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Partitioning Inversion of a Bimodal Polymer Solution in Confined Geometries

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ABSTRACT: The partitioning of solvated polymer molecules with a bimodal molecular weight distribution between a confined geometry such as a porous medium and an external free volume has been investigated. Applying the results of renormalization group theory, we derive the chemical potentials in the interior and exterior of the pore for each fraction of the polymer in equilibrium. It was found that, as the concentration of the high molar mass macromolecule exceeds the overlap concentration in the exterior, the low molar mass fraction is driven into the restricted pore channels, while the high molar mass fraction remains outside. We note that this segregation effect could in principle be used to recover a low molar mass fraction in high purity from a mixture. The implication of this finding with respect to size-exclusion chromatography is also briefly mentioned.

Introduction

The partitioning of polymer chains in solution between a confined but accessible geometry and the surrounding free solution is fundamental to size-exclusion chromatography (SEC).[1–3] The parameter of interest, the partition coefficient, is simply the ratio of the polymer concentration in a porous medium, a typical confined geometry, to the concentration in the exterior. SEC utilizes the sharp decrease in the partition coefficient as a function of the chain dimension of the injected material and the concomitant faster elution. This principle works, however, only for very dilute solution.[4–6] In our recent contribution,[7] we showed generally that the partition coefficient p for a given system of a polymer solute in a good solvent exhibits a rapid increase toward unity as the polymer concentration in the exterior of the porous medium exceeds the overlap concentration. When there is significant chain overlap, a buildup in the osmotic pressure in the exterior drives the polymer chains into narrow pore channels even at the expense of their reduced configurational entropy. Thus as the exterior concentration further increases, p approaches 1. Chain contraction in the semidilute regime augments the increase in p, but the effect is minor relative to the osmotic pressure effect. The transition from the weak to the strong penetration regimes[8,9] is more prominent for a higher molecular weight fraction, which has a smaller p in the dilute limit of the exterior concentration.

In this contribution, we extend our previous work[7] to a polymer solution in which there is a bimodal molecular weight distribution. It is exemplified by a mixture of two monodisperse fractions of the same polymer, the fractions thus differing only in chain dimensions. The solvent is considered to be good. We consider how the partition coefficient for each fraction changes when the concentrations of the two fractions in the free solution are allowed to vary. First, using the well-known results of renormalization group theory,[10] we derive equations for chemical potential equilibrium between the interior and the exterior for each fraction. Solving the equations self-consistently, we show that there can be an *inversion* of the partition coefficient of the *low* molar mass fraction when the concentration of the *high* molar mass fraction exceeds the overlap concentration in the free solution. In contrast to the usual partitioning of a single monodisperse polymer, the confined geometry in this case can accommodate a larger population density than the unrestricted exterior can. We will also discuss how to apply the partitioning inversion to fractionation of polydispersed polymer samples and mention the effect of the presence of a small amount of a high molar mass fraction in the injected material on the elution profile in SEC.

Theory

As the polymer concentration c (total number of polymer chains per unit volume) increases, the osmotic pressure Π deviates from that for an ideal dilute solution. Concurrently, the chain begins to contract as a result of the screening of the excluded volume. Ohta and Oono[10] obtained approximate expressions for Π and the contraction factor of the mean-square end-to-end distance $R_F{}^2$ for a polydisperse polymer solution. The degree of polymerization N has a distribution characterized by a polydispersity index $\beta \equiv \langle N^2\rangle/\langle N\rangle^2$, where $\langle\ \rangle$ is the average with respect to the distribution. At a reduced concentration $X \equiv \alpha_N c\langle N\rangle^{3\nu}$ with $\nu \cong 0.588$ and a coefficient α_N determined below; the approximations are in the forms $\Pi/ck_BT = P(X;\beta)$ and $R_g/R_g^{(0)} = R(X;\beta)$, where k_B is the Boltzmann constant, T is the absolute temperature, and R_g and $R_g^{(0)}$ are the radii of gyration at concentration X and in the dilute solution limit, respectively.[11] The functions are

