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ORIGINAL CONTRIBUTION

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Non-equilibrium adsorption at solid/liquid interfaces from polyelectrolyte solutions

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Abstract The poly(2-vinylpyridine) layer was established at the Pyrex glass/water interface with periodic phases of adsorption/desorption runs observed over several days. This was evidenced by determining the concentration of radio-labelled molecules in the solution equilibrating the glass beads as a function of time (the effluent) while the same radio-labelled polymer was slowly supplied by injecting the polymer solution into the reactor containing the adsorbent at a controlled extremely slow rate. Although the adsorption (or the desorption) steps seemed to present some periodic character, they were better correlated with the successive bulk concentration thresholds that were established with time when the initial surface was free of polymer at time zero. Even when the adsorbent was coated at different degrees, desorption steps were correlated to the overstepping of decreasing concentration thresholds. Adsorption and desorption runs were attributed to the existence of different typical interfacial conformations of the adsorbed macromolecules that only can be stabilised in the adsorbed state when the layer was "equilibrated" with the polymer solution of a certain concentration. Macromolecule were definitely adsorbed when the reconformation process led to a flat conformation (trains). Macromolecules adsorbed with a conformation close to their solution conformation may be desorbed as a result of the reconformation process affecting previously adsorbed neighbour molecules (in the case of partially coated surfaces at time zero of injection). Macromolecules with loops and tails were retained on the surface when the polymer concentration in the bulk was progressively increased (for uncoated surfaces at time zero of injection). All these effect were attributed to the combined influence of topological effects on adsorption and reconformation of adsorbed macromolecules that characterise the non-equilibrium adsorption processes.

Keywords Polyelectrolyte adsorption · Polyelectrolyte desorption · Polyelectrolyte reconformation · Non-equilibrium adsorption · Overshoot

Introduction

Adsorption of polyelectrolytes on solid/liquid interfaces has been a domain of great interest due to the high implication of relevant processes in the industrial, environmental, agricultural and biological areas [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Therefore, numerous theoretical studies have addressed several problems inherent to

equilibrium adsorption phenomena and to the ways to reach equilibrium [14, 15, 16, 17, 18, 19, 20]. However, the kinetics of adsorption of polyelectrolytes sustaining reconformation in the adsorbed state has hardly been investigated [21, 22]. One manifestation of non-equilibrium adsorption is overshoot, when the amount of polymer adsorbed as a function of time develops a peaked variation and polymer adsorbed "in excess" desorbs. Reconformation and related phenomena (overshoot, instability, oscillation) were determined to occur for different systems [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33].

Poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) belong to this class of polyelectrolytes and, in the latter case, the existence of overshoot occurred on varying the rate of polymer supply to the solid adsorbent dispersed as micro-spheres in aqueous medium [25]. When the polymer was very slowly supplied to the adsorbent, no overshoot was observed. When the polymer was rapidly added to the adsorbent, the adsorption went to a maximum and then decreased. No polymer transfer from surface to bulk occurred when one half of the polymer rapidly adsorbed left the surface. From the kinetic point of view, reconformation of isolated adsorbed poly(4-vinylpyridine) molecules was determined to be a relatively slow process while the reconformation of molecules within saturated layers was found to be relatively fast [25]. This troubling event was recently investigated by applying the surface area exclusion chromatography (SAEC) method to polyvinylamine adsorbed on glass microfibres [33]. Adsorbed polyvinylamine sustains fast extended reconformation during surface area filling [34, 35] but no characteristic time for the reconformation rate affecting saturated layers could be determined in experiments lasting between 15 and 117 min. The conclusion of this investigation was that the extent of reconformation is a function of the variable $T \times C_{eq}$, where C_{eq} is the concentration of polymer molecules in the liquid phase equilibrating the adsorbed layer and T is the period of contact between bulk solution and interfacial layer [33].

Clearly, establishment of the P2VP layer at the Pyrex/water interface was found to not be a straightforward process since transitory polymer adsorption and desorption steps occurred when the amount of polymer adsorbed was determined for one week. Similarly, the role of the polymer layer in the colloid stability of dispersed silica particles and the wettability of the silica/polymer system was determined to evolve with time [36, 37]. The present results aimed at a supplementary information relative to kinetic characteristics of the non-equilibrium adsorption of polyelectrolytes differing by their molecular weight or of a mixture of these polymers. Two fractionated samples of P2VP were selected and the "reactor" method was employed to determine the kinetics of establishment of the interfacial layer.

