Studies on the Effect of Particle Size and Copolymer Polydispersity on the Adsorption of a PEO/PPO/PEO Copolymer on PS Latex Particles

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ABSTRACT: A commercial block copolymer poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) sold under the trade name of Pluronic F108 was adsorbed on polystyrene (PS) latex particles. The adsorption isotherm of the copolymer on the PS latex particles was measured using an indirect method (colorimetric depletion). Factors such as the diameter and the concentration of the PS latex particles as well as the concentration of the copolymer were investigated. The presence of a copolymer fraction with a small molecular weight in the F108 copolymer modified significantly the adsorption isotherms: a slanted linear domain appeared in the intermediate range of copolymer concentration. This change was in accordance with the predictions of previously described models. Contrary to previous findings, there was no apparent effect of particle size on F108 surface density and layer thickness. This result was confirmed by measurements performed with a direct method (sedimentation field-flow fractionation). However, the initial slope of the adsorption isotherm was increased by an increase of particle size and a decrase of particle concentration. Moreover, the maximum adsorbed amount was decreased by an increase of particle concentration. The latter observations are believed to be due to particle aggregation.

Introduction

The use of polymer adsorbates to stabilize colloidal dispersions has been the subject of numerous studies. However, relatively little attention has been paid to the effect of particle curvature on adsorption characteristics. Several studies suggest indeed that the size of particles may be of importance in their adsorption properties. In studies done on the adsorption of triblock copolymers made of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) on polystyrene (PS) latex particles, Li et al.[1,2] and Baker et al.[3] observed that the layer thickness of PEO/PPO/PEO copolymers increased with increasing particle sizes. Using the same system, Tan and coworkers[4,5] observed a decrease of layer thickness with an increase of particle size but then demonstrated with Li and Caldwell[6] that such an effect was due to flocculation and that the opposite result was found. Faers and Luckham[7] observed no particle size effect on the copolymer adlayer thickness. The results relative to the copolymer surface density are also rather contradictory. Both Faers and Luckham[7] and Baker et al.[3] did not notice any change of copolymer surface density with particle size, contrary to Li et al.,[1,2] who saw a 2-fold increase with particle size. In a different chemical system (e.g., poly(vinyl alcohol) (PVA) adsorbed on PS latex particles), Ahmed et al.[8] and Garvey et al.[9] measured an increase of the PVA layer thickness vs particle size. For end-functionalized polystyrene adsorbed on colloidal silica beads on Al-coated silicon substrates, Singh et al.[10] measured a decrease of surface coverage with increasing particle size. According to the theoretical studies of Wijmans et al.,[11] Dan and Tirrell,[12] and Biver et al.,[13] curvature effects are only important if the radius of curvature of the substrate is of the same order of magnitude as the adsorbed layer thickness. In the latter case, these authors predicted an increase of adlayer thickness with increasing particle size. Wijmans et al.[11] predicted a decrease of surface density with increasing particle sizes, but the effect was also restricted to small particle sizes compared with the adlayer thickness. Considering the diversity in the experimental results presented in the literature and discrepancies between the latter results and theoretical predictions, a systematic and extensive study of the effect of particle size on polymer adsorption was undertaken to try to reconcile the various findings.

Table 1. Listing of the Particles Used in This Study

nominal size [nm]	PCS size [nm]	SedFFF size [nm]	manufacturer
52	61.1 ± 0.4		Bangs
70	76.5 ± 1.2		Bangs
90	79.3 ± 0.5		Seradyn
98	117.2 ± 0.6		Bangs
127	136.2 ± 0.8		Bangs
130	149.3 ± 1.0[a]	150.0 ± 0.0	Seradyn
165	167.9 ± 1.2[a]	168.5 ± 0.4	Bangs
214	212.7 ± 1.3[a]	214.4 ± 0.2	Bangs
252	251.6 ± 1.7[a]	251.5 ± 0.4	Seradyn
261	264.6 ± 1.4[a]	267.0 ± 0.6	Seradyn
270	270.1 ± 1.6[a]	273.0 ± 0.3	Bangs
314	348.1 ± 2.0[a]	351.7 ± 1.5	Bangs
360	357.8 ± 2.4[a]	355.2 ± 1.3	Bangs

[a] These samples were first filtered by SedFFF.

A PEO−PPO−PEO triblock copolymer sold under the trade name Pluronic F108 and PS latex particles (Table 1) ranging in size from 60 to 360 nm are used for this investigation. PS latex particles are useful as model substrates because they have a broad range of uniform particle sizes and have well-characterized properties. PEO−PPO−PEO triblock copolymers possess a high

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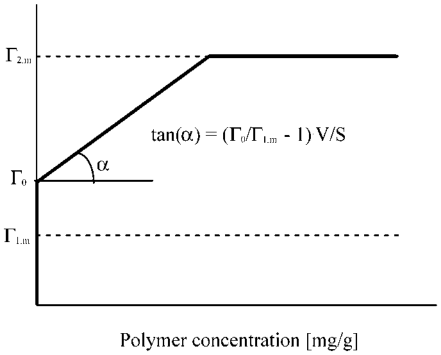

Figure 1. Cohen-Stuart's model. The dashed lines correspond to the (square) adsorption isotherm of the two polymer fractions, whose maxima are $\Gamma_{1,m}$ (small molecular weight) and $\Gamma_{2,m}$ (large molecular weight). The plain line corresponds to the adsorption isotherm of the polymer mix. V is the volume of solution, and S is the surface area of the adsorbing particles. $\Gamma_0 = (w_1/\Gamma_{1,m} + w_2/\Gamma_{2,m})^{-1}$, where w_1 and w_2 are the weight fraction of the small and large molecular weight fraction, respectively.

chemical and thermal stability and have generated considerable interest in biotechnology and medical applications due to their low toxicity and lack of immunogenic activity.[2] For example, Illum et al.[14] and Tan et al.[15] have shown that the lifetime of polystyrene (PS) latex particles injected into the bloodstream of rabbits and rats could be increased from a few dozens of minutes to a few dozens of hours by coating them with PEO−PPO−PEO copolymers. PEO−PPO−PEO copolymers have therefore a great potential for use in conjunction with slow release drug delivery systems.

