MATHEMATICAL ANALYSIS OF SOME DIFFUSION PROBLEMS ASSOCIATED TO THE MODELING OF SURFACTANT COMPOUNDS AT THE AIR-WATER INTERFACE

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MATHEMATICAL ANALYSIS OF SOME DIFFUSION PROBLEMS ASSOCIATED TO THE MODELING OF SURFACTANT COMPOUNDS AT THE AIR-WATER INTERFACE

fue realizada bajo su dirección por Doña Cristina Núñez García, estimando que la interesada se encuentra en condiciones de optar al grado de Doctor en Ciencias Matemáticas, por lo que solicitan que sea admitida a trámite para su lectura y defensa pública.

En Santiago de Compostela, a 30 de Septiembre de 2013.

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A mis padres,
Antonio y Elena.

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Contents

Introduction

A surfactant is a chemical compound with molecules having both a hydrophobic part and a hydrophilic part, this structure being the responsible for the surfactant behavior in a solution. When a new surface is formed in a surfactant solution, surfactant molecules tend to migrate from the bulk of the solution to the surface and, in doing so, this process varies the surface properties, one of the most important being the *dynamic surface tension*. For a plane surface, which is the situation considered in this work, the surface tension is the force that acts along a unit of length, parallel to the surface (see [14]). This force is a consequence of the inward attraction, normal to the surface, to which surface molecules are subject, due to the fact that the molecules situated at the surface have less neighbor molecules to establish intermolecular interactions than the molecules of the bulk of the solution (see [1]). The incorporation of surfactant molecules to the surface breaks the intermolecular interactions between the surface molecules and their neighbors, and hence, the surface tension of the solution is drastically reduced. The variation of the surface tension does not occur instantaneously, that is to say, its equilibrium value is reached after a certain period of time depending on the particular molecular dynamics.

Indeed, the dynamics of this process may vary depending on the type of surfactant, its concentration, its temperature, its salinity, etc, and it is closely related to the transport of molecules from the bulk of the solution to the surface. This transport occurs through two different phenomena: diffusion and adsorption-desorption. We emphasize that, in this work, we deal with quiescent surfactant solutions, so the mass transfer produced by convection is negligible (see [29]). In order to understand the physics of the whole dynamic process, it is very important to take into account the layer, usually called *subsurface*, depicted in Figure 1, which is an imaginary boundary located a few molecular diameters below the air-water interface that splits the region in which only diffusion occurs from the domain in which only adsorption-desorption takes place. Then, surfactant molecules diffuse from the bulk of the solution to the subsurface and, once in the subsurface, they move to the surface by adsorption, whilst they also achieve the correct orientation. However, sometimes, as the surface gets crowder, it can happen that surfactant molecules do not find an empty space at the surface, so they are desorbed at the subsurface and come back to the bulk of the solution. In this context, there are two families of models to describe the adsorption dynamics: the *diffusion-controlled models* and the *mixed kinetic-diffusion* ones (see [7, 16]). In the former family, it is assumed that after diffusing from the bulk into the subsurface, surfactant molecules are directly adsorbed into the surface. So, the timescale for equilibration between the surface and the subsurface is very fast compared to the timescale for diffusion. On the contrary, the mixed kinetic-diffusion models suppose that the equilibrium between the surface and subsurface layers is not achieved instantaneously and, once surfactant molecules are in the subsurface, they have to pass any of the following situations: undergoing a potential energy barrier, evolving in a correct orientation for adsorption or finding an empty space at the surface. Consequently, in this family of models, the adsorption-desorption timescale is comparable to the diffusion one.

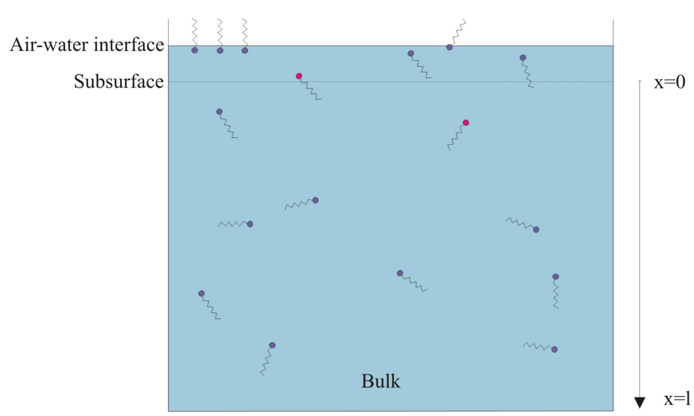

Figure 1: Air-water interface and location of the subsurface.

The study of the dynamic surface tension behavior of surfactant solutions has been revealed a determinant issue for the important role it plays in several industrial, biological and biochemical processes (see [2, 7, 14, 16, 33, 37]). For instance, in agrochemicals, surfactants are one part of the pesticide components since a low dynamic surface tension favors wettability, and then pesticides can spread onto leaves more easily. Moreover, dynamic surface tension is also important in food processing, metal and textile production, cleaning processes and foam and emulsion science. As for biological processes, the control of the dynamic surface tension is very important in lungs, where the presence of surfactants avoids the alveoli collapse. In medicine, the study of the dynamic surface tension of some human liquids comprising surfactants is helpful for diagnosing rheumatic, neurological or oncological diseases and also for the monitoring of therapeutic interventions (see [33]). Besides, surfactant treatments are used to decrease risks from embolisms created during cardiac surgery or rapid decompression and also to reopen collapsed pulmonary airways (see [2]).

All the huge applications of the dynamic surface tension make it a subject of study in which many authors were interested for a long period of time (see [16]). In the 19th century, Dupré published the first work indicating that the variation of the surface tension in a surfactant solution was a dynamic process. His theory was supported by other authors like Gibbs and Rayleigh. At the beginning of the 20th century, explanations of different mechanisms to describe how surface tension changes with time were introduced. First, Milner thought that the process could be explained only by diffusion, but later, some authors proved that only considering a diffusion mechanism the process would be quite fast compared to experimental data, and the idea of the existence of an adsorption barrier came forth. In 1946, the first mathematical contribution in this branch appeared. The work of Ward and Tordai (see [45]) pioneered a mathematical research concerned in achieving analytical solutions, by using the Laplace transform technique, for the diffusion-controlled model considering both a plane surface and infinite diffusion length. However, the theory of Ward and Tordai is hard to apply since their solution gives the surface concentration in terms of a time integral over the subsurface concentration, and this concentration depends on the diffusion and also on the adsorption dynamics model. For this reason, approximations for long and short times were obtained (see [27, 41]). During the decade of 50s, the existence of an adsorption barrier was attributed to the presence of some impurities in the surfactant solutions, so it was thought that if the surfactant was pure, then the process would be explained by a diffusion-controlled model. This difficulty, together with the fact that measurement techniques were indefinite, were the reasons why the interest in the study of the dynamic surface tension decreased until 1990, when the commercialization of some new measurement techniques made this field more accessible. A lot of works comparing experimental data and numerical results obtained with different adsorption models and for different surfactants have been published since those years. Some of them deal with the adsorption dynamics of surfactant solutions at a plane interface and taking into account finite diffusion length (see for instance [5, 6, 7, 30]). Besides plane surfaces, many surfaces of interest are droplets and bubbles because some experimental methods create these structures to measure the dynamic surface tension of solutions. So, there are many publications focusing on surfactant behavior adsorbing onto bubble shaped interfaces (see [28, 29, 34]). Moreover, some of these works regard how the curvature aspects affect on the adsorption dynamics (see [36, 46]).

Nowadays, the experimental measurements can be performed with several methods, which are classified as (see [7]): force methods (Du Noüy ring and Wilhelmy plate), shape methods (pendant drop, spinning drop, and so on), pressure methods (small bubble surfactometer) and other methods. Depending on the time needed for the surface tension equilibration, one can choose the more appropriate method. For example, the Maximum Bubble Pressure Method is useful when the adsorption is fast, which is common in surfactant solutions with concentrations around and above their *critical micelle concentration* (cmc), that is the value of the concentration from which micelles appear in the solution. All the experimental data shown in this manuscript are obtained with the Wilhelmy plate method (see [1]). This method consists in measuring the force exerted on a thin plate that is suspended from one arm of a balance and oriented perpendicularly to the surface, see Figure 2. The plate is partially immersed on a liquid and either a tensiometer or a microbalance measures the force on the plate due to wetting. Then, the surface tension is calculated by means of this force by using the Wilhelmy equation (see [7]).

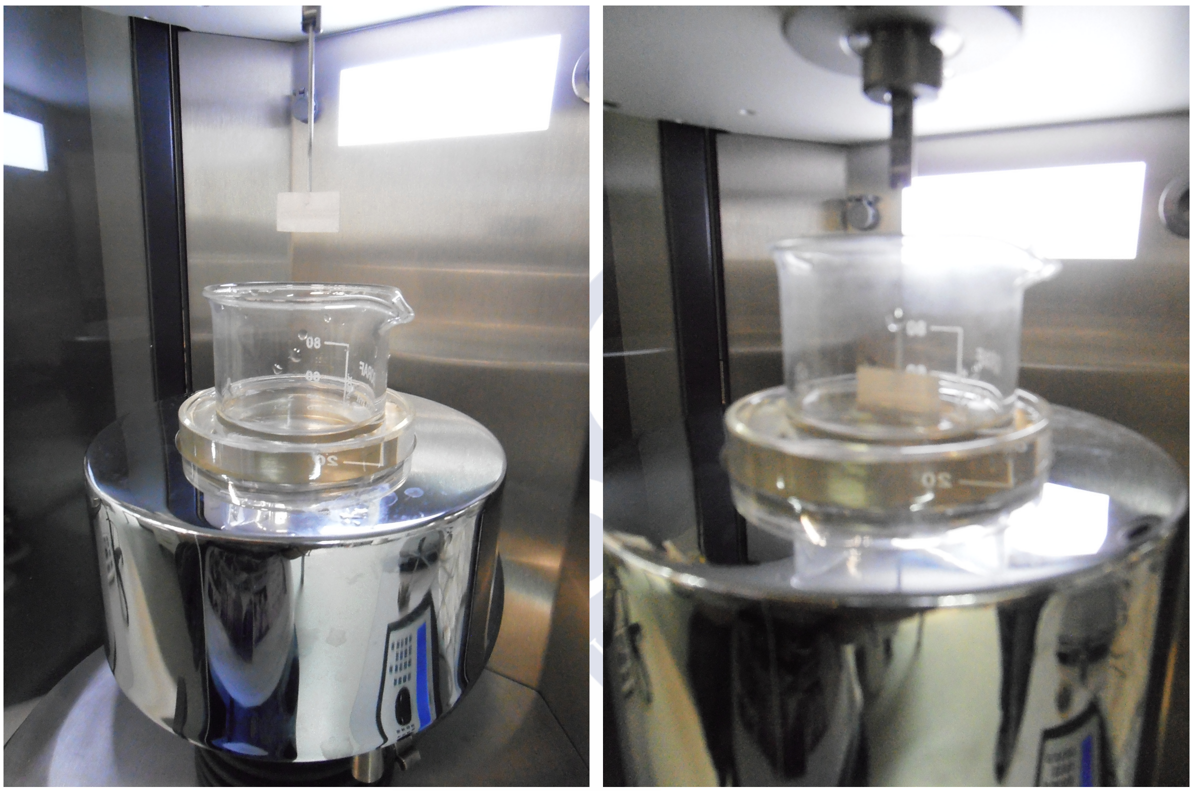

Figure 2: Wilhelmy plate tensiometer. Photographs courtesy of Prof. L. García Río and Mr. S.I. Arias, CIQUS, University of Santiago de Compostela.

Now, we turn to the mathematical treatment of the problem. In this thesis we concern on the analysis of the mathematical problem arising in surfactant solutions at a plane air-water interface. From a mathematical point of view, this dynamic process is modeled by the partial differential equation of diffusion in one spatial dimension, together with suitable initial and boundary conditions. In order to establish the system of equations that describes the process, let us denote by x the distance from the subsurface, see Figure 1, and $c(t, x)$ the concentration of surfactant at time $t \in [0, T]$ and point $x \in [0, l]$. The boundary $x = 0$ of the spatial interval corresponds to the location of the subsurface. Denoting by $\Gamma(t)$ the time-dependent surface concentration, we have the following formulation of the problem (see [7, 35]):

$$\frac{\partial c}{\partial t}(t,x) - D\,\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \qquad t \in (0,T), \quad x \in (0,l), \tag{1}$$

with boundary conditions:

$$D\,\frac{\partial c}{\partial x}(t,0) = \frac{d\Gamma}{dt}(t), \quad t > 0, \tag{2}$$

$$c(t,l) = c_b, \quad t > 0, \tag{3}$$

and initial conditions:

$$c(0,x) = c_0(x), \quad x \in (0,l), \tag{4}$$

$$\Gamma(0) = \Gamma_0. \tag{5}$$

In this system of equations, the positive constants c_b and D denote the bulk concentration and the diffusion coefficient, respectively. We note that, in this thesis, we deal with surfactant solutions below their *cmc*, so a constant diffusion coefficient can be assumed (see [46]). Besides, $c_0(x)$ is a function defined in $[0,l]$, which equals c_b at $x = l$ and Γ_0 is a nonnegative constant.

Then, the transport of molecules from the bulk of the solution to the surface is modeled by equations (1)-(5). Equation (1), that describes the diffusion in the bulk of the solution considering a finite diffusion length, is obtained from the general transport equation by neglecting the convective term since, as we said previously, we are in the framework of quiescent surfactant solutions. Boundary condition (2) describes the surfactant flux from the subsurface to the surface (adsorption) and vice versa, from the surface to the subsurface (desorption). Moreover, we assume that the boundary $x = l$ is kept at a constant concentration, c_b, during the process, so a Dirichlet boundary condition, given by expression (3), is imposed there. In terms of the initial conditions, we assume that, at the beginning, the surface concentration is equal to Γ_0 and the concentration in the bulk of the solution is given by the function $c_0(x)$, $x \in [0,l]$.

Therefore, given l, T, D, c_b, $c_0(x)$ and Γ_0, the problem consists in finding both the surface and subsurface concentrations.

Since the surface concentration, $\Gamma(t)$, is also an unknown of the system, an additional condition must be given in order to close the problem. In this sense, the additional condition, that is coupled to the system of equations (1)-(5) by means of the boundary condition at the subsurface, is established by the adsorption mechanism; so either the diffusion-controlled model or the mixed kinetic-diffusion one has to be used. When considering a **diffusion-controlled model**, a thermodynamic adsorption isotherm states the dependence between the surface and subsurface concentrations. Three of the most commonly used isotherms in the literature are (see [7, 16, 28, 29, 34]):

- The *Henry isotherm*: it is the simplest isotherm and it is only valid for low surface concentrations since it does not take into account interactions between adsorbed molecules. Besides, in this model there is no limit on the surface concentration (see [7, 16]). This isotherm establishes a linear dependence between the surface and subsurface concentrations,

$$\Gamma(t) = K_H \, c(t,0), \qquad t \geq 0, \tag{6}$$

  where K_H is the Henry equilibrium adsorption constant, which is a measure of the surface activity of the surfactant.

- The *Langmuir isotherm*: it defines a nonlinear dependence between the surface and subsurface concentrations,

$$\Gamma(t) = \Gamma_m \frac{K_L \, c(t,0)}{1 + K_L \, c(t,0)}, \qquad t \geq 0, \tag{7}$$

  being Γ_m and K_L the maximum surface concentration and the Langmuir equilibrium adsorption constants, respectively.

- The *Frumkin isotherm*: as in the case of the Langmuir isotherm, this expression states a nonlinear dependence between both surface and subsurface concentrations,

$$\Gamma(t) = \Gamma_m \frac{K_F\, c(t,0)}{e^{-A\frac{\Gamma(t)}{\Gamma_m}} + K_F\, c(t,0)}, \qquad t \geq 0, \tag{8}$$

where K_F is the Frumkin equilibrium adsorption constant and A is a parameter that indicates if the adsorption is anticooperative or not. In the case of negative A, then the adsorption is anticooperative; that is to say, it becomes more difficult as the coverage of the surface increases. The case of A positive describes the existence of cohesive intermolecular forces, which increases the surface coverage and which makes that the desorption rate decreases (see [29]). Finally, if $A = 0$, then Langmuir isotherm is actually recovered.

On the other hand, in **mixed kinetic-diffusion models**, a kinetic expression identifies the rate of change of the surface concentration with the balance between the adsorption and desorption rates. The most studied equations are (see [7]):

- The *linear kinetic model*: in which the rate of adsorption is proportional to the subsurface concentration, while the rate of desorption is proportional to the surface concentration,

$$\frac{d\,\Gamma}{dt}(t) = k_H^a\, c(t,0) - k_H^d\, \Gamma(t), \qquad t > 0, \tag{9}$$

  where k_H^a and k_H^d are the adsorption and desorption constants, respectively.

- The *Langmuir-Hinshelwood kinetic model*: in which the rate of adsorption depends on the subsurface concentration, but also on the fraction of empty space at the surface,

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big) - k_L^d\, \Gamma(t), \qquad t > 0, \tag{10}$$

  being k_L^a and k_L^d the adsorption and desorption constants for the Langmuir-Hinshelwood kinetic model, respectively.

- The *modified Langmuir-Hinshelwood kinetic model*: the modification of the Langmuir-Hinshelwood equation was proposed by Chang and Franses in 1992 (see [6]), because the previous kinetic equation did not fit the experimental data of some surfactants well. With this modification, better results for those surfactants were obtained (see [6, 7]),

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big)e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\, \Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad t > 0, \qquad (11)$$

where the real constant B is an empirical parameter. In the case that $B = 0$, the classical Langmuir-Hinshelwood expression (10) is recovered.

Once the problem is solved, then both surface and subsurface concentrations are known. Now, the surface tension is calculated through the so-called equation of state, that is deduced from the Gibbs adsorption isotherm. This equation relates the surface concentration, $\Gamma(t)$, to both surface tension, $\widetilde{\gamma}(t)$, and subsurface concentration, $c(t,0)$, at a constant temperature, and its expression is given by:

$$\Gamma(t) = -\frac{1}{n\,R\,\theta}\left(\frac{\partial\,\widetilde{\gamma}(t)}{\partial \ln c(t,0)}\right)_\theta,$$

where R is the gas constant, n is a constant which is equal to 1 for non-ionic surfactants and θ is the temperature.

As we mentioned previously, in the chemical literature, we can find several publications devoted to solve numerically some of these problems (see, for instance, [5, 6, 7, 30]). However, to our knowledge, none of those works deal with the study of the existence and uniqueness of weak solutions for both the variational formulations of the problems and their discrete approximations. Furthermore, error estimates for the differences between the continuous solutions and the discrete ones, as well as convergence order results, were not introduced yet. Therefore, the main contribution of this thesis is that we perform variational and numerical analyses of a diffusion problem coupled with a dynamical boundary condition.

The outline of this Ph.D. Thesis is as follows. In Chapter 1, we concern on the variational and numerical formulation of the diffusion problem considering the linear kinetic model. The existence of solution to the weak problem is proved by formulating an auxiliary problem followed by the application of the Banach fixed-point theorem. Uniqueness of solution of the weak problem is also shown. Moreover, fully discrete approximations of the problem are obtained by using the finite element method and a combination of both backward and forward Euler schemes. Under additional regularity conditions, an error estimate result is obtained from which the linear convergence is deduced. Some numerical simulations, in order to show the accuracy of the algorithm and its behavior for a commercial surfactant, are provided. We point out that this chapter has given rise to [20] and [22].

In Chapter 2, we focus on the diffusion problem regarding the Langmuir isotherm. For this problem, the existence of a unique weak solution is proved by using the Rothe's method and fixed-point techniques. Besides, a semi-discrete problem in time is analyzed for which we get the linear convergence under additional regularity conditions. Also, following the same ideas as in Chapter 1, fully discrete approximations of the problem are presented. An error estimate result is proved from which the linear convergence is followed under suitable regularity conditions. We indicate that the work introduced in this chapter has been collected in [11] and [21].

Finally, in Chapter 3, the diffusion problem together with either the Langmuir-Hinshelwood equation or the modified Langmuir-Hinshelwood one is taken into account. The main results of this chapter deal with the existence and uniqueness of weak solution for the truncated versions associated to both problems. Their proofs are obtained by dividing the truncated problems into two auxiliary problems and the application of the Schauder fixed-point theorem. A numerical analysis is performed using some of the ideas already applied in the previous chapters, and numerical simulations that exhibit the accuracy and the behavior of the algorithm for some surfactants are also shown. The work presented in this chapter has led to the manuscripts [23] and [24].

Chapter 1

Mixed kinetic-diffusion model for the Henry isotherm

In this chapter, we describe the adsorption-desorption dynamics of a surfactant solution at the air-water interface by considering a linear mixed kinetic-diffusion model. It is given by the simplest kinetic expression modeling this behavior, which establishes that the rate of change of the surface concentration is related to the balance between the amount of surfactant molecules that migrate from the subsurface to the surface and the amount of surfactant molecules that move from the surface to the subsurface.

From a mathematical point of view, the whole dynamic process is modeled by a coupled nonlinear system of a parabolic equation, for the description of the diffusion dynamics, and an ordinary differential equation, for the adsorption-desorption mechanism. Here, we prove the existence and uniqueness of solution to the weak problem by using classical results for linear parabolic equations and fixed-point techniques. Then, fully discrete approximations are obtained by using the finite element method and a hybrid combination of both backward and forward Euler schemes. An a priori error estimates result is presented from which, under adequate additional regularity conditions, the linear convergence of the algorithm is derived. Finally, numerical simulations are introduced to demonstrate the accuracy of the algorithm and the behavior for two commercially available surfactants.

1.1 The mathematical model

Let us denote by x the distance from the interface and $c(t,x)$ the concentration of surfactant at time $t \in [0,T]$ and point $x \in [0,l]$. The boundary $x = 0$ of the spatial interval corresponds to the location of the subsurface, an imaginary layer between the region in which only diffusion takes place and the domain where only adsorption-desorption occurs. Denoting by $\Gamma(t)$ the time-dependent surface concentration and taking into account the Fick's law, we consider the diffusion partial differential equation:

$$\frac{\partial c}{\partial t}(t,x) - D\,\frac{\partial^2 c}{\partial x^2}(t,x) \quad = \quad 0, \quad t > 0, \quad x \in (0,l), \tag{1.1}$$

together with the boundary conditions (see [7, 35]):

$$D\,\frac{\partial c}{\partial x}(t,0) = \frac{d\Gamma}{dt}(t), \quad t > 0, \tag{1.2}$$

$$c(t,l) = c_b, \quad t > 0, \tag{1.3}$$

and the initial conditions:

$$c(0,x) = c_0(x), \quad x \in (0,l), \tag{1.4}$$

$$\Gamma(0) = \Gamma_0. \tag{1.5}$$

In equations (1.1)-(1.3), the positive constants D and c_b represent the diffusion coefficient and the bulk concentration, respectively. Besides, $c_0(x)$ is a function defined in $[0,l]$ which is equal to c_b on $x = l$. We remark that the time-dependent surface concentration, $\Gamma(t)$, actually becomes an unknown of the system and then an additional condition must be given in order to close the problem. Hereinafter, in this chapter, we consider a linear mixed kinetic-diffusion model, given by the simplest kinetic expression modeling the mass transfer between the surface and subsurface at low concentrations which leads to the following ordinary differential equation (see [7, 44]):

$$\frac{d\,\Gamma}{dt}(t) = k_H^a\, c(t,0) - k_H^d\, \Gamma(t), \qquad t > 0, \tag{1.6}$$

where k_H^a and k_H^d are the adsorption and desorption constants, respectively. This expression identifies the rate of change of the surface concentration with the balance between the adsorption and desorption rates. Moreover, it leads to the Henry isotherm at equilibrium (see [19]).

Remark 1.1 *We note that Henry's isotherm is the simplest equation for describing the adsorption dynamics. It establishes a linear dependence between the subsurface and surface concentrations, assuming that the surface concentration is proportional to the subsurface concentration. Its expression is given by:*

$$\Gamma(t) = K_H\, c(t,0), \quad t \geq 0,$$

K_H being the Henry equilibrium isotherm. At equilibrium or steady-state, $d\,\Gamma/dt = 0$ and, from equation (1.6), the classical Henry's isotherm is recovered with $K_H = k_H^a/k_H^d$.

The study of the surfactant behavior at the air-water interface accounting the Henry isotherm was studied in [19]. In that work, the existence and uniqueness of solution to the weak problem was proved. Moreover, fully discrete approximations of the problem were presented for which error estimates were obtained, and under adequate additional regularity conditions, the linear converge of the algorithm was derived. Finally, some numerical simulations were shown to demonstrate the accuracy of the algorithm and the behavior of the solution.

Assuming that the solution is regular enough, the previous ordinary differential equation, (1.6), together with the initial condition (1.5) can be straightforwardly integrated to obtain:

$$\Gamma(t) = \Gamma_0\, e^{-k_H^d\, t} + k_H^a\, e^{-k_H^d\, t} \int_0^t e^{k_H^d \tau} c(\tau, 0) d\,\tau.$$

Therefore, boundary condition (1.2) reads

$$D\,\frac{\partial c}{\partial x}(t,0) = k_H^a\, c(t,0) - \phi(t, c(\cdot,0)), \qquad t>0, \tag{1.7}$$

where

$$\phi(t,\zeta) = k_H^d\,\Gamma_0\, e^{-k_H^d\, t} + k_H^d\, k_H^a\, e^{-k_H^d\, t} \int_0^t e^{k_H^d \tau}\zeta(\tau)d\,\tau. \tag{1.8}$$

We emphasize that boundary condition (1.7) determines a non-local boundary condition in time since, for the construction of the flux at time t, the values of the subsurface concentration at previous times are also required.

We are now concerned in analyzing problem (1.1), (1.3) and (1.4), together with the new boundary condition (1.7). Moreover, for the sake of clarity in the presentation of this chapter, and in order to simplify the calculations of the following sections, we assume, without loss of generality, that c_b equals zero and so a homogeneous boundary condition is imposed on the right end of the spatial interval.

1.2 Weak formulation of the problem

Before establishing the weak formulation of the problem, we introduce the notation we use hereinafter in this manuscript. Let V be the Hilbert space

$$V = \{v \in H^1(0,l); v(l)=0\},$$

endowed with the inner product and the associated norm given, respectively, by

$$((v,w)) = \int_0^l \frac{\partial v}{\partial x}\frac{\partial w}{\partial x}dx, \quad \|v\|_V = ((v,v))^{1/2}.$$

As usual, we denote by V' the dual space to V and by $\langle\cdot,\cdot\rangle$ the scalar product for the duality V', V. Furthermore, we recall the inner product in $H=L^2(0,l)$ given by

$$(v,w)_H = \int_0^l v(x)\, w(x) dx,$$

with associated norm $\|v\|_H = (v,v)_H^{1/2}$. Moreover, we consider the Hilbert space $\mathcal{V} = L^2(0,T;V)$ with dual space $\mathcal{V}' = L^2(0,T;V')$ together with

$$W_2(0,T) = \{v \in \mathcal{V};\ \frac{\partial v}{\partial t} \in \mathcal{V}'\},$$

where the time derivative is understood in distributional sense (see [40]). Furthermore, for a Banach space X and a nonnegative integer r, here $\mathcal{C}^r([0,T];X)$ denotes the space of r times continuously differentiable functions from $[0,T]$ to X. We denote by $\gamma_0 : H^1(0,l) \to \mathbb{R}$ be the trace operator on $x=0$ given by $\gamma_0(v) = v(0)$. From the continuity of the trace operator (see, for instance, Theorem 3.9.34 in [12]), it follows that

$$|\gamma_0(v)| \leq C_{tr}\,\|v\|_V \ \text{ for all } \ v \in V \ \text{ with } \ C_{tr} = \|\gamma_0\|_{\mathcal{L}(V,\mathbb{R})}. \tag{1.9}$$

Now, let c be a smooth function which solves the problem given by equations (1.1), (1.3), (1.4) and (1.7). Multiplying expression (1.1) by a smooth function z defined in $[0,l]$, such that $z(l)=0$, integrating in $(0,l)$ and using the integration by parts formula, we obtain, for a.e. $t \in (0,T)$,

$$\int_0^l \frac{\partial c}{\partial t}(t,x)z(x)dx + \int_0^l D\frac{\partial c}{\partial x}(t,x)\frac{\partial z}{\partial x}(x)dx + D\frac{\partial c}{\partial x}(t,0)z(0) = 0.$$

Using equation (1.7), we find that, for a.e. $t \in (0,T)$,

$$\int_0^l \frac{\partial c}{\partial t}(t,x)z(x)dx + \int_0^l D\,\frac{\partial c}{\partial x}(t,x)\,\frac{\partial z}{\partial x}(x)dx + k_H^a\, c(t,0)\, z(0) = \phi(t,c(\cdot,0))\, z(0).$$

Therefore, we have the following weak formulation of problem (1.1), (1.3), (1.4) and (1.7):

Problem P_W^H. For a given $c_0 \in H$, find a function $c \in W_2(0,T)$ such that

$$\langle\frac{\partial c}{\partial t}(t), v\rangle_{V'\times V} + D\,((c(t),v)) + k_H^a\,\gamma_0(c(t))\,\gamma_0(v) = \phi(t,\gamma_0(c))\,\gamma_0(v),$$
$$\text{for a.e. } t \in (0,T), \quad \forall v \in V, \tag{1.10}$$

$$c(0) = c_0. \tag{1.11}$$

Note that the initial condition (1.11) makes sense since $W_2(0,T) \hookrightarrow \mathcal{C}([0,T];H)$ (see Chapter 3, Proposition 1.2 in [40]).

1.3 Existence and uniqueness result

A proof of existence and uniqueness of solution to Problem P_W^H is detailed in this section, and it is based on classical results for linear parabolic equations and fixed-point techniques.

Theorem 1.1 *Let k_H^a, k_H^d and D be positive constants. If $c_0 \in H$, then there exists a unique solution $c \in W_2(0,T)$ to Problem P_W^H.*

Proof. *Existence.* For every $\eta \in L^2(0,T)$ we consider the following auxiliary problem:
Problem P_η. Find a function $c_\eta \in W_2(0,T)$ such that,

$$\langle \frac{\partial c_\eta}{\partial t}(t), v\rangle_{V'\times V} + D\left((c_\eta(t), v)\right) + k_H^a\,\gamma_0(c_\eta(t))\,\gamma_0(v)$$
$$= k_H^d\,\Gamma_0\,e^{-k_H^d\,t}\,\gamma_0(v) + k_H^a\,\eta(t)\,\gamma_0(v), \quad \text{for a.e. } t \in (0,T), \quad \forall v \in V, \tag{1.12}$$
$$c_\eta(0) = c_0. \tag{1.13}$$

In order to prove the existence of a unique solution to Problem P_η, we consider the bilinear form $a : V \times V \to \mathbb{R}$ given by

$$a(u,v) = D\left((u,v)\right) + k_H^a\,\gamma_0(u)\,\gamma_0(v), \quad \forall u, v \in V,$$

and the function $f : [0,T] \to V'$ defined by

$$\langle f(t), v\rangle_{V'\times V} = k_H^d\,\Gamma_0\,e^{-k_H^d\,t}\,\gamma_0(v) + k_H^a \eta(t)\,\gamma_0(v).$$

Since $a(\cdot,\cdot)$ is continuous on $V\times V$ (that is to say, $|a(u,v)| \le M\|u\|_V\|v\|_V$, for all $u, v \in V$ with $M > 0$), and coercive on V(that is to say, $a(u,u) \ge \alpha\|u\|_V^2$, for all $u \in V$ with $\alpha > 0$) and $f \in \mathcal{V}'$, we are allowed to apply Theorem 3.1 in [42] and we conclude that there exists a unique solution $c_\eta \in W_2(0,T)$ to Problem P_η.

Now, we define the operator $\Lambda : L^2(0,T) \to L^2(0,T)$ as follows,

$$\eta \to \Lambda\eta(t) = k_H^d \int_0^t e^{k_H^d(\tau - t)} \gamma_0(c_\eta(\tau))\, d\tau,$$

c_η being the solution to Problem P_η. First, we note that the operator Λ maps $L^2(0,T)$ into itself. Indeed, taking into account the definition of Λ and the Cauchy-Schwarz inequality, we have

$$\begin{aligned} \Lambda\eta(t) &\leq k_H^d \left(\int_0^t e^{2k_H^d(\tau - t)} d\tau \right)^{1/2} \left(\int_0^t |\gamma_0(c_\eta(\tau))|^2 d\tau \right)^{1/2} \\ &\leq \left(\frac{k_H^d}{2} \right)^{1/2} \left(\int_0^t |\gamma_0(c_\eta(\tau))|^2 d\tau \right)^{1/2}, \end{aligned}$$

and therefore $\Lambda\eta \in L^2(0,T)$ regarding that $\gamma_0(c_\eta) \in L^2(0,T)$ and

$$\int_0^T |\Lambda\eta(t)|^2 dt \leq \frac{k_H^d}{2} \int_0^T \|\gamma_0(c_\eta)\|^2_{L^2(0,t)} dt \leq \frac{T\, k_H^d}{2} \|\gamma_0(c_\eta)\|^2_{L^2(0,T)}.$$

Let us prove that Λ is a contraction on $L^2(0,T)$. Indeed, taking $\eta_1, \eta_2 \in L^2(0,T)$ we consider the respective solutions c_{η_1}, c_{η_2} to Problem P_η. Subtracting equation (1.12) for $\eta = \eta_1$ and $\eta = \eta_2$, taking $v = c_{\eta_1}(t) - c_{\eta_2}(t) \in V$ as a test function, we get, for a.e. $t \in (0,T)$,

$$\begin{aligned} \langle \frac{\partial c_{\eta_1}}{\partial t}(t) - \frac{\partial c_{\eta_2}}{\partial t}(t), c_{\eta_1}(t) - c_{\eta_2}(t) \rangle_{V' \times V} + D\, \|c_{\eta_1}(t) - c_{\eta_2}(t)\|_V^2 \\ + k_H^a \left(\gamma_0(c_{\eta_1}(t)) - \gamma_0(c_{\eta_2}(t)) \right) \gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)) \\ = k_H^a (\eta_1(t) - \eta_2(t))\, \gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)). \end{aligned}$$

Using the Cauchy-Schwarz inequality and the linearity of the trace operator, we find that, for a.e. $t \in (0,T)$,

$$\begin{aligned} \frac{1}{2}\frac{d}{dt} \|c_{\eta_1}(t) - c_{\eta_2}(t)\|_H^2 + D\, \|c_{\eta_1}(t) - c_{\eta_2}(t)\|_V^2 + k_H^a\, |\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t))|^2 \\ \leq k_H^a |\eta_1(t) - \eta_2(t)|\, |\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t))| \\ \leq \frac{k_H^a}{2} |\eta_1(t) - \eta_2(t)|^2 + \frac{k_H^a}{2} |\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t))|^2. \end{aligned}$$

Then, we have, for a.e. $t \in (0,T)$,

$$\frac{1}{2}\frac{d}{dt}\|c_{\eta_1}(t)-c_{\eta_2}(t)\|_H^2 + D\,\|c_{\eta_1}(t)-c_{\eta_2}(t)\|_V^2 + \frac{k_H^a}{2}\,|\gamma_0(c_{\eta_1}(t)-c_{\eta_2}(t))|^2 \\ \leq \frac{k_H^a}{2}|\eta_1(t)-\eta_2(t)|^2.$$

Integrating from 0 to t we obtain, for all $t \in [0,T]$,

$$\frac{1}{2}\|c_{\eta_1}(t)-c_{\eta_2}(t)\|_H^2 + D\int_0^t \|c_{\eta_1}(\tau)-c_{\eta_2}(\tau)\|_V^2\,d\tau + \frac{k_H^a}{2}\int_0^t |\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|^2\,d\tau \\ \leq \frac{k_H^a}{2}\int_0^t |\eta_1(\tau)-\eta_2(\tau)|^2\,d\tau,$$

and, since all the terms of the left-hand side of the latter expression are nonnegative, we get, for all $t \in [0,T]$,

$$\int_0^t |\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|^2\,d\tau \leq \int_0^t |\eta_1(\tau)-\eta_2(\tau)|^2\,d\tau. \tag{1.14}$$

Recalling the definition of Λ, subtracting its expression for $\eta=\eta_1$ and $\eta=\eta_2$ and using the Cauchy-Schwarz inequality, we find that, for a.e. $t \in (0,T)$,

$$\begin{aligned}|\Lambda\eta_1(t)-\Lambda\eta_2(t)| &\leq k_H^d\int_0^t e^{k_H^d(\tau-t)}|\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|d\tau \\ &\leq k_H^d\left(\int_0^t e^{2k_H^d(\tau-t)}d\tau\right)^{1/2}\left(\int_0^t |\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|^2 d\tau\right)^{1/2} \\ &\leq \left(\frac{k_H^d}{2}\right)^{1/2}\left(\int_0^t |\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|^2 d\tau\right)^{1/2}.\end{aligned}$$

Therefore, using estimate (1.14) it follows that, for a.e. $t \in (0,T)$,

$$\begin{aligned}|\Lambda\eta_1(t)-\Lambda\eta_2(t)|^2 &\leq \frac{k_H^d}{2}\int_0^t |\gamma_0(c_{\eta_1}(\tau)-c_{\eta_2}(\tau))|^2 d\tau \\ &\leq \frac{k_H^d}{2}\,\|\eta_1-\eta_2\|_{L^2(0,t)}^2.\end{aligned}$$

Integrating this expression from 0 to t we obtain

$$\|\Lambda\eta_1 - \Lambda\eta_2\|^2_{L^2(0,t)} \le \frac{k_H^d}{2} \int_0^t \|\eta_1 - \eta_2\|^2_{L^2(0,\tau)}\, d\tau, \quad \text{for all } t \in [0,T], \tag{1.15}$$

and then

$$\|\Lambda\eta_1 - \Lambda\eta_2\|^2_{L^2(0,T)} \le \frac{k_H^d\, T}{2}\, \|\eta_1 - \eta_2\|^2_{L^2(0,T)}.$$

Moreover, using (1.15), we find that

$$\begin{aligned}
\|\Lambda^2\eta_1 - \Lambda^2\eta_2\|^2_{L^2(0,t)} &\le \frac{k_H^d}{2} \int_0^t \|\Lambda\eta_1 - \Lambda\eta_2\|^2_{L^2(0,\tau)} d\tau \\
&\le \frac{k_H^d}{2} \int_0^t \frac{k_H^d}{2} \int_0^\tau \|\eta_1 - \eta_2\|^2_{L^2(0,s)} ds\, d\tau \\
&\le \left(\frac{k_H^d}{2}\right)^2 \frac{t^2}{2} \|\eta_1 - \eta_2\|^2_{L^2(0,t)}, \quad \text{for all } t \in [0,T].
\end{aligned}$$

Following this reasoning and using the induction in n, we assume that the following inequality is satisfied

$$\|\Lambda^{n-1}\eta_1 - \Lambda^{n-1}\eta_2\|^2_{L^2(0,t)} \le \left(\frac{k_H^d}{2}\right)^{n-1} \frac{t^{n-1}}{(n-1)!}\, \|\eta_1 - \eta_2\|^2_{L^2(0,t)}, \quad \text{for all } t \in [0,T].$$

Thus,

$$\begin{aligned}
\|\Lambda^n\eta_1 - \Lambda^n\eta_2\|^2_{L^2(0,t)} &\le \frac{k_H^d}{2} \int_0^t \|\Lambda^{n-1}\eta_1 - \Lambda^{n-1}\eta_2\|^2_{L^2(0,\tau)}\, d\tau \\
&\le \left(\frac{k_H^d}{2}\right)^n \frac{t^n}{n!} \|\eta_1 - \eta_2\|^2_{L^2(0,t)}, \qquad \text{for all } t \in [0,T].
\end{aligned}$$

Consequently

$$\|\Lambda^n\eta_1 - \Lambda^n\eta_2\|^2_{L^2(0,T)} \le \left(\frac{k_H^d\, T}{2}\right)^n \frac{1}{n!}\, \|\eta_1 - \eta_2\|^2_{L^2(0,T)},$$

and then, for n large enough, the operator Λ^n is a contraction on $L^2(0,T)$. Therefore, the Banach fixed-point theorem (see [47]) guarantees the existence of a unique fixed point $\eta \in L^2(0,T)$ of Λ^n, which is also the unique fixed point of Λ and so, there exists a solution to problem (1.10)-(1.11).

Uniqueness. Let c_1 and c_2 be two solutions to problem (1.10)-(1.11). Subtracting equation (1.10) for $c = c_1$ and $c = c_2$, taking $v = c_1(t) - c_2(t) \in V$ as a test function and using the following version of Cauchy's inequality (see [17])

$$r\, s \leq \varepsilon r^2 + \frac{1}{4\,\varepsilon} s^2, \quad \text{for all } r, s \in \mathbb{R},\ \varepsilon > 0, \tag{1.16}$$

with $\varepsilon = k_H^a/2$, we get, for a.e. $t \in (0, T)$,

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_1(t) - c_2(t)\|_H^2 + D\ \|c_1(t) - c_2(t)\|_V^2 + k_H^a\, |\gamma_0(c_1(t) - c_2(t))|^2 \\
&\qquad \leq |\phi(t, \gamma_0(c_1)) - \phi(t, \gamma_0(c_2))|\, |\gamma_0(c_1(t) - c_2(t))| \\
&\qquad \leq \frac{1}{2\, k_H^a}(\phi(t, \gamma_0(c_1)) - \phi(t, \gamma_0(c_2)))^2 + \frac{k_H^a}{2}\gamma_0(c_1(t) - c_2(t))^2.
\end{aligned} \tag{1.17}$$

Taking into account the inequality

$$\begin{aligned}
|\phi(t, \gamma_0(c_1)) - \phi(t, \gamma_0(c_2))| &\leq k_H^d\, k_H^a e^{-k_H^d t} \int_0^t e^{k_H^d \tau} |\gamma_0(c_1(\tau) - c_2(\tau))| d\tau \\
&\leq k_H^d\, k_H^a e^{-k_H^d t} \left(\int_0^t e^{2k_H^d \tau} d\tau \right)^{1/2} \left(\int_0^t |\gamma_0(c_1(\tau) - c_2(\tau))|^2 d\tau \right)^{1/2} \\
&\leq \left(\frac{k_H^d}{2} \right)^{1/2} k_H^a \left(\int_0^t |\gamma_0(c_1(\tau) - c_2(\tau))|^2 d\tau \right)^{1/2},
\end{aligned}$$

estimate (1.17) implies that

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_1(t) - c_2(t)\|_H^2 + D\ \|c_1(t) - c_2(t)\|_V^2 + \frac{k_H^a}{2}\, |\gamma_0(c_1(t) - c_2(t))|^2 \\
&\qquad \leq \frac{k_H^d}{4} k_H^a \int_0^t |\gamma_0(c_1(\tau) - c_2(\tau))|^2 d\tau, \quad \text{for a.e. } t \in (0, T).
\end{aligned} \tag{1.18}$$

Writing

$$\xi(t) := \int_0^t |\gamma_0(c_1(s) - c_2(s))|^2 ds,$$

and integrating estimate (1.18) from 0 to t we get

$$\frac{1}{2}\|c_1(t)-c_2(t)\|_H^2 + D\int_0^t \|c_1(s)-c_2(s)\|_V^2\,ds + \frac{k_H^a}{2}\,\xi(t) \le \frac{k_H^d}{4}k_H^a\int_0^t \xi(s)\,ds, \quad \text{for all } t\in[0,T]. \tag{1.19}$$

Since every term of the left-hand side of the latter expression is nonnegative, we find that

$$\xi(t) \le \frac{k_H^d}{2}\int_0^t \xi(s)\,ds, \quad \text{for all } t\in[0,T].$$

Using Gronwall's inequality (see [17]), it follows that

$$\xi(t)=0 \quad \text{for a.e. } t\in(0,T),$$

and, from inequality (1.19), we have $c_1-c_2\equiv 0$ and the result holds. □

1.4 Fully discrete approximations: numerical analysis

In this section, we consider a fully discrete approximation of problem (1.10)-(1.11); that is to say, we discretize the problem both in time and space. For the spatial discretization we use the finite element method by means of a finite-dimensional space $V^h\subset V$, which approximates the space V. Here, as it is usual in this framework, the positive parameter h denotes the spatial discretization parameter. Moreover, we consider a partition of the time interval $[0,T]$, denoted by $0=t_0<t_1<\dots<t_N=T$. In this case, we use a uniform partition of the time interval $[0,T]$ with step size $k=T/N$ and nodes $t_n=n\,k$ for $n=0,1,\dots,N$. For a continuous function $z(t)$, we use the notation $z_n=z(t_n)$ and, for the sequence $\{z_n\}_{n=0}^N$, we denote by $\delta z_n=(z_n-z_{n-1})/k$ its corresponding divided differences.

Therefore, using a hybrid combination of both backward and forward Euler schemes, the fully discrete approximations are considered as follows.

Problem P_H^{hk}. Find $c^{hk} = \{c_n^{hk}\}_{n=0}^N \subset V^h$ such that

$$c_0^{hk} = c_0^h, \tag{1.20}$$

and, for $n = 1, \dots, N$ and for all $v^h \in V^h$,

$$(\delta c_n^{hk}, v^h)_H + D\,((c_n^{hk}, v^h)) + k_H^a\, \gamma_0(c_n^{hk})\, \gamma_0(v^h) = \phi_{n-1}^{hk}\, \gamma_0(v^h), \tag{1.21}$$

where $c_0^h \in V^h$ is an appropriate approximation of the initial condition c_0 and

$$\phi_{n-1}^{hk} = k_H^d\, \Gamma_0\, e^{-k_H^d\, t_n} + k_H^d\, k_H^a\, k \sum_{j=0}^{n-1} e^{k_H^d (t_j - t_n)} \gamma_0(c_j^{hk}). \tag{1.22}$$

For Problem P_H^{hk}, we have the following result.

Theorem 1.2 *Assume that the hypotheses of Theorem 1.1 hold. Then, Problem* P_H^{hk} *has a unique solution.*

Proof. Let us consider the bilinear form $a_H : V \times V \to \mathbb{R}$ given by

$$a_H(u,v) = \int_0^l u\, v\, dx + D\, k \int_0^l \frac{\partial u}{\partial x}\, \frac{\partial v}{\partial x}\, dx + k\, k_H^a\, \gamma_0(u)\, \gamma_0(v),$$

and the linear form $L_H : V \to \mathbb{R}$ defined by

$$L_H(v) = \int_0^l c_{n-1}^{hk}\, v\, dx + k\, \phi_{n-1}^{hk}\, \gamma_0(v).$$

The bilinear form a_H is continuous on $V \times V$ and coercive on V. Indeed, taking into account both Hölder and trace inequalities (see (1.9)) and that the norms $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$ are equivalent on the space V, we have

$$\begin{aligned} |a_H(u,v)| &\leq \|u\|_H \|v\|_H + D\, k \|u\|_V \|v\|_V + k\, k_H^a\, C_{tr}^2 \|u\|_V \|v\|_V \\ &\leq \max\{1, D\, k, k\, k_H^a\, C_{tr}^2\} \|u\|_{H^1(0,l)} \|v\|_{H^1(0,l)} \leq M^*\, \|u\|_V \|v\|_V, \quad \forall\, u, v \in V, \end{aligned}$$

where M^* is a positive constant large enough, and,

$$\begin{aligned} a_H(v,v) &= \int_0^l v^2\,dx + D\,k\int_0^l \left(\frac{\partial v}{\partial x}\right)^2 dx + k\,k_H^a(\gamma_0(v))^2 \\ &\geq \min\{1, D\,k\}\|v\|^2_{H^1(0,l)} \geq \alpha\|v\|_V^2, \qquad \forall\, v \in V, \end{aligned}$$

α being a positive constant small enough. Moreover, considering both Hölder and trace inequalities again, the equivalence between the norms $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$ on V and that the function ϕ_{n-1}^{hk} is bounded for $n \in \{1,2,\ldots,N\}$, we deduce that

$$|L_H(v)| \leq \|c_{n-1}^{hk}\|_H\|v\|_H + k\,|\phi_{n-1}^{hk}|\,|\gamma_0(v)| \leq M^{**}\|v\|_V, \qquad \forall\, v \in V,$$

where M^{**} is a positive constant large enough. Then, L_H is continuous on V.

