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| | **Experiment title:**<br>**Hydratation study of monovalent ions in supercritical conditions by X-ray Absorption Spectroscopy** | **Experiment number**:<br>CH 2132 |
| **Beamline**:<br>BM25A | **Date of experiment**:<br>from: 22/02/2006 to: 28/02/2006 | **Date of report**:<br>25/07/2007 |
| **Shifts:**<br>18 | **Local contact(s)**:<br>German Rafael CASTRO | *Received at ESRF:* |

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## Context

The initial aim of the experiment was a comparative and systematic study of the solvation phenomena for alkaline bromides (Br-X, X=Li, Na, K, Rb and Cs) in supercritical water (SCW). A decrease of the permittivity of SCW leads to a lowering of the solubility of inorganic salts. By characterizing the ion-water (hydration), ion-ion (ion pairing) and water-water (hydrogen bonding) interactions, the unique properties of such a system can be inspected. One of the most appropriate technique for the structural study of the local order around the ions in solution is the X-ray Absorption Spectroscopy (XAS). A High Temperature and High Pressure (HP/HT) cell dedicated to fluorescence XAS measurements, among other techniques, was developed and is now used routinely.[1] However, the lack of focusing system on the beamline did not allow to have a sufficient flux with such an HP/HT set-up due to the limited size of the X-ray Be-windows of the vessel. We choose then to probe the influence of the permittivity decrease not by increasing the temperature from sub- to supercritical region but by changing the nature of the solvent in ambient conditions (table 1). Moreover, in order to increase the ion-pairing effect, not experimentaly observed for the monovalent species but only theoreticaly predicted[2], we choose to study the trivalent specie $GaBr_3$, where ion-pairing effect was already observed for highly concentrated aqueous solutions in ambient conditions.[3] Experiment was performed at the Ga K-edge in the transmission mode for different concentrations of $GaBr_3$ in solution.

| **Solvent** | | **Dipole moment** | **Permittivity (300K)** | **[$GaBr_3$] (mol/l)** |
|---|---|---|---|---|
| **Water** | $H_2O$ | 1.855 D | ~80 | 0.17, 0.68 |
| **Methanol** | $CH_3OH$ | 1.7 D | ~33 | 0.085, 0.17 |
| **Ethyl Acetate** | $CH_3CH_2OC(O)CH_3$ | 1.78 D | 6.05* | 0.085, 0.17 |

**Table 1**. Dipole moment and static permittivity of the solvents in ambient conditions.
Concentration of the studied solutions. * measurement at 1MHz [4]

## Results

The results obtained for the 0.17mol/l solutions are shown on figure 1. The results of the fits are gathered on table 2. The main result is that when the permittivity is high (for water), the Ga atoms are completely solvated, surrounded by approximately 6 O atoms at 1.97Å for both concentrations studied. Smirnov et al.[3] observed Ga-Br ion pairing with water but at concentration three times higher. When the permittivity decreases, Ga-Br ion pairing is observed (increase of the amplitude of the oscillations in the 6-10$Å^{-1}$ range), such effect being slightly larger for ethyl acetate than for methanol.

