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SHORT COMMUNICATION

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A theory of adsorption kinetics with time delay and its application to overshoot and oscillation in the surface tension of gelatin solution

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Abstract A theory of adsorption kinetics with time delay [Ohshima et al. (1992) *Colloid Polym. Sci.* 270:707] is developed and applied to the surface tension of a polymer solution. It is found that the general appearance of the overshoot and oscillation in the time course of the surface tension of aqueous gelatin solution observed by Sato and Ueberreiter [(1979) *Makromol. Chem.* 180:829, 1107; (1979) *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 20:907) can be explained by the present theory.

Keywords Overshoot · Oscillation · Adsorption kinetics · Time delay · Surface tension

Introduction

The overshoot and oscillation phenomena in polymer adsorption kinetics have been studied by many investigators [1, 2, 3, 4, 5, 6, 7, 8, 9]. In a previous paper [4], in particular, a theory of adsorption kinetics of solutes onto a solid surface from the solution phase was proposed in which a time delay was introduced into the solute concentration on the surface. This theory is based on equations for membrane transport with time delay [10, 11]. It has been found [4] that introduction of time delay, τ, causes, under certain conditions, overshoot or oscillation in the solute concentration on the surface. The reason for this can be explained as follows. During the time interval $t=0$ and $t=\tau$ only adsorption takes place. At the time instant $t=\tau$, in addition to adsorption, desorption starts. If, therefore, the time delay is sufficiently large, then the amount of solute accumulated on the surface may exceed the equilibrium value, resulting in overshoot or oscillation around the equilibrium value. It may be likely that polymers with complex structures, when adsorbed on the solid surface, need some time to be able to desorb from the surface as a result of their conformational changes.

Similar phenomena are expected to occur in adsorption kinetics at the interface between air and a polymer solution, as shown schematically in Fig. 1. Sato and Ueberreiter [1, 2, 3] indeed observed overshoot and

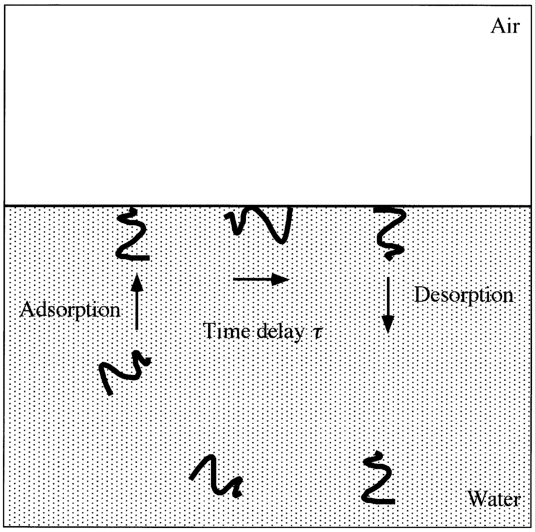

Fig. 1 Schematic representation of adsorption kinetics with a time delay τ at the interface between air and a polymer solution

oscillation in the time course of the surface tension of aqueous gelatin solutions. The surface tension of an aqueous solution of gelatin molecules, which are surface-active, decreases when gelatin molecules are adsorbed at the air/solution interface. After the surface tension reaches a certain minimum value, association of gelatin molecules with their hydrophobic segments occurs at the interface. Associated gelatin molecules become hydrophilic and desorb back into the solution, resulting in an increase in the surface tension of the gelatin solution. Overshoot or oscillation of the surface tension thus appears. In the present paper, by regarding the time required to start desorption of gelatin molecules from the interface as the time delay, we analyze a typical example of the data on adsorption kinetics in aqueous gelatin solutions [3].

Adsorption kinetics with time delay and surface tension of the polymer solution

Following the theory presented in Ref. [4], we consider adsorption of diffusing polymers from a polymer solution (of volume V) onto an interface (of area A) between the solution and air. We assume that there are N_m sites per unit area of the interface that are capable of adsorbing polymers. We denote the polymer concentration in the solution phase and on the air/solution interface by $C(t)$ and $N(t)$, respectively. We set the following initial conditions:

$$C(0) = C_0, \tag{1}$$

$$N(0) = 0. \tag{2}$$

We imagine that polymers with complex structures, when adsorbed on the air/solution interface, need some time to be able to desorb from the interface as a result of their conformational changes. That is, there is a certain time delay, τ, in the time course of the solute concentration on the interface. The time course of $C(t)$ and $N(t)$ may be described by the following kinetic equations with a delay time τ:

