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CFD Modelling of Mass Transfer and Interfacial Phenomena on Single Droplets

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Abstract

In this work, mass transfer from a single spherical droplet to a surrounding continuous liquid phase is modelled and simulated based on a commercial Computational Fluid Dynamics (CFD) software package. The model takes into consideration the droplet size change caused by mass transfer. This is realised using moving grids to readjust the actual position of the phase interface. Furthermore, Marangoni convection due to mass transfer is accounted for by extended interfacial boundary conditions considering surface tension effects. The calculated results are compared with experimental data and good agreement between them is established.

Keywords: CFD, liquid-liquid extraction, Marangoni convection, moving boundaries

1. Introduction

Liquid-liquid extraction has found a wide application as a reliable and efficient method for numerous industrial applications. However, several process phenomena are not yet fully understood, which makes the design of extraction units difficult and requires additional expensive pilot plant experiments. To improve process understanding, it is necessary to consider the phenomena at the smallest representative scale. For most extraction operations, this scale is a single droplet and its surface. Mass transfer of one or more components between the droplet and the surrounding phase, droplet size change due to mass transfer and the onset of Marangoni convection – all these interdependent phenomena have significant influence on extraction processes. The term Marangoni convection generally encompasses phenomena caused by surface tension gradients at fluid interfaces. These gradients lead to enhanced mixing of fluid elements near the interface and thus may accelerate mass transfer considerably (Sawistowski, 1974). It is very difficult to investigate this complex interplay of phenomena experimentally, and thus, rigorous theoretical methods are necessary to understand and describe liquid-liquid extraction processes properly. In this respect, Computational Fluid Dynamics (CFD) allowing the numerical simulation of complex fluid flow patterns inside and outside single droplets represent a powerful method for the description of transport and interfacial phenomena.

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Some first theoretical models describing mass transfer at a single droplet are based on simplifying assumptions and analytical solution methods, e.g. the well known work of Kronig and Brink (1950). However, the complexity of the observed phenomena require development of more sophisticated approaches. Recently, Piarah et al. (2001), Waheed (2001) and Petera et al. (2001) have modelled mass transfer of one component from a single droplet to a continuous liquid phase based on CFD methods. In contrast to Piarah et al. (2001) and Waheed (2001), Petera et al. (2001) considered droplet shape changes due to hydrodynamic phenomena, however changes in droplet size related to mass transfer have been neglected in all these works.

In our study, the Moving Grid method (Ferziger and Peric, 1993), a typical front tracking technique, is applied to simulate the motion of the phase interface due to mass transfer. This method provides both mass conservation during simulations and the exact localisation of the interface which is necessary when complex coupled boundary conditions have to be implemented. In literature, some simulations of droplet deformation by tracking the interface with moving grids can be found (e.g. Christini et al., 2001, Dai et al., 2002). In these works, again, only droplet shape change caused by hydrodynamic phenomena is considered, whereas mass transfer effects are not included.

Our work aims at a detailed description of mass transfer phenomena at a single droplet with moving boundaries. The relevant model is developed and used for simulations to yield concentration profiles for laminar flow inside and outside the droplet. The model is validated using experimental data of Henschke and Pfennig (1999) and Dittmar (2003).

2. Model formulation and implementation

The interactions in the dynamic two-phase system studied are manifold. Momentum and mass transfer phenomena in each phase are coupled by the relevant fluid velocity distributions. Diffusional interactions of different components result in a coupled system of mass transfer equations which should be solved simultaneously. In addition, the variables of the two liquid phases are conjugated in a complex way at the droplet interface. Finally, the droplet changes its size due to mass transfer, and thus, a moving boundary arises. For an accurate description of liquid-liquid extraction processes, all these coupling effects should be properly taken into account.

The following assumptions are imposed on the process considered:

- Newtonian fluids
- Incompressible flow
- Isothermal system
- No mass transfer the two carrier fluids across the phase interface (mutual saturation)
- Laminar flow of both phases
- Absence of surface active contaminants
- No chemical reactions in the system

The process can then be described by the following equation set.