Consequently, we can apply Lax-Milgram theorem and the result follows. $\square$

In the sequel, we will derive an error estimate for the difference $c_n - c_n^{hk}$ assuming the following additional regularity:

$$c \in \mathcal{C}([0,T];V) \cap \mathcal{C}^1([0,T];H). \tag{1.23}$$

Taking $v = c_n - v^h \in V$ in equation (1.10) at time $t = t_n$, we find that, for $n = 1,2,\ldots,N$,

$$\left(\frac{\partial c}{\partial t}(t_n), c_n - v^h\right)_H + D\,((c_n, c_n - v^h)) + k_H^a\,\gamma_0(c_n)\,\gamma_0(c_n - v^h) = \phi_n\,\gamma_0(c_n - v^h),$$

where $\phi_n = \phi(t_n, \gamma_0(c))$, and therefore, since the previous expression holds also for $v^h = c_n^{hk}$, it follows

$$\begin{aligned} &\left(\frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H + D\,((c_n, c_n - c_n^{hk})) \\ &\qquad + k_H^a\,\gamma_0(c_n)\,\gamma_0(c_n - c_n^{hk}) - \phi_n\,\gamma_0(c_n - c_n^{hk}) \\ &= \left(\frac{\partial c}{\partial t}(t_n), c_n - v^h\right)_H + D\,((c_n, c_n - v^h)) \\ &\qquad + k_H^a\,\gamma_0(c_n)\,\gamma_0(c_n - v^h) - \phi_n\,\gamma_0(c_n - v^h). \end{aligned} \tag{1.24}$$

On the other hand, taking $v^h - c_n^{hk} \in V^h$ as a test function in (1.21) and writing $v^h - c_n^{hk} = v^h - c_n + c_n - c_n^{hk}$ we have, for all $v^h \in V^h$,

$$\begin{aligned}
&(\delta c_n^{hk}, c_n - c_n^{hk})_H + D\,((c_n^{hk}, c_n - c_n^{hk})) \\
&\qquad\qquad + k_H^a\ \gamma_0(c_n^{hk})\,\gamma_0(c_n - c_n^{hk}) - \phi_{n-1}^{hk}\,\gamma_0(c_n - c_n^{hk}) \\
&\quad = (\delta c_n^{hk}, c_n - v^h)_H + D\ ((c_n^{hk}, c_n - v^h)) \\
&\qquad\qquad + k_H^a\ \gamma_0(c_n^{hk})\,\gamma_0(c_n - v^h) - \phi_{n-1}^{hk}\,\gamma_0(c_n - v^h).
\end{aligned} \tag{1.25}$$

Subtracting now equations (1.24) and (1.25) and taking into account the linearity of the trace operator, we obtain, for all $v^h \in V^h$,

$$\begin{aligned}
&\left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - c_n^{hk}\right)_H + D\ \|c_n - c_n^{hk}\|_V^2 + k_H^a\ |\gamma_0(c_n - c_n^{hk})|^2 \\
&\qquad\qquad -(\phi_n - \phi_{n-1}^{hk})\ \gamma_0(c_n - c_n^{hk}) \\
&\quad = \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + D\ ((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad + k_H^a\ \gamma_0(c_n - c_n^{hk})\,\gamma_0(c_n - v^h) - (\phi_n - \phi_{n-1}^{hk})\ \gamma_0(c_n - v^h).
\end{aligned}$$

Taking into account that $\dfrac{\partial c}{\partial t}(t_n) - \delta c_n^{hk} = \dfrac{\partial c}{\partial t}(t_n) - \delta c_n + \delta c_n - \delta c_n^{hk}$ and after easy algebraic manipulations we find that, for all $v^h \in V^h$,

$$\begin{aligned}
&(\delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H + D\,\|c_n - c_n^{hk}\|_V^2 + k_H^a\ |\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad = \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + D\,((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad + (\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - c_n^{hk}) - (\phi_n - \phi_{n-1}^{hk})\,\gamma_0(c_n - v^h) \\
&\qquad + k_H^a\gamma_0(c_n - c_n^{hk})\gamma_0(c_n - v^h) + \left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H,
\end{aligned} \tag{1.26}$$

where we recall that $\delta c_n = (c_n - c_{n-1})/k$.

Moreover, using the following property of the divided differences:

$$\begin{aligned}(\delta a_n - \delta b_n, a_n - b_n)_H &= (\frac{a_n - a_{n-1}}{k} - \frac{b_n - b_{n-1}}{k}, a_n - b_n)_H \\ &= \frac{1}{k}\|a_n - b_n\|_H^2 - \frac{1}{k}(a_{n-1} - b_{n-1}, a_n - b_n)_H, \qquad (1.27)\end{aligned}$$

equation (1.26) reads

$$\begin{aligned}&\frac{1}{k}\|c_n - c_n^{hk}\|_H^2 + D\,\|c_n - c_n^{hk}\|_V^2 + k_H^a|\gamma_0(c_n - c_n^{hk})|^2 \\ &\quad = \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + D\,((c_n - c_n^{hk}, c_n - v^h)) \\ &\qquad +(\phi_n - \phi_{n-1}^{hk})\,\gamma_0(c_n - c_n^{hk}) - (\phi_n - \phi_{n-1}^{hk})\,\gamma_0(c_n - v^h) \\ &\qquad +k_H^a\gamma_0(c_n - c_n^{hk})\gamma_0(c_n - v^h) + \left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H \\ &\qquad +\frac{1}{k}(c_{n-1} - c_{n-1}^{hk}, c_n - c_n^{hk})_H, \quad \forall\, v^h \in V^h. \qquad (1.28)\end{aligned}$$

Using both Cauchy-Schwarz and Cauchy inequalities, it follows that

$$\begin{aligned}&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \frac{D}{2}\,\|c_n - c_n^{hk}\|_V^2 + k_H^a|\gamma_0(c_n - c_n^{hk})|^2 \\ &\quad \leq \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + \frac{D}{2}\,\|c_n - v^h\|_V^2 \\ &\qquad +(\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - c_n^{hk}) - (\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - v^h) \\ &\qquad +k_H^a\,\gamma_0(c_n - c_n^{hk})\,\gamma_0(c_n - v^h) + \left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H \\ &\qquad +\frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2, \quad \forall\, v^h \in V^h. \qquad (1.29)\end{aligned}$$

We will use now the following technical lemmas.

Lemma 1.1 *The following estimate holds:*

$$|\phi_n - \phi_{n-1}^{hk}|^2 \leq 2\, I_n^2 + \beta k \sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})|^2,$$

β being a positive constant independent of k, h and n and I_n the integration error given by

$$I_n := k_H^a k_H^d \, e^{-k_H^d t_n} \Big| \int_0^{t_n} e^{k_H^d \tau} \gamma_0(c(\tau)) \, d\tau - \sum_{j=0}^{n-1} k \, e^{k_H^d t_j} \gamma_0(c_j) \Big|. \tag{1.30}$$

Proof. First, we find that

$$\begin{aligned} |\phi_n - \phi_{n-1}^{hk}| &= \Big| k_H^d \, k_H^a \, e^{-k_H^d \, t_n} \Big(\int_0^{t_n} e^{k_H^d \, \tau} \gamma_0(c(\tau)) \, d\tau - \sum_{j=0}^{n-1} k \, e^{k_H^d \, t_j} \gamma_0(c_j^{hk}) \Big) \Big| \\ &= k_H^d \, k_H^a \, e^{-k_H^d \, t_n} \Big| \int_0^{t_n} e^{k_H^d \, \tau} \gamma_0(c(\tau)) \, d\tau - \sum_{j=0}^{n-1} k \, e^{k_H^d \, t_j} \gamma_0(c_j) \\ &\qquad + \sum_{j=0}^{n-1} k \, e^{k_H^d \, t_j} \gamma_0(c_j - c_j^{hk}) \Big|, \end{aligned}$$

and therefore, reminding the definition of the integration error, I_n, given in (1.30), we obtain

$$|\phi_n - \phi_{n-1}^{hk}| \le I_n + k_H^d \, k_H^a \, k \sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})|.$$

Using the following property (see [38])

$$(a+b)^{\wp} \le 2^{(\wp-1)^+} (a^{\wp} + b^{\wp}), \quad \text{for } a, b \ge 0, \text{and } \wp > 0, \tag{1.31}$$

with $\wp = 2$, we deduce

$$|\phi_n - \phi_{n-1}^{hk}|^2 \le 2 \, I_n^2 + 2 \, (k_H^d \, k_H^a \, k)^2 \left(\sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})| \right)^2 . \tag{1.32}$$

Since

$$\sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})| \le n^{1/2} \left(\sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})|^2 \right)^{1/2},$$

from estimate (1.32) we have

$$|\phi_n - \phi_{n-1}^{hk}|^2 \leq 2\, I_n^2 + 2\,(k_H^d\, k_H^a\, k\,)^2 n \sum_{j=0}^{n-1} |\gamma_0(c_j - c_j^{hk})|^2,$$

and, keeping in mind that $k\,N = T$, the result holds. □

Lemma 1.2 *There exist two positive constants, α and β, $\alpha < \beta$, independent of h, k and n such that, using the notation*

$$\begin{aligned}
a_n \quad &:= \|c_n - c_n^{hk}\|_H^2 + k \sum_{j=0}^{n} [D\|c_j - c_j^{hk}\|_V^2 + \alpha|\gamma_0(c_j - c_j^{hk})|^2],\\
b_n(v^h) \quad &:= 2\Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + \|c_n - v^h\|_H^2 + D\|c_n - v^h\|_V^2\\
&\quad +\beta\,|\gamma_0(c_n - v^h)|^2 + \beta I_n^2,\\
d_n(v^h) \quad &:= (c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H,
\end{aligned}$$

it follows that

$$a_n \leq a_{n-1} + k\,(b_n(v^h) + \beta\, a_n) + 2\, d_n(v^h), \quad \forall v^h \in V^h, \quad n \geq 1. \tag{1.33}$$

Proof. Since

$$\begin{aligned}
\left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H &= \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n, c_n - v^h\right)_H\\
&\quad + \frac{1}{k}(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H\\
&\leq \frac{1}{2}\Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + \frac{1}{2}\|c_n - v^h\|_H^2\\
&\quad + \frac{1}{k}(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H, \quad \forall\, v^h \in V^h,
\end{aligned}$$

then estimate (1.29) implies that

$$
\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \frac{D}{2}\,\|c_n - c_n^{hk}\|_V^2 + k_H^a|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad \le \frac{1}{2}\Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + \frac{1}{2}\|c_n - v^h\|_H^2 + \frac{D}{2}\,\|c_n - v^h\|_V^2 + \frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2 \\
&\qquad +(\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - c_n^{hk}) - (\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - v^h) \\
&\qquad +k_H^a\,\gamma_0(c_n - c_n^{hk})\,\gamma_0(c_n - v^h) + \left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H \\
&\qquad +\frac{1}{k}(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H, \quad \forall v^h \in V^h. \qquad (1.34)
\end{aligned}
$$

Moreover, using both Hölder and Cauchy inequalities, estimate (1.34) leads to the following estimate, for all $v^h \in V^h$,

$$
\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \frac{D}{2}\,\|c_n - c_n^{hk}\|_V^2 + k_H^a|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad \le \Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + \frac{1}{2}\|c_n - v^h\|_H^2 + \frac{D}{2}\|c_n - v^h\|_V^2 + \frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2 \\
&\qquad +(\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - c_n^{hk}) - (\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - v^h) \\
&\qquad +k_H^a\,\gamma_0(c_n - c_n^{hk})\,\gamma_0(c_n - v^h) + \frac{1}{2}\|c_n - c_n^{hk}\|_H^2 \\
&\qquad +\frac{1}{k}(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H. \qquad (1.35)
\end{aligned}
$$

Finally, since we have

$$
\begin{aligned}
\gamma_0(c_n - c_n^{hk})\,\gamma_0(c_n - v^h) &\le \frac{1}{2}|\gamma_0(c_n - c_n^{hk})|^2 + \frac{1}{2}|\gamma_0(c_n - v^h)|^2, \\
(\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - c_n^{hk}) &\le \frac{1}{4\varepsilon}|\phi_n - \phi_{n-1}^{hk}|^2 + \varepsilon|\gamma_0(c_n - c_n^{hk})|^2, \\
-(\phi_n - \phi_{n-1}^{hk})\gamma_0(c_n - v^h) &\le \frac{1}{2}|\phi_n - \phi_{n-1}^{hk}|^2 + \frac{1}{2}|\gamma_0(c_n - v^h)|^2,
\end{aligned}
$$

for a parameter $\varepsilon > 0$ assumed small enough, estimate (1.35) implies that, for all $v^h \in V^h$,

$$
\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \frac{D}{2}\ \|c_n - c_n^{hk}\|_V^2 + \frac{\alpha}{2}|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad \le \left\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\right\|_H^2 + \frac{1}{2}\|c_n - v^h\|_H^2 + \frac{D}{2}\|c_n - v^h\|_V^2 + \frac{1}{2}\|c_n - c_n^{hk}\|_H^2 \\
&\qquad + \frac{\beta}{2}|\phi_n - \phi_{n-1}^{hk}|^2 + \frac{\beta}{2}|\gamma_0(c_n - v^h)|^2 \\
&\qquad + \frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2 + \frac{1}{k}(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H,
\end{aligned}
$$

where α and β are generic positive constants, $\alpha < \beta$, assumed to be small and large enough, respectively, independent of h, k and n and whose value may vary from line to line.

Therefore, multiplying by $2k$ we get, for all $v^h \in V^h$,

$$
\begin{aligned}
&\|c_n - c_n^{hk}\|_H^2 + D\,k\ \|c_n - c_n^{hk}\|_V^2 + \alpha k\,|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad \le k\left(2\left\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\right\|_H^2 + \|c_n - v^h\|_H^2 + D\,\|c_n - v^h\|_V^2 + \|c_n - c_n^{hk}\|_H^2\right. \\
&\qquad \left. + \beta|\phi_n - \phi_{n-1}^{hk}|^2 + \beta|\gamma_0(c_n - v^h)|^2\right) + \|c_{n-1} - c_{n-1}^{hk}\|_H^2 \\
&\qquad + 2(c_n - c_n^{hk} - (c_{n-1} - c_{n-1}^{hk}), c_n - v^h)_H. \qquad (1.36)
\end{aligned}
$$

Lemma 1.2 is now a consequence of estimate (1.36) and Lemma 1.1. Indeed, adding

$$
k\sum_{j=0}^{n-1}(D\|c_j - c_j^{hk}\|_V^2 + \alpha|\gamma_0(c_j - c_j^{hk})|^2),
$$

in both sides of inequality (1.36) and using Lemma 1.1, (1.33) holds. $\square$

Consequently, from (1.33) we obtain

$$
a_n \le a_0 + \sum_{j=1}^{n}(k\,(b_j(v_j^h) + \beta\,a_j) + 2\,d_j(v_j^h)), \quad \forall \{v_j^h\}_{j=1}^n \subset V^h. \qquad (1.37)
$$

Since

$$\sum_{j=1}^{n} k\, b_j(v_j^h) \leq k \sum_{j=1}^{N} b_j(v_j^h) \leq TM,$$

where $M = \max\limits_{1\leq j\leq N} b_j(v_j^h)$, estimate (1.37) reads

$$a_n \leq a_0 + T\,M + \sum_{j=1}^{n}(k\,\beta\,a_j + 2\,d_j(v_j^h)), \quad \forall\,\{v_j^h\}_{j=1}^n \subset V^h. \tag{1.38}$$

Taking into account (1.20), we notice now that, for all $\{v_j^h\}_{j=1}^n \subset V^h$,

$$\begin{aligned}\sum_{j=1}^{n} d_j(v_j^h) &= (c_n - c_n^{hk}, c_n - v_n^h)_H - (c_0 - c_0^h, c_1 - v_1^h)_H \\ &\quad + \sum_{j=1}^{n-1}(c_j - c_j^{hk}, c_j - v_j^h - (c_{j+1} - v_{j+1}^h))_H \\ &\leq \varepsilon\|c_n - c_n^{hk}\|_H^2 + \frac{1}{4\varepsilon}\|c_n - v_n^h\|_H^2 + \frac{1}{2}\|c_0 - c_0^h\|_H^2 + \frac{1}{2}\|c_1 - v_1^h\|_H^2 \\ &\quad + \sum_{j=1}^{n-1} k\|c_j - c_j^{hk}\|_H^2 + \sum_{j=1}^{n-1}\frac{1}{4k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2, \end{aligned} \tag{1.39}$$

where $\varepsilon > 0$ is a positive parameter assumed to be small enough. Then, using the fact that $a_0 = \|c_0 - c_0^h\|_H^2$, we get, for all $\{v_j^h\}_{j=1}^n \subset V^h$,

$$\begin{aligned}\sum_{j=1}^{n} d_j(v_j^h) &\leq \varepsilon\, a_n + \Big(\frac{1}{4\varepsilon} + \frac{1}{2}\Big)M + \frac{1}{2}a_0 \\ &\quad + \sum_{j=1}^{n-1} k\|c_j - c_j^{hk}\|_H^2 + \sum_{j=1}^{n-1}\frac{1}{4k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2,\end{aligned}$$

and thus, estimate (1.38) can be written as follows,

$$\begin{aligned}(1 - 2\,\varepsilon)\,a_n &\leq 2a_0 + T\,M + k\sum_{j=1}^{n}\beta\,a_j + \frac{1}{2\varepsilon}M + M \\ &\quad + 2\sum_{j=1}^{n-1} k\|c_j - c_j^{hk}\|_H^2 + \frac{1}{2}\sum_{j=1}^{n-1}\frac{1}{k}\,\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2, \quad \forall\,\{v_j^h\}_{j=1}^n \subset V^h,\end{aligned}$$

and finally

$$a_n \le \ell\, g_n + \ell\, k \sum_{j=1}^{n} a_j, \quad n = 1, 2, \ldots, N,$$

where ℓ is a positive constant and

$$g_n := a_0 + M + \sum_{j=1}^{n-1} \frac{1}{k} \, \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2.$$

Applying a discrete version of Gronwall's inequality with $\ell\, k \le 1/2$ (see [18]), we find that

$$\max_{0\le n\le N} a_n \le (\ell\,(1 + \ell\, T\, e^{2\ell T})) \max_{0\le n\le N} g_n.$$

Therefore, we have proved the following result.

Theorem 1.3 *Under the assumptions of Theorem 1.1 and assuming that regularity condition (1.23) holds, there exists a positive constant $\beta > 0$, independent of the discretization parameters h and k, such that the following error estimates are satisfied for all $\{v_n^h\}_{n=1}^N \subset V^h$,*

$$\begin{aligned} \max_{0\le n\le N} \|c_n - c_n^{hk}\|_H^2 &+ k \sum_{j=0}^{N} \left[\|c_j - c_j^{hk}\|_V^2 + |\gamma_0(c_j - c_j^{hk})|^2 \right] \\ &\le \beta \Bigg[\|c_0 - c_0^h\|_H^2 + \max_{1\le n\le N} \left\{ \left\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \right\|_H^2 + \|c_n - v_n^h\|_V^2 + I_n^2 \right\} \\ &\quad + \sum_{j=1}^{N-1} \frac{1}{k} \, \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 \Bigg]. \end{aligned} \tag{1.40}$$

Estimates (1.40) are the basis for the analysis of the convergence order. From now on and in order to approximate the space V, we consider the finite element space V^h defined in the following form:

$$\begin{aligned} V^h = \{ v^h \in \mathcal{C}([0, l])\,;\, v^h_{|[x_{i-1}, x_i]} \in P_1([x_{i-1}, x_i]), \text{ for } i = 1, \ldots, \hat{M}, \\ v^h(l) = 0 \}, \end{aligned} \tag{1.41}$$

where the spatial discretization of the interval $[0, l]$ is given by $0 = x_0 < x_1 < \ldots <$

$x_{\hat{M}} = l$ and $h = l/\hat{M}$. Moreover, $P_1([x_{i-1}, x_i])$ denotes the set of polynomials of degree less or equal to one in the interval $[x_{i-1}, x_i]$, $i = 1, \ldots, \hat{M}$. Furthermore, as an example of the application of estimates (1.40), let us assume further regularity conditions on the solution to the continuous problem:

$$c \in \mathcal{C}([0,T]; H^2(0,l)), \quad \frac{\partial c}{\partial t} \in L^2(0,T;V), \quad \frac{\partial^2 c}{\partial t^2} \in \mathcal{C}([0,T];H). \tag{1.42}$$

Corollary 1.1 *Under the assumptions of Theorem 1.3 and the additional regularity conditions (1.42), the linear convergence of the algorithm is obtained; i.e. there exists a positive constant $\beta > 0$, independent of h and k, such that*

$$\max_{0 \le n \le N} \|c_n - c_n^{hk}\|_H \le \beta\,(h+k).$$

Proof. Let $\pi^h : \mathcal{C}([0,l]) \to V^h$ denote the standard finite element projection operator, and let us take $v_j^h = \pi^h c_j$, $j = 1, \ldots, N$. Moreover, assume that the discrete initial condition is given by $c_0^h = \pi^h c_0$. Since $c \in \mathcal{C}([0,T]; H^2(0,l))$ we obtain (see [10]),

$$\max_{0 \le n \le N} \|c_n - \pi^h c_n\|_V \le \beta\, h\, \|c\|_{\mathcal{C}([0,T];H^2(0,l))}.$$

Keeping in mind the regularity condition (1.42), we can write

$$\frac{\partial c}{\partial t}(t_n) - \delta c_n = \frac{1}{k}\int_{t_{n-1}}^{t_n} \left(\frac{\partial c}{\partial t}(t_n) - \frac{\partial c}{\partial t}(t) \right) dt = \frac{1}{k}\int_{t_{n-1}}^{t_n}\int_t^{t_n} \frac{\partial^2 c}{\partial t^2}(s)\, ds\, dt, \tag{1.43}$$

and therefore, regarding that $\dfrac{\partial^2 c}{\partial t^2} \in \mathcal{C}([0,T];H)$, we have

$$\begin{aligned}
\Big\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \Big\|_H &\le \frac{1}{k}\int_{t_{n-1}}^{t_n}\int_t^{t_n} \Big\| \frac{\partial^2 c}{\partial t^2}(s) \Big\|_H ds\, dt \\
&\le \frac{1}{k}\int_{t_{n-1}}^{t_n}\int_t^{t_n} \Big\| \frac{\partial^2 c}{\partial t^2} \Big\|_{\mathcal{C}([0,T];H)} ds\, dt \\
&\le \frac{1}{k} \Big\| \frac{\partial^2 c}{\partial t^2} \Big\|_{\mathcal{C}([0,T];H)} \int_{t_{n-1}}^{t_n}\int_{t_{n-1}}^{t_n} ds\, dt,
\end{aligned}$$

and then

$$\max_{1\le n\le N} \left\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \right\|_H \le k \left\| \frac{\partial^2 c}{\partial t^2} \right\|_{\mathcal{C}([0,T];H)}.$$

The last term in estimates (1.40) is bounded following the ideas applied to estimate the damage error terms (see, for instance, [4]). First, note that both functions c_j and c_{j+1} belong to $H^1(0,l)$ and then, taking into account the linearity of the projection operator, we get (see [10])

$$\|c_{j+1} - c_j - \pi^h(c_{j+1} - c_j)\|_H^2 \le \beta\, h^2 \|c_{j+1} - c_j\|_V^2.$$

On the other hand, using regularity condition (1.42) we deduce that

$$c_{j+1} - c_j = \int_{t_j}^{t_{j+1}} \frac{\partial c}{\partial t}(s)\, ds.$$

Thus, we have

$$\|c_{j+1} - c_j\|_V \le \int_{t_j}^{t_{j+1}} \left\| \frac{\partial c}{\partial t}(s) \right\|_V ds \le \sqrt{k} \left(\int_{t_j}^{t_{j+1}} \left\| \frac{\partial c}{\partial t}(s) \right\|_V^2 ds \right)^{1/2},$$

and therefore,

$$\begin{aligned} \frac{1}{k} \sum_{j=1}^{N-1} \|c_{j+1} - \pi^h c_{j+1} - (c_j - \pi^h c_j)\|_H^2 &\le \beta\, h^2 \sum_{j=1}^{N-1} \int_{t_j}^{t_{j+1}} \left\| \frac{\partial c}{\partial t}(s) \right\|_V^2 ds \\ &\le \beta\, h^2 \left\| \frac{\partial c}{\partial t} \right\|_{L^2(0,T;V)}^2. \end{aligned}$$

Finally, from definition (1.30) we get

$$I_n = k_H^a\, k_H^d\, e^{-k_H^d t_n} \left| \sum_{j=0}^{n-1} \left(\int_{t_j}^{t_{j+1}} e^{k_H^d \tau} \gamma_0(c(\tau))\, d\tau - k\, e^{k_H^d t_j} \gamma_0(c_j) \right) \right|.$$

Moreover, taking into account that

$$\int_{t_j}^{t_{j+1}} \left(e^{k_H^d \tau} \gamma_0(c(\tau)) - e^{k_H^d t_j} \gamma_0(c_j) \right) d\tau = \int_{t_j}^{t_{j+1}} \int_{t_j}^{\tau} \frac{\partial \omega}{\partial t}(s)\, ds\, d\tau,$$

where $\omega(s) = e^{k_H^d s}\gamma_0(c(s))$, we obtain, for $1 \le n \le N$,

$$I_n = k_H^a k_H^d e^{-k_H^d t_n} \left| \sum_{j=0}^{n-1} \int_{t_j}^{t_{j+1}} (e^{k_H^d \tau}\gamma_0(c(\tau)) - e^{k_H^d t_j}\gamma_0(c_j)) d\tau \right|$$
$$\le k_H^a k_H^d e^{-k_H^d t_n} \sum_{j=0}^{n-1} \int_{t_j}^{t_{j+1}} \int_{t_j}^{t_{j+1}} \left| \frac{\partial \omega}{\partial t}(s) \right| ds\, d\tau.$$

Keeping in mind the properties of the trace operator and that $k\,N = T$ it follows that, for $1 \le n \le N$,

$$\begin{aligned} I_n &\le k_H^a\, k_H^d\, e^{-k_H^d t_n}\, k^{1/2} \sum_{j=0}^{n-1} \int_{t_j}^{t_{j+1}} \left\| \frac{\partial \omega}{\partial t} \right\|_{L^2(t_j,t_{j+1})} d\tau \\ &\le k_H^a\, k_H^d\, e^{-k_H^d t_n}\, k^{3/2} \sum_{j=0}^{n-1} \left\| \frac{\partial \omega}{\partial t} \right\|_{L^2(t_j,t_{j+1})} \\ &\le k_H^a\, k_H^d\, e^{-k_H^d t_n}\, k^{3/2} n^{1/2} \left(\sum_{j=0}^{n-1} \left\| \frac{\partial \omega}{\partial t} \right\|^2_{L^2(t_j,t_{j+1})} \right)^{1/2} \\ &\le \beta\, k \left(\sum_{j=0}^{N-1} \left\| \frac{\partial \omega}{\partial t} \right\|^2_{L^2(t_j,t_{j+1})} \right)^{1/2} \\ &\le \beta\, k \left(\left\| \frac{\partial \omega}{\partial t} \right\|^2_{L^2(t_0,t_1)} + \left\| \frac{\partial \omega}{\partial t} \right\|^2_{L^2(t_1,t_2)} + \cdots + \left\| \frac{\partial \omega}{\partial t} \right\|^2_{L^2(t_{N-1},t_N)} \right)^{1/2}, \end{aligned}$$

being β a large enough constant independent of h and k. Thus, we deduce that

$$I_n \le \beta\, k \left\| \frac{\partial \omega}{\partial t} \right\|_{L^2(0,T)}, \qquad \text{for } 1 \le n \le N.$$

Finally, we have

$$\max_{1 \le n \le N} I_n^2 \le \beta\, k^2,$$

and the linear convergence of the algorithm is now obtained from estimates (1.40). $\square$

1.5 Numerical results

In this section, we first introduce the numerical scheme and the algorithm implemented in MATLAB which is used in order to obtain the numerical approximations of Problem P_H^{hk}. Then, we present some numerical results in order to exhibit its accuracy in an academic example and its behavior in the simulation of two commercially available surfactants.

Considering the finite element space defined in (1.41), for $n = 1, 2, \ldots, N$ and given $c_{n-1}^{hk} \in V^h$, the discrete concentration of surfactant at time $t = t_n$, c_n^{hk}, is then obtained from equation (1.21); namely, it solves the linear system:

$$
\begin{aligned}
(c_n^{hk}, v^h)_H + D\,k\,((c_n^{hk}, v^h)) + k_H^a\,k\,\gamma_0(c_n^{hk})\,\gamma_0(v^h) \\
= (c_{n-1}^{hk}, v^h)_H + k\,\phi_{n-1}^{hk}\,\gamma_0(v^h), \quad \forall v^h \in V^h,
\end{aligned}
$$

where value ϕ_{n-1}^{hk} is given in (1.22). Now, we describe the algorithm we have implemented to solve this problem:

1. **Initial time step.** At the beginning both c_0^{hk} and Γ_0 are given. We calculate

$$\phi_0^{hk} = k_H^d\,\Gamma_0.$$

2. **(n)th time step.** The surfactant concentration at time t_{n-1}, c_{n-1}^{hk}, and the value ϕ_{n-1}^{hk} are known. Then, at time t_n, c_n^{hk}, ϕ_n^{hk} and Γ_n^{hk} are obtained using the following algorithm:

   (a) We calculate c_n^{hk} by solving the following linear problem:

$$
\begin{aligned}
\int_0^l c_n^{hk}\,v^h\,dx + D\,k \int_0^l \frac{\partial c_n^{hk}}{\partial x}\,\frac{\partial v^h}{\partial x}\,dx + k_H^a\,k\,\gamma_0(c_n^{hk})\gamma_0(v^h) \\
= k\,\phi_{n-1}^{hk}\,\gamma_0(v^h) + \int_0^l c_{n-1}^{hk}\,v^h\,dx, \quad \forall v^h \in V^h.
\end{aligned}
$$

(b) Then, the value of ϕ_n^{hk} is determined with the formula:

$$\phi_n^{hk} = k_H^d\,\Gamma_0\,e^{-k_H^d\,t_{n+1}} + k_H^d\,k_H^a\,k\sum_{j=0}^{n} e^{k_H^d(t_j-t_{n+1})}\gamma_0(c_j^{hk}).$$

(c) Once ϕ_n^{hk} is known, Γ_n^{hk} is easily calculated:

$$\Gamma_n^{hk} = \phi_n^{hk}/k_H^d.$$

This numerical algorithm has been implemented on a 3.2 Ghz PC using MATLAB, and a typical run ($h = k = 0.01$) takes about 0.6 seconds of CPU time.

1.5.1 First example: numerical convergence

As a first example, we consider the following test problem:

$$\begin{aligned}
&\frac{\partial c}{\partial t}(t,x) - 5\,\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \quad t\in(0,0.1), \quad x\in(0,1),\\
&5\,\frac{\partial c}{\partial x}(t,0) = c(t,0) - \phi(t,c(t,0)), \quad t\in(0,0.1),\\
&c(t,1) = 1, \quad t\in(0,0.1),\\
&c(0,x) = c_0(x),
\end{aligned}$$

with the initial condition $c_0(x) = \min\{1,\,1000\,x\}$. This problem corresponds to problem (1.1), (1.3)-(1.4) and (1.7) with the following data:

$$l = 1, \quad T = 0.1, \quad c_b = 1, \quad D = 5, \quad k_H^a = 1, \quad k_H^d = 1, \quad \Gamma_0 = 0.$$

Taking the solution obtained with parameters $h = 1/16384$ and $k = 10^{-6}$ as the "exact solution", c, the numerical errors (multiplied by 10^4), which are given by

$$\max_{1\le n\le N}\|c_n - c_n^{hk}\|_H,$$

are presented in Table 1.1 for several values of the discretization parameters h and k. As it can be seen, the numerical error tends to zero as both h and k do. Moreover, the graph of the error with respect to the parameter $h+k$ is shown in Figure 1.1, where the linear convergence, stated in Corollary 1.1, is clearly achieved.

h ↓ k →	**0.01**	**0.005**	**0.002**	**0.001**	**0.0005**
1/8	2.026437	2.037885	2.044993	2.047404	2.048617
1/16	0.900869	0.961206	0.998666	1.011371	1.017766
1/32	0.337594	0.422319	0.474919	0.492760	0.501739
1/64	0.056607	0.153505	0.213663	0.234067	0.244336
1/128	0.083628	0.019351	0.083284	0.104968	0.115882
1/256	0.153668	0.047651	0.018168	0.040493	0.051729
1/512	0.188668	0.081131	0.014369	0.008275	0.019672
1/1024	0.206162	0.097866	0.030633	0.007829	0.003648
1/2048	0.214908	0.106232	0.038763	0.015879	0.004362
1/4096	0.219281	0.110415	0.042828	0.019904	0.008367

Table 1.1: Numerical errors ($\times 10^4$) for several time and spatial discretization parameters.

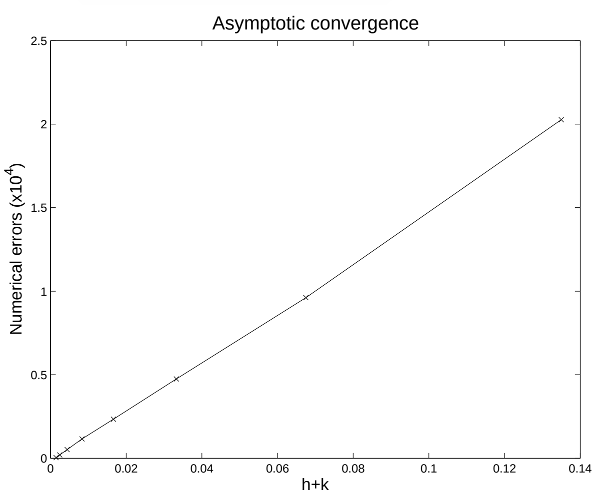

Figure 1.1: Example 1: linear convergence.

1.5.2 Second example: simulation of hexanol

As a second problem, we consider a dilute solution of the commercial alcohol hexanol, using the data from references [7] and [44], namely:

$$
\begin{aligned}
&c_b = 3.44\,\mathrm{mol/m^3}, \quad D = 7.16 \times 10^{-10}\mathrm{m^2/s}, \quad l = 10^{-4}\,\mathrm{m}, \\
&T = 0.5\,\mathrm{s}, \quad \Gamma_0 = 0\,\mathrm{mol/m^2}.
\end{aligned}
$$

Moreover, the initial condition c_0 is here defined as $c_0(x) = c_b$ for all $x \in [0, 10^{-4}]$.

Using the discretization parameters $h = 10^{-8}\,\mathrm{m}$ and $k = 10^{-4}\,\mathrm{s}$ and the adsorption and desorption constants, $k_H^a = 1.73 \times 10^{-4}\,\mathrm{m/s}$ and $k_H^d = 157\,\mathrm{s^{-1}}$, the concentration at final time and the evolution in time of the subsurface concentration are shown in Figure 1.2.

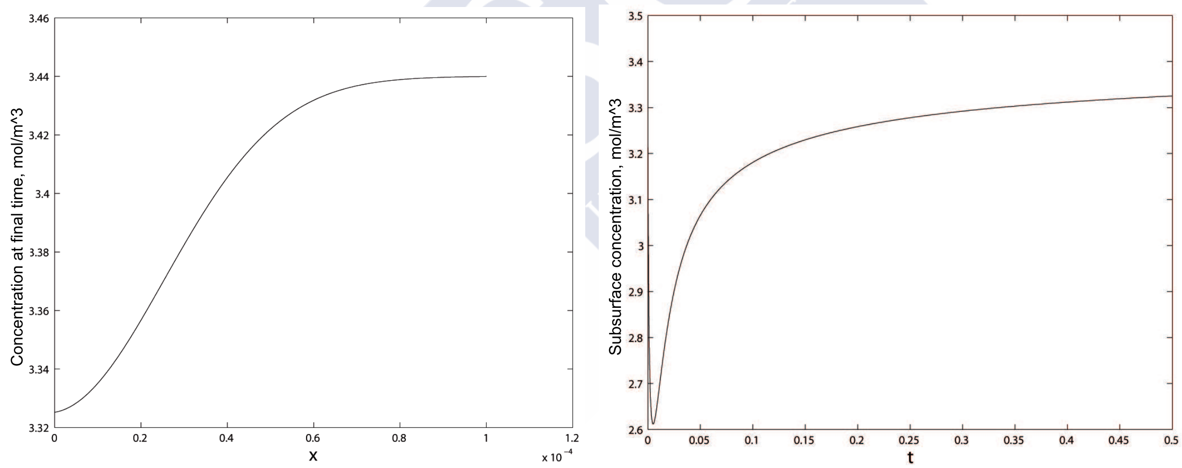

Figure 1.2: Concentration at final time (left) and evolution in time of subsurface concentration (MATLAB results).

Now, these results are compared to those obtained by using the commercial code COMSOL Multiphysics. Indeed, in Figure 1.3 the concentration at final time and the evolution in time of the subsurface concentration are plotted again. As it can be seen, these results are in good agreement with those obtained with our algorithm.

Moreover, in Figures 1.4 and 1.5 we compare the evolution in time of both subsurface and surface concentrations, respectively, obtained with the linear mixed kinetic-diffusion model described in this chapter, with that results obtained with the diffusion-

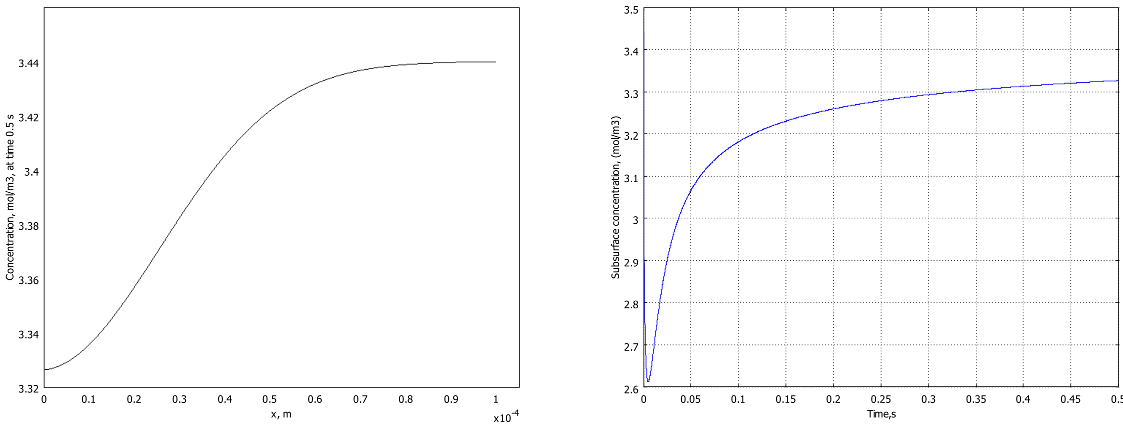

Figure 1.3: Concentration at final time (left) and evolution in time of subsurface concentration (COMSOL results).

controlled model for the classical Henry's isotherm, where the Henry equilibrium adsorption constant K_H equals k_H^a/k_H^d. As it can be seen in Figures 1.4 and 1.5, the diffusion-controlled model predicts a faster equilibration of both subsurface and surface concentrations than the mixed kinetic-diffusion one. In the case of the latter model, the adsorption-desorption dynamics limits the mass transfer from the bulk solution to the surface due to the existence of an adsorption barrier that surfactant molecules have to undergo in order to move from the subsurface to the surface and viceversa. However, in the diffusion-controlled model, diffusion mechanics limits the entire process since the equilibration between the subsurface and surface layers is assumed to be immediate.

Next, we analyze the dependence on the adsorption and desorption rate constants, k_H^a and k_H^d, so we choose different values of these constants as reported in [44], leading to the following six cases:

- **Case i**: $k_H^a = 2.583 \times 10^{-3}\,\mathrm{m/s}$ and $k_H^d = 2348\,\mathrm{s}^{-1}$.
- **Case ii**: $k_H^a = 6.456 \times 10^{-4}\,\mathrm{m/s}$ and $k_H^d = 587\,\mathrm{s}^{-1}$.
- **Case iii**: $k_H^a = 1.73 \times 10^{-4}\,\mathrm{m/s}$ and $k_H^d = 157\,\mathrm{s}^{-1}$.
- **Case iv**: $k_H^a = 1.96 \times 10^{-5}\,\mathrm{m/s}$ and $k_H^d = 18\,\mathrm{s}^{-1}$.
- **Case v**: $k_H^a = 0\,\mathrm{m/s}$ and $k_H^d = 0\,\mathrm{s}^{-1}$.

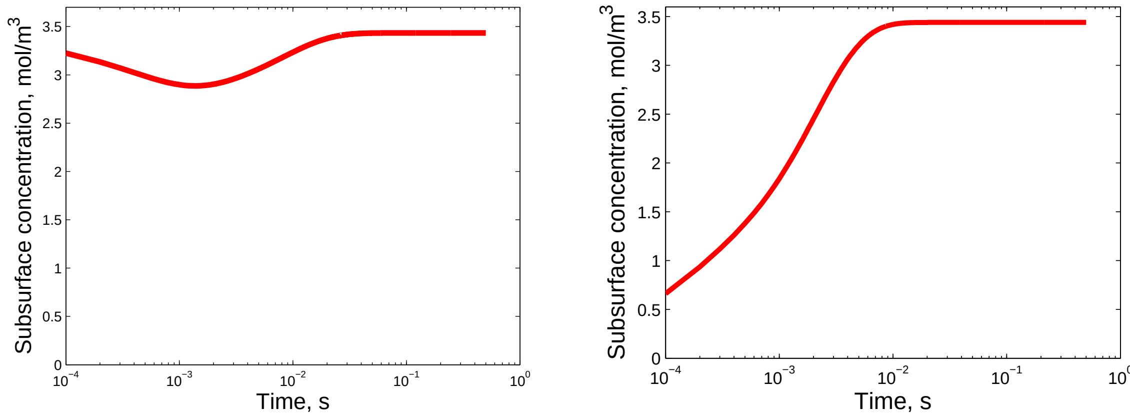

Figure 1.4: Evolution in time of the subsurface concentration with the mixed kinetic model (left) and that obtained with the diffusion-controlled model for Henry's isotherm (right), semi-log scale.

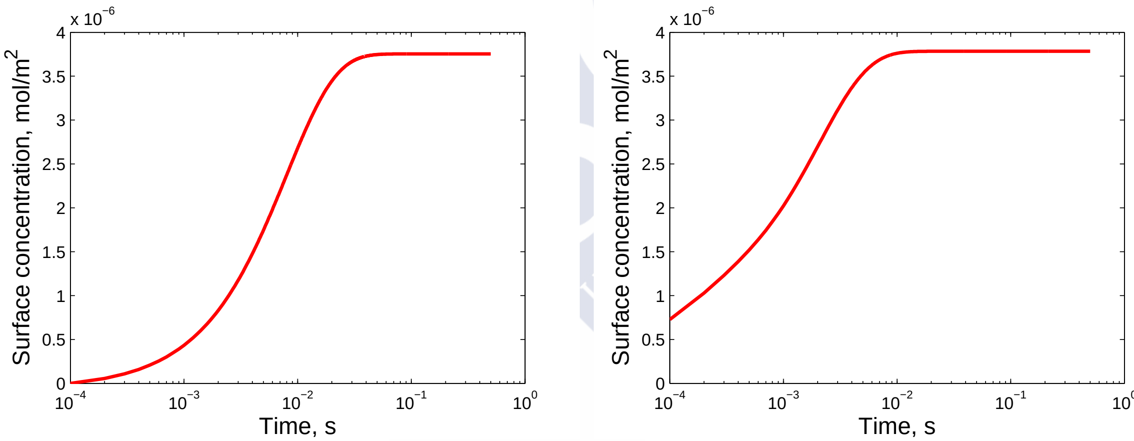

Figure 1.5: Evolution in time of the surface concentration $\Gamma(t)$ with the mixed kinetic model (left) and that obtained with the diffusion-controlled model using Henry's isotherm (right), semi-log scale.

- **Case vi**: diffusion-controlled model with Henry's isotherm, $K_H = 1.1 \times 10^{-6}\,\mathrm{m}$.

Our aim is to compare the surface tension $\widetilde{\gamma}$ given by

$$\widetilde{\gamma}(t) = \widetilde{\gamma}_0 - n\,R\,\theta\,\Gamma(t),$$

for each of the above cases, where $\widetilde{\gamma}_0 = 0.072\,\mathrm{N/m}$ denotes the surface tension of pure water, $\theta = 293.71\,\mathrm{K}$ is the temperature, $R = 8.31\,\mathrm{J/(K\,mol)}$ represents the gas constant and n is a constant which is equal to one for a non-ionic surfactant. Using the discretization parameters $h = 10^{-8}$ m and $k = 10^{-5}$ s for cases ii-vi and $k = 10^{-6}$ s for case i, in Figure 1.6 the evolution in time of the surface tension obtained for each of the above six cases is represented (semi-log scale). We point out that these numerical calculations are in good agreement with the experimental and theoretical values of the surface tensions of the hexanol solution reported in Figure 6 of [44] and Figure 27 of [7]. As it can be expected, the time needed to reach the stationary value decreases meanwhile the value of the adsorption rate constant, k_H^a, increases. This is because, if k_H^a increases, then the incorporation of surfactant molecules at the surface becomes faster and, the increasing of the surface concentration is closely related to the decreasing of the surface tension. Furthermore, as the value of the adsorption rate constant increases, the behavior predicted by the mixed kinetic-diffusion model approaches to the behavior predicted by the diffusion-controlled one.

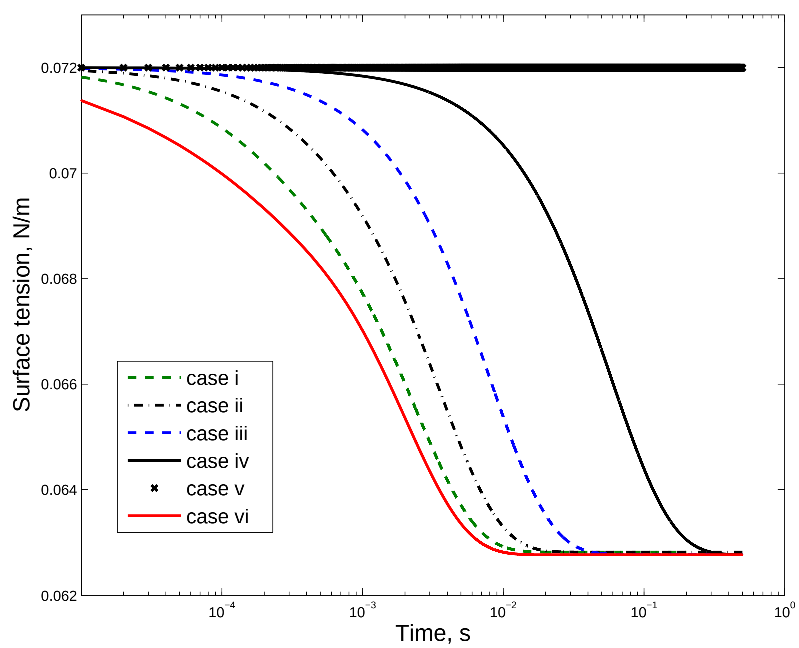

Figure 1.6: Surface tension graphs obtained for the six cases of adsorption and desorption constants, semi-log scale.

Finally, the evolution in time of the surface concentration is shown in Figure 1.7 for the above six cases using the same discretization parameters utilized to obtain Figure

1.6. As we can observe in Figure 1.7, the surface concentration reaches its equilibrium value faster in the diffusion-controlled model than in the mixed kinetic-diffusion one. Moreover, as the adsorption rate constant k_H^a decreases, the adsorption process becomes slower and more time is needed to achieve the saturation at the surface.

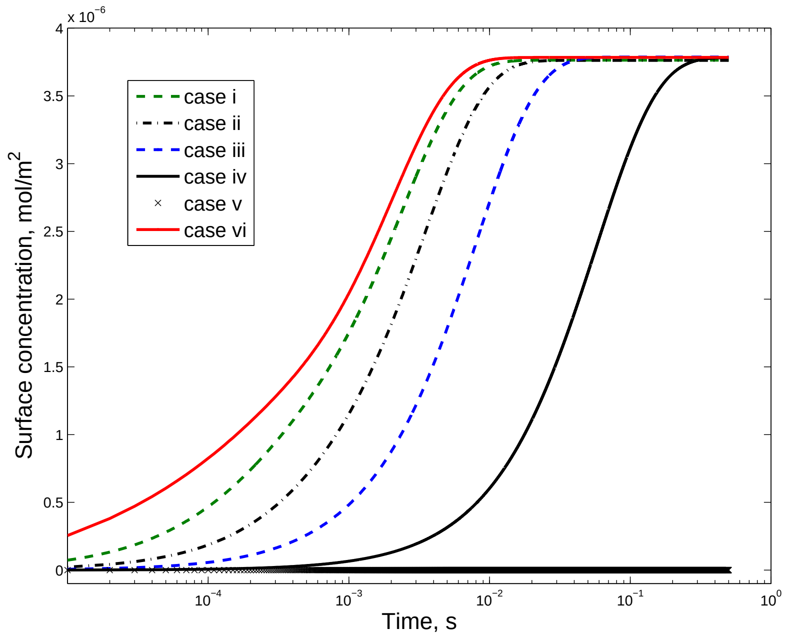

Figure 1.7: Evolution in time of the surface concentration obtained for the six cases of adsorption and desorption constants, semi-log scale.

1.5.3 Third example: simulation of heptanol

As a third example, we consider now a dilute solution of the commercial alcohol heptanol (see [44] for further details):

$$c_b = 0.1\,\mathrm{mol/m^3}, \quad D = 6.5 \times 10^{-10}\mathrm{m^2/s}, \quad k_H^a = 7.04 \times 10^{-4}\,\mathrm{m/s},$$
$$k_H^d = 190.27\,\mathrm{s^{-1}}, \quad l = 10^{-6}\,\mathrm{m}, \quad T = 1\,\mathrm{s}, \quad \Gamma_0 = 0\,\mathrm{mol/m^2}.$$

Moreover, the initial condition c_0 is defined as $c_0(x) = c_b$ for all $x \in [0, 10^{-6}]$.

Using the discretization parameters $h = 10^{-8}$ m and $k = 10^{-4}$ s, the evolution in time of the subsurface and the surface concentrations are shown in Figure 1.8 (left-hand side and right-hand side, respectively). We note that the subsurface concentration evolves to the constant bulk concentration c_b in a fast way.

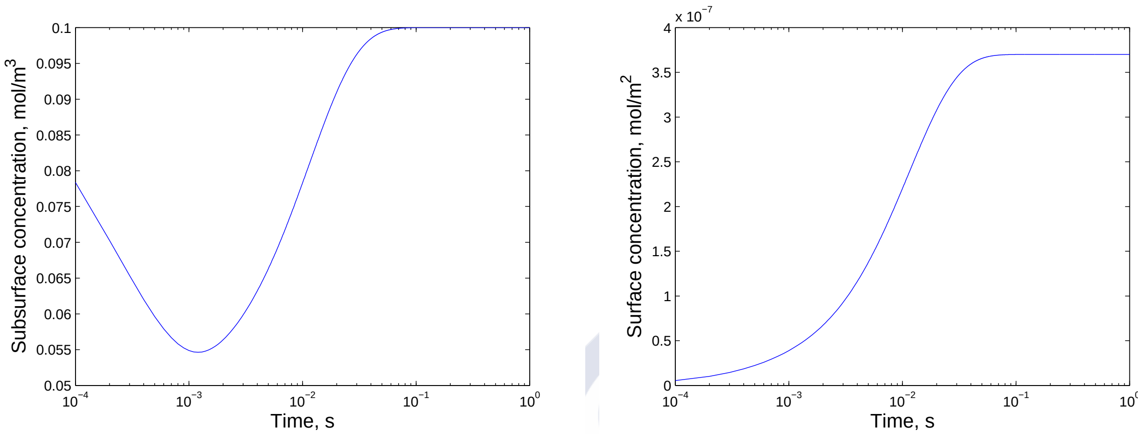

Figure 1.8: Evolution in time of the subsurface concentration (left) and the surface concentration (right), semi-log scale.

