[430g] - Evaluation of operational process parameters for nanoparticle precipitation in microemulsions using a Monte-Carlo Simulation approach

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Abstract

A Monte-Carlo simulation approach for the nanoparticle precipitation in microemulsions has been developed and adapted to $BaSO_4$ nanoparticle precipitation. The simulation includes especially technical process parameters like feed rate, initial volume ratio or molar ratio of initial reactant concentrations. A set of experiments with different initial reactant concentrations of $BaCl_2$ and K_2SO_4 is compared to the simulated final particle size. An adaptation of certain internal parameters of the Monte-Carlo simulation leads to a good agreement between simulated and experimental data. The same internal parameters are then used for other variations of the technical process conditions like the feeding rate or initial volume ratio. It is shown how those process parameters influence the particle size and the size distribution. The simulation results help in finding appropriate control parameters in an up-scale approach of the microemulsion technology for nanoparticle production.

Key words: Monte-Carlo simulation, Particle precipitation, Microemulsion, Model control

Introduction

Nanomaterials are becoming increasingly important in various technological applications [1] but especially the large-scale production of tailor-made nanoparticles still represents a challenge. Different engineering approaches like gas-phase synthesis or bulk phase precipitation in liquids show several disadvantages as the non-ideal mixing in these processes leads to broad particle size distributions and an average particle size which is diffi cult to control [2,3].

Recently microemulsions have shown their potential as an interesting alternative reaction medium for the production of nanoparticles [4]. The nanodroplets in these microemulsions are fi lled with different reactants and act as small reactors where the coalescence-redispersion phenomena between the droplets lead to a controlled uniform micromixing. This enables the control of both the particle size and the particle size distribution. In order to use the microemulsion in a production technology one has to study a multitude of process parameters in order to fi nd suitable variables to control and adjust the properties of the particles [5]. This research can be very costly and time consuming. Appropriate computer simulations will help to reduce both experimental research time and costs. In the present work a Monte-Carlo simulation approach for the description of a microemulsion precipitation process was developed and applied for a process simulation.

Experiments on $BaSO_4$ precipitation in microemulsions

In our experiments two identical microemulsion (cyclohexane / Marlipal O13/40 / water) with two different reactants $BaCl_2$ and K_2SO_4 in the aqueous droplets were mixed. The initial volumes (proportional to the number of droplets N_d) of both reactants were the same ($X_{mix} = 0.5$). One microemulsion was fi lled into a stirred tank and the other was fed into the reactor with a constant feed rate X_{feed} (see Fig.1). Nanoparticles precipitated during this process were analyzed after the batch time with a Transmission Electron Microscope. An extensive overview on these experiments is given elsewhere [6].

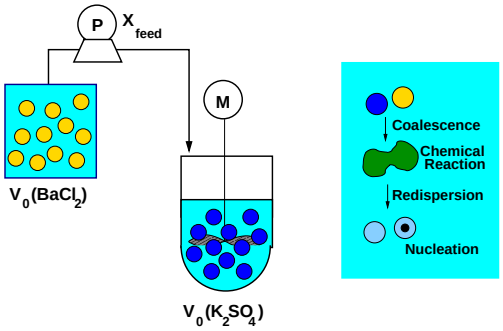

Fig. 1. Left: Experimental setup with a feed pump (P) and a stirred tank for the $BaSO_4$ precipitation in microemulsion. Right: Coalescence and redispersion of microemulsion droplets with chemical reaction and particle nucleation.

One of the main results of our experiments is the signifi cant dependence of the particle size on the molar ratio of initial reactant concentrations $X_{conc} = c^0_{BaCl_2}/c^0_{K_2SO_4}$. The K_2SO_4 concentration was constant ($c^0_{K_2SO_4} = 0.1\ mol/l$) and the $BaCl_2$ concentration was varied ($c^0_{BaCl_2} = 0.05 - 0.1\ mol/l$). It could be shown that a decrease of X_{conc} led to a signifi cant increase of the mean particle diameter (see Fig.2).

