Surface Area Exclusion Chromatography of Diblock Copolymers from Micellar Solutions

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ABSTRACT: We present results of a study of chromatographic separation based on surface area exclusion induced by the irreversible adsorption of the diblock copolymer poly(vinylpyridine)-polystyrene on silica from toluene solutions using a radiolabeled polymer. This characteristic of the copolymer enabled the number of adsorbed copolymers to be determined as a function of the plate number inside the chromatographic column. We find that the initial step of the surface coverage may be simulated by the random sequential adsorption of a mixture of unimers (isolated copolymer) and micelles (structured form). The influences of the relative length of the two PV2P blocks and the concentration of the copolymer solution on the chromatogram were investigated by simulation and experimentally. The chromatograms showed that the surface area availability conditioned the copolymer distribution in the successive plates of the column, and a direct correlation between simulation and experiment could be found for a copolymer of size asymmetry ratio equal to 1. Deviation from this simple behavior was observed in other copolymers. Notably, the influence of the interfacial reconformation was investigated, and we found that the rate at which the process developed depended on the structure (unimer or micelle) of the adsorbed copolymer. Unimer and micelle adsorption was attributed to the existence of strong interactions between the pyridine group of the polymer and the silanol group of the silica.

Introduction

The adsorption of polymers from organized structures in solution onto solid-liquid interfaces constitutes a stimulating domain of investigation. One typical example is the diblock copolymer in selective solvent.[1] Renewed interest in this subject issues from the possibility of inducing the steric stabilization of colloids by a physical adsorption mechanism.[2] It is well known that homopolymers constitute quite efficient agents of colloid aggregation, either by screening the colloid surface charges or by a bridging mechanism.[3,4] We have previously determined that colloid stabilization in the presence of homopolymers constitutes a complex phenomenon.[5] The mode of action of the diblock copolymer in the steric protection of colloids is already evident in selective solvent at the molecular scale because one block of the polymer is protected against precipitation by the other chain segments in good solvent. This schema is valid in very dilute solutions, below the critical micellar concentration (cmc), where the diblock polymer chains are individually solubilized in the medium as unimers. It is also true above the cmc, where the central core of the micelles is solubilized by the corona of the chain segments in good solvent.[6] The protective action can be exerted by adsorbing the poorly soluble segments on the colloid surface and using the soluble moiety, which protrudes into the liquid phase, as a steric protection acting against colloid aggregation.[7] Maximal efficiency is obtained by using a diblock copolymer well designed for this objective. The adsorbing block should adsorb strongly and irreversibly on the colloid surface. Strong adsorption between the colloid and the chain segments may be promoted by hydrophobic or electrostatic attractive interactions while irreversibility may depend on the adsorption mechanism, as previously determined.[8] The interaction between the stabilizing moiety of the polymer and the colloid should however be refused. This situation may be easily verified by a study of the adsorptivity of the corresponding homopolymer on the same adsorbent, but modified by adsorption of the anchoring chains. This schema corresponds to the idealized situation which has been investigated theoretically.[9,10]

The objective of the present paper was to investigate the mode and the kinetics of the adsorption process of diblock copolymers of polystyrene and poly(2-vinylpyridine) in the concentration range above the cmc, where unimers and structured micelles are present in the solution at the same time. We have previously determined the mode and the rates of adsorption of the corresponding unimers on the same toluene-silica interface.[11] The kinetics of the adsorption of unimers from solutions below the cmc could be schematized by the random sequential adsorption model.[8] This relatively fast surface-filling process is followed by a very slow process for a very long period, so that the increase in the amount of polymer adsorbed was very large. We implemented a similar experimental procedure to characterize the polymer adsorption rate and mechanism from solutions above the cmc. The conclusion of this study was that both unimers and micelles adsorb onto silica from toluene solution.[12]

The adsorption of micelles appeared to be very questionable insofar as they constituted stable thermodynamic entities. The most general assumption used in the theoretical study of the adsorption kinetics was that the adsorption of the unimers induces a relaxation of the micelles, acting as a source of unimers, and that the micelle relaxation constituted the rate-limiting process in the unimer adsorption.[13-15] This assumption has been developed on the basis of experimental results indicating that micelle relaxation constituted a fast process.[16] This adsorption mechanism where micelle relaxation is required prior to adsorption seems to be too restrictive in light of recent results of Hong *et al.*[17] based on an investigation of the adsorption of similar diblock copolymers in toluene onto silver substrates using surface-enhanced Raman scattering. These authors concluded that micelles were initially adsorbed from solutions having concentrations above the cmc. Our experiments too invalidate these

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Table 1. Molecular Characteristics

code	M_w[a]	$M_{w,PS}$[a]	$M_{w,PV2P}$[a]	n_{PS}[b]	n_{PV2P}[b]	β_m[c]	β_s[d]
532	28000	22000	6000	211	57	65	33
552	113700	32700	81000	314	771	3.4	1.1
555	61900	18600	43300	179	412	3.0	1.1
569	184400	18400	166000	177	1581	1.9	0.5

[a] g/mol. [b] Polymerizationn index of the corresponding block. [c] Bulk size asymmetry ratio: $\beta_m = (n_{PS})^{0.6}/(n_{PV2P})^{0.33}$. [d] Surface size asymmetry ratio: $\beta_s = (n_{PS})^{0.6}/(n_{PV2P})^{0.5}$.

assumptions, at least for the adsorption of diblock copolymers of size asymmetry ratios close to 1.[12] In the present work, our experimental investigation of the adsorption of micelles was based on an unusual chromatographic technique, where adsorption and surface exclusion were expected to induce the separation of the constituents of the liquid phase being injected. The chromatograms were analyzed using the models issuing from simulation of the adsorption of a mixture of constituents of small and large sizes.