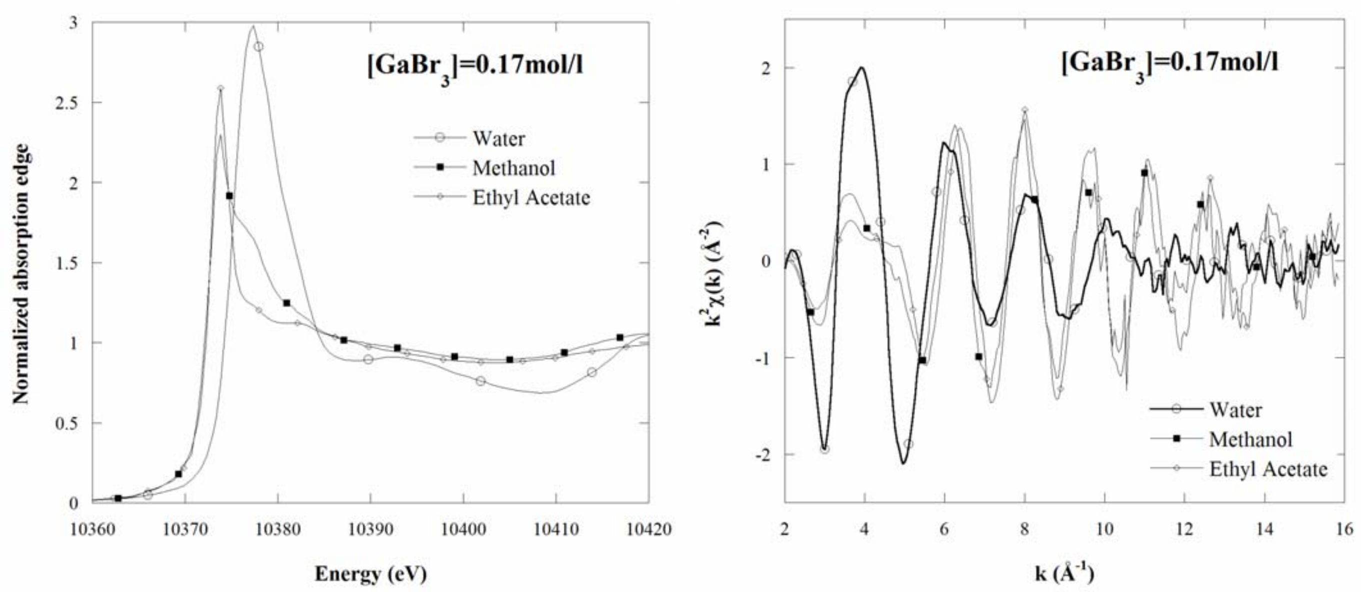

**Figure 1**. normalized XANES spectra (left) and $k^2.\chi(k)$ EXAFS oscillations (right) obtained for the 0.17mol/l solutions.

| **Solvent / [GaBr$_3$]** | **neighbour** | **N** | **R (Å)** | **ΔE (eV)** | **$\sigma^2$ (Å$^2$)** | **R factor** |
|---|---|---|---|---|---|---|
| **Water / 0.17M** | O | 6.4±0.5 | 1.974±0.008 | 4.2±1.0 | 0.0059±0.001 | 0.01 |
| **Water / 0.68M** | O | 6.3±0.4 | 1.965±0.008 | 3.6±0.4 | 0.0053±0.0008 | 0.009 |
| **Water / 2M**<br>**(Smirnov et al. [3])** | O<br>Br | 6.1±0.2<br>0.6±0.2 | 1.96±0.02<br>2.34±0.02 | 7.5<br>4.3 | 0.069±0.005<br>0.076±0.005 | 0.06 |
| **Methanol / 0.085M** | O<br>Br | 1.3±0.5<br>3.2±0.7 | 1.965±0.03<br>2.330±0.001 | -0.8±2.7 | 0.0030<br>0.0048±0.001 | 0.02 |
| **Methanol / 0.17M** | O<br>Br | 2.0±0.3<br>3.2±0.2 | 1.943±0.008<br>2.324±0.003 | -1.8±0.8 | 0.0030±0.0012<br>0.0051±0.0004 | 0.002 |
| **Ethyl Acetate / 0.085M** | O<br>Br | 1.1±0.5<br>3.7±0.4 | 1.908±0.008<br>2.305±0.002 | -2.4±1.5 | 0.0055<br>0.0044±0.0005 | 0.008 |
| **Ethyl Acetate / 0.17M** | O<br>Br | 1.3±0.2<br>3.3±0.1 | 1.908±0.008<br>2.305±0.002 | -1.5±0.8 | 0.0055±0.0019<br>0.0038±0.0002 | 0.001 |

**Table 2**. Results of the simulations performed on the $k^2.\chi(k)$ EXAFS spectra obtained at the Ga K-edge. k-range for the analysis: [2.3 - 14.5Å$^{-1}$], $S_0^2=1$

## Conclusion and perspectives

The experiment allowed to probe the solvation and ion pairing effect around gallium atoms in different solvents with various permittivity values. These results have to be compared to those obtained for this same trivalent system in SCW.[5]

## References:

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