

Nonlinear Spreading Dynamics of a Localized Soluble Surfactant on a Thin Liquid Film

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This paper focuses on the study of the spreading behavior of soluble surfactant in a thin liquid film system. For the convenience of numerical calculation, the system coordinate of the evolution equation is transformed. The generalized Frumkin model is used to simulate the adsorption/desorption process of soluble surfactant. Nonlinear coupling evolution equations are derived using the long-wave approximation and the cross-sectional averaging method. The spreading rate of a liquid film predicted by the generalized Frumkin model is faster than predicted by the Langmuir model. When the prediction using the generalized Frumkin model is performed at a smaller β (relative surface concentration), the effect of solubility of surfactant will be enhanced. Consequently, a small β will lead to the acceleration of spreading behavior; however, contrary results will come out while the value of β exceeds 2.0. The dimensionless bulk diffusion constant D_1 (the molecular interaction parameter, K and the activation energy of desorption, v_d) will enhance (weaken) the desorption of surfactant and decelerate (accelerate) the spreading rate of thin liquid film.

KEYWORDS: thin liquid films, nonlinear, spreading, soluble surfactant, generalized Frumkin, adsorption/desorption

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1. Introduction

The monolayer spreading processes of a liquid film is one of the important research subjects in recent years.^{1–4)} The spreading process of liquid flow has been widely applied to the research areas of medicine and general industry. For the application in medicine, the surfactant replacement therapy (SRT) saves many premature babies. The respiratory distress syndrome is very common in premature babies. The respiratory distress syndrome is treated with the delivery of surfactant to the airway and alveoli. However, the physical mechanism of interaction is not clear. Many researchers indicated that it is important to clarify the mechanism of the medicine or aerosol transport process in the alveoli or airway.^{5–9)}

The long-wave approximation was the method used by most of previous studies, which assumed that the critical wavelength of the liquid system is far larger than the liquid film's characteristic depth. This method used the lubrication theory to derive the evolution equations for a liquid film system.^{11–15)} The adsorption process of surfactant on the free surface is the main cause of the spreading behavior. The absorption of surfactants causes the distribution of surfactant concentration that will yield the surface tension gradient. The monolayer spreading of the liquid film will not stop till the easing of surface tension gradient.¹⁶⁾

Most reports concerned with monolayer spreading problems discussed a liquid film with insoluble surfactants.^{6–8,18–21)} However, the existence of soluble surfactant is more common than the existence of insoluble surfactant. The spreading process of a liquid film with soluble surfactant has been studied by Halpern and Grotberg.²²⁾ They mentioned that the gradient of surface tension will

yield a spreading flow of the liquid film. They also reported that the increase of solubility will decrease the surface concentration of surfactant. This process will generate a back-flow that is driven by adsorption. The slow and fast sorption processes of surfactant molecules have been discussed by Jensen and Grotberg.⁹⁾ They stated that the process of fast sorption is created by the transient desorption of surfactant molecules from the surface to the bulk. The process of the slow sorption is created by the slow movement of surfactant molecules. They also discovered that the spreading rate of a liquid film with insoluble surfactant predicted by fast sorption is much lower than the slow sorption; and the liquid film will generate much larger disturbance.

In the previous studies, researchers usually used a more simplified Langmuir adsorption model to study liquid film systems with soluble surfactant.^{9,22–29)} However, the Langmuir adsorption model is not able to simulate the adsorption/desorption kinetics of soluble surfactant on the liquid film surface and in its bulk phase. Therefore, a more general model is needed to simulate the adsorption/desorption kinetics. Recent studies of adsorption theory have shown that the effect of adsorption/desorption kinetics could be expressed by the molecular interaction and its sorption activation energies. The activation energies of sorption was indicated to be a function of surfactant concentration on the fluid surface,^{30–34)} which was based on the Frumkin adsorption model. Lin *et al.*^{35,36)} showed the Langmuir and the Frumkin adsorption models can not describe and simulate correctly the adsorption/desorption kinetics of the soluble surfactant between the surface and the bulk phase of fluid. After that, they proposed a more complete model, the generalized Frumkin adsorption model which had been shown to agree well with the experimental results. The generalized Frumkin adsorption model assumes that the behavior of absorption is governed by the interaction among

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molecules, which is the activation energy of absorption/desorption. The relationship between adsorption/desorption rate and activation energy can be expressed as the Arrhenius equation. A generalized Frumkin adsorption model presented by Lin *et al.*³⁷⁾ is used to further analyze the nonlinear rupture behaviors of thin liquid films with soluble surfactant.