The problem of the polymer adsorption from solutions above the cmc, where unimers and micelles are present at the same time and at a relative concentration only as a function of the total polymer concentration, appeared to be similar to the deposit of a mixture of disks of two different sizes on a plane interface. On saturation of the plane area, the relative concentration of the adsorbed species should be different from the initial concentration and from the relative concentration of the nonadsorbed species. The separation is only obtained by size exclusion, which is amplified by the use of the chromatographic technique.

Experimental Section

1. **Materials.** The copolymers and the dissolution procedure in toluene are described in the companion paper.[12] The main characteristics are reproduced in Table 1. Ageing for 1 week was required to set the equilibrium characteristics after dissolution.

The chromatographic column is constituted of a calibrated glass syringe (Tacussel, Lyon) and the corresponding pistons, which are modified to be fitted with input and output apertures of 0.5 mm, allowing the polymer solution to be injected at one point and recovered at the other. Two "nonadsorbing" Teflon disks of large porosity are clamped close to the input piston inside the column to guarantee that the injected solution is homogeneously distributed among the third and successive adsorbing filters. Whatman glass fiber filters are used as adsorbents in the chromatographic experiments. The column is composed of a stack of 56 filters over a length of 8 cm. The column is initially carefully saturated with toluene, the corresponding void volume being equal to 0.77 mL. The effluent is collected at the output during elution with the solvent and the polymer solution. In each case, it is analyzed for radioactivity content using a liquid scintillation spectrometer (Tricarb Packard).

2. **Chromatography.** The concentration pulse method is used in our procedure. The experiment starts by injection of the solvent at a controlled rate. Then the solvent injection is stopped to give priority to the copolymer solution which is instantaneously injected at the same rate. The sustained flow of copolymer solution moves down the column, enabling the copolymer to be adsorbed onto the successive filters. When a given volume of solution is passed through the column, the polymer injection is stopped to give priority to the solvent injection. The amount of the injected copolymer is always smaller than the amount required to saturate the column.

The filters are successively taken out of the column with care, individually deposited into the glass vial, and counted for radioactivity content in the scintillation liquid. The radioactivity (cpm) is converted to the number of adsorbed copolymers. The chromatogram is obtained by plotting the adsorbed amount $N_{s,i}$ *vs* the filter number i.

Theoretical Section

1. **Excluded Area Effects and Surface Occupation.** We use a simple plate model to describe the solute partition between the solid and the liquid phases as long as the suspension or solution is flowing through the chromatographic column. The plate concept was introduced by Mayer and Tompkins[18] and later modified by Glueckauf.[19,20] In fact, in chromatographic columns consisting of stacks of beads or porous disks, the adsorbent is discontinuous while the flow of solution is continuous. In the initial model of Mayer and Tompkins, thermodynamic equilibrium was assumed to occur at each plate between the solute and the sorbed phases. Glueckauf considered the lack of equilibrium in the presence of fast rates of mass transfer through the column.

Taking into account the adsorption resulting from a Langmuirian process where adsorption and desorption contribute to establishing a thermodynamic equilibrium, one obtains that the ratio of the concentrations of the adsorbed $N_{s,i}$ and of the solute species N_i is related to the adsorption energy. In irreversible adsorption and in many reversible adsorption processes, as the solute remains a long time in the adsorbed state, the progress of the surface filling modifies the thermodynamic partition.

2. **Random Adsorption of Equal Disks.**[21-26] The purpose of this section is to given an equation expressing the solute distribution in the successive plates of the column when only one species of area πr^2 is injected. To simplify the model, we schematize the plate of the column by a plane of area S able to adsorb a number $N_{s,max}$ of solutes and the corresponding liquid phase by the number of solute N per area S of the adsorbent. Let $N_{n,i}$ denote the number of the constituents in the solution of the ith plate after n injections. Similarly, let $\Delta N_{ns,i}$ be the fraction adsorbed on the same plate at the same time. Taking into account the excluded area effect, by definition one has[11]

$$\Delta N_{ns,i} = K(N_{s,i}) N_{n,i} \tag{1}$$

where $K(N_{s,i})$ defines the probability of adsorption of one solute onto the plate i if $N_{s,i}$ solutes are previously adsorbed at random.

The corresponding curves of $K(N_{s,i})$ as a function of $N_{s,i}$ are represented in Figure 1 of ref 12; the captions of the coordinates $K(N_s)$ and N_s are simpler because the nonadsorbed constituent remained in the liquid phase (one unique plate) and contributed to increasing the concentration in the supernatant. In the present "experiments", the nonadsorbed constituent $N_{n,i}$ is transferred in the $(i+1)$th plate while the solute phase of the $(i-1)$th plate moves in front of the ith plate.

We note that the adsorption probability $K(N_{s,i})$ is only a function of the surface coverage, has a finite value even in the initial step of adsorption onto a bare surface, and decreases strongly as a function of the surface coverage. The problem of the rate of surface filling is beyond the scope of the present paper. Today, simulation seems to be unable to verify the scaling behavior of the rate of approach to the saturationn coverage. We note that the rate of coverage is determined here up to a relative surface filling of about 38% of the available area. Simulation indicates that the full coverage corresponds to 54.7% as previously found (jamming limit).

