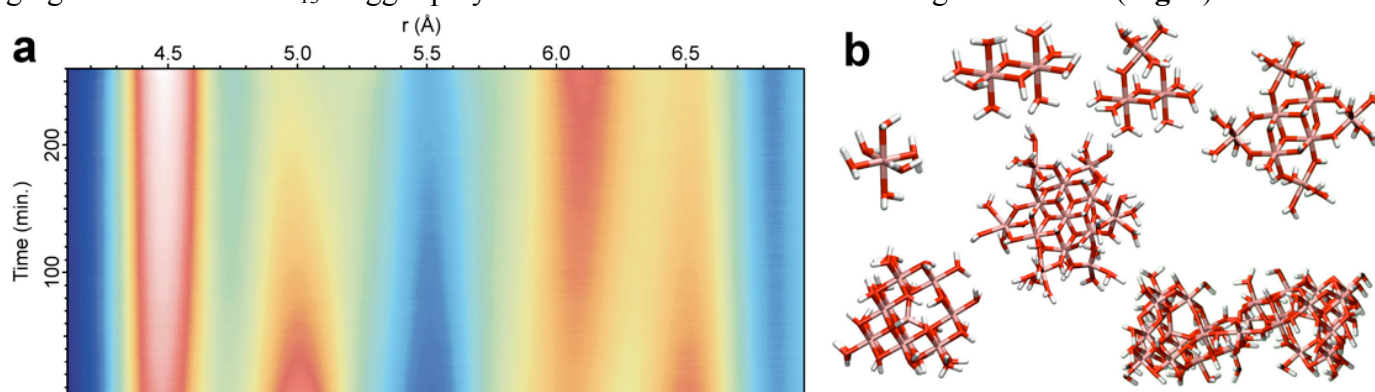|	**Experiment title:** Evolution of Al speciation during polyoxocations glass formation from Al$_{13}$ Keggin species	**Experiment number**: 26-02-830
Beamline: BM26B	**Date of experiment**: from:10 March 2017 at 08:00 to: 13 March 2017 at 08:00	**Date of report**: 16/11/2017
Shifts: 9	**Local contact(s)**: HERMIDA MERINO Daniel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Olivier DESCHAUME*, Department of Physics and Astronomy, KU Leuven, Belgium

Eric BREYNAERT*and Maarten HOULLEBERGHS*, **Centre for Surface Chemistry and Catalysis, KU Leuven, Belgium**

Report

Aluminium polycations are essential for many key applications such as water treatment, cosmetics, nuclear liquid waste treatment and materials science. [1] The critical aspect in the development of new applications is the complexity of aluminium speciation in aqueous solutions, rendering the exploitation of the versatile aluminium polycation, oxide and hydroxide chemistry difficult. Highly concentrated solutions of pure ε-Al$_{13}$ Keggin polycations tend to convert into repulsive gels, behaving like a glass. Whereas such solutions would be highly attractive for the use in applications, the glass formation prevents such developments. Combining NMR, HEXS/PDF and SAXS, the time and distance resolution of HEXS/PDF is ideal to reveal the internal structure and conversions between the polycations, while NMR provides a direct handle on the speciation, revealing the number of components, and the SAXS profile provides access to the size, shape and interactions between the aluminium polyoxometalate clusters. Recently the evolution of Al speciation upon aging concentrated ε-Al$_{13}$ Keggin polycation solutions was observed using HEXS/PDF (**Fig. 1**).

Figure 1: (a) Evolution of the pair distance distribution function of concentrated ε-Al$_{13}$ Keggin polycation solutions as function of aging time (data recorded at id31). (b) Al species potentially interconverting during the course of concentrated ε-Al$_{13}$ aging.

Full interpretation of this dataset requires knowledge on the evolution of the size and shape of these polycation clusters, which can be obtained from SAXS. In the case of Al, solid state NMR coupled to single crystal diffraction currently are the dominant techniques exploited for the analysis of the aluminium chemical environment in polycations. However, NMR based elucidation of Al species intramolecular structure in

solution remains hampered by quadrupolar broadening.[2] Recently, the potential of HEXS in combination with PDF analysis for solution state cluster crystallography was demonstrated by elucidating the solution-phase structure of $[PW_{12}O_{40}]^{3-}$ under equilibrium and photo-reduced conditions. The same approach has revealed unexpected evolutions in the Al speciation upon aging of highly concentrated ε-Al_{13} Keggin polycation solutions. Whereas the combination of XAS and PDF turned out to be extremely powerful in case of heavy element polyoxometalates, the combination of PDF with SAXS and solution state ^{27}Al NMR can be expected to be even more fruitful.

