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ORIGINAL CONTRIBUTION

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# Diffusion-controlled adsorption kinetics at the air/solution interface

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**Abstract** To describe diffusion-controlled adsorption, the diffusion equation is solved under different initial and boundary conditions by means of a Laplace transformation. By solving this equation, it has been found that the solution, which Ward and Tordai used, is only applicable for $x > 0$; therefore, it is incorrect if the derivation is made at $x = 0$. Ward and Tordai did not notice this and the first derivation was made at $x = 0$ in order to get the dynamic surface adsorption, $\Gamma(t)$. In this paper, an accurate solution, which is applicable for $x \geq 0$, is given and the expression for $\Gamma(t)$ is obtained. Furthermore the relationship between the dynamic surface tension and $\Gamma(t)$ is derived. As an example, the dynamic surface tensions of an aqueous octyl-$\beta$-D-glucopyranosid solution were measured by means of the maximum bubble pressure method. By using the derived theory it has been proved that the controlling mechanism of the adsorption process of this surfactant at the long-time-adsorption limits changes as a function of the bulk concentration; only at dilute concentration is it controlled by diffusion.

**Key words** Diffusion-controlled adsorption kinetics · Dynamic surface tension · Maximum bubble pressure method · Air/solution interface

## Introduction

The adsorption process of an aqueous surfactant solution at the air/solution interface 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, the whole process is controlled by diffusion. This kind of diffusion-controlled adsorption is the case which we discuss in this paper.

Diffusion-controlled adsorption kinetics was first treated quantitatively by Ward and Tordai [1]. From the solution of the diffusion equation, an expression for the dynamic surface adsorption, $\Gamma(t)$, which was called the Ward and Tordai equation, was derived by using the first Fick equation at the subsurface $x = 0$. The Ward and Tordai equation has always been used in reports in the literature [2–4]; however, the solution of the diffusion equation, which was used by Ward and Tordai, is only valid for $x > 0$. Considering this, the diffusion equation is solved in this paper by means of a Laplace transformation [5, 6]. A solution which is valid for $x \geq 0$ is given; from this accurate solution, $\Gamma(t)$ is derived.

$\Gamma(t)$ decides the dynamic surface tensions, $\sigma(t)$; therefore the relationship between them is important. Bendure [7] attempted to obtain this relationship but no distinction was made between the equilibrium state and the non equilibrium state. The equation, which is used to describe the equilibrium state was directly adopted for the non equilibrium state; however it seems that the result is not reliable. For this reason, a reliable relationship between $\sigma(t)$ and $\Gamma(t)$ has been strictly derived on the basis of a reasonable assumption which reflects the nature of the surface adsorption.

Octyl-$\beta$-D-glucopyranosid was chosen for study and $\sigma(t)$ of its aqueous solutions were measured with the maximum bubble pressure method [8]. It has been proved that at the long-time limit the diffusion-controlled mechanism of the adsorption is a function of the bulk concentration.

## Theory

For diffusion-controlled adsorption, the diffusion equation (Fick's second law) should be the starting point,

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \quad , \tag{1}$$

where $c(x,t)$ is the concentration at the coordinate normal to the surface, $x$, and at time $t; D$ represents the diffusion coefficient.

To solve this equation the necessary initial condition is

$$c(x,0) = c_0 \quad . \tag{2}$$

This means that the concentration is uniform everywhere before the new surface is created in the solution.

One of the boundary conditions is

$$\lim_{x\to\infty} c(x,t) = c_0 \quad . \tag{3}$$

The other boundary condition is the so-called subsurface concentration. From this subsurface concentration we have the following three cases:

1. Adsorption with no back-diffusion – the short-time-limit adsorption.
2. Adsorption with back-diffusion.
3. Long-time-limit adsorption.

### Adsorption with no back-diffusion – the short-time-limit adsorption

If the subsurface concentration is 0, i.e.,

$$c(0,t) = 0 \quad , \tag{4}$$

then we call it adsorption with no back-diffusion or short-time-limit adsorption. At the initial stage the subsurface is empty enough to take up the arriving molecules and back-diffusion will not happen.

