FK 128656

Structural study of hydroxy-containing compounds in aqueous solutions

Final report

The hydroxyl groups (-OH groups) in sugars and alcohols play a decisive role in the structure and function of the molecules and their – biologically also significant – interactions with the water environment. Therefore, the main aim was to provide a complete picture of the behaviour of the hydrogen-bonded network in the aqueous solutions of alcohols and monosaccharides. In addition, the concentration and the temperature can significantly influence the characteristics of these networks. Even though these systems are composed of simple molecules, revealing the H-bonded properties in detail can be very complex due to the competition between hydrophobic and hydrophilic interactions.

The H-bonded network formed in these systems may be described using a local structural parameter like the average H-bonding number, the number of molecules acting as donors or acceptors, cluster size distributions, and cyclic and non-cyclic properties. On the other hand, these systems as a complex network can be characterized by their topological properties.

The results achieved within the project are summarized in three sections based on 9 articles in refereed international journals including an invited "*Perspective*" article of the Journal of Physical Chemistry B. The total impact factor is over 40, and the independent citation is around 60.

In Sec.1, results of H-bonding properties of alcohol-water systems are presented including findings for ethanol-water and isopropanol-water systems. Outstanding properties of the hydration shell around β-D-glucose based on computational study are discussed in Sec.2. Sec. 3 deals with results concerning Laplace spectra and spectral clustering of H-bonded network. Sec. 4 briefly summarizes the effects of H-bond asymmetry on the electronic properties of liquid water.

1. Hydrogen-bonded networks in alcohol-water systems

Description of methodology

J. Phys. Chem. B. 2023, 127, 3109-3118 [8]

A series of simple alcohol-water mixtures were studied to better understand the occurring changes in the H-bonded network as a result of varying the concentration and decreasing the temperature. The steps of the suggested approach from diffraction experiments to network theories are the following:

(1) X-ray and/or neutron diffraction experiments
(2) Molecular dynamics simulations
(3) Consistency check: establishing the quality of agreement between measured and simulated total scattering structure factors. Depending on the quality of agreement, simulated particle arrangements may (or may not) be considered as representations of the real systems

(4) Provided that the outcome of the consistency check is positive, hydrogen-bonded assemblies are scrutinized within a continuously expanding neighbourhood of molecules:
    a) hydrogen bonds are found
    b) simple descriptors like the number of H-bonds/molecule are determined
    c) H-bond related three-dimensional (3D) distribution functions are calculated for the 1st and 2nd coordination shells of molecules participating in H-bonds
    d) small cyclic entities, up to 8(-10) members, are identified
    e) non-cyclic assemblies are identified
    f) clusters of any size are identified and size distributions are determined, and percolation thresholds can be discussed
    g) Laplace spectra, reflecting genuine cooperative effects that extend over the entire H-bonded network, may be calculated.

This approach proved very useful by the results on ethanol-water and isopropanol-water liquid mixtures. It is important to emphasize that as a result of applying the novel approach, these calculated quantities characterizing H-bond interactions are always consistent with experimental (diffraction) data, thus it is also establishing a direct link between measurements and elements of network theories.

All measurements and computer simulations were performed as a function of composition and temperature to reveal additional aspects of hydrogen bonding.

Hydrogen bonding properties of aqueous solutions of ethanol

J. Phys. Chem. B 2021, 125, 23, 6272–6279 [5]

New X-ray diffraction experiments over the entire composition range, as well as new neutron diffraction experiments over the water rich region were carried out on ethanol-water mixtures, as a function of temperature, down to the freezing points of the liquids. At each point on the temperature-concentration curve, where we had measurement data, molecular dynamic (MD) simulations were performed. It was established that the combination of OPLS-AA (ethanol) and TIP4P/2005 (water) potentials have reproduced individual experimental data sets with more than satisfactory accuracy. That is, after comparing the total scattering structure factors calculated from the models with the results of the measurements, it was concluded that the models were adequate for further calculations of characterizing hydrogen bonded networks.

Concerning H-bonding, a more detailed picture of tendencies can be obtained by distinguishing H-bonds according to whether the molecules are involved in bonding as donors or acceptors. The most populated groups for ethanol molecules is the “one donor – one acceptor” case, while for water molecules is the “two donors – two acceptors” one. As the temperature decreases, the occurrence of the “two donors – two acceptors” combination increases linearly at every concentration.

