

[270a] - Multidimensional Population Balance Modeling of Barium Sulfate Precipitation in Microemulsions

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Motivation

Deterministic population balance models including aggregation phenomena with more than two internal coordinates and without reduction to e.g. moments are to the best of the authors knowledge not published in literature so far. The problem of such models is the high computational demand and long simulation times which can easily reach the duration of weeks. Here the authors present a 3-dimensional probability density function (PDF) model with coalescence & redispersion phenomena for precipitation in emulsions. By the use of a PDF model it is possible to reduce the simulation time due to the fact that the area under a PDF is always exact 1.

Emulsion system properties

By performing precipitation reactions inside emulsion droplets it is possible to get rid of unwanted particle properties caused by non-ideal mixing conditions in the bulk phase process like broad particle size distributions and multiple morphologies. Non-ideal mixing results from the fact that in general the reaction proceeds faster than the mixing process, hence results a partially segregated system with strongly varying local kinetics [Baldyga and Bourne (1999), Bandyopadhyaya et al. (1997), Rauscher and Sundmacher (2004)]. In order to control the particle properties in a desired way either the reactor design or, like in our case, fundamental system changes have to take care for better mixing conditions. The coalescence & redispersion phenomena between the emulsion droplets (for microemulsion systems the notation 'fusion & fission' is also widely used) control the mixing in two ways. First they slow down the progress of the chemical reaction, because after the depletion of all reactants in one droplet the reaction can only proceed after a coalescence & redispersion event and second the limited volume of one droplet prevents the appearance of high concentration gradients. Additionally the emulsion process not only improves the mixing conditions but also has the advantage that a conventional CSTR under normal conditions (ambient temperature and pressure) could be used. The structure of this 3 phase system is shown in Figure 1a. The continuous phase only acts as a surrounding medium which is not involved in the material transport but important parameters like the coalescence & redispersion rate depend on the composition of the continuous phase. The main interactions are between the droplets themselves (see Figure 1b) and between the disperse droplet phase and the disperse particle phase. Interactions between the particles can almost be excluded, because they are shielded by the surrounding droplets.

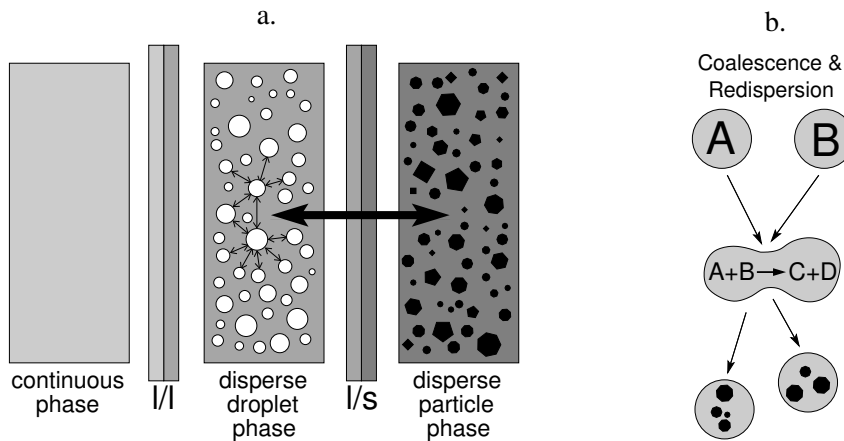
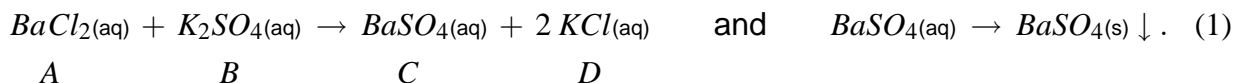


Fig. 1. a. Scheme of the 3 phase system; b. Scheme of the coalescence and redispersion phenomena

The specific emulsion system under investigation is a so called microemulsion. Compared with macroemulsions, microemulsions have certain useful properties like:

- thermodynamical stability,
- almost monodisperse droplet size distributions,
- adjustable droplet size between 3 and 100 nm.

The experiments for the validation of the model were done with a water-in-oil (cyclohexane) microemulsion. The surfactant for the stabilization was Marlipal O13/40 (non-ionic). As model reaction the precipitation of barium sulfate according to Eq. 1 has been chosen.



Our experiments have been performed in a semibatch operating mode. However, this process can be also carried out in batch or continuous mode, which could give additional means for the influence of the particle properties.

