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Conservative Mathematical Model and Numerical Simulation of Batch Gravity Settling with

Coalescence of Liquid-Liquid Dispersions

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Abstract

The coalescence and sedimentation of drops in liquid/liquid systems is a very common and important stage in many industries (crude oil production, metallurgy extraction, wastewater treatment and pharmaceutical processes). Several models have been proposed on this topic. Population balance equations (PBE) provide a suitable a framework for dealing with drop breakage and coalescence. In addition, modeling of the solid particle sedimentation process based on Kynch's theory has been successfully used and validated in mineral processing and wastewater treatment. In this work, we present a model that merges the coalescence process with hindered polydisperse sedimentation. The PBE model is projected onto a partial differential equation (PDE) system by discretizing the droplet volume. Because there is loss of mass in the system when the daughter droplets are greater than the larger species considered for the numerical solution, two terms that produce the conservation of the mass or total volume of the dispersed phase are incorporated into the PDE system. The resulting PDE system is split into two systems: homogeneous PDEs and ordinary differential equations (ODEs). The homogeneous PDEs and the ODEs are discretized using a first-order central differencing scheme and the second-order, two-stage Runge-Kutta method, respectively. The model predicts the vertical variation of the composition of the dispersed phase layer that forms at the top or bottom of the gravity settler. The proposed model was calibrated and validated through an experiment with an oil and water system. In particular, simulations illustrate the effects of: the continuity of the dispersion (oil-in-water and water-in-oil) and the standard deviation of the initial droplet volumes on phase separation quality, as well as the influence of the coalescence frequency on the average droplet volume.

Keywords: Liquid-liquid separation, Mathematical modeling; Simulation; Hindered settling; Dispersion; Population Balance; Coalescence.

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Introduction

1.1. Motivation

The importance of immiscible liquid-liquid system separation is well known in many industrial fields such as metallurgy, wastewater treatment and the pharmaceutical, food and crude oil industries. Liquid-liquid dispersion separation is carried out in gravity settlers and centrifuges and is a complex process in which drop sedimentation and coalescence are involved. Due to the high complexity and cost of physical experimentation in a pilot plant or laboratory, mathematical modeling and simulation is very attractive for analyzing and designing gravity settlers and centrifuges. Moreover, for design and automatic control purposes, it is necessary to know the time to reach steady state in a gravity settler; therefore, merely solving the easier steady-state equations does not yield enough valuable information.

In recent decades, there has been particular interest in the industry in the use of population balance models for different systems, including particle, droplet and bubble aggregation and breaking phenomena, especially for the control of particle size, thanks to the availability of advanced equipment for on-line particle size measurement (Ramkrishna, D., Mahoney, A., 2002).

1.2. Related work

The population balance concept is suitable for modeling the multiphase flow systems occurring in unit operations of liquid-liquid separation carried out in batch and continuous equipment. The dynamic behavior of the droplets (dispersed phase) in such operations makes it necessary to consider a sophisticated mathematical model that describes the variation in the concentration of the different droplet sizes as a function of position and time as a result of sedimentation and coalescence phenomena. The first researchers to incorporate population balance equations (PBE) into the modeling of chemical processes involving dispersed phase operations were Hulburt and Katz (1964) and Valentas and Amundson (1966).

Regarding mathematical models of gravitational settling with liquid-liquid mixture coalescence, Barnea and Mizrahi (1975) studied the separation of phases in a deep-layer gravity settler and proposed a semi-empirical model by considering

the hindered settling of the smaller drops in the dispersion band, together with the rate of drop growth by coalescence. Hartland and Jeelani (1987) proposed a method to predict the variations in height of the sedimentation and dense-packed zones with the throughput in a continuous settler, using parameters determined from experimental batch sedimentation and coalescence data. Ruiz and Padilla (1996) developed a mathematical model for the steady-state operation of a deep-layer gravity settler using a population balance approach, which takes into account the size distribution of drops within the dispersion band and uses rate expressions to describe drop-drop and drop-interface coalescence phenomena. Yu and Mao (2004) developed a mathematical method for predicting the phase separation profiles of a batch liquid-liquid dispersion based on the empirical description of drops resting at a liquid-liquid plane interface. Gomes et al. (2007), based on the work of Ruiz and Padilla (1996), presented a direct numerical technique for computing the thickness and drop-size composition of the dispersion band formed in a shallow-layer settler under steady-state and transient conditions. Mohebbi et al. (2011) used commercial computational fluid dynamics (CFD) modeling software accompanied by experimental field measurements to study the behavior of aqueous-organic dispersion in the performance of the launder of a copper solvent extraction plant settler. In the petroleum field, Noïk et al. (2013) proposed a sedimentation and coalescence model without considering the PBE, which described the position of the sedimentation interface, free water and dense-packed zone based only on ODE. The model was validated through several experiments using a dispersion rig set up with capacitance sensors, and good agreement between the experiments and the model was reported. Grimes (2012) proposed a model that combined sedimentation and PBM by considering the settling velocity of the dispersed phase (polydisperse) given by a Richardson and Zaki expression and by solving the obtained ODE systems with Gear's backward algorithm. In a second paper, Grimes et al. (2012) compared experimental data obtained from a crude oil/water system with results obtained from their model, finding good agreement.

With respect to numerical methods for the solution of the PBE, a general treatment is presented by Ramkrishna (2000). These existing methods focus primarily on the solution of models in a single distributed dimension. The most frequently used numerical methods could be grouped into three categories: stochastic, higher-order and zero-order methods (Ramkrishna 2000; Attarakih et al., 2004). The final type could be classified into two broad classes according to Kumar and Ramkrishna (1996a): internally consistent and inconsistent discretization schemes with respect to selected integral properties (e.g., dispersed phase volume fraction and droplet number concentration). Internal consistency means that the desired integral property associated with the average number concentration obtained from the discrete PBE should be the same as that obtained from the continuous equation. An internally consistent numerical scheme allows the desired integral properties to be accurately predicted and at the same time improves the accuracy of the predicted droplet distribution on

coarse meshes (Hounslow et al., 1988; Lister et al., 1995; Kumar and Ramkrishna, 1996a; Attarakih et al., 2004b). Kumar and Ramkrishna (1996a) used the advantage of internal consistency and introduced a general framework of zero-order discretization that is internally consistent with respect to any two integral properties, irrespective of the grid structure. This scheme is called the fixed-pivot technique because it concentrates the droplet population from a given size range at a single point (called the pivot) through the use of the Dirac delta function. The idea of this technique is that when a droplet is formed by either breakage or coalescence on a discrete mesh (with respect to droplet volume), its volume will not coincide with any of the representative volumes except for the linear discretization. In the classical discretization techniques the daughter droplet volume is assigned to the nearest pivot and thus it could be shown that only one integral property could be conserved (Attarakih et al., 2004a). To conserve at least two integral properties the daughter droplet volume is linearly interpolated between two adjacent pivots; consequently, any two integral properties are conserved.

