Effects of Substrate Interactions in Liquid Chromatography of Star Homopolymers and Star Block Copolymers

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ABSTRACT: A theoretical study of the behavior in liquid chromatography of star polymers of two different kinds of arms is presented, including the special cases of diblock copolymers and regular star polymers. The two different kinds of interactions between the substrate and the monomeric units which can be repulsive attractive or neutral combine in these heteroarm stars. They can act cooperatively or antagonistically determining, in connection with the effects of the architecture and the sizes of the branches, the mode of retention of the macromolecules. The compensation point, where no surface effects remain when the surface−monomer interactions are negligible, can also be reached by cancellation of the opposite but not negligible interactions of the two different kinds of arms with the substrate.

1. Introduction

In liquid chromatography of polymers, the macromolecular chains in a solvent flow through a porous substrate in a column and the elution time, t_e, necessary for the polymers to travel from the top of the column to its bottom is the experimental observable. The technique is very important for the separation and identification not only of different polymers but also of polymers of the same monomeric units having different molecular weights or architecture.[1] The success of the method is based on the excellent effective separation which can be achieved by changing parameters like the temperature T, the size d of the pores of the substrate, or the nature of the solvent. These parameters determine the average interactions between the monomeric units and the solid surface of the substrate which influence the conformational behavior of the chains in the presence of the substrate. The mode of retention of the chains in the column is highly affected by the monomer−surface interactions, and three different modes of elution have been observed, depending on the nature of these interactions.[2,3] For repulsive interactions the probability of the chains to be far from the surface is large, the partition coefficient k of the chains between the stationary phase close to the surface and the mobile phase far from the surface is small, the macromolecules move fast and elute at the bottom of the column in short times t_e. In this exclusion mode the larger the molecular weights of the chains are, the smaller the values of k and the shorter the elution times t_e are.[4] For average attractions between the monomeric units and the substrate the chains are closer to the surface and the partition coefficients k and elution times t_e are large. Larger chains elute in larger times in this adsorption mode.[5] Of importance is also the critical region where the average interactions between the chains and the substrate are negligible, no dependence on the molecular weight M is observed and other characteristics of the chains can be studied.[6]

Though both thermodynamic and kinetic effects contribute to the retention behavior of the chains, the quasi equilibrium character of the phenomenon is dominant and the thermodynamic analysis which in any case is the first necessary step, can describe in a large extend liquid chromatography of polymers. The thermodynamic contribution leads to a partitioning of the chains between the mobile and the stationary phases and can be determined from the laws of statistical thermodynamics. Casassa et al. enhanced this thermodynamic aspect of liquid chromatography of polymers and studied linear and star chains by means of random flight statistics. The partition coefficient of chains in pores of special geometry's has been calculated as the ratio of the partition functions C of the stationary phase to that of the mobile phase.[7,8] In this way, the effects of pore geometry and architecture of the chains on size exclusion chromatography have been successfully described.[7] Corbunov et al. introduced the interactions of the monomeric units with the surface of the substrate which can determine the mode of retention.[9] The three different modes of elution, which have also been seen experimentally, can be described by a unified equation and a single interaction parameter u which is proportional to the intensity of these interactions.[3] Lattice methods and Monte Carlo stimulations have also been employed for the study of the effects of the surface interactions and the architecture of the chains.[10] The study of the effects coming from the size of the pores of the substrate and the way in which this influences the partition coefficients and elution times are also of importance.[11] Despite of the many efforts, the necessity for further theoretical treatment and understanding of the subject is large because of the increasing use of macromolecules with complicated structures. The comparison of the retention behavior of complex macromolecules of special interactions and architecture features with that of linear polymers is often employed. Unless the effects of microscopic parameters are determined, such comparisons and the use of calibration curves of linear chains to derive results for chains of other architectures are not always understandable and accurate.[12]

In this paper, we extend our recent study of the liquid chromatography of linear chains to the description to chains of more complex architectures. We include two different kinds of monomers and see how chain characteristics affect the three modes of elution of the chains. The behavior of special characteristic cases are given in sections 3 and 4. In section 3, we present the behavior

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of the class of regular star polymers, and in section 4, we explain the main characteristics of diblock copolymers. In section 5 we derive certain regularities for the general case of stars of two different species, and in section 6, we end with a conclusion.

