Adsorption Theory for Polydisperse Polymers[†]

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ABSTRACT: Most polymers are polydisperse. We extend the self-consistent field polymer adsorption theory due to Scheutjens and Fleer to account for an arbitrary polymer molecular weight distribution with a cutoff chain length $N_{\max}$. In this paper, the treatment is restricted to homopolymers. For this case a very efficient scheme is proposed for which the enumerations to compute adsorption characteristics for a complete set of molecules $\{n_i\}$ is only a factor of 2 larger than for monodisperse polymers with a chain length $N_{\max}$. For polydisperse polymer, adsorption fractionation takes place, with the long chains preferentially adsorbing from dilute solutions. This fractionation depends on the volume/surface ratio and the polymer concentration; it leads to rounded adsorption isotherms when $N_w/N_n > 1$. It is shown that the hystereses between the adsorption and desorption isotherms, which is often observed, can be explained from an equilibrium point of view. The full calculations corroborate the trends predicted by a simple model proposed by Cohen Stuart *et al.* In addition, in the numerical method many more details are retained.

Introduction

Polymers are excellent surface modifiers. They often adsorb very efficiently from solution onto interfaces. Only a very small entropy loss upon adsorption has to be compensated. When the adsorption energy exceeds a critical adsorption energy of order $0.2kT$ per segment, an adsorbed amount of typically 1 mg/m^2 is found. A higher surface excess may be found when the polymers are marginally soluble in the solvent. Under θ conditions the adsorbed amount diverges as $\ln N$. Due to the high-affinity character of the adsorption process, in most practical cases the polymer system is in the pseudoplateau of the adsorption of isotherm.

The adsorbed polymer layer can be characterized by the train, loop, and tail size distributions.[2] The tails are important (*e.g.*, for colloidal (de)stabilization) because they protrude far into solution and determine, in most practical systems, the hydrodynamic layer thickness of the layer.[3] For extremely long polymers it has been shown that in the overall density profile three parts can be distinguished: (1) the "proximal" region next to the surface, (2) the "central" regime in the semidilute part, and (3) "distal" region in the outer part of the profile.[4,5] The profile of polymer units has universal properties in the latter two regimes, obeying a power law in the central region and decaying exponentially toward the bulk density in the distal region of the profile.

It was long believed that polymer adsorption is usually an irreversible process. This belief rested on some misinterpretations of experimental observations. One of the puzzling findings was that the adsorption and desorption isotherms differ: once the polymers are adsorbed, they do not readily desorb upon dilution of the solution. Clearly, polymer adsorption and probably even more polymer desorption are slow processes, but recent experiments showed that polymers can easily be displaced from a surface when a suitable displacer is added.[6–10] Howard and Woods,[11] Felter *et al.*,[12–14] and Vander Linden and Van Leemput[15,16] showed that a polydisperse polymer has a more rounded adsorption isotherm than a monodisperse one. Cohen Stuart *et al.*,[17] Hlady *et al.*,[18] and Koopal[19] proved that the volume/surface ratio does effect the adsorbed amount of polymer. More than a decade ago, a simple model gave the insight that a proper accounting for the polydispersity of the polymeric samples (which is nearly always present) can explain the experimental observations.[17] In this simple model it was assumed that the boundary between adsorbed (long) molecules and nonadsorbed (short) ones in the solution is sharp. This model initiated this work which gives a full analysis on the basis of the Scheutjens–Fleer theory. The purpose of the present paper is to give the technical details of the extension of this polymer adsorption theory for polydispersity. Although various results of this approach have already been published in several papers,[20–24] the full model has never been published before.

Theory

In this section we define the symbols and show that a proper choice of reference system and boundary conditions leads directly to simple generalizations of the equations for adsorption of monodisperse polymers. We briefly review and generalize the derivation given before,[25] except that a few ambiguities are removed and that now the method of Lagrange multipliers is used. A more general derivation of the theory, which is applicable to multicomponent copolymer systems, is given by Evers *et al.*[26]

(a). Model. A polymer molecule i is represented by a chain of segments, numbered $s = 1$ to N_i. In a sample of n polymer molecules, n_i of the chains are of length N_i. The molecular size distribution is denoted by $\{n_i\}$. It is assumed that solvent molecules and polymer segments are equal in size. In order to enumerate the number of configurations

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[†] Tribute to Jan Scheutjens. The work presented here was performed more than a decade ago as part of the M.Sc. work of one of us [S. P. F. M. Roefs[1]], which was supervised by Jan Scheutjens, who died tragically in 1992. This paper adds a small part to the well-recognized contributions Jan Scheutjens made to the field of polymer adsorption. A brute force method to account for polydispersity would be to compute the adsorption characteristics for each chain length separately. This was not Jan's approach. The proposed method carries some elegance in it, because it accounts for a broad arbitrary molecular weight distribution of chain lengths with only a factor of 2 increase in computation effort as compared to the monodisperse homopolymer case. Therefore it is now possible to cover long chains and a wide range of the relevant parameter space. Most of this paper was prepared by Jan Scheutjens; we found it in his files after his death.