During this experimental session we investigated aluminium polyoxocations in the presence of aminoacids (**Fig. 2**). Weakly interacting aminoacids such as glycine or alanine promote the isomerisation from ε- to δ-Al_{13}, while more strongly interacting aminoacids such as glutamic and aspartic acid lead to a reorganisation of the Keggin ions into large species which structure still needs to be determined.

Experiments were also carried out during ε-Al_{13} release form lyophilised powders, and during the dissolution/dilution of ε-Al_{13} glasses. Moreover we characterised different polycations obtained during the course of neutralisation of aluminium chloride solutions by ion exchange, from hydrolysis ratio 0 to 2.40, to enable us to have a clear picture of Al speciation including monomers, dimers, trimers, ε-Al_{13}, together with intermediate, yet poorly understood species.
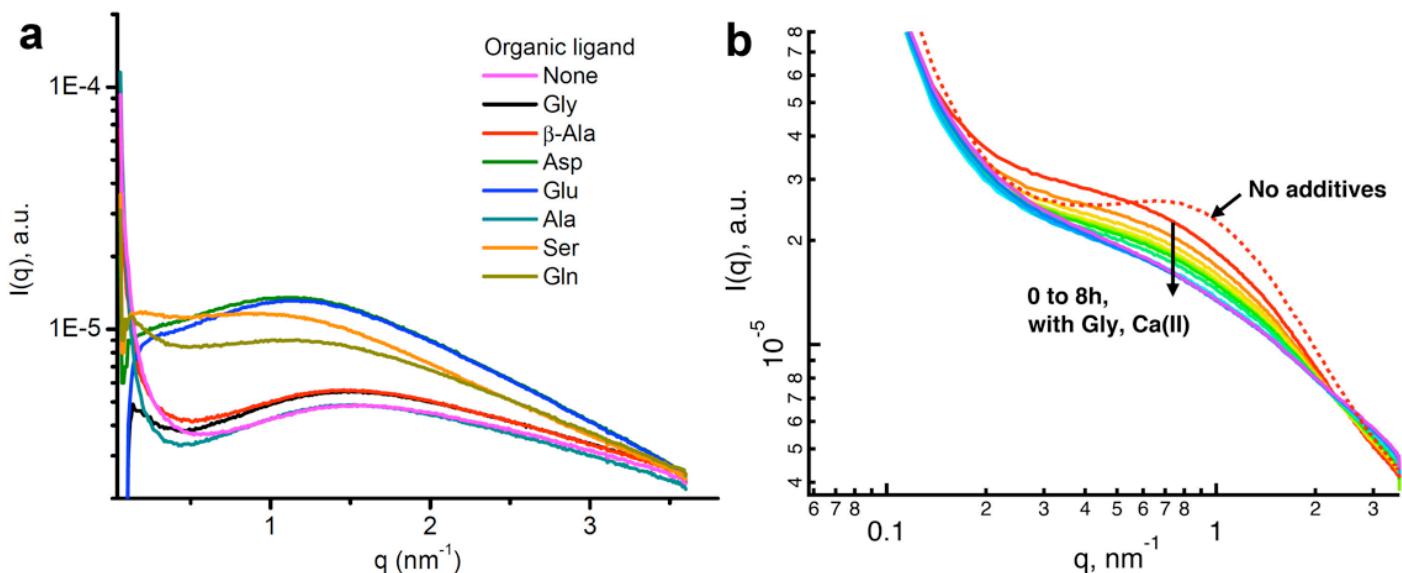

Figure 2: (a) SAXS data for ε-Al_{13} heated in the presence of different aminoacids, clearly defining different classes of aminoacids effect, in aggreement with ^{27}Al NMR and dissolution data. (b) Evolution of SAXS pattern during aging of an aluminium chlorohydrate solution in the presence of calcium and glycine at 90 ºC for 8 h.

We monitored the vitrification process occuring upon aging of concentrated ε-Al_{13} mer solution, and the aging of the resulting glass at 70 to 90 ºC. The resulting SAXS information now needs to be treated in relation with our existing PDF, NMR and dielectric spectroscopy data. In particular a strong structure factor is observed down to very low concentrations of the polycations. This structure factor can be experimentally eliminated by the use of strong Al binders such as acetate anions, for a better observation of the polycations shape and size. However these strong ligands compete with softer ones such as aminoacids, therefore precluding the study of softer interactions. Knowing that the efficacy of Al polycations is based in large part on their size/size ratio, the structure factor and underlying size information could also help us predict the efficacy (protein flocculation) of complex polycation / ligand mixtures.

References

[1] Casey, W. H. (2006). *Chemical reviews*, *106*(1), 1-16.

[2] Haouas, M. *et al.* (2016). *Progress in nuclear magnetic resonance spectroscopy*, 94, 11-36.