FINAL REPORT
OF THE
RESEARCH PROJECT

The influence of pressure and temperature on the structure of alcohol-water mixtures

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Project duration: 01.12.2018 – 31.08.2021
Number of publications: 16
Cumulative impact factor: 67.86

General scheme of the research work

The pressure and temperature dependent microscopic structure and dynamics of alcohol-water liquid mixtures have been studied experimentally by diffraction methods, and by follow-up computer simulations (molecular dynamics, MD, and Reverse Monte Carlo, RMC), as a function of composition. As complementary research, we have also considered the atomic level structure of amorphous solid systems (covalent and metallic glasses) via diffraction and EXAFS methods, and RMC modeling. Although this part of the work is only an extension to the original proposal, the methodology is essentially the same as used for alcohol-water mixtures: this is why this activity fits perfectly into the framework of the research planned. Particle configurations (sets of 3D Cartesian coordinates) provided by MD and RMC have been subjected to further (mostly geometrical) analyses. As a result, detailed descriptions of the local structure, in terms of neighbour- and angular distributions, hydrogen bond statistics, etc…, are obtained.

Results concerning alcohol-water liquid mixtures

(1) Total scattering structure factors of per-deuterated methanol and heavy water, CD_3OD and D_2O, have been determined across the entire composition range as a function of pressure up to 1.2 GPa, by neutron diffraction. The largest variations due to increasing pressure were observed below a scattering variable value of 5 $Å^{-1}$, mostly as shifts in terms of the positions of the first and second maxima. Molecular dynamics computer simulations, using combinations of all-atom potentials for methanol and various water force fields, were conducted at the experimental pressures with the aim of interpreting neutron diffraction results. The peak-position shifts mentioned above could be qualitatively reproduced by simulations, although in terms of peak intensities, the accord between neutron diffraction and molecular dynamics was much less satisfactory. However, bearing in mind that increasing pressure must have a profound effect on repulsive forces between neighboring molecules, the agreement between experiment and computer simulation can certainly be termed as satisfactory. In order to reveal the influence of changing pressure on local intermolecular structure in these “simplest of complex” hydrogen-bonded liquid mixtures, simulated structures were analyzed in terms of hydrogen bond-related partial radial distribution functions and size distributions of hydrogen-bonded cyclic entities. Distinct differences between pressure-dependent structures of water-rich and methanol-rich composition regions were revealed.

(2) Structural details, viscosity trends and dynamic phenomena in t-butanol/water solutions are closely related on the molecular scales across the entire composition range. Utilizing the experimental small- and wide-angle x-ray scattering (SWAXS) method, molecular dynamics (MD) simulations and the ‘complemented-system approach’ it is possible to comprehensively describe the structure-viscosity-

dynamics relationship in such structurally versatile hydrogen-bonded molecular liquids, as well as in similar, self-assembling systems with pronounced molecular and supramolecular structures at the intra-, inter-, and supra-molecular scales. SWAXS and x–ray diffraction experiments and MD simulations were performed for aqueous t-butanol solutions at 25 °C. Literature viscosity and self-diffusion data were also used. The interpretive power of the proposed scheme was demonstrated by the extensive and diverse results obtained for aqueous t–butanol solutions across the whole concentration range. Four composition ranges with qualitatively different structures and viscosity trends were revealed. The experimental and calculated zero-shear viscosities and molecular self-diffusion coefficients were successfully related to the corresponding structural details. The hydrogen bonds that were, along with hydrophobic effects, recognized as the most important driving force for the formation of t–butanol aggregates, show intriguing lifetime trends and thermodynamic properties of their formation.

(3) Methanol-water liquid mixtures have been investigated by high-energy synchrotron X-ray and neutron diffraction at low temperatures. We are thus able to report the first complete sets of both X-ray and neutron weighted total scattering structure factors over the entire composition range (at 12 different methanol concentrations (x_M) from 10 to 100 mol%) and at temperatures from ambient down to the freezing points of the mixtures. The new diffraction data may later be used as reference in future theoretical and simulation studies. The measured data are interpreted by molecular dynamics simulations, in which the all atom OPLS/AA force field model for methanol is combined with both the SPC/E and TIP4P/2005 water potentials. Although the TIP4P/2005 water model was found to be somewhat more successful, both combinations provide at least semi-quantitative agreement with measured diffraction data. From the simulated particle configurations, partial radial distribution functions, as well as various distributions of the number of hydrogen bonds have been determined. As a general trend, the average number of hydrogen bonds increases upon cooling. However, the number of hydrogen bonds between methanol molecules slightly decreases with lowering temperatures in the concentration range between ca. 30 and 60 mol% alcohol content. The same is valid for water-water hydrogen bonds above 70 mol% of methanol content, from room temperature down to 193 K.

