311+G(d) structures are carried out. It is well
30 known that MP2 results with Pople basis sets present larger BSSE than DFT
31 methods. For this reason, single point calculations using aug-cc-pVDZ and
32 aug-cc-pVTZ basis set are also carried out to evaluate the effect on our con-
33 clusions. The CP correction using the procedure of Boys and Bernardi[50]
34 is computed. In all cases, fully optimized structures are characterized by
35 computing second energy derivatives. Computations are carried out by the
36 Gaussian09 program.[62]

1 **3. Results and Discussion.**

2 *3.1. ILs-ethanol and ILs-water clusters.*

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

19 The interaction energy of each cluster is computed as usual as the differ-
20 ence among the whole cluster and the monomers,

$$\Delta E_{\text{int}} = E(X_1, X_2, \dots, X_n) - \sum_i^n E(1)(X_i) \quad (1)$$

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

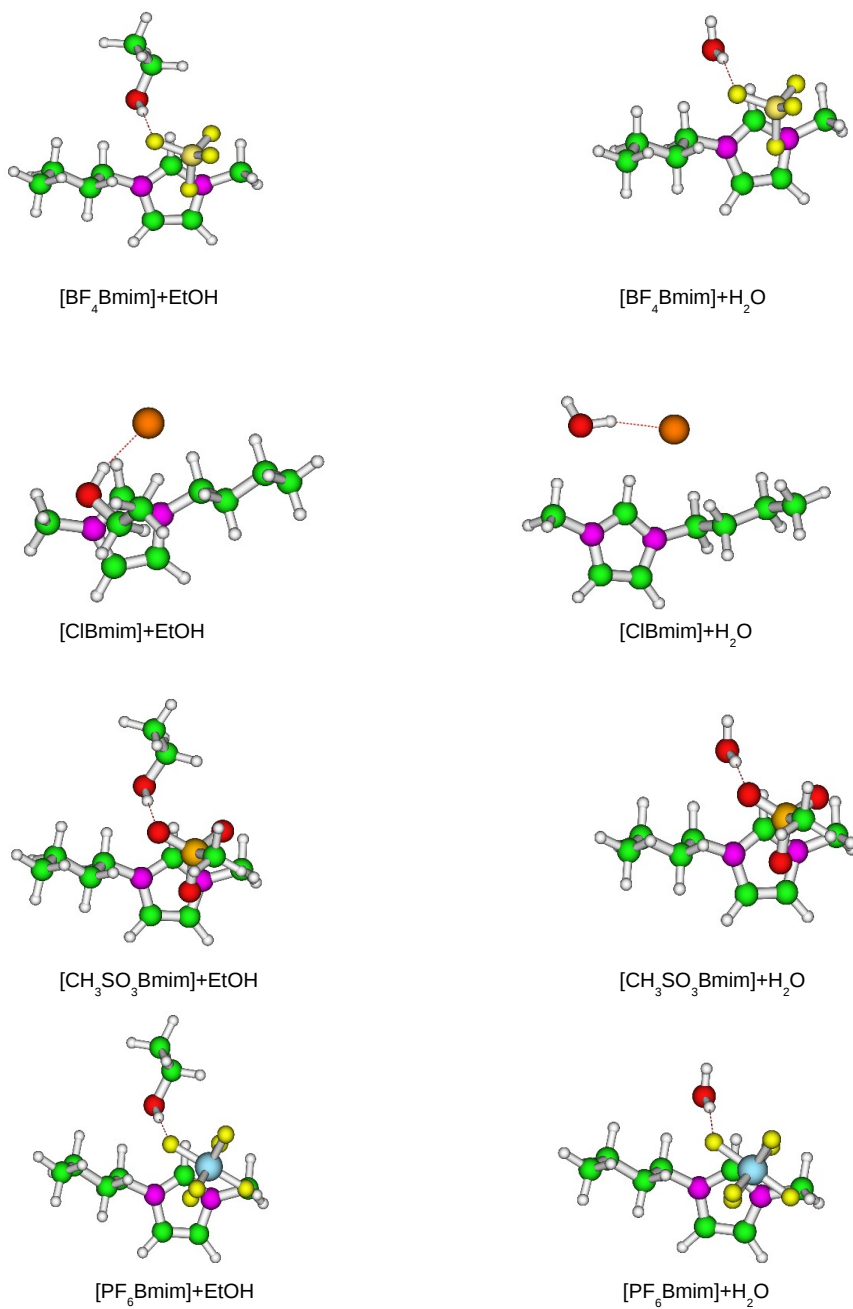
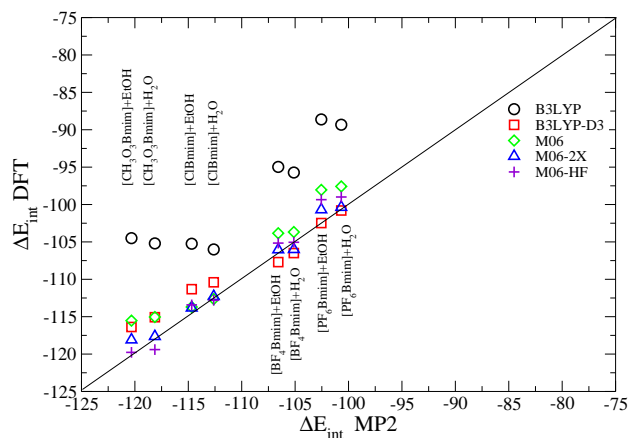
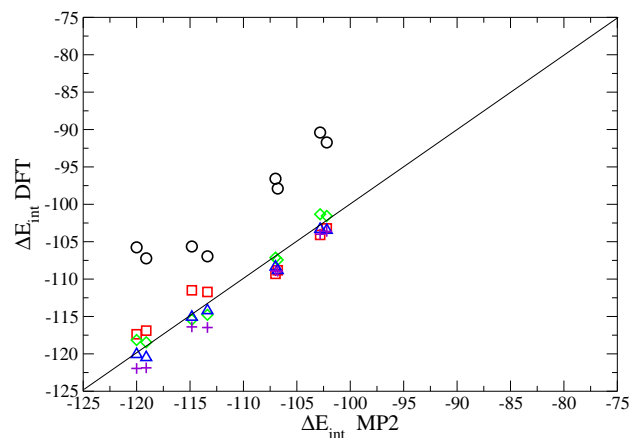