Finally, in Figure 1.9 we plot the evolution in time of the surface tension for several bulk concentrations ($c_b = 0.1\,\mathrm{mol/m^3}$, $c_b = 0.5\,\mathrm{mol/m^3}$ and $c_b = 0.9\,\mathrm{mol/m^3}$).

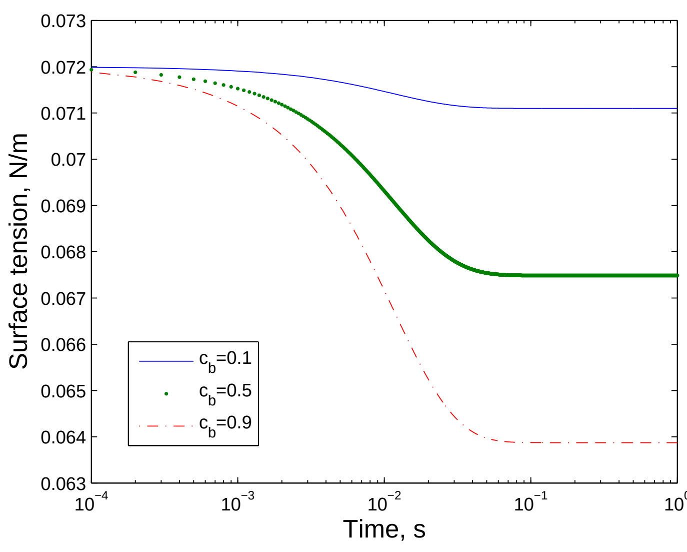

Figure 1.9: Evolution in time of the surface tension for several heptanol bulk concentrations, semi-log scale.

As it can be observed, the time needed to reach stationary values of the surface tension depends both on the values for the adsorption rate constants (see Figure 1.6) and on the bulk concentration (see Figure 1.9). Moreover, increasing the bulk concentration, the equilibrium value of the surface tension decreases and so, the fall of the surface tension curve is greater as the concentration increases. Besides, as the bulk concentration decreases, the number of molecules in the solution becomes smaller. Therefore, the quantity of molecules achieving the surface decreases which implies that the rate of adsorption also decreases (see equation (1.6)) and consequently, the time needed for reaching the equilibrium surface tension increases.

Chapter 2

Diffusion-controlled model with Langmuir isotherm

In this chapter, we focus on the problem of modeling the surfactant behavior at the air-water interface considering a diffusion-controlled model. As it was said in the introduction of this manuscript, in this family of models, diffusion is the mechanism that governs the process since adsorption is assumed to be instantaneous. The adsorption dynamics is described here by the Langmuir isotherm, which has been used in a huge amount of literature (see, for example, [6, 7, 35]). This expression states a nonlinear relationship between the surface and subsurface concentrations and it is based on a lattice-type model (see [7, 16]) which assumes that the adsorption places on the lattice are equivalent, the probability of adsorption of the monomers at one empty space is independent of the occupied sites in its neighborhood and neither interactions nor intermolecular forces between the monomers in the lattice are considered.

Mathematically, in this chapter, we deal with a non-standard parabolic problem. The reason why this problem is non-standard is because the boundary condition at the subsurface is coupled with the Langmuir isotherm, which makes the system to be nonlinear. For this problem, we prove the existence of weak solution by using the Rothe's method, an intermediate problem (for which the existence of a unique weak solution is obtained applying Brouwer's fixed-point theorem), a priori estimates and passing to the limit. The uniqueness issue is solved using some arguments already introduced in [25], as the integration in time of the respective weak equations and the definition of adequate test functions. Moreover, a semi-discrete problem in time associated to an equivalent formulation of the weak problem is analyzed, proving some a priori estimates from which the linear convergence is achieved under additional regularity conditions. Then, fully discrete approximations, obtained by using the finite element method for the spatial discretization and a hybrid combination of both backward and forward Euler schemes, are presented. An error estimate result is proved from which the linear convergence is deduced under suitable regularity conditions. Finally, some numerical examples are shown to demonstrate the accuracy of this algorithm and the behavior of two commercially available surfactants.

2.1 The mathematical model

Denoting by $\tilde{c}(t,x)$ the concentration of surfactant at time $t \in [0,T]$ and point $x \in [0,l]$ and by $\Gamma(t)$ the time-dependent surface concentration, as it is usual, and taking into account the Fick's law, we consider the diffusion partial differential equation:

$$\frac{\partial \tilde{c}}{\partial t}(t,x) - D\,\frac{\partial^2 \tilde{c}}{\partial x^2}(t,x) \;=\; 0, \quad t>0, \;\; x \in (0,l), \tag{2.1}$$

together with the boundary conditions (see [7, 35]):

$$D\,\frac{\partial \tilde{c}}{\partial x}(t,0) = \frac{d\,\Gamma}{dt}(t), \quad t>0, \tag{2.2}$$

$$\tilde{c}(t,l) = c_b, \quad t>0, \tag{2.3}$$

and the initial conditions:

$$\tilde{c}(0,x) = \tilde{c}_0(x), \;\; x \in (0,l), \tag{2.4}$$

$$\Gamma(0) = \Gamma_0. \tag{2.5}$$

In equation (2.4), $\tilde{c}_0(x)$ is a function defined in $[0, l]$ which equals c_b on $x = l$. We remind that the time-dependent surface concentration, $\Gamma(t)$, is also an unknown of the system, so an additional condition is needed in order to close the problem. As we said previously, in this chapter, we consider the well-known and classical Langmuir isotherm (see [7]):

$$\Gamma(t) = \Gamma_m \frac{K_L \, \tilde{c}(t, 0)}{1 + K_L \, \tilde{c}(t, 0)}, \quad t \geq 0, \tag{2.6}$$

where Γ_m is the maximum surface concentration and K_L is the Langmuir equilibrium adsorption constant. Here, we are interested in surfactant solutions below their *cmc* (critical micelle concentration), that is to say, we are interested in single-molecule transport (see [5]), therefore, the parameter Γ_m, which is a theoretical limit, cannot be reached. Moreover, it is usual in chemistry literature (see [7, 35]) to approximate the Langmuir isotherm by the Henry isotherm when the concentration is low or when $K_L c(t) << 1$. Then

$$K_H = \Gamma_m K_L.$$

The Langmuir isotherm (2.6) was first deduced using kinetic arguments (see [7, 16]), by assuming that the rate of change of the surface concentration due to adsorption is equal to the rate of change of the surface concentration due to desorption. However, the Langmuir isotherm can also be deduced by molecular thermodynamic arguments for ideal non-localized adsorption.

For the sake of clarity in the presentation of this chapter and without lost of generality, hereinafter we assume that the constants D, K_L and Γ_m are equal to 1 and we define the nondecreasing Lipschitz function $F : \mathbb{R} \to \mathbb{R}$ as follows

$$F(z) = \begin{cases} \dfrac{z}{1+z} & \text{if } z \geq 0, \\ 0 & \text{if } z < 0. \end{cases} \tag{2.7}$$

Notice that a primitive to F given by

$$H(z) = \begin{cases} z - \ln(1+z) & \text{if } z \geq 0, \\ 0 & \text{if } z < 0, \end{cases} \tag{2.8}$$

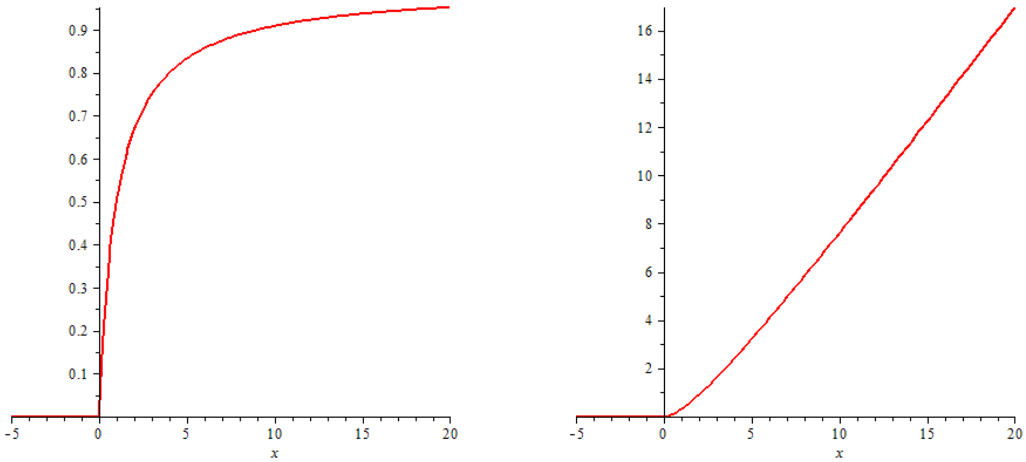

Figure 2.1: Function F (left) and its primitive H (right).

is nondecreasing and convex (see Figure 2.1).

Therefore, using (2.7), boundary condition (2.2) can be written

$$D\frac{\partial \tilde{c}}{\partial x}(t,0) = \frac{d(F \circ \tilde{c}(t,0))}{dt}, \quad t > 0. \tag{2.9}$$

We remark that equation (2.9) determines a nonlinear and dynamical boundary condition due to the function F coming from Langmuir isotherm.

Now, in order to obtain a homogeneous boundary condition in the bulk of the solution and simplify the calculations, we define a new variable $c = \tilde{c} - c_b$ and then problem (2.1), (2.3)-(2.5) and (2.9) can be written as follows

$$\frac{\partial c}{\partial t}(t,x) - \frac{\partial^2 c}{\partial x^2}(t,x) = 0, \quad t > 0, \quad x \in (0,l), \tag{2.10}$$

$$\frac{\partial c}{\partial x}(t,0) = \frac{d(F \circ (c(t,0) + c_b))}{dt}, \quad t > 0, \tag{2.11}$$

$$c(t,l) = 0, \quad t > 0, \tag{2.12}$$

$$c(0,x) = c_0(x), \quad x \in (0,l), \tag{2.13}$$

where $c_0(x) = \tilde{c}_0(x) - c_b$.

Now, we turn to obtain the variational formulation of problem (2.10)-(2.13).

2.2 Weak formulation of the problem

Before establishing the weak formulation, we point out that we follow the notation introduced in Section 1.2 of Chapter 1. Moreover, we assume the following hypothesis: **(H1)**. The initial condition c_0 belongs to V and $-\mathfrak{C} \leq c_0 \leq 0$ a.e. in $(0, l)$, where $\mathfrak{C}$ is a positive constant.

Now, assume that c is a smooth function which solves problem (2.10)-(2.13) and let v be a smooth function such that $v(t, l) = 0$ a.e. $t \in (0, T)$; multiplying equation (2.10) by v, integrating in $(0, l)$ and using the integration by parts formula, we obtain

$$\int_0^l \frac{\partial c}{\partial t}(t,x)v(t,x)dx + \int_0^l \frac{\partial c}{\partial x}(t,x)\frac{\partial v}{\partial x}(t,x)dx + \frac{\partial c}{\partial x}(t,0)v(t,0) = 0,$$

for a.e. $t \in (0, T)$. Using equation (2.11), we find that

$$\int_0^l \frac{\partial c}{\partial t}(t,x)v(t,x)dx + \int_0^l \frac{\partial c}{\partial x}(t,x)\frac{\partial v}{\partial x}(t,x)dx + \frac{d(F \circ (c(t,0) + c_b))}{dt}v(t,0) = 0, \quad (2.14)$$

for a.e. $t \in (0, T)$. Integrating now in $(0, T)$, we have the following weak formulation of the problem (2.10)-(2.13):

Problem P_W^L. For a given $c_0 \in H$, find a function $c \in W_2(0, T)$ such that $F(\gamma_0(c(t)) + c_b) \in H^1(0, T)$, and

$$\int_0^T \langle \frac{\partial c}{\partial t}(t), v(t)\rangle_{V' \times V}\, dt + \int_0^T ((c(t), v(t)))dt + \int_0^T \frac{d(F(\gamma_0(c(t)) + c_b))}{dt}\gamma_0(v(t))\, dt = 0,$$

$$\forall v \in \mathcal{V}, \quad (2.15)$$

$$c(0) = c_0. \quad (2.16)$$

We remark that the initial condition (2.16) makes sense since $W_2(0, T) \hookrightarrow \mathcal{C}([0, T]; H)$.

2.3 Existence and uniqueness results

In this section, following the ideas introduced in [25], in order to prove the existence of solution to Problem P_W^L, we use the Rothe method of semi-discretization in time (see [39]). The scheme of the proof is as follows: the first step is to consider the semi-discretrization in time of problem (2.14) and show that this problem has a unique solution; secondly, using this solution, we construct a piecewise constant and a piecewise linear in time functions and then, using some estimates of these functions and passing to the limit, we arrive to the existence result.

First of all, before dealing with the proof of existence, we introduce the following technical lemma gathering the properties of the functions F and H that will be useful later.

Lemma 2.1 *Functions F and H, defined in (2.7) and (2.8), respectively, satisfy the following properties:*

$$F(z)z - H(z) \geq 0, \quad \forall\, z \in \mathbb{R}, \tag{2.17}$$

$$(F(z_1) - F(z_2))(z_1 - z_2) \geq (F(z_1) - F(z_2))^2, \quad \forall\, z_1, z_2 \in \mathbb{R}. \tag{2.18}$$

Proof. Taking into account the definitions of functions F and H given by (2.7) and (2.8), respectively, (2.17) is trivially obtained for $z < 0$. Otherwise, if z is nonnegative, we get

$$F(z)z - H(z) = \frac{z^2}{1+z} - z + \ln(1+z), \quad \forall\, z \geq 0,$$

then, defining the variable $\alpha := 1 + z$, we have that (2.17) is equivalent to

$$\alpha \ln(\alpha) \geq \alpha - 1, \quad \text{for}\, \alpha \geq 1. \tag{2.19}$$

On the other hand, the function $f : \mathbb{R}^+ \to \mathbb{R}$ defined by

$$f(\alpha) = \alpha \ln(\alpha)$$

verifies that

$$f'(\alpha) = \ln(\alpha) + 1 > 0 \quad \text{in} \quad (e^{-1}, +\infty),$$

$$f''(\alpha) = \frac{1}{\alpha} > 0 \quad \text{in} \quad (e^{-1}, +\infty).$$

Then f is convex in $(e^{-1},+\infty)$ and consequently (see [17])

$$f(\alpha)-f(1)\geq f'(1)(\alpha-1),\quad \forall\,\alpha\in(e^{-1},+\infty),$$

thus, (2.17) follows. Now, taking into account that F is nondecreasing and 1-Lipschitz it follows that

$$(F(z_1)-F(z_2))(z_1-z_2)=|F(z_1)-F(z_2)|\,|z_1-z_2|\geq(F(z_1)-F(z_2))^2,\quad \forall\,z_1,z_2\in\mathbb{R},$$

and (2.18) is obtained. □

Now, we prove the following preliminary result.

Lemma 2.2 *Assuming that $c_{s-1}\in V$ and $\tau>0$, there exists a unique function $c_s\in V$ such that*

$$\begin{aligned}\int_0^l\frac{(c_s-c_{s-1})}{\tau}\,vdx\quad &+\quad\frac{F(\gamma_0(c_s)+c_b)-F(\gamma_0(c_{s-1})+c_b)}{\tau}\,\gamma_0(v)+\\ &+\quad\int_0^l\frac{\partial c_s}{\partial x}\frac{\partial v}{\partial x}dx=0,\quad\forall v\in V.\end{aligned}\tag{2.20}$$

Moreover, if $-\mathfrak{C}\leq c_{s-1}\leq 0$ a.e. in $(0,l)$ then

$$-\mathfrak{C}\leq c_s\leq 0\ \ a.e.\ \ in\ (0,l),\tag{2.21}$$

$\mathfrak{C}$ being a positive constant.

Proof. *Existence.* The proof of the existence of solution to the nonlinear problem (2.20) is based on the study of an intermediate problem, followed by the application of Brouwer's fixed point theorem (see [17]).

Intermediate problem. For a given $c_{s-1}\in V$, $\tau>0$ and $c^\star\in\mathbb{R}$, find $c\in V$ such that, for all $v\in V$,

$$\int_0^l\frac{(c-c_{s-1})}{\tau}\,vdx+\frac{F(c^\star+c_b)-F(\gamma_0(c_{s-1})+c_b)}{\tau}\,\gamma_0(v)+\int_0^l\frac{\partial c}{\partial x}\frac{\partial v}{\partial x}dx=0.\tag{2.22}$$

The existence of a unique solution to problem (2.22) can be proven applying the Lax-Milgram theorem by taking into account that the bilinear mapping

$$a(u,v) = \int_0^l u\, v dx + \tau \int_0^l \frac{\partial u}{\partial x}\frac{\partial v}{\partial x} dx,$$

is continuous and coercive in V and the functional

$$L(v) = \int_0^l c_{s-1}\, v dx + (F(\gamma_0(c_{s-1}) + c_b) - F(c^\star + c_b))\,\gamma_0(v),$$

belongs to V'.

Now, we define the operator $G : \mathbb{R} \to \mathbb{R}$ given by $G(c^\star) = \gamma_0(c)$, where $c \in V$ is the unique solution to problem (2.22) corresponding to $c^\star$. Moreover, for the operator G, we find that G maps $[-M, M]$ into itself, where

$$M := \frac{C_{tr}\, C_e \|c_{s-1}\|_H + C_{tr}^2}{\tau},$$

being C_{tr} the trace constant, see (1.9), and C_e the equivalence constant between the norms $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$, such that $\|v\|_{H^1(0,l)} \leq C_e\|v\|_V$, for all v in V.

Indeed, in order to prove that G maps $[-M, M]$ into itself, we take $c \in V$ as a test function in (2.22) and we get

$$\int_0^l c^2 dx + \int_0^l \tau \left(\frac{\partial c}{\partial x}\right)^2 dx = \int_0^l c_{s-1}\, c\, dx + (F(\gamma_0(c_{s-1}) + c_b) - F(c^\star + c_b))\gamma_0(c).$$

Using the Hölder and trace inequalities and the fact that $|F(a) - F(b)| \leq 1$, for all $a, b \in \mathbb{R}$ and taking into account that the first term of the previous equality is nonnegative and that $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$ are equivalent norms, we have

$$\tau\|c\|_V^2 \leq C_e\|c_{s-1}\|_H\|c\|_V + C_{tr}\|c\|_V.$$

Now, dividing by $\|c\|_V$ and using the trace inequality again, we obtain

$$|\gamma_0(c)| \leq C_{tr} \frac{C_e \|c_{s-1}\|_H + C_{tr}}{\tau} = M.$$

In order to be able to apply the Brouwer's fixed point theorem, we have to show that G is a continuous operator. For that purpose, let us consider $\{c_m^\star\}_{m\in\mathbb{N}} \subset \mathbb{R}$ such that $\{c_m^\star\}_{m\in\mathbb{N}} \to c^\star$ in $\mathbb{R}$ and, for each $c_m^\star, m \in \mathbb{N}$, let c_m be the solution to the problem:

$$\int_0^l \frac{(c_m - c_{s-1})}{\tau} v dx + \frac{F(c_m^\star + c_b) - F(\gamma_0(c_{s-1}) + c_b)}{\tau} \gamma_0(v) \quad + \quad \int_0^l \frac{\partial c_m}{\partial x} \frac{\partial v}{\partial x} dx = 0, \quad \forall v \in V. \tag{2.23}$$

Subtracting (2.23) and (2.22) and taking $v = c_m - c \in V$ as a test function, we get

$$\int_0^l (c_m - c)^2 \, dx + \tau \int_0^l \left(\frac{\partial (c_m - c)}{\partial x} \right)^2 dx = (F(c^\star + c_b) - F(c_m^\star + c_b))\gamma_0(c_m - c).$$

Since the first term of the previous equality is nonnegative, it follows that

$$\tau \|c_m - c\|_V^2 \leq |F(c_m^\star + c_b) - F(c^\star + c_b)| \, |\gamma_0(c_m - c)|.$$

Using the trace inequality, (1.9), we obtain

$$\frac{\tau}{C_{tr}^2} |\gamma_0(c_m - c)|^2 \leq |F(c_m^\star + c_b) - F(c^\star + c_b)| \, |\gamma_0(c_m - c)|.$$

Finally, taking into account that F is 1-Lipschitz , we have

$$|\gamma_0(c_m - c)| \leq \frac{C_{tr}^2}{\tau} |c_m^\star - c^\star|.$$

Since $|c_m^\star - c^\star| \to 0$, we get the continuity of G. Therefore, the Brouwer's fixed-point theorem guarantees the existence of a fixed point of G, i.e. there exists an element $c^\star \in [-M, M]$ such that $G(c^\star) = c^\star$ and the result follows.

Uniqueness. Let us assume that there exist two solutions, c_s^1 and c_s^2, to problem (2.20).

We subtract the resulting two equations obtained for $c_s = c_s^1$ and $c_s = c_s^2$, respectively, and take $c_s^1 - c_s^2 \in V$ as a test function, then

$$\int_0^l (c_s^1 - c_s^2)^2 dx + \tau \int_0^l \left(\frac{\partial (c_s^1 - c_s^2)}{\partial x} \right)^2 dx$$
$$+ (F(\gamma_0(c_s^1) + c_b) - F(\gamma_0(c_s^2) + c_b))\gamma_0(c_s^1 - c_s^2) = 0. \qquad (2.24)$$

Since F is nondecreasing, all terms in the left-hand side are nonnegative. Therefore, we can conclude from (2.24) that all its terms are equal to zero, and then $c_s^1 = c_s^2$ for $x \in (0, l)$.

In order to prove (2.21), we take $v = c_s^+ = \max\{c_s, 0\} \in V$ as a test function in (2.20) to get

$$\int_0^l (c_s^+)^2 \, dx + (F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))\gamma_0(c_s^+) + \tau \int_0^l \left(\frac{\partial c_s^+}{\partial x} \right)^2 dx = \int_0^l c_{s-1} \, c_s^+ dx.$$

Notice that, if $\gamma_0(c_s^+) = 0$, then the second term of the previous equation disappears. On the contrary, if $\gamma_0(c_s^+)$ is positive then $\gamma_0(c_s)$ is positive. Moreover, since $c_{s-1} \leq 0$ a.e. in $(0, l)$ and $c_{s-1} \in V \subset \mathcal{C}([0, l])$ (see [38]), it follows that $\gamma_0(c_{s-1}) \leq 0$. Then, due to the nondecreasing behavior of function F we know that $F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b) \geq 0$. Therefore, in both cases, the left-hand side of the previous equality is nonnegative, while the right-hand side is nonpositive and we can conclude that $c_s^+ = 0$ a.e. in $(0, l)$. Thus $c_s \leq 0$ a.e. in $(0, l)$.

Finally, we take $v = (c_s + \mathfrak{C})^- = \max\{0, -(c_s + \mathfrak{C})\} \in H^1(0, l)$. Notice that $v(l) = \max\{0, -(c_s(l) + \mathfrak{C})\} = \max\{0, -\mathfrak{C}\} = 0$, then $v \in V$ and it can be taken as a test function in equation (2.20) to obtain

$$\int_0^l (c_s - c_{s-1})(c_s + \mathfrak{C})^- dx + (F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))\gamma_0(c_s + \mathfrak{C})^-$$
$$-\tau \int_0^l \left(\frac{\partial (c_s + \mathfrak{C})^-}{\partial x} \right)^2 dx = 0. \qquad (2.25)$$

By using the hypothesis $-\mathfrak{C} \le c_{s-1}$ a.e. $x \in (0,l)$ we have

$$\int_0^l (c_s - c_{s-1})(c_s + \mathfrak{C})^- dx = \int_{[c_s \le -\mathfrak{C}]} (c_s - c_{s-1})(c_s + \mathfrak{C})^- dx \le 0.$$

Moreover, if $\gamma_0(c_s) < -\mathfrak{C}$, then $\gamma_0(c_s + \mathfrak{C})^- > 0$ and $\gamma_0(c_s) < \gamma_0(c_{s-1})$. Taking into account that F is nondecreasing we get $F(\gamma_0(c_s) + c_b) \le F(\gamma_0(c_{s-1}) + c_b)$. Hence, all terms in equation (2.25) are nonpositive and then $(c_s + \mathfrak{C})^- = 0$ a.e. in $(0,l)$ and, consequently, $-\mathfrak{C} \le c_s$ a.e. in $(0,l)$. $\square$

Now, regarding c_s as the solution to problem (2.20) in time $t = s$ we define the following both piecewise constant and piecewise linear in time functions.

Definition 2.1 *Assuming that $c_0 \in V$, let c_s be the solution to problem (2.20) at time $t = s$, $s \in \mathbb{N}$. Then, for $(0,T] = \bigcup_{s=1}^{K}((s-1)\tau, s\tau]$, with $\tau = T/K$ and $K \in \mathbb{N}$, we define a piecewise linear and a piecewise constant in time functions:*

$$\tilde{c}_\tau,\ c_\tau :\ [0,T] \to V$$

by

$$\tilde{c}_\tau(t,x) \ := \ c_s(x), \tag{2.26}$$

$$c_\tau(t,x) \ := \ (s - \frac{t}{\tau})\, c_{s-1}(x) + (\frac{t}{\tau} - s + 1)\, c_s(x), \tag{2.27}$$

for $x \in (0,l)$ and $(s-1)\tau \le t < s\tau$, $s = 1, \ldots, K$. Moreover, we define $F_\tau :\ [0,T] \to \mathbb{R}$ as follows

$$F_\tau(t) \ := \ (s - \frac{t}{\tau})\, F(\gamma_0(c_{s-1}) + c_b) + (\frac{t}{\tau} - s + 1)\, F(\gamma_0(c_s) + c_b), \tag{2.28}$$

for $(s-1)\tau \le t < s\tau$, $s = 1, \ldots, K$.

Remark 2.1 *Note that*

$$\frac{\partial c_\tau}{\partial t}(t,x) = \frac{c_s(x) - c_{s-1}(x)}{\tau}, \tag{2.29}$$

$$\frac{dF_\tau}{dt}(t) = \frac{F(\gamma_0(c_s)+c_b) - F(\gamma_0(c_{s-1})+c_b)}{\tau}, \tag{2.30}$$

for $x \in (0,l)$ *and* $(s-1)\tau < t < s\tau$, $s = 1, \ldots, K$, *and problem (2.20) can be written for a.e.* $t \in (0,T)$ *as follows:*

$$\int_0^l \frac{\partial c_\tau}{\partial t}\, v\, dx + \frac{d\,F_\tau}{dt}\, \gamma_0(v) + \int_0^l \frac{\partial \tilde{c}_\tau}{\partial x}\, \frac{\partial v}{\partial x}\, dx = 0, \quad \forall v \in V. \tag{2.31}$$

Note also that

$$c_\tau - \tilde{c}_\tau \;=\; (\frac{t}{\tau} - s)\,(c_s - c_{s-1}) = (\frac{t}{\tau} - s)\,\tau\,\frac{\partial c_\tau}{\partial t}, \tag{2.32}$$

for $x \in (0,l)$ *and* $(s-1)\tau < t < s\tau$, $s = 1, \ldots, K$.

Definition 2.2 *Regarding the functions* F *and* H *defined in (2.7) and (2.8), respectively, for* $s = 1, \ldots, K$, *we define*

$$M_s := \int_0^l \frac{c_s^2}{2} dx + F(\gamma_0(c_s)+c_b)(\gamma_0(c_s)+c_b) - H(\gamma_0(c_s)+c_b),$$

and

$$N_s := c_b F(\gamma_0(c_s)+c_b).$$

We have the following energy decay property.

Lemma 2.3 *Assuming that the hypothesis (H1) holds with* $\mathfrak{C} = c_b$, *it follows that*

$$M_s + \tau \int_0^l \left(\frac{\partial c_s}{\partial x}\right)^2 dx \le M_{s-1} + c_b,\ s = 1, \ldots, K. \tag{2.33}$$

$$M_K - N_K \le \cdots \le M_s - N_s \le M_{s-1} - N_{s-1} \le \cdots \le M_0 - N_0, \tag{2.34}$$

where $c_s \in V$, $s = 1, \ldots, K$, *are the solutions to problem (2.20). Moreover,*

$$\sum_{n=1}^{s} \tau \int_0^l \left(\frac{\partial c_n}{\partial x}\right)^2 dx \le M_0 + c_b,\ s = 1, \ldots, K, \tag{2.35}$$

and,

$$M_s \leq M_0 + c_b,\ s = 1, \ldots, K. \tag{2.36}$$

Proof. Taking $v = c_s$ as test function in problem (2.20), we get, for $s = 1, \ldots, K$,

$$\int_0^l (c_s - c_{s-1}) c_s dx + \Big(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)\Big)\gamma_0(c_s) + \tau \int_0^l \left(\frac{\partial c_s}{\partial x}\right)^2 dx = 0.$$

Furthermore, using the fact that $x(x-y) \geq (x^2 - y^2)/2$, for $x, y \in \mathbb{R}$, in the first term of the latter expression, we have, for $s = 1, \ldots, K$,

$$\begin{aligned}\int_0^l \frac{c_s^2}{2} dx - \int_0^l \frac{c_{s-1}^2}{2} dx + \Big(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)\Big)(\gamma_0(c_s) + c_b - c_b) \\ + \tau \int_0^l \left(\frac{\partial c_s}{\partial x}\right)^2 dx \leq 0.\end{aligned} \tag{2.37}$$

Keeping in mind that

$$\begin{aligned}(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))(\gamma_0(c_s) + c_b) &= F(\gamma_0(c_s) + c_b)(\gamma_0(c_s) + c_b) \\ &- F(\gamma_0(c_{s-1}) + c_b)(\gamma_0(c_{s-1}) + c_b) \\ &+ F(\gamma_0(c_{s-1}) + c_b)\big((\gamma_0(c_{s-1}) + c_b) - (\gamma_0(c_s) + c_b)\big),\end{aligned} \tag{2.38}$$

and, since the primitive H of F, defined in (2.8), is convex, we get (see [17])

$$H(\gamma_0(c_{s-1}) + c_b) - H(\gamma_0(c_s) + c_b) \leq F(\gamma_0(c_{s-1}) + c_b)\big(\gamma_0(c_{s-1}) - \gamma_0(c_s)\big). \tag{2.39}$$

Taking into account (2.38) and (2.39) in (2.37), we obtain, for $s = 1, \ldots, K$,

$$\begin{aligned}\int_0^l \frac{c_s^2}{2} dx - \int_0^l \frac{c_{s-1}^2}{2} dx + F(\gamma_0(c_s) + c_b)(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)(\gamma_0(c_{s-1}) + c_b) \\ + H(\gamma_0(c_{s-1}) + c_b) - H(\gamma_0(c_s) + c_b) - c_b F(\gamma_0(c_s) + c_b) + c_b F(\gamma_0(c_{s-1}) + c_b) \\ + \tau \int_0^l \left(\frac{\partial c_s}{\partial x}\right)^2 dx \leq 0.\end{aligned}$$

Therefore, it follows that, for $s = 1, \ldots, K$,

$$M_s - M_{s-1} - N_s + N_{s-1} + \tau \int_0^l \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq 0, \tag{2.40}$$

and we find that, for $s = 1, \ldots, K$,

$$M_s + \tau \int_0^l \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq M_{s-1} - N_{s-1} + N_s. \tag{2.41}$$

We remark here that, since hypothesis (H1) holds with $\mathfrak{C} = c_b$, we have $-c_b \leq \gamma_0(c_{s-1}) \leq 0$ and then $0 \leq \gamma_0(c_{s-1}) + c_b \leq c_b$. Therefore, $0 \leq N_{s-1} \leq c_b$. Analogously and applying Lemma 2.2 we get $0 \leq N_s \leq c_b$ and, from (2.41), we conclude that

$$M_s + \tau \int_0^l \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq M_{s-1} + N_s \leq M_{s-1} + c_b, \qquad s = 1, \ldots, K, \tag{2.42}$$

and then (2.33) holds. Moreover, from (2.40) and taking into account that its fifth term is nonnegative, we get

$$M_s - N_s \leq M_{s-1} - N_{s-1}, \qquad s = 1, \ldots, K,$$

and (2.34) holds. Also, from (2.40) we have

$$M_s - N_s + \tau \int_0^l \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq M_{s-1} - N_{s-1}, \qquad s = 1, \ldots, K,$$

and adding the term $\tau \sum_{n=1}^{s-1} \int_0^l \left(\frac{\partial c_n}{\partial x} \right)^2 dx$ in both sides of the latter inequality it follows that

$$M_s - N_s + \tau \sum_{n=1}^{s} \int_0^l \left(\frac{\partial c_n}{\partial x} \right)^2 dx \leq M_0 - N_0, \qquad s = 1, \ldots, K.$$

Finally, considering that $N_s \in [0, c_b], s = 0, \ldots, K$, we obtain, for $s = 1, \ldots, K$,

$$M_s + \tau \sum_{n=1}^{s} \int_0^l \left(\frac{\partial c_n}{\partial x} \right)^2 dx \leq M_0 - N_0 + N_s \leq M_0 + N_s \leq M_0 + c_b. \tag{2.43}$$

Note that we can guarantee that $M_s \geq 0$ taking into account that its first term is nonnegative and using (2.17). Thus, from (2.43) we obtain (2.35) and (2.36). □

We have the following a priori error estimates.

Proposition 2.1 *Assuming the hypothesis (H1) with $\mathfrak{C} = c_b$, then functions $\tilde{c}_\tau$ and c_τ, defined in (2.26) and (2.27), respectively, are bounded in the space $L^2(0,T;H^1(0,l))$. Moreover, c_τ is bounded in $H^1(0,T;H)$ and F_τ, defined in (2.28), is bounded in $H^1(0,l)$ independently of τ. Furthermore,*

$$\|c_\tau - \tilde{c}_\tau\|^2_{L^2(0,T;H)} \leq C_1 \tau^2, \tag{2.44}$$

$$\|\gamma_0(c_\tau) - \gamma_0(\tilde{c}_\tau)\|^2_{L^2(0,T)} \leq C_2 \tau^2, \tag{2.45}$$

where C_1 and C_2 are real, positive constants independent of τ.

Proof. First, we prove that $\tilde{c}_\tau$ is bounded in $L^2(0,T;H^1(0,l))$. Indeed, by definition we have

$$\begin{aligned}
\|\tilde{c}_\tau\|^2_{L^2(0,T;H)} &= \int_0^T \|\tilde{c}_\tau(t)\|^2_H dt \\
&= \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} \left(\int_0^l (\tilde{c}_\tau(t,x))^2 dx \right) dt \\
&= \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} \left(\int_0^l (c_s(x))^2 dx \right) dt.
\end{aligned} \tag{2.46}$$

Using property (2.17) and Lemma 2.3, we know that

$$\int_0^l \frac{(c_s(x))^2}{2} dx \leq M_s \leq M_0 + c_b, \qquad s = 1, \ldots, K,$$

and thus,

$$\int_0^l (c_s(x))^2 dx \leq 2(M_0 + c_b), \qquad s = 1, \dots, K. \tag{2.47}$$

Keeping in mind (2.46) and (2.47), it follows that

$$\|\tilde{c}_\tau\|^2_{L^2(0,T;H)} \leq \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} (2M_0 + 2c_b)dt = (2M_0 + 2c_b)\tau K = (2M_0 + 2c_b)T. \tag{2.48}$$

Moreover, considering inequalities (2.35), (2.47) and (2.48), we have

$$\begin{aligned}
\|\tilde{c}_\tau\|^2_{L^2(0,T;H^1(0,l))} &= \int_0^T \|\tilde{c}_\tau(t)\|^2_{H^1(0,l)} dt \\
&= \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} \left(\int_0^l (c_s(x))^2 dx + \int_0^l \left(\frac{\partial c_s}{\partial x}(x) \right)^2 dx \right) dt \\
&\leq (2M_0 + 2c_b)T + \sum_{s=1}^{K} \tau \int_0^l \left(\frac{\partial c_s}{\partial x}(x) \right)^2 dx \\
&\leq (2M_0 + 2c_b)T + M_0 + c_b.
\end{aligned}$$

Thus, we can conclude that $\tilde{c}_\tau$ is bounded in $L^2(0,T;H^1(0,l))$ independently of τ. The following step is to show that c_τ is bounded in $L^2(0,T;H^1(0,l))$ as well. Indeed, by definition we get

$$\|c_\tau\|^2_{L^2(0,T;H)} = \int_0^T \|c_\tau(t)\|^2_H dt = \int_0^T \|(s - \frac{t}{\tau})c_{s-1} + (\frac{t}{\tau} - s + 1)c_s\|^2_H dt.$$

Regarding that $f(x) = \|x\|^2$ is a convex function and for $(s-1)\tau \leq t \leq s\tau$, $s = 1, \dots, K$, we get that $0 \leq s - \frac{t}{\tau} < 1$, then

$$\begin{aligned}
\|c_\tau\|^2_{L^2(0,T;H)} &\leq \int_0^T \left((s - \frac{t}{\tau})\|c_{s-1}\|^2_H + (\frac{t}{\tau} - s + 1)\|c_s\|^2_H \right) dt \\
&= \int_0^T \left((s - \frac{t}{\tau}) \int_0^l (c_{s-1}(x))^2 dx + (\frac{t}{\tau} - s + 1) \int_0^l (c_s(x))^2 dx \right) dt.
\end{aligned}$$

Now, using inequality (2.47), we have

$$\|c_\tau\|^2_{L^2(0,T;H)} \leq \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} \left((s - \frac{t}{\tau})2(M_0 + c_b) + (\frac{t}{\tau} - s + 1)2(M_0 + c_b) \right) dt$$

$$= \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} 2(M_0 + c_b)\, dt = 2(M_0 + c_b) \sum_{s=1}^{K} \tau = 2(M_0 + c_b)T.$$

Using the same arguments, we also get

$$\left\| \frac{\partial c_\tau}{\partial x} \right\|^2_{L^2(0,T;H)} = \int_0^T \left\| \frac{\partial c_\tau}{\partial x}(t) \right\|^2_H = \int_0^T \left\| (s - \frac{t}{\tau}) \frac{\partial c_{s-1}}{\partial x} + (\frac{t}{\tau} - s + 1) \frac{\partial c_s}{\partial x} \right\|^2_H dt$$

$$\leq \sum_{s=1}^{K} \int_{(s-1)\tau}^{s\tau} \left((s - \frac{t}{\tau}) \int_0^l \left(\frac{\partial c_{s-1}}{\partial x}(x) \right)^2 dx + (\frac{t}{\tau} - s + 1) \int_0^l \left(\frac{\partial c_s}{\partial x}(x) \right)^2 dx \right) dt$$

$$= \frac{\tau}{2} \int_0^l \left(\frac{\partial c_0}{\partial x}(x) \right)^2 dx + \sum_{s=1}^{K-1} \frac{\tau}{2} \int_0^l \left(\frac{\partial c_s}{\partial x}(x) \right)^2 dx + \sum_{s=1}^{K} \frac{\tau}{2} \int_0^l \left(\frac{\partial c_s}{\partial x}(x) \right)^2 dx,$$

and, using (2.35) and keeping in mind that $\tau \leq T$, we obtain

$$\left\| \frac{\partial c_\tau}{\partial x} \right\|^2_{L^2(0,T;H)} \leq \frac{\tau}{2} \|c_0\|^2_V + \frac{1}{2}(M_0 + c_b) + \frac{1}{2}(M_0 + c_b) \leq \frac{T}{2} \|c_0\|^2_V + M_0 + c_b.$$

Now, in order to prove that c_τ is bounded in $H^1(0,T;H)$, it is enough to show that $\dfrac{\partial c_\tau}{\partial t}$ is bounded in $L^2(0,T;H)$ since the boundedness of c_τ in $L^2(0,T;H)$ has been already proved. Taking $c_s - c_{s-1} \in V$ as a test function in (2.31), we get, for a.e. $t \in (0,T)$ and $s = 1, \ldots, K$,

$$\int_0^l \frac{\partial c_\tau}{\partial t}(c_s - c_{s-1})\, dx + \frac{d F_\tau}{dt} \gamma_0(c_s - c_{s-1}) + \int_0^l \frac{\partial c_s}{\partial x} \frac{\partial (c_s - c_{s-1})}{\partial x} dx = 0.$$

Then, considering (2.29) and (2.30), it follows that, for a.e. $t \in (0,T)$ and $s = 1, \ldots, K$,

$$\int_0^l \frac{(c_s - c_{s-1})^2}{\tau} dx + \frac{F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)}{\tau} \gamma_0(c_s - c_{s-1}) + \int_0^l \frac{\partial c_s}{\partial x} \frac{\partial (c_s - c_{s-1})}{\partial x} dx = 0.$$

Using the fact that $x(x-y) \geq \dfrac{x^2}{2} - \dfrac{y^2}{2}$, for $x, y \in \mathbb{R}$, in the third term of the previous equality, we have, for $s = 1, \ldots, K$,

$$\int_0^l \frac{(c_s - c_{s-1})^2}{\tau} dx + \frac{F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)}{\tau} \gamma_0(c_s - c_{s-1}) + \int_0^l \frac{1}{2} \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq \int_0^l \frac{1}{2} \left(\frac{\partial c_{s-1}}{\partial x} \right)^2 dx. \tag{2.49}$$

Now, using (2.18), we obtain, for $s = 1, \ldots, K$,

$$\int_0^l \frac{(c_s - c_{s-1})^2}{\tau} dx + \frac{(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))^2}{\tau} + \int_0^l \frac{1}{2} \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq \int_0^l \frac{1}{2} \left(\frac{\partial c_{s-1}}{\partial x} \right)^2 dx.$$

Adding the term

$$\sum_{n=1}^{s-1} \left(\int_0^l \frac{(c_n - c_{n-1})^2}{\tau} dx + \frac{(F(\gamma_0(c_n) + c_b) - F(\gamma_0(c_{n-1}) + c_b))^2}{\tau} \right),$$

in both sides of the previous inequality, we find that, for $s = 1, \ldots, K$,

$$\sum_{n=1}^{s} \int_0^l \frac{(c_n - c_{n-1})^2}{\tau} dx + \sum_{n=1}^{s} \frac{\big(F(\gamma_0(c_n) + c_b) - F(\gamma_0(c_{n-1}) + c_b)\big)^2}{\tau} + \int_0^l \frac{1}{2} \left(\frac{\partial c_s}{\partial x} \right)^2 dx \leq \int_0^l \frac{1}{2} \left(\frac{\partial c_0}{\partial x} \right)^2 dx.$$

Then, since all terms of the left-hand side are nonnegative, it follows that, for $s =$

$1,\dots,K$,

$$\sum_{n=1}^{s}\int_0^l \frac{(c_n-c_{n-1})^2}{\tau}dx \le \int_0^l \frac{1}{2}\left(\frac{\partial c_0}{\partial x}\right)^2 dx, \tag{2.50}$$

$$\sum_{n=1}^{s}\frac{(F(\gamma_0(c_n)+c_b)-F(\gamma_0(c_{n-1})+c_b))^2}{\tau} \le \int_0^l \frac{1}{2}\left(\frac{\partial c_0}{\partial x}\right)^2 dx. \tag{2.51}$$

Therefore, using (2.29) and (2.50) we have

$$\begin{aligned}
\left\|\frac{\partial c_\tau}{\partial t}\right\|^2_{L^2(0,T;H)} &= \int_0^T \left\|\frac{\partial c_\tau}{\partial t}(t)\right\|^2_H dt = \sum_{s=1}^{K}\int_{(s-1)\tau}^{s\tau}\int_0^l \left(\frac{\partial c_\tau}{\partial t}(t,x)\right)^2 dx\,dt \\
&= \sum_{s=1}^{K}\int_{(s-1)\tau}^{s\tau}\int_0^l \frac{(c_s-c_{s-1})^2}{\tau^2}dx\,dt = \sum_{s=1}^{K}\tau\int_0^l \frac{(c_s-c_{s-1})^2}{\tau^2}dx \\
&\le \int_0^l \frac{1}{2}\left(\frac{\partial c_0}{\partial x}\right)^2 dx = \frac{\|c_0\|_V^2}{2},
\end{aligned}$$

and the result follows.

Moreover, regarding F_τ and keeping in mind (2.30), we obtain

$$\begin{aligned}
\|F_\tau\|^2_{H^1(0,T)} &= \int_0^T |F_\tau(t)|^2 dt + \int_0^T \left|\frac{dF_\tau}{dt}(t)\right|^2 dt \\
&\le \sum_{s=1}^{K}\int_{(s-1)\tau}^{s\tau}\left((s-\frac{t}{\tau})|F(\gamma_0(c_{s-1})+c_b)|^2+(\frac{t}{\tau}-s+1)|F(\gamma_0(c_s)+c_b)|^2\right)dt \\
&\quad +\sum_{s=1}^{K}\int_{(s-1)\tau}^{s\tau}\frac{(F(\gamma_0(c_s)+c_b)-F(\gamma_0(c_{s-1})+c_b))^2}{\tau^2}dt.
\end{aligned}$$

Taking into account that $|F(z)|\le 1$, for all $z\in\mathbb{R}$ and applying (2.51), we get

$$\begin{aligned}
\|F_\tau\|^2_{H^1(0,T)} &\le \sum_{s=1}^{K}\tau + \sum_{s=1}^{K}\tau\frac{(F(\gamma_0(c_s)+c_b)-F(\gamma_0(c_{s-1})+c_b))^2}{\tau^2} \\
&\le T + \int_0^l \frac{1}{2}\left(\frac{\partial c_0}{\partial x}\right)^2 dx = T + \frac{\|c_0\|_V^2}{2}.
\end{aligned}$$

Note also that

$$
\begin{aligned}
\|c_\tau - \tilde{c}_\tau\|^2_{L^2(0,T;H)} &= \int_0^T \|c_\tau(t) - \tilde{c}_\tau(t)\|^2_H dt \\
&= \sum_{s=1}^K \int_{(s-1)\tau}^{s\tau} (\frac{t}{\tau} - s)^2 \int_0^l (c_s(x) - c_{s-1}(x))^2 dx\, dt \\
&= \sum_{s=1}^K \frac{\tau}{3} \int_0^l (c_s(x) - c_{s-1}(x))^2 dx \\
&= \frac{\tau^2}{3} \sum_{s=1}^K \int_0^l \frac{(c_s(x) - c_{s-1}(x))^2}{\tau} dx,
\end{aligned}
$$

and using (2.50) we get

$$
\|c_\tau - \tilde{c}_\tau\|^2_{L^2(0,T;H)} \leq \frac{\tau^2}{3} \int_0^l \frac{1}{2} \left(\frac{\partial c_0}{\partial x} \right)^2 dx = C_1\, \tau^2,
$$

where $C_1 = \|c_0\|^2_V/6$. Finally, we find that

$$
\begin{aligned}
\|\gamma_0(c_\tau(t)) - \gamma_0(\tilde{c}_\tau(t))\|^2_{L^2(0,T)} &= \int_0^T |\gamma_0(c_\tau(t)) - \gamma_0(\tilde{c}_\tau(t))|^2 dt \\
&= \sum_{s=1}^K \int_{(s-1)\tau}^{s\tau} (\frac{t}{\tau} - s)^2 (\gamma_0(c_s) - \gamma_0(c_{s-1}))^2 dt \\
&= \frac{\tau^2}{3} \sum_{s=1}^K \frac{(\gamma_0(c_s) - \gamma_0(c_{s-1}))^2}{\tau}. \qquad (2.52)
\end{aligned}
$$

By using the hypothesis (H1) for $\mathfrak{C} = c_b$ and Lemma (2.2), it follows that $-c_b \leq c_s \leq 0$ for $s = 1, \ldots, K$. Hence, we have

$$
-c_b \leq \gamma_0(c_s) \leq 0, \qquad s = 1, \ldots, K, \qquad (2.53)
$$

and then

$$
0 \leq \gamma_0(c_s) + c_b \leq c_b, \qquad s = 1, \ldots, K. \qquad (2.54)
$$

Considering the definition of function F and (2.53), we have, for $s = 1, \ldots, K$,

$$\begin{aligned}
&(F(\gamma_0(c_s)+c_b) - F(\gamma_0(c_{s-1})+c_b))(\gamma_0(c_s)-\gamma_0(c_{s-1})) \\
&\qquad = \left(\frac{\gamma_0(c_s)+c_b}{1+\gamma_0(c_s)+c_b} - \frac{\gamma_0(c_{s-1})+c_b}{1+\gamma_0(c_{s-1})+c_b}\right)(\gamma_0(c_s)-\gamma_0(c_{s-1})) \\
&\qquad = \frac{(\gamma_0(c_s)-\gamma_0(c_{s-1}))^2}{(1+\gamma_0(c_s)+c_b)(1+\gamma_0(c_{s-1})+c_b)} \\
&\qquad \geq \frac{(\gamma_0(c_s)-\gamma_0(c_{s-1}))^2}{(1+c_b)^2},
\end{aligned}$$

and, using this inequality in (2.49), we obtain, for $s = 1, \ldots, K$,

$$\int_0^l \frac{(c_s - c_{s-1})^2}{\tau} dx + \frac{(\gamma_0(c_s)-\gamma_0(c_{s-1}))^2}{\tau(1+c_b)^2} + \int_0^l \frac{1}{2}\left(\frac{\partial c_s}{\partial x}\right)^2 dx \leq \int_0^l \frac{1}{2}\left(\frac{\partial c_{s-1}}{\partial x}\right)^2 dx.$$

Adding the term

$$\sum_{n=1}^{s-1}\left(\int_0^l \frac{(c_n - c_{n-1})^2}{\tau} dx + \frac{(\gamma_0(c_n)-\gamma_0(c_{n-1}))^2}{\tau(1+c_b)^2}\right)$$

in both sides of the previous inequality, we get, for $s = 1, \ldots, K$,

$$\begin{aligned}
&\sum_{n=1}^{s}\int_0^l \frac{(c_n - c_{n-1})^2}{\tau} dx + \sum_{n=1}^{s}\frac{(\gamma_0(c_n)-\gamma_0(c_{n-1}))^2}{\tau(1+c_b)^2} + \int_0^l \frac{1}{2}\left(\frac{\partial c_s}{\partial x}\right)^2 dx \\
&\qquad \leq \int_0^l \frac{1}{2}\left(\frac{\partial c_0}{\partial x}\right)^2 dx.
\end{aligned}$$

From this inequality, we have, for $s = 1, \ldots, K$,

$$\sum_{n=1}^{s}\frac{(\gamma_0(c_n)-\gamma_0(c_{n-1}))^2}{\tau} \leq \frac{(1+c_b)^2}{2}\int_0^l \left(\frac{\partial c_0}{\partial x}\right)^2 dx,$$

and using this expression in (2.52), we conclude that

$$\|\gamma_0(c_\tau) - \gamma_0(\tilde{c})\|^2_{L^2(0,T)} \leq C_2\tau^2,$$

where $C_2 = \dfrac{(1+c_b)^2}{6}\|c_0\|_V^2$. $\square$

The following theorem establishes the existence of a unique solution to Problem P_W^L. Its proof is based on the proof given in [25] which we reproduce here for the reader's sake.

