Interfacial Instabilities During Interphase Mass Transfer of Propionic Acid

Fettar Leila[1], Bekkouche Samia[1,*], Kadja Mahfoud[1], Lachi Mohammed[2]

[1] Applied Energetic and Pollution Laboratory Department of Mechanical Engineering University Frères Mentouri Constantine 1, Algeria
[2] Materials and Mechanical Engineering Laboratory, Faculty of Exact and Natural Sciences, University of Reims Champagne Ardenne, Reims, France

ARTICLE INFO	ABSTRACT
	We present a numerical study of the transient two-dimensional solutal Marangoni convection which occurs at the interface of a two isothermal layers' system made of two immiscible liquids. The solute is propionic acid and is transferred through the interface from the organic phase to the aqueous phase under gravity condition. The unsteady state of this interfacial convection problem is mathematically described by the Navier-Stokes and solute mass transfer equations in both phases. The Hele Shaw approximation was incorporated in these equations and the resulting equations were solved using the COMSOL Multiphysics software. The latter is based on the finite elements' method. The results obtained are in good agreement with the experiments and suggest that the mass transfer rate is stronger when the acid diffusion and the instability occur together.

1. Introduction

Mass transfer refers to the net movement of substances from one location to another. When mass is transported from one phase to another, we call this process interphase mass transfer. Many physical situations occur in nature where two phases are in contact and the phases are separated by an interface. The Marangoni effect is a small-scale flow driven by local inhomogeneities of interfacial tension, either caused by temperature (thermocapillary flow) or concentration gradients (solute capillary flow) [1]. It plays a crucial role in interfacial flows where mass transfer processes occur accompanied by interfacial instabilities. In such flows, the Marangoni effect alters the hydrodynamic behavior of the liquid layers near the interface.

The Marangoni effect underlies many natural and technological applications in a wide variety of fields such as geology, hydrometallurgy, pharmacy, petro chemistry, food engineering, wastewater treatment and many other processes [2]. It is for these reasons that this phenomenon has received considerable attention from a large number of researchers.

In that respect, there is a vast literature studying the influence of interfacial tension on interphase mass transfer processes. In 1855, Thompson observed convective patterns in drops at an alcohol-

* *Corresponding author.*
E-mail address: samix21000@yahoo.fr

water interface and suggested that they were caused by surface tension-driven flows [3,4]. The credit for identifying this effect has been given to Carlo Marangoni in 1871, who was able to explain the effect in terms of fluid flows and surface tension variations. In 1953, Lewis and Pratt [5] described violent spontaneous movements of the liquid-liquid interface which they observed during measurements of interfacial tension in the presence of mass transfer by the drop-weight method [5,6]. A detailed quantitative theory study on the solutal Marangoni convection by the solute transfer through a planar liquid interface was produced for the first time by Sternling and Scriven [7,8] in 1957. They carried out the classical linear instability analysis. Several previous studies and many efforts have been conducted to elucidate the convective structures during mass transfer [9-15]. In most cases, they are studied under Sternling-Scriven conditions. However, there are many situations where convection occurs even though these conditions are not satisfied.

In this work, it should be noted that changes in the interfacial tension occur solely due to changes in the interfacial composition. The assumption of isothermal conditions was given credibility by Heines and Westwater's work in 1972, in which they demonstrated that heat effects in ternary systems were not powerful enough to generate fluctuations in interfacial tension that led to Marangoni convection [4]. Therefore, convective structures appear under solute transfer in systems with a liquid-liquid interface [16]. Here we aim, by using a finite element analysis solver (COMSOL Multiphysics), to demonstrate numerically the Marangoni impact during mass transfer between two immiscible liquids inside a Hele-Shaw cell. The studied system is the transfer of propionic acid between isobutyl alcohol and water. We recall that we are going to study the transfer of the acid from the organic phase to the aqueous phase, considering both stable and unstable cases, so we are going to take into account two directions: in the first case, the transfer is downward, while in the second case, it is upward.

