Insight into $CaCO_3$ nucleation from the liquid-liquid phase diagram predicted by COSMO-RS

M.P. ANDERSSON* AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (* ma@nano.ku.dk)

Classical nucleation theory predicts a barrier on the order 100 kT for calcite formation, which excludes direct nucleation. Alternate theories have been put forward, such as the formation of prenucleation clusters[1] and liquid-liquid phase separation[2]. In both theories, liquid species similar to amorphous calcium carbonate are formed before calcite. Here we present a quantitative phase diagram for these amorphous phases, as liquid-liquid phase separation, from supersaturated $CaCO_3$ solutions, predicted using density functional theory and the COSMO-RS implicit solvent model (Fig. 1).

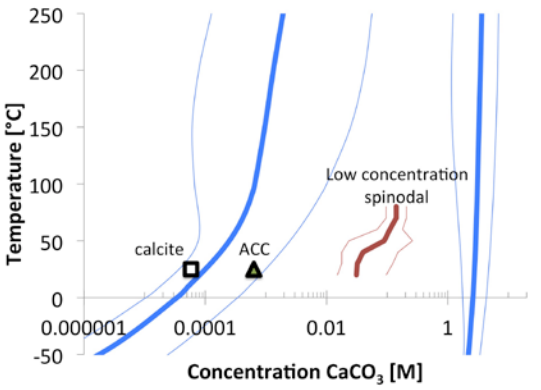

Figure 1. Liquid-liquid phase diagram for $CaCO_3$ solutions. The binodal lines are thick blue. Thin lines represent uncertainty estimates. The square and triangle show concentrations of solutions in equilibrium with the corresponding solid.

Several important conclusions arise from our calculations:

The critical point lies below -170 °C, i.e. liquid-liquid phase separation occurs at all temperatures.

The barrier for phase separation at the binodal line is only ~2 kT and the spinodal concentration is very high, therefore, no spinodal decomposition occurs < 0.01 M.

The number of clusters of the high density phase scales linearly with the Ca^{2+} concentration. Thus, the classical theory of liquid-liquid phase separation can explain the concentration behavior of the non-classical prenucleation model.

[1] D. Gebauer *et al.*, *Science*, 322, 5909, **2008.**
[2] A.F. Wallace *et al.*, *Science*, 341, 6148, **2013.**