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SHORT COMMUNICATION

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Theory of diffusion-controlled adsorption kinetics at the expanding planar surface with a constant area rate

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Abstract The diffusion equation for the expanding surface was solved and a corresponding general expression of dynamic surface adsorption was derived. For the short-time adsorption, a special factor 1/3, which reflected the effect of the expanding surface on the adsorption, appeared in the equation. In addition, the effects of the surface expansion on subsurface concentration ($\phi(t)$), dynamic surface adsorption ($\Gamma(t)$), dynamic surface tension ($\gamma(t)$) and the adsorption mechanism were discussed. In contrast to the adsorption on a still planar surface, $\phi(t)$ and $\Gamma(t)$ are smaller, but $\gamma(t)$ increased. The adsorption mechanism will be the same as long as the corresponding theories are used.

Keywords Adsorption kinetics · Dynamic surface tension · Expanding planar surface

Introduction

In studying diffusion-controlled adsorption kinetics at air/solution interface, Ward–Tordai equation was always used [1]:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \frac{1}{2}\int_0^t \frac{\phi(u)}{\sqrt{t-u}}\,\mathrm{d}u\right], \tag{1}$$

where $\Gamma(t)$ is the dynamic adsorption, D represents the diffusion coefficient of solute, c_0 is the bulk concentration and $\phi(t)$ is the subsurface concentration. To derive this equation, the following diffusion equation (Fick's second law) (Eq. 2) was solved under the necessary initial and boundary conditions (Eqs. 3, 4, 5):

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}, \tag{2}$$

$$\text{initial condition}: \quad c(x,0) = c_0, \tag{3}$$

$$\text{first boundary condition}: \quad \lim_{x\to\infty} c(x,\ t) = c_0, \tag{4}$$

$$\text{second boundary condition}: \quad c(0,t) = \phi(t). \tag{5}$$

The solution of Eq. 2 was [2, 3]

$$c(x,t) = \phi(t) + \frac{2[c_0 - \phi(0)]}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} \exp(-z^2)\,\mathrm{d}z - \frac{2}{\sqrt{\pi}} \int_0^t \phi'(u) \left[\int_0^{x/\left(2\sqrt{D(t-u)}\right)} \exp(-z^2)\,\mathrm{d}z \right] \mathrm{d}u. \quad (6)$$

By inserting Eq. 6 in the following equation (Fick's first law at $x=0$)

$$\left.\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right|_{x=0} = D \left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} \quad (7)$$

Ward–Tordai equation (Eq. 1) was obtained. Here, it should be pointed out that the diffusion equation 2 was applied only for the surface that does not change with time. But in the measuring of the dynamic surface tensions by means of different methods, for example, the maximum bubble pressure method [2, 4–6], drop volume method [7], inclined plate method [8], reversed funnel method [9], the surface changes with time. Therefore, the diffusion equation should be corrected. In previous works [10], although a correction was made, no general equation was given. In addition, the correction is only for the growing surface with a constant (volume) flow rate. It is only suitable for the maximum bubble pressure method and drop volume method. In this paper a similar correction, in the case of adsorption at an expanding surface with a constant rate was made and the general expression for dynamic surface adsorption Γ (t) was derived. The derived results are suitable for inclined plate method [8] and reversed funnel method [9]. Furthermore, the results have been discussed by comparing with that of Ward and Tordai.

Theory

For the adsorption process of aqueous solution at the expanding air/solution interface, the physical model is shown in Fig. 1. The surface expands with the time t. In the meantime, the adsorption process happens in the solution phase. The adsorption process consists of two steps: the first step is the transport of surfactant molecules from the bulk phase to the subsurface due to a concentration gradient, i.e., the diffusion step; the second one is the transport of molecules from the subsurface to the surface, i.e., the adsorption step. If the rate of the first step is much slower than that of the second one, then the whole process is controlled by the diffusion. This kind of diffusion-controlled adsorption has been discussed in this paper.

