Terminally Anchored Chain Interphases: Their Chromatographic Properties

John H. van Zanten†

Polymers Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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ABSTRACT: A previously developed Flory-type mean-field analysis of the mixing of a multicomponent, polydisperse solvent with an interphase of terminally anchored chains of finite extensibility is utilized in the determination of the chromatographic properties of the interphase. In the limit of dilute solute species this approach leads to simple, analytical expressions which describe the partitioning and retention of solute molecules in the interphase. These interphases could be surface-grafted polymer layers or block copolymers at interfaces. The partitioning and retention of solute molecules in the interphase depend on the chain configurations, the entropy of mixing, and the contact interactions among the species present. The theory allows for the calculation of average or global properties such as the polymer, solvent, and solute volume fractions in the interphase, the interphase thickness, and solute partition coefficients and retention factors. The partitioning and retention of the solute molecules are found to depend explicitly on the surface density of the terminally anchored chains, solvent strength, terminally anchored chain length, solute size, and the various interactions among the species present. Size exclusion and enhancement, affinity, and gradient chromatography are considered.

I. Introduction

The process of transferring a solute from one medium to another is of widespread importance. This process is characterized by a free energy of transfer and a corresponding partition coefficient. The assumption that these processes can be modeled in terms of bulk phase solution thermodynamics is common. Additionally, oftentimes it is assumed that the solutions are ideal, that the relevant concentration variable is the mole fraction, and that surface or interfacial effects are negligible. In many situations these assumptions are not valid. Two examples are amphiphilic aggregates, such as monolayers, bilayers, micelles, and vesicles, and stationary phases composed of terminally anchored chains. These systems are interfacial phases or interphases; they have large surface-to-volume ratios, there are configurational constraints on the disorder of the system, and their properties are usually spatially dependent. Partitioning of molecules into phases of these types has applications in liquid chromatographic separation, micellar extraction, drug delivery, biomembrane transport, selective adsorption of pollutants, biocompatibility, colloidal stability, and supported catalysis, among others.

Terminally anchored chain interphases have received considerable theoretical interest in the scientific literature of the past several years.[1-21] These systems present an interesting theoretical and experimental challenge due to the complex nature of the situation wherein one has chain molecules in a constrained geometry. The fundamental interest in such systems is due to the interesting conformations that terminally anchored chains adopt when the unperturbed chain dimensions begin to overlap. As one would expect, the equilibrium properties of a terminally anchored chain interphase in contact with a solvent phase are intimately related to the nature of the solvent molecules in contact with the interphase.

Many theoretical approaches have been utilized to describe terminally anchored chain interphases.[1,2] Among these are scaling or mean-field theories,[3-7] self-consistent field methods,[8-11] statistical mechanical models,[12-18] and numerical simulations.[19-21] The scaling approaches yield, in an elegant way, the correct trends over a variety of conditions. Unfortunately, they only allow one to calculate the bulk properties of the interphase. However, they are relatively simple and provide a significant amount of insight into the factors which have the strongest influence on the equilibrium properties. The other methods allow for the detailed (*i.e.*, spatially dependent) prediction of the local interphase properties at different levels of detail. Unfortunately, these methods are not as computationally transparent as the scaling approaches. The self-consistent field methods allow the development of analytical expressions under limiting conditions such as for strongly stretched chain interphases. Statistical mechanical and numerical simulation techniques require somewhat complex numerical calculations.

These difficulties led this author[22] to extend the Lai and Halperin[5,6] Flory-type mean-field theory for terminally anchored long, polymer-like chain interphases of finite extensibility to account for both solvent quality and *size*. Only the situation wherein the solvent molecules are completely immersed in either the terminally anchored chain interphase or in bulk solvent solution in contact with the interphase was considered in that report. That is, the situation in which any mobile species (*i.e.*, for the case in which the given mobile species is larger than the terminally anchored chain monomer size) straddle the interface between the terminally anchored chain interphase and the bulk solution is neglected. This assumption limits the applicability of the theory to situations in which the dimensions of the solvent molecules are small relative to the terminally anchored chain interphase thickness (*i.e.*, $N_i^{1/2} \ll N$, where N_i is the solvent size and N is the size of the terminally anchored chain). This assumption, to a lesser degree, will also account for the neglect of solvent conformational effects in the model presented here. The relative simplicity of this approach led to a theory which accounted for the effect of solvent size in a straightforward, albeit approximate, manner. A more general approach which would allow the existence of mobile species which straddle the interface and account for solvent conformational effects would most likely require one of the

† E-mail: johnvz@enh.nist.gov.