Materials and methods

The adsorbent

Spherical Pyrex glass beads of diameter 0.5–10 μm were employed as adsorbent. The typical composition of Corning Pyrex Borosilicate glass is as follows: SiO_2 80.6%, Na_2O 4.0%, B_2O_3 13.0%, Al_2O_3 2.3% and K_20 0.1%. This material is classified as being the least reactive glass and is highly resistant to strong alkalis and acids. Before use at pH 3.0, the adsorbent was thoroughly washed with water and equilibrated for a long time at pH 3.0 to ensure pH stability.

The polymer

Two fractionated samples of P2VP molecules, (Polymer Source) were used . Mn and Mw were equal to 9,100 and 9,900 or 358,000 and 385,400, and the mass polydispersity was very close to 1.08. In order to determine the polymer concentrations in very dilute solution and the amounts of polymer adsorbed on the glass microfibre filters, radio-labelled P2VP samples of the different fractions were obtained by quaternisation with $I^{14}CH_3$ of a few pyridine groups (0.1%) in ethylene glycol solution [25]. The specific radioactivity of samples of molecular weights of 358,400 and 9,900 was equal to 3,574,550 and 4,338,610 cpm/mg of polymer, respectively. This labelling allowed very precise detection of extremely small amounts of polymer, the lower limit of detection being close to 5–10 ng.

The reactor method

The adsorption experiments were performed at pH 3.0 and at 22 °C. To enable precise determinations of the polymer concentration in the reactor as a function of time the following methods were implemented (Fig. 1).

A reactor of 21.50 mL containing 15 mL water at pH 3.0 and a given weight of suspended Pyrex glass beads was first degassed to generate a true water/glass interface. Then, after addition of the weighted dose of polymer solution under stirring, the cell was completely filled with solvent. This operation fixed the initial concentration C_0 of the polymer in the liquid phase prior adsorption close to 15 mg/100 mL (in some experiments, C_0 was set to zero). The initial time of contact between the glass beads and the solution of concentration C_0 was held within a period of 5 min but was not strictly the same for the different experiments since the syringe and the sample collector must be connected to the inlet and outlet

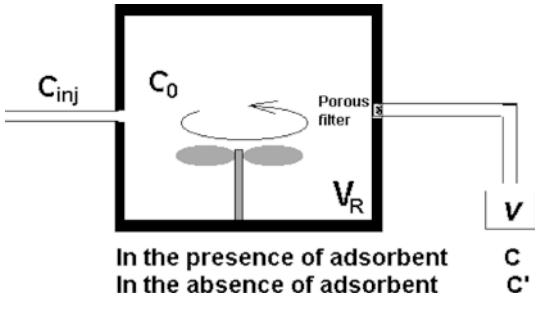

Fig. 1 Representation of the reactor cell. The polymer solution of concentration C_{inj} is injected into the reactor of volume V_R containing the polymer solution at the concentration C_0. Aliquots of volume v are collected at the outlet fitted with a porous filter. In the presence or in the absence of adsorbent, the polymer concentration is noted as C or C', respectively

apertures, respectively. Adsorption during this period changes the polymer concentration of C_0 to a smaller value C_1. A solution of polymer of concentration C_{inj} equal to 3 mg/100 mL was then very slowly injected through the inlet aperture of the reactor at the rate of 0.35 mL/h for about 4–7 days while the liquid effluent was sampled as aliquots of 0.30 mL and analysed for polymer concentration. This sampling allowed calculation of the time-dependent polymer concentration in the supernatant. The sample collected first provided information on the concentration C_0 of the polymer solution. The initial adsorption is derived from the balance between C_0 and C_1. Then, the mean transfer of polymer molecules from the solution to the surface or from the surface to the bulk was derived from the variation in the polymer concentration within the reactor corresponding to each aliquot sampling time. For mixed polymer systems, the experiment was duplicated, and in each case one polymer was radio-labelled while the other one was unlabelled.

