

Kinetics of Adsorption and Desorption of Water-Soluble Associative Polymers on Planar Titanium Dioxide Surfaces by Ellipsometry

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SYNOPSIS

The adsorption and desorption kinetics of water-soluble associative polymers with different molecular weights on crystals of titanium dioxide [$\text{TiO}_2(001)$] have been studied by ellipsometry. The model water-soluble associative polymers used in the kinetic study are nonionic polyurethanes based on polyethylene glycol, and have average molecular weights of 17,000, 51,000, and 100,000 with a $\text{C}_{16}\text{H}_{33}$ linear alkyl group on each end of the molecule. It is shown that the adsorption and desorption kinetics over a wide range of polymer concentrations is governed by: (1) the kinetics of adsorption and desorption of polymer chains at the interface, (2) the kinetics of adsorption and desorption at the interfaces as well as simultaneous diffusion in the adsorbed layer, and/or (3) diffusion in the adsorbed layer. The existence of regimes (1), (2), and (3) of the adsorption and desorption kinetics are justified by using the experimental data for the adsorption and desorption of water-soluble associative polymers with different molecular weights. It is shown that the adsorption is an irreversible process for the strongly convex adsorption isotherms. Equations were derived to calculate: (a) the rate constant for polymer adsorption and desorption processes, (b) the coefficient of diffusion, (c) the activation energy of diffusion in the adsorbed layer, and (d) the time needed to attain the equilibrium states for the adsorption and desorption processes by using adsorption and desorption kinetics data with associative polymers of different molecular weights at different polymer concentrations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The study of adsorption and desorption processes of polymers on solid interfaces is very important to comprehend the resulting structures of the adsorbed films (and/or adsorption layers), as well as their kinetics of formation are essential in order to find ways of controlling them. The kinetics of adsorption and desorption on a planar surface has been treated theoretically and experimentally by a number of investigators.¹⁻²⁵ The suggestion that the diffusion process of the solute to surface was the cause of the alternation of adsorption and desorption with time was made by Millner,¹ and described by Langmuir

and Schafer.¹ Diffusion-controlled adsorption kinetics has been analyzed theoretically by Ward and Tordai³ by using an integral equation. Delay, Fike, and Hansen⁵⁻⁷ have found analytical solutions in the form of three terms for the short-time approximation and in the form of the first term for the adsorption process obeying the Langmuir adsorption isotherms. Miller and Wasan^{12-14,16} analyzed the different numerical schemes and showed that numerical solutions of the nonlinear equation describing the adsorption process may be obtained only by making sets of simplified assumptions even in the case in which the diffusion coefficient is constant. We examined the analytical approaches and the simplifying assumptions of the earlier investigations. Despite several attempts, there was no treatment of the problem that achieved a general analytical approach for solving the nonlinear equations for the

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adsorption and desorption processes without making sets of simplifying assumptions. Therefore, the motivations for this article are: (a) to develop a theory for the adsorption and desorption processes obeying arbitrary adsorption isotherms over a wide range of time, (b) to estimate the effects of the adsorption/desorption kinetics and the diffusion in the adsorbed layer in an analytical form for the short-time and long-time approximations, and (c) to apply the relaxation function [see eqs. (6a) and (6b)] in order to find the parameters characterizing the adsorption and desorption processes. The effect of adsorption and desorption kinetics on the adsorption and desorption processes may be also significant.^{8,10,15-22} The kinetics of the formation of adsorbed polymer layers can be separated into three stages.^{10,16-18,22,25} (1) the kinetics of adsorption and desorption of the polymer molecules on the bare surface, (2) the kinetics of adsorption and desorption of the polymer molecules onto the interface and simultaneous diffusion of polymer molecules within the adsorbed layer, and (3) diffusion of the polymer molecules in the adsorbed layer. The first process (1) occurs for short times or at low concentrations of polymer in the adsorbed layers. This process is governed by the kinetics of adsorption and desorption. Therefore, this process is called kinetic-controlled adsorption and desorption. The relaxation time (or the time scale), characteristic of this process, is relatively small (on the order of tens or 100 s). The second process (2) is governed simultaneously by the kinetics of adsorption and desorption, and diffusion. Therefore, this process is called kinetic-diffusion-controlled adsorption and desorption. The third process (3) takes place for long times or high concentrations of polymer in the adsorbed layer when interaction between the polymer molecules are essential. This process (3) is governed by diffusion and is called the diffusion-controlled adsorption and desorption. This process has relaxation times (or the time scale) on the order of hours for adsorption and days for desorption. The relaxation times of all three adsorption and desorption regimes depend on: (a) the molecular weights of the polymer molecules, (b) the structure of the adsorbed layer, (c) the surface coverage, and (d) interaction between molecules of polymer, solvent, and adsorbent.

A theory of kinetic-diffusion-controlled adsorption and desorption has been developed for linear and nonlinear adsorption and desorption isotherms. Equations are derived to calculate the relaxation times and the time needed to attain the equilibrium states for both the kinetic-controlled adsorption and diffusion-controlled adsorption and desorption.

We have reported earlier on the adsorption kinetics and dynamics of polymers onto particulate surfaces of titanium dioxide.²⁶ In this article, new results are presented on the adsorption kinetics of polymers onto a planar surface of titanium dioxide single crystal. For this purpose, an optical technique based on the use of ellipsometry^{25,27} have been used, which allows measurements of the time-dependent adsorbed polymer concentrations and the adsorbed layer thickness during the polymer adsorption process at an interface and to calculate the equilibrium adsorption, the rate of polymer adsorption, the diffusion coefficient, and the activation energy for diffusion in the adsorbed layer.

EXPERIMENTAL

Titanium Dioxide Crystal

The titanium dioxide crystals [TiO₂(001)] were purchased from Commercial Crystal Laboratories, Inc. A glass cell, shown in Figure 1, was used to measure the values for the refractive index of the titanium dioxide crystal (001) in DDI (distilled-deionized) water and polymer solutions during the adsorption and desorption processes at room temperature. The optical model, shown in Figure 2, was used to calculate: (a) the thickness of the adsorbed layer, (b) the refractive index of the adsorbed layer, (c) the weight fraction of polymers in the adsorbed layer, and (d) the adsorption of polymers onto a planar surface. After adsorption runs lasting 110 min, desorption runs were made by quickly replacing the polymer solution with DDI water. Ellipsometric measurements were performed with a Rudolph Auto El ellipsometer, using a He/Ne laser, with $\lambda = 632.8$ nm, and at an incident angle of 70°.

Characterization of the Surface of Titanium Dioxide Crystal

The morphology of the titanium dioxide crystal [TiO₂(001)] was determined using a Park Scientific Instruments (Sunnyvale, CA) Autoprobe CP contact-mode force microscope (AFM) using an ultralever and scanning at 4 kHz with constant force in air. The image shows a uniform pattern with heights of about 0.4 nm.

Polymers

The model water-soluble associative polymers used in the kinetic study were obtained from the Union Carbide Company. These polymers are nonionic

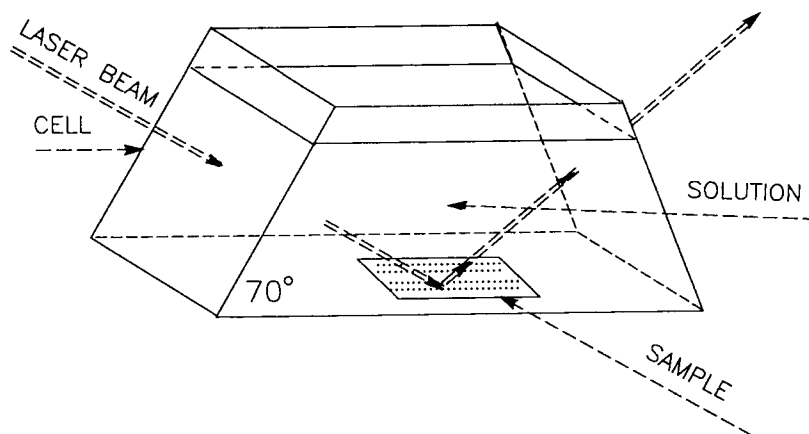


Figure 1 The glass cell to measure the adsorption onto a planar of the titanium dioxide crystal (001).

polyurethanes based on poly(ethylene glycol) and have average molecular weights of 17,000, 51,000, and 100,000 with a $C_{16}H_{33}$ linear alkyl group on each end of the molecule.

Theory of Kinetic-Diffusion-Controlled Adsorption and Desorption Processes

The adsorption and desorption processes take place in a thin layer at a planar interface. In the general case, these processes are governed by the kinetics of adsorption and desorption of polymer molecules at the interface and diffusion of these molecules into the adsorbed layer. Therefore, the adsorption and desorption processes on a planar surface may be described in a one dimensional model as:^{21,25}

$$\partial c/\partial t = \partial[D(c)\partial c/\partial x]/\partial x \quad (1a)$$

$$d\Gamma/dt = K^{ad}[c(0, t)]^m(\Gamma_m^o - \Gamma)^p - K^{des}\Gamma \quad (1b)$$

with the initial boundary conditions for the adsorption (1c) and the desorption (1d) processes, respectively:

$$c(x > 0, 0) = c_o, c(\infty, t) = c_o, \Gamma(0) = 0 \quad (1c)$$

$$c(x > 0, 0) = 0, c(\infty, t) = 0, \Gamma(0) = \Gamma(c_o) \quad (1d)$$

$$d\Gamma/dt = D[c(0, t)]\partial c(0, t)/\partial x \quad (1e)$$

where $c(x, t)$ is the concentration of polymer at a coordinate x normal to the surface ($x = 0$), $c(0, t)$ is the surface concentration on the interface, c_o is the bulk concentration, $D(c)$ is the diffusion coefficient in the bulk, $D[c(0, t)]$ is the diffusion coefficient in the adsorbed layer, Γ is the adsorption on a planar surface, Γ_m^o is the maximum adsorption when the surface coverage, θ , is equal to unity, K^{ad} and K^{des} are the rate constants for adsorption and desorption processes, respectively, m and p are the parameters of adsorption and adsorption kinetics. The inhomogeneous adsorption model in the form of eqs. (1) is complex and it is reasonable to consider the simplified homogeneous adsorption model, which may be written in the form of eqs. (1b), (2a), and (2b) with the initial boundary conditions (1c) and (1d):

$$\partial c/\partial t = D_o \partial^2 c/\partial x^2 \quad (2a)$$

$$d\Gamma/dt = D(\theta)\partial c(0, t)/\partial x \quad (2b)$$

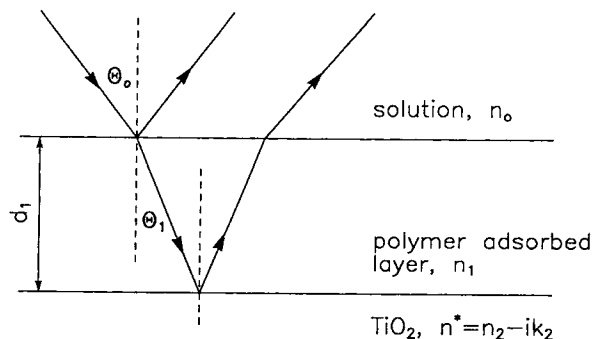


Figure 2 The optical model to calculate the adsorption onto a planar of the titanium dioxide crystal (001).

