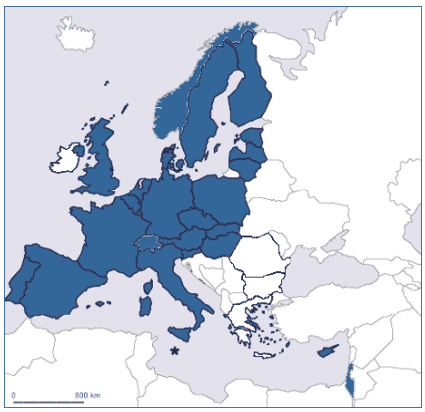
Déposer un projet

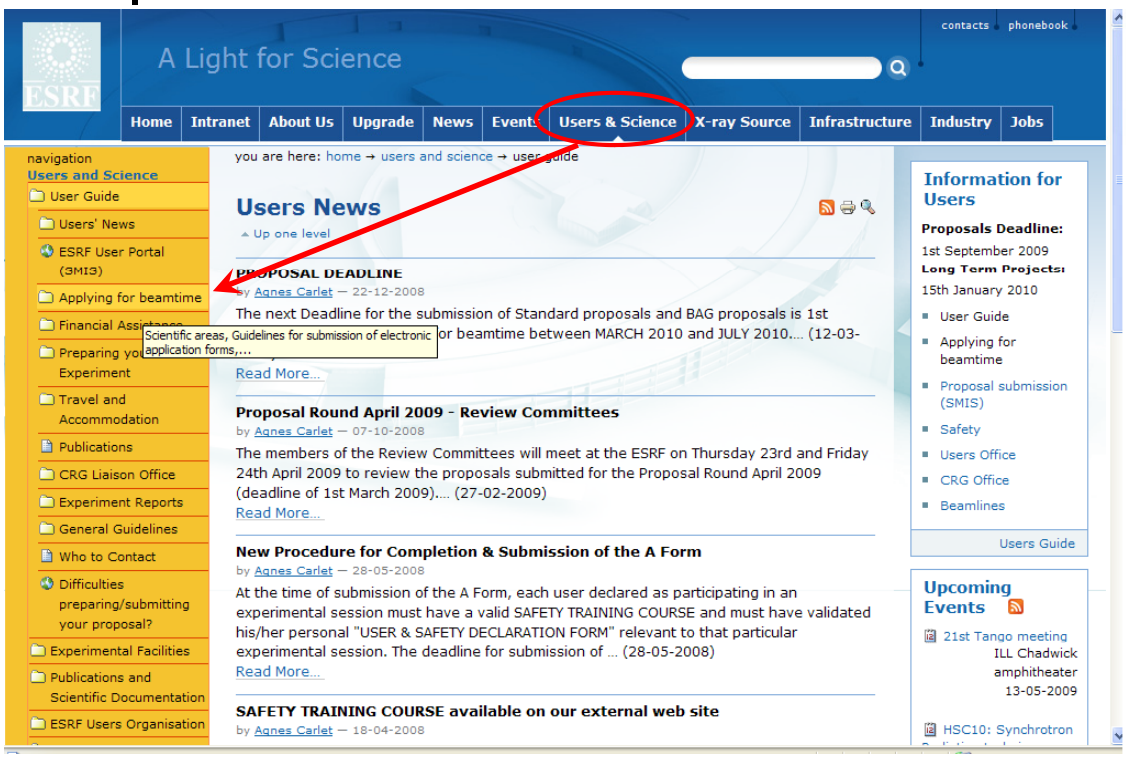
FAME+

Deux comités de programme

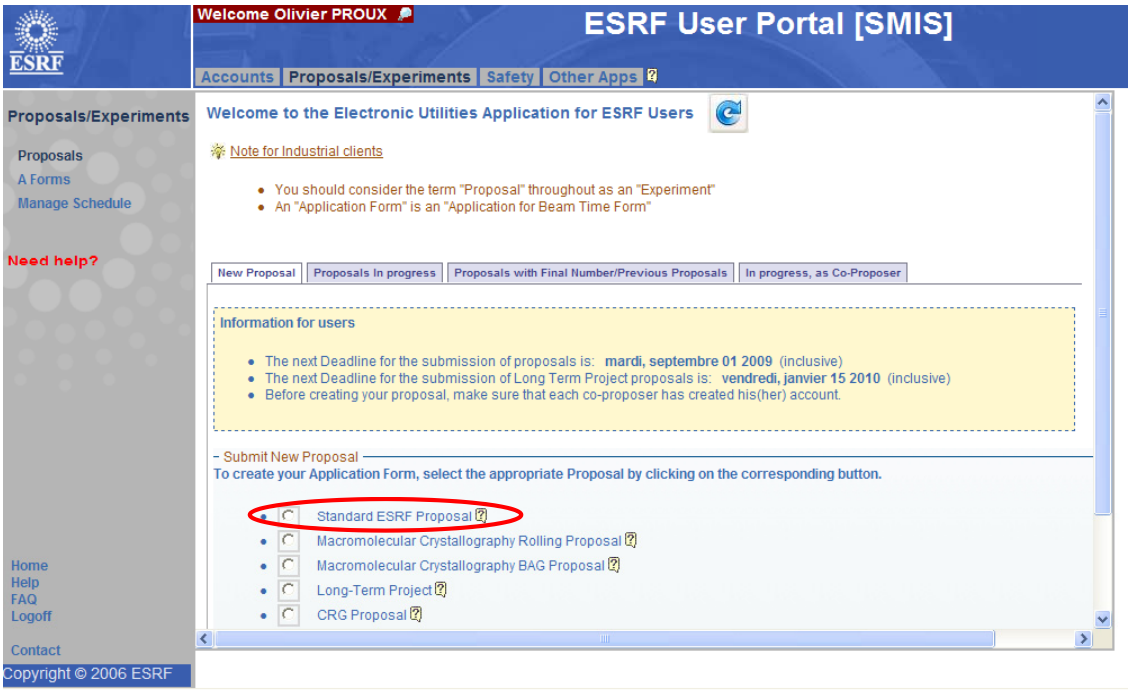
- Comité commun CRG-SOLEIL : 2/3 du temps
  http://sunset.synchrotron-soleil.fr/sun/
- Comité ESRF: 1/3 du temps
  https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do