$$P(X;\beta)=1+\frac{1}{2}X\exp\left\{\frac{1}{4}\left[\frac{1}{\beta X}+\frac{\ln\beta}{(\beta X)^2}+\left(1-\frac{1}{(\beta X)^2}\right)\ln(X+1/\beta)\right]\right\}$$

and

$$R(X;\beta)=\exp\left\{\frac{X}{16}\left[\frac{3}{Y}-\left(\frac{3}{2Y^2}+\frac{1}{Y}\right)\times(\ln(2Y)+\gamma)+e^{2Y}\,\mathrm{Ei}(-2Y)\left(1-\frac{2}{Y}+\frac{3}{2Y^2}\right)\right]\right\}$$

where $Y = X + 1/\beta$, $\gamma \cong 0.5772$ is Euler's constant, and $\mathrm{Ei}(-\chi) \equiv -\int_x^\infty t^{-1}\exp(-t)\,\mathrm{d}t$.[12]

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We now apply these expressions to a solution of polymer with a bimodal molecular weight distribution. Let us define a reduced concentration X_i for fraction i, with a degree of polymerization N_i, by $X_i = \alpha_C c_i/c_i^*$ (i = 1, 2), where α_C is a numerical coefficient, c_i is the number concentration of the fraction $i (c_1 + c_2 = c)$, and the overlap concentration c_i^* is defined[13] by $c_i^*(\sqrt{2}R_{gi}^{(0)})^3 = 1$ for a pure solution of the fraction i. Comparison of the linear terms in $P(X;1)$ and an expression for Π in virial expansion[13] yields $\alpha_C \cong 3.49$.[7] By definition $X_i = \alpha_N c_i N_i^{3\nu}$; therefore, $\alpha_N = \alpha_C(\sqrt{2}R_{gi}^{(0)}/N_i^{\nu})^3$. Thus, the reduced concentration X and the polydispersity index β for the mixture of the two fractions are given by

$$X^{1/3\nu} = (1 + c_2/c_1)^{1/3\nu-1}[X_1^{\ 1/3\nu} + (c_2/c_1)^{1-1/3\nu}X_2^{\ 1/3\nu}] \qquad (1)$$

$$\beta = \frac{(1 + c_2/c_1)[1 + (c_2/c_1)(N_2/N_1)^2]}{[1 + (c_2/c_1)(N_2/N_1)]^2} \qquad (2)$$

with $c_2/c_1 = (X_2/X_1)(R_{g1}^{(0)}/R_{g2}^{(0)})^3$ and $N_2/N_1 = (R_{g2}^{(0)}/R_{g1}^{(0)1/\nu}$. The Gibbs free energy of the polymer solution is given as

$$G/k_BT = n_1 \ln c_1 + n_2 \ln c_2 + (n_1 + n_2)\, I(X;\beta) \qquad (3)$$

where $n_i \equiv Vc_i$ (V is the volume) is the total number of molecules of the fraction i, and the interaction $I(X;\beta) \equiv P(X;\beta) - 1 + \int_0^X x^{-1}[P(x;\beta) - 1]\, dx$ vanishes at $X = 0$.

Let us consider a porous medium equilibrated with a large volume of a free solution of a bimodal polymer. We assume that the vacant spaces of the porous medium can be represented by cylinders of radius R_P and that the surface of the solid walls is inert. Therefore, the geometrical restriction of the pore merely changes the configurational entropy of a polymer chain relative to that in the unrestricted space. For a polymer chain of the fraction i in the pore, the free energy is increased by an entropy term ΔS_i due to the restriction on the number of conformations available.[14] When the reduced concentrations of the two fractions are given in the exterior of the pore as X_{1E} and X_{2E}, the interior counterparts X_{1I} and X_{2I} are determined by equilibration of the chemical potentials for the two fractions. From eq 3, the relationship