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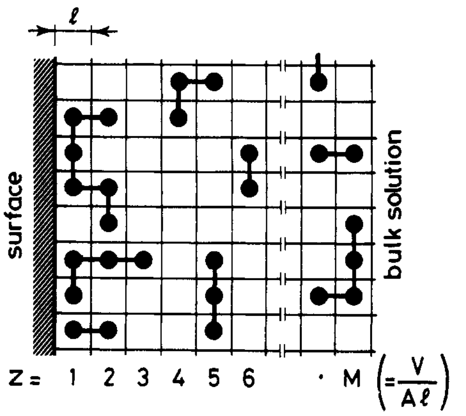

Figure 1. A two-dimensional representation of the lattice used. Quantities defined in the text are indicated. Solvent molecules are not drawn, but fill up the open sites. In this example the coordination number Z is $Z = 4$.

in a system of adsorbing polymer, the molecules are distributed over a lattice with coordination number Z in such a way that each lattice site is occupied by either a solvent molecule or a polymer segment (see Figure 1). The lattice is divided into M layers of L lattice sites each, numbered $z = 1$ to M. Segments and solvent molecules in the firsty layer are considered to be adsorbed. Layer M is in the bulk solution. The thickness of a lattice layer is ℓ, so that the solution volume-to-surface ratio V/A is given by

$$V/A = M\ell \tag{1}$$

Within each layer a random distribution of polymer segments and solvent (0) is assumed to apply (Bragg–Williams approximation), their volume fractions being $\varphi(z) = \sum_{i\neq 0}\varphi_i(z)$ and $\varphi_0(z)$, respectively. The energy difference U of the system with respect to a reference state of pure solvent and amorphous pure polymer is given by

$$U = Lu\varphi(1) + Lu_0\varphi_0(1) + kTL\chi\sum_z \varphi_0(z)\langle\varphi(z)\rangle \tag{2}$$

where u is the adsorption energy of a segment and u_0 that of a solvent molecule. The last term in eqn 2 accounts for the mixing energy of polymer and solvent. The transfer of one solvent molecule from pure solvent into pure polymer is accompanied by a contact energy change of χkT, χ being the Flory–Huggins polymer–solvent interaction parameter, and k is Boltzmann's constant and T the temperature. For a solvent molecule in layer z the fraction of contacts with polymer is given by the average volume fraction $\langle\varphi(z)\rangle$ of segments around a site in layer z. If a site has a fraction λ_0 of its nearest neighbors in the same layer (*e.g.*, $\lambda_0 = 4/6$ for a cubic lattice) there will be a fraction $\lambda_1 = (1 - \lambda_0)/2$ in each of the adjacent layers. Hence,

$$\langle\varphi(z)\rangle = \lambda_1\varphi(z-1) + \lambda_0\varphi(z) + \lambda_1\varphi(z+1) \tag{3}$$

The entropy is a function of the conformation distribution $\{n_i^c\}$ of the molecules. A conformation c is characterized by the distribution $\{N_i^c(z)\}$, which gives the number of segments that a molecule i in conformation c has in each layer z. The volume fraction of polymer can be calculated from the conformation distribution by

$$\varphi(z) = \sum_{i\neq 0}\sum_c N_i^c(z)n_i^c/L \tag{4}$$

In a lattice there are $L\omega_i^c$ spatial arrangements of the chain i in conformation c, where the factor L accounts for translation parallel to the surface and ω_i^c for the (lattice dependent) orientational freedom of bond directions within the segment distribution $\{N_i^c(z)\}$. When $N_i = 1$, $\omega_i^c = 1$, but for $N_i > 1$ this quantity is given by $\omega_i^c = \prod_{s=2}^{N_i} Z\lambda_i^c(s|s-1)$. Here $\lambda_i^c(s|s-1) = \lambda_0$ if segment s and $s-1$ in conformation c are in the same layer and λ_1 otherwise. Evers *et al.*[26] write $\omega_i^c = Z^{N_i-1}\prod_{s=2}^{N_i}\lambda_i^c(s|s-1) = Z^{N_i-1}\lambda_i^c$.

When the lattice is already filled with some solvent and polymer, the empty site distribution is denoted as $\{\vartheta(z)\}$. For an empty lattice $\vartheta(z) = L$ for any z, and its value decreases as each layer becomes more occupied. The probability that a certain lattice site in layer z is empty equals $\vartheta(z)/L$ and the probability that a given sequence of N_i sites with distribution $\{N_i^c(z)\}$ is vacant is given by $L^{-N_i}\sum_{z=1}^{M} \vartheta(z)!/(\vartheta(z) - N_i^c(z)!$, assuming again a random distribution of vacancies within each layer. This gives the correction factor for the lattice occupancy on the $L\omega_i^c$ arrangements in an empty lattice. Consequently, we can place one of the $\{N_i^c(z)\}$ molecules in $L\omega_i^c L^{-N_i}\sum_{z=1}^{M} \vartheta(z)!/(\vartheta(z) - N_i^c(z))!$ ways on this lattice. One of the $n_j(z)$ monomers or $n_0(z)$ solvent molecules could have been placed in $\vartheta(z)$ ways. It follows that, starting with an empty lattice ($\vartheta(z) = \mathrm{L}$), the placement of all molecules in a given conformation distribution $\{n_i^c\}$ produces one out of