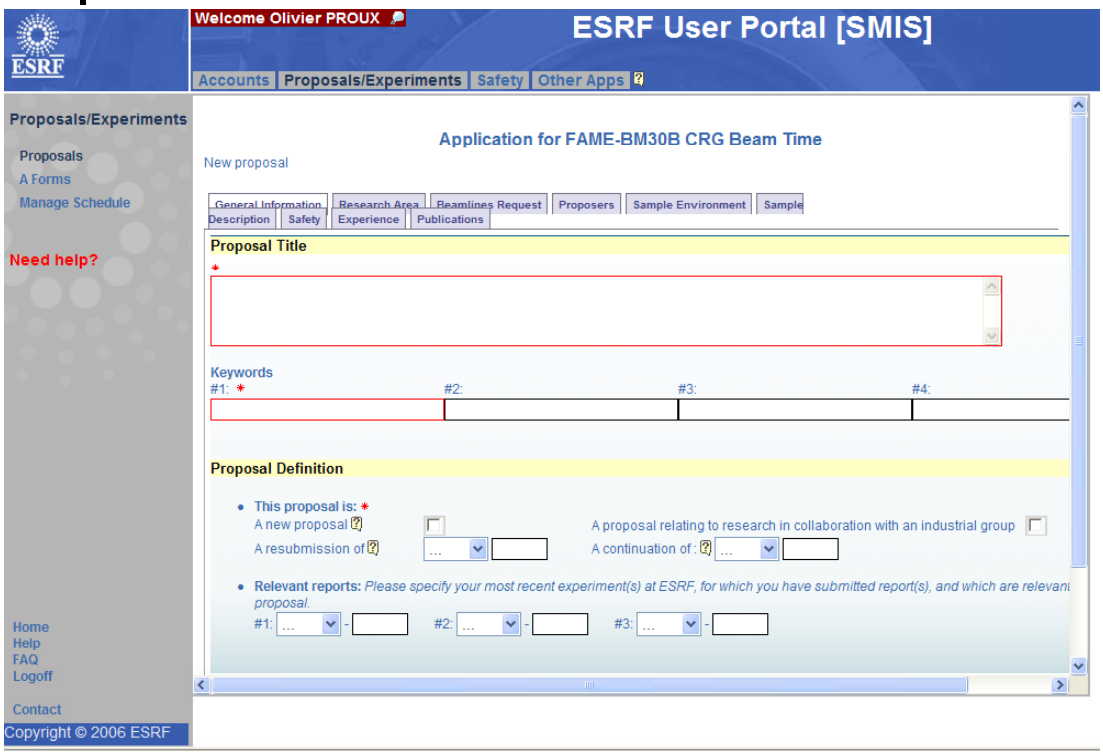
L'interface ESRF: SMIS



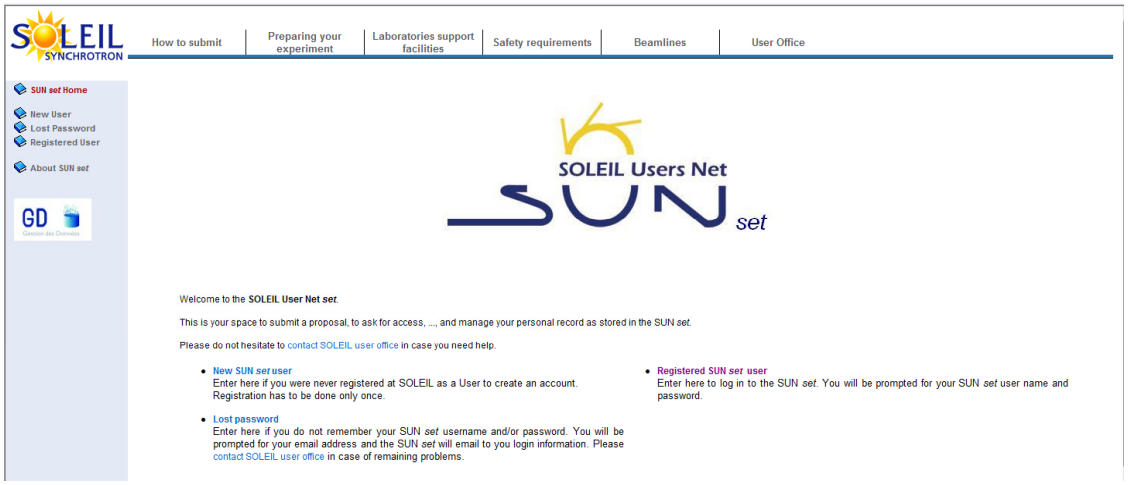
L'interface ESRF: SMIS



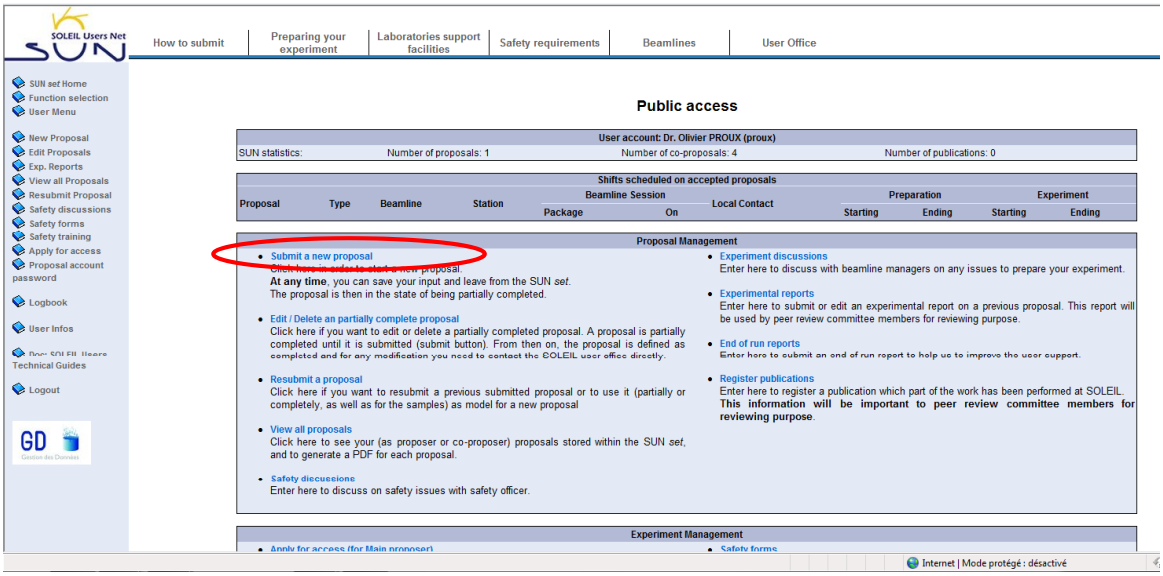
L'interface ESRF: SMIS



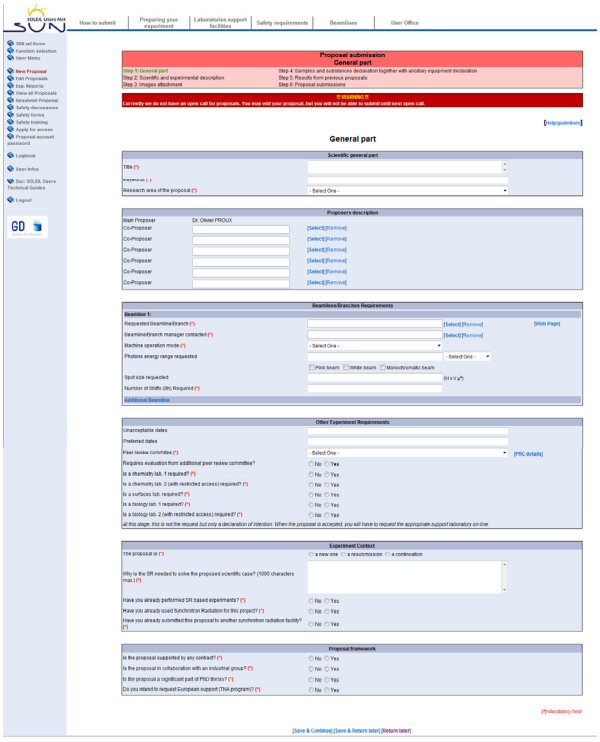
L'interface SOLEIL: SUNSet



