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## Numerical Modeling of Mass Transfer for Solvent-Carbon Dioxide System at Supercritical (Miscible) Conditions

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**Abstract:** A numerical procedure of mathematical model for mass transfer between a droplet of organic solvent and a compressed antisolvent is presented for conditions such that the two phases are fully miscible. The model is applicable to the supercritical antisolvent (SAS) method of particle formation. In this process, solute particles precipitate from an organic solution when sprayed into a compressed antisolvent continuum. Effects of operating temperature and pressure on droplet behavior were examined. The CO<sub>2</sub> critical locus and the conditions for which the densities of solvent and carbon dioxide are equal are identified. Calculations were performed using Peng-Robinson equation of state. The model equations were put into the form that allowed the application of the Matlab standard solver pdepe. Calculations with toluene, ethanol, acetone (solvents) and carbon dioxide (antisolvent) demonstrated that droplets swell upon interdiffusion when the solvent is denser than the antisolvent and shrink when the antisolvent is denser. Diffusion modeling results might be used for data interpretation or experiments planning of the more complex real SAS process.

**Key words:** Diffusion, supercritical antisolvent method, droplets swell, droplets shrink

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### INTRODUCTION

A literature survey Reverchon and Adami (2006) over the last decade shows that supercritical fluid processes such as SAS (supercritical antisolvent), RESS (rapid expansion of supercritical solutions) and GAS (gas antisolvent) have attracted increasing attention for particle engineering, including fine particle formation, coating and encapsulation. Supercritical carbon dioxide (SC CO<sub>2</sub>), in particular, is a feasible processing medium for particle encapsulation because of its relatively mild critical condition ( $T_c = 304.1$  K,  $P_c = 7.38$  MPa). Furthermore, SC CO<sub>2</sub> is nontoxic, nonflammable, relatively inexpensive, readily available and chemically stable.

In SAS, SC CO<sub>2</sub>, is used as an antisolvent to extract an organic solvent from a solution containing solute, which is considered as the coating or encapsulation material. The solution is in the form of tiny droplets, produced by a nozzle through which the solution is sprayed into a high-pressure vessel. When the droplets contact the SC CO<sub>2</sub> very rapid diffusion takes place, including phase separation and precipitation of the solute. SAS exhibits the capacity of producing free-flowing particles in a single step at moderate pressure and temperature.

In order to achieve a rational understanding of the SAS process, theoretical investigation of the underlying phenomena and their interaction can play a valuable role. With this aim it is useful to break down the whole into its constituent parts. A detailed analysis of each aspect of SAS, leading to understanding of how these basic processes interact to influence particle characteristics, will eventually allow for the design and control of SAS experiments and for engineering design of industrial SAS units.

In this study, we consider two-way diffusion process between a solvent droplet and its antisolvent environment at supercritical conditions. Following, we refer throughout the single-phase region as supercritical for simplicity, although strictly speaking it is pressure and not temperature, that is supercritical in the single-phase region.

In most extent, we followed the formulation of the model done by Werling and Debenedetti (2000) but we achieved the analogous results applying more simple numerical routine procedure subject to assumptions on the source term of the diffusion equation.

Solution of governing mass transfer equations allowed for the calculation of composition and density profiles as a function of time. The droplet radius was also

defined and calculated as a function of time. For the toluene-CO<sub>2</sub>, acetone-CO<sub>2</sub> and ethanol-CO<sub>2</sub> systems it was found that droplets swell, often dramatically, due to mass transfer with CO<sub>2</sub> rich continuum.

**PROBLEM FORMULATION**

Under typical SAS temperatures and pressures 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 used to calculate the binary system density:

$$P = \frac{RT}{v - b_m} - \frac{a_m}{v^2 + 2vb_m - b_m^2} \tag{1}$$

where, the mixture parameters a<sub>m</sub> and b<sub>m</sub> were obtained from the following mixing rules (Poling *et al.*, 2001):

$$\begin{aligned} a_m &= \sum_i \sum_j x_i x_j a_{ij} \\ a_{ij} &= \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \\ b_m &= \sum_i \sum_j x_i x_j b_{ij} \\ b_{ij} &= \frac{(b_{ii} + b_{jj})}{2} (1 - l_{ij}) \end{aligned} \tag{2}$$

where, parameters a<sub>ii</sub> ≡ a<sub>i</sub> and b<sub>ii</sub> ≡ b<sub>i</sub> for a pure species were determined by following relationships Eq. 4:

$$a_i(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha_i(T) \tag{3}$$

$$b_i = 0.07780 \frac{RT_c}{P_c} \tag{4}$$

$$\alpha_i(T) = \left[ 1 - \kappa \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \tag{5}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{6}$$