Determination of the characteristics of the polymer adsorption

Taking into account the variables appearing in Fig. 1, the concentration C' of polymer in the effluent is expressed as a function of the injected volume v by:

$$C' = C_{inj} - [C_{inj} - C_0] \exp(\frac{v}{V_R}) \quad (1)$$

and the variation dC' is given by:

$$\frac{dC'}{dv} = \frac{C_{inj} - C'}{V_R} \quad (2)$$

In the presence of adsorbent, the concentration C_0 dropped to C_1 (the concentration corresponding to that of the aliquot collected first) and the initial mass Γ_0 of polymer adsorbed is given by:

$$\Gamma_0 = [C_0 - C_1] \times V_R \quad (3)$$

The variations in the adsorption $d\Gamma$ as a function of the injected volume v were determined using the relationship:

$$d\Gamma = [C_{inj} - C] \times dv - V_R \times dC \quad (4)$$

Finally, one obtains:

$$\frac{d\Gamma}{dv} = C_{inj} - C - V_R \frac{dC}{dv} \quad (5)$$

and the total amount of polymer adsorbed Γ after injection of a volume v of the polymer solution is given by:

$$\Gamma(v) = \Gamma_0 + \sum_v \frac{d\Gamma}{dv} \quad (6)$$

The reliability of the method was checked as follows: the solution of radio-labelled polymer of concentration C_{inj} and volume v was injected into the reactor which initially was filled with the polymer solution of concentration C_0. Figure 2 shows the experimental result to fit the expected variation of $\log \frac{C_{inj}-C'}{C_{inj}-C_0}$ as a function of the reduced volume v/V_R of the injected solution that obviously can only be predicted in the absence of adsorbent.

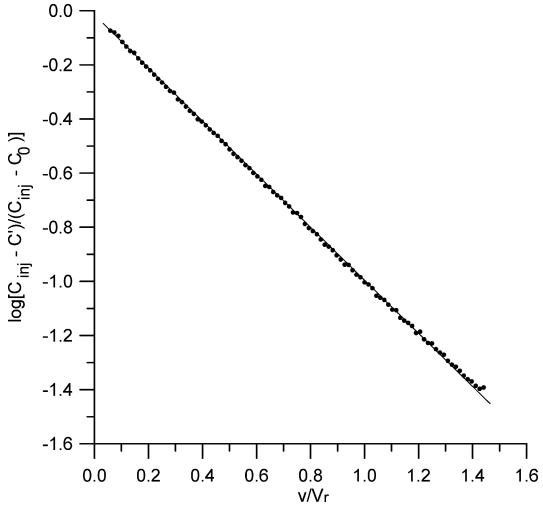

Fig. 2 Theoretical (*line*) and experimental (*black circle*) representation of $\log \frac{C_{inj}-C'}{C_{inj}-C_0}$ as a function of the reduced volume of the injected solution

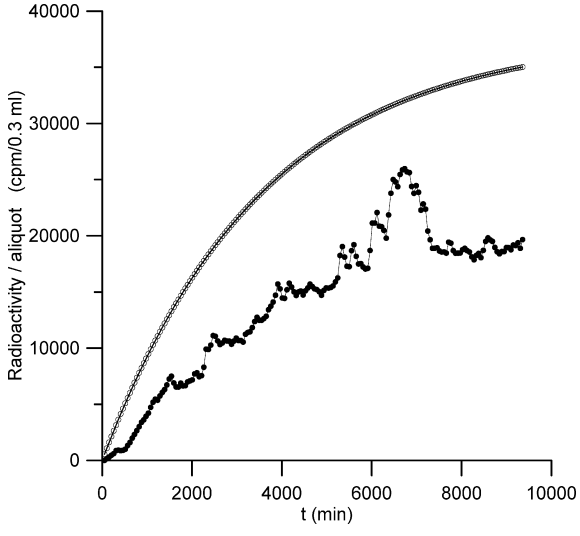

Fig. 3 Representation of the radioactivity of the aliquot as a function of time. The *upper curve* was obtained in the absence of adsorbent and the *lower curve* was determined in the presence of 1.5 g Pyrex glass beads. Experimental conditions: $C_0 = 0$ mg/mL, $C_{inj} = 0.029$ mg/mL, injection rate 0.35 mL/h

Results and discussion

Polymer adsorption under controlled polymer supply at the initially polymer free Pyrex surface

Figure 3 represents the variations of the radioactivity of the successive aliquots as a function of time, corresponding to two experiments of polymer injection into the reactor for which C_0 was equal to zero. The upper curve corresponds to the situation in the absence of adsorbent while the lower curve was determined in the presence of 1.5 g Pyrex glass.

