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Kinetics of Exchange between Adsorbed and Free Polymers at a Solid/Liquid Interface

Emile Pefferkorn,* Abdelkrim Haouam, and Raphael Varoqui

Institut Charles Sadron (CRM-EAHP), 6, Rue Boussingault, 67083 Strasbourg Cedex, France.

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ABSTRACT: Adsorption of polystyrene on silica was performed at 25 and 35 °C in carbon tetrachloride. The adsorption isotherm displays two distinct regions: a plateau at low concentration, followed by a region where the adsorption amount increases steeply with the solution concentration. Radioactive ^{3}H labeled polymers enabled us to measure, in both regions, the intrinsic self-mobility of the polymers at the interface at constant chemical composition. As previously reported, surface molecules exchange very slowly with solution molecules. The kinetic properties are, however, very different in both regions of the isotherm. In the plateau region, fluxes can be expressed in terms of one relaxation time, whereas in the zone of high adsorption, the interfacial exchange of labeled and nonlabeled polymers cannot be characterized by one kinetic constant. The dynamical properties are connected with the specific conformational properties of polymer layers in both regions.

Introduction

The formation of an adsorbed polymer layer and its desorption raise many questions: when the bare solid surface is exposed to a polymer solution, how does the coverage increase with time? Can polymers exchange between surface and bathing solution fast enough so that thermodynamic equilibrium is rapidly established? How are kinetic and conformational properties related?

Different experimental approaches have been attempted to characterize some of these points. The main observations relative to the desorption of polymers are the following: polymer desorption is promoted by changing some parameters of the system such as temperature, solvent, pH, etc. or by using monomeric or polymeric displacers of different nature or of the same nature but of different size.[1-7] In these experiments, the adsorption equilibrium was, however, always modified and information on the intrinsic mobility of polymer species in the adsorbed state cannot be obtained.

Recently, we have used a method in which preliminary adsorption of radioactively labeled polymers was carried out, the surface then being exposed to a solution of unlabelled polymers.[8] In this way, flux measurements of labeled polymers from the surface to the solution can be measured at chemical equilibrium, and the mean time spent by a polymer at the interface, which characterizes its self-mobility in the adsorbed state, is obtained. In a systematic study of polyacrylamide adsorbed in aqueous media onto modified silica, we found that surface molecules exchange very slowly (on the laboratory time scale) with solution molecules. A metastable equilibrium is then reached in which solution is replaced by pure (or nearly pure) solvent. These kinetic aspects were analyzed from the theoretical viewpoint by de Gennes in several reports.[9,10] In this paper, we present in the same context kinetic data on the rate of exchange of labeled polystyrene adsorbed in carbon tetrachloride on silica. The polystyrene/carbon tetrachloride system is familiar in adsorption studies of polymers.[11-13] However, aerosil was most often used as sorbent. This is a pyrogenic silica which develops a large specific surface area but has siloxane and silanol groups on its surface which have different thermodynamic affinities toward the styrene ring.[12-15] Moreover, the aerosil grains are complex assemblies of elementary spheres and are not suitable models for adsorption at plane interfaces.[16] The sorbent we used is a nonporous, spherical, fully hydrated silica which bears only hydroxyl groups on its surface. In that respect, it is a better model for the study of adsorption in the presence of interacting surface sites.[17]

Experimental Section

Materials. (a) Polymer. Radioactive techniques proved useful to measure the amount of polymer adsorbed on metal surfaces.[18] In order to synthesize unlabeled polystyrene and radioactively labeled polystyrene having the same macromolecular characteristics, we prepared, by radical polymerization of styrene in the presence of traces of acrolein, a statistical copolymer of styrene and 0.2% acrolein. After purification, unlabeled polymer

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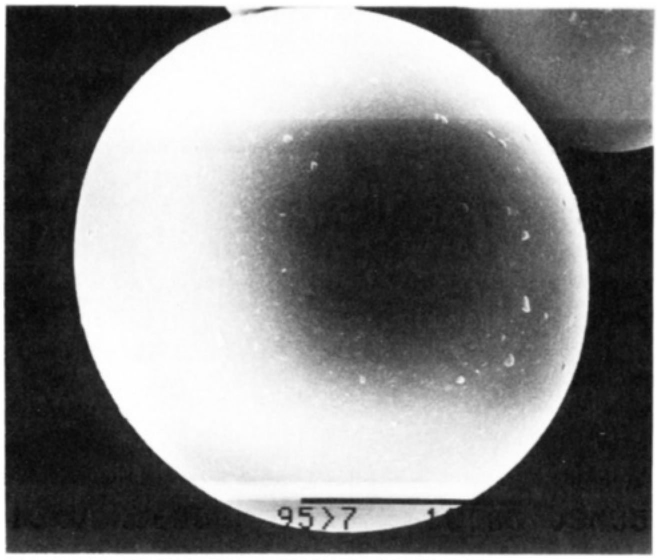

