RESEARCH NOTES

Diffusion-controlled Adsorption Kinetics at Air/Solution Surface Studied by Maximum Bubble Pressure Method*

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Abstract In studying the diffusion-controlled adsorption kinetics of aqueous surfactant solutions at the air/solution surface by means of the maximal bubble pressure method, Fick's diffusion equation for a sphere should be used. In this paper the equation was solved by means of Laplace transformation under different initial and boundary conditions. The dynamic surface adsorption $\Gamma(t)$ for a surfactant solution, which was used to describe the diffusion-controlled adsorption kinetics at the solution surface, was derived. Different from the planar surface adsorption, the dynamic surface adsorption $\Gamma(t)$ for the short time consists of two terms: one is the same as Ward-Tordai equation and the other reflects the geometric effect caused by the spherical bubble surface. This effect should not be neglected for the very small radius of the capillary. The equilibrium surface tension γ_{eq} and the dynamic surface tension $\gamma(t)$ of aqueous $C_{10}E_6$ [$CH_3(CH_2)_9(OCH_2CH_2)_6OH$] solution at temperature 25°C were measured by means of Wilhelmy plate method and maximal bubble pressure method respectively. As $t \to 0$, the theoretical analysis is in good agreement with experimental results and the dependence of $\gamma(t)$ on $\left(\sqrt{t} + \dfrac{r_0}{\sqrt{\pi D}}\right)^2$ is linear.

Keywords diffusion-controlled adsorption kinetics, dynamic surface tension, maximum bubble pressure method

1 INTRODUCTION

Diffusion-controlled adsorption was discussed in many papers[1−15]. In studying such diffusion-controlled kinetics, dynamic surface tensions were measured. One of the methods to measure dynamic surface tensions is the maximum bubble pressure method[6−15]. According to the basic principle of this method, the geometric effect of the bubble should be considered. However, this kind of effect has been simply neglected in the literatures and the diffusion equation for the planar surface has always been used. This paper will be focused on this point and a general equation of dynamic surface adsorption for the maximum bubble pressure method will be derived and discussed.

2 THEORY

In measuring the surface tensions of aqueous solutions by means of the maximum bubble pressure method, the gas bubbles are formed in the solution at the end of the capillary. The surface tension γ can be calculated through measuring the maximum pressure (p_{max}) in the bubbles. If during the measurement the equilibrium state is established slowly, the measured maximum pressure will be a function of time $t[p_{max}(t)]$ and the calculated surface tension will correspond to the dynamic surface tension $\gamma(t)$. This time dependence is caused by the diffusion of surfactant molecules from the bulk phase to the sub-surface phase. Here the diffusion profile is not a plane (Fig. 1). The diffusion is in radial direction and the adsorption is at air/solution surface $r = r_0$, where r_0 is the radius of the capillary. This is different from the planar model[1]. It is assumed that the solution is initially of uniform concentration (c_0), and at a certain time a half-spherical solution/air surface is developed (Fig. 1). The diffusion in the r-direction (pointing to the center of the bubble) is considered. The time derivative of $c(r,t)$ at a given position follows from mass conservation. The starting point for the theoretical analysis is the diffusion equation (Fick's second law) in spherical coordinates

$$\frac{\partial c(r,t)}{\partial t} = D\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{2D}{r}\frac{\partial c(r,t)}{\partial r} \qquad (1)$$

where $c(r,t)$ is the concentration for $r \geqslant r_0$ and D is the diffusion coefficient. The initial condition is

$$c(r,0) = c_0 \qquad (2)$$

c_0 is the bulk concentration. This initial condition means that the concentration in the solution is the same everywhere before the surface is created.
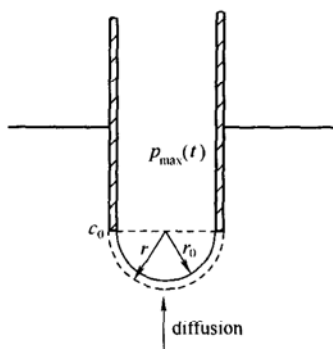
Figure 1   Schematics of a gas bubble in solution

To solve Eq. (1) by means of Laplace transformation, two boundary conditions are necessary except the initial condition. The first one is

$$\lim_{r \to \infty} c(r,t) = c_0 \qquad (3)$$

The second boundary condition is the so-called subsurface concentration $c(r_0, t)$, which corresponds to two cases: adsorption without and with back-diffusion. The first case is the short-time approximation, where the back-diffusion is neglected. The second one takes the back-diffusion into consideration.