Regarding to the solution of the PDE for the sedimentation process for polydisperse suspensions, many authors have faced the problem (Berres and Bürger, 2003; Bürger et al., 2008, 2010, 2011; Betancourt et al., 2014; Boscarino et al., 2015; Torf et. al, 2017 ...; this list is far from being complete). Here we follow the approach developed by Berres et al. (2004).



Figure 1: Sketch of a batch-settling experiment and respective settling curve with notation for different heights (Pfennig et al., 2002).

1.3. Description of drop coalescence and sedimentation process

In an unsteady-state batch settler (Figure 1), the height h of the dispersion decreases with time as two clear phases are formed, with the total separation time being $t_{\rm f}$. In a decaying batch dispersion the drops settle while growing in size due to binary coalescence before entering the dense-packed zone and finally coalescing with their bulk homophase at the coalescing interface. The thickness of the dense-packed zone initially increases when the sedimentation rate is faster than the interfacial coalescence rate and finally decreases, from time t_i , when sedimentation is complete; thus, interfacial coalescence predominates. Therefore, the total dispersion height h is the sum of the heights h_s and h_p of the sedimentation and dense-packed zones at any time t'. However, if the sedimentation rate is always less than the interfacial coalescence rate during the decay, then no dense-packed zone is formed.

1.4. Objectives

The objective of this work is to model and simulate the phenomenon of batch separation of liquid-liquid dispersions in a gravity settler. The specific objectives are to predict the transient composition of the dispersed phase within the unit to study the behavior of different droplet volumes, the effects of the standard deviation of the initial droplet volumes and the continuity of the dispersion (oil-in-water and water-in-oil) on phase separation quality and the effect of the coalescence frequency constant on the average droplet volume.

The mathematical model proposed here is based on population balance equations for coalescence and a PDE for sedimentation, which is applicable for dynamic operation; the numerical method is first-order accurate in space and secondorder accurate in time. In addition, the numerical scheme is programmed into the specialized language for scientific computation, FORTRAN, and can be synthesized in an executable file that can run on the Windows operating system. The model is calibrated and validated through comparison with experimental measurements.

The paper is organized as follows: Section 2 describes the proposed mathematical model. Section 3 is devoted to the numerical method for solving the model. In Section 4, the experimental set-up, conditions and results are reported. Section 5 shows the numerical examples and compares them with the experiments.

2. Derivation of the mathematical model

2.1. Mathematical model for gravity settling of polydisperse suspensions

We adopt the model described by Berres and Bürger (2003), who assume that particles of species *i* have size d_i ; i = 1, ..., *M*, where $d_1 > d_2 > \cdots > d_M$, and the same density ρ_s . The solutions depend on time *t* and on depth *z* as the unique space variable. The system of equations that remains to be solved is

$$\frac{\partial \phi_i}{\partial t} + \frac{\partial}{\partial z} f_i(\Phi, z) = 0, \quad i = 1, \dots, M$$
(1)

where f_i is a flux function, $\Phi = [\phi_1, \phi_2, ..., \phi_M]^T$ is volume fraction vector and g is the acceleration of gravity. Berres and Bürger (2003) used the well-known MLB flux function proposed by Masliyah and Lockett and Bassoon, which, for equal density spheres, is given by

$$f_i(\Phi, z) = f_i^{M}(\Phi) := (\rho_s - \rho_f)\phi_i(1 - \phi)\tilde{V}(\phi)\frac{g}{18\mu_f} \left[d_i^2 - \sum_{k=1}^M d_k^2 \phi_k \right],$$

where ρ_f and μ_f are the density and the dynamic viscosity of the fluid, respectively, and the function $\tilde{V}(\phi)$ is a hindered settling factor.

The relevant zero-flux boundary conditions are

$$f_i\Big|_{z=z_i} = 0 \quad \text{for} \quad z_b \in 0, H \tag{2}$$

and the condition defining the initial composition of the suspension is

$$\phi_i(z,0) = \phi_i^0(z), \quad 0 < z < H, \quad \phi_i^0(z) \in D_{\phi_{max}}, \tag{3}$$

where $D_{\phi_{max}}$ is the phase space of admissible concentration:

$$D_{\phi_{\max}} \coloneqq \{\phi_i, i = 1, \dots, M : \phi_i \ge 0, \phi \le \phi_{\max}\}$$

where $\phi = \phi_1 + \dots + \phi_M$ is the total solids volume fraction and $0 < \phi_{max} \le 1$ is the maximal dispersed phase concentration.

Bürger et al. (2010) proved that for equal-density particles and arbitrary particle size distributions, the system (1) with the MLB flux functions is strictly hyperbolic for all $\Phi \in D_{\phi_{max}}$.

2.2. The population balance equation for a batch gravitational separator

The spatially one-dimensional population balance equation for a batch gravitational liquid–liquid separator (settler) (see Figure 1) without mass transfer and diffusion could be written as

$$\frac{\partial n}{\partial t} + \frac{\partial \mathcal{F}}{\partial z} = \beta(n, v) \tag{4}$$

where v is the droplet volume, z is the vertical coordinate and n(v; z, t)dv := N(t, z)f(v)dv is the average number concentration of droplets having a volume between v and v + dv at the time instant t and position z, where N(t, z) is the total number concentration and f(v) is a number density function. The convective flux density function of these droplets is represented by

$$\mathcal{F}(n,v,\phi,z):=u_d n,$$

where $u_d = u_d (v, \phi, z)$ is the velocity of the dispersed phase relative the settler walls and will be derived later on.

The term on the right-hand side of (4) is the net number of droplets produced by coalescence per unit time and unit volume and is defined by Valentas and Amundson (1966):

$$\beta(n,v) := -n(v;z,t) \int_{v_{\min}}^{v_{\max}} \lambda(v,\xi,\phi,z) n(\xi;z,t) d\xi + \frac{1}{2} \int_{v_{\min}}^{v} \lambda(\xi,v-\xi,\phi,z) n(\xi;z,t) n(v-\xi;z,t) d\xi$$
(5)

The coalescence frequency, λ , is dependent on the system physical properties, the internal vessel geometry and the dispersed phase hold-up, ϕ , which is given by

$$\phi(z,t) \coloneqq \int_{\nu_{\min}}^{\nu_{\max}} \xi n(\xi;z,t) d\xi \,. \tag{6}$$