$$\ln c_{iE} + I\,(X_E;\beta_E) = \ln c_{iI} + I(X_I;\beta_I) + \Delta S_i/k_B \quad (i = 1,2) \qquad (4)$$

can be derived, where the subscripts E and I denote the exterior and the interior of the pore, respectively. Note that the interaction term in the chemical potential of the fraction i depends on the total concentration X_E and the polydispersity index β_E, because the interaction is between two monomers common to the two fractions. The interaction term applies also to the solution in the interior of the pore, as long as $R_g^{(0)}$ is not extremely large compared with R_P, as was discussed by Teraoka et al.[7]

Casassa[14] obtained an expression for the entropy reduction ΔS for an isolated Gaussian coil with radius of gyration R_g confined in a cylindrical pore with radius R_P as $\exp(-\Delta S/k_B) = f(R_g/R_P)$ with

$$f(x) = 4\sum_{m=1}^{\infty} b_m^{\ -2} \exp(-b_m^{\ 2}x^2)$$

where b_m (m = 1,2, ...) is the mth root of the zeroth-order Bessel function $J_0(b) = 0$. We assume here that this expression can be applied to a solution of polymer with excluded volume, and, on the basis of this assumption, we obtain the following expression for the concentration-dependent entropy reduction:[15]

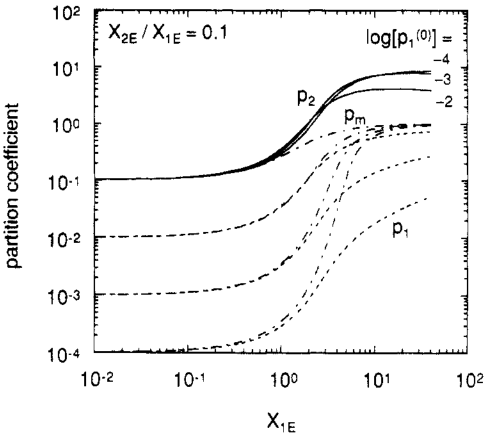

Figure 1. Partition coefficients p_1 (dashed line) and p_2 (solid line) for fractions 1 and 2, plotted as a function of X_{1E} for $X_{2E}/X_{1E} = 0.1$, $p_2^{(0)} = 10^{-1}$ ($R_{g2}^{(0)}/R_P \cong 0.585$), and $p_1^{(0)} = 10^{-2}, 10^{-3}$, and 10^{-4} ($R_{g1}^{(0)}/R_P \cong$ 0.861, 1.068, and 1.240, respectively). For reference, the partition coefficient p_m (dash-dotted line) for a monodisperse polymer is plotted for $p_m^{(0)} = 10^{-1}, 10^{-2}, 10^{-3}$, and 10^{-4}. Plots of p_1 and p_m can be identified by their values in the limit of $X_{1E} \to 0$.

$$\Delta S_i/k_B = -\ln f((R_{gi}^{(0)}/R_P)R(X_I;\beta_I)) \qquad (5)$$

In the dilute limit, the partition coefficient $p_i \equiv X_{iI}/X_{iE} = c_{iI}/c_{iE}$ of the fraction i (i = 1, 2) is determined purely by an entropic factor, $p_i^{(0)} = f(R_{gi}^{(0)}/R_P)$. Therefore, $p_i^{(0)}$ can be regarded as a parameter reflecting the dimension of an isolated chain of the fraction i relative to the pore radius.

The set of equations, eqs 1, 2, 4 and 5 can be solved self-consistently to yield X_{1I} and X_{2I} for given external concentrations X_{1E} and X_{2E} and the partition coefficients $p_1^{(0)}$ and $p_2^{(0)}$ in the dilute limit. In the following, we show the results of the calculation for $N_1 > N_2$.

