474e Nucleation and Growth Kinetics for the Nanoparticle Precipitation of Barium Sulfate in Microemulsions

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The formation of nanoparticles in microemulsion droplets is a promising technology for the control of the particle properties, e.g. the particle size distribution or particle shape [1]. Results from barium sulfate precipitation experiments in a semi-batch rushton tank reactor [2] confirmed that the particle size distribution can be controlled by the variation of the initial reactant concentrations inside the droplets. A population balance model was used to analyze this behavior paying particular attention to the nucleation and growth kinetics.

The challenge in the model derivation of this process originates from the occurrence of two nested populations (particles inside droplets) and a high number of distributed properties, e.g. the concentrations of the reactants and the particle size. The two populations with their properties are strongly coupled by phenomena like the droplet exchange (coalescence/ redispersion or also named fusion/ fission), the chemical reaction, nucleation and growth of particles. Especially the droplet exchange concerning more than two properties (internal coordinates of the population balance) makes the solution of the resulting deterministic partial integro-differential equation via numerical methods difficult and computationally expensive [3]. Without any model reduction this system is only solvable by Monte-Carlo simulations [2,4], which have as well a high computational demand and are therefore not appropriate for an extensive study of the nucleation and growth kinetics. A significant model reduction can be obtained by the assumption that the time constant for the droplet exchange is much smaller than the time constants for nucleation and growth. This means that the concentrations of the liquid species inside the droplet are distributed following an equilibrium distribution, which is in the case of microemulsions Poissonian [5]. Further assuming that only one particle can exist per droplet and that the chemical reaction proceeds instantaneously the population balance model has to consider two internal coordinates, namely the particle size and the number of the liquid barium sulfate molecules within one droplet, which are distributed inside the droplet population according to the discrete Poisson distribution. Mathematically speaking the model is reduced to a partial differential equation with a high number (20 - 30) of convective terms, representing particle growth, for each number of barium sulfate molecules due to the dependence of the growth kinetics on the supersaturation.

Different rate approaches obtained from bulk precipitation experiments for nucleation and growth kinetics [6-8] were implemented in this model and simulations using the same process parameters as described by [2] were performed. The comparison of particle size distributions from experiments and the simulations shows that the kinetics from literature for the bulk phase process are not applicable in the nanosized droplets of a microemulsion without any modification. A simultaneous parameter estimation of the rate constants for nucleation and growth with the whole set of experimental data has been performed and a good agreement with the experimental data could be achieved. The location as well as the broadness of the particle size distribution could be adapted by the two rate constants. These corrected parameters were several order of magnitude smaller than the original ones in the bulk phase process. Possible explanations for this slow-down effect are that the kinetics derived for particle sizes in the micrometer range cannot be directly applied at the nanoscale or that the assumption of an instantaneous droplet exchange is wrong. In fact many theoretical studies assume that the droplet exchange is the rate determining step [4], but the high computational demand constricts such models too much. With the present model the whole process can be simulated in less than ten seconds on a standard 3 GHz PC in Matlab, which utilizes this very flexible and accurate model for further applications in CFD codes and online process control strategies.

In addition to the parameter estimations the sensitivity of the nucleation and growth kinetics concerning the critical number of molecules needed to form a stable nucleus and the droplet size have been investigated. The present model is currently extended to take excess of one reactant into account, too. Therefore two liquid species, both Poissonian distributed, have to be considered, leading to 400 - 900 convective terms in the partial differential equation. This will result in more reliable kinetics at high concentration gradients.

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