In this work, the parameter λ , as a function of the volumes, v and \hat{v} , of two coalescing droplets, is expressed as follows:

$$\lambda(v, \hat{v}, \phi, z) = \begin{cases} 0, & \text{for } \phi < 0, \\ K_{c,s} \left[v^{1/3} + \hat{v}^{1/3} \right]^2 \left| u(v, \phi, z) - u(\hat{v}, \phi, z) \right|, & \text{for } 0 \le \phi < \phi_{cr}, \\ K_{c,p} \left[v^{-1/3} + \hat{v}^{-1/3} \right]^2 \left| z - z_{cr} \right| + \lambda_{cr}, & \text{for } \phi_{cr} \le \phi, \end{cases}$$
(7)

where $K_{c,s}$ and $K_{c,p}$ are coalescence frequency coefficients, ϕ_{cr} is the critical concentration at which the droplets touch each other and depends on droplet size distribution and z_{cr} is the height at which ϕ_{cr} is reached; for continuity of the function λ , λ_{cr} is given by

$$\lambda_{\mathrm{cr}} = K_{\mathrm{c,s}} \left[v^{1/3} + \hat{v}^{1/3} \right]^2 \left| u(v,\phi_{\mathrm{cr}},z_{\mathrm{cr}}) - u(\hat{v},\phi_{\mathrm{cr}},z_{\mathrm{cr}}) \right|$$

The formula for the sedimentation zone $(0 \le \phi < \phi_{cr})$ was introduced by Rogers and Davis (1990) for modeling coalescence of droplets of Zn-Bi immiscible alloys during a micro-gravitational process, as well as by Zhang and Davis (1991) and Zhang et al. (1993) for modeling coalescence of droplets in gravitational motion, and the formula for the dense-packed zone ($\phi_{cr} \le \phi$) was introduced by Ruiz and Padilla (1996), but with $\lambda_{cr} = 0$, for modeling coalescence in aqueous-organic dispersions in a gravity settler. For the treatment of unphysical values of ϕ greater than 1, we propose a correction technique in the numerical scheme that involves "turning off" the birth (positive) term of the equation (5) when $\phi > 1$ (see equation (30)).

Ruiz and Padilla (1996) reported ϕ_{cr} values of around 0.53 for the condition in which the hold-up of the incoming dispersion was less than or equal to 0.53; otherwise, ϕ_{cr} was equal to the feed hold-up. Note that the volume fraction of spheres of the same diameter for a simple cubic packing is $\pi/6 \approx 0.5236$.

We can observe that in the sedimentation zone two droplets of the same size cannot collide, and that there is no coalescence if no droplet exists ($\phi = 0$).

As an approximation of the value of the critical height z_{cr} , here we consider that its value is that which is reached in steady state (infinite time), that is:

$$z_{\rm cr} = \begin{cases} (1-\phi_0)L, & \text{if } \rho_d \ge \rho_c \\ \phi_0 L, & \text{if } \rho_d < \rho_c \end{cases}$$

2.3. Model discretization with respect to droplet volume

Here we follow the ideas of Attarakih et al. (2004). We discretize the droplet volume, v, according to the discrete set $\{v_{i-1/2} \mid i = 1, ..., M + 1\}$ with $v_{\min} = v_{1/2} < v_{3/2} < \cdots < v_{M+1/2} = v_{\max}$, where *M* identifies the species composed of droplets with volumes greater than $v_{M-1/2}$ plus the corresponding homophase, hereinafter species *M*.

Let the ith subdomain be defined as $V_i := [v_{i-1/2}, v_{i+1/2}]$, i = 1,..., M and the middle of this subdomain $v_i := (v_{i-1/2} + v_{i+1/2})/2$, called the pivot.

The number concentration of droplets in the ith subdomain, $N_i(r, t)$, is defined by

$$N_i(z,t) \coloneqq \int_{v_{i-1/2}}^{v_{i+1/2}} n(\xi;z,t) d\xi \tag{9}$$

The population of the *i*th subdomain is concentrated at the pivot v_i through the use of the Dirac delta function:

$$\widehat{n}(v;z,t) \coloneqq \sum_{i=1}^{M} N_i(z,t) \delta(v-v_i)$$
(10)

With the definitions of v_i and N_i , it is now possible calculate an approximate value of ϕ as

$$\widehat{\phi} = \sum_{i=1}^{M} N_i v_i \, .$$

Kumar and Ramkrishna (1996) showed that when the source term $\rho(n,v)$ is discretized by integrating it with respect to v from $v_{i+1/2}$ to $v_{i+1/2}$, the formation term due to coalescence is a source of internal inconsistency. They solved the problem of internal inconsistency by modifying the formation term due to coalescence by multiplying it with a triangular function that it is defined as

$$w_{i}(v) \coloneqq \begin{cases} w_{i}^{(1)}(v) = \frac{v - v_{i-1}}{v_{i} - v_{i-1}}, & \text{for } v_{i-1} \leq v < v_{i}, \\ \\ w_{i}^{(2)}(v) = \frac{v_{i+1} - v}{v_{i+1} - v_{i}}, & \text{for } v_{i} \leq v < v_{i+1}. \end{cases}$$
(11)

Then we can integrate equation (4) with respect to v from $v_{i-1/2}$ to $v_{i+1/2}$, using equation (10), to get the following system of balance equations:

$$\frac{\partial N_i}{\partial t} + \frac{\partial}{\partial z} F_i(\mathbf{N}, \mathbf{v}, z) = \beta_i(\mathbf{N}, \mathbf{v}), \quad i = 1, \dots, M.$$
(12)

where $\mathbf{N} = [N_1, N_2, ..., N_M]^T$, $\mathbf{v} = [v_1, v_2, ..., v_M]^T$ and the flux function F_i is defined by

$$F_i(\mathbf{N}, \mathbf{v}, z) \coloneqq u_d(v_i, \phi, z) N_i.$$

The velocity of droplet species of volume v_i relative to the continuous phase or slip velocity of species *i* is defined by

$$u_{r,i}(\phi, z) \coloneqq u_d(v_i, \phi, z) - u_c(\phi, z), \tag{13}$$

where $u_d(v_i, \phi, z)$ and $u_c(\phi, z)$ are the dispersed and continuous phase velocity with respect to the settler walls.

