Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Depolarization of water in protic ionic liquids

Supporting Information

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We carried out additional static quantum chemistry calculations to highlight the influence of solvation on hydrogen bond strength. At first, we calculated the reaction energy of several model reactions (**RX**) shown in table 1. The corresponding structures/clusters shown in Fig.1 were obtained by structure optimization with the TURBOMOLE[1] program package. We used the BLYP-D[2–4] density functional in combination with a def2-TZVP[5] basis set and the RI[6–8] approximation. Please note that all start configurations consisted of the ionic forms, i.e. monomethylammonium cations and nitrate anions. Only in the case of **C4**, a proton transfer between the two ions occurred during optimization. This is a result of the gas phase calculation which neglects solvation in opposite to our AIMD simulations. It already highlights the important role of solvation for charged species and the difficulties in comparing gas phase results to liquid state ones. However, by increasing the cluster size, cooperative effects are included progressively. For instance, proton transfer was not observed in the larger ion cluster **C6** which was in agreement with the CPMD simulation of neat MMAN.[9]

As one can see in table 1, the reaction energy of **R1** is significantly smaller than for **R2** or **R3**. Thus, the hydrogen bond between one water molecule and one ion is significantly stronger than a hydrogen bond between two water molecules. To approximate the influence of solvation on the hydrogen bond strength, we compare the calculated reactions energies ΔE_{calc} for the reactions shown in table 1 to a assumed value ΔE_{asum}. ΔE_{asum} is calculated in the following way: We assume for each hydrogen bond type in the reactant the same hydrogen bond energy as obtained by the related equation **R1**, **R2**, **R3**, and **R4** and add up the corresponding interaction energies. For example, the reactant of **R5** is cluster **C5**. This cluster has six hydrogen bonds between two water molecules. If cooperativity plays no role for the hydrogen bond strength, the reaction energy of **R5** should be about 6·**R1**. However, the value ΔE_{asum} is significantly smaller than ΔE_{calc}. Thus, cooperativity increases significantly the hydrogen bond strength (from about 25 kJ/mol to 40 kJ/mol) in this cluster as reported before.[10] Therefore, hydrogen bonds in pure water are much stronger than between two water molecules in the gas phase. The opposite trend is found for the other reactions in table 1 which are the dissociation of larger ion clusters or water-ion clusters (Please note, that ΔE_{asum} considers only interactions which are highlighted by a dashed line in Fig. 1.). Thus, cooperativity in MMAN weakens the hydrogen bond strength in MMAN.

Table 1: Reaction energy ΔE_{calc} (def2-TZVP/BLYP-D(RI)) of model reactions **RX** ass well as assumed interaction energy ΔE_{asum} if cooperativity is neglected and only the interactions shown by the dashed lines in Fig. 1 are considered. Additionally, the difference between these two energies ΔE_{calc}-ΔE_{asum}. All values are given in kJ/mol.

	reaction	ΔE_{calc}	ΔE_{asum}	ΔE_{calc}-ΔE_{asum}
R1	**C1** $\longrightarrow$ 2·**W**	26.5	—	—
R2	**C2** $\longrightarrow$ **W** + **K**	86.3	—	—
R3	**C3** $\longrightarrow$ **W** + **A**	63.3	—	—
R4	**C4** $\longrightarrow$ **K** + **A**	536.3	—	—
R5	**C5** $\longrightarrow$ 6·**W**	235.1	159.0	76.5
R6	**C6** $\longrightarrow$ 3·**K** + 3·**A**	1804.1	3217.8	−1413.7
R7	**C7** $\longrightarrow$ **K** + 2·**A**	687.1	1072.6	−385.5
R8	**C8** $\longrightarrow$ 2·**K** + **A**	675.0	1072.6	−397.6
R9	**C9** $\longrightarrow$ **W** + **K** + **A**	580.1	685.9	−105.8
R10	**C10** $\longrightarrow$ **W** + **K** + 2·**A**	745.6	1222.2	−476.6
R11	**C11** $\longrightarrow$ 2·**W** + 2·**K** + 2·**A**	1277.8	1372.4	−94.6
R12	**C12** $\longrightarrow$ **W** + 2·**K** + 2·**A**	1233.6	2358.1	−1124.5