Figure 1. SEM of 34-μm sorbent glass beads.

was obtained by reaction of the primary polymer in freshly distilled dioxane with potassium borohydride in alkaline medium. Radioactive labeled polystyrene was obtained by reaction of the primary polymer with tritiated potassium borohydride to yield the following chemical structure:

$$-[-\mathrm{CH_2}-\mathrm{CH(C_6H_5)}-]_{m_1}-[-\mathrm{CH_2}-\mathrm{CH(CH^3HOH)}-]_{m_2}-$$
$$-m_2/m_1 = 2 \times 10^{-3}$$

The polymer characteristics were the following: $M_w = 3.6 \times 10^5$, $M_w/M_n = 1.6$ (GPC); specific radioactivity $R_s = 2 \times 10^8$ counts min^{-1} g^{-1}. The radioactivity of the "tritiated" polystyrene was determined by using a liquid scintillation spectrometer (SL 3000 Kontron). Since carbon tetrachloride exerts a strong quenching effect, the solvent was extracted before addition of the liquid scintillator (Instagel Packard) to the polymer sample. The concentration of the radioactive polymer solution was then determined by counting the radioactivity of the solvent-free sample.

(b) Adsorbent and Solvent. The adsorbent used was a lot of nonporous glass beads (furnished by Verre et Industrie) of 34-μm average diameter and a specific surface area S of 7.8×10^{-2} m^2 g^{-1}. The glass beads were treated with hot hydrochloric acid in order to generate a surface bearing Si–OH silanol groups. The beads were then washed free of acid and the excess water was evaporated under reduced pressure at 40 °C. This mild drying process maintains the surface in its fully hydrated state.

Figure 1 represents a SEM picture of the sorbent. The surface can be considered as plane and without roughness on the scale of 0.1 μm, which compares with the polymer dimensions.

Carbon tetrachloride was dried over $\mathrm{CaH_2}$, distilled under nitrogen, and stored over molecular sieves.

(c) The cell used in adsorption/desorption experiments consisted of a cylindrical chrome reservoir of 50-mL volume (Figure 2) with a magnetic rotating bar fixed on its bottom. On the top cover, an inlet (A) and an outlet (B) were fitted with Teflon filters, to avoid loss of beads during injection of solution. The solution or the glass bead suspension was introduced at the orifice (C) into the cell.

The cell design is similar to the one previously used in the determination of the exchange rate of labeled/nonlabeled polyacrylamide adsorbed on modified silica beads and more details can be found in ref 8 and 19. The chief advantage of this technique is the possibility of a quasi-continuous recording of the radioactivity of the effluent as a function of time, by which a high accuracy in the determination of the adsorption amount can be reached. It was also shown that under the hydrodynamic conditions of strong agitation, the diffusion of macromolecules in stagnant layers around each glass bead can be neglected (cf. the discussion and particularly eq 1–8 and paragraph 2.2 in ref 19), so that the kinetic data on adsorption or exchange rate can be interpreted in terms of the structure of the adsorbed layer.

Adsorption Isotherm Determination. The suspension of the silica beads was degassed under reduced pressure to generate the true solid/solvent interface. A given mass of radioactive solution was then added to 50 mL of suspension. Controlled agitation was used to prevent the sedimentation of silica beads. The amount of adsorbed polymer was determined by counting the radioactivity of the supernatant solution. This was done at different time intervals and the amount adsorbed was recorded when no systematic variation could be detected over 3 days.

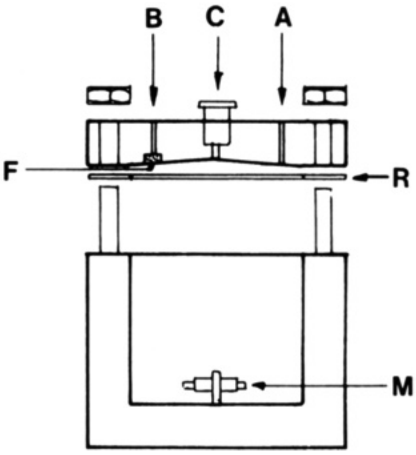

Figure 2. Representation of the cell used in exchange experiments: (A), (B) inlet and outlet for polymer solution; (C) inlet for beads; (F) Millipore Teflon filter; (R) solvent-proof Teflon ring; (MB) magnetic bar.