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = k_\mathrm{a}C(t)[N_\mathrm{m} - N(t)], \quad 0 \leqslant t \leqslant \tau, \tag{3}$$

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = k_\mathrm{a}C(t)[N_\mathrm{m} - N(t)] - k_\mathrm{d}N(t-\tau), \quad t > \tau, \tag{4}$$

where k_a and k_d are, respectively, the rate constants of adsorption and desorption. Equations (3) and (4) state that during the time interval between $t = 0$ and $t = \tau$, only adsorption occurs and at the time instant $t = \tau$, in addition to adsorption, desorption starts. The solute concentrations $C(t)$ in the solution phase and $N(t)$ at the interface must satisfy the conservation relation

$$VC(t) + AN(t) = VC_0. \tag{5}$$

We treat the case in which the condition $VC(t) \gg AN(t)$ holds so that $C(t)$ in Eqs. (3) and (4) may be replaced by C_0. In such a case, Eqs. (3) and (4) are simplified into the following linear equations:

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = k_\mathrm{a}C_0[N_\mathrm{m} - N(t)], \quad 0 \leqslant t \leqslant \tau, \tag{6}$$

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = k_\mathrm{a}C_0[N_\mathrm{m} - N(t)] - k_\mathrm{d}N(t-\tau), \quad t > \tau. \tag{7}$$

Now we use the Laplace transform of $N(t)$,

$$\bar{N}(p) = \int_0^\infty \mathrm{e}^{-pt} N(t)\mathrm{d}t. \tag{8}$$

Then we have from Eqs. (6) and (7)

$$\begin{aligned}\bar{N}(p) &= \frac{\alpha}{p\left(p+\alpha+\frac{\alpha}{K}\mathrm{e}^{-p\tau}\right)}N_\mathrm{m} \\ &= \frac{\alpha}{p(p+\alpha)}\sum_{n=0}^{\infty}(-1)^n\left[\frac{\alpha}{K(p+\alpha)}\right]^n \mathrm{e}^{-np\tau}N_\mathrm{m},\end{aligned} \tag{9}$$

with

$$\alpha = k_\mathrm{a}C_0 \tag{10}$$

and

$$K = \frac{k_\mathrm{a}}{k_\mathrm{d}}C_0, \tag{11}$$

where K is the product of the binding constant ($k_\mathrm{a}/k_\mathrm{d}$) of polymers onto the air/solution interface and C_0. Equation (9) gives

$$N(t) = N_\mathrm{m}\sum_{n=0}^{\infty}\frac{(-1)^n}{K^n} \times \left\{1 - \mathrm{e}^{-\alpha(t-n\tau)}\left[\sum_{r=0}^{n}\frac{\alpha^r(t-n\tau)^r}{r!}\right]\right\}E(t-n\tau), \tag{12}$$

where $E(t)$ is the step function defined by

$$E(t) = \begin{cases} 1, & t > 0 \\ 0, & t<0 \end{cases}. \tag{13}$$

Note that at $t \to \infty$, $N(t)$ tends to a Langmuir-type equilibrium concentration,

$$N(\infty) = \frac{K}{1+K}N_\mathrm{m}. \tag{14}$$

In order to calculate $N(t)$, it is convenient to obtain the inverse Laplace transform of $\bar{N}(p)$ given by Eq. (9) with the help of, for example, Mathematica rather than using directly Eq. (12), which involves the step functions.

The time course of the surface tension, $\sigma(t)$, of a polymer solution caused by polymer adsorption may be expressed as

$$\sigma(t) = \sigma(0) - BN(t), \tag{15}$$

B being a constant. Equation (15) can be rewritten in terms of the equilibrium surface tension, $\sigma(\infty)$, as

$$\begin{aligned}\sigma(t) &= \sigma(0) - [\sigma(0) - \sigma(\infty)]\tfrac{N(t)}{N(\infty)} \\ &= \sigma(0) - [\sigma(0) - \sigma(\infty)]\left(\tfrac{1+K}{K}\right)\tfrac{N(t)}{N_\mathrm{m}},\end{aligned} \tag{16}$$

where the last equation was derived using Eq. (14).