Theorem 2.1 *Assuming that hypothesis (H1) holds with $\mathfrak{C} = c_b$, then there exists a unique solution to Problem P_W^L with the regularity*

$$c \in H^1(0,T;H) \cap L^2(0,T;H^1(0,l)),$$

$$F(\gamma_0(c)+c_b) \in H^1(0,T), \quad F(\gamma_0(c(0))+c_b) = F(\gamma_0(c_0)+c_b).$$

Moreover, this solution also satisfies

$$-c_b \le c(t,x) \le 0 \quad a.e. \ in \ Q_T = (0,T)\times(0,l). \tag{2.55}$$

Proof. *Existence.* The estimates of Proposition 2.1 and the reflexivity of the space $L^2(0,T;V)$ lead to the existence of a function $c \in L^2(0,T;V)$ such that, for a subsequence (not relabelled), it holds

$$\tilde{c}_\tau \rightharpoonup c \text{ weakly in } L^2(0,T;V), \tag{2.56}$$

$$c_\tau \rightharpoonup c \text{ weakly in } L^2(0,T;V). \tag{2.57}$$

Notice that the weak limits of these sequences coincide in $L^2(0,T;H)$ due to (2.44). Moreover, the estimates of Proposition 2.1 establish that the sequence c_τ is bounded in

$$W = \{u \in L^2(0,T;V); \quad \frac{\partial u}{\partial t} \in L^2(0,T;H)\}.$$

Since W is reflexive, there exists an element $c_\star \in W$ and a subsequence, still denoted by τ, such that

$$c_\tau \rightharpoonup c_\star \text{ weakly in } W.$$

That is, we have

$$c_\tau \rightharpoonup c_\star \text{ weakly in } L^2(0,T;V), \quad \frac{\partial c_\tau}{\partial t} \rightharpoonup \frac{\partial c_\star}{\partial t} \text{ weakly in } L^2(0,T;H). \tag{2.58}$$

By (2.57) and the uniqueness of the weak limit we deduce that $c = c_\star$. Furthermore, using Lions-Aubin Lemma (see [40]) with $B_0 = V$ and $B = B_1 = H$ and taking into account that $V \hookrightarrow H$ is a compact embedding, we get

$$c_\tau \to c \text{ in } L^2(0,T;H). \tag{2.59}$$

Moreover, since $H \hookrightarrow (H^1(0,l))'$, there exists a subsequence of c_τ (still relabelled by τ) weakly convergent to c in

$$W_1 = \{u \in L^2(0,T;H^1(0,l));\ \frac{\partial u}{\partial t} \in L^2(0,T;(H^1(0,l))'\}.$$

Taking into account the following space (see [38]):

$$W^{\varepsilon,2}(0,l) = \{u \in H; \frac{|u(x)-u(y)|}{|x-y|^{\varepsilon+\frac{1}{2}}} \in L^2((0,l)\times(0,l))\},$$

for $\frac{1}{2} < \varepsilon < 1$ and using Lions-Aubin Lemma again, with $B_0 = H^1(0,l)$, $B = W^{\varepsilon,2}(0,l)$ and $B_1 = (H^1(0,l))'$ and regarding that $H^1(0,l) \hookrightarrow W^{\varepsilon,2}(0,l)$ is compact (see [38]) and $W^{\varepsilon,2}(0,l) \hookrightarrow (H^1(0,l))'$, we have

$$c_\tau \to c \text{ in } L^2(0,T;W^{\varepsilon,2}(0,l)).$$

Now, taking into account that the trace operator is linear and continuous (see [15]), we obtain

$$\gamma_0(c_\tau) \to \gamma_0(c) \text{ in } L^2(0,T).$$

Besides, using (2.45) we find that

$$\gamma_0(\tilde{c}_\tau) \to \gamma_0(c) \text{ in } L^2(0,T). \tag{2.60}$$

Since F_τ is bounded in $H^1(0,T)$ and this space is reflexive, we can extract a subsequence of τ, still denoted by τ, such that, for some $F_\star \in H^1(0,T)$ we get

$$F_\tau \rightharpoonup F_\star \text{ weakly in } H^1(0,T). \tag{2.61}$$

Due to the inclusion $H^1(0,T) \hookrightarrow L^2(0,T)$ is compact, it follows that

$$F_\tau \to F_\star \text{ in } L^2(0,T). \tag{2.62}$$

Moreover, taking $t \in ((s-1)\tau, s\tau)$, $s = 1, \ldots, K$ and using

$$\begin{aligned}
&F_\tau(t) - F(\gamma_0(\tilde{c}_\tau(t)) + c_b) \\
&\quad = (s - \frac{t}{\tau})F(\gamma_0(c_{s-1}) + c_b) + (\frac{t}{\tau} - s + 1)F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_s) + c_b) \\
&\quad = (\frac{t}{\tau} - s)(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b)),
\end{aligned}$$

together with (2.51), we get

$$\begin{aligned}
\|F_\tau - F(\gamma_0(\tilde{c}_\tau) + c_b)\|^2_{L^2(0,T)} &= \int_0^T |F_\tau(t) - F(\gamma_0(\tilde{c}_\tau(t)) + c_b)|^2 dt \\
&= \sum_{s=1}^K \int_{(s-1)\tau}^{s\tau} (\frac{t}{\tau} - s)^2 (F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))^2 dt \\
&= \sum_{s=1}^K \frac{\tau}{3}(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))^2 \\
&= \frac{\tau^2}{3} \sum_{s=1}^K \frac{(F(\gamma_0(c_s) + c_b) - F(\gamma_0(c_{s-1}) + c_b))^2}{\tau} \leq \tau^2 \frac{\|c_0\|_V^2}{6}.
\end{aligned}$$

Then, letting $\tau \to 0$, we deduce

$$F_\tau - F(\gamma_0(\tilde{c}_\tau) + c_b) \to 0 \text{ in } L^2(0,T),$$

and using (2.60) and (2.62), we find that $F_\star = F(\gamma_0(c(t)) + c_b)$ a.e. in $(0,T)$ and, consequently,

$$F_\tau \to F(\gamma_0(c(t)) + c_b) \text{ in } L^2(0,T). \tag{2.63}$$

Taking $v \in \mathcal{V}$, and integrating (2.31) from $t = 0$ to $t = T$, we obtain

$$\int_0^T \int_0^l \frac{\partial c_\tau}{\partial t}\, v\, dx\, dt + \int_0^T \frac{\partial F_\tau}{\partial t}\, \gamma_0(v(t))\, dt \quad + \quad \int_0^T \int_0^l \frac{\partial \tilde{c}_\tau}{\partial x}\, \frac{\partial v}{\partial x} dx\, dt = 0.$$

Using (2.56), (2.58) and (2.61) and passing to the limit when $\tau \to 0$, it holds

$$\int_0^T \int_0^l \frac{\partial c}{\partial t}\, v\, dx\, dt + \int_0^T \frac{dF(\gamma_0(c) + c_b)}{dt}\, \gamma_0(v)\, dt + \int_0^T \int_0^l \frac{\partial c}{\partial x}\, \frac{\partial v}{\partial x} dx\, dt = 0,$$

for any $v \in \mathcal{V}$ and therefore (2.15) holds. Moreover, let us take $v \in \mathcal{V}$ independent of t, that is to say $v(t,x) = v(x)$, using the integration by parts formula and considering the definition of c_τ given in (2.27), we get for a.e. $t \in (0,T)$

$$\int_0^t (\frac{\partial c_\tau}{\partial t}(t), v)_H\, dt = (c_\tau(t), v)_H - (c_\tau(0), v)_H = (c_\tau(t), v)_H - (c_0, v)_H. \tag{2.64}$$

Furthermore, using (2.59), we have

$$c_\tau(t) \longrightarrow c(t) \quad \text{in } H, \quad \text{for a.e. } t \in (0,T).$$

Thus, passing to the limit in (2.64), taking into account (2.58) and the integration by parts formula, we obtain

$$(c(t), v)_H - (c(0), v)_H = \int_0^t (\frac{\partial c}{\partial t}(t), v)_H\, dt = (c(t), v)_H - (c_0, v)_H, \quad \text{for a.e. } t \in (0,T).$$

Therefore

$$(c(0) - c_0, v)_H = 0, \qquad \forall\, v \in V,$$

and, since V is dense in H, (2.16) holds a.e. in $(0,l)$.

Note also that, using the integration by parts formula, we have

$$\int_0^t \frac{dF_\tau}{dt}(t)\,dt = F_\tau(t) - F_\tau(0) = F_\tau(t) - F(\gamma_0(c_0) + c_b), \quad \text{for a.e. } t \in (0,T).$$

Besides, using (2.63), passing to the limit in the previous expression and applying the integration by parts formula, we get, for a.e. $t \in (0,T)$,

$$\begin{aligned} F(\gamma_0(c(t)) + c_b) - F(\gamma_0(c(0)) + c_b) &= \int_0^t \frac{dF(\gamma_0(c(t)) + c_b)}{dt}\,dt \\ &= F(\gamma_0(c(t)) + c_b) - F(\gamma_0(c_0) + c_b). \end{aligned}$$

The previous expression yields

$$F(\gamma_0(c(0)) + c_b) = F(\gamma_0(c_0) + c_b), \tag{2.65}$$

and, using (2.44) and (2.59), we deduce that

$$\tilde{c}_\tau \to c \text{ in } L^2(Q_T).$$

Then, for a subsequence it holds (see [3])

$$\tilde{c}_\tau \to c \text{ a.e. in } Q_T. \tag{2.66}$$

By using hypothesis (H1), $-c_b \leq c_s(x) \leq 0$ a.e. in $(0,l)$ and then, by construction, $-c_b \leq \tilde{c}_\tau \leq 0$ also holds a.e. in Q_T and, keeping in mind (2.66), we get (2.55).

Uniqueness. In order to prove the uniqueness of solution to Problem P_W^L, we proceed using several arguments already introduced in [25]. Anyway, for the sake of clarity of the presentation, we detail the main steps of the proof. Therefore, we consider $\psi \in V$ and we define

$$v_{\tau,n}(t,x) = \varphi_{\tau,n}(t)\psi(x),$$

where

$$\varphi_{\tau,n}(t) = \begin{cases} 1 & \text{if } t \in [0,\tau], \\ n(\tau - t) + 1 & \text{if } t \in [\tau, \tau + \frac{1}{n}], \\ 0 & \text{if } t \in [\tau + \frac{1}{n}, T], \end{cases}$$

for $\tau \in (0,T)$ and $n \in \mathbb{N}$. Since $v_{\tau,n} \in \mathcal{V}$, we can use it as a test function in equation (2.15) to get

$$\int_0^T \langle \frac{\partial c}{\partial t}(t), v_{\tau,n}(t)\rangle_{V'\times V}\, dt + \int_0^T ((c(t), v_{\tau,n}(t)))\, dt + \int_0^T \frac{d(F(\gamma_0(c(t)) + c_b))}{dt} \gamma_0(v_{\tau,n}(t))\, dt = 0. \tag{2.67}$$

Notice that $v_{\tau,n} \in H^1(0,T;V)$ and therefore, using Theorem 11.5 in [8] and taking into account that $v_{\tau,n}(T,x) = 0$ for a.e. $x \in (0,l)$, the first term of the previous expression reads, for all $\tau \in (0,T)$,

$$\begin{aligned} \int_0^T \langle \frac{\partial c}{\partial t}(t), v_{\tau,n}(t)\rangle_{V'\times V}\, dt &= -\int_0^T \langle c(t), \frac{\partial v_{\tau,n}}{\partial t}(t)\rangle_{V\times V'} - (c(0), v_{\tau,n}(0))_H \\ &= n \int_\tau^{\tau+\frac{1}{n}} (c(t),\psi)_H dt - (c_0,\psi)_H, \end{aligned} \tag{2.68}$$

Furthermore, using the integration by parts formula, considering $\varphi_{\tau,n}(T) = 0$ in the third term of equations (2.67) and taking into account expression (2.65), we obtain, for all $\tau \in (0,T)$,

$$\begin{aligned} \int_0^T \frac{d(F(\gamma_0(c(t)) + c_b))}{dt} \gamma_0(v_{\tau,n}(t))\, dt &= -\int_0^T F(\gamma_0(c(t)) + c_b)\, \gamma_0(\psi)\, \frac{d\,\varphi_{\tau,n}}{dt}(t)\, dt \\ &\quad - F(\gamma_0(c_0) + c_b)\, \gamma_0(\psi)\, \varphi_{\tau,n}(0) \\ &= \int_\tau^{\tau+\frac{1}{n}} n\, F(\gamma_0(c(t)) + c_b)\, \gamma_0(\psi)\, dt - F(\gamma_0(c_0) + c_b)\, \gamma_0(\psi). \end{aligned} \tag{2.69}$$

Therefore, taking into account (2.68) and (2.69), equation (2.67) reads

$$\int_\tau^{\tau+\frac{1}{n}} (c(t),\psi)_H \, n \, dt + \int_0^T \varphi_{\tau,n}(t)\,((c(t),\psi))\,dt + \int_\tau^{\tau+\frac{1}{n}} n\,F(\gamma_0(c(t))+c_b)\,\gamma_0(\psi)\,dt$$
$$= (c_0,\psi)_H + F(\gamma_0(c_0)+c_b)\,\gamma_0(\psi), \qquad \forall\tau\in(0,T). \tag{2.70}$$

Now, let c_1 and c_2 be two solutions to Problem P_W^L. Subtracting the resulting equations obtained from the previous expression for $c = c_1$ and $c = c_2$, we get, for all $\tau \in (0,T)$,

$$\int_\tau^{\tau+\frac{1}{n}} (c_1(t)-c_2(t),\psi)_H \, n \, dt + \int_0^{\tau+\frac{1}{n}} ((c_1(t)-c_2(t),\psi))\varphi_{\tau,n}(t)\,dt$$
$$+ \int_\tau^{\tau+\frac{1}{n}} (F(\gamma_0(c_1(t))+c_b) - F(\gamma_0(c_2(t))+c_b))\,n\,\gamma_0(\psi) = 0, \quad \forall\psi\in V. \tag{2.71}$$

Now, taking into account that c_1, $c_2 \in W_2(0,T) \subset \mathcal{C}([0,T];H)$ (see [39]) and using the mean value theorem, we have, for $t^\star \in [\tau, \tau+\frac{1}{n}]$,

$$\int_\tau^{\tau+\frac{1}{n}} (c_1(t)-c_2(t),\psi)_H \, n \, dt = (c_1(t^\star)-c_2(t^\star),\psi)_H. \tag{2.72}$$

We notice that

$$\int_0^{\tau+\frac{1}{n}} ((c_1(t)-c_2(t),\psi))\,\varphi_{\tau,n}(t)\,dt$$
$$= \int_0^T \chi(0,\tau+\frac{1}{n})\,((c_1(t)-c_2(t),\psi))\,\varphi_{\tau,n}(t)\,dt, \tag{2.73}$$

where $\chi(0,\tau+\frac{1}{n})$ denotes the characteristic function over the interval $(0,\tau+\frac{1}{n})$. Now, we define a sequence of functions given by

$$f_n(t) := \chi(0,\tau+\frac{1}{n})\,((c_1(t)-c_2(t),\psi))\varphi_{\tau,n}(t), \quad n\in\mathbb{N}.$$

We remark that $f_n \in L^1(0,T)$ for each $n \in \mathbb{N}$, and the family of functions f_n, $n \in \mathbb{N}$ satisfies that

$$f_n(t) \longrightarrow f(t), \text{ a.e. } t\in(0,T),$$

where

$$f(t) = \chi(0,\tau)((c_1(t) - c_2(t), \psi))$$

and

$$|f_n(t)| \leq g(t), \text{ a.e. } t \in (0,T), \tag{2.74}$$

being

$$g(t) = ((c_1(t) - c_2(t), \psi)).$$

Then, applying the Lebesgue dominated convergence theorem, we can conclude that $f \in L^1(0,T)$ and

$$\int_0^{\tau+\frac{1}{n}} ((c_1(t) - c_2(t), \psi))\, \varphi_{\tau,n}(t)\, dt \longrightarrow \int_0^{\tau} ((c_1(t) - c_2(t), \psi))\, dt. \tag{2.75}$$

Moreover, considering that $F(\gamma_0(c_i(t)) + c_b) \in H^1(0,T) \subset \mathcal{C}([0,T])$, for $i = 1, 2$, and using the mean value theorem, it follows that, for a given $t^{\star\star} \in [\tau, \tau + \frac{1}{n}]$,

$$\begin{aligned} &\int_\tau^{\tau+\frac{1}{n}} (F(\gamma_0(c_1(t)) + c_b) - F(\gamma_0(c_2(t)) + c_b))\, n\, \psi(0)\, dt \\ &\qquad = (F(\gamma_0(c_1(t^{\star\star})) + c_b) - F(\gamma_0(c_2(t^{\star\star})) + c_b))\, n\, \frac{1}{n}\, \psi(0). \end{aligned} \tag{2.76}$$

Therefore, passing to the limit when $n \to \infty$ in (2.71) and taking into account (2.72), (2.75) and (2.76), it follows that

$$\begin{aligned} &(c_1(\tau) - c_2(\tau), \psi)_H + \int_0^{\tau} ((c_1(t) - c_2(t), \psi))\, dt \\ &\quad + (F(\gamma_0(c_1(\tau)) + c_b) - F(\gamma_0(c_2(\tau)) + c_b))\, \psi(0) = 0, \quad \forall \psi \in V, \text{ a.e. } \tau \in (0,T). \end{aligned} \tag{2.77}$$

Now, we fix $\tau \in (0,T)$ and we take $\psi = c_1(\tau) - c_2(\tau)$ in (2.77) to obtain

$$\begin{aligned} &\int_0^l (c_1(\tau,x) - c_2(\tau,x))^2 dx + \int_0^{\tau} ((c_1(t) - c_2(t), c_1(\tau) - c_2(\tau)))\, dt \\ &\quad + (F(\gamma_0(c_1(\tau)) + c_b) - F(\gamma_0(c_2(\tau)) + c_b))(\gamma_0(c_1(\tau)) - \gamma_0(c_2(\tau))) = 0. \end{aligned}$$

Since F is nondecreasing, the last term of the previous equality is nonnegative, and then, for a.e. $\tau \in (0,T)$,

$$\begin{aligned} &\|c_1(\tau) - c_2(\tau)\|_H^2 \\ &\quad + \int_0^\tau \int_0^l (\frac{\partial c_1}{\partial x}(t,x) - \frac{\partial c_2}{\partial x}(t,x))(\frac{\partial c_1}{\partial x}(\tau,x) - \frac{\partial c_2}{\partial x}(\tau,x))\, dx\, dt \leq 0. \end{aligned} \tag{2.78}$$

Taking into account $\frac{\partial c_1}{\partial x} - \frac{\partial c_2}{\partial x} \in L^2(0,T;H)$, we define the function

$$\beta(\tau) := \int_0^\tau (\frac{\partial c_1}{\partial x}(s) - \frac{\partial c_2}{\partial x}(s))ds$$

which belongs to $W^{1,2}(0,T;H)$ (see [40], page 104), being

$$\frac{d\beta}{d\tau}(\tau) = \frac{\partial c_1}{\partial x}(\tau) - \frac{\partial c_2}{\partial x}(\tau).$$

Thus, we deduce (see Chapter III, Corollary 1.1, in [40]),

$$\begin{aligned} \frac{1}{2}\frac{d}{d\tau}\|\beta(\tau)\|_H^2 &= (\frac{d\beta}{d\tau}(\tau), \beta(\tau))_H \\ &= \int_0^l \int_0^\tau (\frac{\partial c_1}{\partial x}(s) - \frac{\partial c_2}{\partial x}(s))ds\, (\frac{\partial c_1}{\partial x}(\tau) - \frac{\partial c_2}{\partial x}(\tau))dx. \end{aligned}$$

Therefore, taking into account the Fubini Theorem (see Theorem IV.5 in [3]), we can change the order of the integrals and then replace the previous equality in estimate (2.78) to obtain, for a.e. $\tau \in (0,T)$,

$$\|c_1(\tau) - c_2(\tau)\|_H^2 + \frac{1}{2}\frac{d}{d\tau}\|\beta(\tau)\|_H^2 \leq 0.$$

Integrating from 0 to T, we have

$$\int_0^T \|c_1(\tau) - c_2(\tau)\|_H^2 d\tau + \frac{1}{2}\int_0^T \frac{d}{d\tau}\|\beta(\tau)\|_H^2 d\tau \leq 0,$$

and therefore

$$\int_0^T \|c_1(\tau) - c_2(\tau)\|_H^2 d\tau + \frac{1}{2}\|\beta(T)\|_H^2 \le 0.$$

Consequently, $c_1 = c_2$ a.e in Q_T. □

2.4 Analysis of a semi-discrete problem

In this section, we study the approximation in time of Problem P_W^L, proving some a priori estimates depending on the time discretization parameter.

First, we rewrite Problem P_W^L in the following equivalent form, in terms of the derivative of function F taking into account that $F(\gamma_0(c)) \in H^1(0,T)$.

Problem $P_W^{L,eq}$. For a given $c_0 \in V$, find a function $c \in H^1(0,T;H) \cap L^2(0,T;V)$ such that $c(0) = c_0$ and, for every $v \in V$ and a.e. $t \in (0,T)$, we get

$$(\frac{\partial c}{\partial t}(t), v)_H + ((c(t), v)) + h(\gamma_0(c(t)) + c_b, \frac{\partial(\gamma_0(c))}{\partial t}(t))\gamma_0(v) = 0, \tag{2.79}$$

where function $h : \mathbb{R}^2 \to \mathbb{R}$ is defined as

$$h(u,v) = \begin{cases} \dfrac{v}{(1+u)^2} & \text{if} \quad u \ge 0, \\ 0 \quad \text{elsewhere.} \end{cases}$$

Now, in order to obtain an approximation in time of Problem $P_W^{L,eq}$, we consider the uniform partition of the time interval $[0,T]$ given in Section 1.4 of Chapter 1. Moreover, the same notation introduced there is also used hereinafter in this chapter.

Therefore, applying a hybrid combination of both implicit and explicit Euler schemes, we get the following semi-discrete form of Problem $P_W^{L,eq}$.

Problem P_L^k. Find a sequence of functions $c^k = \{c_n^k\}_{n=0}^N \subset V$ such that

$$\begin{aligned}\left(\frac{c_n^k - c_{n-1}^k}{k}, v\right)_H + ((c_n^k, v)) + h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k})\gamma_0(v) \\ = 0, \quad \forall v \in V,\end{aligned} \tag{2.80}$$

where $c_0^k = c_0$.

After a straightforward application of Lax-Milgram theorem and proceeding as in the proof of Lemma 2.2, assuming hypothesis (H1) we can prove that Problem P_L^k has a unique solution $c^k \subset V$ such that

$$-c_b \leq c_n^k(x) \leq 0 \text{ for a.e. } x \text{ in } (0,l), \quad n = 0, \dots, N. \tag{2.81}$$

Hereafter, in this section, we will obtain some a priori estimates depending on the time discretization parameter assuming the following additional regularity condition:

$$c \in \mathcal{C}^1([0,T]; V). \tag{2.82}$$

Theorem 2.2 *Assuming that hypothesis (H1) holds with $\mathfrak{C} = c_b$. Let c and c^k denote the respective solutions to problems $P_W^{L,eq}$ and P_L^k. Under the additional regularity condition (2.82), we have the following a priori error estimates:*

$$\max_{0 \leq n \leq N} \|c_n - c_n^k\|_H^2 + k \sum_{j=1}^N \|c_j - c_j^k\|_V^2 + \max_{0 \leq n \leq N} |\gamma_0(c_n) - \gamma_0(c_n^k)|^2$$
$$\leq Ck \sum_{j=1}^N \left\{ \left\| \frac{\partial c}{\partial t}(t_j) - \frac{c_j - c_{j-1}}{k} \right\|_V^2 + k^2 \right\},$$

where C denotes a generic positive constant which may depend on the continuous solution c but it is independent of the discretization parameter k, and whose value may change from line to line.

Proof. Writing equation (2.79) at time $t = t_n$ and subtracting it to equation (2.80) we find that, for all $v \in V$,

$$\left(\frac{\partial c}{\partial t}(t_n) - \frac{c_n^k - c_{n-1}^k}{k}, v \right)_H + ((c_n - c_n^k, v))$$
$$+ \left(h(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}) - h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k}) \right) \gamma_0(v)$$
$$+ \left(h(\gamma_0(c_n) + c_b, \frac{\partial(\gamma_0(c))}{\partial t}(t_n) - \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}) \right) \gamma_0(v) = 0.$$

Then, taking in the previous expression $v = c_n - c_n^k$ as a test function we have

$$
\begin{aligned}
&\left(\frac{\partial c}{\partial t}(t_n) - \frac{c_n^k - c_{n-1}^k}{k}, c_n - c_n^k\right)_H + ((c_n - c_n^k, c_n - c_n^k)) \\
&+ \left(h(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}) - h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k})\right) \gamma_0(c_n - c_n^k) \\
&\quad + \left(h(\gamma_0(c_n) + c_b, \frac{\partial(\gamma_0(c))}{\partial t}(t_n) - \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\right) \gamma_0(c_n - c_n^k) = 0.
\end{aligned}
$$

Taking into account that

$$
\begin{aligned}
&\left(\frac{\partial c}{\partial t}(t_n) - \frac{c_n^k - c_{n-1}^k}{k}, c_n - c_n^k\right)_H = \left(\frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k}, c_n - c_n^k\right)_H \\
&\qquad + \left(\frac{c_n - c_{n-1}}{k} - \frac{c_n^k - c_{n-1}^k}{k}, c_n - c_n^k\right)_H, \\
&\left(\frac{c_n - c_{n-1}}{k} - \frac{c_n^k - c_{n-1}^k}{k}, c_n - c_n^k\right)_H \geq \frac{1}{2k}\left(\|c_n - c_n^k\|_H^2 - \|c_{n-1} - c_{n-1}^k\|_H^2\right), \\
&((c_n - c_n^k, c_n - c_n^k)) = \|c_n - c_n^k\|_V^2, \\
&h(\gamma_0(c_n) + c_b, \frac{\partial(\gamma_0(c))}{\partial t}(t_n) - \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k) \\
&\qquad \leq C\left\|\frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k}\right\|_V \|c_n - c_n^k\|_V,
\end{aligned}
$$

where Hölder, Cauchy and trace inequalities and estimate (2.55) has been employed, we find that

$$
\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^k\|_H^2 + \|c_n - c_n^k\|_V^2 + h\Big(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}\Big)\gamma_0(c_n - c_n^k) \\
&\quad -h\Big(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k}\Big)\gamma_0(c_n - c_n^k) \\
&\qquad \leq \frac{1}{2k}\|c_{n-1} - c_{n-1}^k\|_H^2 + C\left\|\frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k}\right\|_V \|c_n - c_n^k\|_V \\
&\qquad\quad - \left(\frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k}, c_n - c_n^k\right)_H.
\end{aligned}
$$

Using the Cauchy inequality with a small parameter, see (1.16), the fact that the norms $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$ are equivalent and multiplying by $2k$, it follows that

$$
\begin{aligned}
&\|c_n - c_n^k\|_H^2 + \beta\, k \|c_n - c_n^k\|_V^2 + 2k\, h\Big(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}\Big)\gamma_0(c_n - c_n^k)\\
&\qquad -2k\, h\Big(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k}\Big)\gamma_0(c_n - c_n^k)\\
&\qquad \le \|c_{n-1} - c_{n-1}^k\|_H^2 + Ck\left\|\frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k}\right\|_V^2 + Ck\|c_n - c_n^k\|_H^2,
\end{aligned}
$$

where β is a positive constant, which is independent of the time discretization parameter k, but, as in the case of constant C, it may change from line to line. Now, keeping in mind that

$$
\begin{aligned}
&\Big(h(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k}) - h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k})\Big)\gamma_0(c_n - c_n^k)\\
&\quad = h(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\qquad -h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\qquad +h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\qquad -h(\gamma_0(c_{n-1}^k) + c_b, \tfrac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k})\gamma_0(c_n - c_n^k),
\end{aligned}
$$

the Lipschitz behavior of function $N(z) = \dfrac{1}{(1+z)^2}$ for $z \in [0, c_b]$ and

$$
\begin{aligned}
&h(\gamma_0(c_n) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\quad -h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\qquad \le R_n\left|\frac{1}{(1+\gamma_0(c_n)+c_b)^2} - \frac{1}{(1+\gamma_0(c_{n-1}^k)+c_b)^2}\right| |\gamma_0(c_n - c_n^k)|\\
&\qquad \le CR_n |\gamma_0(c_n) - \gamma_0(c_{n-1}^k)|\, |\gamma_0(c_n - c_n^k)|\\
&\qquad \le CR_n \left(|\gamma_0(c_n) - \gamma_0(c_{n-1})| + |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|\right) |\gamma_0(c_n - c_n^k)|\\
&\qquad \le CR_n \left(|\gamma_0(c_n) - \gamma_0(c_n^k)|^2 + |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|^2 + |\gamma_0(c_n) - \gamma_0(c_{n-1})|^2\right),
\end{aligned}
$$

$$
\begin{aligned}
&h(\gamma_0(c_{n-1}^k) + c_b, \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k})\gamma_0(c_n - c_n^k)\\
&\qquad -h(\gamma_0(c_{n-1}^k) + c_b, \tfrac{\gamma_0(c_n^k) - \gamma_0(c_{n-1}^k)}{k})\gamma_0(c_n - c_n^k)\\
&\qquad \ge \frac{\beta}{2k}\left(|\gamma_0(c_n) - \gamma_0(c_n^k)|^2 - |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|^2\right),
\end{aligned}
$$

where Cauchy's inequality and estimate (2.81) have been used and R_n is the error

$$R_n = \left| \frac{\gamma_0(c_n) - \gamma_0(c_{n-1})}{k} \right| \leq C \|c\|_{C^1([0,T];V)}, \tag{2.83}$$

we get

$$\begin{aligned}
&\|c_n - c_n^k\|_H^2 + \beta\, k \|c_n - c_n^k\|_V^2 + \beta |\gamma_0(c_n) - \gamma_0(c_n^k)|^2 \\
&\quad \leq \|c_{n-1} - c_{n-1}^k\|_H^2 + Ck \left\| \frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k} \right\|_V^2 + Ck \|c_n - c_n^k\|_H^2 \\
&\qquad + \beta |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|^2 + Ck |\gamma_0(c_n) - \gamma_0(c_n^k)|^2 + Ck |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|^2 \\
&\qquad + Ck |\gamma_0(c_n) - \gamma_0(c_{n-1})|^2.
\end{aligned}$$

Considering inequality (2.83) and using the following notation

$$\begin{aligned}
\alpha_n^L &:= \|c_n - c_n^k\|_H^2 + \beta |\gamma_0 c_n - \gamma_0 c_n^k|^2, \\
\lambda_n^L &:= \beta \|c_n - c_n^k\|_V^2, \\
\phi_n^L &:= C \left\| \frac{\partial c}{\partial t}(t_n) - \frac{c_n - c_{n-1}}{k} \right\|_V^2 + C\|c_n - c_n^k\|_H^2 + C\, k^2 + C|\gamma_0(c_n) - \gamma_0(c_n^k)|^2 \\
&\qquad + \beta |\gamma_0(c_{n-1}) - \gamma_0(c_{n-1}^k)|^2,
\end{aligned}$$

we deduce that

$$\alpha_n^L + k\, \lambda_n^L \leq \alpha_{n-1}^L + k\, \phi_n^L,$$

and then, we get

$$\begin{aligned}
&\|c_n - c_n^k\|_H^2 + \beta\, k \sum_{j=1}^n \|c_j - c_j^k\|_V^2 + \beta |\gamma_0(c_n) - \gamma_0(c_n^k)|^2 \leq Ck \sum_{j=1}^n \Big\{ \|c_j - c_j^k\|_H^2 \\
&\quad + \left\| \frac{\partial c}{\partial t}(t_j) - \frac{c_j - c_{j-1}}{k} \right\|_V^2 + |\gamma_0(c_j) - \gamma_0(c_j^k)|^2 + k^2 \Big\},
\end{aligned}$$

where the initial condition $c_0^k = c_0$ has been used. Then, defining

$$\begin{aligned}
a_n^L &:= \|c_n - c_n^k\|_H^2 + \beta\, k \sum_{j=1}^n \|c_j - c_j^k\|_V^2 + \beta |\gamma_0(c_n) - \gamma_0(c_n^k)|^2, \\
g_n^L &:= k \sum_{j=1}^n \left(k^2 + \left\| \frac{\partial c}{\partial t}(t_j) - \frac{c_j - c_{j-1}}{k} \right\|_V^2 \right),
\end{aligned}$$

we have

$$a_n^L \leq Ck \sum_{j=1}^{n} a_j^L + C g_n^L, \qquad n = 1, \ldots, N.$$

Finally, taking into account that a_n^L, g_n^L, $n = 1, \ldots, N$ are nonnegative, we can apply the discrete version of Gronwall's lemma introduced in Section 1.4 of Chapter 1 (see, for example, [26]) to obtain the desired result. □

As a particular case of application of Theorem 2.2, let us assume that the continuous solution has the additional regularity

$$c \in H^2(0, T; V). \tag{2.84}$$

Corollary 2.1 *Under the assumptions of Theorem 2.2 and the additional regularity condition (2.84), the semi-discrete approximation in time is linearly convergent; that is to say, there exists a positive constant, independent of the time discretization parameter k, such that*

$$\max_{0 \leq n \leq N} \|c_n - c_n^k\|_H + \max_{0 \leq n \leq N} |\gamma_0(c_n) - \gamma_0(c_n^k)| \leq Ck.$$

Proof. Regarding the regularity condition (2.84), we can write

$$\begin{aligned}
\Big\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \Big\|_V &= \Big\| \frac{1}{k} \int_{t_{n-1}}^{t_n} \Big(\frac{\partial c}{\partial t}(t_n) - \frac{\partial c}{\partial t}(t) \Big) dt \Big\|_V \\
&= \frac{1}{k} \Big\| \int_{t_{n-1}}^{t_n} \int_t^{t_n} \frac{\partial^2 c}{\partial t^2}(s)\, ds\, dt \Big\|_V,
\end{aligned}$$

and hence, keeping in mind that $c \in H^2(0, T; V)$, it follows that

$$\begin{aligned}
k \sum_{j=1}^{N} \Big\| \frac{\partial c}{\partial t}(t_j) - \delta c_j \Big\|_V^2 &\leq \frac{1}{k} \sum_{j=1}^{N} \left(\int_{t_{j-1}}^{t_j} \int_t^{t_j} \Big\| \frac{\partial^2 c}{\partial t^2}(s) \Big\|_V ds\, dt \right)^2 \\
&\leq \frac{1}{k} \sum_{j=1}^{N} \left(\int_{t_{j-1}}^{t_j} \Big\| \frac{\partial^2 c}{\partial t^2} \Big\|_{L^2(t, t_j; V)} \sqrt{t_j - t}\, dt \right)^2 \\
&\leq C\, k^2 \sum_{j=1}^{N} \Big\| \frac{\partial^2 c}{\partial t^2} \Big\|_{L^2(t_{j-1}, t_j; V)}^2 = C\, k^2 \Big\| \frac{\partial^2 c}{\partial t^2} \Big\|_{L^2(0, T; V)}^2.
\end{aligned} \tag{2.85}$$

Moreover, we have

$$k\sum_{j=1}^{N} k^2 = k^3 N = T\,k^2.$$

Therefore, combining both estimates, the linear convergence of the algorithm is achieved.

$\square$

2.5 Fully discrete approximations: a priori error estimates

Before obtaining some a priori error estimates for the fully discrete approximations of the problem, let us define the truncation operator $R_L : \mathbb{R} \to [0, c_b]$ by

$$R_L(z) = \begin{cases} 0 & \text{if} \quad z \le 0, \\ z & \text{if} \quad 0 \le z \le c_b, \\ c_b & \text{if} \quad z \ge c_b, \end{cases}$$

which leads to the following truncated version of the problem, associated to Problem $P_W^{L,eq}$:

Problem P_{R_L}. For a given $c_0 \in V$, find a function $c \in H^1(0,T;H) \cap L^2(0,T;V)$ such that $c(0) = c_0$ and, for every $v \in V$ and a.e. $t \in (0,T)$, we get

$$(\frac{\partial c}{\partial t}(t), v)_H + ((c(t), v)) + h(R_L(\gamma_0(c(t)) + c_b), \frac{\partial\,(\gamma_0(c))}{\partial t}(t))\gamma_0(v) = 0. \tag{2.86}$$

Now, a fully discrete approximation of Problem P_{R_L} is obtained by following the steps indicated in Section 1.4 of Chapter 1 and taking into account both spatial and time discretizations described there.

Then, using a hybrid combination of both backward and forward Euler schemes, the fully discrete approximations are considered as follows.

Problem P_L^{hk}. Find a sequence $c^{hk} = \{c_n^{hk}\}_{n=0}^N \subset V^h$ such that

$$c_0^{hk} = c_0^h, \tag{2.87}$$

and, for $n = 1, \ldots, N$ and for all $v^h \in V^h$,

$$(\delta c_n^{hk}, v^h)_H + ((c_n^{hk}, v^h)) + h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\, \gamma_0(v^h) = 0, \tag{2.88}$$

where $c_0^h \in V^h$ is an appropriate approximation of the initial condition c_0.

We note that, under the assumptions of Theorem 2.1 and using Lax-Milgram theorem, we easily deduce the existence of a unique discrete solution to Problem P_L^{hk}.

Remark 2.2 *An important and open issue now would be to prove that the discrete solution c^{hk} also satisfies the boundedness property stated in Theorem 2.1; that is, to show that $-c_b \le c_n^{hk} \le 0$, for all $n = 1, \ldots, N$, assuming that $c_0^h(x) \in [-c_b, 0]$ for all $x \in [0, l]$. However, even if this question remains open yet we can prove the following partial result.*
Let us assume that $c_0^h(x) \in [-c_b, 0]$ for all $x \in [0, l]$ and that, for $n = 1, \ldots, N$, if $c_n^{hk}(x) = 0$ (or $-c_b$) for some $x \in (a_{i-1}, a_i)$ and $i = 1, \ldots, M$, then $c_n^{hk}(x) = 0$ (or $-c_b$) for all $x \in [a_{i-1}, a_i]$. Therefore, we have

$$-c_b \le c_n^{hk} \le 0, \quad n = 1, \ldots, N.$$

The proof of this discrete boundedness property follows from the arguments used in the continuous case (see the proof of Theorem 2.1 for details). The main idea is to use the fact that the test functions $v^h = (c_n^{hk})^+ = \max\{c_n^{hk}, 0\}$ and $v^h = (c_n^{hk} + c_b)^- = \max\{-(c_n^{hk} + c_b), 0\}$ belong to the finite element space V^h.

In the sequel, we derive an error estimate for the difference $c_n - c_n^{hk}$ assuming the additional regularity given in (2.82). But first, we introduce the following result which states two lower boundedness properties, where, here and in what follows in this section, C is a positive constant whose value may change from line to line and which may depend on the continuous solution c, although it is independent of the discretization parameters h and k.

Lemma 2.4 *Given $c^{hk} = \{c_n^{hk}\}_{n=0}^N$ the unique solution to Problem P_L^{hk}, we have, for $n = 1, \ldots, N$,*

$$\|c_n^{hk}\|_V \leq \|c_0^h\|_V, \tag{2.89}$$

$$\gamma_0(c_n^{hk} - c_{n-1}^{hk})^2 \leq Ck(\|c_{n-1}^{hk}\|_V^2 - \|c_n^{hk}\|_V^2) \leq Ck\|c_0^h\|_V^2. \tag{2.90}$$

Proof. Taking $v^h = c_n^{hk} - c_{n-1}^{hk} \in V^h$ as a test function in (2.88) we find that

$$\frac{1}{k}\|c_n^{hk} - c_{n-1}^{hk}\|_H^2 + \|c_n^{hk}\|_V^2 - ((c_n^{hk}, c_{n-1}^{hk})) + \frac{1}{k}\frac{(\gamma_0(c_n^{hk} - c_{n-1}^{hk}))^2}{(1 + R_L(c_b + \gamma_0(c_{n-1}^{hk})))^2} = 0. \tag{2.91}$$

Since the first and the forth terms of the previous expression are nonnegative, we get

$$\|c_n^{hk}\|_V^2 \leq \|c_n^{hk}\|_V \|c_{n-1}^{hk}\|_V,$$

and (2.89) follows.

Using equation (2.91) and taking into account that its first term is nonnegative and that

$$h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(v))\gamma_0(v) \geq \beta|\gamma_0(v)|^2, \quad \forall v \in V,$$

and applying both Hölder and Cauchy inequalities, we get

$$\|c_n^{hk}\|_V^2 + \frac{\beta}{k}|\gamma_0(c_n^{hk} - c_{n-1}^{hk})|^2 \leq \frac{1}{2}(\|c_{n-1}^{hk}\|_V^2 + \|c_n^{hk}\|_V^2).$$

Thus, estimate (2.89) leads to estimate (2.90). □

Now, we turn to obtain some a priori error estimates on the numerical errors $c_n - c_n^{hk}$.

Theorem 2.3 *Under the assumptions of Theorem 2.1 and assuming that regularity condition (2.82) holds, there exists a positive constant $C > 0$, independent of the* *discretization parameters h and k, such that the following error estimates are satisfied for all $\{v_n^h\}_{n=1}^N \subset V^h$,*

$$\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H^2 + k\sum_{n=1}^N \|c_n - c_n^{hk}\|_V^2 + \max_{0\le n\le N} |\gamma_0(c_n - c_n^{hk})|^2 \le C\|c_0 - c_0^h\|_H^2$$
$$+C|\gamma_0(c_0 - c_0^h)|^2 + Ck\sum_{n=1}^N \Big\{ \Big\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \Big\|_H^2 + \|c_n - v_n^h\|_V^2 + \Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big)\Big|^2$$
$$+|\gamma_0(c_n - v_n^h)|^2 + |\gamma_0(c_n - c_{n-1})|^2 \Big\} + C\max_{1\le n\le N} \|c_n - v_n^h\|_H^2$$
$$+\frac{C}{k}\sum_{n=0}^{N-1} \{ \|c_n - v_n^h - (c_{n+1} - v_{n+1}^h)\|_H^2 + |\gamma_0(c_n - v_n^h - (c_{n+1} - v_{n+1}^h))|^2 \}$$
$$+C\max_{0\le n\le N} |\gamma_0(c_n - v_n^h)|^2 + C\sum_{n=0}^{N-1} |\gamma_0(c_{n+1} - v_{n+1}^h)|^2. \tag{2.92}$$

Proof. Taking $v = c_n - v^h \in V$ in equation (2.86) at time $t = t_n$, we find that, for $n = 1, 2, \ldots, N$,

$$\Big(\frac{\partial c}{\partial t}(t_n), c_n - v^h\Big)_H + ((c_n, c_n - v^h)) + h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\,\gamma_0(c)}{\partial t}(t_n)\Big)\,\gamma_0(c_n - v^h) = 0, \tag{2.93}$$

and using equation (2.88) we have, for all $v^h \in V^h$,

$$(\delta c_n^{hk}, c_n - c_n^{hk})_H + ((c_n^{hk}, c_n - c_n^{hk})) + h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\,\gamma_0(c_n - c_n^{hk})$$
$$= (\delta c_n^{hk}, c_n - v^h)_H + ((c_n^{hk}, c_n - v^h))$$
$$+h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\,\gamma_0(c_n - v^h). \tag{2.94}$$

Subtracting now equations (2.93) and (2.94) and taking into account the linearity of the trace operator, after easy algebraic manipulations we obtain, for all $v^h \in V^h$,

$$\Big(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - c_n^{hk}\Big)_H + \|c_n - c_n^{hk}\|_V^2$$
$$+\Big(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial \gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\Big)\,\gamma_0(c_n - c_n^{hk})$$

$$= \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + ((c_n - c_n^{hk}, c_n - v^h))$$
$$+ \left(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\,\gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\right) \gamma_0(c_n - v^h),$$

and therefore, taking into account that $\dfrac{\partial c}{\partial t}(t_n) - \delta c_n^{hk} = \dfrac{\partial c}{\partial t}(t_n) - \delta c_n + \delta c_n - \delta c_n^{hk}$, it follows that, for all $v^h \in V^h$,

$$(\delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H + \|c_n - c_n^{hk}\|_V^2$$
$$+ \left(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\right) \gamma_0(c_n - c_n^{hk})$$
$$= \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + ((c_n - c_n^{hk}, c_n - v^h))$$
$$+ \left(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\right) \gamma_0(c_n - v^h)$$
$$+ \left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n - c_n^{hk}\right)_H. \tag{2.95}$$

Now, considering the property of the divided differences (1.27)— see Chapter 1— and using the Cauchy inequality, we get

$$(\delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H \geq \frac{1}{2k}\left(\|c_n - c_n^{hk}\|_H^2 - \|c_{n-1} - c_{n-1}^{hk}\|_H^2\right). \tag{2.96}$$

Moreover, the following equality holds

$$\left(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\right) \gamma_0(v)$$
$$= \left(h\Big(R_L(c_b + \gamma_0(c_n)), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big) - h\Big(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big)\right) \gamma_0(v)$$
$$+ \left(h\Big(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \frac{\partial\gamma_0(c)}{\partial t}(t_n)\Big) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n))\right) \gamma_0(v)$$
$$+ \left(h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n)) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\right) \gamma_0(v).$$

Taking into account that the functions R_L and $N(z) = \dfrac{1}{(1+z)^2}$, $z \in [0, c_b]$ are Lipschitz, considering the trace inequality and the regularity condition (2.82) and keeping in mind that $0 \leq R_L(\cdot) \leq c_b$, we obtain the following estimates, for all $v \in V$,

$$|(h(R_L(c_b+\gamma_0(c_n)),\frac{\partial\,\gamma_0(c)}{\partial t}(t_n)) - h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\frac{\partial\,\gamma_0(c)}{\partial t}(t_n)))\,\gamma_0(v)|$$
$$\leq C|\gamma_0(c_n-c_{n-1}^{hk})||\gamma_0(v)|, \qquad (2.97)$$

$$|(h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\frac{\partial\gamma_0(c)}{\partial t}(t_n)) - h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\gamma_0(\delta c_n)))\,\gamma_0(v)|$$
$$\leq C|\gamma_0(\frac{\partial c}{\partial t}(t_n)-\delta c_n)||\gamma_0(v)|, \quad (2.98)$$

$$\big(h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\gamma_0(\delta c_n)) - h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\gamma_0(\delta c_n^{hk}))\big)\;\gamma_0(c_n-c_n^{hk})$$
$$\geq \frac{\beta}{2k}\left(|\gamma_0(c_n-c_n^{hk})|^2 - |\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\right), \qquad (2.99)$$

where β is a positive constant which is independent of the discretization parameters. We recall that $\delta c_n = (c_n - c_{n-1})/k$. Therefore, using (2.96), (2.97), (2.98) and (2.99), equation (2.95) leads to the following estimates

$$\begin{aligned}
&\frac{1}{2k}\|c_n-c_n^{hk}\|_H^2 + \|c_n-c_n^{hk}\|_V^2 + \frac{\beta}{2k}|\gamma_0(c_n-c_n^{hk})|^2 \leq \frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2\\
&\quad+\frac{\beta}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2 + \left(\frac{\partial c}{\partial t}(t_n)-\delta c_n^{hk}, c_n-v^h\right)_H + ((c_n-c_n^{hk},c_n-v^h))\\
&\quad+\big(h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\gamma_0(\delta c_n)) - h(R_L(c_b+\gamma_0(c_{n-1}^{hk})),\gamma_0(\delta c_n^{hk}))\big)\;\gamma_0(c_n-v^h)\\
&\quad+C|\gamma_0(c_n-c_{n-1}^{hk})||\gamma_0(c_n-c_n^{hk})| + C\Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_n)-\delta c_n\Big)\Big||\gamma_0(c_n-c_n^{hk})|\\
&\quad+C|\gamma_0(c_n-c_{n-1}^{hk})||\gamma_0(c_n-v^h)| + C\Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_n)-\delta c_n\Big)\Big||\gamma_0(c_n-v^h)|\\
&\quad+\left(\delta c_n - \frac{\partial c}{\partial t}(t_n), c_n-c_n^{hk}\right)_H, \quad \forall v^h \in V^h.
\end{aligned} \qquad (2.100)$$

Taking into account that

$$\left(\frac{\partial c}{\partial t}(t_n)-\delta c_n^{hk}, c_n-v^h\right)_H = \left(\frac{\partial c}{\partial t}(t_n)-\delta c_n, c_n-v^h\right)_H + \left(\delta c_n-\delta c_n^{hk}, c_n-v^h\right)_H,$$

$$|\gamma_0(c_n-c_{n-1}^{hk})| \leq |\gamma_0(c_n-c_{n-1})| + |\gamma_0(c_{n-1}-c_{n-1}^{hk})|,$$

and using several times Hölder and both Cauchy and Cauchy with ε, see (1.16), inequalities, and considering the property (1.31) with $\wp = 2$, we have, for all $v^h \in V^h$,

$$\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \|c_n - c_n^{hk}\|_V^2 + \frac{\beta}{2k}|\gamma_0(c_n - c_n^{hk})|^2 \le \frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2 \\
&\quad + \frac{\beta}{2k}|\gamma_0(c_{n-1} - c_{n-1}^{hk})|^2 + C\Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + C\|c_n - v^h\|_V^2 \\
&\quad + \big(h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n)) - h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n^{hk}))\big)\ \gamma_0(c_n - v^h) \\
&\quad + (\delta c_n - \delta c_n^{hk}, c_n - v^h)_H + \varepsilon\|c_n - c_n^{hk}\|_V^2 + C|\gamma_0(c_n - c_{n-1})|^2 + C|\gamma_0(c_{n-1} - c_{n-1}^{hk})|^2 \\
&\quad + C|\gamma_0(c_n - c_n^{hk})|^2 + C\Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big)\Big|^2 + C|\gamma_0(c_n - v^h)|^2 + C\|c_n - c_n^{hk}\|_H^2.
\end{aligned}$$