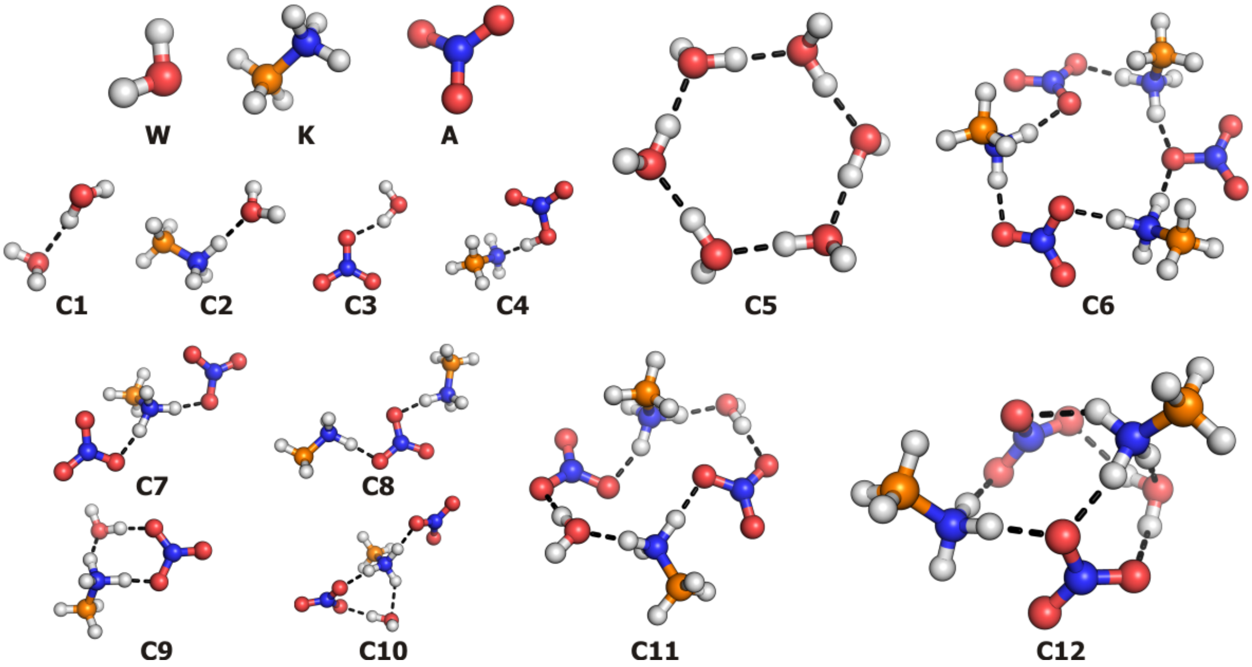

Figure 1: Ball-and-stick model of investigated structures

Additionally, we took snapshots of our simulations and removed one water molecule. The energy gap between the snapshot with and without the water is a rough estimation of the solvation energy of the water molecule. On average, we calculate a solvation energy of about 104 kJ/mol. We can now take the same snapshot and calculate the hydrogen bond strength between the removed water molecule and *e.g.* one cation in the gas phase in the following way: We remove all other molecules except the two which participate in the hydrogen bond. Subsequently, we calculate the interaction energy of these two molecules in the gas phase (all structures from the snapshot are not relaxed). We found on average a water-anion hydrogen bond strength of about 52 kJ/mol and a water-cation hydrogen bond strength of about 63 kJ/mol for the isolated systems in the gas phase. Adding up both values and, hence, neglecting cooperativity and interactions with any other ions than the nearest anion and the nearest cation, we obtained an average value of about 115 kJ/mol. This energy is already larger than the calculated solvation energy of about 104 kJ/mol while only half of the possible hydrogen bond contacts of a water molecule are not even considered. Thus, solvation must weaken significantly the hydrogen bond strength obtained by our snapshot gas phase calculations.

In summary, solvation influences significantly the hydrogen bond strength. The hydrogen bond strength in MMAN is decreased while the hydrogen bonds in neat water are increased.

References

[1] Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.

[2] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.

[3] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

[4] Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

[5] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[6] Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396–3402.

[7] Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41–51.

[8] Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

[9] Zahn, S.; Thar, J.; Kirchner, B. *J Chem Phys* **2010**, *132*, 124506.

[10] Wendler, K.; Thar, J.; Zahn, S.; Kirchner, B. *J. Phys. Chem. A* **2010**, *114*, 9529–9536.