2. Methodology
2.1 System Under Study

The configuration to be studied is shown in Figure 1. We aim to study the Marangoni solutal convection which occurs at the interface, considered flat and non-deformable, between two superposed immiscible liquids (water and isobutyl alcohol). The two liquids are confined in a Hele-Shaw cell composed of two parallel solid plates. The cell has an aspect ratio H/L = 0.5. We recall here that the organic phase (isobutyl alcohol) and the aqueous one (water) are in equilibrium due to mutual saturation. The only transfer that occurs is the diffusion of propionic acid which is dissolved in the organic phase placed above the aqueous phase in the first case and below the water in the second case.
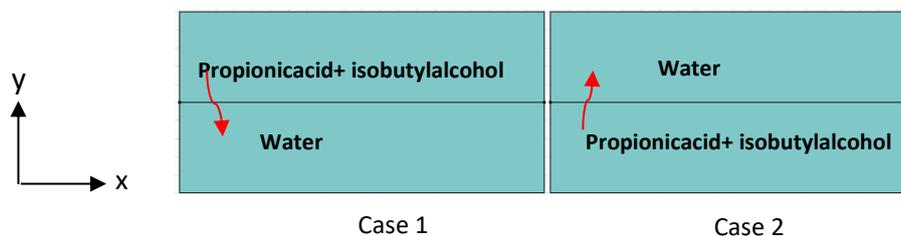
Fig. 1. Schematic of the system under study

2.2 Mathematical Formulation

In the present work, the flow is considered to be two-dimensional, laminar and isothermal. The flowing liquids are assumed immiscible and incompressible with constant properties except for the density in the buoyancy term, which is given by

$$\rho = \rho_0\big(1 - \beta(C - C_0)\big) \tag{1}$$

where ρ_0 is the reference density, C is the solute concentration, C_0 is the initial concentration and β is the solutal expansion coefficient.

By taking into account the Hele-Shaw approximation for velocity (the approximation assumes that the flow velocity profile in the y direction is parabolic throughout the gap), the governing equations for continuity, momentum and mass, may be written in vectorial form as follows

$$\rho \nabla . U = 0 \tag{2}$$

$$\rho \frac{\partial U}{\partial t} + \rho(U.\nabla)U = \nabla[-PI + \mu(\nabla U + (\nabla U^T)] - 12\left(\mu \frac{U}{d^2}\right) + F \tag{3}$$

$$\rho \frac{\partial C}{\partial t} + U.\nabla C = \nabla.(D\nabla C) \tag{4}$$

Where t is the time, U, P and "I" are the flow velocity vector, the pressure and the identity tensor respectively. F is the body acceleration due to gravity g. The parameters D, and ρ are the fluid solutal diffusion coefficient and the density, respectively. "T" stands for "transpose".

The initial conditions for solving Eq. (2) to Eq. (4) are

For case 1:

$$C_0 = 0 \ [mol/l] \ \text{for} \ 0 \le x \le L, \ 0 \le y \le H/2, \ C = C_0. \tag{5}$$

$$C_0 = 0.6 \ [mol/l] \ \text{for} \ 0 \le x \le L, \ H/2 \le y \le H, \ C = C_0. \tag{6}$$

For case 2:

$$C_0 = 0.6 \ [mol/l] \ \text{for} \ 0 \le x \le L, \ 0 \le y \le H/2, \ C = C_0. \tag{7}$$

$$C_0 = 0 \ [mol/l] \ \text{for} \ 0 \le x \le L, \ H/2 \le y \le H, \ C = C_0. \tag{8}$$

And the boundary conditions of the problem are as follows

Impermeable solid walls (x= 0, x = L, y= 0 and y = H)

$$u = v = 0 \ \text{and} \ \frac{\partial C}{\partial x} = 0 \text{for } 0 \le x \le L \text{ and } y = \frac{H}{2} \tag{9}$$

The flow in both phases is coupled via the shear-stress-surface tension balance [17,18]

$$\frac{\partial \sigma}{\partial x} = \mu_{aq} \frac{\partial v_{aq}}{\partial y} - \mu_{org} \frac{\partial v_{org}}{\partial y} \tag{10}$$

and it is assumed that the excess concentration of the interface is related to the interfacial tension σby a linear relationship, which leads to [19]

$$\sigma = \sigma_{ref} + \sigma_{ref}.C \tag{11}$$

At the interface the normal velocity components vanish and we impose the continuity of the acid concentration, of the U velocity component and of the acid mass fluxes

$$v_{aq} = v_{org} = 0 \tag{12}$$

$$C_{acid\ in\ aq} = C_{acid\ in\ org} \tag{13}$$

$$u_{aq} = u_{org} \tag{14}$$

$$D_{acidinaq} \frac{\partial C_{aq}}{\partial y} = D_{acidinorg} \frac{\partial C_{org}}{\partial y} \tag{15}$$

