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NUMERICAL ANALYSIS OF A DYNAMIC PROBLEM INVOLVING BULK-SURFACE SURFACTANTS

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Abstract. *Here, we numerically study a dynamic problem which models the evolution of the concentration of surfactants, including the effects of the diffusion and the surface diffusion. A kinetic expression which can be reduced to the well-known Langmuir-Hinshelwood equation is used to model the relation between the surfactant concentration and the surface concentration. The variational formulation is written as a coupled system of parabolic elliptic partial differential equations, for which an existence and uniqueness result is recalled. Then, fully discrete approximations are introduced by using the classical finite element method to approximate the spatial variable and the implicit Euler scheme to discretize the time derivatives. An a priori error estimates result is shown, from which the linear convergence of the approximation is derived under suitable additional regularity conditions.*

1 INTRODUCTION

The effect of surfactants is a very important issue in many real world applications, in which the surface tension plays a significant role. For instance, some examples could be the control of the droplet size when forming emulsions, foams, suspensions and pharmaceuticals, the inkjet printing, etc. In this paper, we assume that the process is governed by a mixed kinetic-diffusion model, that is, a kinetic relation between the surfactant and surface concentrations which is written in terms of an expression that generalizes the Langmuir-Hinshelwood ordinary differential equation.

Recently, we have published several papers dealing with related problems as the linear Henry isotherm [7], the mixed kinetic-diffusion case [8] or the Langmuir-Hinshelwood equation [6]. However, in all these papers we reduced the problem to its one-dimensional setting, because we considered that the molecules moved in a vertical direction and that no diffusion took place on the surface. Therefore, following other authors (see, e.g., [1]), in this work we consider that the problem is either two- or three-dimensional and that there is diffusion of the surface concentration.

2 THE MODEL

Let $\Omega \subset \mathbb{R}^{n+1}$, $n = 1, 2$, be an open and bounded domain with a Lipschitz continuous boundary denoted by $\partial\Omega$. Here, we assume that it is the union of three disjoint parts Γ_D, Γ_N and Γ_S such that meas (Γ_D), meas $(\Gamma_S) > 0$; the latter being assumed as a compact C^∞ Riemannian manifold with a Lipschitz boundary.
Let us denote by $\mathbf{n}$ the unit normal vector to Γ_S exterior to Ω and by $\boldsymbol{\mu}$ the outer unit normal vector to $\partial\Gamma_S$, which is tangent to Γ_S at every boundary point.

For a function g, being defined and regular in a neighbourhood of Γ_S, the surface (or tangent) gradient is given by

$$\nabla_S\, g = Dg - (\mathbf{n} \cdot Dg)\,\mathbf{n},$$

where $Dg(y)$ is the gradient of g at point $y \in \Gamma_S$. Thus, the surface gradient at a point $y \in \Gamma_S$ is the projection of the gradient at y onto the tangent plane to Γ_S at y. Furthermore, denoting by $(\underline{D}_1 g, \ldots, \underline{D}_{n+1} g)$ the components of the surface gradient, the Laplace-Beltrami operator is defined by the surface divergence of the surface gradient, that is,

$$\Delta_S g := \nabla_S \cdot \nabla_S\, g = \sum_{i=1}^{n+1} \underline{D}_i\, \underline{D}_i g.$$

Therefore, in this work we consider the following problem which models the evolution of concentration of surfactant for a solution with concentration below the so-called critical micelle concentration (cmc), see [1]:

$$\frac{\partial c(x,t)}{\partial t} - D\,\Delta c(x,t) + \boldsymbol{u}(x,t) \cdot \nabla c(x,t) = 0 \quad \text{in} \quad \Omega \times (0,T), \tag{1}$$

$$c(x,t) = c_b(x,t) \quad \text{on} \quad \Gamma_D \times (0,T), \tag{2}$$

$$D\frac{\partial c(x,t)}{\partial \mathbf{n}} = 0 \quad \text{on} \quad \Gamma_N \times (0,T), \tag{3}$$

$$D\frac{\partial c(x,t)}{\partial \mathbf{n}} = -\dot{S}_\Gamma \quad \text{on} \quad \Gamma_S \times (0,T), \tag{4}$$

$$c(x,0) = c_0(x) \quad \text{in} \quad \Omega, \tag{5}$$

$$\frac{\partial \xi}{\partial t}(x,t) - D_S\,\Delta_S \xi(x,t) + \xi(\nabla_S \cdot \boldsymbol{u}(x,t)) + \boldsymbol{u}_\tau(x,t)\cdot\nabla_S\xi(x,t) = \dot{S}_\Gamma \quad \text{on} \quad \Gamma_S\times(0,T), \tag{6}$$

$$D_S\,\nabla_S\xi(x,t)\cdot\boldsymbol{\mu}(x) = 0 \quad \text{on} \quad \partial\Gamma_S\times(0,T), \tag{7}$$

$$\xi(x,0) = \xi_0(x) \quad \text{on} \quad \Gamma_S, \tag{8}$$

with the source term in (6) given by (see [1])

$$\dot{S}_\Gamma = k_L^a c(x,t)\left(1 - \frac{\xi(x,t)}{\xi_m}\right) - k_L^d \xi(x,t). \tag{9}$$