Modeling

General aspects

The modeling of an emulsion system with precipitation inside droplets is quite difficult due to a necessarily high number of distributed variables (properties). Table 1 shows a list for such a system which could be easily extended to variables like morphology or the concentrations of byproducts, non-reactive components (e.g. surfactants), etc.. Different solution methods, like discretization of the Population Balance Equation (PBE), Monte-Carlo Simulations or the Method of Moments could be used to solve this population dynamics problem. The Method of Moments is not appropriate for this kind of model, because the reduction to mean values reduces the system to a pseudo-homogeneous one which is not able to represent the influences of the kinetics on the resulting particle size distribution. Both, discretization of the PBE and Monte-Carlo Simulation, can be equally used for problems with no more than 3 dimensions. For problems with a higher number of dimensions, calculations are only possible with acceptable effort if the Monte-Carlo Method is used,

Table 1

Internal and external coordinates (dimensions) for a population balance model of precipitation in (micro-)emulsion droplets and the assumptions for the microemulsion process.

properties of the model	variable type (dimensions)	assumptions: microemulsions
droplet size	size distribution (1)	monodisperse distribution (-)
particle size	size distribution (1)	- (1)
concentrations inside droplets	conc. distributions (≥ 4)	limitation to main comp. (≥ 2)
number of particles in 1 droplet	number distribution (1)	one particle per droplet (-)
flow field	vector field (3)	ideally mixed (-)
temperature	scalar field (1)	isothermal (-)
Σ dimensions	≥ 10	≥ 3

because the computational demand for a solution via discretization of the PBE would be too high in this case.

Basic Model

The basic structure of the 3-dimensional model is based on a 1-dimensional model for simple chemical reactions in droplets published by Curl (1963). This model describes the concentration distribution of one component A in form of a PDF $p(c_A, t)$, which equals a normalized number density function generally used for population balances. The model (Eq. 2) considers accumulation (l.h.s), depending on the operation mode inlet and outlet fluxes (1st term r.h.s.), chemical reactions inside the droplets (2nd term r.h.s) and coalescence & redispersion of droplets (3rd term r.h.s.).

$$\frac{\partial p(c_A, t)}{\partial t} = \frac{1}{\tau} \cdot (p_{in}(c_A, t) - p(c_A, t)) - \frac{\partial}{\partial c_A} (v_i \cdot r(c_A) \cdot p(c_A, t)) + \beta \cdot \left(4 \cdot \int_0^{c_A^*} p(c_A + \alpha, t) \cdot p(c_A - \alpha, t) d\alpha - p(c_A, t) \right). \quad (2)$$

With: $c_A^* = \text{Min}(c_A, c_{A, \text{max}} - c_A)$, τ = residence time, v_i = matrix of stoichiometric coefficients, $r(c_A)$ = chemical reaction rate and β = coalescence & redispersion rate. The chemical reaction is modeled as convection flux along the property coordinate c_A . The assumptions for this model are listed below:

- ideally mixed = no spatial gradients,
- constant number of droplets,
- all droplets have the same size (monodisperse droplets),
- after coalescence instantaneous redispersion in two identical droplets,
- power law approach for the chemical reaction.

The most complex part in this equation is the coalescence & redispersion term. The integral in this term has not the typical convolution structure like other aggregation phenomena, because here the concentrations of the two coalescing droplets are averaged and

not add together like it is done with the particle size in agglomeration processes. Figure 2 illustrates the mathematical structure of the coalescence & redispersion integral. Values

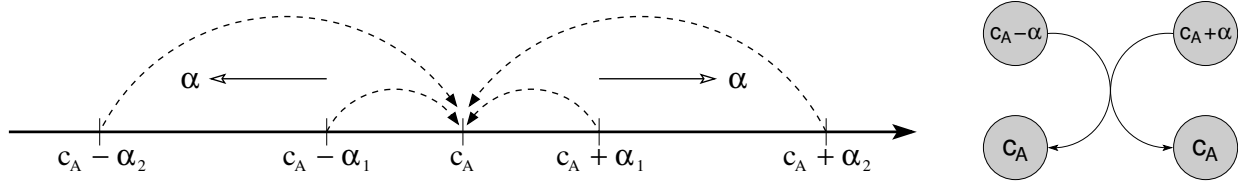


Fig. 2. Principle of the coalescence & redispersion integral

with the same range of α left and right from c_A are used to calculate the new value for c_A . Results for a batch reactor with no chemical reaction and an initial distribution with 50% empty droplets and 50% droplets with 1 mol/l A are shown in Figure 3 for different simulation time steps ($t_1 < t_2 < t_3 < t_4$). A 2-dimensional extension of the 1-dimensional model was recently presented by Niemann et al. (2004). The second property coordinate in this model is the liquid concentration c_B , so that simple chemical reactions inside droplets with at least two components can be described.

