Aqueous salt solutions

Concerning the structure of aqueous salt solutions, highly concentrated aqueous lithium and cesium chloride solutions have been investigated by classical molecular dynamics (MD) and reverse Monte Carlo (RMC) simulations. At first, MD calculations were carried out applying twenty-nine (LiCl) and thirty (CsCl) combinations of ion-water interaction models at four (LiCl) and three (CsCl) salt concentrations. Characteristic properties obtained from various experiments, such as density, static dielectric constant, and self-diffusion coefficients, have been compared with simulation results originating to the (many) different type of force fields.

Particle configurations obtained from MD simulations were used to calculate the partial radial distribution functions (PRDF) and the neutron and X-ray weighted total scattering structure factors (TSSF). The TSSFs were compared with experimental data (measured earlier by some of the participants), in order to find the best force field (FF) models that reproduce measured structure factors correctly.

Although none of the tested MD models can describe the structure perfectly at the highest investigated LiCl concentration, the (at least) semi-quantitative agreement with experiment made it possible to determine basic structural features in each solution. Four nearest neighbors (oxygen atoms and chloride ions together) are found around a lithium ion at each concentration, while in the surroundings of the chloride ion, hydrogen atom pairs are replaced by one lithium ion as the concentration increases. While in pure liquid water four water molecules can be found around a central water molecule, near the solubility limit nearly all water molecules are connected to two chloride ions (via their hydrogen atoms) and one lithium ion (by their oxygen atoms). It was also shown that in addition to models in which the number of contact ion pairs is too high, models in which this number is too low are also unable to reproduce the experimental data on CsCl solutions.

In addition, we performed ab initio molecular dynamics simulations (blyp/d3 level) on concentrated LiCl and CsCl solutions (3.75 and 19.55 mol/kg). The total coordination number of Li+ is found to be around 4 at each investigated concentration. In the more dilute solutions we can find only 0.2 Cl contacts of Li ions on average. One of the drawbacks of nearly all of the classical simulations was that the diffusion constants of Li, Cl and water are very small (in the range of 10^{-10} m^2/s). In our AIMD simulations the diffusion constants are in the range of $0.2\text{-}0.4*10^{-9}$ m^2/s, even in the concentrated solution. Furthermore, we can get acceptable agreement with both the measured X-ray and neutron diffraction data by AIMD simulations. On the other hand, in the case of CsCl solutions we showed that the applied DFT theory cannot predict properly the experimentally estimated Cs-O distance.

In order to understand the main problem with our DFT calculations, a series of electronic structure calculations for ‘Cs-8water’ (sandwich) style structures have been performed from an optimized geometry, using the def2qzvpp basis set together with the m062x functional. In addition to these calculations, we examined how the interaction energy of these ‘Cs-8water’ systems change if the Cs-O distance is systematically varied while maintaining the symmetry of the system.

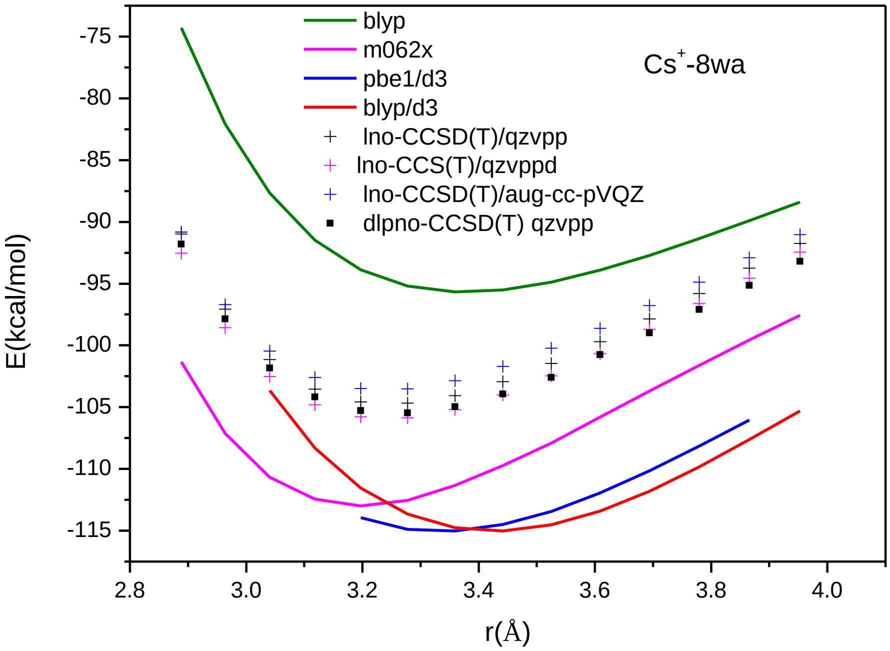

Figure 1 Calculated interaction energies between the Cs+ ion and water in ‘Cs--8water‘ (sandwich like) systems as a function of the Cs…O distance.