In the function of the slip velocity of species *i*, $u_{r,i}$, F_i is given by

$$F_i(\mathbf{N}, \mathbf{v}, z) = N_i \left(u_{r,i} - \sum_{i=1}^M N_i v_i u_{r,i} \right)$$

The source term for droplet coalescence could be written by introducing the *i*th interaction coalescence matrix, $C^{(i)}$ (Attarakih et al., 2004) and, in addition, with the purpose of favoring the conservation of the mass, the death (negative) term for the largest species (*M*) is cancelled out, as

$$\beta_{i}(\mathbf{N}, \mathbf{v}) \coloneqq \begin{cases} \sum_{j=1}^{i-1} \sum_{k=j}^{i-1} C_{jk}^{(i)} \lambda_{jk} N_{j} N_{k} - N_{i} \sum_{j=1}^{M} \lambda_{ij} N_{j}, & i = 1, \dots, M - 1, \\ \sum_{j=1}^{i-1} \sum_{k=j}^{i-1} C_{jk}^{(i)} \lambda_{jk} N_{j} N_{k}, & i = M. \end{cases}$$

$$(14)$$

where $\lambda_{ij} := \lambda(v_i, v_j)$ and the elements in the *i*th coalescence interaction matrix are given by

$$C_{jk}^{(i)} \coloneqq \begin{cases} 1 - \delta_{jk} / 2 \ w_i^{(1)}(v_j + v_k), & \text{for } v_{i-1} \le v_j + v_k < v_i, \\ 1 - \delta_{jk} / 2 \ w_i^{(2)}(v_j + v_k), & \text{for } v_i \le v_j + v_k < v_{i+1}, \\ 0 & , & \text{otherwise.} \end{cases}$$
(15)

where δ_{ik} is the Kronecker delta.

2.4. The droplet velocity of the dispersed phase relative to the continuous phase

For the sedimentation zone, the equation for the slip velocity in the vertical direction, $u_{r,i} = V_{s,i} := V_{s,i}(d_i,\phi)$, according to Kumar and Hartland (1985), is adopted:

$$0.53V_{s,i}^{2} + \frac{24\mu_{c}}{d_{i}\rho_{c}}V_{s,i} + \frac{4d_{i}g(\rho_{c}-\rho_{d})(1-\phi)}{3\rho_{c}(1+4.56\phi^{0.73})} = 0, \qquad i = 1, \dots, M.$$
(16)

where ρ_c and μ_c are the density and the viscosity of the continuous phase, respectively, ρ_d is the density of the dispersed phase and d_i is the diameter of the droplet species *i*.

Equation (16) provides good agreement between experimental and predicted values of slip velocity over a wide range of hold-ups ϕ (0.01 to 0.76) and Reynolds numbers $\text{Re}_i = d_i u_{r,i} \rho_c / \mu_c$ (0.16 to 3169), as reported in Kumar and Hartland (1985).

For the dense-packed zone it is necessary to find an appropriate formula for the slip velocity or the flux function. Here, it is assumed that the formula for the sedimentation zone is also valid for the dense-packed zone.

2.5. Conservation of mass of the dispersed phase in a batch process

Because the fixed-pivot technique is not applicable when the daughter drops are greater than the largest species considered for the numerical solution, it is necessary to incorporate into the system of balance equations (12) a term that

produces the conservation of the total mass or volume of the dispersed phase, in a batch process (see Example 1, Fig. 5). This will be done by means of a source that corrects the mass of the species M (see definition in section 2.3).

An average velocity of corrective source of mass of species M, $q_{corr,M}$ at the end of the vessel where it is deposited is proposed.

Since the volumetric fraction of this source is 1, the number concentration [drops / volume] is the inverse of the volume v_M of a drop of species *M*. Then, the corrective flux density of the species *M* is given by

$$F_{\text{corr},M}(t) = \frac{q_{\text{corr},M}(t)}{v_M} \quad [\text{drops/(area \times \text{time})}]. \tag{17}$$

The corrective flux density of the other species is zero:

$$F_{\text{corr},i} = 0, \quad i = 1, \dots, M - 1.$$
 (18)

In addition, the presence of the flux density $F_{corr,M}$ must produce a displacement of the mixture toward the zone of lower dispersed phase concentration, at the same velocity $q_{corr,M}$. Thus, the flux density of drop displacement is the product of the concentration in number of drops and the displacement velocity:

$$F_{\text{disp},i}(N_i,t) = N_i q_{\text{corr},M}(t), \quad i = 1,...,M.$$
 (19)

The corrective flux is added to the balance equations (12) as a singular source term, while the displacement flux is added to the batch flux, resulting in the balance equations:

$$\frac{\partial N_i}{\partial t} + \frac{\partial}{\partial z} F_i(\mathbf{N}, \mathbf{v}, z) + F_{\text{disp}, i}(N_i, t) = \beta_i(\mathbf{N}, \mathbf{v}) + F_{\text{corr}, i}(t)\delta(z - z_{\text{end}}), \quad i = 1, \dots, M ,$$
(20)

where $\delta(z - z_{end})$ is the Dirac delta centered at $z = z_{end}$, which is the position of the bottom or top end of the vessel where species *M* is deposited.

2.6. Final form of the mathematical model

Using the Heaviside function, we may absorb the last term of the right-hand side of (20) into the flux function. This leads to the equations:

$$\frac{\partial N_i}{\partial t} + \frac{\partial}{\partial z} F_i(\mathbf{N}, \mathbf{v}, z) + F_{\text{disp},i}(N_i, t) - F_{\text{corr},i}(t)H(z - z_{\text{end}}) = \beta_i(\mathbf{N}, \mathbf{v}), \quad i = 1, \dots, M.$$
(21)

This system is solved together with the zero-flux boundary conditions:

$$F_i|_{z=z_b} = 0 \text{ for } z_b \in 0, L , \quad i = 1, ..., M$$
 (22)

and the initial condition:

$$N_i(z,0) = N_i^0(z), \quad 0 < z < L, \text{ with } \hat{\phi}_i^0(z) = \sum_{i=1}^M N_i^0 v_i \in D_{\phi_{\max}}$$
(23)

3. Numerical scheme

3.1. Discretization of the settler interior.

We discretize the spatial domain into cells $[z_{j-1/2}, z_{j+1/2}]$, j = 0, 2, ..., J, where $z_j = j\Delta z$ for j = -1/2, 0, 1/2, ..., J+ 1/2. Similarly, the time interval (0, T) is discretized via $t_n = n\Delta t$ for n = 0, ..., N, where N is the nearest integer to $T/\Delta t + 1$, which results in the time strips $[t_n, t_{n+1}]$, n=0,...,N-1. Here $\Delta z > 0$ and $\Delta t > 0$ denote the spatial and temporal discretization parameters. We set $\Delta z := (L + L_{ex})/J$, where L is the height of the settler, L_{ex} is an extra length for numerical reasons and J is a natural number. Δt is chosen such that the following stability condition (CFL condition) holds (Le Veque, 1992):

$$\frac{\Delta t}{\Delta z} \max SR \ J_{\mathbf{G}}(\mathbf{N}, \mathbf{v}, z) \le 1,$$
(24)

where $SR(\cdot)$ denotes the spectral radius and $J_{\mathbf{G}}(\mathbf{N}, \mathbf{v}, z)$ the $M \times M$ Jacobian of $\mathbf{G}(\mathbf{N}, \mathbf{v}, z) \coloneqq [G_1, \dots, G_M]^{\mathrm{T}}$, with $G_i = F_i + F_{\mathrm{disp},i} - F_{\mathrm{corr},i}H(z - z_{\mathrm{end}})$.