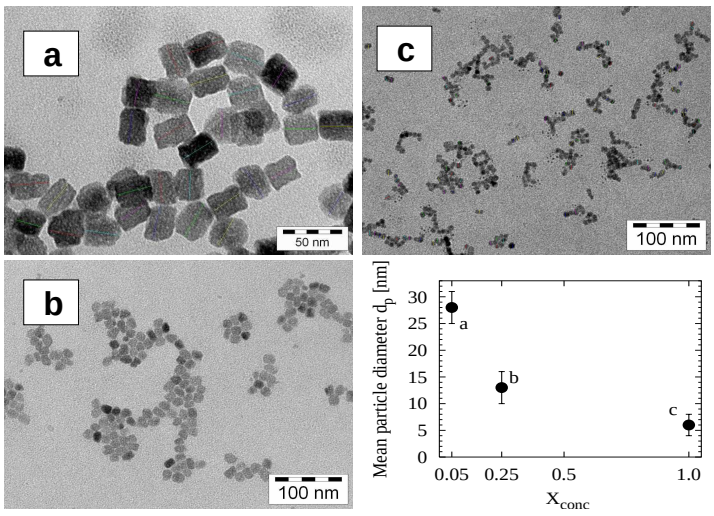

Fig. 2. TEM pictures of $BaSO_4$ particles and particle diameter dependence on the molar ratio of initial reactant concentrations.

The chosen process conditions of the presented experimental data were used for the adaptation of internal parameters of the Monte-Carlo simulation discussed in the following.

Monte-Carlo Simulation

A Monte-Carlo simulation approach for the nanoparticle precipitation in microemulsions was developed and applied to $BaSO_4$ nanoparticle precipitation. The simulation program is especially designed to take technical process parameters like the feed rate X_{feed}, the initial volume ratio X_{mix} and the molar ratio of initial reactant concentration X_{conc} into account. The flow chart of the simulation is shown in Fig.3.

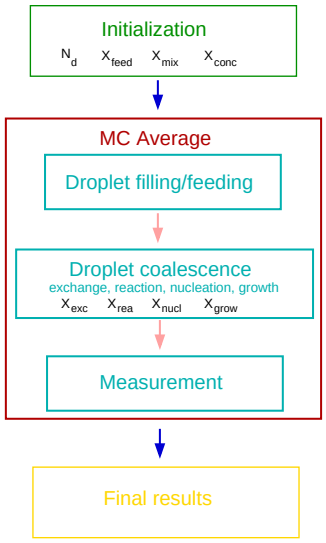

Fig. 3. Flow chart of the Monte-Carlo simulation.

The program is initialized with a given number of droplets $N_d = N_d(BaCl_2) + N_d(K_2SO_4)$. The initial volume ratio $X_{mix} = N_d(BaCl_2)/N_d(K_2SO_4)$ is set and the droplets are fi lled with the two reactants $BaCl_2$ or K_2SO_4. From experimental values at $X_{conc} = 1$ with $c^0_{K_2SO_4} = c^0_{BaCl_2} = 0.1 mol/l$ and a measured microemulsion droplet size of $6\ nm$ one can calculate the number of reactant molecules in each droplet which is ≈ 10. As in the experiments droplets with $BaCl_2$ are fed into the reactor with a feed rate $X_{feed} = N_d^{feed}(BaCl_2)/N_d(BaCl_2)$ per Monte-Carlo step to the $N_d(K_2SO_4)$ droplets. We assume perfect macromixing of the total reactor volume, i.e. the coalescence and redispersion of droplets is independent on their spatial position within the tank.

The coalescence and redispersion process is the basic step of the Monte-Carlo simulation (see Fig.1). For a coalescence event a pair of droplets is randomly chosen and mixed. $BaCl_2$ and K_2SO_4 in the droplets react instantaneously to $BaSO_4$ because this chemical reaction is very fast compared to all other sub-processes taking place in the system. In a second step the number of $BaSO_4$ molecules present in the droplet is compared to a critical value X_{nucl}. This value X_{nucl} is related to supersaturation and to homogeneous nucleation theory values [7] which in the present system is assumed to be $X_{nucl} \approx 10$. If the number of $BaSO_4$ molecules exceeds this value, a particle nucleation can occur, depending on a rate coeffi cient for such an event. In the redispersion step the remaining liquid reactants are distributed randomly back into two identical droplets. The particle is put randomly into just one of the droplets. If a particle is already present in one of the droplets then all dissolved $BaSO_4$ (just reacted due to present $BaCl_2$ and K_2SO_4 or just still present due to a former reaction in some other droplet) will be used to let that particle grow. This is due to the fact that growth is energetically more favored than nucleation [7].