$$\Omega = \prod_{z=1}^{M} L! \prod_{i,c} \frac{(L^{1-N_i}\omega_i^c)^{n_i^c}}{n_i^c!} \tag{5}$$

states. We note that the multiple product in eq 5 runs over all molecules i including the solvent. The factorials $n_i^c!$ are included to correct for the indistinguishability of the n_i^c chains (or solvent molecules) in the same conformation c. Note that the given conformation distribution and solvent profile must yield a total volume fraction of 1 in each layer.

The reference state (which will be denoted by an asterisk) consists of the unmixed components, *i.e.*, pure solvent and a series of liquid monodisperse polymers. The combinatory factor for the solvent is 1 and that of the polymer with chain length N_i has been given by Flory:[27]

$$\Omega_i^* = (N_in_i)!\frac{\{(N_in_i)^{1-N_i}\omega_i^*\}^{n_i}}{n_i!} \tag{6}$$

where ω_i^* is the conformational degeneracy of a chain in the melt, often approximated by Z^{N_i-1} for a Z choice lattice. Equation 6 is a reduced version of eq 5, which is easily shown by realizing that L can be substituted by N_in_i. The ratio between the partition functions of the system and the reference state is now given by

$$\frac{Q(M,L,T,\{n_i^c\})}{Q^*} = \frac{\Omega}{\prod_i \Omega_i^*}\exp\left(\frac{-U}{kT}\right) \tag{7}$$

and the free energy $F = -kT\ln(Q/Q^*)$ with respect to the reference state follows after a few substitutions and rearrangements:

$$\frac{F}{kT} = \sum_{i\neq 0}\sum_{c} n_i^c \ln\left\{\frac{N_i n_i^c \omega_{\mathrm{i}}^*}{\mathrm{L}\omega_i^c}\right\} + \sum_{z=1}^{M} n_0(z) \ln \varphi_0(z) + \frac{(un(1) + u_0 n_0(1))}{kT} + \chi \sum_{z=1}^{M} n_0(z)\langle\varphi(z)\rangle \quad (8)$$

where Stirling's approximation $\ln(x!) \approx x\ln(x) - x$ was used for the factorials.

Due to the given choice of the reference system, the only effect of polydispersity in eq 8 appears to be a summation of the first term over all molecules $i \neq 0$. Of course, the equilibrium profile is also affected, but it is gratifying that the complexity of the equations hardly increases for a larger number of different species.

(b). Equilibrium Distribution. In the previous section we arrived at the free energy for a given set of conformations and a distribution of solvent such that the total volume fraction in each lattice layer equals unity. In this section we derive the equilibrium distribution by minimizing the free energy with respect to the number of chains $i \neq 0$, n_i^c in conformation c, and the number of solvent molecules $n_0(z)$ in layer z. We fix the total number of polymer units and solvent molecules in each layer to L and keep the number of molecules constant by imposing the boundary conditions

$$n_0(z) + \sum_{i\neq 0}\sum_{c} N_i^c(z) n_i^c = L \qquad (1 \le z \le M) \quad (9)$$

and

$$\sum_{c} n_i^c = n_i \qquad i \neq 0 \quad (10)$$

Applying Lagrange's method we need to determine the multipliers $\alpha(z)$ and β_i by minimizing the Lagrange function

$$\Psi = \frac{F}{kTL} - \sum_{z=1}^{M}\alpha(z)\left(n_0(z) + \sum_{i\neq 0}\sum_{c} N_i^c(z) n_i^c - L\right) - \sum_{i\neq 0}\beta_i\left(\sum_{c} n_i^c - n_i\right)/L \quad (11)$$

with respect to n_i^c ($i \neq 0$) and $n_0(z)$. Setting the partial differentials to zero gives for all conformations n_i^c

$$\ln\left(\frac{N_i n_i^c \omega_i^*}{L\omega_i^c}\right) + 1 - \beta_i + N_i^c(1)\frac{u}{kT} + \sum_{z=1}^{M} N_i^c(z)[\chi\langle\varphi_0(z)\rangle - \alpha(z)] = 0 \quad (12)$$

and for all layers z

$$\ln\varphi_0(z) + 1 + \delta_{1,z}\frac{u_0}{kT} + \chi\langle\varphi(z)\rangle - \alpha(z) = 0 \quad (13)$$

respectively, where we have used the relation $\sum_z n_0(z)\langle\varphi(z)\rangle = \sum_z n(z)\langle\varphi_0(z)\rangle$, *i.e.*, the total number of solvent–segment contacts equals the total number of segment–solvent contacts. The Kronecker $\delta_{1,z}$ in eq 13 switches on u_0 when $z = 1$.