where D_o is the diffusion coefficient in the bulk, $D(\theta)$ is the diffusion coefficient in the adsorbed layer, $\theta (= \Gamma/\Gamma_m^o)$ is the fraction of the total surface coverage. For the simplified adsorption model, the diffusion coefficient, D_o , in the bulk is assumed to be constant. The simplified adsorption model in the form of eqs. (2) has been already discussed by Ravera and co-workers;²¹ the authors interpreted the diffusion coefficient, $D(\theta)$, in the framework of an interfacial potential barrier in the adsorbed layer. Inhomogeneities within the adsorbed layer can be estimated by

using the homogeneous model with the diffusion coefficient, $D(\theta)$, depending on the interaction between adsorbate molecules in the adsorbed layer and the architecture of the adsorbed layer. The equations of adsorption and desorption isotherms are calculated from eq. (1b) when equilibrium takes place, i.e., $d\Gamma/dt = 0$. The Henry (3a), the Langmuir (3b), and the Freundlich (3c) adsorption isotherms are given by:

$$\Gamma(c) = K_p c,$$

where $K_p = K^{\text{ad}}/K^{\text{des}}$, $m = 1$, $p = 0$ in eq. (1b) (3a)

$$\Gamma(c) = \Gamma_m^o K_p c / (1 + K_p c),$$

where $m = 1$, $p = 1$ in eq. (1b) (3b)

$$\Gamma(c) = (K_p)_{\text{Fr}} c^m,$$

where $0 < m \leq 1$, $p = 0$ in eq. (1b) (3c)

where K_p and $(K_p)_{\text{Fr}}$ are the constants of adsorption equilibrium. By using the Laplace transform,^{28,29} the system of eqs. (2a) and (2b) may be reduced to the system of integral-differential equations given by eqs. (4a) and (4b) for the adsorption process and eqs. (5a) and (5b) for the desorption process as:

$$\gamma(\theta(t)) = c_o (4D_o t / \pi)^{1/2} - \int_0^t (4D_o / \pi)^{1/2} c(0, t - \rho) d\rho^{1/2} \quad (4a)$$

$$c(0, t) = c_o - \frac{d}{dt} \int_0^t \gamma(\theta(t - \rho)) d\rho / (\pi D_o \rho)^{1/2} \quad (4b)$$

$$\gamma(\theta(t)) = \gamma(\theta(c_o)) - (4D_o / \pi)^{1/2} \int_0^t c(t - \rho) d\rho^{1/2} \quad (5a)$$

$$c(0, t) = \gamma(\theta(c_o)) / (\pi D_o t)^{1/2} - \frac{d}{dt} \int_0^t \gamma(\theta(t - \rho)) (\pi D_o \rho)^{-1/2} d\rho \quad (5b)$$

where

$$\gamma(\theta(t)) = \Gamma_m^o \int_0^{\theta(t)} d\rho / g(\rho), \quad \theta(t) = \Gamma(t) / \Gamma_m^o,$$

$$g(\theta) = D(\theta) / D_o, \quad D_o = D(\theta = 0),$$

$g(\theta)$ is the dimensional function taking into account the dependence of the diffusion coefficient in the adsorbed layer on the surface coverage and $\gamma[\theta(t)]$ is the function taking into account the fact that the diffusion coefficient in the adsorbed layer depends on the surface coverage θ ; $\gamma[\theta(t)] = \Gamma(t)$ when the diffusion coefficient in the adsorbed layer does not

depend on the surface coverage (i.e., $g = 1$). To describe the adsorption process over a wide range of times, it is reasonable to use eq. (4a) for short times, and eq. (4b) for long times. To describe the desorption process over a wide range of times, it is reasonable to use eq. (5a) for short times, and eq. (5b) for long times. The solution of the system of eqs. (4) and (5) over a wide range of times may be found by using the relaxation function $F(t)$, which may be written in the following form for the adsorption $F^{\text{ad}}(t)$ and the desorption $F^{\text{des}}(t)$ processes, respectively, as:^{19,20,25}

$$F^{\text{ad}}(t) = -\log[\Gamma_o / \Gamma(t) - 1] = n \log(t / t_{\text{rel}}) \quad (6a)$$

$$F^{\text{des}}(t) = \log[\Gamma_o / \Gamma(t) - 1] = n^* \log(t / t_{\text{rel}}^*) \quad (6b)$$

where t_{rel} and t_{rel}^* are the relaxation times characterizing the rate of the adsorption and desorption processes, respectively, at the interface and in the adsorbed layer, n is the slope of the relaxation function $F^{\text{ad}}(t)$ vs. $\log(t)$, and n^* is the slope of the relaxation function $F^{\text{des}}(t)$ vs. $\log(t)$.

Kinetic-Controlled Adsorption

For short times or low polymer concentrations the adsorption process may be governed by the adsorption kinetics in the form of eq. (1b). For the Henry adsorption kinetics with $m = 1$ and $p = 0$, the relative adsorption expressed in terms of the relative time $\tau = t/t_o$ is:

$$\Gamma(\tau) / \Gamma_o = 1 - G^*(\tau) \quad (7a)$$

$$G^*(\tau) = a_1 \exp(b_1^2 \tau) \operatorname{erfc}(b_1 \tau^{1/2}) - a_2 \exp(b_2^2 \tau) \operatorname{erfc}(b_2 \tau^{1/2}) \quad (7b)$$

where

$$\tau = t/t_o, \quad t_o = (\Gamma_o / c_o)^2 / D_o, \quad \beta = 4 / (K^{\text{des}} t_o),$$

$$a_1 = [1 + (1 - \beta)^{1/2}] / [2(1 - \beta)^{1/2}],$$

$$b_1 = 2[1 - (1 - \beta)^{1/2}] / \beta,$$

$$a_2 = [1 - (1 - \beta)^{1/2}] / [2(1 - \beta)^{1/2}],$$

$$b_2 = 2[1 + (1 - \beta)^{1/2}] / \beta, \quad \operatorname{erfc}(y) = 1 - \operatorname{erf}(y),$$

and where:

$$\operatorname{erf}(y) = (2/\pi^{1/2}) \int_0^y \exp(-z^2) dz$$

is the error function.^{28,29}

The function $\exp(z^2)\text{erfc}(z)$ is a complex variable, when $\beta > 1$, and may be calculated from the published tables.²⁹ The relaxation function of $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$ for different values of the parameter β is shown in Figure 3. Applying eq. (7a) for short times, the approximations of the first and third order, respectively, are given by:

$$\Gamma(t)/\Gamma_o \approx (K^{\text{ad}}c_o/\Gamma_o)t, \quad \Gamma(\tau)/\Gamma_o \approx 4\tau/\beta, \quad (8a)$$

$$\beta = (t_{\text{rel}}^o)_{\text{kin}}/(t_{\text{rel}}^o)_{\text{dif}}, \quad (t_{\text{rel}}^o)_{\text{kin}} = 4\Gamma_o/(K^{\text{ad}}c_o), \quad (t_{\text{rel}}^o)_{\text{dif}} = (\Gamma_o/c_o)^2/D_o \quad (8b)$$

$$\Gamma(\tau)/\Gamma_o \approx 4\tau/\beta - 64\tau^{3/2}/(\beta^2\pi^{1/2}) + 8(4 - \beta)\tau^2/\beta^3 \quad (8c)$$

where $(t_{\text{rel}}^o)_{\text{kin}}$ is the relaxation time characterizing the rate of adsorption kinetics and $(t_{\text{rel}}^o)_{\text{dif}} (= t_o)$ is the relaxation time characterizing the rate of the adsorption process because of diffusion. From Figure 3 and eqs. (8a) and (8b) it follows that for the Henry adsorption kinetics, the relative adsorption, $\Gamma(t)/\Gamma_o$, is controlled by the rate of adsorption kinetics, i.e., $K^{\text{ad}}c_o/\Gamma_o$. For long times the approximations of the first and third order, respectively, are given by:

$$\Gamma(\tau)/\Gamma_o \approx 1/(\pi\tau)^{1/2} \quad (9a)$$

$$\Gamma(\tau)/\Gamma_o \approx 1/(\pi\tau)^{1/2} - (2/\beta - 1)/\tau^{3/2} + 3[3 + 10(1 - \beta) + 3(1 - \beta)^2]/(64\tau^{5/2}) \quad (9b)$$

According to eqs. (6a), (8a), and (9a) for the Henry adsorption kinetics, the adsorption may be described in the form of two straight lines of $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$, as shown in Figure 3.

$F^{\text{ad}}(t)$

$$\approx \begin{cases} \log(t/t_{\text{rel}}^o), & 0 \leq t \leq t_{\text{cr}}^*, \quad t_{\text{rel}}^o = \Gamma_o/(c_oK^{\text{ad}}) \\ 0.5 \log(t/t_{\text{rel}}^{\infty}), & t \geq t_{\text{cr}}^*, \quad t_{\text{rel}}^{\infty} = (\Gamma_o/c_o)^2/(\pi D_o) \end{cases} \quad (10a)$$

$$t_{\text{cr}}^* = (t_{\text{rel}}^o)^2/t_{\text{rel}}^{\infty} = \pi D_o/(K^{\text{ad}})^2, \quad \tau_{\text{cr}}^* = t_{\text{cr}}^*/t_o = \pi\beta^2/16 \quad (10b)$$

where t_{cr}^* and τ_{cr}^* are the dimensional and dimensionless critical times, respectively. Now we consider the critical times, τ_{cr}^* , for different values of the rate of the adsorption kinetics, K^{ad} . If the rate of the adsorption kinetics is infinite ($K^{\text{ad}} \rightarrow \infty$), then $\beta = 0$, $\tau_{\text{cr}}^* = 0$, and $n_o = 0.5$, according to eqs. (8b), (10a), and (10b). As shown in Figure 3, in this case the adsorption process is governed by the diffusion