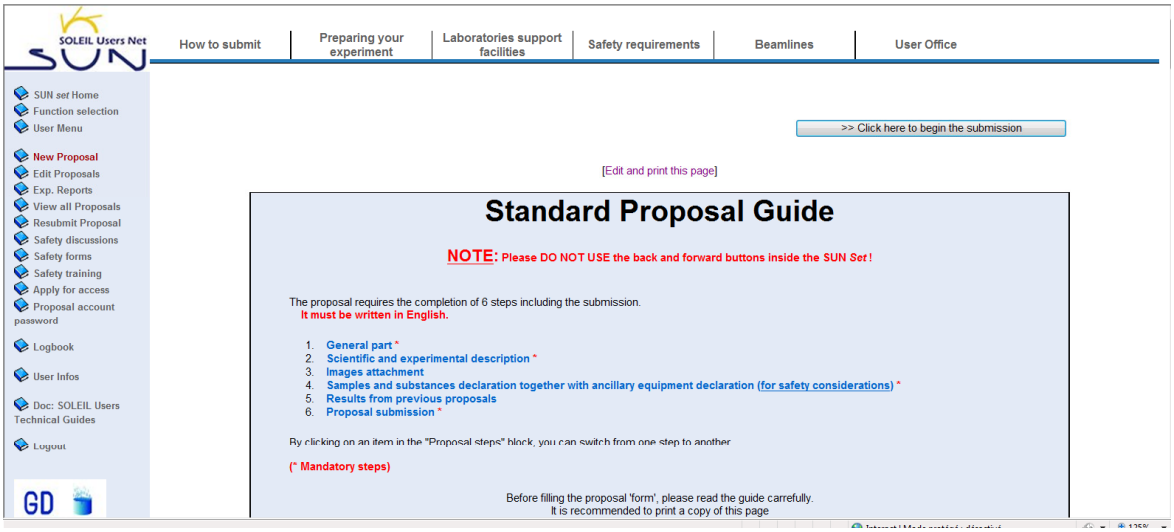
L'interface SOLEIL: SUNSet



L'interface SOLEIL: SUNSet

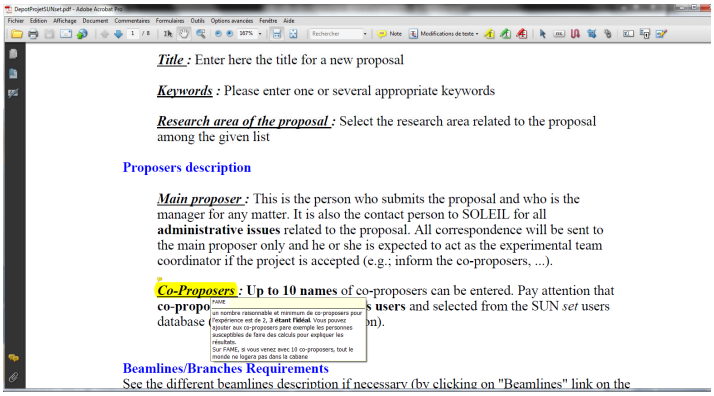


L'interface SOLEIL: SUNSet



Aide en ligne sur le site de SOLEIL

L'interface SOLEIL: SUNSet



Fichier: DepotProjetSUNset.pdf

- PDF commenté