Under these initial (Eq. 2) and boundary conditions (Eqs. 3, 4), we can solve the diffusion equation by means of a Laplace transformation [5, 6]: the solution is

$$c(x,t) = c_0\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2c_0}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-u^2)\mathrm{d}u \quad . \tag{5}$$

In order to get the surface adsorption, Fick's first law should be used at $x = 0$:

$$\left.\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right|_{x=0} = D\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} \quad . \tag{6}$$

Inserting Eq. (5) in Eq. (6) and integrating it we have the amount of diffusion of the surfactant molecules from the subsurface to the surface in the time range $0 \to t$,

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{\pi}} \quad . \tag{7}$$

It should be pointed out that this is an approximation for the short-time adsorption. For the long-time adsorption, back-diffusion must be considered.

### Adsorption with back-diffusion

The subsurface concentration should be a function of time. We assume this function to be $\phi(t)$, i.e.,

$$c(0,t) = \phi(t) \quad . \tag{8}$$

Under the initial condition (Eq. 2) and the boundary conditions (Eqs. 3, 8), Ward and Tordai gave the following solution [1]:

$$\begin{aligned} c(x,t) = &\frac{2c_0}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-u^2)\mathrm{d}u \\ &+ \frac{x}{2\sqrt{\pi D}}\int_0^t \frac{\phi(u)}{(t-u)^{3/2}}\exp\left[-\frac{x^2}{4D(t-u)}\right]\mathrm{d}u \ (x>0) \quad . \end{aligned} \tag{9}$$

We would like to emphasize that this solution is only valid for $x > 0$. If we set $x = 0$ in this solution, we cannot get back the boundary condition (Eq. 8); therefore, this solution can not be used in Eq. (6) to calculate $\Gamma(t)$. Ward and Tordai did not notice this.

In order to get a solution, which is also valid for $x = 0$, the Laplace transformation has been used [5, 6]. Our solution is

$$\begin{aligned} c(x,t) = \phi(t) &+ \frac{2[c_0 - \phi(0)]}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-z^2)\mathrm{d}z \\ &- \frac{2}{\sqrt{\pi}}\int_0^t \phi'(u)\left[\int_0^{\frac{x}{2\sqrt{D(t-u)}}} \exp(-z^2)\mathrm{d}z\right]\mathrm{d}u \\ &(x \geq 0) \quad . \end{aligned} \tag{10}$$

With $x = 0$ in Eq. (10) we now have the correct boundary condition (Eq. 8). It should be pointed out that Eqs. (9) and (10) are identical for $x > 0$: this is easy to prove. By substituting Eq. (10) in Eq. (6) and integrating one gets

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left\{[c_0 - \phi(0)]\sqrt{t} - \int_0^t \phi'(u)\sqrt{t-u}\,\mathrm{d}u\right\}$$
$$= 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \frac{1}{2}\int_0^t \frac{\phi(u)}{\sqrt{t-u}}\mathrm{d}u\right] \quad . \tag{11}$$

This is the general equation to describe diffusion-controlled adsorption. One can see that this equation will reduce to Eq. (7) by setting $\phi(t) = 0$.

## The long-time-limit adsorption

The other special case of the general equation (Eq. 11) is the long-time adsorption. It has also been discussed in the literature [3, 9]. After a certain long time, $t_1$, the subsurface concentration will also tend to a constant; here we assume it to be $c_s$. Then the whole time range can be divided into two parts: $0 \to t_1$ and $t_1 \to t$. For the first time range, we have

$$\Gamma_1(t)|_{0\to t_1} = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t_1} - \frac{1}{2}\int_0^{t_1} \frac{\phi(u)}{\sqrt{t_1-u}}\mathrm{d}u\right] \quad . \tag{12}$$

For the second one, we have

$$\Gamma_2(t)|_{t_1\to t} = 2\sqrt{\frac{D}{\pi}}(c_0 - c_s)\cdot\left(\sqrt{t} - \sqrt{t_1}\right) \quad . \tag{13}$$