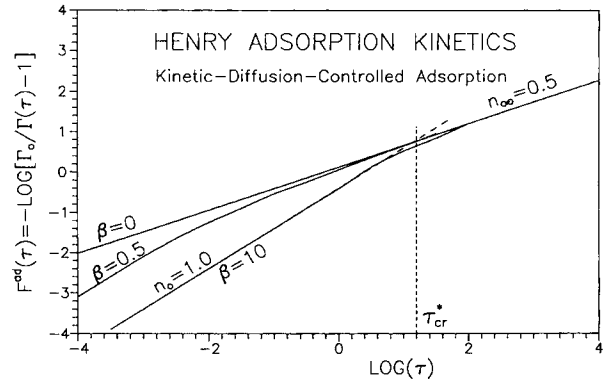


Figure 3 The time dependence of the relaxation function $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$ for the kinetic-diffusion-adsorption obeying the Henry adsorption kinetics for different values of the parameter β [$\beta = 4/(K^{\text{des}}t_o)$]. For $\beta = 10$, the slope, n , of a straight line of $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$, is equal to $n_o = 1.0$ for the kinetic-controlled adsorption process ($0 \leq \tau \leq \tau_{\text{cr}}^*$, $\tau_{\text{cr}}^* = 15.8t_o$), and equal to $n_{\infty} = 0.5$ for the diffusion-controlled adsorption process ($\tau \geq \tau_{\text{cr}}^*$).

over a wide range of time. If $\beta = 0.5$ and $\beta = 10$, then from eq. (10b) the critical times, τ_{cr}^* , are to be 0.05 and 19.6, respectively, as shown in Figure 3. If the rate of adsorption kinetics is finite ($\beta \neq 0$), then for short times ($0 \leq \tau \leq \tau_{\text{cr}}^*$) the adsorption process is governed by the adsorption kinetics. The slope, n_o , of the straight line [the relaxation function, $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$] is to be 1.0, as shown in Figure 3. For long times ($\tau \geq \tau_{\text{cr}}^*$) the adsorption process is governed by the diffusion. The slope, n_{∞} , of the straight line [the relaxation function, $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$] is to be 0.5, as shown in Figure 3. For the kinetic-controlled adsorption obeying the Henry, Langmuir, and Freundlich adsorption kinetics over short times, the relative adsorption is given by:

$$\Gamma(t)/\Gamma_o \approx t/t_{\text{rel}}^o \quad (11a)$$

where:

$$t_{\text{rel}}^o = \Gamma_o/[K^{\text{ad}}c_o^m(\Gamma_m^o)^p].$$

From eqs. (6a) and (11a) it follows that the time-dependence adsorption for short time periods for the kinetic-controlled model may be described by a straight line as:

$$F^{\text{ad}}(t) \approx n_o \log(t) + s_o \quad (11b)$$

where $n_o = 1.0$, $t_{\text{rel}}^o = \Gamma_o/[c_o^m(\Gamma_m^o)^p K^{\text{ad}}]$, and $s_o = -\log(t_{\text{rel}}^o)$ is the shift of the straight lines of the relaxation function $F^{\text{ad}}(t)$ vs. $\log(t)$ for short times.

Eq. (11a) may be used to find the adsorption rate constant from the experimental data.

It is of interest to analyze different stages of the adsorption process obeying arbitrary adsorption isotherms from the phenomenological point of view. For short times ($t \rightarrow 0$), from eq. (11a) the rate of the adsorption process is to be $(1/t_{\text{rel}})$; therefore, the resistance, Z_{kin} , because of the adsorption kinetics equals (t_{rel}) . For short times ($t \rightarrow 0$), from eq. (15b) the rate of adsorption process is to be $2/[\pi(t_o t)^{1/2}]$; therefore, the resistance, Z_{dif} , because of the diffusion equals $(\pi/2)(t_o t)^{1/2}$. The resistance, $R_{\text{ad,proc}}$, for overall adsorption process is equal to $(Z_{\text{kin}} + Z_{\text{dif}})$. From the previous analysis, it follows that for short times ($t \rightarrow 0$) $Z_{\text{ad,proc}} \approx Z_{\text{kin}}$, since $Z_{\text{kin}} \gg Z_{\text{dif}}$. Thus, for short times the adsorption process are governed by the adsorption kinetics. The critical time, t_{*cr} , when resistances of adsorption because of the adsorption kinetics and the diffusion are equal ($Z_{\text{kin}} = Z_{\text{dif}}$), is given by:

$$t_{*cr} \approx t_{\text{rel}}^2/(\pi t_o) = D_o/[\pi K^{\text{ad}}\Gamma_o(\Gamma_m^o)^p c_o^{m-2}] \quad (12)$$

From the previous analysis it follows that the adsorption process is governed by the adsorption kinetics for short times ($0 \leq t \leq t_{*cr}$) and is governed by the diffusion at $t \geq t_{*cr}$. For intermediate times, $Z_{\text{kin}} \approx Z_{\text{dif}}$, therefore $Z_{\text{ad,proc}} = Z_{\text{kin}} + Z_{\text{dif}}$. Thus, for intermediate times, the adsorption process is governed by the adsorption kinetics and diffusion simultaneously. For long times ($t \rightarrow \infty$), $Z_{\text{kin}} \ll Z_{\text{dif}}$, therefore $Z_{\text{ad,proc}} \approx Z_{\text{dif}}$. Thus, for long times, the adsorption process is governed by the diffusion.

Diffusion-Controlled Adsorption

The adsorption process is governed by diffusion of adsorbed molecules in the adsorbed polymer layer when the rate of adsorption or desorption are infinite, i.e., $d\Gamma/dt = 0$. In this case, the adsorption process is described by using eq. (4a). In the simplest case, when the diffusion coefficient is constant [$D(\theta) = D_o = \text{constant}$; $g(\theta) = 1$] and the equilibrium adsorption obeys the linear Henry eq. (3a), the relative adsorption and the relative surface concentration expressed in terms of the relative time $\tau = t/t_o$ are:

$$\Gamma(\tau)/\Gamma_o = c(0, \tau)/c_o = G(\tau) \quad (13)$$

where $G(\tau) = 1 - \exp(\tau) \text{erfc}(\tau^{1/2})$, $t_o = (K_p)^2/D_o$.

For high adsorbed concentrations of polymer, the diffusion coefficient, $D(\theta)$, in the adsorbed layer depends on the fraction of the total surface coverage as:¹⁸

$$D(\theta) = g(\theta)D_o, \quad g(\theta) = \exp(-\alpha\theta), \\ \alpha = Q/RT, \quad D_o = D(\theta = 0) \quad (14)$$

where Q is the activation energy for the diffusion process, characterizing the interaction of the adsorbed molecules in the adsorbed layer, θ is the fraction of the total surface coverage, R is the universal gas constant, and T is the absolute temperature.

Now we consider the case when the adsorption isotherms are nonlinear and the diffusion coefficient in the adsorbed layer is variable. For short times, and applying the Langmuir adsorption isotherms, the relative surface concentration and the relative adsorption are given, respectively, by:

$$c(0, \tau)/c_o = (4\tau/\pi)^{1/2}/(1+b) \\ - \tau[1 - 4b(1 - \alpha/2)/\pi]/(1+b)^2 \\ + 4\tau^{3/2}\pi^{-1/2}\{[1 - 4b(1 - \alpha/2)/\pi] \\ \times [1 - 3b(1 - \alpha/2)]/3 \\ - 2b^2(1 + \alpha + \alpha^2/6)/\pi\} \quad (15a)$$

$$\Gamma(\tau)/\Gamma_o = (4\tau/\pi)^{1/2} - \tau(1 + 2\alpha b/\pi)/(1+b) \\ + 4\tau^{3/2}[3\pi^{1/2}(1+b)^2]^{-1} \\ \times \{[1 - 4b(1 - \alpha/2)/\pi](1 + 3\alpha b/2) \\ - \alpha b^2(6 + \alpha)/\pi\} \quad (15b)$$

where

$$\tau = D_o t(1+b)^2/(\Gamma_m^o K_p)^2 \quad (15b)$$

where Γ_m^o is the maximum adsorption on a planar surface, $b = K_p c_o$ is the parameter for the Langmuir adsorption isotherm, and K_p is the equilibrium constant in the equation for the Langmuir adsorption isotherm.

For long times ($t \rightarrow \infty$), and applying arbitrary adsorption isotherms from eq. (4b), we find the asymptotic solutions for the relative surface concentration, $c(0, t)/c_o$, and the relative adsorption, $\Gamma(t)/\Gamma_o$, in the following form:

$$c(0, t)/c_o = 1 - [\gamma(\theta(c_o))/c_o]/(\pi D_o t)^{1/2}, \\ \Gamma(t)/\Gamma_o = 1 - 1/(t/t_{\text{rel}}^\alpha)^{1/2} \quad (16a)$$

where

$$\gamma_o = \int_0^{\theta_o} d\rho/g(\rho), \quad \gamma(\theta(c_o)) = \Gamma_m^o \gamma_o, \quad \theta_o = \Gamma_o/\Gamma_m^o,$$

$$\Gamma_o = \Gamma(c_o), \quad t_o = (\Gamma_o/c_o)^2/D_o, \quad t_{rel}^\infty = (a_o \gamma_o/\theta_o)^2 t_o/\pi,$$

$$a_o = [d\Gamma(c_o)/dc]/[\Gamma(c_o)/c_o],$$

and the parameter of a_o is:

$$a_o = \begin{cases} 1 & \text{(for linear isotherms)} \\ 1/(1+b) & \text{(for the Langmuir isotherms)} \\ m & \text{(for the Freundlich isotherms)} \end{cases} \quad (16b)$$

Figure 4 shows the relaxation function $F^{ad}(\tau)$ for the Langmuir adsorption isotherm. From eqs. (15) and (16), and the results shown in Figure 4, it follows that the time-dependent adsorption for the diffusion-controlled model may be described over a wide range of time by using the three straight lines as:

$$F^{ad}(t) = \begin{cases} n_o \log(t) + s_o, & n_o = 0.5, \\ & s_o = -\log(t_{rel}^o), \quad 0 \leq t \leq t_{cr1} \\ n_{mid} \log(t) + s_{mid}, & t_{cr1} \leq t \leq t_{cr2} \\ n_\infty \log(t) + s_\infty, & \\ & s_\infty = \log(t_{rel}^\infty), \quad n_\infty = 0.5, \quad t \geq t_{cr2} \end{cases} \quad (17a)$$

where s_o , s_{mid} , and s_∞ are the shift of the straight lines of the relaxation function $F^{ad}(t)$ vs. $\log(t)$ for short, intermediate, and long times, respectively. The critical times, t_{cr1} and t_{cr2} , are given by:

$$\log(t_{cr1}) = (s_o - s_{mid})/(n_{mid} - 0.5) \quad (17b)$$

$$\log(t_{cr2}) = (s_\infty - s_{mid})/(n_{mid} - 0.5) \quad (17c)$$

From the analysis of eqs. (15) through (17), the slope, n_{mid} , and the shift, s_{mid} , are equal to:

$$n_{mid} \approx dF(t_{mid})/d \log(t); \quad F(t_{mid}) \approx 0;$$

$$\Gamma(t_{mid})/\Gamma_o \approx \frac{1}{2}, \quad s_{mid} \approx n_{mid} \log(t_{mid}) \quad (17d)$$

The time-dependent diffusion-controlled adsorption may be described for arbitrary adsorption isotherms by using eqs. (17) over a wide range of times.

