Macromolecules **1992,** *25,* 5416-5423

Kinetics of Polymer Adsorption and Desorption in Capillary Flow

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Received December 7, 1991; Revised Manuscript Received June 2, 1992

ABSTRACT: With streaming potential measurements we performed kinetic and static experiments on the adsorption of poly(ethylene oxide) on glass, in order to obtain the rates of adsorption and desorption and the equilibrium thickness of the polymer layer. The hydrodynamic layer thickness δ_h is very sensitive to small changes in the adsorbed amount, especially for high molecular weights near saturation. This enabled us to perform measurements of the kinetics and thickness isotherms in the region near saturation with unprecedented accuracy. It was found that both the adsorption and desorption rate are determined by mass transfer between bulk solution and the surface region. In the case of adsorption the observed increase of the hydrodynamic layer thickness with time could be quantitatively predicted by a model which combines the mass-transfer equation with the equilibrium relation between δ_h and the adsorbed amount Γ. For desorption into a flow of pure solvent the rate is proportional to the surface concentration of nonadsorbed molecules. Assuming a local equilibrium between the adsorbed layer and the subsurface region and a logarithmic isotherm, we derived an explicit expression for the adsorbed amount as a function of time: the desorbed amount is proportional to log *t*. The model predicts that the absolute values of the slopes of the desorption curve $\Gamma(\log t)$ and the adsorption isotherm $\Gamma(\log c)$ should be the same. This prediction is verified experimentally for molecular weights ranging from 7×10^3 to 8.47×10^5. Moreover, the absolute value of the observed desorption rate agrees well with that predicted by our model.

Introduction

The rate of adsorption of polymers is mainly determined by two processes: (i) transport of the polymer by convection and/or diffusion from the solution to the surface, and (ii) attachment to the interface. The second step may consist of the reconformation of the chain toward an adsorbed state and of the formation of entanglements between different molecules. When the adsorption takes place from a well-defined flow, the rate of transport can be calculated and thereby separated from the attachment step. In a previous paper[1] we showed in this way that for the adsorption of poly(ethylene oxide) (PEO) from water onto silica the transport is rate limiting until close to saturation. A similar behavior was found in time-dependent ATR-IR measurements by Van der Beek et al.[2] with polytetrahydrofuran, by Johnson and Granick[3] with poly(methyl methacrylate), and by Frantz et al.[4] with polystyrene. For all these polymers it was found that 70–100% of the plateau value of the isotherm adsorbs already in the first few minutes after introduction of the polymer solution in the cell. It is likely that this rapid inital adsorption was mass-transfer-limited, although not always a quantitative analysis was made. The mass-transfer limitation seems to be a general feature for uncharged homopolymers.

However, it is quite possible that in adsorbed layers processes occur that are not revealed by merely following the adsorbed amount. We therefore decided to study a different property of interfacial layers, namely the hydrodynamic thickness δ_h. Generally, we expect that the hydrodynamic thickness is a quantity rather sensitive to the conformation of adsorbed molecules. For instance, in equilibrated adsorbed layers of long chains the nonadsorbed ends of the molecules ("tails") protrude far into the solution, determining almost completely the hydrodynamic thickness.[5] However, these tails contribute only slightly to the adsorbed amount. We therefore expect that the hydrodynamic thickness can be used as a probe of the tails, whereas the adsorbed amount cannot be used as such. A claim that δ_h can indeed be used to monitor reconformations was made earlier by Cohen Stuart and Tamai.[6,7] They concluded from streaming potential measurements on the adsorption of poly(ethylene oxide) and poly(vinylpyrrolidone) on glass that a thickness relaxation of the adsorbed layer could be observed following a short, pulsewise injection of polymer in the capillary.

Another reason for monitoring the adsorption process by means of the hydrodynamic layer thickness is the high sensitivity of δ_h to the adsorbed amount of high molecular weight polymers at saturation. It may be interesting to study changes in such layers, for instance those due to desorption. The amounts of long chains desorbed into solvent are expected to be very low, due to the high adsorption energy per chain. Therefore desorption of long chains is very difficult to study via the adsorbed amount, but we expect much larger changes in the hydrodynamic thickness. Experimental information on desorption is only available for low molecular weights of PEO ($<1.00 \times 10^5$).[1] By reflectometry we observed that in about 10 min only a small amount (up to 10%) desorbs when a flow of pure solvent is applied. When a polymer solution is injected again, readsorption to the original saturated level occurs. No quantitative analysis was possible, but the reversibility of the adsorption suggests that no barrier to desorption is present. This leads us to the interesting question whether the desorption rate, just as the adsorption rate, is mainly determined by mass transfer between the bulk solution and the interfacial region.

A suitable method to obtain the hydrodynamic thickness under well-defined hydrodynamic conditions is the measurement of streaming potentials in glass capillaries. Cohen Stuart and Tamai[6,7] showed that by this method the adsorption of uncharged polymers can be studied as a function of time. By using a suitable injection system one can switch quickly between a flow of polymer solution or of pure solvent.

For a correct analysis of our data it is necessary to know how the adsorbed amount changes under the hydrodynamic conditions of the experiments. Therefore, we will first carefully consider the mass transfer in a capillary, both for adsorption and desorption conditions.

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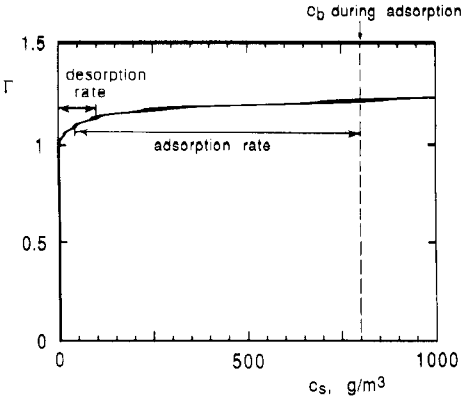

Figure 1. Illustration of adsorption and desorption rates using the local equilibrium concept. The full curve is an equilibrium adsorption isotherm $\Gamma(c_s)$. The ad- and desorption rates are proportional to $c_b - c_s$, where c_b is the bulk solution concentration. For adsorption c_b has a constant (non-zero) value and the rate is proportional to the lower horizontal bar. For desorption $c_b = 0$ and the rate is represented by the upper bar. In this example, the adsorption isotherm was calculated with the theory of Scheutjens and Fleer. The adsorbed amount Γ is given in equivalent monolayers. The bulk volume fraction as given by the theoretical model was converted to ppm (g/m^3) using a specific volume of 10^{-3} m^3/kg. Parameters: number of statistical segments $r = 100$, solvency parameter $\chi = 0.5$, segmental adsorption energy $\chi_s = 1.0$, cubic lattice with $\lambda_0 = {}^2/_3$.