The critical locus line represented P<sub>c</sub> vs. T<sub>c</sub> for the binary mixture was calculated as follows:

Since, the critical isotherm exhibits a horizontal inflection at the critical point, the mathematical conditions imply as:

$$\left( \frac{\partial P}{\partial v} \right)_{T_c} = \left( \frac{\partial^2 P}{\partial v^2} \right)_{T_c} = 0 \tag{7}$$

Differentiating Peng-Robinson Eq. 1 with respect to v and applying condition Eq. 7 we obtain the following equations:

$$\frac{RT_c}{(v - b_m)^2} - 2a_m(T_c) \frac{v + b_m}{(v^2 + 2b_m v - b_m^2)^2} = 0 \tag{8}$$

$$\frac{RT_c}{(v - b_m)^3} - a_m(T_c) \frac{3v + 6b_m v + 5b_m^2}{(v^2 + 2b_m v - b_m^2)^3} = 0 \tag{9}$$

Multiplying Eq. 9 by 1/v-b<sub>m</sub> and then equating RT/(v-b<sub>m</sub>)<sup>3</sup> term yields:

$$\frac{2(v + b_m)}{v - b_m} - \frac{3v^2 + 6b_m v + 5b_m^2}{v^2 + 2b_m v - b_m^2} = 0 \tag{10}$$

Equation 10 and 1-6 for reducing carbon dioxide mole fraction values x<sub>1</sub> = 1, 0.99, 0.98 ... were solved by iteration giving critical pressure P<sub>c</sub> and temperature T<sub>c</sub> of binary mixture to plot the locus line.

Physical properties, critical values and the binary interaction parameters for C<sub>7</sub>H<sub>8</sub> - CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>O - CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>O - CO<sub>2</sub> systems used in this paper were those reported in the publications by Poling *et al.* (2001), Chang *et al.* (1997), Kikic and Lora (1997) and Kordikowski *et al.* (1995).

**MODEL FORMULATION**

In order to formulate a model, time-dependent mass conservation equations and an equation of state are used. We assume spherical symmetry and a stagnant droplet. Hence the only convective motion is that actuated by diffusion process. The isothermal case has been considered here suggesting that the thermal effects are not important under practical SAS conditions.

All calculations were performed for toluene-CO<sub>2</sub>, acetone-CO<sub>2</sub> mixtures and ethanol-CO<sub>2</sub> mixtures.

The most general expression given by Poling *et al.* (2001) for the diffusive flux states that the flux is proportional to the chemical potential gradient as:

$$N_A = -\rho D_\phi \nabla x_A + x_A N \tag{11}$$

Where:

$$D_\phi = D \left[ 1 + \left( \frac{\partial \ln \hat{\phi}_A}{\partial \ln x_A} \right)_{T,P} \right] \tag{12}$$

However, since in this study the conditions considered are far from critical point the second term in Eq. 12 is neglected for the majority of calculations, so that the diffusive flux is assumed to be proportional to the concentration gradient as described by Fick's law:

$$N_A = -\rho D_\phi \Delta x_A + x_A N \tag{13}$$

Under supercritical conditions the antisolvent and solvent are completely miscible. Therefore, only one equation is needed to describe the mole fraction profile, which can be obtained from the continuity equation and Fick's law. The following equations are written in terms of molar quantities and the subscript A in these equations denotes carbon dioxide. The mass balance on carbon dioxide reads:

$$\frac{\partial}{\partial t}(\rho x_A) + \nabla \cdot (-\rho D \nabla x_A + x_A N) = 0 \quad (14)$$

The continuity equation is required to find the convective flux N:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot N = 0 \quad (15)$$

The expression for the diffusion coefficient in Eq. 13 requires an estimate of D, the proportionality constant from Fick's law. To approximate the change in the diffusivity of the system as the liquid solvent mixes with its dense gas environment, the Vignes equation was used over the entire region (Werling and Debenedetti, 2000):

$$D = (D_g^\circ)^{x_A} (D_l^\circ)^{1-x_A} \quad (16)$$

The liquid phase diffusion coefficient at infinite dilution ( $D_l^\circ$ ) and gas phase diffusion coefficient at infinite dilution with correction for high pressure ( $D_g^\circ$ ) were calculated using the methods presented by Poling *et al.* (2001).

