

[REDACTED]	Experiment title: SAXS study of the structural evolution of water and methanol in sub- and supercritical conditions	Experiment number: SC-1533
Beamline:	Date of experiment: from: 08/09/2004 to: 14/09/2004	Date of report: 13/10/2004
Shifts: 18	Local contact(s): Françoise BLEY	<i>Received at ESRF:</i>
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#### Report:

We report preliminary results of Small Angle X-Ray Scattering measurements done at the CRG beamline D2AM at ESRF. The purpose was to determine the differences in the structure of density fluctuations in pure water and methanol. These fluctuations exist as long range inhomogeneities at high temperature/high pressure conditions and are maximum along the critical isochore. They consist of the existence of dynamical dense clusters of solvent molecules. The purpose is to know if the size of these clusters is identical or not in both solvents in order to correlate this result to the role of the hydrogen bond in these clusters. For that reason, we performed SAXS measurement to benefit from the high sensitivity of the SAXS signal to density contrast. An Ornstein-Zernike analysis of the signals lead to the determination of the compressibility of the fluid and its typical correlation length (i.e. the mean size of the inhomogeneities).

In order to compare results of both systems we worked at similar conditions, relatively to the critical point: along two isobars (1.1, and 1.3  $P_c$ ), from ambient to temperatures beyond the critical isochore. In addition, we studied 2 solutions of ZnBr<sub>2</sub> dissolved (0.3 mol/l) in methanol and water along one isobar (1.1  $P_c$ ). Indeed, it is of particular interest to understand the effect of the presence of ions on the density fluctuations, or, put the other way, to understand the effect of density fluctuations on the properties of hydration of ions in those conditions of high temperature and high pressure. We proposed in a recent work based on previous SAXS measurements on ZnBr<sub>2</sub> aqueous solutions made on D2AM at ESRF [1] that the onset of density fluctuations enhance the hydration of ions (i.e. the hydration shell denser locally denser than the bulk is a nucleus for development of density fluctuations when the temperature is raised). As a result these water molecules screen the coulombic attraction between ions and stops the ion pairing and clustering effect that takes place for temperature below 300°C [2]. Since the interactions between methanol molecules and ions are not identical to water-ions interactions, it is of interest to determine how ZnBr<sub>2</sub> methanol solutions behave.

All the results are summarized in Figures 1 and 2. They represent the evolution of the correlation length, but it is important to note that a similar evolution is measured for the compressibility of the fluids. For clarity, these plots are not presented here. We observe in Figure 1 that at a pressure of 1.1  $P_c$ , density fluctuations in water and methanol have the same "size" (the correlation length has the same amplitude). However, it seems that when the pressure is increased (1.3  $P_c$ ), i.e. further from the critical point, the correlation length in

methanol does not decrease as it is the case in water. This decrease is normal and follows the exponential laws of the 3D Universality class of fluids [3]. It is important to determine if this experimental result is an artefact or not. Then, Figure 2 indicates that at  $1.1 P_c$ , the correlation length in electrolyte solutions is lower than in pure solvents. This result is in contradiction with our previous measurements [1] where the presence of ions would increase the correlation length. But, in the present case, the conditions are closer to the critical point, and a precipitation of  $ZnBr_2$  is systematically observed. Consequently, the evolution of the correlation length (the same decrease is observed for the compressibility) can be explained by the ion pairing and precipitation of the ions out of the clusters of solvent molecules. For higher pressures, this had been prevented by the screening effect mentioned above, but a dramatic decrease of the dielectric constant because of the proximity of the critical point can be at the origin of such ions interactions. Further experiments in aqueous and water solutions are to be done.

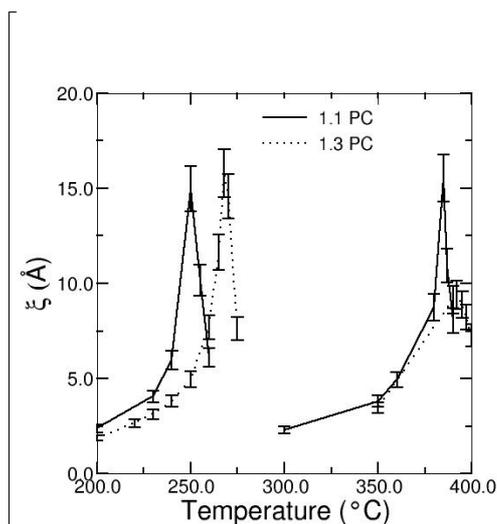


Fig. 1: Correlation length measured in methanol (left) and water (right) as a function of temperature, along two isobars ( $1.1$  and  $1.3 P_c$ ).

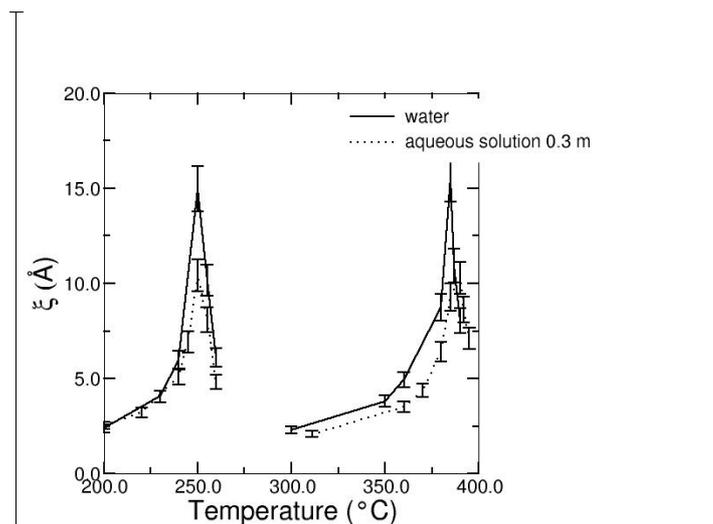


Fig.2: Correlation length measured in solutions of  $ZnBr_2$  dissolved ( $0.3 \text{ mol/l}$ ) in methanol (left) and water (right), as a function of temperature at  $1.1 P_c$ .

[1] D. Testemale, M. V. Coulet, J.-L. Hazemann, J.-P. Simon, O. Geaymond, R. Argoud, J. Chem. Phys., submitted.

[2] V. Simonet, Y. Calzavara, J.-L. Hazemann, R. Argoud, O. Geaymond, D. Raoux, J. Chem. Phys., 117, 2771 (2002).

[3] J.-P. Hansen, I. R. McDonald, Theory of simple liquids, Academic Press, 1976.