In the numerical scheme, we approximate $\max SR(J_G(\mathbf{N}, \mathbf{v}, z))$ by $2u_{r,max}$, where:

$$u_{r,\max} \coloneqq \max_{\phi,z,i} \left| u_{r,i}(\phi,z) \right|,\tag{25}$$

is the maximum settling velocity of the species in the system.

3.2. Solution of the model in the discretized domain

To solve our problem we use the well-known Fractional-Step Method (Le Veque, 1992).

The proposed numerical scheme for the first step, i.e., to solve the homogeneous conservation laws:

$$\frac{\partial N_i}{\partial t} + \frac{\partial}{\partial z} G_i(\mathbf{N}, \mathbf{v}, z) = 0, \quad i = 1, \dots, M,$$
(26)

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is the Lax-Friedrichs Method (Le Veque, 1992). Let $\mathbf{N}_{j}^{n} \coloneqq [N_{1,j}^{n}, ..., N_{M,j}^{n}]^{\mathrm{T}}$ denote our approximation to $\mathbf{N}(z_{j}, t_{n})$ Expressed in terms of the forward Euler solver, we consider the one-parameter family of Runge-Kutta schemes:

$$\mathbf{N}_{j}^{(1)} = \mathbf{N}_{j}^{n} - \frac{\Delta t}{\Delta z} \Delta_{-} \mathbf{g}(\mathbf{N}_{j}^{n}, \mathbf{N}_{j+1}^{n}),$$

$$\mathbf{N}_{j}^{(k+1)} = (1 - \eta_{k}) \left(\mathbf{N}_{j}^{(k)} - \frac{\Delta t}{\Delta z} \Delta_{-} \mathbf{g}(\mathbf{N}_{j}^{(k)}, \mathbf{N}_{j+1}^{(k)}) \right) + \eta_{k} \mathbf{N}_{j}^{n}, \quad k = 1, 2, \dots, s - 1,$$

$$\mathbf{N}_{j}^{n+1} \coloneqq \mathbf{N}_{j}^{(s)},$$
(27)

where we introduce the difference operators $\Delta_{-}V_{j} \coloneqq V_{j} - V_{j-1}$ and $\Delta_{+}V_{j} \coloneqq V_{j+1} - V_{j}$ and define $\mathbf{N}_{j}^{0} \coloneqq \mathbf{N}_{0}(z_{j}^{-})$. Here $G(z^{-})$ denotes the limit of a function $G(\xi)$ for $\xi \rightarrow z, \xi < z$. We employ second-order time differencing (s = 2), for which $\eta_{1} = 1/2$. The numerical flux vector **g** appearing in equation (27) is given by

$$\mathbf{g}(\mathbf{N}_{j}^{n},\mathbf{N}_{j+1}^{n}) \coloneqq \frac{1}{2} \Big[\mathbf{F}(z_{j},\mathbf{N}_{j}^{n}) + \mathbf{F}(z_{j+1},\mathbf{N}_{j+1}^{n}) \Big] - \frac{\Delta z}{2\Delta t} \Big[\mathbf{N}_{j+1}^{n} - \mathbf{N}_{j}^{n} \Big].$$
(28)

The second step means solving the ordinary differential equations:

$$\frac{\partial N_i}{\partial t} = \tilde{\beta}_i(\mathbf{N}, \mathbf{v}), \quad i = 1, \dots, M,$$
(29)

where, in order to avoid solutions of the volume fraction above its maximum value by definition, 1, a correction technique is proposed to evaluate the source terms $\beta_i(\mathbf{N}, \mathbf{v})$, i = 1,...,M, which consists of canceling out the birth term when the volume fraction is greater than 1, as follows

$$\tilde{\beta}_{i}(\mathbf{N}, \mathbf{v}) = \begin{cases} \sum_{j=1}^{i-1} \sum_{k=j}^{i-1} C_{jk}^{(i)} \lambda_{jk} N_{j} N_{k} - N_{i} \sum_{j=1}^{M} \lambda_{ij} N_{j} & \text{if } \phi \leq 1, \text{ for } i = 1, \dots, M - 1, \\ -N_{i} \sum_{j=1}^{M} \lambda_{ij} N_{j} & \text{if } \phi > 1, \text{ for } i = 1, \dots, M - 1, \\ \sum_{j=1}^{i-1} \sum_{k=j}^{i-1} C_{jk}^{(i)} \lambda_{jk} N_{j} N_{k} & \text{if } \phi \leq 1, \text{ for } i = M, \\ 0 & \text{if } \phi > 1, \text{ for } i = M. \end{cases}$$
(30)

The proposed numerical scheme for this step is the well-known second-order, two-stage Runge-Kutta method (Le Veque, 1992).

3.3. Calculation of the average velocity of corrective source $q_{corr,M}^n$

The total volume of the dispersed phase is defined as

$$V(t) \coloneqq \int_0^L \phi(z,t) A(z) dz$$

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If A(z) is constant, and replacing $\phi(z, t)$ with $\hat{\phi}(z, t)$, V at time t_n is numerically approximated by

$$V_n = A\Delta z \sum_{j=0}^{J} \left(\sum_{i=1}^{M} N_{i,j}^n v_i \right)$$

The volume of species M, calculated from its number concentration N_M , which deviates from its conservative value, is given by

$$V_{M, \text{ not cons.}}^{n} = A\Delta z \sum_{j=0}^{J} N_{M,j}^{n} v_{M} .$$
(31)

In addition, because the system is closed, we define the conservative volume of species M as the difference between the total initial volume V_0 of the dispersed phase and the sum of the volumes of the species other than species M, i. e.:

$$V_{M, \text{ cons.}}^{n} = V_{0} - A\Delta z \sum_{j=0}^{J} \left(\sum_{i=1}^{M-1} N_{i,j}^{n} v_{i} \right).$$
(32)

It is proposed that the average velocity of corrective source of mass of species M at time t_n be obtained from the difference between its conservative volume and non-conservative volume, divided by the cross-sectional area of the vessel and the time step Δt , namely:

$$\hat{q}_{\text{corr},M}^{n} = \frac{V_{M,\text{ cons.}}^{n} - V_{M,\text{ not cons.}}^{n}}{A\Delta t} = \frac{1}{A\Delta t} \left[V_{0} - A\Delta z \sum_{j=0}^{J} \left(\sum_{i=1}^{M} N_{i,j}^{n} v_{i} \right) \right].$$
(33)

In order to maintain the stability of the numerical method, we limit the value of $\hat{q}_{\text{corr},M}^n$ to the maximum settling velocity of the species, $u_{r,\text{max}}$ (eq. 25), thus:

$$q_{\text{corr},M}^{n} = \begin{cases} \hat{q}_{\text{corr},M}^{n} & \text{if } \hat{q}_{\text{corr},M}^{n} \leq u_{r,\max}, \\ u_{r,\max} & \text{otherwise.} \end{cases}$$
(34)

In all the examples shown here, it is true that $\hat{q}_{corr,M}^n \leq u_{r,max}$, but the definition of a general limit, instead of $u_{r,max}$, remains pending.