3. Numerical Simulation and Discussion
3.1 Considering the Shear Stress at the Interface ($\tau \neq 0$)
3.1.1 Temporal evolution of the instability

Case 1 (Mass transfer downwards)

The transfer of solutes in a liquid-liquid system changes the concentration of these liquids and can induce a gradient of interfacial tension between them by changing the density of a solution.

Figure 2 shows a series of simulation states at different times after the onset of instability; it shows the temporal evolution of the instability defined by streamlines at different times. Soon after contact, the acid enters the aqueous solution, and after a few seconds ($\approx$10e-^{7}s), movements are obtained in the interface in both phases. In fact due to its diffuvity($D_{acid\ in\ org} \cong D_{acid\ in\ aq}$) and because it is less viscous in water($\frac{\mu_{aq}}{\mu_{org}} < 1$) the acid moves towards the lower phase which makes the fluid layers of the organic phase which are close to the interface, poor in acid and creates a concentration gradient (Figure 3 and Figure 4) which in turn generates a surface tension gradient (Figure 5). The decrease in surface tension drives the interface flow and creates small-scale circulating eddy cells on either side of the interface; this is called Marangoni convection and confirms the findings of several authors who have worked in this area [5,14]. In the upper phase, the fluid layers far from the interface are now richer in acid compared to the lower layers. This change in concentration creates large-scale cells directed from the bottom to the top of the Hele-Shaw cell, as shown in Figure 2 with the red velocity vectors, and as time passes, they become two large counter-rotating cells (solutal convection). This phenomenon is also observed in the aqueous phase, but in the opposite direction, because the upper fluid layers are now richer in acid.
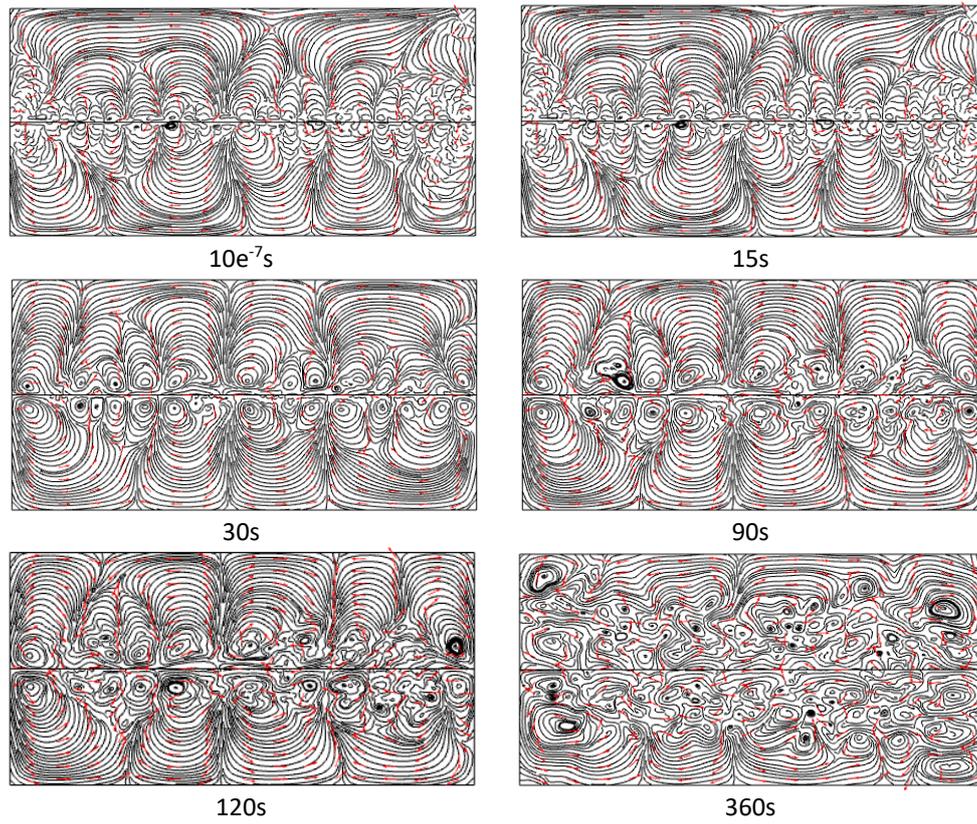
Fig. 2. Temporal evolution of the instability in the Hele Shaw cell (case 1)
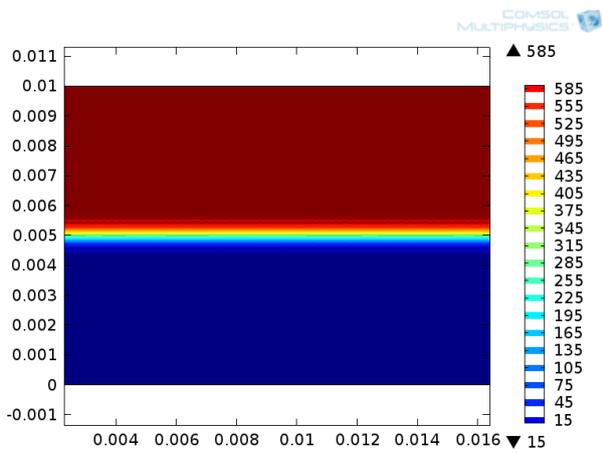
Fig. 3. Concentration disribution in the Hele Shaw Cell(C_o=0.6[g/l])