These calculations were performed at the BLYLP/D3, PBE/D3, revPBE/D3, m062x/D3 and B2PLYP/D3 levels. Additionally, we performed on these sets of geometries LNO-CCSD(T) calculations, using the MRCC code with qzvpp, qzvppd and aug-cc-pVQZ basis sets, with ecp-46 effective core potentials for Cs ions. The results are presented in the Figure 1 (just above). It is clear that the BLYP and PBE functionals significantly overestimated the position of the energy minimum obtained from very accurate QM calculations.

A new energy decomposition (LED) calculation was also performed on ’Cs-1water’ and ‘Cs-8water’ energy minimum configurations, using the DLPNO-CCSD(T) method at the def2qzvpp level. The interaction energy difference for this system is smaller than 0.2 kcal/mol between calculations with LNO or DLPNO-CCSD(T) methods on the same basis sets. Results from these calculations are presented in Table 1.

Table 1. The various energy components in the ‘Cs—8water’ system with optimized geometry (kcal/mol)

Tot E	el.stat	exchange	nondisp	triple ex.	repulsion	dispersion
-100,46	-319,64	-43,69	3,25	-13,54	289,09	-15,92

It is clear that the most important contribution is the electrostatic one. Here we would like to remark that the main part of the repulsive interactions is arising from the water-water contact in the hydration shell.

In our related publication we showed that the concept of ‘mixed’ water-anion hydrogen bonded network provides a sensible characterization of highly concentrated lithium chloride salt solutions. The existence a “real” H-bond between the Cl- anion and water molecules are also proven now, via a quantum chemical QM calculation on the $Cl(H_2O)_6$ cluster. The applied QM descriptor (bond order, bond critical point properties, CECA decomposition) have proven that the interaction between Cl^- and water is not purely electrostatic.

Taking this type of H-bond into account explains the apparent homogeneity of such systems, contrary to what the concept of a ‘pure’ water network would suggest. The approach has brought about the observation of ‘solvent separated anion pairs’ that are the dominant motifs in cyclic hydrogen bonded entities at high LiCl concentration. The characterization of, as well as the distinction between, ‘good’ and ‘bad’ potential models of aqueous LiCl solutions becomes very natural via the ‘mixed’ network concept: good models facilitate mixing of ions and water molecules at the atomic scale, whereas inappropriate force fields tend to result in separation of solvent and solute (micro-)phases.

Electronic properties of ions and water in aqueous environments

In the related works we studied cooperative effects in bulk liquid water and in water clusters. We analysed the two- and three-body interaction energy components in water clusters containing up to 30 water molecules, using the “hierarchical” basis set superposition error (BSSE)-corrected energy decomposition scheme. We found that the average BSSE-corrected two- and three-body interaction energy terms are about 74 to 80 and 20 to 26%, respectively, of the total BSSE-corrected interaction energy for all investigated clusters. We showed, while investigating the two-body energy distribution, that this function presents two distinct peaks at -5.0 kcal/mol and 0.0 kcal/mol, respectively. The first peak corresponds to the H-bonded interaction, as we can prove by calculating the OO-distance/interaction energy 2D distribution. It was observed that the three-body interaction energy component is significantly negative/positive if there are two H-bonds and one attraction/repulsion interaction in the corresponding trimer, respectively. Our calculations also revealed that the deformation energy of water molecules depends on their H-bonded environment.

The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system, that is, a measure of the system's overall polarity. The dipole moment is one of the simplest quantities that is related to the distribution of electronic density in a polar molecule. In the absence of the knowledge of the dipole moment, the induction, long-range electrostatic interactions and the information incorporated in structure of infrared and sum-frequency generation spectra cannot be interpreted. It is well established that in condensed phases the dipole moment of polar molecules increases due to the interaction with the environment (polarization, charge transfer, geometrical deformation, etc. ...) Recent studies indicated a significant enhancement (up to ~2.9-3.05 D) of the dipole moment of individual water, methanol and acetonitrile molecules in clusters and in liquid phase. It is conceivable that the more than 40 % increase of dipole moments of water and methanol molecules in the liquid state should be considered as a collective effect that is connected with the existence of H-bonded structures in these liquids. In a previous study we showed that the average dipole moment of water molecules depends on the H-bonded environment of the central molecule. Additionally, in our earlier paper we showed that the dipole moment of a large water cluster can be reproduced only if one takes into account that there is a significant electron delocalization along the hydrogen bonds. The dipole moments of individual molecules contain significant components originating to the “tails” of the orbitals due to this delocalization (‘quantum chemical bond formation’). This even questions the concept of a water cluster consisting of individual molecules (as opposed to the concept of the whole clusters is considered as single molecules).