Local Equilibrium Concept

Both for adsorption and desorption the steady-state rate of mass transfer in a capillary is given by the equation of Lévêque.[8] The flux J of polymer is a function of the mean fluid velocity v_m, of the diffusion constant D of the polymer and of the concentration difference $c_b - c_s$, where c_b and c_s are the polymer concentrations in the bulk solution and in the subsurface region, respectively:

$$J = 0.855(D^2 v_m / Rz)^{1/3}(c_b - c_s) \qquad (1)$$

In this equation, R is the radius of the capillary and z the lateral distance downstream from the capillary entrance. Both c_b and c_s are assumed to be independent of z. For adsorption we have $c_b > c_s$ and $J > 0$, whereas in desorption experiments (where $c_b = 0$) we must have $J < 0$.

At a fixed flow rate the flux of polymer is only determined by the concentration difference $c_b - c_s$ between bulk solution and surface. The bulk solution concentration c_b is either maintained at a constant level (adsorption) or is zero (desorption in pure solvent). The problem is to find a reasonable expression for c_s.

From reflectometry on the adsorption of PEO we know that the adsorption rate is mass-transfer-limited till close to saturation.[1] This mass-transfer limitation implies that the attachment to the interface is faster than the arrival of new molecules. This, in turn, leads us to the assumption that the adsorbed layer and its immediate surroundings are continuously in a local equilibrium. Then the adsorption isotherm $\Gamma(c_s)$ applies near the surface, where c_s is the local equilibrium concentration of nonadsorbed molecules. These free molecules can take part in diffusion and convection, and therefore this local equilibrium concentration should also be used in eq 1.

In the case of local equilibrium the difference between the kinetics of adsorption and that of desorption can be qualitatively explained using an adsorption isotherm (Figure 1). According to eq 1 the mass-transfer rate is proportional to $c_b - c_s$. For an adsorption experiment c_b is the concentration of the flowing polymer solution, which may be chosen arbitrarily, e.g., at the value indicated by the vertical dashed line in Figure 1. The concentration c_s is, at each Γ, given by the adsorption isotherm. Now the mass-transfer rate for adsorption is proportional to the (horizontal) distance from c_b to a point on the isotherm. According to the isotherm, the (sub)surface concentration is very small indeed until close to saturation, making the concentration difference between the bulk and surface and, hence, the mass transport constant. Then also the adsorption rate is constant till close to saturation.

For desorption the same reasoning leads to totally different kinetics. Now c_b is zero and the concentration difference $c_b - c_s$ is completely determined by the surface concentration. The desorption rate is given by the distance from an isotherm point to the ordinate axis (see Figure 1). According to the isotherm c_s and thus the rate of mass transport decrease sharply upon a minute desorption. Thus the desorption rate decreases continuously during desorption. For a high-affinity adsorption isotherm of a polymer the concentration c_s drops over decades for only a small decrease in the adsorbed amount. If Γ has decreased so far that the "vertical section" of the isotherm is entered, the desorption rate is hardly measurable because c_s is then extremely small. As will be derived below, for a typical polymer adsorption isotherm, the adsorbed amount decreases linearly with log t.

These typical differences between adsorption and desorption kinetics depend highly on the shape of the adsorption isotherm. If the isotherm would be linear over the concentration range $0 < c_s < c_b$, adsorption and desorption rates would follow the same pattern. However, it is well-known that polymer adsorption isotherms show a pronounced high-affinity character, making desorption much slower than adsorption. The isotherm given in Figure 1 was calculated with the theory of Scheutjens and Fleer[9,10] but any other high-affinity isotherm would lead to the same general conclusions. In the following sections we will consider the kinetics of adsorption and desorption quantitatively in order to be able to make a quantitative comparison between experiment and theory. For the case of desorption we shall make an explicit assumption about the isotherm shape.

Adsorption. In the analysis of the adsorption experiments we want to answer the question whether the observed change in the streaming potential can be interpreted in a way similar to the results found by reflectometry in stagnation point flow.[1] There we found that the adsorption rate was mass-transfer-limited, except for the final approach to saturation, which was much slower.

The analysis of the streaming potential experiments involves three steps. First, the adsorbed amount $\Gamma(t,z)$ as a function of time t and position z in the capillary is calculated, using the mass-transfer equation in combination with reflectometric data on the adsorption of PEO. Then the adsorbed amount $\Gamma(t,z)$ is converted into the hydrodynamic layer thickness $\delta_h(t,z)$ by means of an experimental relation between the two quantities. Finally, from the local hydrodynamic layer thickness $\delta_h(t,z)$ the expected streaming potential $V_s(t)$ is calculated.

Before we calculate $\Gamma(t,z)$ with the transport equation, we first examine the adsorption kinetics of PEO from a stagnation point flow as found by reflectometry.[1] In this type of experiment the flow of polymer solution hits the surface perpendicularly. A typical example is shown in Figure 2. From these experiments we concluded that the initial adsorption rate equals the maximum mass-transfer rate, i.e. c_s equals zero initially. Only close to saturation does dΓ/dt start to decrease. In order to incorporate the approach to saturation in the transport equation we define

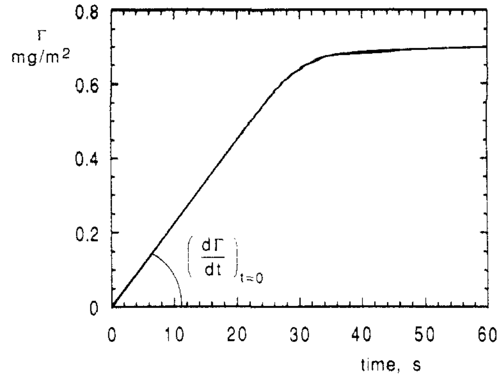

Figure 2. Adsorption kinetics of PEO from water, using stagnation point flow toward an oxidized silicon wafer: $M = 1.05 \times 10^5$ $c_b = 10$ g/m³, Reynolds number $Re = 6.1$.

an adsorption probability β as

$$\beta = (\mathrm{d}\Gamma/\mathrm{d}t)/(\mathrm{d}\Gamma/\mathrm{d}t)_{t=0} \tag{2}$$

Clearly, in the initial, linear regime $\beta = 1$, and at saturation $\beta = 0$. In the transition region we found that, at least qualitatively, β only depends on Γ, and not on mass-transport conditions. From the reflectometry experiment we can now determine $\beta(\Gamma)$ and we can use this in combination with eq 1 to calculate $\mathrm{d}\Gamma/\mathrm{d}t$ in the capillary:

$$\mathrm{d}\Gamma(t,z)/\mathrm{d}t = J_0(z)\beta(\Gamma) \tag{3}$$

where $J_0(z)$ is the flux J of polymer at $c_s = 0$ and position z in the capillary. From this $\Gamma(t,z)$ is obtained by integration:

$$\Gamma(t,z) = \int_{t=0}^{t} J_0(z)\beta(\Gamma)\,\mathrm{d}t \tag{4}$$

where the injection of polymer solution in the capillary starts at $t = 0$ (i.e., $\Gamma(0,z) = 0$).