2. Interactions with the Surface of the Substrate

When a chain is in the vicinity of a surface the monomeric units interact with the surface and the probability distribution $P\{R_i\}$ of the positions R_i ($i = 1, 2, ..., N$) of the N units of the chain can be written as the product of two factors:

$$P\{R_i\} = P_o\{R_i\} \exp\left\{-u \sum_{i=1}^{N} \delta(z_i)\right\} \qquad (2.1)$$

The first one, $P_o\{R_i\}$, is the probability distribution of the positions of the units of the ideal noninteracting chain, and the exponential term represents the contribution from the interactions with the surface. The parameter u is connected with the molecular interaction potential $V(z)$ by means of the binary cluster integral

$$u = \int_0^\infty dz\, [1 - \exp\{-V(z)/(kT)\}] \qquad (2.2)$$

and expresses the intensity of the interactions from each unit approaching the surface at a distance z_i. The probability $p \sim \exp\{-u\delta(z_i)\}$ of a contact, for large positive values of u, becomes small, indicating an increased repulsive character of the interactions, while negative values of u give large probabilities of contact describing attractions. Though the amount of adsorbed monomeric units depends also on the boundary conditions posed on the chains,[13,14] the region around $u = 0$, between repulsions and attractions, can be used to describe the situation where the chains do not feel special interactions with the surface. This arbitrariness in the values of u gives the possibility of adjustment for a proper description of experimental results. By integration with respect to all positions of the units of the chain but the position of the last unit, the probability of a linear chain localized with one end at the distance z from the surface has been obtained.[14] For reflecting boundary conditions, with zero the derivative of the probability at the surface, it is equal to

$$P(z) = 1 + F(z),$$
$$F(z) = \exp\left\{U^2 + \frac{Uz}{S_o}\right\} \mathrm{erfc}\left\{U + \frac{z}{2S_o}\right\} - \mathrm{erfc}\left\{\frac{z}{2S_o}\right\} \qquad (2.3)$$

with the interaction parameter $U = u(6N)^{1/2}/2$ and $S_o = l_o N^{1/2}/6^{1/2}$ the radius of gyration of the chain,[14] written in terms of the number N of the units of the chain which is proportional to the molecular weight of the polymer and the length l_o of each unit. Close to the surface (z small), $F(z)$ can be positive or negative for negative or positive u, respectively. This makes $P(z)$ larger or smaller than unity in the two cases, indicating larger or smaller probabilities to find a chain in the vicinity of the surface, for attractions or repulsions, respectively. At large distances z where no surface effects survive, $F(z)$ dies out, affecting no more $P(z)$. The ideal state with $u = 0$ is somehow arbitrary and the amount of monomeric units adsorbed depends also on the boundary conditions posed on the chains.[13,14] Varying u all situations from the full adsorption to complete desorption can be described giving thus the possibility of the adjustment of the value of u in order to be in accord with experimental findings.

For a heteroarm star macromolecule of two species with f_a arms of the first kind and f_b arms of the second, all starting from the same junction point, the probability to find the common junction at the point z is equal to the product $(1 + F_a(z))^{f_a} (1 + F_b(z))^{f_b}$ of the probabilities of all arms starting at z. $F_i(z)$ (i = a, b) refer to the two different kinds of arms with different radii of gyration $S_{oi} = l_i N_i^{1/2}/6^{1/2}$ and different interaction parameters $U_i = u_i(6N_i)^{1/2}/2$. Though the arms are ideal in the sense that no excluded volume interactions are considered, their behaviors are correlated. The first source of correlations comes through their starting from the common core which for example differentiates the behavior of the arms of a star from a mixture of linear homopolymers which behave independently. Second the arms are correlated through the interactions with the surface. When for example an arm is adsorbed the probability to find the rest arms of the macromolecule in the vicinity of the surface is increased. The configurational partition function C at the stationary phase is taken after the integration over all available positions z so that

$$C = S \int_0^d dz\, (1 + F_a(z))^{f_a} (1 + F_b(z))^{f_b} \qquad (2.4)$$

S is the total area of the available surface and d is the extension along the perpendicular axis z, which expresses the depth of the stationary phase, providing also a first description of the size of the pores of the substrate.[3] A useful step is to separate the volume contribution of C by writing it as

$$C = V\left\{1 - \frac{\Delta}{d}\right\},$$
$$\Delta = \int_0^d dz\, [1 - (1 + F_a(z))^{f_a}(1 + F_b(z))^{f_b}] \qquad (2.5)$$

where Δ is a finite quantity even in the limit of very large size d. In what follows the depth d will be considered to be much larger than the size of the chains so that the calculation of Δ in the limit $d \to \infty$ will be used. Through the division with the partition function in the mobile phase being proportional to the total available volume V, the partition coefficient $k = 1 - \Delta/d$ can be found which depends on Δ but also on the pore size d, describing in this way the chromatographic behavior of a large class of substrates with different average pore sizes. Δ which determines k describes the interactions with the substrate, and it is the central quantity in our analysis.

