The Influence of $\{Ba^{2+}\}:\{SO_4^{2-}\}$ Solution Stoichiometry on $BaSO_4$ Crystal Nucleation and Growth in Aqueous Solutions

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Abstract

The impact of solution stoichiometry, upon formation of $BaSO_4$ crystals in 0.02 M NaCl suspensions, on the development of particle size was investigated using Dynamic Light Scattering (DLS). Measurements were performed on a set of suspensions prepared with predefined initial supersaturation ($\Omega_{barite} = \{Ba^{2+}\}\{SO_4^{2-}\}/K_{sp} = 1000$) and dissolved ion activity stoichiometries ($r_{aq} = \{Ba^{2+}\}:\{SO_4^{2-}\} = 0.01$, 0.1, 1, 10 and 100), at a pH of 5.5 to 6.0, and ambient temperature and pressure. At this Ω_{barite} and set of r_{aq}, the average apparent hydrodynamic particle size of the largest population present in all suspensions grew from ~ 200 nm to ~ 700 nm within 10 to 15 minutes. This was independently confirmed by TEM imaging. Additional DLS measurements conducted at the same conditions in flow confirmed that the $BaSO_4$ formation kinetics were very fast for our specifically chosen conditions. The DLS flow measurements, monitoring the first minute of $BaSO_4$ formation, showed strong signs of aggregation of prenucleation clusters forming particles with a size in the range of 200 – 300 nm for every r_{aq}. The estimated initial bulk growth rates from batch DLS results show that $BaSO_4$ crystals formed fastest at near stoichiometric conditions and more slowly at non-stoichiometric conditions. Moreover, at extreme SO_4-limiting conditions barite formation was slower compared to Ba-limiting conditions. Our results show that DLS can be used to investigate nucleation and growth at carefully selected experimental and analytical conditions. Additional SEM imaging on formed $BaSO_4$ crystals for a range of initial conditions of Ω_{barite} (i.e. 31, 200, 1000 and 6000), r_{aq} (0.01, 0.1, 1, 10 and 100) and different background electrolytes (i.e. NaCl, KCl, $NaNO_3$, $MgSO_4$ and $SrCl_2$) confirms that $\{Ba^{2+}\}:\{SO_4^{2-}\}$ impacts the growth rate significantly in different directions for the different background electrolytes at the different Ω_{barite}-values. Furthermore, the $BaSO_4$ crystal morphology varies with r_{aq} and the type of background electrolyte. The combined DLS, TEM and SEM results imply that solution stoichiometry should be considered when optimizing antiscalant efficiency to regulate $BaSO_4$ (scale) formation processes.