For the whole time range, we have

$$\Gamma(t) = \Gamma_1(t)|_{0\to t_1} + \Gamma_2(t)|_{t_1\to t}$$
$$= 2\sqrt{\frac{D}{\pi}}\left[(c_0 - c_s)\sqrt{t} + c_s\sqrt{t_1} - \frac{1}{2}\int_0^{t_1} \frac{\phi(u)}{\sqrt{t_1-u}}\mathrm{d}u\right]$$
$$(t \geq t_1) \quad . \tag{14}$$

## The relationship between $\Gamma(t)$ and $\sigma(t)$

We have derived the expressions for $\Gamma(t)$ for the three different cases; however, $\Gamma(t)$ cannot be measured directly. What we can measure directly is $\sigma(t)$. Now in order to derive the relationship between them, we begin from the classical Gibbs' adsorption equation

$$\Gamma_{\mathrm{eq}} = -\frac{c_0}{RT}\frac{\mathrm{d}\sigma_{\mathrm{eq}}}{\mathrm{d}c_0} \quad . \tag{15}$$

This equation is used to describe the relationship between the equilibrium adsorption, $\Gamma_{\mathrm{eq}}$, and the bulk concentration, $c_0$. Rearranging gives

$$\mathrm{d}\sigma_{\mathrm{eq}} = -\frac{RT\Gamma_{\mathrm{eq}}}{c_0}\mathrm{d}c_0 \quad . \tag{16}$$

The Langmuir isotherm can be used to describe the adsorption of surfactant at the solution surface,

$$\Gamma_{\mathrm{eq}} = \Gamma_\infty \frac{bc_0}{1 + bc_0} \quad , \tag{17}$$

where $\Gamma_\infty$ is the saturated adsorption at $c_0 \to \infty$ and $b$ is the Langmuir isotherm parameter. From Eq. (17) we have

$$c_0 = \frac{\Gamma_\infty}{b\left(\Gamma_\infty - \Gamma_{\mathrm{eq}}\right)} \quad . \tag{18}$$

Inserting this equation in Eq. (16) and rearranging yields

$$\mathrm{d}\sigma_{\mathrm{eq}} = RT\Gamma_\infty \mathrm{d}\ln\left(\Gamma_\infty - \Gamma_{\mathrm{eq}}\right) \quad . \tag{19}$$

It should be emphasized that Eqs. (15)–(18) are applicable only for the equilibrium state. Equation (19) indicates the relationship between the equilibrium surface tension, $\sigma_{\mathrm{eq}}$, and $\Gamma_{\mathrm{eq}}$.

In order to derive the relation between $\Gamma(t)$ and $\sigma(t)$, the following assumption is made. We think that the surface tension, $\sigma$, depends only on the surface adsorption, $\Gamma$. This means the surface tension is only a function of the surface adsorption. If the surface adsorption is the equilibrium adsorption, $\Gamma_{\mathrm{eq}}$, then the surface tension is the equilibrium surface tension, $\sigma_{\mathrm{eq}}$. If the surface adsorption is the nonequilibrium adsorption, $\Gamma(t)$, then the surface tension corresponds to the nonequilibrium surface tension, $\sigma(t)$. This kind of dependent relationship should be the same; namely, Eq. (19) is valid not only for the equilibrium state but also for the nonequilibrium state. We think this assumption is reasonable considering the nature of the adsorption at the air/solution interface. Under this assumption we can use Eq. (19) to derive the relation between $\Gamma(t)$ and $\sigma(t)$. Integrating Eq. (19), we have

$$\int_{\sigma_0}^{\sigma(t)} \mathrm{d}\sigma = RT\Gamma_\infty \int_0^{\Gamma(t)} \mathrm{d}\ln(\Gamma_\infty - \Gamma) \tag{20}$$

or

$$\int_{\sigma_{\mathrm{eq}}}^{\sigma(t)} \mathrm{d}\sigma = RT\Gamma_\infty \int_{\Gamma_{\mathrm{eq}}}^{\Gamma(t)} \mathrm{d}\ln(\Gamma_\infty - \Gamma) \quad , \tag{21}$$

where $\sigma_0$ is the equilibrium surface tension of water (pure solvent).