By elimination of $\alpha(z)$ from eqs 12 and 13, we arrive at the original equations for the equilibrium value for n_i^c:[25]

$$\frac{n_i^c}{L} = \mathrm{C}_i \frac{\omega_i^c}{\omega_i^*}\prod_{z=1}^{M} G(z)^{N_i^c(z)} \qquad i \neq 0 \quad (14)$$

In eq 14 we have introduced the segment weighting factor $G(z)$, which in ref 25 was called the free segment probability and referred to with the symbol P_i. It is given by

$$G(z) = \varphi_0(z)\exp(\chi_s\delta_{1,z} + \chi\langle\varphi(z) - \varphi_0(z)\rangle) \quad (15)$$

The parameter χ_s is the net adsorption energy per segment, in kT units:

$$\chi_s = (u_0 - u)/kT \quad (16)$$

and $C_i = N_i^{-1}\exp(\beta_i + N_i - 1)$ is a normalization constant. [Note that in the definition of C in ref 25 a factor $\exp(N_i - 1)$ is missing.] The constant C_i follows from eqs 10 and 14:

$$C_i = \frac{n_i}{LG(N_i|1)} \qquad i \neq 0 \quad (17)$$

where $G(N_i|1) = \sum_c(\omega_i^c/\omega_i^*)\prod_{z=1}^{M} G(z)^{N_i^c(z)}$ is the chain weighting factor, for which we will give a more convenient expression below. We note that the volume fraction of solvent is given by $\varphi_0(z) = 1 - \sum_{i\neq 0}\varphi_i(z)$.

The segment volume fraction profile is determined by the conformation profile, whereas the conformation profile is a function of the volume fraction profile through the segment weighting factors $G(z)$. The self-consistent solution is to be obtained by solving M equations in M unknowns by successive approximation.

However, when the chains are longer than a few segments the number of conformations is too large for an exact enumeration of $\{\varphi(z)\}$ from $\{G(z)\}$. A suitable sampling technique can shift the feasible chain length, but not more than 1 order of magnitude. The convenient way out to cover the whole molecular weight range encountered in practice is using step-weighted random walks. The next section describes the equations needed for polydisperse polymer.

(c). Concentration Profile. In principle, it is easy to obtain the total segment volume fraction profile from the segment weighting factors since eq 14 applies for any degree of polydispersity. The equations for monodisperse polymer can be used to compute the density profile for each individual chain length present in the system and the sum over all these components gives the overall volume fraction profile of segments:[25,26]

$$\varphi(z) = \sum_{i\neq 0}\sum_{s=1}^{N_i} C_i G(z,s|1) G(z,s|N_i)/G(z) \quad (18)$$

where we have introduced the chain-end distribution functions $G(z,s|1)$ and $G(z,s|N)$, which are the overall statistical weights of all possible subconformations that include segment s in layer z; therefore they are summed over all allowing positions for segment number 1 and for segment number N_i, respectively.

In the case of polydispersity eq 18 is not very convenient, because there are many chain molecules i involved. Let us thus group the chains in sets, wherein the molecules within a set only differ with respect of their chain length. We would number the sets $j = 0, 1, ...,$ where again $j = 0$ refers to the solvent and $j = 1$ to the present case of (polydisperse) chains of the same chemical nature. The case $j > 1$ discribes the situation that more than one type