The total concentration $N_{s,i}$ of the adsorbed species in each plate i after n injections is obtained as follows:

$$N_{s,i} = \sum_n K(N_{s,i}) N_{n,i} \tag{2}$$

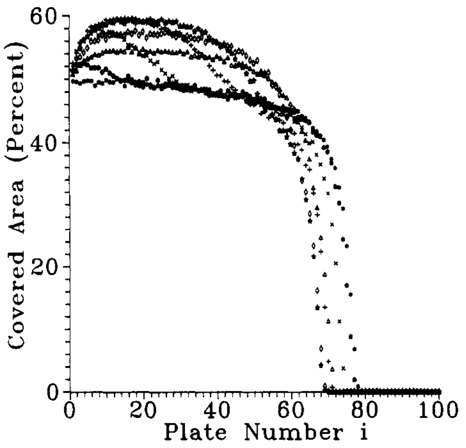

Figure 1. Simulation using the algorithm of the random sequential adsorption of disks of radii $r_1 = 1$ and $r_2 = 3$ on successive plates of the chromatographic column. Representation of the relative area covered with disks as a function of the plate number i for the different relative concentrations c_{rel}: 0.0 (*); 0.15 (○); 0.5 (×); 0.7 (+); 0.8 (◇); 0.9 (☆); 0.95 (△).

On the other hand, the solute concentration in the effluent is obtained similarly by $N_{n,i}$ for the last plate.

3. Random Adsorption of a Mixture of Disks of Two Different Radii. We are interested in generalizing this problem to a mixture of two monosized species of radii r_1 and r_2. The parameters of interest are their relative concentration $c_{rel} = c_1/(c_1 + c_2)$ and size $r_{rel} = r_1/r_2$. The two parameters c_{rel} and r_{rel} are thus expected to modify the adsorption profile in the column.

In simulation, the chromatographic column with 100 plates is schematized by 100 successive adsorbing square planes, each with an areal equal to 62 500. At each run, 500 disks are injected into the column, the different disks succeeding each other at random. For each plate i we determined (1) the total number $N_{s,i}(r_1+r_2)$ of adsorbed disks, (2) the number $N_{s,i}(r_1)$ of adsorbed disks of radius r_1, (3) the number $N_{s,i}(r_2)$ of adsorbed disks of radius r_2, and (4) the relative area occupied by the adsorbed disks. The number of runs was selected to obtain a surface coverage independent of the disk radius at the end of each simulation run.

The simulation comprised five successive situations. The radius r_1 of the small disk was chosen to be equal to 1 in each situation. The radius r_2 of the large disk was chosen to be 3, 4, 6, 7, and 10 successively to thoroughly investigate the influence of this parameter on the compactness of the disk packing. Different values of the relative concentration of species 1 and 2 were taken into account to determine the dependence of the shape of the chromatogram on the composition of the injected copolymer solution.

Results

1. Simulation. Figures 1–4 represent the percentage of the area of each plate i occupied by the adsorbed disks.

Figure 1 shows the chromatogram corresponding to the random deposition of disks of radii $r_1 = 1$ and $r_2 = 3$ for the different values of the relative concentration c_{rel}, 0.95, 0.90, 0.80, 0.70, 0.50, 0.15, and 0. For injection of disks of identical size, the chromatogram, independent of the size r, is characterized by a montonically and slowly decreasing curve which suddenly drops to zero between plates 70 and 80. The degree of surface coverage in plate 1, 0.500, is smaller than the expected value 0.547 of the jamming limit, indicating that the limiting coverage is not reached when 77 500 disks of radius $r = 3$ or 696 500 disks of radius $r =$ 1 attempted to adsorb into this first plate. The chromatograms are strongly modified in the presence of mixtures of disks of radii r_1 and r_2 and typically, the degree of coverage increases from plate 1 to a maximal value, a function of c_{rel}, and decreases thereafter in different ways. The maximal coverage, close to 0.6, is obtained for $c_{rel} = 0.70$.

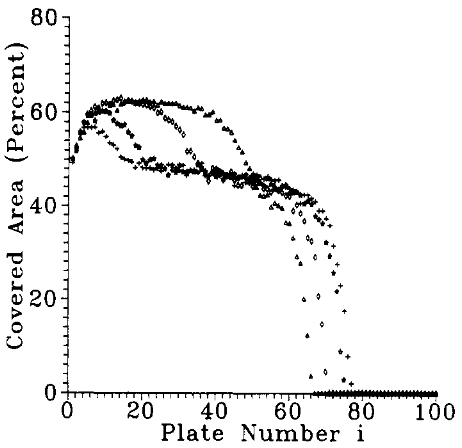

Figure 2. Simulation using the algorithm of the random sequential adsorption of disks of radii $r_1 = 1$ and $r_2 = 6$ on successive plates of the chromatographic column. Representation of the relative area covered with disks as a function of the plate number i for the different relative concentrations c_{rel}: 0.7 (+); 0.8 (☆); 0.9 (◇); 0.95 (△).