Fig. 4. Temporal evolution of the concentration at a point in the interface (C_o=0.6[g/l])
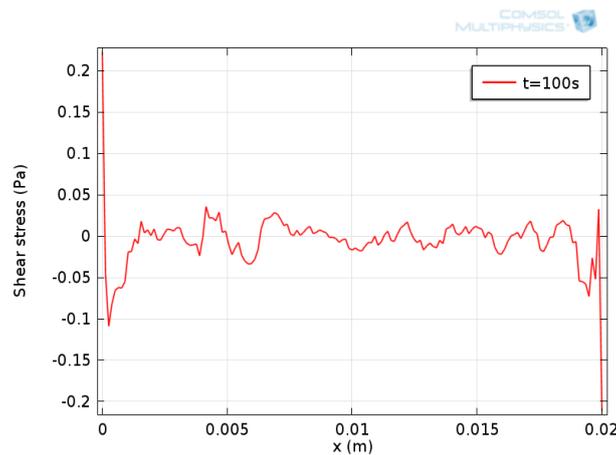
Fig. 5. Variation of the shear stress along the interface (Case 1)

Case 2 (mass transfer upwards)

When the mass transfer is upward, we see the same trends as in case 1: small scale roll cells of 1 mm length appear on both sides close to the interface, but after 120 seconds, each of the two sides becomes unstable and those cells disappear, leaving erratic shapes (Figure 6).
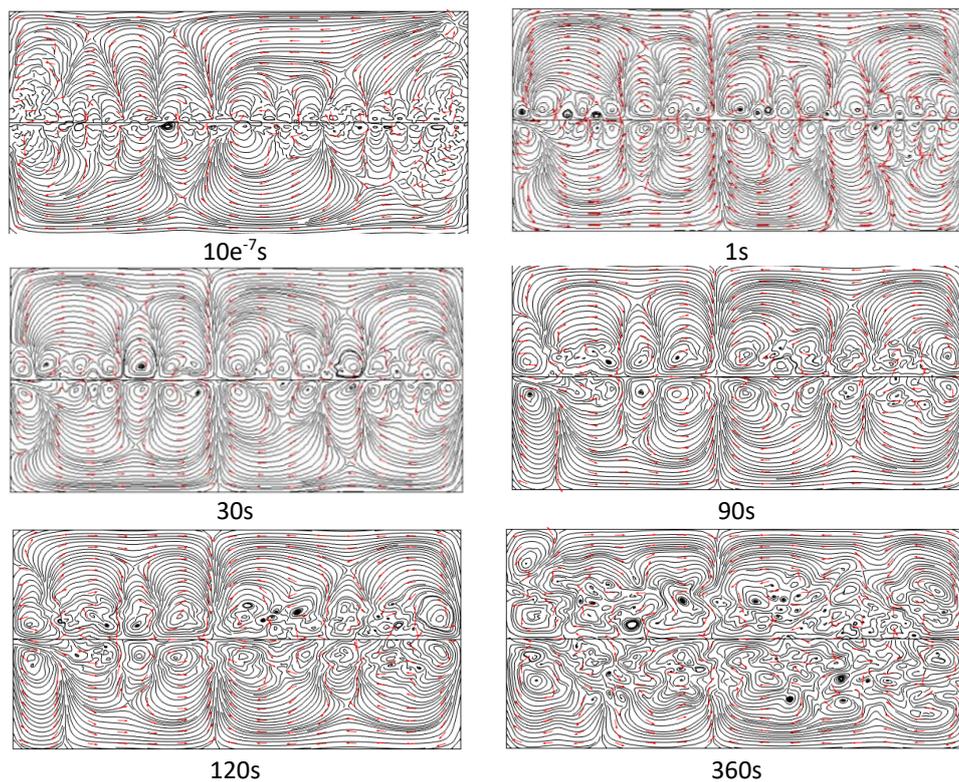
Fig. 6. Temporal evolution of the instability (Case 2)