2.1 Adsorption without back-diffusion—short time limit

In the early stage of diffusion, the backward movement of solute can be neglected, because the surface is sufficiently empty to take up solute molecules as soon as they arrive. Hence the second boundary condition is

$$c(r_0, t) = 0 \qquad (4)$$

Solving the diffusion Eq. (1) under the initial condition [Eq. (2)] and the two boundary conditions [Eqs. (3) and (4)] by means of Laplace transformation, we have

$$c(r,t) = c_0 - \frac{r_0}{r} c_0 + \frac{2c_0}{\sqrt{\pi}} \frac{r_0}{r} \int_0^{\frac{r-r_0}{2\sqrt{Dt}}} \exp\left(-u^2\right) \mathrm{d}u \quad (5)$$

At any time, surface adsorption $\Gamma(t)$ is related to the concentration in the solution adjacent to the surface. Surface adsorption formally is a function of time t and radial distance r. If this function is considered only at the surface $r = r_0$, a function $\Gamma(t)$ results. During adsorption, $\Gamma(t)$ increases at a rate determined by the diffusion flux corresponding to Fick's first law

$$\left.\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right|_{r=r_0} = \left.\frac{\partial c(r,t)}{\partial r}\right|_{r=r_0} \qquad (6)$$

Insertion of Eq. (5) into Eq. (6) and integration at $r = r_0$ yields

$$\Gamma(t) = \frac{Dc_0 t}{r_0} + 2c_0 \sqrt{\frac{Dt}{\pi}} \qquad (7)$$

The dynamic adsorption for the spherical model consists of two terms. The second term is the same as the Ward and Tordai equation[1], while the first one reflects the geometric effect on adsorption. By setting $r_0 \to \infty$, the first term is zero, Ward and Tordai equation is obtained.

In contrast to the short adsorption time range, the adsorption behavior during longer time is influenced by back-diffusion. The next part of the paper will deal with this phenomenon.

2.2 Adsorption with back-diffusion

As soon as the concentration near the surface is considerably different from zero, back-diffusion of surfactant molecules from the surface to the bulk may take place. Experimental data indicate that for the long time range $c(r_0, t)$ should be a function of time. This leads to the following boundary condition

$$c(r_0, t) = \phi(t) \qquad (8)$$

The solution of Eq. (1) under the initial condition [Eq. (2)] and the boundary conditions [Eqs. (3) and (8)] is

$$\begin{aligned}
c(r,t) =& c_0 - \frac{r_0}{r}[c_0 - \phi(t)] + \frac{2[c_0 - \phi(0)]}{\sqrt{\pi}} \frac{r_0}{r} \\
& \int_0^{\frac{r-r_0}{2\sqrt{Dt}}} \exp\left(-z^2\right)\mathrm{d}z - \frac{2}{\sqrt{\pi}} \frac{r_0}{r} \int_0^t \phi'(u) \\
& \left[\int_0^{\frac{r-r_0}{2\sqrt{D(t-u)}}} \exp\left(-z^2\right)\mathrm{d}z\right]\mathrm{d}u \quad (r \geqslant r_0)
\end{aligned}$$
$$(9)$$

Substitution of Eq. (9) into Eq. (6) and integration at $r = r_0$ leads to

$$\begin{aligned}
\Gamma(t) =& \frac{Dc_0}{r_0} t - \frac{D}{r_0} \int_0^t \phi(u)\mathrm{d}u + \\
& 2\sqrt{\frac{D}{\pi}} \left[c_0\sqrt{t} - \int_0^t \frac{\phi(u)}{2\sqrt{t-u}}\mathrm{d}u\right]
\end{aligned}$$
$$(10)$$

This solution is our general diffusion-controlled equation for spherical surface adsorption. The difference between Eq. (10) and the result of Ward and Tordai [Eq. (22) in Ref.[1]] for adsorption with back-diffusion is reflected in the two terms which are functions of r_0. They reflect the geometric effect of the spherical surface on the adsorption. For the limiting case $r_0 \to \infty$, they approach 0 and the result reduces

to that for the planar surface, Ward and Tordai equation. Thus Ward and Tordai equation is only a particular result of our equation as $r_0 \to \infty$.

In contrast to the result of adsorption without back-diffusion [Eq. (7)], the two terms with $\phi(t)$, which are always negative because $\phi(t) \geqslant 0$, are the flow of the back diffusion. By setting $\phi(t) = 0$ (neglecting back-diffusion), Eq. (10) reduces to Eq. (7).

