Distance Angle Descriptors of the Interionic and Ion-Solvent Interactions in Imidazolium-based Ionic Liquids Mixtures with Aprotic Solvents: a Molecular Dynamics Simulation Study

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The main physicochemical properties of the studied ILs are collected in Table . One can see that the neat ILs differ significantly in their transport properties, *i.e.*, viscosity and conductivity. At same time, they have rather close polarity (slightly higher value of the relative static dielectric permittivity of BmimTfO is related to significant contribution of its polar anion).

Table 1 Selected properties of ILs used in the present study: molar mass, M, density. d. dynamic viscosity, η, relative static dielectric permittivity, ε_r, electrical conductivity, κ, at 298.15 K

Property	BmimBF$_4$	BmimPF$_6$	BmimTfO	BmimTFSI
M / g mol^{-1}	226.02	284.18	288.29	419.36
d / g cm^{-3}	1.20164[a]	1.36832[a]	1.29963[b]	1.43430[c]
η / mPa s	90-219[d]	207-450[d]	75-93[d]	49-69[d]
ε_r	11.7[e]	11.4[e]	13.2[e]	11.6[e]
κ / mS cm^{-1}	3.53[a]	1.469[a]	2.90[f]	3.90[f]

[a]Ref. [1], [b]ref. [2], [c]ref. [3]; [d]data scatter a lot depending on the origin and purity of the sample and on the method, extreme values are given in refs. [4] and [5] for BmimBF$_4$, refs. [6] and [7] for BmimPF$_6$, refs. [8] and [7] for BmimTfO, refs. [4] and [5] for BmimTFSI; [e]ref. [9], [f]ref. [10].

The main physicochemical properties of the solvents are given in Table 2. They differ in terms polarity both on macro and microscopic scales as quantified by relative static dielectric permittivity and molecular dipole moment values, respectively. They follow the sequence AN < γ-BL < PC. However, their solvating capabilities towards cations, described by their electron donicities or nucleophilic properties in the framework of Gutmann's donor numbers, follow a slightly different trend AN < <PC < γ-BL. Note that donor numbers of other common polar aprotic organic solvents like acetone or dimethyl sulfoxide are 17 and 29.8. respectively.[11] In terms of electrophilic properties as quantified by Gutmann's acceptor numbers, which indirectly characterize solvent's capability of anion solvation all the solvents show comparable values which are typical for this class of polar aprotic molecular solvents.[11]

Table 2 Selected properties of molecular solvents used in the present strudy: molar mass, M, density. d. dynamic viscosity, η, relative static dielectric permittivity, ε_r, molecular dipole moment, μ, Gutmann's donor and acceptor numbers at 298.15 K

Property	AN	γ-BL	PC
M / g mol^{-1}	41.05	86.09	102.09
d / g cm^{-3}	0.776565[a]	1.124210[b]	1.19993[c]
η / mPa s	0.339[a]	1.76[d]	2.5120[c]
ε_r	35.96[e]	41.7[f]	64.96[c]
μ / Debye	3.90[g]	4.19[h]	4.95[g]
Donor number	14.1[g]	18.0[i]	15.1[g]
Acceptor number	18.9[g]	17.3[g]	18.3[g]

[a]Ref. [12], [b]ref. [13], [c]ref. [14], [d]ref. [15], [e]ref. [16], [f]ref. [17], [g]ref. [11], [h]ref. [18], [i]ref. [19].

In this part of the supporting information we are showing the comparison between the calculated density and the experimental ones is illustrated in Fig. S1. Indeed, to validate the simulated IL-molecular solvent mixtures, the basic physicochemical properties were predicted and compared with available experimental data as a function of mixture composition, namely density and self-diffusion coefficient. In this way, we validate suitability of the physical model of the combined force fields for describing the macroscopic properties.