In our most recent paper we show that the dipole moment of polar (water, methanol, formamide, acetone and acetonitrile) molecules in the neighbourhood of cations is increased primarily by polarization from the bare electrostatic charge of the cations. This is so despite that the effective value of the latter is somewhat reduced by “back donation” of electrons from neighbouring polar molecules. It was found that the geometrical arrangement of polar molecules in the first solvation shell is such that their mutual polarization reduces the dipole moments of individual molecules, so that in some cases they become smaller than the dipole moment of the free protic or aprotic molecule. We conjecture, for the first time, that this behaviour, namely the about 10-20 % decrease of the dipole moment of water molecules in the first shell of cations, with the cation itself removed, is essentially a manifestation of the Le Chatelier–Braun principle.

The polarizability of a water molecule within a condensed phase is expected to be different from its value in the gas phase because of inter-molecular interactions. As a follow-up, the polarizability of cations and anions in a hydrated environment was determined using the finite difference method. Results are shown in Table 2.

Table 2: Polarizability of anions, cations and water molecules in supramolecular environments.

	Polarizability ion (A^3)	Polarizability water (A^3)
Cl^-(6wa)	3.151	1.142
F^-(6wa)	1.065	1.068,1.171
Li^+(6wa)	0.026	1.167
Na^+(6wa)	0.095	1.120
Mg^{2+}(6wa)	0.040	1.122
Ca^{2+}6wa	0.505	1.184
Ca^{2+}8wa	0.512	1.194
Zn^{2+}(6wa)	0.201	1.123
Al^{3+}6wa	0.019	1.085
Ga3+(6wa)	0.021	1.081

Nuclear quantum effects in hydrogen bonded liquids

We proposed a new method, GSTA (Generalized Smoothed Trajectory Analysis) for quantum correction of classical and BOMD (Born-Oppenheimer molecular dynamics) simulations. We showed that the capability and accuracy of GSTA is comparable to concurrent methods. A clear advance of GSTA, as compared to the well established 1PT(+AC) or 2PT methods, is that the effect of anharmonicity can be determined rigorously using a smoothing function. Another novelty is that structural NQEs can be investigated with the filtration of the coordinates. In more advanced methods, by which anharmonicity can be described, the classical dynamics is modified to incorporate NQEs, for instance ZPEs (zero point energies) are added to the different normal modes of vibrations. The good agreement with the experiments indicates the plausibility of our smoothing technique. Zero point vibrations do not need to be introduced into classical simulations: similar effect can be achieved with the proper enhancement of high frequency motions from unmodified trajectories. The necessary simulations are orders of magnitudes faster than those of the golden standard (exact) technique, PIMD.

It is well known for molecular liquids that can form hydrogen bonds that their structural and dynamical properties are influenced by nuclear quantum effects, too. Differences in terms of density, dynamic and thermodynamic properties between deuterated and hydrogenated forms of many liquids are well known. We applied our new method, GSTA for quantum correcting classical simulations. We presented an application of the GSTA method for classical and ab initio molecular dynamics simulation models of light (H_2O) and heavy (D_2O) water. NQEs have somewhat smaller influence on the O-D and D-D partial radial distribution functions of heavy water than on the O-H and H-H ones of light water. After correcting for NQEs the O-’H’ bond lengths in light and heavy water have become different: the O-D ones are about 0.5 % shorter than the O-H ones. Based on a cross-check procedure (calculate GSTA-corrected PRDFs for light, heavy and ’null’ water; compose total RDFs; separate partials by assuming that H=D), it can be stated that concerning the structure of liquid water, the assumption that H and D are equal is valid, to a very good approximation for isotopic substitution method for liquid water. This statement is important from the point of view of the isotopic substitution method.

We continued our systematic investigations for comparing the two available methods (2PT and 1PT+AC) for taking the NQE effect into account in the case of the heat capacity calculation. We clearly proved that the heat capacity calculated by the 2PT method (this was the most acceptable in the literature) contains a significant mathematical error. We performed a benchmark calculation for more than 100 organic liquids using our newly developed correction method for heat capacity. Our results help to improve the accuracy of the calculated thermodynamic properties of large systems.

As a continuation of this research, we analyzed in detail the cooperative effects of water in the percolated three-dimensional hydrogen bonding network. This phenomenon was investigated through the dependence of the average hydrogen bond distance on the number of hydrogen bonded neighbours. We found that NQE effects did not influence these properties. For simulations using ab initio, or classical polarization models, the mean H-bond distance decreases with increasing H-bond number. However, in the case of the classical rigid models, the opposite behaviour was observed.