3.1.2 Dynamic field

Figure 7 depicts the magnitude and variation of the velocity components at three points in the Hele Shaw cell "1, 2, and 3". The coordinates of point 1 are: $(x_1=0.01, y_1=0.005)$, those of point 2 are: $(x_2=0.017, y_2=0.007)$ and those of point 3 are $(x_3=0.004, y_3=0.004)$. The initial concentration of

propionic acid is 0.6 g/l. It can be seen that the horizontal component has a higher order of magnitude than the vertical component, indicating that the movement is caused by changes in interfacial tension. In fact, surface tension gradients induce liquids to flow from low to high tension regions due to the greater force generated by a concentration gradient (Figure 8, Figure 9, and Figure 10). The value of the horizontal velocity varies with the position of the point under consideration.
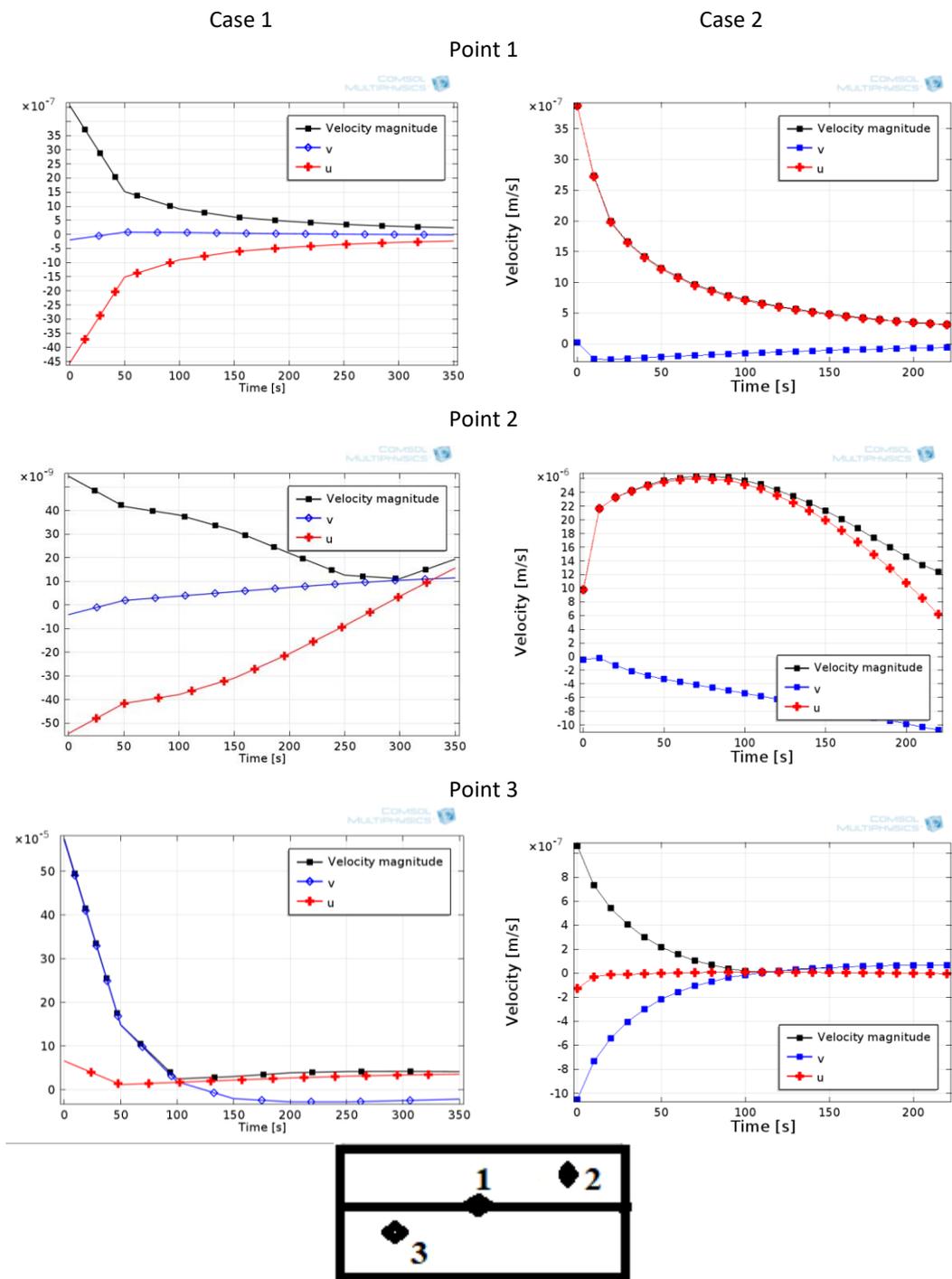
Fig. 7. Temporal evolution of velocity at three points in the Hele Shaw Cell
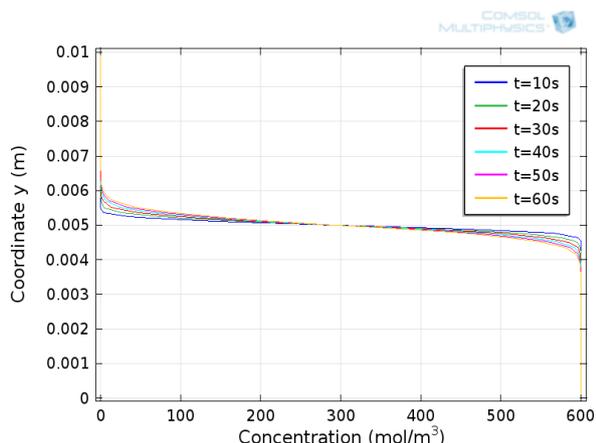
Fig. 8. Concentration profile at vertical midline of the hele shaw cell (case 2; C_o=0.6[g/l])
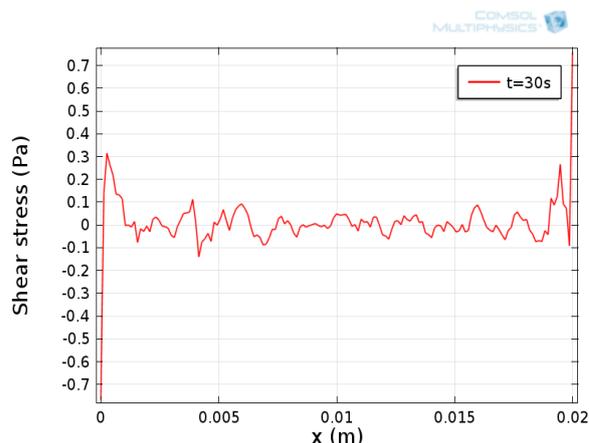
Fig. 9. Variation of shear stress along the interface (case 2)
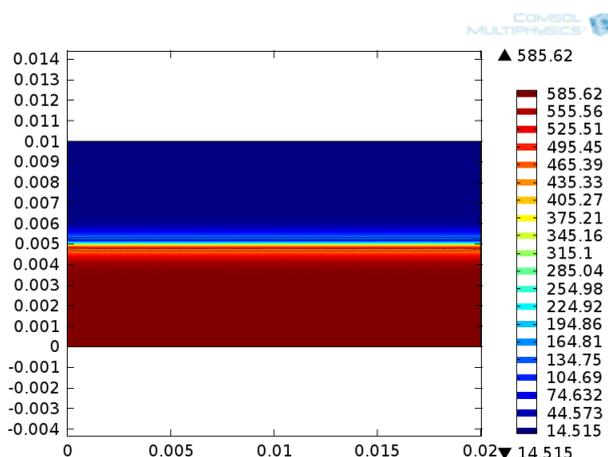
Fig. 10. Concentration distribution in the Hele Shaw cell (t= $1.e^{-6}$ s, case 2)