The calculated densities of the IL-solvents mixtures further were compared with several experimental measurements. The obtained results are in satisfactory agreement with experimental results at the entire range of mixture compositions. Comparing the behavior of the three different solvents one can see that the great changes are inherent to the binary mixtures with AN and to a less extent for GBL and PC. Indeed, in case of the binary mixtures with AN the respective densities of the mixture decreases only slightly in the mole fraction range $x_{IL} > 0.3$, staying almost steady. With further decreasing of x_{IL}, densities decrease exponentially with increasing of solvent content. For the binary mixtures with GBL and PC the respective densities increases with decreasing of x_{IL}, and pass through a maximum at $x_{IL} \sim 0.30$. With further addition of the solvent, the density of the binary mixture gradually decreases. The calculated densities of the mixtures of ILs with GBL and PC are characterized by the minor difference with experimental values, however due to the small spread of the experimental values it is rather difficult to reproduce the same trend, particularly for the binary mixtures with PC.
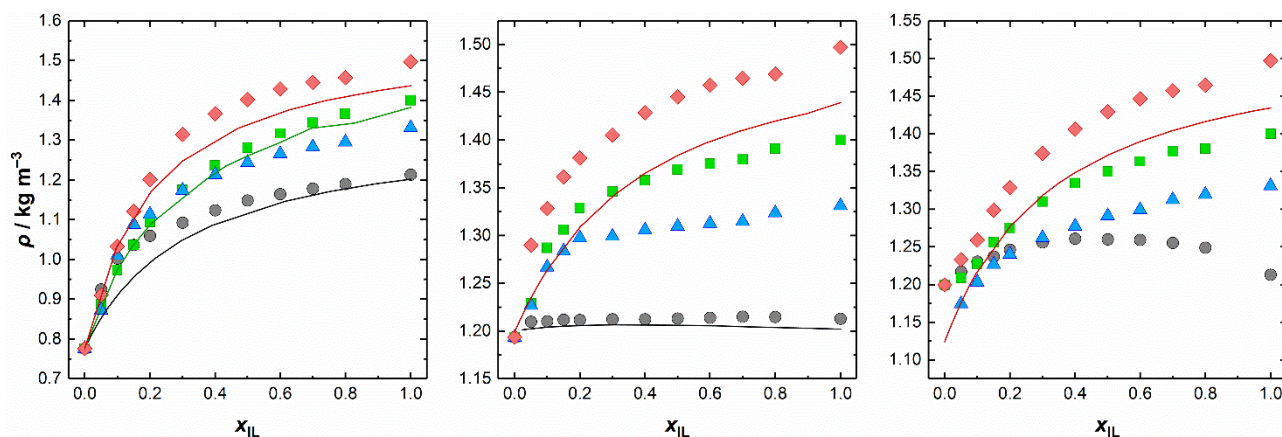

Figure S1. Densities calculated for BmimBF$_4$ (○), BmimPF$_6^-$ (□), BmimTFO (△) and BmimTFSI (◇) and their mixtures with AN (*left*), GBL (*right*) and PC (*middle*) in comparison with experimental data (*solid lines*) for AN-BmimBF$_4$ (*black*),[1] AN-BmimPF$_6$ (*green*),[20] AN-BmimTFSI (*red*),[21] PC-BmimBF$_4$ (*black*),[1] PC-BmimTFSI (*red*),[22] GBL-BmimTFSI (*red*).[23]

