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A study on the method of short-time approximation–curvature effect

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ABSTRACT

The short-time approximation method is known as a simple way to determine the adsorption mechanisms and to estimate the surfactant diffusivity. Three assumptions are needed in order to obtain the linear short-time approximation relationship between $\gamma(t)$ and $t^{1/2}$ to fit the experimental dynamic surface tension data: the surfactant backward diffusion process is negligible, the forward adsorption contributed from the spherical geometry is much smaller than that to a planar surface, and surfactant follows Henry's equation of state.

Recently, a general criterion, in terms of adsorption time and surface pressures for short-time approximation applicability on solution systems assuming a planar gas–liquid interface, has been explored by Casandra et al. (2015). How are the criteria applicable for spherical surfaces? Surface tension relaxes faster and reaches its equilibrium earlier for surfactant molecules mass-transporting onto a spherical interface than onto a planar interface due to the geometrical effect. Ignoring this geometrical effect may cause a serious error in estimating diffusivity and in determining the adsorption mechanism when applying the short-time approximation technique. In this study, a theoretical numerical simulation of the short-time approximation method was conducted, and the general criteria for accurately utilizing the short-time approximation were investigated.

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1. Introduction

Mass transport of surfactant molecules is an important issue for many practical processes, including detergents, inks, adhesives, pesticides and cosmetics, particularly those involving the motion of fluid particles or gas bubbles [1]. Determination of the diffusivity of a surfactant in the bulk phase of a solution is one of the main issues when studying mass transport of surfactants. Diffusivity has usually been determined from dynamic surface tension data, especially when the process involves diffusion-control. In 1946, Ward and Tordai introduced a general equation for interpreting the surfactant adsorption kinetics for a planar gas–liquid interface [2]. This well-known diffusion-controlled adsorption model assumes that the surfactant diffusion between the bulk and sublayer is the rate-limiting step. This *diffusion-controlled* approach has been widely applied for many small surfactants [3].

Although the Ward–Tordai equation was widely applied for simulating experimental data of dynamic surface tension (DST), its application has been hindered for decades due to its complicated numerical calculations. There are various equations which have been proposed in order to circumvent the complicated integration of Ward–Tordai equation. Defay and Hommelen [4] and Hansen and Wallace [5] simplified the Ward–Tordai equation by assuming that at the beginning of the adsorption process the surfactant backward diffusion from the sublayer to the bulk solution could be omitted. In 1980, van den Bogaent and Joos [6] proposed a systematic way to use this simplified Ward–Tordai equation by coupling it with Gibb's adsorption equation. This systematic equation became well-known as a short-time approximation equation.

This linear short-time approximation equation has been widely used to evaluate the surfactant diffusivity or to determine the adsorption mechanism by simply applying a linear fitting, $\gamma(t)$ vs. $t^{1/2}$ to experimental DST data. Recently, a theoretical study was reported for (i) a diffusion controlled adsorption, (ii) a surfactant following the Langmuir adsorption isotherm and (iii) a solution with a planar gas–liquid interface. Simple rules were developed in terms of limiting surface pressure and dimensionless time as a function of dimensionless surfactant concentration [7].

Recently, most of the DST data have been obtained by utilizing a surface with a significant curvature, such as the methods of maximum bubble pressure [8–16], drop weight/volume [12,16,17] and pendant bubble/drop [18–21]. A literature review on the methods for DST measurement used for estimating diffusivity with a short-

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time approximation was detailed in Table S1 of the Supplementary materials. In these cases the adsorption of surfactant molecules is no longer onto a planar interface and utilizing the short-time approximation method may lead to a significant measurement error on the diffusivity estimation. This planer assumption will no longer work unless the surfactant concentration is high enough and the adsorption depth is very thin, making the surfactant molecules adsorb onto a plane-like interface.

Munoz et al. [18] evaluated the diffusivity of Pluronic F68 by applying the short-time approximation equation and linearly fitting the DST data, which were obtained from the pendant bubble method. They reported a significant disagreement between the diffusivity obtained from the short-time approximation and the diffusivity measured using the Quasi Elastic Light Scattering (QELS) method. Eastoe et al. [22] measured the DST data of C_mE_n and di-C_8 (dialkylphosphatidyl-cholines) by using the maximum bubble pressure method. Quite a diverse value of diffusivity resulted when the DST data at different time ranges were fitted by the short-time approximation. Similar results have been reported [11,18] when the short-time approximation was applied. Therefore, an investigation on the effect of the interfacial curvature of the short-time linear approximation is conducted in this study to clarify its applicability.

In this work, a theoretical study on curvature effect for the short-time approximation method was performed. All calculations were conducted with two assumptions: (1) the diffusion-controlled adsorption process has a diffusivity of $D_{set} = 5 \times 10^{-6}$ cm^2/s and (2) the surfactant follows the Langmuir adsorption isotherm with model parameters Γ_∞ (maximum surface concentration) = 5×10^{-10} mol/cm^2 and a (surfactant activity) = 1×10^{-9} mol/cm^3.

