

Zirconium speciation in lactate solutions and polyacrylate gels

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Controlling gelation kinetics is an important objective for several applications (ceramic and thin film syntheses, reduction in permeability of porous rock, etc). There is a growing interest in studying the gelation of polymers by zirconium, a crosslinker of lower toxicity than the chromium which is still commonly used. XAS at the Zr K-edge was performed at the European Synchrotron Radiation Facility (ESRF) on the BM32 beamline. The fluorescence detection was used to carry out successful *in situ* speciation at concentrations as low as 36 ppm. The Zr speciation was determined both in ZrLa (where La stands for lactate) aqueous solutions and in gels of a terpolymer of acrylamide having 2% of zirconium reactive acrylate side groups and 2% of sulfonate groups introduced to prevent syneresis. XANES results show that Zr is always in a dodecahedral geometry. In ZrLa solutions, EXAFS results indicate that Zr species grow from a dimer $Zr_2(La)_6$ to a tetramer $(Zr_4(La)_x)$ and then to larger polymers resulting from tetramer associations, as the Zr concentration decreases from 51840 ppm to 36 ppm. In polymer gels, Zr species appear to be dimers at pH 6 while tetramers are found when gelation occurred at pH 7. Calculations taking into account multiple scattering effects as well as dynamic molecular calculation confirmed conclusions derived from conventional EXAFS analysis.

1. Introduction

The control of gelation kinetics in sol-gel systems is an important objective for several applications such as ceramic and thin film syntheses, reduction in permeability of porous rock, . . . Two main sol-gel processes are generally studied. The first is based on the hydrolysis and condensation of metal alkoxides leading to the formation of oxopolymers which transform into a gel. The second is based on the gelling of organic polymers (polyacrylate, . . .) using a crosslinker like di-, tri- or tetra-valent cations.

Concerning the gelling of organic polymers, there is a growing interest in studying the efficiency and properties of gels containing Zr as crosslinker, which is more environment friendly than the commonly used Cr. In that context, Chauveteau *et al.* (1999-2000) have developed an original approach and a new model for predicting crosslinking of polyacrylate solutions by Zr-lactate (=ZrLa where La stands for lactate) solutions under shear. The complete control of gelation process requires to determine the Zr species both in ZrLa solutions and after gelling in presence of polyacrylate. Although Zr species have not been determined in these particular systems, the evolution of the Zr speciation in water solutions is known. From very acidic to neutral solutions, Zr species evolve from a monomer (Jolivet, 1994) to cyclic tetramers (Johnson and

Krauss, 1956, Aberg, 1977, . . .) and larger polymers. Depending on the kinetic of hydrolysis, several compounds could be formed by polymerization of cyclic tetramers (gels or $Zr(OH)_4$, (Clearfield, 1964)). In the presence of strong complexing ligand, and under conditions which prevents hydrolysis (i.e. low pH and excess of ligands) complex $Zr(\text{ligand})_4$ represents the major species (Peter *et al.*, 1995). A polymerization of such complexes, leading to the formation of the Zr dimer: $Zr_2(\text{ligand})_6$ (Clearfield, 1964, Intorre and Martell, 1960, Peter *et al.*, 1994 and 1995) could occur if the pH slightly is increased. But the general trend is that strong complexing ligands hinder the Zr polymerization.

This paper reports analysis of the Zr speciation in aqueous system containing lactate, polyacrylate and sodium chloride. Experiment were performed by using X-ray Absorption Spectroscopy in both ZrLa solutions at different concentrations and gel systems resulting from the crosslinking by Zr of acrylate groups beared by the polymers.

2. Materials and methods

2.1. Solutions and gels

The effects of the dilution of a ZrLa solution in salted solutions on zirconium species was investigated. The dilution of the concentrated solution provided by Benchmark Research and Technology Inc. ($C_{ZrO_2} = 72000$ ppm, pH = 7.53, $X = [ZrO_2]/[La] = 3$ in molar ratio) was carried out in 20 g/l NaCl water. Then the pH is adjusted to 6 or 7 by addition of HCl or NaOH depending on the dilution. After 15 min, the dilute Zr solution is directly analyzed, lyophilized or mixed in 50/50 volume ratio with a polymer solution at the same pH for gelling. The polymer used for gelling experiments is a high molecular weight ($M_w \approx 5.10^6$ daltons) copolymer provided by Floerger containing 96% acrylamide groups, 2% sulfonates to prevent syneresis and 2% acrylates for ensuring crosslinks with zirconium.

