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ORIGINAL PAPER

Numerical analysis of surfactant dynamics at air-water interface using the Henry isotherm

J. R. Fernández · M. C. Muñiz

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Abstract This paper focuses on the surfactant behavior at air-water interface, taking into account the diffusion-controlled model together with the Henry isotherm to model the relation between the surface and the subsurface concentrations. The existence and uniqueness of a weak solution is stated. Fully discrete approximations are obtained by using a finite element method and the backward Euler scheme. Error estimates are then proved from which, under adequate additional regularity conditions, the linear convergence of the algorithm is derived. Finally, some numerical simulations are presented in order to demonstrate the accuracy of the algorithm and the behavior of the solution.

Keywords Henry isotherm · Surfactant · Surface concentration · Surface tension · Finite element approximation · Error estimates · Numerical simulations

1 Introduction

A huge amount of chemical literature has reported the importance of the dynamic surface tension behavior of surfactants at the air-water interface in several areas such

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J. R. Fernández
Departamento de Matemática Aplicada I, Universidade de Vigo, ETSI Telecomunicación,
Campus As Lagoas Marcosende s/n, 36310 Vigo, Spain
e-mail: jose.fernandez@uvigo.es

M. C. Muñiz (✉)
Facultade de Matemáticas, Departamento de Matemática Aplicada, Universidade de Santiago de Compostela, Campus Sur s/n, 15782 Santiago de Compostela, Spain
e-mail: mcarmen.muniz@usc.es

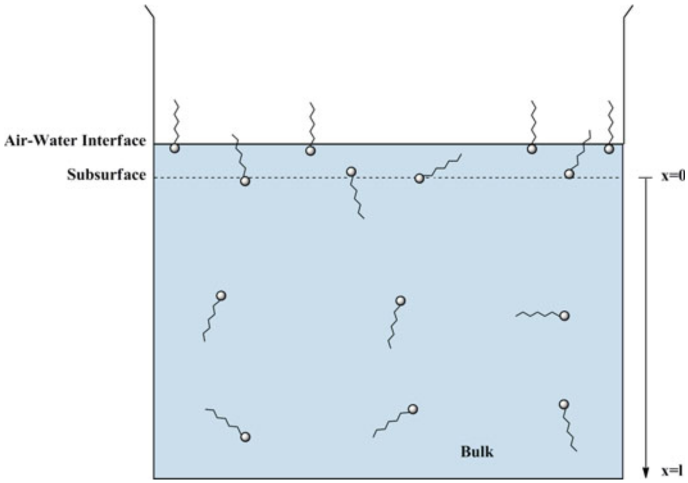

Fig. 1 Air-water interface and location of the subsurface

as biochemistry, medicine, agrochemistry, metallurgy, food processing and so on (see [1,4,5,8,12,14]). When a new surface is formed, the surfactant molecules tend to migrate to the interface in order to reduce its surface tension. This dynamic process may vary depending on the type of surfactant and its concentration ranging from milliseconds to several hours in order to reach its equilibrium. The analysis of the dynamic surface tension is then closely related to molecules transport and adsorption from the bulk of the solution to the interface and vice versa; that is to say, desorption from the surface and back diffusion into the bulk.

In order to get an insight into the physics of the whole process, it is important to take into account the so-called *subsurface* (see Fig. 1 and [1,4]), located a few molecular diameters below the interface, being the boundary between the domain where only diffusion takes place and the region in which only adsorption-desorption occurs. In this context, there are two models for describing adsorption dynamics:

- The *diffusion-controlled model* in which the timescale for equilibration of the surface and subsurface is very fast compared to the timescale for diffusion. In this case, a thermodynamic adsorption isotherm establishes a relationship between the concentration of the surface and the subsurface during the process.
- The *mixed kinetic-diffusion model* in which the adsorption-desorption timescale is comparable to the diffusion one. In this case, a kinetic expression identifies the rate of change of the surface concentration with the balance between adsorption and desorption rates.

From the mathematical point of view, the process is modeled by the diffusion partial differential equation in one spatial dimension, coupled with the corresponding adsorption model by means of the boundary condition at the subsurface, the unknowns being the concentration in the bulk and the surface concentration. To our knowledge, considering the aforementioned adsorption dynamics models yields to non-standard boundary conditions worthy of being analyzed from a theoretical point of view. In this paper, we are concerned with the modeling and numerical analysis of the diffusion problem for the diffusion-controlled model considering the so-called Henry isotherm described below.

The outline of the paper is as follows. In Sect. 2 we describe some of the most well-known mathematical models regarding surfactant dynamics at air-water interface. Then, in Sect. 3 we introduce the variational formulation of the problem for which an existence and uniqueness result is recalled. Fully discrete approximations are introduced in Sect. 4 by using a finite element method and the implicit Euler scheme for the spatial and time discretizations, respectively. An error estimate result is proved, from which the linear convergence is deduced under suitable regularity assumptions. Finally, in Sect. 5 some numerical examples are shown to demonstrate the accuracy of the algorithm and the behavior of the solution.

2 Statement of the problem. Mathematical modeling

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

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

together with the boundary conditions:

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

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

In Eqs. (1)–(3), D is the diffusion coefficient and the positive constant c_b is the bulk concentration. We remark that Γ actually becomes an unknown of the system and so, either the diffusion-controlled model or the mixed kinetic-diffusion one has to be considered in order to state the problem together with suitable initial conditions.

2.1 Diffusion-controlled model

When considering this model, a thermodynamic adsorption isotherm states the dependence between $\Gamma(t)$ and $c(0,t)$. Two of the isotherms studied in the literature are (see [4,12]):

– *The Henry isotherm*: it is the simplest one and it defines a linear dependence between the subsurface and surface concentrations,

$$\Gamma(t) = K_H\, c(0,t), \quad t \geq 0, \tag{4}$$

K_H being the Henry equilibrium adsorption constant.

– *The Langmuir isotherm*: it is commonly used and it defines a nonlinear dependence between the subsurface and surface concentrations,

$$\Gamma(t) = \Gamma_m \frac{K_L\, c(0,t)}{1 + K_L\, c(0,t)}, \quad t \geq 0, \tag{5}$$

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

2.2 Mixed kinetic-diffusion model

In this model, the equilibrium between the surface and the subsurface is not instantaneous and it is assumed that the surfactant has to whether undergo a potential energetic barrier, to evolve in a correct orientation or to look for an empty space at the surface. The kinetic expression modeling this behavior becomes

$$\frac{d\,\Gamma}{dt} = r_{ads} - r_{des}, \tag{6}$$

where r_{ads}, r_{des} are the adsorption and desorption rates, respectively. It is necessary to know the equilibrium adsorption isotherm of the surfactant in order to use a specific kinetic equation. We describe below two of the kinetic relations most studied in the literature (see [1]):

– *Linear kinetic model*: the rate of adsorption is proportional to the subsurface concentration meanwhile the rate of desorption is proportional to the surface concentration, thus Eq. (6) reads

$$\frac{d\,\Gamma}{dt}(t) = k_H^a\, c(0,t) - k_H^d\, \Gamma(t), \tag{7}$$

where k_H^a and k_H^d are the adsorption and desorption constants, respectively. At equilibrium or steady-state, $d\,\Gamma/dt = 0$ and from Eq. (7) the Henry isotherm (4) is recovered with $K_H = k_H^a/k_H^d$.