The objective of present study is to further discuss the spreading process of a liquid film with soluble surfactant. The study used the generalized Frumkin model to simulate the adsorption/desorption process of the surfactant molecules in the bulk and on the top surface of the liquid film. The long-wave approximation and cross-section averaging method was first utilized to derive a set of nonlinear coupling evolution equations. The strip spreading property was used to transform the nonlinear coupling evolution equations to a much simplified coordinate system. The numeric analysis was then used to solve the nonlinear evolution equation. Finally, based on the result of present study, the mechanism of dynamic kinetics of soluble surfactant will be discussed. Besides, the results were also compared with those obtained previously using Langmuir adsorption model.^{9,22)}

2. The Physical Model

2.1 Governing equations and associated boundary conditions in dimension-less form

The physical model used in this study represents soluble surfactants on a thin film system, which is assumed to be an incompressible Newtonian viscous liquid coated on a flat plate. The liquid is assumed to have surface tension of the thin film, σ_0 ; kinematic viscosity, ν ; density, ρ ; dynamic viscosity, $\mu = \rho\nu$ and other general physical properties. The local thickness of the film, h , is assumed to be thin enough to neglect the gravity effect. In this study, the dimensionless physical quantities are introduced using the following scales: spatial scale h_0 , the average local thickness of the thin liquid

film; L_0 , the initial horizontal length of the liquid films; parameter $\varepsilon = h_0/L_0 \ll 1$; time $\mu L_0/\sigma_0 h_0$; velocity $\sigma_0 h_0/L_0$; pressure σ_0/L_0 ; surface tension σ_0 ; density $\mu L_0/\sigma_0 h_0^2$. The surfactant concentration on the surface and in the bulk of a liquid film is represented by the uniform equilibrium surface concentration Γ_0 and the uniform equilibrium surfactant concentration c_0 as a measurement unit of the dimensionless physical quantities. In this paper we consider the spreading is dominated by surface tension, the Marangoni effect, and solubility. However, the relatively weaker van der Waals attraction is neglected.^{7-9,21)} From these definitions, the dimensionless governing equations and their boundary conditions can be formulated to describe the proposed liquid film system.

$$u_x + w_z = 0, \tag{1}$$

$$u_t + uu_x + wu_z = -p_x + (u_{xx} + u_{zz}), \tag{2}$$

$$w_t + uw_x + ww_z = -p_z + (w_{xx} + w_{zz}), \tag{3}$$

$$c_t + uc_x + wc_z = D_1(c_{xx} + c_{zz}), \tag{4}$$

Where u and w are dimensionless velocity components in x and z directions, respectively; p is the dimensionless pressure. The dimensionless bulk diffusion constant is denoted by $D_1 = D/\nu$, where D is the bulk diffusion coefficient. Equation (1) is the continuity equation. Equations (2) and (3) are the momentum equations. Equation (4) is the advection-diffusion equation for bulk concentration.

The boundary conditions (no-slip and no-flux) on the solid surface, $z = 0$, are

$$u = w = 0, \tag{5}$$

$$c_z = 0. \tag{6}$$

For the free surface $z = h(x, t)$, the boundary conditions (tangential shear, normal stress and kinetic) at the interface can be expressed by

$$[(w_x + u_z)(1 - h_x^2) - 2h_x(u_x - w_z)] = (1 - h_x^2)^{-1/2} \Sigma_x, \tag{7}$$

$$-p + 2(1 - h_x^2)^{-1}[u_x(h_x^2 - 1) - h_x(w_x + u_z)] = (1 - h_x^2)^{-3/2} h_{xx} \Sigma, \tag{8}$$

$$h_t + uh_x = w, \tag{9}$$

The surface tension of liquid film is directly affected by the surfactant concentration. One could use Gibbs' adsorption equation²³⁾ to describe the relationship between surface tension and surfactant concentration. The dimensionless equation can then be expressed by (Lin *et al.*³⁷⁾)

$$\Sigma = T + M(1 + \beta) \left[\ln \left(\frac{1 + \beta - \Gamma}{1 + \beta} \right) - \frac{nK}{n + 1} \left(\frac{\Gamma}{1 + \beta} \right)^{n+1} \right], \tag{10}$$

Where the dimensionless surface tension $T = \sigma_0 h_0/\rho\nu^2$; the Marangoni number $M = RT^* \Gamma_0/\sigma_0\nu^2$; the dimensionless parameter of relative surface concentration strength $\beta = \Gamma_0/(\Gamma_\infty - \Gamma_0)$; n is the index of power law (obtained by an optimal fit to the experiment data, detailed in Lin *et al.*³⁵⁾), when $n = 1$ the generalized Frumkin equation reduces to the Frumkin equation;³⁵⁾ and K is the molecular interaction parameter. For cohesive interaction, the energy barrier for desorption increases more steeply than that for adsorption ($\nu_d > \nu_a$) and K is negative. When the cohesive interaction is disappear, K is zero and the generalized