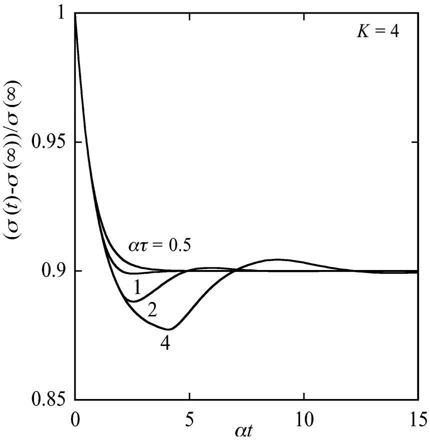

Fig. 2 Surface tension, $\sigma(t)$, of a polymer solution as a function of the scaled time, αt, for several values of the time delay $\alpha\tau$ at $K = 4$. Calculated via Eq. (16)

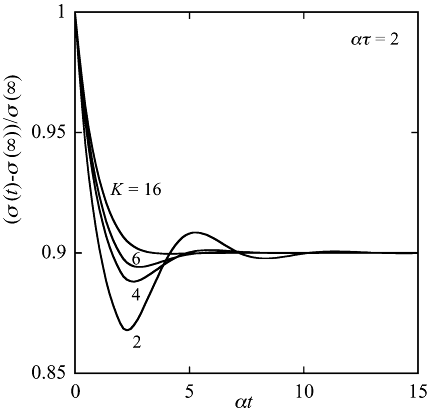

Fig. 3 Surface tension of a polymer solution as a function of the scaled time for several values of K at $\alpha\tau = 2$. Calculated via Eq. (16)

Results and discussion

We have obtained the solution (Eq. 12) to equations for the adsoption kinetics with a time delay τ (Eqs. 3, 4) and an expression for the time course of the surface tension, $\sigma(t)$, of a polymer solution (Eq. 16), which involves two nondimensional parameters: a scaled delay time $\alpha\tau$ and a scaled adsorption constant K. Some examples of the calculation of the surface tension of a polymer solution on the basis of Eq. (16) are shown in Figs. 2 and 3, where the calculation was made for several values of $\alpha\tau$ and K at $[\sigma(0)-\sigma(\infty)]/\sigma(0) = 0.1$.

The dependence of $\sigma(t)$ upon $\alpha\tau$ at $K = 4$ is shown in Fig. 2. It is seen that for small $\alpha\tau$, there is neither overshoot nor oscillation (curve with $\alpha\tau = 0.5$), whereas for large $\alpha\tau$ overshoot does occur ($\alpha\tau = 1$), and with further increase in τ damped oscillation appears ($\alpha\tau = 2$ and 4). Note that the overshoot in our model is such that the amplitude of oscillation is damped so rapidly that all extrema, except for the first minimum, are negligible and, therefore, that the oscillation is in practice observed as an overshoot. The reason why introduction of the time delay causes overshoot and oscillation can be explained as follows. During the time interval between $t = 0$ and $t = \tau$, only adsorption of polymers, i.e., solute accumulation at the air/water interface, occurs following $N(t) = N_\mathrm{m}(1-\mathrm{e}^{-\alpha t})$. At the time instant $t = \tau$, in addition to adsorption, desoption commences, i.e., solutes begin to diffuse from the interface into the solution phase. Therefore, if τ is sufficiently large, the amount of solute accumulated at the air/water interface between $t = 0$ and $t = \tau$ may exceed the equilibrium value $N_\mathrm{m}K/(1+K)$, resulting in overshoot or oscillation around the equilibrium value.

The dependence of $\sigma(t)$ upon K at $\alpha\tau = 2$ is shown in Fig. 3. For large K, there is neither overshoot nor oscillation (curve with $K = 16$), whereas for small K overshoot occurs ($K = 6$), and with further decrease in K

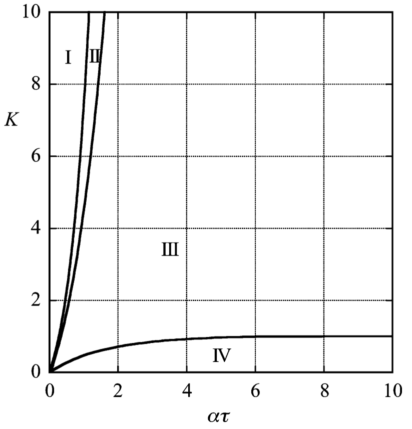

Fig. 4 Four regions in which different types of the time course of $N(t)$ and $\sigma(t)$ appear: monotonic exponential-type change without oscillation (*I*); overshoot (*II*); stable oscillation (*III*); unstable oscillation (*IV*). The boundary between I and II corresponds to values of K and $\alpha\tau$ satisfying $\gamma = 1/\mathrm{e}$ (γ defined by Eq. 18)

damped oscillation appears ($K = 4$ and 2). For very small K ($K < 1$ for $\alpha\tau > 7$), oscillation in $\sigma(t)$ becomes unstable, i.e., the amplitude of oscillation increases with time (divergent oscillation).