Next, we consider how the adsorption, $\Gamma(t)$, may approach the equilibrium state Γ_o . Strictly speaking, this equilibrium state may be reached at infinitely long times, i.e., with asymptotic $t \rightarrow \infty$. However, if we reduce the range of equilibrium amount of adsorption value by some relative value ϵ ($\epsilon \rightarrow 0$), i.e., if we take the following ranges of quasi-equilibrium

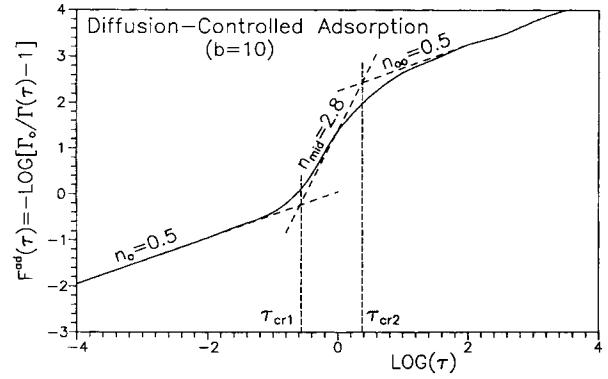


Figure 4 The time dependence of the relaxation function $F^{ad}(\tau)$ vs. $\log(\tau)$ for the diffusion-adsorption process obeying the Langmuir adsorption isotherms for the parameter $b = 10$ ($b = K_p c_o$): for short times: $n_o = 0.5$, $0 \leq \tau \leq \tau_{cr1}$, $\tau_{cr1} = 0.18t_o$; for intermediate times: $n_{mid} = 2.8$, $\tau_{cr1} \leq \tau \leq \tau_{cr2}$, $\tau_{cr2} = 2.3t_o$; and for long times: $n_\infty = 0.5$, $\tau \geq \tau_{cr2}$.

adsorption $(1 - \epsilon)\Gamma_o$, then the quasi-equilibrium state becomes realizable for finite times.

From eq. (16a) for arbitrary adsorption isotherm, the time t_{Γ}^{ad} , when the adsorption, $\Gamma(t_{\Gamma}^{ad})$, reaches the quasi-equilibrium state, $(1 - \epsilon)\Gamma_o$, is given as:

$$t_{\Gamma}^{ad} = (a_o)^2 t_o / (\pi \epsilon^2) + \pi t_o / 4 \quad (18a)$$

For the strong convex adsorption isotherms, ($a_o \rightarrow 0$), the equilibrium state, Γ_o , is approached in a time of $\pi t_o / 4$. From eq. (18a) for the Langmuir adsorption isotherm we write:

$$t_{\Gamma}^{ad} = t_o / \{ \pi [\epsilon(1+b)]^2 \} + \pi t_o / 4$$

$$= (1 - \theta)^2 t_o / (\pi \epsilon^2) + \pi t_o / 4 \quad (18b)$$

where $\theta = \Gamma/\Gamma_m^o$ is the surface coverage. From eq. (18b) it follows that the time, t_{Γ}^{ad} , depends on the surface coverage θ .

Kinetic-Controlled Desorption

For short times the desorption process may be governed by the desorption kinetics in the form of eq. (1b). In the simple case, when the desorption process obeys the linear Henry kinetics given by eq. (1b) with $m = 1$ and $p = 0$, the relative surface concentration and the relative desorption expressed in terms of the relative time $\tau = t/t_o$ are given by:

$$c(0, \tau)/c_o = \Gamma(\tau)/\Gamma_o = G^*(\tau) \quad (19)$$

where $G^*(\tau)$ is found from eq. (7a). From eq. (5), the relative desorption are given for short and long times, respectively, by:

$$\Gamma(t)/\Gamma_o \approx 1 - t/t_{\text{rel}}^{*o} \quad (20a)$$

$$\Gamma(t)/\Gamma_o \approx (t_{\text{rel}}^{*\infty}/t)^{1/2} \quad (20b)$$

where t_{rel}^{*o} ($= 1/K^{\text{des}}$) is the relaxation time for short times for the linear desorption isotherm and $t_{\text{rel}}^{*\infty}$ ($= t_o/\pi$) is the relaxation time for long times. From eqs. (6b) and (20), it follows that the desorption process is controlled by the desorption kinetics for short times and diffusion for long times. For arbitrary desorption isotherms over short times, the relative desorption is given by:

$$\Gamma(t)/\Gamma_o \approx 1 - t/t_{\text{rel}}^{*o} \quad (21)$$

where

$$t_{\text{rel}}^{*o} (= (\Gamma_m^o - \Gamma_o)/\{K^{\text{des}}[\Gamma_m^o + (p-1)\Gamma_o]\})$$

is the relaxation time at short times for arbitrary desorption isotherms.

Now we consider the relaxation function $F^{\text{des}}(t)$. According to eqs. (6b), and (21), for arbitrary desorption isotherms, the relaxation function $F^{\text{des}}(t)$ for short times ($t \rightarrow 0$) may be written as:

$$\begin{aligned} F^{\text{des}}(t) &= \log[\Gamma_o/\Gamma(t) - 1] \\ &= n_{*o}^* \log(t/t_{\text{rel}}^{*o}) = \log(t) + s_{*o}^* \quad (22) \end{aligned}$$

where

$$s_{*o}^* = -\log(t_{\text{rel}}^{*o})$$

and

$$n_{*o}^* = 1.0$$

are the shift and the slope of the straight lines of the relaxation function $F^{\text{des}}(t)$ vs. $\log(t)$ for short times, respectively. Equation (22) may be used to find the desorption rate constant from the experimental data.

Diffusion-Controlled Desorption

The desorption of macromolecules from a planar surface may be a reversible or irreversible process.^{10,15,25} For the reversible processes, the desorption is described by eq. (5) when the rate of adsorption and desorption are infinite, i.e., $d\Gamma/dt = 0$. In the simplest case, when the diffusion coefficient is constant [i.e., $D(\theta) = D_o = \text{constant}$, $g(\theta) = 1$] and the equilibrium desorption obeys the linear Henry eq. (3a), the relative desorption and the relative sur-

face concentration expressed in terms of the relative time, $\tau = t/t_o$, are:

$$\Gamma(\tau)/\Gamma_o = c(0, \tau)/c_o = 1 - G(\tau) \quad (23)$$

where $G(\tau)$ is found from eq. (13).

Now we consider the desorption process for non-linear desorption isotherms. The relative surface concentration, $c(0, \tau)/c_o$ and the relative desorption, $\Gamma(\tau)/\Gamma_o$, for short times ($\tau \rightarrow 0$), for the Langmuir desorption isotherms are given by:

$$\begin{aligned} c(0, \tau)/c_o &= 1 - g_o(1+b)(4\tau/\pi)^{1/2} + \tau g_o^2(1+b)^2 \\ &\quad \times \{1 + 4b[1 - \alpha/(1+b)]/[\pi(1+b)]\} \\ &\quad - 4\tau^{3/2} g_o^3(1+b)^3 (3\pi^{1/2})^{-1} \\ &\quad \times \{[1 + 4b(\pi(1+b))^{-1}] \\ &\quad \times (1 - \alpha(2(1+b))^{-1})\} \\ &\quad \times [1 + 3b(1 - \alpha(2(1+b))^{-1})/(1+b)] \\ &\quad - 6b^2[1 - \alpha/(1+b) \\ &\quad + \alpha^2/(6(1+b)^2)]/[\pi(1+b)^2] \} \quad (24a) \end{aligned}$$

$$\begin{aligned} \Gamma(\tau)/\Gamma_o &= 1 - g_o(4\tau/\pi)^{1/2} + \tau g_o^2(1+b) \\ &\quad \times \{[1 + 4b(1 - \alpha/(1+b))]/[\pi(1+b)] \\ &\quad - 4b/\pi\} - 4/(3\pi^{1/2})\tau^{3/2} g_o^3 \{6b^2/\pi \\ &\quad - 3(1+b)^2 + (1+b)^2 \\ &\quad \times [(1 + 4b(\pi(1+b))^{-1}) \\ &\quad \times (1 - \alpha(2(1+b))^{-1})] \\ &\quad \times (1 + 3b(1 - \alpha(2(1+b))^{-1})/(1+b)) \\ &\quad - 6b^2(1 - \alpha/(1+b) \\ &\quad + \alpha^2/(6(1+b)^2))/(\pi(1+b)^2)\} \} \quad (24b) \end{aligned}$$

where

$$g_o = g(\theta(c_o)), \Gamma_m^o$$

is the maximum adsorption on a planar surface, $b = K_p c_o$ is the parameter for the Langmuir desorption isotherm, and K_p is the equilibrium constant in the equation for the Langmuir desorption isotherm.

For long times ($t \rightarrow \infty$) and arbitrary desorption isotherms, the relative surface concentration and relative desorption are given, respectively, by:

$$c(0, t)/c_o = [\gamma(\theta(c_o))/c_o]/(\pi D_o t)^{1/2} \quad (25a)$$

$$\Gamma(t)/\Gamma_o = (t_{\text{rel}}^{*\infty}/t)^{1/2} \quad (25b)$$

where

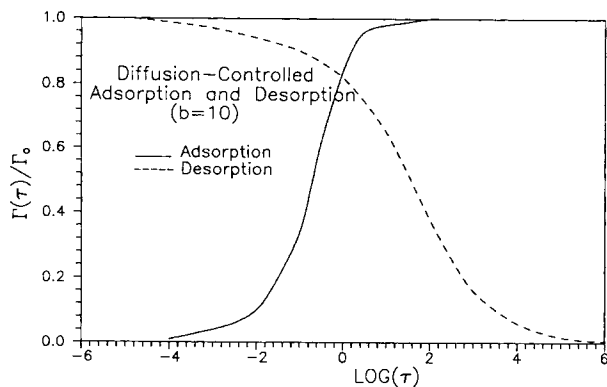


Figure 5 The relative adsorption and desorption, $\Gamma(\tau)/\Gamma_0$ vs. $\log(\tau)$ for the diffusion-adsorption obeys the Langmuir adsorption isotherms for the parameter $b = 10$.

$$t_{\text{rel}}^{*\alpha} = (a_o^* \gamma_o / \theta_o)^2 t_o / \pi$$

is the relaxation time for long times, for arbitrary desorption isotherms and the parameter $a_o^* = [d\Gamma(c=0)/dc]/(\Gamma_0/c_0)$ is:

$$a_o^* = \begin{cases} 1 & \text{(for linear desorption isotherms)} \\ 1 + b & \text{(for the Langmuir desorption isotherms)} \\ \infty & \text{(for the Freundlich desorption isotherms)} \end{cases} \quad (25c)$$

Now we consider the relaxation function $F^{\text{des}}(t)$. According to eqs. (6b), (24b), and (25b) for arbitrary adsorption isotherms, the relaxation function $F^{\text{des}}(t)$ for short times ($t \rightarrow 0$) is given by eq. (26a), and for long times ($t \rightarrow \infty$) is given by eq. (26b), may be written as:

$$F^{\text{des}}(t) = \log[\Gamma_0/\Gamma(t) - 1] = n_o^* \log(t/t_{\text{rel}}^{*o}) = 0.5 \log(t) + s_o^* \quad (26a)$$

$$F^{\text{des}}(t) = \log[\Gamma_0/\Gamma(t) - 1] = n_{\infty}^* \log(t/t_{\text{rel}}^{*\alpha}) = 0.5 \log(t) + s_{\infty}^* \quad (26b)$$

$$s_o^* = -0.5 \log(t_{\text{rel}}^{*o}); t_{\text{rel}}^{*o} = \pi t_o / (4g^2) \quad (26c)$$

$$s_{\infty}^* = -0.5 \log(t_{\text{rel}}^{*\alpha}); t_{\text{rel}}^{*\alpha} = (a_o^* \gamma_o / \theta_o)^2 t_o / \pi \quad (26d)$$

where $t_o = (\Gamma_0/c_0)^2/D_o$ is the time characterizing the rate of desorption processes for the diffusion-controlled model, s_o^* and s_{∞}^* are the shift of the straight lines of the relaxation function $F^{\text{des}}(t)$ vs. $\log(t)$ for short and long times, respectively. For the diffusion-controlled model obeying the Langmuir desorption isotherm, the relative adsorption, $\Gamma(\tau)/\Gamma_0$, and the relaxation function $F^{\text{des}}(\tau)$ are shown, respectively, in Figures 5 and 6. According to eqs.

