

## **Spectroscopic features of tetrahedrally coordinated aluminate dimer, $K_2Al_2O(OH)_6$**

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Formation of oligomeric aluminum hydroxide species such as the aluminate dimer has been historically called upon to account for anomalously high Al concentrations observed in radioactive tank waste located at the Hanford Nuclear Site and as the possible cause for remarkably slow precipitation kinetics of Bayer liquors. Despite its importance detailed studies of the only crystallographically characterized, tetrahedrally coordinated aluminate dimer,  $K_2Al_2O(OH)_6$  are rare. We investigate the Al/KOH/H<sub>2</sub>O tertiary system to determine the conditions governing the identity of the solubility limiting phase (gibbsite, Al(OH)<sub>3</sub> vs.  $K_2Al_2O(OH)_6$ ) and perform extensive analytical analysis of both the resulting solid and solution phases. We implement X-ray absorption spectroscopy (XAS) and X-ray scattering techniques in conjunction with well characterized and synthetically pure  $K_2Al_2O(OH)_6$  and other solid oligomers to develop standards that will be used to model complex solutions containing mixtures of these species along with the aluminate Al(OH)<sub>4</sub><sup>-</sup> monomer. Solution phases are initially analyzed using-high field (750 MHz) <sup>27</sup>Al NMR, Raman, and IR spectroscopy to establish baseline monomer, Al(OH)<sub>4</sub><sup>-</sup> to dimer, Al<sub>2</sub>O(OH)<sub>6</sub><sup>2-</sup> ratios which are then compared with results obtained from solution-phase X-ray scattering. This work establishes a set of standards and standard procedures for quantification of oligomeric species present in caustic aluminate solutions.