Frumkin equation reduces to the Langmuir equation³⁵⁾ of state. RT is the product of the ideal gas constant and the absolute temperature. ν_a, ν_d are activation energy for absorption and desorption to the change of slope of surface concentration Γ^n ; The transport equation of surfactant concentration Γ along the free surface is given by (Tsai and Yue²³⁾):

$$-\Gamma_t + (1 + h_x)^{-1} \{ (u\Gamma)_x + h_x [(w\Gamma)_x] + h_x^2 \Gamma w_z \} = D_2 [(1 + h_x^2)^{-1} \Gamma_{xx} - h_x h_{xx} (1 + h_x^2)^{-2} \Gamma_x] + B, \tag{11}$$

Where Γ is dimensionless surface concentration; D_2 is dimensionless surface diffusion constant defined by $D_2 = D_s/\nu$ (D_s is the surface diffusion coefficient). B is the normal diffusion flux of surfactant from the bulk phase, which, according to Fick's law of diffusion, can be expressed by

$$B = -D_1[(n \cdot \nabla)c] = -\frac{D_1}{\lambda}(1 + h_x^2)^{1/2}(-h_x c_x + c_z), \quad (12)$$

where λ is the equilibrium rate between the surface and the bulk phase of the thin liquid film, which is defined by $\lambda = \Gamma_0/h_0 c_0$. For a highly elevated c_0 , λ will approach zero since Γ_0 is bounded by Γ_∞ . In this limit, diffusion is more rapid compared with the surface convection, and the surfactant transport is adsorption/desorption-controlled. For an extremely diluted c_0 , λ will increase to infinitely large. In this limit, diffusion is slow compared to the surface convective flux, and the surfactant transport is diffusion controlled. Note that λ measures the degree of solubility (23): for decreasing λ , the surfactant become more soluble in the substrate; while for large λ , the surfactant adsorbs preferentially on the free surface. For the case of insoluble surfactant, there is no surfactant in the bulk fluid, i.e., $B = 0$. However, to solve the soluble surfactant transportation problem, eqs. (4) and (12) are required and the diffusive flux B must be known. The generalized Frumkin adsorption model (Lin *et al.*³⁵⁾ has been derived, which can be normalized and expressed in a dimensionless mode by

$$B = J \left[c \left(1 + \frac{1 - \Gamma}{\beta} \right) - \Gamma \right] \exp(\nu_d \Gamma^n), \quad (13)$$

The equation concerned with the equilibrium concentration of the surfactant, in the dimensionless process the following equilibrium equation is introduced to simplify the equation above.

$$\begin{aligned} c_0 &= \frac{k_d}{k_a} \frac{\Gamma_0}{\Gamma_\infty - \Gamma_0} \exp[(E_a - E_d)/RT] \\ &= \frac{k_d}{k_a} \frac{1}{\beta} \exp[(E_a - E_d)/RT], \end{aligned} \quad (14)$$

In eq. (13), $J = \mu L_0 k_d / \sigma_0$ is a dimensionless parameter of the rate constant for desorption rate; If $J = 0$, there are no sorptive fluxes, the bulk concentration equation the transport of a passive scalar by a surfactant-driven flow. In the case $J \rightarrow \infty$, the bulk and surface surfactant distributions arrive at equilibrium rapidly according to the linearized Langmuir isotherm.³⁵⁾ and $\nu_d = \Gamma_0^n \nu_d^* / RT^* \exp(-E_d/RT^*)$ is a dimensionless parameter of ν_d^* . As described in eq. (11), the magnitude of B will be decreased as Γ is increased. The surfactant molecules will diffuse from the fluid surface into the bulk of fluid. In contrast, the adsorption rate will be increased as the bulk concentration, c , is increased. And therefore the surfactant molecules will diffuse from the bulk to the surface. In the following we will use long wave approximation and cross-sectional averaging methods to solve the evolution equation that governing the fluid system.

2.2 Long-wave approximation and cross-sectional averaging method

A long wave approximation method described in Williams and Davis's study³⁸⁾ is used to obtain successive approximations for the solutions of eqs. (1) to (3). Here, we re-define

the dimensionless variables that are scaled by a small parameter ε in the following measures:

$$\begin{aligned} x &= \varepsilon^{-1} \xi, \quad z = \zeta, \quad t = \varepsilon^{-1} \tau, \quad h = H, \\ u &= U, \quad w = \varepsilon W, \quad p = \varepsilon^{-1} P, \quad \phi = \varepsilon^{-1} \Phi. \end{aligned} \quad (15)$$