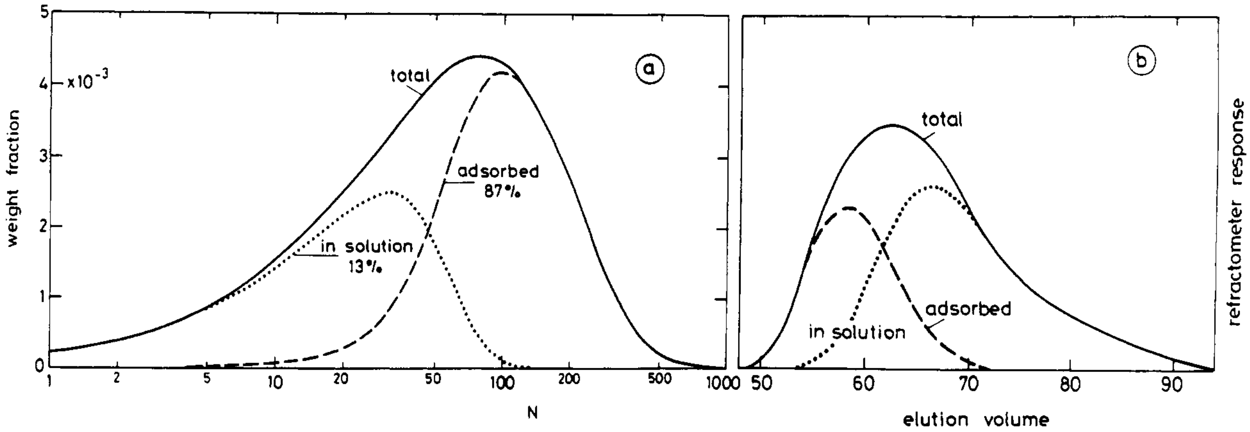

Figure 2. Adsorption fractionation of polydisperse polymers. Part 2a is the theoretical result for a Schulz–Flory distribution with $N_n = 80$, $N_w/N_n = 2.06$, $V/A = 120\ell$, $\varphi^b = 1.55 \times 10^{-3}$, $\chi_s = 1$, $\chi = 0.5$. Part b gives experimental GPC data for polydisperse polystyrene adsorbed from CCl_4 on SiO_2.[16] In the experimental sample $N_w/N_n = 1.69$, we note that there is a logarithmic dependence of the elution volume on the molecular weight, with a decreasing elution volume for higher chain lengths.

of chain molecules is present in the system. We will illustrate the formalism with only two sets (solvent and polydisperse homopolymers), and drop the index j for convenience. For the given set ($j = 1$) we will assume that there is a maximum chain length $N^{\max}$. The maximum number of members in this set is thus limited to the cutoff chain length $N^{\max}$. In this set we order the polymer molecules from low to high chain length by giving them ranking number $k = 1, ..., N^{\max}$, so that a molecule k has a degree of polymerization $N_k = k$. The number of molecules of chain k in the system is n_k and the normalization constant $C_k = n_k/LG(N_k|1)$. Note, that when a molecule length k is not present in the set then $n_k = C_k = 0$.

We now return to eq 18, where the summation over i is now replaced by a summation over k. Upon inspection we notice that the order of the two summations can be interchanged. Further, the division by $G(z)$ can be taken out of both summations. We now realize that all chains in the set have a first segment, and thus we can take $G(z,1|1)$ out of the summation over k. Similarly, $G(z,2|1)$ can be taken out of the summation for all chains which have a second segment. This can be repeated for the whole set, and it is easily shown that eq 18 can be written as

$$\varphi(z) = \frac{1}{G(z)} \sum_{s=1}^{N^{\max}} [G(z,s|1) \sum_{k \geq s} C_k G(z,s|N_k)] \qquad (19)$$

which implies nothing else than a change in the order of summation of the terms in eq 18. By defining a chain-end distribution function $G(z,s|\{N_k \geq s\}) \equiv \sum_{k \geq s} C_k G(z,s|N_k)$, expressing the combined statistical weight of a properly normalized set of chain fragments with lengths between 1 and $N^{\max} - s + 1$, we can rewrite eq 19 as

$$\varphi(z) = \frac{1}{G(z)} \sum_{s=1}^{N^{\max}} G(z,s|1) G(z,s|\{N_k \geq s\}) \qquad (20)$$

The chain-end distribution functions in eq 20 can be evaluated recursively by defining a starting relation $G(z,1|1) = G(z)$ and using

$$G(z,s|1) = \langle G(z,s-1|1) \rangle G(z) \qquad (21)$$

which is successively applied to $s = 2, 3$, etc. Here $\langle G(z,s-1|1) \rangle$ is defined, completely analogously to eq 3, as the weighted average over three neighboring layers $\lambda_1 G(z-1,s|1) + \lambda_0 G(z,s|1) + \lambda_1 G(z+1,s|1)$, an operation which ensures chain connectivity. Due to the presence of the wall (at layer $z = 0$) $G(0,s|1) = 0$ for all s. We define $G(z,N^{\max}|N^{\max}) = C_{N^{\max}} G(z)$ and evaluate $G(z,s|\{N_k \geq s\})$ from the recurrence relation:

$$G(z,s|\{N_k \geq s\}) = \langle G(z,s+1|\{N_k \geq s+1\}) \rangle G(z) + C_s G(z) \qquad (22)$$

where again $G(0,s|\{N_k \geq s\}) = 0$ for all s. The quantity C_s is given by $C_s = n_s/LG(s|1)$, where $G(s|1) = \sum_{z=1}^{M} G(z,s|1)$. We note that only eq 22 and the calculation of C_s differ from the usual computation of the volume fraction profile for monodisperse polymers.[25] Thus a remarkable simple and efficient scheme is obtained. The set of equations can be solved numerically.

Results and Discussion

The theoretical results in this section have been obtained for a hexagonal lattice ($\lambda_0 = 6/12$), an adsorption energy parameter $\chi_s = 1$, and a cutoff chain length $N_{\max} = 1000$ segments.

Preferential Adsorption. In a polydisperse sample of polymers adsorbing from dilute solution onto a solid interface one should not expect that all chains have the same affinity for the surface. Thus, at the interface the composition will be different from the overall composition in the system. The expected adsorption fractionation is indeed predicted by the present theory. The preferential adsorption depends on the solution concentration of the polymer, but hardly on the adsorption energy and the solvent quality.