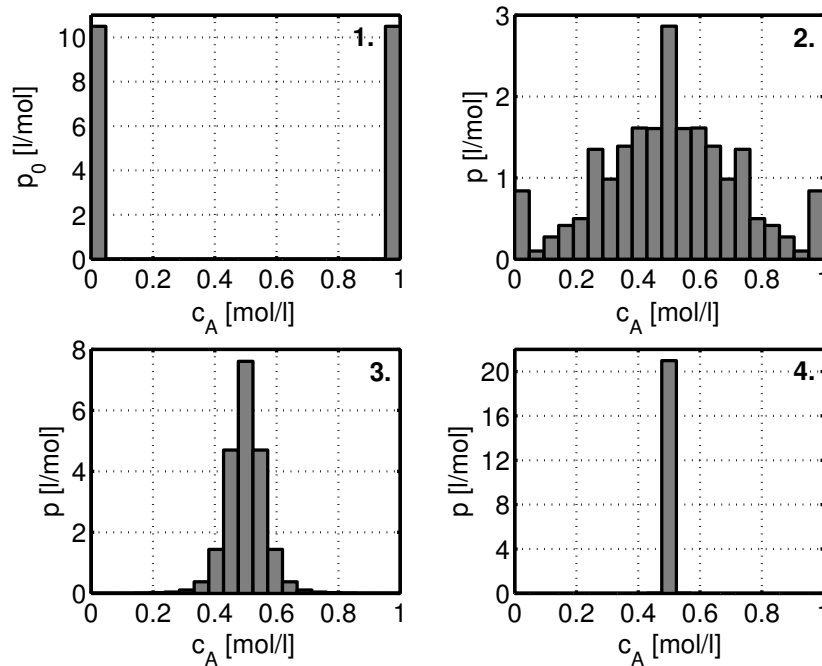


Fig. 3. Simulation results for a batch system without reaction: only coalescence & redispersion

3-dimensional Population Balance Model

The three property coordinates are two liquid concentrations and one solid concentration. The use of a solid concentration instead of a particle size is only possible in the case of monodisperse droplets, because it is possible to calculate the particle size after the simulation by the use of the following equation:

$$V_P = c_s \cdot \frac{V_{drop} \cdot M_s}{\rho_s} \quad (3)$$

With: V_p = particle volume, c_s = solid concentration, V_{drop} = droplet volume, M_s = molecular weight of the solid and ρ_s = solid density.

The structure of the 3-dimensional model (Eq. 4) is almost the same as the 1-dimensional model with the exception that the coalescence & redispersion term only redistributes the liquid concentrations and not the solid concentration:

$$\begin{aligned} \frac{\partial p(c_A, c_B, c_s, t)}{\partial t} = & \frac{1}{\tau} \cdot (p_{in}(c_A, c_B, c_s, t) - p(c_A, c_B, c_s, t)) \\ & - \sum_i \frac{\partial}{\partial c_i} (v_i \cdot r(c_A, c_B) \cdot p(c_A, c_B, c_s, t)) \\ & + \beta \cdot \left(4 \cdot \int_0^{c_s^{max}} \int_{-c_A^*}^{c_A^*} \int_{-c_B^*}^{c_B^*} p(c_A + \alpha_A, c_B + \alpha_B, c_s, t) \right. \\ & \left. \cdot p(c_A - \alpha_A, c_B - \alpha_B, c_s, t) d\alpha_B d\alpha_A dc_s - p(c_A, c_B, c_s, t) \right). \end{aligned} \quad (4)$$

This model is only valid for systems which fulfill the following additional assumptions (see also Table 1):

- no agglomeration and breakage of particles
- overall kinetics for the chemical reaction and nucleation (Eq. 5) \Rightarrow no critical nucleus size and no liquid product concentration.

The parameters of the barium sulfate system were used to analyze this model. Due to the assumptions the chemical reaction equations (see Eq. 1) are lumped together:



The concentration of the byproduct KCl is being neglected, so that the two liquid concentrations in the model are $BaCl_2$ and K_2SO_4 and the solid concentration is $BaSO_4$. Figure 4 shows the results for the simulation of a continuous reactor with a microemulsion droplet size V_{drop} of 5 nm and feed concentrations ($BaCl_2$ and K_2SO_4) of about 0.1 mol/l. Data from semibatch experiments (Adityawarman et al. (2004)) with the same parameters were used for a first comparison in order to check the general applicability of the proposed model. The partial-integro-differential equation was solved by Finite-Volume-Discretization and a standard ODE solver in the software tool Matlab. Due to the high computational demand only about 4000 discrete volumes were used for the simulation runs. Figure 4 (l.h.s.) shows the steady state particle size distribution for the simulation of a continuous stirred tank reactor and data from a selected semibatch experiment. The higher fraction of small particles in the simulation can be explained by the short residence time and the neglect of a critical nucleus size in the model. The figure on the r.h.s. gives an interesting insight to one of the liquid concentration layers at a fixed solid concentration. For the chosen parameters which are typical for emulsions with high droplet exchange rates and fast chemical reactions (precipitation) it becomes clear that the two liquid concentrations never coexist in one droplet, so that a model reduction with the assumption of an instantaneous chemical reaction is possible.