(6b), (13), and (23), for the diffusion-controlled model, the behavior of the relaxation functions $F^{\text{ad}}(\tau)$ and $F^{\text{des}}(\tau)$ are the same for the linear desorption isotherms and are dramatically different for Langmuir desorption isotherms, as shown in Figures 4 and 5. From eqs. (6b) and (23) through (26), and results shown in Figure 6, it follows that the time-dependent desorption for the diffusion-controlled model may be described over a wide range of times by using the three straight lines as:

$$F^{\text{des}}(t) = \begin{cases} n_o^* \log(t) + s_o^*, & n_o^* = 0.5, \\ s_o^* = -\log(t_{\text{rel}}^{*o}), & 0 \leq t \leq t_{\text{cr1}}^* \\ n_{\text{mid}}^* \log(t) + s_{\text{mid}}^*, & t_{\text{cr1}}^* \leq t \leq t_{\text{cr2}}^* \\ n_{\infty}^* \log(t) + s_{\infty}^*, & s_{\infty}^* = \log(t_{\text{rel}}^{*\alpha}), \\ n_{\infty}^* = 0.5, & t \geq t_{\text{cr2}}^* \end{cases} \quad (27a)$$

where s_o^* , s_{mid}^* , and s_{∞}^* are the shift of the straight lines of the relaxation function $F^{\text{des}}(t)$ vs. $\log(t)$ for short, middle, and long time, respectively. The critical times, t_{cr1}^* and t_{cr2}^* , are given by:

$$\log(t_{\text{cr1}}^*) = (s_o^* - s_{\text{mid}}^*) / (n_{\text{mid}}^* - 0.5) \quad (27b)$$

$$\log(t_{\text{cr2}}^*) = (s_{\infty}^* - s_{\text{mid}}^*) / (n_{\text{mid}}^* - 0.5) \quad (27c)$$

From the analysis of eqs. (27), the slope, n_{mid}^* , and the shift, s_{mid}^* , are equal to:

$$n_{\text{mid}}^* \approx dF(t_{\text{mid}}^*)/d \log(t), \quad (28)$$

$$s_{\text{mid}}^* \approx F^{\text{des}}(t_{\text{mid}}^*) - \frac{1}{2} \log(t_{\text{mid}}^*)$$

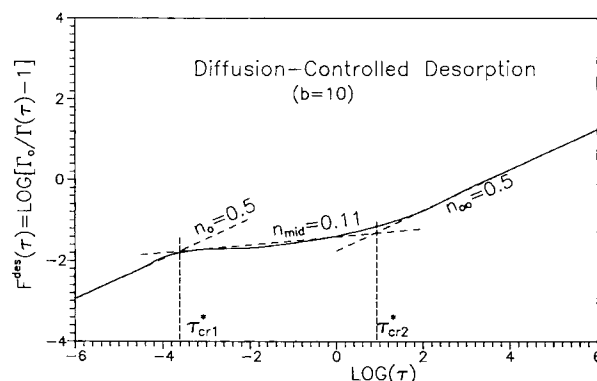


Figure 6 The relaxation function $F^{\text{des}}(\tau)$ versus $\log(\tau)$ for the diffusion-desorption process obeying the Langmuir desorption isotherms for the parameter $b = 10$ ($b = K_p c_o$). The slope, n , of a straight line of $F^{\text{ad}}(\tau)$ vs. $\log(\tau)$ is equal to $n_o = 0.5$ for short times ($0 \leq \tau \leq \tau_{\text{cr1}}^* = 1.6 \cdot 10^{-4} t_o$), is equal to $n_{\text{mid}} = 0.11$ for intermediate times ($\tau_{\text{cr1}}^* \leq \tau \leq \tau_{\text{cr2}}^*$, $\tau_{\text{cr2}}^* = 7.9 t_o$), and is equal to $n_{\infty} = 0.5$ for long times ($\tau \geq \tau_{\text{cr2}}^*$).

The time-dependent diffusion-controlled desorption may be described for an arbitrary desorption isotherms by using eqs. (27) and (28) over a wide range of times.

Below, we consider how the desorption, $\Gamma(t)$, may approach the equilibrium state, $\Gamma = 0$. Strictly speaking, this equilibrium state may only be reached at infinitely long times, i.e., asymptotic $t \rightarrow \infty$. However, if we reduce the range by some relative value ϵ ($\epsilon \rightarrow 0$), i.e., if we take the following range of the quasi-equilibrium desorption $\epsilon\Gamma_0$, then the quasi-equilibrium state becomes realizable for finite times, t_{Γ}^{des} . From eq. (25b) for arbitrary desorption isotherms in the form of eq. (29a) and for the Langmuir desorption isotherms in the form of eqs. (29b), the times, t_{Γ}^{des} , are given by:

$$t_{\Gamma}^{\text{des}} = t_{\text{rel}}^{\alpha} / \epsilon^2 = (a_{\sigma}^* \gamma_o / \theta_o)^2 t_o / (\pi \epsilon^2) \quad (29a)$$

$$t_{\Gamma}^{\text{des}} = (1 + b)^2 (\gamma_o / \theta_o)^2 t_o / (\pi \epsilon^2) \quad (29b)$$

From the preceding analysis it follows that for the strong convex adsorption isotherm (i.e., $b \rightarrow \infty$) the equilibrium state for desorption processes cannot be reached for real, finite times. In these cases the desorption is an irreversible process.

ELLIPSOMETRY

We have used the ellipsometer to measure the amount of polymer adsorbed on a planar surface comprised of the crystal $\text{TiO}_2(001)$. The thickness of the adsorption layer depends on changes in the polarization of light due to reflection from the smooth interface. The thickness, $d_{\text{ad.layer}}$, and the refractive index, $n_{\text{ad.layer}}$, of adsorption layer were found simultaneously by using the following equations^{25,30}:

$$\begin{aligned} \text{Re}(\delta) &= (2\pi/\lambda) d_{\text{ad.layer}} \\ &\times [n_{\text{ad.layer}}^2 - n_{\text{sol}}^2 \sin^2 \theta_{\text{sol}}]^{1/2}; \text{Im}(\delta) = 0 \end{aligned} \quad (30)$$

where $\text{Re}(\delta)$ and $\text{Im}(\delta)$ are the real and imaginary parts of the phase shift, respectively, λ is the wavelength of light, $d_{\text{ad.layer}}$ is the thickness of the adsorbed polymer layer, $n_{\text{ad.layer}}$ and n_{cr} are the refractive index of the adsorbed layer and the polymer solution, respectively. The values of $d_{\text{ad.layer}}$ and $n_{\text{ad.layer}}$ from eqs. (30) are calculated by using ellipsometric experimental data. The amount of polymer adsorbed on a planar surface is given by:

$$\Gamma = d_{\text{ad.layer}} X_{\text{polym}} \rho_{\text{polym}} \quad (31)$$

where Γ is the amount of polymer adsorbed expressed in mg per cm^2 of surface, $X_{\text{ad.layer}}$ is the weight fraction of polymer in the adsorbed layer, and ρ_{polym} is the polymer density (g/cm^3).

The weight fraction of polymer in the adsorption layer $X_{\text{ad.layer}}$ may be found from the Lorentz-Lorenz equation.³¹ This equation for the molar refraction, $R_{\text{ad.layer}}^*$, of a mixture of solvent and polymer, can be written as:

$$R_{\text{ad.layer}}^* = x_{\text{polym}} R_{\text{polym}}^* + x_{\text{sol}} R_{\text{sol}}^*;$$

$$\text{where } R_i^* = (M_i / \rho_i) (n_i^2 - 1) / (n_i^2 + 2) \quad (32)$$

where x_{polym} and x_{sol} are the mol fraction of polymer (polym) and solvent (sol), respectively, and M_i , ρ_i , and n_i represent the molecular weight, density, and refractive index of component i , respectively.

The experimental values for the thickness, $d_{\text{ad.layer}}$, and the refractive index, $n_{\text{ad.layer}}$, are found simultaneously by ellipsometric measurements. The molar fraction, $x_{\text{ad.layer}}$, and the weight fraction, $X_{\text{ad.layer}}$, of polymer in the adsorption layer may be calculated by using eq. (32). Finally, the amount of polymer adsorbed, Γ , is found by using eq. (31).

RESULTS AND DISCUSSION

The above theory for the kinetic-diffusion-controlled adsorption and desorption was developed in order to estimate the time dependence of adsorption and desorption over a wide range of times. According to the developed theory, the adsorption process for arbitrary adsorption isotherms is governed by: (1) the adsorption kinetics on the bare surface for short times ($0 \leq t \leq t_{\text{cr1}}$), (2) the adsorption kinetics and diffusion in the adsorbed layer for intermediate times ($t_{\text{cr1}} \leq t \leq t_{\text{cr2}}$), and (3) diffusion in the adsorbed layer for long times ($t \geq t_{\text{cr2}}$). The values of the critical times t_{cr1} and t_{cr2} depend on the structure of the adsorbed layer, molecular weight of polymer molecules, and interaction between molecules of polymer, solvent, and adsorbent.