For the homopolymer case Δ can be found analytically, and it has been given before.[3,15] It is equal to

$$\Delta_h = -\int_0^\infty dz\, F(z) = S_o\left\{\frac{2}{\pi^{1/2}} - \frac{1}{U} + \frac{1}{U}\exp(U^2)\,\mathrm{erfc}\{U\}\right\}, \quad S_o = \frac{l_o N^{1/2}}{6^{1/2}}, \quad U = \frac{u(6N)^{1/2}}{2} \qquad (2.6)$$

with a plot of Δ_h/S_o appearing in Figure 1(normal line with crosses). All three modes are quantitatively explained by means of eq 2.6. For attractions, U is negative and Δ_h is negative, so that the partition

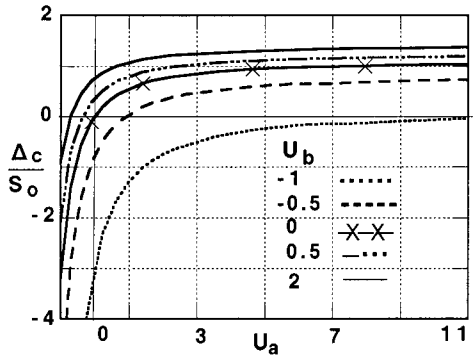

Figure 1. Δ_c/S_o of block copolymers of equal radii of gyration of the two blocks but different U_a and U_b interactions, as a function of the U_a parameter, eq 4.9. The cases with $U_b = -1$, -0.5, 0.5, 2 are the dotted, dashed, normal-dotted, and normal lines, respectively. The normal line with crosses represent the homopolymer case Δ_h/S_o, as a function of the interaction parameter $U_a = U(U_b = 0)$, eq 2.6.

coefficient k and the retention time t_e are large, describing the adsorption mode. As the molecular weight N is increased, U takes more negative values indicating that larger chains need indeed larger times to elute in this mode. For U positive, the interactions between the monomers and the surface are repulsive, Δ_h is positive and k and the elution times become smaller, describing the exclusion mode. Larger chains lead to larger Δ_h and smaller elution times, in accordance with what is observed in this mode. The compensation point where the interactions give zero net effect, takes place at $U = 0$. At this point, $\Delta_h = 0$, and no dependence on the molecular weight is observed. Another observed regularity which can be explained by means of the analytic expression, eq 2.6 is the broadening of the peak of chromatograms in certain regions. It has been observed that peak broadening increases significantly going from the exclusion to the critical region.[16] From eq 2.6 and Figure 1, we see that approaching the critical region the dependence of Δ_h on U, becomes steeper, indicating that small variation of the molecular weight of the chains will affect significantly retention times leading to the observed broadening. A similar tendency must be true also at the adsorption region.

3. Regular Star Polymers

For normal stars of f equal branches each of length N, Δ of eq 2.5 takes the form

$$\Delta_f = \int_0^\infty dz\,[1 - (1+ F(z))^f]$$

$$\text{with } F(z) = \exp\left\{U^2 + \frac{Uz}{S_o}\right\} \operatorname{erfc}\left\{U + \frac{z}{2S_o}\right\} - \operatorname{erfc}\left\{\frac{z}{2S_o}\right\}$$

with

$$S_o = \frac{l_o N^{1/2}}{6^{1/2}}, \quad U = \frac{u(6N)^{1/2}}{2} \tag{3.1}$$

and N the molecular weight of a branch. While the integrals for different values of f and U can generally be performed only numerically, useful analytical results can be derived at the limits of the three different modes. To describe the critical region of chromatography where compensation between the effects of repulsive and attractive forces occur, first-order calculation in U is adequate. The result is

$$\Delta_f = fUS_o = \frac{fNl_o u}{2} = \frac{Ml_o u}{2}, \quad \text{critical region of stars} \tag{3.2}$$

and at $u = 0$, the value of Δ_f is zero giving for the partition coefficient $k = 1 - \Delta_f$/d the value1 as expected. For u positive or negative, Δ_f becomes positive or negative, and the partition coefficient k becomes smaller or bigger than unity. This designates the leaving of the critical point and the beginning of the exclusion or adsorption regions for repulsions or attractions, respectively. In the critical region a proportionality between Δ_f and the total molecular weight M of the stars is obtained, eq 3.2, something which has also be seen before for linear chains by means of molecular simulations[11] and it is a challenge to experimental verification. This linear relation of the retention time on the total molecular weight M of the chains, in the neighborhood of the critical point, seems to be true for all polymers of a single species, regardless of the architecture of their chains, and it can be proven useful for quantitative measurements.

