

SIMULATION OF HEAT AND MASS TRANSFER OF A CO₂ BINARY MIXTURE, IN THE MISCIBLE CONDITIONS OF A SUPERCRITICAL ANTISOLVENT PROCESS

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A complete description of the Supercritical Antisolvent Process requires the modelling of several complex physical phenomena such as heat and mass transfer, hydrodynamic, phase equilibria of ternary mixtures, and nucleation /growth of the specie to be precipitated; moreover, the description should also account for the biphasic case, where the jet of organic solvent breaks up as droplets.

As a first step, we focus on the simulation of mass and heat transfer of a binary CO₂-solvent mixture in miscible conditions, based on the pioneer work developed by Werling and Debenedetti. The system is described as a spot of pure solvent immersed in pure carbon dioxide, but compared to Werling's work and further publications, we explore conditions where the temperatures of the solvent and the fluid are different; hence, our calculations allow to take into account the heat transfer in the mixture. The evolution of the spot size is detailed for various conditions of pressure and temperature, and for two CO₂-mixtures.

INTRODUCTION

Crystallization is a key operation in powder technology since characteristics of produced particles will influence the material final properties, and more specifically bioavailability or stability when active pharmaceutical ingredients are considered. Properties like particle mean size and particle size distribution are influenced by both thermodynamic and kinetic factors, and when precipitation is induced by the addition of a third specie, the time and space scales at which the mixing occurs become significant. Literature provides numerous examples of crystallisation induced by CO₂; although the effect of several operating parameters on the product characteristics is evidenced, contradictory trends could be obtained. Moreover, the potential interactions between parameters and the diversity of the processed systems render the interpretation quite difficult. Hence, a numerical approach becomes fundamental either to identify the controlling phenomena, either to optimize the process according to sustainability concepts.

In this article, we focus on the description of heat and mass transfers that occur when a 'pseudo' droplet of solvent is immersed in a compressed antisolvent in miscible conditions, in the aim of investigating more specifically temperature effects. This work is based on the mathematical model for mass transfer already proposed by Werling and Debenedetti [1]. Elvassore et al. [2] further refined the Werling's approach by taking in account the solute. The diffusion in the ternary is taken into account with the generalised Maxwell-Stefan equations. In the first part, the modelling of the heat and mass transfers in the binary mixture is presented. In a second part, the model is applied for two mixtures, i.e. toluene/carbon dioxide

and ethanol/carbon dioxide. Simulations are achieved in isothermal conditions and non isothermal conditions, i.e. when temperatures of solvent and CO₂ are different.

MODELING OF THE HEAT AND MASS TRANSFER IN THE BINARY MIXTURE

The equations are in term of molar quantities and the subscript “a” denotes the carbon dioxide and “b” the solvent.

In the supercritical regime, the solvent and the antisolvent are fully miscible so only one equation is needed to describe the mass transfer. We assume that the medium is stagnant so the convective flux can be neglected. The mass transfer is only affected by diffusion so the mass balance equation, according to the Fick’s law, reads to:

$$\frac{\partial \rho x_a}{\partial t} + \nabla \cdot (-\rho D \nabla x_a) = 0 \quad 1$$

where ρ represents the density of the binary mixture, x_a the mole fraction of the carbon dioxide and D the diffusion coefficient of the solvent in the carbon dioxide estimated with the Wilke and Chang correlation [3]. The viscosity of the medium, required in the calculation of the diffusion coefficient, is estimated with the Stiel and Thodos relationship [4].

The mole fraction of the solvent is directly deduced by the relation:

$$x_b = 1 - x_a \quad 2$$

The temperature field is obtained by solving the conservation equation of energy. Assuming that the viscous energy dissipation can be neglected and by considering that there is no heat source, the conservation equation of energy is written as follows:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) \quad 3$$

where C_p and λ are respectively the heat capacity and the heat conductivity of the mixture.

We consider that in the range of the investigation, heat capacity and thermal conductivity for each component are constant at a given pressure. So the heat capacity and thermal conductivity for the binary mixture is given by:

$$C_p = x_a C_{pa} + x_b C_{pb} \quad 4$$

$$\lambda = x_a \lambda_a + x_b \lambda_b \quad 5$$

In the supercritical regime, carbon dioxide is a dense fluid which will alter the composition and the density of the droplet in a highly non ideal way. The Peng Robinson equation of state was chosen to calculate the fluid density because of its ability to predict phase equilibria, its relative accurate density prediction at high pressures, and its ease of application. The Peng Robinson equation is written as:

$$P = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad 6$$

where the mixture parameters a_m and b_m are given by the following mixing rules, with the a and b parameters function of the critical properties of individual species:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij})$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2} (1 - l_{ij})$$

The critical properties and the binary interaction parameters for carbon dioxide, toluene and ethanol used in this work are reported in the table 1.