In this problem, we denote by $c(x,t)$ and $\xi(x,t)$ the volumetric and surface surfactant concentrations, respectively, at point $x \in \Omega$ and time $t \in (0,T)$ ($T > 0$ is the final time). Moreover, c_b denotes the bulk concentration, the positive constants D and D_S are the bulk and the surface diffusion coefficients, respectively, c_0 is a function defined in Ω, which gives the initial concentration of surfactant, and ξ_0 is a function defined on Γ_S which denotes the initial surface concentration. Note that equation (6) allows diffusion along the surface Γ_S, and equation (9) describes the adsorption-desorption transport of surfactant molecules between the bulk phase and the surface, as stated in [1]. The convective terms in (1) and (6) have been included here for the sake of completeness, where $\boldsymbol{u}(x,t)$ represents the velocity of the bulk molecules and $\boldsymbol{u}_\tau$ is its tangential component given by $\boldsymbol{u}_\tau = \boldsymbol{u} - (\boldsymbol{u}\cdot\mathbf{n})\mathbf{n}$. The positive constants k_L^a and k_L^d denote the adsorption and desorption rate constants, respectively, and $\xi_m > 0$ is the maximum surface coverage.

Therefore, the dynamic process considered is governed by two mechanisms: diffusion from the bulk phase to the sublayer and adsoption from the sublayer to the surface. We remark that, since surfactant solutions below the level of cmc are taken into account, a constant diffusivity and an incompressible bulk phase can be assumed.

Now, we obtain the variational formulation of this problem. Denote by V the following subspace of $H^1(\Omega)$:

$$V = \{v \in H^1(\Omega);\ v_{|\Gamma_D} = 0\},$$

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

$$((u,v)) = \int_\Omega \nabla u \cdot \nabla v\,dx, \quad \|v\|_V = ((v,v))^{1/2}.$$

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

$$(u,v)_H = \int_\Omega u\,v\,dx,$$

with the associated norm $\|v\|_H = (v,v)_H^{1/2}$. Furthermore, we consider the Hilbert space

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

the time derivative being understood in the distributional sense and endowed with the norm

$$\|v\|^2_{\mathcal{W}(0,T)} = \|v\|^2_{L^2(0,T;V)} + \|v'\|^2_{L^2(0,T;V')}.$$

On the other hand, on the boundary Γ_S we consider the space $X = L^2(\Gamma_S)$ with the inner product and norm given, respectively, by

$$(u,v)_X = \int_{\Gamma_S} u\, v\, d\Gamma, \quad \|v\|_X = (v,v)_X^{1/2},$$

where $d\Gamma$ is the surface element on Γ_S. Regarding Sobolev spaces on surfaces we also consider the space

$$H^1(\Gamma_S) = \{f \in X;\, \underline{D}_i f \in X, i = 1, \dots, n+1\},$$

endowed with the inner product and its associated norm given by (see [4])

$$(u,v)_{H^1(\Gamma_S)} = \int_{\Gamma_S} u\, v d\Gamma + \int_{\Gamma_S} \nabla_S u \cdot \nabla_S v\, d\Gamma, \quad \|v\|_{H^1(\Gamma_S)} = (v,v)^{1/2}_{H^1(\Gamma_S)}.$$

Let $\gamma\colon V \to X$ denote the trace operator on Γ_S. From the continuity of the trace operator, it follows that

$$\|\gamma v\|_X \le K\, \|v\|_V \ \text{ for all } \ v \in V \ \text{ with } \ K = \|\gamma\|_{\mathcal{L}(V,X)}. \tag{10}$$

We denote by $H^1(\Gamma_S)'$ the dual space to $H^1(\Gamma_S)$. Since Γ_S is a compact manifold with Lipschitz boundary we consider the Gelfand triple (see [9], p. 267):

$$H^1(\Gamma_S) \hookrightarrow X \hookrightarrow H^1(\Gamma_S)', \tag{11}$$

and we define the Banach space

$$\mathcal{W}_S(0,T) = \{v \in L^2(0,T;H^1(\Gamma_S));\, v' \in L^2(0,T;H^1(\Gamma_S)')\}.$$