Discussion

First, we consider the case where the high molar mass fraction has a higher reduced concentration in the exterior, i.e., $X_{1E} > X_{2E}$. Note, however, that this condition does not necessarily mean that the high molar mass fraction is the majority component in terms of monomer unit concentration. Figure 1 shows the partition coefficients of the two fractions as a function of X_{1E} for $X_{2E}/X_{1E} = 0.1$ and $p_2^{(0)} = 0.1$. For reference, the partition coefficient p_m for a monodisperse polymer is also plotted for several values of $p_m^{(0)}$. A transition from weak to strong penetration for the low molar mass fraction takes place when the concentration of the high molar mass fraction exceeds its overlap concentration ($X_{1E} \cong 4$) for all the values of $p_1^{(0)}$ employed here. Note that, at this concentration, the *low* molar mass fraction is still in the dilute regime in the exterior of the pore ($X_{2E} \cong 0.4$). Around $X_{1E} \cong 2$, the parameter p_2 *exceeds unity* (partitioning inversion), the asymptotic partition coefficient in the strong penetration limit for a monodisperse system. The higher molecular weight of fraction 1 yields an even larger p_2 for $X_{1E} > 10$. In contrast, p_1 approaches unity gradually with increasing X_{1E}. The transition to strong penetration for the high molar mass fraction is suppressed.

There are two factors that contribute to increasing the partition coefficient as the exterior concentration increases.

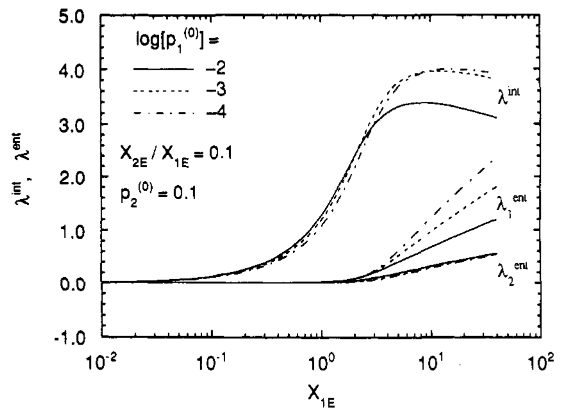

Figure 2. Contributions of interaction $\lambda^{\rm int}$ and of chain contraction $\lambda_i^{\rm ent}$ (i = 1, 2) to the increases in the partition coefficients shown for the same parameters used in Figure 1.

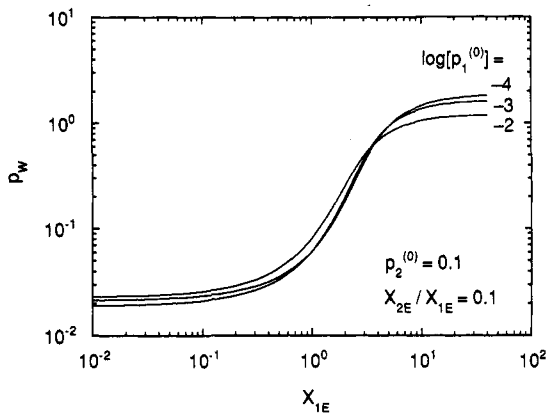

Figure 3. Partition coefficients for the monomer unit concentration p_W shown for the same parameters used in Figure 1.

One is an interaction factor $\lambda^{\rm int} \equiv I(X_E;\beta_E) - I(X_I;\beta_I)$, and the other is an entropic factor $\lambda_i^{\rm ent} \equiv (\Delta S_i^{(0)} - \Delta S_i)/k_B$ due to chain contraction, where $\Delta S_i^{(0)}$ is the value of ΔS_i in the dilute limit. Then, from eq 4, $p_i = p_i^{(0)} \exp(\lambda^{\rm int} + \lambda_i^{\rm ent})$. Figure 2 shows these two factors as a function of X_{1E} for the same parameters used in Figure 1. Comparison of Figures 1 and 2 reveals that the increase in $\lambda^{\rm int}$ causes the transition of p_2. The inverted population of the low molar mass fraction is caused by the high osmotic pressure of the high molar mass fraction exterior to the pore. The retardation of the transition in p_1 is due to the relatively high osmotic pressure in the interior caused by the high concentration of the low molar mass fraction. The parameter p_1 begins to increase only when the contribution of $\lambda_1^{\rm ent}$ becomes large enough to overcome the osmotic pressure in the interior, especially for larger chain dimensions of the fraction and a resultant smaller $p_1^{(0)}$.