Simplifying these two equations, we obtain

$$\sigma(t) = \sigma_0 + RT\Gamma_\infty \ln\left[1 - \frac{\Gamma(t)}{\Gamma_\infty}\right] \tag{22}$$

and

$$\sigma(t) = \sigma_{\mathrm{eq}} + RT\Gamma_\infty \ln\left[\frac{\Gamma_\infty - \Gamma(t)}{\Gamma_\infty - \Gamma_{\mathrm{eq}}}\right] \quad . \tag{23}$$

We would like to distinguish the meanings of the three adsorptions: $\Gamma(t)$, $\Gamma_{\mathrm{eq}}$ and $\Gamma_\infty$. The relations among them are

$$\lim_{t\to\infty}\Gamma(t)=\Gamma_{\mathrm{eq}} \tag{24}$$

and

$$\lim_{c_0\to\infty}\Gamma_{\mathrm{eq}}=\Gamma_\infty \quad \text{(see Eq. 17)} \ . \tag{25}$$

Compared with Eq. (23), Eq. (22) is simple. We do not need to determine $\sigma_{\mathrm{eq}}$ and $\Gamma_{\mathrm{eq}}$; therefore we use Eq. (22) in this paper.

For a dilute solution, $\Gamma(t)$ is small; thus

$$\ln\left[1-\frac{\Gamma(t)}{\Gamma_\infty}\right]\approx-\frac{\Gamma(t)}{\Gamma_\infty} \ . \tag{26}$$

Hence, Eq. (22) reduces to

$$\sigma(t)=\sigma_0-RT\Gamma(t) \ . \tag{27}$$

Inserting Eqs. (7), (11) and (14) in Eq. (27) results in

$$\sigma(t)=\sigma_0-2RTc_0\sqrt{\frac{Dt}{\pi}} \ , \tag{28}$$

for the short-time-limit adsorption

$$\sigma(t)=\sigma_0-2RT\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t}-\frac{1}{2}\int_0^t\frac{\phi(u)}{\sqrt{t-u}}\mathrm{d}u\right] \tag{29}$$

for adsorption with back-diffusion

$$\sigma(t)=\sigma_0-2RT\sqrt{\frac{D}{\pi}}\left[(c_0-c_\mathrm{s})\sqrt{t}+c_\mathrm{s}\sqrt{t_1}-\frac{1}{2}\int_0^{t_1}\frac{\phi(u)}{\sqrt{t_1-u}}\mathrm{d}u\right]\ (t\geq t_1) \tag{30}$$

and for the long-time-limit adsorption.

We can see that for the two limiting cases, the short-time-limit adsorption and the long-time-limit adsorption, there should be a linear relationship between $\sigma(t)$ and $\sqrt{t}$.

## Experimental

The dynamic surface tension measurements were carried out by means of a maximum bubble pressure tensiometer (BP-2 made by Krüss, Hamburg, Germany). The measuring range in the time window was from 0.005 to 60 s. The capillary diameter was 0.264 mm. The principle and a detailed description of the method are given in Ref. [8] . Octyl-$\beta$-D-glucopyranosid was purchased from Bachem Biochemica, Heidelberg, Germany. The surfactants were used without any further purification. The critical micelle concentration (cmc) of octyl-$\beta$-D-glucopyranosid is $2.5\times10^{-2}$ mol/l. Four aqueous surfactant solutions, below the cmc, were prepared using double-distilled, deionized water. The last distillation was performed over alkaline $KMnO_4$ in order to remove the effect of surface-active impurities. All dynamic surface tension measurements were performed at 25 ± 0.1 °C.