Approximately one half of the injected polymer that remains in the reactor is globally adsorbed on the Pyrex glass beads. The amount of polymer adsorbed, as derived from the variations of the radioactivity C and C', is reported as a function of time in Fig. 4 and as a function of the polymer bulk concentration C_{bulk} (mg

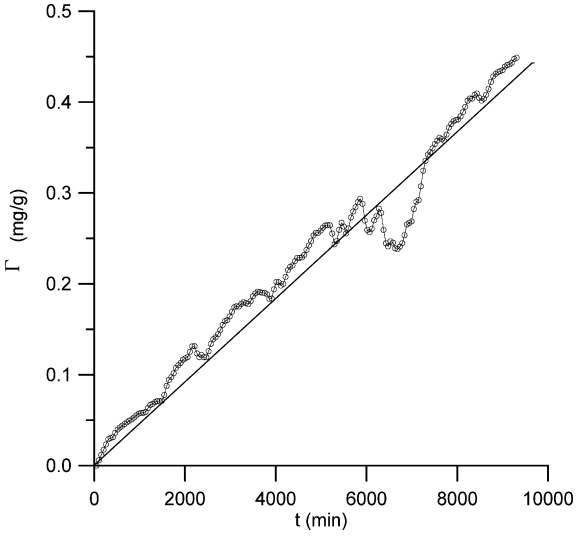

Fig. 4 Representation of the amount Γ of polymer adsorbed as a function of injection time. Experimental conditions: $C_0 = 0$ mg/mL, $C_{inj} = 0.029$ mg/mL, injection rate 0.35 mL/h

polymer/g Pyrex) in Fig. 5. Obviously, the amount of polymer adsorbed globally increases with time but the bulk concentration seems to be the parameter that transitorily limits the amount of polymer adsorbed Γ. Apart from the initial adsorption run, the successive runs a–f appear to present the characteristics of the non-equilibrium adsorption with overshoot. The adsorption jumps progressively, being longer with the increasing bulk concentrations C_{bulk} of 0.035, 0.06, 0.075, 0.115, 0.16 and 0.20 mg/g Pyrex at A, B, C, D, E and F, respectively.

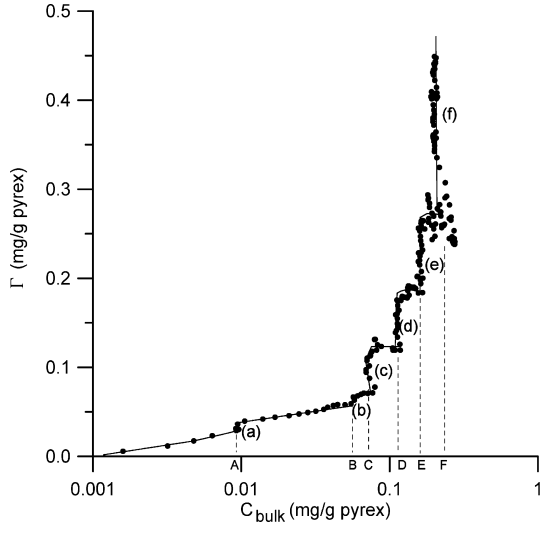

Fig. 5 Representation of the amount Γ of polymer adsorbed as a function of the polymer concentration C_{bulk} in the supernatant. Experimental conditions: $C_0 = 0$ mg/mL, $C_{inj} = 0.029$ mg/mL, injection rate 0.35 mL/h

Polymer adsorption under controlled polymer supply at polymer coated Pyrex surfaces

Adsorption from monodisperse systems

Figures 6 (polymer [9,900]) and 7 (polymer [385,400]) show the adsorption values Γ (mol/g Pyrex) to present fluctuations as a function of injection time. The adsorption at time zero corresponds to the polymer initially adsorbed when 20.75 mL of polymer solution at the concentration of 0.15 mg/mL was initially supplied to 1.5 g of adsorbent within the reactor for various periods (within 5–10 min). The amplitude of the oscillation in the adsorption Γ decreases with the adsorption determined at time 0 and for polymer [385,400] the oscillations are not visible when the initial coverage was equal to 0.910 mg/g Pyrex. Furthermore, the delay in the progress of adsorption in the initial period of injection decreases with the initial adsorption Γ.