Measurements of the Rate of Exchange of Radioactive and Nonradioactive Polymers. At the same time as an adsorption run of labeled polymers was performed, a similar adsorption run was carried out, using nonradiolabeled polymer under identical conditions of concentration, volume/surface ratio, and temperature. At equilibrium, agitation was stopped, and in both cases the supernatant solution was separated from the silica sediment. One part of the supernatant nonlabeled solution was then quickly brought into contact with the beads covered with radioactive polymers, and at the same time (zero time), the other part of the nonlabelled solution was introduced into the closed cell at the inlet (A) with an automatically driven syringe with a constant flow rate of 0.6 mL/min. The effluent was collected at the outlet (B), and n successive samples corresponding to time intervals Δt were analyzed for radioactivity. After correction for a very low activity originating from the residual radioactive solution inside the bead sediment at $t = 0$, the radioactivity of the effluent furnished the rate of the transference of the radioactive polymers from the solid/liquid interface to the solution.

Let A_n be the total activity (counts per minute) of the nth sample collected during the time interval Δt. The loss ΔA_s of the radioactivity of the sorbent surface during Δt is given by

$$\Delta A_s = A_n + \Delta A_v \tag{1}$$

ΔA_v being the difference of the total radioactivity of the solution in the cell at time t and time $t + \Delta t$. Provided Δt is small (compared to the exchange rate), ΔA_v is given by

$$\Delta A_v = \frac{V(A_{n+1} - A_{n-1})}{2\Delta t J_v} \tag{2}$$

J_v is the volume flow of injection (mL min^{-1}) and V the volume of solution in contact with the beads. The recorded values of A_n are reported for successive samples in Figure 3: J_v was equal to 0.6 mL min^{-1} and ΔT was equal to 20 min.

The value of A_0 is given by

$$A_0 = vV^{-1}N^*M_wR_sJ_v\Delta t \tag{3}$$

v is the volume of the residual liquid inside the bead sediment, and N^* (mol mL^{-1}), the concentration of radioactive polymer in the solution at adsorption equilibrium, is reported in Figure 6. The rate $\mathrm{d}N^*_s/\mathrm{d}t$ (of negative sign) of radioactive polymer leaving a unit surface area per minute was then calculated by

$$\frac{\mathrm{d}N_s^*}{\mathrm{d}t} = \frac{\Delta A_s}{60\Delta t R_s M_w S} \tag{4}$$

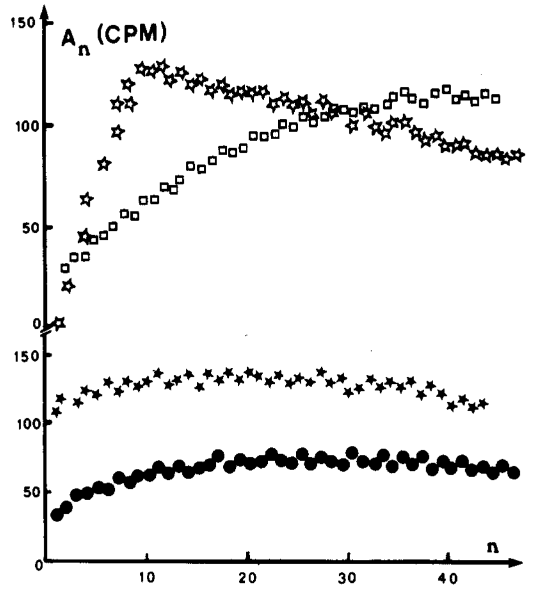

Figure 3. Radioactivity A_n (cpm) of effluent as a function of the sample number n for different exchange experiments: (☆) 35 °C, $N = 5.00 \times 10^{-11}$ mol/mL, $N_s = 4.20 \times 10^{-13}$ mol/cm^2; (□) 25 °C, $N = 0.90 \times 10^{-11}$ mol/mL, $N_s = 3.40 \times 10^{-13}$ mol/cm^2; (★) 25 °C, $N = 6.35 \times 10^{-11}$ mol/mL, $N_s = 6.76 \times 10^{-13}$ mol/cm^2; (●) 25 °C, $N = 2.34 \times 10^{-11}$ mol/mL, $N_s = 4.27 \times 10^{-13}$ mol/cm^2.