The important part in describing the supercritical diffusion is to define what constitutes a solvent droplet. Werling and Debenedetti (2000) tested several definitions for the droplet radius during the diffusion process. With cutoff value definition, regions with densities significantly different from the density of the continuum were considered as part of droplet. The following criteria were adopted for our calculations:

$$\rho_{\text{cutoff}} = \rho_{\text{CO}_2} + 0.33(\rho_{\text{maximum}} - \rho_{\text{CO}_2}) \quad (17)$$

if  $\rho_{\text{solvent}} \gg \rho_{\text{CO}_2}$

$$\rho_{\text{cutoff}} = \rho_{\text{CO}_2} - 0.33(\rho_{\text{CO}_2} - \rho_{\text{solvent}}) \quad (18)$$

if  $\rho_{\text{solvent}} \ll \rho_{\text{CO}_2}$

The model formulation then completed with the following initial and boundary conditions:

$$t = 0 \quad x_A(r, 0) = \begin{cases} 0 & r \leq R_o \\ 1 & r > R_o \end{cases} \quad (19)$$

$$r = 0 \quad \frac{\partial x_A(0, t)}{\partial r} = 0 \quad (20)$$

$$r = \infty \quad \frac{\partial x_A(0, t)}{\partial r} = 0 \quad (21)$$

It has been assumed that Eq. 21 is satisfied at  $r = 20R_o$ .

Equation 19 states that initially the droplet contains no CO<sub>2</sub> and the surroundings contain no solvent. However, in order to avoid potential convergence problems the condition Eq. 19 was approximated by parabolic tangent profile:

$$t = 0 \quad x_A(r, 0) = \frac{1}{2} \{ \tanh[\alpha(r - R_o)] + 1 \}, \alpha = 10^8 \quad (22)$$

### NUMERICAL PROCEDURE

Werling and Debenedetti (2000) applied the procedure that involves the reduction of the partial differential equations system to the system of ordinary differential equations. It requires replacing the radial dependence with second-order finite difference approximation using, for example, the method of lines by Zanderer (2006). The total number of equations makes the calculations rather difficult to control and requests non-trivial advanced mathematical software.

In this study, we transform the above system of equations into the form that under certain assumptions allows application of standard Matlab pdepe solver for the parabolic PDE system. It is worth to mention that Matlab built-in routine also converts PDEs into the system of the ordinary differential equations as well however there is practical advantage of having the opportunity to apply a reliable well documented code. It considerably saves time and bulk of work. The arrangements and assumptions are as follows:

Multiplying Eq. 15 by  $x_A$  and combining with Eq. 14 yields:

$$\rho \frac{\partial x_A}{\partial t} = \nabla \cdot (\rho D \nabla x_A) - N \nabla x_A \quad (23)$$

Equation 23 written for spherical system of coordinates has the form:

$$\rho \frac{\partial x_A}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \rho D \frac{\partial x_A}{\partial r} \right] - \frac{N}{r^2} \frac{\partial}{\partial r} (r^2 x_A) \quad (24)$$

MATLAB solver pdepe solves initial-value problems for system of parabolic and elliptic partial differential equations in one space variable and time and of the general form:

$$c\left(r, t, x_A, \frac{\partial x_A}{\partial r}\right) \frac{\partial x_A}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 f\left(r, t, x_A, \frac{\partial x_A}{\partial r}\right) \right] + s\left(r, t, x_A, \frac{\partial x_A}{\partial r}\right) \quad (25)$$

(Equation 25 is rewritten here using the nomenclature of this study).

The principal difference between Eq. 24 and 25 refers to the last term in RHS, namely Eq. 25 has one unknown variable  $x_A(r, t)$  whereas Eq. 24 contains two variables  $x_A(r, t)$  and  $N(r, t)$  hence strictly speaking the solver pdepe is not applicable to Equation 24. Werling and Debenedetti (2000) calculated convective flux  $N$  from the continuity Eq. 15 in the process of simultaneous solution of 14, 15 and accompanied equations which requested a complicated procedure).

Here, we suggest approximation of the convective flux satisfying the source term,

$$s\left(r, t, x_A, \frac{\partial x_A}{\partial r}\right)$$

that allows for the direct application of Matlab's pdepe solver.