Thus, by induction we find that

$$\begin{aligned}
&\|c_n - c_n^{hk}\|_H^2 + k\sum_{j=1}^n \|c_j - c_j^{hk}\|_V^2 + |\gamma_0(c_n - c_n^{hk})|^2 \le C\|c_0 - c_0^h\|_H^2 \\
&\quad + C|\gamma_0(c_0 - c_0^h)|^2 + Ck\sum_{j=1}^n \Big\{\Big\|\frac{\partial c}{\partial t}(t_j) - \delta c_j\Big\|_H^2 + \|c_j - v_j^h\|_V^2 \\
&\quad + \big(h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j)) - h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j^{hk}))\big)\ \gamma_0(c_j - v_j^h) \\
&\quad + (\delta c_j - \delta c_j^{hk}, c_j - v_j^h)_H + |\gamma_0(c_j - c_{j-1})|^2 + |\gamma_0(c_j - c_j^{hk})|^2 + \Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_j) - \delta c_j\Big)\Big|^2 \\
&\quad + |\gamma_0(c_j - v_j^h)|^2 + \|c_j - c_j^{hk}\|_H^2\Big\}, \quad \forall v^h = \{v_j^h\} \subset V^h. \qquad (2.101)
\end{aligned}$$

Now, denoting by $s_j = \dfrac{1}{(1 + R_L(c_b + \gamma_0 c_{j-1}^{hk}))^2}$, keeping in mind that functions $N(z) = \dfrac{1}{(1+z)^2}$ for $z \in [0, c_b]$ and R_L are Lipschitz and using both (2.87) and (2.90), we deduce that, for all $v^h = \{v_j^h\} \subset V^h$,

$$\begin{aligned}
&k\sum_{j=1}^n \big(h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j)) - h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j^{hk}))\big)\ \gamma_0(c_j - v_j^h) \\
&\quad = \sum_{j=1}^n \big(\gamma_0(c_j - c_j^{hk}) - \gamma_0(c_{j-1} - c_{j-1}^{hk})\big)\ s_j\, \gamma_0(c_j - v_j^h) \\
&\quad = \sum_{j=1}^{n-1} \gamma_0(c_j - c_j^{hk})\big(s_j\, \gamma_0(c_j - v_j^h) - s_{j+1}\, \gamma_0(c_{j+1} - v_{j+1}^h)\big) \\
&\qquad + \gamma_0(c_n - c_n^{hk})\gamma_0(c_n - v_n^h)s_n + \gamma_0(c_0^h - c_0)\gamma_0(c_1 - v_1^h)s_1,
\end{aligned}$$

$$|s_j\gamma_0(c_j - v_j^h) - s_{j+1}\gamma_0(c_{j+1} - v_{j+1}^h)|$$
$$\leq \left|s_j\left(\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))\right)\right| + |\gamma_0(c_{j+1} - v_{j+1}^h)(s_j - s_{j+1})|,$$
$$|s_j - s_{j+1}| \leq C|\gamma_0(c_j^{hk} - c_{j-1}^{hk})| \leq C\sqrt{k}\|c_0^h\|_V.$$

Therefore, taking into account both Cauchy and Cauchy with $\varepsilon > 0$ (see (1.16)) inequalities, we notice that

$$\begin{aligned}
&k\sum_{j=1}^{n}\left(h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j)) - h(R_L(c_b + \gamma_0(c_{j-1}^{hk})), \gamma_0(\delta c_j^{hk}))\right)\gamma_0(c_j - v_j^h)\\
&\leq C\sum_{j=1}^{n-1}(k|\gamma_0(c_j - c_j^{hk})|^2 + \frac{1}{k}|\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))|^2 + \|c_0^h\|_V^2|\gamma_0(c_{j+1} - v_{j+1}^h)|^2)\\
&\qquad + C\,\varepsilon|\gamma_0(c_n - c_n^{hk})|^2 + C|\gamma_0(c_n - v_n^h)|^2 + C|\gamma_0(c_0 - c_0^h)|^2 + C|\gamma_0(c_1 - v_1^h)|^2.
\end{aligned}$$

Using the previous estimate and estimate (1.39), see Chapter 1, expression (2.101) reads

$$\begin{aligned}
&\|c_n - c_n^{hk}\|_H^2 + k\sum_{j=1}^{n}\|c_j - c_j^{hk}\|_V^2 + |\gamma_0(c_n - c_n^{hk})|^2 \leq C\|c_0 - c_0^h\|_H^2\\
&\quad + C|\gamma_0(c_0 - c_0^h)|^2 + Ck\sum_{j=1}^{n}\left\{\left\|\frac{\partial c}{\partial t}(t_j) - \delta c_j\right\|_H^2 + \|c_j - v_j^h\|_V^2 + \left|\gamma_0\left(\frac{\partial c}{\partial t}(t_j) - \delta c_j\right)\right|^2\right.\\
&\quad \left. + |\gamma_0(c_j - c_j^{hk})|^2 + |\gamma_0(c_j - v_j^h)|^2 + \|c_j - c_j^{hk}\|_H^2 + |\gamma_0(c_j - c_{j-1})|^2\right\}\\
&\quad + C\|c_n - v_n^h\|_H^2 + C\|c_1 - v_1^h\|_H^2 + C|\gamma_0(c_n - v_n^h)|^2 + C|\gamma_0(c_1 - v_1^h)|^2\\
&\quad + \frac{C}{k}\sum_{j=1}^{n-1}\{\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 + |\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))|^2\}\\
&\quad + C\sum_{j=1}^{n-1}|\gamma_0(c_{j+1} - v_{j+1}^h)|^2, \quad \forall v^h = \{v_j^h\} \subset V^h.
\end{aligned}$$

Now, defining

$$b_n^L := \|c_n - c_n^{hk}\|_H^2 + k\sum_{j=1}^{n}\|c_j - c_j^{hk}\|_V^2 + |\gamma_0(c_n - c_n^{hk})|^2,$$

$$d_n^L := \|c_0 - c_0^h\|_H^2 + |\gamma_0(c_0 - c_0^h)|^2 + k\sum_{j=1}^n \Big\{ \Big\| \frac{\partial c}{\partial t}(t_j) - \delta c_j \Big\|_H^2 + \|c_j - v_j^h\|_V^2$$
$$+ \Big|\gamma_0\Big(\frac{\partial c}{\partial t}(t_j) - \delta c_j\Big)\Big|^2 + |\gamma_0(c_j - v_j^h)|^2 + |\gamma_0(c_j - c_{j-1})|^2 \Big\} + \|c_n - v_n^h\|_H^2$$
$$+ \|c_1 - v_1^h\|_H^2 + |\gamma_0(c_n - v_n^h)|^2 + |\gamma_0(c_1 - v_1^h)|^2 + C\sum_{j=1}^{n-1} |\gamma_0(c_{j+1} - v_{j+1}^h)|^2$$
$$+ \frac{1}{k}\sum_{j=1}^{n-1} \big\{ \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 + |\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))|^2 \big\},$$

it follows that

$$b_n^L \leq C\,k\sum_{j=1}^n b_j^L + C\,d_n^L, \quad n = 1, \ldots, N.$$

Finally, applying the discrete version of Gronwall's inequality presented in Section 1.4 of Chapter 1 (see, for example, [18]), the result follows. □

Remark 2.3 *We note that estimates (2.92) could be also obtained without the estimates on function h, keeping in mind that*

$$\begin{aligned} & h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n - \delta c_n^{hk}))\gamma_0(c_n - c_n^{hk}) \\ & = h\left(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \frac{1}{2k}\left[k^2\gamma_0(\delta c_n - \delta c_n^{hk})^2 + \gamma_0(c_n - c_n^{hk})^2 - \gamma_0(c_{n-1} - c_{n-1}^{hk})^2\right]\right) \\ & \geq \frac{C}{2k}\left[k^2\gamma_0(\delta c_n - \delta c_n^{hk})^2 + \gamma_0(c_n - c_n^{hk})^2 - \gamma_0(c_{n-1} - c_{n-1}^{hk})^2\right], \end{aligned}$$

and the estimate

$$\begin{aligned} & h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(\delta c_n - \delta c_n^{hk}))\gamma_0(c_n - v^h) \\ & \qquad \leq C\varepsilon k\gamma_0(\delta c_n - \delta c_n^{hk})^2 + \frac{C}{k}\gamma_0(c_n - v^h)^2, \end{aligned}$$

where $\varepsilon > 0$ is assumed small enough.

Estimates (2.92) are the basis for the convergence analysis. As an example, recall that the finite element space V^h is given in (1.41), and let us assume further regularity conditions on the solution to the continuous problem:

$$c \in H^1(0,T;H^2(0,l)), \quad \frac{\partial^2 c}{\partial t^2} \in L^2(0,T;V). \qquad (2.102)$$

Denoting by $\pi^h : \mathcal{C}([0,l]) \to V^h$ the standard finite element interpolation operator (see [9]) and considering $c_0^h = \pi^h c_0$, we are able to prove the following.

Corollary 2.2 *Let the assumptions of Theorem 2.3 and the additional regularity conditions (2.102) hold. Then the linear convergence of the algorithm is obtained; i.e. there exists a positive constant $C > 0$, independent of h and k, such that*

$$\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H + \max_{0\le n\le N} |\gamma_0(c_n - c_n^{hk})| \le C\,(h+k).$$

Proof. Let us take $v_j^h = \pi^h c_j$, $j = 1,\dots,N$. Since $c \in \mathcal{C}([0,T];H^2(0,l))$ because $H^1(0,T) \subset \mathcal{C}([0,T])$ we obtain (see [9]),

$$\begin{aligned} &k\sum_{n=1}^{N}\left[\|c_n - \pi^h c_n\|_V^2 + |\gamma_0(c_n - \pi^h c_n)|^2\right] + \|c_0 - c_0^h\|_H^2 + |\gamma_0(c_0 - c_0^h)|^2 \\ &\quad + \max_{0\le n\le N}\|c_n - \pi^h c_n\|_H^2 + \max_{0\le n\le N}|\gamma_0(c_n - \pi^h c_n)|^2 \le C\,h^2\,\|c\|^2_{\mathcal{C}([0,T];H^2(0,l))}. \end{aligned}$$

Keeping in mind the regularity $\dfrac{\partial^2 c}{\partial t^2} \in L^2(0,T;V)$ and expression (2.85), considering the trace inequality, the fact that $\|\cdot\|_V$ and $\|\cdot\|_{H^1(0,l)}$ are equivalent norms in V and the inequality (2.85), we have

$$\begin{aligned} k\sum_{n=1}^{N}\left[\left\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\right\|_H^2 + \left|\gamma_0\Big(\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big)\right|^2\right] &\le C\,k\sum_{n=1}^{N}\left\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\right\|_V^2 \\ &\le Ck^2\left\|\frac{\partial^2 c}{\partial\,t^2}\right\|^2_{L^2(0,T;V)}. \end{aligned}$$

Now, following the ideas applied to estimate the damage error terms (see, for instance, [4]) we bound the terms

$$\frac{1}{k}\sum_{n=0}^{N-1}\left[\|c_n - v_n^h - (c_{n+1} - v_{n+1}^h)\|_H^2 + |\gamma_0(c_n - v_n^h - (c_{n+1} - v_{n+1}^h))|^2\right].$$

First, note that both c_n and c_{n+1} belong to $H^2(0,l)$ and then, taking into account the linearity of the interpolation operator, we get (see [9]),

$$\|c_{n+1}-c_n-\pi^h(c_{n+1}-c_n)\|_H^2+|\gamma_0(c_{n+1}-c_n-\pi^h(c_{n+1}-c_n))|^2\leq C\,h^4\|c_{n+1}-c_n\|_{H^2(0,l)}^2.$$

We point out now that the second term in the latter expression, as well as the last term in estimates (2.92), are zero taking into account that $\gamma_0(c_n)=\gamma_0(\pi^h c_n)$, $n=0,\ldots,N$, and the linearity of the trace operator.

On the other hand, using regularity condition (2.102) we deduce that

$$c_{n+1}-c_n=\int_{t_n}^{t_{n+1}}\frac{\partial c}{\partial t}(s)\,ds.$$

Thus, we have

$$\|c_{n+1}-c_n\|_{H^2(0,l)}\leq\int_{t_n}^{t_{n+1}}\Big\|\frac{\partial c}{\partial t}(s)\Big\|_{H^2(0,l)}ds\leq\sqrt{k}\left(\int_{t_n}^{t_{n+1}}\Big\|\frac{\partial c}{\partial t}(s)\Big\|_{H^2(0,l)}^2ds\right)^{1/2},$$

and therefore, keeping in mind that $h\leq l$ it follows that

$$\begin{aligned}\frac{1}{k}\sum_{n=0}^{N-1}\|c_n-\pi^h c_n-(c_{n+1}-\pi^h c_{n+1})\|_H^2 &\leq C\,h^4\sum_{j=1}^{N-1}\int_{t_n}^{t_{n+1}}\Big\|\frac{\partial c}{\partial t}(s)\Big\|_{H^2(0,l)}^2ds\\ &\leq C\,h^2\Big\|\frac{\partial c}{\partial t}\Big\|_{L^2(0,T;H^2(0,l))}^2.\end{aligned}$$

Combining all these estimates, the linear convergence is obtained. □

2.6 Numerical results

In this section, we first describe the numerical scheme implemented in MATLAB in order to obtain the numerical approximations of Problem P_L^{hk} and then, we present some numerical results to exhibit its accuracy in an academic example and its behavior in the simulation of two commercially available surfactants.

Considering the finite element space defined in (1.41), for $n=1,2,\ldots,N$ and given $c_{n-1}^{hk}\in V^h$, the discrete concentration at time $t=t_n$ of surfactant, c_n^{hk}, is then obtained from equation (2.88); namely, it solves the problem:

$$(c_n^{hk}, v^h)_H + k\,((c_n^{hk}, v^h)) + h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(c_n^{hk}))\,\gamma_0(v^h)$$
$$= (c_{n-1}^{hk}, v^h)_H + h(R_L(c_b + \gamma_0(c_{n-1}^{hk})), \gamma_0(c_{n-1}^{hk}))\,\gamma_0(v^h), \quad \forall v^h \in V^h.$$

The algorithm implemented to solve this problem is described below:

1. **Initial time step.** At the beginning both c_0^{hk} and Γ_0 are given. We calculate

$$\mu_0^{hk} = \frac{1}{(1 + R_L(c_b + \gamma_0(c_0^{hk})))^2}.$$

2. **(n)th time step.** The surfactant concentration at time t_{n-1}, c_{n-1}^{hk}, and the value μ_{n-1}^{hk} are known. Then, at time t_n, c_n^{hk}, μ_n^{hk} and Γ_n^{hk} are obtained using the following algorithm:

   (a) We calculate c_n^{hk} by solving the following linear problem:

$$\int_0^l c_n^{hk}\, v^h\, dx + k \int_0^l \frac{\partial c_n^{hk}}{\partial x}\,\frac{\partial v^h}{\partial x}\, dx + \mu_{n-1}^{hk}\,\gamma_0(c_n^{hk})\,\gamma_0(v^h)$$
$$= \mu_{n-1}^{hk}\,\gamma_0(c_{n-1}^{hk})\,\gamma_0(v^h) + \int_0^l c_{n-1}^{hk}\, v^h\, dx, \quad \forall v^h \in V^h.$$

   (b) Now, μ_n^{hk} is obtained by using the formula:

$$\mu_n^{hk} = \frac{1}{(1 + R_L(c_b + \gamma_0(c_n^{hk})))^2},$$

   (c) and the value of Γ_n^{hk} is easily deduced:

$$\Gamma_n^{hk} = \frac{\gamma_0(c_n^{hk})}{1 + R_L(c_b + \gamma_0(c_n^{hk}))}.$$

This numerical scheme has been implemented on a 3.2 Ghz PC using MATLAB, and a typical run ($h = k = 0.01$) takes about 0.6 seconds of CPU time.

2.6.1 First example: numerical convergence

As a first example, we consider the following test problem:

$$\begin{aligned}
&\frac{\partial \tilde{c}}{\partial t}(t,x) - 5\,\frac{\partial^2 \tilde{c}}{\partial x^2}(t,x) = 0, \quad x \in (0,1), \quad t \in (0,0.1),\\
&5\,\frac{\partial \tilde{c}}{\partial x}(t,0) = h(\tilde{c}(t,0), \frac{\partial \tilde{c}}{\partial t}(t,0)), \quad t \in (0,0.1),\\
&\tilde{c}(t,1) = 1, \quad t \in (0,0.1),\\
&\tilde{c}(0,x) = \tilde{c}_0(x),
\end{aligned}$$

with the initial condition $\tilde{c}_0(x) = \min\{1, 1000\,x\}$. This problem corresponds to problem (2.1), (2.3)-(2.4) and (2.9) with the following data:

$$l = 1, \quad T = 0.1, \quad c_b = 1, \quad D = 5, \quad \Gamma_m = 1, \quad K_L = 1, \quad \Gamma_0 = 0.$$

Taking the solution obtained with parameters $h = 1/16384$ and $k = 10^{-6}$ as the "exact solution", c, the numerical errors, which are given by

$$\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H + \max_{0\le n\le N} |\gamma_0(c_n - c_n^{hk})|,$$

are presented in Table 2.1 for several values of the discretization parameters h and k. As it can be seen, the numerical error tends to zero as both h and k do. Moreover, the graph of the error with respect to the parameter $h+k$ is shown in Figure 2.2, where the linear convergence, stated in Corollary 2.2, seems to be achieved.

2.6.2 Second example: simulation of propanol

As a second problem, we consider a solution of propanol, using the following data from reference [6], namely:

$$\begin{aligned}
&c_b = 333\,\mathrm{mol/m^3}, \quad D = 5.2\times 10^{-10}\,\mathrm{m^2/s}, \quad K_L = 5.5\times 10^{-3}\,\mathrm{m^3/mol},\\
&\Gamma_m = 7.1\times 10^{-6}\,\mathrm{mol^2/m^2}, \quad l = 10^{-4}\,\mathrm{m}, \quad T = 10^{-4}\,\mathrm{s}, \quad \Gamma_0 = 0\,\mathrm{mol/m^2}.
\end{aligned}$$

$h\downarrow k\rightarrow$	0.01	0.005	0.002	0.001	0.0005
1/8	0.437554	0.365515	0.312296	0.291710	0.280590
1/16	0.324326	0.247134	0.188115	0.164276	0.150916
1/32	0.267746	0.187936	0.125745	0.099936	0.085071
1/64	0.239626	0.158547	0.094766	0.067912	0.052196
1/128	0.225634	0.143942	0.079381	0.052003	0.035847
1/256	0.218658	0.136667	0.071724	0.044087	0.027711
1/512	0.215176	0.133037	0.067905	0.040136	0.023654
1/1024	0.213518	0.131309	0.066087	0.038261	0.021724
1/2048	0.213497	0.131288	0.066065	0.038238	0.021699
1/4096	0.213487	0.131277	0.066054	0.038227	0.021688

Table 2.1: Numerical errors ($\times 10^1$) for several time and spatial discretization parameters.

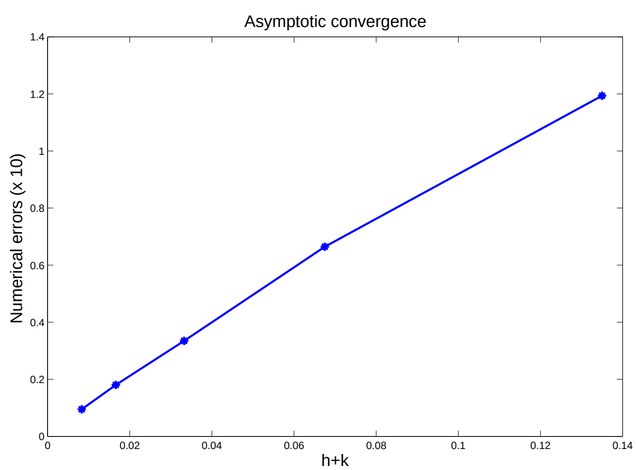

Figure 2.2: Example 1: linear convergence.

Moreover, the initial condition $\tilde{c}_0$ is here defined as

$$\tilde{c}_0(x) = \begin{cases} 0 & \text{if } x = 0, \\ 333 & \text{if } x \in (0, 10^{-4}]. \end{cases}$$

Using the time discretization parameter $k = 10^{-9}$ s and a non-uniform spatial mesh, refined as we approach to the point $x = 0$ and with the smallest element length 10^{-11} m, the evolution in time of both surface and subsurface concentrations are shown in Figure

2.3. As it can be seen, the subsurface concentration tends to the bulk concentration as time evolves, while the surface concentration increases but it converges to a value below Γ_m and determined by the Langmuir isotherm (2.6).

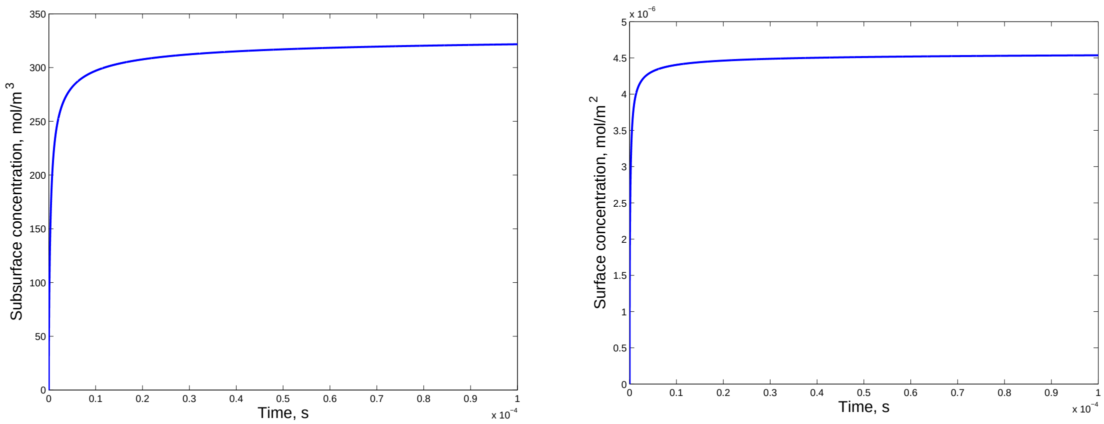

Figure 2.3: Evolution in time of subsurface and surface concentrations, respectively.

The surface equation of state, relating the surface tension $\widetilde{\gamma}$ with the subsurface concentration $c(t,0)$, is given by

$$\widetilde{\gamma}(t) = \widetilde{\gamma}_0 - n\,R\,\theta\,\Gamma_m\,\ln(1 + K_L\,c(t,0)), \tag{2.103}$$

where we take $\widetilde{\gamma}_0 = 0.0725\,\mathrm{N/m}$, $\theta = 293\,\mathrm{K}$ and we recall that $R = 8.31\,\mathrm{J/(K\,mol)}$ and $n = 1$. In Figure 2.4 the evolution in time of the surface tension obtained with our algorithm is compared with the results provided in [6]. We observe that both results are in good agreement.

2.6.3 Third example: simulation of sodium dodecylsulfate

In this last example, we consider a solution of sodium dodecylsufate (SDS) and we use the following data, obtained from [6]:

$$D = 0.1\times 10^{-10}\,\mathrm{m^2/s},\quad K_L = 0.11\,\mathrm{m^3/mol},\quad l = 10^{-4}\,\mathrm{m},$$
$$\Gamma_m = 10\times 10^{-6}\,\mathrm{mol^2/m^2},\quad T = 10\,\mathrm{s},\quad \Gamma_0 = 0\,\mathrm{mol/m^2}.$$

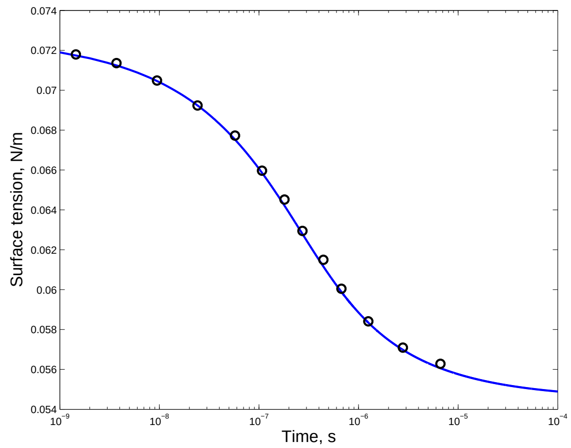

Figure 2.4: Comparison between the numerical surface tension obtained with our algorithm (solid curve) and that numerically obtained in [6] ($\circ$), semi-log scale.

Moreover, the bulk concentration considered is $c_b = 3.6\,\text{mol/m}^3$ and the initial condition $\tilde{c}_0$ is defined as

$$\tilde{c}_0(x) = \begin{cases} 0 & \text{if } x = 0, \\ 3.6 & \text{if } x \in (0, 10^{-4}]. \end{cases}$$

Here, we use a uniform time mesh composed of elements with length $k = 10^{-4}\,\text{s}$ and a non-uniform spatial mesh, refined as we approach to $x = 0$ and with the smallest element length $10^{-8}\,\text{m}$. In Figure 2.5 the concentration at final time and the evolution in time of the surface concentration are shown. Again, we point out that the subsurface and surface concentrations are increasing functions and that they converge to the bulk concentration and to a value less than Γ_m, respectively.

The numerical surface tension, obtained from equation (2.103) considering $\widetilde{\gamma}_0 = 0.072\,\text{N/m}$, $\theta = 298\,\text{K}$, $R = 8.31\,\text{J/(K mol)}$ and $n = 1$, and for different values of the diffusion coefficient, are plotted in Figure 2.6. Regarding that, at equilibrium, the subsurface concentration is equal to the bulk concentration, c_b, and that equation (2.103) does not depend on the diffusion coefficient, the value of the surface tension at equilibrium for the three experiments considered in Figure 2.6 is the same.

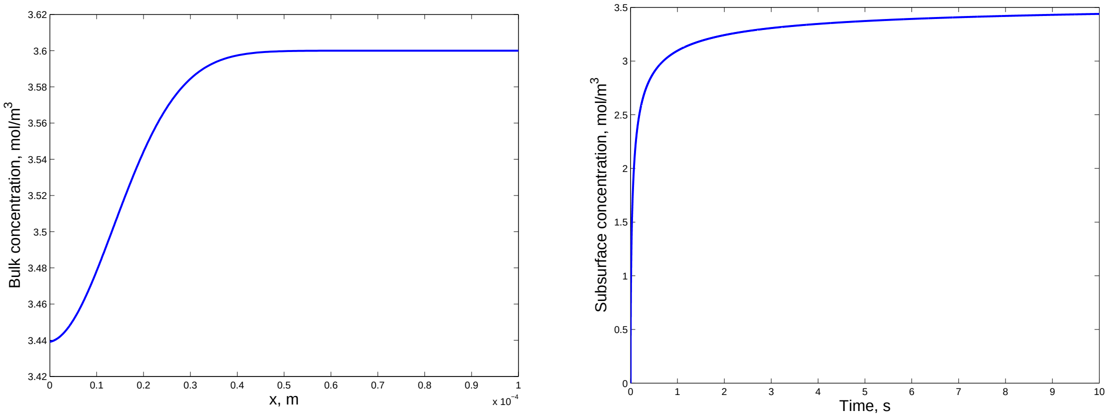

Figure 2.5: Concentration at final time (left) and evolution in time of subsurface concentration.

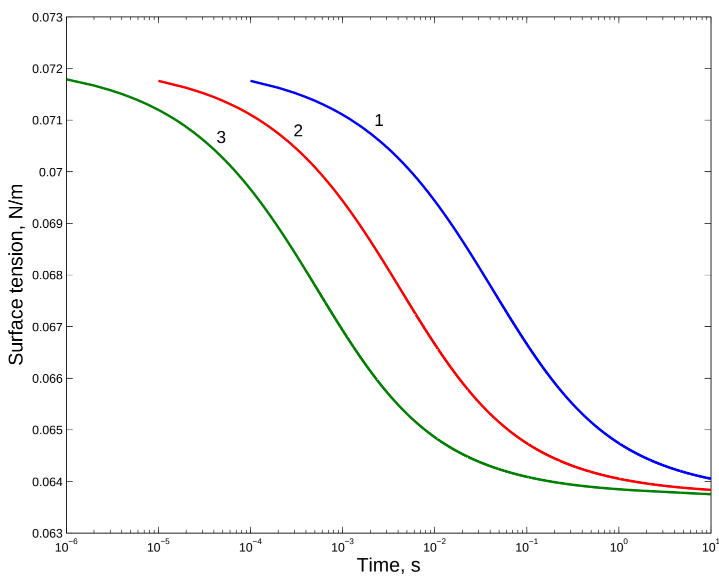

Figure 2.6: Evolution in time of the surface tension obtained for $D = 0.1 \times 10^{-10}\mathrm{m}^2/\mathrm{s}$ (**curve 1**), $D = 1 \times 10^{-10}\mathrm{m}^2/\mathrm{s}$ (**curve 2**) and $D = 8 \times 10^{-10}\mathrm{m}^2/\mathrm{s}$ (**curve 3**), semi-log scale.

Chapter 3

Mixed kinetic-diffusion model with the Langmuir-Hinshelwood equation

In this chapter, as we did in Chapter 1, we describe the adsorption-desorption dynamics of a surfactant solution at the air-water interface by means of a mixed kinetic-diffusion model. However, in this case, we first take into account the well-known Langmuir-Hinshelwood kinetic equation and then a modification of this expression which can be found in [6]. Physically, the difference between these models and the one introduced in Chapter 1 relies on the description of the adsorption dynamics. Indeed, in the case of the linear kinetic expression considered in Chapter 1, the rate of adsorption only depends on the subsurface concentration; however in the models presented here, this rate also depends on the fraction of the empty surface. So, the former model does not take into account the increase of the surface coverage and this is the reason why it predicts a faster equilibration between both surface and subsurface layers than the models considered here. Moreover, the modified Langmuir-Hinshelwood equation assumes a more pronounced deceleration of the adsorption rate with the incorporation of surfactant molecules into the surface than the original Langmuir-Hinshelwood expression (see [7]).

Mathematically, in this chapter, we first describe the model consisting of the diffusion partial differential equation in one spatial dimension together with the boundary and initial conditions and Langmuir-Hinshelwood equation, coupled to the system through the boundary condition at the subsurface. Secondly, we present the variational formulation of the problem and its truncated version providing results on existence and uniqueness of solution to both models. Then, fully discrete approximations obtained with the finite element method and a hybrid combination of both backward and forward Euler schemes are introduced. An a priori error estimate result is proved and, under adequate additional regularity conditions, the linear converge of the algorithm is derived. Numerical simulations are presented in order to illustrate the accuracy of the algorithm and the behavior of the model. Finally, we perform the same mathematical and numerical analyses for the modified Langmuir-Hinshelwood equation, presenting some simulations in order to show the behavior of this algorithm.

3.1 Mixed kinetic adsorption: Langmuir-Hinshelwood equation

In this section, in order to describe the adsorption dynamics we use the nonlinear Langmuir-Hinshelwood equation. We note that this work has been published in [23].

3.1.1 Model setting and its weak formulation

The system of equations to describe the diffusion process is the same as in the previous chapters, that is to say, it consists of the diffusion partial differential equation in one spatial dimension, together with suitable boundary and initial conditions. We recall it here in order to make the reading easier:

$$\frac{\partial c}{\partial t}(t,x) - D\,\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \quad t > 0, \quad x \in (0,l), \tag{3.1}$$

$$D\,\frac{\partial c}{\partial x}(t,0) = \frac{d\Gamma}{dt}(t), \quad t > 0, \tag{3.2}$$

$$c(t,l) = c_b, \quad t > 0, \tag{3.3}$$

$$c(0,x) = c_0(x), \quad x \in (0,l) \tag{3.4}$$

$$\Gamma(0) = \Gamma_0. \tag{3.5}$$

In order to close the problem, we consider here the Langmuir-Hinshelwood equation which is given by the following kinetic expression:

$$\frac{d\Gamma}{dt}(t) = k_L^a c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big) - k_L^d\,\Gamma(t), \qquad t > 0, \tag{3.6}$$

where the positive constant Γ_m is the maximum surface concentration, and the positive constants k_L^a and k_L^d denote the adsorption and desorption rate constants, respectively. Note that, in this model, the rate of adsorption depends on the term $1 - \dfrac{\Gamma(t)}{\Gamma_m}$, which represents the fraction of empty space at the surface. We remark that, at equilibrium (i.e. when $d\Gamma(t)/dt = 0$), this model yields to the classical Langmuir isotherm (see Chapter 2) with constant $K_L = \dfrac{k_L^a}{k_L^d\,\Gamma_m}$.

In order to simplify the writing, we define the function $f\colon \mathbb{R}^2 \to \mathbb{R}$ by

$$f(r,s) = k_L^a\, r\Big(1 - \frac{s}{\Gamma_m}\Big). \tag{3.7}$$

Using this function, equation (3.6) can be written as follows,

$$\frac{d\Gamma}{dt}(t) = f(c(t,0),\Gamma(t)) - k_L^d\,\Gamma(t), \qquad t > 0. \tag{3.8}$$

We are now interested in analyzing problem (3.1)-(3.5) coupled with the ordinary differential equation (3.8). Now, for the sake of clarity in the presentation of this model, and in order to simplify the calculations in the next sections, we assume that c_b equals zero and so, a homogeneous Dirichlet boundary condition is imposed on the right end of the spatial interval.

We turn now to the variational formulation of problem (3.1)-(3.5) and (3.8). So, assuming regularity, multiplying equation (3.1) by a smooth function z defined in $[0,l]$ such that $z(l)=0$; integrating in $(0,l)$ and using the integration by parts formula, we obtain

$$\int_0^l \frac{\partial c}{\partial t}(t,x)z(x)\,dx + D\int_0^l \frac{\partial c}{\partial x}(t,x)\,\frac{\partial z}{\partial x}(x)\,dx + D\,\frac{\partial c}{\partial x}(t,0)\,z(0) = 0,$$

for a.e. $t \in (0,T)$. Using the equations (3.2) and (3.8), we find

$$\int_0^l \frac{\partial c}{\partial t}(t,x)z(x)\,dx + D\int_0^l \frac{\partial c}{\partial x}(t,x)\,\frac{\partial z}{\partial x}(x)\,dx + f(c(t,0),\Gamma(t))\,z(0) = k_L^d\,\Gamma(t)\,z(0),$$

for a.e. $t \in (0,T)$. From the latter, using (3.4), (3.5) and (3.8) and taking into account the notations introduced in Chapter 1, we obtain the following weak formulation of the problem:

Problem P_W^{LH}. For given $c_0 \in H$ and $\Gamma_0 \in \mathbb{R}$, find $c \in W_2(0,T)$ and $\Gamma \in H^1(0,T)$ such that

$$\begin{aligned}
&\langle \frac{\partial c}{\partial t}(t), v\rangle_{V'\times V} + D((c(t),v)) + f(\gamma_0(c(t)),\Gamma(t))\gamma_0(v) = k_L^d\,\Gamma(t)\,\gamma_0(v),\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{for a.e. } t\in(0,T),\ \forall\, v \in V,\\
&\frac{d\,\Gamma}{dt}(t) = f(\gamma_0(c(t)),\Gamma(t)) - k_L^d\,\Gamma(t), \quad \text{for a.e. } t \in (0,T),\\
&c(0) = c_0, \quad \Gamma(0) = \Gamma_0.
\end{aligned}$$

Besides, in the sequel, we need the truncation operator $R\colon \mathbb{R}\to\mathbb{R}$ given by

$$R(s) = \begin{cases} 0 & \text{if} \quad s < 0,\\ s & \text{if} \quad 0 \le s \le (1-\sigma)\Gamma_m,\\ (1-\sigma)\Gamma_m & \text{if} \quad s > (1-\sigma)\Gamma_m, \end{cases} \tag{3.9}$$

where $0 \leq \sigma < 1$ is a given small constant. Indeed, we use the previously defined function f and the truncation operator R to introduce the following truncated version of the Langmuir–Hinshelwood equation, which becomes a modification of equation (3.8) and reads

$$\frac{d\Gamma}{dt}(t) = f(c(t,0), R(\Gamma(t))) - k_L^d\, \Gamma(t), \qquad t > 0. \tag{3.10}$$

We notice that, in spite of being a mathematical tool, the truncated operator R has also physical sense since it acts on the surface concentration, its real values being nonnegative but below Γ_m, since, as mentioned, we are interested in surfactant concentrations below their *cmc*.

Similarly as we did previously, from (3.1)-(3.5) and (3.10), we arrive to the following truncated problem associated to Problem P_W^{LH}:

Problem P_R^{LH}. For given $c_0 \in H$ and $\Gamma_0 \in \mathbb{R}$, find $c \in W_2(0,T)$ and $\Gamma \in H^1(0,T)$ such that

$$\begin{aligned}
&\langle \frac{\partial c}{\partial t}(t), v\rangle_{V'\times V} + D((c(t), v)) + f(\gamma_0(c(t)), R(\Gamma(t)))\gamma_0(v) = k_L^d\, \Gamma(t)\, \gamma_0(v), \\
&\hspace{6cm} \text{for a.e. } t \in (0,T),\ \forall\, v \in V, \\
&\frac{d\,\Gamma}{dt}(t) = f(\gamma_0(c(t)), R(\Gamma(t))) - k_L^d\, \Gamma(t), \quad \text{for a.e. } t \in (0,T), \\
&c(0) = c_0, \quad \Gamma(0) = \Gamma_0.
\end{aligned}$$

We remark that the initial conditions in Problems P_W^{LH} and P_R^{LH} make sense since $W_2(0,T) \subset \mathcal{C}([0,T]; H)$ and $H^1(0,T) \subset \mathcal{C}([0,T])$. Here and in what follows, by $\mathcal{C}([0,T])$ we denote the space of continuous functions from $[0,T]$ to $\mathbb{R}$ with the maximum norm $\|v\|_{\mathcal{C}([0,T])} = \max\{|v(t)|; t \in [0,T]\}$.

In the following two sections we study the existence and uniqueness of solution to Problems P_R^{LH} and P_W^{LH} and we also analyze the relation between these two problems and their solutions.

3.1.2 Existence and uniqueness results for Problem P_R^{LH}

In this section we formulate and prove the main existence and uniqueness result for Problem P_R^{LH}.

Theorem 3.1 *Assume that D, k_L^d, k_L^a and Γ_m are positive constants, and $\Gamma_0 \in \mathbb{R}$, $c_0 \in H$. Then Problem P_R^{LH} has a unique solution $(c, \Gamma) \in W_2(0,T) \times H^1(0,T)$.*

The proof of Theorem 3.1 is carried out in several steps and it is based on the study of two intermediate problems, followed by the application of the Schauder fixed-point theorem. So, before demonstrating this result, we introduce all the tools needed to prove it. To simplify the presentation in this section, and without loss of generality, we can suppose that $D = k_L^d = k_L^a = \Gamma_m = 1$, and therefore the nonlinear term in Problem P_R^{LH} is of the form $f(r,s) = r(1-s)$ for r, $s \in \mathbb{R}$. Let a be a given positive constant, which represents an arbitrary time.

Intermediate parabolic problem. Let $\eta \in \mathcal{C}([0,a])$ and consider the following problem:

Problem P_1^η. Given $c_0 \in H$, find $c_\eta \in W_2(0,a)$ such that

$$\langle \frac{\partial c_\eta}{\partial t}(t), v\rangle_{V'\times V} + ((c_\eta(t), v)) + \gamma_0(c_\eta(t))(1 - R(\eta(t)))\gamma_0(v) = \eta(t)\,\gamma_0(v),$$
$$\text{for a.e. } t \in (0,a),\ \forall\, v \in V,$$
$$c_\eta(0) = c_0.$$

For Problem P_1^η we have the following result regarding that C_{tr} denotes the $\mathcal{L}(V,\mathbb{R})$-norm of the trace operator, see (1.9).

Lemma 3.1 *Problem P_1^η has a unique solution $c_\eta \in W_2(0,a)$. Moreover, we have*

$$\|\gamma_0(c_\eta)\|_{L^2(0,a)} \leq C_{tr}^2\,\sqrt{a}\,\|\eta\|_{\mathcal{C}([0,a])} + C_{tr}\,\|c_0\|_H. \tag{3.11}$$

Proof. The existence and uniqueness of solution is based on the classical result on evolution problems. We define a family of bilinear forms $a_\eta\colon (0,a)\times V\times V\to\mathbb{R}$ by

$$a_\eta(t;u,v) = ((u,v)) + \gamma_0(u)\,(1-R(\eta(t)))\gamma_0(v), \quad t\in(0,a), \ \ \forall\, u,v\in V,$$

and the function $g_\eta\colon (0,a)\to V'$ by

$$\langle g_\eta(t),v\rangle_{V'\times V} = \eta(t)\,\gamma_0(v), \quad t\in(0,a), \ \ \forall\, v\in V.$$

Under this notation, Problem P_1^η has the form

$$\langle \frac{\partial c_\eta}{\partial t}(t),v\rangle_{V'\times V} + a_\eta(t;c_\eta(t),v) = \langle g_\eta(t),v\rangle_{V'\times V}, \ \ \text{for a.e.}\ t\in(0,a), \ \forall\, v\in V,$$
$$c_\eta(0) = c_0.$$

Exploiting the properties that $a_\eta(\cdot,u,v)$ is measurable for all u, $v\in V$, $a_\eta(t;\cdot,\cdot)$ is continuous on $V\times V$ for a.e. $t\in(0,a)$ (i.e. $|a_\eta(t;u,v)|\le M\|u\|\|v\|$ for all u, $v\in V$, a.e. $t\in(0,a)$ with $M>0$), $a_\eta(t;\cdot,\cdot)$ is coercive for a.e. $t\in(0,a)$ (i.e. $a_\eta(t;u,u)\ge\alpha\|u\|^2$ for all $u\in V$, a.e. $t\in(0,a)$ with $\alpha>0$) and $g_\eta\in\mathcal{V}'$, we apply Theorem 3.4 in [42] and we conclude that there exists a unique solution $c_\eta\in W_2(0,a)$ to Problem P_1^η.

Next, we establish estimate (3.11). Taking $c_\eta(t)$ as a test function in Problem P_1^η, we get

$$\frac{1}{2}\frac{d}{dt}\|c_\eta(t)\|_H^2 + \|c_\eta(t)\|_V^2 + (1-R(\eta(t)))\,(\gamma_0(c_\eta(t)))^2 = \eta(t)\,\gamma_0(c_\eta(t)),$$

for a.e. $t\in(0,a)$. Taking into account the fact that $0\le 1-R(\eta(t))$ for $t\in(0,a)$ and using the following version of the Cauchy inequality with ε

$$r\,s \le \frac{1}{2\,\varepsilon^2}\,r^2 + \frac{\varepsilon^2}{2}\,s^2, \quad \forall\, r,s\in\mathbb{R},\ \varepsilon>0, \tag{3.12}$$

we have

$$\frac{1}{2}\frac{d}{dt}\|c_\eta(t)\|_H^2 + \|c_\eta(t)\|_V^2 \le \eta(t)\,\gamma_0(c_\eta(t)) \le \frac{1}{2\varepsilon^2}(\eta(t))^2 + \frac{\varepsilon^2}{2}(\gamma_0(c_\eta(t)))^2,$$

for a.e. $t \in (0,a)$ with an arbitrary and positive ε. Using the trace inequality with constant C_{tr} (see (1.9) in Chapter 1) and integrating from 0 to t, we obtain

$$\|c_\eta(t)\|_H^2 \,+\, \frac{2}{C_{tr}^2}\int_0^t (\gamma_0(c_\eta(s)))^2\,ds \le \frac{1}{\varepsilon^2}\int_0^t (\eta(s))^2\,ds + \varepsilon^2\int_0^t (\gamma_0(c_\eta(s)))^2\,ds \,+\, \|c_0\|_H^2,$$

for all $t \in [0,a]$. Choosing $\varepsilon = 1/C_{tr}$, we have

$$\frac{1}{C_{tr}^2}\int_0^t (\gamma_0(c_\eta(s)))^2\,ds \le C_{tr}^2\int_0^t (\eta(s))^2\,ds \,+\, \|c_0\|_H^2 \quad \text{for all} \quad t \in [0,a].$$

Since $\eta \in \mathcal{C}([0,a])$, it follows that

$$\|\gamma_0(c_\eta)\|_{L^2(0,t)}^2 \le C_{tr}^4\, t\,\|\eta\|_{C([0,t])}^2 + C_{tr}^2\|c_0\|_H^2, \quad \text{for all} \quad t \in [0,a],$$

hence applying the property (1.31) with $\wp = 1/2$, we conclude that (3.11) holds. $\square$

Intermediate ordinary differential equation. Let $\eta \in \mathcal{C}([0,a])$ and let $c_\eta \in W_2(0,a)$ be the unique solution to Problem P_1^η corresponding to η. Consider the following problem.

Problem P_2^η. Given $\Gamma_0 \in \mathbb{R}$, find $\Gamma_\eta \in H^1(0,a)$ such that

$$\frac{d\,\Gamma_\eta}{dt}(t) = \gamma_0(c_\eta(t))(1 - R(\eta(t))) - \Gamma_\eta(t), \quad \text{for a.e. } t \in (0,a),$$
$$\Gamma_\eta(0) = \Gamma_0.$$

For Problem P_2^η we have the following existence and uniqueness result.

Lemma 3.2 *Problem P_2^η has a unique solution $\Gamma_\eta \in H^1(0,a)$ given by*

$$\Gamma_\eta(t) = \Gamma_0\,e^{-t} + e^{-t}\int_0^t \gamma_0(c_\eta(s))(1 - R(\eta(s)))\,e^s\,ds, \quad \textit{for all} \quad t \in [0,a]. \tag{3.13}$$

Moreover, we have

$$\|\Gamma_\eta\|_{\mathcal{C}([0,a])} \leq |\Gamma_0| + \sqrt{a}\,\|\gamma_0(c_\eta)\|_{L^2(0,a)}. \tag{3.14}$$

Proof. Let us define the function

$$F(t,r) = \gamma_0(c_\eta(t))(1 - R(\eta(t))) - r, \quad \text{for a.e. } t \in (0,a),\ \forall\, r \in \mathbb{R}.$$

It is clear that $F(t,\cdot)$ is Lipschitz continuous for a.e. $t \in (0,a)$ and $F(\cdot,r) \in L^2(0,a)$ for all $r \in \mathbb{R}$. The existence and uniqueness of the solution to Problem P_2^η follows from the classical theorem of Cauchy–Lipschitz which can be found in Theorem 2.1 of [43]. A short computation entails the formula (3.13). From (3.13), using the estimate $1 - R(\eta(t)) \leq 1$ for $t \in [0,a]$ and applying the Hölder inequality, we obtain

$$|\Gamma_\eta(t)| \leq |\Gamma_0| + \sqrt{t}\,\|\gamma_0(c_\eta)\|_{L^2(0,t)}, \quad \text{for all } \ t \in [0,a].$$

Since $\Gamma_\eta \in \mathcal{C}([0,a])$, the last estimate implies (3.14). $\square$

Next, we define the operator $\Lambda_1 \colon \mathcal{C}([0,a]) \to W_2(0,a)$ which to $\eta \in \mathcal{C}([0,a])$ assigns the unique solution $c_\eta \in W_2(0,a)$ to Problem P_1^η. Moreover, we introduce the operator $\Lambda_2 \colon \mathcal{C}([0,a]) \times W_2(0,a) \to H^1(0,a)$ which to $\eta \in \mathcal{C}([0,a])$ and $c_\eta \in W_2(0,a)$ assigns the unique solution $\Gamma_\eta \in H^1(0,a)$ to Problem P_2^η. From Lemmata 3.1 and 3.2, it follows that the operators Λ_1 and Λ_2 are well defined. Now we define the operator $\Lambda \colon \mathcal{C}([0,a]) \to H^1(0,a) \subset \mathcal{C}([0,a])$ by

$$\Lambda(\eta) = \Lambda_2(\eta, \Lambda_1(\eta)) \quad \text{for} \quad \eta \in \mathcal{C}([0,a]). \tag{3.15}$$

We turn to investigate the properties of Λ. Given $r > 0$, we introduce the following notation

$$B_a(r) = \{\, u \in \mathcal{C}([0,a]);\, \|u\|_{\mathcal{C}([0,a])} \leq r \,\}$$

and two constants

$$T^* = \frac{1}{2C_{tr}^2}, \tag{3.16}$$

$$r^* = 2|\Gamma_0| + \sqrt{2}\|c_0\|_H, \tag{3.17}$$

where C_{tr} is the trace constant.

In the next step, we show that there exists a ball in $\mathcal{C}([0,T^*])$ which is invariant under the operator Λ.

Lemma 3.3 *For the operator Λ defined by (3.15), we have $\Lambda(B_{T^*}(r^*)) \subset B_{T^*}(r^*)$.*

Proof. It is enough to prove that if $\eta \in B_{T^*}(r^*)$, then $\Lambda(\eta) \in B_{T^*}(r^*)$. Let $\eta \in B_{T^*}(r^*)$, i.e. $\eta \in \mathcal{C}([0,T^*])$ and $\|\eta\|_{\mathcal{C}([0,T^*])} \le r^*$. From the estimates (3.11), (3.14) with $a = T^*$ and taking into account (3.16) and (3.17), we obtain

$$\begin{aligned}
\|\Gamma_\eta\|_{\mathcal{C}([0,T^*])} &\le |\Gamma_0| + \sqrt{T^*}\|\gamma_0(c_\eta)\|_{L^2(0,T^*)} \\
&\le |\Gamma_0| + \sqrt{T^*}(C_{tr}^2\sqrt{T^*}\|\eta\|_{\mathcal{C}([0,T^*])} + C_{tr}\|c_0\|_H) \\
&\le |\Gamma_0| + C_{tr}^2 T^*(2|\Gamma_0| + \sqrt{2}\,\|c_0\|_H) + C_{tr}\sqrt{T^*}\,\|c_0\|_H = r^*.
\end{aligned}$$

This means that $\|\Gamma_\eta\|_{\mathcal{C}([0,T^*])} \le r^*$, i.e. $\Lambda(\eta) \in B_{T^*}(r^*)$, which proves the lemma. □

The next two lemmata show that the operator Λ is compact.