Figure 8 (decreasing x axis) shows the adsorption of polymer [9,900] (refers to the experiments of Fig. 6) as a function of the normalised polymer concentration C_{bulk} (mg/g Pyrex) in the reactor. Taking into account that the concentration C_{inj} is smaller than the initial concentration C_0, C_{bulk} globally decreases with time. It is clearly shown that for the three different degrees of initial coverage of 0.200, 0.361 and 0.558 mg/g Pyrex, the observed successive desorption steps start at the critical bulk concentrations of 1.32 (A), 1.0 (B), 0.75 (C) and 0.61 mg/g Pyrex (D). Despite the fact that the global

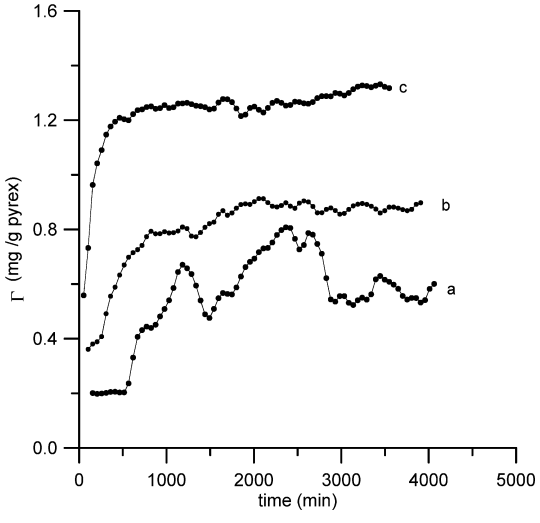

Fig. 6 Adsorption from the monodisperse system. Representation of the amount Γ (mg/g Pyrex beads) of polymer [9,900] as a function of the injection time. Due to increasing initial contact times between the polymer solution and the adsorbent for experiments *a–c*, the adsorption determined at time zero was equal to 0.200, 0.361 and 0.558 mg/g Pyrex beads, respectively. Experimental conditions: $C_0 = 0.15$ mg/mL, $C_{inj} = 0.029$ mg/mL, injection rate 0.35 mL/h

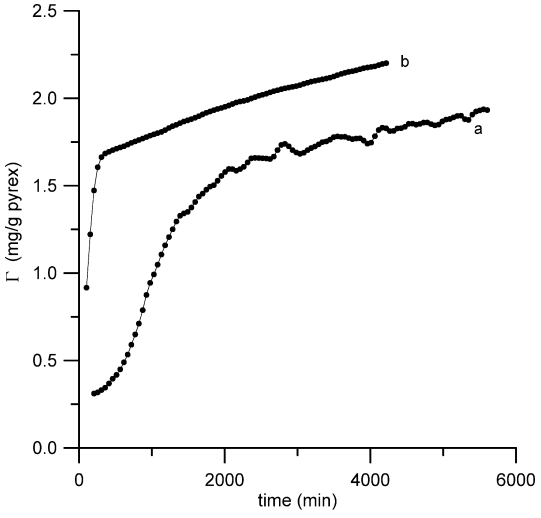

Fig. 7 Adsorption from the monodisperse system. Representation of the amount Γ (mg/g Pyrex beads) of polymer [385,400] as a function of the injection time. Due to increasing initial contact times between the polymer solution and the adsorbent for experiments *a* and *b*, the adsorption determined at time zero was equal to 0.310 and 0.910 mg/g Pyrex beads, respectively. Experimental conditions: $C_0 = 0.15$ mg/mL, $C_{inj} = 0.029$ mg/mL, injection rate 0.35 mL/h