Based on the assumptions of the model the convective flux approximation is invoked by diffusion and hence is pronounced through the gradient of concentration term  $\partial x_A / \partial r$  that is rather zero beyond mixing region. A simple approximation rationale is based on dimensional analysis of the characteristic value of the radial velocity that has been generated purely by diffusion. From diffusion coefficient units  $[D] = m^2/s$  and the characteristic length as the radius of the particle  $[R] = m$  we have suggested that the apparent average value of radial velocity induced by diffusion is proportional to  $D_g^0 / R_o$ , i.e.,  $\bar{V}_r = K(D_g^0 / R_o)$  where, a constant  $K$  has to be evaluated. Typical value of  $D_g^0 \approx 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ , a value much less than for a low-pressure gas but still significantly higher than for a typical liquid (Poling *et al.*, 2001). Werling and Debenedetti (2000) results of the toluene-carbon dioxide modeling with finding  $N$  from unabridged system were also used for comparison in evaluation of  $K$  (for example,  $K \approx 0.016$  for toluene-CO<sub>2</sub> diffusion process).

We presume that even a rude evaluation of radial velocity could produce satisfactory results because the entire term:

$$\frac{N}{r^2} \frac{\partial}{\partial r} (r^2 x_A) = \frac{\rho \bar{V}_r}{r^2} \frac{\partial}{\partial r} (r^2 x_A)$$

works in the diffusion equation and thus one intuitively expects that introducing an apparent radial flux however keeping non-distorted the multiplier  $\partial / \partial r (r^2 x_A)$  the solution would still yield realistic results.

After approximation of the source term we obtain the alternative form of the working equation that is consistent with pdepe solver requirements:

$$\rho \frac{\partial x_A}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \rho D \frac{\partial x_A}{\partial r} \right] - \frac{\rho \bar{V}_r}{r^2} \frac{\partial}{\partial r} (r^2 x_A) \quad (26)$$

Under fixed pressure and temperature the system density is function of composition  $\rho = \rho(x_A) = v^{-1}$  and was calculated from the Peng-Robinson Eq. 1.

Near the droplet center (0-4 times the initial droplet radius), a constant mesh spacing was used. Whereas away from the droplet center (4-20 times the initial droplet radius) a logarithmic scaling was applied due to slow changes of the variables and their derivatives at the remote distance from the front of the mixing zone.

In the total, the space mesh consisted of 1000 radial nodes providing sufficient accuracy for computing. Total calculation time via common PC (1.8 GHz, 0.97 GB of RAM) was about 3-4 min.

### RESULTS AND DISCUSSIONS

Figure 1 maps the location of swelling/shrinking regimes identified for the toluene-CO<sub>2</sub> system. Our calculations mainly correspond to Werling and Debenedetti (2000) results except the different trend of the critical locus. This disagreement might need further clarification. However, it didn't affect the presented results on the diffusion process since the selected temperature and pressure sets were quite away from the locus line.

Figure 2 and 3 demonstrate the advancement of initially stepwise CO<sub>2</sub> mole fraction and mixture density profiles: due to fast interdiffusion the curves are becoming flat within a fraction of a second.

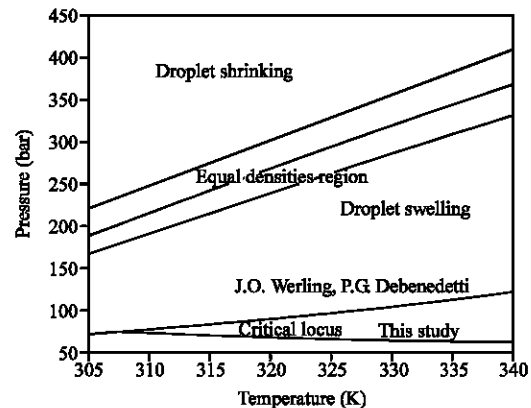


Fig. 1: Effect of operating temperature and pressure on droplet behavior for toluene-CO<sub>2</sub> system

