

Ionic Liquid Glassification to Observe Aluminate Ion Speciation in Low Water Alkaline Environments

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Aluminum (Al), originating from nuclear fuel cladding, plays a commanding role in high level radioactive waste (HLW) chemistry. Hanford Site HLW is composed of saltcakes and sludges in concentrated highly alkaline solutions of sodium hydroxide containing octahedral (O_h) Al in colloidal solid phases and a distribution of tetrahedral (T_d) aluminates. Transient solute species with strained T_d geometries may be intermediates in $T_d - O_h$ transitions during dissolution and precipitation processes. These T_d Al species are poorly resolved, undergoing rapid ligand exchange with water. The glass transition of an ionic liquid presents an opportunity to slow the dynamics of structural rearrangements to a rate where they are resolvable with nuclear magnetic resonance spectroscopy (NMR). The dissolution of boehmite in sodium hydroxide monohydrate was monitored with *in-situ* ^1H , ^{17}O , ^{23}Na and ^{27}Al magic angle spinning NMR and *in-situ* X-ray diffraction. Upon cooling, the ionic liquid phase transitions into an amorphous glass in which multiple T_d Al(III) can be resolved. These T_d Al(III) species slowly crystallize as O_h Al(III) species in nonasodium bis(hexahydroxy aluminate) trihydroxide hexahydrate, in a thermally reversible process. Thermal cycling enables concerted Al(III) coordination change and ligand exchange with limited water to be directly probed with *in-situ* NMR.