

Understanding oligomerization in alkaline sodium aluminate solutions using reactive force field molecular dynamics simulations

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Understanding mechanisms governing chemical transformations of aluminum between aqueous solutes and mineralogical forms is important in mineral weathering, soil composition, and in industrial Al processing. Compared to acidic conditions, less is known about these mechanisms in alkaline systems, particularly in highly concentrated electrolytes. Here, the mechanism of the transformation of aluminate $\text{Al}(\text{OH})_4^-$ to gibbsite $\text{Al}(\text{OH})_3$, respectively consisting of AlO_4 tetrahedra and AlO_6 octahedra, remains unknown. Although evidence exists for the aluminate dimer $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ as one condensation product of two $\text{Al}(\text{OH})_4^-$, no other solution species with higher Al-O coordination have been observed. Experimental studies typically feature NMR or optical spectroscopies, which are not sufficiently time-resolved to indicate when the change in coordination from 4 to 6 occurs during the nucleation-crystallization process.

Therefore, to make advances, molecular simulations are essential. However, the complexity of this system places constraints on simulation approaches, which must be both computationally efficient but also capable of accurately encompassing the dynamics of solvation, pH effects, and bond breaking/making. We report the development of a reactive force field for this purpose, which uses a simple formalism based on Lennard-Jones two-body terms, Stillinger-Weber three-body terms and QEq charge equilibration that is parameterized using density functional theory (DFT)-based molecular dynamics (MD) and validated against solution diffraction data and free energy profiles from DFT and DFTB-based MD. A combination of parallel tempering and umbrella sampling is used to probe the initial clustering of aluminate species then their oligomerization. Complementary global optimization is performed for a small number of Al^{3+} to validate the structure of the low-lying oligomers, accompanied by DFT calculations with implicit solvation. The free energy of the formation of oligomers with 4-coordinated Al bridged by oxo ligands is lower than that of gibbsite-like oligomers with 6-coordinated Al bridged by hydroxo ligands. Larger-scale simulations indicate the possible formation of an amorphous phase based on 4-coordinated Al, of which precipitation is also observed experimentally alongside gibbsite. Ongoing simulations and experiment ultimately will help us determine whether a solid phase with 4-coordinated Al is