DETERMINATION OF Kw OF CONFINED WATER IN NANODROPLETS

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INTRODUCTION

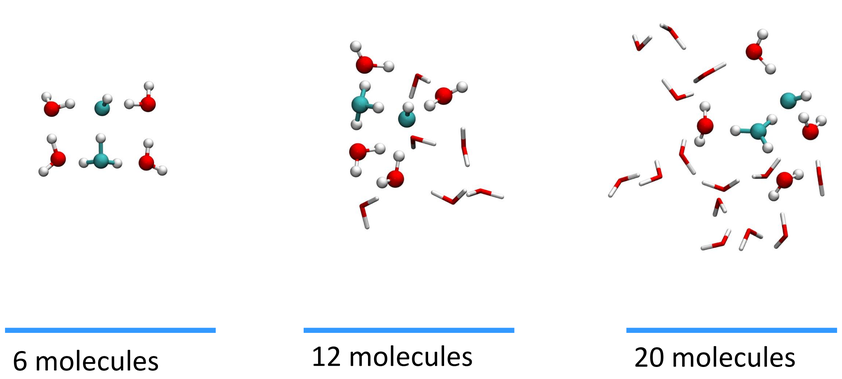
The self-dissociation of water is a matter of interest given the role that aqueous reactivity plays in many natural and technological processes [1,2,3,4] . However, even though there is a great amount of studies on this subject, there are still many questions to be answered regarding the reactivity in confined systems. In this work we aimed to determine the effect of confinement on the value of Kw in nanodroplets of different sizes, comparing the obtained values with the one corresponding to bulk water.

METHODOLOGY

- DFT Car-Parrinello Molecular Dynamics (CPMD) with Umbrella Sampling scheme[5], as implemented in the Quantum-Espresso program[6] .
- Reaction coordinate: hydrogen coordination number for the oxygen of the dissociating molecule[7].
- Temperature of 300 K.
- BLYP functional and plane wave basis set.
- Vanderbilt ultrasoft pseudopotentials.

STUDIED SYSTEMS

Nanodroplets of different size were studied in order to analyse the effect of confinement.
The figure below presents the structures of the droplets with a hydroxide/hydronium pair resulting from the dissociation of a water molecule, highlighting the first solvation shell of the ions.

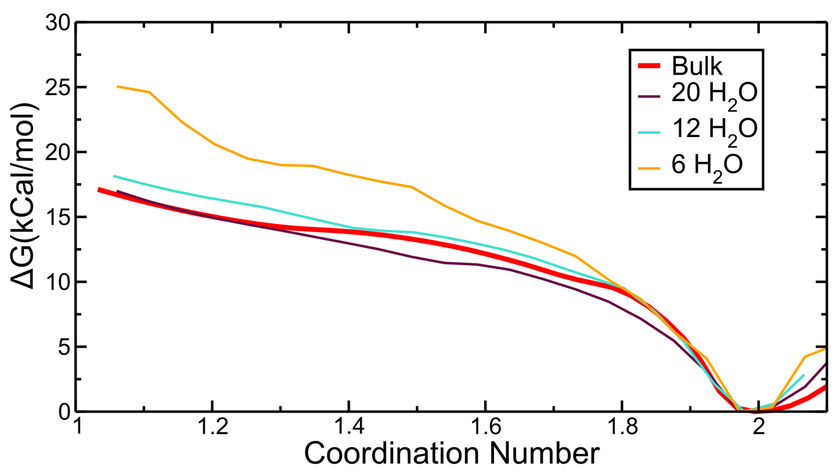


6 molecules | 12 molecules | 20 molecules

RESULTS

Free energies of dissociation

The free energy curves obtained with the methodology described before are presented in the following figure.

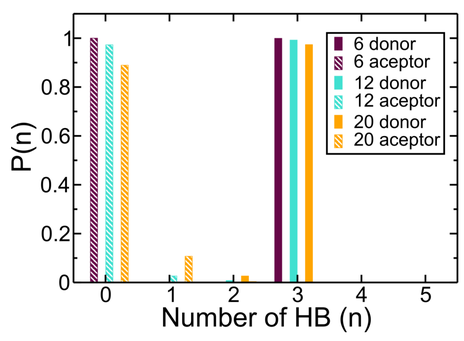


- For the larger clusters (12 and 20 molecules) there is no difference in **Δ**G with respecto to the bulk.
- In the hexamer the **Δ**G of dissociation is of about 4 kcal/mol higher than in the bulk which represents a drop of 3 orders of magnitude in Kw.

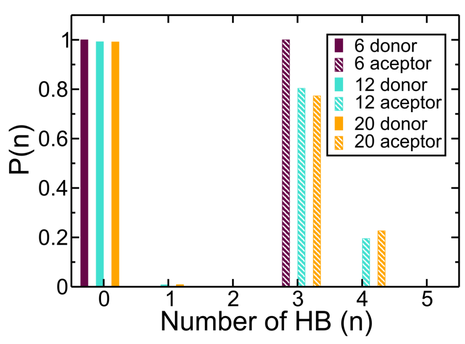
Solvation Structure of Hydronium and Hydroxide

The distribution of hydrogen bonds for the hydronium and hydroxide ions, products of the reaction, was calculated in each cluster.

Hydronium Hydrogen Bond Coordination



Hydroxide Hydrogen Bond Coordination



- In the larger clusters the solvation structure of the hydroxide and hydronium is similar to the one reported for these ions in bulk water.
- In the hexamer the solvation structure is more rigid compared with the other two clusters and the bulk.

CONCLUSIONS AND PERSPECTIVES

- These results suggest that the increase in the free energy of self-dissociation (or equivalently a drop in the value of Kw) observed in the smallest droplet is due to a deficient solvation of the products becuase of the structural constraints present in the hexamer.
- It seems that most of the energetics in the self-ionization of water is captured by the first hydration shell of the hydronium and hydroxide ions which is present in the two larger clusters but not in the hexamer .
- Similar studies in 2D water slabs are being carried out in order to further support these results with systems of different geometry.

ACKNOWLEDGEMENT

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