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	Experiment title: Clustering tendency in supercritical aqueous $ZnBr_2$ solution : a small angle scattering study.	**Experiment number**: HS-1246
Beamline: D2AM	**Date of experiment**: from: 01 February 2000 to: 06 February 2000	**Date of report**:
Shifts: 15	**Local contact(s)**: Jean-Paul Simon	*Received at ESRF:*

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Report:

Let recall that our work is devoted to the investigation of new possibilities of depollution using supercritical water. Indeed, by a solvation/precipitation process, toxic inorganic salts (Zn, Pb, U, Cr) present in water might be extracted. In order to expertise this field, we have started a thorough study of solvation and ion clustering properties of toxic salts in aqueous solutions using different methods (XAS, SAXS).

The SAXS experiment on which we report here, were performed in order to verify the formation of solute clusters in diluted zinc bromide ($ZnBr_2$) aqueous solutions. Such a behaviour was expected from EXAFS experiments carried out on same aqueous solutions [1]. These experiments, performed at two different concentrations (0.1mol/l and 1mol/l) respectively at the Zn-K edge and Br-K edge, could be consistent with ion precipitation processes [1]. Using the evolution of the height of the edge of the XAFS spectra (directly proportional to the ion density in the beam path) one can have an indication of the behaviour of the solution concentration from ambient to supercritical conditions. While at 0.1 mol/l the ion density follows very closely the water density up to the highest temperatures, at 1mol/l, the ion quantity decreases faster than the water density, and the Br edge jump even disappears. This could be attributed to a precipitation of solid salt occurring in the more concentrated solution. Moreover, the analysis of the EXAFS oscillations, at both the Zn and Br edges, clearly showed a shrinking of the hydration sphere and the presence of ions pairs. This effect of ion pair association is of course of particular interest because it could lead, by formation of solute clusters, to precipitation phenomena.

In order to verify the existence of these clusters and get some insight on their structure, we performed Small Angle X-rays Scattering experiments on zinc bromide aqueous solution. The supercritical conditions were experimentally obtained using the specific diffraction cell developed in the Laboratoire de Cristallographie.

Experiments were carried out at 600 bar, the temperature varying from ambient until 500°C. The concentration of ZnBr2 of the experiment was 0.6 mol/l.

The CCD detector was used with a beamstop whose diameter was equal to 0.28cm. The distance between sample and detector was equal to 84cm, thus wave vector values was varying from 0.025 to $0.25A^{-1}$.

Let note that we first tried to work around the K edge of Br (13.5keV) performing anomalous x-ray scattering. The energies values (13,376 ; 13,444 and 13,465keV) were chosen in order to minimise the fluorescence of bromide near the edge. However, due to the low concentration of $ZnBr_2$ in solution, this method was not efficient to enhance the contrast of $ZnBr_2$ domains in supercritical water.

We thus worked at higher energy (E=18 keV) and the scattering intensities I(q) obtained for various temperature are shown in figure 1. Spectra were corrected from dark variation of the CCD camera and normalised with transmission. Signal of the empty cell in the same pressure condition was subtracted to the total scattered intensity.

We can see in figure 1 that at low temperatures *i.e.* far from the critical point, the signal is flat which is characteristic of a homogeneous fluid. When increasing the temperature, the amplitude of the small angle scattered intensity is increasing and two different kinds of variation can be observed depending on the q range. At low q, the augmentation of the signal is a signature of density fluctuations present in supercritical water. This results are in good agreement with the one published by Nishikawa on pure supercritical water [2]. Moreover at higher q values, we can observe a change in the shape of the curves. Plotted as 1/I(q) vs q^2, (figure 2) clearly two different slopes can be observed. If the first one can be undoubtedly attributed to critical fluctuations in water, the second one could be related to the formation of clusters.

We could interpret these first observation as following : the signal related to the supercritical state of water and the one related to the formation of $ZnBr_2$ clusters are weakly correlated and the total observed scattered intensity is the sum of this two signals. The density fluctuations are predominant at low q values (large object = thin and intense central diffraction peak) whereas the clusters are predominant at high q values (smaller object = large and weak central diffraction peak). However, this still a first qualitative interpretation of these SAXS experiment. In order to perform a more detailed analysis the scattered intensity of pure water has to be measured in exactly the same condition than the scattered intensity of both water and zinc-bromide. Moreover it could be interesting to study different concentrations of zinc bromide in solution in order to verify if the size of the clusters depends on the concentration.

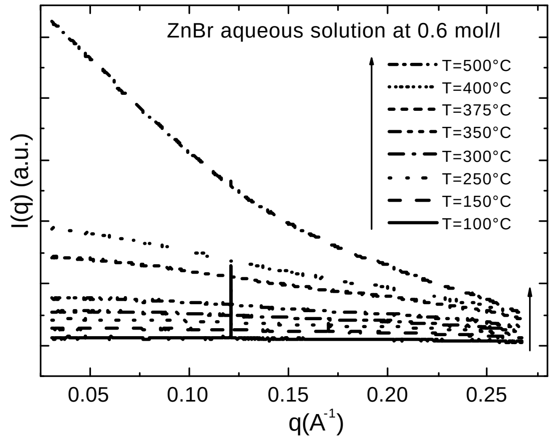

Figure 1 : SAXS intensity of zinc bromide solution at different temperatures

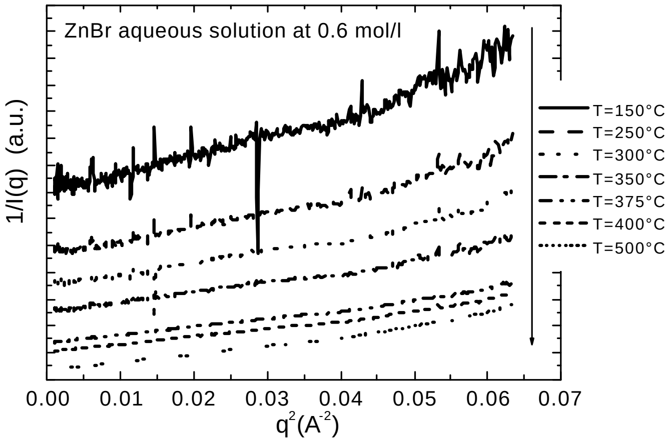

Figure 2: OZ plots of the SAXS intensities plotted in figure 1

References :

[1] V. Simonet, Y. Calavara, J.-L. Hazemann, R. Argoud, O. Geaymond and D. Raoux, *Temperature, pressure and concentration dependance of local order around cation and anion in sub and super-critical conditions*, submitted to J. Chem. Phys.

[2] T. Morita, K. Kusano, H. Ochiai, K. Saitow and K. Nishikawa, J. Chem. Phys. **112** (9), 2000