Figure 2 shows the adsorption fractionation of a polymer with polydispersity ratio N_w/N_n around 2. Here, N_w and N_n are the weight and number averaged chain lengths, respectively. Figure 2a shows the theoretical result for a (truncated) Schulz–Flory distribution ($N_w/N_n = 2.06$), and Figure 2b is reconstructed from the experimental gel permeation chromatography data given by Vander Linden and Van Leemput (Figures 1 and 3a of ref 16) for adsorption of polydisperse polystyrene ($N_w/N_n = 1.69$) on silica. The experimental elution volume decreases logarithmically with the molecular weight, and thus parts a + b of Figure 2, are mirror images. The full curves represent the overall molecular weight distributions, the dashed curves give the distribution of the adsorbed fraction, and the dotted curves that of nonadsorbed polymer in solution. The correspondence between the theoretical and experimental data is remarkable. The position of the transition region between nonadsorbed and adsorbed molecules depends on the solution concentration (in this case about 1000 ppm) and volume/surface ratio (V/S) (about 120ℓ),

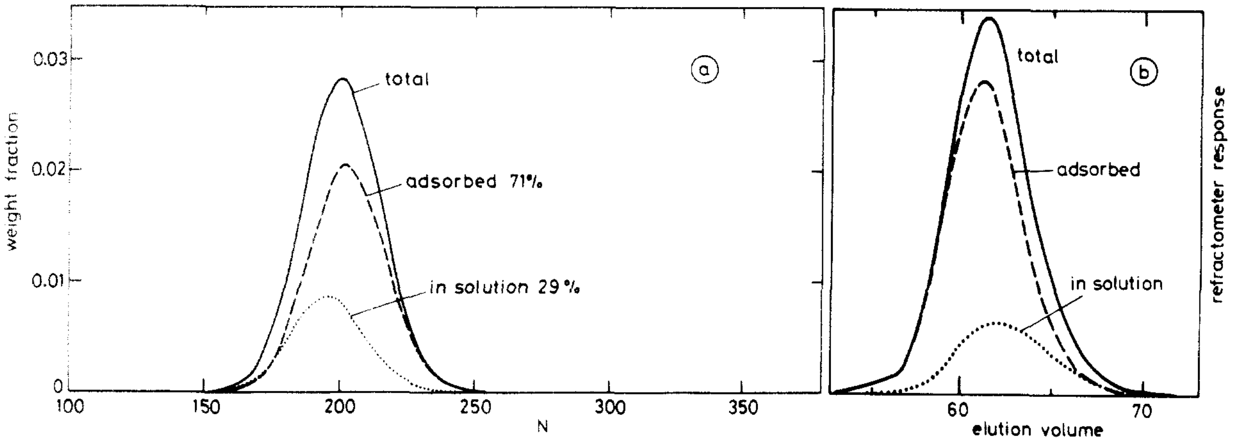

Figure 3. Same as in Figure 2, but now for a narrow Poison distribution $N_n = 200$, ($N_w/N_n = 1.005$), $\varphi^b = 5 \times 10^{-4}$, $V/A = 5000\ell$. Figure 2b is again taken from Vander Linden and Van Leemput (ref 16).

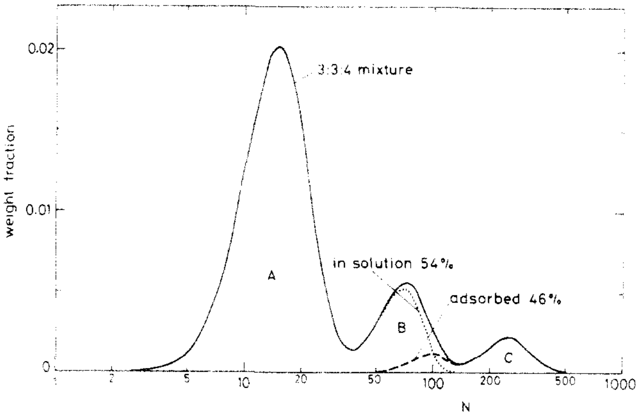

Figure 4. Adsorption of a 3:3:4 w/w mixture of three narrow Schulz–Flory polydisperse fractions A ($N_n = 15$, $N_w/N_n = 1.15$), B ($N_n = 70$, $N_w/N_n = 1.09$), and C ($N_n = 250$, $N_w/N_n = 1.08$). A considerable reduction in polydispersity is obtained, both at the surface and in the solution. Overall: $N_n = 39$, $N_w/N_n = 3.46$. In solution: $N_n = 23$, $N_w/N_n = 1.78$. Adsorbed: $N_n = 202$, $N_w/N_n = 1.23$. $V/A = 10\,000\ell$.