The adsorption of water-soluble associative polymer ($\text{C}_{16}\text{H}_{33}$ end groups with a molecular weight of 17,000, 51,000, or 100,000) from aqueous solution onto the titanium dioxide crystal (001) was studied for a concentration range of 3 mg/kg to 300 mg/kg by ellipsometry with a Rudolph Auto El ellipsometry at room temperature. The adsorption isotherms of the associative polymer with different molecular weights are shown in Figure 7. The adsorption isotherms are strongly convex for low polymer concentrations (less than 3 mg/kg). For intermediate and

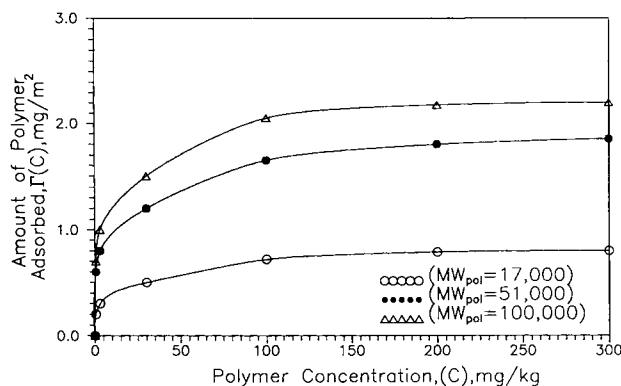


Figure 7 Adsorption isotherms of the water-soluble associative polymer on TiO_2 substrate with different polymer molecular weights.

high polymer concentrations (greater than 30 mg/kg), the adsorption isotherms may be approximated by using the Langmuir adsorption isotherms. The maximum amounts of polymer adsorbed as a function of molecular weights of the associative polymers are given in Table I, along with several other characteristics of the adsorbed layers.

From the experimental adsorption isotherms one can determine the surface area occupied by one polymer molecule, σ_m , in the adsorbed state corresponding to the plateau:

$$\sigma_m (\text{nm}^2) = MW_{\text{polym}} / (\Gamma_m^\circ N_A) \quad (33)$$

where MW_{polym} is the polymer molecular weight, Γ_m° is the amount of the adsorbed polymer on a planar surface corresponding to the isotherm plateau, and N_A is Avagadro's number. Table I represents the molecular weight dependence of the surface σ_m for the water-soluble associative polymers. The value of σ_m increases from 36 nm^2 to 77 nm^2 (approximately 2.1 times) as the polymer molecular weight is increased from 17,000 to 100,000 (approximately six times). From this date, it follows that the surface coverage density (the degree of packing in the adsorbed layer) increases with increasing the polymer molecular weights.

The thickness of the adsorbed polymer layers (d_{ad}) for $c_o = 300$ mg/kg, obtained by using eq. (30), is given in Table I. From the experimental values and the Lorentz-Lorenz eq. (32), the weight fraction, X_{polym} , of water-soluble associative polymer in the adsorption layer is found. As shown in Figure 8, the weight fraction of water-soluble associative polymer depends on the molecular weight of polymers and increases with increasing the polymer concentration in bulk. For example, for the 100,000 molecular weight polymer at the polymer concen-

Table I Characteristics of the Adsorbed Layers of Associative Polymers onto Planar TiO_2

MW_{pol} [g/mol]	Γ_m° [mg/m ²]	σ_m [nm ²]	d_{ad} [nm]	Wt_{plat}	χ_{Arch}
17,000	0.79	35.7	11.9	0.11	0.57
51,000	1.95	43.4	12.6	0.145	0.59
100,000	2.15	77.2	14.3	0.175	0.69

MW_{pol} = Molecular weight of associative polymer.

Γ_m° = Amount adsorbed per unit area.

σ_m = Area occupied by one polymer molecule.

d_{ad} = Thickness of the adsorbed layer.

Wt_{plat} = weight fraction of the associative polymer in the adsorbed layer.

χ_{Arch} = Parameter characterizing the architecture of the adsorbed layer.

tration c_o corresponding to the plateau, the weight fraction of polymer in the adsorbed layer is approximately about 0.18; thus, in this case, the adsorption layer consists of 18 wt % water-soluble associative polymer and 82 wt % water. The weight fractions Wt_{plat} for $c_o = 300$ mg/kg, when the quasi plateau is reached for the three polymer samples, are also given in Table I. From results in Figure 8 and Table I, it follows that the adsorbed layers are compressed when the polymer concentration in the bulk increases from 3 mg/kg to 300 mg/kg. The length, L_{suf} , characterizing the surface area on a planar surface occupied by one polymer molecule, may be estimated as:

$$L_{\text{suf}} \approx (4\sigma_m/\pi)^{1/2} \quad (34)$$

The ratio, χ_{Arch} , equals to

$$\chi_{\text{Arch}} = L_{\text{suf}}/d_{\text{ad}} \quad (35)$$

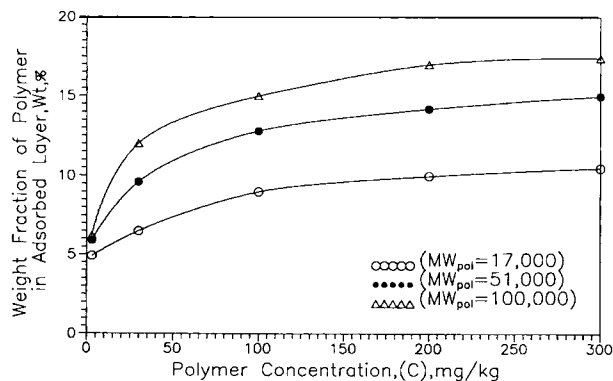


Figure 8 The concentration dependence of the weight fraction of the associative polymers in the adsorbed layer in the adsorbed state corresponding to the plateau of the adsorption isotherm.

characterizes the architecture of the adsorbed layer. Table I shows the ratio, χ_{Arch} , vs. the molecular weight of polymers. The values of χ_{Arch} are calculated from eqs. (34) and (35), and the experimental data in Table I. The values of χ_{Arch} are listed in Table I, which show that the compressibility of the adsorbed layers increases with the increase in the molecular weight of polymers.

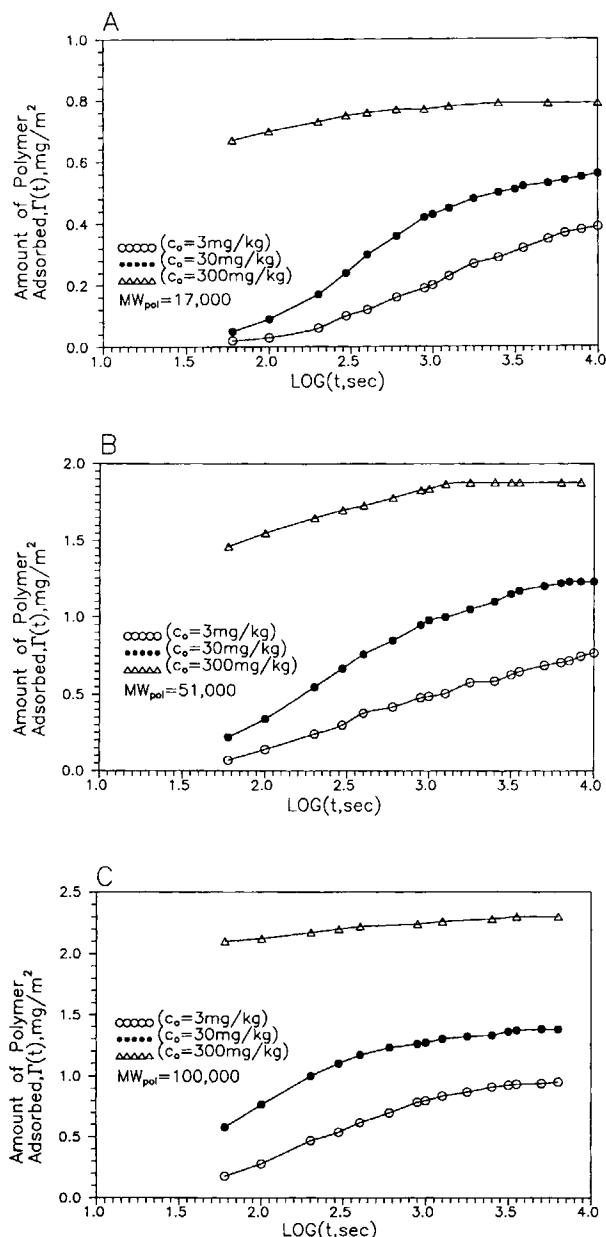


Figure 9 The time dependence of the amount of polymer adsorbed vs. log time for water-soluble associative polymer for a wide concentration range of 3 mg/kg to 300 mg/kg: A—with a molecular weight of 17,000, B—with a molecular weight of 51,000, and C—with a molecular weight of 100,000.

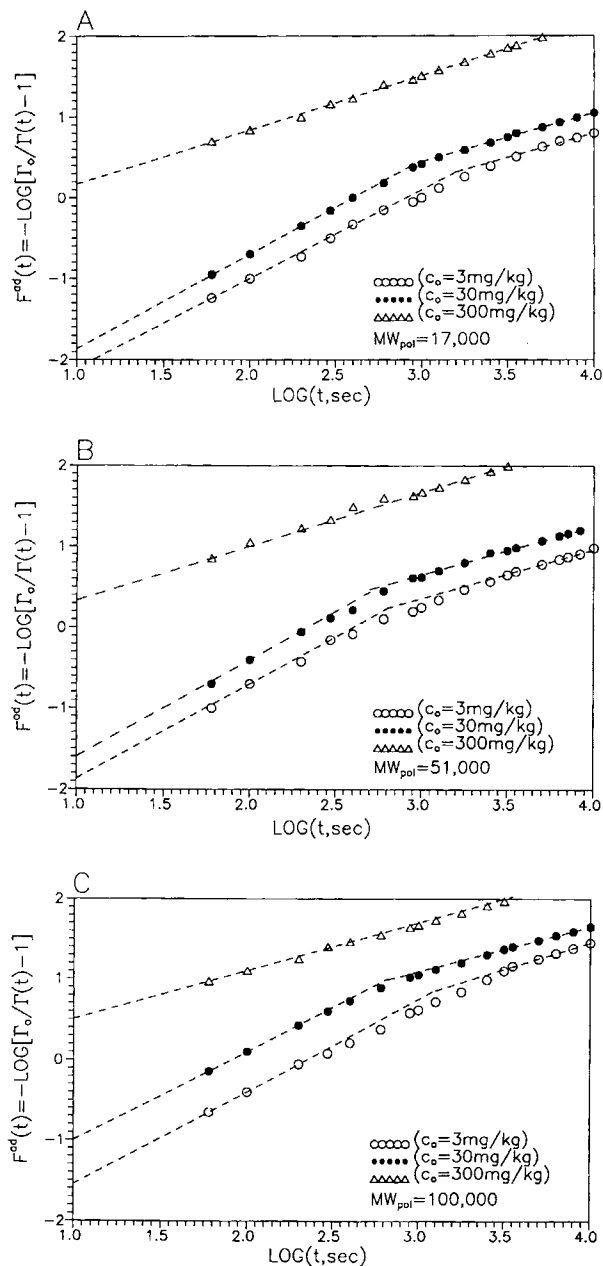


Figure 10 The time dependence of the relaxation function $F^{ad}(t)$ vs. $\log(t)$ for water-soluble associative polymer for a wide concentration range of 3 mg/kg to 300 mg/kg: A—with a molecular weight of 17,000, B—with a molecular weight of 51,000, and C—with a molecular weight of 100,000.