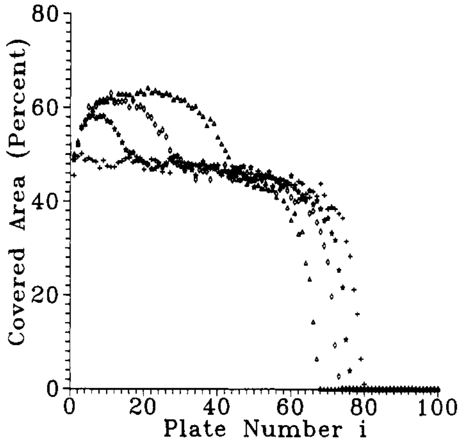

Figure 3. Simulation using the algorithm of the random sequential adsorption of disks of radii $r_1 = 1$ and $r_2 = 7$ on successive plates of the chromatographic column. Representation of the relative area covered with disks as a function of the plate number i for the different relative concentrations c_{rel}: 0.5 (+); 0.8 (☆); 0.9 (◇); 0.95 (△).

Figure 2 shows the chromatogram corresponding to the random deposition of disks of radii $r_1 = 1$ and $r_2 = 6$ for the different values of the relative concentration c_{rel}, 0.95, 0.90, 0.80, and 0.70. As in Figure 1, one observes that the degree of surface coverage in the first plates increases from 0.50 to 0.62 and decreases thereafter. A high plateau is seen for the larger values of c_{rel}, 0.95, 0.90, and 0.80, which disappears for 0.70.

Figure 3 shows the chromatogram corresponding to the random deposition of disks of radii $r_1 = 1$ and $r_2 = 7$ for the different values of the relative concentration c_{rel}, 0.95, 0.90, 0.80, and 0.50. Trends similar to those of Figure 2 are evidenced. Moreover, for $c_{rel} = 0.50$, the shape of the chromatogram is quite similar to that corresponding to the deposition of monosized disks.

Figure 4 shows the chromatogram corresponding to the random deposition of disks of radii $r_1 = 1$ and $r_2 = 10$ for

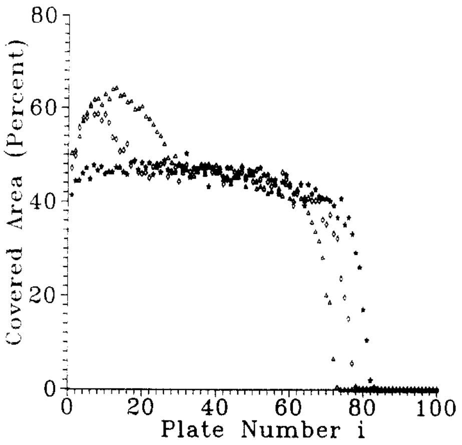

Figure 4. Simulation using the algorithm of the random sequential adsorption of disks of radii $r_1 = 1$ and $r_2 = 10$ on successive plates of the chromatographic column. Representation of the relative area covered with disks as a function of the plate number i for the different relative concentrations c_{rel}: 0.5 (☆); 0.9 (◇); 0.95 (△).

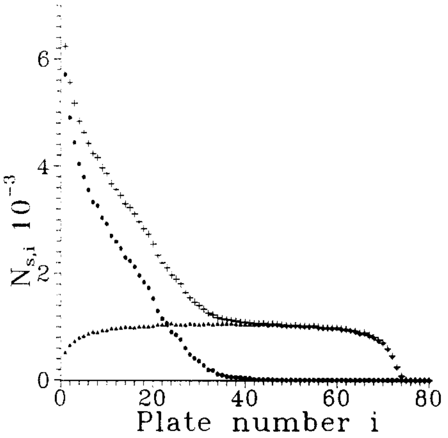

Figure 5. Simulation using the algorithm of the random sequential adsorption of disks of radii $r_1 = 1$ and $r_2 = 3$ on successive plates of the chromatographic column. Representation of the number $N_{s,i}$ deposited on each of the successive plates as a function of the plate number i for the relative concentration c_{rel} equal to 0.5: total number of disks (+); number of disks of radius 1 (●); number of disks of radius 3 (▲).

the different values of the relative concentration c_{rel}, 0.95, 0.90, and 0.50. The maximal coverage, close to 0.65, is obtained for $c_{rel} = 0.95$. For the experiment carried out for $c_{rel} = 0.50$, the degree of coverage in the first plates is close to 0.40, indicating that the disks of small radius exclude about 10% of the surface available to the coverage in the case of the deposition of monosized disks.

It is important to note that small differences in the composition of the injected mixture lead to very different chromatograms. The low plateau of the degree of coverage in the domain 0.45–0.40 corresponds to the sole deposition of disks of radius r_2, indicating that coverage higher than 0.5 results from the deposition of the small disks in the free area portions available between the area occupied by the large disks. Figure 5 shows this particular behavior resulting from the surface exclusion on adsorption chromatography of an equal mixture of disks of radii 1 and 3. The relatively large coverage of the first plates by the disks of size 1 induced a lower degree of coverage by disks of size 3.

2. Experiments. The influence of the following parameters on the chromatogram has been determined to assess the information resulting from the different particular shapes experimentally determined.

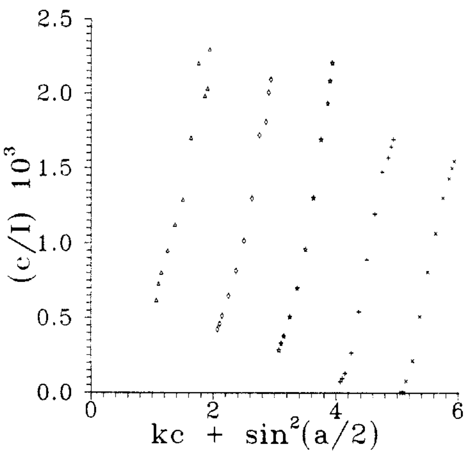

Figure 6. Zimm plot. Light scattering experiments for micellar solutions of copolymer 552 at concentrations increasing from 10^{-9} to 4×10^{-8} mol/mL.