All the scaled variables and their derivatives with respect to other variables are taken with the first order. Moreover, it is assumed that the orders of the following parameters are

$$T = O(1), \quad M = O(\varepsilon^2), \quad D_1 = O(\varepsilon^2), \quad D_2 = O(\varepsilon^2). \quad (16)$$

By introducing the following regular perturbation expansion for U , W and P , which are expressed by

$$(U, W, P) = (U_0, W_0, P_0) + \varepsilon(U_1, W_1, P_1) + \dots, \quad (17)$$

into eqs. (1)–(3), the governing equations and associated boundary conditions in the leading-order can be obtained as follows.

$$U_{0\xi} + W_{0\zeta} = 0, \quad (18)$$

$$U_{\xi\xi} = P_{0\xi}, \quad (19)$$

$$P_{0\xi} = 0, \quad (20)$$

and the boundary condition at the interface of solid and fluid, $\zeta = 0$, is

$$U_0 = 0, \quad (21)$$

The boundary conditions at free liquid surface, $\zeta = h$, are

$$U_{0\zeta} = -M \left[\frac{1 + \beta}{1 + \beta - \Gamma} + nK \left(\frac{\Gamma}{1 + \beta} \right)^n \right] \Gamma_\xi, \quad (22)$$

$$P_0 = -TH_{\xi\xi}, \quad (23)$$

$$H_\tau + U_0 H_\xi = W_0. \quad (24)$$

The cross-sectional averaging technique was used to solve the transport eqs. (4) and (11). One could take $\kappa^2/D_1 \ll 1$ and decompose c into two independent components, as given below once the leading terms in the average of C taken with respect to z are given

$$c = c_0(x, t) + \frac{\kappa^2}{D_1} c_1(x, z, t), \quad (25)$$

Finally, one can obtain the following evolution equations:

$$h_t + \left\{ \frac{1}{3} Th^3 h_{xxx} - \frac{1}{2} M \left[\frac{1 + \beta}{1 + \beta - \Gamma} + nK \left(\frac{\Gamma}{1 + \beta} \right)^n \right] h^2 \Gamma_x \right\}_x, \quad (26)$$

$$\begin{aligned} c_t + \left\{ \frac{1}{3} Th^3 h_{xxx} - \frac{1}{2} M \left[\frac{1 + \beta}{1 + \beta - \Gamma} + nK \left(\frac{\Gamma}{1 + \beta} \right)^n \right] h \Gamma_x \right\} c_x \\ = \frac{D_1}{h} (hc_x)_x + \frac{J\lambda}{h} \left[c \left(1 + \frac{1 - \Gamma}{\beta} \right) - \Gamma \right] \exp(\nu_d \Gamma^n), \end{aligned} \quad (27)$$

$$\begin{aligned} \Gamma_t + \left\{ \frac{1}{3} Th^2 h_{xxx} - M \left[\frac{1 + \beta}{1 + \beta - \Gamma} + nK \left(\frac{\Gamma}{1 + \beta} \right)^n \right] h \Gamma_x \right\}_x \\ = D_2 \Gamma_{xx} + J \left[c \left(1 + \frac{1 - \Gamma}{\beta} \right) - \Gamma \right] \exp(\nu_d \Gamma^n). \end{aligned} \quad (28)$$

Using the above coupling evolution eqs. (26)–(28), one could obtain the thickness of liquid films and the surfactant

concentration in the fluid bulk and on the fluid surface.

3. Nonlinear Numerical Analysis Results

This article focuses on the spreading process of a liquid film with soluble surfactant. The generalized Frumkin model was used to simulate the film system. The results were compared with those estimated by the Langmuir adsorption model. The results of the spreading process were also compared with those of a liquid film with insoluble surfactant. At $x = 0$, it is assumed that there is no surfactant flux ($u = \Gamma_x = c_x = 0$). Otherwise, it is assumed that there exists the flux of surfactant. As $x \rightarrow \infty$, it is assumed that $h \rightarrow 1$, $c \rightarrow 0$, and $\Gamma \rightarrow 0$. From the mass conservation rule, eqs. (7) and (13), the total mass per unit length of the surfactant can be obtained as Jensen and Grotberg:⁹⁾

$$m = \int_0^\infty \Gamma(x,t) + \frac{1}{\lambda} \int_0^h c(x,z,t) dz dx. \quad (29)$$

In Jensen and Grotberg's paper,⁹⁾ they proposed that the monolayer spreading growth rate of planar strip system is proportional to $t^{1/3}$. Naturally, this condition can be used to define the following forms:

$$\begin{aligned} \xi &= \frac{x}{t^{1/3}}, \quad \tau = t, \quad H(\xi, \tau) = h(x,t), \\ F(\xi, \tau) &= c_0(x,t)^{1/3}, \quad G(\xi, \tau) = \Gamma_0(x,t)^{1/3}, \end{aligned} \quad (30)$$