We thus see that four different forms of the time course of $\sigma(t)$, and $N(t)$, appear, namely, a simple exponential-type monotonic change without oscillation, overshoot, stable damped oscillation and unstable oscillation, depending on the magnitudes of $\alpha\tau$ and K. Four regions, I–IV, corresponding to the different time courses are shown in Fig. 4. In region I, $\sigma(t)$ varies monotonically, tending to the equilibrium value. In region II, $\sigma(t)$ shows overshoot. In region III, $\sigma(t)$ shows convergent oscillation around its equilibrium value. Region IV corresponds to unstable oscillation. As shown later, the boundary between regions I and II coincides with $\gamma = 1/\mathrm{e}$ (γ given in Eq. 18).

The position of the extrema in $\sigma(t)$ in regions II and III is given by setting d $N(t)$/d $t = 0$. Differentiating Eq. (12) with respect to t, we obtain

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \gamma^n \left(\frac{t}{\tau} - n\right)^n E(t - n\tau) = 0, \tag{17}$$

where

$$\gamma = \frac{\alpha\tau}{K} \mathrm{e}^{\alpha\tau}. \tag{18}$$

The solution to Eq. (17) gives the positions of the extrema of $\sigma(t)$. Note that the position of the extrema (scaled by the delay time τ) depends on only one parameter, γ. It can be shown that if $\gamma \geq 1$, then the position t_{m} of the first minimum of $\sigma(t)$ is given by

$$t_{\mathrm{m}} = \tau\left(1 + \frac{1}{\gamma}\right), \quad (\text{if } \gamma \geqslant 1), \tag{19}$$

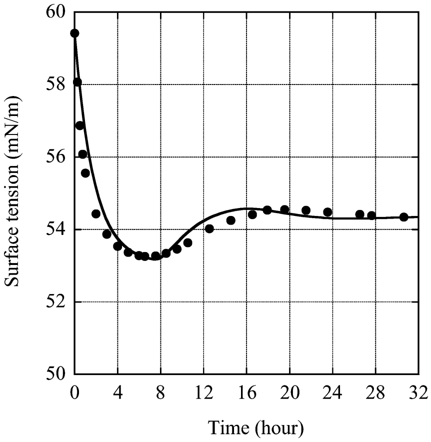

Fig. 5 Surface tension of aqueous gelatin solution as a function of time. *Circles* represent the experimental data of Sato and Ueberreiter for 0.05% aqueous gelatin solution at pH 6.93 and 30 °C, taken from Fig. 3 of Ref. [3]. The *solid line* is the theoretical result calculated via Eq. (16) with $\alpha = 0.56$ h^{-1}, $K = 4.0$, $\tau = 7.4$ h, $\sigma(0) = 59.42$ mN m^{-1} and $\sigma(\infty) = 54.34$ mN m^{-1}

which lies between τ and 2τ, tending to τ in the limit of very large γ.

Sato and Ueberreiter [1, 2] measured the time course of the surface tension, $\sigma(t)$, of aqueous gelatin solutions under various conditions, finding that in some cases $\sigma(t)$ exhibits overshoot or oscillation. The circles in Fig. 5 correspond to the experimental data showing an oscillation for 0.05% aqueous gelatin solution at pH 6.93 and 30 °C, taken from Fig. 3 of Ref. [3]. The first minimum is seen to appear around $t = 7$ h, suggesting that τ for this case is about 7 h. This time delay, which is much longer than typical molecular relaxation times, should correspond to association of gelatin molecules with their hydrophobic segments at the air/solution interface. The solid line in Fig. 5 represents the theoretical results calculated via Eq. (16) with $\alpha = 0.56$ h^{-1}, $K = 4.0$, $\tau = 7.4$ h, $\sigma(0) = 59.42$ mN m^{-1} and $\sigma(\infty) = 54.34$ mN m^{-1}. Agreement between theory and experiment is good. We thus see that while the present model cannot truly yield insight into the detailed mechanism of the change in conformation of gelatin molecules at the water/solution interface, Eq. (16) can explain the general appearance of overshoot and oscillation in the surface tension of polymer solutions with a proper choice of the parameters τ, K and α.

Conclusion

We have proposed a theory for the time course of the surface tension of polymer solutions by incorporating a time delay into the kinetics equations for polymer adsorption at the interface between air and the polymer solution. Criteria for the appearance of overshoot and oscillation in $\sigma(t)$ have been given. The general features of the overshoot and oscillation observed in the surface tension of aqueous solutions by Sato and Ueberreiter [1, 2, 3] can be explained by the present theory.

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