



## Imaging the supersaturation in high-pressure systems for particle generation

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### ABSTRACT

The supersaturation which is the driving force for particle precipitation was quantified in situ for the injection of a solution into a supercritical antisolvent. Firstly, saturation mole fractions of the solute yttrium acetate were measured via elastic light scattering in the homogeneous ternary system, which is composed of the solute itself, the solvent dimethylsulfoxide and the antisolvent carbon dioxide. The saturation experiments were carried out at pressures of 8.5, 12 and 16 MPa and at a temperature of 313 K. Secondly, applying a Raman based optical measurement technique the actual solute mole fraction was imaged in situ during the injection of the solution (solute dissolved in solvent) into the antisolvent. The injection experiments were carried out at pressures of 12 and 16 MPa and at a temperature of 313 K. Finally, the ratio of the actual solute mole fractions and the saturation solute mole fractions, which were measured during the injection experiment and during the saturation experiment, respectively, quantifies the supersaturation. High supersaturation values are evidenced already close to the nozzle exit. For the first time, an optical method was developed to measure the supersaturation in situ in a dynamic process under high-pressure.

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## 1. Introduction

The field of nanomaterials is a fascinating area of research that has found many applications of technological interest in diverse fields such as pigments, drugs, metal oxides, pharmaceuticals and inorganic materials [1,2]. In recent years, significant progress has been made in supercritical fluid technology, particularly in the generation of a large number of nano-sized particles by precipitation [3–6]. Therefore, an important question that needs to be satisfactorily addressed in supercritical particle precipitation is the mechanism of particle formation. A significant factor that mainly influences the particle formation process is the degree of supersaturation of the solution which can be influenced by the process conditions. There are several methods to measure supersaturation for liquid and vapour phase processes at ambient conditions [7], but the experimental data concerning supersaturation in high-pressure processes is fairly poor [8]. As there is an increasing interest in the application of supercritical fluid technologies to generate different kinds of particles at different operative

conditions, the principles of these processes need to be further enlightened.

Several advantages must be considered using supercritical fluids compared to conventional routes. Among them, supercritical carbon dioxide (scCO<sub>2</sub>) is preferred because of its extremely moderate critical parameters ( $\rho_c = 7.4$  MPa,  $T_c = 304$  K) [9]. In the last years, different antisolvent processes based on the antisolvent CO<sub>2</sub> have been proposed to produce micro or nanoparticles. Besides, in the post-processing step, the solid particles can be separated from the fluid phase (solvent and antisolvent) on a filter and the antisolvent CO<sub>2</sub> can be separated from the solvent easily by reducing the pressure [10]. Supercritical precipitation techniques have the capability to produce several different kinds of particles with controlled morphology and a very narrow size distribution [11]. At different operation conditions, nanoparticles, microparticles, balloons or crystals can be produced [2,12,13]. Among the numerous particle formation processes, the supercritical antisolvent (SAS) technology is especially useful to gently treat thermo-labile particulate, mechanical sensitive and other high purity materials which must not be spoiled with residuals of harmful organic solvents.

In this work, the supersaturation measurements have been applied to the supercritical antisolvent process (SAS). The solute to be precipitated is dissolved in the liquid organic solvent to form a solution. Most suitable, the solute is totally insoluble in the antisolvent/solvent mixture while the solvent is completely miscible in

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the antisolvent. When the solution is injected into the scCO<sub>2</sub>, rapid mixing induces a high degree of supersaturation and nucleation is a matter to overcome the metastable solution.

## 2. Supersaturation in high-pressure processes

Solute precipitation is a two-step process which incorporates nucleation and growth since it involves a very rapid phase change and the formation of a solid phase from a former homogeneous solution. Statistical fluctuations of the solute concentration in the system lead to an aggregation of molecules of the precipitating substance. If these clusters reach a critical size, they are thermodynamically stable and called nuclei. The probability for the formation of these nuclei, their critical size and the nucleation rate are a function of the degree of supersaturation  $S$  [14,15]. In general, the supersaturation

$$S = \frac{x_{\text{solute}}}{x_{\text{solute}}^* (x_{\text{antisolvent}}, \rho_{\text{antisolvent}})} \quad (1)$$

is defined by the ratio of the actual solute mole fraction  $x_{\text{solute}}$  and the saturation mole fraction  $x_{\text{solute}}^* (x_{\text{CO}_2}, \rho_{\text{CO}_2})$  [16–18], which is a function of the antisolvent mole fraction  $x_{\text{antisolvent}}$  and the antisolvent partial density  $\rho_{\text{antisolvent}}$  [19,20]. The mole fraction

$$x_i = \frac{n_i}{n_{\text{total}}} = \frac{n_i}{n_{\text{solute}} + n_{\text{solvent}} + n_{\text{antisolvent}}} \quad (2)$$

of one component “ $i$ ” in a ternary system composed of the solute, the solvent and the antisolvent is defined by the ratio of the amount of the component  $n_i$  and the sum of all components  $n_{\text{total}}$ . According to Eq. (1) a solution is supersaturated, when the actual mole fraction of the solute  $x_{\text{solute}}$  exceeds the saturation mole fraction of the solute for a given temperature and pressure. In common SAS applications the solute mole fraction is much smaller than one ( $x_{\text{solute}} \ll 1$ ). Therefore the simplification

$$x_{\text{solute}} + x_{\text{solvent}} + x_{\text{antisolvent}} \approx x_{\text{solvent}} + x_{\text{antisolvent}} = 1 \quad (3)$$