Lemma 3.4 *The operator $\Lambda\colon B_{T^*}(r^*) \to B_{T^*}(r^*)$ is Lipschitz continuous with respect to the $\mathcal{C}([0,T^*])$- topology.*

Proof. We prove that Λ is Lipschitz continuous from $B_{T^*}(r^*)$ into itself. Indeed, for η_1, $\eta_2 \in B_{T^*}(r^*)$, let c_{η_1}, $c_{\eta_2} \in W_2(0,T^*)$ be the unique solutions to Problem P_1^η corresponding to η_1 and η_2, respectively. Moreover, let Γ_{η_1}, $\Gamma_{\eta_2} \in H^1(0,T^*)$ be the unique solutions to Problem P_2^η related to η_1, c_{η_1} and η_2, c_{η_2}, respectively. Thus we have

$$\langle \frac{\partial c_{\eta_1}}{\partial t}(t), v\rangle_{V'\times V} + ((c_{\eta_1}(t), v)) + \gamma_0(c_{\eta_1}(t))(1 - R(\eta_1(t)))\gamma_0(v) = \eta_1(t)\,\gamma_0(v),$$
$$\langle \frac{\partial c_{\eta_2}}{\partial t}(t), v\rangle_{V'\times V} + ((c_{\eta_2}(t), v)) + \gamma_0(c_{\eta_2}(t))(1 - R(\eta_2(t)))\gamma_0(v) = \eta_2(t)\,\gamma_0(v),$$
$$\text{for a.e. } t \in (0, T^*),\ \forall\, v \in V,$$
$$c_{\eta_1}(0) = c_{\eta_2}(0) = c_0.$$

Subtracting the above equations and taking $v = c_{\eta_1}(t) - c_{\eta_2}(t) \in V$, a.e. $t \in (0, T^*)$ as a test function, we get

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_{\eta_1}(t) - c_{\eta_2}(t)\|_H^2 + \|c_{\eta_1}(t) - c_{\eta_2}(t)\|_V^2 \\
&\qquad + \Big(\gamma_0(c_{\eta_1}(t))\big(1 - R(\eta_1(t))\big) - \gamma_0(c_{\eta_2}(t))\big(1 - R(\eta_2(t))\big)\Big)\,\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)) \\
&= (\eta_1(t) - \eta_2(t))\,\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)), \qquad \text{for a.e. } t \in (0, T^*).
\end{aligned}$$

Hence, adding and subtracting the term $\gamma_0(c_{\eta_1}(t))(1 - R(\eta_2(t)))\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t))$ in the left hand-side of the previous expression and taking into account the linearity of the trace operator, it follows that

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_{\eta_1}(t) - c_{\eta_2}(t)\|_H^2 + \|c_{\eta_1}(t) - c_{\eta_2}(t)\|_V^2 + (1 - R(\eta_2(t)))\,(\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)))^2 \\
&\quad = (\eta_1(t) - \eta_2(t))\,\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)) \\
&\qquad - \gamma_0(c_{\eta_1}(t))\big(R(\eta_2(t)) - R(\eta_1(t))\big)\,\gamma_0(c_{\eta_1}(t) - c_{\eta_2}(t)), \qquad \text{for a.e. } t \in (0, T^*).
\end{aligned}$$

Using the inequality $1 - R(\eta_2(t)) \geq 0$ and integrating the last equation from 0 to t, we have

$$\begin{aligned}
&\frac{1}{2}\|c_{\eta_1}(t) - c_{\eta_2}(t)\|_H^2 + \int_0^t \|c_{\eta_1}(s) - c_{\eta_2}(s)\|_V^2\, ds \\
&\qquad \leq \int_0^t |\eta_1(s) - \eta_2(s)||\gamma_0(c_{\eta_1}(s) - c_{\eta_2}(s))|\, ds \\
&\qquad\quad + \int_0^t |\gamma_0(c_{\eta_1}(s))|\,|R(\eta_2(s)) - R(\eta_1(s))|\,|\gamma_0(c_{\eta_1}(s) - c_{\eta_2}(s))|\, ds,
\end{aligned}$$

for all $t \in [0,T^*]$. Next, taking into account the trace inequality and the fact that the truncation operator R is 1-Lipschitz continuous, from the Cauchy inequality with positive ε, see expression (3.12), it follows

$$\frac{1}{C_{tr}^2}\int_0^t |\gamma_0(c_{\eta_1}(s)-c_{\eta_2}(s))|^2\,ds \le \frac{1}{2\varepsilon^2}\int_0^t |\eta_1(s)-\eta_2(s)|^2\,ds$$
$$+\varepsilon^2\int_0^t |\gamma_0(c_{\eta_1}(s)-c_{\eta_2}(s))|^2\,ds + \frac{1}{2\varepsilon^2}\int_0^t |\gamma_0(c_{\eta_1}(s))|^2\,|\eta_1(s)-\eta_2(s)|^2\,ds,$$

for all $t \in [0,T^*]$. Choosing $\varepsilon^2 = \dfrac{1}{2C_{tr}^2}$, we obtain

$$\frac{1}{2C_{tr}^2}\|\gamma_0(c_{\eta_1}-c_{\eta_2})\|^2_{L^2(0,t)} \le C_{tr}^2\,t\,\|\eta_1-\eta_2\|^2_{\mathcal{C}([0,t])} + C_{tr}^2\,\|\gamma_0(c_{\eta_1})\|^2_{L^2(0,t)}\,\|\eta_1-\eta_2\|^2_{\mathcal{C}([0,t])},$$

for all $t \in [0,T^*]$. Hence

$$\|\gamma_0(c_{\eta_1}-c_{\eta_2})\|^2_{L^2(0,T^*)} \le 2C_{tr}^4\,\|\eta_1-\eta_2\|^2_{\mathcal{C}([0,T^*])}\big(T^*+\|\gamma_0(c_{\eta_1})\|^2_{L^2(0,T^*)}\big). \tag{3.18}$$

Now, subtracting the two equations obtained from (3.13) for $\eta=\eta_1$, $c_\eta = c_{\eta_1}$ and for $\eta=\eta_2$, $c_\eta=c_{\eta_2}$, respectively, we find

$$\Gamma_{\eta_1}(t)-\Gamma_{\eta_2}(t) = e^{-t}\int_0^t \Big(\gamma_0(c_{\eta_1}(s))\big(1-R(\eta_1(s))\big)-\gamma_0(c_{\eta_2}(s))\big(1-R(\eta_2(s))\big)\Big)\,e^s\,ds,$$

for all $t\in[0,T^*]$. Adding and subtracting the term $\gamma_0(c_{\eta_1}(t))(1-R(\eta_2(t)))$ under the integral in the last equation, we get

$$|\Gamma_{\eta_1}(t)-\Gamma_{\eta_2}(t)| \le \int_0^t |\gamma_0(c_{\eta_1}(s))|\,|R(\eta_2(s))-R(\eta_1(s))|\,ds$$
$$+\int_0^t |\gamma_0(c_{\eta_1}(s)-c_{\eta_2}(s))|\,|1-R(\eta_2(s))|\,ds, \qquad \text{for all } t\in[0,T^*].$$

Exploiting the fact that $0\le R(\eta(\cdot))\le 1$ and, again, the property that R is 1-Lipschitz continuous, by the Hölder inequality we have

$$|\Gamma_{\eta_1}(t) - \Gamma_{\eta_2}(t)| \leq \sqrt{t}\,\|\gamma_0(c_{\eta_1} - c_{\eta_2})\|_{L^2(0,t)} + \sqrt{t}\,\|\gamma_0(c_{\eta_1})\|_{L^2(0,t)}\|\eta_1 - \eta_2\|_{\mathcal{C}([0,t])},$$

for all $t \in [0, T^*]$. Consequently

$$\begin{aligned} \|\Gamma_{\eta_1} - \Gamma_{\eta_2}\|_{\mathcal{C}([0,T^*])} \leq{} & \sqrt{T^*}\,\|\gamma_0(c_{\eta_1} - c_{\eta_2})\|_{L^2(0,T^*)} \\ & + \sqrt{T^*}\,\|\gamma_0(c_{\eta_1})\|_{L^2(0,T^*)}\|\eta_1 - \eta_2\|_{\mathcal{C}([0,T^*])}. \end{aligned} \tag{3.19}$$

Using (3.18) in (3.19), we arrive at the following estimate

$$\begin{aligned} \|\Gamma_{\eta_1} - \Gamma_{\eta_2}\|_{\mathcal{C}([0,T^*])} \leq{} & \sqrt{2T^*}\,C_{tr}^2\|\eta_1 - \eta_2\|_{\mathcal{C}([0,T^*])}\left(\sqrt{T^*} + \|\gamma_0(c_{\eta_1})\|_{L^2(0,T^*)}\right) \\ & + \sqrt{T^*}\,\|\gamma_0(c_{\eta_1})\|_{L^2(0,T^*)}\,\|\eta_1 - \eta_2\|_{\mathcal{C}([0,T^*])}. \end{aligned}$$

Finally, using the estimate (3.11), we deduce that there exists a constant $C > 0$ depending on T^*, r^* and on the problem data such that

$$\|\Gamma_{\eta_1} - \Gamma_{\eta_2}\|_{\mathcal{C}([0,T^*])} \leq C\|\eta_1 - \eta_2\|_{\mathcal{C}([0,T^*])}.$$

Hence, it follows that the operator Λ is Lipschitz continuous from $B_{T^*}(r^*)$ into itself.

□

Lemma 3.5 *The operator* $\Lambda\colon B_{T^*}(r^*) \to B_{T^*}(r^*)$ *is compact with respect to the* $\mathcal{C}([0,T^*])$-*topology.*

Proof. From Lemma 3.4 we know that Λ is continuous. In order to prove the compactness of the operator Λ, let B be a bounded subset of $B_{T^*}(r^*)$. We show that $\Lambda(B)$ is relatively compact in $\mathcal{C}([0,T^*])$. Indeed, it is clear from Lemma 3.3 that all functions from $\Lambda(B)$ are norm-bounded by r^*, thus $\Lambda(B)$ is equibounded. We prove that the set $\Lambda(B)$ is equicontinuous, that is, for every $\varepsilon > 0$ there exists $\bar{\delta} > 0$ such that for all t_1,

$t_2 \in [0,T^*]$ and for all $\Gamma \in \Lambda(B)$, we have

$$|t_1 - t_2| \leq \bar{\delta} \quad \Longrightarrow \quad |\Gamma(t_1) - \Gamma(t_2)| \leq \varepsilon. \tag{3.20}$$

Let us choose $\Gamma \in \Lambda(B)$ and t_1, $t_2 \in [0,T^*]$ such that $t_1 < t_2$. We obtain

$$\begin{aligned}\Gamma(t_2) - \Gamma(t_1) = \Gamma_0\, e^{-t_2} + \, e^{-t_2} \int_0^{t_2} \gamma_0(c_\eta(s))\big(1 - R(\eta(s))\big)\, e^s\, ds \\ -\Gamma_0\, e^{-t_1} - \, e^{-t_1} \int_0^{t_1} \gamma_0(c_\eta(s))\big(1 - R(\eta(s))\big) e^s\, ds.\end{aligned}$$

Therefore, we have

$$\begin{aligned}|\Gamma(t_2) - \Gamma(t_1)| \leq |\Gamma_0|\, |e^{-t_2} - e^{-t_1}| + |e^{-t_2} - e^{-t_1}| \int_0^{t_1} |\gamma_0(c_\eta(s))|\, |1 - R(\eta(s))|\, e^s\, ds \\ + e^{-t_2} \int_{t_1}^{t_2} |\gamma_0(c_\eta(s))|\, |1 - R(\eta(s))|\, e^s\, ds.\end{aligned}$$

Using the mean value theorem, the Hölder inequality and the fact that $|1-R(\eta(\cdot))| \leq 1$, we get

$$\begin{aligned}|\Gamma(t_2) - \Gamma(t_1)| &\leq |\Gamma_0|\, |t_2 - t_1| + \, e^{t_1}|t_2 - t_1| \int_0^{t_1} |\gamma_0(c_\eta(s))|\, ds + \int_{t_1}^{t_2} |\gamma_0(c_\eta(s))|\, ds \\ &\leq |\Gamma_0|\, |t_2 - t_1| + e^{T^*}\, |t_2 - t_1|\, \sqrt{T^*}\, \|\gamma_0(c_\eta)\|_{L^2(0,T^*)} + \sqrt{t_2 - t_1}\, \|\gamma_0(c_\eta)\|_{L^2(0,T^*)}.\end{aligned}$$

By the estimate (3.11), we have

$$|\Gamma(t_2) - \Gamma(t_1)| \leq C_1\, |t_2 - t_1| + C_2 \sqrt{t_2 - t_1},$$

where the positive constants C_1, C_2 depend only on T^*, r^*, $|\Gamma_0|$, $\|c_0\|_H$ and C_{tr}. We conclude that if we choose $\bar{\delta} = \frac{\varepsilon^2}{(C_2 + \sqrt{\varepsilon C_1})^2}$, then (3.20) is obtained. Since the choice of $\bar{\delta}$ is independent of Γ, we deduce that the set $\Lambda(B)$ is equicontinuous. It follows now from the Arzelá-Ascoli theorem (see Theorem 1.6.16 of [12]) that the set $\Lambda(B)$ is relatively compact in $\mathcal{C}([0,T^*])$, which completes the proof of the lemma. $\square$

Proof of Theorem 3.1. We choose T^* and r^* as in (3.16) and (3.17), respectively. It is straightforward to show that $B_{T^*}(r^*)$ is a nonempty, closed, bounded and convex set in the Banach space $\mathcal{C}([0,T^*])$. Besides, the choice of T^* and r^* guarantees, by Lemma 3.3, that $\Lambda(B_{T^*}(r^*)) \subset B_{T^*}(r^*)$. Moreover, it follows from Lemmata 3.4 and 3.5 that the operator Λ defined by (3.15) is a compact operator. Therefore, by exploiting the Schauder fixed-point theorem (see Theorem 2.A in [47]), we deduce that Λ has a fixed point, i.e. there exists an element $\eta^* \in B_{T^*}(r^*)$ such that $\Lambda(\eta^*) = \eta^*$. Let $c_{\eta^*} \in W_2(0,T^*)$ and $\Gamma_{\eta^*} \in H^1(0,T^*)$ denote the solutions to Problems P_1^η and P_2^η, respectively, with the choice $\eta = \eta^*$. It follows now that $\eta^* = \Gamma_{\eta^*}$. Thus, we conclude that $(c_{\eta^*}, \Gamma_{\eta^*}) \in W_2(0,T^*) \times H^1(0,T^*)$ is a solution to Problem P_R^{LH} on the time interval $(0,T^*)$.

If $T^* \geq T$, then the proof is complete. Otherwise, we continue the proof and we repeat the argument above to extend the solution to the time interval $(T^*, 2T^*)$, see Section 9.2 of [17]. Continuing, after finitely many steps, we construct the solution on the whole interval $(0,T)$.

We are now keen to prove the uniqueness of solution to Problem P_R^{LH}. Let (c_1, Γ_1), $(c_2, \Gamma_2) \in W_2(0,T) \times H^1(0,T)$ be two solutions to Problem P_R^{LH}. We subtract the two equations obtained from Problem P_R^{LH} for $c = c_1$, $\Gamma = \Gamma_1$ and $c = c_2$, $\Gamma = \Gamma_2$, respectively, and take $v = c_1(t) - c_2(t) \in V$ a.e. $t \in (0,T)$ as a test function. We have

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_1(t) - c_2(t)\|_H^2 + \|c_1(t) - c_2(t)\|_V^2 \\
&\qquad + \Big(\gamma_0(c_1(t))\big(1 - R(\Gamma_1(t))\big) - \gamma_0(c_2(t))\big(1 - R(\Gamma_2(t))\big)\Big)\,\gamma_0(c_1(t) - c_2(t)) \\
&\quad = (\Gamma_1(t) - \Gamma_2(t))\,\gamma_0(c_1(t) - c_2(t)), \qquad \text{for a.e. } t \in (0,T).
\end{aligned}$$

Adding and subtracting the term $\gamma_0(c_1(t))(1 - R(\Gamma_2(t)))\gamma_0(c_1(t) - c_2(t))$, considering the linearity of the trace operator, the fact that R is 1-Lipschitz and using the Cauchy inequality with ε, (3.12), we obtain

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_1(t)-c_2(t)\|_H^2+\|c_1(t)-c_2(t)\|_V^2+(1-R(\Gamma_2(t)))(\gamma_0(c_1(t)-c_2(t)))^2\\
&\quad=(\Gamma_1(t)-\Gamma_2(t))\,\gamma_0(c_1(t)-c_2(t))+\gamma_0(c_1(t))\big(R(\Gamma_1(t))-R(\Gamma_2(t))\big)\,\gamma_0(c_1(t)-c_2(t))\\
&\quad\le(1+|\gamma_0(c_1(t))|)\,|\Gamma_1(t)-\Gamma_2(t)|\,|\gamma_0(c_1(t)-c_2(t))|\\
&\quad\le\frac{\varepsilon^2}{2}\,(\gamma_0(c_1(t)-c_2(t)))^2+\frac{1}{2\varepsilon^2}\,(1+|\gamma_0(c_1(t))|)^2\,(\Gamma_1(t)-\Gamma_2(t))^2,\quad\text{for a.e. } t\in(0,T).
\end{aligned}$$

Since $0\le 1-R(\Gamma_2(t))$ for all $t\in[0,T]$, we estimate the third term of the left hand-side of the previous inequality by below by zero. Taking into account the trace inequality, using the inequality (1.31) with $\wp=2$, and choosing $\varepsilon^2=1/C_{tr}^2$, we have

$$\begin{aligned}
&\frac{1}{2}\frac{d}{dt}\|c_1(t)-c_2(t)\|_H^2+\frac{1}{2C_{tr}^2}\,(\gamma_0(c_1(t)-c_2(t)))^2\\
&\qquad\le C_{tr}^2\,\big(1+(\gamma_0(c_1(t)))^2\big)\,(\Gamma_1(t)-\Gamma_2(t))^2,\qquad\text{for a.e. } t\in(0,T).
\end{aligned}\tag{3.21}$$

Integrating the ordinary differential equation in Problem P_R^{LH}, from

$$\frac{d\,\Gamma}{dt}(t)=\gamma_0(c(t))(1-R(\Gamma(t)))-\Gamma(t),\qquad\text{for a.e.} t\in(0,T),$$

we have

$$\Gamma(t)=\Gamma_0\,e^{-t}+e^{-t}\int_0^t\gamma_0(c(s))\,\big(1-R(\Gamma(s))\big)\,e^s\,ds,\qquad\text{for all } t\in[0,T].\tag{3.22}$$

We subtract the two equations obtained from (3.22) for $c=c_1$, $\Gamma=\Gamma_1$ and $c=c_2$, $\Gamma=\Gamma_2$, respectively, to get

$$\Gamma_1(t)-\Gamma_2(t)=e^{-t}\int_0^t\Big(\gamma_0(c_1(s))\big(1-R(\Gamma_1(s))\big)-\gamma_0(c_2(s))\big(1-R(\Gamma_2(s))\big)\Big)\,e^s\,ds,$$

for all $t\in[0,T]$. Adding and subtracting the term $\gamma_0(c_1(t))(1-R(\Gamma_2(t)))$ under the integral sign in the previous equality, considering that R is 1-Lipschitz, using the fact that $t \mapsto e^t$ is an increasing function and using the Hölder inequality, it follows that

$$
\begin{aligned}
|\Gamma_1(t) - \Gamma_2(t)| \leq & \int_0^t |\gamma_0(c_1(s))| \, |\Gamma_1(s) - \Gamma_2(s)| \, ds \\
& + \int_0^t |1 - R(\Gamma_2(s))| \, |\gamma_0(c_1(s) - c_2(s))| \, ds \\
\leq & \int_0^t |\gamma_0(c_1(s))| \, |\Gamma_1(s) - \Gamma_2(s)| \, ds + \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)}, \quad \text{for all } t \in [0,T].
\end{aligned}
$$

Hence, using the Gronwall inequality (see Proposition 1.7.85 in [13]), we obtain

$$
\begin{aligned}
|\Gamma_1(t) - \Gamma_2(t)| \leq & \sqrt{t} \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} \\
& + \int_0^t e^{\int_s^t |\gamma_0 c_1(\tau)| d\tau} |\gamma_0(c_1(s))| \, \sqrt{s} \|\gamma_0(c_1 - c_2)\|_{L^2(0,s)} ds, \quad \text{for all } t \in [0,T],
\end{aligned}
$$

and since the function $t \to \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)}$ is nondecreasing, we get

$$
|\Gamma_1(t) - \Gamma_2(t)| \leq \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} \left(1 + \int_0^t e^{\int_s^t |\gamma_0 c_1(\tau)| d\tau} |\gamma_0(c_1(s))| ds \right),
$$

for all $t \in [0,T]$. Now, we note that, for t fixed, it holds that

$$
\frac{d}{ds} \left(e^{\int_s^t |\gamma_0(c_1(\tau))| d\tau} \right) = e^{\int_s^t |\gamma_0(c_1(\tau))| d\tau} (-|\gamma_0(c_1(s))|),
$$

and therefore, from the previous expression we have

$$
\begin{aligned}
|\Gamma_1(t) - \Gamma_2(t)| \ \leq \ & \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} \left(1 + \int_0^t \frac{d}{ds} \Big(- e^{\int_s^t |\gamma_0(c_1(\tau))| d\tau} \Big) ds \right) \\
\leq \ & \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} \left(1 + (-e^0 + e^{\int_0^t |\gamma_0(c_1(\tau))| d\tau}) \right) \\
= \ & \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} e^{\int_0^t |\gamma_0(c_1(\tau))| d\tau}, \qquad \text{for all } t \in [0,T].
\end{aligned}
$$

Then, applying the Hölder inequality, it follows that

$$
|\Gamma_1(t) - \Gamma_2(t)| \leq \sqrt{t} \, \|\gamma_0(c_1 - c_2)\|_{L^2(0,t)} \, e^{\sqrt{t} \, \|\gamma_0(c_1)\|_{L^2(0,t)}}, \tag{3.23}
$$

for all $t \in [0,T]$. Using this estimate in (3.21) and integrating from 0 to t, we get

$$\frac{1}{2}\|c_1(t)-c_2(t)\|_H^2 + \frac{1}{2C_{tr}^2}\int_0^t (\gamma_0(c_1(s)-c_2(s)))^2\,ds$$
$$\leq C_{tr}^2 \int_0^t s\left(1+(\gamma_0(c_1(s)))^2\right)e^{2\sqrt{s}\,\|\gamma_0(c_1)\|_{L^2(0,s)}}\,\|\gamma_0(c_1-c_2)\|_{L^2(0,s)}^2\,ds, \quad (3.24)$$

for all $t \in [0,T]$. From the latter, denoting $\xi(t) = \displaystyle\int_0^t (\gamma_0(c_1(s)-c_2(s)))^2\,ds$, we have

$$\xi(t) \leq 2C_{tr}^4 \int_0^t s\left(1+(\gamma_0(c_1(s)))^2\right)e^{2\sqrt{s}\,\|\gamma_0(c_1)\|_{L^2(0,s)}}\xi(s)\,ds, \qquad \text{for all } t\in[0,T].$$

From the Gronwall inequality, we find that $\xi(t) = 0$ for all $t \in [0,T]$. Subsequently, using (3.24), we obtain $c_1(t) = c_2(t)$ for a.e. $t \in (0,T)$ and from (3.23) it follows that $\Gamma_1(t) = \Gamma_2(t)$ for all $t \in [0,T]$. The proof of the theorem is now complete. □

3.1.3 Existence and uniqueness results for Problem P_W^{LH}

In this section we investigate the relation between Problems P_R^{LH} and P_W^{LH} and we study the uniqueness of solution to Problem P_W^{LH}. The next lemma provides an existence result for Problem P_W^{LH} under the assumption that $\gamma_0(c(t))$ is nonnegative for a.e. $t \in (0,T)$. Let us define the set

$$W_2^+(0,T) = \{\, c \in W_2(0,T); \gamma_0(c(t)) \geq 0 \text{ for a.e. } t \in (0,T)\,\}.$$

Lemma 3.6 *Assume that $\sigma = 0$ in the definition (3.9) of the truncation operator and assume that the initial condition $\Gamma_0 \in [0,\Gamma_m]$. If $(c,\Gamma) \in W_2^+(0,T)\times H^1(0,T)$ is a solution to Problem P_R^{LH}, then $\Gamma(t) \in [0,\Gamma_m]$ for all $t \in [0,T]$, and, in consequence, (c,Γ) is a solution to Problem P_W^{LH}.*

Proof. Let $\sigma = 0$, $\Gamma_0 \in [0,\Gamma_m]$ and let $(c,\Gamma) \in W_2^+(0,T)\times H^1(0,T)$ be a solution to Problem P_R^{LH}. Then, obviously, $\Gamma \in H^1(0,T) \subset \mathcal{C}([0,T])$. We will show that $\Gamma(t) \leq \Gamma_m$ for all $t \in [0,T]$. Suppose not, that is, that there exists $t^* \in [0,T]$ such that $\Gamma(t^*) > \Gamma_m$. Define $t^{**} = \max\{t \in [0,t^*] \mid \Gamma(t) = \Gamma_m\}$. Obviously, we obtain $0 \leq t^{**} < t^*$ and $\Gamma(t) > \Gamma_m$ for all $t \in (t^{**}, t^*)$. Thus, $R(\Gamma(t)) = \Gamma_m$ for all $t \in (t^{**}, t^*)$ and, from the ordinary differential equation of Problem P_R^{LH}, we have

$$\frac{d\,\Gamma}{dt}(t) = -k_L^d\,\Gamma(t), \qquad \text{for a.e. } t \in (t^{**}, t^*).$$

Integrating this expression from t^{**} to t, we obtain, for all $t \in [t^{**}, t^*]$

$$\Gamma(t) = \Gamma(t^{**})\, e^{k_L^d(t^{**}-t)} = \Gamma_m\, e^{k_L^d(t^{**}-t)}.$$

Hence $\Gamma(t^*) = \Gamma_m\, e^{k_L^d(t^{**}-t^*)} < \Gamma_m$ and we have obtained the contradiction.

In order to show that $\Gamma(t) \geq 0$ for all $t \in [0,T]$, assume that this is not the case, i.e. $\Gamma(t^*) < 0$ for some $t^* \in [0,T]$. We define $t^{**} = \max\{t \in [0,t^*] \mid \Gamma(t) = 0\}$. So, we have that $0 \leq t^{**} < t^*$ and $\Gamma(t) < 0$ for all $t \in (t^{**}, t^*)$. Consequently, taking into account (3.10), we obtain

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\,\gamma_0(c(t)) - k_L^d\,\Gamma(t).$$

Then, integrating from t^{**} to t, we have, for every $t \in [t^{**}, t^*]$,

$$\Gamma(t) = \Gamma(t^{**}) + \int_{t^{**}}^{t} \Gamma'(s)\,ds = \int_{t^{**}}^{t} \Big(k_L^a \gamma_0(c(s)) - k_L^d\,\Gamma(s)\Big)\,ds.$$

Since $\Gamma(t) < 0$ for all $t \in (t^{**}, t^*)$, the right hand side of the previous equality is positive. Consequently, the left hand side, $\Gamma(t)$, is positive too for every $t \in [t^{**}, t^*]$ and therefore, $\Gamma(t^*) > 0$, a contradiction. The proof of the lemma is complete. $\square$

Remark 3.1 *Note that, if in Lemma 3.6 we assume that $\gamma_0(c) \in L^\infty(0,T)$ and, instead of assuming that $\sigma = 0$, we suppose that*

$$\sigma \in \Big[0, \frac{k_L^d\,\Gamma_m}{k_L^d\,\Gamma_m + k_L^a \|\gamma_0(c)\|_{L^\infty(0,T)}}\Big),$$

and $\Gamma_0 \in [0, (1-\sigma)\Gamma_m]$, then we have that $\Gamma(t) \in [0, (1-\sigma)\Gamma_m]$ for all $t \in [0,T]$, and, consequently, the solution, (c,Γ), to Problem P_R^{LH} is also a solution to Problem P_W^{LH}.

Indeed, the fact that $\Gamma(t) \geq 0$ *for all* $t \in [0,T]$ *follows from the proof of Lemma 3.6. Moreover, proceeding as in that proof, it is easy to show that* $\Gamma(t) \leq (1-\sigma)\Gamma_m$ *for all* $t \in [0,T]$. *In fact, we suppose that there exists* $t^* \in [0,T]$ *such that* $\Gamma(t^*) > (1-\sigma)\Gamma_m$ *and we denote by* $t^{**} = \max\{t \in [0,t^*] \mid \Gamma(t) = (1-\sigma)\Gamma_m\}$. *Then,* $\Gamma(t) > (1-\sigma)\Gamma_m$ *for all* $t \in (t^{**}, t^*)$. *Then, using the ordinary differential equation of Problem* P_R^{LH}, *we obtain*

$$\frac{d\Gamma}{dt}(t) = k_L^a \gamma_0(c(t))\Big(1 - \frac{(1-\sigma)\Gamma_m}{\Gamma_m}\Big) - k_L^d \Gamma(t), \quad \textit{for a.e. } t \in (t^{**}, t^*).$$

Integrating from t^{**} *to* t, *we have*

$$\begin{aligned}
\Gamma(t) &= \Gamma(t^{**}) + \int_{t^{**}}^{t} \Big(\sigma\, k_L^a\, \gamma_0(c(s)) - k_L^d \Gamma(s)\Big) ds \\
&< (1-\sigma)\Gamma_m + \sigma\, k_L^a \|\gamma_0(c)\|_{L^\infty(0,T)}(t - t^{**}) - k_L^d (1-\sigma)\Gamma_m (t - t^{**}) \\
&< (1-\sigma)\Gamma_m, \qquad \textit{for all } t \in [t^{**}, t^*],
\end{aligned}$$

and then, we arrive to a contradiction.

In the following two lemmata we show that if $\gamma_0(c) \in L^\infty(0,T)$, then the similar properties as in Lemma 3.6 hold also for the solutions to Problem P_W^{LH}.

Lemma 3.7 *If* $(c,\Gamma) \in W_2^+(0,T) \times H^1(0,T)$ *solves Problem* P_W^{LH} *with* $\Gamma_0 \in [0,\Gamma_m]$ *and* $\gamma_0(c) \in L^\infty(0,T)$, *then* $\Gamma(t) \in [0,\Gamma_m]$ *for all* $t \in [0,T]$.

Proof. First, we show that $\Gamma(t) \leq \Gamma_m$ for all $t \in [0,T]$. Analogously to the proof of Lemma 3.6, we proceed by contradiction. Assume that $\Gamma(t^*) > \Gamma_m$ for some $t^* \in [0,T]$ and define $t^{**} = \max\{t \in [0,t^*] \mid \Gamma(t) = \Gamma_m\}$. We have $0 \leq t^{**} < t^*$. Obviously, for $t \in (t^{**}, t^*)$ it follows that $\Gamma(t) > \Gamma_m$. Moreover, for $t \in (t^{**}, t^*)$, we have

$$\begin{aligned}
\Gamma(t) &= \Gamma(t^{**}) + \int_{t^{**}}^{t} \frac{k_L^a}{\Gamma_m}\, \gamma_0(c(s))\, (\Gamma_m - \Gamma(s)) - k_L^d \Gamma(s)\, ds \\
&\leq \Gamma_m + \frac{k_L^a}{\Gamma_m} \|\gamma_0(c)\|_{L^\infty(0,T)} \int_{t^{**}}^{t} |\Gamma_m - \Gamma(s)|\, ds - k_L^d\, \Gamma_m (t - t^{**}).
\end{aligned}$$

If $\|\gamma_0 c\|_{L^\infty(0,T)} = 0$, then $\Gamma(t) \leq \Gamma_m$ for $t \in (t^{**}, t^*)$. Otherwise, we choose $\varepsilon = \frac{k_L^d\,\Gamma_m^2}{k_L^a\,\|\gamma_0(c)\|_{L^\infty(0,T)}}$. Since $\Gamma \in \mathcal{C}([0,T])$, there exists $\bar{\delta} > 0$ such that if $|t - t^{**}| \leq \bar{\delta}$, then $|\Gamma(t^{**}) - \Gamma(t)| \leq \varepsilon$. For $t \in (t^{**}, \min\{t^*, t^{**} + \bar{\delta}\})$, we have

$$\Gamma(t) \leq \Gamma_m + \frac{k_L^a}{\Gamma_m}\,\|\gamma_0(c)\|_{L^\infty(0,T)}\,(t - t^{**})\frac{k_L^d\,\Gamma_m^2}{k_L^a\,\|\gamma_0(c)\|_{L^\infty(0,T)}} - k_L^d\,\Gamma_m(t - t^{**}) = \Gamma_m.$$

So we obtain a contradiction. Next, we prove that $\Gamma(t) \geq 0$ for all $t \in [0,T]$. Suppose, by contradiction, that $\Gamma(t^*) < 0$ for some $t^* \in [0,T]$ and define $t^{**} = \max\{t \in [0,t^*] \mid \Gamma(t) = 0\}$. We have $0 \leq t^{**} < t^*$ and $\Gamma(t) < 0$ for all $t \in (t^{**}, t^*)$. Moreover, for all $t \in [t^{**}, t^*]$ we have

$$\Gamma(t) = \Gamma(t^{**}) + \int_{t^{**}}^{t} \frac{k_L^a}{\Gamma_m}\,\gamma_0(c(s))\,(\Gamma_m - \Gamma(s)) - k_L^d\,\Gamma(s)\,ds \geq 0,$$

which is a contradiction. The proof of the lemma is complete. □

Lemma 3.8 *Assume that $\sigma = 0$ in the definition (3.9) of the truncation operator and $\Gamma_0 \in [0, \Gamma_m]$. Let $(c_1, \Gamma_1) \in W_2^+(0,T) \times H^1(0,T)$ with $\gamma_0(c_1) \in L^\infty(0,T)$ and $(c_2, \Gamma_2) \in W_2^+(0,T) \times H^1(0,T)$ with $\gamma_0(c_2) \in L^\infty(0,T)$ be two solutions to Problem P_W^{LH}. Then $c_1(t) = c_2(t)$ and $\Gamma_1(t) = \Gamma_2(t)$ for a.e. $t \in (0,T)$.*

Proof. It follows from Lemma 3.7 that $\Gamma_1(t) \in [0, \Gamma_m]$ and $\Gamma_2(t) \in [0, \Gamma_m]$ for all $t \in [0,T]$. Hence, (c_1, Γ_1) and (c_2, Γ_2) are two solutions to Problem P_R^{LH}. Now, the conclusion is a consequence of Theorem 3.1 and the proof of the lemma is complete. □

3.1.4 Fully discrete approximation: a priori error estimate

In this section, we consider a fully discrete approximation of Problem P_R^{LH} which is done following the same two steps explained in Chapter 1. Moreover, we also use the same notation introduced there.

Without loss of generality, we suppose in this section that $D = k_L^d = k_L^a = \Gamma_m = 1$. Using a hybrid combination of both backward and forward Euler schemes, we consider the following fully discrete approximations of Problem P_R^{LH}.

Problem P_{LH}^{hk}. Find $c^{hk} = \{c_n^{hk}\}_{n=0}^N \subset V^h$ and $\Gamma^{hk} = \{\Gamma_n^{hk}\}_{n=0}^N \subset \mathbb{R}$ such that

$$c_0^{hk} = c_0^h, \quad \Gamma_0^{hk} = \Gamma_0, \tag{3.25}$$

and, for $n = 1, \dots, N$ and for all $v^h \in V^h$, it holds

$$(\delta c_n^{hk}, v^h)_H + ((c_n^{hk}, v^h)) + f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\,\gamma_0(v^h) = \Gamma_{n-1}^{hk}\,\gamma_0(v^h), \tag{3.26}$$

$$\delta\Gamma_n^{hk} = f(\gamma_0(c_n^{hk}), R(\Gamma_n^{hk})) - \Gamma_n^{hk}, \tag{3.27}$$

where $c_0^h \in V^h$ is an appropriate approximation of the initial condition c_0.

Under the assumptions of Theorem 3.1, using the Lax-Milgram lemma, we easily deduce the existence of a unique discrete solution to Problem P_{LH}^{hk}.

In the sequel, we derive an error estimate for the differences $c_n - c_n^{hk}$ and $\Gamma_n - \Gamma_n^{hk}$. Under the following additional regularity of the solution to Problem P_R^{LH}

$$c \in \mathcal{C}([0,T];V) \cap \mathcal{C}^1([0,T];H) \ \text{ and } \ \Gamma \in \mathcal{C}^1([0,T]), \tag{3.28}$$

we get the result presented below. We note that assuming regularity (3.28), we have $\gamma_0(c) \in \mathcal{C}([0,T])$.

Theorem 3.2 *Assume the hypotheses of Theorem 3.1 and the regularity conditions (3.28) hold. Then there exists a positive constant C, independent of the discretization parameters h and k, such that the following error estimate is satisfied, for all $\{v_n^h\}_{n=1}^N \subset V^h$,*

$$\begin{aligned}
&\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H^2 + k \sum_{n=1}^N \Big(\|c_n - c_n^{hk}\|_V^2 + \sigma(\gamma_0(c_n - c_n^{hk}))^2 \Big) + \max_{0\le n\le N} |\Gamma_n - \Gamma_n^{hk}|^2 \\
&\qquad \le C\,\|c_0 - c_0^h\|_H^2 + C\,k \sum_{n=1}^N \Big(\|c_n - v_n^h\|_V^2 + k^2 + \Big\| \frac{\partial c}{\partial t}(t_n) - \delta c_n \Big\|_H^2 \Big) + \max_{0\le n\le N} I_n^2 \\
&\qquad\quad + C \max_{0\le n\le N} \|c_n - v_n^h\|_H^2 + C \sum_{n=1}^{N-1} \frac{1}{k} \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2,
\end{aligned} \tag{3.29}$$

where I_n denotes the integration error given by

$$I_n = \left| \int_0^{t_n} f(\gamma_0(c(s)), R(\Gamma(s))) - \Gamma(s)\, ds - k \sum_{j=1}^{n} [f(\gamma_0(c_j), R(\Gamma_j)) - \Gamma_j] \right|. \tag{3.30}$$

Proof. Taking $v = c_n - v^h \in V$ in the parabolic equation in Problem P_R^{LH} at time $t = t_n$, we find that

$$\begin{aligned} \left(\frac{\partial c}{\partial t}(t_n), c_n - v^h\right)_H + ((c_n, c_n - v^h)) + f(\gamma_0(c_n), R(\Gamma_n))\gamma_0(c_n - v^h) \\ = \Gamma_n \gamma_0(c_n - v^h), \end{aligned} \tag{3.31}$$

for $n = 1, 2, \ldots, N$, and using equation (3.26) we have, for all $v^h \in V^h$,

$$\begin{aligned} &(\delta c_n^{hk}, c_n - c_n^{hk})_H + ((c_n^{hk}, c_n - c_n^{hk})) + f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\, \gamma_0(c_n - c_n^{hk}) \\ &\quad = (\delta c_n^{hk}, c_n - v^h)_H + ((c_n^{hk}, c_n - v^h)) + \Gamma_{n-1}^{hk}\, \gamma_0(c_n - c_n^{hk}) \\ &\qquad - \Gamma_{n-1}^{hk}\, \gamma_0(c_n - v^h) + f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\, \gamma_0(c_n - v^h). \end{aligned} \tag{3.32}$$

From (3.31) and (3.32), we obtain, for all $v^h \in V^h$,

$$\begin{aligned} &\left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - c_n^{hk}\right)_H + \|c_n - c_n^{hk}\|_V^2 \\ &\qquad + \left(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\right)\, \gamma_0(c_n - c_n^{hk}) \\ &\quad = \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n^{hk}, c_n - v^h\right)_H + ((c_n - c_n^{hk}, c_n - v^h)) \\ &\qquad + (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - c_n^{hk}) - (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - v^h) \\ &\qquad + \left(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\right)\, \gamma_0(c_n - v^h), \end{aligned}$$

and therefore, for all $v^h \in V^h$,

$$\begin{aligned} &(\delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H + \|c_n - c_n^{hk}\|_V^2 \\ &\qquad + \left(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\right)\, \gamma_0(c_n - c_n^{hk}) \end{aligned}$$

$$
\begin{aligned}
&= (\delta c_n - \delta c_n^{hk}, c_n - v^h)_H + ((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad + (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - c_n^{hk}) - (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - v^h) \\
&\qquad - \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n, c_n - c_n^{hk} \right)_H + \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n, c_n - v^h \right)_H \\
&\qquad + \big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk})) \big)\ \gamma_0(c_n - v^h),
\end{aligned}
$$

where we recall that $\delta c_n = (c_n - c_{n-1})/k$.

Moreover, reminding the following property of the divided differences

$$
(\delta a_n - \delta b_n, a_n - b_n)_H \geq \frac{1}{2k} \|a_n - b_n\|_H^2 - \frac{1}{2k} \|a_{n-1} - b_{n-1}\|_H^2,
$$

the previous equation reads

$$
\begin{aligned}
&\frac{1}{2k} \|c_n - c_n^{hk}\|_H^2 + \|c_n - c_n^{hk}\|_V^2 \\
&\qquad\qquad + \big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk})) \big)\, \gamma_0(c_n - c_n^{hk}) \\
&\quad \leq \frac{1}{2k} \|c_{n-1} - c_{n-1}^{hk}\|_H^2 + (\delta c_n - \delta c_n^{hk}, c_n - v^h)_H + ((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad\qquad + (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - c_n^{hk}) - (\Gamma_n - \Gamma_{n-1}^{hk})\, \gamma_0(c_n - v^h) \\
&\qquad\qquad - \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n, c_n - c_n^{hk} \right)_H + \left(\frac{\partial c}{\partial t}(t_n) - \delta c_n, c_n - v^h \right)_H \\
&\qquad\qquad + \big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk})) \big)\ \gamma_0(c_n - v^h),
\end{aligned}
$$

for all $v^h \in V^h$. Now, using the equality

$$
\begin{aligned}
&\big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk})) \big)\ \gamma_0(v) \\
&\qquad = \big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n), R(\Gamma_{n-1}^{hk})) \big)\ \gamma_0(v) \\
&\qquad\qquad + \big(f(\gamma_0(c_n), R(\Gamma_{n-1}^{hk})) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk})) \big)\ \gamma_0(v), \quad \text{for all } v \in V,
\end{aligned}
$$

and taking into account the following estimates

$$\big(f(\gamma_0(c_n), R(\Gamma_{n-1}^{hk})) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\big)\ \gamma_0(c_n - c_n^{hk}) \geq \sigma(\gamma_0(c_n - c_n^{hk}))^2,$$

$$\big(f(\gamma_0(c_n), R(\Gamma_n)) - f(\gamma_0(c_n), R(\Gamma_{n-1}^{hk}))\big)\ \gamma_0(v) \leq |\gamma_0(c_n)|\,|\Gamma_n - \Gamma_{n-1}^{hk}|\,|\gamma_0(v)|,$$

$$\begin{aligned}&\big(f(\gamma_0(c_n), R(\Gamma_{n-1}^{hk})) - f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\big)\ \gamma_0(c_n - v^h)\\ &\qquad\qquad \leq |\gamma_0(c_n - c_n^{hk})|\,|\gamma_0(c_n - v^h)|,\end{aligned}$$

for all $v \in V$, it follows that

$$\begin{aligned}&\frac{1}{2k}\,\|c_n - c_n^{hk}\|_H^2 + \|c_n - c_n^{hk}\|_V^2 + \sigma(\gamma_0(c_n - c_n^{hk}))^2\\
&\quad \leq \frac{1}{2k}\,\|c_{n-1} - c_{n-1}^{hk}\|_H^2 + (\delta c_n - \delta c_n^{hk}, c_n - v^h)_H + \|c_n - c_n^{hk}\|_V\,\|c_n - v^h\|_V\\
&\qquad + |\Gamma_n - \Gamma_{n-1}^{hk}|\,|\gamma_0(c_n - c_n^{hk})| + |\Gamma_n - \Gamma_{n-1}^{hk}|\,|\gamma_0(c_n - v^h)|\\
&\qquad + \Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H \|c_n - c_n^{hk}\|_H + \Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H \|c_n - v^h\|_H\\
&\qquad + |\gamma_0(c_n - c_n^{hk})|\,|\gamma_0(c_n - v^h)| + |\gamma_0(c_n)|\,|\Gamma_n - \Gamma_{n-1}^{hk}|\,|\gamma_0(c_n - c_n^{hk})|\\
&\qquad + |\gamma_0(c_n)|\,|\Gamma_n - \Gamma_{n-1}^{hk}|\,|\gamma_0(c_n - v^h)|, \qquad\qquad \text{for all } v^h \in V^h.\end{aligned}$$

Using now the Cauchy inequality with a small parameter and the property (1.31) with $\wp = 2$, considering the regularity condition (3.28) and the fact that $\|\cdot\|_{H^1(0,l)}$ and $\|\cdot\|_V$ are equivalent norms in V and keeping in mind that

$$|\Gamma_n - \Gamma_{n-1}^{hk}| \leq |\Gamma_n - \Gamma_{n-1}| + |\Gamma_{n-1} - \Gamma_{n-1}^{hk}| \leq C\,k\,\|\Gamma\|_{\mathcal{C}^1([0,T])} + |\Gamma_{n-1} - \Gamma_{n-1}^{hk}|, \quad (3.33)$$

we find

$$\begin{aligned}&\frac{1}{2k}\,\|c_n - c_n^{hk}\|_H^2 + \alpha\,\|c_n - c_n^{hk}\|_V^2 + \alpha\,\sigma\,(\gamma_0(c_n - c_n^{hk}))^2\\
&\quad \leq \frac{1}{2k}\,\|c_{n-1} - c_{n-1}^{hk}\|_H^2 + C\,\Big((\delta c_n - \delta c_n^{hk}, c_n - v^h)_H + \|c_n - v^h\|_V^2\\
&\qquad + |\Gamma_{n-1} - \Gamma_{n-1}^{hk}|^2 + |\gamma_0(c_n - v^h)|^2 + \Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 + \|c_n - c_n^{hk}\|_H^2 + k^2\Big),\end{aligned}$$

for all $v^h \in V^h$, where the positive constants α and C, which are small and large enough, respectively, are independent of the discretization parameters h and k. Thus, from the previous estimate, by an induction argument with respect to n, we obtain

$$\|c_n - c_n^{hk}\|_H^2 + \alpha\, k \sum_{j=1}^{n} \|c_j - c_j^{hk}\|_V^2 + \alpha\, k\, \sigma \sum_{j=1}^{n} (\gamma_0(c_j - c_j^{hk}))^2$$
$$\leq \|c_0 - c_0^h\|_H^2 + C\, k \sum_{j=1}^{n} \Big((\delta c_j - \delta c_j^{hk}, c_j - v_j^h)_H + \|c_j - v_j^h\|_V^2 + |\Gamma_{j-1} - \Gamma_{j-1}^{hk}|^2$$
$$+ |\gamma_0(c_j - v_j^h)|^2 + \Big\| \frac{\partial c}{\partial t}(t_j) - \delta c_j \Big\|_H^2 + \|c_j - c_j^{hk}\|_H^2 + k^2 \Big), \tag{3.34}$$

for all $\{v_j^h\}_{j=1}^N \subset V^h$. Now, we turn to obtain some estimates on the numerical errors for the surface concentration. We integrate the ordinary differential equation in Problem P_R^{LH} and we get

$$\Gamma_n = \Gamma_0 + \int_0^{t_n} \Big(f(\gamma_0(c(s)), R(\Gamma(s))) - \Gamma(s) \Big)\, ds.$$

From (3.27) and using (3.25), we have

$$\Gamma_n^{hk} = \Gamma_{n-1}^{hk} + k\, f(\gamma_0(c_n^{hk}), R(\Gamma_n^{hk})) - k\, \Gamma_n^{hk} = \Gamma_0 + k \sum_{j=1}^{n} \Big(f(\gamma_0(c_j^{hk}), R(\Gamma_j^{hk})) - \Gamma_j^{hk} \Big).$$

Using the last two equations, we find that

$$|\Gamma_n - \Gamma_n^{hk}| \leq I_n + k \sum_{j=1}^{n} \Big[|f(\gamma_0(c_j), R(\Gamma_j)) - f(\gamma_0(c_j^{hk}), R(\Gamma_j^{hk}))| + |\Gamma_j - \Gamma_j^{hk}| \Big], \tag{3.35}$$

where we recall that the integration error I_n is defined by expression (3.30).