Then, the numerical corrective flux density of species M at time t_n is given by $F_{\text{corr},M}^n = q_{\text{corr},M}^n / v_M$, but the numerical corrective flux density of the other species is zero, i. e., $F_{\text{corr},i}^n = 0$, i = 1, ..., M - 1, and the numerical flux density of displacement of drops is the product of the drop number concentration and the displacement velocity: $F_{\text{dis},i}^n = N_i^n q_{\text{corr},M}^n$, i = 1, ..., M.

4. Experimental methodology

The following equipment was required to perform the liquid-liquid gravity separation tests: a $3 \times 100 \times 350$ -mm³ glass cell, a digital camera with a tripod, a desk lamp, a laptop computer, a mixing vessel and a mechanical stirrer. Figure **2** shows the glass cell used to perform the tests.

Commercial-quality vegetable oil and demineralized water were used for the experiments. The appropriate O/W mixture volume for the tests is was defined as 60 ml.



Figure 2: Cell for experimental tests.

For the experimental design, three important parameters were considered for the investigation: stirring speed (2, 3 and 4 Hz), stirring time (10, 20 and 30 s) and percentage of oil (10, 15 and 20%). The selected settings for the model fitting were 3 Hz, 10 s and 20%.

To capture images of the gravity separation process, a Canon EOS Rebel T5 camera with a zoom lens, connected to a laptop computer, was used. At the moment of image capture the sample was illuminated from behind at an angle of approximately 45° by means of a halogen light source, which was diffused through a sheet of white paper to produce a reasonably homogeneous background of adequate intensity. The images were taken at the following times after cessation of agitation: first photo: 12 s and second photo: 32 s.

The images captured during the experiment were analyzed using an own code in the Image Processing Toolbox of Matlab. The code allows the minimum diameter of drops to measure to be selected; for example, the smallest droplets that adhere to the surface of the larger droplets can be disregarded. It is worth mentioning that these analyses were performed for the respective times of each experiment (12 s and 32 s) and their respective duplicates. From this study of images, the variables of interest for the study of liquid-liquid separation were selected: average droplet volume and standard deviation of droplet volume.

In Figure 3 (a) and (b), photographs are of the experiment at 12 s and 32 s, respectively, are shown.



(a)

(b)

Figure 3: Photographs of the experiment: (a) 12 s and (b) 32 s from the cessation of agitation.

Figure 4 presents: (a) the average drop volume and (b) the standard deviation of drop volume, after image processing.



Figure 4: Image processing results: (a) average drop volume and (b) standard deviation of drop volume.

5. Results and Discussion

In all the examples the initial droplet volume distribution, at a specific *z* level, is represented by a lognormal distribution with average droplet volume μ_{vol} and standard deviation of droplet volume σ_{vol} . The representative probability density function is

$$f(x;\mu_{vol},\sigma_{vol}) = \frac{1}{x\sigma_{vol}\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln x - \mu_{vol}}{\sigma_{vol}}\right)^2\right],\tag{31}$$

where *x* is the droplet volume.

The droplet volume is discretized by $v_{i-1/2} = \frac{\pi}{6} d_{i-1/2}^3$, where the diameter is calculated with the exponential formula:

$$d_{i-1/2} = d_{\min} \left[rac{d_{\max,0}}{d_{\min}}
ight]^{rac{i-1}{M_0}}, \quad i = 1, 2, \dots, M+1$$

Here d_{\min} and $d_{\max,0}$ are the minimum and the initial maximum droplet diameters and M_0 is the initial number of species for the simulation, all given in the tables.

We emphasize that the species identified with the letter M (species M) represents the group composed of droplets with volumes greater than $v_{M-1/2}$ plus the corresponding homophase, and the average droplet volume is calculated considering the species that are different from species M.

Furthermore, we assume that the rate of coalescence in the sedimentation zone is negligible compared to that in the dense-packed zone, i.e., we take $K_{c,s} = 0$. This assumption is possible when the sedimenting interface curve, which separates the clear continuous phase zone from the sedimentation zone, has no inflection points (Hartland and Jeelani, 1987). (See Figure 9 (b) of Example 1).

5.1. Model Validation

To validate the model, we compared the results of our model with those of our experiment on gravitational phase separation of an oil-in-water dispersion in a rectangular vessel. The experiment was focused on the movement and coalescence of oil droplets in the dense-packed zone, assuming the coalescence in the sedimentation zone to be negligible. The same hypothesis was also made by Hartland and Jeelani (1987).

To fit the model to data, first, we probed with different values of $K_{c,p}$ until finding one that produced average droplet volume values at time 20 s close to the curve of the quadratic polynomial adjusted to the experimental values. Next, we did

simulations with three values of $K_{c,p}$ near the found value -2.0×10^{-14} , 1.11×10^{-13} and 2.0×10^{-13} (m⁴/s) – and then we calculated the error between each simulated value and the experimental values of the average droplet volume at time 20 s. The errors were calculated with the Euclidian norm or 2-norm, presented in Table **4**.

For the simulations, the initial and total number of droplet species are $M_0 = 14$ and M = 20, respectively. The initial droplet size distribution (23) is a function of depth z, as shown in Table 2. The physical and discretization parameters are given in Tables 1 and 3, respectively.

 Table 1. Physical parameters for examples.

Parameter	Quantity
d_{\min} [mm]	0.500
$d_{\max,0}$ [mm]	2.762
$ ho_{\rm O} [{\rm kg/m^3}]$	920
μ_0 [Pa s]	6.05×10^{-2}
$\phi_{\rm max}$ [-]	1
$ ho_{\rm A} [{\rm kg/m^3}]$	998.0
$\mu_{\rm A}$ [Pa s]	1.002×10^{-3}

Table 2. Initial parameters of droplet size distribution and concentration for the model fitting.

(The variations of the mean and the standard deviation of droplet volume at z are assumed to be continuous).

z (mm)	3.5	7.5	11	13 to 26
$\mu_{vol} [\mathrm{mm}^3]$	4.766	2.080	1.207	1.207
$\sigma_{\rm vol} [\rm mm^3]$	12.372	5.352	1.736	1.736
ϕ_0 [-]	0.651	0.604	0.621	0.360

Table 3. Discretization parameters for the model fitting.