The next step, the conversion of $\Gamma(t,z)$ into $\delta_h(t,z)$, will be done using static, equilibrium data of Γ and δ_h at saturation. The experimental results needed to establish the relation between Γ and δ_h will be given under Results and Discussion, and therefore at the moment we simply assume that

$$\delta_h(t,z) = f(\Gamma(t,z)) \tag{5}$$

where f is a monotonously increasing function of Γ, which can be determined experimentally.

We now want to find from $\delta_h(t,z)$ the streaming potential $V_s(t)$ between the two ends of the capillary. For a surface homogeneously covered with polymer Cohen Stuart et al.[11,12] showed that the streaming potential V_s is related to the hydrodynamic layer thickness δ_h by

$$V_s = V_s^0 e^{-\kappa\delta_h} \tag{6}$$

where V_s^0 is the streaming potential of the bare capillary and κ^{-1} is the Debye screening length. This equation is valid as long as (i) $\delta_h < \kappa^{-1}$, (ii) the polymer is uncharged, and (iii) the adsorbed layer is homogeneous. However, during the adsorption the coverage in the capillary is not homogeneous, but it depends on z, as is seen from eq 1. Therefore eq 6 cannot be used directly to calculate $V_s(t)$. In order to overcome this restriction, we will assume that eq 6 can be applied to small sections of the capillary for which the adsorbed layer can be considered to be homogeneous. The streaming potential of the whole capillary is obtained as the sum of the contributions of the individual sections. Equation 6 applied to a small section of the capillary turns into

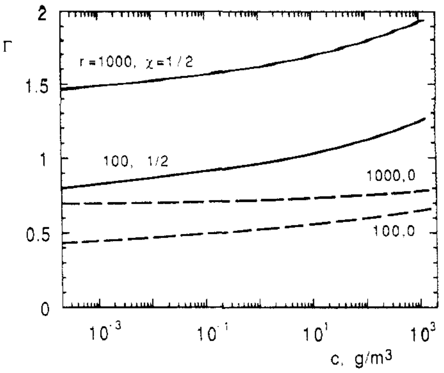

Figure 3. Theoretical adsorption isotherms $\Gamma(\log c)$ for homopolymers, showing that the slope $\mathrm{d}\Gamma/\mathrm{d}\log c$ is constant over several decades of c. The isotherms are calculated with the Scheutjens–Fleer theory, using the same parameters as in Figure 1, except for the chain length r and the solvency parameter χ (indicated).

$$\mathrm{d}V_S = e^{-\kappa\delta_h}\,\mathrm{d}V_s^0 \tag{7}$$

where $\mathrm{d}V_s$ and $\mathrm{d}V_s^0$ are the contributions to the streaming potential due to a length $\mathrm{d}z$ of the section with and without polymer adsorbed, respectively. In a bare capillary this contribution is the same everywhere, and therefore $\mathrm{d}V_s^0$ is proportional to V_s^0 and the length $\mathrm{d}z$ of the section

$$\mathrm{d}V_s^0 = V_s^0\,\mathrm{d}z/L \tag{8}$$

where L is the length of the capillary. Finally, the streaming potential $V_s(t)$ of a capillary inhomogeneously covered with polymer is obtained by combining eqs 7 and 8 and by integrating over the length of the capillary

$$V_S(t) = \frac{V_s^0}{L}\int_0^L e^{-\kappa\delta_h(t,z)}\,\mathrm{d}z \tag{9}$$

With eqs 1–5, in combination with (9) we can now calculate $V_s(t)$ as it should be expected on the basis of the adsorption kinetics as found by reflectometry. These latter kinetics were mass-transfer-limited, except for the final approach to saturation. The calculated time dependence $V_s(t)$ can be compared directly to experimental results.

Desorption. In order to describe the desorption of polymer in a flow of pure solvent we will derive in this section a desorption equation which is based on the mass-transfer equation in combination with the local equilibrium concept.

When solvent is injected into a capillary with an adsorbed polymer layer, the mass transfer will take place from the surface region (concentration c_s) to the bulk solution, where $c_b = 0$. We assume that continuously a local equilibrium exists between the adsorbed layer and the solution directly adjacent to it, as is discussed above. In this case the desorption rate can be written as

$$\mathrm{d}\Gamma/\mathrm{d}t = -kc_s(\Gamma) \tag{10}$$

where $k = 0.855(D^2V_m/(Rz))^{1/3}$ according to eq 1 and $c_s(\Gamma)$ is the inverse of the adsorption isotherm $\Gamma(c_s)$. In order to get an impression of the shape of the adsorption isotherm we performed model calculations with the theory of Scheutjens and Fleer. In Figure 3 adsorption isotherms of homopolymers of 100 and 1000 statistical segments for good ($\chi = 0$) and θ-solvents ($\chi = {}^1/_2$) are shown. The concentrations of interest are those below $c < 100$ g/m³. It is seen that for all cases the slope $p = \mathrm{d}\Gamma/\mathrm{d}\log c$ is nearly constant over several decades of c, its value being of the order of a few percent per decade. As long as the slope

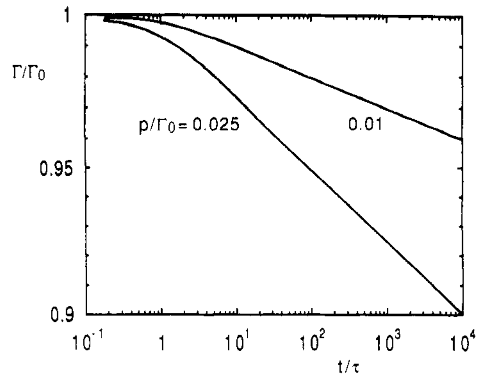

Figure 4. Mass-transfer-controlled desorption kinetics according to eq 12 for a polymer with a high affinity adsorption isotherm, for $p/\Gamma_0 = 0.025$ and 0.01. For times $t > 5\tau$ the slope $d\Gamma/d \log t$ equals $-p$.

p is constant, we can describe the adsorption isotherm equation as $\Gamma - \Gamma_0 = p \log (c_s/c_s^0)$, where Γ_0 and c_s^0 refer to some reference point of the isotherm (for example, the point $\Gamma(c_b)$ in Figure 1). Equivalently

$$c_S = c_s^0 10^{(\Gamma-\Gamma_0)/p} \tag{11}$$

Taking for c_s^0 and Γ_0 the values at the start of the solvent injection (at $t = 0$) we obtain a simple differential equation for $\Gamma(t)$ by substitution of eq 11 into eq 10. Integrating this from $t = 0$, $\Gamma = \Gamma_0$ to t, Γ we find

$$\Gamma = \Gamma_0 - p \log (1 + t/\tau) \tag{12}$$

where $\tau = 0.43p/kc_s^0$. This equation describes the kinetics of the mass-transfer-controlled desorption of polymer and is graphically shown in Figure 4, for two values of p/Γ_0. In our experiments τ is typically well below 1 s, and the time scale well above (≈15 min), so that Γ is expected to decrease essentially as $p \log (t/\tau)$. A few remarks are in place at this point.