shows that either the mole fraction of the antisolvent  $x_{\text{antisolvent}}$  or the mole fraction of the solvent  $x_{\text{solvent}}$  is sufficient to define the overall mixture composition in the respective ternary system (if  $x_{\text{solute}} \ll 1$ ). Hence, the overall mixture composition ( $x_{\text{antisolvent}}$  or  $x_{\text{solvent}}$ ) puts the antisolvent and solvent power of the competing antisolvent and solvent, respectively, into relation. This quantity affects the amount of solute, which can be dissolved in a ternary system of solute, solvent and antisolvent. Therefore, the saturation mole fraction of the solute in Eq. (1) is given as a function of the antisolvent mole fraction  $x_{\text{antisolvent}}$ . Furthermore, the amount of solute, which can be dissolved in ternary mixtures of constant composition, is a function of the density (pressure) of the ternary system. Therefore, the saturation mole fraction of the solute in Eq. (1) is given as a function of the antisolvent partial density  $\rho_{\text{antisolvent}}$  next to  $x_{\text{antisolvent}}$ .

The ratio  $c_{\text{solute/solvent}}$  of the amount of substance of the solute and solvent

$$c_{\text{solute/solvent}} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{n_{\text{solute,initial}}}{n_{\text{solvent,initial}}} \quad (4)$$

is assumed to be constant during the mixing of the injected original solution and is defined by the amount of solute  $n_{\text{solute,initial}}$ , which is dissolved in the initial solution in a particular amount of substance of the solvent  $n_{\text{solvent,initial}}$  (before mixing with the antisolvent). Consequently, the actual solute mole fraction  $x_{\text{solute}}$  during mixing of the injected solution and the antisolvent can be derived from

$$x_{\text{solute}} = c_{\text{solute/solvent}} \cdot x_{\text{solvent}} = c_{\text{solute/solvent}} \cdot (1 - x_{\text{antisolvent}}), \quad (5)$$

if either the solvent or the antisolvent mole fraction is known.

In supercritical fluid precipitation processes, high abrupt supersaturations are obtained as a consequence of the rapid mixing process between the injected solution and the antisolvent CO<sub>2</sub> [11] and additionally as a consequence of the high antisolvent power of CO<sub>2</sub> [21]. Hence, in supercritical precipitation processes, primary homogeneous nucleation is favoured [16,22]. The rate of nucleation depends strongly on the degree of supersaturation and the temperature. Increasing both parameters also increases the nucleation rate.

According to supersaturation measurements in antisolvent precipitation processes, there is a big lack of knowledge with almost no data for high-pressure processes available. As it is a big challenge to obtain those data, some authors tried to model the process of supersaturation and nucleation. Mukhopadhyay et al. [15] stated in their work, that the size of the critical nucleus and the rate of nucleation only depends on the degree of supersaturation and the nucleus size ranges from 1.0 nm to 0.1 nm for very high supersaturations. An influence of the pressure on the nucleation rate and the critical size of the nucleus for a given temperature and supersaturation could not be evidenced. Türk [23] described the supersaturation and the nucleation rate in the “Rapid Expansion of Supercritical Solutions” process in dependence on the interfacial tension and the solubility of the solute in different solvents and the effect on the supersaturation of the solution. The maximum attainable supersaturation in the free jet was between 10 E5 and 10 E8 with a decreasing particle size at higher supersaturations [24]. Bristow et al. [14] used supersaturation to define the mixing process in the vessel, and found smaller, agglomerated crystal sizes at higher supersaturations corresponding to a pressure below the mixture critical point (MCP), and larger crystal sizes at lower supersaturations corresponding to a pressure above the MCP. Computational fluid analysis of the SAS micronization have been carried out by Cardoso et al. [25], who visualized the modelled pseudo-supersaturation distribution in a plane through the centre of the SAS vessel and quantified it contrary to other publications to be rather small between 12 and 16.

These several contradictory statements ask for a closer look at the driving force for particle nucleation. Supersaturation is influenced by the mixing process to obtain a homogeneous supersaturation of the solution and to generate particles with a narrow size distribution [19]. In this work, the supersaturation was imaged in situ experimentally during the SAS experiment. Yttrium acetate (YAc), dimethylsulfoxide (DMSO) and carbon dioxide (CO<sub>2</sub>) were used as solute, solvent and antisolvent, respectively. The applied imaging technique relied onto a combination of elastic and inelastic (Raman based) light scattering mechanisms. Firstly, in a homogeneously mixed system the YAc saturation mole fraction  $x_{\text{YAc}}^*$  was measured as a function of the CO<sub>2</sub> mole fraction  $x_{\text{CO}_2}$  for pressures of 8.5, 12 and 16 MPa and a temperature of 313 K. Secondly, the actual YAc mole fraction  $x_{\text{YAc}}$  was imaged in situ during the turbulent jet mixing inside the SAS vessel with a high temporal and spatial resolution. Third, phase boundary distributions were imaged two-dimensionally by elastic light scattering to identify the location of first particle precipitation (LFPP). The approach to measure quantitative mole fraction distributions and phase boundary distributions via inelastic Raman scattering and elastic light scattering in the jet is explained elsewhere [26]. Consequently all parameters are accessible, which are required to compute the supersaturation distribution according to Eq. (1).

## 3. Materials and methods

For the investigation into the YAc saturation mole fraction  $x_{\text{YAc}}^*$  in a homogeneous system (saturation experiment) and for the investigation into the actual YAc mole fraction  $x_{\text{YAc}}$  during jet mixing (SAS experiment), the same experimental setup (minor

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