Journal of Molecular Liquids 147 (2009) 83–95

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# X-ray absorption spectroscopy study of solvation and ion-pairing in aqueous gallium bromide solutions at supercritical conditions

Cécile Da Silva [a], Olivier Proux [b,*], Jean-Louis Hazemann [a], Julianne James-Smith [a,c], Denis Testemale [a], Toshio Yamaguchi [d]

[a] Institut Néel, CNRS, Grenoble, France
[b] Laboratoire de Géophysique Interne et Tectonophysique, UMR CNRS/Université Joseph Fourier, Grenoble, France
[c] School of Earth and Environmental Sciences, University of Adelaide, South Australia, Australia
[d] Advanced Materials Institute and Department of Chemistry, Faculty of Science, Fukuoka University, Japan

ARTICLE INFO

Available online 16 July 2008

*Keywords:*
Gallium bromide solution
Ion solvation
Ion-pairing
Supercritical fluids

ABSTRACT

X-ray absorption spectroscopy measurements have been performed both at the Ga and Br *K*-edges on aqueous $GaBr_3$ solutions. The isobaric experiments have been recorded at 30 MPa from ambient temperature to 670 K for two $GaBr_3$ concentrations (0.017 and 0.17 mol/dm$^3$). At room temperature, $Ga^{3+}$ and $Br^-$ ions are fully solvated, surrounded by water O atoms at 1.97 Å (Ga–O) and 3.37 Å (Br–O). When the temperature is elevated, $Ga^{3+}$ cations precipitate as gallium oxy-hydroxide colloids while $Br^-$ anions remain solvated. With a further increase in temperature, the gallium solid precipitates remarkably re-dissolved (25% and 50% for 0.017 and 0.17 mol/dm$^3$ respectively), due to the formation of $[GaBr_n(H_2O)_{4-n}]^{3-n}_{(aq)}$ ($n=2$, 3 or 4) tetrahedral complexes.



## 1. Introduction

Compared to water at ambient conditions, supercritical water (SCW) is unique in that it exhibits both gas-like and liquid-like properties. The high diffusivity and low viscosity of supercritical fluids enable them to penetrate and transport solutes from solid matrices. The smaller dielectric constant of SCW is responsible of the low solubility of inorganic salts. Since the solvation capacity of supercritical fluids depend on pressure and temperature, one can achieve the optimum conditions for a particular separation process by adjusting the temperature and pressure of the fluid phase, in decontamination process [1] or metal extraction [2] for example. By characterizing the ion–water (hydration), ion–ion (ion-pairing) and water–water (hydrogen bonding) interactions, the unique properties of such system can be inspected. However, these features remain in some cases unexplored because of experimental difficulties in structural and/or spectroscopic measurements at high temperatures and high pressures. One of the most appropriate techniques for the structural study of the local order around the ions in solution is the X-ray absorption spectroscopy (XAS) including both the X-ray-absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectroscopic techniques. This spectroscopy allows characterization of the local atomic environment around the absorbing element (selected from its absorption edge) to extract structural information on ions of interest. This is one reason why these techniques can be applied to dilute systems (several mM). These advantages also make it an ideal technique to study supercritical aqueous electrolyte solutions of low density in which the solubility of salts can be much lowered. Thus a high pressure and high temperature (HP/HT) cell dedicated to simultaneous fluorescence and transmission XAS measurements was developed and is now used routinely [3].

The behaviour with *P* and *T* of the bromide anion associated to monovalent [4–6] or divalent cations [7–11] as counter ions in aqueous solutions is now well understood. The effect of ion-pairing in aqueous solutions, i.e. formation of pairs of oppositely charged ions with a common solvation shell, is a very rich topic. Ion-pair formations at high temperature and high pressure conditions, from an aqueous solution in which the ions are completely dissolved at ambient conditions, is mainly related to the strong decrease of the solvent permittivity with *T* [12]: it leads to the increase of the coulombic force between ions, a decrease of the solvation sphere and then ion-pairing and formation of multi-ionic complexes. A limitation of the ion-pairing occurs close to the supercritical temperature and along the critical isochore: the onset of density fluctuations promotes the development of dense dynamic clusters of water molecules around the ions, leading to a screening effect which possibly inhibits the ion-pairing processes [13]. Previous studies of $MBr_2$ (M = Mn [11], Ni [7], Zn [8–9]) aqueous solutions have clearly described this effect. An increase of the number of M–Br pairs associated to a dehydration

* Corresponding author. CNRS 1381 Rue de la Piscine, BP 53X 38041 Grenoble, France. Tel.: +33 4 76 88 25 46; fax: +33 4 76 88 23 25.
*E-mail address:* olivier.proux@grenoble.cnrs.fr (O. Proux).

0167-7322/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2008.06.022

phenomenon (drop of the number of O neighbours) is observed when increasing the temperature at a constant high pressure. Then, when reaching the supercritical conditions, M–Br and M–O distances decrease, while Br–O distances are invariant or tend to increase slightly.

In the present study we focus our effort on the trivalent cation, $Ga^{3+}$, with an ionic force superior than monovalent and divalent cations. Previous results from EXAFS, X-ray diffraction and Raman experiments on the $GaBr_3$ system showed that the ion-pairing effect occurred at ambient conditions in concentrated aqueous solutions ($[GaBr_3] = 2.4$ mol/dm$^3$) [14] and is not observed for concentrations lower than 1 mol/dm$^3$ [15]. The main aim of this experiment was to determine the evolution of the structure of the ionic hydration and/or pairing at various $P$ and $T$ in aqueous $GaBr_3$ solutions. XAS measurements have been performed simultaneously in fluorescence and transmission modes with the HP/HT cell, both at the Ga and Br $K$-edges. The isobaric experiments have been recorded at 30 MPa from ambient temperature to 673 K for two $GaBr_3$ concentrations (0.017 and 0.17 mol/dm$^3$). The goal of this study is to probe the evolution of the local structure around $Ga^{3+}$ and $Br^-$ ions in solution, from ambient to supercritical state.