## Results and discussion

The dynamic surface tensions of aqueous octyl-$\beta$-D-glucopyranosid solutions are shown in Fig. 1. For all four concentrations, the surface tensions decreased with time until a constant value was reached. This kind of decrease is much stronger at the beginning than at the end. It shows us that the adsorption happens mainly in the initial stage. The rate of adsorption, $\mathrm{d}\Gamma(t)/\mathrm{d}t$, at the beginning is very high (see Fig. 2). In the short-time limit the reduction follows a square-root decay (Fig. 3), corresponding to Eq. (28). This region was used to determine the diffusion coefficient of the surfactant in water. The calculated diffusion coefficient, $D$, is $1.31\times10^{-10}$ m$^2$/s. For the long-time limit, there should also be a linear relationship between $\sigma(t)$ and $\sqrt{t}$ according to Eq. (30) although we do not know the values of the constant variables $c_\mathrm{s}$ and $t_1$. The linear relationship between $\sigma(t)$ and $1/\sqrt{t}$, which was proposed in Refs. [3, 9], is incorrect for this surfactant. The

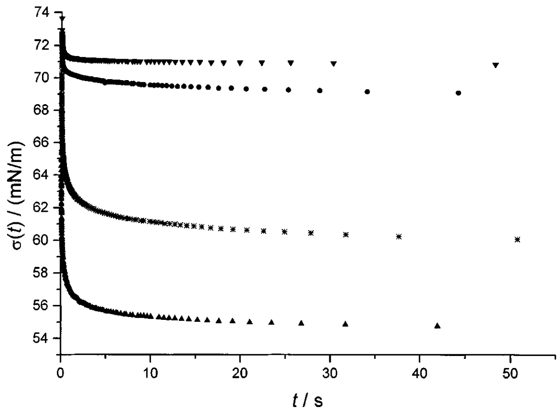

**Fig. 1** Experimental dynamic surface tension, $\sigma(t)$, of aqueous octyl-$\beta$-D-glucopyranosid solution at 25 °C and at different surfactant concentrations: $c_0 = 6.84\times10^{-5}$ mol/l (▼), $c_0 = 1.82\times10^{-4}$ mol/l (●), $c_0 = 8.13\times10^{-4}$ mol/l (∗), $c_0 = 1.79\times10^{-3}$ mol/l (▲)

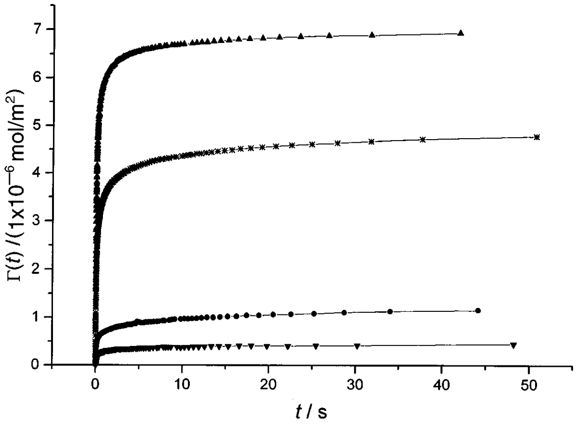

**Fig. 2** The dynamic surface adsorption, $\Gamma(t)$, for aqueous octyl-$\beta$-D-glucopyranosid solution at 25 °C and at different surfactant concentrations: $c_0 = 6.84\times10^{-5}$ mol/l (▼), $c_0 = 1.82\times10^{-4}$ mol/l (●), $c_0 = 8.13\times10^{-4}$ mol/l (∗), $c_0 = 1.79\times10^{-3}$ mol/l (▲)

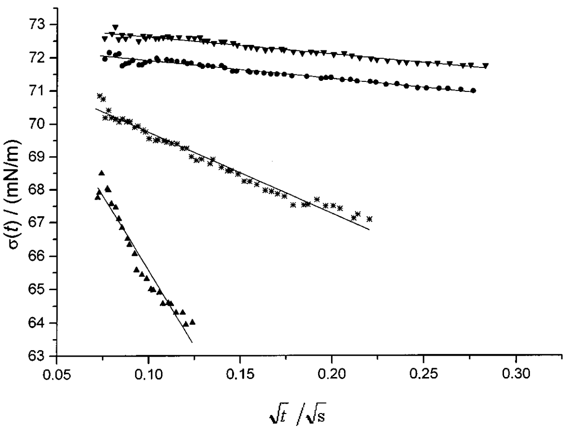

**Fig. 3** The short-time-limit dependence of $\sigma(t)$ on $\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution (Eq. 28) at 25 °C; $c_0 = 6.84 \times 10^{-5}$ mol/l (▼), $c_0 = 1.82 \times 10^{-4}$ mol/l (●), $c_0 = 8.13 \times 10^{-4}$ mol/l (∗), $c_0 = 1.79 \times 10^{-3}$ mol/l (▲).