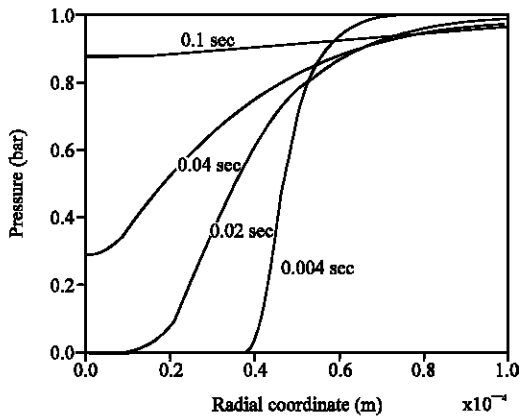


Fig. 2: Evolution of CO<sub>2</sub> mole fraction. Toluene -CO<sub>2</sub> system, T = 318K, P = 100 bar. Initial radius of all droplets is 50 μm

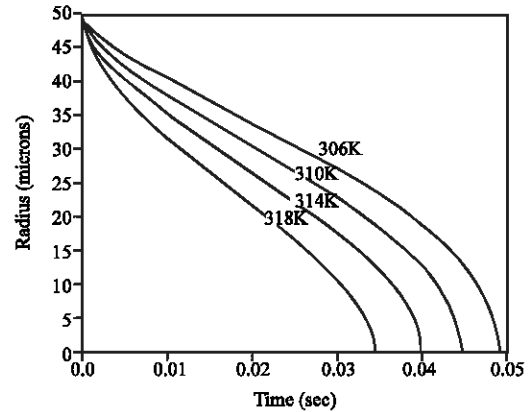


Fig. 4: Evolution of toluene droplet radius at 275 bar and different temperatures. Initial radius of all droplets is 50 μm

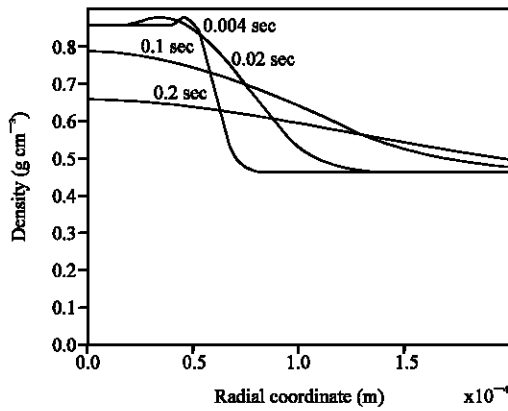


Fig. 3: Evolution of density profiles. CO<sub>2</sub> - toluene diffusion, T = 318K, P = 100 bar

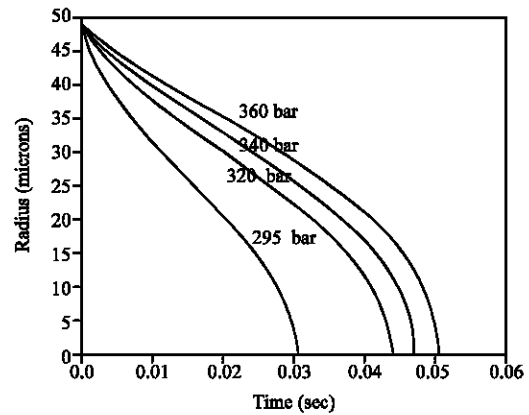


Fig. 5: Evolution of toluene droplet radius at 318 K and at different pressures

Application of the droplet radius criteria (Eq. 17-18) to the mixture density profiles allows to monitor the evolution of the drop under the fixed pressures and temperatures. Figure 4 and 5 show the droplet shrinking behavior whereas in Figure 6 and 7 under the corresponding pressure and temperature the droplet's radius increases in times before collapsing; namely such expansion is considered as a crucial stage in SAS process. Results from Fig. 8 shows that under the specified pressure and temperature the selection of the solvent is also having an appreciable effect (through the physical properties) on the droplet expansion magnitude.

Usage of the general expression for the diffusive flux (Eq. 12) instead of Fick's law (Eq. 13) yields certain alternation on the particle lifetime curves which is shown in Fig. 9. However the computing time with Eq. 12 increases substantially putting away the advantage of the suggested procedure as a tool for fast preliminary

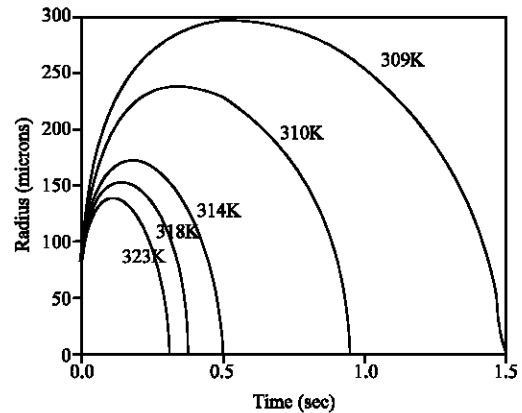


Fig. 6: Evolution of acetone droplet radius at 110 bar and at different temperatures

exploring of the interdiffusion process. Besides scattering of input data of the physical properties of the solvents