2.2. XAS experiments

Zr K-edge XAS experiments have been carried out at the ESRF (Grenoble-France) on the BM32 beamline with 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 and 6 hours scan for each spectrum, we were able to obtain spectra with a very high signal/noise ratio even at so low Zr concentration. XAS Spectra were scanned from 100 eV below to 800 eV above the Zr K-edge.

Pre-edge part has been extracted from XANES region. XANES spectra intensity were normalized by fitting the photoelectric background above the absorption edge with a 2^{nd} order polynomial function. The standard procedure for data reduction was used to analyze the measured EXAFS data. This was done using a series of programs developed by Michalowicz (1991). Background was removed by fitting pre and post-edge with a polynomial fit function and a spline function fit procedure respectively. Then the resulting normalized EXAFS data $\chi(E)$ were converted from energy to wave vector $\chi(k)$ by reference to threshold energy E_0 , k^3 weighted and Fourier transformed to R space using a Kaiser apodization window with $\tau=2.5$. The analysis of the $\chi(k)$ was based on the curved wave EXAFS formalism (Rehr and Albers, 1990). EXAFS parameters were calibrated and validated for each scattering path by reference to well-characterized crystalline model compounds for which $\chi(k)$ is measured experimentally. Amplitude and phase shift functions

used to recalculate partial EXAFS spectra were extracted from the FEFF7 code (Zabinsky *et al.*, 1995). FEFF7 was also performed to estimate the contribution of multiple scattering (MS) paths on the EXAFS signal.

2.3. Molecular modelling

All forcefield results were generated by using the Universal Force Field (Rappe *et al.*, 1992) from the Cerius package (MSI Corp.). Optimal conditions concerning the calculation were determined from the structure of the Zr-Acetylacetonate crystal (Clegg, 1987).

Table 1

Structural parameters derived from EXAFS analysis of the samples

Sample	Shell	R(Å)	σ (Å)	N	Q*
ZrLa(mother sol.)	Zr-C	2.76	0.02	0.9	0.06
	Zr-C	3.20	0.06	6.1	
	Zr-Zr	3.54	0.06	0.9	
	Zr-O	4.05	0.10	2.9	
ZrLa(1400 ppm)	Zr-C	2.72	0.02	0.3	0.06
	Zr-C	3.15	0.08	5.1	
	Zr-Zr	3.53	0.06	1.9	
	Zr-O	4.00	0.11	2.3	
ZrLa(800 ppm)	Zr-C	3.16	0.04	3.7	0.03
	Zr-Zr	3.53	0.06	2.4	
	Zr-O	4.01	0.11	0.8	
ZrLa(200 ppm)	Zr-C	2.83	0.02	0.5	0.06
	Zr-C	3.12	0.08	4.6	
	Zr-Zr	3.57	0.07	1.7	
	Zr-O	3.94	0.06	0.7	
ZrLa(50 ppm)	Zr-C	2.95	0.02	1.3	0.06
	Zr-C	3.18	0.07	2.7	
	Zr-Zr	3.53	0.06	2.6	
	Zr-O	4.20	0.06	0.5	
Gel(pH6)	Zr-C	3.12	0.02	1.9	0.03
	Zr-C	3.36	0.02	1.3	
	Zr-Zr	3.56	0.05	0.9	
	Zr-O	3.71	0.11	1.6	
Gel(pH7)	Zr-C	3.06	0.10	2.5	0.06
	Zr-C	3.19	0.02	0.6	
	Zr-Zr	3.55	0.09	2.1	
	Zr-O	3.69	0.11	1.3	

$$*Q = \frac{\sum [(k^3 \chi_{\text{calculated}} - k^3 \chi_{\text{experimental}})]^2}{(k^3 \chi_{\text{experimental}})^2}$$

3. Results and discussion

XANES results show that Zr is always in a dodecahedral geometry both in lactate solutions and in polyacrylate gels. This coordination is different from that found in Zr-alkoxide system (Peter *et al.*, 1995). In that case the number of oxygen atoms in the first coordination sphere of Zr (Zr-O distance $\approx 2.2\text{\AA}$) increases from 6 to 8 during gelation.

i) Zr speciation in lactate solutions:

