Ethanol-water structures at the microscopic level studied by X-ray Compton scattering: extreme sensitivity to geometries

Water-ethanol mixtures are industrially important substances, but surprisingly little is known about them at the detailed microscopic level. In general, characterization and understanding of liquid mixtures at the molecular level is needed in order to explain and design their macroscopic properties. Liquid mixtures are ubiquitous in our environment, ranging from household chemicals to seawater. Industry handles and manufactures a wide variety of liquid mixtures, which could be in many cases better tailored if one had the precise knowledge of the microscopic structure and behavior. From a purely scientific perspective, the most interesting questions are related to structural inhomogeneities and hydration structures, and how for example the water molecules behave in complicated structures, when they are not any more in their bulk environment.

Accurate computer simulations on the structure of complicated liquids are still at their infancy. In principle, quantum mechanical molecular dynamics (MD) simulations should reveal all the aspects of the liquid, but in practice such calculations cannot be yet performed even at supercomputers. The difficulty stems first of all from the heavy computational demand regarding the time-scale of the simulation runs. Secondly, the complexity of the physical interaction model for the electrons is such that only very small systems can be studied highly accurately. These challenges require new experimental approaches.

In a joint experimental and theoretical study [1], an X-ray Compton scattering experiment on ethanol-water mixtures was carried out at beamline **BL08W**. The purpose of the experiment was to characterize the hydrogen bond and solvation structures in the mixtures at various alcohol concentrations. X-ray Compton scattering experiments suit to this project since the measured data is extremely sensitive to subtle changes in the molecular level geometries [2]. The experiments are demanding, since very large statistics are needed to observe the sub-Ångström scale effects. The samples were prepared by researchers from Suntory, Japan. The molar concentration of ethanol in the samples was chosen to be 5.5-73.1%, which corresponds to the volume percentages 20-90%.

In the experiment an interesting behavior was found, which suggests that there is a structural change in the water-ethanol mixture between the concentrations 5.5% and 15.7% (see Fig 1). The data is shown as difference profiles, for which the Compton profiles of pure liquids are subtracted from the Compton profile of the mixture according to the molar percentages. The experimental data was analyzed by scientists at the University of Helsinki using model calculations based on modified structures obtained from classical molecular dynamics simulations. In the models, systematic changes were made in the internal covalent bonds and in the intermolecular distances between the molecules. An example of the results of these changes is shown in Fig. 2. A noteworthy point is that changes in the covalent bond lengths produce qualitatively different effects compared to changes in the intermolecular distances.

The comparison of the model calculations to the experimental data led to the characterization and interpretation of the structure. In the low-concentration sample (5.5 mol-%), there is a lengthening of the O-H covalent bonds by approx. 0.003 Å. Based on other studies in the literature, this lengthening can be interpreted as a stronger hydrogen-bond network of water in the mixture as compared to the pure liquids. In the higher-concentrations samples (15.7-73.1 mol-%), it was found that the intermolecular distances between the molecules became shorter. Macroscopically, this means a denser system compared to the pure liquids, which is a well-known

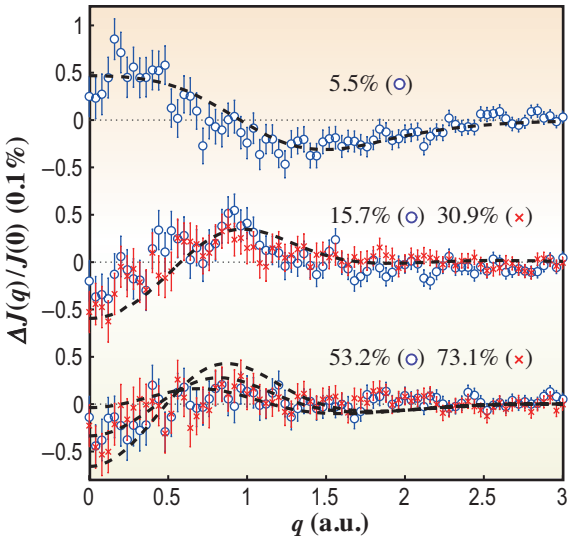

Fig. 1. Experimental Compton profile differences. The experimental data are given by red crosses (×) and blue circles (o). The molar percentages of ethanol have been indicated, and the data have been shifted for clarity. The black dashed curves are model calculations from modified MD clusters. Uppermost curve: O-H bonds elongated by 0.003 Å in the 5% mixtures; middle curve: O…O distances decreased by 1% in the 15% mixtures; lowermost three curves: O…O distances decreased by 1%, 2%, and 3% in the 95% mixtures.