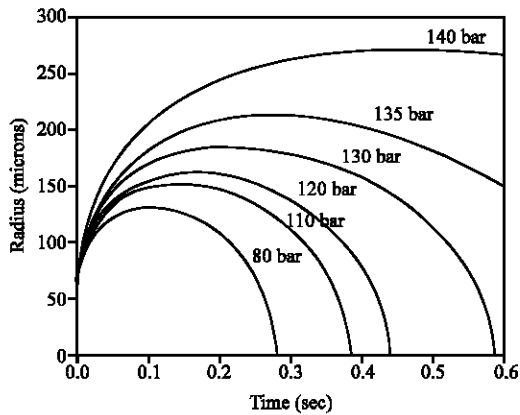


Fig. 7: Evolution of acetone droplet radius at 318 K and at different pressures. The mixture critical pressure at this temperature is 70 bar

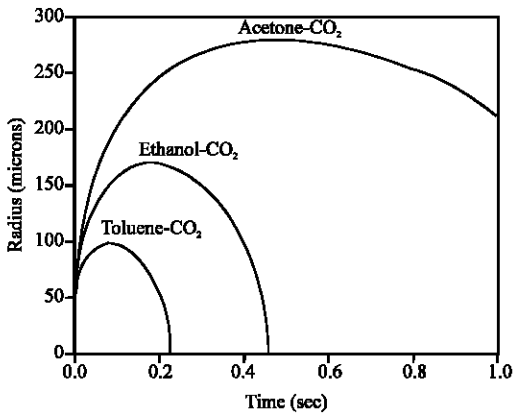


Fig. 8: Evolution of acetone, ethanol, toluene droplets radius at T = 318 K and at P = 140 bar

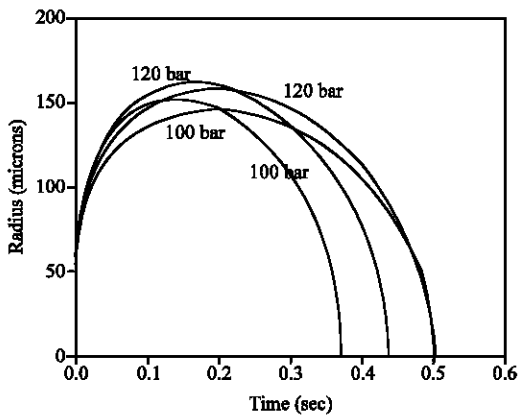


Fig. 9: T = 318 K, CO<sub>2</sub> - acetone mixture, solid lines - calculations on the basis of Fick's Law, dashed lines - using Eq. 12

and some parameters (mixing rule coefficients) is capable to bring more deviation comparing with differences due to formulae on flux.

### CONCLUSION

The developed approach on the calculation of the diffusion process makes the numerical procedure comparatively simple in practice for the estimation of the essential aspects of the solvent droplet behavior and might be helpful in planning, exploring and optimization SAS technique of particles formation.

### NOMENCLATURE

- a, b = Parameters in Peng-Robinson equation of state
- $a_m, b_m$  = Parameters in Peng-Robinson equation of state of binary mixture
- D = Diffusion coefficient from Fick's law
- $D_\phi$  = Modified diffusion coefficient containing thermodynamic correction
- k, l = Binary interaction parameters
- N = Flux due to composition gradients
- P = Pressure (Pa)
- $P_c$  = Critical pressure (Pa)
- R = Radial coordinate
- R = Instantaneous droplet radius (m)
- $R_o$  = Initial droplet radius (m)
- t = Time (sec)
- T = Temperature (K)
- $T_c$  = Critical temperature (K)
- V = Radial velocity (m sec<sup>-1</sup>)
- $\bar{v}$  = Apparent radial velocity (m sec<sup>-1</sup>)
- v = Molar volume (m<sup>3</sup> kmol<sup>-1</sup>)
- $x_A$  = Mole fraction of carbon dioxide
- $\rho$  = Density (kmol m<sup>-3</sup>)
- $\Phi$  = Fugacity coefficient
- $\omega$  = Acentric factor

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