Table 2. Solution Characteristics: Relative Concentration of Unimers for Different Degrees of Micellization *m*

concn (mol/mL)	$m = 10$ c_{rel}	$m = 100$ c_{rel}
7.5×10^{-11}	1	1
1.0×10^{-10}	1	1
1.5×10^{-10}	0.95	0.99
2.5×10^{-10}	0.87	0.98
3.5×10^{-10}	0.80	0.97
7.5×10^{-10}	0.61	0.92
1.0×10^{-9}	0.52	0.90
1.5×10^{-9}	0.42	0.85
1.0×10^{-8}	0.09	0.45

Ageing of the Copolymer Solution. Experiments carried out by injecting nonaged copolymer solutions showed poor reproducibility in the chromatograms. We assumed that these artifacts resulted from the presence of micelles and/or aggregates of very large molecular weight existing when the solution is freshly prepared. Static light scattering measurements were carried out on aged copolymer solutions (5–8 days) above the cmc to determine the molecular weight of the micelles. The corresponding Zimm plot is given in Figure 6 for copolymer 552 [314–771]. It is noteworthy that the Zimm plot is characteristic of a macromolecular system in poor solvent, as evidenced by the negative value of the second virial coefficient. The shape of the angular variation of the scattered intensity is characteristic of that of interacting spheres[27] and confirms the spherical structure of this class of micelles. The mean degree of micellization was determined to be of the order of 10. To facilitate the discussion of the experimental results, the correlation between the copolymer concentration and the relative concentration of micelles in terms of c_{rel} is given in Table 2 for the degree of micellization equal to 10 as well as for the value 100 estimated by Sikora and Tuzar for the same copolymer.[28]

Volume of the Elutant. The shape of the chromatogram was found to be independent of the solvent volume used as elutant. This characteristic is valid for a copolymer with a large anchoring block (166 000 for copolymer 569) as well as for one with the smallest block (6000 for copolymer 532). In addition to the mechanism of the adsorption shown previously,[12] these experiments clearly indicate the irreversible nature of this adsorption. It has to be related to the flat structure adopted by the PV2P block on the adsorbent surface.

Rate of Injection of the Copolymer Solution. Experiments carried out with different rates of injection of the same copolymer solution at the cmc showed that the linear

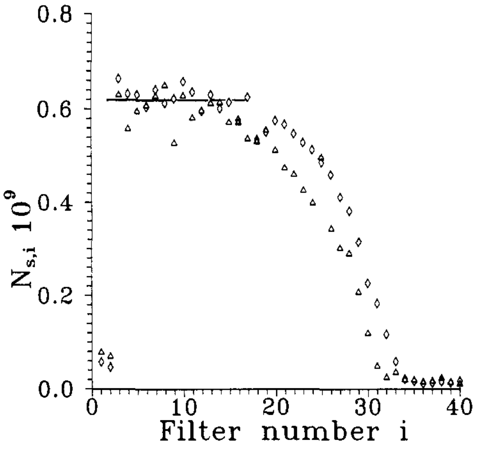

Figure 7. Chromatograms obtained with copolymer 532 [211–57]. Injection of 1.7×10^{-8} mol during 6 min from a solution of concentration equal to 2.02×10^{-9} mol/mL (◇); injection of 1.45 $\times 10^{-8}$ mol during 36 s from a solution of concentration equal to 1.92×10^{-8} mol/mL (△).

velocity of the macromolecules in the porous medium did not influence the chromatogram. The macromolecules adsorbed as if the adsorption were only controlled by the excluded area per plate, as already demonstrated in ref 12, the hydrodynamic characteristics of the transport probably exerting a very minor influence on the macromolecule deposition process.

Two sets of experiments were carried out above the cmc (10 × (cmc) and 20 × (cmc)) with copolymers 552 [314–771] and 555 [179–412] by varying only the rate of the solution injection by a factor of 10. Each experiment was repeated five times and all of the corresponding chromatograms were found to be superimposed. The fact that the chromatograms obtained from micellar solutions are also insensitive to the period of injection—1.5–15 min was experienced–apparently implies two conflicting assumptions. First, the micelle relaxation leading to the expulsion of unimers is a very fast process,[14,15] which, however, contradicts the previous results.[12] Second, the relaxation time is very long and unimers and micelles are above to interact individually with the adsorbent. This assertion seems to be valid because the total radioactivity which is collected in the effluent only represents 1% of the injected radioactivity. The radioactivity passing through the column may possibly result from the presence of very small polymer-covered filter fragments migrating through the column and which are recovered in the effluent. Another explanation is that a small portion of copolymers displays such a structural conformation that interaction with the adsorbent is continuously disabled.

Total Number of Copolymers Adsorbed. From experiments carried out at and above the cmc, for increasing total amounts of the adsorbed copolymer 552 [314–771], we determined that in the range (1–2.5) $\times 10^{-9}$ mol adsorbed, the chromatogram tended toward a well-charactrized shape only as a function of the injected copolymer concentration.