In the second part of the supporting information, the radial distributions functions describing the local structure around the acidic hydrogen atoms of the Bmim$^+$ cation in position 4, and 5 as well as the distance angle descriptors of the C^{4,5}-H^2 …A and C^{4,5}-H^2 …S interactions .
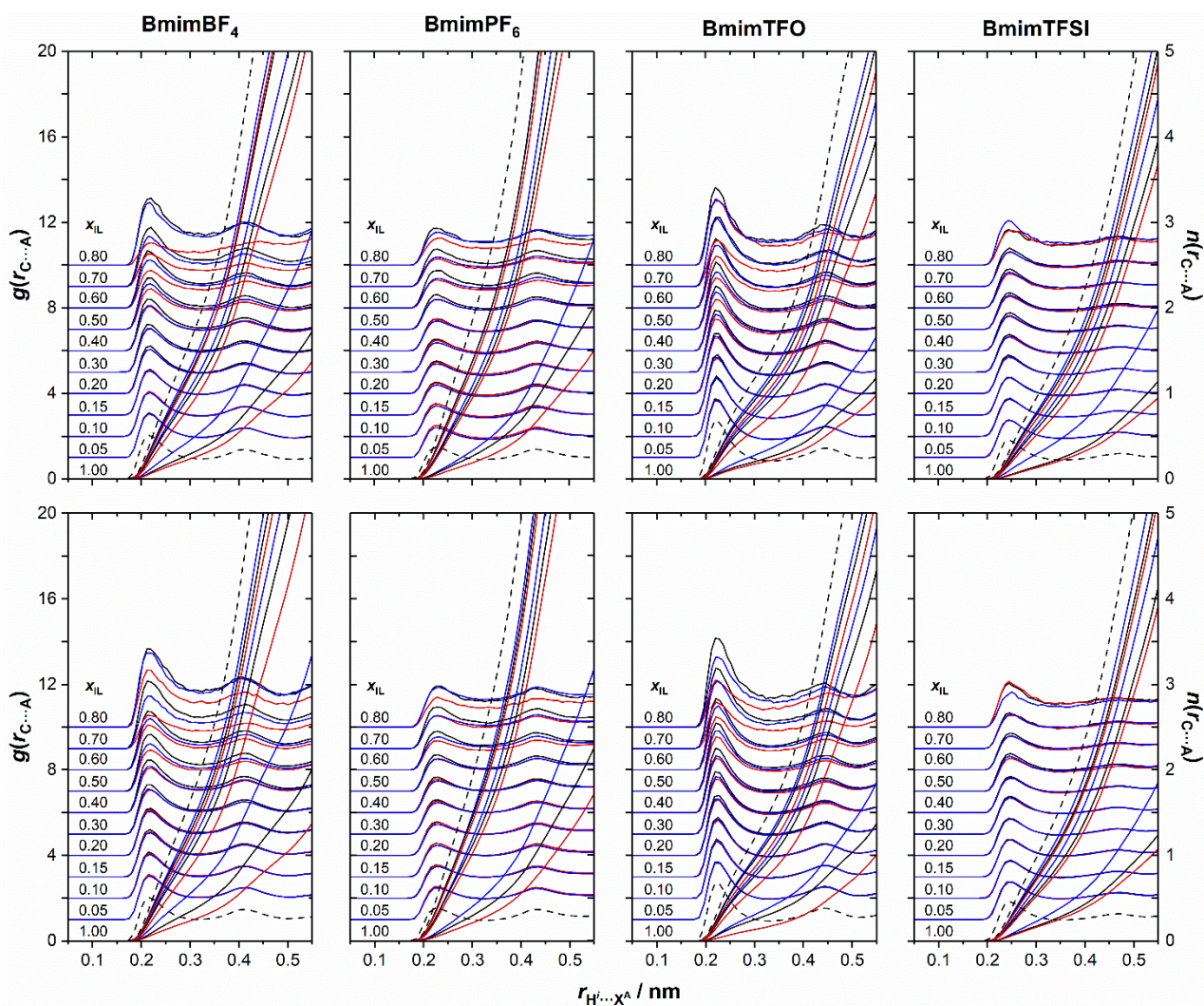
Figure S2. The radial distributions functions, $g(r_{C\cdots A})$, describing the cation$\cdots$anion, C$\cdots$A, interactions between the H^4 (*top*) and H^5 (*bottom*) site of Bmim$^+$ and the X^A site of anion (F atom of BF$_4^-$ and PF$_6^-$, and the O atom of TFO$^-$ and TFSI$^-$) in neat ILs (-----) and their binary mixtures (—) with AN (*blue*), GBL (*black*) and PC (*red*) for the different mixtures compositions along with the corresponding coordination numbers, $n(r_{C\cdots A})$, given only for x_{IL} equal to 0.05, 0.30, 0.50 and 1.00 at the right side *y*-axes.
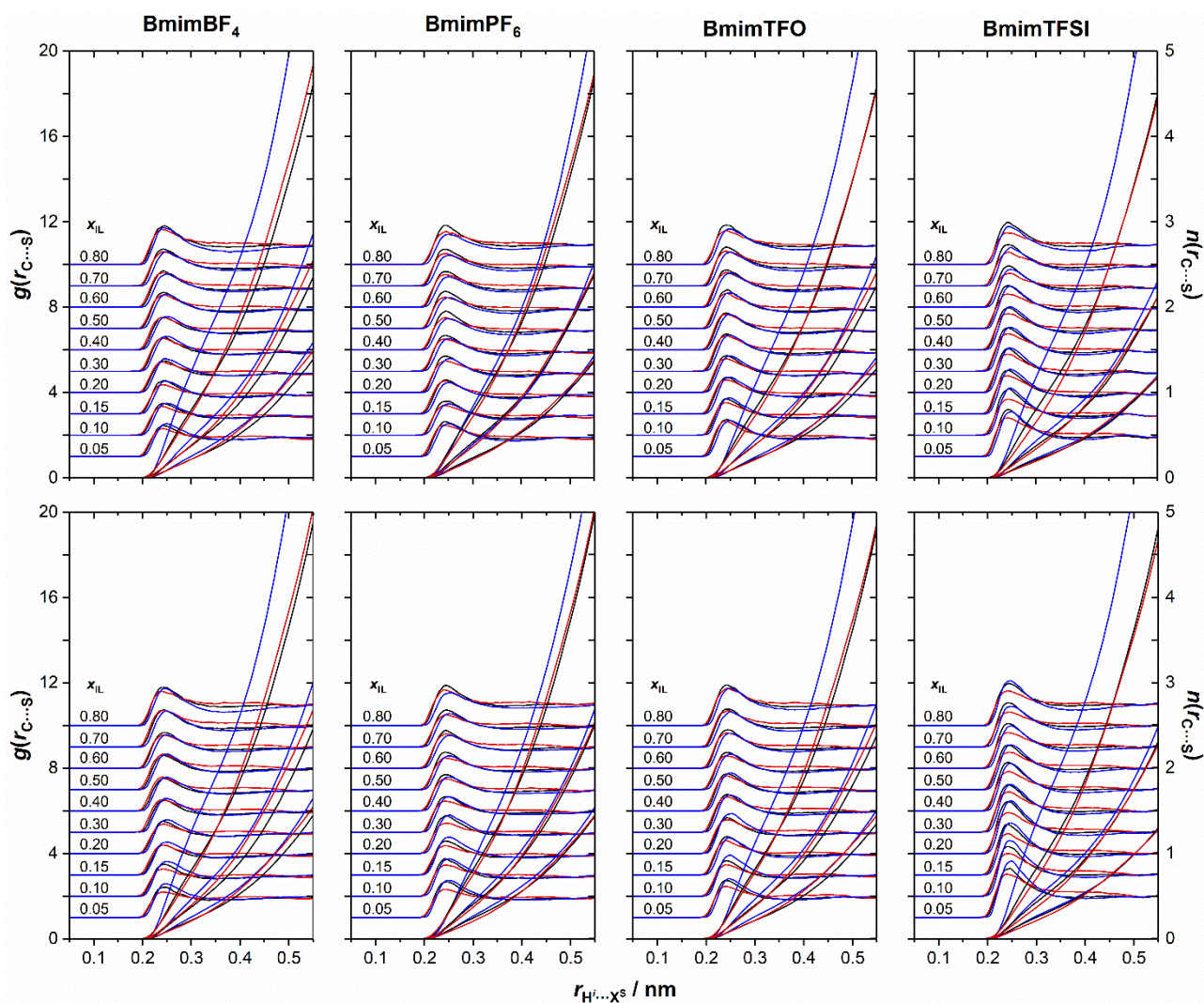