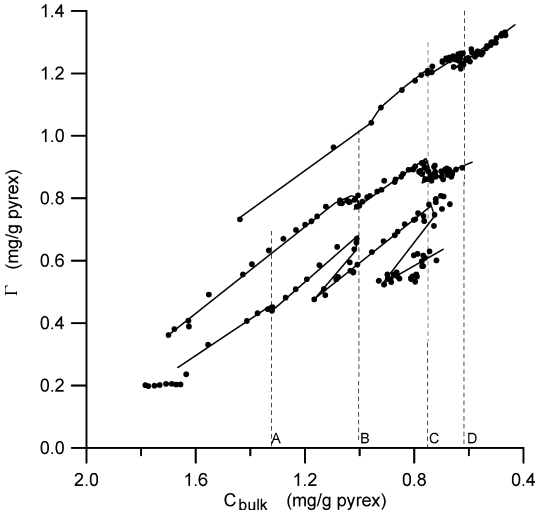

Fig. 8 Representation of the adsorption Γ (mg/g Pyrex) as a function of the bulk concentration C_{bulk} (mg/g Pyrex) for experiments represented in Fig. 6. Note: descending x axis

bulk concentration is decreasing, each desorption step gives rise to a further growth in adsorption.

Adsorption from bidisperse systems

In these experiments, 0.5 g Pyrex glass beads were brought in contact with a polymer solution containing an equal weight of the two polymers [385,400] and [9,900] at the total concentration of 0.15 mg/mL but the contact time was limited to the smallest manageable period. Then, the same mixture at the concentration of 0.03 mg/mL was slowly injected into the reactor.

Figure 9 shows the concomitant adsorption of polymer [385,400] (curve a) and [9,900] (curve c). In a second set of experiments using 0.15 g Pyrex glass beads and a slightly longer period of initial contact, the specific adsorption of polymer [385,400] as a function of injection time is represented by curve b. It is clear that the presence of polymer [9,900] strongly increases the amplitude of the oscillations in adsorption. Previously, adsorption profiles of similar shapes were determined to occur for adsorption of a polydisperse sample of P2VP on the same Pyrex glass beads. The oscillations were attributed to the polydispersity in molecular weight, thus referring to the probable exchange between low and high molecular weight molecules [32]. The present result of Fig. 9 confirms this assumption, although the former assumption of very fast adsorption rate—based on results determined for the poly(4-vinylpyridine)/polystyrene sulphate latex systems [25])—should be amended by taking into account the concentration-dependent adsorption rate on Pyrex glass beads as evidenced in Fig. 5 and the time of initial contact as evidenced in Figs. 6 and 7.

Figure 9 shows that the polymer [9,900] of low molecular weight rapidly adsorbs on the adsorbent, slowly increases after a delay of 500 min and reaches a value of Γ close to 0.08 mg/g Pyrex. Then, most of the adsorbed polymer [9,900] is desorbed and the adsorption in the remaining layer is close to 0.015 mg/g Pyrex. The

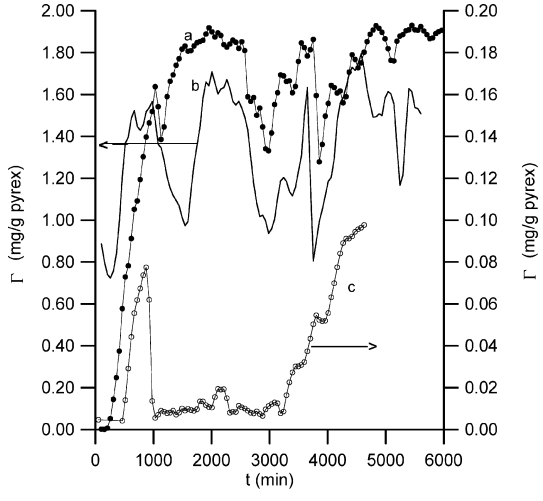

Fig. 9 Adsorption from the bidisperse system. Representation of the amount of polymer adsorbed as a function of time. *Curves a* and *b* correspond to adsorption of polymer [385,400] and *curve c* corresponds to adsorption of polymer [9,900] when the two polymer were concomitantly supplied at the relative weight concentration of 1. Experimental conditions: $C_0 = 0.15$ mg/mL, $C_{inj} = 0.03$ mg/mL, injection rate 0.35 mL/h. For experiments represented by *curves a* and *c*, the weight of adsorbent was 0.5 g while for the experiment of *curve b*, the weight of adsorbent was 0.15 g

