

Numerical behavior of a linear mixed kinetic-diffusion model for surfactant adsorption at the air-water interface

José R. Fernández · María del Carmen Muñiz ·
Cristina Núñez

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Abstract This paper concerns the numerical behavior of the solution to a problem including a linear mixed kinetic-diffusion model for surfactant adsorption at the air-water interface. The existence and uniqueness of a weak solution is recalled. Then, fully discrete approximations are obtained by using a finite element method and the backward Euler scheme. Error estimates are stated from which, under adequate additional regularity conditions, the linear convergence of the algorithm is deduced. Finally, several numerical simulations are presented in order to demonstrate the behavior of the solution for commercially available surfactants.

Keywords Mixed kinetic-diffusion model · Surfactant · Adsorption dynamics · Finite element approximation · Numerical simulations

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J. R. Fernández (✉)

Departamento de Matemática Aplicada I, Universidade de Vigo, ETSI de Telecomunicación,
Buzón 104, Campus As Lagoas Marcosende s/n, 36310 Vigo, Spain
e-mail: jose.fernandez@uvigo.es

M. del Carmen Muñiz · C. Núñez

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

C. Núñez

e-mail: cristina.nunez.garcia@usc.es

1 Introduction

Surfactant adsorption dynamics at the air-water interface has determinant applications in areas such chemistry, medicine, food processing and so on (see [1, 2] and the references therein). When a new air-water interface is formed in a surfactant solution, the surfactant molecules tend to migrate to this interface changing its properties as, for instance, reducing drastically its surface tension (see [1, 2]). This problem is modeled using the diffusion partial differential equation in one spatial dimension, coupled with the corresponding adsorption-desorption model by means of a suitable boundary condition at the interface. In this paper we address the research began in [4] concerning a linear mixed kinetic-diffusion model, where the existence of a unique solution and the theoretical numerical analysis were shown, and also in [3], where the diffusion-controlled model for the so-called Henry isotherm was studied from the numerical point of view. Here, we provide several numerical examples in order to demonstrate the behavior of the solution.

The outline of this paper is as follows. In Sect. 2, we briefly describe the mathematical model and we introduce the variational formulation of the problem, for which an existence and uniqueness result is recalled. Fully discrete approximations are introduced in Sect. 3 by using a finite element method and a hybrid combination of the explicit and implicit Euler schemes for the spatial and time discretizations, respectively. An error estimate result is stated from which the linear convergence is deduced under suitable regularity assumptions. Finally, in Sect. 4 numerical examples are shown to demonstrate the behavior of the solution for commercially available surfactants.

2 The model and its variational formulation

First, we introduce the so-called *subsurface* (see [1, 2]), which is located a few molecular diameters below the air-water interface, being the limit between the domain where only diffusion takes place and the region in which only adsorption-desorption occurs.

Then, let x be the distance from the interface and denote by $c(x, t)$ 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 (see Fig. 1). Denoting by $\Gamma(t)$ the time-dependent surface concentration and taking into account the Fick's law, we have the following problem (see [4] and the references therein for details):

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

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

$$c(l, t) = c_b, \quad t \geq 0, \quad (3)$$

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

$$\Gamma(0) = \Gamma_0, \quad (5)$$

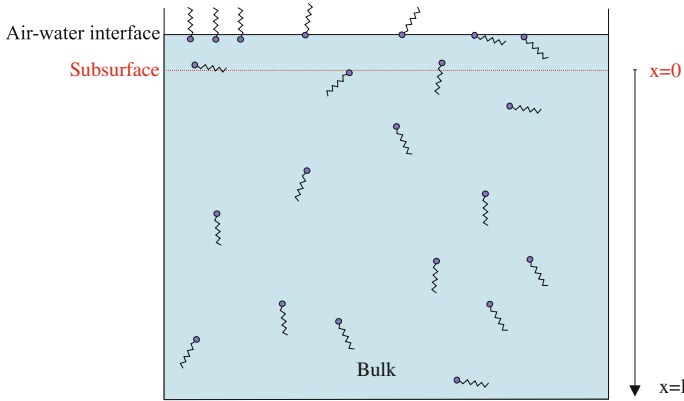


Fig. 1 Air-water interface and location of the subsurface

where D denotes the diffusion coefficient and the positive constant c_b is the bulk concentration. Moreover, $c_0(x)$ is a function defined in $[0, l]$ and being equal to c_b on $x = l$ which represents an initial condition for the concentration. We point out that the surface concentration, Γ , is, in fact, an unknown of the system and then an additional condition must be given in order to complete the problem. In this work, we use a linear kinetic expression modeling the mass transfer between the surface and subsurface at low concentrations, leading to the following ordinary differential equation (see [1, 6]):