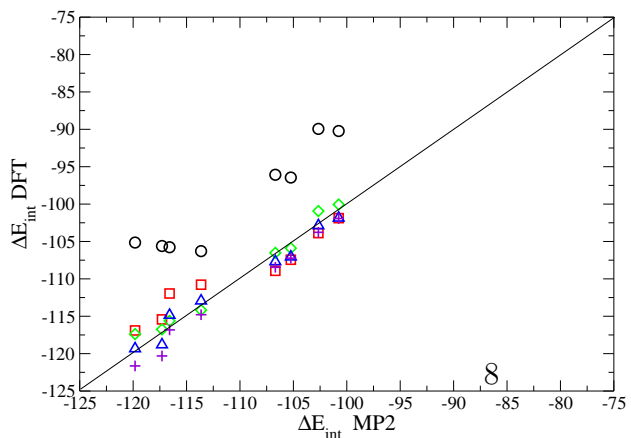
Figure 1: Optimized structures obtained at MP2/6-311+G(d) for the ILs-cosolvent clusters.



a)



b)



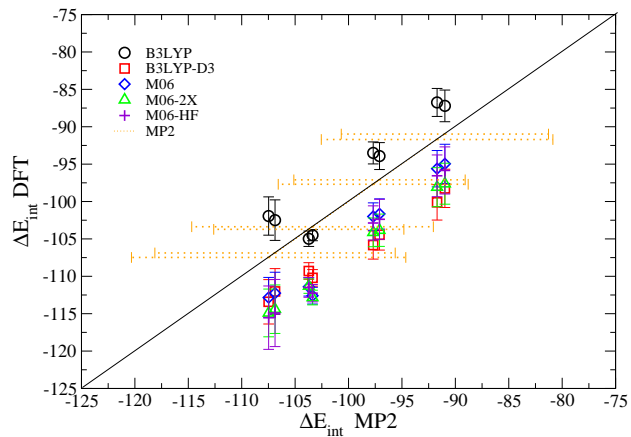
c)

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.

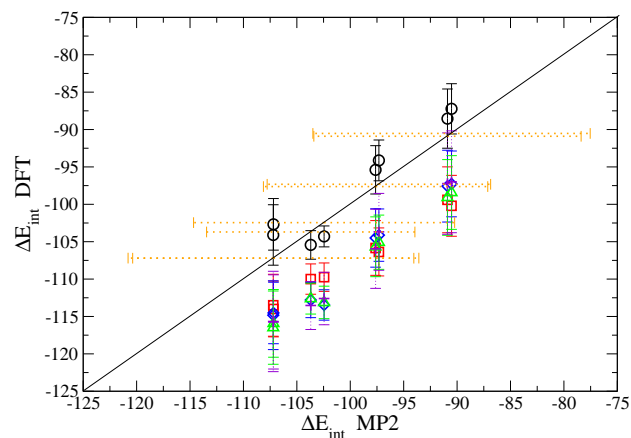
1 with ILS in ILS/water/ethanol mixtures.[34, 63]. The results for the remain-
2 ing functionals depend on the basis sets. The interaction energies with extra
3 diffuse and polarization basis sets (6-31++G(d,p) and 6-311++G(d,p)) fol-
4 low the MP2 trend whereas those with 6-311+G(d) basis sets are between
5 B3LYP and MP2. It is well-known[64, 65] the importance of the diffuse func-
6 tions in the description of the H bonding, specially when anionic species are
7 involved. This fact can be an issue in the differences between 6-31++G(d,p)
8 and 6-311++G(d,p), and 6-311+G(d) results. This topic will be treated in
9 more detailed in the next section.

10 Fig. 3 shows the CP DFT interaction energies *vs.* the CP MP2 values
11 for the ILS-ethanol and ILS-water clusters optimized at 6-31++G(d,p), 6-
12 311+G(d) and 6-311++G(d,p) basis sets. For the sake of comparison, BSSE
13 has been included as a bar error. The analysis of Fig. 3 shows that BSSE
14 correction represents only a small fraction ($\pm 1-5\%$) of the interaction energy
15 for B3LYP, B3LYP-D3, M06 and M06-2X. Although still small, BSSE is
16 a bit larger for M06-HF ($\pm 1-7\%$). However, it is far more important for
17 MP2 results ($\pm 8-13\%$). As a rule, BSSE increases with increasing number
18 of electrons, *i.e.* size of the anion.[43] This way, BSSE contribution is the
19 smallest for ILS containing the Cl^- anion and the largest for those with the
20 CH_3SO_3^- one. Finally, Fig. 4 plots the averCP DFT interaction energies *vs.*
21 the averCP MP2 values for the ILS-ethanol and ILS-water clusters optimized
22 at 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets. Certainly, the
23 inclusion of BSSE correction changes the interpretation of the results.

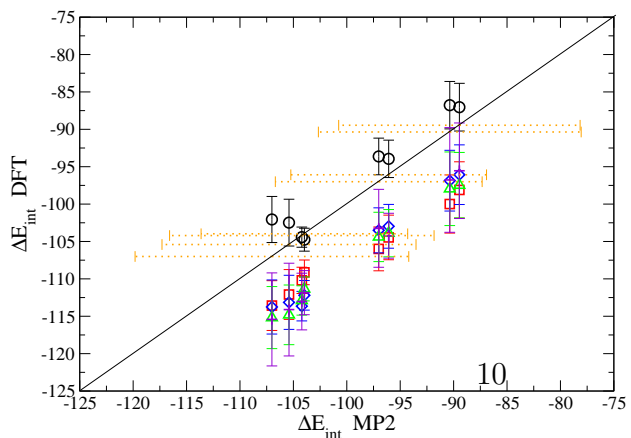
24 When BSSE is neglected, Fig. 2 shows that M06-2X results present the
25 best resemblance to the MP2 interaction energies using 6-31++G(d,p), the
26 largest deviation is 2.23 kcal/mol for the $[\text{CH}_3\text{SO}_3\text{Bmim}]+\text{EtOH}$ aggregate.
27 M06-HF interaction energies also present a small divergence from MP2 re-
28 sults followed by B3LYP-D3 and M06 functionals. With no doubt, B3LYP
29 functional underestimates MP2 interactions energies giving the worst results.
30 The analysis of Fig. 2 considering 6-311+G(d) and 6-311++G(d,p) basis sets
31 produces similar conclusions but now M06-2X and M06 can be considered
32 the most accurate functionals in comparison with the MP2 reference data.
33 Although still close, M06-HF and B3LYP-D3 interaction energies present
34 higher mean absolute errors, specially in the case of polar anions. Again,
35 the B3LYP functional disagrees more than 10 kcal/mol with the MP2 re-
36 sults. No matter the basis sets, the B3LYP functional does quite poorly for
37 the resemblance with MP2 results. The behaviour of the rest of functionals
38 depends on the the cluster and basis sets but, in general, B3LYP-D3 func-



a)