Water-alcohol systems

Concerning the temperature dependence of the structure of ethanol-water mixtures, extensive molecular dynamics computer simulations have been conducted in the water-rich side of the composition range, with 10, 20 and 30 mol % of the alcohol, at temperatures between room temperature and the experimental freezing point of the given mixture. All-atom type (OPLS) interatomic potentials have been assumed for ethanol, in combination with two kinds of rigid water models (SPC/E and TIP4P/2005). Both combinations have provided excellent reproductions of the experimental X-ray total structure factors at each temperature; this provided a strong basis for further structural analyses. Beyond partial radial distribution functions, various descriptors of hydrogen bonded assemblies, as well as of the hydrogen bonded network, have been determined from the simulated particle configurations. A clear tendency was observed towards that an increasing proportion of water molecules participate in hydrogen bonding with exactly 2 donor- and 2 acceptor sites as temperature decreases. Concerning larger assemblies held together by hydrogen bonding, the main focus was put on the properties of cyclic entities: it was found that, similarly to methanol-water mixtures, the number of hydrogen bonded rings has increased with lowering temperature. However, for ethanol-water mixtures the dominance of not the six-, but of the five-fold rings could be observed.

Concerning the atomic level dynamics of ethanol-water mixtures, temperature dependent hydrogen bond energetics and dynamical features, such as the diffusion coefficient and re-orientational times, have been determined for ethanol-water mixtures with 10, 20 and 30 mol % of ethanol. Concerning pairwise interaction energies between molecules, it is found that water-water interactions become stronger, while ethanol-ethanol ones become significantly weaker in the mixtures, than the corresponding values characteristic to the pure substances. Concerning the diffusion processes, for all concentrations the activation barriers of water and ethanol molecules become very similar to each other. Re-orientational motions of water and ethanol become slower as ethanol concentration is increasing. Characteristic re-orientational times of water in the mixtures are substantially longer than these values in the pure substance. On the other hand, this change for ethanol is only moderate. Re-orientational motions of water (especially the ones related to the H-bonded interaction) become very similar for those of ethanol in the mixtures.

Concerning the temperature dependence of the structure of 2-propanol-water mixtures, extensive molecular dynamics computer simulations have been conducted on the water-rich side of the composition range, with 5, 10 and 20 mol % of the alcohol, at temperatures between room temperature and the experimental freezing point of the given mixture. Here we focus on characteristics related to hydrogen bonds (HB): cluster-, and in particular, ring formation, energy distributions, and lifetimes of HB-s have been scrutinized for the entire system, as well as for the water and isopropanol subsystems. It is demonstrated that, similar to ethanol–water mixtures, the occurrence of 5-membered-hydrogen-bonded rings are significant, particularly at higher alcohol concentrations. We investigated the energetic properties of these mixtures and found that a double maximum appears on the alcohol–alcohol HB energy distribution function in the attractive region. HB lifetimes, calculated using the autocorrelation method, have been found significantly longer in the mixtures than they are in the pure liquids. These studies help us to perform more sophisticated analyses of the H-bonded network in aqueous salt solutions.

Scrutinizing the properties of the hydrogen-bonded network in water, methanol and ethanol, a number of computer-generated models are considered at room temperature and ambient pressure, and also as a function of temperature (for water and ethanol), and the potential model (for water only). The Laplace matrices have been determined, and various characteristics of them, such as eigenvalues and eigenvectors, as well as the corresponding Laplace spectra have been calculated. It is revealed how the width of the spectral gap in the Laplace matrix of H-bonded networks may be applied for characterising the stability of the network. A novel method for detecting the presence of percolated networks in these systems was also introduced.

A series of Molecular Dynamics simulations were performed using TIP4P/2005 water model to study the effects of periodic boundary conditions on the community in H-bonded networks based on eigenvectors and eigenvalues analyses of the Laplace spectra, via applying spectral clustering method. The results suggest that periodic boundary conditions always introduce clustering in our systems. Thus, we are not dealing only with local structural information about the actual structure of the fluid, but an additional distribution, which can be considered as a perturbation arising from periodic boundary conditions. Unfortunately, this effect cannot be eliminated. We hypothesize that these properties of the Laplace spectrum are significantly influenced by the shape of the simulation box. Ultimately, these results suggest that six clusters are always formed in our simulation systems in the cubic box due to the periodic boundary conditions. The H-bonded environment on the surface is organized more tetrahedrally than the “core” molecules in the cluster, as we showed using several local order parameters such as tetrahedrality and different LSI approaches. Our results revealed that in the case of simulation based investigations, the possible existence of low (LDL) and high density liquid (HDL) phases in liquid water, it is always necessary to take into account the effect of periodic boundary conditions. Finally, we would like to point out that similar analyses for neat HDL and LDL water (below, of course, the hypothetical liquid-liquid critical point) would be worth performing.

In addition, we have summarised our results in a(n invited) “perspective” article, already submitted to *J. Phys. Chem B.*

Number of research articles: 17 (+1 submitted).

Cumulative impact factor: 78.

Number of independent citations: 110.