Model equations for each phase:

Continuity and momentum equation

$$\nabla \cdot \mathbf{u} = 0 \tag{1}$$

$$\rho\left[\frac{\partial \mathbf{u}}{\partial t}+\mathbf{u}\cdot\nabla\mathbf{u}\right]=-\nabla p+\mu\Delta\mathbf{u} \tag{2}$$

Mass transfer equation for a multicomponent system

$$\frac{\partial(\mathbf{C})}{\partial t}+\mathbf{u}\cdot\nabla(\mathbf{C})=\nabla\left([\boldsymbol{D}]\nabla(\mathbf{C})\right) \tag{3}$$

Boundary conditions at the droplet surface
Normal and shear stress

$$\left(p-2\mu\frac{\partial u_r}{\partial r}\right)_p-\left(p-2\mu\frac{\partial u_r}{\partial r}\right)=\frac{2\sigma}{R(t)} \tag{4}$$

$$\mu_p\left[r\frac{\partial}{\partial r}\left(\frac{u_\theta}{r}\right)+\frac{1}{r}\frac{\partial u_r}{\partial\theta}\right]_p-\mu\left[r\frac{\partial}{\partial r}\left(\frac{u_\theta}{r}\right)+\frac{1}{r}\frac{\partial u_r}{\partial\theta}\right]=\frac{1}{R(t)}\frac{d\sigma}{d\theta} \tag{5}$$

Normal and tangential velocity

$$u_{r,p}=u_r \tag{6}$$

$$u_{\theta,p}=u_\theta \tag{7}$$

Thermodynamic equilibrium

$$(\mathbf{C})_p=[\boldsymbol{M}](\mathbf{C}) \tag{8}$$

Component fluxes

$$\left[\boldsymbol{D}_p\right]\frac{\partial(\mathbf{C})_p}{\partial r}+(\mathbf{C})_p\cdot\mathbf{u}_p=[\boldsymbol{D}]\frac{\partial(\mathbf{C})}{\partial r}+(\mathbf{C})\cdot\mathbf{u} \tag{9}$$

Transient change of the droplet radius

$$R(t+dt)=\sqrt[3]{R(t)^3-\frac{3dt}{4\pi}\cdot\sum_{i=1}^{m}\left(\frac{M_i}{\rho_i}\int_A(J_i)\,dA\right)} \tag{10}$$

Here, $\mathbf{u}$ is velocity, ($\mathbf{C}$) is concentration vector; ρ is density, μ viscosity and σ surface tension in the given system; p is the system pressure, t is time, whereas [$\boldsymbol{D}$] and [$\boldsymbol{M}$] represent the matrix of diffusion and distribution coefficients, respectively. R is the droplet radius, whereas r and θ are cylindrical coordinates. The subscript p stands for the droplet phase. In equation (10), M_i is the molar mass and J_i is the molar flux of the component i, respectively.

The model is complemented by additional boundary conditions at the symmetry axis. For the continuous phase far away from the droplet, constant velocities and concentrations are specified. Initially, for the velocity and concentration fields in both phases, constant values are assumed.

The system of partial differential equations together with initial and boundary conditions cannot be solved analytically and require a numerical solution technique. The

principle of numerical fluid mechanics is based on the discretisation of the derivatives of Navier-Stokes and mass transfer equations in respect to time and space. In this work, the commercial CFD tool CFX4.3 (Ansys Inc.) is used for the model implementation. A droplet surrounded by a laminar liquid flow is studied. Because of the flow conditions and the initial droplet diameter of about two millimetres the problem can be considered as axisymmetric. Due to this assumption, the system can be modelled as a two-dimensional one which reduces computational expense significantly (Figure 1).

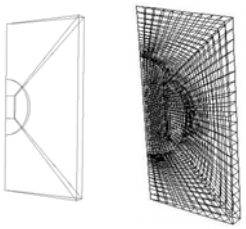

Figure 1. Multi-block geometry of the system without (left) and with body-fitted grids (right)

Interfacial boundary conditions are implemented in CFX4.3 via Fortran subroutines. This permits an extension or replacement of standard boundary conditions available in CFX4.3. The system geometry is represented as seven blocks to enable reasonable meshing of the system with structured grids. For the grid generation, body-fitted grids are used to account for the spherical shape of the droplet. The structure of the chosen finite volume grid is shown in Figure 1 with a lowered number of grid cells to ensure good visualisation. For numerical simulations, the geometrical system is meshed with 25,000 grid cells. This guarantees that the simulation results are independent of the number of cells.

3. Results

To allow for a change in droplet size due to mass transfer, the component flow across the droplet surface should be calculated. Based on the mass flow for each time step, the volume and radius change of the droplet with time can be estimated (eq.(10)). The system grid is then shifted according to the radius change to localise the new position of the phase interface.