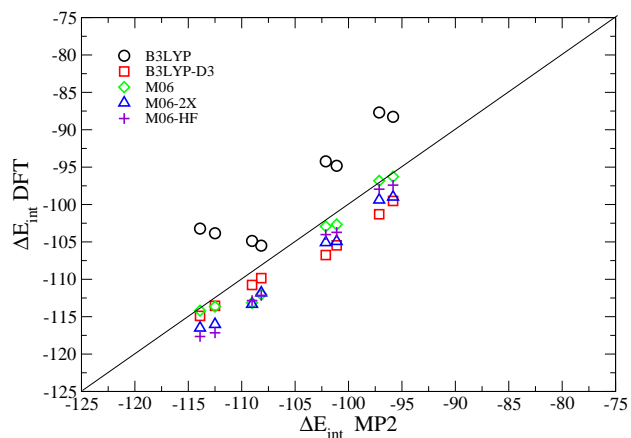


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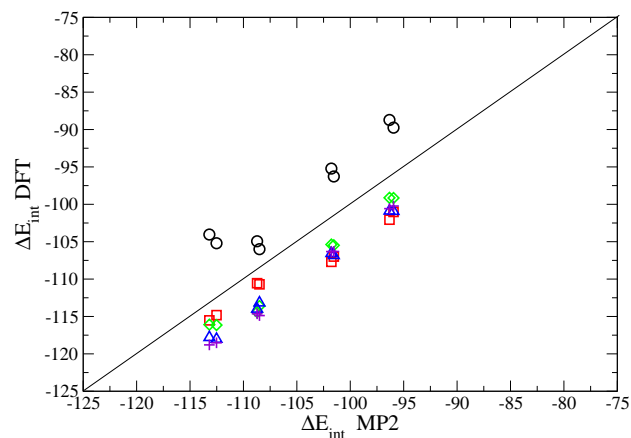


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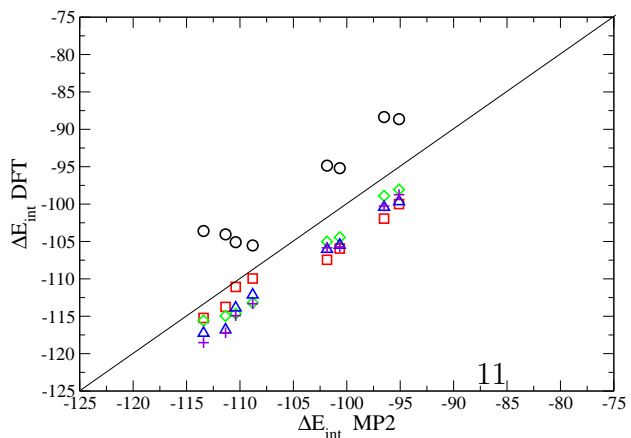
Figure 3: Plot of CP ΔE_{int} DFT vs. CP ΔE_{int} MP2 for the optimized ILS-ethanol and ILS-water clusters using a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets. BSSE has been included as a bar error.



a)



b)



c)

Figure 4: Plot of averCP $\Delta E_{int}DFT$ vs. averCP $\Delta E_{int}MP2$ 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.

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

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

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

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

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

35 The analysis of Fig. 5 indicates that the behaviour is not exactly the same
36 as that obtained in optimized clusters. The order from better to worse repro-
37 duction of the unCP MP2 results is the following: $\text{M06-2X} \sim \text{M06-HF} > \text{M06}$
38 $> \text{B3LYP-D3} > \text{B3LYP}$ (but in the case of 6-31++G(d,p) where the order