Several different approaches were used to describe the temperature-dependent percolation transition. As a result, we found that even at the highest ethanol concentration, the entire system percolates at the lowest studied temperature. The percolation transition in the water subsystems occurs between 40 mol% and 50 mol% ethanol content at 300 K and between 50 mol% and 60 mol% ethanol content at 200 K.

Concerning the topology of H-bonded assemblies, 5-membered ring takes the leading role between 30 mol% and 70 mol% ethanol content. The number of rings are significantly less, when 80 mol% ethanol content were reached. This tendency is most pronounced at low temperatures.

Hydrogen bonding properties of aqueous solutions of 2-propanol

J. Phys. Chem B. 2019, 123, 7599-7610 [1]
J. Mol. Liq. 2021, 329, 115592 [4]

Molecular dynamic (MD) simulations were performed on aqueous solutions of isopropanol as a function of temperature (from room temperature to freezing) over the entire isopropanol concentration range (10 mol%, 16 mol%, 23 mol%, 36 mol%, 45 mol%, 56 mol%, 74 mol%, 90 mol%, 100 mol%). For isopropanol molecules, OPLS all-atom force field was used. For water molecules, SPC / E and TIP4P / 2005 water models were applied. We validated our simulation procedure by comparing measured and calculated total structure factors. Based on this comparison with the measurement, both water models well matched with the measurements, but TIP4P / 2005 proved to be a slightly better model.

To verify that the model systems remained liquid at lower temperatures, the self-diffusion coefficient for both water and isopropanol molecules was calculated. Although these values also decreased with the decrease in temperature, but the molecules were sufficiently mobile even at the lowest temperature tested.

Furthermore, we examined how the formation of rings in these systems is affected by temperature and concentration. We found that the number of cyclic entities is decreasing with increasing the alcohol concentration. For a given composition, the number of hydrogen-bonded rings increases when lowering the temperature. The dominant ring is the 5-fold one.

We estimated by various methods the boundary where the system can no longer be considered a coherent network. At room temperature, the percolation transition occurs at around xip = 0.62–0.74, whereas at 230 K, the threshold is above 90 mol% isopropanol content. Concerning the size of hydrogen-bonded assemblies, not only the mixture as a whole but also the water subsystem is percolating at each temperature and composition studied.

Additionally, the changes in hydrogen bond lifetime were studied in different hydrogen-bonded environments as a function of temperature. H-bonding lifetimes in the mixtures tend to be significantly longer than they are in pure water. The longest 'survival times', regardless of temperature and concentration, were found in the case of n=3 and n=4 H-bonded states for 2-propanol and water molecules, respectively.

2. Hydration shell properties in aqueous solutions of monosaccharides

ACS Omega, 2024, ASAP [9]

Hydrogen bonding (HB) properties were scrutinized based on ab initio molecular dynamics (AIMD) simulations on aqueous solutions of four simple sugars, α-D-glucose, β-D-glucose, α-D-mannose and α-D-galactose. We found that α-D-glucose forms one of the smallest, while β-D-glucose forms the highest number of hydrophilic hydrogen bonds both as an acceptor and as a donor with surrounding water molecules. Concerning hydrophobic interactions, β-D-glucose has the smallest number of water bounded by hydrophobically. These findings are in accord with the fact that β-D-glucose is the most, whereas α-D-glucose is the least soluble in water. For each of the sugar molecules we have studied, the ring oxygen atom has the fewest water molecules attached to it by H-bonds. The largest number of water molecules that H-bonds to the ring oxygen position in β-D-glucose. The strengths of the donor and acceptor types of H-bonds can be estimated by the distances between hydrogen and oxygen atoms which formed them. The shortest average donor H-bond length was found in β-D-glucose related to the strongest H-bond strength, while the weakest H-bond strength was revealed in α-D-glucose.

The Bader charges derived from AIMD simulations for oxygen atoms at positions 2,3,4 and 6 are very similar for all monosaccharides studied. On the other hand, the O atom at position 1 has a significantly more negative charge. Of all the O atoms, the one at position 5 has the least negative charge.

Scrutinizing the spatial structure of the hydration spheres of sugar molecules has revealed apparent asymmetries of the hydrophobic shell, whereas the hydrophilic shell is much more symmetric. β-D-glucose appears to be outstanding in terms of both of its hydrophilic and hydrophobic hydration shells.