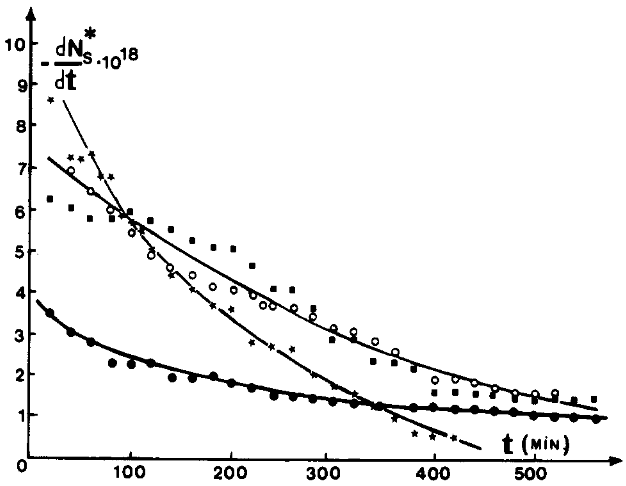

Figure 4. Specific exchange rate of radiolabeled polymer, from surface to solution, as a function of time (min) corresponding to different equilibrium conditions: (★) 25 °C, $N = 6.35 \times 10^{-11}$ mol/mL, $N_s = 6.76 \times 10^{-13}$ mol/cm^2; (■) 25 °C, $N = 4.72 \times 10^{-11}$ mol/mL, $N_s = 6.10 \times 10^{-13}$ mol/cm^2; (○) 25 °C, $N = 4.74 \times 10^{-11}$ mol/mL, $N_s = 6.05 \times 10^{-13}$ mol/cm^2; (●) 25 °C, $N = 2.34 \times 10^{-11}$ mol/mL, $N_s = 4.27 \times 10^{-13}$ mol/cm^2.

The experimental values of $-\mathrm{d}N^*_s/\mathrm{d}t$ recorded are reported in Figures 4 and 5 as a function of time. Time zero corresponds to the moment where the beads covered by radioactive polymers and the nonradioactive polymer solution were brought into contact.

Results and Discussion

Figure 6 shows the adsorption isotherm of polystyrene at the silica/carbon tetrachloride interface at 25 and 35 °C. $N^*_{s,0}$ is the number of polymers adsorbed per cm^2 of sorbent area when the polymer concentration in the solution, expressed in number of polymers per milliliter, is N^*. The adsorption isotherm was determined by using radioactive polymers and, henceforth, an asterisk indicates the concentration of radioactive polymers. We suppose that molecules differing only by minute amounts in their isotopic composition have the same thermodynamic and kinetic properties.

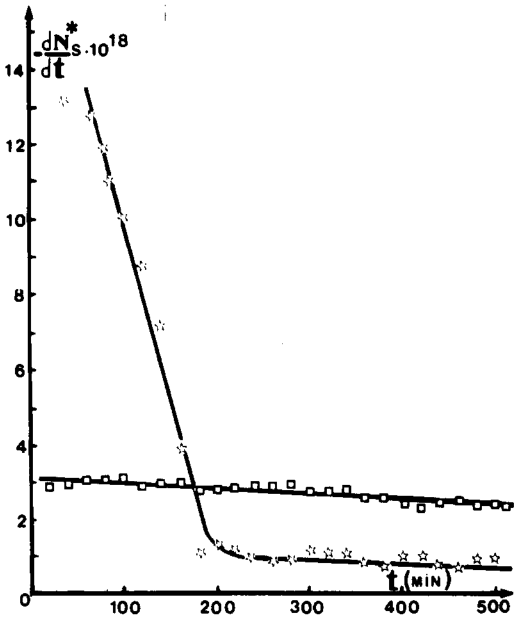

Figure 5. Specific exchange rate of radiolabeled polymer, from surface to solution, as a function of time (min) corresponding to different equilibrium conditions: (☆) 35 °C, $N = 5.00 \times 10^{-11}$ mol/mL, $N_s = 4.20 \times 10^{-13}$ mol/cm^2; (□) 25 °C, $N = 0.90 \times 10^{-11}$ mol/mL, $N_s = 3.40 \times 10^{-13}$ mol/cm^2.

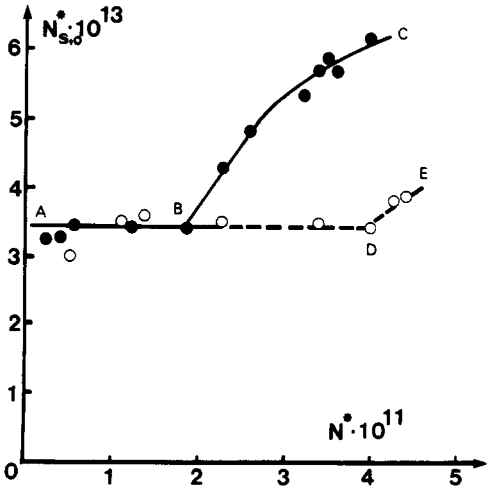

Figure 6. Adsorption isotherms of radiolabeled polystyrene at different temperatures. Representation of the surface coverage $N^*_{s,0}$ (mol/cm^2) as a function of the polymer concentration N^* (mol/mL) in solution at adsorption equilibrium: (●) 25 °C; (○) 35 °C.