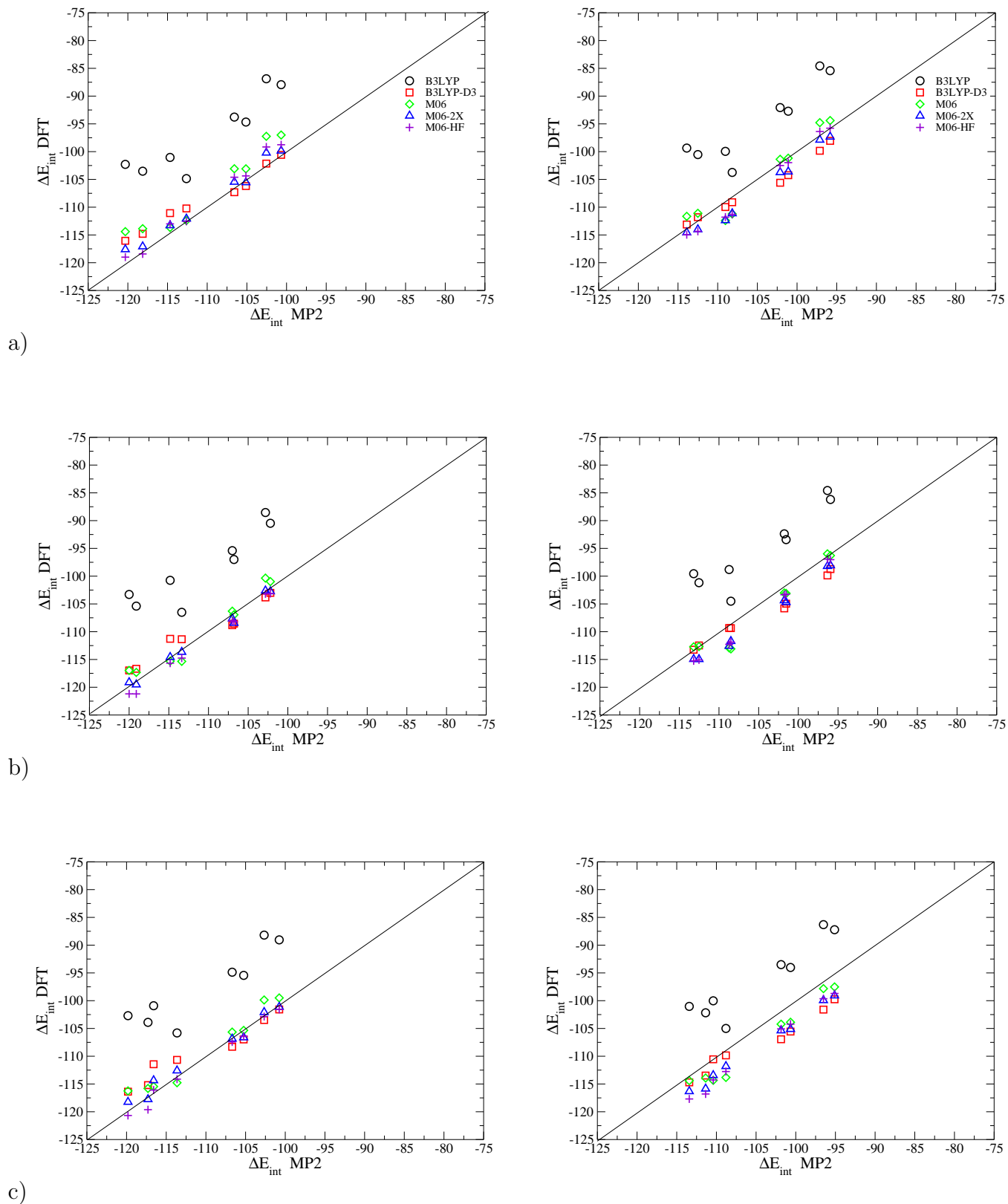


Figure 5: Plot of unCP $\Delta E_{int}DFT$ vs. unCP $\Delta E_{int}MP2$ (left) and averCP $\Delta E_{int}DFT$ vs. averCP $\Delta E_{int}MP2$ (right) for the ILs-ethanol and ILs-water clusters optimized at MP2 level with a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets.

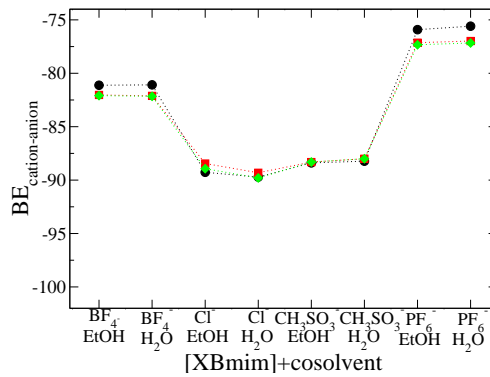
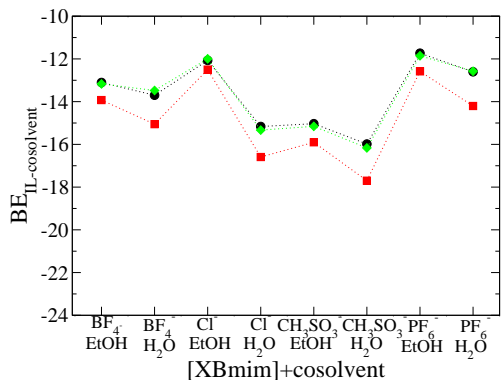
1 between M06 and B3LYP-D3 is exchanged). Again, B3LYP energies differ
2 from MP2 results in an important amount but now M06-HF improves its
3 accuracy. As occurred in the case of the optimized clusters when the averCP
4 results are analyzed, B3LYP-D3 functional reproduces better the aggregates
5 with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

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

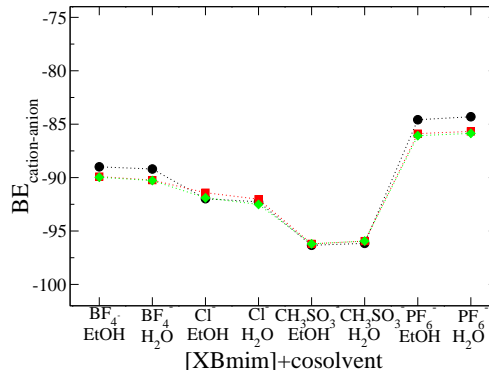
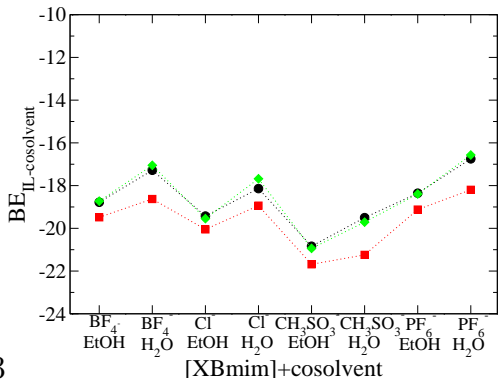
19 Due to the discrepancies found on the relative stabilities of the ILs-ethanol
20 and ILs-water clusters as a function of the method, IL-cosolvent and cation-
21 anion interactions in the geometry of the cluster are also evaluated. Fig. 6
22 shows the comparison of IL-cosolvent and cation-anion binding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