The exclusion mode of regular stars can be described from the general expression eq 3.1, by taking U to go to infinity. In this limit $F(z) = -\operatorname{erfc}(z/2S_o)$, and we have that

$$\Delta_f = \int_0^\infty dz\,[1 - (\operatorname{erf}(z/2S_o))^f] = 2S_o\alpha_f,$$

$$\alpha_f = \int_0^\infty dx\,[1 - (\operatorname{erf}(x))^f], \quad S_o = \frac{l_o N^{1/2}}{6^{1/2}}, \quad \text{exclusion mode} \tag{3.3}$$

In terms of the total molecular weight of the star $M = Nf$, we can write that

$$\Delta_f = 2(l_o M^{1/2}/6^{1/2})\alpha_f/f^{1/2} \tag{3.4}$$

The values of $\alpha_f/f^{1/2}$ are found numerically and are written in Table 1 for the first six values of f. Beyond the first two members of the series which represent linear chains, $\alpha_f/f^{1/2}$ is a decreasing function of f. This means that for constant total molecular weight M, increasing the number of branches of a regular star, Δ_f decreases and C and k increase, in accordance with previous results.[7,17] On the other hand, by increasing the number f of branches of a regular star, all of them being of equal length N, α_f and $\Delta_f = 2S_o\alpha_f$, increase. Therefore, the partition coefficient k decreases, indicating that larger regular stars elute in smaller elution times. The radius of gyration of a regular star is equal to $S_f = S_o((3 - (2/f))^{1/2}$ with S_o the radius of gyration of a branch.[18] For linear chains ($f = 1$, 2), we have $\Delta_f = 1.128S_f = 2S_o\alpha_{of}$ with $\alpha_{of} = 0.564((3-(2/f))^{1/2}$ written also in Table 1, while for compact stars with larger values

Table 1

f	α_f	α_{of}	$\alpha_f/f^{1/2}$	k_f
1	0.564	0.564	0.564	2.000
2	0.798	0.798	0.564	2.000
3	0.938	0.862	0.542	2.267
4	1.036	0.892	0.518	4.000
5	1.110	0.910	0.496	6.400
6	1.170	0.921	0.478	10.667

of f, $\Delta_f = 2S_o\alpha_f$, which is larger than $2S_o\alpha_{of}$. This indicates that the presence of the surface differentiates the real Δ_f of stars, making it bigger in this exclusion mode than what is found from the radius of gyration. The influence of the surface interactions on the behavior of macromolecules is profound, even in the region of exclusion where the chains are far from the surface and the influence of the surface is smaller than in the other two regions of adsorption or criticality.

Finally the adsorption mode is taken in the limit of $U \rightarrow -\infty$ where $F(z) = 2\exp\{U^2 - |U|z/S_o\}$, and Δ_f of regular stars becomes equal to

$$\Delta_f = -\frac{S_o 2^f \exp\{fU^2\}}{f|U|}, \quad \text{adsorption mode, regular stars} \quad (3.5)$$

For constant molecular weight $M = Nf$, we take

$$\Delta_f = -\exp\left\{\frac{3u^2 M}{2}\right\}\frac{l_o}{3|u|}k_f, \quad k_f = \frac{2^f}{f} \quad (3.6)$$

The values of k_f are written in Table 1 and we see that larger f values give smaller (more negative) Δ_f and larger partition coefficients k, in this mode of adsorption. More compact structures, like these of stars of larger f and constant total molecular weight M, elute over longer times. The tendency of the elution times to increase on increasing the compactness of the chains seems to be true in both exclusion and adsorption modes, although of course the retention times are generally larger in the adsorption modes.

4. Block Copolymers

For the interesting class of block copolymers of two blocks a and b,[19] Δ takes the form

$$\Delta_c = -\int_0^\infty dz\,[F_a(z) + F_b(z) + F_a(z)F_b(z)],$$

$$F_i(z) = \exp\{U_i^2 + (U_i z/S_i)\}\,\mathrm{erfc}\{U_i + (z/2S_i)\} - \mathrm{erfc}\{z/2S_i\}, \quad S_i = l_i N_i^{1/2}/6^{1/2}, \quad U_i = u_i(6N_i)^{1/2}/2, \quad i = a, b$$

$$\Delta_c = \Delta_a + \Delta_b + K,$$

$$\Delta_i = S_i\left\{\frac{2}{\pi^{1/2}} - \frac{1}{U_i} + \frac{1}{U_i}\exp(U_i^2)\,\mathrm{erfc}\{U_i\}\right\},$$

$$K = -\int_0^\infty dz\,F_a(z)F_b(z)] \quad (4.1)$$

While the first two terms in eq 4.1 describe the contribution from the two separate blocks acting as independent homopolymers, the K term gives the cross effects of the presence of both blocks and expresses the degree of their correlation. The interactions of the surface with the two different blocks may be of the same or opposite nature, and the elution mode of the copolymer is therefore the result of the cooperation or the competition of the two blocks. The chromatographic behavior of the whole macromolecule can be found by means of the study of the dependence of both Δ_a and Δ_b and the factor K on the interaction parameters and the molecular weights of the blocks. K can be written as

$$K = -I(a,b) + I(a,o) + I(o,b) - I(o,o)$$

$$\text{with } I(a,b) = \int_0^\infty dz\,\exp\left\{U_a^2 + U_b^2 + \left(\frac{U_a}{S_a} + \frac{U_b}{S_b}\right)z\right\}\mathrm{erfc}\left\{U_a + \frac{z}{2S_a}\right\}\mathrm{erfc}\left\{U_b + \frac{z}{2S_b}\right\} \quad (4.2)$$