- guide en fonction de FAME

Aide en ligne commentée sur la clef USB de la formation

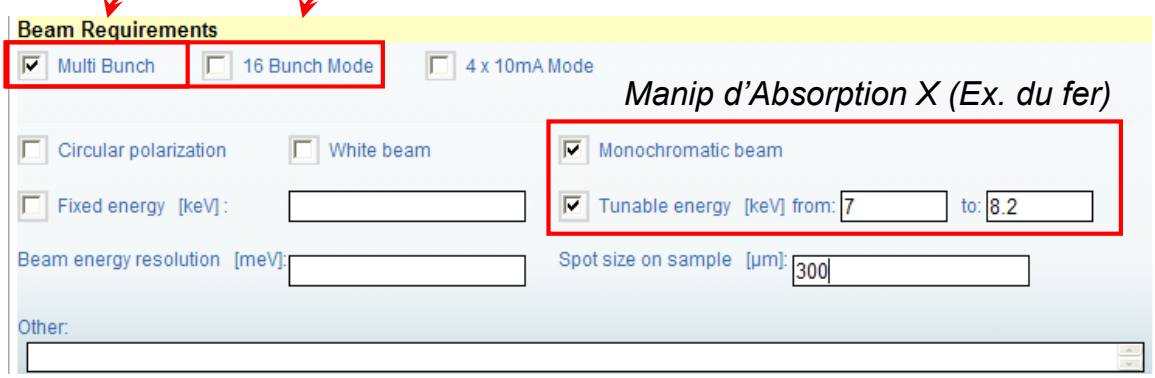
Quelles informations…?

- Deux procédures
  - Présentation différente
  - Contenu identique
- Deux possibilités d'avoir du temps de faisceau

Quelles informations…?