The adsorption $\Gamma(t)$ and the function $F^{ad}(t)$ vs. $\log(t)$ are shown in Figures 9 (A, B, and C) and 10 (A, B, and C), respectively, for the water-soluble associative polymer of three molecular weights over a wide range of concentrations, from 3 mg/kg to 300 mg/kg. According to eqs. (16) and (17), the relaxation time t_{rel}^{∞} , characterizing the rate of the adsorption process, decreases when the polymer con-

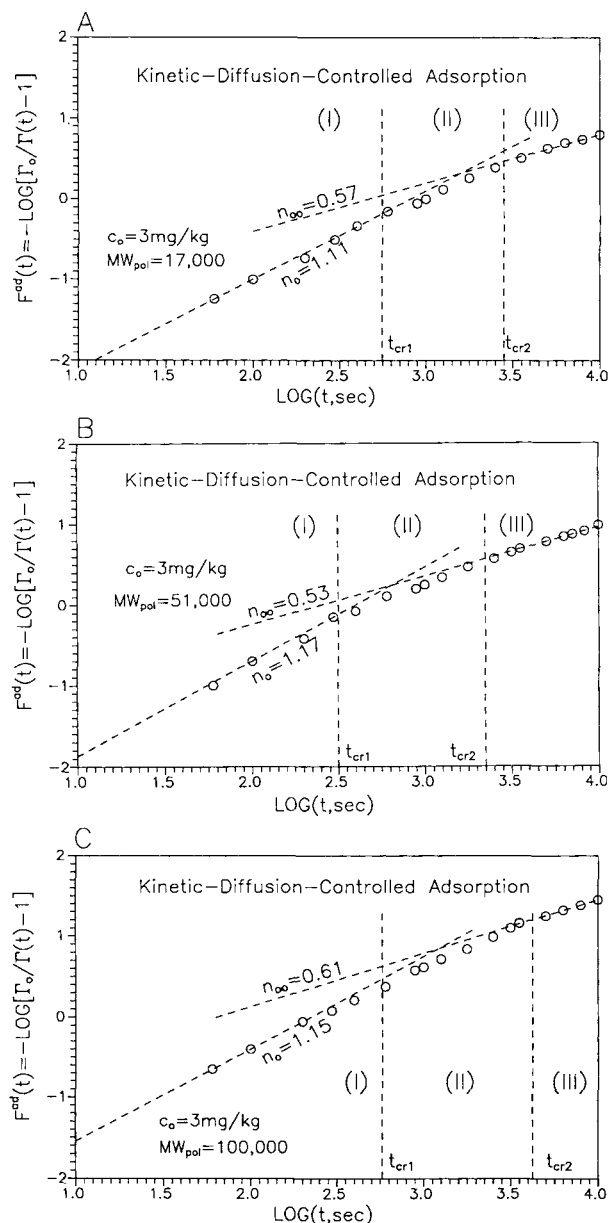


Figure 11 The time dependence of the relaxation function $F^{\text{ad}}(t)$ vs. $\log(t)$ for water-soluble associative polymer for 3 mg/kg polymer concentration: A—(with a molecular weight of 17,000) (I) the kinetic-controlled adsorption process, $n_0 = 1.11$; $0 \leq t \leq t_{\text{cr1}}$, $t_{\text{cr1}} = 9.4$ min; (II) the kinetic-diffusion-controlled adsorption process, $n = \text{variable}$; $t_{\text{cr1}} \leq t \leq t_{\text{cr2}}$, $t_{\text{cr2}} = 46.9$ min; and (III) the diffusion-controlled adsorption process, $n_\infty = 0.57$; $t \geq t_{\text{cr2}}$; B—(with a molecular weight of 51,000) (I) the kinetic-controlled adsorption process, $n_0 = 1.17$; $0 \leq t \leq t_{\text{cr1}}$, $t_{\text{cr1}} = 5.3$ min; (II) the kinetic-diffusion-controlled adsorption process, $n = \text{variable}$; $t_{\text{cr1}} \leq t \leq t_{\text{cr2}}$, $t_{\text{cr2}} = 37.3$ min; and (III) the diffusion-controlled adsorption process, $n_\infty = 0.53$; $t \geq t_{\text{cr2}}$; and C—(with a molecular weight of 100,000) (I) the kinetic-controlled adsorption process, $n_0 = 1.15$; $0 \leq t \leq t_{\text{cr1}}$, $t_{\text{cr1}} = 3.7$ min; (II) the kinetic-diffusion-controlled adsorption process, $n = \text{variable}$; $t_{\text{cr1}} \leq t \leq t_{\text{cr2}}$, $t_{\text{cr2}} = 66.3$ min; and (III) the diffusion-controlled adsorption process, $n_\infty = 0.61$; $t \geq t_{\text{cr2}}$.

centration increases. Therefore, the rate of the adsorption process for the water-soluble associative polymer decreases when the polymer concentration increases from 3 mg/kg to 300 mg/kg, as shown in Figures 9 and 10. The experimental data in Figures 10 and 11 show that for short times and low concentrations of water-soluble associative polymers that the slopes, n_0 , of the straight lines [of the relaxation function $F^{\text{ad}}(t)$ vs. $\log(t)$] are approximated to 1.0. In order to analyze these results, one must consider that the overall adsorption process is governed by the step with the least rate, and according to eqs. (8a) and (15b), for the kinetic-controlled step the adsorption is proportional to t (time) and the rate of adsorption is constant; for the diffusion-controlled step, the adsorption is proportional to $t^{1/2}$ and the rate of adsorption is proportional to $t^{-1/2}$. Therefore, according to the experimental data in Figures 10 and 11 and eqs. (11a) and (11b), the rate-determining step of the overall adsorption process for short times ($0 \leq t \leq t_{\text{cr1}}$) is the kinetic-controlled step. From the experimental data shown in Figures 10 (A, B, and C) and 11 (A, B, and C), it also follows that for long times and high concentrations of water-soluble associative polymer concentrations the slopes, n_∞ , of the straight lines are approximately 0.5. For the intermediate times ($t_{\text{cr1}} \leq t \leq t_{\text{cr2}}$), the rates of the kinetic-controlled step and the diffusion-controlled step are comparable; therefore, the rate-determining step is the kinetic-diffusion-controlled step. According to eqs. (17), for long times ($t \geq t_{\text{cr2}}$) the rate of the adsorption kinetics is greater than the rate of the adsorption process because of the diffusion; therefore, the rate-determining step for long times is the diffusion-controlled step. Thus, the kinetic-diffusion-controlled adsorption takes place for water-soluble associative polymer concentrations from 3 mg/kg to 30 mg/kg over a wide range of times, as shown in Figures 10 (A, B, and C) and 11 (A, B, and C). Diffusion-controlled adsorption takes place at water-soluble associative polymer concentrations greater than 30 mg/kg over a wide range of times.

From the experimental data presented in Figures 10 (A, B, and C) and 11 (A, B, and C), and eqs. (11), (12), and (16) through (17), the following values, characterizing adsorption processes for the water-soluble associative polymers, are calculated and listed in Table II: (1) the adsorption rate constant, K^{ad} , (2) the diffusion coefficient in the bulk, D_0 , and in the adsorbed layer, $D[\theta(c)]$, and (3) the activation energy in the adsorbed layer, Q . The adsorption rate constant decrease with increasing the molecular weight of the polymers due to the greater mobility of molecules with low molecular weights.

Table II Characteristics of the Adsorption Process of Associative Polymer onto TiO₂

MW_{pol} [g/mol]	K^{ad} [10 ⁻⁴ kg/(mg·s)]	D_o [10 ⁻⁶ (cm ² /s)]	Q [kJ/mol]
17,000	1.26	0.63	10.6
51,000	1.05	0.42	11.8
100,000	0.79	0.33	12.3

K^{ad} = Adsorption rate constant.
 D_o = Diffusion coefficient in bulk.
 Q = Activation energy.

From the data in Table II the diffusion coefficient in the bulk, D_o , is given by:

$$\log[D_o(\text{cm}^2/\text{s})] = -4.67 - 0.36 \log(MW_{\text{pol}}) \quad (36)$$

The proportionality of D_o to $MW^{-0.36}$ is in accordance with the phenomenological theory for polymer solutions.³² The concentration dependence of the diffusion coefficient, $D[\theta(c)]$, in the adsorbed associative polymer layer on the titanium dioxide crystal (001) is shown in Figure 12. The diffusion coefficient in the adsorbed layer decreases significantly when the fraction of the total surface coverage increases due to strong interactions between molecules of water-soluble associative polymer and water in the adsorbed layer. As shown in Table II, the activation energy, Q , increases weakly (about 25%) as the polymer molecular weights increase almost one order of magnitude; this results from interactions between molecules in the adsorbed layer. Based on the experimental results given in Tables I and II, the following eqs. (37) through (42) may be used to estimate the values characterizing the adsorption processes for the water-soluble associative polymers on the titanium dioxide planar surface:

$$\Gamma_m^o(\text{mg}/\text{m}^2) = -7.6 + 2 \log(MW_{\text{pol}}) \quad (37)$$

$$d_{\text{ad}}(\text{nm}) = 62.1 - 24.5 \log(MW_{\text{pol}}) + 3[\log(MW_{\text{pol}})]^2 \quad (38)$$

$$W_{\text{t,plat}}(\%) = -27.5 + 9.1 \log(MW_{\text{pol}}) \quad (39)$$

$$K^{\text{ad}}(\text{kg}/\text{mg}\cdot\text{s}) = [3.82 - 0.6 \log(MW_{\text{pol}})] 10^{-4} \quad (40)$$

$$D[\theta(c)] = D_o \exp[-\theta(c)Q/RT], \quad \theta = \Gamma(c)/\Gamma_m^o \quad (41)$$

$$Q(\text{kJ}/\text{mol}) = 1.22 + 2.22 \log(MW_{\text{pol}}) \quad (42)$$

Next, we consider the desorption process for the water-soluble associative polymers with different molecular weights. The time dependence of desorption, $\Gamma(t)$, and the relaxation function, $F^{\text{des}}(t)$, vs. $\log(t)$ are shown in Figures 13 (A, B, and C) and 14 (A, B, and C), respectively. The adsorption isotherms, as shown in Figures 13 (A, B, and C), are weakly convex for polymer concentrations greater than 30 mg/kg and are strongly convex for polymer concentrations less than 30 mg/kg. According to the above theory for the kinetic-diffusion-controlled desorption process, the adsorption is a reversible process for weakly convex adsorption isotherms and is an irreversible process for strongly convex adsorption isotherms, shown in Figures 13 (A, B, and C). From the experimental data shown in Figures 14 (A, B, and C), it follows that for short times the slope, n_o^* , of the straight line [the relaxation function $F^{\text{des}}(t)$ vs. $\log(t)$] are approximately 1.0. The overall desorption process is governed by the step with the least rate. According to eqs. (20a) and (24b), for the kinetic-controlled step the desorption is proportional to t (time) and the rate of desorption is constant; for the diffusion-controlled step, the desorption is proportional to $t^{1/2}$ and the rate of desorption is proportional to $1/t^{1/2}$ for short times ($0 \leq t \leq t_{\text{cr1}}^*$). Therefore, according to eqs. (21) and (22), the rate-determining step of the overall desorption process for short times is the kinetic-controlled step in the case of the weakly convex adsorption isotherms. From the experimental data in Figures 14 (A,B,C), it also follows that (a) $t_{\text{cr1}}^* \rightarrow 0$ and (b) for intermediate times ($t \leq t_{\text{cr2}}^*$) the slope, n_{mid}^* , is approximately 0.18 and for long time ($t \geq t_{\text{cr2}}^*$) the slope, n_{∞}^* , is of about 0.5. According to eqs. (25) through (27), the desorption process is