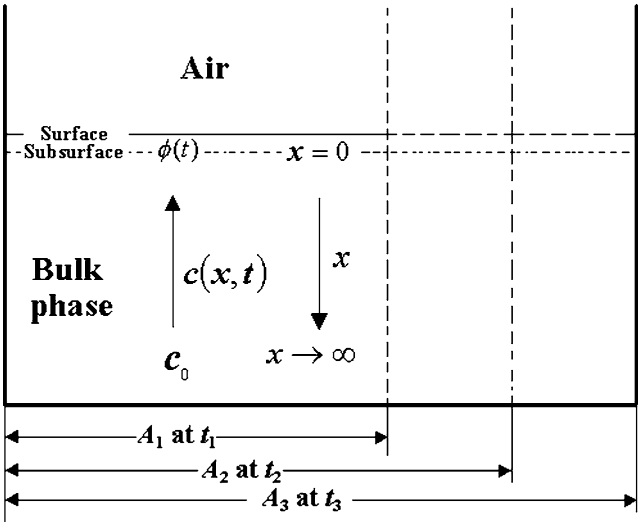

Fig. 1 Schematics of the adsorption on expanding planar surface

For the diffusion-controlled adsorption at air/solution interface, the start point is the diffusion equation. For the expanding surface it reads [11]

$$\frac{\partial c(x,t)}{\partial t} = D \cdot \frac{\partial^2 c(x,t)}{\partial x^2} + \theta \cdot x \frac{\partial c(x,t)}{\partial x}, \quad (8)$$

where c (x, t) is the concentration at x and at the time t. θ is the dilatation,

$$\theta = \frac{1}{A} \cdot \frac{\mathrm{d}A}{\mathrm{d}t}, \quad (9)$$

where A is the surface area.

In contrast to Eq. 2, an extra term $\theta\ x(\partial c\ (x,t)/\partial x)$, which is the convective flux due to the expanding surface, appeared in this equation. If the surface expands with a constant area rate $\dot{A}$, then the surface area is

$$A = \dot{A}t. \quad (10)$$

Inserting Eq. 9 into 10, we get

$$\theta = \frac{1}{t}, \quad (11)$$

then Eq. 8 becomes

$$\frac{\partial c(x,t)}{\partial t} = D \cdot \frac{\partial^2 c(x,t)}{\partial x^2} + \frac{x}{t} \cdot \frac{\partial c(x,t)}{\partial x}. \quad (12)$$

This is the diffusion equation for the surface with a constant expanding rate.

In order to solve this equation, two new variables τ and β will be defined:

$$\begin{cases} \tau = \frac{1}{3}t^3 \\ \beta = tx \end{cases} \quad (13)$$

By using these two new variables, the diffusion equation (Eq. 12) can be written in the following way:

$$\frac{\partial c(\beta,\tau)}{\partial \tau} = D \cdot \frac{\partial^2 c(\beta,\tau)}{\partial \beta^2}. \tag{14}$$

This equation is analogous to Eq. 2. It can be solved by means of Laplace transformation [3].

To solve it, the following initial condition and boundary conditions, which are from Eqs. 3, 4, 5, are necessary:

$$\text{Initial condition}: \quad c(\beta,0) = c_0, \tag{15}$$

$$\text{First boundary condition}: \quad \lim_{\beta\to\infty} c(\beta,\tau) = c_0, \tag{16}$$

$$\text{Second boundary condition}: \quad c(0,\tau) = \psi(\tau). \tag{17}$$

Naturally, the following is the relationship between the both subsurface functions,

$$\phi(t) = \phi\left((3\tau)^{\frac{1}{3}}\right) = \psi(\tau) = \psi\left(t^3/3\right). \tag{18}$$

Under these conditions (Eqs. 15, 16, 17), the solution of Eq. 14 is the following:

$$c(\beta,\tau) = \psi(\tau) + \frac{2[c_0-\psi(0)]}{\sqrt{\pi}} \int\limits_0^{\beta/2\sqrt{D\tau}} \exp(-z^2)\mathrm{d}z - \frac{2}{\sqrt{\pi}} \int\limits_0^{\tau} \psi'(u) \int\limits_0^{\beta/\left(2\sqrt{D(\tau-u)}\right)} \exp(-z^2)\,\mathrm{d}z\,\mathrm{d}u \quad (\beta \geqslant 0). \tag{19}$$

Using the first Fick's equation at the surface $x=0$,

$$\frac{\mathrm{d}(\Gamma A)}{\mathrm{d}t}\Big|_{x=0} = DA \cdot \frac{\partial c(x,t)}{\partial x}\Big|_{x=0} \tag{20}$$

one can derive the expression of the dynamic surface adsorption $\Gamma(t)$.