The peculiar shape of the isotherm is interpreted as follows: it was shown that polystyrene is able to hydrogen bond with surface hydroxyls.[20] For the toluene/silica/carbon tetrachloride system, the excess enthalpy corresponding to the replacement of 1 mol of CCl_4 by 1 mol of toluene was estimated to be approximately 1 kcal.[21,22] This figure corresponds to a large amount of energy gain, and it is reasonable to suppose that styrene binds to hydrated silica with the same strength. We expect therefore that the adsorption proceeds first through a 1–1 stoichiometric association of styrene monomers and surface hydroxyls. In other words, in region AB of the isotherm at 25 °C, polystyrene is in an almost flat conformation at the interface. The available amount of OH groups per cm^2 is 7.9×10^{14}, which compares quite well with the number of 6.7×10^{14} styrene monomers in contact with the surface at point B of the isotherm.[23,24] The model of a quasi-two-dimensional adsorption is therefore reasonable. Weak adsorption would correspond to a compact regular packing of polymer coils at the surface. For this model, $N^*_{s,0}$ is given by

$$N^*_{s,0} = (N_v/M_w)^{2/3}\mathcal{N}^{-1/3} \qquad (5)$$

$$N_v = 0.77/[\eta] \qquad (6)$$

$\mathcal{N}$ is Avogadro number and $[\eta]$ is the intrinsic viscosity (expressed in mL g) of the polymer solution. N_v is the number of coils per unit volume in a three-dimensional close packing.[25] $N^*_{s,0}$(35 °C) and $N^*_{s,0}$(25 °C) calculated in this way are equal respectively to 0.52×10^{13} mol/cm^2 and $0.57\ 10^{-13}$ mol/cm^2. Since the experimental value is 3.4×10^{-13} mol/cm^2, this model is far from reality. We suppose the two-dimensional adsorption holds true in the first plateau region. Figure 6 shows that for N^* values above 1.7×10^{-11} mol/mL at 25 °C and 4×10^{-11} mol/mL at 35 °C, the adsorption increases. As a result of the formation of extended loops and/or tails, a distinct population appears above points B and D of the isotherm. The fraction of segments not in direct contact with the surface grows continuously with N^*. We propose that the loop/tail formation results from a slow exchange which takes place at the interface between adsorbed and solution polymers.

Radioactive exchange fluxes were measured as reported in the Experimental Section. The isotopic fraction N^*/N in the solution phase did not exceed in any case 3%, so that the following condition was always fulfilled:

$$N^*_s(t)/N_s \gg N^*(t)/N \qquad (7)$$

Index s indicates surface concentrations, and symbols without index indicate solution concentrations. N_s is the total amount of adsorbed polymer. Actually, N_s is equal to $N^*_{s,0}$ reported in Figure 6. During the isotopic exchange, the surface is, however, populated by inactive polymers (of concentration $N^*_{s,0} - N^*_s$) and by radioactive polymers (of concentration N^*_s); in order to avoid confusion, we use in eq 7 and henceforth the symbol N_s for the surface concentration when both isotopic species are present. N is the concentration of the solution (mol mL^{-1}). The strong isotopic asymmetry, indicated by eq 7, was maintained in keeping the flow velocity of inactive solution through the cell at a sufficiently high level (the exchange proceeds as if the glass beads were in contact with a very large reservoir of almost inactive solution). In account of eq 7, the number $\mathrm{d}N^*_s/\mathrm{d}t$ of radioactive molecules leaving the surface in unit time is the unidirectional flux $J^*_{s\to b}$, where index s → b means directed from the surface to the solution. The total unidirectional flux, including inactive and radioactive molecules, is given by

$$J_{s\to b} = (\rho^*_s)^{-1}J^*_{s\to b} \qquad (8)$$

ρ^*_s being the surface fraction N^*_s/N_s of radioactive polymers. At chemical equilibrium, N_s is constant and

$$J_{s\to b} = -J_{b\to s} \qquad (9)$$

$J_{b\to s}$, the unidirectional flux directed from the solution to the surface, is proportional to the concentration N of the solution:

$$J_{b\to s} = KN \qquad (10)$$

K, a positive constant, is expected to be a function of N_s. If eq 9 and 10 are substituted into eq 8, we obtain