The first point was to identify the Zr species present in the stock

Zr-La solution. EXAFS results indicates that the number of Zr-O₂-Zr linkages ($d_{\text{Zr-Zr}}=3.54\text{\AA}$) was equal to 1($\pm 20\%$) suggesting the presence of Zr dimers (table 1). The number of C atoms around Zr at $3.0\text{-}3.2\text{\AA}$ ($=d_{\text{Zr-C}}$) is approximately 6($\pm 20\%$). In the case of bidentate Zr-lactate complex this result indicates that 3 lactates are linked to each Zr dodecahedron. Since the determination of light element like C is difficult at the Zr k-edge, this EXAFS result was analyzed in detail. The effect of multiple scattering (MS) was analyzed on the EXAFS spectrum of the ZrLa stock solution. A 3D structure was optimized using forcefield calculations (figure 1). The theoretical EXAFS spectrum from this cluster was adjusted using FEFFit (Newville *et al.*, 1995) to the experimental $\chi(k)$. The good adjustment between experimental and calculated EXAFS curves (figure 2) strongly suggests that MS is not a predominant phenomenon, and that the previous EXAFS calculation and the cluster proposed for the dimer are reasonable.

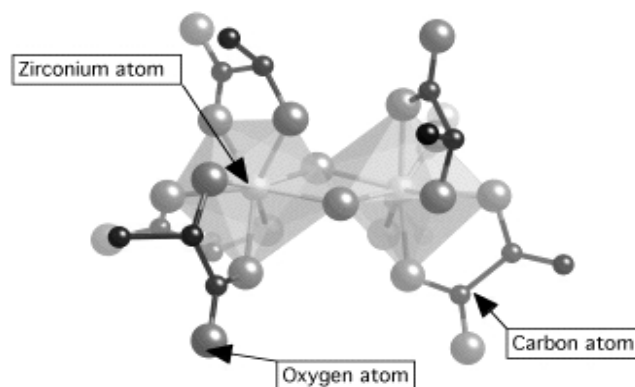


Figure 1

3D cluster of the Zr₂La₆ calculated with the UFF forcefield

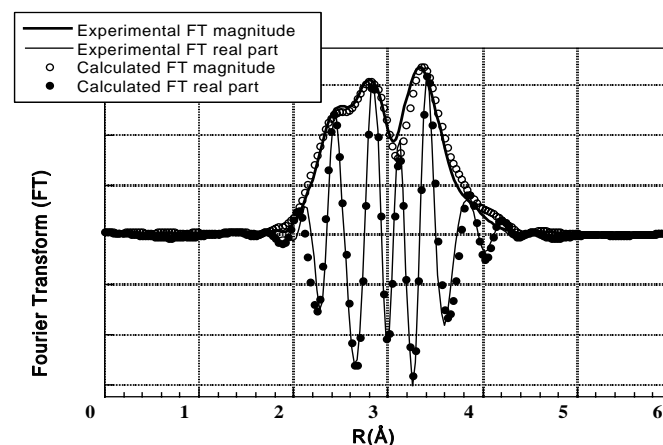


Figure 2

Magnitude and real part of the Fourier Transform of the partial EXAFS curve of the ZrLa mother solution compared with calculated curves

At pH 6, the number of Zr-O-Zr linkages increases when ZrLa concentration decreases from 51840 ppm to 36 ppm. In term of structure it seems that Zr polymers grow from a dimer Zr₂(La)₆ in concentrate solutions ([Zr]=51840 ppm) to a tetramer (Zr₄(La)_x) at

[Zr]=1400 ppm & 800 ppm and to larger polymers resulting from tetramer associations at lower concentrations (table 1). In addition the number of carbon atoms around Zr at a distance of 3.2Å decreases showing that lactate complexes are replaced by OH groups during the polymerization.

ii) Zr speciation in Zr-lactate-polyacrylate gels:

The different analyzed gels resulted from the gelation of a mixture between polyacrylate solutions at pH=6 and 7 and ZrLa solutions. The final Zr concentration was very low (36 ppm). For gelation at pH=6 Zr species appear to be dimers while Zr tetramers are present when gelation occurred at pH=7. The Zr-C distance decreases from 3.2Å in a pure lactate solutions down to 3.1Å 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 groups on the polymers. The modification of the Zr-C distance could be due to a modification of the structure of the complexing ligand. In the case of Zr-La, the complexation occurs through a bidentate structure while in the case of Zr-acrylate a monodentate structure seems to exist. This hypothesis needs to be validated using molecular modelling. Ab initio calculations using DFT theory are under progress to classify the complexing energies between all Zr ligands (lactate, acrylate, OH, water).

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