Parameter	Quantity
<i>M</i> [-]	20
<i>M</i> ₀ [-]	14
J [-]	1920

$\Delta z [m]$	2.031×10^{-5}
Δt [s]	2.066×10^{-4}

Table 4. Errors of the simulated values of the average droplet volume at time 20 s.

$K_{\rm c,p}~({\rm m}^4/{\rm s})$	Error in 2-norm
2.00×10^{-14}	4.333×10^{-8}
1.11×10^{-13}	1.682×10^{-8}
2.00×10^{-13}	4.203×10^{-8}

A quadratic polynomial was adjusted to the set of ($K_{c,p}$, Error) points, and its minimum error point was calculated: error = 5.089×10^{-9} . Thus, the optimal $K_{c,p}$, for the given number of species, is 7.73×10^{-14} (m⁴/s).

Figure **5** shows the experimental and simulated average oil droplet volume in the dense-packed zone at time 20 s, and indicates that the model fits the experimental data of the average oil droplet volume curve at time 20 s, which has been obtained by digital image analysis, reasonably well.



Figure 5: Comparison of the average oil droplet volume (of species different from specie *M*) in the dense-packed zone at time 20 s, between the simulation and the quadratic polynomial fitted to the experimental data.

Figure 6 presents the simulated oil volume fraction in the gravity settler after the model fitting and illustrates the accumulation of the dispersed phase near the top of the vessel, as was to be expected, due to its lower density.



Figure 6: Simulated oil volume fraction after the model fitting

Figure 7 presents the simulated volume fraction of species M in the gravity settler after the model fitting, and shows this species (formed by the largest oil drops and oil homophase) filling the upper layer of the vessel, due to its higher weight.



Figure 7: Simulated volume fraction of species M after the model fitting.

Figure **8** shows the comparison between the simulated dispersed phase volume per unit area, as a function of time, by the mathematical model with (conservative) and without the corrective source term (non-conservative). It is observed that the simulated volume without the corrective source declines at a decreasing rate.



Figure 8: Simulated dispersed phase (oil) volume per unit area, as a function of time, by the model with and without the corrective source term.

5.2. Example 1: Effect of the continuity of the dispersion

Here the effect of dispersion continuity on phase separation quality is shown through the study of separation of O/W and W/O dispersions.

The set-up and the physical parameters are the same as in the model fitting. The initial composition of the dispersion is constant throughout the gravity settler for each species. The initial and discretization parameters for both cases are given in Table 5, and the time steps for O/W and W/O dispersions are $\Delta t = 2.119 \times 10^{-4}$ s and $\Delta t = 5.522 \times 10^{-4}$ s, respectively.

Table 5. Initial droplet size distribution, concentration and discretization parameters in Example 1.

z (mm)	0 to 26	Parameter	Quantity
$\mu_{vol} [\mathrm{mm}^3]$	1.207	<i>M</i> [-]	10
$\sigma_{\rm vol}~[{\rm mm}^3]$	1.736	M_0 [-]	7
ϕ_0 [-]	0.5	J [-]	1920
		$\Delta z [m]$	2.031×10^{-5}

Figure **9** presents the simulated dispersed phase volume fraction for different dispersion continuities. It is observed that organic droplets in an aqueous matrix (Figure 9 (a)) settle faster than aqueous droplets in an organic matrix (Figure 9 (b)) due to the lower viscosity of the water in spite of the lower density of the oil; thus, the organic phase is better separated when it is discontinuous than when it is continuous.



Figure 9: Example 1. Simulated volume fraction of the dispersed phase for different dispersion types. Plot (a): aqueous continuity. Plot (b): organic continuity.

Figure **10** presents the simulated dispersed phase average droplet volume for both dispersion continuities. It is observed that the average organic droplet volume in an aqueous matrix (Figure 10 (a)) has a lower maximum than that of aqueous droplets in an organic matrix (Figure 10 (b)). This can be explained by the faster incorporation of the oil droplets into their homophase due to the lower viscosity of the water.



Figure 10: Example 1. Simulated average droplet volume (of species other than specie *M*) for different dispersion types. Plot (a): aqueous continuity. Plot (b): organic continuity.

In this example, it is verified that sedimentation and coalescence are strongly interdependent.

5.3. Example 2: Influence of the coalescence frequency coefficient

In this example, we show the influence of increasing the coalescence frequency coefficient on the behavior of the

numerical solution of our mathematical model through the study of five cases: $K_{c.p.} = 1.0 \times 10^{-13}$, 1.0×10^{-12} , 1.0×10^{-11} and 1.0×10^{-10} (m⁴/s). The set-up and physical properties are the same as in the model fitting. The initial and discretization parameters are given in Table **6**.

z (mm)	0 to 26	Parameter	Quantity
$\mu_{vol} [\mathrm{mm}^3]$	1.207	<i>M</i> [-]	10
$\sigma_{\rm vol} [{\rm mm}^3]$	17.36	M_0 [-]	7
ϕ_0 [-]	0.5	J [-]	480
		Δ <i>z</i> [m]	8.125×10^{-5}
		Δt [m]	4.238×10^{-4}

Table 6. Initial droplet size distribution, concentration and discretization parameters in Example 2.

Figure 11 shows that by increasing the value of $K_{c.p.}$, the maximum simulated average droplet volume of the organic phase increases. This occurs because at higher $K_{c.p.}$, larger droplets are generated faster, before they become species M, which includes the homophase and is deposited at the top (z = 0). Figure 11 also shows that at the top at lower $K_{c.p.}$, larger droplets after the peak slowly begin to grow again.



Figure 11: Example 2. Simulations of average organic phase droplet volume (of species other than specie *M*) for different $K_{c.p.}$: (a) 1.0×10^{-13} , (b) 1.0×10^{-12} , (c) 1.0×10^{-11} and (d) 1.0×10^{-10} (m⁴/s).

Figure 12 shows simulations of organic phase volume fraction for different coalescence frequency coefficients, $K_{c.p.}$, at T = 100 s, a time that seems close to the steady state. It is observed that by increasing the value of $K_{c.p.}$, the simulated organic phase volume fraction at time T = 100 s is practically unaffected. This is the case because for this example we assume that the coalescence in the sedimentation zone is negligible ($K_{c.s.} = 0$) and that the maximal dispersed phase volume fraction is 1 ($\phi_{max} = 1$).



Figure 12: Example 2. Simulations of organic phase volume fraction for different coalescence frequency coefficients, $K_{c.p.}$, at time T = 100 s (near the steady state).

Figure 13 shows simulations of average organic phase droplet volume for different coalescence frequency coefficients, $K_{c.p.}$, at T = 100 s (near the steady state). It is observed that upon increasing the value of $K_{c.p.}$, the simulated average organic phase droplet volume at time T = 100 s, tends to decrease throughout the dense-packed zone and therefore improves phase separation. Again, this occurs because at higher $K_{c.p.}$, larger droplets are generated faster, and then they become species M, which includes the homophase and is deposited at the top (z = 0).