One can use the above definitions to transform the system coordinates for the above three coupling eqs. (26), (31) and (32). These equations consequently become:

$$\tau H_\tau = \frac{1}{3} \xi H_\xi + \left[-\frac{1}{3} TH_{\xi\xi\xi} H^3 \tau^{-1/3} + \frac{1}{2} M^* H^2 G_\xi \right], \quad (31)$$

$$\begin{aligned} \tau F_\tau &= \frac{1}{3} (\xi F)_\xi + \left[-\frac{1}{3} TH_{\xi\xi\xi} H^2 \tau^{-1/3} + \frac{1}{2} M^* H G_\xi \right] F_\xi + \frac{D_1 \tau^{1/3}}{H} \\ &\quad (HF_\xi)_\xi - \frac{J\lambda\tau}{H} \left[F \left(1 + \frac{1 - G\tau^{1/3}}{\beta} \right) - G \right] \exp(\nu_d G^n \tau^{-nb}), \end{aligned} \quad (32)$$

$$\begin{aligned} \tau G_\tau &= \frac{1}{3} (\xi G)_\xi + \left[-\frac{1}{2} TH_{\xi\xi\xi} G \tau^{-1/3} + \frac{1}{2} M^* H G_\xi G \right] + D_2 G_{\xi\xi} \tau^{1/3} \\ &\quad + J\tau \left[F \left(1 + \frac{1 - G\tau^{1/3}}{\beta} \right) - G \right] \exp(\nu_d G^n \tau^{-nb}), \end{aligned} \quad (33)$$

where

$$M^* = M \frac{1 + \beta}{1 + \beta - G\tau^{-1/3}}.$$

The relative boundary and the initial conditions are given as follows.

The boundary conditions are:

For the downstream, $H(\xi, \tau) = 1$, $G(\xi, \tau) = 0$, and $F(\xi, \tau) = 0$.

For the upstream, $G_\xi = 0$, $F_\xi = 0$, $G_\xi = 0$, and $H_{\xi\xi\xi} = 0$.

The initial conditions are $H(\xi, 1) = 1$, $F(\xi, 1) = 0$. and

$$G(\xi, 1) = \frac{1}{2} \left[1 - \tanh \left(\frac{\xi - \xi_m}{\xi_m} \right) \right], \quad (34)$$

where $\xi_m = 0.5$, $\xi_m = 0.1^9$.

After coordinate transformation, the numerical solutions can be obtained. The finite difference method was used to expand the coupling evolution equations into algebraic equations. The center difference is employed for spatial domain while the Crank–Nicholson method is used for time domain. The Newton–Raphson iteration scheme is introduced to solve the non-linear difference equations and the convergence tolerance is selected to 10^{-5} .

4. Results and Discussion

Previous studies have reported that many factors would affect the spreading of a liquid film.^{5–8,22)} This article discusses the effect of solubility on the surface and bulk concentration of a liquid film. It also discusses the factors that influence the spreading of liquid film. For comparison,

the same parameters used in previous studies^{8,9,35)} were also used in this study, they are: $T = 0.0001$, $D_2 = 0.01$, $M = 1.0$, $\lambda = 1.0$, $J = 1.0$.

Before starting to analyze the spreading process of a liquid film with soluble surfactant, the spreading process of a liquid film with insoluble surfactant will first be discussed. For the latter film system, the surfactants on the surface and in the bulk of a liquid film do not show the absorption/desorption process. In this condition that the J is equal to zero ($J = 0$), the surfactant exists only on the surface of a liquid film system. The equations left in the evolution coupling equations are eqs. (31) and (33). The predicted spreading process of a liquid film system with insoluble surfactant is illustrated in Fig. 1(a). The distributions of surface surfactant concentration and shear stress are shown in Figs. 1(b) and 1(c), respectively. In these figures, one can observe that the distribution of surface shear stress is induced by the given initial distribution of surfactant concentration. This force will create a significant up front shock at the surfactant distribution in a liquid film system. This leads to the spreading of surfactant. This force will be smoothed out by the spreading of surfactant.⁸⁾ Next, the spreading of soluble surfactants in the liquid film system is discussed. Here, the adsorption/desorption process at the surface and in the bulk of a liquid film system is considered. Comparing this prediction to that by the Langmuir model, it is obvious that the surface concentration of soluble surfactant predicted by the Langmuir model is decreased faster than that predicted by the generalized Frumkin model. This prediction will lead to a much faster decline of