The simulation runs till complete conversion of one or both initial reactants is reached and all $BaSO_4$ molecules are grown onto particles. Then, the number of $BaSO_4$ molecules inside each droplet is determined, converted to a particle size (assuming bulk crystal structure with the known solid density). From the whole droplet ensemble the particle size distribution is also calculated.

The statistical analysis of the Monte-Carlo data, the study of fi nite size effects and other internal numerical requirements like appropriate random number generation will be presented elsewhere [8].

As pointed out already in the beginning, a set of experiments of $BaSO_4$ nanoparticle precipitation with different molar ratios of initial reactant concentrations X_{conc} (see Fig.2) has been compared to simulated data. The initial process conditions are chosen according to the experiments ($X_{mix} = 0.5$ and $X_{feed} = 1$). The remaining internal parameters are adapted so that the experiments are reproduced qualitatively. The simulated data of the mean particle diameter for different X_{conc} are given in Fig.4.

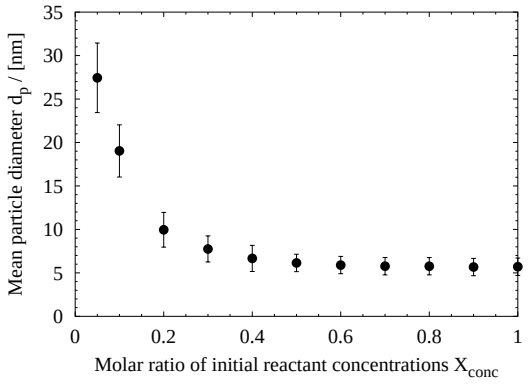

Fig. 4. Simulated dependence of the mean particle diameter d_p *on the molar ratio of the initial reactant concentrations* X_{conc}.

Now, with the obtained internal parameters, the Monte-Carlo simulation approach can be used to fi nd suitable operational process parameters which influence particle properties in a desired way. The fi rst such parameter will be the feeding rate. So far a very quick feeding has been assumed corresponding to the experimental setup. In our simulation this corresponds to a feeding rate of $X_{feed} = 1$, i.e. the number of droplets fed per Monte-Carlo step equals the number of total droplets applicable: $N_d^{feed}(BaCl_2) = N_d(BaCl_2)$. A lower feeding rate would correspond to a smaller number of droplets $N_d^{feed}(BaCl_2)$ fed into the system per Monte-Carlo step. The lowest possible number would then be just one droplet per Monte-Carlo step. In Fig.5 the change of the mean particle diameter and some selected particle size distributions for such a simulation run are shown.

It can be seen that only a very small feeding rate has a measurable impact on the particle size. The mean particle diameter does not change down to $X_{feed} \approx 0.01$. Only at a lower feeding rate the mean particle diameter increases. Additional calculation of the number of nucleated particles in such a system reveals that the increase in diameter is connected to a decrease in this number. As similar scenario has been found already for the change of mean particle diameter when the molar ratio of initial reactant concentrations was varied [6].

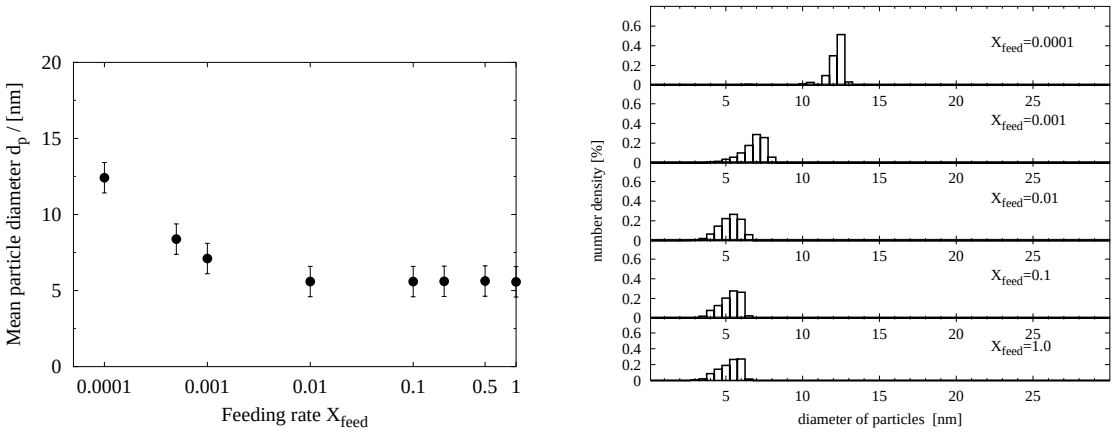

Fig. 5. Left: Simulated dependence of the mean particle size d_p *on the feeding rate* X_{feed} *(*$X_{mix} = 0.5, X_{conc} = 1$*). Right: Particle size distributions for selected values of* X_{feed}*.*