One identified source of confusion related to the adsorption of the copolymer Pluronic F108 used in this study is the fact that this product is not monodisperse but bidisperse (see below). Several studies indicate that the adsorption characteristics of polymers in solution may vary a lot depending on their molecular weight.[16−24] It is for example known that large homopolymers adsorb preferentially over smaller ones.[16,17] For diblock copolymers, where adsorption occurs via a short-chain end, the opposite behavior is observed: long chains are replaced by short chains.[20−24] As a result, the shape of an adsorption isotherm obtained with a polydisperse polymer can be very different from that of a monodisperse polymer. Cohen-Stuart et al.[18] proposed a model predicting isotherms for an arbitrary molecular weight distribution, provided the dependency of the plateau adsorbance on molecular weight is known. They compared this model with experimental data obtained with poly(vinylpyrrolidone) adsorbed on silica particles and showed good agreement. Other experimental evidence was given by Hlady et al.,[19] who studied the adsorption of dextran on silver iodide particles. Again, a good agreement between theory and experimental results was observed.

The model of Cohen-Stuart contains two basic assumptions: (1) large molecules adsorb preferentially over smaller ones, and (2) all the polymer adsorption isotherms are square, i.e., have an infinite slope below the plateau region. Therefore, the adsorption isotherm of a polymer containing a mixture of two monodisperse fractions is composed of three line segments: one vertical and one horizontal line linked by a slanted line (Figure 1). The plateau value corresponds to that of the large molecular weight polymer fraction, $\Gamma_{2,m}$. The slanted-line area corresponds to the zone where small molecular weight polymers are displaced by large molecular weight polymers. The slope of the slanted line depends on the ratio V/S, where V is the volume of solution and S is the area of the adsorbing surface. Therefore, the shape of the adsorption isotherm is expected to depend on the particle concentration in solution. To negate this concentration effect, the adsorption isotherm is expressed as a function of the surface normalized concentration of unadsorbed polymer (concentration divided by S/V).

The first assumption of the Cohen-Stuart model is valid for homopolymers. For block copolymers, the situation may be different. For example, if the two block copolymers adsorb via a strong anchoring block of identical length (like PPO in F108), the block copolymer with the shortest nonadsorbing side chain is expected to displace the block copolymer with the longest nonadsorbing side chain.[20,22,24] As a result, the plateau value of the adsorption isotherm of the mixture is not equal to the plateau value of the adsorption isotherm of the long-chain polymer fraction, as in Figure 1, but to that of the short-chain polymer fraction. Here, the nature of the short-chain polymer fraction is not known (see also below). GPC measurements showed that the low-molecular-weight fraction has almost the same molecular weight as the PEO block. Therefore, it was assumed that the low-molecular-weight fraction of the F108 mixture consisted of PEO, i.e., the nonadsorbing or poorly adsorbing polymer fraction. As a result, the Cohen-Stuart model was used to analyze the adsorption isotherms of Pluronic F108 on latex particles.

Experimental Section

1. Materials. Pluronic F108 was provided by BASF Corp (No. 583062, Lot No. WP10-549B). F108 is a triblock copolymer PEO−PPO−PEO. The nominal molecular weights of PEO and PPO are 5.68 and 3.25 kDa, respectively, for a total molecular weight of approximately 14.6 kDa. The sizes of the three constitutive blocks are 129−56−129 repeat units, respectively. The F108 molecular weight distribution was measured by gel permeation chromatography (GPC), using a liquid chromatography controller LCC-500 linked to two P-500 pumps and one peristaltic pump P-1 (all devices from Pharmacia, Sweden). The column Superose 12 was purchased from Pharmacia (No. 17-0538-01) and is suitable for molecular weights in the range 1−300 kDa. Sodium azide (NaN_3; Sigma No. S-2002, Lot No. 43H0291), TRIZMA base (Sigma No. 1503, Lot No. 64H5767), and sodium chloride (Mallinckrodt AR No. 7581, Lot No. 7581KMJC) were used to prepare the elution buffer (0.05 M TRIS + 0.5 M NaCl; pH adjusted to 8.0 with concentrated HCl). The refractive index of the eluting solution was measured with a differential refractometer (Knauer). The GPC chromatogram for the F108 copolymer is shown in Figure 2. F108 is made of two fractions with the following molecular weights: 13.7 ± 0.1 and 6.1 ± 0.1 kDa. These values were determined using a calibration curve, based on PEO standards, and three chromatograms. The largest molecular weight is slightly lower than the value given by BASF for F108 (14.6 kDa); meanwhile, the second fraction has a molecular weight slightly larger than the molecular weight of the PEO block indicated by BASF (5.68 kDa). Assuming that both fractions are monodisperse and that the molar refractive index is proportional to molecular weight, the molar fraction of the small component can be roughly estimated using the area under both peaks. This gives a value of 42%. An infrared spectrophotometer was used to identify the different molecular weight fractions collected by GPC. The FTIR spectra of the collected fractions were compared to methoxypoly(ethylene glycol) (Sigma No. M-7268, Lot No. 66F-0296) and poly(propylene glycol) (Aldrich No. 20′235-5, Lot No. 07025BG) spectra. However, the results were inconclusive. A certain

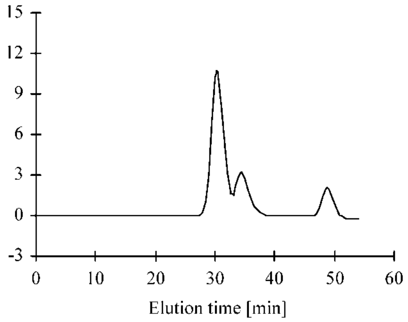

Figure 2. F108 GPC chromatogram. The largest and the smallest fraction (left peaks) have a molecular weight of 13700 ± 100 and 6100 ± 100 Da, respectively. This has been determined using the calibration curve: $\log(M_w) = 6.67 - 0.0839t$ (t = elution time; $r^2 = 0.993$). The right peak corresponds to the solvent.