2. Theoretical framework

2.1. Ward–Tordai equation

In the case of surfactant adsorption onto a spherical interface from a bulk phase initially containing uniformity of surfactant, the one-dimensional diffusion of the surfactant in the bulk continuous phase is described by Fick's law [23]:

$$\frac{\partial C}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) \tag{1}$$

with initial and boundary conditions:

$$C(r > b, t = 0) = C_0 \tag{2}$$

$$C(r \to \infty, t > 0) = C_0 \tag{3}$$

$$\frac{d\Gamma(t)}{dt} = D\frac{\partial C}{\partial r}\bigg|_{r=b} \tag{4}$$

$$\Gamma(t=0) = 0 \tag{5}$$

where r is the radial coordinate, b is the radius of the spherical bubble, D denotes the diffusivity, C is the surfactant concentration in the bulk phase, C_0 is the initial bulk concentration and Γ is the surface concentration of the surfactant. Initial condition (5) indicates an initially clean air–water surface. By using the Laplace transform, the adsorption of surfactant molecules as a function of time can be formulated in terms of an unknown sublayer concentration $C_s(t) = C(r = b,t)$ [21,24]:

$$\Gamma(t) = (D/b)\left[C_0 t - \int_0^t C_S(\tau)\,d\tau\right] + 2(D/\pi)^{1/2}\left[C_0 t^{1/2} - \int_0^{\sqrt{t}} C_S(t-\tau)\,d\tau^{1/2}\right] \tag{6}$$

where C_s is the subsurface concentration. This relation is the spherical analogue of Ward and Tordai's equation, which is applicable for a mass transport process with an initially clean spherical gas–liquid surface. This subsurface concentration can be determined numerically [25,26]. The first term on the right-hand side of Eq. (6) shows a spherical effect in the diffusion process. Eq. (6) becomes the well-known Ward and Tordai equation for diffusion toward a planar surface when bubble radius b becomes very large:

$$\Gamma(t) = 2(D/\pi)^{1/2}\left[C_0 t^{1/2} - \int_0^{\sqrt{t}} C_S(t-\tau)\,d\tau^{1/2}\right] \tag{7}$$

2.2. Dynamic surface tension

To obtain theoretical DST profiles, the modified Ward–Tordai equation (Eq. (6)) has to be combined with two additional relations: the adsorption isotherm and the equation of state. The adsorption isotherm relates the surface concentration and subsurface concentration of the surfactant. When the mass transport process is diffusion-controlled and the adsorbed surfactants at the air–water surface do not interact with each other, the Langmuir adsorption isotherm is commonly used to describe the relationship between the surface concentration and the bulk concentration:

$$\frac{\Gamma}{\Gamma_\infty} = x = \frac{C/a}{1 + C/a} \tag{8}$$

where Γ_∞ (maximum surface concentration) and a (surfactant activity) are the model parameters of the Langmuir isotherm. The modified Ward–Tordai equation (Eq. (6)) coupled with the Langmuir adsorption isotherm (Eq. (8)) can be solved numerically to obtain the relaxation of surface concentration $\Gamma(t)$.

If the surfactant solution is considered ideal, the Gibbs adsorption equation, $d\gamma = -RT\Gamma\, d\ln C$, and the Langmuir isotherm (Eq. (8)) will allow for the calculation of the surface tension (γ) explicitly in terms of surface concentration:

$$\gamma(t) = \gamma_0 + RT\Gamma_\infty ln[1 - (\Gamma(t)/\Gamma_\infty)] \tag{9}$$

where R is the universal gas constant, T is temperature and γ_0 is the surface tension of the solvent.

2.3. Short-time approximation

Three assumptions are needed in order to obtain the linear relationship between $\gamma(t)$ and $t^{1/2}$, the short-time approximation for a spherical solution drop or a spherical bubble inside surfactant solution: the backward surfactant diffusion process is negligible, the forward adsorption contributed from the spherical geometry is much smaller than the forward adsorption to a planar interface and $\sqrt{t}/C_S$ remains nearly constant during the adsorption process.

The first assumption, the backward surfactant diffusion process from the sublayer to the bulk phase is negligible, works generally in the initial stage of the adsorption process, *i.e.*, $\int_0^t C_S(\tau)\,d\tau << C_0 t$ and $\int_0^{\sqrt{t}} C_S(t-\tau)\,d\tau^{1/2} << C_0 t^{1/2}$. Then, Eq. (6) becomes:

$$\Gamma(t) = (D/b)[C_0 t] + 2(D/\pi)^{1/2}\left[C_0 t^{1/2}\right] \tag{10}$$

Next, the forward adsorption contributed from the spherical geometry, $(D/b)C_0 t = \text{Term}_{\text{S-Fw}}$, is assumed to be much smaller than the forward adsorption to a planar interface, $2(D/\pi)^{1/2}C_0 t^{1/2}$. Therefore Eq. (10) becomes:

$$\Gamma(t) = 2C_0\sqrt{\frac{Dt}{\pi}} \tag{11}$$

There are two ways for the third assumption. First way follows the idea of Joos and Rillaerts [16]. They assumed that the surfactant follows Henry's equation of state ($\gamma_0 - \gamma = \Gamma RT$) for a

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