$$\frac{d\Gamma}{dt}(t) = k_H^a c(0, t) - k_H^d \Gamma(t), \tag{6}$$

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

If we assume now that the solution to this ODE is regular enough, the previous equation together with the initial condition (5) can be straightforwardly integrated and boundary condition (2) reads

$$D \frac{\partial c}{\partial x}(0, t) = k_H^a c(0, t) - \phi(t, c(0, \cdot)), \tag{7}$$

where

$$\phi(t, \zeta) = k_H^d \Gamma_0 e^{-k_H^d t} + k_H^d k_H^a e^{-k_H^d t} \int_0^t e^{k_H^d \tau} \zeta(\tau) d\tau. \tag{8}$$

Thus, we are interested in the problem defined by equations (1), (3), (4) and boundary condition (7). Moreover, for the sake of clarity in this paper, we assume that c_b equals zero and so a homogeneous boundary condition is imposed on the right end of the spatial interval.

We turn now to obtain the variational formulation of problem (1), (3), (4) and (7).

Let V be the Hilbert space

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

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 $\|v\|_V = ((v, v))^{1/2}$. We denote by $\gamma_0 : H^1(0, l) \rightarrow \mathbb{R}$ the trace operator on $x = 0$. 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 space

$$W_2(0, T; V) = \{v \in L^2(0, T; V); \dot{v} \in L^2(0, T; V')\},$$

where we denote the time derivative by a dot above.

Using the integration by parts formula, the weak formulation of problem (1), (3), (4) and (7) is written as follows.

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

$$\langle \dot{c}(t), v \rangle_{V' \times V} + D((c(t), v)) + k_H^a \gamma_0(c(t)) \gamma_0(v) = \phi(t, \gamma_0(c)) \gamma_0(v),$$

for a.e. $t \in (0, T)$, $\forall v \in V$, (9)

$$c(0) = c_0. \quad (10)$$

The existence and the uniqueness of solution to Problem P is stated in the next theorem. Its proof is based on classical results for linear parabolic equations and fixed-point techniques (see [4]).

Theorem 1 *Let k_H^a , k_H^d and D be positive constants. If $c_0 \in H$ then there exists a unique solution $c \in W_2(0, T; V)$ to Problem P.*

3 Fully discrete approximations: numerical analysis

We introduce now a fully discrete approximation of problem (9), (10). First, we consider the finite-dimensional space $V^h \subset V$ to approximate the variational space V given by

$$V^h = \{v^h \in C([0, l]); v^h|_{[a_{i-1}, a_i]} \in P_1([a_{i-1}, a_i]), \text{ for } i = 1, \dots, M, v^h(l) = 0\}, \quad (11)$$

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

Secondly, let $0 = t_0 < t_1 < \dots < t_N = T$ be a uniform partition of the time interval $[0, T]$, with nodes $t_n = nk$ for $n = 0, 1, \dots, N$, and denote by $k = T/N$ the time step size. 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 approximation of Problem P is written in the following form.

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

$$c_0^{hk} = c_0^h, \tag{12}$$

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

$$(\delta c_n^{hk}, v^h)_H + D((c_n^{hk}, v^h)) + k_H^a \gamma_0(c_n^{hk}) \gamma_0(v^h) = \phi_{n-1}^{hk} \gamma_0(v^h), \tag{13}$$

where $c_0^h = \pi^h c_0 \in V^h$ is an approximation of the initial condition c_0 , π^h being the standard finite element interpolation operator, and

$$\phi_{n-1}^{hk} = k_H^d \Gamma_0 e^{-k_H^d t_n} + k_H^d k_H^a k \sum_{j=0}^{n-1} e^{k_H^d(t_j - t_n)} \gamma_0(c_j^{hk}). \tag{14}$$

Under the assumptions of Theorem 1 and using Lax–Milgram theorem, we easily deduce the existence of a unique discrete solution to Problem P^{hk}.

In the sequel, we present some error estimates for the difference $c_n - c_n^{hk}$ assuming the following additional regularity:

$$c \in C([0, T]; V) \cap C^1([0, T]; H). \tag{15}$$

Applying a discrete version of Gronwall’s inequality (see [5]), after some algebraic manipulations (see [4] for details) we have the following result which states some a priori error estimates on the approximate solutions.