(4) New X-ray and neutron diffraction experiments have been performed on ethanol–water mixtures as a function of decreasing temperature, so that such diffraction data are now available over the entire composition range. Extensive molecular dynamics simulations show that the all-atom interatomic potentials applied are adequate for gaining insight into the hydrogen-bonded network structure, as well as into its changes on cooling. Various tools have been exploited for revealing details concerning hydrogen bonding, as a function of decreasing temperature and ethanol concentration, like determining the H-bond acceptor and donor sites, calculating the cluster-size distributions and cluster topologies, and computing the Laplace spectra and fractal dimensions of the networks. It is found that 5-membered hydrogen-bonded cycles are dominant up to an ethanol mole fraction xeth = 0.7 at room temperature, above which the concentrated ring structures nearly disappear. Percolation has been given special attention, so that it could be shown that at low temperatures, close to the freezing point, even the mixture with 90% ethanol ($x_{eth} = 0.9$) possesses a three-dimensional (3D) percolating network. Moreover, the water subnetwork also percolates even at room temperature, with a percolation transition occurring around $x_{eth} = 0.5$.

(5) Synchrotron X-ray diffraction measurements have been conducted on aqueous mixtures of propan-2-ol (a.k.a. isopropanol, or 2-propanol), for alcohol contents between 10 and 90 mol%, from room temperature down to 230 K. Molecular dynamics simulations, by using an all-atom parametrization

of the propan-2-ol molecule and the well-known TIP4P/2005 water model, were able to provide semi-quantitative descriptions of the measured total structure factors. Various quantities related to hydrogen bonding, like hydrogen bond numbers, size distri- bution of cyclic entities and cluster size distributions, have been determined from the particle co-ordinates ob- tained from the simulations. The percolation threshold at room temperature could be estimated to be between isopropanol concentrations of 62 and 74 mol%, whereas at very low temperature, calculations yielded a value above 90 mol%.

(6) Aqueous mixtures of 1-propanol have been investigated by high-energy synchrotron X-ray diffraction upon cooling. X-ray weighted total scattering structure factors of 6 mixtures, from 8 mol% to 89 mol% alcohol content, as well as that of pure 1-propanol are reported from room temperature down to the freezing points of the liquids. Molecular dynamics simulations have been performed, in order to interpret measured data. The all atom OPLS-AA potential model was used for 1-propanol, combined with both the SPC/E and the TIP4P/2005 water models: both combinations provide a semi-quantitative description of the measured total structure factors at low and high alcohol contents, while the agreement is qualitative for the mixture with 71 mol% of 1-propanol. From the simulated particle configurations, partial radial dis- tribution functions were calculated. Furthermore, detailed description of the hydrogen bonded network is provided, in terms of hydrogen bond numbers, analysis of proton donor–acceptor ratios, size distribu- tions of hydrogen bonded clusters and ring size statistics. Strong temperature dependence of the perco- lation threshold, as well as of the participation of the number of doubly hydrogen bonded molecules in cyclic entities, has been found for the mixture with 89 mol% of 1-propanol. Above an alcohol content of 20 mol%, 5-fold rings are the most frequent cyclic entities, with a strong temperature dependence in terms of the number of rings.

Results concerning hydrogen-bonded sytems in general

(7) Corrections for nuclear quantum effects (NQE) have been calculated for classical molecular dynamics (MD) simulation models of light (H_2O), heavy (D_2O) and 'null' [$(H_2O)_{0.64}(D_2O)_{0.36}$] water. New path integral molecular dynamics (PIMD) simulations have also been conducted for the same systems. 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' bondlengths in light and heavy water have become differ- ent: the O-D ones are about 0.5% shorter than the O-H ones. Following NQE corrections, the total RDF of 'null' water does show hydrogen related features at the position of the intramolecular O-'H' peak. Based on a cross- check procedure involving the NQE-corrected total and partial radial distribution functions, 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 intermolecular correlations. These findings are also supported by our path integral molecular dynamics simulations.

(8) We demonstrated that the concept of 'mixed' water-anion hydrogen bonded network provides a sensible characterization of highly concentrated lithium chloride salt solutions. It can account for the homogeneity of such systems, contrary to what the 'pure' water network suggests 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.

(9) The orientational correlation scheme introduced earlier for tetrahedral molecules is extended for being able to classify orientational correlations between pairs of high symmetry molecules. While in the original algorithm a given orientation of a pair of tetrahedral molecules is characterized unambiguously by the number of ligand atoms that can be found between two planes that contain each centre and perpen- dicular to the centre-centre connecting line, in the generalized algorithm, the planes are replaced by cones, whose apex angles are set according to the symmetry of each molecule. To demonstrate the applicability of the method, the octahedral-shaped SF_6 molecule is studied in a wide range of phases (gaseous, supercritical fluid, liquid and plastic crystalline) using classical molecular dynamics. By analyzing the ori- entational correlations, a close-contact region in the first coordination shell and a medium-range order behaviour are identified in the non-crystalline phases. While the former is invariant to changes of the density, the latter showed longer-ranged correlations as density is raised. In the plastic crystalline state, fluorine atoms are oriented along the lattice directions with higher probability. To test the method for icosahedral symmetries, the crystalline structures of room temperature C_{60} is generated by three sets of potentials that produce different local arrangements. The novel analysis provided quantitative result on preferred arrangements.

