Kinetics of ^{17}O-exchange reactions in aqueous metal-oxo nanoclusters

J. R. BLACK[1], M. NYMAN [2] AND W. H. CASEY[1]

[1] Department of Geology, University of California, Davis;
[2] Department of Geochemistry, Sandia National Laboratories, Albuquerque, U.S.A.;

Nanometer-sized aqueous clusters can serve as useful models for the surfaces of extended structures such as minerals. Unlike mineral surfaces, however, these molecules have well-defined structures in solution and the various structural sites yield distinct spectroscopic signatures. These signatures allow us to collect kinetic data on oxygen-isotope-exchange reactions and interpret the mechanisms via computer models. We also can follow polymerization reactions in situ. In this presentation, the target molecules are niobate polyoxoanions ($[H_xNb_6O_{19}]^{(8-x)-}$ (x = 0-3), see inset (1) in Fig. 1). We investigate the speciation and reactivity of these clusters using a number of techniques; ^{17}O-NMR to follow exchange of bridging (O_b), terminal (O_t) and central (O_c) oxygen sites over time; UV-Vis spectra following the reaction to form a larger cluster over time (Fig. 1); and capillary electrophoresis, which confirms the formation of a higher molecular weight cluster over time, that we tentatively identify as a decaniobate (see inset (2) in Fig. 1). Using previous work as a guide [1], we can follow changes in the intensities of peaks in the ^{17}O-NMR spectra to assign rate laws for exchange of both O_b and O_t sites in the $[H_xNb_6O_{19}]^{(8-x)-}$ molecule. The rates for exchange of μ_2-O_b sites is pH dependent, even at pH > 12. O_t sites react much slower than the μ_2-O_b bridges under these conditions. ^{17}O-NMR data also show the slow growth of a peak (~ +28 ppm) that we presume to be the μ_6-O_c site in the larger cluster.

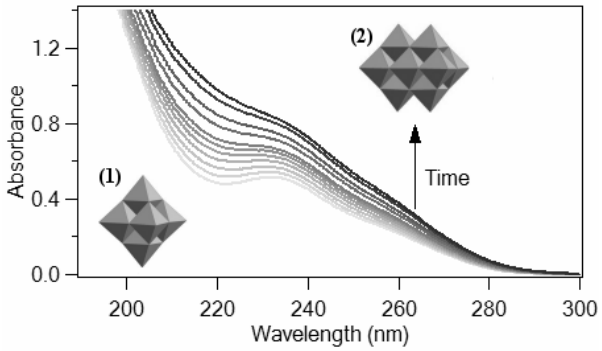

Figure 1. UV spectra as a function of time. pH = 8.45, 20°C, aging = 4 hours and $\Sigma[([H_xNb_6O_{19}]^{(8-x)-}$= 20.6 mM.

References

[1] Alam, T. M., Nyman, M., Cherry, B. R., Segall, J. M. and Lybarger, L. E. (2004). *J. Amer. Chem. Soc.*, **126(17)**, 5610-5620.