## 2. Experimental details

### 2.1. Sample preparation and the high pressure/high temperature device

Gallium bromide aqueous solutions were prepared by dissolving weighted amounts of $GaBr_3$ salts ($GaBr_3$, 99.999%, Sigma-Aldrich) in deionised water. The $GaBr_3$ solution concentrations are 0.017 and 0.17 mol/dm$^3$, with a measured pH equal to 2.7 and 1.9 respectively at ambient conditions. These concentrations are low enough in order to avoid any ion-pairing at ambient conditions [15].

The HP/HT cell used for these experiments has been described in details by Testemale et al. [3]. A schematic view of the set-up is shown in Fig. 1. The general principle consists of a helium-pressurized autoclave, and an internal sample container embedded in the heater. The main feature of the cell is then that the temperature and the pressure can be adjusted independently and are both stabilized by two independent pressure and temperature regulation devices [16]. For this particular study, the internal cell was in glassy carbon with a wall thickness machined down to 100 μm at the X-ray beam position, in order to limit the absorbance of the set-up as much as possible. The path length of the X-rays on the sample is 5 mm, the internal diameter of the carbon tube. Three apertures are present in the heater and vessel for the incident, transmitted and fluorescence beams. These apertures induce a small temperature difference between the value given by the thermocouple close to the furnace and the real sample temperature. A temperature calibration was then performed with pure water at 30 MPa, by determining the water density through X-ray absorption measurements. This is done by precisely estimating the total X-ray absorption of all the constituents of the experimental system at 30 MPa: the two 0.8 mm beryllium windows of the vessel, the glassy carbon cell, the pressurized helium and the water at different furnace temperatures. The experimental estimation of the density of the water sample allows then to estimate the temperature of the sample area, by comparing to the theoretical density of water [17] and then to establish a temperature calibration curve. In the following, all the mentioned temperatures are the sample real temperature. The precision on the furnace temperature measurement equals to 0.1 K. Due to the uncertainty of the calibration curve, one can estimate the error bar on the sample temperature to ±2 K.

The following procedure was followed to run an isobaric experiment: the pressure was progressively applied with a constant slope of 1 MPa/min; when the pressure inside the cell reached 30 MPa, the target temperature was reached (with a slope of 10°/min), acquisitions were done (for each temperature, 3 spectra were acquired); then the temperature was increased to the next target temperature, and so on.

### 2.2. X-ray absorption measurements

X-ray absorption spectroscopy experiments were performed on the CRG-FAME beamline (BM30B), located at the European Synchrotron Radiation Facility storage ring in Grenoble, operating in 2*1/3 filling mode at 6 GeV. Spectra were recorded both in fluorescence and transmission modes (~40 min/scan data collection time), at the Ga and Br $K$-edges, using a double-crystal Si(220) monochromator [18]. The size, around 300×200 μm$^2$ ($H \times V$, full width half maximum values), and the position of the X-ray spot on the sample were kept constant during the data acquisition. The full beam delivered by the bending magnet source was focused in the horizontal plane by the 2nd crystal of the monochromator and by the 2nd Rh-coated mirror in the vertical plane. Finally, a feedback system was used to maximize the output of the two-crystal X-ray monochromator [19]. Acquisitions of the XAS spectra $\mu(E)$ were performed simultaneously in the transmission ($\mu_t(E) \cdot d = \ln(I_0/I_t)$) and in the fluorescence modes ($\mu_f$

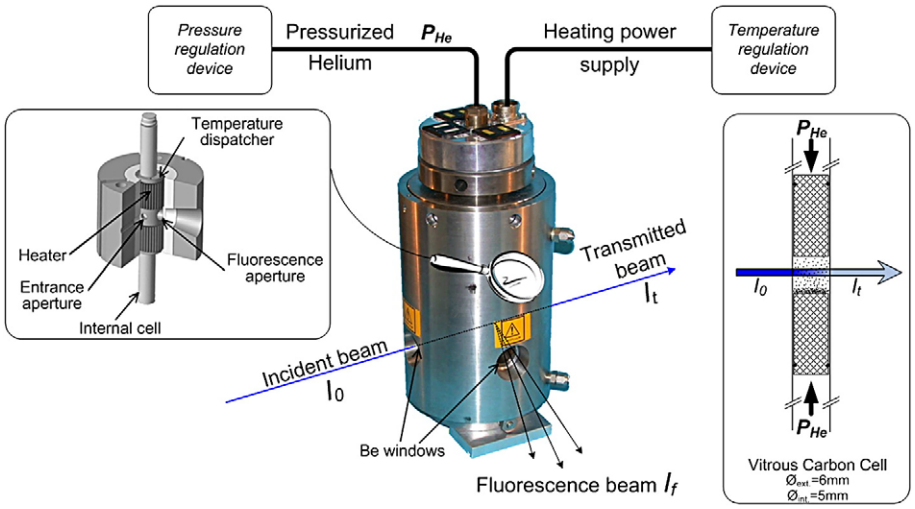


**Fig. 1.** Schematic view of the high pressure/high temperature vessel used for XAS measurements [3]. The gas pressure inside the vessel is stabilized with a special pressure regulation device [16]. Details of the internal heating system is shown in the left inset.