Considering the relation

$$|f(\gamma_0(c_j), R(\Gamma_j)) - f(\gamma_0(c_j^{hk}), R(\Gamma_j^{hk}))| \leq |f(\gamma_0(c_j), R(\Gamma_j)) - f(\gamma_0(c_j), R(\Gamma_j^{hk}))|$$
$$+ |f(\gamma_0(c_j), R(\Gamma_j^{hk})) - f(\gamma_0(c_j^{hk}), R(\Gamma_j^{hk}))| \leq |\gamma_0(c_j)|\, |\Gamma_j - \Gamma_j^{hk}| + |\gamma_0(c_j - c_j^{hk})|,$$

where the fact that the operator R is 1-Lipschitz continuous and the inequality $1 - R(\cdot) \leq 1$ have been used; and applying several times inequality (1.31) with $\wp = 2$, taking into account the regularity $c \in \mathcal{C}([0,T];V)$ and Cauchy-Schwarz inequality and recalling that $k\,N = T$, from expression (3.35), we find that

$$|\Gamma_n - \Gamma_n^{hk}|^2 \leq C\,I_n^2 + C\,k\sum_{j=1}^{n}|\Gamma_j - \Gamma_j^{hk}|^2 + C\,k\sum_{j=1}^{n}|\gamma_0(c_j - c_j^{hk})|^2. \tag{3.36}$$

Moreover, keeping in mind that

$$\begin{aligned}
k\sum_{j=1}^{n}(\delta c_j - \delta c_j^{hk}, c_j - v_j^h)_H &= (c_n - c_n^{hk}, c_n - v_n^h) + (c_0^h - c_0, c_1 - v_1^h)\\
&\quad + \sum_{j=1}^{n-1}(c_j - c_j^{hk}, c_j - v_j^h - (c_{j+1} - v_{j+1}^h))_H\\
&\leq \frac{1}{2}\|c_0 - c_0^h\|_H^2 + \frac{1}{2}\|c_1 - v_1^h\|_H^2 + \frac{1}{2}\|c_n - c_n^{hk}\|_H^2 + \frac{1}{2}\|c_n - v_n^h\|_H^2\\
&\quad + \sum_{j=1}^{n-1}\left(k\,\|c_j - c_j^{hk}\|_H^2 + \frac{1}{4k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2\right),
\end{aligned}$$

combining the estimates (3.34) and (3.35), and using (3.36) and the initial condition $\Gamma_0 = \Gamma_0^{hk}$, we have

$$\begin{aligned}
&\|c_n - c_n^{hk}\|_H^2 + \alpha\,k\sum_{j=1}^{n}\|c_j - c_j^{hk}\|_V^2 + \alpha\,k\,\sigma\sum_{j=1}^{n}(\gamma_0(c_j - c_j^{hk}))^2 + |\Gamma_n - \Gamma_n^{hk}|^2\\
&\quad \leq C\,\|c_0 - c_0^h\|_H^2 + C\,k\sum_{j=1}^{n}\Big(\|c_j - v_j^h\|_V^2 + k^2 + |\Gamma_j - \Gamma_j^{hk}|^2\\
&\qquad + |\gamma_0(c_j - v_j^h)|^2 + \left\|\frac{\partial c}{\partial t}(t_j) - \delta c_j\right\|_H^2 + \|c_j - c_j^{hk}\|_H^2\Big) + C\,I_n^2 + C\,\|c_1 - v_1^h\|_H^2\\
&\qquad + C\,\|c_n - v_n^h\|_H^2 + C\sum_{j=1}^{n-1}\frac{1}{k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2.
\end{aligned}$$

Using now the notation

$$\widetilde{a}_n := \|c_n - c_n^{hk}\|_H^2 + \alpha\, k \sum_{j=1}^{n} \|c_j - c_j^{hk}\|_V^2 + \alpha\, k\, \sigma \sum_{j=1}^{n} (\gamma_0(c_j - c_j^{hk}))^2 + |\Gamma_n - \Gamma_n^{hk}|^2,$$

where $\widetilde{a}_0 = \|c_0 - c_0^h\|_H^2$ and considering the trace inequality, see (1.9), we find that

$$\widetilde{a}_n \leq C\, \widetilde{a}_0 + C\, k \sum_{j=1}^{n} \widetilde{a}_j + C\, k \sum_{j=1}^{n} \left(\|c_j - v_j^h\|_V^2 + k^2 + \left\| \frac{\partial c}{\partial t}(t_j) - \delta c_j \right\|_H^2 \right) + C\, I_n^2$$
$$+ C\, \|c_1 - v_1^h\|_H^2 + C\, \|c_n - v_n^h\|_H^2 + C \sum_{j=1}^{n-1} \frac{1}{k} \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2.$$

Denoting by

$$\widetilde{g}_n := \widetilde{a}_0 + k \sum_{j=1}^{n} \left(\|c_j - v_j^h\|_V^2 + k^2 + \left\| \frac{\partial c}{\partial t}(t_j) - \delta c_j \right\| \right) + I_n^2$$
$$+ \|c_1 - v_1^h\|_H^2 + \|c_n - v_n^h\|_H^2 + \sum_{j=1}^{n-1} \frac{1}{k} \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2,$$

we can conclude that

$$\widetilde{a}_n \leq C\, \widetilde{g}_n + C\, k \sum_{j=1}^{n} \widetilde{a}_j.$$

Finally, applying a discrete version of the Gronwall inequality, like in Section 1.4 of Chapter 1 (see, for instance, [4]), the result is achieved. □

Estimate (3.29) is the basis for the convergence analysis. As an example, we state the following corollary under the assumption that the finite element space V^h is given by (1.41) and under further regularity conditions on the solution to the continuous problem:

$$c \in \mathcal{C}([0,T]; H^2(0,l)) \cap H^1(0,T;V) \cap H^2(0,T;H). \tag{3.37}$$

Corollary 3.1 *Assume the hypotheses of Theorem 3.2 and the regularity condition (3.37) hold. Then, the convergence of the algorithm in Problem P_{LH}^{hk} is linear, i.e.*

there exists a constant $\beta > 0$, independent of h and k, such that

$$\max_{0\leq n\leq N} \|c_n - c_n^{hk}\|_H + \max_{0\leq n\leq N} |\Gamma_n - \Gamma_n^{hk}| \leq \beta\,(h+k).$$

Proof. Let $\pi^h : \mathcal{C}([0,l]) \to V^h$ denote the standard finite element projection operator, and let us take $v_j^h = \pi^h c_j$ for $j = 1,\dots,N$. Moreover, assume that the discrete initial condition is given by $c_0^h = \pi^h c_0$. Since $c \in \mathcal{C}([0,T]; H^2(0,l))$, we obtain (see [10])

$$\max_{0\leq n\leq N} \|c_n - \pi^h c_n\|_V \leq \beta\, h\, \|c\|_{\mathcal{C}([0,T];H^2(0,l))},$$
$$\max_{0\leq n\leq N} \|c_n - \pi^h c_n\|_H \leq \beta\, h^2\, \|c\|_{\mathcal{C}([0,T];H^2(0,l))}.$$

Keeping in mind (1.43), using Hölder inequality and from the regularity hypothesis $c \in H^2(0,T;H)$, we get

$$k\sum_{n=1}^{N} \Big\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\Big\|_H^2 \leq k \sum_{n=1}^{N} \frac{1}{k^2}\left(\int_{t_{n-1}}^{t_n}\int_t^{t_n}\Big\|\frac{\partial^2 c}{\partial t^2}(s)\Big\|_H ds\,dt\right)^2$$
$$\leq \frac{1}{k}\sum_{n=1}^{N}\left(\int_{t_{n-1}}^{t_n} k^{1/2}\Big\|\frac{\partial^2 c}{\partial t^2}\Big\|_{L^2(t_{n-1},t_n;H)} dt\right)^2 \leq \sum_{n=1}^{N} k^2\Big\|\frac{\partial^2 c}{\partial t^2}\Big\|^2_{L^2(t_{n-1},t_n;H)}$$
$$= k^2\Big\|\frac{\partial^2 c}{\partial t^2}\Big\|^2_{L^2(0,T;H)}.$$

From the definition of the integration error I_n, we obtain

$$I_n \leq \Big|\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}\Big(f(\gamma_0(c(s)),R(\Gamma(s))) - f(\gamma_0(c_j),R(\Gamma_j))\Big)\,ds\Big|$$
$$+\Big|\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}(\Gamma_j - \Gamma(s))\,ds\Big|. \tag{3.38}$$

Now, using the regularity condition (3.28) and the mean value theorem, on one hand we have

$$\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}|\Gamma_j - \Gamma(s)|\,ds \leq \|\Gamma\|_{\mathcal{C}^1([0,T])}\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}|t_j - s|\,ds \leq T\,k\,\|\Gamma\|_{\mathcal{C}^1([0,T])}. \tag{3.39}$$

On the other hand, taking into account the regularity conditions (3.28) and (3.37), the properties of both R and trace operators and expression (3.39), we obtain

$$\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}|f(\gamma_0(c_j),R(\Gamma_j))-f(\gamma_0(c(s)),R(\Gamma(s)))|\,ds$$
$$\leq \|c\|_{\mathcal{C}([0,T];V)}\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}|\Gamma(s)-\Gamma_j|+C_{tr}\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}\|c_j-c(s)\|_V\,ds,$$
$$\leq T\,k\,\|\Gamma\|_{\mathcal{C}^1([0,T])}\|c\|_{\mathcal{C}([0,T];V)}+C_{tr}\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}\int_{s}^{t_j}\left\|\frac{\partial c}{\partial t}(r)\right\|_V\,dr\,ds.$$

Now, from the relation

$$\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}\int_{s}^{t_j}\left\|\frac{\partial c}{\partial t}(r)\right\|_V\,dr\,ds=\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}\int_{t_{j-1}}^{r}\left\|\frac{\partial c}{\partial t}(r)\right\|_V\,ds\,dr$$
$$\leq C\sum_{j=1}^{n}\left\|\frac{\partial c}{\partial t}\right\|_{L^2(t_{j-1},t_j;V)}k^{3/2}\leq C\,k^{3/2}\,n^{1/2}\left(\sum_{j=1}^{n}\left\|\frac{\partial c}{\partial t}\right\|^2_{L^2(t_{j-1},t_j;V)}\right)^{1/2},$$

where the Hölder and Cauchy-Schwarz inequalities have been considered, the previous estimate reads

$$\sum_{j=1}^{n}\int_{t_{j-1}}^{t_j}|f(\gamma_0(c_j),R(\Gamma_j))-f(\gamma_0(c(s)),R(\Gamma(s)))|\,ds$$
$$\leq C\,k\Big(\|c\|_{\mathcal{C}([0,T];V)}\|\Gamma\|_{\mathcal{C}^1([0,T])}+\left\|\frac{\partial c}{\partial t}\right\|_{L^2(0,T;V)}\Big). \tag{3.40}$$

Therefore, combining (3.38), (3.39) and (3.40), it follows that

$$\max_{0\leq n\leq N} I_n\leq C\,k\,\left(\|c\|_{H^1(0,T;V)}+(1+\|c\|_{\mathcal{C}([0,T];V)})\|\Gamma\|_{\mathcal{C}^1([0,T])}\right).$$

Reminding that both c_j and c_{j+1} belong to $H^1(0,l)$, the last term in the inequality (3.29) can be estimated following the same reasoning as in Chapter 1.

The proof of the corollary is complete. □

3.1.5 Numerical results

In this section, we first describe the numerical scheme implemented in MATLAB in order to obtain the numerical approximations of Problem P_{LH}^{hk} and then, we present some numerical results to exhibit its accuracy in an academic example and its behavior in the simulation of a commercially available surfactant.

Given the finite element space defined by (1.41), $c_{n-1}^{hk} \in V^h$ and $\Gamma_{n-1}^{hk} \in \mathbb{R}$ for $n = 1, 2, \ldots, N$, the discrete concentration at time $t = t_n$ of surfactant, c_n^{hk}, is then obtained from equation (3.26), but here with generic constants, namely, it solves the following linear problem

$$(c_n^{hk}, v^h)_H + k\, D((c_n^{hk}, v^h)) + k\, f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))\, \gamma_0(v^h)$$
$$= (c_{n-1}^{hk}, v^h)_H + k\, k_L^d \Gamma_{n-1}^{hk}\, \gamma_0(v^h), \quad \text{for all} \quad v^h \in V^h.$$

Then, the discrete concentration Γ_n^{hk} is updated from equation (3.27) by the formula

$$\Gamma_n^{hk} = \Gamma_{n-1}^{hk} + k\, f(\gamma_0(c_n^{hk}), R(\Gamma_n^{hk})) - k\, k_L^d \Gamma_n^{hk}. \tag{3.41}$$

This problem is solved with the following algorithm:

1. **Initial time step.** At the beginning, both c_0^{hk} and Γ_0 are given.

2. **(n)th time step.** The bulk and surface concentrations at time t_{n-1}, c_{n-1}^{hk} and Γ_{n-1}^{hk}, respectively, are known. Then, at time t_n, c_n^{hk} and Γ_n^{hk} are obtained using the following algorithm:

   (a) We calculate c_n^{hk} by solving the following linear problem:

   $$\int_0^l c_n^{hk}\, v^h\, dx + D\, k \int_0^l \frac{\partial c_n^{hk}}{\partial x}\, \frac{\partial v^h}{\partial x}\, dx + k\, k_L^a\, \gamma_0(c_n^{hk}) \left(1 - \frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}\right) \gamma_0(v^h)$$
   $$= \int_0^l c_{n-1}^{hk}\, v^h\, dx + k\, k_L^d\, \Gamma_{n-1}^{hk} \gamma_0(v^h), \quad \forall v^h \in V^h.$$

   (b) Then, the value of Γ_n^{hk} is determined by the formula (3.41).

This numerical scheme has been implemented on a 3.2 GHz PC using MATLAB, and a typical run ($h = k = 0.01$) takes about 0.577 seconds of CPU time.

First example: numerical convergence

As a first example, we consider the following test problem:

$$\begin{aligned}
&\frac{\partial c}{\partial t}(t,x) - 5\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \quad t \in (0, 0.1), \quad x \in (0,1),\\
&5\,\frac{\partial c}{\partial x}(t,0) = f(c(t,0), R(\Gamma(t))) - k_L^d\,\Gamma(t), \quad t \in (0, 0.1),\\
&c(t,1) = 4, \quad t \in (0, 0.1),\\
&c(0,x) = c_0(x), \quad x \in (0,1),
\end{aligned}$$

with the initial condition $c_0(x) = 4$. This problem corresponds to Problem P_R^{LH} with the following data:

$$l = 1, \quad T = 0.1, \quad c_b = 4, \quad D = 5, \quad k_L^a = 0.5, \quad k_L^d = 0.5, \quad \Gamma_m = 1, \quad \Gamma_0 = 0.$$

$h \downarrow k \rightarrow$	0.01	0.005	0.002	0.001	0.0005
1/8	4.035107	1.949628	0.667269	0.266453	0.204185
1/16	4.190719	2.106177	0.819612	0.384867	0.167339
1/32	4.229873	2.145791	0.859353	0.424341	0.205675
1/64	4.239675	2.155719	0.869349	0.434346	0.215657
1/128	4.242127	2.158204	0.871850	0.436853	0.218169
1/256	4.242739	2.158824	0.872476	0.437479	0.218795
1/512	4.242893	2.158979	0.872632	0.437636	0.218948
1/1024	4.242931	2.159019	0.872672	0.437676	0.218989
1/2048	4.242941	2.159028	0.872681	0.437686	0.219000
1/4096	4.242943	2.159030	0.872684	0.437687	0.219001

Table 3.1: Numerical errors ($\times 10^3$) for several time and spatial discretization parameters.

Choosing the solution obtained with parameters $h = 1/16384$ and $k = 10^{-6}$ as the "exact solution", c, the numerical errors given by

$$\max_{1\leq n\leq N}\left\{\|c_n - c_n^{hk}\|_H + |\Gamma_n - \Gamma_n^{hk}|\right\}$$

are presented in Table 3.1 for several values of the discretization parameters h and k. It can be seen that the numerical error tends to zero as both h and k do. Moreover, the graph of the error with respect to the value of parameter $h+k$ is shown in Figure 3.1, where the linear convergence, stated in Corollary 3.1, is achieved.

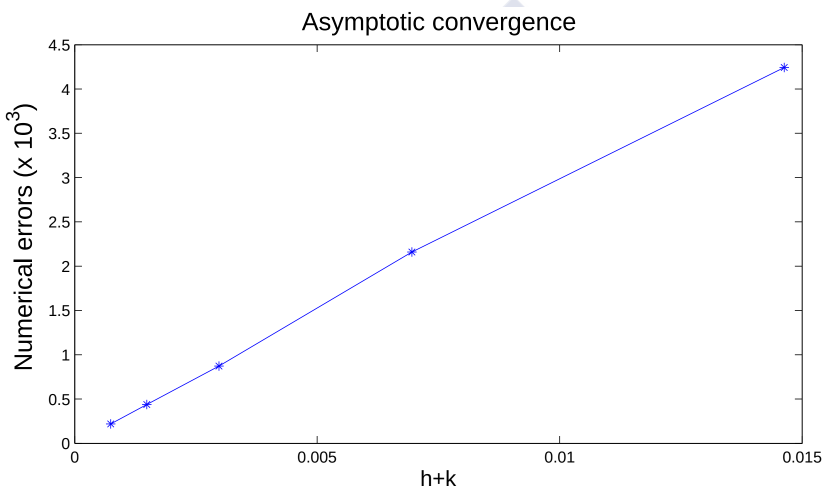

Figure 3.1: The linear convergence of the algorithm.

Second example: simulation of propanol

As a second problem, we consider a solution of the numerical problem for the propanol, using the following data taken from [6]:

$$l = 10^{-4}\,\mathrm{m}, \qquad T = 0.1\,\mathrm{s}, \qquad c_b = 333\,\mathrm{mol/m^3}, \qquad D = 5.2\times 10^{-10}\mathrm{m^2/s},$$
$$k_L^a = 7.8\times 10^{-6}\,\mathrm{m/s}, \qquad k_L^d = 199.74392\,\mathrm{s^{-1}}, \qquad \Gamma_m = 7.1\times 10^{-6}\,\mathrm{mol/m^2}.$$

Moreover, the initial conditions c_0 are defined as $c_0(x) = 333\,\mathrm{mol/m^3}$, for all $x\in[0,l]$, and $\Gamma_0 = 0\,\mathrm{mol/m^2}$.

Using the time discretization parameter $k = 10^{-5}\,\mathrm{s}$ and a non-uniform spatial mesh, refined as we approach to the point $x = 0$ its smallest parameter being 10^{-7} m, the concentration at final time and the evolution in time of the subsurface concentration are shown in Figure 3.2. As it can be seen, both concentrations tend to the bulk concentration as time evolves.

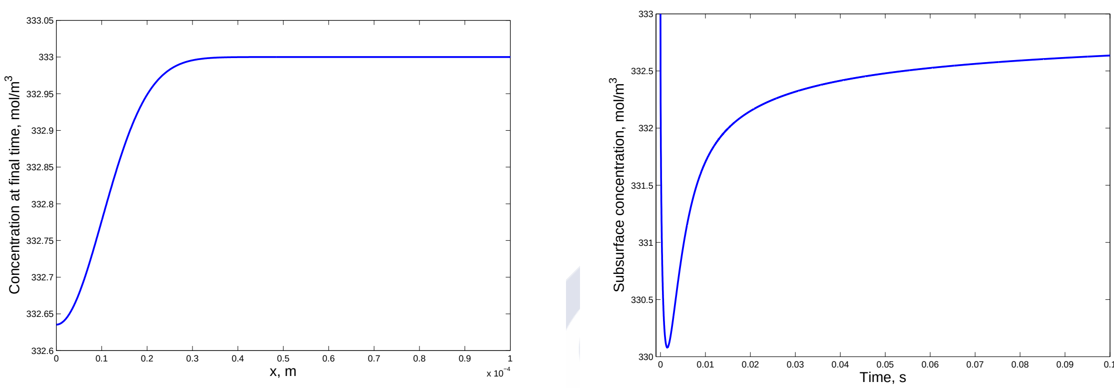

Figure 3.2: Concentration at the final time (left) and evolution in time of the subsurface concentration (right).

The surface equation of state, relating the surface tension $\widetilde{\gamma}$ with the surface concentration Γ, is given by

$$\widetilde{\gamma}(t) = \widetilde{\gamma}_0 - n\,R\,\theta\,\Gamma_m\,\log\left(\frac{\Gamma_m}{\Gamma_m - \Gamma(t)}\right), \tag{3.42}$$

where we take $\widetilde{\gamma}_0 = 0.0725$ N/m and $\theta = 293$ K and we remind that $R = 8.31$ J/(K mol) and $n = 1$. In Figure 3.3 the evolution in time of the surface tension obtained with our algorithm is presented, compared to that obtained in Figure 2 of [6] and also to some experimental data taken from [31].

As it can be seen in Figure 3.3, our numerical results are in good agreement with the numerical results obtained in [6] and the experimental data shown in [31]. We conclude that the very good agreement between both experimental and numerical dynamic surface tension results, strongly supports the Langmuir-Hinshelwood adsorption mechanism for the propanol. Indeed, results given in [6] show that the timescale for the propanol adsorption at the air-water interface for the diffusion-controlled model with the Langmuir isotherm is at least 10^3 times faster than the experimental measurements.

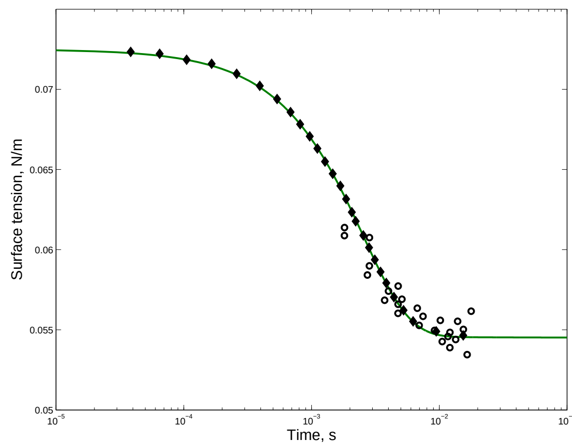

Figure 3.3: Evolution in time of the surface tension. Comparison of our numerical simulation (solid curve) with the numerical results obtained in [6] (♦) and with the experimental data (○) taken from [31].

3.2 Mixed kinetic adsorption: modified Langmuir-Hinshelwood equation

Sometimes the adsorption-desorption process in a surfactant solution is slower than the Langmuir-Hinshelwood mechanism (3.6) predicts. In 1992, Chang and Franses proposed a modification of this equation in order to obtain a model which best fits the experimental data of some surfactant solutions. In what follows, in this chapter, we consider the following modification of the Langmuir-Hinshelwood equation (see [6]):

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0) \left(1 - \frac{\Gamma(t)}{\Gamma_m}\right) e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\, \Gamma(t) e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad t > 0, \tag{3.43}$$

where B is an empirical parameter that can be positive, negative or zero. Note that, in the case that B equals zero, then Langmuir-Hinshelwood equation (3.6) is recovered. Expression (3.43) considers an activation barrier, that depends on the surface coverage, for both adsorption and desorption processes.

This model, in spite of being more general than the previous one, represents a small modification from the mathematical point of view. For this reason, the results presented in this section can be proved following the same techniques we use in the previous section, and so we omit all the proofs. We have decided to perform a detailed mathematical analysis of the model concerning the Langmuir-Hinshelwood equation and not its modification because the former is actually the classical model that appears in several chemical literature and, on the contrary, the model presented in this section is only a modification of the classical one proposed by two authors.

3.2.1 Model setting and its weak formulation

Now, we are interested in the problem consisting of the system of equations (3.1)-(3.5) and (3.43). In order to simplify the notation and taking into account the function f, defined in (3.7), expression (3.43) can be written as follows:

$$\frac{d\Gamma}{dt}(t) = f(c(t,0),\Gamma(t))e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\,\Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad t > 0. \tag{3.44}$$

Therefore, we are concerned in analyzing problem (3.1)-(3.5) coupled with (3.44). As we did in the analysis of problem (3.1)-(3.5) and (3.8), here, to simplify the calculations, we also assume that c_b equals zero.

Assume that c is a smooth function which solves the problem we are considering. Multiplying equation (3.1) by smooth function z defined in $[0,l]$ such that $z(l) = 0$, integrating in $(0,l)$, using the integration by parts formula and equations (3.3) and (3.44), we get

$$\int_0^l \frac{\partial c}{\partial t}(t,x)\,z(x)\,dx + D\int_0^l \frac{\partial c}{\partial x}(t,x)\,\frac{\partial z}{\partial x}(x)\,dx + f(c(t,0),\Gamma(t))e^{-B\frac{\Gamma(t)}{\Gamma_m}}\,z(0)$$

$$= k_L^d\,\Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}\,z(0),$$

for a.e. $t \in (0,T)$. Then, using (3.4), (3.5) and (3.44), we get the following weak formulation of the problem.

Problem P_W^{mLH}. Given $c_0 \in H$ and $\Gamma_0 \in \mathbb{R}$, find $c \in W_2(0,T)$ and $\Gamma \in H^1(0,T)$ such that

$$\langle \frac{\partial c}{\partial t}(t), v\rangle_{V'\times V} + D((c(t),v)) + f(\gamma_0(c(t)),\Gamma(t))e^{-B\frac{\Gamma(t)}{\Gamma_m}}\gamma_0(v) = k_L^d\,\Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}\,\gamma_0(v),$$

$$\text{for a.e. } t\in(0,T),\ \forall\ v\in V,$$

$$\frac{d\,\Gamma}{dt}(t) = f(\gamma_0(c(t)),\Gamma(t))e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\,\Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad \text{for a.e. } t\in(0,T),$$

$$c(0)=c_0, \quad \Gamma(0)=\Gamma_0.$$

Analogously as in the previous section, we need the truncation operator given in (3.9), and we work with the following truncated version of the modified Langmuir-Hinshelwood equation:

$$\frac{d\,\Gamma}{dt}(t) = f(c(t,0),R(\Gamma(t)))e^{-B\frac{R(\Gamma(t))}{\Gamma_m}} - k_L^d\,R(\Gamma(t))e^{-B\frac{R(\Gamma(t))}{\Gamma_m}}, \qquad t>0. \tag{3.45}$$

Proceeding as before, we define the following weak formulation of the truncated problem, associated to Problem P_W^{mLH}.

Problem P_R^{mLH}. For given $c_0\in H$ and $\Gamma_0\in\mathbb{R}$, find $c\in W_2(0,T)$ and $\Gamma\in H^1(0,T)$ such that

$$\langle \frac{\partial c}{\partial t}(t), v\rangle_{V'\times V} + D((c(t),v)) + f(\gamma_0(c(t)),R(\Gamma(t)))e^{-B\frac{R(\Gamma(t))}{\Gamma_m}}\gamma_0(v)$$

$$= k_L^d\,\Gamma(t)e^{-B\frac{R(\Gamma(t))}{\Gamma_m}}\,\gamma_0(v), \quad \text{for a.e. } t\in(0,T),\ \forall\ v\in V,$$

$$\frac{d\,\Gamma}{dt}(t) = f(\gamma_0(c(t)),R(\Gamma(t)))e^{-B\frac{R(\Gamma(t))}{\Gamma_m}} - k_L^d\,R(\Gamma(t))e^{-B\frac{R(\Gamma(t))}{\Gamma_m}}, \quad \text{for a.e. } t\in(0,T),$$

$$c(0)=c_0, \quad \Gamma(0)=\Gamma_0.$$

3.2.2 An existence and uniqueness result for Problem P_R^{mLH}

In this section, we introduce an existence and uniqueness result for Problem P_R^{mLH}. Its proof is obtained proceeding as in the proof of Theorem 3.1 and so, here we only give a brief scheme of this proof indicating the main steps.

Theorem 3.3 *Let D, k_L^a, k_L^d and Γ_m be positive constants, $B, \Gamma_0 \in \mathbb{R}$ and $c_0 \in H$. Then Problem P_R^{mLH} has a unique solution $(c, \Gamma) \in W_2(0,T) \times H^1(0,T)$.*

The proof is done in two steps: we first split the truncated problem into two intermediate problems for which the existence and uniqueness of solution is obtained. Then, the application of Schauder fixed-point theorem leads to the desired result. In order to simplify the notation, in this section we assume that $D = k_L^a = k_L^d = \Gamma_m = 1$. Now, let a be a given positive constant representing an arbitrary time.

Intermediate parabolic problem. Let $\eta \in \mathcal{C}([0,a])$ and consider the following parabolic problem:

Problem $\widetilde{P}_1^\eta$. Given $c_0 \in H$, find $c_\eta \in W_2(0,a)$

$$\begin{aligned}
&\langle \frac{\partial c_\eta}{\partial t}(t), v\rangle_{V' \times V} + ((c_\eta(t), v)) + \gamma_0(c_\eta(t))(1 - R(\eta(t)))\, e^{-BR(\eta(t))}\gamma_0(v) \\
&\qquad\qquad = \eta(t) e^{-BR(\eta(t))}\,\gamma_0(v), \quad \text{for a.e. } t \in (0,T),\ \forall\, v \in V, \\
&c_\eta(0) = c_0.
\end{aligned}$$

Lemma 3.9 *There exists a unique solution $c_\eta \in W_2(0,a)$ to Problem $\widetilde{P}_1^\eta$. Moreover*

$$\|\gamma_0(c_\eta)\|_{L^2(0,a)} \leq \bar{C}\, C_{tr}^2 \sqrt{a} \|\eta\|_{\mathcal{C}([0,a])} + C_{tr}\|c_0\|_H, \tag{3.46}$$

where C_{tr} is the trace constant given by (1.9) and $\bar{C} := \max\{1, e^{-B}\}$.

Intermediate ordinary differential equation. Let $\eta \in \mathcal{C}([0,a])$ and $c_\eta \in W_2(0,a)$ be the unique solution to Problem $\widetilde{P}_1^\eta$ corresponding to η. We formulate the following:

Problem $\widetilde{P}_2^\eta$. Given $\Gamma_0 \in \mathbb{R}$, find $\Gamma_\eta \in H^1(0,a)$ such that

$$\begin{aligned}
&\frac{d\Gamma_\eta}{dt}(t) = \gamma_0(c_\eta(t))(1 - R(\eta(t)))e^{-BR(\eta(t))} - R(\eta(t))e^{-BR(\eta(t))}, \quad \text{for a.e. } t \in (0,a), \\
&\Gamma_\eta(0) = \Gamma_0.
\end{aligned}$$

The following lemma establishes the existence and uniqueness of solution to Problem $\widetilde{P}_2^\eta$.

Lemma 3.10 *There exists a unique solution $\Gamma_\eta \in H^1(0,a)$ to Problem $\widetilde{P}_2^\eta$ given by*

$$\Gamma_\eta(t) = \Gamma_0 + \int_0^t \left(\gamma_0(c_\eta(s))(1 - R(\eta(s)))e^{-BR(\eta(s))} - R(\eta(s))e^{-BR(\eta(s))}\right) ds, \qquad (3.47)$$

for all $t \in [0,a]$. Moreover, the following estimate holds

$$\|\Gamma_\eta\|_{\mathcal{C}([0,a])} \le |\Gamma_0| + \bar{C}\sqrt{a}\,\|\gamma_0(c_\eta)\|_{L^2(0,a)} + \bar{C}\,a. \qquad (3.48)$$

We define the operator $\widetilde{\Lambda}_1 \colon C([0,a]) \to W_2(0,a)$ as follows,

$$\eta \to \widetilde{\Lambda}_1(\eta) = c_\eta,$$

where c_η is the unique solution to Problem $\widetilde{P}_1^\eta$. Moreover, we consider the operator $\widetilde{\Lambda}_2 \colon \mathcal{C}([0,a]) \times W_2(0,a) \to H^1(0,a)$ given by

$$(\eta, c_\eta) \to \widetilde{\Lambda}_2(\eta, c_\eta) = \Gamma_\eta,$$

being Γ_η the unique solution to Problem $\widetilde{P}_2^\eta$. We remark that Lemmata 3.9 and 3.10 guarantee both operator $\widetilde{\Lambda}_1$ and operator $\widetilde{\Lambda}_2$ are well defined. Furthermore, we introduce the operator $\widetilde{\Lambda} \colon \mathcal{C}([0,a]) \to H^1(0,a) \subset \mathcal{C}([0,a])$ by

$$\widetilde{\Lambda}(\eta) = \widetilde{\Lambda}_2(\eta, \widetilde{\Lambda}_1(\eta)) \quad \text{for} \quad \eta \in \mathcal{C}([0,a]). \qquad (3.49)$$

For $\widetilde{T} = \dfrac{1}{2\bar{C}^2\, C_{tr}^2}$ and $\widetilde{r} = 2|\Gamma_0| + \sqrt{2}\|c_0\|_H + \dfrac{1}{\bar{C}\, C_{tr}^2}$ we obtain the following properties of the operator $\widetilde{\Lambda}$.

Lemma 3.11 *The operator $\widetilde{\Lambda}$ maps the ball $B_{\widetilde{T}}(\widetilde{r})$ into itself. Moreover, it is compact with respect to the $\mathcal{C}([0,\widetilde{T}])$-topology.*

We remark that the existence of solution to Problem P_R^{mLH} follows from Lemma 3.11 and the Schauder fixed-point theorem. Moreover, the uniqueness of solution can be demonstrated arguing as in the proof of Theorem 3.1.

3.2.3 An existence and uniqueness result for Problem P_W^{mLH}

In this section, we present three results that establish relations between the solutions of Problems P_R^{mLH} and P_W^{mLH}. The following two lemmata study the existence of solution to Problem P_W^{mLH} under the assumption that $c \in W_2^+(0,T)$. The third one deals with the uniqueness of solution to Problem P_W^{mLH}. Some proofs are omitted because they follow proceeding as in the proofs of the corresponding lemmata in Section 3.1.3.

Lemma 3.12 *Assume that $\sigma = 0$ in the definition of the truncation operator (3.9) and that the initial condition $\Gamma_0 \in [0, \Gamma_m]$. If $(c, \Gamma) \in W_2^+(0,T) \times H^1(0,T)$ is a solution to Problem P_R^{mLH}, then $\Gamma(t) \in [0, \Gamma_m]$ for all $t \in [0,T]$, and, consequently, (c, Γ) is a solution to Problem P_W^{mLH}.*

The following lemma states that a solution to Problem P_W^{mLH} verifying that $\gamma_0(c) \in L^\infty(0,T)$ is also a solution to Problem P_R^{mLH}.

Lemma 3.13 *If $(c, \Gamma) \in W_2^+(0,T) \times H^1(0,T)$ solves Problem P_W^{mLH} with $\Gamma_0 \in [0, \Gamma_m]$ and $\gamma_0(c) \in L^\infty(0,T)$, then $\Gamma(t) \in [0, \Gamma_m]$ for all $t \in [0,T]$.*

Proof. The fact that $\Gamma(t) \geq 0$ directly follows from the proof of Lemma 3.7 in the previous section. So, here we only show that $\Gamma(t) \leq \Gamma_m$ for all $t \in [0,T]$. Assume now that there exists $t^* \in [0,T]$ such that $\Gamma(t^*) > \Gamma_m$. We define $t^{**} = \max\{t \in [0, t^*] \mid \Gamma(t) = \Gamma_m\}$ and we note that this definition makes sense since Γ is a continuous function from $[0,T]$ to $\mathbb{R}$. Obviously, for all $t \in (t^{**}, t^*)$, we have $\Gamma(t) > \Gamma_m$. Integrating the ordinary differential equation in Problem P_W^{mLH} from t^{**} to t and taking into account that $\gamma_0(c) \in L^\infty(0,T)$, we obtain

$$\begin{aligned}\Gamma(t) \leq \Gamma_m + \frac{k_L^a}{\Gamma_m} \|\gamma_0(c)\|_{L^\infty(0,T)} \int_{t^{**}}^{t} (\Gamma_m - \Gamma(s)) e^{-B\frac{\Gamma(s)}{\Gamma_m}} ds \\ -k_L^d \int_{t^{**}}^{t} \Gamma(s)\, e^{-B\frac{\Gamma(s)}{\Gamma_m}} ds, \qquad \text{for all } t \in (t^{**}, t^*). \qquad (3.50)\end{aligned}$$

Now, two different cases are considered depending on the sign of B (the case $B = 0$ is done in the previous section). If $B > 0$, then the following estimates hold for all

$t \in (t^{**}, t^*)$,

$$e^{-B\frac{\Gamma(t)}{\Gamma_m}} \leq e^{-B}, \qquad -e^{-B\frac{\Gamma(t)}{\Gamma_m}} \leq -e^{-B\frac{\|\Gamma\|_{\mathcal{C}([0,T])}}{\Gamma_m}}.$$

Therefore, from (3.50), we have for all $t \in (t^{**}, t^*)$

$$\Gamma(t) \leq \Gamma_m + \frac{k_L^a}{\Gamma_m}\|\gamma_0(c)\|_{L^\infty(0,T)}e^{-B}\int_{t^{**}}^t (\Gamma_m - \Gamma(s))ds - k_L^d\Gamma_m\, e^{-B\frac{\|\Gamma\|_{\mathcal{C}([0,T])}}{\Gamma_m}}(t - t^{**}).$$

If $\|\gamma_0(c)\|_{L^\infty(0,T)} = 0$, then $\Gamma(t) \leq \Gamma_m$ for $t \in (t^{**}, t^*)$. Otherwise, choosing

$$\varepsilon = \frac{k_L^d\,\Gamma_m^2\, e^{-B\frac{\|\Gamma\|_{\mathcal{C}([0,T])}}{\Gamma_m}}}{k_L^a\,\|\gamma_0(c)\|_{L^\infty(0,T)}e^{-B}},$$

there exists $\bar{\delta} > 0$ such that if $|t - t^{**}| \leq \bar{\delta}$, then $|\Gamma(t^{**}) - \Gamma(t)| \leq \varepsilon$. For $t \in (t^{**}, \min\{t^*, t^{**} + \bar{\delta}\})$, we get

$$\begin{aligned}\Gamma(t) \leq \Gamma_m + \frac{k_L^a}{\Gamma_m}\,\|\gamma_0(c)\|_{L^\infty(0,T)}\, e^{-B}(t - t^{**})\frac{k_L^d\,\Gamma_m^2\, e^{-B\frac{\|\Gamma\|_{\mathcal{C}([0,T])}}{\Gamma_m}}}{k_L^a\,\|\gamma_0(c)\|_{L^\infty(0,T)}e^{-B}} \\ -k_L^d\,\Gamma_m\, e^{-B\frac{\|\Gamma\|_{\mathcal{C}([0,T])}}{\Gamma_m}}(t - t^{**}) = \Gamma_m.\end{aligned}$$

So we have a contradiction. The case $B < 0$ is analogous. $\square$

Lemma 3.14 *Assume that $\sigma = 0$ in the definition (3.9) of the truncation operator and $\Gamma_0 \in [0, \Gamma_m]$. Let $(c_1, \Gamma_1) \in W_2^+(0,T) \times H^1(0,T)$ with $\gamma_0(c_1) \in L^\infty(0,T)$ and $(c_2, \Gamma_2) \in \mathcal{W}_+(0,T) \times H^1(0,T)$ with $\gamma_0(c_2) \in L^\infty(0,T)$ be two solutions to Problem P_W^{mLH}. Then $c_1(t) = c_2(t)$ and $\Gamma_1(t) = \Gamma_2(t)$ for a.e. $t \in (0,T)$.*

3.2.4 Fully discrete approximation: a priori error estimate

In this section, we introduce a fully discrete approximation to Problem P_R^{mLH} and, in doing so, the same notations as the ones taken in Section 1.4 are used here. We also assume, without loss of generality, that $D = k_L^d = k_L^a = \Gamma_m = 1$. Moreover, by using the finite element method to obtain the spatial discretization and a hybrid combination of both backward and forward Euler schemes to discretize the time derivatives, we deal with the following fully discrete approximation of Problem P_R^{mLH}:

Problem P_{mLH}^{hk}. Find $c^{hk} = \{c_n^{hk}\}_{n=0}^N \subset V^h$ and $\Gamma^{hk} = \{\Gamma_n^{hk}\}_{n=0}^N \subset \mathbb{R}$ such that

$$c_0^{hk} = c_0^h, \quad \Gamma_0^{hk} = \Gamma_0, \tag{3.51}$$

and, for $n = 1, \dots, N$, and all $v^h \in V^h$, it holds

$$(\delta c_n^{hk}, v^h)_H + ((c_n^{hk}, v^h)) + f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))e^{-BR(\Gamma_{n-1}^{hk})}\gamma_0(v^h)$$
$$= \Gamma_{n-1}^{hk} e^{-BR(\Gamma_{n-1}^{hk})}\gamma_0(v^h), \tag{3.52}$$

$$\delta\Gamma_n^{hk} = f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))e^{-BR(\Gamma_{n-1}^{hk})} - R(\Gamma_{n-1}^{hk})e^{-BR(\Gamma_{n-1}^{hk})}, \tag{3.53}$$

where $c_0^h \in V^h$ is an appropriate approximation of the initial condition c_0.

Under the assumptions of Theorem 3.3, Lax-Milgram lemma guarantees the existence and uniqueness of solution to Problem P_{mLH}^{hk}.

The results presented in what follows focus on deriving an error estimate for the differences $c_n - c_n^{hk}$ and $\Gamma_n - \Gamma_n^{hk}$. Their proofs are omitted since they follow the same ideas and techniques proposed in Section 3.1.5. Assuming the additional regularity conditions of the solution to Problem P_R^{mLH} given in (3.28), we get the following result.

Theorem 3.4 *Assume the hypotheses of Theorem 3.3 and the regularity condition (3.28) hold. Then, there exists a constant* $\beta > 0$, *independent of the discretization parameters* h *and* k, *such that the following error estimate is satisfied, for all* $\{v_n^h\}_{n=1}^N \subset V^h$,

$$\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H^2 + k\sum_{n=1}^N \left(\|c_n - c_n^{hk}\|_V^2 + \sigma(\gamma_0(c_n - c_n^{hk}))^2\right) + \max_{0\le n\le N} |\Gamma_n - \Gamma_n^{hk}|^2$$
$$\le \beta\,\|c_0 - c_0^h\|_H^2 + \beta\,k\sum_{n=1}^N \left(\|c_n - v_n^h\|_V^2 + k^2 + \left\|\frac{\partial c}{\partial t}(t_n) - \delta c_n\right\|_H^2\right) + \max_{0\le n\le N} I_n^2$$
$$+\beta \max_{0\le n\le N} \|c_n - v_n^h\|_H^2 + \beta\sum_{n=1}^{N-1} \frac{1}{k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2, \tag{3.54}$$

where I_n is the integration error defined now as follows,

$$I_n = \Big| \int_0^{t_n} \Big(f(\gamma_0(c(s)), R(\Gamma(s)))e^{-B(R\Gamma(s))} - R(\Gamma(s))e^{-B(R\Gamma(s))} \Big)\, ds$$
$$-k \sum_{j=1}^{n} \big(f(\gamma_0(c_j), R(\Gamma_j))e^{-BR(\Gamma_j)} - R(\Gamma_j)e^{-BR(\Gamma_j)} \big) \Big|.$$

As an example of the convergence given by estimate (3.54), we state the following corollary under the assumption that the finite element space V^h is given by (1.41) and under further regularity condition on the solution to the continuous problem given by (3.37).

Corollary 3.2 *Assume the hypotheses of Theorem 3.4 and the regularity condition (3.37) hold. Then, the convergence of the algorithm in Problem P^{hk}_{mLH} is linear, i.e. there exists a constant $\beta > 0$, independent of h and k, such that*

$$\max_{0\le n\le N} \|c_n - c_n^{hk}\|_H + \max_{0\le n\le N} |\Gamma_n - \Gamma_n^{hk}| \le \beta\,(h+k).$$

3.2.5 Numerical results

The numerical scheme, implemented in MATLAB, for approximating Problem P^{hk}_{mLH} is presented in this section. Moreover, some numerical simulations are introduced in order to show the behavior of this model.

Given the finite element space defined in (1.41) and given $c^{hk}_{n-1} \in V^h$ and $\Gamma^{hk}_{n-1} \in \mathbb{R}$ for $n = 1, 2, \ldots, N$, we calculate the discrete concentration at time $t = t_n$ of surfactant, denoted by c_n^{hk}, by using equation (3.52), but here with generic constants; that is to say, we find the solution of the following linear problem

$$(c_n^{hk}, v^h)_H + D\,k((c_n^{hk}, v^h)) + k\, f(\gamma_0(c_n^{hk}), R(\Gamma^{hk}_{n-1}))e^{-B\frac{R(\Gamma^{hk}_{n-1})}{\Gamma_m}}\, \gamma_0(v^h)$$
$$= (c^{hk}_{n-1}, v^h)_H + k\, k_L^d\, \Gamma^{hk}_{n-1}\, e^{-B\frac{R(\Gamma^{hk}_{n-1})}{\Gamma_m}}\, \gamma_0(v^h), \quad \forall \;\; v^h \in V^h.$$

Once c_n^{hk} is known, the discrete surface concentration Γ_n^{hk} is calculated from equation

(3.53) by the expression

$$\Gamma_n^{hk} = \Gamma_{n-1}^{hk} + k\, f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))e^{-BR(\Gamma_{n-1}^{hk})} - k\, k_L^d\, R(\Gamma_{n-1}^{hk})e^{-BR(\Gamma_{n-1}^{hk})}.$$

Besides, we describe below the implemented algorithm which solves this problem.

1. **Initial time step.** At the beginning both c_0^{hk} and Γ_0 are given.

2. **(n)th time step.** The bulk and surface concentrations at time t_{n-1}, c_{n-1}^{hk} and Γ_{n-1}^{hk}, respectively, are known. Then, at time t_n, c_n^{hk} and Γ_n^{hk} are obtained using the following algorithm:

   (a) We calculate c_n^{hk} by solving the following linear problem:

$$\int_0^l c_n^{hk} v^h\, dx + Dk \int_0^l \frac{\partial c_n^{hk}}{\partial x}\frac{\partial v^h}{\partial x}\, dx + k\, k_L^a\, \gamma_0(c_n^{hk})\Big(1 - \frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}\Big)e^{-B\frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}}\gamma_0(v^h)$$
$$= \int_0^l c_{n-1}^{hk}\, v^h\, dx + k\, k_L^d\, \Gamma_{n-1}^{hk} e^{-B\frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}}\gamma_0(v^h), \quad \forall v^h \in V^h.$$

   (b) Then, the value of Γ_n^{hk} is determined by the formula:

$$\Gamma_n^{hk} = \Gamma_{n-1}^{hk} + k\, f(\gamma_0(c_n^{hk}), R(\Gamma_{n-1}^{hk}))e^{-B\frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}} - k\, k_L^d R(\Gamma_{n-1}^{hk})e^{-B\frac{R(\Gamma_{n-1}^{hk})}{\Gamma_m}}.$$

This algorithm has been implemented on a 3.2 GHz PC using MATLAB, and a typical run ($h = k = 0.01$) takes about 0.047 seconds of CPU time.

First example: numerical convergence

We consider the following test problem:

$$\frac{\partial c}{\partial t}(t,x) - 5\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \quad t \in (0, 0.1), \quad x \in (0,1),$$
$$5\,\frac{\partial c}{\partial x}(t,0) = f(c(t,0), R(\Gamma(t)))e^{-BR\Gamma(t)} - k_L^d\, R(\Gamma(t))e^{-BR(\Gamma(t))}, \quad t \in (0, 0.1),$$
$$c(t,1) = 1, \quad t \in (0, 0.1),$$
$$c(0,x) = c_0(x), \quad x \in (0,1),$$

with the initial condition $c_0(x) = 1$. This problem corresponds to Problem P_R^{mLH} with the following data:

$$l = 1, \quad T = 0.1, \quad c_b = 1, \quad D = 5, \quad k_L^a = 1, \quad k_L^d = 0.25,$$
$$B = -1, \quad \Gamma_m = 1, \quad \Gamma_0 = 0.$$

Choosing the solution obtained with parameters $h = 1/16384$ and $k = 10^{-6}$ as the "exact solution", c, the numerical errors given by

$$\max_{1\leq n\leq N} \left\{ \|c_n - c_n^{hk}\|_H + |\Gamma_n - \Gamma_n^{hk}| \right\}$$

are presented in Table 3.2 for several values of the discretization parameters h and k. In Figure 3.4, the error with respect to the value of parameter $h + k$ is plotted. It can be seen that the linear convergence is achieved as Corollary 3.2 states.

$h \downarrow k \rightarrow$	0.01	0.005	0.002	0.001	0.0005
1/8	20.251566	9.730384	3.196324	1.066322	0.438502
1/16	21.179591	10.672453	4.136028	1.917607	0.802959
1/32	21.41244	10.909478	4.375164	2.156568	1.039592
1/64	21.4707	10.968818	4.435143	2.216719	1.099735
1/128	21.48527	10.983659	4.450149	2.231776	1.114816
1/256	21.48891	10.987369	4.453902	2.235543	1.118588
1/512	21.489825	10.988297	4.454839	2.236485	1.119532
1/1024	21.490052	10.988529	4.455074	2.236721	1.119768
1/2048	21.490109	10.988587	4.455133	2.2367791	1.119826
1/4096	21.490123	10.988601	4.455148	2.2367939	1.119843

Table 3.2: Numerical errors ($\times 10^4$) for several time and spatial discretization parameters.

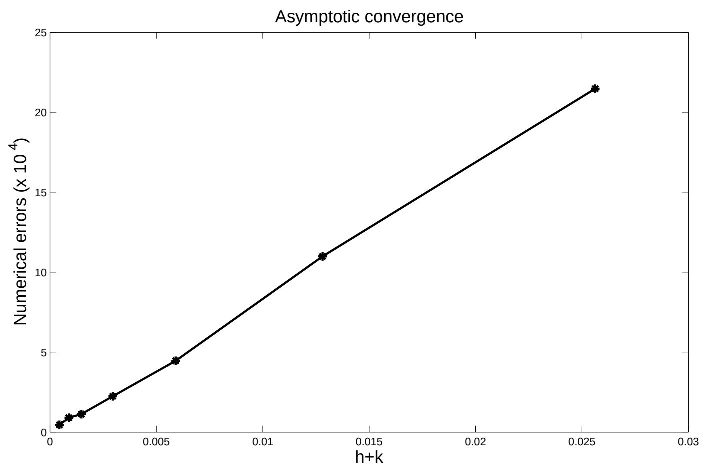

Figure 3.4: The linear convergence of the algorithm.

Second example: simulation of octanol

As a second example, we take into account a solution of octanol, considering the following data, taken from [6]:

$$l = 10^{-4}\,\mathrm{m}, \quad T = 0.1\,\mathrm{s}, \quad c_b = 3.44\,\mathrm{mol/m^3}, \quad D = 6\times 10^{-10}\mathrm{m^2/s}, \quad B = -28,$$

$$k_L^a = 6.5\times 10^{-5}\,\mathrm{m/s}, \quad k_L^d = 3.47\,\mathrm{s^{-1}}, \quad \Gamma_m = 7.5\times 10^{-6}\,\mathrm{mol/m^2}.$$

Besides, as initial conditions c_0 and Γ_0, we consider $c_0(x) = 3.44\,\mathrm{mol/m^3}$, for all $x \in [0, 10^{-4}]$ and $\Gamma_0 = 0\,\mathrm{mol/m^2}$.

Employing a uniform time discretization, considering elements with size $k = 10^{-5}\,\mathrm{s}$ and a non-uniform spatial mesh, refined as we approach to the point $x = 0$ and whose smaller parameter is 10^{-9}m, we obtain the evolution in time of both surface and subsurface concentrations shown in Figure 3.5. As we can observe in this figure, at time $t = 0$, since the solution is well stirred, the subsurface concentration is the same as the bulk concentration. Moreover, the surface is empty and then, its concentration equals zero. At initial stages of the process, the migration of surfactant molecules from the subsurface to the surface produces a great decreasing of the subsurface concentration and a pronounced increasing of the surface concentration. However, as time evolves and the surface becomes crowded, the molecules that diffuse from the bulk of the solution have to remain at the subsurface because they do not find an empty site into the surface. This is the reason why the subsurface concentration increases again until the equilibrium value and the surface concentration stabilizes.