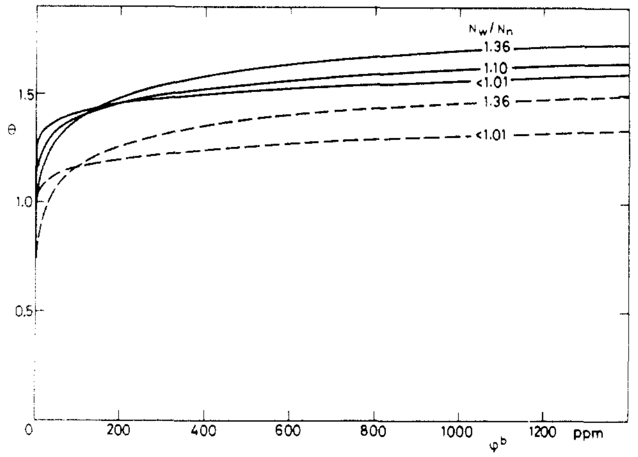

Figure 5. Effect of polydispersity on the shape of the adsorption isotherm. Isotherms with $N_n = 100$ (dashed curves) and $N_n = 200$ are given for different degrees of polydispersity, N_w/N_n (Schulz–Flory distribution). A higher degree of polydispersity leads to a more rounded shape of the isotherm and a less horizontal (pseudo)-plateau. $V/A = 5000\ell$.

but in all cases we found that the transition extends over less than half a decade in molecular weight. The fractionation results in a sharper molecular weight distribution in solution and also in a sharper distribution of the adsorbed molecules. In Figure 2a we find $N_w/N_n = 1.65$ in solution and $N_w/N_n = 1.48$ at the interface.

The preferential adsorption is very pronounced. Even if the molecular weight distribution is extremely narrow a significant fractionation occurs if the V/S ratio is large. In Figure 3a an example is given for a Poisson distribution ($N_w/N_n \approx 1 + (1/N_n) = 1.005$, $V/A = 5000\ell$). Even for this narrow distribution the adsorbed fraction has a higher molecular weight ($N_n = 202$) than the polymer in solution ($N_n = 195$). Figure 3b gives a comparable experimental result (reproduced from Figures 1 and 4c of ref 16) for the adsorption of polystyrene with a relatively narrow molecular weight distribution ($N_w/N_n = 1.17$) on silica. Clearly, the theoretical predictions are fully supported by experimental observations.

There is no restriction as to the shape of the chain-length distribution that can be dealt with by the theory. An examine is given in Figure 4, which shows the adsorption fractionation of a 3:3:4 w/w mixture of three polymer fractions, A, B, and C. In this case, polymer A ($N_n = 15$) is completely in the solution and polymer C ($N_n = 250$) is completely on the surface, whereas the major part of polymer B ($N_n = 70$) is in the solution and only a small fraction is adsorbed. A considerable reduction in polydispersity is obtained, both in the solution and on the surface, as can be seen from the numerical details given in the legend of Figure 4.

Adsorption Isotherms. The effect of polydispersity on the adsorption isotherm is demonstrated in Figure 5 for $N_n = 100$ (dashed curves) and $N_n = 200$ (full curves). The isotherms have been computed for Schulz–Flory distributions of various polydispersity ratios, as indicated along the curves; the volume/area (V/A) ratio was kept constant (5000ℓ). The curves for $N_w/N_n < 1.01$ are essentially identical to adsorption isotherms of monodisperse polymer and illustrate the high affinity character of polymer adsorption and its molecular weight effect. With an increasing degree of polydispersity the isotherms become more rounded because short chains are progressively displaced by longer ones as the polymer dose (and, hence, the concentration in solution) is increased. Even a polydispersity ratio of 1.1 already shows a significant effect. The isotherms for a given N_n show a common intersection point which depends on the adsorption energy and chain length. Below this point the solution concentration is higher and the adsorption is lower for a polydisperse polymer, because of the weak affinity of the shorter molecules for the (saturated) surface, whereas beyond this point an increasing number of longer molecules on the surface raises the adsorbed amount.

For a polydisperse polymer the initial slope of the isotherm is proportional to the volume/surface ratio.[17] This is best illustrated by isotherms for a mixture of two

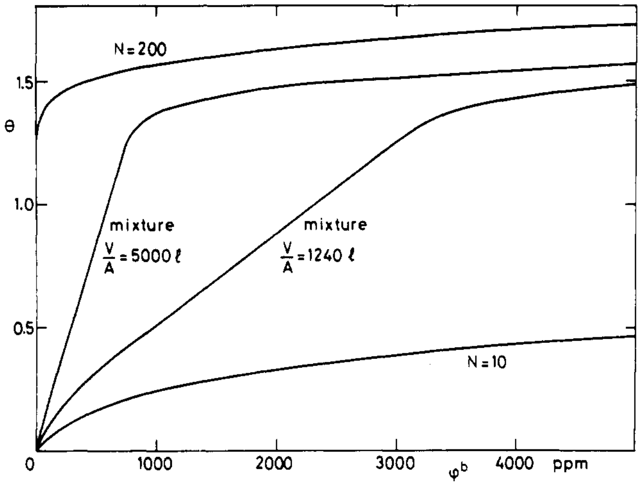

Figure 6. Theoretical adsorption isotherms for a bimodal mixture of short ($N = 10$) and long ($N = 200$) chains, at two V/A ratios. The weight fraction of long chains in the mixture is 0.25. For comparison, the isotherms for the monodisperse samples are also shown; these do not depend on V/A.