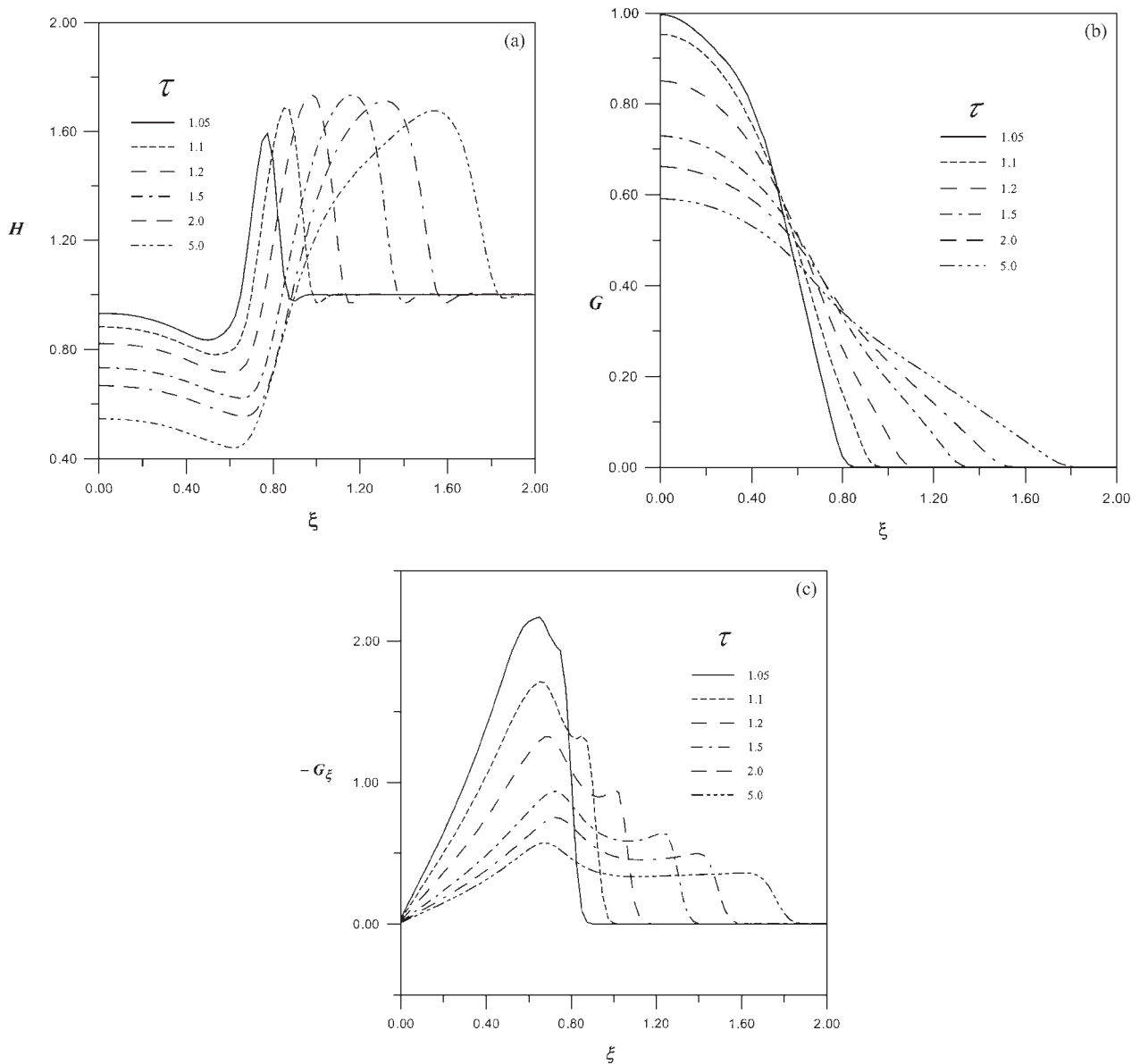


Fig. 1. (a) The predicted spreading process of a liquid film system with insoluble surfactant at different times, $\tau = 1.05, 1.1, 1.2, 1.5, 2$ and 5 , respectively. (b) The predicted surface concentration of a spreading liquid film with insoluble surfactant at different t times, $\tau = 1.05, 1.1, 1.2, 1.5, 2$ and 5 , respectively. (c) The predicted shear stress of spreading liquid film with insoluble surfactant at different times, $\tau = 1.05, 1.1, 1.2, 1.5, 2$ and 5 , respectively.

concentration gradient and a slower spreading of surfactant.