Inserting

$$\begin{aligned} \left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} &= \frac{\partial c(\beta,\tau)}{\partial \beta} \cdot \left.\frac{\partial \beta}{\partial x}\right|_{x=0} + \frac{\partial c(\beta,\tau)}{\partial \tau} \cdot \left.\frac{\partial \tau}{\partial x}\right|_{x=0} \\ &= \left\{ (c_0-\psi(0))\left(\frac{1}{\pi D\tau}\right)^{\frac{1}{2}} - \sqrt{\frac{1}{\pi D}} \int\limits_0^{\tau} \frac{\psi'(z)}{\sqrt{\tau-z}}\mathrm{d}z \right\} t \end{aligned} \tag{21}$$

and

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \frac{\mathrm{d}\Gamma}{\mathrm{d}\tau} \cdot \frac{\mathrm{d}\tau}{\mathrm{d}t} = \frac{\mathrm{d}\Gamma}{\mathrm{d}\tau} \cdot t^2 \tag{22}$$

in Eq. 20 and after rearranging it, we get

$$\begin{aligned} \frac{\mathrm{d}\Gamma}{\mathrm{d}\tau} + \frac{\Gamma}{3\tau} = {} & (c_0-\psi(0))\left(\frac{D}{\pi}\right)^{\frac{1}{2}} (3)^{-\frac{1}{3}}(\tau)^{-\frac{5}{6}} \\ & - (3)^{-\frac{1}{3}}(\tau)^{-\frac{1}{3}} \sqrt{\frac{D}{\pi}} \int\limits_0^{\tau} \frac{\psi'(z)}{\sqrt{\tau-z}}\mathrm{d}z. \end{aligned} \tag{23}$$

Solving this equation by using the initial condition $t=0$, Γ $(\tau)=0$, we get

$$\Gamma(\tau) = 2c_0\sqrt{\frac{D\tau}{\pi}}(3)^{-\frac{1}{3}}(\tau)^{-\frac{1}{3}} - (3)^{-\frac{1}{3}}(\tau)^{-\frac{1}{3}}\sqrt{\frac{D}{\pi}} \int\limits_0^{\tau} \frac{\psi(z)}{\sqrt{\tau-z}}\mathrm{d}z. \tag{24}$$

In order to compare with the Ward–Tordai equation (Eq. 1), the subsurface concentration $\phi(t)$ should be used instead of $\psi(t)$. Changing the integral variable by using Eq. 18, we get

$$\int\limits_0^{\tau} \frac{\psi(z)}{\sqrt{\tau-z}}\mathrm{d}z = \int\limits_0^{t} \frac{\phi(u)\cdot u^2}{\sqrt{(t^3-u^3)/3}}\,\mathrm{d}u. \tag{25}$$

Combining Eqs. 24 and 25 and substituting the expressions for τ and β, the general expression of the dynamic surface adsorption for the expanding surface with a constant area rate is derived as follows:

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{3\pi}} - \sqrt{\frac{D}{\pi}} \cdot t^{-1} \int\limits_0^{t} \frac{\phi(u)\cdot u^2}{\sqrt{(t^3-u^3)/3}}\,\mathrm{d}u. \tag{26}$$

The following case is always discussed:

At the beginning of adsorption, the subsurface concentration is zero, i.e.,

$$\phi(t) = 0 \tag{27}$$

then Eq. 26 is reduced to

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{3\pi}}. \tag{28}$$

Eq. 28 can be used in the short-time limit ($t \to 0$).