We define a partition coefficient p_W in terms of the total monomer unit concentration as $p_W \equiv (c_{1I}N_1 + c_{2I}N_2)/(c_{1E}N_1 + c_{2E}N_2)$, and this coefficient is shown in Figure 3 for the same conditions as those used to plot Figure 1. For $X_{1E} > 10$, p_W is larger than unity, which means that the concentration of polymer expressed in the usual weight/volume dimension is larger in the interior of the pore than in the free exterior volume. This result appears paradoxical, because the partition coefficient for the majority component (high molar mass fraction) is small. Note, however, that $p_w = (p_1 + w_{21}p_2)/(1 + w_{21})$ is approximated by $w_{21}p_2$ for $X_{1E} > 10$, where w_{21} is the ratio of fraction 2 to fraction 1 in terms of the total monomer unit concentration in the exterior: $w_{21} \equiv (c_{2E}N_2)/(c_{1E}N_1)$. For the three values of $p_1^{(0)}$ (10^{-2}, 10^{-3}, and 10^{-4}), $w_{21} \cong 0.165$, 0.219, and 0.265, respectively, in the exterior solution. The large partition coefficient p_2 (close to 10) raises p_W to a value above unity.

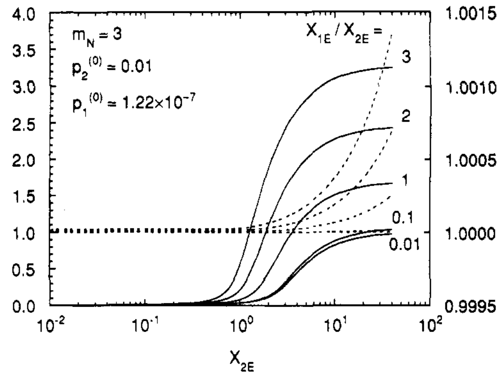

Figure 4. Partition coefficients p_2 for the low molar mass fraction (solid line) and corresponding polydispersity index β_I in the interior of the pore (dashed line) plotted as functions of X_{2E} for $m_N \equiv N_1/N_2 = 3$, $p_2^{(0)} = 0.01$, and X_{1E}/X_{2E} = 0.01, 0.1, 1, 2, and 3. The plots of β_I for X_{1E}/X_{2E} = 0.01 and 0.1 are nearly overlapped.

This result for the segregation of two polymer fractions differing in molecular weight suggests that a porous medium might be used to extract with high purity and efficiency a low molar mass fraction from a mixture. We performed appropriate calculations for various chain dimensions of the two fractions and various ratios of the free volume concentrations. An example of such a calculation is shown in Figure 4 for the ratio of the molecular weights of the two fractions $m_N \equiv N_1/N_2 = 3$ and $p_2^{(0)} = 0.01$ ($R_{g2}^{(0)}/R_P \cong 0.861$), which yields $p_1^{(0)} \cong 1.22 \times 10^{-7}$ ($R_{g1}^{(0)}/R_P \cong 1.643$). Like the situation in Figure 1, this case produces a transition from weak to strong penetration for fraction 2, the low molar mass fraction. The partitioning is inverted when X_{2E} is large, the concentration in the interior then becoming higher than that in the exterior. For a given ratio of the molecular weights, the transition in p_2 takes place at a lower concentration of X_{2E}, and p_2 reaches a larger value—specifically, when the low molar mass fraction is mixed with a larger amount of the large molar mass fraction.