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

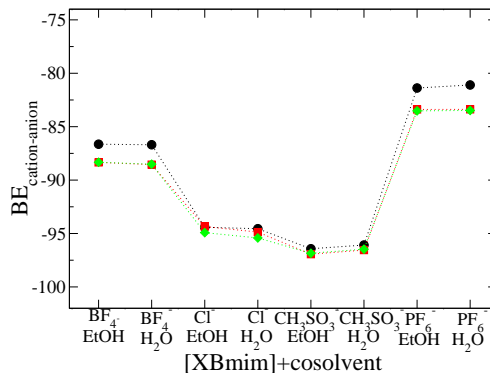
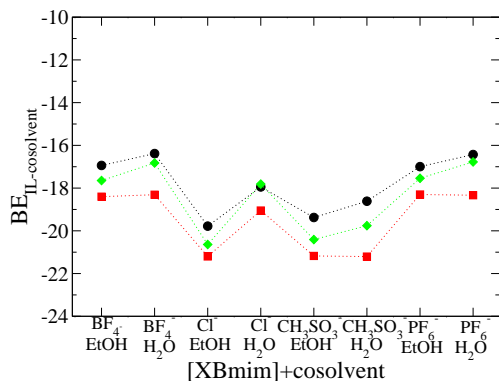
$$BE_{\text{cation-anion}} = E(\text{IL}) - E(\text{cation}) - E(\text{anion}) \quad (3)$$



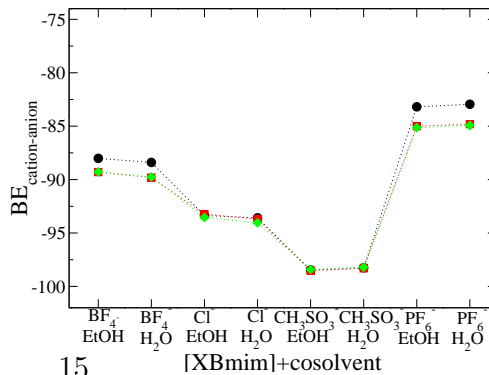
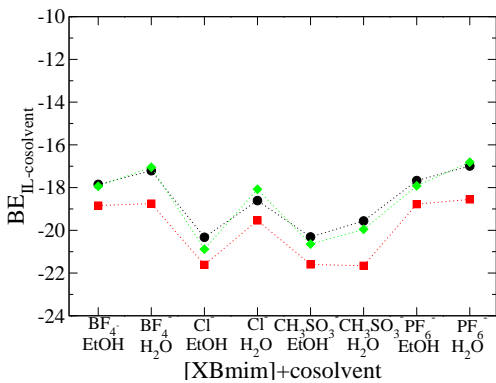
B3LYP



B3LYP-D3

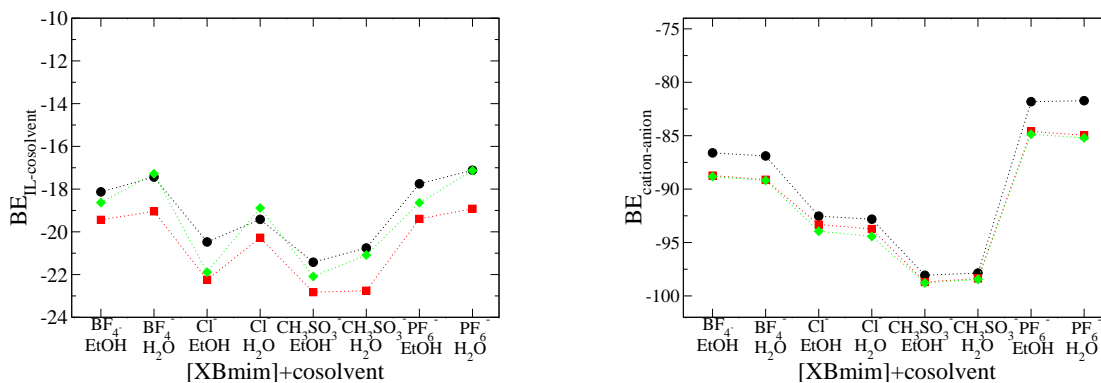


M06



M06-2x

M06-HF



MP2

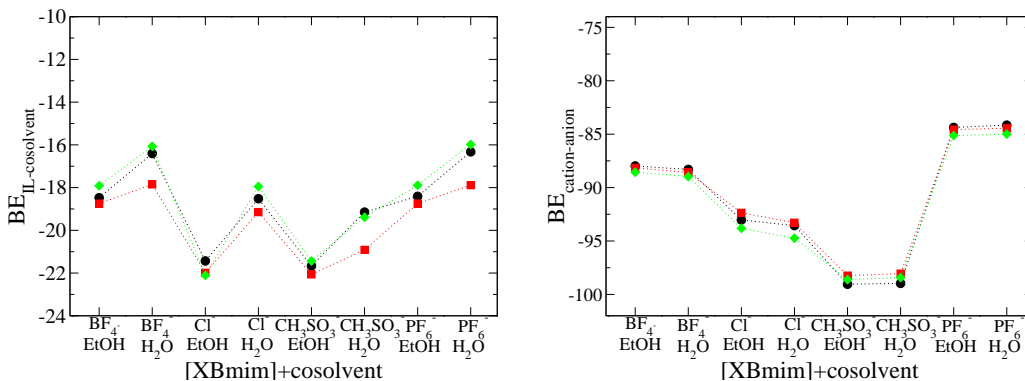


Figure 6: Plot of the DFT and MP2 IL-cosolvent (left) and cation-anion (right) binding energies for the ILs-cosolvent clusters optimized at MP2 level with 6-31++G(d,p) (black), 6-311+G(d) (red) and 6-3111++G(d,p) (green) basis sets.

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.

	6-31++G(d,p)						6-31+++G(d)						6-31++++G(d,p)											
	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X				
Distance ^a																								
BF ₃ 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	0.18	0.14	0.20	0.13	0.14	0.16	0.17	0.15	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	0.19	0.22	0.28	0.13	0.19	0.13	0.19	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	0.11	0.15	0.13	0.16	0.16	0.16	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	0.14	0.14	0.22	0.13	0.14	0.16	0.15	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	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X
BF ₃ 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	11.82	4.42	7.65	5.94	5.94	11.82	4.42	7.65	5.94	
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	26.05	12.19	17.96	25.19	25.19	25.32	26.05	12.19	17.96	
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	4.09	13.50	6.16	8.86	12.37	4.77	6.16	8.86	12.37	
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	12.11	3.24	4.66	2.60	2.60	1.22	3.24	4.66	2.60	
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	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X	B3LYP	B3LYP-D3	M06	M06-HF	M06-2X
BF ₃ 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	17.62	4.53	7.53	5.79	5.79	11.09	4.53	7.53	5.79	
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	59.18	23.24	26.13	40.53	40.53	34.11	23.24	26.13	40.53	
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	19.58	8.31	11.30	5.52	5.52	3.12	8.31	11.30	5.52	
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	18.15	3.00	6.56	3.12	3.12	1.41	3.00	6.56	3.12	

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

^aThe 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. ^bThe 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. ^cThe 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.