To our knowledge eq 12 is the first theoretical expression for the desorption rate that has ever been derived. It is expected to apply whenever a constant flow of solvent is maintained; i.e., the desorbed material is transported away. Nevertheless, the desorption is for all practical cases far from complete, even after long times, due to the logarithmic dependence on time. The reason is, obviously, the (extremely) low value of c_s obtained after some desorption has taken place.

For $t > 5\tau$ we see that the slope $d\Gamma/d \log t$ equals $-p$, whereas the slope of the adsorption isotherm $d\Gamma/d \log c$ is $+p$. Thus the coupling of the mass transfer with the local equilibrium concept leads to a remarkable congruence between the shape of the desorption curve $\Gamma(\log t)$ and the adsorption isotherm $\Gamma(\log c)$. The equality $d\Gamma/d \log t = -d\Gamma/d \log c$ can be used as an experimental check on the local equilibrium assumption and, hence, on eq 12. However, a direct check on eq 12 is difficult to carry out since p and thus also the desorbed amounts for polymers are usually very small. The key idea in our experiments is to follow the hydrodynamic thickness δ_h (rather than Γ) over time and to compare these data to static values of δ_h at various concentrations. Since $d\Gamma = (d\Gamma/d\delta_h)d\delta_h$, where $d\Gamma/d\delta_h$ is constant as long as points of the same Γ are compared, we can equally well test whether $d\delta_h/d \log t = -d\delta_h/d \log c$.

Finally, we expect that the desorption equation even holds for polymers where the local equilibration takes some time. An effect of equilibration on the desorption can only be observed when its rate is lower than the mass-transfer rate. Since the mass-transfer rate falls by orders of magnitude upon a small desorption, the same applies to the equilibration rate that can be observed. In fact, it is likely that the mass-transfer rate is nearly always lower than the equilibration rate and thus rate determining.

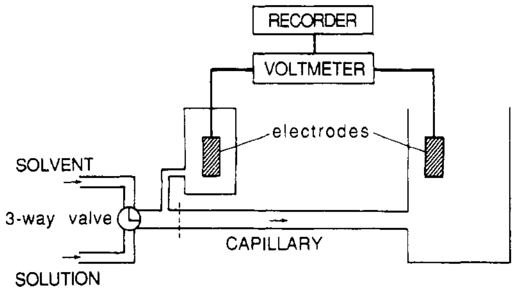

Figure 5. Schematic diagram of the experimental setup for measuring the streaming potential in adsorption or desorption kinetics.

Table I
Polymer Samples

$10^{-3}M_w$	M_w/M_n	$10^{-3}M_w$	M_w/M_n
7.1	1.03	105	1.06
23	1.08	400	1.08
56	1.05	847	1.16

Experimental Setup and Materials

The experimental setup used is schematically drawn in Figure 5. A glass capillary (length 20 cm, inner diameter 0.30 mm) is mounted between an inlet valve and a flask at the outlet side. The electronic inlet valve is connected to two bottles containing solvent and polymer solution, respectively. The bottles were under 0.300 atm N_2 with respect to the outlet pressure and through the valve either of the two solutions was injected into the capillary. An electronic pressure control was used, and the pressure drop over connecting tubes and valve was found to be negligible. Hydrostatic pressure differences were at most 1% of the applied N_2 overpressure. Under the conditions of the experiment the Reynolds number was 127, and the entrance length according to the Boussinesq expression,[13] approximately 1.3 mm. The flow can thus be considered to be laminar over nearly the whole length of the capillary. The total flux was 1.79 mL/min and the wall shear rate 11 300 s^{-1}.

The streaming potential was measured with a special high-impedance voltmeter connected to two reversible Ag/AgCl electrodes, one of which is in the flask at the outlet side and the other in a separate vessel connected via a small opening to the space between valve and capillary. The drift in the potential at zero pressure drop was in all cases less than 1% of V_s^0. The dead volume between valve and capillary was estimated from recording the adjustment time of the streaming potential after a switch to a solution of different salt concentration. After 10 s (≈0.3 mL) the adjustment was complete.

As the solvent 1.00 mM NaCl was used throughout. The Debye screening length κ^{-1} for this ionic strength is 10 nm. Monodisperse poly(ethylene oxide) purchased from Polymer Laboratories (see Table I) was dissolved without further purification, and the solution was stirred for one night at room temperature before use. The glass capillaries were cleaned by immersion for 24 h in concentrated sulfochromic acid, followed by 24 h in 2 N HNO_3, after which they were stored in the solvent. The streaming potential of the clean capillaries varied between 140 and 155 mV (corresponding to an electrokinetic ζ-potential of 80–90 mV).

The hydrodynamic layer thickness was calculated from the streaming potential using eq 6. The reported thickness is therefore an average over the length of the capillary.

Results and Discussion

In Figure 6 we show the result of a typical experiment. First ($t < 0$), only solvent is injected and, hence, $\delta_h = 0$. At $t = 0$ the valve is switched to polymer solution and we see an increase of δ_h due to the adsorption of polymer.

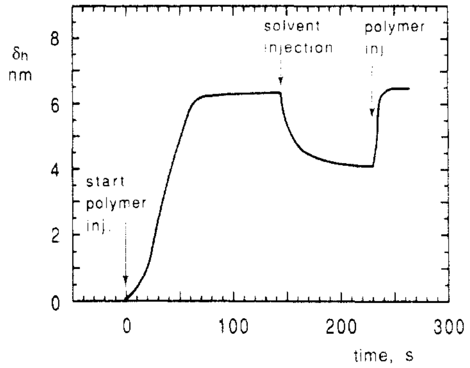

Figure 6. Typical example of $\delta_h(t)$ for PEO adsorption in a streaming potential experiment. At $t = 0$ s the injection of the polymer solution starts, at $t = 150$ s this flow was changed into solvent, followed by a switch to the same polymer solution at $t = 225$ s. Parameters: $M = 1.05 \times 10^5$, $c = 10$ g/m^3, $Re = 127$.