When $m_N(c_1/c_2) \ll 1$, $c_1/c_2 \cong (\beta\text{-}1)/(m_N\text{-}1)^2$. Thus β-1 is proportional to the concentration of the high molar mass fraction relative to that of the low molar mass fraction. In the exterior, $\beta_E \cong$ 1.00571, 1.0529, 1.281, 1.332, and 1.328 for X_{1E}/X_{2E} = 0.01, 0.1, 1, 2, and 3, respectively. Figure 4 shows that, for all the values plotted in $X_{2E} \leq 40$, $(\beta_I\text{-}1)/(\beta_E\text{-}1) \ll 1$, a result denoting an enrichment of the low molar mass fraction in the porous media. Of course, enrichment in terms of a smaller $(\beta_I\text{-}1)/(\beta_E\text{-}1)$ is optimal when $X_{2E} \ll 1$. In practice, however, a low concentration is not favorable for extraction. It is important to note that the internal concentration can be raised without diminishing the purity of the low molar mass fraction.

Finally we consider the effect of a small amount of high molar mass impurity (component 1) on an SEC elution time for the low molar mass majority fraction (component 2). Let us assume that, in the injected sample, $c_{2E} = c_2^*/10$ (dilute regime for the component 2) and add a small amount of component 1 (a fraction by weight $f_W \ll 1$ with $c_{1E}N_1 = f_W c_{2E}N_2$) of molecular weight m_N times that of the component 2. Then, $X_{1E} = 0.349 f_W m_N^{3\nu-1}$. If $m_N = 10^3$, then X_{1E} = 6.84 at f_W = 0.1, which will increase p_2 close to or larger than unity, thereby distorting the elution curve of SEC to a longer time.

In this contribution, we have employed the expressions for $P(X;\beta)$ and $I(X;\beta)$ obtained by Ohta and Oono, because they are given as explicit functions of X and β and cover a wide range of X. The driving force for the partitioning inversion is the drastic increase in the osmotic pressure as the exterior concentration exceeds the overlap concentration. The increase is most simply expressed by the widely accepted scaling theory. The power dependence between Π and X for $X \gg 1$ is essential for the inversion to take place. Other expressions for P and R more elaborate than those obtained by Ohta and Oono, if available, would not greatly change the characteristics of the partitioning inversion described here.

In conclusion, we have shown that a bimodal polymer solution can exhibit a partitioning inversion between a confined geometry and an unrestricted exterior. We propose that this population inversion can be used to enrich the low molar mass fraction from a mixture of different molecular weights. An interesting extension to a ternary system comprising two different polymers and a common solvent is currently being studied.

To our knowledge, no experimental data on this phenomenon of partitioning inversion are available. In principle, the inversion characteristics can be demonstrated by interferometric study to measure the interior concentration. By selecting a solvent isorefractive with the pore material, the interior concentration of the polymer can be obtained as an increment in the average of the refractive index of the pore. This experiment would demonstrate the inversion in p_w. To investigate the separate inversion characteristics p_1 and p_2, we have to use another method. For example, if the porous medium can be made proton free, the use of a deuterated solvent and high molar mass fraction could lead to the measurement of p_2 by proton NMR imaging techniques. The imaging, however, would need to possess a sufficient spatial resolution and a well-defined focal depth.

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(12) The large X limit of $P(X;\beta)$ agrees with the result of the scaling argument based on the blob picture, but that of $R(X;\beta)$ does not.

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(15) The interaction term I in eq 4 contains the increase in the configurational entropy due to the screening of excluded volume with reference to the dilute limit. The entropy term ΔS_i is defined as a decrease in the configurational entropy of a confined polymer chain in a hypothetical situation where the interaction terms are the same in the interior and the exterior of the pore. Thus, ΔS_i is solely a function of the ratio of the chain dimension at a given interior concentration to the pore radius.