Figure S3. The radial distributions functions, $g(r_{C \cdots S})$, describing the cation$\cdots$anion, C$\cdots$S, interactions between the H^4 (*top*) and H^5 (*bottom*) site of $Bmim^+$ and the X^S site of solvent (N atom of AN (*blue*), $O^{C=O}$ atom of GBL (*black*) and PC (*red*)) for the different mixtures compositions along with the corresponding coordination numbers, $n(r_{C \cdots S})$, given only for x_{IL} equal to 0.05, 0.30 and 0.50 at the right side *y*-axes.
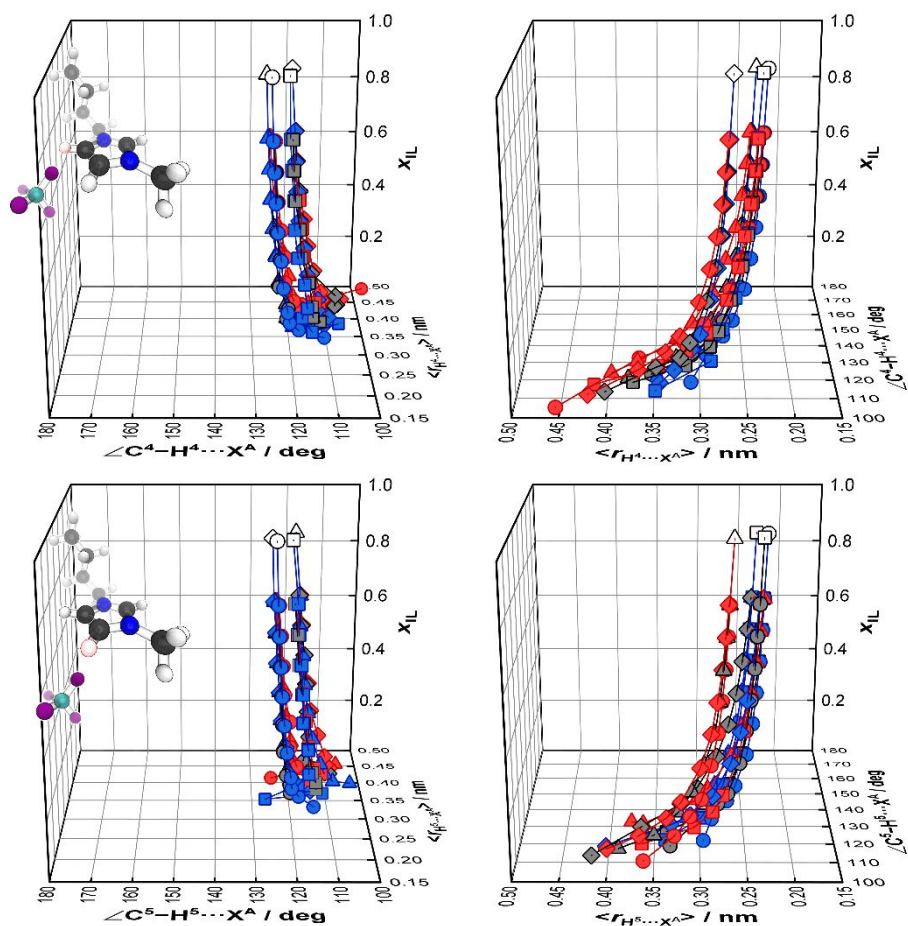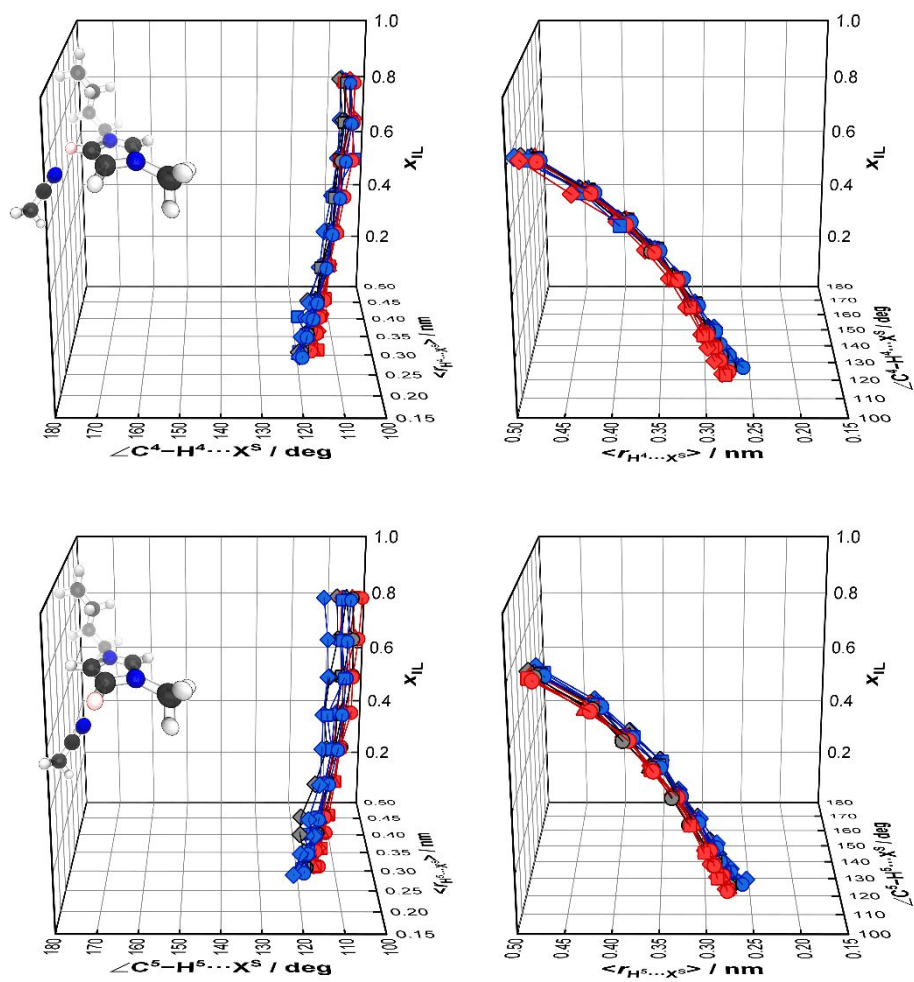
Figure S4. The behavior of the average geometrical H-bonding characteristics, $<r_{H^4\cdots X^A}>$ and $\angle C^4-H^4\cdots X^A$ (*top*) and $<r_{H^5\cdots X^A}>$ and $\angle C^5-H^5\cdots X^A$ (*bottom*), of the cation$\cdots$anion interactions for the different mixtures compositions with AN (*blue*), GBL (*black*) and PC (*red*), where X^A denote F atom of BF_4^- ($\bigcirc$) and PF_6^- ($\square$), O atom of TFO^- ($\triangle$) and $TFSI^-$ ($\diamond$).