After some time ($\approx$70 s in this example) δ_h has attained a constant level, indicating that the polymer layer is saturated. We indicate the saturated level by δ_h^m. When the valve is switched back to solvent the ensuing decrease in δ_h reflects the desorption of polymer. When polymer is injected again the same level of δ_h^m is reached, but more quickly than the first time. This cycle of desorption and readsorption can be repeated many times with reproducible results. The picture sketched for this experiment was found for all molecular weights and all concentrations studied. Only the time scales and layer thicknesses are different. We shall first describe the adsorption kinetics in more detail, followed by an analysis of the (equilibrium) thickness isotherms and, finally, the desorption kinetics.

Adsorption Kinetics. Before we can apply the adsorption model, we have to establish the relation between δ_h and Γ. Cohen Stuart et al.[14] found from theoretical calculations that for low volume fractions of polymer the relation between δ_h and Γ does not depend on molecular weight. Moreover, their experimental data of PEO adsorbed on polystyrene latex were in good agreement with this result. We therefore decided to measure δ_h and Γ at saturation as a function of molecular weight, using different methods, and to combine these results to a universal curve $\delta_h(\Gamma)$. Adsorbed amounts of PEO on silica in water are available from reflectometry[1] and δ_h^m was measured by the streaming potential technique as described above. All measurements were carried out at the same polymer concentration of 10 g/m^3, and the results are shown in Figure 7 as $\delta_h(\Gamma)$. For the two highest molecular weights, δ_h is somewhat greater than κ^{-1}, and therefore the reported values may underestimate the actual δ_h. For comparison, values of δ_h (at a higher concentration) measured by means of dynamic light scattering by Van der Beek and Cohen Stuart[15] are also combined with the reflectometry results and included in Figure 7. There is good agreement between values of δ_h found by the latter authors and those obtained from the streaming potential technique, which confirms the idea that both methods measure the same quantity. Also, the shape of the curve $\delta_h(\Gamma)$ is in good agreement with the theoretical predictions of Cohen Stuart et al.[14] We therefore conclude that we can use our present data as an empirical relation $\delta_h(\Gamma)$. In order to have explicit expressions we represented the data by combination of a linear ($\Gamma \leq 0.5$ mg/m^2) and a fourth-order polynomial function ($\Gamma \geq .5$ mg/m^2).

Model calculations for the adsorption of PEO of $M = 1.05 \times 10^5$ were carried out as described in the theoretical section, using Poiseuilles law to calculate v_m and a diffusion coefficient of 2.34×10^{-11} m^2/s, which was taken from Sauer and Yu.[16] The result is shown in Figure 8. The maximum adsorbed amount is used as a variable parameter to obtain a good fit at saturation. This optimum value was found to be 0.636 mg/m^2. From Figure 7 we see that this is well within the experimental range of adsorbed amounts found for this molecular weight. We conclude that there is excellent agreement between model and experiment. We emphasize that the time scale of the experiment predicted by the model is correct. This corroborates our conclusion that the adsorption rate of PEO is mass-transfer-controlled. The precise shape of the dashed curve in Figure 8 is explained as follows. The slow increase of δ_h in the first 50 s is mainly due to the flat conformation of the polymer at low coverage. The slowing down close to saturation of the decrease of V_s/V_s^0 is largely caused by the rapid decrease of β. We also checked the effect of the variation of the deposition rate along the z-direction. The curve labeled "average J" is the result of a calculation with a uniform, average mass-transfer rate in the z-direction. We see that this leads to a quite different prediction for $V_s(t)$. The sharp kink at $t = 200$ s is an artifact resulting from the transition from a linear to a polynomial approximation for $\delta_h(\Gamma)$. We conclude that the deposition rate is nonuniform along the lateral direction. Agreement between theory and experiment is

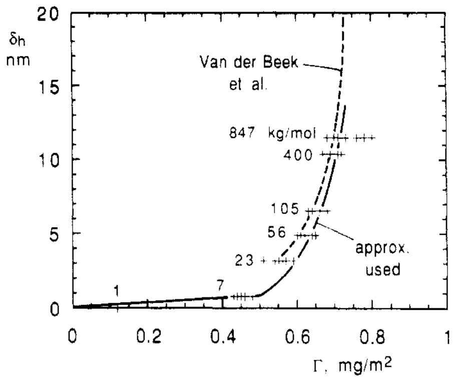

Figure 7. Relation between the hydrodynamic layer thickness δ_h and the adsorbed amount Γ for PEO. The + symbols represent the combination of δ_h (from the streaming potential in saturated layers) and Γ (from reflectometry) for different molecular weights (indicated). The dashed curve gives results of Van der Beek and Cohen Stuart.[15] The full curve is the approximation used for further calculations (see text).

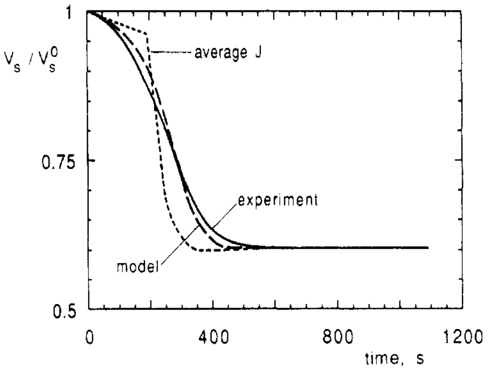

Figure 8. Comparison of model calculations and streaming potential experiments for the adsorption of PEO. The full curve represents the experimental V_s/V_s^0 during injection of PEO (at constant $c_b = 1$ g/m^3). The dashed curve was calculated using the Lévêque equation and reflectometric data on the adsorption of PEO and accounts for the inhomogeneous PEO deposition. Calculations with an assumed homogeneous mass-transfer rate, which equals the average over the length of the capillary, are shown in the dotted curve. Parameters: $M = 1.05 \times 10^5$ and $Re = 127$.

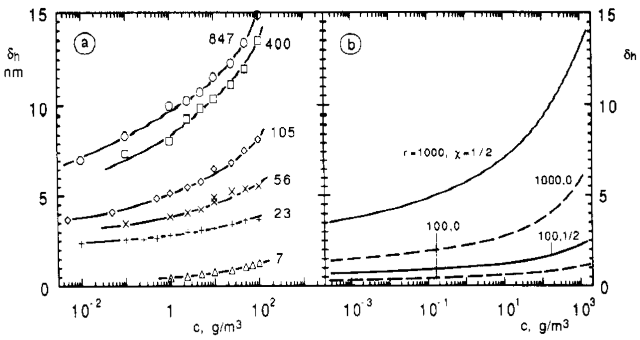

Figure 9. Experimental equilibrium thickness isotherms δ_h^m-(log c_b) for PEO of six different molecular weights (a). Theoretical hydrodynamic layer thickness for the adsorption isotherms of Figure 3 (b). Chain length r and solvency parameter χ are indicated. The hydrodynamic constant C_h was assumed to be 1.0; δ_h is given as the number of lattice layers.

only obtained if this nonuniform deposition is explicitly taken into account.