fast desorption of the small molecules corresponds to a fast increase in adsorption of the high molecular weight molecules. Nevertheless, the presence of the small macromolecules [9,900] at the huge relative number concentration, close to 40 in the supernatant, strongly perturbs the mechanism of the establishment of the polymer layer. Actually, at this moment, the layer is constituted by 5×10^{-9} and 1.5×10^{-9} mol/g Pyrex of large and small molecular weight molecules, respectively. Finally, after a period of 3,000 min, the adsorption of [9,900] slowly increases stepwise whereas the adsorption of [385,400] levels off while displaying strong variations with injection time. Polymers [9,900] and [385,400] may sustain concomitant relaxation but the desorption appears to affect polymer [385,400] at a greater extent than polymer [9,900]. Adsorption runs of the two polymers are engaged at the same time and one is lead to conclude that the two polymers continue to compete stepwise for the remaining free surface area, while the layer sustains adsorption and desorption runs.

Transitory adsorption/desorption processes

In our opinion, the stepwise increase in adsorption determined during establishment of the polymer layer on adsorbent initially dispersed in the polymer-free suspension (results of Figs.3, 4 and 5) and the oscillations in the surface coverage determined for layers characterised by a relatively stabilised adsorption (results of Figs. 6, 7 and 8) should be interpreted on slightly different bases.

In the first case, Fig. 4 clearly shows the adsorption to be an extremely slow process taking into account the very long period of contact between adsorbent and polymer solution. Only a fraction of the injected polymer is adsorbed. Additionally, due to the controlled injection of the polymer that slowly increases the bulk concentration, one expects that thermodynamic factors may exert the mass action effect. At the critical values A–F of the bulk concentration, the adsorption increases while the bulk concomitantly becomes impoverished (Fig. 3). Moreover, the gain in adsorption becomes amplified at higher critical bulk concentrations while the adsorption levels off as long as these critical concentrations are not successively established (Fig. 5). Clearly, each adsorption run displays the typical non-equilibrium adsorption with overshoot (Fig. 4).

In the second case, when at time zero of injection the polymer layer is partially established, the oscillations are connected with reconformation of adsorbed molecules that obviously induces overshoot effects (monodisperse systems). They are additionally connected with the particular characteristic of the layer (coexistence of molecules of small and high molecular weight) that amplifies the oscillations.

The controlled slow decrease in the bulk polymer concentration is expected to strongly slow down the already low rate of adsorption (as determined for the initially free surface in Fig. 4). Additionally, it is possible that the reconformation of adsorbed molecules succeeds in inverting the net interfacial transfer from the bulk to the surface at the critical concentrations A–D.

Origin of the stepwise adsorption

Since oscillations in the amount of polymer adsorbed were obtained for bulk concentrations that globally increase or decrease with injection time, the energy of the polymer adsorption should be very small. Then, the success of the encounter between polymer and adsorbent towards adsorption must be very uncertain. We have to note that in similar experiments, when the Pyrex was replaced by polystyrene sulphate latex, the adsorption was determined to be extremely fast since the injected polymer was instantaneously fully adsorbed up to a given surface coverage and the process was only slightly retarded thereafter [25]. This process could be modelled by the ''mobile'' adsorption process since adsorbed molecules remain able to diffuse within the adsorbent surface by taking advantage of the high density of negatively charged sulphate sites that exist on the latex surface [38]. The reconformation of isolated adsorbed molecules adsorbed on the latex particle was determined to increase the adsorbed area of the single macromolecule by a factor of 5 within 1,000 min [27]. Apparently, Pyrex develops a surface with lower adsorption affinities for the P2VP molecule in water at pH 3.0, certainly resulting from the high chemical stability of the borosilicate glass employed in industrial and laboratory processes (ASTM Glass Type I).The stepwise adsorption may originate from the history of the slow adsorption. According to the growing disc model, which was used to describe the kinetics and the final level of adsorption of poly(4-vinylpyridine) on latex particles when the rate of polymer supply was extremely low, the adsorbed molecules relax as long as no neighbour molecules interact with them [27]. At intermediary degrees of coverage, the extent of reconformation is lower and adapts to the available free area. For poly(4-vinylpyridine) adsorbed on latex particles, continuous in-plane diffusion of the molecules with various conformations rapidly produces an average molecular conformation. This averaging effect may be greatly delayed in the present situation. Possibly, P2VP molecules adsorbed on Pyrex maintain their respective position in the adsorbed state and the growing of the interfacial cross sectional area during reconformation develops around this position. The adsorption energy may be high when the macromolecule can be stabilised in the surface in a flat conformation. When the polymer-coated surface area progressively increases with injection time, the area

