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Variational analysis of the Langmuir–Hinshelwood dynamic mixed-kinetic adsorption model[☆]

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ABSTRACT

The paper deals with the mathematical and numerical analysis of surfactants behavior at the air–water interface, by using a mixed-kinetic adsorption model which is known as the Langmuir–Hinshelwood model and which is consistent with the classical Langmuir isotherm at equilibrium. The model consists of a coupled nonlinear system of a parabolic equation for the surfactant concentration and an ordinary differential equation for the surface concentration. The existence and uniqueness of the weak solution is proved by applying a result for the linear parabolic equation and fixed-point techniques. Then, fully discrete approximations are introduced by using a finite element method and a hybrid combination of both backward and forward Euler schemes. An a priori error estimate result is proved from which, under adequate additional regularity conditions, the linear convergence of the algorithm is derived. Finally, numerical simulations are presented to demonstrate the accuracy of the algorithm and the behavior of the solution for a commercially available surfactant.

1. Introduction

The surface tension behavior of aqueous surfactants is important in biological and biochemical processes, and in many diverse areas of application. It affects foamability and foam stability, wettability, coating flows, and the formation of soap–lather (see, e.g., [1–5]). In all the processes, the new formed surface in the surfactant solution is generated with the incorporation of surfactant molecules to this surface, which reduces considerably its surface tension. This variation has a great importance because, for instance, in the production of thin films in gelatin solutions (slide coating), this tension affects the stresses which control flow and film deformation. As it is well known, this dynamic process may vary depending on temperature, salinity, 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 the transportation of molecules

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as a consequence of an adsorption–desorption mechanism from the bulk of the solution to the interface and vice versa. There are two types of models which are used to describe this process: the diffusion-controlled model and the mixed kinetic-diffusion model (see [6]). In the former an isotherm describes the relation between the surface and subsurface concentrations, whereas in the latter, a kinetic relation between these concentrations is written in terms of an ordinary differential equation. The simplest model from this family relies on the assumption that the rate of adsorption is proportional to the subsurface concentration and the rate of desorption is proportional to the surface concentration. This leads to the linear kinetic model which was studied in [7]. Besides, the rate of adsorption being proportional to the fraction of empty space at the surface yields to the so-called Langmuir–Hinshelwood dynamic mixed-kinetic diffusion model (hereafter the L–H model), the one we are concerned about in this paper.

From the mathematical point of view, the problem consists of the classical diffusion partial differential equation in one spatial dimension coupled with the L–H model by means of a boundary condition at the subsurface, the unknowns being both bulk and surface concentrations. More precisely, we are concerned with the mathematical and numerical analysis of the diffusion problem with finite diffusion length coupled with the nonlinear L–H model, evolving into the so-called Langmuir isotherm at equilibrium. The main result of the paper (cf. Theorem 1) deals with the existence and uniqueness of solution to the truncated problem. Its proof is based on the study of two intermediate problems followed by the application of the Schauder fixed point theorem.

This paper is outlined as follows. In Section 2, we briefly describe the model and present its variational formulation. In Section 3 we provide results on the existence and uniqueness of solutions to the model and its truncated version. The proof of our main result is given in Section 4. In Section 5 we introduce a fully discrete approximation by using a finite element method and a hybrid combination of both backward and forward Euler schemes. An a priori error estimate result is proved from which the linear convergence is deduced under some additional regularity conditions. Finally, in Section 6 some numerical examples are provided to show the accuracy of the algorithm and the behavior of the solution for a commercially available surfactant.

2. Problem setting and its variational formulation

In the mathematical modeling of surfactants behavior at the air–water interface, it is important to define the boundary called *subsurface*, which is located a few molecular diameters below the air–water interface, and splits the domain into a part where only diffusion takes place and the region in which only adsorption–desorption occurs.

Let x and t be the distance from the interface and the time, respectively, and denote by $c(x,t)$ the concentration of surfactant at point $x \in [0,l]$ and a time instant $t \in [0,T]$, $l > 0$ and $T > 0$ being the final diffusion length and the final time, respectively. 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 law, we consider the following problem (see [1,4]):

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

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

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

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

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

In Eqs. (1)–(3), the constant $D > 0$ is the diffusion coefficient and the positive constant c_b is the bulk concentration. Moreover, c_0 is a function defined on $[0,l]$ which denotes the initial concentration of surfactant, and Γ_0 stands for the initial surface concentration. We remark that the surface concentration, $\Gamma = \Gamma(t)$, actually becomes an unknown of the system and therefore an additional condition must be given in order to close the problem.

In this paper, we consider the following well-known Langmuir–Hinshelwood equation which governs the time-dependent surface concentration and which is consistent with the classical Langmuir's equilibrium isotherm (see [8,1]):

$$\frac{d\Gamma}{dt}(t) = K_L^a c(0,t)\left(1 - \frac{\Gamma(t)}{\Gamma_m}\right) - K_L^d\,\Gamma(t), \tag{6}$$

where $\Gamma_m > 0$ is the maximum surface concentration, and $K_L^a > 0$ and $K_L^d > 0$ are the adsorption and desorption rate constants, respectively. Here, we are interested in surfactant solutions below the cmc (critical micelle concentration); therefore Γ_m, which is a theoretical limit, can never be reached. Moreover, we notice that at equilibrium (i.e. when $d\Gamma(t)/dt = 0$), this model yields to the classical Langmuir isotherm with constant $K_L = \frac{K_L^a}{K_L^d \Gamma_m}$.

In order to simplify the notation, we define the function $f : \mathbb{R}^2 \to \mathbb{R}$ by

$$f(r,s) = K_L^a\, r\left(1 - \frac{s}{\Gamma_m}\right) \quad \text{for } r, s \in \mathbb{R}.$$