Table 2. Conditions Used To Centrifuge the Sols Containing the Coated Latex Particles

nominal size [nm]	centrifugation acceleration [*g*]	duration [min]	nominal size [nm]	centrifugation acceleration [*g*]	duration [min]
52[a]	138 000	60	165[b]	16 000	150
69[a]	138 000	60	214[b]	16 000	90
70[a]	138 000	30	252[b]	16 000	60
90[a]	138 000	15	261[b]	16 000	60
98[a]	138 000	15	270[b]	16 000	60
127[b]	16 000	180	314[b]	16 000	45
130[b]	16 000	180	360[b]	16 000	45

[a] Beckman TL-100 ultracentrifuge. Centrifuge tubes in polyallomer purchased from Beckman (No. 347′357, Lot No. P5 O2 20, 11 × 34 mm). [b] Eppendorf 5415C centrifuge.

amount of the two F108 fractions was collected by GPC. The monodispersity of these two fractions was checked by GPC using the same conditions as those used for the collection except for the higher sensitivity of the differential refractometer. The F108 fractions were dialyzed with a polymer membrane Spectra/Por 7 purchased from Spectrum (No. 132′104, M_w = 1 kDa) and used for adsorption experiments under the names of "small F108 component" and "large F108 component".

The latex particles were purchased from Bangs Laboratories and Seradyn (Table 1). Their size was measured by photon correlation spectroscopy (PCS) and sedimentation field-flow fractionation (SedFFF).[1] The measurements were done in FL-70 solution (1 mL/L; Fisher Scientific Co. No. SO-F-105, Lot No. 873′121). Both techniques gave comparable results (Table 1). SedFFF was also used to measure the F108 maximum surface density on the particles. The principle for such a measurement is given elsewhere.[1] The elution solution was a 0.01 M NaCl solution.

2. Sample Preparation. The adsorption experiments were made in small polypropylene Eppendorf tubes (ISC No. C-3260-1, 1.7 mL). All the reactants added to the Eppendorf tubes were weighed. The deionized water and the desired amount of F108 solution (taken from a previously prepared F108 stock solution) were rapidly mixed in the Eppendorf tube. Then, the latex particles were added, and the sol was end-over-end mixed for 24 h. The total amount of the sol was 1 mL. Unless otherwise specified, the particle concentration was 0.05% w/w; the initial F108 concentration was usually in the range 0.001−0.030% w/w. After F108 adsorption, the samples were centrifuged, and part of the supernatant was removed for analysis. The centrifugation conditions are listed in Table 2 depending on the particle size since small particles require higher gravitation field for longer times to be completely separated. No detectable amount of Pluronic F108 was adsorbed on the walls of the Eppendorf tubes.

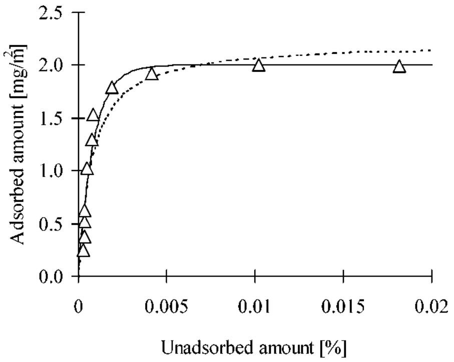

Figure 3. Adsorption isotherm fit of the large F108 component: plain line, exponential fit ($r^2 = 0.93$); dashed line, Langmuir fit ($r^2 = 0.89$). Particle diameter: 252 nm.

3. Baleux Method. The colorimetric method used to measure the amount of F108 adsorbed on the PS latex particles has been described by Baleux.[25] This method is based upon the formation of a reddish brown complex when an iodine solution is added to PEO or PPO. This complex can be selectively dosed with a spectrophotometer at a 500 nm wavelength. A sample of the F108 solution (supernatant obtained in part 1) is diluted in deionized water (final volume: 5 mL) so that the final F108 concentration is in the range 0−20 mg/L (0−0.002% w/w). Then, 1.25 mL of a KI_3 solution (1 g of I_2—Mallinckrodt AR No. 1008, Lot No. 1008KECX—and 2 g of KI—Mallinckrodt AR No. 1127, Lot No. 1127KLHE—in 100 mL of deionized water) is added to the diluted F108 solution. After a minimum of 5 min, the solution absorbance is measured at a wavelength of 500 nm. The F108 concentration of the diluted solution, and also the initial solution concentration, can be calculated knowing the calibration curve. In this study, it was assumed that the absorbance of the iodate complex of the low F108 component is the same as that of the iodate complex of the large F108 component.

4. Curve Fitting. In most studies, polymer adsorption isotherms are fitted with the Langmuir equation:

$$\frac{\theta}{1-\theta} = k'c \tag{1}$$

where θ is the fraction coverage, c the concentration of the adsorbing species, and k' the adsorption constant. This equation is based on the assumption that the size of the adsorbing species is the same as that of the solvent, which is not the case here since the F108 polymer is much larger than water molecules. Despite this, the Langmuir equation has been commonly used to fit the adsorption isotherms of polymers onto particles and has proved to work well. However, this equation is inappropriate to fit our data. Contrary to our data, the Langmuir equation does not have a sharp curvature just below reaching the adsorption plateau (Figure 3). Taking into account the number of solvent molecules displaced per polymer molecule, ν, the Langmuir equation becomes[26]

$$\frac{\theta}{\nu(1-\theta)^{\nu}} = k''c \tag{2}$$

This equation fits our data only when ν is close to one, as in eq 1. When θ is high, the curve is too rounded, especially at the plateau region. Since eqs 1 and 2 do not provide a good fit, we decided to use an exponential fit equation, which gives a much better fit of the data (Figure 3).

