Faraday Discussions, vol.235, pp.95-108, July, 2022.

Multistep nucleation compatible with a single energy barrier: catching the non-classical culprit

A.R. Lauer; M.A. Durán Olivencia; A. Fernández Martínez; A.E.S. Van Driessche

Abstract-

In this work we link experimental results of SrSO4 precipitation with a nucleation model based on mesoscopic nucleation theory (MeNT) to stride towards a cohesive view of the nucleation process that integrates both classical and non-classical views. When SrCl2 and Na2SO4 are co-titrated at slow dosing rates, time-resolved turbidity, conductivity and ion-specific data reveal that the initial stage of the nucleation process is driven by neutral species, i.e. ion-pairs or larger, akin to the prenucleation cluster model. However, when co-titrations are conducted at higher rates, the onset of nucleation is dominated by the consumption of free ions, akin to the explanation provided by classical nucleation theory (CNT). The occurrence of both mechanisms for the same system is explained by a toy model that includes both the thermodynamics (consisting of a single energy barrier) and kinetics of cluster formation formally obtained from MeNT. This gives rise to an effective energy barrier exhibiting a local intermediate minimum, which does not originate from a minimum in the thermodynamic free energy. Rather, it is associated with an increased probability of observing a specific class (in terms of size/density) of precursor clusters due to their slower kinetics. At high supersaturations this minimum in the kinetics of cluster formation becomes less pronounced and the effective barrier is also significantly lowered. Consequently, the probability of observing an intermediate state is blurred and we recover a nucleation pathway more closely following the one envisaged by the classical model. Thus, our model is capable of capturing both single and multistep nucleation mechanisms observed experimentally considering only a single energy barrier.

Index Terms- Nucleation, Mesoscopic Nucleation Theory, Stochastic Processes

Citation:
Andrew Lauer, A.R.; Durán-Olivencia, M.A.; Fernández-Martínez, A.; Van Driessche, A.E.S. "Multistep nucleation compatible with a single energy barrier: catching the non-classical culprit", Faraday Discussions, vol.235, pp.95-108, July, 2022.