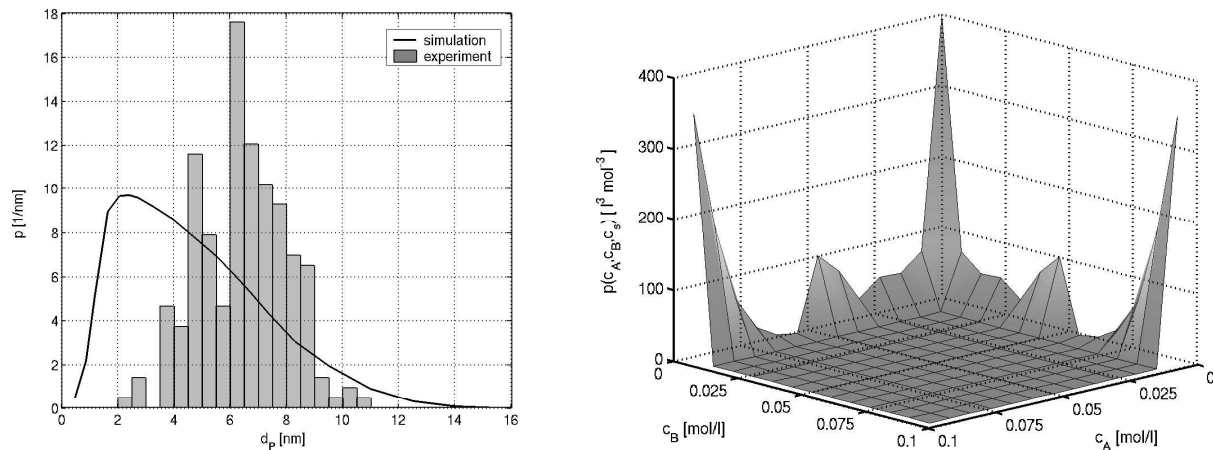


Fig. 4. Results of the 3-dimensional model. Parameters: $\tau = 10$ s, $\beta = 200$ s⁻¹, $k = 5 \cdot 10^6$ l mol⁻¹ s⁻¹ ($r = k \cdot c_A \cdot c_B$). Left: Steady state particle size distribution; Right: Concentration distribution at steady state for $d_p = 1$ nm.

Conclusions & Outlook

The comparison of the simulation results with experimental data (see Figure 4) proves the applicability of our modeling idea for the system under investigation, although the operating modes of the experiments and the model are different. It is also obvious that a model reduction (instantaneous reaction) will result in an almost equivalent model with an increase of the computational performance. Such a model would consist of two coupled 2-dimensional PDF's ($p(c_A, c_s, t)$ and $p(c_B, c_s, t)$) and one ODE for the droplet fraction in both populations. Against the tendency of a reduction to low dimensional models it is necessary to find a way for the consideration of the liquid barium sulfate concentration due to the large amount of small particles. Thus a further reduction with e.g. the Method of Moments or the Method of Weighted Residuals could be the inevitable consequence of this extension.

References

- Adityawarman, D., Veit, P., Sundmacher, K., 2004. Precipitation of BaSO₄ nanoparticles in non-ionic microemulsions. 7th International Conference on Nanostructured Materials, Wiesbaden, Germany, June 20-24 .
- Baldyga, J., Bourne, J. R., 1999. Turbulent Mixing and Chemical Reactions. John Wiley & Sons.
- Bandyopadhyaya, R., Kumar, R., Gandhi, K. S., Ramkrishna, D., 1997. Modeling of precipitation in reverse micellar systems. Langmuir 13 (14), 3610–3620.
- Curl, R. L., 1963. Dispersed phase mixing: I. Theory and effects in simple reactors. A.I.Ch.E. Journal 9 (2), 175–181.
- Niemann, B., Mahoney, A. W., Sundmacher, K., 2004. Two-dimensional PDF model of chemical reactions in liquid-liquid dispersions. 2nd Population Balance Modelling Conference, Valencia, Spain, May 5-7 .
- Rauscher, F., Sundmacher, K., 2004. Precipitation in microemulsions - A method for large scale production of nanoparticles. PARTEC, Nürnberg, Germany, March 16-18 .