Finally, we introduce the following truncation operator $R\colon X \to X$ given by

$$R(\eta) = \eta_+ - (\eta - (1-\sigma)\xi_m)_+, \tag{12}$$

with $\sigma \in [0,1]$ and $\eta_+ = \max\{0,\eta\}$ denotes the positive part of η. We note that this operator is required for mathematical reasons. Using it, we introduce the following truncated version of equation (9):

$$\dot{S}_\Gamma = k_L^a c(x,t)\left(1 - \frac{R(\xi(x,t))}{\xi_m}\right) - k_L^d \xi(x,t). \tag{13}$$

Using Green's formula, boundary conditions (2), (3), (4) and (7), and equation (13), we obtain the following weak formulation of problem (1)-(8).
Problem P. Given $c_0 \in H$, $\xi_0 \in X$ and $u \in L^\infty(0,T;L^\infty(\Omega;\mathbb{R}^{n+1}))$, find $c \in \mathcal{W}(0,T)$ and $\xi \in \mathcal{W}_S(0,T)$ such that $c(0) = c_0$, $\xi(0) = \xi_0$ and, for a.e. $t \in (0,T)$,

$$\langle c'(t), v\rangle_{V'\times V} + D((c(t),v)) + (\boldsymbol{u}(t)\cdot\nabla c(t), v)_H + (k_L^a \gamma c(t)\Big(1 - \frac{R(\xi(t))}{\xi_m}\Big), \gamma v)_X$$

$$= (k_L^d \xi(t)\,,\, \gamma v\,)_X, \quad \forall v \in V, \tag{14}$$

$$\langle \xi'(t), w\rangle_{H^1(\Gamma_S)'\times H^1(\Gamma_S)} + D_S \int_{\Gamma_S} \nabla_S \xi(t)\cdot\nabla_S w d\Gamma + (k_L^d \xi(t),\, w\,)_X + (\boldsymbol{u}_\tau(t)\cdot\nabla_S\xi(t), w)_X$$

$$= (k_L^a \gamma c(t)\Big(1 - \frac{R(\xi(t))}{\xi_m}\Big), w\,)_X - ((\nabla_S\cdot \boldsymbol{u}(t))\xi(t), w\,)_X, \quad \forall w \in H^1(\Gamma_S), \tag{15}$$

where we suppressed the dependence on the spatial variable for the sake of clarity.

The following is the main result concerning Problem P (see [5] for details).

Theorem 1. *Assume that D, D_S, k_L^d , k_L^a and ξ_m are positive constants, and $c_0 \in H$, $\xi_0 \in X$ and $\boldsymbol{u} \in L^\infty(0,T;L^\infty(\Omega;\mathbb{R}^{n+1}))$ with $\nabla_S\cdot\boldsymbol{u} \in L^\infty(0,T;L^\infty(\Gamma_S))$ and $\boldsymbol{u}_\tau \in L^\infty(0,T;L^\infty(\Gamma_S;\mathbb{R}^{n+1}))$. Then problem P has a unique solution $c \in \mathcal{W}(0,T)$ and $\xi \in \mathcal{W}_S(0,T)$.*

The proof of Theorem 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.

3 FULLY DISCRETE APPROXIMATIONS

Now, we provide a finite element algorithm to approximate solutions to Problem P and we will show an a priori error estimates result.

The discretization of Problem P is done as follows. First, we assume that $\overline{\Omega}$ is a polyhedral domain and we consider a finite dimensional space $V^h \subset V$, approximating the variational space V, given by

$$V^h = \{v^h \in C(\overline{\Omega})\ ;\ v^h_{|_K} \in P_1(K), \quad \forall K \in \mathcal{T}^h, \quad v^h = 0 \text{ on } \Gamma_D\}, \tag{16}$$

where $P_1(K)$ represents the space of polynomials of global degree less or equal to one in K and we denote by $(\mathcal{T}^h)_{h>0}$ a regular family of triangulations of $\overline{\Omega}$ (in the sense of [3]), compatible with the partition of the boundary $\partial\Omega$ into Γ_D, Γ_N and Γ_S; i.e. the finite element space V^h is composed of continuous and piecewise affine functions. Let h_K be the diameter of an element $K \in \mathcal{T}^h$ and let $h = \max_{K\in\mathcal{T}^h} h_K$ denote the spatial discretization parameter. Moreover, let $(\tilde{\mathcal{T}}^h)_{h>0}$ be the triangulation induced by $(\mathcal{T}^h)_{h>0}$ onto Γ_S. Then, we construct the finite element space X^h, approximating the Sobolev space $H^1(\Gamma_S)$, in the form:

$$X^h = \{w^h \in C(\overline{\Gamma_S})\ ;\ w^h_{|_{\tilde{K}}} \in P_1(\tilde{K}), \quad \forall \tilde{K} \in \tilde{\mathcal{T}}^h\}, \tag{17}$$

where $P_1(\tilde{K})$ represents the space of polynomials of global degree less or equal to one in $\tilde{K}$.