- Beamlines request
  - durée… pas moins de 12 shifts!
  - beam requirements

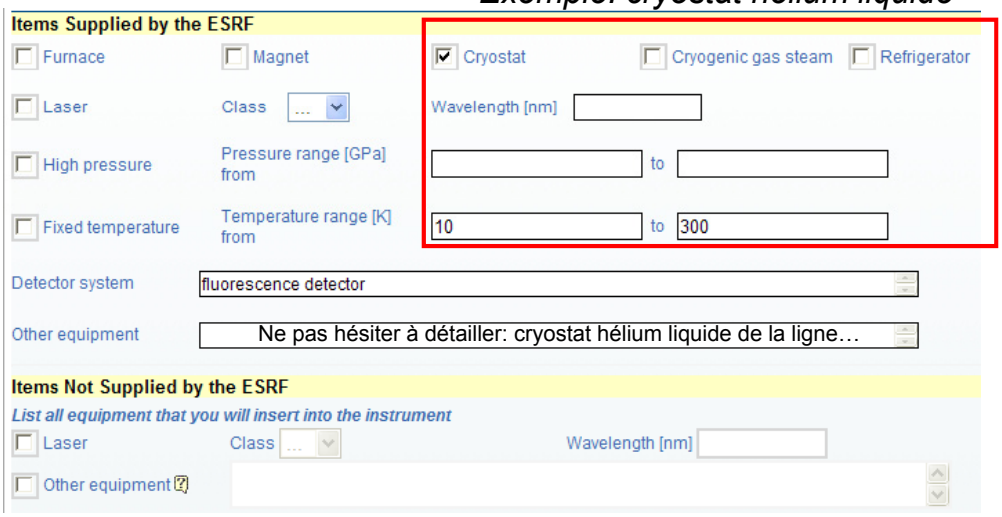
éléments dilués, expériences basse température, haute pression…



Quelles informations…?

- Sample environment

Exemple: cryostat hélium liquide



Quelles informations…?

