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SUPPORTING MATERIAL: The properties of residual water molecules in ionic liquids: a comparison between direct and inverse Kirkwood-Buff approaches

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1 Number of hydrogen bonds between water molecules

In order to study the pairing of water molecules, we calculated the number of hydrogen bonds between water molecules at different mole fractions in the individual IL solutions. The results are depicted in Fig. 1. The results reveal that the values for the number of hydrogen bonds N_{HB}^{W} are very small. Based on these results, one can conclude that the formation of hydrogen bonds is a rare event and that the considered water molecules significantly differ from water molecules in the bulk phase. In fact, the values for identical mole fractions of water are slightly higher for EMIM/BF4. Most importantly, we observe a constant slope with increasing water content in the number of hydrogen bonds for both ILs. This finding indicates that no significant phase transitions, *e. g.* the formation of higher number water clusters, occur which induce a jump in the corresponding values. Hence, the number of hydrogen bonds increases linearly with the number of water molecules and thus it can be concluded that the increase can be purely related to a higher fraction of water in the solution instead of local water cluster aggregation phenomena.

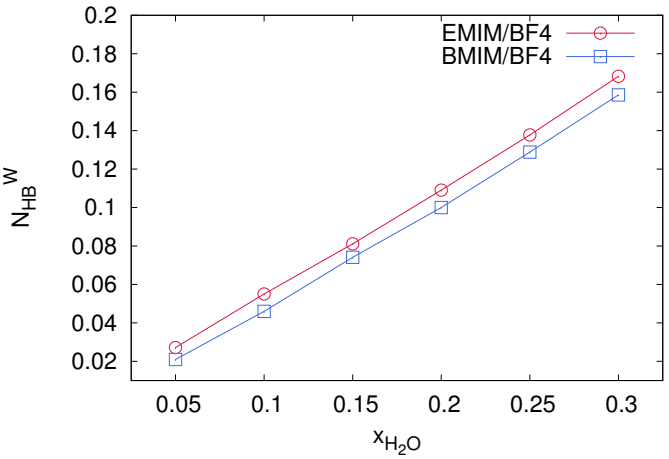

Fig. 1 Number of hydrogen bonds N_{HB}^{W} between water molecules at different mole fractions of water in EMIM/BF4 (red circles) and BMIM/BF4 (blue squares). The lines are guides for the eyes only.

2 Partial structure factor

The partial structure factors $S_{++}(q)$ for the cation-cation arrangement at different water content are shown in Fig. 2. Both ILs reveal a maximum peak at $q = 10$ nm^{-1}. Furthermore, it can be seen that BMIM/BF4 shows a more defined structural arrangement for $q \geq 11$ nm^{-1}. Both findings are in good agreement with the radial distribution functions as discussed in the main text. The varying content of water in the solution does not seriously affect the results.

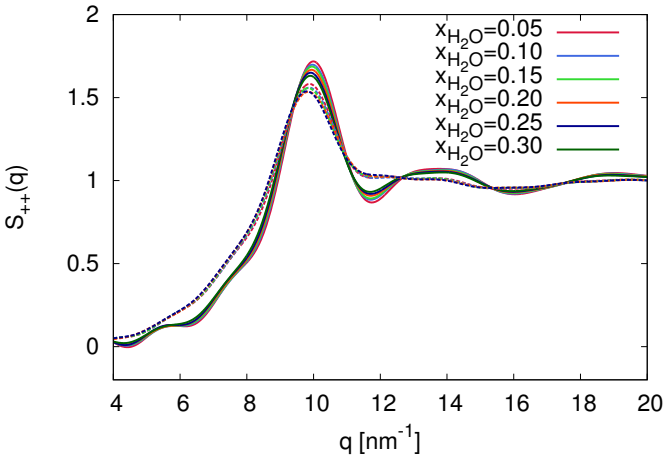

Fig. 2 Partial structure factors S_{++} for cation-cation arrangement in EMIM/BF4 (solid lines) and BMIM/BF4 (dashed lines) with different water content.

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