$$\Gamma = \Gamma_m[1 - e^{(-kc)}] \tag{3}$$

where Γ is the surface density and Γ_m the maximum surface density ($\Gamma/\Gamma_m = \theta$). k is not a real adsorption constant but is similar in meaning since an increase of k increases the initial slope of the adsorption isotherm. If it is assumed that the adsorption isotherm of one polymer fraction is not influenced by that of the other polymer fraction (as long as the particles

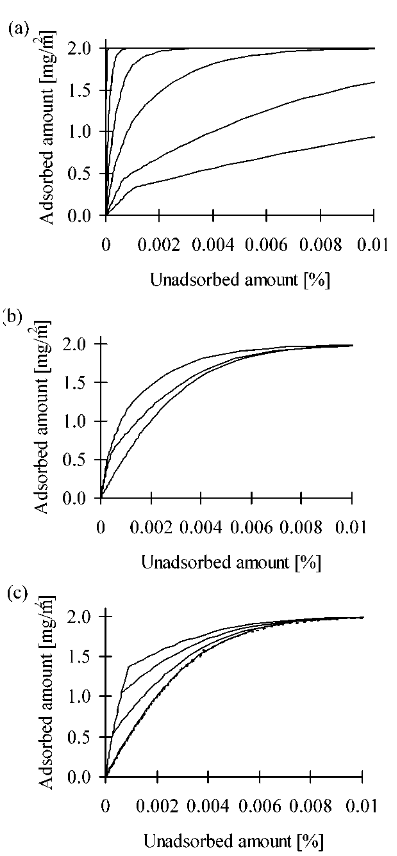

Figure 4. Effect of (a) k_2, (b) k_1, and (c) $\Gamma_{1,m}$ on the adsorption isotherm (model). Initial conditions: 252 nm particles, 0.1% w/w concentration, $\Gamma_{2,m} = 2.0$ mg/m^2. (a) $\Gamma_{1,m} = 0.2$ mg/m^2, $k_1 = 10^{10}$, $k_2 = 10^8$, 10^7, 3×10^6, 10^6, 3×10^5, and 10^5 (from left to right); (b) $\Gamma_{1,m} = 0.2$ mg/m^2, $k_2 = 10^6$, $k_1 = 10^{10}$, 10^7, and 10^3 (from left to right: the first two curves are almost completely superimposed); (c) $k_1 = 10^{10}$, $k_2 = 10^6$, $\Gamma_{1,m} = 0.8$, 0.5, 0.2, and 0.001 mg/m^2 (from left to right). These results show that the main parameters determining the shape of the adsorption isotherm of the copolymer mixture are the parameters of the large molecular weight fraction.

are not fully covered), the surface density of a bidisperse polymer mixture can be written

$$\Gamma = \Gamma_{1,m}[1 - e^{(-k_1 c_1)}] + \Gamma_{2,m}[1 - e^{(-k_2 c_2)}] \tag{4}$$

In the text below, eq 4 is used to fit the adsorption data. We use this exponential fit instead of the Cohen-Stuart square isotherms.

The F108 adsorption isotherms are fitted by means of a Microsoft Excel program using the following assumptions: (i) Large molecules adsorb preferentially to small molecules. (ii) The two polymer fractions present in the F108 product are adsorbed onto the PS latex surface according to eq 4. (iii) The mole fraction of the small polymer component is estimated to be 42% on the basis of GPC. From these assumptions, the four unknown variables (k_1, k_2, $\Gamma_{1,m}$, $\Gamma_{2,m}$) can be determined. The first step in fitting the data is to allocate an approximate value to the four different parameters (k_1, k_2, $\Gamma_{1,m}$, $\Gamma_{2,m}$). These four values are then modified by the fitting algorithms of Excel until the differences between measured and calculated data are minimized.

Results

To get a good feeling of the effect of the different parameters (k_1, k_2, $\Gamma_{1,m}$, $\Gamma_{2,m}$) on the shape of the adsorption isotherms, several simulations were performed (Figure 4). Among the four different parameters, the maximum adsorbed amount of the large molecular weight fraction, $\Gamma_{2,m}$, and the adsorption constant of the large molecular weight fraction, k_2, are the most important. $\Gamma_{2,m}$ determines the maximum adsorbed amount of the particles (Figure 1), whereas k_2 determines the slope of the adsorption isotherm (Figure 4a). The other two parameters (k_1, $\Gamma_{1,m}$) have an influence on the initial shape of the adsorption isotherm. An increase of k_1 provokes a small increase of the initial slope of the adsorption isotherm, but only if k_1 is larger than k_2 (Figure 4b). Finally, large $\Gamma_{1,m}$ values lead to the appearance of a shoulder in the adsorption isotherm (Figure 4c). If k_1 is much smaller than k_2, the shoulder disappears, and the curve is similar to that obtained with a very low $\Gamma_{1,m}$ value, e.g., $\Gamma_{1,m} = 0.001$ mg/m^2 (Figure 4c).

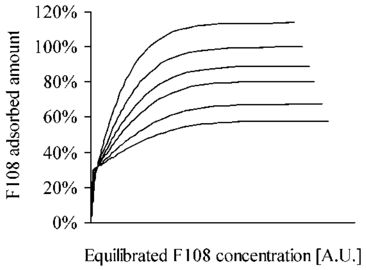

Figure 5. Effect of the absorbance ratio, λ, on the F108 adsorption isotherm. Initial conditions: 252 nm particles, 0.1% w/w concentration, $\Gamma_{2,m} = 2.0$ mg/m^2, $\Gamma_{1,m} = 0.2$ mg/m^2, $k_1 = 10^{10}$, $k_2 = 10^7$. The adsorption isotherm with a 100% plateau value corresponds to the adsorption isotherm that would be determined assuming that $\lambda = 1$. The other curves represent the real adsorption isotherms for a given absorbance ratio: $\lambda = 0.5$, 1, 1.5, 2, 3, and 4 (from top to bottom). When the value of the maximum adsorbed amount is larger than 100%, it means that the height of the adsorption plateau would be overestimated by experimental results due to the fact that $\lambda < 1.0$. The opposite is true when $\lambda > 1.0$.