– *Langmuir-Hinshelwood kinetic model*: here, the rate of adsorption is proportional to the fraction of empty space at the surface

$$\frac{d\,\Gamma}{dt}(t) = k_L^a\, c(0,t)\left(1 - \frac{\Gamma(t)}{\Gamma_m}\right) - k_L^d\, \Gamma(t), \tag{8}$$

where k_L^a and k_L^d are the adsorption and desorption constants for this kinetic model, respectively. At equilibrium or steady-state, $d\,\Gamma/dt = 0$ and from Eq. (8) the Langmuir isotherm (5) is recovered with $K_L = k_L^a/(k_L^d\, \Gamma_m)$.

The work of Ward and Tordai (see [14]) pioneered a mathematical research concerned in achieving analytical solutions for the diffusion controlled model, with the

Henry isotherm, and for the linear kinetic model and then, obtaining approximations for long and short times (see [7,13]). Regarding the nonlinear isotherms, in [10] a solution is given in terms of power series, in the square root of time, for Langmuir and Freundlich isotherms and, in general, for the nonlinear problems, numerical methods were used to approximate their solutions (see [11]). However, to our knowledge, their numerical analysis is nowadays an open problem.

3 Weak formulation of the diffusion-controlled model for the Henry isotherm

We are here concerned in analysing problem (1)–(3) together with the Henry isotherm (4) and the following initial conditions:

$$\Gamma(0) = \Gamma_0, \tag{9}$$

$$c(x, 0) = c_0(x), \quad x \in (0, l), \tag{10}$$

where Γ_0 is the initial surface concentration and $c_0(x)$ is a continuous function in $[0, l]$ being equal to Γ_0/K_H and c_b on $x = 0$ and $x = l$, respectively.

Note that if $\Gamma_0 = c_b K_H$ and $c_0(x) = c_b$ then the constant functions $c(x, t) = c_b$ and $\Gamma(t) = \Gamma_0$ are solutions to problem (1)–(4), (9)–(10). We are interested in problems where

$$\Gamma_0 < c_b K_H. \tag{11}$$

Furthermore, in order to obtain homogeneous boundary conditions, with no loss of generality, we assume hereafter that $c_b = 0$ and Γ_0 is negative.

Multiplying Eq. (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. $t \in [0, T]$,

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

Using Eq. (4), we find that, for a.e. $t \in [0, T]$,

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

Let V be the Hilbert space

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

endowed with the inner product

$$((v, w)) = \int_0^l \frac{\partial v}{\partial x}\frac{\partial w}{\partial x} dx,$$

and the associated norm $\|v\| = ((v, v))^{1/2}$. We denote by $\gamma_0 : H^1(0, l) \to \mathbb{R}$ the trace operator on $x = 0$. Furthermore, we recall the inner product in $H = L^2(0, l)$

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

with associated norm $\|v\|_H = (v, v)_H^{1/2}$. Besides, we use the classical notation for the space $H^1(0, T; V)$, we denote the time derivative by a dot above and we now state the weak formulation of the problem (1)–(4), (9)–(10).

Problem P. Find a function $c : [0, T] \to V$ such that

$$(\dot{c}(t), v)_H + D((c, v)) + K_H \gamma_0(\dot{c})\, \gamma_0(v) = 0, \quad \forall v \in V, \quad \text{a.e. } t \in (0, T), \quad (12)$$

$$c(0) = c_0. \quad (13)$$

Here, we remark that Banach fixed-point arguments similar to those employed in [6] can not be used here to obtain the existence, uniqueness and regularity of weak solutions to the previous problem. Furthermore, the existence and uniqueness of solution is based on the theory of pseudomonotone operators and it is directly obtained applying the abstract theorem provided in [9].

Theorem 1 *Let c_b be zero and K_H, D two positive constants. If $c_0 \in V$, $\gamma_0(c_0) = \Gamma_0/K_H$ and assumption (11) holds, then there exists a unique solution to a weaker formulation of problem (12)–(13) with regularity:*

$$c \in L^2(0, T; V), \quad \dot{c} \in L^2(0, T; V').$$

4 Fully discrete approximations: numerical analysis

We now consider a fully discrete approximation of problem (12)–(13), taking into account a finite-dimensional space $V^h \subset V$ to approximate the space V, obtained, for instance, by a finite element method. Here, $h > 0$ denotes the spatial discretization parameter. Besides, we consider a partition of the time interval $[0, T]$, denoted by $0 = t_0 < t_1 < \cdots < t_N = T$. 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 $n = 0, 1, \ldots, N$. 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 the backward Euler scheme, the fully discrete approximations are considered as follows.

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

$$c_0^{hk} = c_0^h, \tag{14}$$

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

$$\left(\delta c_n^{hk}, v^h\right)_H + D\left(\left(c_n^{hk}, v^h\right)\right) + K_H\, \gamma_0\left(\delta c_n^{hk}\right)\gamma_0\left(v^h\right) = 0, \tag{15}$$

where c_0^h is an appropriate approximation of the initial condition c_0.

Under the assumptions of Theorem 1 and using Lax-Milgram theorem, we easily deduce the existence of a unique discrete solution to problem (14)–(15). First, we are interested, for a known $c_{n-1}^{hk} \in V^h$, in the behavior of $c_n^{hk} \in V^h$.

Proposition 1 *Under the assumptions of* Theorem 1*, if c_{n-1}^{hk} and c_n^{hk} are two consecutive solutions to* Eq. (15)*, then it follows that*

$$\left\|c_n^{hk}\right\| \le \left\|c_{n-1}^{hk}\right\|. \tag{16}$$

Proof Taking $v^h = c_n^{hk} - c_{n-1}^{hk} \in V^h$ as a test function in Eq. (15), taking into account the linearity of the trace operator, we get

$$\int_0^l \left(c_n^{hk} - c_{n-1}^{hk}\right)^2 dx + k\,D \int_0^l \frac{\partial c_n^{hk}}{\partial x} \frac{\partial\left(c_n^{hk} - c_{n-1}^{hk}\right)}{\partial x}\,dx$$
$$+K_H\,\left(\gamma_0\left(c_n^{hk}\right) - \gamma_0\left(c_{n-1}^{hk}\right)\right)^2 = 0. \tag{17}$$

On the other hand, we remark the property of the convex function $z \to z^2$ that, for a fixed $b \in \mathbb{R}$, it holds

$$\forall z \in \mathbb{R}, \quad z^2 \ge b^2 + 2b(z - b).$$

Therefore, we have

$$\forall z \in \mathbb{R}, \quad \frac{b^2}{2} - \frac{z^2}{2} \le b(b - z). \tag{18}$$