(10) It has been shown how the dipole moment of a single molecule in a cluster can be calculated and used for describing the polarization effect. Additionally, we review the accuracy of the calculation of the dipole moment of several simple protic and aprotic molecules. It is shown that the dipole moment of polar (water, methanol, formamide, acetone and acetonitrile) molecules in the neighborhood of a cation is increased primarily 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 neighboring polar molecules. In other words, the classical picture may be viewed as if a point charge slightly smaller than the nominal charge of the cation would be placed at the cation site. It was found that the geometrical arrangement of the 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 behavior, namely the about 10%–20% decrease of the dipole moment of water in the first shell of cations, with the cation itself removed, is essentially a manifestation of the Le Chatelier– Braun principle. We also remark that if the cation-molecule bond order is too large then the calculated dipole moment for these complexes can be questionable, due to the questionable definition of a single molecule within the “supermolecule”-like cluster.

Results concerning amorphous solids

(1) Chemical short range order and topology of $Ge_xGa_xTe_{100-2x}$ glasses was investigated by neutron- and x-ray diffraction as well as Ge and Ga K-edge extended x-ray absorption fine structure (EXAFS) measurements. Large scale structural models were obtained by fitting experimental datasets simultaneously with the reverse Monte Carlo simulation technique. Models, relying only on experimental data and basic physical information without constraining the average coordination numbers, give 3.9–4.1 for the number of the atoms in the first coordination sphere of Ge atoms, while the average number of first neighbors of Ga atoms scatters around 3.8. The average coordination number of Te atoms is significantly higher than 2 for x = 12.5 and 14.3. It is found that the vast majority of MTe_4 (M = Ge or Ga) tetrahedra have at least one corner sharing MTe_4 neighbor.

(2) Structural order in the chalcogenide glasses of $(As_2S_3)_x(GeS_2)_{1-x}$ (x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) system is examined in terms of the parameters of local atomic structure as a function of composition x, obtained using high-resolution Raman spectroscopy, high-energy synchrotron X-ray diffraction, extended X-ray absorption fine structure spectroscopy and reverse Monte-Carlo modeling of diffraction data. As a result of the research carried out it is revealed that the structural order of As-rich (x > 0.4) and Ge-rich (x < 0.4) glasses is organized by the main As− S and Ge− S structural motifs based on pyramidal AsS_3 and tetrahedral GeS_4 units. Based on the structural studies, it is also established that the balance between corner-shared and edge-shared GeS_4 tetrahedra in the glass backbone of the investigated GeS_2-based glasses seems to be responsible for the interconnectivity between two speculative Raman modes at 370 and 430 cm− 1. Compositional changes in studied glasses result in the evolution of the observed Raman bands. Such dependences of characteristic constituent Raman bands' intensities showed that $(As_2S_3)_x(GeS_2)_{1-x}$ samples contain different nanophases whose concentration is changing along chosen compositional cross-section.

(3) In order to improve the reliability of short- and intermediate-range atomic structures of Ge_xSe_{1-x} glasses, high quality neutron diffraction data, in both the real and reciprocal spaces, were added to the existing anomalous x-ray scattering and x-ray diffraction datasets during Reverse Monte Carlo modeling. This addition proved to be highly effective for obtaining well-refined structural data and for revealing a close relationship between the compositional stiffness transition occurring at about x = 0.20–0.26 and the partial structures. Although the $S_{ij}(Q)$ and $g_{ij}(r)$ functions gradually change with varying x, important indications on the stiffness transition are confirmed on the basis of the intermediate-range element-selective atomic structures (hyper-ordered structures) more clearly than it was possible by previous results. An abrupt decrease in terms of the the prepeak intensity of $S_{GeGe}(Q)$, a rapid disappearance of the Ge–Ge homopolar bonds, anomalies in the ratio of edge- and corner-sharing $Ge(Se_{1/2})_4$ tetrahedra, and characteristic changes in the tetrahedral connections with decreasing x across the so-called intermediate phase have all been observed.

(4) Amorphous alloys consisting of elements present in the human body, such as magnesium, zinc and calcium, are currently extensively studied in order to utilize them as a material for biodegradable orthopaedic implants. amongst all Mg-Zn-Ca alloys investigated up to date, the $Mg_{66}Zn_{30}Ca_4$ composition has the greatest potential for applications. Its critical casting thickness reaches a value of 5 mm, the compressive strength (716–854 MPa) is about 4 times the limit of human cortical bone while elastic modulus is (31 GPa) is only 3 times higher than that of human bone. During dissolution the alloy shows only marginal hydrogen evolution. Here we present a detailed, experiment-based structural investigation of $Mg_{66}Zn_{30}Ca_4$. Structural and topological analysis of its atomic structure reveals a high number of predominantly icosahedral densely packed Zn-centred clusters. It is believed that the existence of these structural units is responsible for the suppression of internal diffusion and thus greatly improves glass formability.

Date: 20 September 2021

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