All the latter calculations were based on the assumption that the quantification, i.e., the measured absorbance of the complex between iodine and the small F108 component, is the same as that of the complex between iodine and the large F108 component. In practice, this may not be true. To estimate the potential effect of an absorbance difference, some calculations were performed (Figure 5). The adsorption isotherm was determined as a function of the absorbance ratio, λ, which is defined as the ratio of the absorbance of the complex formed between iodine and the small F108 component divided by the absorbance of the complex formed between iodine and the large F108 component. The results show that the F108 adsorption isotherm is modified, but only in and above the range where the molecules of the small F108 component are replaced by the molecules of the large F108 component (Figure 5). An increase of λ decreases markedly the plateau value of the adsorption isotherm (Figure 5). In this study, all adsorption isotherms are obtained assuming that $\lambda = 1$. Thus, the calculations show that if λ is in reality below one, the use of the Baleux method underestimates the plateau value. If λ is in reality above one, the plateau value is overestimated. Interestingly, a change of particle size or particle concentration does not modify these results.

The commercial F108 sample used in this study was subjected to molecular characterization by GPC (see above). The chromatogram shown in Figure 2 gives clear evidence of the heterogeneity of the polymer which appears to consist of two discrete molecular weight

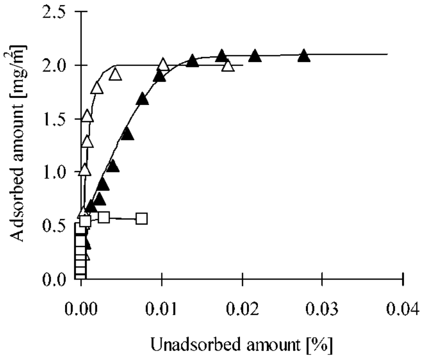

Figure 6. Adsorption isotherm of (△) the large F108 component, (□) the small F108 component, and (♦) the commercial grade F108 on PS latex particles. Particle concentration: 0.4% w/w. Particle diameter: 252 nm. The lines correspond to the best fits of the data using eq 4. The plateau value of the adsorption isotherm of the commercial grade F108 corresponds to the plateau value of the large F108 component.

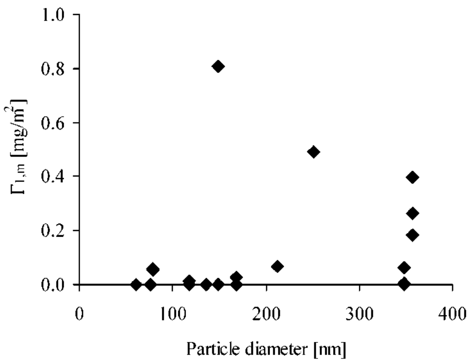

Figure 7. Effect of particle size on the plateau value of the adsorption isotherm of the short F108 component ($\Gamma_{1,m}$ values). Particle concentration: 0.05% (w/w).

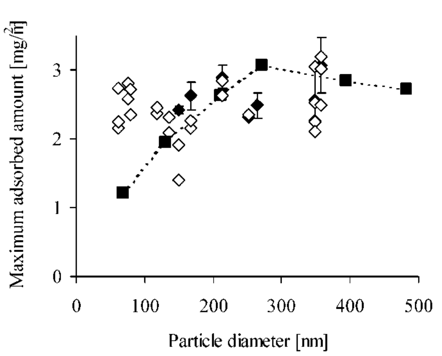

Figure 8. Particle size effect on the maximum F108 adsorbed amount. Particle concentration: 0.05% (w/w). Method used: (◇) Baleux; (♦) SedFFF; (■) isotope labeling (Li et al.[1]). The error bars correspond to a 95% level of confidence on the average.

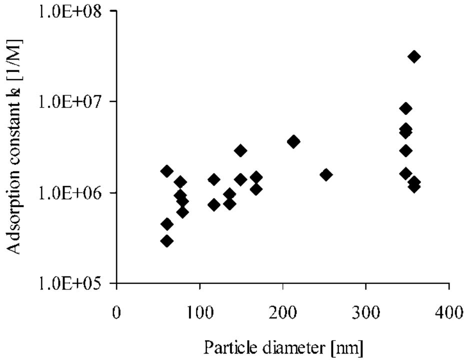

Figure 9. Particle size effect on the adsorption constant k_2. The average value is represented for each particle size. Particle concentration: 0.05% (w/w). An increase of adsorption constant leads to an increase of the initial slope of the adsorption curve (see Figure 4).

Table 3. F108 Layer Thickness on F108-Coated PS Latex Particles As Measured by PCS with Prior Fractionation[a]

nominal size [nm]	adlayer thickness [nm]	nominal size [nm]	adlayer thickness [nm]
130	8.2 ± 0.9	261	8.9 ± 1.6
165	7.7 ± 1.0	314	10.4 ± 2.0
214	7.3 ± 1.2	360	8.7 ± 1.6

[a] F108 concentration: 3% (w/w). Particles concentration: 2.5% (w/w).