$$\mathrm{d}N^*_s/\mathrm{d}t = -KNN^*_s/N_s \qquad (11)$$

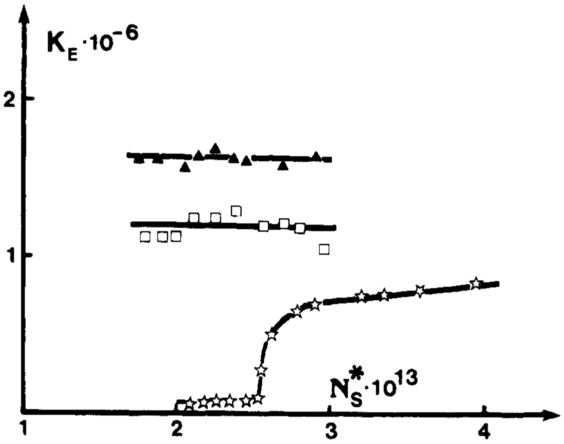

Figure 7. Specific rate coefficient K_E (mL mol^{-1} s^{-1}) of radiolabeled polymer versus surface concentration N^*_s (mol cm^{-2}) corresponding to different equilibrium conditions: (▲) 25 °C, $N = 0.35 \times 10^{-11}$ mol/mL, $N_s = 3.40 \times 10^{-13}$ mol/cm^2; (□) 25 °C, $N = 0.90 \times 10^{-11}$ mol/mL, $N_s = 3.40 \times 10^{-13}$ mol/cm^2; (☆) 35 °C, $N = 5.00 \times 10^{-11}$ mol/mL, $N_s = 4.20 \times 10^{-13}$ mol/cm^2.

We now discuss our experimental results on the basis of eq 11. First we note that despite the strong asymmetry of the isotopic distribution indicated by eq 7, the unidirectional flux $J^*_{x\to b}$ is very small at any time. For example, taking $N = 0.9 \times 10^{-11}$ mol/mL and $N_s = 3.4 \times 10^{-13}$ mol/cm^2, we note, in Figure 5, that $\mathrm{d}N^*_s/\mathrm{d}t$ is a linear function of time t. By straightforward integration and in view of the small variation of $\mathrm{d}N^*_s/\mathrm{d}t$ with t, we obtain

$$N^*_{s,0} - N^*_s(t) = V^*_0\tau^{-1}[1 - \exp(-\tau t)] \qquad (12)$$

V^*_0 is the rate $\mathrm{d}N^*_s/\mathrm{d}t$ at time zero. The relaxation time τ^{-1} is of the order of 1.5×10^3 min. It takes therefore hours to obtain the surface free of radioactivity. The same conclusion holds also true for the data reported in Figure 4. This important result demonstrates that polymers have an unusually long lifetime in the adsorbed state.

Such "frozen" interfacial states were also reported previously for polyacrylamide adsorbed in aqueous medium on modified silica.[8] Recent results obtained with a different technique by Granick on polystyrene adsorbed on quartz in CCl$_4$ are in line with our observation, which thus appears to be a general phenomenon.[26]

If we apply eq 11 in the plateau region of the isotherm where N_s is constant, we can lump K and N_s together to define a new constant K_E (mol^{-1} mL s^{-1}) and eq 11 transforms to

$$\mathrm{d}N^*_s/\mathrm{d}t = -K_E NN^*_s \qquad (13)$$

This equation has formally the structure of a bimolecular chemical reaction rate. It does, however, not signify any 1-1 "chemical" association between surface and bulk molecules but originates from the strong requirement of constant chemical composition N_s of the interface during the isotopic exchange ($K_E N$ and τ of eq 12 and 13 represent the same quantity).

K_E values calculated according to eq 13 for $N = 0.9 \times 10^{-11}$ mol/mL, $N^*_{s,0} = 3.4 \times 10^{-13}$ mol/cm^2 and $N = 0.35 \times 10^{-11}$ mol/mL, $N^*_{s,0} = 3.4 \times 10^{-13}$ mol/cm^2 are reported on Figure 7 as a function of the concentration N^*_s of residual surface active polymers. They are remarkably constant with N^*_s. The difference of K_E with respect to the concentration N_s is of the order of 26%; this can be ascribed to the large experimental error which occurs in the determination of polymer concentrations of the order of 10^{-4} wt % in the supernatant of two independent adsorption experiments.

We consider now the data of kinetic exchange in the ascending part BC of the isotherm. Previous considerations leading to eq 11 do still apply; however, N_s is no

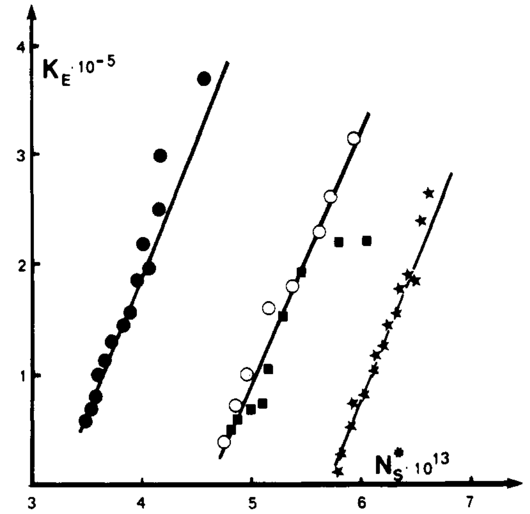

Figure 8. Specific rate coefficient K_E (mL mol^{-1} s^{-1}) of radiolabeled polymer versus surface concentration N^*_s (mol cm^{-2}) corresponding to different equilibrium conditions: (●) 25 °C, $N = 2.34 \times 10^{-11}$ mol/mL, $N_s = 4.27 \times 10^{-13}$ mol/cm^2; (■) 25 °C, $N = 4.72 \times 10^{-11}$ mol/mL, $N_s = 6.10 \times 10^{-13}$ mol/cm^2; (○) 25 °C, $N = 4.74 \times 10^{-11}$ mol/mL, $N_s = 6.05 \times 10^{-13}$ mol/cm^2; (★) 25 °C, $N = 6.35 \times 10^{-11}$ mol/mL, $N_s = 6.76 \times 10^{-13}$ mol/cm^2.