A. Chromatogram Obtained with Copolymer 532 [211–57]. Light scattering measurements show that this copolymer did not form structured micelles in the concentration domain between 1.0×10^{-9} and 2.0×10^{-8} mol. Figure 7 presents two chromatograms. One is obtained by injecting 1.7×10^{-8} mol for 6.25 min from a solution of concentration equal to 2.02×10^{-9} mol/mL. The second is obtained by injecting 1.45×10^{-8} mol for 36 s from a solution of concentration equal to 1.92×10^{-8} mol. The filling of the first 20 filters does not depend on the concentration, and a true plateau is formed. The limiting coverage is close to 6.5×10^{-10} mol.

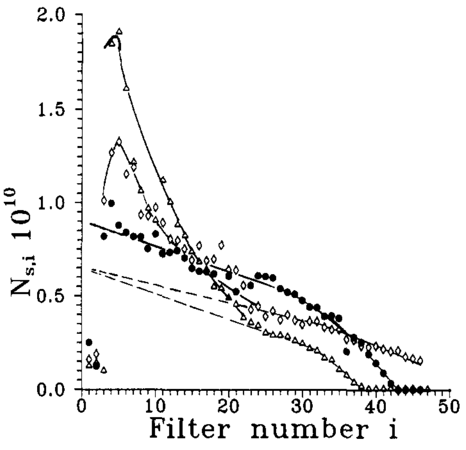

Figure 8. Chromatograms obtained with copolymer 569 [117–1581]. Injection of 2.6×10^{-9} mol from a solution of concentration equal to 1.0×10^{-10} mol/mL (◇), from a solution of concentration equal to 1.18×10^{-9} mol/mL (△), and from a solution of concentration equal to 1.018×10^{-8} mol/mL (◇).

B. Manifestation of the Interfacial Reconformation of the Adsorbed Copolymer with Copolymer 569 [177–1581]. Figure 8 shows the number of adsorbed copolymers per plate $N_{s,i}$ as a function of the filter number i. In each experiment, the total number of adsorbed copolymers was equal to 2.6×10^{-9} mol. When the concentration of the injected solution is equal to the cmc, the first adsorbing filter retains 0.9×10^{-10} mol and the adsorption as a function of the filter number displays the usual variation. In a second experiment, the solution at a concentration of 1.18×10^{-9} mol/mL was injected for 13.5 min. The corresponding variation of the amount adsorbed per plate decreases strongly down to a plateau which can be extrapolated to a value close to 0.65×10^{-10} mol. In a third experiment, the solution at a concentration of 1.018×10^{-8} mol/mL was injected for 9 s. The chromatogram displays the same behavior and the plateau can also be extrapolated to the same value of 0.65×10^{-10} mol. As evidenced by the simulation, the coverage in the lower plateaus is indicative of the surface area occupied by the micelles. These experiments show that the adsorbed micelles of copolymer 569 undergo interfacial reconformation while being adsorbed.

C. Influence of the Concentration of the Injected Solution Investigated Using Copolymer 552 [314–771]. Figures 9–12 shows the number of adsorbed copolymers $N_{s,i}$ as a function of the filter number i.

Figure 9 shows the chromatograms obtained by injecting a solution of concentration 1.1×10^{-10} mol/mL (cmc) at a rate of 1.5 mL/min (1.6 mol/min) for 8 min. The total number of adsorbed macromolecules inside the column was equal to 1.10×10^{-9} mol. Three identical experiments are presented to qualify the reproducibility of the experiments. The adsorption in the first adsorbing filter (filter no. 3) was close to 0.75×10^{-10} mol. A value of 0.755×10^{-10} mol was determined from the batch experiment, where the filter was immersed in the same solution for 40 h.

Figure 10 shows the chromatograms obtained by injecting a solution of concentration 2.5×10^{-10} mol/mL (2.5 × (cmc)) at a rate of 0.6 mL/min (1.5×10^{-10} mol/min) for 8 min. The total number of adsorbed macromolecules inside the column was equal to 1.13×10^{-9} mol.

Figure 11 shows the chromatograms obtained by injecting a solution of concentration 1.01×10^{-9} mol/mL (10 ×

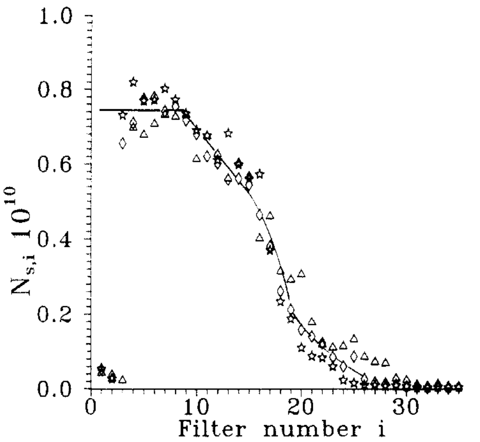

Figure 9. Chromatograms obtained with copolymers 552 [314–771]. Injection of 1.1×10^{-9} mol from a solution of concentration equal to 1.0×10^{-10} mol/mL at a rate of 1.5 mL/min (1.6×10^{-10} mol/min); three similar experiments.

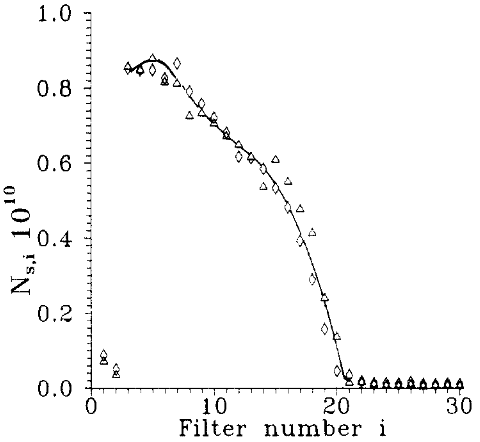

Figure 10. Chromatograms obtained with copolymer 552 [314–771]. Injection of 1.13×10^{-9} mol from a solution of concentration equal to 2.5×10^{-10} mol/mL at a rate of 0.6 mL/min (1.5×10^{-10} mol/min); two similar experiments.