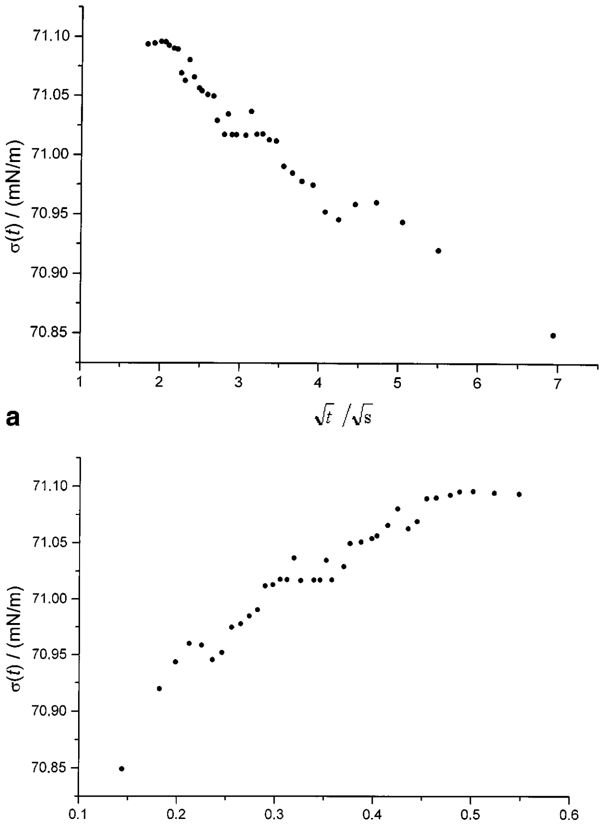

**Fig. 4a** The long-time-limit ($t$ > 4000 ms) dependence of $\sigma(t)$ on $\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution (Eq. 30) at 25 °C; $c_0 = 6.84 \times 10^{-5}$ mol/l. **b** The long-time-limit ($t$ > 4000 ms) dependence of $\sigma(t)$ on $1/\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution at 25 °C; $c_0 = 6.84 \times 10^{-5}$ mol/l