3.2 Neglecting the Shear Stress at the Interface ($\tau = 0$)

To investigate the effect of surface tension on the instability induced in the Hele Shaw's cell by propionic acid's diffusion, we omitted the surface tension at the interface and ran a series of simulations that depicted the progression of instability over the first few minutes. Figure 11 illustrates a different behavior than the first case (Figure 2 and Figure 6); large-scale cells appear in both phases, indicating the generation of solutal convection due to gravity and acid diffusion, but at the interface, the small convection fingers disappear and irregularly shaped convective cells arise on both sides of the interface.

Case 1

1s

40s

60s   120s

360s

Case 2

1s   10s

60s   120s

360s
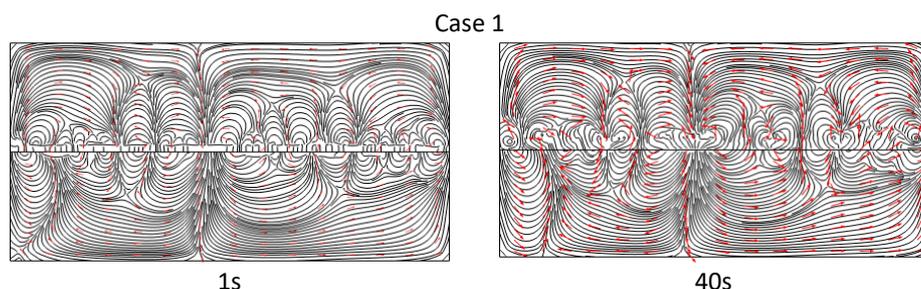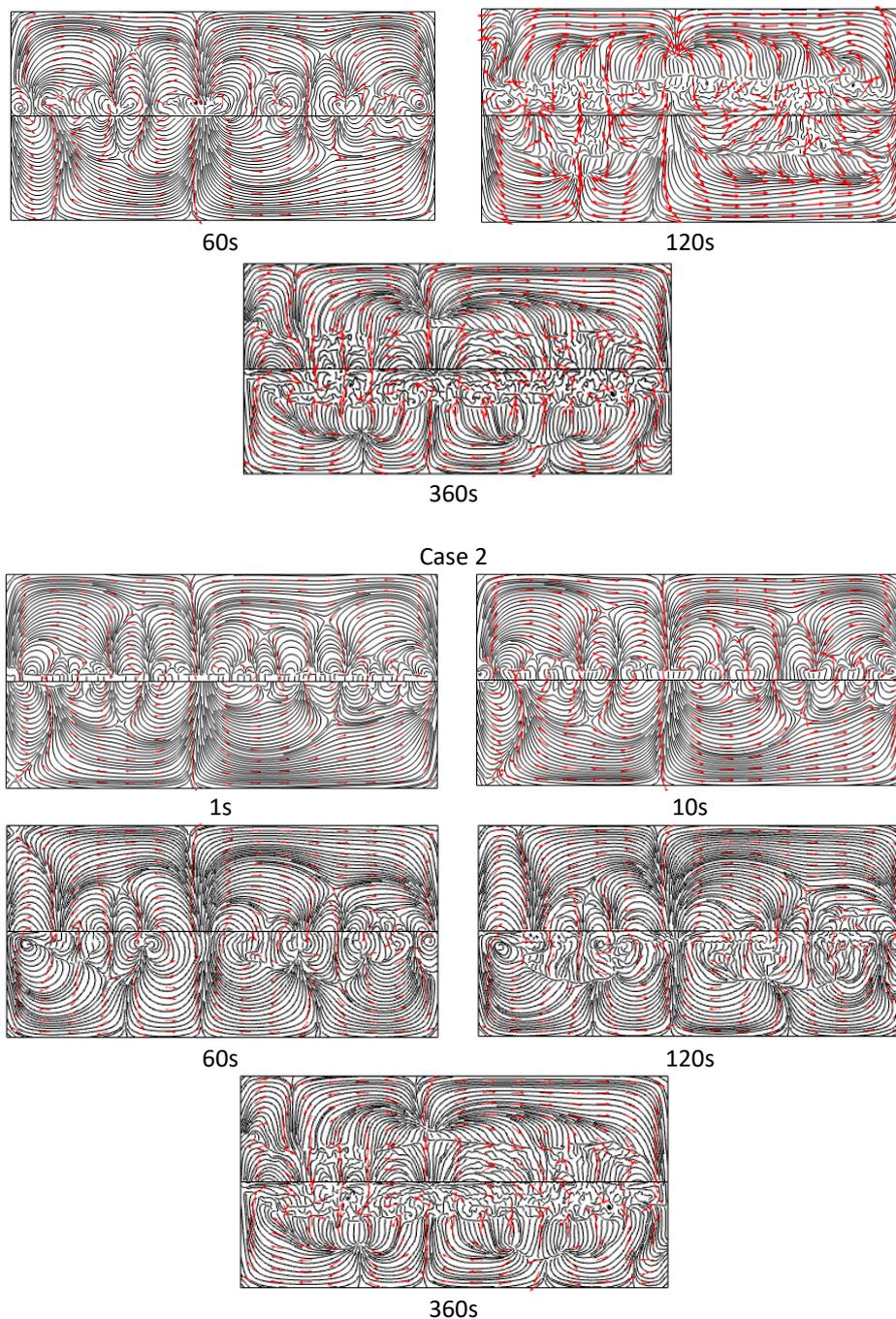
Fig. 11. Temporal evolution of the instability omitting shear stress