Taking $b = \frac{\partial c_n^{hk}}{\partial x}$ and $z = \frac{\partial c_{n-1}^{hk}}{\partial x}$ we obtain

$$\frac{1}{2}\left(\frac{\partial c_n^{hk}}{\partial x}\right)^2 - \frac{1}{2}\left(\frac{\partial c_{n-1}^{hk}}{\partial x}\right)^2 \le \frac{\partial c_n^{hk}}{\partial x}\frac{\partial\left(c_n^{hk} - c_{n-1}^{hk}\right)}{\partial x},$$

and then Eq. (17) yields to

$$\int_0^l \left(c_n^{hk} - c_{n-1}^{hk}\right)^2 dx + k\,\frac{D}{2} \int_0^l \left(\frac{\partial c_n^{hk}}{\partial x}\right)^2 dx + K_H \left(\gamma_0\left(c_n^{hk}\right) - \gamma_0\left(c_{n-1}^{hk}\right)\right)^2$$
$$\leq k\,\frac{D}{2} \int_0^l \left(\frac{\partial c_{n-1}^{hk}}{\partial x}\right)^2 dx. \tag{19}$$

Since the first and the third terms of the latter expression are nonnegative, we obtain the result. □

Proposition 2 *Under the assumptions of* Theorem 1, *if c_{n-1}^{hk} and c_n^{hk} are two consecutive solutions to* (15), *then for $\mathfrak{C}_n := \int_0^l (c_n^{hk})^2 dx + K_H\,(\gamma_0(c_n^{hk}))^2$, it holds*

$$\mathfrak{C}_n \leq \mathfrak{C}_{n-1}. \tag{20}$$

Proof Taking $v^h = c_n^{hk} \in V^h$ as a test function in (15), we get

$$\int_0^l \left(c_n^{hk} - c_{n-1}^{hk}\right) c_n^{hk}\, dx + k\,D \int_0^l \left(\frac{\partial c_n^{hk}}{\partial x}\right)^2 dx$$
$$+K_H \left(\gamma_0\left(c_n^{hk}\right) - \gamma_0\left(c_{n-1}^{hk}\right)\right) \gamma_0\left(c_n^{hk}\right) = 0. \tag{21}$$

Using Eq. (18) with both $b = c_n^{hk}$, $z = c_{n-1}^{hk}$ and $b = \gamma_0(c_n^{hk})$, $z = \gamma_0(c_{n-1}^{hk})$, we get

$$\frac{\mathfrak{C}_n}{2} + k\,D \int_0^l \left(\frac{\partial c_n^{hk}}{\partial x}\right)^2 dx \leq \frac{\mathfrak{C}_{n-1}}{2}. \tag{22}$$

Since all the terms of the latter expression are nonnegative, we obtain the desired result. □

Corollary 1 *Under the assumptions of* Theorem 1, *the sequence $\{\mathfrak{C}_n\}_{n=0}^{\infty}$ is convergent with limit $\ell \geq 0$.*

Proof From Proposition 2 we find that $\{\mathfrak{C}_n\}_{n=0}^{\infty}$ is a monotone and bounded sequence of nonnegative real numbers, thus the result follows. □

Corollary 2 *Under the assumptions of* Theorem 1, *the sequence $\{\|c_n^{hk}\|\}_{n=0}^{\infty}$ is convergent with limit $\tilde{\ell} = 0$.*

Proof From Proposition 1 we get that $\{\|c_n^{hk}\|\}_{n=0}^{\infty}$ is a monotone and bounded sequence of nonnegative real numbers, thus it is convergent to a limit $\tilde{\ell} \geq 0$. Moreover, from Proposition 2 and Corollary 1, passing to the limit in estimate (22), it follows that

$$\ell + 2\,k\,D\,\tilde{\ell} \leq \ell. \tag{23}$$

Since both k and D are positive constants, we deduce that $\tilde{\ell}$ is zero. □

In the sequel, we will derive an error estimate for the difference $c_n - c_n^{hk}$. We assume the following regularity condition:

$$c \in C^1([0, T]; V). \tag{24}$$

Taking $v = c_n - v^h \in V$ in Eq. (12) at time $t = t_n$, we find that, for $n = 1, 2, \ldots, N$ and $v^h \in V^h$,

$$(\dot{c}_n, c_n - v^h)_H + D\,((c_n, c_n - v^h)) + K_H\,\gamma_0(\dot{c}_n)\,\gamma_0(c_n - v^h) = 0. \tag{25}$$

Thus, taking $v^h = c_n^{hk}$ in Eq. (25), it follows that

$$(\dot{c}_n, c_n - c_n^{hk})_H + D\,((c_n, c_n - c_n^{hk})) + K_H\,\gamma_0(\dot{c}_n)\,\gamma_0(c_n - c_n^{hk}) = 0. \tag{26}$$

On the other hand, using Eq. (15) we have, for all $v^h \in V^h$,

$$\begin{aligned}(\delta c_n^{hk}, c_n - c_n^{hk})_H &+ D\,((c_n^{hk}, c_n - c_n^{hk})) + K_H\,\gamma_0(\delta c_n^{hk})\,\gamma_0(c_n - c_n^{hk})\\ &= (\delta c_n^{hk}, c_n - v^h)_H + D\,((c_n^{hk}, c_n - v^h)) + K_H\,\gamma_0(\delta c_n^{hk})\,\gamma_0((c_n - v^h).\end{aligned} \tag{27}$$

Subtracting now Eqs. (26) and (27) and taking into account the linearity of the trace operator, we obtain, for all $v^h \in V^h$

$$\begin{aligned}(\dot{c}_n - \delta c_n^{hk}, c_n - c_n^{hk})_H &+ D\,\|c_n - c_n^{hk}\|^2 + K_H\,\gamma_0(\dot{c}_n - \delta c_n^{hk})\,\gamma_0(c_n - c_n^{hk})\\ &= (-\delta c_n^{hk}, c_n - v^h)_H - D\,((c_n^{hk}, c_n - v^h)) - K_H\,\gamma_0(\delta c_n^{hk})\,\gamma_0(c_n - v^h).\end{aligned} \tag{28}$$

Using Eq. (25), Eq. (28) leads to the following relation,

$$\begin{aligned}(\dot{c}_n - \delta c_n^{hk}, c_n - c_n^{hk})_H &+ D\,\|c_n - c_n^{hk}\|^2 + K_H\,\gamma_0(\dot{c}_n - \delta c_n^{hk})\,\gamma_0(c_n - c_n^{hk})\\ &= (\dot{c}_n - \delta c_n^{hk}, c_n - v^h)_H + D\,((c_n - c_n^{hk}, c_n - v^h))\\ &\quad + K_H\,\gamma_0(\dot{c}_n - \delta c_n^{hk})\,\gamma_0(c_n - v^h)), \quad \forall v^h \in V^h.\end{aligned}$$

Adding and subtracting δc_n in the first and third terms, we obtain

$$\begin{aligned}(\dot{c}_n - \delta c_n + \delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H + D\,\|c_n - c_n^{hk}\|^2\\ + K_H\,\gamma_0(\dot{c}_n - \delta c_n + \delta c_n - \delta c_n^{hk})\,\gamma_0(c_n - c_n^{hk})\\ = (\dot{c}_n - \delta c_n^{hk}, c_n - v^h)_H + D\,((c_n - c_n^{hk}, c_n - v^h))\\ + K_H\,\gamma_0(\dot{c}_n - \delta c_n^{hk})\,\gamma_0(c_n - v^h), \quad \forall v^h \in V^h,\end{aligned}$$

and therefore,

$$
\begin{aligned}
&(\delta c_n - \delta c_n^{hk}, c_n - c_n^{hk})_H + D\ \|c_n - c_n^{hk}\|^2 + K_H\ \gamma_0(\delta c_n - \delta c_n^{hk})\, \gamma_0(c_n - c_n^{hk}) \\
&\quad = (\dot{c}_n - \delta c_n^{hk}, c_n - v^h)_H + D\ ((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad + K_H\ \gamma_0(\dot{c}_n - \delta c_n^{hk})\, \gamma_0(c_n - v^h) + (\delta c_n - \dot{c}_n, c_n - c_n^{hk})_H \\
&\qquad + K_H\ \gamma_0(\delta c_n - \dot{c}_n)\, \gamma_0(c_n - c_n^{hk}), \quad \forall v^h \in V^h.
\end{aligned} \tag{29}
$$