and $I(a,o)$, $I(o,b)$, $I(o,o)$ equal to $I(a,b)$ for $U_a = 0$, $U_b = 0$ and U_a, $U_b = 0$, respectively. It is straightforward to show that

$$I(a,b) = -\frac{\exp\{U_a^2 + U_b^2\}}{\frac{U_a}{S_a} + \frac{U_b}{S_b}}\mathrm{erfc}\{U_a\}\,\mathrm{erfc}\{U_b\} + \frac{I(U_a) + I(U_b)}{\left(\frac{U_a}{S_a} + \frac{U_b}{S_b}\right)\pi^{1/2}}$$

with

$$I(U_a) = \frac{\exp\{U_a^2\}}{S_b}\int_0^\infty dz\,\exp\left\{\frac{U_a z}{S_a} - \frac{z^2}{4S_b^2}\right\}\mathrm{erfc}\left\{U_a + \frac{z}{2S_a}\right\} \quad (4.3)$$

and a symmetrical relation for $I(U_b)$. A convenient form for $I(U_a)$ in terms of a finite integral is the following:

$$I(U_a) = \exp\left\{\frac{U_a^2 S^2}{S_a^2}\right\}\left\{\frac{2}{\pi^{1/2}}\tan^{-1}\left(\frac{S_a}{S_b}\right) - \pi^{1/2}\,\mathrm{erf}\left(U_a\frac{S}{S_a}\right) + \pi^{1/2}\mathrm{erf}\left(U_a\frac{S_b}{S_a}\right) - 2\int_0^{U_a S_b/S_a} dy\,\exp\{-y^2\}\,\mathrm{erf}\left(\frac{yS_a}{S_b}\right)\right\}, \quad S = (S_a^2 + S_b^2)^{1/2} \quad (4.4)$$

with a symmetrical expression for $I(U_b)$. Equations 4.1−4.4 can be used to derive the limit of the linear homopolymer chain and derive also a useful analytical result.

To recover the limit of a homopolymer from the diblock expression we must have $u_a = u_b = u$. For simplicity we take also $l_a = l_b = l_o = 1$ so that

$$\frac{U_a}{S_a} = \frac{U_b}{S_b} = 3u$$

Under these circumstances Δ_c must be identical to that of a homopolymer chain of length N equal to the sum $N = N_a + N_b$ of the lengths of the two blocks. By means of the definition $\mathrm{erf}(x) = 2/\pi^{1/2}\int_0^x dy\,\exp\{-y^2\}$, it can be proved that

$$\frac{2}{\pi^{1/2}}\exp\{U_b^2 S^2/S_b^2\}\int_0^{U_b S_a/S_b} dy\,\exp\{-y^2\}\,\mathrm{erf}\left(\frac{yS_b}{S_a}\right) + \frac{2}{\pi^{1/2}}\exp\{U_a^2 S^2/S_a^2\}\int_0^{U_a S_b/S_a} dy\,\exp\{-y^2\}\,\mathrm{erf}\left(\frac{yS_a}{S_b}\right) = \exp\{9u^2S^2\}\mathrm{erf}\{3uS_a\}\,\mathrm{erf}\{3uS_b\} \quad (4.5)$$

so that $I(a,b)$ can be written as

$$I(\mathrm{a,b}) = \frac{\exp\{9u^2S^2\}}{3u}\{\mathrm{erf}\{3uS_a\} + \mathrm{erf}\{3uS_b\} - \mathrm{erf}\{3uS\} - \mathrm{erf}\{3uS_a\}\,\mathrm{erf}\{3uS_b\}\} \quad (4.6)$$

Similarly we obtain that

$$I(\mathrm{a,o}) + I(\mathrm{o,b}) = -\frac{\exp\{9u^2S_a{}^2\}}{3u}\mathrm{erfc}\{3uS_a\} - \frac{\exp\{9u^2S_b{}^2\}}{3u}\mathrm{erfc}\{3uS_b\} + \frac{1}{3u}\{\exp(9u^2S^2)[1 - 2\mathrm{erf}\{3uS\} + \mathrm{erf}\{3uS_a\} + \mathrm{erf}\{3uS_b\} - \mathrm{erf}\{3uS_a\}\,\mathrm{erf}\{3uS_b\}] + 1\}$$

and

$$I(\mathrm{o,o}) = [2/\pi^{1/2}]\,[S_a + S_b - S]$$

Substituting in eq 4.2 we finally take that

$$\Delta_c = S\left[\frac{2}{\pi^{1/2}} - \frac{1}{U} + \frac{1}{U}\exp(U^2)\,\mathrm{erfc}\{U\}\right]$$

with

$$S = (S_a{}^2 + S_b{}^2)^{1/2} \quad \text{and} \quad U = \frac{u6(N_a + N_b)^{1/2}}{2} \quad (4.7)$$

which indeed corresponds to the Δ of a homopolymer chain of length $N = N_a + N_b$, equal to the sum of the lengths of the two blocks.