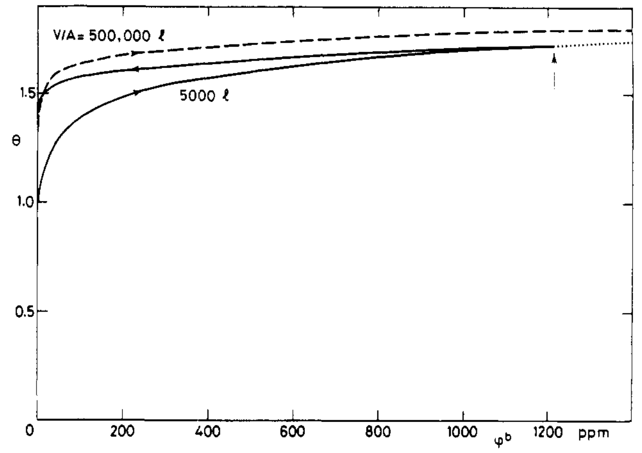

Figure 7. Two adsorption isotherms and one desorption isotherm for a polydisperse polymer sample with a Schulz–Flory distribution ($N_w/N_n = 1.36$). Although for each case the system is in full equilibrium, the isotherms do not coincide because of surface fractionation effects. The adsorption isotherms (arrows pointing to the right) are given for $V/A = 5000\ell$ (solid curve) and $V/A = 500\,000\ell$ (dashed curve). The desorption isotherm (arrow point to the left) simulates desorption by dilution and is given for a constant amount of polymer in the system (7.7 equivalent monolayers, corresponding to the amount present in the system at the vertical arrow). For this desorption isotherm, V/A increases from right to left.

monodisperse samples, as plotted in Figure 6. Two chain lengths are chosen for which the adsorption plateaus differ considerably. (The top curve is for a monodisperse sample with $N = 200$; the bottom curve is for $N = 10$.) A mixture of these polymers (with a mass fraction 0.25 for the long chains) shows adsorption isotherms with an essentially linear initial section, where the surface accommodates all the long molecules and a decreasing fraction of the short ones. The slope of the isotherm in this region is indeed proportional to V/A: the two curves differ a factor of 4.13 in slope and 4.03 in V/A. Beyond this linear section, in the pseudoplateau region, only long molecules are adsorbed, but the plateau does not coincide with that of the unmixed long chains: it is always lower and the isotherms run more or less parallel. The reason is that the concentration of long chains in the solution for mixture isotherm in the plateau region is only 25% of that for the isotherm of the monodisperse sample; the remaining 75% of short chains just sit in the solution, without affecting the adsorption equilibrium.

Although adsorption isotherms are rounded for polydisperse polymer, desorption by dilution hardly occurs because this does not alter the preferential adsorption but rather the volume/surface ratio. In Figure 7 an adsorption–desorption sequence is simulated. The bottom curve represents an adsorption isotherm for $V/A = 5000\ell$. A similar adsorption isotherm for $V/A = 500\,000\ell$ is indicated by the dashed curve. The total amount of polymer in the system at 1200 ppm and low V/A is about 7.7 monolayers (1.7 adsorbed and 6 in the solution). Three desorption isotherms were calculated by increasing V/A while keeping the total amount of polymer (7.7 monolayers) constant. The curve follows a high affinity isotherm, as hardly any desorption of long molecules takes place. When $V/A = 500\,000\ell$ (at the intersection point of the desorption curve and the dashed curve) the solution concentration is 12.45 ppm and the adsorbed amount is 1.5 monolayers.

We conclude that the difference between adsorption and desorption isotherms is not an indication that polymer adsorption is irreversible, since Figure 7 shows that it occurs in full equilibrium as well. The desorption isotherm (with varying V/A) corresponds to a series of points on adsorption isotherms, each with a different value of V/A. This does not reflect irreversibility, but simply a change of the mass balance.

Conclusions

The present theory is able to fully account for any molecular weight distribution of adsorbing polymer. The agreement with experimental results is excellent and trends predicted from previous simple models are fully corroborated.

The preferential adsorption of longer molecules is very pronounced in dilute solutions but decreases with increasing polymer concentration and eventually reverses at a critical concentration around a few tens of a percent.[28] At polymer concentrations around 1000 ppm the transition between nonadsorbed and adsorbed molecules occurs within half a decade in molecular weight. Adsorption isotherms of polydisperse polymers differ significantly from isotherms of monodisperse polymers, even if the degree of polydispersity is only 1.1. For increasing degree of polydispersity the adsorbed amount decreases at very low solution concentrations and increases at higher concentrations.

The slope of the isotherm of polydisperse polymer is proportional to the ratio between solution volume and surface area. The difference between adsorption and desorption isotherms can be reproduced by proper accounting for the change in volume/surface ratio.

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