3. Laplace spectra of H-bonded network

J. Mol. Liq. 2019, 273, 670 [2]

The Laplace matrices are determined, and various characteristics of them, such as eigenvalues and eigenvectors, as well as the corresponding Laplace spectra are calculated for the ethanol-water solutions. We showed how the size of the spectral gap in the Laplace matrix of H-bonded networks may be applied for characterising the stability of the network. This quantity does not depend on the applied water model. We introduced a new method for detecting the presence percolated network in these systems, too, via the investigation of the properties of the distribution of inverse participation ratio for eigenvalue ‘0’. We showed that the localisation of water molecules that belong to the network is significantly different from the ones that are not part of the percolated cluster.

J. Mol. Liq. 2021, 327, 114802 [6]

Molecular dynamics simulations of pure ambient liquid water were performed. Hydrogen bond network properties were determined by calculation of eigenvectors and eigenvalues of the Laplace matrix. We investigated how these quantities depend on the system size, the coordination number and periodic boundary conditions taking into account different hydrogen bond definitions. It was found that the first peak of the Laplace spectra contains six eigenvalues. These results suggest that six communities are always formed in our simulated systems independently of the number of molecules in the cubic box. By the help of the spectral clustering method, which is an acceptable indicator of the global properties of H-bonded network, two different H-bonded environments were identified. The tetrahedrality of the water molecules is significantly larger at the surface than inside the clusters. This difference can be related to the coexistence of HDL and LDL domains in liquid water.

Furthermore, our work also emphasizes that the periodic boundary conditions always cause clustering in the system.

J. Mol. Liq. 2022, 363, 119860 [7]

Topological descriptors related to the size distribution of hydrogen bonded clusters are scrutinized systematically, primarily from the point of view of their applicability for locating the percolation transition point. As a first step, we focus on regular, relatively simple systems like ice polymorphs (cubic, hexagonal, ice VI and ice VII), in order to monitor the evolution of these descriptors with varying the hydrogen bonding probability. Further quantities are also introduced, like the ratio of the number of molecules that do not belong to any ring structure, by which it is possible to determine a critical bonding probability below that the system shows dominantly chain-like behaviour. By means of calculating the smallest eigenvalues of the Laplace spectra of hydrogen bonded networks, yet another way has been developed for determining the percolation transition point. Results concerning the percolation transition agree well with those arising from more traditional 'toolbox' calculations. Finally, the aforementioned descriptors have been calculated for more realistic systems, with the aim of understanding better the properties of hydrogen bonded networks in important alcohol-water solutions.

4. Effects of H-bond asymmetry on the electronic properties of liquid water

J. Mol. Liq. 2019, 293, 111579 [3]

Molecular dipole moments, density of states (DOS) and charge distributions are reported for liquid water at two temperatures, 300 K and 350 K, from ab initio molecular dynamics simulations, using the BLYP functional with empirical dispersion corrections. The distributions of the molecular dipole moments have been determined according to various definitions, like the Bader and the Wannier type descriptions. By calculating the self-diffusion coefficient, it is confirmed that our systems are in the normal liquid state. It is demonstrated that the properties mentioned above, and in particular, the molecular dipole moment, depend on the hydrogen bonded local environment of the molecules.

List of publications supported by project NKFI FK 128656

Research articles

[1] **Pothoczki, S.**; Pusztai, L.; Bako, I.: Molecular Dynamics Simulation Studies of the Temperature-Dependent Structure and Dynamics of Isopropanol-Water Liquid Mixtures at Low Alcohol Content
JOURNAL OF PHYSICAL CHEMISTRY B 123, 7599-7610 (2019)
https://doi.org/10.1021/acs.jpcb.9b05631

[2] Bakó, I.; Pethes, I.; **Pothoczki, S.**; Pusztai, L.: Temperature dependent network stability in simple alcohols and pure water: The evolution of Laplace spectra
JOURNAL OF MOLECULAR LIQUIDS 273, 670-675 (2019)
https://doi.org/10.1016/j.molliq.2018.11.021 [Arxiv: https://arxiv.org/abs/1803.06660]