components, with relative molecular weights of 13.7 and 6.1 kDa. The presence of a small component in the F108 product strongly affects the F108 adsorption isotherm (Figure 6), as predicted by Cohen-Stuart theory.[18] Interestingly, the maximum adsorbed amount of the commercial grade F108 corresponds to the plateau value of the adsorption isotherm of the large F108 component. Therefore, the data were fitted with a biexponential function (eq 4), where the low-molecular-weight polymer corresponds to the small F108 component and the high molecular weight polymer to the large F108 component. In this work, particle size, particle concentration, and F108 concentration were varied over a large range, and as a result, about 60 isotherms were collected and fitted with the exponential expression given in eq 4. As previously mentioned, an approximate value had to be allocated to the four different parameters (k_1, k_2, $\Gamma_{1,m}$, $\Gamma_{2,m}$) to perform the fitting procedure. The initial value for k_1 and k_2 was taken as 1.6×10^{11} M^{-1}. The calculations showed that, contrary to k_2, the value of k_1 was not decreased during the fitting procedure, indicating that k_1 has little influence on the adsorption isotherms as long as it is larger than k_2, as previously calculated (Figure 4b). The $\Gamma_{1,m}$ values obtained from the data fit are generally very low. All values are between 0 and 0.8 mg/m^2, with an average of 0.1 mg/m^2 (Figure 7). The $\Gamma_{1,m}$ values are 3−20 times lower than the $\Gamma_{2,m}$ values. These values are also much lower than the maximum surface density of the small F108 component (Figure 6). Despite the scattering of the data, the particle size does not have any significant effect on the $\Gamma_{2,m}$ values measured by the Baleux method (Figure 8). For all particle sizes but one (149 nm), the $\Gamma_{2,m}$ values are in the range of 1.8 and 3.2 mg/m^2 and are close to those obtained by SedFFF measurements. However, the adsorption constant k_2 (adsorption constant of the large molecular weight polymer) is increased by an increase in particle size (Figure 9): there is a 5−10-fold increase of k_2 between 61 nm particles and 358 nm particles. Interestingly, the layer thickness of F108 adsorbed on PS latex particles is not significantly modified by particle size (Table 3).

As previously mentioned, the presence of a low-molecular-weight polymer fraction in the F108 product strongly affects the F108 adsorption isotherm (Figure 6). Therefore, and as predicted by Cohen-Stuart theory,[18] the shape of the adsorption isotherm changes with particle concentration (Figure 10a). At low particle concentration (0.1 and 0.2% w/w), the adsorption isotherm has a smooth shape, looking very much like a single Langmuir-type adsorption isotherm. At a higher particle concentration (0.4 and 0.7% w/w), the adsorption isotherm becomes a juxtaposition of three straight

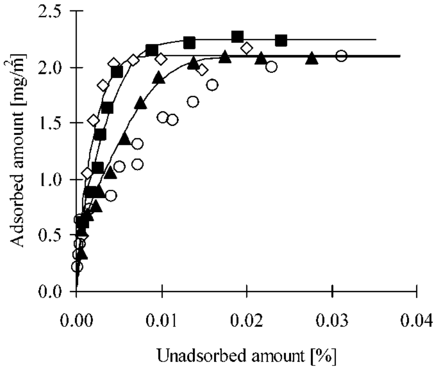

Figure 10. Effect of particle concentration expressed in (a) weight percent and (b) mg/m² on the F108 adsorption isotherm. Particle diameter: 252 nm. Particle concentration (in w/w): (◇) 0.1%, (▲) 0.2%, (♦) 0.4%, (○) 0.7%. Lines correspond to best fits of the data using eq 4. For 0.7% w/w, the number of data points at large F108 concentration is insufficient to fit the measured values using eq 4.

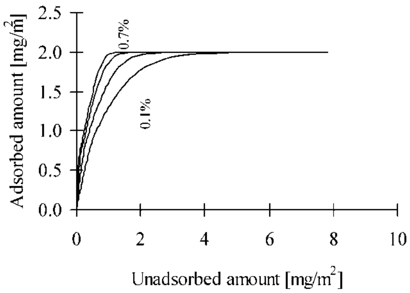

Figure 11. Particle concentration effect on the F108 adsorption isotherm as calculated with eq 4 using $k_1 = k_2 = 10^6$ M^{-1}, $\Gamma_{1,m}$ = 0.17 mg/m², and $\Gamma_{1,m}$ = 2.00 mg/m². Particle diameter: 252 nm. Particle amount (in w/w): 0.1%, 0.2%, 0.4%, and 0.7%.

lines as shown in Figure 1. When these adsorption isotherms are corrected for the amount of particles, i.e., when the concentration in solution is expressed in mg/m², all the adsorption isotherms fall on the same curve as predicted by Cohen-Stuart theory[18] (Figure 10b). However, the latter conclusion is only valid if the adsorption isotherm of each polymer fraction is square, as presented in Figure 1. In our experiments, the adsorption isotherms are rounded (Figure 3). In that case, the particle concentration should influence the shape of the adsorption isotherm as shown by our calculations, done at constant k_1, k_2, $\Gamma_{1,m}$, and $\Gamma_{2,m}$ but various particle concentrations: the larger the particle concentration, the larger the initial slope (Figure 11). To account for our experimental results where no significant effect of particle concentration is observed, the adsorption constant, k_2, must decrease with an increase in particle concentration, as summarized for different particles sizes in Figure 12. An increase of the particle concentration provokes also a decrease of the maximum F108 surface density (Figure 13), but no significant effect on $\Gamma_{1,m}$ values (Figure 14).

Discussion

1. Cohen-Stuart Model. The result of the fitting calculations show that the small F108 component has a strong effect on the shape of the adsorption isotherm, as predicted by Cohen-Stuart[18] (Figures 6 and 10). This may appear surprising because the $\Gamma_{1,m}$ values are much lower than the $\Gamma_{2,m}$ values (Figures 7 and 8). However, this is compensated by the fact that the k_1 values are much larger than the k_2 values (Figure 4b).

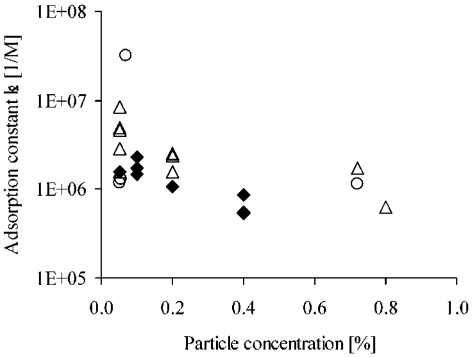

Figure 12. Particle concentration effect on the adsorption constant k_2. Particle diameter: (○) 358, (△) 348, and (♦) 252 nm.