3.3 Interphase Mass Transfer Coefficient

The mass transfer efficiency of propionic acid can be estimated by the coefficient of mass transfer. Figure 12 depicts the time evolution of the average mass transfer coefficient of propionic acid along the interface. The decreasing shape of the curve leads us to presume that the transfer of acid was rapid at first but slowed after 120 seconds, explaining why convective cells vanished on both sides of the interface (Figure 2 and Figure 6).
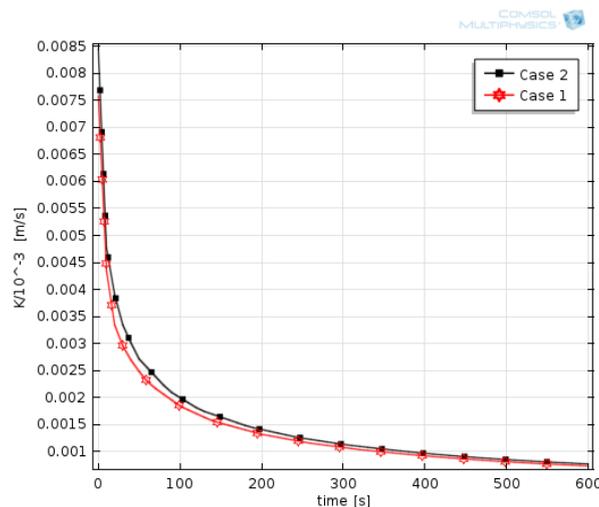
Fig. 12. Temporal development of the interphase mass transfer coefficient along the interface

4. Conclusions

This work presents a numerical simulation of the Marangoni effect at the interface between two immiscible isothermal layers filling a Hele-Shaw cell oriented vertically in the gravity field, and like many authors, this study allowed us to accurately depict the interfacial processes [20-24]. The linear relationship of the interfacial tension versus the solute concentration was incorporated into a mathematical model accounting for liquid flow and mass transfer in both phases to better understand the regularity of this phenomenon generated by surface tension sensitivity to the surface concentration of the transferred solute. Our findings from this work are as follows

i. The interfacial tension varies due to acid diffusion, which induces the Marangoni effect at the interface. The movement of the liquid interface transfers momentum to the adjacent bulk liquid, which carries itself and any solutes within it to a new location that finally appears as roll cells.
ii. The Marangoni instability works only for a brief period.
iii. When propionic acid diffusion and interfacial convection occur together, mass transfer becomes a much faster process [25].

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