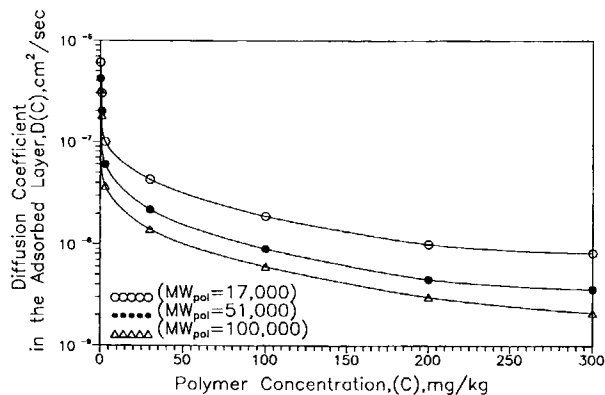


Figure 12 The dependence of the diffusion coefficient of the water-soluble associative polymers in the adsorbed layer [$D(c)$] vs. polymer concentrations with different polymer molecular weights.

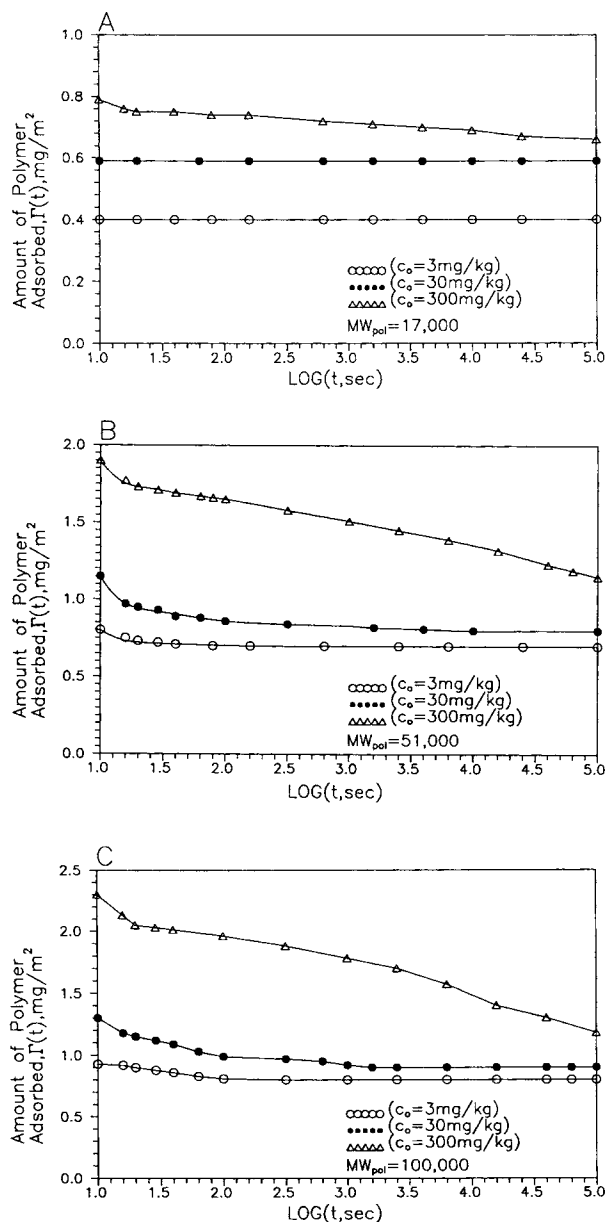


Figure 13 The time dependence of the amount of polymer desorbed vs. log time for water-soluble associative polymer for a wide concentration range of 3 mg/kg to 300 mg/kg: A—with a molecular weight of 17,000, B—with a molecular weight of 51,000, and C—with a molecular weight of 100,000.

controlled by the diffusion in the adsorbed layer for $t \geq t_{cr1}^*$. The slopes n_{mid}^* and n_{∞}^* characterize the rate of the desorption when the desorption process is controlled by the diffusion in the adsorbed layer. As shown in Figures 13 (A,B,C) and 14 (A,B,C), the rate of the desorption process for intermediate times ($t \leq t_{cr2}^*$) is much less than that for long times ($t \geq t_{cr2}^*$). Equations (22), (27), and (28) may be used to predict time-dependence desorption over a

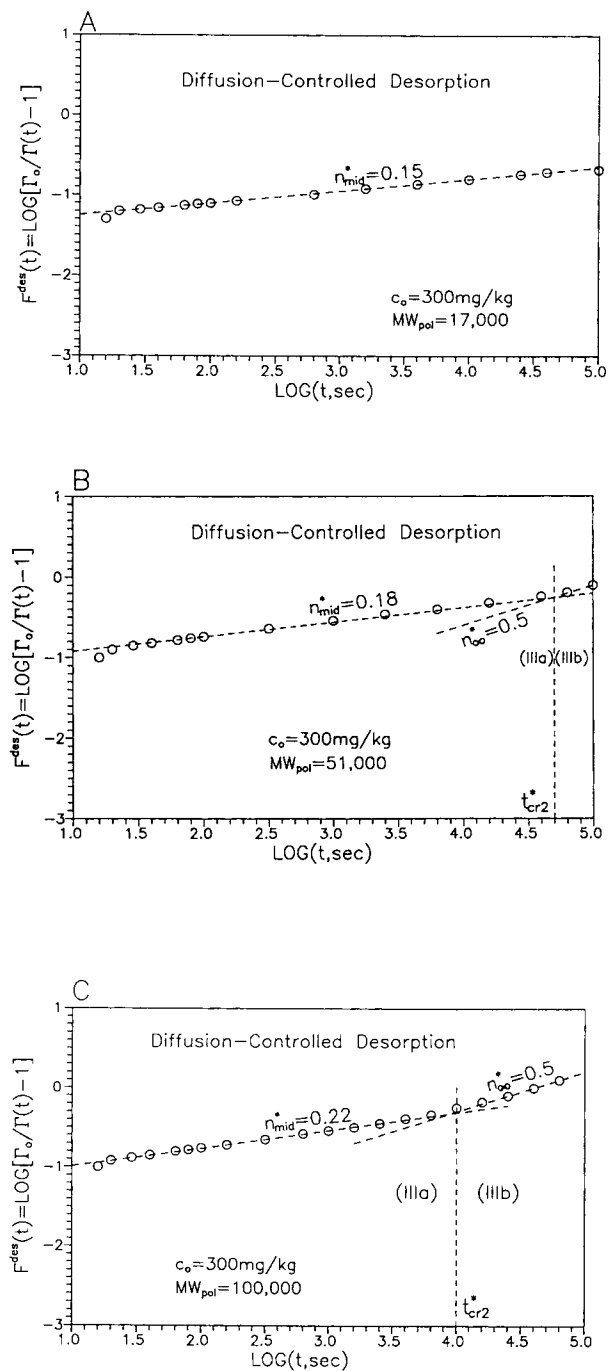


Figure 14 The time dependence of the relaxation function $F^{des}(t)$ vs. $\log(t)$ for water-soluble associative polymer for 300 mg/kg polymer concentration: A—with a molecular weight of 17,000) the diffusion-controlled desorption process, $n_{mid}^* = 0.15$; B—(with a molecular weight of 51,000) (IIIa) the diffusion-controlled desorption process, $n_{mid}^* = 0.18$; $t \leq t_{cr2}^*$, $t_{cr2}^* = 14$ h; and (IIIb) the diffusion-controlled desorption process, $n_{\infty}^* = 0.53$; $t \geq t_{cr2}^*$; and C—(with a molecular weight of 100,000) (IIIa) the diffusion-controlled desorption process, $n_{mid}^* = 0.22$; $t \leq t_{cr2}^*$, $t_{cr2}^* = 2.8$ h; and (IIIb) the diffusion-controlled desorption process, $n_{\infty}^* = 0.5$; $t \geq t_{cr2}^*$.

wide range of times for arbitrary adsorption isotherms.

It should be noted that the rates for the adsorption and desorption processes for the convex adsorption isotherms are significantly different. The times for establishing the equilibrium states for these processes are also significantly different. Figure 5 shows the time dependence of the adsorption for the Langmuir adsorption isotherms. From data in Figure 5 and eqs. (18) and (29), it follows that the time to establish the equilibrium state for the adsorption processes, t_F^{ad} , is equal to $29t_0$ ($\epsilon = 0.01$), and the time to establish the equilibrium state for the desorption processes, t_F^{des} , is equal to $3.8 \times 10^5 t_0$ ($\epsilon = 0.01$). Thus, the ratio of $t_F^{\text{des}}/t_F^{\text{ad}} = 1.3 \times 10^4$. From the preceding analysis it follows that for the strongly convex adsorption isotherms, the adsorption process is irreversible.

CONCLUSIONS

We have developed a theory for the kinetic-diffusion-controlled adsorption and desorption of polymers on planar surfaces. Equations are derived to calculate the parameters characterizing these adsorption and desorption processes. Using a theoretical approach and analysis of the experimental data, it is shown that the adsorption processes for arbitrary adsorption isotherms on a planar surface are governed: (a) by the kinetics of polymer adsorption for short times or low polymer concentrations (less than 30 mg/kg), (b) simultaneously by the kinetics of polymer adsorption and diffusion of polymer molecules in the adsorbed layer for intermediate times or midrange polymer concentrations (greater than 10 mg/kg and less than 100 mg/kg), and (c) by the diffusion of polymer molecules in the adsorbed layer for long times or high polymer concentrations (greater than 100 mg/kg). The equations are derived to calculate the times needed to establish the equilibrium states for the adsorption and desorption processes. It is shown that for the strongly convex adsorption isotherms the equilibrium state for desorption processes cannot be reached for real finite times; therefore, in these cases the adsorption is an irreversible process.

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