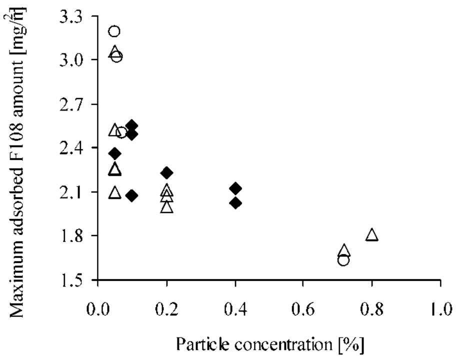

Figure 13. Particle concentration effect on the maximum adsorbed amount. Particle diameter: (○) 358, (△) 348, and(♦) 252 nm.

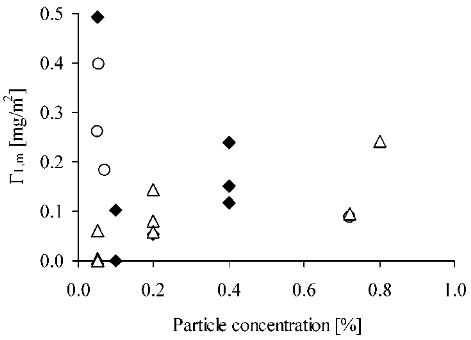

Figure 14. Particle concentration effect on $\Gamma_{1,m}$. Particle diameter: (○) 358, (△) 348, and (♦) 252 nm.

Large k_1 values occur when the interactions between the small F108 component and the PS surface are strong. Because of its high hydrophobicity, PPO is expected to interact with the hydrophobic PS surface much more extensively than the hydrophilic PEO. Therefore, the present results suggest that the small F108 component may consist of PPO polymer. The adsorption isotherm of the small F108 component does indeed show a very steep initial slope (Figure 6). However, the results of Klein et al.[20] suggest that if there is a strong binding between the small F108 component and the PS latex particles, the small F108 component would displace the large F108 component. As a result, the plateau value of the adsorption isotherm of the commercial grade F108 would correspond to the plateau value of the adsorption isotherm of the small F108 component, which was not observed experimentally (Figure 6). As the molecular weight of the small F108 component is close to the molecular weight of the PEO side blocks (6.1 vs 5.7 kDa), the best explanation for the experimental results is that the small F108 component consists of PEO. The reason that PEO would have a large k_1 value is unclear but could be an artifact of the fitting program. The $\Gamma_{1,m}$ values obtained by fitting the experimental data are much lower than the plateau value of the adsorption isotherm of the small F108 component (Figures 6 and 7). To obtain the latter adsorption isotherm, it was first necessary to determine the concentration of the solution containing the small F108 component collected by GPC. This determination was based on the absorbance of this solution after reacting with the iodine solution assuming that the absorbance ratio, λ, is equal to 1. If λ 1, the determination is inaccurate, and the plateau value of the adsorption isotherm obtained with the small F108 component is shifted. Such a shift could be the origin of the discrepancy between the $\Gamma_{1,m}$ values obtained by fitting the experimental and the plateau value of the adsorption isotherm of the small F108 component.

2. Particle Size Effect. By plotting all the $\Gamma_{2,m}$ values obtained in the fitting calculations as a function of particle size (Figure 8), it can be seen that particle size does not have any significant effect on $\Gamma_{2,m}$. For all particle sizes but one (149 nm), the $\Gamma_{2,m}$ values are in the range of 1.8−3.2 mg/m^2. Interestingly, the $\Gamma_{2,m}$ values obtained with the Baleux method were close to those obtained by SedFFF, but always smaller. Contrary to the Baleux method, SedFFF is a direct technique, where only the amount of F108 adsorbed on the particles is measured. Therefore, the smaller values obtained with the Baleux method could be explained by some particle aggregation. Despite the fact that the $\Gamma_{2,m}$ values measured by the Baleux method are always lower than the $\Gamma_{2,m}$ values measured by SedFFF, these differences remain small. In fact, the latter differences are much smaller than the variations observed between different particle sizes (e.g., 149 and 270 nm particles). In an attempt to determine the cause of these large variations, the surface charge of the different particle sizes was measured by electrophoresis. A large scatter of the data was observed, but no trend and no correlation with the $\Gamma_{2,m}$ and k_2 values was found. Kronberg et al.[27,28] suggested that the main parameter for the adsorption of nonionic polymers was not the surface charge, but rather the surface hydrophobicity. For example, Schröen et al.[29] observed that hydrophilic surfaces adsorbed much less F108 than hydrophobic surfaces: 0.7 vs 1.8 mg/m^2, respectively. Consulting Figure 8, the $\Gamma_{2,m}$ values obtained here are slightly higher than those measured by Schröen et al.[29] for hydrophilic particles (reflectometry; 0.7 mg/m^2), Kayes and Rawlins[30] (Baleux method; 1.15 mg/m^2), Faers and Luckham[7] (Baleux method; 1.4 ± 0.2 to 1.85 ± 0.2 mg/m^2), and Baker et al.[3,31] (Static adsorption method; 1.35 mg/m^2), but are very similar to those obtained by Schröen et al. for hydrophobic particles (reflectometry; 1.8 mg/m^2) and by Li et al.[1,15] Considering the large scattering of the $\Gamma_{2,m}$ values presented here and in the literature, and the large effect that surface hydrophobicity can play, our results do not demonstrate an effect of particle size on the maximum F108 surface density. The low value measured with 149 nm PS particles could be due to a difference in surface hydrophobicity. The absence of particle size effect is in accordance with theoretical predictions.[11,12] According to geometric arguments, significant particle size effects should not be seen as long as the particle radius is larger than the adsorbed layer thickness. As the F108 layer thickness is close to 8 nm (Table 3), the investigated particle sizes are not in the critical range.

