ESRF	**Experiment title:** Sol/Gel process in Zr/lactate-Citrate/polyacrylate systems.	**Experiment number**: **32-1-135**
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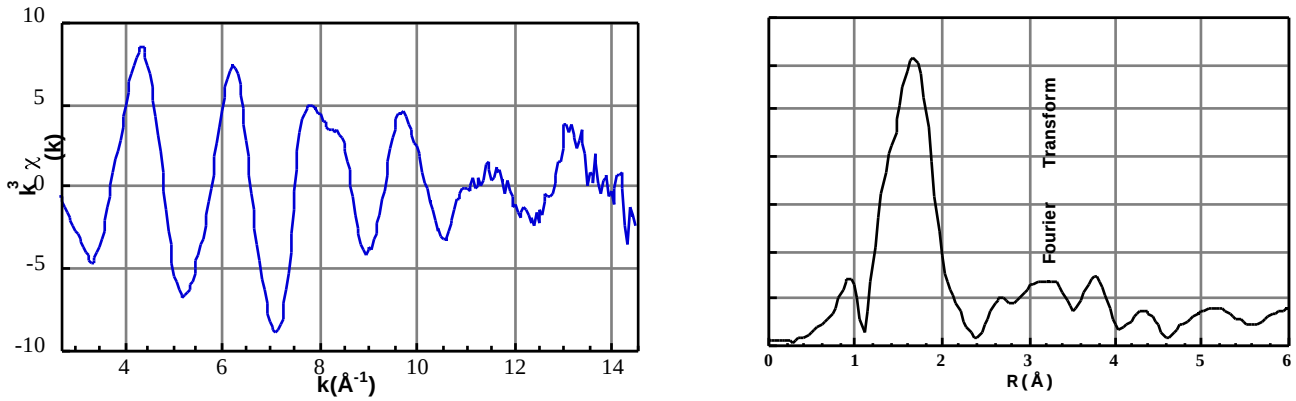
Report:

The control of gelation kinetics in sol-gel systems is an important objective for several applications (ceramic and thin film synthesis, modification of permeability in porous rock, etc…). There is a growing interest in studying the efficiency and properties of gels containing zirconium that doesn't suffer the environmental limitation known for Cr usually used in sol-gel process. In that context, Chauveteau et al (1999) have developed an original approach and a new model for predicting crosslinking of polyacrylate solutions by Zr-lactate solutions under shear. The complete understanding of gelation process requires to determine the Zr speciation both in Zr-Lactate solutions and after geling in presence of polyacrylate. Since there is no investigation published in literature we decided to analyze by using X-ray Absorption Spectroscopy i) zirconium lactate solutions at different concentrations ii) gel systems resulting from zirconium lactate and polyacrylate solutions mixture.

Zr K-edge XANES and EXAFS experiments have been carried out with the Si (111) monochromator crystals and by using the fluorescence detection mode due to the very low concentration of Zr in liquid or gel samples (36 ppm for the lowest concentration). By combining the high brilliance from the ESRF synchrotron source with a multi-channel fluorescence detector, we were able to obtain spectra with a very high signal/noise ratio for such a Zr concentration as seen in figure 1. These good spectra quality was also due to the fact that the sample's matrix is composed by light elements (C, O, Cl, Na…).

Our XANES results suggest that Zr ion is always in a dodecahedral geometry both in



a) b)

Figure 1: a) EXAFS spectrum b) Fourier transform of a Zr-lactate-polyacrylate gel ([Zr]=36 ppm).

lactate solutions and in polyacrylate gels. The coordination of zirconium in our systems is different from that found in Zr-alkoxide system (Peter et al, 1995) used as precursors in the Sol-Gel process. In that case the number of oxygen atoms in the first coordination sphere of Zr (Zr-O distance≈2.2Å) increases from 6 to 8 during gelation

i) Zr speciation in lactate solutions: At pH 6, the number of Zr-O-Zr linkages (d_{Zr-Zr}=3.54Å) increases when Zr-lactate concentration decreases from 72000 to 36 ppm. In term of structure it seems that zirconium polymers grow from a dimer $Zr_2(lactate)_6$ in concentrate solutions ([Zr]=72000 ppm) to a tetramer ($Zr_4(lactate)_x$) at [Zr]=1400 & 800 ppm and to larger polymers resulting from tetramer associations at lower concentrations. In addition the number of carbon atoms around Zr at a distance of 3.2 Å decreases showing that lactate complexes are replaced by OH groups during the polymerization.

ii) Zr speciation in Zr-lactate-polyacrylate gels: The different gels analyzed resulted from the gelation of a mixture between polyacrylate solutions (2g/l) containing NaCl salts (20 g/l) at pH 6 and 7 by zirconium lactate solutions. The final Zr concentration was very low (36 ppm). For gelation at pH 6 Zr species appear to be a mixture of monomers and dimers while Zr tetramers are present when gelation occurred at pH7. The Zr-C distance decreases from 3.2Å in a pure lactate solutions down to 3.1 Å for Zr-lactate-polyacrylate systems when gelation has taken place. As a consequence it seems that lactate molecules initially bonded to Zr are partly exchanged by acrylate group borne by polymers.

The analysis of multiple scattering is still in progress using the Feff-7 code. In a near future we will use molecular modeling to validate the 3D structures suggested by EXAFS results.

The very satisfactory and important point is that we where able to determine *in situ* Zr speciation i.e. at very low concentrations without the need of artificially increasing the Zr concentration in solutions and gels to obtain high signal/noise ratio.

References :

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