Figure S5. The behavior of the average geometrical H-bonding characteristics, $\langle r_{\mathrm{H}^4\cdots\mathrm{X}^{\mathrm{S}}}\rangle$ and $\angle\mathrm{C}^4-\mathrm{H}^4\cdots\mathrm{X}^{\mathrm{S}}$ (*top*) and $\langle r_{\mathrm{H}^5\cdots\mathrm{X}^{\mathrm{S}}}\rangle$ and $\angle\mathrm{C}^5-\mathrm{H}^5\cdots\mathrm{X}^{\mathrm{S}}$ (*bottom*), of the cation$\cdots$solvent interactions for the different mixtures compositions with AN (*blue*), GBL (*black*) and PC (*red*), where X^{S} denote N atom of AN, $\mathrm{O}^{\mathrm{C}=\mathrm{O}}$ atom of GBL and PC.
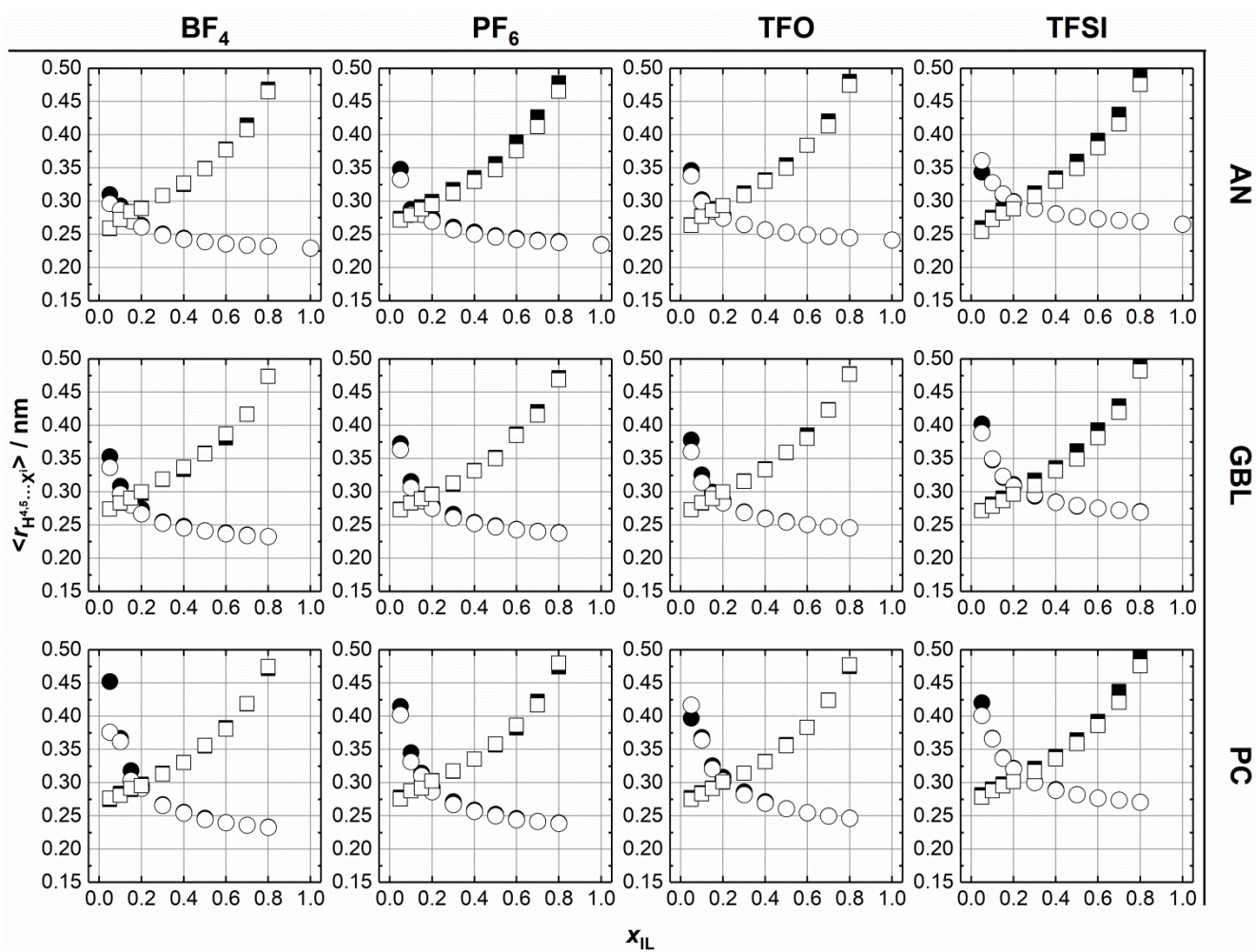
Figure S6a . The behavior of the distance descriptors $<r_H^2\cdots_X>$, of the cation$\cdots$anion ($\bigcirc$) and cation$\cdots$solvent ($\square$) interactions