Results and discussion

1. To derive the dynamic adsorption (Eq. 26), Fick's first law was used at $x=0$. For the expanding surface, Eq. 20, which is different from Eq. 7, was adopted. Equation 20 is the general equation and Eq. 7 can be considered as the special case of Eq. 20 when A = constant.
2. As a boundary condition, the subsurface concentration (ϕ (t)) is introduced. ϕ (t) is a function of time t and it should tend to 0 as $t \to \infty$, i.e.,

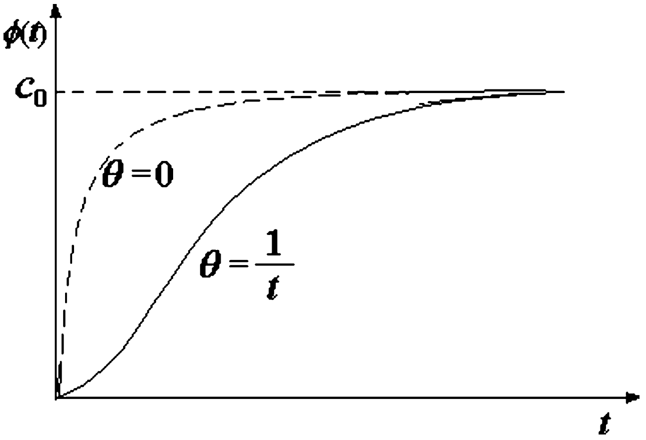

Fig. 2 Schematics of the subsurface concentration. *Solid line* expanding surface, *dotted line* still surface

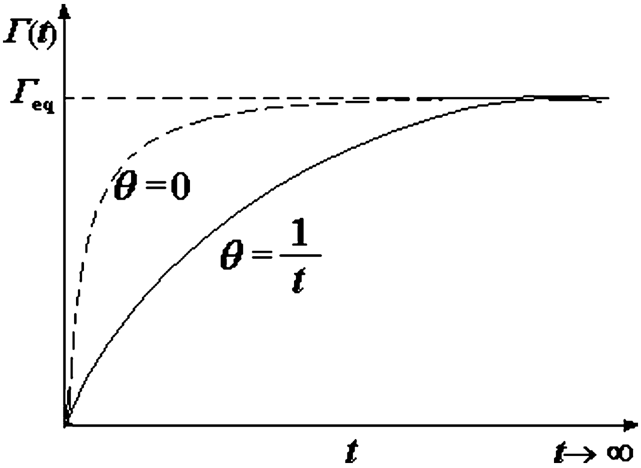

Fig. 3 Schematics of the dynamic adsorption. *Solid line* expanding surface, *dotted line* still surface

$$\lim_{t\to\infty}\phi(t)=c_0. \tag{29}$$

Figure 2 gives a schematic diagram of ϕ (t). Although at the beginning (t $\rightarrow$ 0) and at the end of the adsorption (t $\rightarrow$ ∞), the subsurface concentrations (ϕ (t)) equal to 0 and bulk concentration (c_0) for both cases of expanding surface ($\theta=1/t$) and still surface ($\theta=0$) respectively, ϕ (t) will be different in the other times. In contrast to the case of $\theta=0$, the subsurface concentrations ϕ (t) for the case of expanding surface ($\theta=1/t$) will be lower because of the surface expansion. Thus, a longer time is needed for ϕ (t) to reach the bulk concentration.

3. In contrast to the Ward–Tordai equation ($\theta=0$), for the short-time adsorption [1]

$$\Gamma(t)=2c_0\sqrt{\frac{Dt}{\pi}}, \tag{30}$$

a factor 1/3 appeared in Eq. 28. This factor can be considered as the correction of the effect of expanding surface on the adsorption; also, this factor indicates that the dynamic adsorption at short-time range (Γ (t)$|_{t\,\rightarrow\,0}$) for expanding surface ($\theta=1/t$) becomes smaller due to the surface expansion.

4. In the long-time limit (t $\rightarrow$ ∞), there should be $\lim_{t\to\infty}\Gamma(t)=\Gamma_{\mathrm{eq}}$ for both cases of $\theta=1/t$ and $\theta=0$. Considering the adsorption model, Fig. 3 was plotted for both cases. Similar to the changes of subsurface concentration, the dynamic surface adsorption for the case of expanding surface ($\theta=1/t$) will be lower due to the surface expansion than that in the case of $\theta=0$.