Finally, we assume that the discrete initial conditions, denoted by c_0^h and ξ_0^h, are given by

$$c_0^h = \mathcal{P}_{V^h} c_0, \quad \xi_0^h = \mathcal{P}_{X^h} \xi_0, \tag{18}$$

where $\mathcal{P}_{V^h}$ and $\mathcal{P}_{X^h}$ are the standard L^2-projection operators over the finite element spaces V^h and X^h, respectively.

To discretize the time derivatives, we consider a uniform partition of the time interval $[0,T]$, denoted by $0 = t_0 < t_1 < \ldots < t_N = T$, and let k be the time step size, $k = T/N$. For a continuous function $f(t)$, let $f_n = f(t_n)$.

Therefore, using the implicit Euler scheme and assuming that all the constants are equal to one for the sake of clarity, we obtain the following fully discrete approximation of Problem P.

Problem P^h. Given $c_0^h \in V^h$, $\xi_0^h \in X^h$, find $c^{hk} = (c_n^{hk})_{n=0}^N \subset V^h$ and $\xi^{hk} = (\xi_n^{hk})_{n=0}^N \subset X^h$ such that $c_0^{hk} = c_0^h$, $\xi_0^{hk} = \xi_0^h$ and, for $n = 1, \ldots, N$,

$$\begin{aligned} &((c_n^{hk} - c_{n-1}^{hk})/k, v^h)_H + ((c_n^{hk}, v^h)) + (\boldsymbol{u}_n \cdot \nabla c_n^{hk}, v^h)_H + (\gamma c_n^{hk}(1 - R(\xi_n^{hk})), \gamma v^h)_X \\ &\qquad = (\xi_n^{hk}, \gamma v^h)_X, \quad \forall v^h \in V^h, \end{aligned} \tag{19}$$

$$\begin{aligned} &((\xi_n^{hk} - \xi_{n-1}^{hk})/k, w^h)_X + \int_{\Gamma_S} \nabla_S \xi_n^{hk} \cdot \nabla_S w^h \, d\Gamma + (\xi_n^{hk}, w^h)_X + ((\boldsymbol{u}_\tau)_n \cdot \nabla_S \xi_n^{hk}, w^h)_X \\ &\qquad = (\gamma c_n^{hk}(1 - R(\xi_n^{hk})), w^h)_X - ((\nabla_S \cdot \boldsymbol{u}_n)\xi_n^{hk}, w^h)_X, \quad \forall w^h \in X^h. \end{aligned} \tag{20}$$

Proceeding as in the proof of Theorem 1, we can prove the existence of a unique solution to Problem P^h.

Now, our aim is to obtain a priori error estimates on the numerical errors $c_n - c_n^{hk}$ and $\xi_n - \xi_n^{hk}$. Then, we assume the following additional regularity on the continuous solution:

$$c \in C^1([0,T]; H) \cap C([0,T]; V), \quad \xi \in C^1([0,T]; X) \cap C([0,T]; H^1(\Gamma_S)). \tag{21}$$

We have the following a priori error estimates result.

Theorem 2. *Let the assumptions of Theorem 1 and the additional regularities (21) hold. If we denote by (c,ξ) and (c^{hk}, ξ^{hk}) the respective solutions to problems P and P^h, respectively, then the following estimates are obtained, for all $v^h = \{v_n^{hk}\}_{n=0}^N \subset V^h$ and $w^h = \{w_n^{hk}\}_{n=0}^N \subset X^h$,*

$$\begin{aligned} &\max_{0 \le n \le N} \|c_n - c_n^{hk}\|_H^2 + \max_{0 \le n \le N} \|\xi_n - \xi_n^{hk}\|_X^2 + k \sum_{j=1}^N \Big(\|c_j - c_j^{hk}\|_V^2 + \|\xi_j - \xi_j^{hk}\|_{H^1(\Gamma_S)}^2 \Big) \\ &\quad \le C k^{-1} \sum_{j=1}^{N-1} \Big(\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 + \|\xi_j - w_j^h - (\xi_{j+1} - w_{j+1}^h)\|_X^2 \Big) \\ &\qquad + Ck \sum_{j=1}^N \Big(\|c_j - v_j^h\|_V^2 + \|c_j' - (c_j - c_{j-1})/k\|_H^2 + \|\xi_j - w_j^h\|_{H^1(\Gamma_S)}^2 \end{aligned}$$

$$+\|\xi_j' - (\xi_j - \xi_{j-1})/k\|_X^2\Big) + C \max_{0\le n\le N} \|c_n - v_n^h\|_H^2 + C \max_{0\le n\le N} \|\xi_n - w_n^h\|_X^2$$
$$+C\|c_0 - c_0^h\|_H^2 + C\|\xi_0 - \xi_0^h\|_X^2. \tag{22}$$