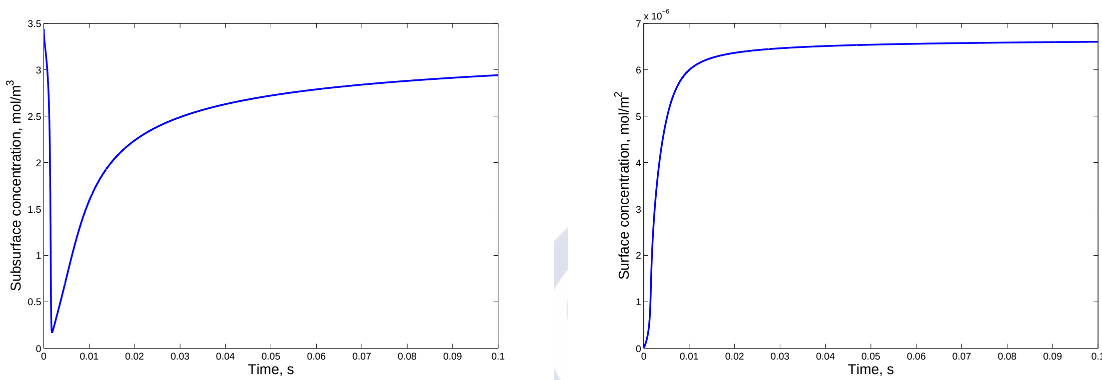

Figure 3.5: Evolution in time of the subsurface (left) and surface (right) concentrations.

The surface tension, calculated with expression (3.42) taking $\widetilde{\gamma}_0 = 0.0725$ N/m and $\theta = 293$ K and keeping in mind that $R = 8.31$ J/(K mol) and $n = 1$, is plotted in Figure 3.6. We present there the numerical surface tension results for two different concentrations of a solution of octanol obtained with our algorithm and we compare them with the numerical results obtained in [6] and the experimental data taken from [32]. It can be seen that our numerical results, the numerical results presented in [6] and the experimental data shown in [32] are in good agreement. Therefore, our algorithm predicts well the experimental data for these solutions of octanol. Furthermore, we can conclude that the very good agreement between experimental and numerical data evidences that the modification of the Langmuir-Hinshelwood equation, proposed by C.H. Chang and E.I. Franses, implied an improvement for the description of the adsorption dynamics for the octanol. In fact, it can be seen in [7] that neither the diffusion-controlled model with the Langmuir isotherm nor the mixed kinetic-diffusion one with the Langmuir-Hinshelwood equation can fit the adsorption behavior of the octanol well.

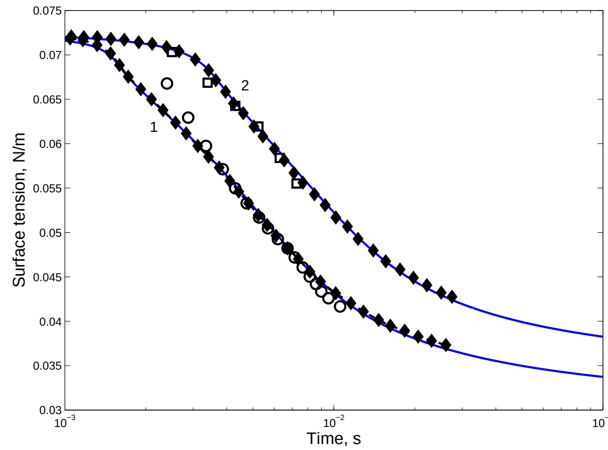

Figure 3.6: Evolution in time of the surface tension. Comparison of our numerical simulations (solid curves) with the numerical results obtained in [6] (♦) and with the experimental data (□ and ∘) taken from [32]. **Curve 1**: $c_b = 3.44$ mol/m^3, **curve 2**: $c_b = 2.7$ mol/m^3 (in this case we take the same data as previously except the constant B, being $B = -17$).

Third example: simulation of heptanol

As a third example, we consider a solution of heptanol, using the following data, taken from [6]:

$$l = 10^{-4}\,\mathrm{m}, \quad T = 0.1\,\mathrm{s}, \quad c_b = 2.58\,\mathrm{mol/m^3}, \quad D = 6.5\times 10^{-10}\mathrm{m^2/s}, \quad B = -8,$$

$$\Gamma_m = 8.8\times 10^{-6}\,\mathrm{mol/m^2}, \quad k_L^a = 1.1\times 10^{-4}\,\mathrm{m/s}, \quad k_L^d = 26.04\,\mathrm{s^{-1}}.$$

Moreover, the initial conditions c_0 and Γ_0 are defined as $c_0(x) = 2.58\,\mathrm{mol/m^3}$ for all $x \in [0, 10^{-4}]$ and $\Gamma_0 = 0\,\mathrm{mol/m^2}$.

Using the time discretization parameter $k = 10^{-5}\,\mathrm{s}$ and a non-uniform spatial mesh, refined as we approach to the point $x = 0$ and whose smaller parameter is $10^{-9}\,\mathrm{m}$, the evolution in time of both surface and subsurface concentrations are shown in Figure 3.7. In this figure, we can notice that the behavior of both surface and subsurface concentrations is quite similar to that explained in the previous example.

The numerical surface tension, calculated using equation (3.42) taking $\widetilde{\gamma}_0 = 0.0725$

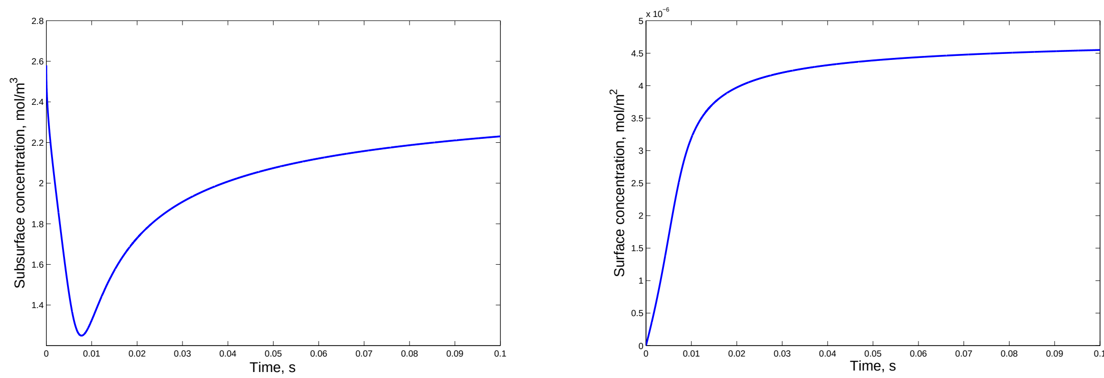

Figure 3.7: Evolution in time of the subsurface (left) and surface (right) concentrations.

N/m, $\theta = 298$ K (we recall that $R = 8.31$ J/(K mol) and $n = 1$), is plotted in Figure 3.8 for three different concentrations of heptanol. We also compare in this figure our numerical results with the numerical results given in [6] and the experimental data of [31]. It can be seen that, for these three concentrations of heptanol, the modified Langmuir-Hinshelwood model fits the experimental data well.

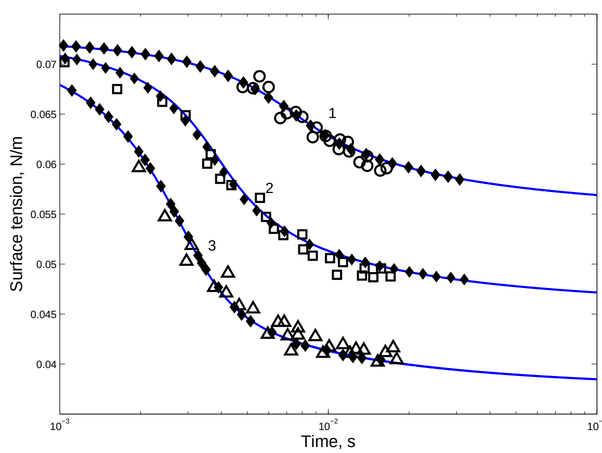

Figure 3.8: Evolution in time of the surface tension. Comparison of our numerical simulation (solid curves) with the numerical results obtained in [6] (⧫) and the experimental data (○, □ and △) of [31]. **Curve 1**: $c_b = 2.58$ mol/m^3, **curve 2**: $c_b = 5.16$ mol/m^3, $k_L^a = 1.2 \times 10^{-4}$ m/s, $k_L^d = 28.4$ s^{-1} and $B = -7$, **curve 3**: $c_b = 8.61$ mol/m^3, $k_L^a = 1.9 \times 10^{-4}$ m/s, $k_L^d = 44.98$ s^{-1} and $B = -4$.

Conclusions and forthcoming research work

In this Ph.D. Thesis we studied several mathematical models describing the surfactant behavior at the plane air-water interface. The problem was modeled by a nonlinear system, consisting of the partial diffusion equation in one spatial dimension and appropriate boundary and initial conditions arising in the diffusion process. Moreover, this system was coupled with the corresponding adsorption-desorption model, given by either an isotherm or an ordinary differential equation by means of the boundary condition at the subsurface. Then, the models considered in this work only differ in the boundary condition at the subsurface, which determines the novelty of this study.

In Chapter 1, the linear mixed kinetic-diffusion model was introduced. The variational formulation of this problem was presented and the existence and uniqueness of weak solution was proved by using fixed-point techniques. Moreover, a fully discrete approximation of the weak problem was obtained by applying the finite element method for the spatial discretization and a hybrid combination of both backward and forward Euler schemes for the discretization in time. For this problem, we got an a priori error estimate result from which, under additional regularity conditions, the linear convergence of the algorithm follows. Furthermore, some numerical simulations were presented to show the accuracy of the algorithm and its behavior for the hexanol and heptanol.

In Chapter 2, we dealt with the Langmuir isotherm for describing the adsorption-desorption dynamics. We introduced the weak formulation of the problem and we presented an existence and uniqueness result. Its proof is based on the Rothe's method and fixed-point techniques. We studied a semi-discrete approximation in time of the weak problem for which an a priori error estimate was proved and, under additional regularity conditions, the linear convergence was achieved. Besides, applying the finite element method and a hybrid combination of both backward and forward Euler schemes to get the spatial and time discretizations, respectively, a fully discrete approximation of the problem was derived. We proved an error estimate result from which, assuming further regularity conditions, the linear convergence was achieved. A test problem showing the linear convergence of the algorithm was presented and, also, two numerical simulations for the propanol and the sodium dodecylsulfate were shown.

Finally, in Chapter 3, we first analyzed the problem consisting of the diffusion equation together with the Langmuir-Hinshelwood expression. The weak formulation of the problem and a truncated version of this weak formulation were introduced. Existence and uniqueness results for both weak versions of the problem were provided. Moreover, a fully discrete approximation of this problem was obtained by using once again the finite element method and a hybrid combination of both forward and backward Euler schemes for approximate the spatial variable and the time derivatives, respectively. An error estimate result was obtained and, under additional regularity conditions, the linear convergence of the algorithm was derived. Some numerical simulations consisting in a test example and an example for propanol were provided. Then, we studied a similar problem, but considering now a modification of the Langmuir-Hinshelwood equation (proposed by C.H. Chang and E.I. Franses in 1992, see [6]). Similar results as in the previous case were obtained for this model. Numerical simulations showing the accuracy of the algorithm and its behavior for octanol and heptanol were presented.

We point out that the numerical algorithms of this thesis were implemented in MATLAB. In order to check the good functioning of them, we compared some simulations obtained with our algorithms with the same simulations proportioned by COMSOL Multiphysics.

As it can be seen with the simulations presented in this study, the models introduced in this work can predict well the behavior of several surfactants. However, they are not able to fit the experimental data of all of them. For this reason, as a future work, we think that it could be interesting to study a more sophisticated model accounting the surface diffusion. The simplification of the model in one dimension does not allow to consider this phenomenon and a two-dimensional model would take into account only the surface diffusion in one direction. So, in our opinion, the natural continuation of this work is the analysis of a three-dimensional model incorporating the surface diffusion. This model predicts a slower equilibration of the surface tension than the one-dimensional model. This is because the surface tension decay occurs in two phases; first the surface tension decreases as a consequence of the adsorption process and then the second fall is due to the compaction of molecules in the surface.

From our point of view, another attractive task is the study of the adsorption-desorption dynamics of surfactant solutions onto bubble shaped surfaces since, both in real life and experiments, the adsorbent surface is not always plane. As it was noticed in [46], the bubble shape of the surface in which the adsorption takes place plays an important role in the analysis of the relaxation of the surface tension. This becomes a problem if one tries to reproduce the behavior of a solution in which the exact shape of the adsorbent bubble is an unknown, as it occurs when measuring, for instance, with a pendant bubble tensiometer. Furthermore, when experimental measurements are performed with this apparatus, it was observed that some surfactant solutions equilibrates faster than the diffusion-controlled model predicts. This was attributed (see [36]) to the possible existence of convective currents in the solution, so the inclusion of a convective term in the model could be also an interesting issue.

Summary

A surfactant is a chemical compound with molecules having two different parts: one hydrophilic part and one hydrophobic part, this structure being the responsible of the surfactant behavior in a solution. When a new surface is formed in a surfactant solution, the surfactant molecules tend to migrate from the bulk of the solution to the surface and, in doing so, they produce a variation of the surface properties (one of the most important properties is the dynamic surface tension). For a plane surface, that is the situation considered in this work, the surface tension is the force that acts along a unit of length, parallel to the surface (see [14]). This force is a consequence of the inward attraction, normal to the surface, to which surface molecules are subjected, due to the fact that they have less neighbor molecules to establish intermolecular interactions than the molecules of the bulk of the solution (see [1]). The presence of surfactant molecules at the surface breaks the intermolecular interactions between the surface molecules and their neighbors, consequently reducing the surface tension drastically. The dynamic surface tension is an important property because its plays a major role in several biological, biochemical and industrial processes like, for example, in foam and pesticides production, cleaning processes, in breathing, in food processing and so on (see, for instance, [2, 7, 14, 16, 33, 37]).

The variation of the surface tension is a dynamic process, that is to say, it is not instantaneous and it needs a certain period of time until the equilibrium is reached by the system. In fact, this dynamic process may vary from a few seconds to several hours or even days, depending on the type of surfactant, its concentration, its temperature, its salinity, etc. However, the analysis of the dynamic surface tension is always related to the study of the transport of molecules from the bulk of the solution to the surface, that can occur by means of two different mechanisms: diffusion and adsorption-desorption. In order to understand the process, it is important to take into account the layer so-called "subsurface" (see Figure A.1), an imaginary boundary located a few molecular diameters below the surface, and that splits the region in which only diffusion takes place from the domain in which only adsorption-desorption occurs. The surfactant molecules diffuse from the bulk of the solution to the subsurface and, once at the subsurface, they are adsorbed into the surface. However, as the surface gets crowder, it can happen that surfactant molecules do not find an empty space at the surface. In this case, they are desorbed at the subsurface and they come back to the bulk of the solution. There are two families of models to describe the adsorption-desorption dynamics (see [7, 16]):

- **Diffusion-controlled models**. These models assume that the timescale needed to reach the equilibrium between the surface and the subsurface is less than the timescale needed for diffusion.

- **Mixed kinetic-diffusion models**. These models suppose that the timescale needed for the adsorption-desorption process is comparable to the timescale for diffusion.

Experimentally, the tensiometers measure the surface tension of a solution. There are many tensiometers and they are classified in (see [7]): force methods, shape methods, pressure methods and others. Some of them measure the surface tension over plane surfaces and others over bubble shaped surfaces. The best choice of the measurement method depends on the timescale that the solution needs to reach the equilibrium. All the experimental data shown in this thesis have been obtained with the Wilhelmy plate method (see [1]). This method consists in measuring the force applied on a thin plate that is suspended from one arm of a balance and oriented perpendicularly to the surface. The plate is partially immersed on a liquid and either a tensiometer or a microbalance measures the force on the plate due to wetting. The surface tension is calculated by means of this force by using the Wilhelmy equation (see [7]).

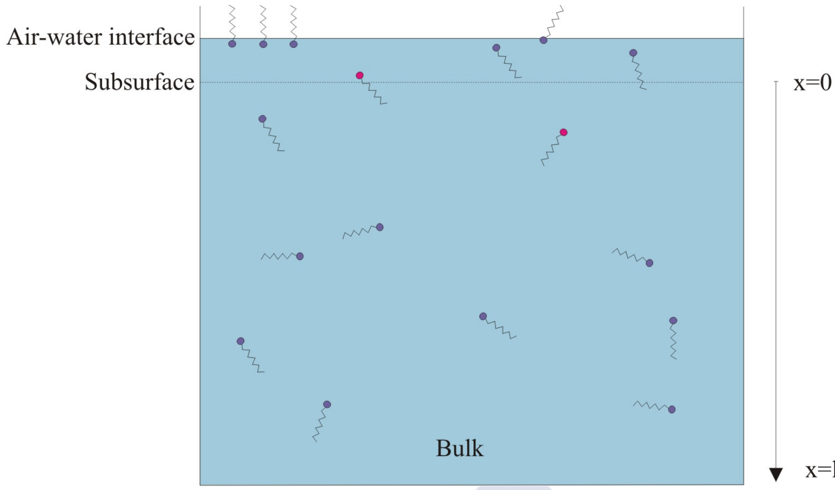

Figure A.1: Air-water interface and location of the subsurface.

The aim of this thesis is to perform a mathematical analysis of the problem concerning surfactant solutions at a plane air-water interface. From a mathematical point of view, this dynamic process is modeled by the partial differential equation of diffusion in one spatial dimension, together with suitable initial and boundary conditions. In order to establish the system of equations that models the process, let us denote by x the distance from the subsurface, and by $c(t,x)$ the surfactant concentration at time $t \in [0,T]$ and at point $x \in [0,l]$. The boundary $x = 0$ of the spatial interval corresponds to the location of the subsurface. Denoting by $\Gamma(t)$ the time-dependent surface concentration, we have the following formulation of the problem (see [7, 35]):

$$\frac{\partial c}{\partial t}(t,x) - D\,\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \qquad t \in (0,T), \quad x \in (0,l), \tag{A.1}$$

with boundary conditions:

$$D\,\frac{\partial c}{\partial x}(t,0) = \frac{d\Gamma}{dt}(t), \quad t > 0, \tag{A.2}$$

$$c(t,l) = c_b, \quad t > 0, \tag{A.3}$$

and initial conditions:

$$c(0,x) = c_0(x), \quad x \in (0,l), \tag{A.4}$$

$$\Gamma(0) = \Gamma_0. \tag{A.5}$$

In this system of equations, D and c_b are two positive constants that denote the diffusion coefficient and the bulk concentration, respectively. Moreover, $c_0(x)$ is a function defined in $[0,l]$, that is equal to c_b on $x = l$, and Γ_0 is a nonnegative constant that denotes the surface concentration at time $t = 0$.

This way, the transport of molecules from the bulk of the solution to the surface is modeled by equations (A.1)-(A.5). Equation (A.1), that describes the diffusion in the bulk of the solution considering finite diffusion length, is obtained from the general transport equation by neglecting the convective term since, in this study, we work with quiescent surfactant solutions. The boundary condition (A.2) describes the flux of monomers from the subsurface to the surface (adsorption) and vice versa, from the surface to the subsurface (desorption). Moreover, we assume that the boundary $x = l$ is kept at a constant concentration, equal to c_b, and so, it is imposed a nonhomogeneous boundary condition, given by expression (A.3) at the right end of the spatial interval. As the initial conditions, we assume that, at the beginning of the process, the surface concentration is equal to Γ_0 and that the bulk concentration is given by the function $c_0(x)$, $x \in [0,l]$. Therefore, given D, c_b, l, T, $c_0(x)$ and Γ_0, the problem consists in finding both the bulk concentration, c, and the surface concentration, Γ.

Since the surface concentration, Γ, is an unknown of the problem, we need an additional condition in order to close the system. In this sense, the additional condition, that is coupled to the system of equations (A.1)-(A.5) by means of the boundary condition at the subsurface, is given by the adsorption-desorption model. Then, either the diffusion-controlled model or the mixed kinetic-diffusion one has to be considered. When considering a diffusion-controlled model, an equation so-called *isotherm* establishes the relation between both surface and subsurface concentrations. The most studied isotherms in the literature are:

- *Henry isotherm:* assumes a linear dependence between the surface and subsurface concentrations,

$$\Gamma(t) = K_H\, c(t,0), \qquad t \geq 0, \tag{A.6}$$

where K_H is the Henry adsorption constant.

- *Langmuir isotherm:* it supposes that the dependence between both concentrations is nonlinear,

$$\Gamma(t) = \Gamma_m \frac{K_L\, c(t,0)}{1 + K_L\, c(t,0)}, \qquad t \geq 0, \tag{A.7}$$

being Γ_m and K_L the maximum surface concentration and the Langmuir adsorption constant, respectively.

- *Frumkin isotherm:* like the Langmuir isotherm, it establishes a nonlinear dependence between the surface and subsurface concentrations,

$$\Gamma(t) = \Gamma_m \frac{K_F\, c(t,0)}{e^{-A\frac{\Gamma(t)}{\Gamma_m}} + K_F\, c(t,0)}, \qquad t \geq 0, \tag{A.8}$$

where K_F is the Frumkin adsorption constant and A is an empirical parameter that indicates if the adsorption is anticooperative; that is to say, if the adsorption becomes difficult with the increasing of the surface coverage.

On the contrary, if we consider a mixed kinetic-diffusion model for describing the adsorption-desorption mechanism, then a kinetic equation relates the rate of change of the surface concentration with the balance between the adsorption and desorption rates. The most commonly expressions are:

- *Lineal kinetic model:* it assumes that the rate of adsorption is proportional to the subsurface concentration while the rate of desorption is proportional to the surface concentration,

$$\frac{d\,\Gamma}{dt}(t) = k_H^a\, c(t,0) - k_H^d\, \Gamma(t), \qquad t > 0, \tag{A.9}$$

where k_H^a and k_H^d are the adsorption and desorption constants, respectively.

- *Langmuir-Hinshelwood model:* the rate of adsorption depends on the subsurface concentration, but also on the fraction of empty space at the surface,

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big) - k_L^d\,\Gamma(t), \qquad t > 0, \tag{A.10}$$

being k_L^a and k_L^d the adsorption and desorption constants for the Langmuir-Hinshelwood model, respectively.

- *Modified Langmuir-Hinshelwood model:* it is a modification of the previous model, proposed in 1992 by C.H. Chang and E.I. Franses (see [6]), due to the fact that Langmuir-Hinshelwood model is not able to fit the behavior of some surfactants,

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big)e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\,\Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad t > 0, \tag{A.11}$$

where the real constant B is an empirical parameter. Note that, in the case of B equals zero, the previous expression leads to the classical Langmuir-Hinshelwood equation.

In the chemical literature, one can find several publications in which these problems are numerically solved. Moreover, the work done by Ward and Tordai, see [45], was the pioneer in carrying out a mathematical research concerning the obtention of analytical solutions, using the Laplace transform technique, for the diffusion-controlled model considering both a plane surface and a finite diffusion length. However, sometimes, the Ward and Tordai theory can not be applied since their solution gives the surface concentration in terms of a time integral over the subsurface concentration and it depends on both the diffusion and adsorption models. For this reason, approximations for short and long times of that solutions were obtained. To our knowledge, none of the works published until now have dealt with the mathematical analysis of the problem. Then, the main contribution of this thesis is that we perform a mathematical study of a diffusion problem that is coupled with a dynamical boundary condition.

In what follows, we introduce a brief abstract of the chapters of this thesis, carried out at the University of Santiago de Compostela, under the supervision of José Ramón Fernández García and María del Carmen Muñiz Castiñeira.

Chapter 1: Mixed kinetic-diffusion model for the Henry isotherm

In this chapter, we take into account the model consisting of the system of equations (A.1)-(A.5) and (A.9). The study developed for this problem consists in introducing its weak formulation and the proof of the existence and uniqueness of weak solution and, in doing so, we use fixed-point techniques.

Moreover, we also carry out the numerical analysis of a fully discrete approximation of the weak problem. This approach is obtained by applying the finite element method in order to approximate the spatial variable and a hybrid combination of both backward and forward Euler schemes to discretize the time derivatives. For this problem, we obtain an a priori error estimates and, under additional regularity conditions, the linear convergence of the algorithm is achieved.

Finally, we present some numerical simulations in order to show the accuracy of the algorithm and its behavior for the hexanol and the heptanol.

We indicate that the work presented in this chapter has given rise to the articles [20] and [22].

Chapter 2: Diffusion-controlled model with the Langmuir isotherm

In the second chapter, we focus on the analysis of the diffusion problem coupled with an adsorption-desorption model given by the Langmuir isotherm. It is a parabolic nonstandard problem since the Langmuir isotherm, coupled to the system through the boundary condition at the subsurface, makes the system to be nonlinear. For this problem, we state its weak formulation and we prove the existence and uniqueness of weak solution. The existence is obtained by using the Rothe method, an intermediate problem, a priori estimates and passing to the limit. Following some arguments already introduced in [25], the uniqueness is proved.

Moreover, a semi-discrete approximation in time of the problem is analyzed and we prove some a priori estimates from which the linear convergence of the algorithm is derived. Furthermore, applying the finite element method and a hybrid combination of both forward and backward Euler schemes for the spatial and time discretizations, respectively, a fully discrete approximation of the weak problem is obtained. A result concerning an error estimate for this problem is shown and, under additional regularity conditions, we get the linear convergence of the algorithm.

Finally, we present three examples. The first one is a test problem in which we show the linear convergence theoretically proved. The other examples deal with simulations of commercial surfactants: propanol and sodium dodecylsulfate.

The work introduced in Chapter 2 has been collected in the articles [11] and [21].

Chapter 3: Mixed kinetic-diffusion model with the Langmuir-Hinshelwood equation

In this last chapter, we take into account two mixed kinetic-diffusion models that describe the adsorption-desorption dynamics. First, we consider the Langmuir-Hinshelwood equation and, then, the modification proposed by C.H. Chang and E.I. Franses in 1992. Physically, the difference between these two models and the model presented in the first chapter (that also belongs to the family of the mixed kinetic-diffusion models) lies in the description of the adsorption dynamics. Indeed, in the case of the linear kinetic expression, considered in Chapter 1, the rate of adsorption only depends on the subsurface concentration; however, in the models introduced in this chapter, it also depends on the fraction of empty space at the surface. Moreover, the modified Langmuir-Hinshelwood equation assumes a more pronounced decelerate of the adsorption rate than the Langmuir-Hinshelwood equation with the increasing of the surface coverage (see [7]).

The mathematical analysis presented in this chapter has been published in [23] and [24].

The algorithms used in this work are implemented in MATLAB. Moreover, in order to prove their good functioning, we have compared the results obtained with them with the results given by the commercial software COMSOL Multiphysics for the same simulations.

Conclusions and forthcoming research work

In this thesis we study some mathematical models that describe the behavior of surfactant solutions at the plane air-water interface. This problem is modeled through a nonlinear system consisting of the diffusion equation in one spatial dimension, together with the suitable initial and boundary conditions. Moreover, this system is coupled with the corresponding adsorption-desorption model by means of the boundary condition at the subsurface. Therefore, the models considered in this work only differ in the boundary condition at the subsurface, which determines the novelty of the study.

In Chapters 1 and 3 of this manuscript, we work with mixed kinetic-diffusion problems in order to model the adsorption-desorption dynamics. In the first chapter, we take into account the linear kinetic equation, while in the third chapter we introduce both Langmuir-Hinshelwood model and one of its modifications.

On the contrary, in Chapter 2, we present a diffusion-controlled model, using the Langmuir isotherm. The physical difference between this model and those presented in the others chapters is that, in this case, the adsorption-desorption process is assumed to be instantaneous while the others suppose that both adsorption-desorption and diffusion processes have a similar timescale.

For each of the models studied in this work, a weak problem is formulated and existence and uniqueness results of weak solution are proved. Furthermore, we carry out the numerical analysis of the fully discrete approximations of the weak problems, obtained by applying the finite element method for the spatial discretization and a hybrid combination of both implicit and explicit Euler schemes to approximate the time derivatives. For these approximations, error estimate results are proved and, under additional regularity conditions, the linear convergence of the algorithm is deduced.

Finally, we present several numerical simulations in order to show how the algorithms work.

As it can be observed in the simulations of this study, the models proposed here are able to predict the behavior of some surfactants. However, they can not fit the experimental data of all of them. For this reason, we think that an interesting continuation of this work would be to consider more sophisticated models. Our proposal is to deal with a three-dimensional model accounting the surface diffusion.

Moreover, from our point of view, another interesting task would be the study of the adsorption-desorption dynamics onto bubble shaped surfaces since, both in real life and in experiments, the adsorbent surface is not always plane. Furthermore, the inclusion of a convective term in the model could be also an interesting issue.

Acknowledgments

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Resumen

Un tensioactivo ("surfactant" en inglés) es un compuesto químico cuyas moléculas constan de dos partes diferentes: una parte hidrófila y una parte hidrófoba, siendo esta estructura la responsable del comportamiento del tensioactivo en una disolución. Cuando se forma una nueva superficie en una disolución de tensioactivos, las moléculas de estos compuestos tienden a viajar desde el seno de la disolución hasta la superficie y, al hacerlo, provocan una variación de las propiedades superficiales (una de las más importantes es la tensión superficial dinámica). Para una superficie plana, que es la situación que se tiene en cuenta en este trabajo, la tensión superficial es la fuerza que actúa paralelamente a la superficie por unidad de longitud (véase [14]). Esta fuerza es una consecuencia de la atracción hacia el interior, en dirección normal a la superficie, a la que están sometidas las moléculas de la superficie, debido a que éstas tienen una cantidad menor de moléculas vecinas para establecer relaciones intermoleculares que las moléculas que se encuentran en el seno de la disolución (véase [1]). La presencia de moléculas de tensioactivo provoca la ruptura de las conexiones intermoleculares entre las moléculas de la superficie y sus vecinas, de manera que la tensión superficial de la disolución se reduce drásticamente. La tensión superficial dinámica es una propiedad muy importante porque juega un papel fundamental en diferentes procesos biológicos, bioquímicos e industriales como, por ejemplo, en la producción de jabones, en la fabricación de pesticidas, en los procesos de limpieza, en la respiración, en el procesado de alimentos, etc (véanse, e.g., [2, 7, 14, 16, 33, 37]).

La variación de la tensión superficial es un proceso dinámico, es decir, no ocurre de manera instantánea y es necesario que transcurra un cierto tiempo hasta que el sistema alcanza el equilibrio. De hecho, la dinámica del proceso puede variar desde unos pocos segundos hasta horas o incluso días, dependiendo del tipo de tensioactivo, de su concentración, su temperatura, su salinidad, etc. Sin embargo, en todos los casos, el análisis de la tensión superficial dinámica está ampliamente ligado al estudio del transporte de moléculas desde el seno de la disolución hasta la superficie, que tiene lugar mediante dos mecanismos diferentes: la difusión y la adsorción-desorción. Para entender el proceso es importante tener en cuenta la capa llamada "subsuperficie" (véase la Figura B.1), una frontera imaginaria situada a unos pocos diámetros moleculares por debajo de la superficie y que separa la región en donde sólo tiene lugar la difusión del dominio en el que se lleva a cabo la adsorción-desorción. Las moléculas de tensioactivo difunden desde el seno de la disolución hasta la subsuperficie y, una vez en la subsuperficie, son adsorbidas a la superficie. Sin embargo, a medida que la superficie se va llenando, los lugares vacantes en ella disminuyen y puede ocurrir que las moléculas no encuentren un sitio libre para posicionarse en la misma. En este caso, las moléculas desorben a la subsuperficie y vuelven de nuevo al seno de la disolución. Existen dos familias de modelos para describir la dinámica de adsorción-desorción (véanse [7, 16]):

- **Modelos controlados por difusión**. Este tipo de modelos asumen que la escala de tiempo necesaria para alcanzar el equilibrio entre la superficie y la subsuperficie es mucho menor que la escala de tiempo necesaria para el proceso difusivo.

- **Modelos cinético mixtos**. Estos modelos suponen que la escala de tiempo necesaria para el proceso de adsorción-desorción es comparable a la escala de tiempo necesaria para la difusión.

Experimentalmente, las mediciones de la tensión superficial de una disolución se realizan con unos aparatos llamados tensiómetros. Existe una gran variedad de tensiómetros y se pueden clasificar en: métodos de fuerza, métodos de forma, métodos de presión y otros métodos (véase [7]). Algunos miden la tensión superficial sobre una superficie plana, otros sobre una superficie esférica y otros sobre superficies con forma de burbuja,

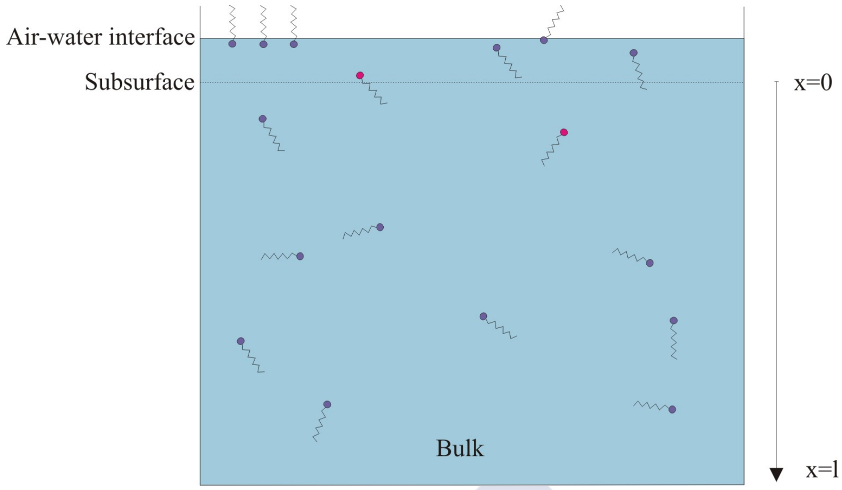

Figure B.1: Interfase aire-agua y localización de la subsuperficie.

pero que no es totalmente esférica. La elección óptima del método de medida depende de la escala de tiempo necesaria para que la disolución alcance el equilibrio. Todos los datos experimentales que se muestran en esta tesis han sido obtenidos con el método de placa de Wilhelmy (véase [1]). Este método consiste en medir la fuerza ejercida en una placa fina que está supendida de un brazo de una balanza y que está orientada perpendicularmente a la superficie. La placa se sumerge parcialmente en la disolución y, o bien el tensiómetro o bien una microbalanza, mide la fuerza ejercida en la placa debido a su humidificación. La tensión superficial se calcula a través de esta fuerza usando la ecuación de Wilhelmy (véase [7]).

El objetivo de esta tesis es llevar a cabo el análisis matemático del problema que concierne a disoluciones de tensioactivos en una superficie aire-agua plana. Desde el punto de vista matemático, este proceso dinámico es modelado por la ecuación en derivadas parciales de difusión en una dimensión espacial, junto con condiciones de contorno e iniciales adecuadas. Con el fin de introducir el sistema de ecuaciones que modela el proceso, denotemos por x la distancia desde la subsuperficie, y por $c(t, x)$ la concentración de tensioactivo en el instante $t \in [0, T]$ y en el punto $x \in [0, l]$. La frontera $x = 0$ del intervalo espacial se corresponde con la localización de la subsuperficie. Denotando por $\Gamma(t)$ la concentración superficial, que depende del tiempo, tenemos la siguiente formulación del problema (véanse [7, 35]):

$$\frac{\partial c}{\partial t}(t,x) - D\,\frac{\partial^2 c}{\partial x^2}(t,x) = 0, \qquad t \in (0,T), \quad x \in (0,l), \tag{B.1}$$

con las condiciones de contorno:

$$D\,\frac{\partial c}{\partial x}(t,0) = \frac{d\Gamma}{dt}(t), \quad t > 0, \tag{B.2}$$

$$c(t,l) = c_b, \quad t > 0, \tag{B.3}$$

y las condiciones iniciales:

$$c(0,x) = c_0(x), \quad x \in (0,l), \tag{B.4}$$

$$\Gamma(0) = \Gamma_0. \tag{B.5}$$

En el sistema de ecuaciones previo, D y c_b son dos constantes positivas que denotan el coeficiente de difusión y la concentración en el seno de la disolución, respectivamente. Además, $c_0(x)$ es una función definida en $[0,l]$, que es igual a c_b en $x = l$, y Γ_0 es una constante no negativa que denota la concentración superficial en el instante inicial.

De esta forma, el transporte de moléculas desde el seno de la disolución hasta la superficie se modela por las ecuaciones (B.1)-(B.5). La ecuación (B.1), que describe la difusión en el seno de la disolución considerando una longitud de difusión finita, se obtiene a partir de la ecuación de transporte despreciando el término convectivo ya que, en este estudio, estamos trabajando con disoluciones quiescentes. La condición de contorno (B.2) describe el flujo de tensioactivos desde la subsuperficie hasta la superficie (adsorción) y viceversa, desde la superficie hasta la subsuperficie (desorción). Además, asumimos que la frontera $x = l$ se mantiene a una concentración constante igual a c_b, por lo que se impone una condición de tipo Dirichlet no homogénea, dada por la expresión (B.3), en el extremo derecho del intervalo espacial. En cuanto a las condiciones iniciales, asumimos que, al principio del proceso, la concentración superficial es igual a Γ_0 y que la concentración en la disolución viene dada por la función $c_0(x)$,

$x \in [0, l]$. Por lo tanto, dados D, c_b, l, T, $c_0(x)$ y Γ_0, el problema consiste en encontrar tanto la concentración en la disolución, c, como la concentración en la superficie, Γ.

Como la concentración superficial, Γ, es una incógnita del probema, necesitamos añadir una condición adicional para cerrar el sistema. En este sentido, la condición adicional, que se acopla al sistema de ecuaciones (B.1)-(B.5) a través de la condición de contorno en la subsuperficie, viene dada por el modelo de adsorción-desorción. Por tanto, se debe utilizar el modelo controlado por difusión o bien el modelo cinético mixto. Cuando se considera un modelo controlado por difusión, una ecuación llamada *isoterma de adsorción* establece la relación entre las concentraciones de superficie y subsuperficie. Las isotermas más estudiadas en la literatura son:

- *Isoterma de Henry:* asume una dependencia lineal entre las concentraciones de superficie y subsurperficie:

$$\Gamma(t) = K_H \, c(t, 0), \qquad t \geq 0, \tag{B.6}$$

  siendo K_H la constante de adsorción de Henry.

- *Isoterma de Langmuir:* supone que la dependencia entre ambas concentraciones es no lineal:

$$\Gamma(t) = \Gamma_m \frac{K_L \, c(t, 0)}{1 + K_L \, c(t, 0)}, \qquad t \geq 0, \tag{B.7}$$

  siendo Γ_m y K_L la concentración superficial máxima y la constante de adsorción de Langmuir, respectivamente.

- *Isoterma de Frumkin:* al igual que la isoterma de Langmuir, establece una dependencia no lineal entre las concentraciones de superficie y subsuperficie:

$$\Gamma(t) = \Gamma_m \frac{K_F \, c(t, 0)}{e^{-A \frac{\Gamma(t)}{\Gamma_m}} + K_F \, c(t, 0)}, \qquad t \geq 0, \tag{B.8}$$

  donde K_F es la constante de adsorción de Frumkin y A es un parámetro que indica si la adsorción es anticooperativa; es decir, si la adsorción se hace más difícil a medida que incrementa la cobertura de la superficie.

Si, por el contrario, consideramos un modelo cinético mixto para describir el mecanismo de adsorción-desorción, entonces una ecuación cinética relaciona la tasa de cambio de la concentración superficial con el balance entre las tasas de adsorción y desorción. Las expresiones más conocidas son:

- *Modelo cinético lineal:* asume que la tasa de adsorción es proporcional a la concentración subsuperficial mientras que la tasa de desorción es proporcional a la concentración superficial:

$$\frac{d\,\Gamma}{dt}(t) = k_H^a\, c(t,0) - k_H^d\, \Gamma(t), \qquad t > 0, \tag{B.9}$$

  donde k_H^a y k_H^d son las constantes de adsorción y desorción, respectivamente.

- *Modelo de Langmuir-Hinshelwood:* supone que la tasa de adsorción depende de, además de la concentración en la subsuperficie, del espacio vacío que hay en la superficie:

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big) - k_L^d\, \Gamma(t), \qquad t > 0, \tag{B.10}$$

  siendo k_L^a y k_L^d las constantes de adsorción y desorción para el modelo de Langmuir-Hinshelwood, respectivamente.

- *Modelo de Langmuir-Hinshelwood modificado:* se trata de una modificación del modelo anterior, que fue propuesta en 1992 por C.H. Chang y E.I. Franses (véase [6]), debido a que la ecuación de Langmuir-Hinshelwood no era capaz de ajustar el comportamiento de algunos tensioactivos:

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(t,0)\Big(1 - \frac{\Gamma(t)}{\Gamma_m}\Big)e^{-B\frac{\Gamma(t)}{\Gamma_m}} - k_L^d\, \Gamma(t)e^{-B\frac{\Gamma(t)}{\Gamma_m}}, \qquad t > 0, \tag{B.11}$$

  donde la constante real B es un parámetro empírico. Nótese que, en el caso de que B sea igual a cero, la expresión anterior se reduce a la ecuación de Langmuir-Hinshelwood.

En la literatura química se pueden encontrar numerosas publicaciones en las que se resuelven numéricamente este tipo de problemas. Además, el trabajo realizado por

Ward y Tordai, véase [45], fue el pionero en llevar a cabo una investigación matemática centrada en la obtención de soluciones analíticas, usando la técnica de la transformada de Laplace, para el modelo controlado por difusión considerado tanto en una superficie plana como con una longitud de difusión infinita. Sin embargo, la teoría de Ward y Tordai no se puede aplicar siempre ya que sus soluciones proporcionan la concentración superficial en términos de una integral temporal sobre la concentración en la subsuperficie, y esta concentración depende de los modelos de difusión y adsorción. Por este motivo, se obtuvieron aproximaciones de estas soluciones para tiempos cortos y largos. En nuestra opinión, ninguno de los trabajos presentados hasta el momento han tratado el análisis matemático del problema. Por lo tanto, la contribución principal de esta tesis, con respecto a las publicaciones existentes, es que nosotros hemos llevado a cabo un estudio matemático de un problema de difusión que incluye una condición de contorno dinámica.

A continuación, hacemos un resumen de los capítulos que forman parte de esta tesis, llevada a cabo en la Universidad de Santiago de Compostela bajo la supervisión de los profesores José Ramón Fernández García y María del Carmen Muñiz Castiñeira.

Capítulo 1: Modelo cinético mixto para la isoterma de Henry

En este capítulo se tiene en cuenta el modelo formado por el sistema de ecuaciones (B.1)-(B.5) y (B.9). El estudio desarrollado para este problema consiste en el planteamiento de su formulación variacional y la demostración de existencia y unicidad de solución débil, para lo que se utilizan técnicas de punto fijo.

Por otra parte, también se lleva a cabo el análisis numérico de una aproximación totalmente discretizada del problema débil. Dicha aproximación se obtiene aplicando el método de elementos finitos para aproximar la variable espacial y una combinación híbrida de los esquemas de Euler implícito y explícito para la discretización de las derivadas temporales. Para este problema se obtiene una estimación a priori del error y, bajo ciertas hipótesis de regularidad adicional, se prueba la convergencia lineal del algoritmo.

Por último, presentamos varias simulaciones numéricas para mostrar la precisión del algoritmo y su comportamiento para el hexanol y el heptanol.

Indicamos que el trabajo presentado en este capítulo ha dado lugar a los artículos [20] y [22].

Capítulo 2: Modelo controlado por difusión con la isoterma de Langmuir

En este segundo capítulo nos centramos en el análisis del problema de difusión acoplado al modelo de adsorción-desorción dado por la isoterma de Langmuir. Se trata de un problema parabólico no estándar puesto que, el acoplamiento de la condición de contorno en la subsuperficie con la isoterma de Langmuir, hace que el sistema sea no lineal. Para este problema, planteamos su formulación variacional y probamos la existencia y unicidad de solución débil. La existencia se demuestra usando el método de Rothe, un problema intermedio, estimaciones a priori y el paso al límite. La unicidad se prueba usando algunos argumentos que ya han sido introducidos en [25].

Además, se analiza un problema semidiscretizado en tiempo asociado al problema débil y se prueban algunas estimaciones a priori de las que se deduce la convergencia lineal del algoritmo bajo unas condiciones de regularidad adicionales. También se tiene en cuenta una aproximación totalmente discreta del problema débil, obtenida usando el método de elementos finitos para la discretización en espacio y una combinación híbrida de los esquemas de Euler progresivo y regresivo para aproximar las derivadas temporales. Se obtiene un resultado de estimación de error y, añadiendo ciertas hipótesis de regularidad, se deduce que el algoritmo converge linealmente.

Por último, presentamos tres ejemplos. El primero de ellos es un ejemplo test en el que se muestra la convergencia lineal probada teóricamente. Los otros dos ejemplos son simulaciones de tensioactivos comerciales: propanol y sodium dodecylsulfate.

El trabajo introducido en el Capítulo 2 ha sido recogido en los artículos [11] y [21].

Capítulo 3: Modelo cinético mixto con la ecuación de Langmuir-Hinshelwood

En este último capítulo, tenemos en cuenta dos modelos cinético mixtos para modelar la dinámica de adsorción-desorción. En primer lugar se tiene en cuenta la ecuación de Langmuir-Hinshelwood y, a continuación, la modificación de esta ecuación propuesta por C.H. Chang y E.I. Franses en 1992. Físicamente, la diferencia entre estos dos modelos y el modelo presentado en el primer capítulo (que también pertenece a la familia de los modelos cinético mixtos) radica en la descripción de la dinámica de adsorción. De hecho, en el caso de la expresión cinética lineal considerada en el Capítulo 1, la variación de la adsorción sólo depende de la concentración en la subsuperficie; sin embargo, en los modelos presentados aquí, ésta depende también de la fracción de espacio vacío que haya en la superficie. Además, la ecuación modificada de Langmuir-Hinshelwood asume una deceleración más pronunciada de la variación de adsorción que la ecuación de Langmuir-Hinshelwood clásica a medida que la cobertura de la superficie incrementa (véase [7]).

El análisis matemático presentado en este último capítulo ha sido publicado en [23] y [24].

En este trabajo, todos los algoritmos que hemos utilizado han sido programados en MATLAB. Además, para probar el buen funcionamiento de nuestros algoritmos, hemos comparado algunos resultados obtenidos con ellos con los resultados proporcionados por el software comercial COMSOL Multiphysics para las mismas simulaciones.

Conclusiones y trabajo futuro

En esta tesis hemos estudiado algunos modelos matemáticos para describir el comportamiento de los tensioactivos en una superficie aire-agua plana. Este problema ha sido modelado a través de un sistema no lineal, formado por la ecuación de difusión en una dimensión espacial, junto con las condiciones de contorno e iniciales adecuadas. Además, para cerrar el problema, es necesario acoplar este sistema con el modelo de adsorción-desorción correspondiente por medio de la condición de contorno en la subsurperficie. Por lo tanto, los modelos que se han considerado en este trabajo sólo se diferencian en la condición de contorno en la subsuperficie, la cual determina la novedad del estudio.

En los Capítulos 1 y 3 de esta tesis hemos trabajado con modelos cinético mixtos para describir la dinámica de adsorción-desorción. En el primer capítulo, hemos tenido en cuenta la ecuación cinética lineal, mientras que en el tercer capítulo hemos introducido tanto el modelo de Langmuir-Hinshelwood, como una de sus modificaciones.

Por el contrario, en el Capítulo 2 hemos presentado un modelo controlado por difusión, usando la isoterma de Langmuir. La diferencia física entre este modelo y los considerados en los otros dos capítulos es que, mientras que en este caso el proceso de adsorción-desorción se asume que ocurre de manera inmediata, los otros modelos suponen que los procesos de adsorción-desorción y el de difusión necesitan una escala de tiempo parecida para desarrollarse.

Para todos los modelos estudiados en este trabajo, se propone una formulación variacional del problema y se proporcionan resultados de existencia y unicidad de solución débil. Además, se lleva a cabo un análisis numérico teniendo en cuenta aproximaciones totalmente discretas de los problemas débiles, obtenidas aplicando el método de elementos finitos para la discretización en espacio y una combinación híbrida de los métodos de Euler progresivo y regresivo para la aproximación de las derivadas temporales. Para estas aproximaciones, se prueban resultados de estimación del error y, bajo ciertas hipótesis de regularidad adicional, se deduce la convergencia lineal del algoritmo. Por último, hemos presentado diversas simulaciones numéricas con el fin de mostrar la precisión de los algoritmos y su comportamiento para distintos tensioactivos comerciales.

Como se puede observar en las simulaciones presentadas en este estudio, los modelos expuestos aquí son capaces de predecir el comportamiento de varios tensioactivos. Sin embargo, no pueden ajustar los datos experimentales de todos ellos. Por esta razón, creemos que una buena continuación del trabajo sería considerar modelos más sofisticados. Nuestra propuesta es tener en cuenta un modelo tridimensional que describa el transporte de moléculas desde el seno de la disolución hasta la superficie como lo hacen los modelos unidimensionales contemplados en este trabajo (mediante mecanismos de difusión y adsorción-desorción), pero que tenga en cuenta además la difusión superficial, es decir, que incluya la descripción del transporte de moléculas dentro de la superficie mediante difusión.

Por otra parte, bajo nuestro punto de vista, otra tarea interesante sería el estudio de la dinámica de adsorción-desorción sobre superficies con forma de burbuja ya que, tanto en la vida real como en los experimentos, la superficie adsorbente no es siempre plana. Como ya ha sido expuesto en [46], la forma de la burbuja en la que tiene lugar la adsorción juega un papel importante en el estudio de la tensión superficial dinámica. Además, en algunas disoluciones de tensioactivos se ha observado la existencia de movimientos del fluido en el seno de la disolución (véase [36]) y, por eso, la inclusión de un término convectivo en el modelo podría ser también una cuestión de interés.

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