Theorem 2 *Under the assumptions of Theorem 1 and assuming that regularity condition (15) 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 $\{v_n^h\}_{n=1}^N \subset V^h$,*

$$\begin{aligned}
& \max_{0 \leq n \leq N} \|c_n - c_n^{hk}\|_H^2 + k \sum_{j=0}^N \left[D \|c_j - c_j^{hk}\|_V^2 + \alpha |\gamma_0(c_j - c_j^{hk})|^2 \right] \\
& \leq \beta \left[\|c_0 - c_0^h\|^2 + \max_{1 \leq n \leq N} \{\|\dot{c}_n - \delta c_n\|_H^2 + \|c_n - v_n^h\|_V^2 + I_n^2\} \right. \\
& \quad \left. + \sum_{j=1}^{N-1} \frac{1}{k} \|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 \right], \quad (16)
\end{aligned}$$

where $\delta c_n = (c_n - c_{n-1})/k$ and the integration error I_n is given by

$$I_n = k_H^a k_H^d e^{-k_H^d t_n} \left| \int_0^{t_n} e^{k_H^d \tau} \gamma_0(c(\tau)) d\tau - \sum_{j=0}^{n-1} k e^{k_H^d t_j} \gamma_0(c(t_j)) \right|.$$

Estimates (16) are the basis for the convergence analysis. As an example, let us assume further regularity conditions on the solution to the continuous problem:

$$c \in \mathcal{C}([0, T]; H^2(0, l)), \quad \dot{c} \in L^2(0, T; V), \quad \ddot{c} \in \mathcal{C}([0, T]; H). \quad (17)$$

We now state the linear convergence of the algorithm under these additional regularity conditions.

Corollary 1 *Let the assumptions of Theorem 2 still hold. If we assume the additional regularity conditions (17), then there exists a positive constant $\beta > 0$, independent of h and k , such that*

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

4 Numerical results

In this final section, we present some numerical simulations involving commercially available surfactants in order to demonstrate the numerical behavior of the solution to Problem P.

Remark 1 The numerical resolution of Problem P^{hk} is done as follows. First, for $n = 1, 2, \dots, N$ 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 Eq. (13) solving the problem:

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

where value ϕ_{n-1}^{hk} is given in (14). This leads to a linear system which is solved by using classical Cholesky's method. This numerical scheme was implemented on a Core i5 2.53 Ghz PC using MATLAB, and a typical run ($h = k = 0.01$) took about 0.6 seconds of CPU time for a final time $T = 5$ s.

4.1 Simulation of hexanol: dependence on the adsorption rate constant

As a first example, we consider a dilute solution of the commercial alcohol hexanol, using the data from references [1] and [6]:

$$c_b = 3.44 \text{ mol/m}^3, \quad D = 7.16 \times 10^{-10} \text{ m}^2/\text{s}, \quad l = 10^{-6} \text{ m}, \\ T = 0.5 \text{ s}, \quad \Gamma_0 = 0 \text{ mol/m}^2.$$

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

Using the discretization parameters $h = 10^{-8}$ and $k = 10^{-4}$ and the adsorption and desorption rate constants, $k_H^a = 1.73 \times 10^{-4} \text{ m/s}$ and $k_H^d = 157 \text{ s}^{-1}$, in Figs. 2 and 3 the evolution in time of the subsurface and surface concentrations are shown, respectively, both obtained with this mixed kinetic model and also that modeling the problem with the diffusion-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

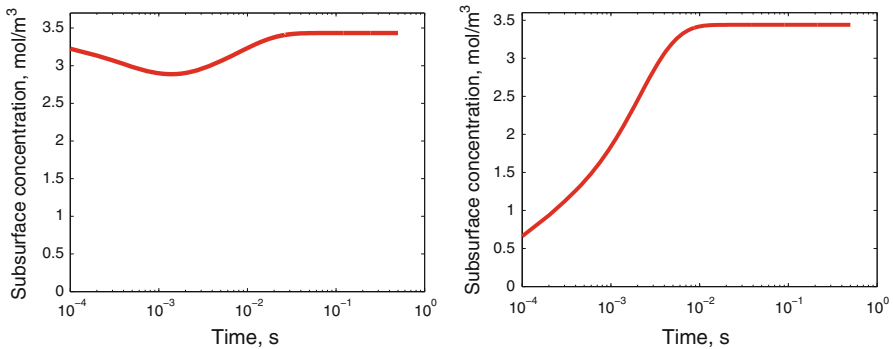


Fig. 2 Evolution in time of the subsurface concentration with the mixed kinetic model (*left*) and that obtained with the diffusion-controlled model for Henry’s isotherm (*right*), semi-log scale