Moreover, using the following property of the divided differences

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

Eq. (29) reads

$$
\begin{aligned}
&\frac{1}{k}\|c_n - c_n^{hk}\|_H^2 + D\ \|c_n - c_n^{hk}\|^2 + \frac{K_H}{k}|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad = (\dot{c}_n - \delta c_n^{hk}, c_n - v^h)_H + D\ ((c_n - c_n^{hk}, c_n - v^h)) \\
&\qquad + K_H\ \gamma_0(\dot{c}_n - \delta c_n^{hk})\, \gamma_0(c_n - v^h) + (\delta c_n - \dot{c}_n, c_n - c_n^{hk})_H \\
&\qquad + K_H\ \gamma_0(\delta c_n - \dot{c}_n)\, \gamma_0(c_n - c_n^{hk}) + \frac{1}{k}(c_{n-1} - c_{n-1}^{hk}, c_n - c_n^{hk})_H \\
&\qquad + \frac{K_H}{k}\gamma_0(c_{n-1} - c_{n-1}^{hk})\, \gamma_0(c_n - c_n^{hk}), \quad \forall v^h \in V^h.
\end{aligned} \tag{30}
$$

On the other hand, using both Cauchy-Schwarz and Cauchy inequalities, we obtain

$$
\begin{aligned}
&\frac{1}{k}(c_{n-1} - c_{n-1}^{hk}, c_n - c_n^{hk})_H \le \frac{1}{k}\|c_{n-1} - c_{n-1}^{hk}\|_H \|c_n - c_n^{hk}\|_H \\
&\quad \le \frac{1}{2k}\|c_{n-1} - c_{n-1}^{hk}\|_H^2 + \frac{1}{2k}\|c_n - c_n^{hk}\|_H^2, \\
&\frac{K_H}{k}\gamma_0(c_{n-1} - c_{n-1}^{hk})\, \gamma_0(c_n - c_n^{hk}) \\
&\quad \le \frac{K_H}{2k}|\gamma_0(c_{n-1} - c_{n-1}^{hk})|^2 + \frac{K_H}{2k}|\gamma_0(c_n - c_n^{hk})|^2, \\
&((c_n - c_n^{hk}, c_n - v^h)) \le \|c_n - c_n^{hk}\|\ \|c_n - v^h\|, \\
&\quad \le \frac{1}{2}\|c_n - c_n^{hk}\|^2 + \frac{1}{2}\|c_n - v^h\|^2.
\end{aligned}
$$

Thus, Eq. (30) yields

$$
\begin{aligned}
&\frac{1}{2k}\|c_n - c_n^{hk}\|_H^2 + \frac{D}{2}\ \|c_n - c_n^{hk}\|^2 + \frac{K_H}{2k}|\gamma_0(c_n - c_n^{hk})|^2 \\
&\quad \le (\dot{c}_n - \delta c_n^{hk}, c_n - v^h)_H + \frac{D}{2}\|c_n - v^h\|^2
\end{aligned}
$$

$$+K_H\ \gamma_0(\dot{c}_n-\delta c_n^{hk})\,\gamma_0(c_n-v^h)+(\delta c_n-\dot{c}_n,c_n-c_n^{hk})_H$$
$$+K_H\ \gamma_0(\delta c_n-\dot{c}_n)\,\gamma_0(c_n-c_n^{hk})$$
$$+\frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2+\frac{K_H}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2,\quad \forall v^h\in V^h. \tag{31}$$

Since

$$\begin{aligned}(\dot{c}_n-\delta c_n^{hk},c_n-v^h)_H &= (\dot{c}_n-\delta c_n,c_n-v^h)_H\\ &\quad+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H\\ &\le \frac{1}{2}\|\dot{c}_n-\delta c_n\|_H^2+\frac{1}{2}\|c_n-v^h\|_H^2\\ &\quad+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H,\end{aligned}$$

estimate (31) implies that

$$\begin{aligned}&\frac{1}{2k}\|c_n-c_n^{hk}\|_H^2+\frac{D}{2}\ \|c_n-c_n^{hk}\|^2+\frac{K_H}{2k}|\gamma_0(c_n-c_n^{hk})|^2\\ &\le \frac{1}{2}\|\dot{c}_n-\delta c_n\|_H^2+\frac{1}{2}\|c_n-v^h\|_H^2+\frac{D}{2}\|c_n-v^h\|^2\\ &\quad+K_H\ \gamma_0(\dot{c}_n-\delta c_n^{hk})\,\gamma_0(c_n-v^h)+(\delta c_n-\dot{c}_n,c_n-c_n^{hk})_H\\ &\quad+K_H\ \gamma_0(\delta c_n-\dot{c}_n)\,\gamma_0(c_n-c_n^{hk})\\ &\quad+\frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2+\frac{K_H}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\\ &\quad+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H,\quad \forall v^h\in V^h.\end{aligned} \tag{32}$$

An analogous expression holds for the trace operator and thus,

$$\begin{aligned}\gamma_0(\dot{c}_n-\delta c_n^{hk})\,\gamma_0(c_n-v^h) &= \gamma_0(\dot{c}_n-\delta c_n)\,\gamma_0(c_n-v^h)\\ &\quad+\frac{1}{k}\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h)\\ &\le \frac{1}{2}|\gamma_0(\dot{c}_n-\delta c_n)|^2+\frac{1}{2}|\gamma_0(c_n-v^h)|^2\\ &\quad+\frac{1}{k}\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h).\end{aligned}$$

Therefore, estimate (32) yields, for all $v^h\in V^h$,

$$\begin{aligned}&\frac{1}{2k}\|c_n-c_n^{hk}\|_H^2+\frac{D}{2}\ \|c_n-c_n^{hk}\|^2+\frac{K_H}{2k}|\gamma_0(c_n-c_n^{hk})|^2\\ &\le \frac{1}{2}\|\dot{c}_n-\delta c_n\|_H^2+\frac{1}{2}\|c_n-v^h\|_H^2+\frac{D}{2}\|c_n-v^h\|^2\end{aligned}$$

$$
\begin{aligned}
&+\frac{K_H}{2}|\gamma_0(\dot{c}_n-\delta c_n)|^2+\frac{K_H}{2}|\gamma_0(c_n-v^h)|^2+(\delta c_n-\dot{c}_n,c_n-c_n^{hk})_H\\
&+K_H\ \gamma_0(\delta c_n-\dot{c}_n)\,\gamma_0(c_n-c_n^{hk})\\
&+\frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2+\frac{K_H}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\\
&+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H\\
&+\frac{K_H}{k}\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h).
\end{aligned}
\tag{33}
$$