- Sample environment
  - Essayer de ne rien oublier
  - Ne pas hésiter à ajouter des commentaires
  - Attention: vérifier que le dispositif est disponible!

Quelles informations…?

- Sample

Utile pour des manips de diffraction

Justificatif scientifique

- *Aims of the experiment and scientific background*
  - cadre scientifique général
  - cadre scientifique spécifique
  - buts et objectifs de l'expérience
  - rappeler les résultats préliminaires (littérature), autres mesures…

Justificatif scientifique

- *Experimental method*
  - pourquoi utiliser une technique synchrotron?
  - préparation des échantillons, *in situ*…
  - justificatif du nombre de shifts demandés
- *Results expected*
  - dans quelle mesure l'expérience répondra au but, au questionnement du début?
- *Références*

Justificatif scientifique

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ESRF User Office
BP 220, F-38043 GRENOBLE CEDEX, France
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Tel: +33 (0)4 7688 2552, fax: +33 (0)4 7688 2020, email: useroff@esrf.fr, web: http://www.esrf.fr

ESRF

Hydratation study of $GaBr_3$ aqueous solution in supercritical conditions by X-ray Absorption Spectroscopy

Aims of the experiment and scientific background

The aim of this experiment is to establish the structure (interatomic distance and coordination number) of ionic hydration and ion association at various temperatures and pressures in the sub- and supercritical states of aqueous $GaBr_3$ solutions. Water above the critical point (371°C, 22.1 MPa) (so called supercritical water, SCW) has unique properties not available in ambient conditions, e.g. a substantial decrease in the dielectric constant leads to lowering the solubility of inorganic salts in SCW.

In the past two decades, there has been considerable interest in utilizing supercritical fluids as solvents for chemical separations or extractions. The development of supercritical fluid extraction technologies is mostly due to the environmental regulations and waste management. Supercritical fluids have 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. Since the solvation power of supercritical fluid depends on pressure and temperature, one can achieve the optimum conditions for a particular separation process by manipulating the temperature and pressure of the fluid phase. Recently, by making use of this property of SCW, attempts have been made to produce funetional metal oxide particles in nano scale as one of the SCW technological applications. Fine metal oxides particles are used for industrial materials, such as magnets, electronic devices, cosmic, catalysts, etc.; however, it is essential to control the size, crystal structure, and morphology of metal oxides required in their materials. When aqueous solutions of inorganic salts are heated, the hydrated meal ions are hydrolysed and dehydrated finally to metal oxides. Since the chemical processes, nucleation, and crystal growth of metal oxides can be continuously controlled as a function of temperature and pressure in SCW, it is anticipated to produce the metal oxides which meet industrial needs.

The effects of ion-pairing in aqueous solution is a very rich subject. Ion-pairs formation in supercritical conditions (from an aqueous solution in which the ions are completely dissolved at ambient condition) is related to the strong decrease of the solvent permittivity. Such an evolution of the permittivity leads to the increase of the ionic force and the resulting decrease of the bond length between the ions. Previous studies lead by our team on $ZnBr_2$ aqueous solutions have clearly shown this effect [1-3]. At ambient conditions, an increase of the number of Zn-Br pairs associated to a dehydration phenomenon (drop of the number of O neighbours) is observed when increasing the temperature and the concentration and increasing the pressure. Then, when reaching the supercritical conditions, Zn-Br and Zn-O distances decrease, while Br-O distances tend to increase. However, ion pairing does not lead to a large clustering (ion pairs concentration increases but remains constant at high temperature): coulombic interactions seems to be limited by the local density enhancements.

The unique properties of supercritical aqueous solutions and hydrothermal reactions in them depend on ion-water (hydration), ion-ion (ion association), and water-water interactions; however, their detailed structure feature remains in some cases unexplored because of experimental difficulties in measurements at high temperatures and high pressures. Our team has a good experience of high temperature and high pressure studies in supercritical fluids and their technical demanding requirements. The HP/HT cell dedicated to fluorescence XAS [4].is now regularly and easily used and numerous experiments attest the efficiency of this setup [1-10].

The behaviour versus pressure and temperature of monovalent anion linked to monovalent [5] or divalent cations such as $ZnBr_2$ in aqueous solutions being now well understood, our will is now to study $GaBr_3$ in aqueous solutions (monovalent anion and trivalent cation).