Of interest is also the case with $S_a = S_b = S_o$ for which the integrals of $I(U_a)$ and $I(U_b)$ are doable giving that

$$\frac{2}{\pi^{1/2}}\int_0^{U_bS_a/S_b} dy\,\exp\{-y^2\}\,\mathrm{erf}\left(\frac{yS_b}{S_a}\right) = \frac{2}{\pi^{1/2}}\int_0^{U_b} dy\,\exp\{-y^2\}\,\mathrm{erf}(y) = \frac{1}{2}\,\mathrm{erf}^2(U_b) \quad (4.8)$$

An analytical expression can then be written for Δ_c, in terms of the error functions, as

$$\Delta_c/S_o = -\frac{1}{2}\left(\frac{1}{U_a} + \frac{1}{U_b}\right) + \frac{22^{1/2}}{\pi^{1/2}} + \frac{1}{U_a + U_b}\exp\{U_a{}^2 + U_b{}^2\}\,\mathrm{erfc}\{U_a\}\,\mathrm{erfc}\{U_b\} + \left(\frac{1}{U_a} - \frac{1}{U_a + U_b}\right)\exp(2U_a{}^2)\left[\frac{1}{2} - \frac{1}{2}\mathrm{erf}^2(U_a) + \mathrm{erf}(U_a) - \mathrm{erf}(2^{1/2}\,U_a)\right] + \left(\frac{1}{U_b} - \frac{1}{U_a + U_b}\right)\exp(2U_b{}^2)\left[\frac{1}{2} - \frac{1}{2}\mathrm{erf}^2(U_b) + \mathrm{erf}(U_b) - \mathrm{erf}(2^{1/2}\,U_b)\right] \quad (4.9)$$

By means of this relation the effects of the simultaneous action of the two different interaction parameters u_a and u_b can be studied. To see for example the effect of varying the intensity of repulsive and attractive interactions of the two blocks, we plot in Figure 1 Δ_c/S_o, as a function of U_a and for the values $U_b = -1, -0.5, 0, 0.5, 2$ (dotted, dashed, normal with crosses, dotted-normal, normal). From the graphs we see that increasing U_a, Δ_c increases leading to a reduction of elution times. A similar increase of Δ_c takes place on increasing the U_b repulsions, going for example from the graph with $U_b = -1$ (dotted) to the graph with $U_b = 2$ (normal). When the molecular weight of a block is increased, if the corresponding interaction is positive we move to higher values of U and Δ, resulting in a smaller elution time. In the case of negative values of the interaction parameter U on increasing the molecular weight of the corresponding block, we move to the opposite direction taking smaller Δ and larger elution time.

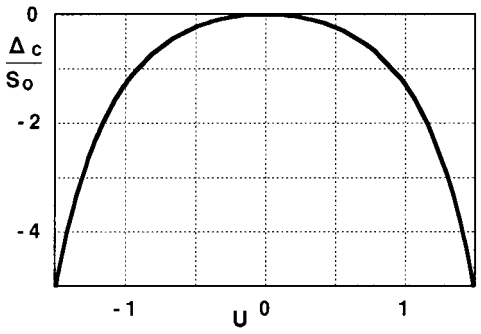

Figure 2. Δ_c/S_o of a block copolymer with the two blocks having the same radii of gyration but with opposite interaction parameters $U_a = -U_b = U$, as a function of U, eq 4.10. Notice that the difference $1 - \Delta/d$ gives the partition coefficient k which determines the elution time t_e.

Of interest is also the study of the case with opposite interactions of the two blocks with $U_a = -U_b = U$. For this case we take from eq 4.9, by finding the limit $U_a = -U_b \to U$, the expression

$$\Delta c = S_o\left\{\frac{4.2^{1/2}}{\pi^{1/2}} - \frac{4}{\pi^{1/2}}\exp(U^2) + 2\exp(2\,U^2)\,[\mathrm{erf}(2^{1/2}U) - \mathrm{erf}(U)]\left(2U - \frac{1}{U}\right)\right\},\ U_a = -U_b = U \quad (4.10)$$

We plot this dependence in Figure 2 and from the graph we see that Δ_c is symmetrical to the change $U \to -U$ as expected and always negative. The negative values of Δ_c prove that the net interactions are always attractive and that k is always larger than unity. The adsorption character, being stronger for equal blocks with $S_a = S_b = S_o$ and $U_a = -U_b$, always dominates. In this case Δ_c becomes more negative on increasing U, indicating an increase of the intensity of adsorption.