	Pc (bar)	Tc (K)	molar mass (g/mol)	k_{ij}	l_{ij}
CO2	73.81	304.21	44		
Ethanol	61.48	513.92	46.069	0.066	0.005
Toluene	40.54	591.75	92.1405	0.094	-0.024

Table 1: Critical properties and the binary interaction parameters for carbon dioxide (antisolvent), toluene and ethanol

SIMULATION AND RESULTS

The system of equations is solved in order to obtain the concentration and temperature fields over the domain. The simulation tool was based on the Computational Fluid Dynamic library Aquilon, developed at TREFLE laboratory. Aquilon contains a set of discretization schemes, solvers and models that were deemed interesting for simulating this kind of problem. The approximations of the conservation equations were based on a regular spherical grid and finite volumes. For concentration and temperature, the time discretization is achieved with an implicit Euler scheme of first order; the space discretization for energy is a second order centered scheme, whilst for the mass transport, a TVD scheme is used (Total Variation Diminishing) since it is particularly well suited for diffusion problems. The linear system is solved at each time step, an iterative bi-conjugate gradient stabilized BICG-Stab II [5] preconditioned under a modified and Incomplete LU method is used.

Configuration and initial/boundary conditions are shown in figure 1. The grid consists in 30 000 cells. The initial radius of the solvent droplet is fixed to 50 μm and the radius of the antisolvent domain to 500 μm .

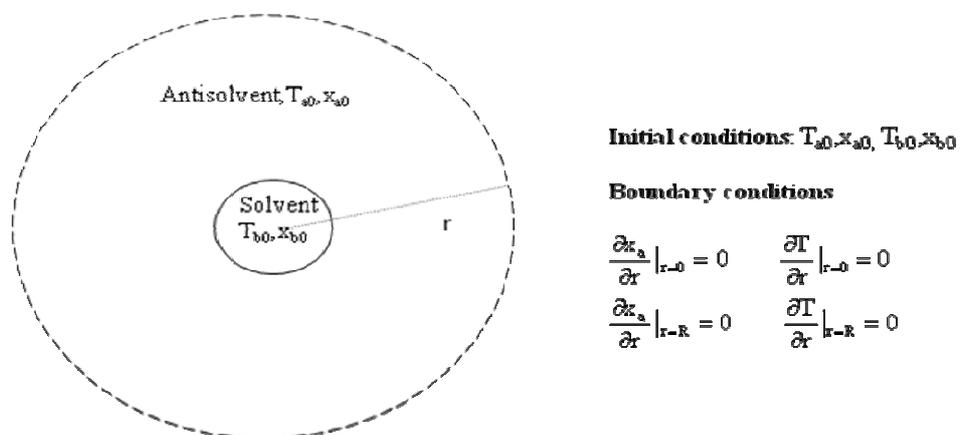


Figure 1: Configuration, initial and boundary conditions for the study

In supercritical conditions, the question of defining the droplet radius rises, because of the complete miscibility of the species even if a “pseudo” droplet exists as we can remark in figure 2 which represents the evolution of the density profiles of the binary mixture. As a first step and in order to match Werling approach, the droplet radius was defined by a “cutoff” value of density which allowed for distinguish a solvent-rich and an antisolvent-rich zones. More details can be found in the article [1]. The “cutoff” value of the density is defined by:

$$\begin{aligned} \rho_{\text{cutoff}} &= \rho_{\text{CO}_2} + 0.33(\rho_{\text{max}} - \rho_{\text{CO}_2}) & \text{if } \rho_{\text{solvent}} \geq \rho_{\text{CO}_2} \\ \rho_{\text{cutoff}} &= \rho_{\text{CO}_2} - 0.33(\rho_{\text{CO}_2} - \rho_{\text{solvent}}) & \text{if } \rho_{\text{solvent}} \leq \rho_{\text{CO}_2} \end{aligned} \quad 8$$

where ρ_{CO_2} and ρ_{solvent} are the pure densities of the carbon dioxide and the solvent and ρ_{max} is the maximum mass density attained by the binary mixture which can be significantly greater than the pure component densities [6].