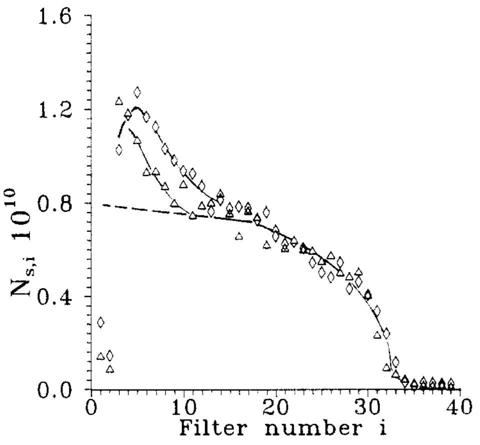

Figure 11. Chromatograms obtained with copolymer 552 [314–771]. Injection of 2.3×10^{-9} mol from a solution of concentration equal to 1.01×10^{-9} mol/mL at a rate of 1.5 mL/min (1.52×10^{-9} mol/min) (△) and at a rate of 0.15 mL/min (1.52×10^{-10} mol/min) (◇).

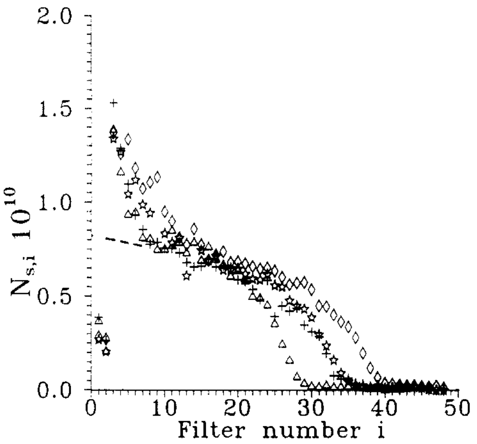

Figure 12. Chromatograms obtained with copolymer 552 [314–771]. Injection of different amounts (between 1.85×10^{-9} and 2.65×10^{-9} mol) from a solution of concentration equal to 9.5×10^{-9} mol/mL at a rate of 1.5 mL/min (1.42×10^{-8} mol/min) (△,◇,☆) and at a rate of 0.15 mL/min (1.42×10^{-9} mol/min) (+). For (☆) and (+) the amount injected was identical.

(cmc)) at a rate of 1.5 mL/min (1.5×10^{-10} mol/min) for 1.5 min and 0.15 mL/min (1.5×10^{-10} mol/min) for 16.5 min. The total number of adsorbed macromolecules inside the column was equal to 2.3×10^{-9} mol. The number of adsorbed moles in the first adsorbing filter was close to 1.3×10^{-10} mol. A value of 2.45×10^{-10} mol was determined from the batch experiment, where the filter was immersed in the same solution for 40 h. This indicates that the interfacial layer composed of adsorbed unimers and micelles undergo a considerable structural reconformation allowing the adsorption to progress with time for periods longer than 2 h. We note that the lower plateau may be extrapolated to a value close to 0.8×10^{-10} mol.

Figure 12 shows the chromatograms obtained by injecting a solution of concentration 9.5×10^{-9} mol/mL (95 × (cmc)) at different rates but at a constant rate of polymer supply equal to 1.42×10^{-8} mol/min for periods of 10 s to 1.75 min. The total number of adsorbed macromolecules inside the column ranges from 1.85×10^{-9} to 2.65×10^{-9} mol. The number of adsorbed moles in the first adsorbing filter is close to 1.5×10^{-10} mol. We note that, like in Figure 9, the lower plateau may be extrapolated to a value close to 0.8×10^{-10} mol. This result shows that this copolymer does not display reconformation when the solution is injected for short periods of time.

Discussion

1. Equivalence between the Covered Area and the Number of Adsorbed Moles. The comparison between the size asymmetry ratios of the different copolymers leads to the conclusion that the surface coverage with the PV2P block of the copolymer 552 (ratio = 1.13) should not be inhibited by the presence of the PS dangling chain. This assumption seems not to be valid for copolymer 532, which is characterized by a larger size asymmetry ratio 3.3. We calculate that the number of adsorbed PV2P chain segments in the first adsorbing filter is equal to 6.2×10^{-8} for copolymers 552 and equal to 3.7×10^{-8} for copolymer 532. For copolymer 569, the situation is very different if we consider the adsorption of the unimers, or that of the micelles, and the chromatogram should be interpreted in light of the results shown in Figure 5. The unimer adsorption in the first plate is equal to 0.9×10^{-10} mol, equivalent to the adsorption of 14.2×10^{-8} chain segments, while the similar coverage formed by the micelle adsorption (0.65×10^{-10} mol) corresponds to 10.2×10^{-8} chain segments. These results demonstrate the complexity of the adsorption process in the two situations where, on the one hand, the anchoring PV2P block is relatively large and, on the other hand, where the dangling PS chain is the largest block.