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techniques which yield a local description of the interphase properties and is beyond the scope of the present report. Additionally it is assumed that the anchoring surface, or interface, is neutral (*i.e.*, there are no favorable interactions between the surface and any of the species present in the system). Therefore wetting effects can be neglected.[23]

Unfortunately, potential technical applications of these interphases, other than colloidal stabilization, have received very little attention. The interphases may be useful as separations media as was noted by Lai and Halperin.[6] Dill and Marqusee have considered the partitioning and retention of small molecules in terminally anchored short-chain interphases via statistical mechanical methods.[24,25] They have considered bilayers, micelles, vesicles, and short terminally anchored chains such as those which occur in reverse-phase high-performance liquid chromatography stationary phases. Their method allows one to calculate the spatial properties, such as the solute distribution, of the short-chain interphases. However, it is not computationally feasible for the long-chain interphases one encounters with terminally attached polymers or polymer brushes. Lecourtier *et al.* considered the partitioning of molecules in terminally anchored polymer phases within the Flory–Huggins theory.[26] This approach leads to predictions of global or average properties within the usual Flory–Huggins formulations. Unfortunately, their approach did not consider the effect of surface coverage explicitly and therefore does not completely account for the severe constraints imposed by the interfacial nature of the problem. They also assumed that the interphase layer thickness is equivalent to the diameter of the unperturbed chains. Since it is known that the layer thickness increases from this value as the chains begin to overlap, it is apparent that this approach is only applicable in the regime up to where the chains are just beginning to overlap and is definitely not applicable in the strong stretching regime, which is the situation considered in this contribution. Therefore, the approach of Lecourtier *et al.*, while computationally much simpler than the other methods, does not explicitly account for the nature of the terminally anchored chain interphase (*i.e.*, the effect of chain surface density on the thermodynamic properties of the interphase). This difficulty led the author to consider the chromatographic properties of terminally anchored chain interphases within a previously developed extension of Lai and Halperin's Flory-type mean-field model.[22] This approach allows one to describe the global conformational properties of the chains and the various species fractions in the interphase in terms of the chain length, the solvent species sizes, the various interactions, and the surface density of the terminally anchored chains. It is also readily amenable to developing closed-form, analytical expressions which describe the various interphase properties such as the solute partition coefficients and retention factors which can provide insight into the design of terminally anchored chain interphases for given applications. However, it should be noted at this point that the approach outlined here will yield at most only a *qualitative* description of the various phenomena. Some fairly recent studies[12,13,21] indicate that the free energy is underestimated by approaches similar to the one described here, although an even more recent study[27] seems to indicate that this is not always the case.

In the present paper the chromatographic properties of terminally anchored chain interphases are considered within the previously developed theory for a terminally anchored chain interphase in contact with a multicomponent, polydisperse solvent.[22] The previously developed theory is briefly reviewed and the partition coefficient and retention factor of a given species are defined. These model equations are applicable to all solvent compositions and interphase configurations. In this report, however, the emphasis will be on the case of very dilute solutes dissolved in a pure or binary bulk phase. This special case leads to analytic expressions for the partition coefficient which contain all of the relevant physics, in addition to the fact that this is typically the situation one commonly encounters in chromatographic separation and selective absorption.

II. Terminally Anchored Chain Interphase in Contact with a Multicomponent, Polydisperse Solvent Mixture: Partition Coefficients and Retention Factors

Recently, a Flory-type mean-field theory of terminally anchored chain interphases in contact with a multicomponent, polydisperse solvent was developed.[22] Within this model the terminally anchored chains are assumed to be of size N and monomer size a. They are connected to a locally flat interface at a surface density $\sigma = a^2/D^2$, where D is the distance between anchoring sites. (In this approach it is explicitly assumed that the terminally anchored chains are overlapping and, therefore, sufficiently stretched such that the terminally anchored chains contribute elastically to the free energy of the interphase.) Following the work of several investigators,[1-10] especially the seminal contributions of Alexander[3] and de Gennes,[4] the free energy of a terminally anchored chain in contact with such a solvent can be written as

$$F = F_{conf} + F_{mix} \tag{1}$$

The first term is due to the configuration of the terminally anchored chain. It is a result of the stretched configurations that terminally anchored chains must adopt as their surface density increases. The second term is due to the various interactions between the solvents and terminally anchored chains.

To allow for high surface densities of terminally anchored chains, an expression for the configurational free energy which accounts for the finite extensibility of the terminally anchored chains is adopted. This configurational energy can be expressed in terms of the inverse Langevin function, $\mathcal{L}^{-1}(x)$, where $\mathcal{L}(x) = \coth x - 1/x$ is the Langevin function.[5,6] If the Flory–Huggins expression is used for the energy of mixing, the following expression for the free energy of the terminally anchored chain interphase is found:[22]

$$F = N \int_0^{(\sigma/N)(N+\sum_{i\neq p} n_i N_i)} \mathcal{L}^{-1}(u)\, du + \sum_{i\neq p} n_i \ln \phi_i + \sum_{i\neq j} \chi_{ij} \frac{n_i N_i n_j N_j}{\sum_i n_i N_i} \tag{2}$$