Estimates (22) are the basis for the analysis of the convergence rate. Hence, as an example, assume the following additional regularity conditions on the continuous solution:

$$\begin{aligned} &c \in C([0,T]; H^2(\Omega)) \cap H^2(0,T;H) \cap H^1(0,T;V), \\ &\xi \in C([0,T]; H^2(\Gamma_S)) \cap H^2(0,T;X) \cap H^1(0,T;H^1(\Gamma_S)). \end{aligned} \tag{23}$$

From these regularities, taking into account the approximation properties of the projection operators we easily obtain that (see [3])

$$\|c_0 - c_0^h\|_H^2 + \|\xi_0 - \xi_0^h\|_X^2 \le Ch^2.$$

We have the following.

Corollary 1. *Let the assumptions of Theorem 2 and the additional regularities (23) hold. Therefore, the numerical approximation of Problem P by Problem P^h is linearly convergent; that is, there exists a positive constant C, independent of the discretization parameters h and k, such that*

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

The proof of Corollary 1 is done by using the classical properties on the approximation by the finite element spaces and the projection operators P_{V^h} and P_{X^h} (see again [3]), and taking into account that (see [2] for details),

$$k^{-1}\sum_{j=1}^{N-1}\Big(\|c_j - v_j^h - (c_{j+1} - v_{j+1}^h)\|_H^2 + \|\xi_j - w_j^h - (\xi_{j+1} - w_{j+1}^h)\|_X^2\Big)$$
$$\le Ch^2\left(\|c\|_{H^1(0,T;V)}^2 + \|\xi\|_{H^1(0,T;H^1(\Gamma_S))}^2\right),$$
$$k\sum_{j=1}^{N}\Big(\|c_j' - (c_j - c_{j-1})/k\|_H^2 + \|\xi_j' - (\xi_j - \xi_{j-1})/k\|_X^2\Big) \le Ck^2\left(\|c\|_{H^2(0,T;H)}^2 + \|\xi\|_{H^2(0,T;X)}^2\right).$$

REFERENCES

[1] S. Adami, X.Y. Hu and N.A. Adams. A conservative SPH method for surfactant dynamics, *J. Comp. Phys.*, Vol. **229**, pp. 1909-1926, (2010).

[2] M. Campo, J.R. Fernández, K.L. Kuttler, M. Shillor and J.M. Viaño. Numerical analysis and simulations of a dynamic frictionless contact problem with damage, *Comput. Methods Appl. Mech. Engrg.*, Vol. **196**(1-3), pp. 476–488, (2006).

[3] P.G. Ciarlet, *Basic error estimates for elliptic problems.* P.G. Ciarlet and J.L. Lions eds., *Handbook of Numerical Analysis*, Vol. **II** (1993), pp. 17–351.

[4] G. Dziuk and C. M. Elliott, Surface finite elements for parabolic equations. *J. Comp. Math.*, Vol. **25**, pp. 385-407, (2007).

[5] J.R. Fernández, P. Kalita, S. Migorski, M.C. Muñiz and C. Núñez, Existence and uniqueness results for a kinetic model in bulk-surface surfactant dynamics, *Submitted*, (2015).

[6] J.R. Fernández, P. Kalita, S. Migorski, M.C. Muñiz and C. Núñez, Variational analysis of the LangmuirHinshelwood dynamic mixed-kinetic adsorption model, *Nonlinear Anal. Real World Applications*, Vol. **15**, pp. 205-220, (2014).

[7] J.R. Fernández and M.C. Muñiz, Numerical analysis of surfactant dynamics at air-water interface using the Henry isotherm, *J. Math. Chem.*, Vol. **49**, pp. 1624-1645, (2011).

[8] J.R. Fernández, M.C. Muñiz and C. Núñez, A mixed kinetic-diffusion surfactant model for the Henry isotherm, *J. Math. Anal. Appl.*, **389**, pp. 670-684, (2012).

[9] J. Wloka, *Partial Differential Equations*, Cambridge University Press, London, (1987).