available to further adsorption decreases, and so does the extent of reconformation of the adsorbing molecules due to nearest neighbour interactions. The adsorption energy of these macromolecules should be smaller than that of flat adsorbed ones and, consequently, the chemical potential in the bulk has to be higher to maintain these molecules at the interface. Near total surface area coverage, the molecules have to experience a great number of attempts before adsorption succeeds, since the adsorption energy is extremely low when the molecule has to adsorb while maintaining its solution conformation. The adsorption of this class of polymers requires greater bulk concentrations. This interpretation of the origin of heterogeneity in adsorbed polymer layers was previously given for polymers adsorbing on highly attractive substrates [39]. The authors focus on the fact that the complex topologically mediated interactions lead to prohibitively long equilibration times and thus to kinetically frozen conformational states. One of their results is that the adaptive random sequential adsorption model exhibits inhomogeneity on multiple scales and finally produces Appolonian packing.

Therefore, one may affect particular conformations to macromolecules adsorbing at the different critical bulk concentrations of 0.035, 0.06, 0.075, 0.115, 0.16 and 0.20 mg/g Pyrex. Low bulk concentration only stabilises flat conformations (trains) whereas higher bulk concentrations are progressively able to stabilise conformations with loops, trains and tails. The relative portion of segments belonging to trains are smaller as soon as the critical bulk concentration shifts towards higher values.

The situation is not profoundly modified when the adsorption develops under globally decreasing bulk concentrations. Actually, the explored range of the bulk concentration (1.6–0.5 mg/g Pyrex as seen in Fig. 8) allowed the establishment of interface layer of higher density. Under these conditions, it is necessary to envisage that the rate of bulk to surface, and the inverse transfer, may be modified by the presence of the bulk molecules that also control the amplitude of the reconformation [33]. Actually, for the system polyvinylamine / silica/water, where the interaction between polyvinylamine and silica was determined to be of high affinity type, surface area exclusion chromatography has shown the extent of reconformation to be limited by $T \times C_{bulk}$, T being the duration of the contact between the layer and the polymer solution of concentration C_{bulk}.

Conclusion

The establishment of the P2VP layer on Pyrex glass beads [32, 36, 37] showed a certain complexity that motivated the present investigation on the adsorption of monodisperse and bidisperse polymer samples. To interpret the successive non-equilibrium adsorption runs evidenced when the polymer was slowly supplied to the adsorbent initially dispersed in water or in a polymer solution, we postulate that typical conformations of the adsorbed molecules emerge from all the possible conformations as a result of the reconformation affecting the adsorbed macromolecule and the topological influences on polymer adsorption. Obviously, adsorption and desorption runs are related to the stability characteristics of the adsorbed polymer molecule when the surface area available to adsorption decreases and the macromolecules have to adsorb while adopting progressively interfacial conformations approaching their solution conformation.

One may wonder at the generality of the observed phenomenon, especially when the pH and/or the ionic strength of the system are modified. We believe that the systems always behave similarly insofar as charge–charge interactions are present. In the present case, increasing the pH of the polyelectrolyte solution tends to decrease the linear charge density of the polymer backbone. Conversely, increasing the pH of the adsorbent suspension tends to increase the surface charge density of the Pyrex glass beads. On mixing polyelectrolyte and adsorbent systems, charge–charge interactions on confined systems may locally increase the linear charge density of the adsorbed polyelectrolyte [40]. Finally, adsorption of P2VP on Pyrex glass beads was determined to progress similarly from ethanol solutions where only Lewis acid/base interactions are operating [32, 41].

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