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

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

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

30 It is necessary to comment that the aggregates involving the Cl^- anion have
31 the most important differences in structure depending on the method and the basis
32 sets used, specially for the [ClBmim]+ H_2O cluster. Clearly, the potential energy
33 surface when the Cl^- anion is involved is more complex than that for the rest of
34 ILs here studied. At the MP2 level, the minimum at 6-31++G(d,p) implies the
35 Cl^- anion and water molecule out of the ring plane (dihedral angles of 19° and
36 77° , respectively) whereas for the 6-311+G(d) basis sets the water molecule is in
37 plane with imidazolium ring. Although only single point calculations at MP2 level
38 are performed at MP2 level with the 6-311++G(d,p) basis sets, an exception is
39 carried out for the [ClBmim]+ H_2O aggregate in order to evaluate if the inclusion
40 of more diffuse and polarization functions gives rise to a different minimum. The

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

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

10 3.2. *ILs-(H_2O)₃ clusters.*

11 As mentioned before, IL network in the presence of water mainly depends
12 on the water concentration. When the content of water is high ($x_{\text{H}_2\text{O}} > 0.8$)
13 clusters of water molecules interact with isolated ionic pairs. In order to know
14 how this situation where H bonding gains importance is described by DFT and
15 different basis sets the analysis of ILs-(H_2O)₃ aggregates is carried out. Three
16 water molecules can interact among them and with ILs in different ways. To
17 sample their potential energy surface (PES) the following procedure is followed:
18 starting from the previous ILs-water clusters, the water molecule is substituted by
19 a) a (H_2O)₃ cluster where the H bonding among the water molecules is maximized,
20 that is, the three molecules interacting altogether forming a trimer. (see Fig. 7)
21 This arrangement allows the three water molecules can interact with the anion and
22 the cation simultaneously; b) a (H_2O)₃ cluster in which the first and third water
23 molecules do not interact. This situation favours the interaction of two water
24 molecules with the anion and the cation at the same time; c) a (H_2O)₃ cluster
25 similar to case b) but where only one water molecule interacts with the IL via
26 hydrogen bond. Empirical evidences preclude the consideration of individual water
27 molecules interacting with the IL, thus these initial configurations have not been
28 taking into consideration. The structures obtained by substitution are optimized
29 at B3LYP/6-31+G(d) level of computation. These resulting minimum structures
30 were in turn used as starting points for the prospection of the ILs-(H_2O)₃ PES by
31 changing the angle and dihedral angle of the water clusters respect to the IL. It
32 is needed to point out that although the identity of water clusters is preserved when
33 the angles and dihedral angles are changed, no restrictions are imposed in the
34 subsequent optimizations and water-water and water-IL arrangement can evolve
35 freely.

36 For each IL the three most stable IL-(H_2O)₃ aggregates resulted from the PES
37 prospection were reoptimized at MP2 level of computation using 6-31++G(d,p)
38 and 6-311+G(d) basis sets. Single point energy calculations using 6-311++G(d)
39 basis sets on the latter geometries are also carried out. For a comparison with other

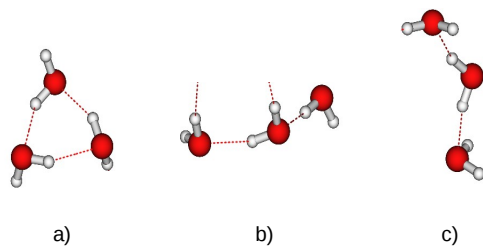


Figure 7: Water clusters used in the prospection of the $\text{ILs}-(\text{H}_2\text{O})_3$ PES.

1 methods single point calculations on the MP2 geometries at B3LYP, B3LYP-D3,
2 M06, M06-2X, M06-HF levels are carried out. Although it has been already seen
3 that B3LYP functional do not perform properly, it was kept in this part of the
4 study to see if the increase of the number of water molecules in the aggregate
5 contributes to a better description in the case of the lack of dispersion corrections.
6 At this point it is worth pointing out that the complexity of the multidimensional
7 ILS-(H₂O)₃ PES does not preclude the existence of other minima. However, the
8 exploration of all the minima is out of the scope of this study.