2.3 The relationship between $\gamma(t)$ and $\Gamma(t)$

For a diffusion-controlled adsorption mechanism, an equilibrium adsorption isotherm, such as the Langmuir isotherm, can be applied as a relation between the dynamic surface tension $\gamma(t)$ and the dynamic adsorption $\Gamma(t)$[15]

$$\gamma(t) = \gamma_0 + RT\Gamma_\infty \ln[1 - \Gamma(t)/\Gamma_\infty] \qquad (11)$$

where Γ_∞ is the saturation adsorption, γ_0 the surface tension of the solvent (water), T is the temperature, and R the ideal gas constant. Expanding the logarithm in Eq. (11) into a power series and breaking off after the first term, we have the following approximation

$$\gamma(t) = \gamma_0 - RT\Gamma(t) \qquad (12)$$

Applying Eqs. (7) and (10) to Eq. (12) yields for the short time limit (adsorption without back-diffusion)

$$\gamma(t) = \gamma_0 - RT\frac{Dc_0 t}{r_0} - 2RTc_0\sqrt{\frac{Dt}{\pi}} \qquad (13)$$

and for the whole time range (adsorption with back-diffusion)

$$\gamma(t) = \gamma_0 - RT\left\{ \frac{Dc_0}{r_0}t - \frac{D}{r_0}\int_0^t \phi(u)\mathrm{d}u + 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \int_0^t \frac{\phi(u)}{2\sqrt{t-u}}\mathrm{d}u \right] \right\} \qquad (14)$$

3 EXPERIMENTAL

The equilibrium surface tension was measured with Wilhelmy plate tensiometer (K12 from the Company Krüss GmbH Hamburg, Germany). The dynamic surface tension was determined by means of a maximum bubble pressure tensiometer (BP-2 made by Krüss GmbH Hamburg, Germany). The capillary radius was $r_0 = 0.132$ mm. $C_{10}E_6$ was purchased from SIGMA-ALDRICH Chemie, Fluka, Swiss, with purity for gas chromatography. The surfactant was used

without any further purification. Three aqueous surfactant solutions, below the CMC (critical micelle concentration), were prepared using distilled water. All measurements of dynamic surface tension were performed at $(25 \pm 0.1)^\circ$C.

4 RESULTS AND DISCUSSION

The equilibrium surface tensions of aqueous $C_{10}E_6$ solutions are shown in Fig. 2. The CMC at 25°C is 0.68 mol·m^{-3}. In the adsorption kinetics studies, the concentration should be below CMC so that the effect of micelle on adsorption does not exist.
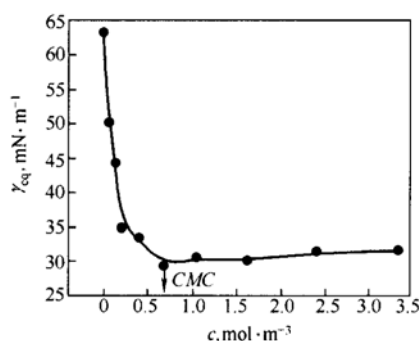
Figure 2   The equilibrium surface tensions
● experimental data

Figure 3 shows the experimental dynamic surface tensions of aqueous $C_{10}E_6$ solutions. Here one can see that the initial value of the surface tension equals that of pure water, which means that the solute is not adsorbed at the surface and the surface is empty at the beginning. This is the reason why the boundary condition [Eq. (4)] was used for the case of adsorption without back-diffusion. It is a reasonable approximation in the short-time range. For the short time range, the diffusion coefficient according to Eq. (13) can be calculated from the measured dynamic surface tensions. Eq. (13) shows a non-linear relationship between $\gamma(t)$ and $\sqrt{t}$, while it is linear for the planar surface adsorption. To overcome this difficulty and obtain diffusion coefficient D, Eq. (13) is rearranged in the following form

$$\sqrt{\frac{r_0(\gamma_0 - \gamma(t))}{RTc_0} + \frac{r_0^2}{\pi}} = \sqrt{Dt} + \frac{r_0}{\sqrt{\pi}} \qquad (15)$$

With $F = \sqrt{\dfrac{r_0(\gamma_0 - \gamma(t))}{RTc_0} + \dfrac{r_0^2}{\pi}}$, Eq. (15) indicates a linear relationship between F and $\sqrt{t}$, as shown in Fig. 4. From the slope, the diffusion coefficient D is calculated, 2.6×10^{-9} m^2·s^{-1}.