Experimental method

X-ray absorption fine structure (XAFS) spectroscopy enables us to extract structure information of the local structure of ions in interest without any contribution from the solvent and counter ion and can thus be applied to dilute systems (several mM). These advantages make it an ideal technique with which to study supercritical aqueous electrolyte solutions, in which the solubility of salts is very lowered. Furthermore, XAFS measurements of supercritical aqueous electrolyte solutions require a suitable high-temperature and high-pressure cell. In the ESRF, such a cell has been developed and successfully utilized for measurements of supercritical fluids in the range of ambient to 1650°C and 60 MPa [4].

X-ray absorption fine structure measurements will be made both in fluorescence and transmission modes with the high-temperature and high-pressure cell at both Ga (10.367 keV) and Br (13.474 keV) *K*-edges on aqueous $GaBr_3$ solutions. Ion association (complex formation) between Ga^{3+} and Br^- depends on ionic strength and temperature of the solutions as revealed in previous study [10]. Concentrated aqueous $GaBr_3$ solutions (ca. 2 M) have been investigated over a temperature range from –193 to 60°C by X-ray diffraction, XAFS and Raman spectroscopy. It has been found that complex formation of Ga^{3+} by Br^- is favoured with increasing temperature and that aqua complex at 25°C has a sixfold coordination, as $[Ga(H_2O)_6]^{3+}$, with a Ga^{3+}–H_2O distance of (1.96 ± 0.02) Å.

These experiments will be performed from the ambient to around the critical point water at 647.06 K and 220.41 bars. Therefore, for two concentrations (0.02 and 0.1 M) and two absorption edge, including time to set up the experiment and measure XANES and EXAFS spectra, a total 18 shifts are requested.

Results expected

The outcomes of the present experiment will be firstly the hydration structure of trivalent Ga ion from the ambient to supercritical temperatures. In previous XAFS measurements of ionic hydration on different valent ions [1-5], it has been proposed that the hydration shell of univalent and divalent cations contract with increasing temperature. The present result on the trivalent ion will give a new result on this open discussion. Secondly, the ion association between Ga^{3+} and Br^- and the nature of the complex formation will be claried as a function of temperature and pressure.

References

[1] Simonet V. et al., "Structure of aqueous $ZnBr_2$ solution probed by X-ray absorption spectroscopy in normal and hydrothermal conditions", *Journal of Chemical Physics* **116** (2002) 2997.
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[3] Calzavara Y. et al., :An XAS Study of the P and T dependence of $ZnBr_2$ aqueous supercritical solutions, Journal of Synchrotron Radiation **8** (2001) 178-181
[4] Testemale D., Argoud R., Geaymond O., Hazemann J.L., "A high-pressure/high-temperature cell for x-ray absorption and scattering techniques", *Review of Scientific Instruments* **76** (2005) 043905
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[6] Pokrovski G.S. et al., "Experimental study of arsenic speciation in vapor phase to 500°C : Implications for As transport and fractionation in low-density crystal fluids and volcanic gases", *Geochimica et Cosmochimica Acta* **66** (2002) 3453-3480
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[8] Testemale D. et al., "Study of the evolution of $As(OH)_3$ arsenious acid structure in supercritical conditions: an EXAFS and XANES investigation", *Journal of Chemical Physics* **121** (2004) 8973-8982
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[10] Wernet Ph. et al., "Spectroscopic characterization of microscopic hydrogen bonding disparities in supercritical water", *Journal of Chemical Physics* **123** (2005)154503
[11] Smirnov P. et al., "Structure of Aqueous Gallium(III) Bromide Solutions over a Temperature Range 80–333 K by Raman Spectroscopy, XAFS and X-ray Diffraction", *J. of Solution Chemistry* **33** (2004) 903-922

Justificatif scientifique

- *Relier le proposal à un rapport d'expérience*
  - Il est possible de la faire simplement lorsque vous restez dans le même cadre (associez un rapport « SOLEIL » dans le SUNset)
  - Sinon, pour associer un rapport « ESRF » sur le SUNset, il faut joindre au pdf de la justification scientifique le pdf du rapport d'expérience

Déposer un projet

- Un bon exercice de concision
- Attention aux dates limites!
  - 1er septembre et 1er mars pour l'ESRF
  - 15 septembre et 15 février pour Soleil
- Ne pas hésiter à nous contacter

http://www.esrf.fr/UsersAndScience/Experiments/CRG/BM30B/BM30Bb-en.html