as well as that of $<r_H^{2(s)}\cdots_X>$ of the solvent$\cdots$anion interactions ($\triangle$) for the different mixture compositions.
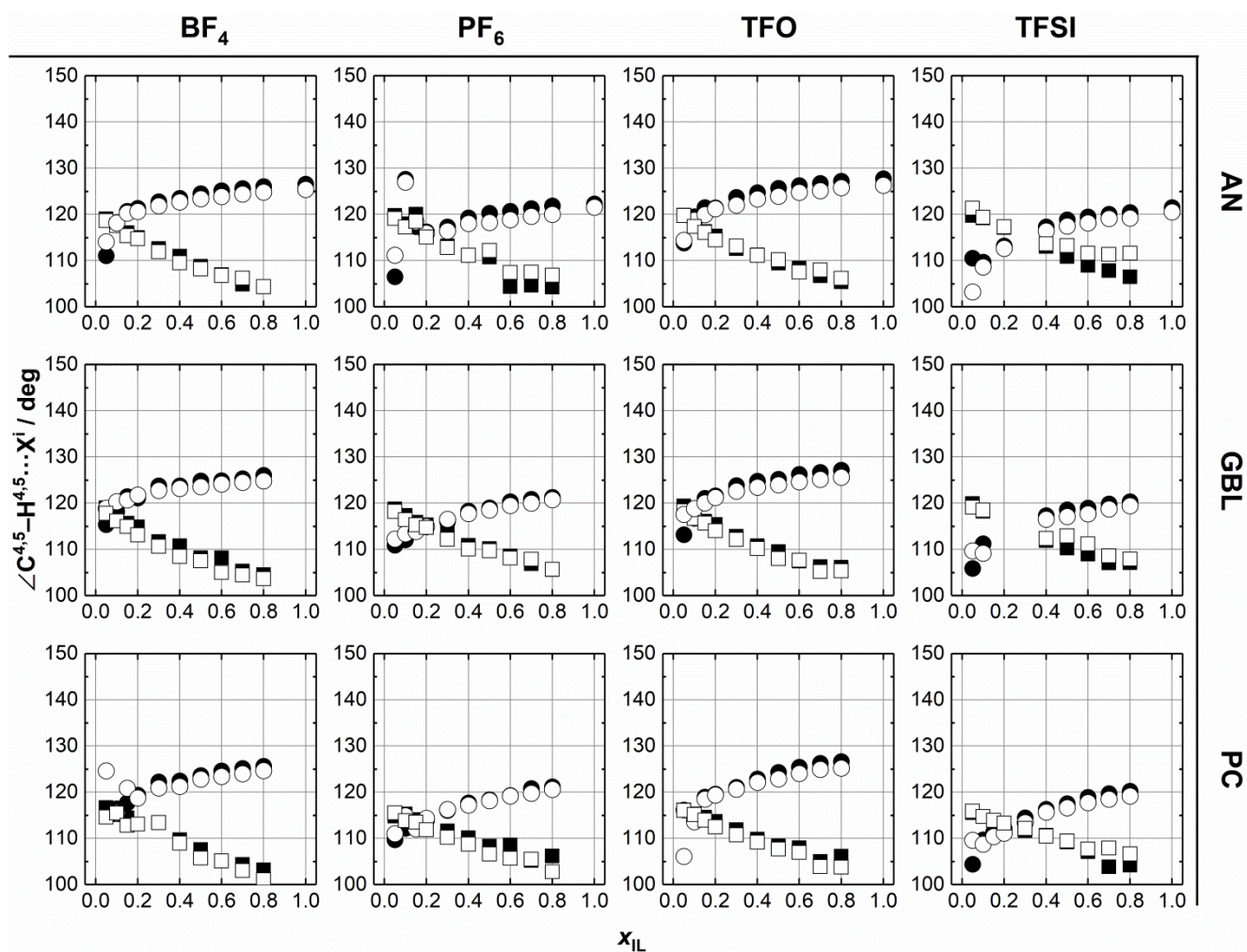
Figure S6b. The behavior of angular descriptor, $\angle C^2-H^2\cdots X$, of the cation$\cdots$anion (○) and cation$\cdots$solvent (□) interactions, and $\angle C^{2(s)}-H^{2(2s)}\cdots X$ of the solvent$\cdots$anion interaction (△) for the different mixture compositions

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