Figure 13: Example 2. Simulations of average organic phase droplet volume (of species different from the specie *M*) for different $K_{c.p.}$, at time T = 100 s (near the steady state).

5.4. Example 3: Effect of the standard deviation of initial droplet volumes

In this example, we use a simulation to show the influence of the standard deviation of the initial organic phase droplet volumes on phase separation quality. We study three cases: $\sigma_{vol} = 0.1736$, 1.736 and 17.36 mm³.

The set-up is the same as in the model fitting. The common physical and discretization parameters are given in Tables 1 and 3, respectively, and the initial parameters are $\mu_{vol} = 1.207 \text{ mm}^3$ and $\phi_0 = 0.5$.

Figure 14 shows simulations of average organic phase droplet volume for three cases of σ_{vol} . It illustrates that the greater the standard deviation of the initial droplet volumes, the lower the maximum average droplet volume. In addition, a higher droplet concentration is observed in the sedimentation zone when the standard deviation is lower.





Figure 14: Example 3. Simulated average droplet volume (of species other than specie *M*) for different standard deviations of the initial droplet volumes. Plot (a): $\sigma_{vol} = 0.1736 \text{ mm}^3$, Plot (b): $\sigma_{vol} = 1.736 \text{ mm}^3$, Plot (c): $\sigma_{vol} = 17.36 \text{ mm}^3$, Plot (d): the three cases at 100 s.

Figure 15 shows simulations of the volume fraction of species M for three cases of σ_{vol} . It illustrates that the greater the standard deviation of the initial organic phase droplet volumes, the faster the formation of species M (including the organic homophase), despite the greater proportion of small droplets. All initial volume distributions are log-normal and have the same initial average volume.



Figure 15: Example 3. Simulated volume fraction of species *M* (including the organic homophase) for different standard deviations of the initial droplet volumes. Plot (a): $\sigma_{vol} = 0.1736 \text{ mm}^3$, Plot (b): $\sigma_{vol} = 1.736 \text{ mm}^3$, Plot (c): $\sigma_{vol} = 17.36 \text{ mm}^3$, Plot (d): the three cases at 100 s.

6. Conclusions

A mathematical model of batch sedimentation and drop coalescence was presented and solved numerically. The model is a population balance model (PBE) with the independent variables time *t*, depth *z* and droplet volume *v*, in the form of an integro-partial differential equation (IPDE). This IPDE was projected onto a system of partial differential equations (PDEs) by discretizing the droplet volume. This was accomplished using the fixed-pivot technique of Kumar and Ramkrishna (1996a), handling any two integral properties associated with population number density such as dispersed phase (droplet) volume fraction and droplet number concentration. Because there is loss of mass in the system when the daughter droplets are greater than the larger species initially considered for the numerical solution, two terms that maintain the mass or total volume of the dispersed phase were incorporated into the PDE system. The model was validated through a comparison with experimental data. The capabilities of the model were illustrated by several numerical examples. In particular, simulations illustrate that: organic droplets in an aqueous matrix settle faster than aqueous droplets in an organic matrix, thus the organic phase is better separated when is discontinuous than when it is continuous; by increasing the value of $K_{c,p}$ the simulated average organic phase droplet volume at a time near steady state tends to decrease throughout the dense-packed zone and therefore improves phase separation; and the greater the standard deviation of the initial organic droplet volumes, the faster the formation of the organic droplet volumes, the faster the formation of the organic droplet volumes, the greater proportion of small droplets.

In a future work, the incorporation of the settling velocity in the dense-packed zone will be incorporated and a less diffusive numerical scheme for the sedimentation (second-order) will be implemented.

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Appendix A: Error Study

We recorded an approximate error defined with respect to a reference solution in order to evaluate the performance of the scheme. We introduced an approximate error, denoted as e_1 , which is defined by

$$e_1 \coloneqq \Delta z \Delta t \sum_{j=J_{\mathrm{L}}}^{J_{\mathrm{R}}} \sum_{k=0}^{m-1} \sum_{n=0}^{N} \left| \phi_j^{mn+k} - \phi_j^n \right|,$$

where $\tilde{\phi}_{j}^{\tilde{n}}$ and ϕ_{j}^{n} are the reference solution at $t = t_{\tilde{n}}$ and the approximate solution at $t = t_{n}$, respectively, of the dispersed phase volume fraction, both at $z = z_{j}$; *m* is the nearest integer of the value of the division between Δt of the approximate solution and that of the reference solution; J_{L} and J_{R} are the indices of the positions between which we calculate the numerical approximation errors; Δt is the temporal discretization parameter of the reference solution and Δz is the common spatial discretization parameter. The reference solution was calculated with M = 160, $M_{0} = 112$ and $\Delta t = 2.011 \times 10^{-4}$ s. The spatial discretization parameter is $\Delta z = 2.031 \times 10^{-5}$ m. The common physical and initial parameters are given in Tables 1 and A.1.

Table A.1. Initial parameters of droplet size distribution and concentration of Example 2.

(The variations of the mean and the standard deviation of the volume of dropiets in 2 are supposed to be continuous	(The	e variations	of the mean	and the standa	rd deviation of	the volume	of droplets	in z are sup	posed to b	be continuous)
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z (mm)	3.5	7.5	11	13 to 26
$\mu_{vol} [\mathrm{mm}^3]$	4.766	2.080	1.207	
$\sigma_{\rm vol}~[{\rm mm}^3]$	12.372	5.352	1.736	
ϕ_0 [-]	0.99	0.99	0.99	0

Figure A.1 presents the simulated dispersed phase volume fraction, at time T = 20 s, for different total numbers of species. It shows that the simulated organic phase volume fraction at time T = 20 s is practically unaffected, as the initial condition of the dispersed phase volume fraction is near the steady state.



Figure A.1: Simulated dispersed phase volume fraction at time T = 20 s, for different numbers of species.

Figure A.2 presents the simulated average droplet volume, at time T = 20 s, for different total numbers of species. It is seen that simulations with a smaller number of species result in a more rapid formation of the largest species. This occurs because if there is a smaller number of species, the larger species have a larger range of droplet sizes and, therefore, grow faster.



Figure A.2: Simulated dispersed phase average droplet volume (of species different from the species M) at time T = 20 s, for different numbers of species.

Figure A.3 presents the approximate error of the simulated dispersed phase volume fraction for different total numbers of species.



Figure A.3: Approximate error of the simulated dispersed phase volume fraction in relation to the reference solution calculated with 160 species.

Figures A.1, A.2 and A.3 illustrate that the sequence of numerical solutions produced by the numerical scheme converge toward the reference solution.

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