Thickness Isotherms. The measurement of a thickness isotherm δ_h^m(log c) and of the desorption kinetics δ_h(log t) was done in one experiment for each molecular weight and proceeded as follows. First, we prepared a saturated polymer layer in equilibrium with a polymer solution of $c = 100$ g/m^3, which is the highest concentration studied. Then for a prolonged time pure solvent was injected into the capillary, and the resulting desorption curve was recorded. Directly following this, without cleaning the capillary or completely desorbing the polymer, we determined the thickness isotherms δ_h^m(log c). In order to do this, polymer solutions of decreasing concentration were injected in the capillary, and for each concentration the final thickness δ_h^m was measured. In Figure 9a the resulting thickness isotherms are shown for molecular weights from 7 to 847 kg/mol. For the two highest molecular weights the condition $\kappa\delta_h < 1$ is no longer fulfilled at concentrations above 10 g/m^3, and therefore the reported values of δ_h underestimate the actual ones.

We shall first show that these isotherms really represent equilibrium by giving an illustration of the reversibility of the polymer layer with respect to concentration changes. Figure 10 shows a recording of the concentration in the capillary, of the streaming potential, and of the pressure when the polymer concentration is switched from $c = 2.5$ to 1 g/m^3, with an intermediate period of pure solvent flow. Initially, the higher concentration is injected and V_s is stable at 82 mV. When the valve is opened to pure solvent, the polymer concentration in the capillary drops to zero, and the streaming potential increases due to desorption. Then the pressure is released for some time in order to replace the polymer solution in the bottle. When the pressure is reapplied and the valve is switched back to the polymer solution of lower concentration, for the first 45 s the polymer solution of the higher concentration, which was still in the connecting tubes, passes the capillary. The streaming potential closely follows the changes in the polymer concentration and stabilizes at a level which corresponds to the adsorbed amount for the lower concentration. It is remarkable to see how fast and completely reversible the streaming potential adjusts itself to the concentration in solution. From this we conclude that the reported values of δ_h^m represent equilibrium. For low concentrations (<0.1 g/m^3) the adjustment time becomes of the order of minutes and (far) more because the rate of mass transfer, which is proportional to the concentration gradient between surface and solution, is very low in that case. In fact, the long-time stability of the apparatus determined the lowest concentration (0.005 g/m^3) at which we were able to measure. Finally, it is worth noting that by performing all the measurements in one experiment we can accurately detect thickness differences corresponding to changes in the streaming potential of only about 1%. The results are not complicated by the variations which inevitably occur when the capillary is cleaned in between.

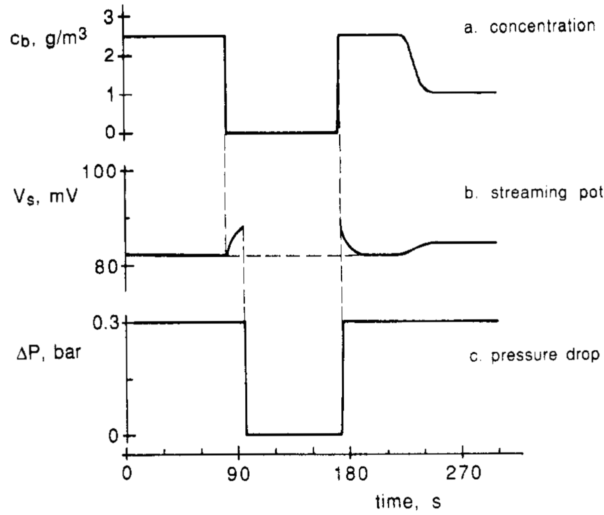

Figure 10. Response of the adsorbed layer to changes in the polymer concentration. Initially, a polymer solution (c = 2.5 g/m^3) is flushed through. At t = 80 s the valve is switched to pure solvent injection. Between t = 96 and 170 s the pressure is released in order to be able to change the polymer solution in the bottle, and directly after this the valve is opened to polymer solution of lower concentration (1 g/m^3). The top diagram (a) gives the bulk polymer concentration in the capillary, the middle curve (b) represents the streaming potential, and the lower figure (c) shows the pressure drop over the capillary. Parameters: $M = 1.05 \times 10^5$ and V_s^0 = 140 mV. For further explanation, see text.

For a comparison of the experimental thickness isotherms with their theoretical counterparts, we calculated theoretical δ_h values according to the method described by Cohen Stuart et al.[14] The result for the adsorption isotherms of Figure 3 is shown in Figure 9b. Qualitatively, there is good agreement: δ_h, dδ_h/d log c (or dδ_h/d log ϕ), and the curvature of the isotherms increase with chain length in both experiment and theory. Note that the chain length dependence of the slope of the thickness isotherms (Figure 9) is reversed as compared to the adsorption isotherms (Figure 3). This indicates that for long chains δ_h is a much more sensitive quantity to measure than Γ.

In Figure 11 the experimental chain length dependence of dδ_h/d log c (plusses) is compared to theory (full curves). For the calculations we assumed, according to Cohen Stuart et al.[14] two EO monomers/statistical segment and an elementary layer thickness of 1 nm. We see that there is good agreement between theory and experiment. For the two highest molecular weights the condition $\kappa\delta_h < 1$ is no longer fulfilled and therefore the experimental data of dδ_h/d log c and dδ_h/d log t underestimate the actual values. The results for dδ_h/d log t (open squares in Figure 11) will be discussed in the next section.

