



	Experiment title: Tenfold amplification of the dielectric loss in mixed alcohols: Break-up of ring-like structures into chains	Experiment number: SC-3916
Beamline: ID20	Date of experiment: from: 04 December 2014 to: 09 December 2014	Date of report: 04.03.2015 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): <i>Christoph J. Sahle</i>	
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Report: The aim of experiment SC-3916 was to study changes in the local structure of monohydroxy alcohols and their mixtures using x-ray Raman scattering at the oxygen K-edge with the ultimate goal to detect the breakup of ring-like supramolecular structures into chain-like ones by mixing of two ring-forming alcohols, such as 4M3H, 2B1O, and 2H1D. This structural ring-opening effect is proposed to be the reason for an up to tenfold amplification of dielectric loss in the mixtures compared to the neat alcohols [1-3] and was found to be significantly enhanced for alcohol mixtures with decreasing temperature.

We used the multi-analyzer spectrometer of beamline ID20 to measure x-ray Raman scattering spectra at the oxygen K-edges of different monohydroxy alcohols and specific mixtures. The samples were contained in glass capillaries of 2 mm in diameter, fixed in a nitrogen cooled copper block sample cell, and temperature controlled via heating foils by a Lakeshore controller. The analyzer energy was set to 9.69 keV scanning the incident energy and an energy resolution of 0.6 eV was achieved. Spectra were measured utilizing 4 analyzer modules at low scattering angles and 2 at high scattering angles related to low and high momentum transfers, respectively, and were analyzed separately.

First we measured oxygen K-edge at room temperature of the octanol isomers 1-octanol, 2E1H, 4M3H, and 4M4H to analyze the sensitivity of the oxygen K-edge to both (i) different location of the OH-group within the alcohol and (ii) general differences due to proposed ring-former (4M3H) and chain former (2E1H). The corresponding results of these measurements are presented in figure 1 and show distinct differences between the alcohols. Moreover, difference spectra using 1-octanol as reference are shown. Apparently, there is a

strong dependence of the K-edges' shape with respect to both the position of the OH group in the molecule and number of nearest neighbor methyl-groups. These results have to be compared to modeled spectra on the basis of structural motives obtained by molecular dynamics simulation which are currently under work.

For a more detailed understanding of possible structural transformations on the supramolecular level, the ring-former 4M3H can be directly compared to the chain-former 2E1H. Although the spectral differences measured at ambient temperature are small, the general shape of the difference between 2E1H and 4M3H spectra might be consistent with calculations of trimer-chains and rings by Tamenori et al. [4], confirming that the experimental approach is suited to study ring opening effects.

In a next step we measured the neat alcohols 2H1D and 4M3H, both assumed to be ring-former, and compared the results with that of a 35:65 mixture (optimized for the largest amplification of the dielectric signal) to identify signatures of ring-opening effects. Only small changes between the K-edge spectra of the mixture and of a superposition of spectra of the neat alcohols was found. This strongly points towards a structuring in alcohols and their mixtures at lower temperatures and increased viscosity. Consequently, to enhance the spectral signatures of supramolecular arrangements, corresponding alcohols and mixtures have to be measured at temperatures below 240 K where slower dynamics and less temperature induced disorder support the formation of supramolecular structures [1]. Hence, we tried to measure in a next step the alcohols 2E1H and 4M3H at temperature of 230 K and 210 K to reveal changes in the alcohols' structure with decreasing temperature at enhanced viscosity. These measurements turned out to be highly sensitive to radiation damage, which was not expected in this temperature range. Neither defocussing of the x-ray beam nor sample movement was able to reduce beam damage significantly on time scales which allow to measure spectra with sufficient statistical quality to draw final conclusion.

To conclude we found spectral signatures of the intramolecular structure of the different isomers and possibly found first hints due to different intermolecular arrangement of the alcohols. However, to confirm and to specify these effects, measurements at low temperature are required which were not possible with the current setup. Hence, we started to develop a liquid jet system that is capable of producing highly stable jet also for highly viscous liquids. The jet is already tested and can provide a liquid sample jet for the alcohols and mixtures for temperatures down to 210 K. Measurements in this low temperature regime then will provide unique information on the structure formation in monohydroxy alcohols.

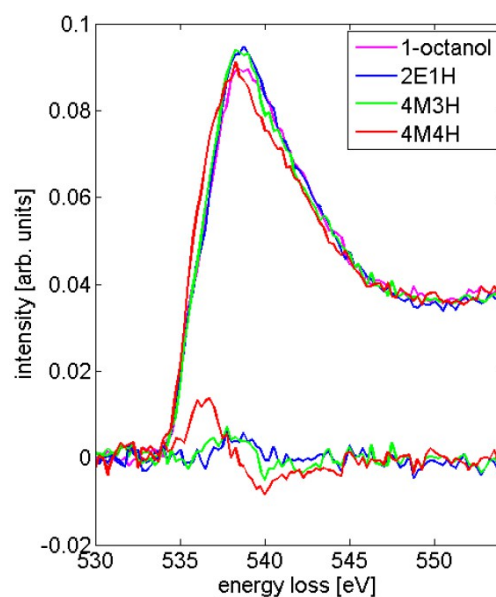


Figure 1: Oxygen K-edge measured at room temperature for different octanol isomers.

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