Figure 2. Droplet in experimental setup (Dittmar, 2003)

Experimental data provided by Dittmar (2003) are used for validation of this model. In Dittmar (2003), single water droplets attached to a capillary were studied (Figure 2). The droplets were pressed through the capillary into a continuous toluene phase with zero fluid velocity. The size change of the droplet due to mass transfer from the toluene phase ($w_0 = 0.07$) to the droplet was analysed. It is assumed that the droplet has already been enriched with acetone during the droplet formation and the initial acetone

concentration in the droplet is set to 0.02. Fluid motion of the toluene phase due to the droplet formation is accounted for by assuming Re = 0.7 in the given system. The comparison in Figure 3 shows a very good agreement between experimental and simulated results. The small discrepancy between the calculated and measured final values can be explained by the model assumption of a spherical droplet. In the experiments, the droplet is attached to a capillary (Figure 2), and this position results in a deviation from the spherical shape with increasing volume which is not matched by the model.

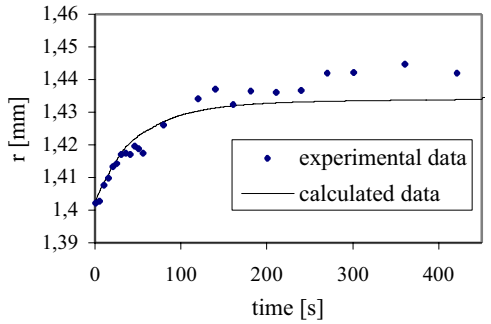

Figure 3. Change in droplet radius - simulated and experimental data (Dittmar, 2003)

For the model validation regarding the mass transfer to a freely moving droplet undergoing to Marangoni convection, experimental data of Henschke and Pfennig (1999) are used, who studied the mass transfer of acetone from a continuous aqueous phase to a butyl acetate droplet. To account for Marangoni phenomena, the surface tension gradient due to mass transfer of acetone is implemented in equation (5) using a correlation derived from experiments (Misek et al., 1985). Figure 4 shows the results of the model validation. Evidently, the experimental mass transfer rate is significantly higher than the rate calculated using the analytical approach of Kronig and Brink (1950). This can be explained with the limitations of the analytical model. It was found experimentally that the model of Kronig and Brink (1950) gives reasonable results for Reynolds numbers smaller than 200 (Brounshtein et al., 1970), whereas the Reynolds number in the experimental studies of Henschke and Pfennig (1999) exceeds this value noticeably. The agreement between the experimental data and our model is much better. Only in the first 20 seconds, the simulated mass transfer rate is slightly lower than the experimental rate. In Figure 4 it can also be seen that the account of Marangoni phenomena improves the agreement. This improvement is about 30%, as in this system, with its high fluid velocities, the onset of Marangoni convection at the interface is at least partly suppressed. Deviations may be explained by effects typical for short residence times in the measuring cell, e.g. mass transfer during drop formation and coalescence. Overall, it can be stated that a fairly good agreement between experimental and simulated data is obtained.

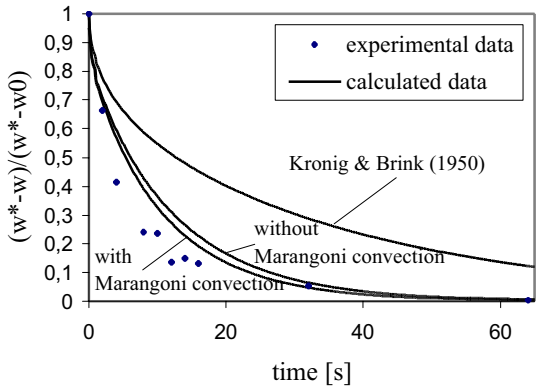

Figure 4. Simulations and experimental results of Henschke and Pfennig (1999) (w - mass fraction; w - mass fraction at $t \rightarrow \infty$; w0 - mass fraction at t=0)*

4. Conclusions

In this work, a new CFD model describing mass transfer to and from single droplets with moving boundaries in liquid-liquid extraction is developed. The evolution in droplet size with time is captured by the Moving Grid method. Additionally, the onset of Marangoni convection due to multicomponent mass transfer is considered. The comparison between simulated and experimental data demonstrates their good agreement.

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