5. The General Case

(A) Exclusion Mode. From the general expression, eq 2.5, the case with both kinds of branches being in the exclusion mode (U_a, $U_b \to \infty$) takes the form

$$\Delta_{f_a,f_b} = \int_0^\infty dz\left[1 - \mathrm{erf}^{f_a}\left(\frac{z}{2S_a}\right)\mathrm{erf}^{f_b}\left(\frac{z}{2S_b}\right)\right] \quad (5.1)$$

Two limits can be seen from relation, eq 5.1. In the limit $S_a \to 0$, $\mathrm{erf}(z/2S_a) \to 1$, and the value $\Delta_{f_b} = = \int_0^\infty dz\,[1 - \mathrm{erf}^{f_b}(z/2S_b)] = 2S_b\alpha_{f_b}$ of the regular star of f_b branches is recovered. On the other hand for large S_a and finite S_b, Δ can be written as $\Delta = S_a\int_0^\infty dx\,[1 - \mathrm{erf}^{f_a}(x/2)\mathrm{erf}^{f_b}(xS_a/2S_b)]$ and since in the limit $S_a \to \infty$, $\mathrm{erf}(xS_a/2S_b) \to 1$, the result of $\Delta_{f_a} = \int_0^\infty dz\,[1 - \mathrm{erf}^{f_a}(z/2S_a)] = 2S_a\alpha_{f_a}$ of a regular star of f_a branches is obtained. In Figure 3, an example of the application of eq 5.1 is presented. $\Delta_{f_a,f_b}/S_a = 2\int_0^\infty dx\,[1 - \mathrm{erf}^{f_a}(x))\mathrm{erf}^{f_b}(x/\lambda)]$ as a function of $\lambda = S_b/S_a$ is seen, for the cases of $f_a = 1$, $f_b = 1, 2, 3$, and $f_a = 2$, $f_b = 1, 2, 3$. The derivative of $\Delta_{f_a,f_b}/S_a$ with respect to λ is always positive proving that $\Delta_{f_a,f_b}/S_a$ is a monotonic increasing function of λ. Increasing the number

of branches, $\Delta_{f_a,f_b}/S_a$ increases, following the same trend as that of regular star polymers. It starts from the value $\Delta_{f_a,f_b}/S_a = 2a_{f_a}$ at the limit $\lambda \rightarrow 0$ and ends up at the function $\Delta_{f_a,f_b}/S_a = 2\,\lambda a_{f_b}$ at large values of λ.

(B) Adsorption Mode. In the case of the adsorption of all branches where both U_a and U_b obtain large negative values, $F_i(z) = 2\exp\{U_i^2 - |U_i|z/S_i\}$ (i = a, b), and we take for Δ_{f_a,f_b} the expression

$$\Delta_{f_a,f_b} = -\frac{2^{f_a+f_b}\exp\{f_a U_a^2 + f_b U_b^2\}}{\frac{|U_a|f_a}{S_a} + \frac{|U_b|f_b}{S_b}} \qquad (5.2)$$

According to eq 5.2, Δ_{f_a,f_b} obtains large negative values, becoming more negative on increasing the number of the branches of the star, the intensities $|U_i|$ of attractions or the size S_i of the two kinds of branches. This explains therefore, quantitatively, the way k increases on increasing the attractions the number of branches and the size of the macromolecule.

(C) Critical Region. The critical region is described with the first-order result with respect to the U_a and U_b interactions. In this limit $F_i(z) = U_i\{z/S_i\ \mathrm{erfc}[z/2S_i] - 2/\pi^{1/2}\exp[-z^2/4S_i^2]\}$ and Δ_{f_a,f_b} becomes equal to

$$\Delta_{f_a,f_b} = f_a S_a U_a + f_b S_b U_b \qquad (5.3)$$

Δ_{f_a,f_b} becomes zero either when both U_a and U_b are zero or when the two interaction parameters obtain certain opposite values. A competition between the two kinds of arms is seen in the later case of small but nonzero interactions. The compensation point for the hole star occurs when the sum of the products of the numbers of branches the radii of gyration of the branches and the intensity of the two opposite interactions vanish that is $\Delta_{f_a,f_b} = f_a S_a U_a + f_b S_b U_b = 0$.