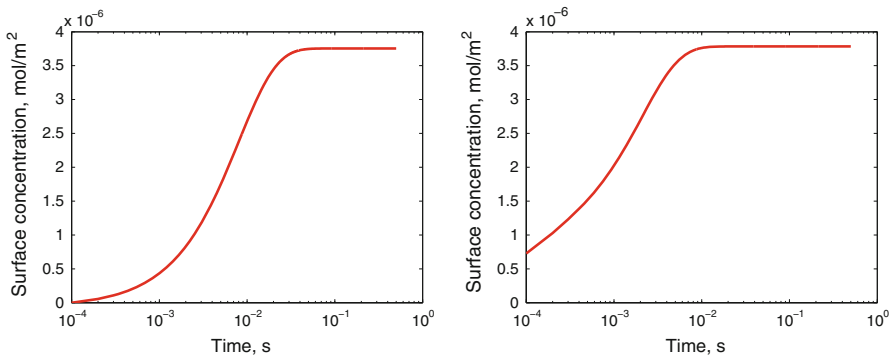


Fig. 3 Evolution in time of the surface concentration $\Gamma(t)$ with the mixed kinetic model (*left*) and that obtained with the diffusion-controlled model using Henry’s isotherm (*right*), semi-log scale

Fig. 2 the adsorption mechanism of the mixed kinetic model is limiting the mass transfer from the solution to the surface.

Next, we choose the adsorption and desorption rate constants, k_H^a and k_H^d as reported in [6], leading to the following six cases:

- **Case i:** $k_H^a = 2.583 \times 10^{-3}$ m/s and $k_H^d = 2348$ s $^{-1}$.
- **Case ii:** $k_H^a = 6.456 \times 10^{-4}$ m/s and $k_H^d = 587$ s $^{-1}$.
- **Case iii:** $k_H^a = 1.73 \times 10^{-4}$ m/s and $k_H^d = 157$ s $^{-1}$.
- **Case iv:** $k_H^a = 1.96 \times 10^{-5}$ m/s and $k_H^d = 18$ s $^{-1}$.
- **Case v:** $k_H^a = 0$ m/s and $k_H^d = 0$ s $^{-1}$.
- **Case vi:** diffusion-controlled model with Henry's isotherm, $K_H = 1.1 \times 10^{-6}$ m.

Our aim is to compare the surface tension σ given by

$$\sigma(t) = \sigma_0 - n R T \Gamma(t),$$

for each of the above cases, where $\sigma_0 = 0.072$ N/m denotes the surface tension of pure water, $T = 293.71$ K is the temperature, $R = 8.31$ 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 $h = 10^{-8}$ and $k = 10^{-5}$ for cases ii–vi and $k = 10^{-6}$ for case i, in Fig. 4 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 Fig. 6 of [6] and Fig. 27 of [1]. As it can be expected, the time needed to reach the stationary value increases meanwhile the value of the adsorption rate constant k_H^a decreases.

The evolution in time of the surface concentration is shown in Fig. 5 for the above six cases using the same discretization parameters employed to obtain Fig. 4.

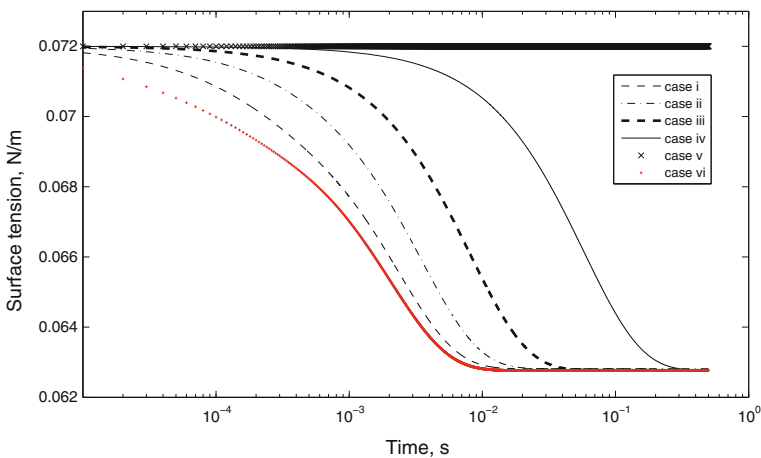


Fig. 4 Surface tension graphs obtained for the six cases of adsorption and desorption constants, semi-log scale