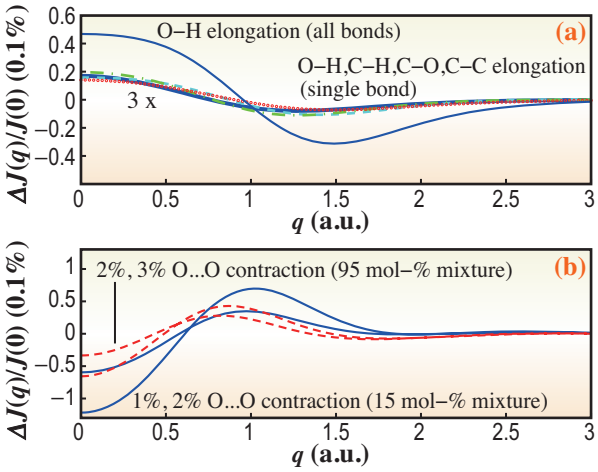

Fig. 2. **(a)** Changes in the Compton profile when all the intramolecular O-H bond lengths are increased by 0.003 Å (blue solid line) and one bond [O-H of water or ethanol (red), C-O (cyan), C-C (green), or C-H (blue)] in a cluster increased by 0.01 Å (latter multiplied by 3 for better clarity). **(b)** Changes in the Compton profile when the density increases: intermolecular O…O distances decreased by 1% and 2% (for 15% mixture) and 2% and 3% (for 95% mixture). For both concentrations, larger features arise for larger contractions.

property of ethanol-water mixtures. The two regimes are represented schematically in Fig. 3.

The present findings are a new way to characterize inhomogeneities in alcohol-water systems. For the first time, the quantitative changes related to the intra- and intermolecular structures were determined. The study demonstrates the power of X-ray Compton scattering to study detailed geometrical properties. It complements a previous demonstration of the observation of configurational energetics of materials [3]. In the future, advanced materials could be characterized in a new and unique way using these methods.

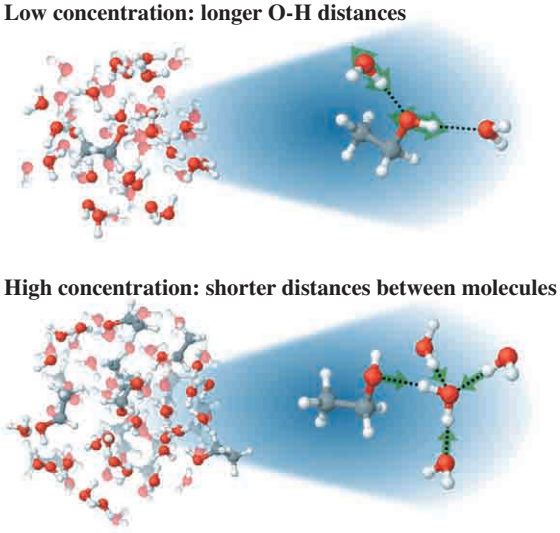

Fig. 3. Schematic representation of the structural changes in the two solvation regimes in water-ethanol mixtures compared to pure liquids.

Mikko Hakala[a,*], Iina Juurinen[a] and Koichi Nakahara[b]

[a] Dept. of Physics, University of Helsinki, Finland
[b] Frontier Center for Value Creation, Suntory Business Expert Limited

*E-mail: mikko.o.hakala@helsinki.fi

References

[1] *I. Juurinen, K. Nakahara, N. Ando, T. Nishiumi, H. Seta, N. Yoshida, T. Morinaga, M. Itou, T. Ninomiya, Y. Sakurai, E. Salonen, K. Nordlund, K. Hämäläinen and M. Hakala: Phys. Rev. Lett.* ***107*** *(2011) 197401.*
[2] M. Hakala *et al.*: Phys. Rev. B **73** (2006) 035432.
[3] K. Nygård *et al.*: Phys. Rev. Lett. **99** (2007) 197401.