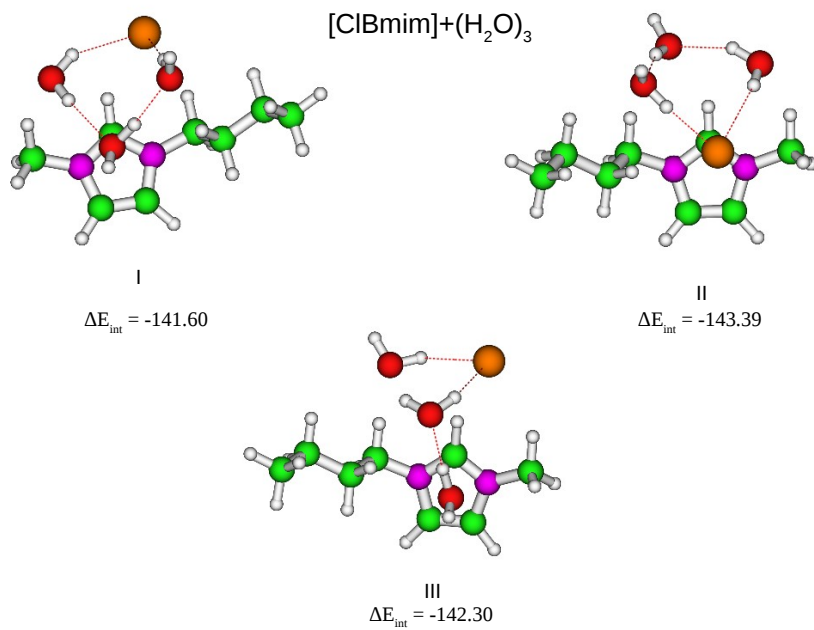
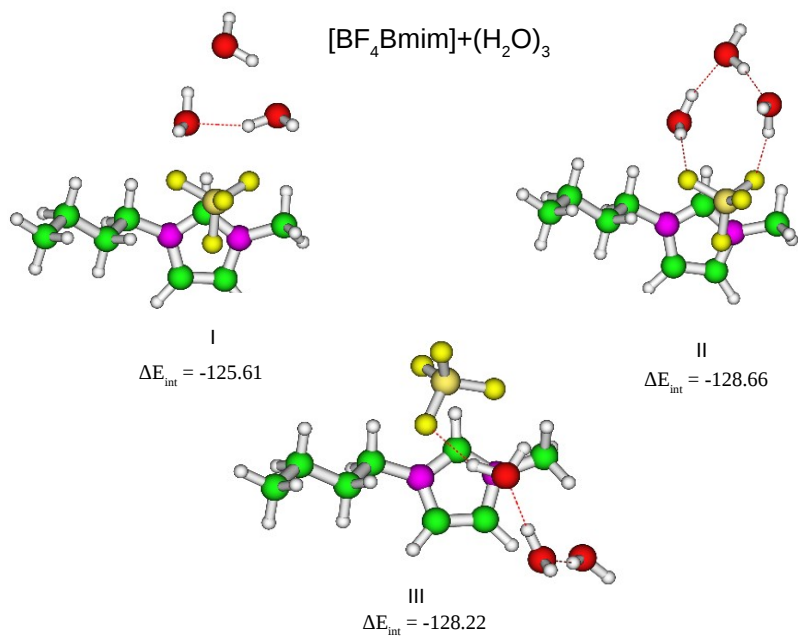
9 There are not important structural differences between the minima obtained
10 with 6-31++G(d,p) and 6-311+G(d) basis sets. Fig. 8 collects the ILS-(H₂O)₃
11 clusters optimized at MP2/6-311+G(d). At the first moment it could be thought
12 that the most stable structures would be those that maximize the interaction
13 among the water molecules with the anion and the H_a atom of the ring. Never-
14 theless, the comparison of the three minima indicates that there is not a unique
15 mode of interaction between water clusters and ILS. Besides, the position of the
16 anion respect to the cation also differs being in the plane of the ring, over or in
17 an intermediate situation. Again, and in spite of the importance of the H bonding
18 among the water molecules it is necessary to take into consideration all the possi-
19 ble interactions including the less H acidic atoms, the π cloud of the ring and the
20 alkyl chains to properly understand the ILS-(H₂O)₃ aggregates.

21 Fig. 9 contains the unCP and averCP interaction energies for the ILS-(H₂O)₃
22 clusters optimized at MP2 level and the single point DFT estimations.

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

31 The analysis of the profiles given by each method shows that the relative
32 stability of the clusters barely changes when the unCP and averCP results are
33 compared. The only exception is found for the [PF₆Bmim]+(H₂O)₃ clusters. In
34 this case the unCP estimations indicate that the stability order of the clusters is
35 II>I>III while the averCP results give rise to I>III>II.

36 The comparison of the results denotes that the trend followed by B3LYP re-
37 garding the ILS containing the Cl⁻ ions is different from that given by the remain-
38 ing methods, in the sense that cluster II is the least stable whereas it is the most
39 stable for the rest of the methods. In addition, a different tendency appears when
40 the stability between cluster III for the Cl⁻ ion and cluster I for the CH₃SO₃⁻ ion