From a comparison of the theoretical adsorption isotherms of Figure 3 with the corresponding thickness isotherms in Figure 9b, we see that the concentration range over which the slope dΓ/d log ϕ is constant is wider than for dδ_h/d log ϕ. Using the equilibrium relation between δ_h and Γ (Figure 7), we can convert the isotherms δ_h(log c) to Γ(log c). This conversion leeds to curves with a constant slope up to higher concentrations, which is in agreement with the theoretical finding. From such a Γ(log c) isotherm we found that for $M = 1.05 \times 10^5$ the

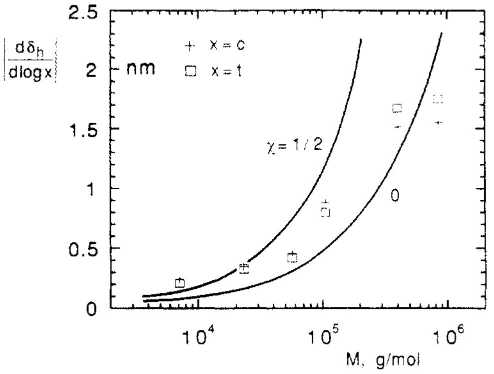

Figure 11. Chain length dependence of $d\delta_h/d\log c$ (plusses), $-d\delta_h/d\log t$ (open squares), and $d\delta_h/d\log \phi$ (full curves). The slopes $d\delta_h/d\log c$ and $d\delta_h/d\log t$ were calculated from the linear parts of Figures 9a ($c < 1$ g/m^3) and 12b ($t > 50$ s), respectively; the theoretical values of $d\delta_h/d\log c$ were calculated at $c = 1$ g/m^3, using the Scheutjens–Fleer model and assuming 2 EO monomers/statistical chain element. The lattice layer thickness was taken to be 1 nm.

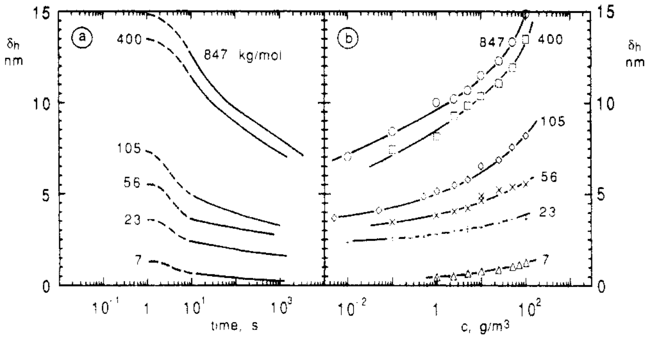

Figure 12. Desorption kinetics during injection of solvent (a) and equilibrium thickness isotherms $\delta_h^m(\log c_b)$ of PEO (b). The latter are replotted from Figure 9a. The desorption experiments start at $t = 0$ s with the injection of pure solvent on a polymer layer initially saturated at $c = 100$ g/m^3. The initial sections ($t < 10$ s) are dashed, because the kinetics are still affected by the dead volume between the valve and capillary.

relative slope $d\Gamma/(\Gamma d\log c)$ is 0.024. The theoretical value for $d\Gamma/(\Gamma d\log \phi)$ for a chain of 1000 segments ($\approx$2 EO monomers/statistical chain element) ranges from 0.015 for $\chi = 0.5$ to 0.04 for $\chi = 0$. The experimental value is in between these limits, which is reassuring. For this molecular weight the relative changes in δ_h are about 5 times higher than those in Γ and therefore much easier to detect. For longer chains this factor is still greater. The conversion was also carried out for the other molecular weights. Again the concentration range over which the slope of the isotherm was constant increased, but the slope $d\Gamma/d\log c$ showed no consistent variation with molecular weight. Since $d\Gamma = (d\Gamma/d\delta_h)d\delta_h$, the slope $d\Gamma/d\log c$ is proportional to the slope $d\Gamma/d\delta_h$ of the equilibrium curve $\delta_h(\Gamma)$. Especially for very low and high molecular weights it was not possible to determine $d\Gamma/d\delta_h$ accurately from our results, because the variations in δ_h and Γ, respectively, are very small in those regions (see Figure 7). Thus, the conversion of δ_h to Γ prohibits a quantitative comparison of the experimental and theoretical chain length dependence of $d\Gamma/(d\log c)$. Nevertheless, the qualitative agreement between theory and experiment is excellent.

Desorption Kinetics. In Figure 12a the results of the desorption experiments are shown, and for comparison, the thickness isotherms of Figure 9a are replotted in Figure 12b. The results apply to desorption starting from a polymer layer in equilibrium with a polymer solution of $c = 100$ g/m^3. At $t = 0$ the injection of pure solvent starts and the layer thickness decreases due to desorption. For the first 10 s the desorption curves are dashed because the kinetics in this time interval are affected by the dead volume between valve and capillary so that a steady state is not yet fully established. We see that for $t > 10$ s (full lines) shape and slope of the desorption curves closely correspond to the $\delta_h(\log c)$ isotherms. In fact, parts a and b of Figure 9 are virtually mirror images of each other. By connecting points of equal thickness in two corresponding curves, it is possible to find at each moment during the desorption the surface concentration c_s according to the thickness isotherm. For instance, for the highest molecular weight c_s is found to be 32, 1.3, and 0.05 g/m^3 at t = 10, 100, and 1000 s, respectively. This decrease of c_s with time reflects directly the slower desorption.

Our model for the desorption kinetics predicts that $d\Gamma/d\log t = -d\Gamma/d\log c$. This is only valid under the condition that p ($=d\Gamma/d\log c$) is constant and for times $t > 5\tau$. For $M = 1.05 \times 10^5$ we calculated τ as 0.03 s, and thus for all t of interest the second condition is fulfilled. With respect to the constancy of the slope p we see in Figure 12b that the curves $\delta_h(\log c)$ are linear up to about 10 g/m^3. As pointed out before, the linear part is even longer after conversion to $\Gamma(\log c)$, and thus also the former condition is met. Consequently, the logarithmic dependence of Γ on c is corroborated. Instead of comparing slopes in terms of Γ we can equally well test whether $d\delta_h/d\log t = -d\delta_h/d\log c$, as pointed out before. In Figure 11 we plotted $-d\delta_h/d\log t$ (open squares) and $d\delta_h/d\log c$ (plusses) as a function of chain length. For all molecular weights $-d\delta_h/d\log t$ and $d\delta_h/d\log c$ are nearly equal. This is a strong indication for the correctness of the desorption model.

We also checked whether the absolute value of $d\Gamma/dt$ equals J as predicted by the Lévêque equation. For $M = 1.05 \times 10^5$ we determined $d\delta_h/dt$ and from this $d\Gamma/dt$ at $t = 18$ s. We found 0.6 μg m^{-2} s^{-1}. Using the value of δ_h at $t = 18$ s in the $\delta_h^m(\log c)$ isotherm, the equilibrium concentration near the surface is found to be $c_s = 0.35$ g/m^3. The Lévêque equation gives, with this c_s, $J = 0.89$ μg m^{-2} s^{-1}. We consider this to be in good agreement with the value found for $d\Gamma/dt$, considering the experimental uncertainty that arises from the conversion of $d\delta_h/dt$ to $d\Gamma/dt$ and from reading c_s from a logarithmic concentration scale. We conclude that our model for desorption kinetics is essentially adequate for PEO: the desorption rate is indeed a logarithmic function of time, the slopes $d\Gamma/d\log t$ are quite reasonable (and correspond to the adsorption isotherms), and the desorption process is transport-limited. The desorption is so slow because the (very) low subsurface concentration of polymer allows only a correspondingly low gradient flux.