Next, the effect of the solubility of surfactant on the liquid film spreading process is further discussed. The initial distributions of surface and bulk concentrations for the present model are shown in Fig. 2, where the initial surfactant concentration at designed locations for two simulated models and the liquid film system with insoluble surfactant are presented. These data indicate that the initial surfactant concentrations for two models are lower than that of a liquid film with insoluble surfactant. The concentration at the initial location predicted by the Langmuir model is dropping faster than predicted by others. The time required for reaching the equilibrium concentration for both the surface and the bulk predicted by the Langmuir model are also shorter than predicted by other models. While, it took longer for the generalized Frumkin model to reach the equilibrium. This reflects that the Langmuir absorption

model will predict a stronger desorption rate for the surfactant. Therefore, one may conclude that the solubility predicted by Langmuir model is stronger than predicted by other models. Resultantly, the surface concentration of a liquid film at the central area is declined dramatically, which will blunt the induced shear stress significantly. In this case, spreading rate will be increased. Furthermore, the spreading rate of a liquid film with surfactant estimated by the generalized Frumkin model and Langmuir model are slower than that predicted in the case of a liquid film with insoluble surfactant.

Finally, the influence of important parameters, β , D_1 , ν_d , K of the generalized Frumkin model on the spreading process is discussed. β , denoted by $(\Gamma_\infty - \Gamma_0)/\Gamma_0$ is the magnitude of dimensionless relative surface concentration. A smaller β means the equilibrium concentration Γ_0 is closer to the saturated concentration Γ_∞ , which means a

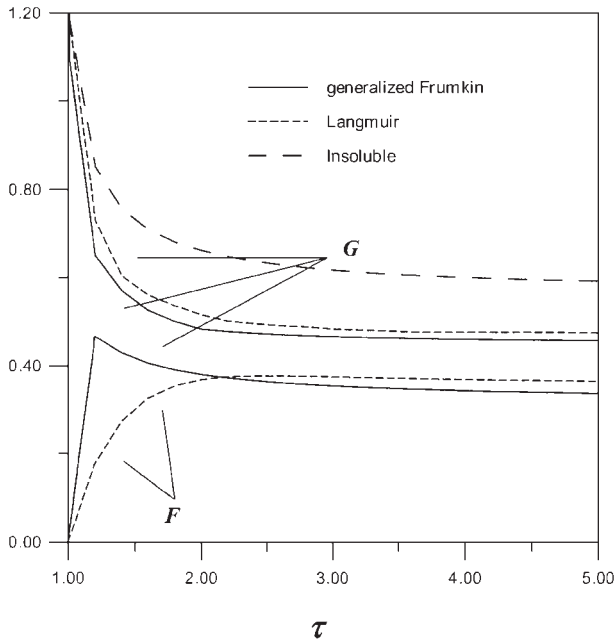


Fig. 2. The surface and bulk concentrations at initial location predicted by concerning models.

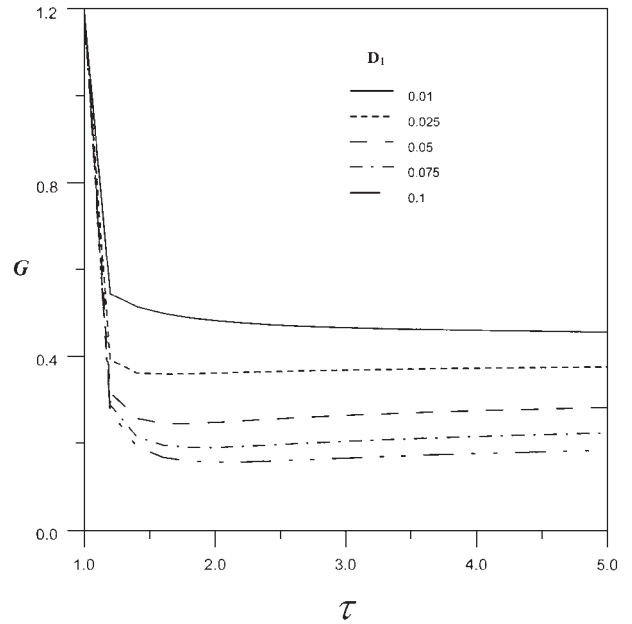


Fig. 4. The variation of surface concentration at the initial location predicted by the generalized Frumkin model with three different values of D_1 .

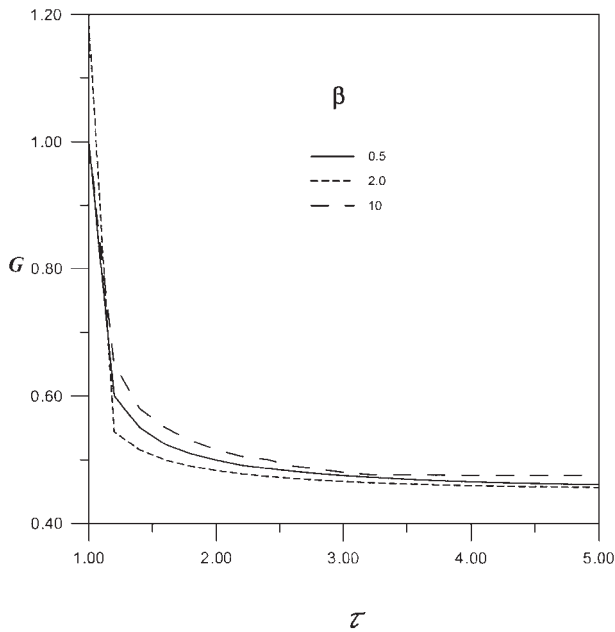


Fig. 3. The variation of surface concentration at the initial location predicted by the generalized Frumkin model with three different values of β .

