



	Experiment title: Small Angle Scattering study of clusters formation in aqueous supercritical ZnBr ₂ solution.	Experiment number: HS-1558
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Report:

We performed Small Angle Scattering experiments on ZnBr₂ solutions in supercritical conditions. One of the goals of our team is to study the evolution, at a microscopic scale, of the solvation properties of water from ambient up to supercritical conditions (critical point of water: 374°C, 221 bar). The synchrotron-based spectroscopic techniques we use are Xray Absorption Spectroscopy, Small Angle Xray Scattering and Inelastic Xray Scattering. The different samples we probe in water are essentially heavy elements dissolved salts. The long-term objective is obviously environmental: we profit from our fundamental investigation to estimate the efficiency of methods which would exploit the precipitation of polluting salts in supercritical conditions.

The present study is the following of a previous SAXS investigation (see experimental report HS-1246). Our previous XAS study [1] had proven the existence of ion pairing under the form of ZnBr₂O₂ clusters. HS-1246 experiment had stressed qualitatively the capability of that method and of our experimental set-up to detect the existence of the clusters. The interest of the study we are reporting on was to get SAXS spectra of both ZnBr₂ aqueous solutions and water at the same experimental conditions. Another interesting point was to probe several supercritical conditions and several concentrations to change both the local configuration of ion pairs and of the solvent itself.

The experimental apparatus has been extensively described elsewhere [1]. The experimental conditions were:

-0.3m at 600, 450 and 300bar, from ambient up to 500°C.

-0.1m at 600bar, from ambient up to 500°C.

-1m at 600bar, from ambient up to 500°C.

–water alone at 600, 450 and 300bar, from ambient up to 500°C.

The geometry of the set-up allowed the scattering vector to vary from 0.35 up to 0.5 angstroms⁻¹. The counting time had been optimized in the last experiment and was 10*100s per temperature step.

In order to decorrelate the influence of density correlations effects in supercritical water from clusters scattering (if any) in ZnBr₂ aqueous solutions, we probed, as already mentioned, both water and aqueous ZnBr₂ at the same experimental conditions. In figure 1a), one can observe the small angle scattering spectra from ambient up to 450°C. The first remark is that one can observe the scattering signal related to density correlations in water near the critical point. That was already observed by Morita and al. [2]. The second remarkable point is the difference between water alone and the aqueous salt. That difference is stressed in figure 1b) where the contribution of water has been taken into account in order to plot the signal only related to clusters.

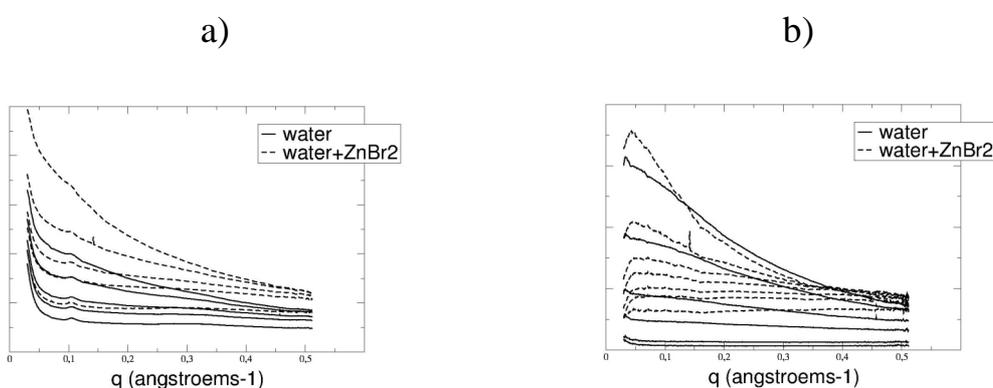


Figure 1a): raw SAXS spectra of water and 0.3m aqueous ZnBr₂ at 600 bar, at different temperature (30, 300, 350, 400 and 450°C from bottom to top).

Figure 1b): SAXS spectra corrected from ambient temperature for water spectra and corrected from ambient temperature and water contribution for 0.3m aqueous ZnBr₂. Pressure is 600 bar and temperatures are 150, 200, 300, 350, 400 and 450°C.

Figure 1) only refers to a specific experimental condition (600 bar and 0.3m concentration). The analysis of the other spectra points at the influence of concentration (the smaller the concentration, the weaker the signal of clusters) and pressure, ie density (the closer to the critical point, the more intense the signals are).

Thanks to an Ornstein Zernike fit, density correlation lengths in water and typical clusters sizes are likely to be calculated. It will be thus possible to compare quantitatively our results to other studies [2], and complete our XAS study of solvation effects in supercritical aqueous ZnBr₂ solutions. The technique of SAXS is promising in the different aqueous solutions we are studying to give an insight on the clustering effect in supercritical conditions.

REFERENCES:

- 1) V. Simonet and al., J. Chem. Phys., 116, **2002**, P2997–3006.
- 2) T. Morita and al., J. Chem. Phys., 112, **2000**.