By means of the results derived in the previous sections in special regions and for characteristic cases, the main regularities of stars of two species have been realized. We can proceed in this stage and search by means of numerical performance of the integrals of eq 2.5, the general behavior of star polymers of two different kinds of branches. We will check the main factors which increase Δ_{f_a,f_b} or decrease k and the elution times. As indicated from the above examples an increase of Δ_{f_a,f_b} is expected on increasing the number of desorbed branches or their molecular weights while the number of adsorbed branches or their molecular weights must decrease in order to obtain larger Δ_{f_a,f_b}'s. Indeed in Figure 4a we see that Δ_{f_a,f_b} is an increasing function of N_b of the desorbed arms. Larger numbers f_b of the b arms lead to larger values of Δ_{f_a,f_b} as well. In Figure 4b we see that increasing N_b we obtain smaller values of Δ_{f_a,f_b} because the b branches are adsorbed. Increasing f_b in this case Δ_{f_a,f_b} becomes smaller. The compensation point for finite interactions where Δ_{f_a,f_b} becomes zero and assigns the beginning of the adsorption or exclusion behavior of the whole macromolecule can also be determined from figures like Figure 4b. We see that for the case of the stars of Figure 4b, the compensation point for the stars with $f_a = 1$, $f_b = 6$ takes place at the smaller value of N_b. The stars with $(f_a,f_b) = (2,6)$ and (1,3) follow at about the same value of N_b and then the stars (1,2) and (2,3) have their compensation points at larger values of N_b. The stars (1,1) and (2,2) have their compensation points at the next same value of N_b, and finally the star (2,1) has its compensation point at the larger value of N_b.

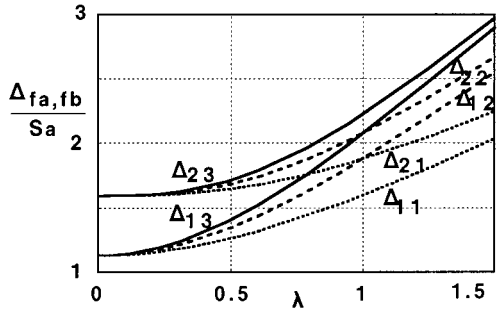

Figure 3. $\Delta_{f_a,f_b}/S_a$ of a heteroarm star at the exclusion mode, eq 5.1, as a function of the ratio $\lambda = S_b/S_a$ of the radii of gyration of two different branches. The values of the numbers of branches are as follows: $f_a = 1$, $f_b = 1$(dotted bottom line); $f_a = 1$, $f_b = 2$ (dashed bottom); $f_a = 1$, $f_b = 3$ (normal bottom); $f_a = 2$, $f_b = 1$ (dotted top); $f_a = 2$, $f_b = 2$ (dashed top); $f_a = 2$, $f_b = 3$ (normal top).

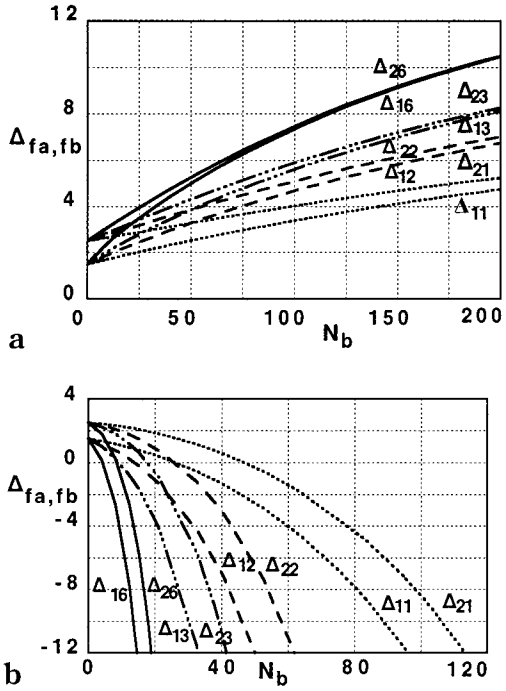

Figure 4. (a) Δ_{f_a,f_b} of a heteroarm star, eq 2.5, *which determines the partition coefficient* $k = 1 - (\Delta_{f_a,f_b}/d)$ *and the elution time,* as a function of the molecular weight N_b of the b branch for the cases with $f_a = 1$ and $f_b = 1$, 2, 3, 6 (bottom lines) and $f_a = 2$ and $f_b = 1$, 2, 3, 6 (top lines) for $N_a = 50$, $u_a = 0.1$, and $u_b = 0.1$. (b) Δ_{f_a,f_b} of a heteroarm star, eq 2.5, as a function of the molecular weight N_b of the b branch for the cases with $f_a = 1$ and $f_b = 1$, 2, 3, 6 (top lines) and $f_a = 2$ and $f_b = 1$, 2, 3, 6 (bottom lines) for $N_a = 50$, $u_a = 0.1$, and $u_b = -0.1$.

6. Conclusions

The quantitative behavior of star polymers of two different kinds of branches, in liquid chromatography, has been given. A quantity Δ has been defined which determines the partition coefficient $k = 1 - (\Delta/d)$ and the elution times t_e of the chains. When the number or the molecular weight of the branches with attractive interactions with the surface of the substrate increase, the elution times increase, while the increase of the number or the molecular weight of the branches with repulsive interactions decreases the elution times. The compensation point where $\Delta = 0$ and no average surface

effects remain can be produced either from vanishing interactions or the cancellation of the opposite interactions of the two different blocks. In the latter case, the compensation point depends on the number of adsorbed and desorbed branches the intensity of their interactions with the substrate and their molecular weights.

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