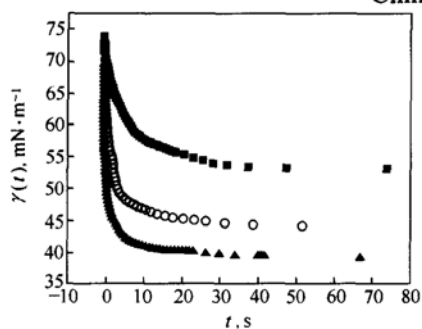**Figure 3　The dynamic surface tensions**
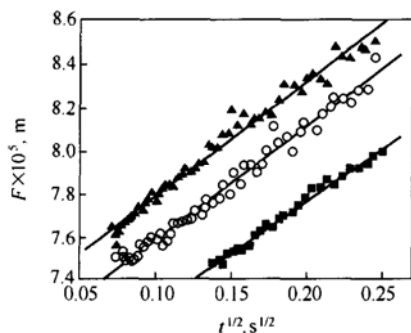c_0, mol·m^{-3}: ■ 0.058; ○ 0.211; ▲ 0.399

Figure 4　The linear relation between F and $\sqrt{t}$ for the adsorption in the short time range
c_0, mol·m^{-3}: ■ 0.058; ○ 0.211; ▲ 0.399;
——— linear fit of data

To check the calculated coefficient, one can also rearrange Eq. (13) in the following form

$$\gamma(t) = \gamma_0 - \frac{RTD}{r_0}c_0\left(\sqrt{t} + \frac{r_0}{\sqrt{\pi D}}\right)^2 + \frac{RTr_0}{\pi}c_0 \quad (16)$$

It means that for the short-time adsorption, there should be a linear relation between the dynamic tension $\gamma(t)$ and $\left(\sqrt{t} + \frac{r_0}{\sqrt{\pi D}}\right)^2$, as shown in Fig.5. It can be seen that the experimental data are in good agreement with the theoretical analysis.
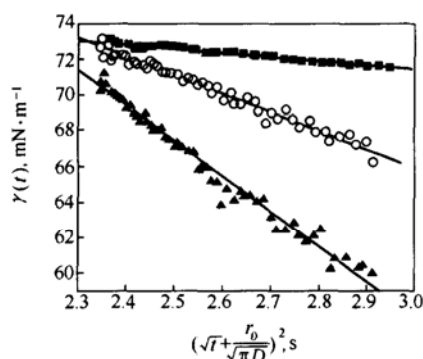

Figure 5　The linear relation between $\gamma(t)$ and $(\sqrt{t} + r_0/\sqrt{\pi D})^2$ for the adsorption in the short time range
c_0, mol·m^{-3}: ■ 0.058; ○ 0.211; ▲ 0.399;
——— linear fit of data

The two parts of Eq. (7) were plotted in Fig. 6. The first term reflects the geometric effect. It should depend on the diffusion coefficient D, the radius of the capillary r_0 and time t. For most of surfactants the diffusion coefficient D are about 10^{-10}—10^{-9} m^2·s^{-1}, so that the contribution of D to the first term is much smaller than that of $\sqrt{D}$ to the second term. However, for very small radius of the capillary r_0, the first term plays an important role in $\Gamma(t)$, so the geometric effect on adsorption must be considered.
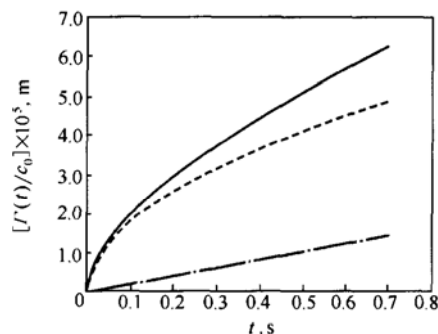

Figure 6　The geometric effect on the adsorption
$(D = 2.6 \times 10^{-9}\,\text{m}^2\text{·s}^{-1})$
——— $\dfrac{Dt}{r_0} + 2\sqrt{\dfrac{Dt}{\pi}}$ (the sum);
- - - - $2\sqrt{\dfrac{Dt}{\pi}}$ [2nd term in Eq.(7)];
—·—·— $\dfrac{Dt}{r_0}$ [1st term in Eq.(7)]

NOMENCLATURE

c_0	bulk concentration, mol·m^{-3}
$c(r,t)$	concentration, mol·m^{-3}
D	diffusion coefficient, m^2·s^{-1}
F	defined function in Eq. (15)
	$\left(F = \sqrt{\dfrac{r_0[(\gamma_0 - \gamma(t)]}{RTc_0} + \dfrac{r_0^2}{\pi}}\right)$, m
$p_{\max}$	maximum pressure, Pa
R	ideal gas constant, J·mol^{-1}·K^{-1}
r	distance in radial direction, m
r_0	capillary radius, m
T	temperature, K
t	times, s
$\Gamma(t)$	dynamic surface adsorption, mol·m^{-2}
Γ_∞	saturation adsorption, mol·m^{-2}
γ_0	surface tension of the solvent (water), mN·m^{-1}
γ_{eq}	equilibrium surface tension, mN·m^{-1}
$\gamma(t)$	dynamic surface tension, mN·m^{-1}
$\phi(t)$	subsurface concentration, mol·m^{-3}

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