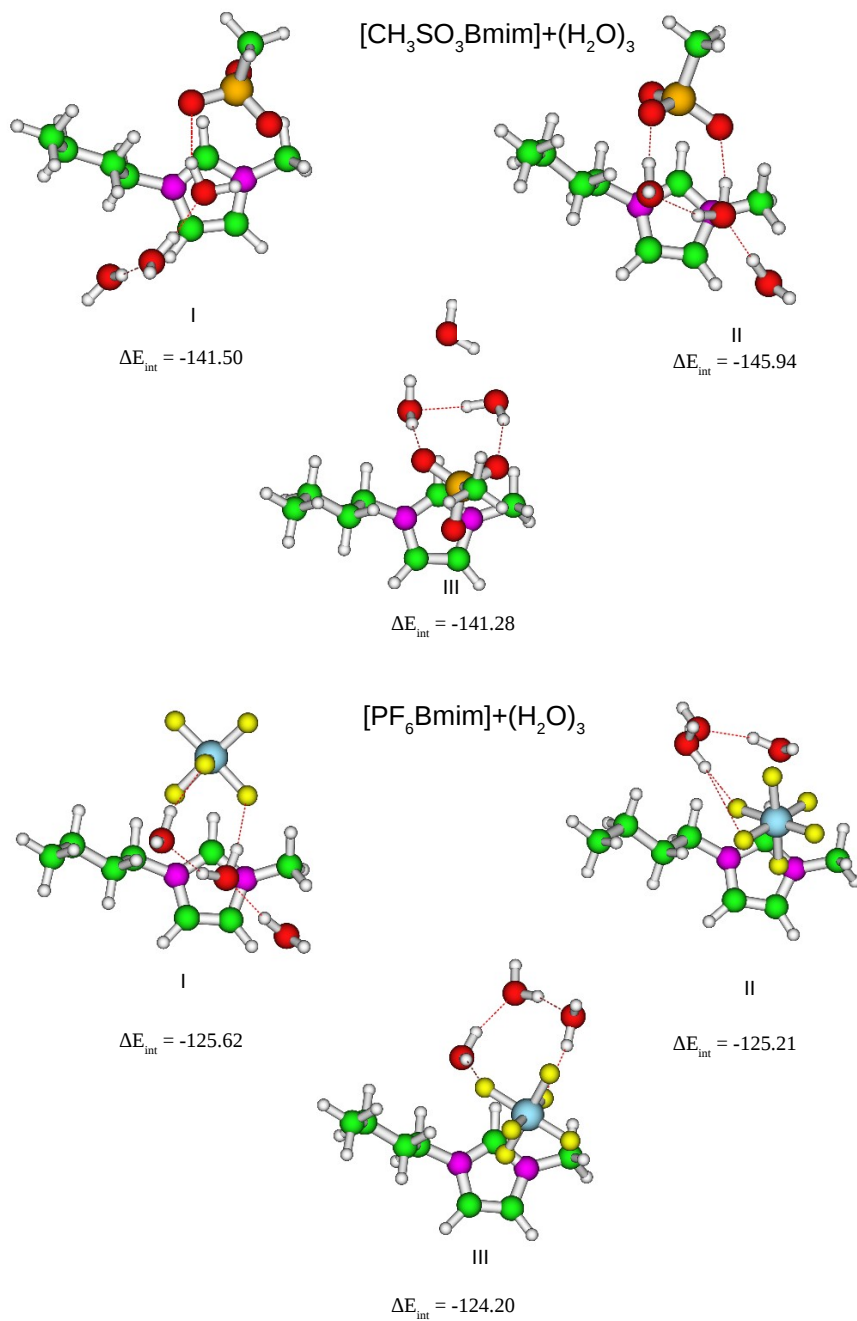


Figure 8: Optimized structures at MP2/6-311+G(d) level and interaction energies in kcal/mol obtained at MP2/6-311+G(d)//MP2/6-311++G(d,p) level for the ILs-(H₂O)₃ clusters.

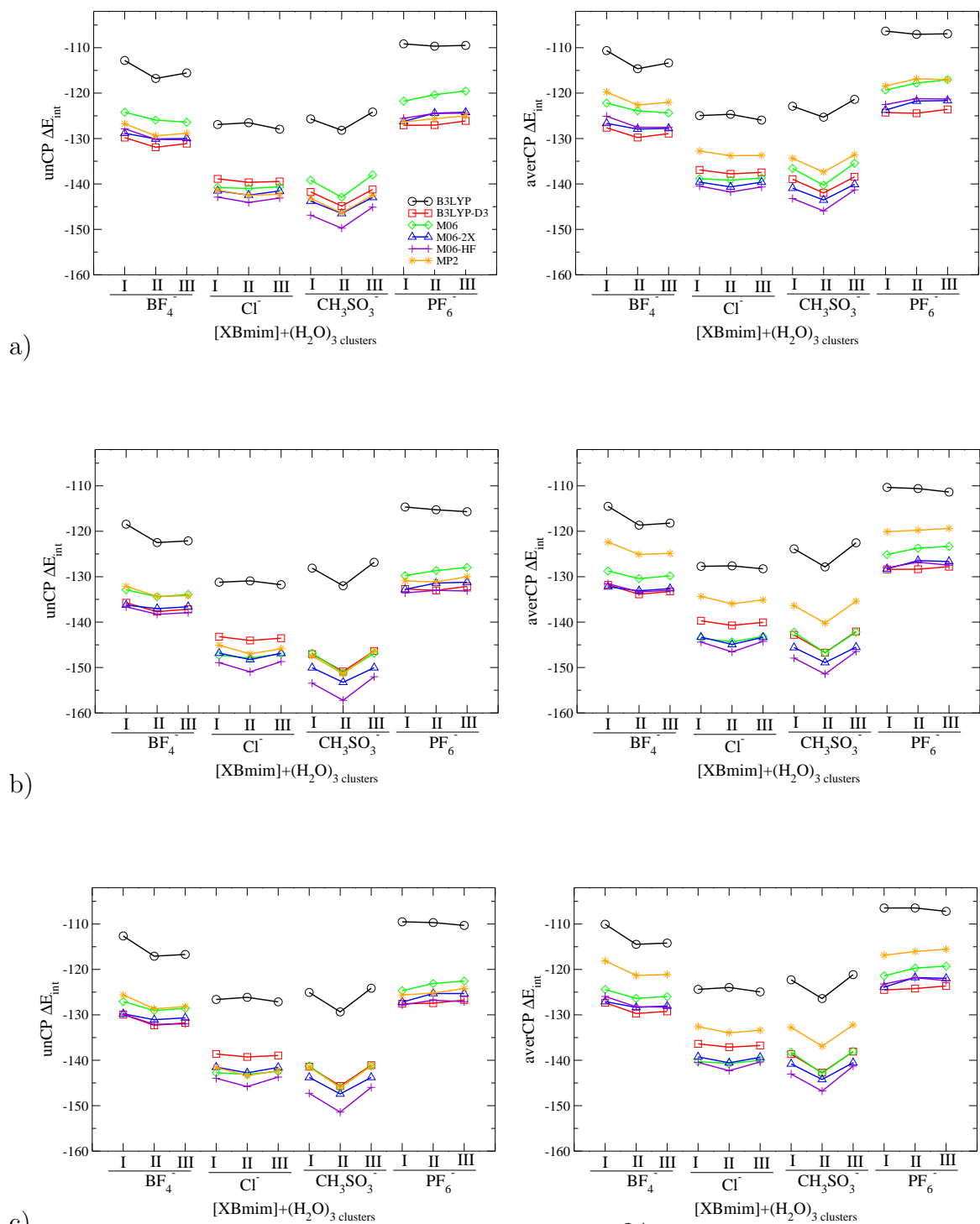


Figure 9: Plot of unCP ΔE_{int} (left) and averCP ΔE_{int} (right) for the ILs-(H₂O)₃ clusters optimized at MP2 level with a) 6-31++G(d,p), b) 6-311+G(d) and c) 6-311++G(d,p) basis sets. The labels are related with the minima shown in Fig. 12.

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

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

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

24 4. Concluding Remarks.

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

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

31 B3LYP functional is not able to recover all the ingredients to describe prop-
32 erly these systems regardless the nature of the anion, cosolvent and the number
33 of cosolvent molecules. The performance of DFT dispersive corrected methods is
34 rather similar for water and ethanol as a cosolvent but it depends on anion nature.
35 This way, M06-2X gives the best accuracy when the unCP energies are consid-
36 ered whereas the averCP energies suggest that M06 and B3LYP-D3 functionals
37 performs better for polar and non polar anions, respectively. The reproduction of
38 the MP2 structures follows the trend $\text{M06-2X} > \text{B3LYP-D3} \sim \text{M06-HF} > \text{M06} >$

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

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

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

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