[3] Bakó, I.; Daru, J.; **Pothoczki, S.**; Pusztai, L.; Hermansson, K.: Effects of H-bond asymmetry on the electronic properties of liquid water – An AIMD analysis
JOURNAL OF MOLECULAR LIQUIDS 293, 111579 (2019)
https://doi.org/10.1016/j.molliq.2019.111579 [REAL: https://real.mtak.hu/100132/]

[4] **Pothoczki, S.**; Pethes, I.; Pusztai, L.; Temleitner, L.; Csókás, D.; Kohara, S.; Ohara, K.; Bakó, I.: Hydrogen bonding and percolation in propan-2-ol – Water liquid mixtures: X-ray diffraction experiments and computer simulations
JOURNAL OF MOLECULAR LIQUIDS 329, 115592 (2021)
https://doi.org/10.1016/j.molliq.2021.115592 [Open Access]

[5] **Pothoczki, S.**; Pethes, I.; Pusztai, L.; Temleitner, L.; Ohara, K.; Bakó, I.: Properties of Hydrogen-Bonded Networks in Ethanol-Water Liquid Mixtures as a Function of Temperature: Diffraction Experiments and Computer Simulations
JOURNAL OF PHYSICAL CHEMISTRY B 125, 6272-6279 (2021)
https://doi.org/10.1021/acs.jpcb.1c03122 [Open Access]

[6] Bakó, I.; Csókás, D.; **Pothoczki, S.**: Molecular aggregation in liquid water: Laplace spectra and spectral clustering of H-bonded network
JOURNAL OF MOLECULAR LIQUIDS 327, 114802 (2021)
https://doi.org/10.1016/j.molliq.2020.114802 [REAL: https://real.mtak.hu/129630/; Arxiv: https://arxiv.org/abs/2009.00955]

[7] Bakó, I.; Pusztai, L.; **Pothoczki, S.**: Topological descriptors and Laplace spectra in simple hydrogen bonded systems
JOURNAL OF MOLECULAR LIQUIDS 363, 119860 (2022)
https://doi.org/10.1016/j.molliq.2022.119860 [Open Access]

[8] Bakó, I.; **Pothoczki, S.**; Pusztai, L.: Connecting Diffraction Experiments and Network Analysis Tools for the Study of Hydrogen-Bonded Networks
JOURNAL OF PHYSICAL CHEMISTRY B 127, 3109-3118 (2023)
https://doi.org/10.1021/acs.jpcb.2c07740 [Open Access]

[9] Bakó, I.; Pusztai, L.; **Pothoczki, S.**: Outstanding Properties of the Hydration Shell Around β-D-Glucose: A Computational Study
ACS OMEGA (2024) ASAP
https://doi.org/10.1021/acsomega.4c00798
[Open Access, Arxiv: https://arxiv.org/abs/2308.03653]

Conference talks

[T1] Changes of H-bond network on cooling in 2-propanol-water liquid mixtures over the entire concentration range, Joint EMLG/JMLG Annual Meeting, September 2019. Kutna Hora, Czech Republic

[T2] Hydration of carbohydrate molecules, Joint EMLG/JMLG Annual Meeting, September 2022. Barcelona, Spain

[T3] Hydration properties in aqueous solutions of fructose, Joint EMLG/JMLG Annual Meeting, September 2023. Bordeaux, France

[T4] Hydration of monosaccharide molecules, 25th International Conference of Horizons in Hydrogen Bond Research, September 2023. Bologna, Italy

[T5] Hydration properties of monosaccharide molecules, RMC-8(+1) Conference, September 2023. Budapest, Hungary

Conference posters

[P1] Temperature induced changes in the hydrogen-bond network of isopropanol-water mixtures at low isopropanol concentration range, Joint Conference of EMLG/JMLG Meeting 2018 and 41st Symposium on Solution Chemistry of Japan, November 2018. Nagoya, Japan

[P2] Hydration of carbohydrate molecules, From water to colloidal water Conference, June 2022, Rome, Italy

Other seminar talks

[O1] Changes of H-bond network on cooling in 2-propanol-water liquid mixtures over the entire concentration range, February 2020. Fukuoka University, Fukuoka, Japan – *invited talk*

[O2] Changes of H-bond network on cooling in 2-propanol-water liquid mixtures over the entire concentration range, February 2020. Saga University, Saga, Japan – *invited talk*

[O3] Investigation of hydrogen bonds in aqueous solutions of isopropanol, May 2020. Seminar of Wigner RCP ISSP – *online talk*