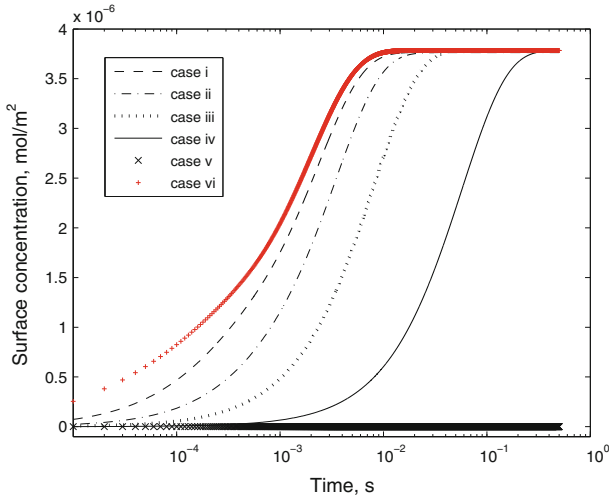


Fig. 5 Evolution in time of the surface concentration obtained for the six cases of adsorption and desorption constants, semi-log scale

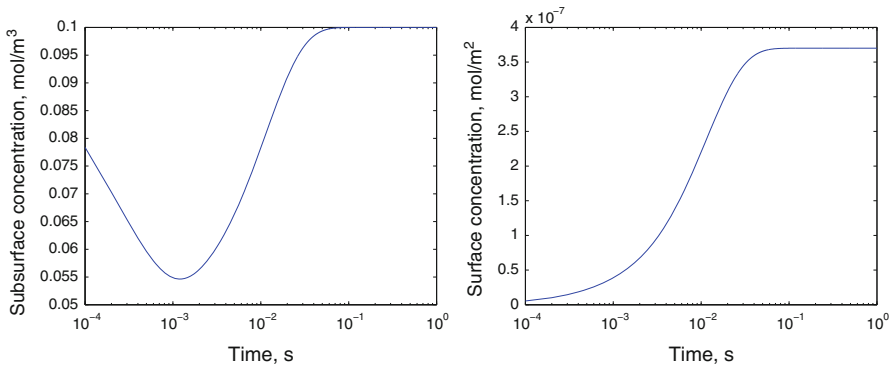


Fig. 6 Evolution in time of the subsurface concentration (*left*) and the surface concentration (*right*) for heptanol, semi-log scale

4.2 Simulation of heptanol

As a second example, we consider now a dilute solution of the commercial alcohol heptanol (see [6] for further details):

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

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 $h = 10^{-8}$ and $k = 10^{-4}$, the evolution in time of the subsurface and the surface concentrations are shown in Fig. 6 (left-hand side

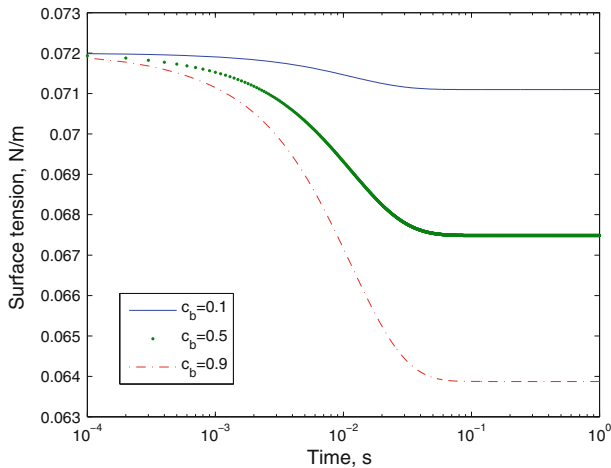


Fig. 7 Evolution in time of the surface tension for several heptanol bulk concentrations, semi-log scale

and right-hand side, respectively). We note that the subsurface concentration evolves to the constant bulk concentration c_b in a fast way.

Finally, in Fig. 7 we plot the evolution in time of the surface tension for several bulk concentrations ($c_b = 0.1 \text{ mol/m}^3$, $c_b = 0.5 \text{ mol/m}^3$ and $c_b = 0.9 \text{ mol/m}^3$).

As it can be seen, the time needed to reach stationary values of the surface tension depends both on the values for the adsorption rate constants (see Fig. 4) and on the bulk concentration (see Fig. 7). Moreover, on increasing the bulk concentration also increases the magnitude of the change of the surface tension, because more alcohol is incorporated to the air-water interface.

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