Moreover, by using the inequality

$$
\begin{aligned}
(\delta c_n-\dot{c}_n,c_n-c_n^{hk})_H &\le \|\delta c_n-\dot{c}_n\|_H\|c_n-c_n^{hk}\|_H\\
&\le \frac{1}{2}\|\delta c_n-\dot{c}_n\|_H^2+\frac{1}{2}\|c_n-c_n^{hk}\|_H^2,
\end{aligned}
$$

estimate (33) leads to the following estimate, for all $v^h\in V^h$,

$$
\begin{aligned}
&\frac{1}{2k}\|c_n-c_n^{hk}\|_H^2+\frac{D}{2}\ \|c_n-c_n^{hk}\|^2+\frac{K_H}{2k}|\gamma_0(c_n-c_n^{hk})|^2\\
&\le \|\dot{c}_n-\delta c_n\|_H^2+\frac{1}{2}\|c_n-v^h\|_H^2+\frac{D}{2}\|c_n-v^h\|^2\\
&\quad+\ \frac{K_H}{2}|\gamma_0(\dot{c}_n-\delta c_n)|^2+\frac{K_H}{2}|\gamma_0(c_n-v^h)|^2+\frac{1}{2}\|c_n-c_n^{hk}\|_H^2\\
&\quad+K_H\ \gamma_0(\delta c_n-\dot{c}_n)\,\gamma_0(c_n-c_n^{hk})\\
&\quad+\frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2+\frac{K_H}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\\
&\quad+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H\\
&\quad+\frac{K_H}{k}\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h).
\end{aligned}
\tag{34}
$$

Finally, since we have,

$$
\gamma_0(\delta c_n-\dot{c}_n)\,\gamma_0(c_n-c_n^{hk})\le\frac{1}{2}|\gamma_0(\delta c_n-\dot{c}_n)|^2+\frac{1}{2}|\gamma_0(c_n-c_n^{hk})|^2,
$$

estimate (34) implies that, for all $v^h\in V^h$,

$$
\begin{aligned}
&\frac{1}{2k}\|c_n-c_n^{hk}\|_H^2+\frac{D}{2}\ \|c_n-c_n^{hk}\|^2+\frac{K_H}{2k}|\gamma_0(c_n-c_n^{hk})|^2\\
&\le \|\dot{c}_n-\delta c_n\|_H^2+\frac{1}{2}\|c_n-v^h\|_H^2+\frac{D}{2}\|c_n-v^h\|^2\\
&\quad+\frac{K_H}{2}|\gamma_0(c_n-v^h)|^2+\frac{1}{2}\|c_n-c_n^{hk}\|_H^2
\end{aligned}
$$

$$
\begin{aligned}
&+K_H|\gamma_0(\delta c_n-\dot{c}_n)|^2+\frac{K_H}{2}|\gamma_0(c_n-c_n^{hk})|^2\\
&+\frac{1}{2k}\|c_{n-1}-c_{n-1}^{hk}\|_H^2+\frac{K_H}{2k}|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\\
&+\frac{1}{k}(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H\\
&+\frac{K_H}{k}\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h).
\end{aligned}
$$

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

$$
\begin{aligned}
&\|c_n-c_n^{hk}\|_H^2+D\,k\ \|c_n-c_n^{hk}\|^2+K_H|\gamma_0(c_n-c_n^{hk})|^2\\
&\quad\le k(\,2\|\dot{c}_n-\delta c_n\|_H^2+\|c_n-v^h\|_H^2+D\,\|c_n-v^h\|^2\\
&\qquad+K_H|\gamma_0(c_n-v^h)|^2+\|c_n-c_n^{hk}\|_H^2\\
&\qquad+2K_H|\gamma_0(\delta c_n-\dot{c}_n)|^2+K_H|\gamma_0(c_n-c_n^{hk})|^2)\\
&\qquad+\|c_{n-1}-c_{n-1}^{hk}\|_H^2+K_H|\gamma_0(c_{n-1}-c_{n-1}^{hk})|^2\\
&\qquad+2(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H\\
&\qquad+2\,K_H\gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h).
\end{aligned}
\tag{35}
$$

Denoting

$$
\begin{aligned}
a_n&:=\|c_n-c_n^{hk}\|_H^2+D\,k\sum_{j=0}^{n}\|c_j-c_j^{hk}\|^2+K_H|\gamma_0(c_n-c_n^{hk})|^2,\\
b_n(v^h)&:=2\|\dot{c}_n-\delta c_n\|_H^2+\|c_n-v^h\|_H^2+D\|c_n-v^h\|^2\\
&\qquad+K_H|\gamma_0(c_n-v^h)|^2+2\,K_H|\gamma_0(\delta c_n-\dot{c}_n)|^2,\\
d_n(v^h)&:=(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}),c_n-v^h)_H,\\
e_n(v^h)&:=\ \gamma_0(c_n-c_n^{hk}-(c_{n-1}-c_{n-1}^{hk}))\,\gamma_0(c_n-v^h),
\end{aligned}
$$

adding the nonnegative term $D\,k\sum_{j=0}^{n-1}\|c_j-c_j^{hk}\|^2$ on both sides of estimate (35) and the nonnegative term $D\,k^2\ \sum_{j=0}^{n}\|c_j-c_j^{hk}\|^2$ on its right hand-side, we find that

$$
a_n\le a_{n-1}+k(\,b_n(v^h)+a_n)+2\,d_n(v^h)+2\,K_H\,e_n(v^h),\quad\forall v^h\in V^h.
$$

Therefore, it follows that

$$
a_n\le a_0+\sum_{j=1}^{n}(k(\,b_j(v_j^h)+a_j)+2\,d_j(v_j^h)+2\,K_H\,e_j(v_j^h)),\quad\forall\{v_j^h\}_{j=1}^n\subset V^h.\tag{36}
$$

Since

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

where $M = \max_{1\leq j\leq N} b_j(v_j^h)$, estimate (36) reads

$$a_n \leq a_0 + T\, M + \sum_{j=1}^{n}(k\, a_j + 2\, d_j(v_j^h) + 2\, K_H\, e_j(v_j^h)), \quad \forall \{v_j^h\}_{j=1}^n \subset V^h. \tag{37}$$