The second investigated operational process parameter studied here is the ratio of initial volumes (or number of droplets respectively) $X_{mix} = N^d_{BaCl_2}/N^d_{K_2SO_4}$. The other operational parameters are kept unchanged ($X_{feed} = 0.5$ and $X_{conc} = 1$) and X_{mix} will be varied. The results of such a simulation for the particle size and the particle size distribution are presented in Fig.6. $X_{mix} = 0.5$ corresponds to the conditions of the experiments. A value of $X_{mix} = 0.9$ corresponds to 90% of K_2SO_4 droplets and 10% of $BaCl_2$ droplets in the whole system.

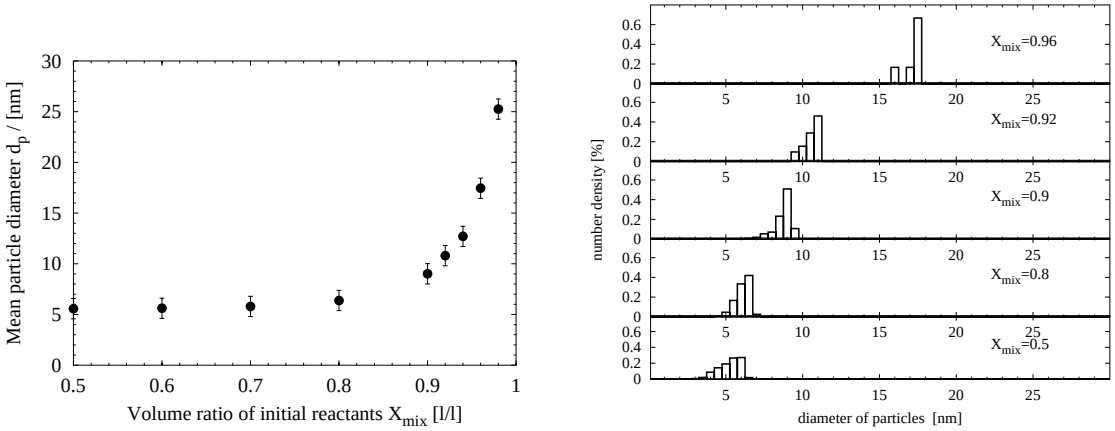

Fig. 6. Left: Simulated dependence of the particle size distribution on the ratio of the initial reactant volumes X_{mix}*. Right: Particle size distributions for selected values of* X_{mix}*.*

The mean particle size does increase with increasing X_{mix}. The particle size distribution seems to narrow slightly with the increase of the mean particle diameter although this behavior will be investigated in more detail elsewhere. Also in this simulation the total number of nucleated particles decreases with the increase in mean particle diameter.

Conclusions

A Monte-Carlo simulation approach for the nanoparticle precipitation in microemulsions has been developed. The simulation especially accounts for some important operational process parameters like feed rate, molar ratio of initial reactant concentrations or initial volume ratios.

Simulation results are compared to experiments of $BaSO_4$ nanoparticle precipitation in a non-ionic microemulsion. Internal parameters of the simulation have been adapted to this experimental systems and reasonable agreement between the two data sets was achieved. With the obtained internal parameters other external operational process parameters like the feed rate or the volume ratio of initial reactants are varied. Measurable changes of the mean particle diameter and the particle size distribution are found. It could be shown that the Monte-Carlo simulation can help to identify suitable operational process parameters which influence the particle properties. Those findings are important as they unveil important control parameters from the point of view of a technical application and industrial production of tailor-made nanoparticles. The presented Monte-Carlo simulation approach will be extended to include other operational parameters and to higher dimensional models for the investigation of additional particle properties like the morphology.

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