

From H-bonded dimer to the H-bond network around protein

Imre Bakó

Research Centre for Natural Sciences, H-1117 Budapest, Magyar tudósok körútja 2., Hungary

The significant cooperative effect between water molecules substantially affects the properties of liquid water. The cooperativity of hydrogen bonds means that the hydrogen bond strength is influenced by the neighboring water molecules. The introduction of an external ion into bulk water also causes a strong perturbation of the water structure in the neighbourhood of the ion in question. The effects of the environment (mainly asymmetric) on the electronic, structural and energetic properties of a water molecule are in focus in this lecture from different point of view. We showed that some quantum chemical descriptor (dipole moment, intra- and intermolecular bond order) can be used to characterise the collective electrostatic and quantum mechanical effects caused by non-immediate environment of water molecules.

These longer-range effects may be basically attributed to the properties of water as a polarizable medium, but the peculiarities of the wave functions of the actual systems do also have some measurable role even for the farther environment.

We performed a detailed analysis of the two- and three-body interaction energies in water clusters containing up to 30 water molecules using the “hierarchical” basis set superposition error (BSSE)-corrected energy decomposition scheme. In this work we showed that the average two and three body interaction energy terms are about 74 to 80 and 20 to 26 percent, respectively, of the total BSSE corrected interaction energy for all investigated clusters. We observed that the three-body interaction energy component is significantly negative/positive if there are two H-bonds and one attraction/repulsion interaction energy in the corresponding trimer, respectively.

I will show based on AIMD calculation that the electronic DOS, XES spectrum and the net charge depend on hydrogen bonding environment in liquid phase too.

We showed in our calculations that the dipole moment of water molecules in a neighborhood of a cation is primarily increased by polarization from the bare electrostatic charge of the cation, although the effective value of the latter is somewhat reduced by “back donation” of electrons from the water. A further important factor is the collective effect of the water molecules: their mutual arrangement and polarization counteract the polarizing effect of the cation, resulting in less increased values of the dipole moments.

Additionally, I will analyze from network science how can we calculate the cooperative effect and several topological descriptors in liquid water, water-alcohol mixture and surface of protein surface using knowledges from network science.

I will discuss a method for the determination of the optimal set of H/D compositions (isotopic substitution method, neutron diffraction) with or without taking into account the experimental error. I make some outline for the effect of nuclear quantum effect too.

Changes of H-bond network on cooling in 2-propanol-water liquid mixtures over the entire concentration range

¹Sz. Pothoczki, ¹I. Pethes, ¹L. Temleitner, ^{1,3}L. Pusztai, ²I. Bakó

¹Institute for Solid State Physics and Optics, Wigner RCP of HAS, Konkoly-Thege M. Út 29-33, H-1121, Budapest, Hungary, pothoczki.szilvia@wigner.mta.hu

²Institute of Organic Chemistry Research Centre for Natural Sciences, HAS, Magyar tudósok körútja 2, H-1117, Budapest, Hungary, bako.imre@ttk.mta.hu

³International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan

Due to the fact that 2-propanol molecules show both hydrophobic and hydrophilic characters, its aqueous mixtures provide a good opportunity for studying effects of temperature and composition on the variations of the hydrogen-bonded (H-bonded) network. Understanding these changes at a microscopic level can be a substantial step toward a better understanding the behaviour of aqueous solutions of more complex amphiphilic molecules.

A series of Molecular Dynamics (MD) simulations were performed for 2-propanol—water mixtures over the entire concentration range, between room temperature and the freezing points of the liquids. All-Atom Optimized Potential for Liquid Simulations (OPLS-AA) [1] was used for isopropanol molecules. For water molecules the improved Transferable Intermolecular Potential with four Particles (TIP4P-2005) [2] was applied. The goodness of our models was assessed by the goodness of agreement between total scattering structure factors from the MD models and measured X-ray diffraction data [3,4].

Percolation was monitored by comparing the calculated cluster size distribution functions for the present systems with that obtained for random percolation on a 3D cubic lattice. In percolating systems the cluster size distribution exceeds this predicted function at large cluster size values. It was found that the size of the percolated clusters is decreasing with the increasing ratio of 2-propanol molecules in the mixtures.

Observable trends on varying the temperature and the composition were revealed in terms of the average H-bond number, the fraction of 2-propanol molecules as H-acceptors and as H-donors in the H-bonds, as well as in terms of size distributions of cyclic entities [6].

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