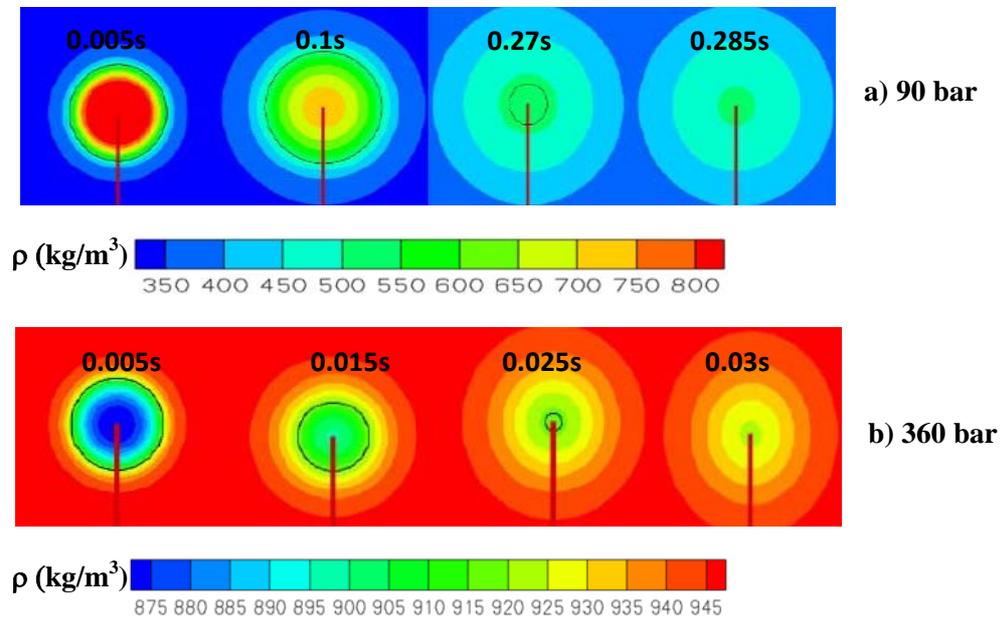


Figure 2: Evolution of the density profiles of the mixture $\text{CO}_2/\text{Toluene}$ at 318K for two pressures. Black circle represent the effective droplet radius defined by the criteria of Debenedetti.

Isothermal conditions

In isothermal conditions, solvent and antisolvent regions have the same temperature. The figure 3a and 3b show the evolution of the droplet radius in case of toluene and ethanol as solvents, for different pressures. The Toluene case displays the same behaviour than described in Werling’s paper, hence, validating our calculations. Compared to toluene, ethanol also undergoes an expansion at low pressure, and a shrinking behaviour for pressure above 14 MPa.

The droplet behaviour is governed by the density differences between the solvent-rich and the antisolvent-rich domains. When the pure solvent density is significantly higher than the antisolvent one, the droplets swell (figure 2a); this swelling is more pronounced at lower pressures due to the largest differences in densities. On the other hand, when the CO_2 density is greater than the solvent one, droplets are shrinking (figure 2b); at very high pressure, the droplet lifetimes are very short.