We notice now that

$$\begin{aligned}
\sum_{j=1}^{n} d_j(v_j^h) &= (c_n - c_n^{hk}, c_n - v_n^h)_H - (c_0 - c_0^h, c_1 - v_1^h)_H \\
&\quad + \sum_{j=1}^{n-1}(c_j - c_j^{hk}, c_j - v_j^h - (c_{j+1} - v_{j+1}^h))_H \\
&\leq \epsilon \|c_n - c_n^{hk}\|_H^2 + \frac{1}{4\epsilon}\|c_n - v_n^h\|_H^2 \\
&\quad + \frac{1}{2}\|c_0 - c_0^h\|_H^2 + \frac{1}{2}\|c_1 - v_1^h\|_H^2 \\
&\quad + \sum_{j=1}^{n-1} \|c_j - c_j^{hk}\|_H\, \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H \\
&\leq \epsilon \|c_n - c_n^{hk}\|_H^2 + \frac{1}{4\epsilon}\, M + \frac{1}{2}\|c_0 - c_0^h\|_H^2 + \frac{1}{2}\, M \\
&\quad + \sum_{j=1}^{n-1} k\|c_j - c_j^{hk}\|_H^2 + \sum_{j=1}^{n-1}\frac{1}{k}\, \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2,
\end{aligned} \tag{38}$$

where $\epsilon > 0$ is a positive parameter assumed to be small enough. Using similar arguments we find that

$$\begin{aligned}
\sum_{j=1}^{n} e_j(v_j^h) &= \gamma_0(c_n - c_n^{hk})\gamma_0(c_n - v_n^h) - \gamma_0(c_0 - c_0^h)\gamma_0(c_1 - v_1^h) \\
&\quad + \sum_{j=1}^{n-1} \gamma_0(c_j - c_j^{hk})\, \gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h)) \\
&\leq \epsilon|\gamma_0(c_n - c_n^{hk})|^2 + \frac{1}{4\epsilon}|\gamma_0(c_n - v_n^h)|^2 \\
&\quad + \frac{1}{2}|\gamma_0(c_0 - c_0^h)|^2 + \frac{1}{2}|\gamma_0(c_1 - v_1^h)|^2
\end{aligned}$$

$$
\begin{aligned}
&+\sum_{j=1}^{n-1} |\gamma_0(c_j - c_j^{hk})|\,|\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))| \\
&\le \epsilon|\gamma_0(c_n - c_n^{hk})|^2 + \frac{1}{4\epsilon}\,M + \frac{1}{2}|\gamma_0(c_0 - c_0^h)|^2 + \frac{1}{2}\,M \\
&+\sum_{j=1}^{n-1} \frac{1}{k}\,|\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))|^2 \\
&+\sum_{j=1}^{n-1} k\,|\gamma_0(c_j - c_j^{hk})|^2.
\end{aligned}
$$

Thus, estimate (37) can be written as follows,

$$
\begin{aligned}
(1 - 2\,\max\{1, K_H\}\,\epsilon)\,a_n \le a_0 + T\,M + \sum_{j=1}^{n} k\,a_j + \frac{1}{2\epsilon}M + \|c_0 - c_0^h\|_H^2 + M \\
+2\sum_{j=1}^{n-1} k\|c_j - c_j^{hk}\|_H^2 \\
+2\sum_{j=1}^{n-1} \frac{1}{k}\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 \\
+\frac{K_H}{2\epsilon}M + K_H|\gamma_0(c_0 - c_0^h)|^2 + K_H\,M \\
+2\,K_H\,\sum_{j=1}^{n-1} k\,|\gamma_0(c_j - c_j^{hk})|^2 \\
+2\,K_H\,\sum_{j=1}^{n-1} \frac{1}{k}\,|\gamma_0(c_j - v_j^h - c_{j+1} - v_{j+1}^h))|^2,
\end{aligned}
$$

and finally

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

where $\alpha = (1 + \max\{2/D, 2K_H\})/(1 - 2\,\max\{1, K_H\}\,\epsilon)$ and

$$
\begin{aligned}
g_n := 2\,a_0 + 5\,\max\{T, \frac{1}{2\epsilon}, 1\}\,M + 2\sum_{j=1}^{n-1} \frac{1}{k}\,\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 \\
+2\,K_H\,\sum_{j=1}^{n-1} \frac{1}{k}\,\left|\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))\right|^2.
\end{aligned}
$$

Applying a discrete version of the Gronwall's inequality with $\alpha\, k \leq 1/2$ (see [6]), we find that

$$\max_{0\leq n\leq N} a_n \leq (\alpha\,(1+\alpha\, T\, e^{2\alpha T}))\, \max_{0\leq n\leq N} g_n. \tag{39}$$

Therefore, we have proved the following result.

Theorem 2 *Under the assumptions of* Theorem 1 *and assuming that the regularity condition* (24) *holds, then we have the following error estimates for all* $\{v_n^h\}_{n=1}^N \subset V^h$*,*

$$\begin{aligned}
&\max_{0\leq n\leq N}\{\|c_n - c_n^{hk}\|_H^2 + K_H\gamma_0(c_n - c_n^{hk})^2\} + Dk\sum_{n=0}^{N}\|c_n - c_n^{hk}\|^2\\
&\leq \alpha\,(1+\alpha\, T\, e^{2\alpha T})\left[2\,\|c_0 - c_0^h\|_H^2 + 2\,D\,k\,\|c_0 - c_0^h\|^2\right.\\
&\quad +2\,K_H|\gamma_0(c_0 - c_0^h)|^2 + 5\,\max\{T, \frac{1}{2\epsilon}, 1\}\max_{1\leq n\leq N}\{2\|\dot{c}_n - \delta c_n\|_H^2\\
&\quad +\|c_n - v_n^h\|_H^2 + D\|c_n - v_n^h\|^2 + 2\,K_H|\gamma_0(\delta c_n - \dot{c}_n)|^2\\
&\quad +K_H|\gamma_0(c_n - v_n^h)|^2\} + 2\sum_{j=1}^{N-1}\frac{1}{k}\,\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2\\
&\quad \left.+2\,K_H\sum_{j=1}^{N-1}\frac{1}{k}\,|\gamma_0(c_j - v_j^h - (c_{j+1} - v_{j+1}^h))|^2\right].
\end{aligned} \tag{40}$$

Estimates (40) are the basis for the convergence analysis. Hereafter, we consider the finite element space V^h consisting of the continuous piecewise affine functions, defined on a mesh of the interval [0,1], which are equal to zero on $x = 1$. Let us assume further regularity conditions on the weak solution:

$$c \in \mathcal{C}([0,T]; H^2(0,l)), \quad \dot{c} \in L^2(0,T; H^2(0,l)), \quad \ddot{c} \in L^2(0,T; V). \tag{41}$$

Corollary 3 *Under the assumptions of* Theorem 2 *and the additional regularity conditions* (41)*, the linear convergence of the algorithm is obtained; i.e. there exists a positive constant* $\beta > 0$*, independent of h and k, such that*

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

Proof Let $\pi^h : \mathcal{C}([0,l]) \to V^h$ denote the standard finite element interpolation operator, and let us take $v_j^h = \pi^h c_j$, $j = 0, \ldots, N$. Since $c \in \mathcal{C}([0,T]; H^2(0,l))$ we obtain (see [2]),

$$\max_{0\leq n\leq N}\|c_n - \pi^h c_n\|_V \leq \beta\, h\, \|c\|_{\mathcal{C}([0,T];H^2(0,l))}. \tag{42}$$

Keeping in mind the regularity $\ddot{c} \in L^2(0, T; V)$, it yields

$$\max_{1\leq n\leq N} \|\dot{c}_n - \delta c_n\|_V \leq \beta\, k\, \|\ddot{c}\|_{L^2(0,T;V)}, \tag{43}$$

and then

$$\max_{1\leq n\leq N} \|\dot{c}_n - \delta c_n\|_H + \max_{1\leq n\leq N} |\gamma_0(\delta c_n - \dot{c}_n)| \leq \beta\, k\, \|\ddot{c}\|_{L^2(0,T;V)}. \tag{44}$$