5. It is difficult to measure the dynamic surface adsorption $\Gamma(t)$, whereas it is easy to measure the dynamic surface tension $\gamma(t)$. The relationship between $\Gamma(t)$ and $\gamma(t)$ is [2]:

$$\gamma(t)=\gamma_0+RT\Gamma_\infty\ \ln\left(1-\frac{\Gamma(t)}{\Gamma_\infty}\right), \tag{31}$$

where γ_0 is the surface tension of solvent (water), Γ_∞ is the saturated adsorption. As $((\Gamma\ (t))/(\Gamma_\infty))\approx0$, we get ln $(1-((\Gamma\ (t))/(\Gamma_\infty))\approx-((\Gamma\ (t))/(\Gamma_\infty))$, and Eq. 31 becomes

$$\gamma(t)=\gamma_0-RT\Gamma(t). \tag{32}$$

As discussed above, Γ (t) is different in both the cases of $\theta=1/t$ and $\theta=0$. Obviously, the dynamic surface tension $\gamma(t)$ should also be different as $\theta=1/t$ and $\theta=0$. The dynamic surface tension for the case of expanding surface ($\theta=1/t$) will be higher because of its lower surface adsorption than that in the case of $\theta=0$. From Fig. 4 it can be seen that the following equation exists for both cases

$$\lim_{t\to\infty}\gamma(t)=\gamma_{\mathrm{eq}}. \tag{33}$$

Figure 4 shows an important conclusion: for different methods, the measured dynamic surface tensions $\gamma(t)$ should be different. Therefore, it is meaningless to compare the experimental dynamic surface tensions, which were measured by means of the different methods. The dynamic surface tensions $\gamma(t)$ are different from the equilibrium surface tensions γ_{eq}, which do not change with the methods.

6. The measured dynamic surface tensions $\gamma(t)$ were always used to analyze the adsorption mechanism. Although the measured dynamic surface tensions $\gamma(t)$ by means of different methods are different, the adsorption mechanism should be the same. The nature of adsorption will not change with the experimental methods. Therefore, for different methods the corresponding theories should be used to analyze

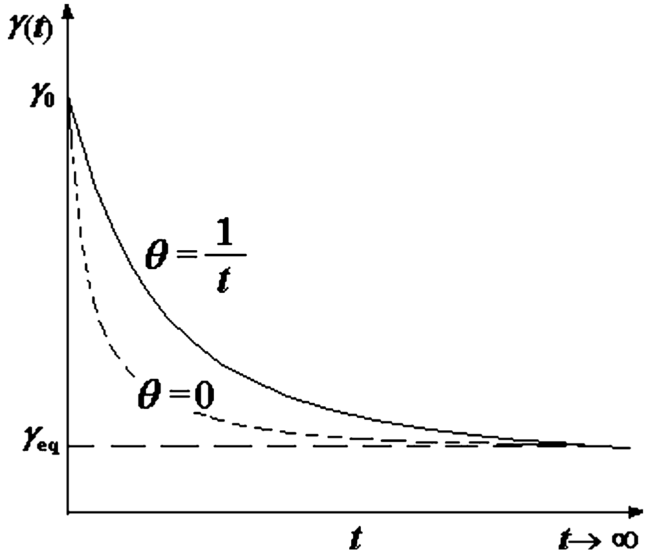

Fig. 4 Schematics of the dynamic surface tension. *Solid line* expanding surface, *dotted line* still surface

the experimental data. Otherwise one cannot get the correct conclusions. For inclined plate method and reversed funnel method, Eq. 26 should be used instead of Eq. 1.

Summary

The diffusion equation for the expanding surface was solved by introducing the new variables. A general expression of dynamic surface adsorption was derived. For the short-time adsorption, a special factor 1/3, which reflected the effect of the expansion of surface on the adsorption, appeared in the equation. For different experimental methods, although the measured dynamic surface tensions can be different, the adsorption mechanism will not change with different experimental methods as long as the corresponding theories are used.

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