As for the $\Gamma_{2,m}$ values, no significant size effect is observed on the adlayer thickness in the diameter range from 150 to 360 nm investigated in this study. All the values are close to 8 nm. This is in good agreement with theoretical predictions[11,12] and the values presented in the literature. Lee et al.[4] measured a layer thickness of 11.8 ± 1.5 nm (dynamic light scattering). Kayes and Rawlins[30] obtained a value of 13.5 ± 2.0 nm by microelectrophoresis and 13.4 ± 4.5 nm by intensity fluctuation spectroscopy. Faers and Luckham[7] determined a thickness of 9.4 ± 0.5 nm (steady-shear measurements) to 13.5 ± 2 nm (PCS). Schröen et al.[29] found a value of 10 nm. Finally, Li et al.[1] measured values in the range of 6.5−24.0 nm. Later, Li et al.[6] corrected these values to 8 ± 3 to 14 ± 3 nm.

3. Particle Concentration Effect. The effect of particle concentration on the adsorption constant k_2 and the $\Gamma_{2,m}$ values (Figures 12 and 13) suggests that the results are distorted either by agglomeration or by kinetic factors. To make sure that kinetics did not play a role in these observations, the adsorption isotherm of 252 nm particles was measured after 1 and 24 h of mixing (the samples were normally mixed for 24 h). No difference could be shown between the isotherm obtained after 1 and 24 h mixing, therefore implying that the system had reached at least a pseudo-equilibrium within the first hour of mixing. The second possible cause for the large effect of particle concentration on k_2 and $\Gamma_{2,m}$ values is particle aggregation. As particle aggregation is eased by a decrease of the interparticle distance, a decrease of the $\Gamma_{2,m}$ values and of the adsorption constant k_2 could be expected with an increase of particle concentration and a decrease of particle size. The adsorption constant k_2 is indeed observed to decrease with an increase of particle concentration (Figure 12) and a decrease of particle size (Figure 9). Moreover, the $\Gamma_{2,m}$ values decrease with an increase in particle concentration (Figure 13).

An increase of the particle concentration has no discernible effect on $\Gamma_{1,m}$ values (Figure 14). However, the scattering of the $\Gamma_{1,m}$ values is so large that it is difficult to see any trend. Interestingly, the scattering of the $\Gamma_{1,m}$ values decreases with an increase of particle concentration. This stems from the fact that when the particle concentration increases, the domain in which the adsorption isotherm is modified by the presence of the low-molecular-weight polymer fraction extends markedly (Figure 10a). As a result, the $\Gamma_{1,m}$ values can be determined more accurately, leading to a decrease in the standard deviation of the $\Gamma_{1,m}$ values (Figure 14).

4. Comparison with Previous Results. The discrepancy between the results obtained in this study and the results obtained previously by Li et al.[1,2] in our lab is intriguing. In the latter studies,[1,2] four different PEO/PPO/PEO copolymers (Pluronics) were adsorbed on PS latex particles with a diameter in the range of 69−482 nm. For three of the four copolymers, there was a significant and simultaneous increase of the adlayer thickness and surface coverage with an increase in particle size.[1,2] Moreover, an increase of the protein adsorption of the copolymer-coated particles was observed with an increase in particle size.[2] The latter results were obtained with two different analytical methods. On the basis of these results, it was believed that particle size had a strong effect on the adsorption of Pluronics. According to a recent model of Biver et al.,[13] the layer thicknesses are indeed well correlated to the surface densities. However, the model does not predict an effect of particle size on surface density. In the present study, an effect of particle size is seen on the adsorption constant k_2. Moreover, an increase of protein adsorption to the F108-coated particles is observed with an increase in particle size (unpublished results). However, no effect of particle size is observed on layer thickness and surface density, in accordance with several theoretical predictions.[11,12] What could explain those discrepancies? Contrary to Li et al.,[1,2] who performed numerous measurements with various analytical methods, but only on a few particle samples, we tested here many particle samples, but mainly with one analytical technique (Baleux) and with sometimes only two measurements per sample. So, two explanations can be proposed. First, the difference could stem from the analytical technique: Li et al.[1] used direct methods (SedFFF, radio-labeling), whereas we mainly used an indirect method (Baleux). Interestingly, the SedFFF method and the radio-labeling technique require the use of a phosphate buffered solution (PBS), contrary to the Baleux method. It is known that the ionic strength can influence the desorption of polymers, in particular polyelectrolytes.[32] However, only a small difference in surface density is observed between the SedFFF method and the radio-labeling technique[1] and between the Baleux and SedFFF method (in this study). The second explanation for the discrepancy is the large scattering of the data obtained with different samples (Figure 8). When the results of Li et al.[1] are compared with the present results (Figure 8), it appears that only the $\Gamma_{2,m}$ value of 69 nm particles is significantly lower than the values obtained here. Considering the large effect of particle hydrophobicity,[29] this low value could be easily explained by a low hydrophobicity. Considering the considerable care that has been taken to collect enough data in our past and present study, more experiments are certainly required to come to a conclusion.

Conclusion

In this study, no effect of particle size was observed on the maximum adsorbed amount of F108 and on the F108 layer thickness. However, the adsorption constant was increased by an increase in particle size. Moreover, the adsorption constant and the maximum adsorbed amount were decreased by an increase of particle size. The latter results could be explained by particle aggregation.

The model of Cohen-Stuart describes well the adsorption of a bidisperse polymer on particles. For example, this model predicts the large effect of the small F108 component on the adsorption isotherm. It also predicts that the shape of the adsorption isotherm changes with particle concentration. Furthermore, it predicts that the effect of particle concentration disappears when the polymer concentration is divided by the particle surface area. However, the assumption of Cohen-Stuart that all the adsorption isotherms are square (infinitely high adsorption constant) has limitations. It is thus recommended to consider that the adsorption isotherm are rounded and not square.

The fact that the maximum adsorbed amout of the commercial grade F108 was close to the maximum adsorbed amount of the large F108 component suggests that the small F108 component consists of PEO. This result is supported by the fact that the small F108 component has almost the same molecular weight as that of the PEO side chain.

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