The last two terms in estimates (40) are bounded following the ideas applied to estimate the damage error terms (see, for instance, [3]). First, note that both c_j and c_{j+1} belong to $H^2(0, l)$, then, taking into account the linearity of the interpolation operator, we get

$$\|c_{j+1} - c_j - \pi^h(c_{j+1} - c_j)\|_V^2 \leq \beta\, h^2 \|c_{j+1} - c_j\|^2_{H^2(0,l)}. \tag{45}$$

On the other hand, using (41) and the Sobolev embedding theorem

$$H^1(0, T; V) \hookrightarrow \mathcal{C}([0, T]; V),$$

we deduce that $\dot{c} \in \mathcal{C}([0, T]; V)$, and then

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

Thus,

$$\|c_{j+1} - c_j\|_{H^2(0,l)} \leq \int_{t_j}^{t_{j+1}} \|\dot{c}(s)\|_{H^2(0,l)}\, ds \leq \sqrt{k} \left(\int_{t_j}^{t_{j+1}} \|\dot{c}(s)\|^2_{H^2(0,l)}\, ds \right)^{1/2}.$$

Finally, from (45) we get

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

The last term is bounded proceeding in a similar way and leading to the following,

$$\frac{1}{k}\sum_{j=1}^{N-1}\left|\gamma_0(c_j-\pi^h c_j-(c_{j+1}-\pi^h c_{j+1}))\right|^2 \leq \beta\, h^2\, \|\dot{c}\|^2_{L^2(0,T;H^2(0,l))}.$$

5 Numerical results

In this section, we first briefly describe the numerical scheme implemented in Matlab in order to obtain the numerical approximations of Problem P^{hk}, and then we present some numerical results to exhibit its accuracy in an academic example and its behavior in the simulation of a more real case.

5.1 Numerical scheme

In order to approximate the space V, we consider the aforementioned finite element space V^h defined in the following form:

$$V^h=\{v^h\in C([0,l])\,;\ v^h_{|[a_{i-1},a_i]}\in P_1([a_{i-1},a_i])\quad \text{for } i=1,\dots,M,\quad v^h(l)=0\},$$

where the spatial discretization of the interval $[0,l]$ is given by $0=a_0<a_1<\cdots<a_M=l$ and $h=l/M$. Besides, $P_1([a_{i-1},a_i])$ denotes the polynomials of degree less or equal to one in the interval $[a_{i-1},a_i]$, $i=1,\dots,M$.

Therefore, for $n=1,2,\dots,N$, given $c^{hk}_{n-1}\in V^h$, the discrete concentration of surfactant c^{hk}_n is then obtained from Eq. (15), namely it solves the problem

$$\begin{aligned}&(c^{hk}_n,v^h)_H+D\,k((c^{hk}_n,v^h))+K_H\,\gamma_0(c^{hk}_n)\,\gamma_0(v^h)\\&\quad=(c^{hk}_{n-1},v^h)_H+K_H\,\gamma_0(c^{hk}_{n-1})\,\gamma_0(v^h),\quad \forall v^h\in V^h.\end{aligned}$$

This leads to a linear system which is solved by using classical Cholesky's method.

The numerical scheme has been implemented on a 3.2 Ghz PC using Matlab, and a typical 1D run ($h=k=0.01$) takes about 0.6 s of CPU time.

5.2 First example: numerical convergence

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

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

with the initial condition $c_0(x) = \min\{1,\ 1000\,x\}$. This problem corresponds to problem (1)–(4), (9)–(10) with the following data:

$$l = 1, \quad T = 1, \quad c_b = 1, \quad D = 1, \quad K_H = 1, \quad \Gamma_0 = 0.$$

Taking the solution obtained with parameters $h = 1/16384$ and $k = 10^{-6}$ as the "exact solution" c, the numerical errors (multiplied by 100), which are given by

$$\max_{1 \le n \le N} \{\|c_n - c_n^{hk}\|_H + |\gamma_0(c_n - c_n^{hk})|\},$$

are presented in Table 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 Fig. 2, where linear convergence, stated in Corollary 3, is achieved.

5.3 Second example: a real case

As a second problem, we consider the data corresponding to octanol, namely (see [1]):

$$l = 10^{-6}\,\text{m}, \qquad T = 0.5\,\text{s}, \qquad c_b = 0.3\,\text{mol/m}^3,$$
$$D = 5 \times 10^{-10}\,\text{m}^2/\text{s}, \qquad K_H = 18 \times 10^{-6}\,\text{m}, \qquad \Gamma_0 = 0.$$

Moreover, the initial condition c_0 is defined as

$$c_0(x) = \begin{cases} 0.3 & \text{if} \quad x \in (0, 10^{-6}], \\ 0 & \text{if} \quad x = 0. \end{cases}$$

Using the discretization parameters $h = 10^{-8}$ and $k = 10^{-4}$, the concentration at different times and the evolution of the sequence $\{\|c_n^{hk}\|\}_{n=0}^{\infty}$ are shown in Fig. 3. It is

Table 1 Numerical errors ($\times 10^2$) for several time and spatial discretization parameters

$h \downarrow k \rightarrow$	0.01	0.005	0.002	0.001	0.0005
1/8	1.855622	2.092109	2.253191	2.309661	2.338383
1/16	0.787802	0.896857	1.024717	1.074946	1.101252
1/32	0.550369	0.404064	0.461319	0.502525	0.526151
1/64	0.605921	0.285868	0.206403	0.229264	0.248897
1/128	0.670589	0.309314	0.121453	0.103285	0.114077
1/256	0.709209	0.236367	0.120818	0.060885	0.051371
1/512	0.729765	0.359217	0.133789	0.060502	0.030209
1/1024	0.740317	0.369411	0.142786	0.066993	0.030117
1/2048	0.745658	0.374668	0.147785	0.071509	0.033433
1/4096	0.748345	0.377334	0.150395	0.074022	0.035726

worth noting that the concentration evolves to the constant bulk concentration c_b in a fast way, as it can be deduced from the monotone evolution to zero of the sequence $\{\|c_n^{hk}\|\}_{n=0}^{\infty}$ (see Corollary 2).

Regarding the evolution in time of the subsurface concentration shown in Fig. 4, the solution provided by the algorithm is compared with its approximation for short times, given by (see [1], formula (26) and [4], formula (18))

$$c(0,t) \backsimeq 2\,\frac{c_b}{K_H}\sqrt{\frac{D\,t}{\pi}}.$$

As it can be seen, the solution behaves like $\sqrt{t}$ for short times. Finally the interfacial tension of the surfactant using the Henry isotherm is given by