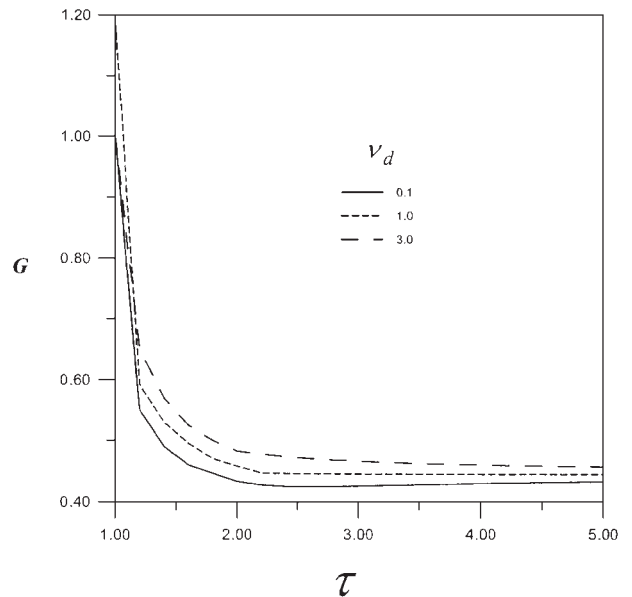


Fig. 5. The variation of surface concentration at the initial location predicted by the generalized Frumkin model with different values of ν_d .

larger surface concentration. From eqs. (10) and (13), it is evident that β will affect not only the adsorption and desorption behaviors of surfactant, but also the shear stress term of the surface tension. The variation of surface concentration at the initial location estimated by the generalized Frumkin model with three different β values As shown in Fig. 3, a faster decrease in the surface concentration G is found at the initial location (that is, the desorption of surfactant will be enhanced) as the relative surface concentration β is increased. However, the surface concentration is increased (that is, the desorption of surfactant will be weakened) when the value of β exceeds

2.0. Factually, the effect of spreading rate should be discussed by considering the Marangoni effect. The distribution of Marangoni flow estimated using small value of β will be much well developed than that is estimated using large β . This means that a higher surface concentration will induce a stronger Marangoni effect when β is small, but there are contrary results while the value of β exceeds 2.0. The variation of surface concentration at the initial location estimated by the generalized Frumkin model with different values of D_1 , ν_d and K were investigated. As shown in Fig. 4, the surface concentration at the initial location shows a faster decline as the value of D_1 is increased. This means D_1 will enhance the desorption of surfactant and decelerate the spreading rate of the thin liquid film. From Fig. 5,

obviously the surface concentration at the initial location shows a faster decline as the values of ν_d and K are decreased. That is ν_d and K will weaken the desorption of surfactant and accelerate the spreading rate of thin liquid film.

5. Conclusions

This article discusses the spreading process of a liquid film system with soluble surfactant. The generalized Frumkin absorption model³⁵⁾ was used to simulate the adsorption and desorption processes of surfactant on the surface and in the bulk of a liquid film system. The important findings are summarized as follows:

1. The desorption (surface concentration) of surfactant from the surface to the bulk predicted by the Langmuir model is faster than that predicated by the generalized Frumkin model. This is because the effect of solubility is overestimated by the Langmuir model and leads to the underestimation of spreading rate. As a result, the prediction using the Langmuir model should be properly corrected.
2. When the prediction using the generalized Frumkin model is performed at a smaller β (a higher surface concentration), the effect of solubility and the Marangoni effect of a liquid film system will be enhanced. However, the Marangoni effect is much more significant than the other. Consequently, a small β value will lead to the acceleration of spreading, but there are contrary results while the value of β exceeds 2.0.
3. The dimensionless bulk diffusion constant D_1 will enhance the desorption of surfactant and decelerate the spreading rate of thin liquid film. But both the activation energy of desorption ν_d and the molecular interaction parameter K will weaken the desorption of surfactant and accelerate the spreading rate of thin liquid film.

The results of this study can be used for further detailed discussion on other fields such as the chemical reaction⁴⁰⁾ and evaporation or condensation of liquid films.⁴¹⁾ the liquid film with soluble surfactant.

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