In two earlier papers Cohen Stuart and Tamai[6,7] attributed the decrease in the layer thickness to a relaxation of adsorbed molecules rather than to desorption. Their main argument against desorption was that the decrease of δ_h continues when the flow is stopped. Using an improved setup, we now find that the opposite is true. In Figure 13 we compare the increase of V_s upon injection of solvent for two cases: the dashed curve represents continuous injection of solvent, whereas for the full curve the flow is interrupted for about 5 min by the release of the pressure drop over the capillary. It is clearly seen that the increase of V_s stops as long as the flow is absent. This corroborates our present analysis that the decrease is due to desorption. We conclude that the previously claimed thickness relaxation was actually due to desorption of polymer.

Finally, we want to summarize and discuss the results obtained for the desorption kinetics. We believe that for

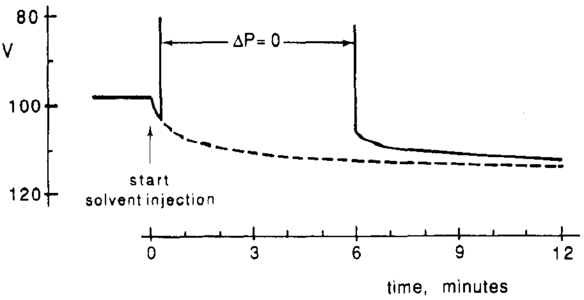

Figure 13. Effect of flow on the desorption of polymer. For $t < 0$ s the polymer layer is saturated at $c = 1.0$ g/m^3, and at $t = 0$ s the injection of pure solvent starts. The dashed curve represents continuous injection of solvent, whereas the full curve is the result of an experiment, during which the flow of solvent is stopped for some time by release of the pressure drop over the capillary ($\Delta P = 0$). Parameters: $M = 1.05 \times 10^5$ and $V_s^0 = 159$ mV.

the first time a quantitative analysis of polymer desorption kinetics has been made and, furthermore, this analysis is also verified by experimental evidence. Using the mass-transfer equation and assuming a local equilibrium near the surface, we derived a desorption equation of the form $\Gamma = \Gamma_0 - p \log (t/\tau)$. It is found that the adsorbed amount decreases linearly with log t and, also, the equilibrium adsorption isotherm $\Gamma(\log c)$ and the desorption curve $\Gamma(\log t)$ are mirror images: $\mathrm{d}\Gamma/\mathrm{d} \log t = -\mathrm{d}\Gamma/\mathrm{d} \log c$. The slope $\mathrm{d}\Gamma/(\Gamma \mathrm{d} \log c)$ is usually very small for polymers, of the order of a few percent per decade in c. As a result, also the desorbed amount is very small. A sensitive quantity, like the hydrodynamic layer thickness, is needed to observe desorption. From our analysis it has become evident that for a desorption experiment it is essential to remove the desorbed material continuously from the system. By doing this a (small) concentration gradient between the surface region and bulk solution is maintained, giving rise to a (correspondingly small) desorption. The adsorbed layer is prevented from establishing an equilibrium with the bulk solution at an extremely low concentration. Only at the local level (c_s) should such an equilibrium take place. We expect that also for more slowly equilibrating polymers than PEO mass transfer will be rate limiting during desorption, because the mass-transfer rate becomes extremely low, and thus rate limiting, after a small amount is desorbed. We therefore presume that eq 12 is a fairly general expression for the desorption of polymers.

Conclusions

From streaming potential measurements we have obtained the kinetics of adsorption and desorption and equilibrium thickness isotherms of PEO adsorbed on the wall of a glass capillary. Using the Lévêque equation, we found that the rates of adsorption and desorption are determined by the rate of mass transfer toward and away from the surface, respectively. On the time scale of the mass transfer there is near the surface continuously a local equilibrium between free and adsorbed molecules.

The hydrodynamic layer thickness δ_h of PEO adsorbed on silica as calculated from the streaming potential is in good agreement with the results of dynamic light scattering, indicating that both methods measure the same quantity.

Especially for high molecular weights δ_h is sensitive to very small changes in the adsorbed amount Γ, which is mainly due to tails protruding far into the solution. This sensitivity enabled us to perform accurate measurements of the kinetics and thickness isotherms in the region near saturation, under conditions where changes in Γ are hardly measurable. Thickness isotherms were measured down to extremely low concentrations (0.005 g/m^3) and are in good agreement with theoretical predictions.

For the adsorption kinetics we propose a simple model combining the mass-transfer equation with the measured dependence of δ_h on Γ. Excellent, quantitative agreement was found between the predicted and observed δ_h as a function of time. This result is entirely consistent with the kinetics, as found by reflectometry.

In the case of desorption into a flow of pure solvent the mass-transfer rate is proportional to the surface concentration c_s of nonadsorbed molecules, which according to the local equilibrium concept is determined by the adsorption isotherm of the polymer. Since, in the relevant range, Γ increases nearly linearly with log c, a simple expression for $c_s(\Gamma)$ can be incorporated into the mass-transfer equation. This leads to the prediction that Γ falls linearly with log t, which constitutes a first result for a desorption equation. Moreover, the slope $-\mathrm{d}\Gamma/\mathrm{d} \log t$ is predicted to be the same as $\mathrm{d}\Gamma/\mathrm{d} \log c$. Experimentally, we found that the slopes of the equilibrium thickness isotherms and kinetic desorption curves are indeed equal for all molecular weights studied. The absolute value of the observed $\mathrm{d}\Gamma/\mathrm{d}t$ agrees quite well with the predictions of our model. The relative slope $\mathrm{d}\Gamma/(\Gamma \mathrm{d} \log c)$ is for polymers usually of the order of a few percent per decade in the concentration c. As a consequence the desorption rate slows down enormously with desorbed amount, and full desorption is therefore impossible in a practical sense. Desorption of polymer by dilution with solvent (where there is no continuous removal of the desorbed material) is impossible. This conclusion is, nevertheless, in complete agreement with thermodynamic equilibrium between the adsorbed layer and the (sub)surface region; it merely reflects that the equilibrium between the surface layer and solution is highly biased toward the surface side (high-affinity adsorption).

Acknowledgment. We thank Dr. J. M. H. M. Scheutjens for his useful suggestions for the analysis of the desorption experiments.

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Registry No. PEO, 25322-68-3; H_2O, 7732-18-5; SiO_2, 7631-86-9.