$$\gamma(t) = \gamma_0 - nRT\,K_H c(0,t),$$

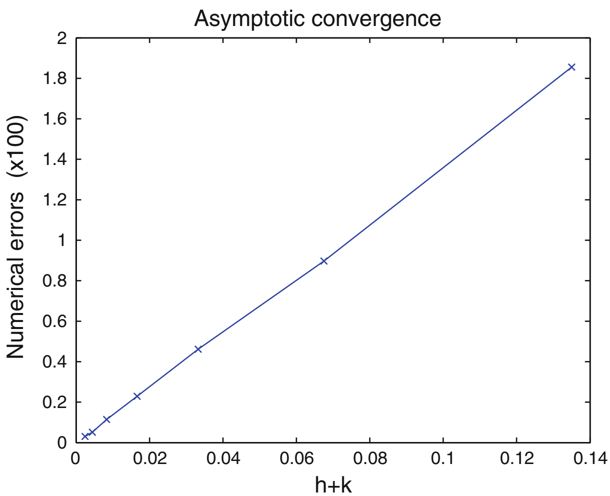

Fig. 2 Example 1: linear convergence

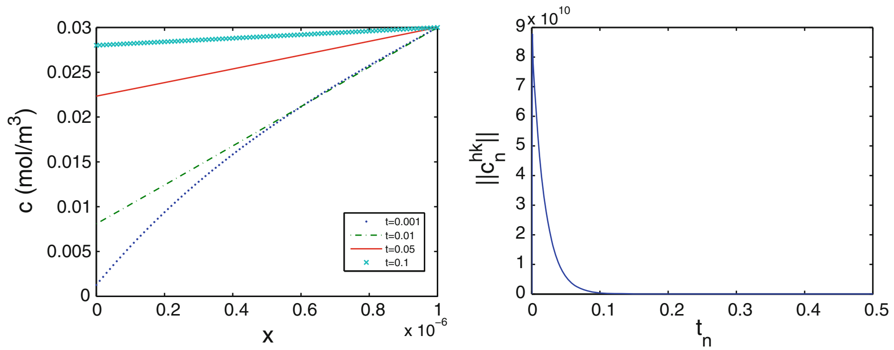

Fig. 3 Concentration at different times (*left*) and sequence $\{\|c_n^{hk}\|\}_{n=0}^{\infty}$ (*right*)

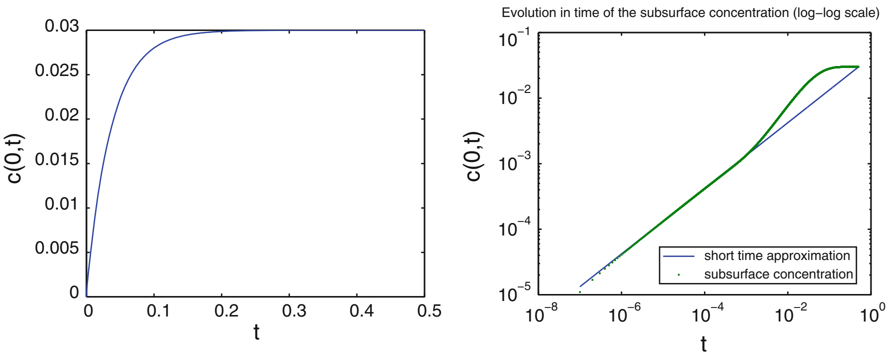

Fig. 4 Evolution in time of the subsurface concentration (*left*) and comparison between the subsurface concentration and its short time approximation (log-log scale) (*right*)

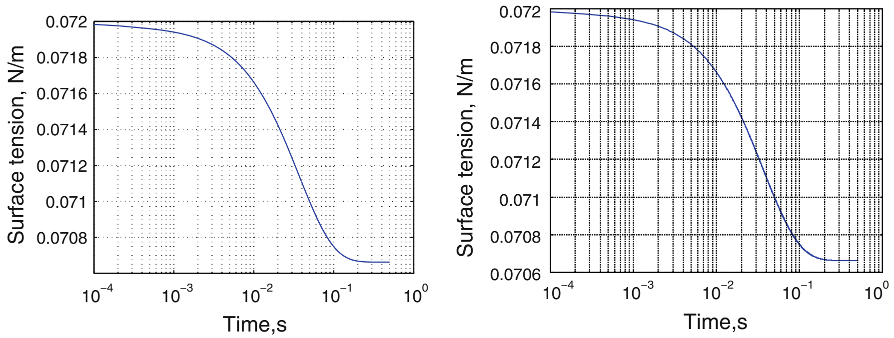

Fig. 5 Comparison between the surface tension obtained with our algorithm (*left*) and with COMSOL (*right*), semi-log scale

where $\gamma_0 = 0.072\,\text{N/m}$ denotes here the surface tension of pure water, $T = 298\,\text{K}$ is the temperature, $R = 8.31\,\text{J/(K mol)}$ represents the gas constant and n is a constant which is equal to one for a non-ionic surfactant. In Fig. 5 the evolution in time of the surface tension obtained with our algorithm is shown (left) and also the one obtained modeling the whole problem with the commercial code Comsol Multiphysics (right), stating the agreement of both results.

References

1. C.H. Chang, E.I. Franses, Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data and mechanisms. Colloids Surf. **100**, 1–45 (1995)
2. P.G. Ciarlet, in *The Finite Element Method for Elliptic Problems*, ed. by P.G. Ciarlet, J.L. Lions. Handbook of Numerical Analysis, vol. II, part 1,(North Holland, 1991), pp. 17–352
3. M. Campo, J.R. Fernández, K.L. Kuttler, M. Shillor, J.M. Viaño, Numerical analysis and simulations of a dynamic frictionless contact problem with damage. Comput. Methods Appl. Mech. Eng. **196**, 476–488 (2006)
4. J. Eastoe, J.S. Dalton, Dynamic surface tension and adsorption mechanisms of surfactants at the air/water interface. Adv. Colloid Interface Sci. **85**, 103–144 (2000)

5. I. Egry, E. Ricci, R. Novakovic, S. Ozawa, Surface tension of liquid metals and alloys recent developments. Adv. Colloid Interface Sci. **159**, 198–212 (2010)
6. W. Han, M. Sofonea, Quasistatic contact problems in viscoelasticity and viscoplasticity, American Mathematical Society-International Press (2002)
7. R.S. Hansen, Diffusion and the kinetics of adsorption of aliphatic acids and alcohols at the water-air interface. J. Colloid Sci. **16**, 549–560 (1961)
8. V.N. Kazakov, A.F. Vozianov, O.V. Sinyachenko, D.V. Trukhin, V.I. Kovalchuk, U. Pison, Studies on the application of dynamic surface tensiometry of serum and cerebrospinal liquid for diagnostics and monitoring of treatment in patients who have rheumatic, neurological or oncological diseases. Adv. Colloid Interface Sci. **86**, 1–38 (2000)
9. K.L. Kuttler, M. Shillor, Set-valued pseudomonotone maps and degenerate evolution inclusions. Commun. Contemp. Math. **1**(1), 87–123 (1999)
10. B.J. McCoy, Analytical solutions for diffusion-controlled adsorption kinetics with nonlinear adsorption isotherms. Colloid Polymer Sci. **261**, 535–539 (1983)
11. R. Miller, On the solution of diffusion controlled adsorption kinetics for any adsorption isotherms. Colloid Polym. Sci. **259**, 375–381 (1981)
12. R. Miller, P. Joos, V.B. Fainerman, Dynamic surface and interfacial tensions of surfactant and polymer solutions. Adv. Colloid Interface Sci. **49**, 249–302 (1994)
13. K.L. Sutherland, The kinetics of adsorption at liquid surfaces. Aus. J. Sci. Res. Series A: Phys. Sci. **5**, 683–696 (1952)
14. A.F.H. Ward, L. Tordai, Time-dependence of boundary tensions of solutions. J. Chem. Phys. **14**(7), 453–461 (1946)