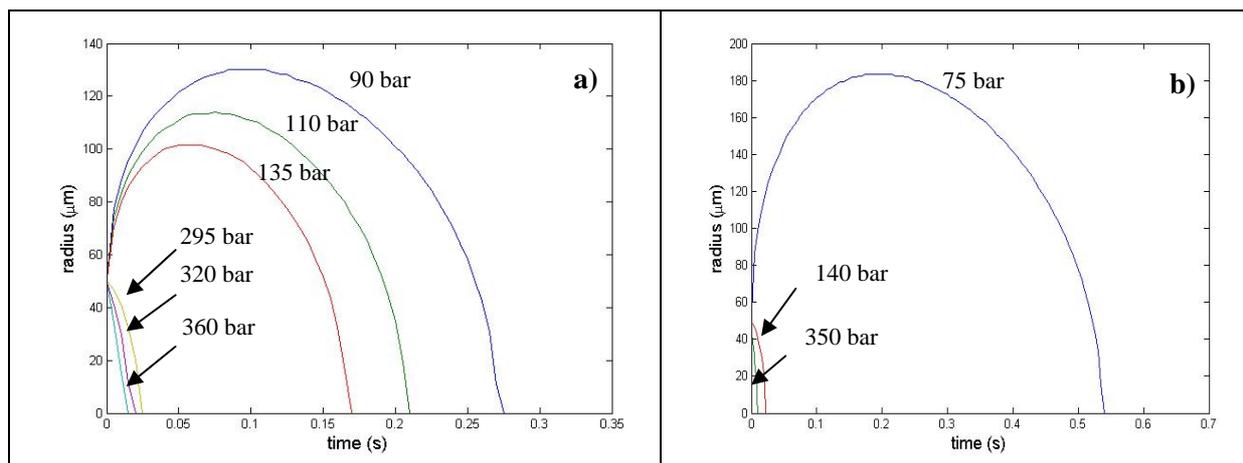


Figure 3: a) Evolution of toluene droplet radius at 318K and for different pressures. b) Evolution of ethanol droplet radius at 300K and for different pressures.

Non-isothermal conditions

Calculations were now performed in case of non-isothermal conditions, where solvent and antisolvent regions have different temperatures. Figures 4a and 4b show the droplet evolution at 14 and 35 MPa in case of ethanol, considering that the solvent (b subscript) is warmer than carbon dioxide.

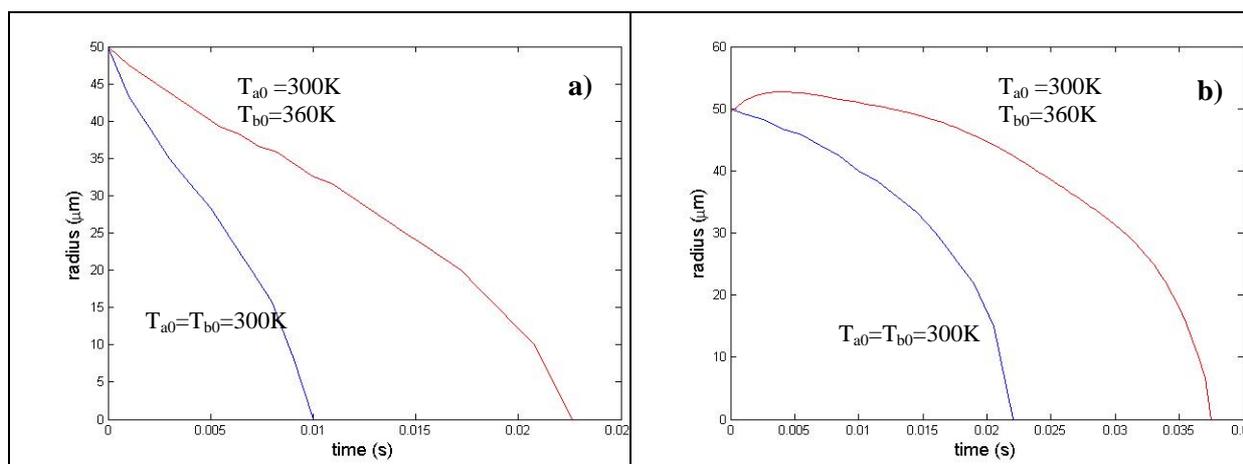


Figure 4: a) Evolution of ethanol droplet radius at 140 bar and for different initial temperatures. b) Evolution of ethanol droplet radius at 350 bar and for different initial temperatures.

The influence of the temperature difference is quite significant. When the solvent temperature increase, the pure density of the solvent decreases and consequently the difference between the solvent-rich region and the antisolvent-rich region is greater; as a result, in coherence with the pressure effect described earlier, the increase of temperature increases the droplet lifetimes. Extra numerical experiments are currently in progress to validate this assumption.

CONCLUSION

This work developed a model of heat and mass transfer between a droplet of solvent and a compressed antisolvent in miscible conditions, in order to emphasize the role of density or temperature on the droplet lifetime. Results for isothermal conditions allows for comforting the numerical scheme since results closely matched the behaviour reported by Werling and

Debenedetti. First results obtained in non-isothermal conditions indicate that temperature gradient can provide an opportunity to tune the droplet lifetime, besides the pressure effect. Extra numerical calculations are currently in progress to enlight the role of the density difference on the expansion/shrinking behaviour and on the shrinking time.

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