Light Scattering for the Masses™

In Situ Analysis of Inorganic and Organometallic Clusters

The detailed *in situ* analysis of inorganic and organometallic clusters is becoming increasingly important as researchers now routinely synthesize cluster compounds for use as secondary building units. In the series of experiments which follow, we used DLS to study the formation and reactivity of the well-characterized zirconium tetramer, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, as well as a recently characterized zirconium-glycine cluster, $[Zr_6(O)_4(OH)_4(H_2O)_8(Gly)_8]^{12+}$.

All solutions are prepared at the temperature of initial measurement using de-ionized water (0.067 μS/cm) and filtered through a 0.02μm filter (Whatman, Anotop) immediately prior to analysis. The reagents used are zirconium dichloride oxide octahydrate ($ZrOCl_2{\cdot}8H_2O$, Alfa Aesar) and Glycine, 99% (Alfa Aesar). Raw data are collected using the DynaPro Titan and hydrodynamic radius measurements are derived from the DYNAMICS software regularization analysis.

Crystal data of ZrOCl2 demonstrates discrete tetrameric units and ZrOCl2 is known to exist as the tetrameric $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ cluster in solution[1] with an expected hydrodynamic radius less than 1nm. Figure 1 depicts the measured particle size in a 0.1M $ZrOCl_2$ solution as it is heated along a linear temperature gradient. It is immediately apparent that both the radius and mass increase as a function of temperature, suggesting aggregative behavior. The high resolution and relatively low noise provide insight into the temperature dependant cluster growth of this system. After the reaction, cooling to 0°C confirmed a permanent transformation from an initially measured radius of 4.2Å to a final radius of 17.6Å.

$ZrOCl_2$ has been previously reported to react with glycine in aqueous solution to form an organometallic moiety of formula $[Zr_6(O)_4(OH)_4(H_2O)_8(Gly)_8]^{12+}$[2]. The heating of a 0.1M $ZrOCl_2$ solution at 80°C in the presence of 0.13M glycine was found to inhibit cluster aggregation, likely by formation of the organometallic cluster. (Figure 2) Decay signals from glycine molecules occur exclusively in the first correlator channel because of their small size; by excluding first-channel decay processes from data analysis, the signal from glycine was eliminated.

The precision with which DLS can measure the size of species on the sub-nanometer scale allows researchers unprecedented insight into aqueous metal systems. By monitoring the effects of adjusting temperature and organic ligand, it is possible to make meaningful predictions about the reactivity and speciation of inorganic and organometallic clusters.

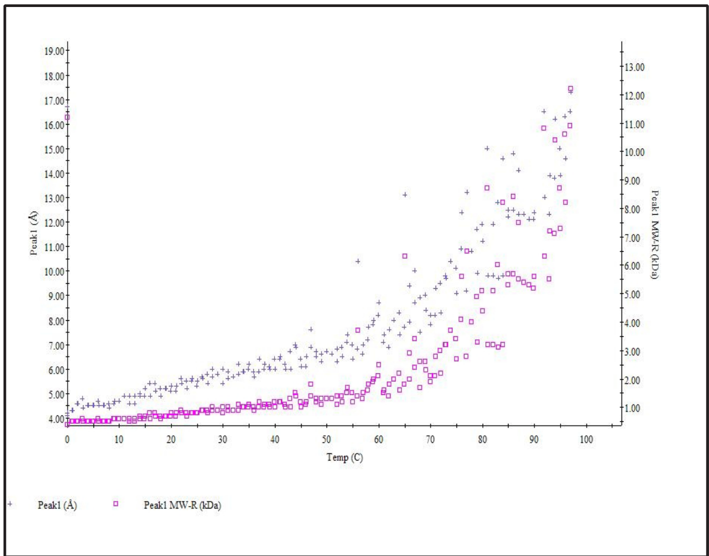

Figure 1: 0.1M ZrOCl2 heated along a linear temperature gradient from 0°C to 100°C over a 5 hour period. Color Code: Blue Cross -Measured radius (Å), Purple Square -Derived MW (kDa)

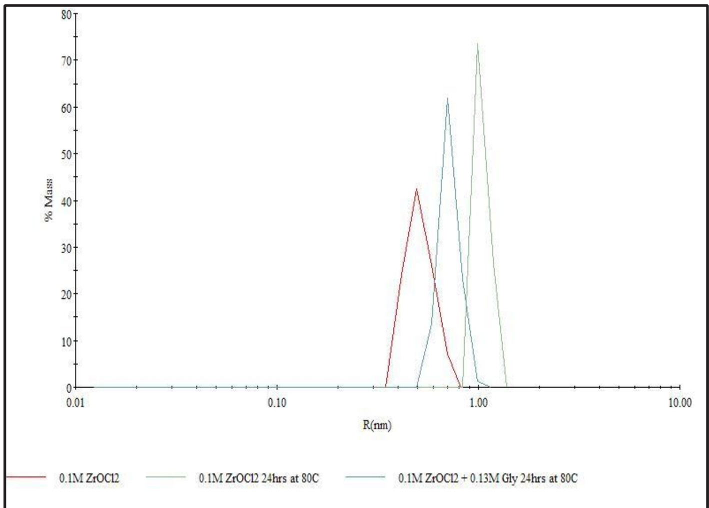

Figure 2: Effect on the measured radius of heating 0.1M ZrOCl2 with and without glycine. Color Code: Purple -Fresh 0.1M ZrOCl2 Teal -0.1M ZrOCl2 after 24 hours heating at 80°C Grey -0.1M ZrOCl2 + 0.13M glycine after 24 hours heating at 80°C

Citations

1. Clearfield, A.; Vaughan, P. A. Acta Crystallogr. 1956, 9, 555.

2. Pan, L.; Heddy, R. Inorg Chem. 2008, 47(13), 5537-5539

This note graciously submitted by Iraklis Pappas, Michael Fitzgerald, LaTonya Kilpatrick, Aixing Fan and Long Pan* Colgate Palmolive Co. 909 River Rd. Piscataway, NJ.

Wyatt Technology CORPORATION
6300 Hollister Avenue • Santa Barbara, CA 93117
TEL (805) 681-9009 • FAX (805) 681-0123
E-mail: info@wyatt.com • URL http://www.wyatt.com