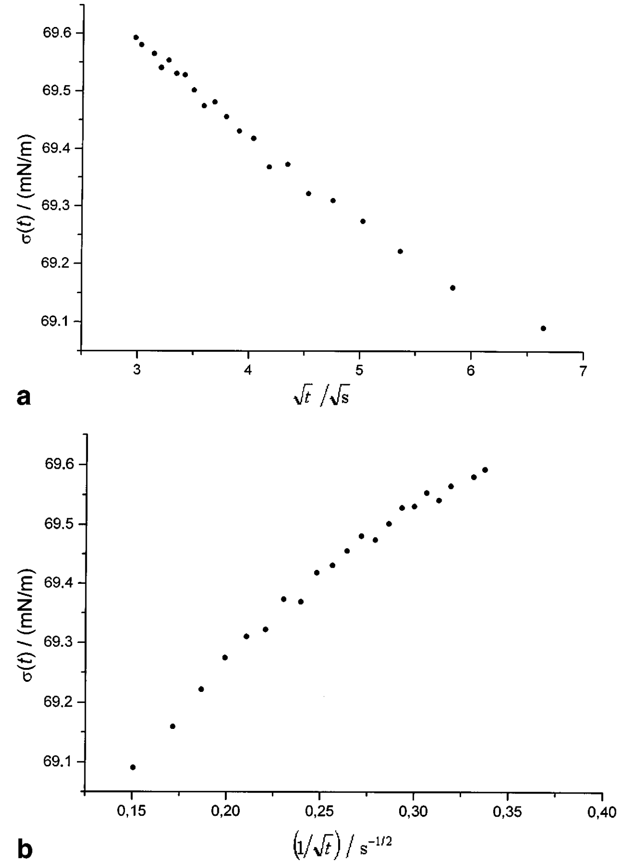

**Fig. 5a** The long-time-limit ($t$ > 8000 ms) dependence of $\sigma(t)$ on $\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution (Eq. 30) at 25 °C; $c_0 = 1.82 \times 10^{-4}$ mol/l. **b** The long-time-limit ($t$ > 8000 ms) dependence of $\sigma(t)$ on $1/\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution at 25 °C; $c_0 = 1.82 \times 10^{-4}$ mol/l

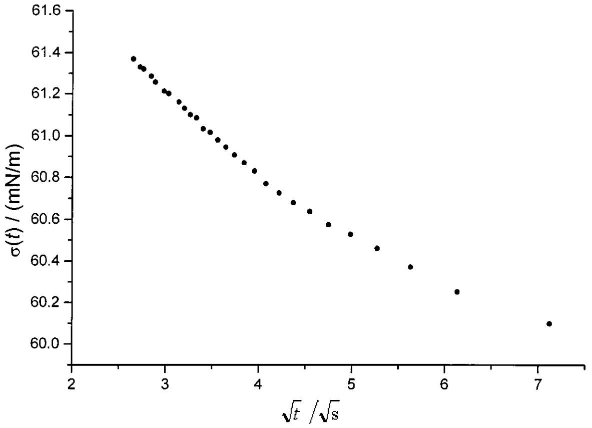

**Fig. 6** The long-time-limit ($t$ > 7000 ms) dependence of $\sigma(t)$ on $\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution at 25 °C; $c_0 = 8.13 \times 10^{-4}$ mol/l

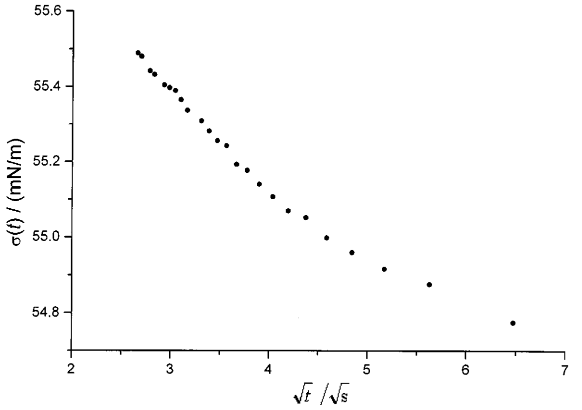

**Fig. 7** The long-time-limit ($t$ > 7000 ms) dependence of $\sigma(t)$ on $\sqrt{t}$ for octyl-$\beta$-D-glucopyranosid solution at 25 °C; $c_0 = 1.79 \times 10^{-3}$ mol/l

experimental results result in the same conclusion (Figs. 4, 5). The expected results in Figs. 4a and 5a mean that for both concentrations the adsorption is really controlled by diffusion; however, for the other two concentrations (Figs. 6, 7), the linear relation between $\sigma(t)$ and $\sqrt{t}$ is not reached. This means that the adsorption process is not controlled by diffusion, but a mixed diffusion-adsorption-controlled mechanism appeared. A similar phenomenon, where the adsorption mechanism changes as a function of the bulk concentration, has been reported for other surfactants [10, 11].

## Conclusion

An expression for the dynamic surface adsorption has been obtained from the accurate solution of the diffusion equation. On the basis of a reasonable assumption, the dependence of the dynamic surface tension on the dynamic surface adsorption has been strictly derived. From the measured dynamic surface tensions of aqueous octyl-$\beta$-D-glucopyranosid solutions, the diffusion coefficient was calculated for the short-time limit. For the long-time-limit adsorption process, the controlling mechanism changes with the bulk concentration.

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