longer constant but rather follows, when N is larger than 2×10^{-11} mol/mL^{-1}, the law

$$N_s = \alpha N \tag{14}$$

From eq 11, we have then

$$dN^*_s/dt = -\alpha^{-1}KN^*_s \tag{15}$$

and a formal relation between K_E and K is obtained by combining eq 13 and 15:

$$K_E = K/N_s \tag{16}$$

In Figure 8, we have reported the values of K_E, according to eq 11, as a function of N^*_s for different adsorption amounts corresponding to region BC. As expected from eq 16, K_E decreases with N_s; however, the prominent feature is that for a given N_s value, K_E is a decreasing function of N^*_s; this means that the value of K is not constant during the isotopic exchange at constant surface coverage. To explain this behavior we must reconsider eq 8–11. A unique relaxation time K_E^{-1} in region AB of the isotherm signifies that polymers are kinetically indistinguishable. However, considering region BC, we must be more careful in expressing the fluxes $J_{s\rightarrow b}$ or $J_{b\rightarrow s}$. On account of the variation of K_E with N^*_s, it is not possible to attribute to all polymers identical kinetic properties; instead we must consider a whole spectrum of K values in expressing $J_{b\rightarrow s}$ by eq 10. Therefore in region BC, the polymer layer cannot be considered as a homogeneous phase. As already stated, the structure of the layer in region BC is like a "hairy" carpet build up by a slow exchange of newcomers with parts of the polymer already adsorbed in a flat conformation.

The exchange kinetics was also determined under good solvent conditions at 35 °C where the stability of the two-dimentional layer is enhanced. The exchange was started in the "hairy" domain corresponding to $N = 5 \times 10^{-11}$ mol/mL, $N_s = 4.2 \times 10^{-13}$ mol/mL and pursued for the part of the adsorbed layer which contains molecules involved in the formation of the flat layer. Two dynamic populations are indeed observed in Figure 7 (bottom curve): about 2.6×10^{-13} mol do exchange with a rate constant $K_E \simeq 10^5$ mol^{-1} mL s^{-1}, whereas the replacement of 1.6×10^{-13} mol proceeds with a rate constant $K_E \simeq 8 \times 10^5$ mol^{-1} mL s^{-1}. From this, one infers that when the bulk concentration is raised to 5×10^{-11} mol/mL, 75% of the molecules which are involved in the construction of the two-dimensional structure up to point D do preserve at point E their flat conformation, while the other 25% makes room for lodging 1.6×10^{-13} mol of newcomers. From the material balance, one deduces that the structure of the molecules in the "hairy" conformation is made up on the average of half trains and half tails.

In a recent paper, de Gennes has shown that the coefficient K in eq 11 can be expressed in terms of a tunneling amplitude T, which is the statistical weight for a chain, when starting at the limit of the diffuse polymer layer, to reach the surface:[9,10]

$$K = K_{si}TN_s \tag{17}$$

K_{si} is a diffusion coefficient divided by the layer thickness; T can be expressed as a function of the chain length. For polyacrylamide the diffuse layer thickness measured by viscosity and inelastic light scattering[27] was found to be of the order of 400–800 Å for $3 \times 10^5 < M_w < 1.2\ 10^6$. For such thick polymer layers, the concept of a resistance due to a repulsive potential in the diffuse layer could be applied. In the present discussion, we suppose, however, strong adsorption and a quasi-two-dimensional structure in the first isotherm region; the application of the concepts leading to eq 16 which express the parameter K in terms of the probality T is therefore doubtful, in the present case.

Conclusion

Adsorption of polystyrene on hydrated silica displays two well-defined regions in the adsorption isotherm. The plateau region at low bulk concentration, usually not observed with aerosil silica (which bears only a small number of hydrophylic surface groups), is explained as the result of a two-dimensional interfacial structure.

As previously reported, polymers at solid/liquid interfaces are firmly attached and exchange very slowly with bulk molecules. In the present study, we were able to correlate the dynamic properties relative to the two regions of the isotherm with the conformational properties of the polymer layer in both regions.