However, from Figures 9–12, we determined that copolymer 552 displays a particular behavior: the extrapolated value of the coverage in the plateau is the same for the unimers as for the micelles. This leads us to the important conclusion that, for copolymer 552, the chain segments occupy an equal area irrespective of their structure (unimer or micelle) in the adsorbed state. Thus, we can adopt the simulation model to interpret the experimental chromatogram. In simulation, the area occupied by a micelle of radius r_2 represents r_2^2 times that of the unimer. In the experiment, the micelle constituted of n unimers occupies n times the area of one unimer. Insofar as the adsorbed unimer is represented by a disk of radius equal to 1, the micelle of average size equal to 9 is simulated by a disk of radius equal to 3. This result constitutes the basis of the discussion relative to the results shown in Figure 8–12 in light of the simulation results shown in Figures 1–4.

2. Surface Exclusion in the Chromatography of a Mixture of Disks. Figures 1–4 show that the surface area exclusion provoked by the progress of the copolymer adsorption gives rise to chromatograms of very different shapes. To open discussion of the experimental results and to determine the optimal conditions potentially leading to the separation of the unimers and micelles, we first interpret typical chromatograms resulting from simulation.

For a mixture of disks of radii 1 and 3, as indicated in Figure 1, a quantitative separation is obtained by the injection of mixtures of relative concentration smaller than 0.15. These conditions favor the deposition of the small disks in the first 20 plates, the large ones being slightly excluded from these portions of the column and essentially occupying the plates numbered from 20 to 70. For an equal mixture of the two disks, the chromatographic separation is of poorer quality. The small disks adsorb from plates 1 to 40, while the large ones occupy the full column, mainly from plates 10 to 70.

For the other systems involving larger disks (1 and 7 as well as 1 and 10), Figures 3 and 4 show that the chromatograms determined for the separation of an equal mixture of the small and large disks do not present a particular shape. We note that, especially for the largest disk, the coverage is relatively smaller in the first plates. In fact, the disappearance of the chromatographic peak is indicative of the optimal separation conditions. The relative surface occupation of each plate by the small and the large disks (not represented) clearly indicates that the small disks occupy the first 10–15 plates only and exclude the large disks from these plates. When c_{rel} increases, the chromatographic peaks of the surface area occupation are formed and the quality of separation decreases as c_{rel} increases.

This study particularly points out that the chromatograms strongly depend on the relative sizes and concentrations of the unimers and micelles in the copolymer solution. The preliminary determination of the degree of micellization and the interfacial area occupied by the unimers and the micelles is essential in the following analysis of the chromatograms.

3. Surface Exclusion in the Chromatography of Micellar Solutions. Taking into account the correspondence between the copolymer concentration and the parameter c_{rel} given in Table 2, we have to discuss the four following situations:

(i) $c_{rel} = 1.0$: The result of Figure 1 representing the surface filling with monosized disks applies to the chromatogram of Figure 9. One third of the plateaus (or filters) are equally covered near the maximal value of 50%. In the second portion, the coverage slowly decreases and in the last portion, the coverage rapidly drops to zero.

(ii) $c_{rel} = 0.87$: From the curve corresponding to $c_{rel} = 0.9$ in Figure 1, the maximal coverage is expected to be larger than in the previous case. A valid comparison may be made between the experimental chromatogram shown in Figure 10 and that of the simulation.

(iii) $c_{rel} = 0.52$: The experimental chromatogram given in Figure 11 presents a good similarity with the curve corresponding to $c_{rel} = 0.50$ in Figure 1. The deviation from the adsorption behavior of monosized disks is in fact observed in the first half of the chromatogram in the simulation and in the experiment.

(iv) $c_{rel} = 0.09$: The experimental chromatogram is given in Figure 12 and has to be compared with the chromatogram in Figure 1 for $c_{rel} = 0.15$, which displays a typical deviation in the initial portion of the "column". We observe that the pseudoplateau is well developed in the simulation and in the experiment.

The choice of the degree of micellization equal to 9 and of the order of the values determined by light scattering measurements ensures that the experimental chromatograms and the simulation data are consistent. Consideration of the larger values of 36, 47, and 100 leads to a strong discrepancy.

Summary

We have demonstrated that unimers and micelles of the copolymers PS–PV2P irreversibly adsorb onto silica surfaces from toluene solutions by taking advantage of the fact that (i) the random sequential adsorption model enables the adsorption process to be schematized from a kinetic point of view, at least in the domain of relatively low coverage, and (ii) surface exclusion chromatography enables the two constituents to be separated by adsorption onto successive plates. From the irreversible nature of the interaction between the pyridine group of the anchoring block and the silanol group of the adsorbent, we conclude that, in the more general situation, the interfacial layer may be strongly inhomogeneous, insofar as the kinetics of the structural relaxation of the anchoring block of the unimers and the micelles may be extremely different as a function of the size asymmetry ratio of the copolymer.

We are aware that our simulation of the copolymer adsorption mechanism is valid for schematizing only the initial surface coverage and the interfacial behavior for short periods. Interfacial reconformation of the anchored block during the chromatographic separation is not taken into account. Neither is the simulation valid for describing the adsorption when bulky dangling chains limit the progress of the adsorption.

The determination of the number of copolymers adsorbed below the cmc and from micellar solution after very long periods of contact between the solution and the adsorbent showed that the adsorption increased slowly but continuously,[11,29] the rate being limited by the quasi-irreversibility of the initial adsorption step.[30] This study evidenced that the initial formation of the polymeric layer involves unimers and micelles, adsorbing onto the adsorbent surface randomly and quite irreversibly.

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