In the plateau region, backward and forward fluxes can be expressed in terms of one kinetic constant. True equilibrium holds, however, if the bulk concentration is suddenly reduced to nearly zero (the very first part of the isotherm at exceedingly small concentrations, not seen here); then because of the very low mobilities, reequilibration takes a long time and the situation is then that of a metastable equilibrium state. In the isotherm region where overadsorption occurs, the interfacial exchange cannot be characterized by one kinetic constant, and the picture of a most probable conformation fails; the train and tail size distributions are not narrow in that region.

Registry No. Polystyrene, 9003-53-6; silica, 7631-86-9.

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Polymer Concentration Profile near a Liquid–Solid Interface: Evanescent Wave Ellipsometry Study

M. W. Kim* and D. G. Peiffer

Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801

W. Chen, H. Hsiung, Th. Rasing, and Y. R. Shen

Department of Physics, University of California, Berkeley, California 94720, and Center for Advanced Materials, LBL, Berkeley, California 94720.

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ABSTRACT: The phase retardation angle, $\Delta\Phi$, as a function of the incident angle was measured to study adsorption and depletion of polymers near a solid substrate from a solution by use of an evanescent wave ellipsometry technique. A lightly sulfonated ionomer dissolved in a polar solvent displayed an appreciable interfacial adsorption layer, while the nonionic precursor in ethyl acetate exhibits a depleted concentration profile. The results are in good agreement with adsorption or depletion layer profiles obtained previously by other techniques, i.e., X-ray fluorescence for polymer adsorption and optical fluorescence evanesent wave technique for depletion.

Introduction

It is widely known that ellipsometry[1] is very useful in the determination of film thickness at air–solid interfaces. However, the lack of sensitivity of conventional ellipsometry has limited its usefulness with regard to a variety of technologically interesting interfaces such as at liquid–solid interfaces where either polymer adsorption or depletion can occur. A recent report[2] shows that a phase-modulated instrument similar to the one used in this study has sufficient sensitivity to probe the phase transition of even a submonolayer of surfactants. The present work is devoted to a dilute macromolecular solution in the vicinity of an impenetrable wall. Such a system, for example, mimics the important role polymer materials play in the stabilization of colloidal particles. It is well-known that the stability of colloidal dispersions[3] depends on a variety of parameters such as polymer composition, molecular weight, solvent quality, and ionic strength. Therefore it is of interest to probe the polymer adsorption or depletion phonomena in terms of these variables.

As previously noted, the central problem in understanding the stabilization mechanism of colloidal particles by macromolecules is related to the detailed structure of the polymer near the liquid–solid interface. For this purpose, a very sensitive phase-modulated ellipsometer is utilized in order to examine whether it possesses sufficient sensitivity to monitor polymer adsorption or depletion at a liquid–solid interface. The initial measurements are compared with previous experimental results obtained from X-ray fluorescence[4] and fluorescence optical evanesent techniques[5] for polymer adsorption and depletion, respectively.

Experimental Section

The optical technique described in this report utilizes the total internal reflection at an interface located between an optically dense medium and a lean one. When there exists an interfacial layer of different optical property, i.e., either enhancement or depletion of the polymer concentration at the boundary in the present situation, the optical phase difference ($\Delta\Phi$) of the p-wave and s-wave reflection varies with the incident angle due to the change of the penetration depth of the evanescent wave. Thus, by measuring the phase difference as a function of the incident angle, one learns about the structure of the interfacial layers. If the thickness of the interfacial layer is small compared to the optical wavelength, then the critical angle of the total internal reflection (θ_t) is determined solely by the dielectric constant ($\epsilon = n^2$) of the bulk phases forming the interfaces. Following the derivation of Drude,[6] the phase difference at an incident angle (θ) is given by

$$\Delta\Phi(\theta) = 2k_0 \cos\theta \, \frac{(\epsilon_2)^{1/2}\epsilon_1 \sin^2\theta}{(\epsilon_2 - \epsilon_1)(\epsilon_2 \sin^2\theta - \epsilon_1 \cos^2\theta)} \, \eta \qquad (1)$$

where

$$\eta = \int_0^\infty \frac{1}{\epsilon(z)}[\epsilon_2 - \epsilon(z)][\epsilon(z) - \epsilon_1] \, dz$$

where $k_0 = 2\pi/\lambda$, λ is the wavelength of laser beam in vacuum, and ϵ_2, ϵ_1, and $\epsilon(z)$ are the dielectric constants of the dense, lean, and interface region at a distance z from the interface, respectively. At the critical angle (θ_t), eq 1 becomes

$$\Delta\Phi(\theta_t) = \frac{2k_0}{(\epsilon_2 - \epsilon_1)^{1/2}} \int_0^\infty \frac{1}{\epsilon(z)} [\epsilon_2 - \epsilon(z)][\epsilon(z) - \epsilon_1] \, dz \qquad (2)$$

The sign of $\Delta\Phi(\theta_t)$ gives a qualitative description of whether the interfacial layer is best described as an adsorbed (positive)

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