where n_i is the number of solvent species i associated with each terminally anchored chain in the interphase, N_i is the size of solvent species i, ϕ_i is the volume fraction of solvent species i in the interphase, and χ_{ij} is the interaction parameter between species i and j. The translational entropy of the grafted chains is neglected because the chains are assumed to be anchored at the interface of the interphase.[4] As noted previously, there are indications[12,13,21] that the free energy functionals of the type

utilized in most scaling, mean-field, and self-consistent field calculations underestimate the terminally anchored chain surface density dependence of the free energy, although another study indicates that this is not necessarily always true.[27] This latter study also included the case wherein free polymer chains occurred in the interphase and the free solution. Some of these studies[12,13,21] predict that the basic structural properties of the interphase, such as its thickness and the monomer density profile, are essentially the same as those found from scaling, mean-field, and self-consistent field approaches, while the free energy and surface osmotic pressure differ from the predictions of these approaches. Carignano and Szleifer[13] note that in the previous scaling[3] and mean-field[2] approaches only the first term of the virial expression has been used to calculate the free energy, while in their approach, and also of course in the molecular dynamics simulations of Grest and co-workers[19,21] and others,[20] higher order monomer–monomer interactions are accounted for explicity. This is also true in the approach considered previously by Lai and Halperin[5,6] and also the model considered here, wherein the full Flory–Huggins free energy of mixing is used to account for all of the various species interactions. It should be noted however that a free energy functional which accounts for all orders of the various species interactions is qualitatively very different from those found for cases wherein only the first term of the virial expansion is retained and does not display a single scaling relationship as was shown by Lai and Halperin.[5] In fact, as Carignano and Szleifer[13] note, for systems in which higher order interactions are accounted for there is not going to be a single scaling relationship for the free energy or the surface pressure.

The bulk solvent solution will also be modeled as a regular solution in the Flory–Huggins approximation with its free energy given by

$$F_{bulk} = \sum_{i \neq P} n_i \ln \Phi_i + \sum_{i \neq j} \chi_{ij} \frac{n_i N_i n_j N_j}{\sum_i n_i N_i} \quad (3)$$

where Φ_i is the volume fraction of species i in the bulk solvent. Here the terminally anchored chains are ignored since due to their immobilization they are not present in the bulk solvent phase. However, the effect of mobile chains of the same species being present in the bulk solvent phase can still be addressed. The subscript P will only refer to the terminally anchored chains.

The equilibrium state of a terminally anchored chain interphase is determined by equating the chemical potential of each mobile species i in the two phases, the bulk solvent and the terminally anchored chain interphase. This condition leads to the following expression:[22]

$$\sigma \mathcal{L}^{-1}(\sigma/\phi_P) + \frac{1}{N_j}\left(\ln \frac{\phi_j}{\Phi_j} + \Phi_j - \phi_j\right) + \sum_{i \neq j,P} \frac{\Phi_i - \phi_i}{N_i} + (1 - \phi_j) \sum_{i \neq j} \chi_{ij}\phi_i + (\Phi_j - 1) \sum_{i \neq j} \chi_{ij}\Phi_i + \sum_{\substack{i,k \neq j \\ i \neq k}} \chi_{ik}(\Phi_i\Phi_k - \phi_i\phi_k) = 0 \quad (4)$$

This condition must be satisfied for all of the mobile species present in the system. The most important observation to be made here is that the equilibrium volume fractions do depend on the various solvent sizes. However, they are independent of the terminally anchored chain size as is typically found for scaling or mean-field descriptions of terminally anchored chain interphases.[3-6] The first term is the contribution due to the cost of stretching the terminally anchored chains as the interphase is swollen with solvent species. The next two terms are the mixing entropy contributions. The last three terms, the heat of mixing contribution, are a result of the interactions between the various species which are present. Given the solvent composition, sizes and interaction parameters, along with the surface density of the terminally anchored chains, the volume fractions of the various species in the terminally anchored chain interphase can be readily calculated including the terminally anchored chain volume fraction since

$$\phi_P = 1 - \sum_{i \neq P} \phi_i \quad (5)$$

Once the volume fractions of the solvent species in the terminally anchored chain interphase are known, the equilibrium layer thickness, h, is readily determined from

$$h = \frac{N\sigma a}{\phi_P} \quad (6)$$

Therefore, the equilibrium thickness of a terminally anchored chain interphase in contact with a multicomponent solvent of varying quality and size is a linear function of the chain size, N. This linear dependence of the layer thickness with respect to the chain size is the signature of strongly stretched terminally anchored chain interphases.[3] Knowledge of the layer thickness is required to calculate the retention factors of various species, therefore making this approach very useful in determining the chromatographic properties of these terminally anchored chain interphases.

The partition coefficient for species i, K_i, is a measure of species i's affinity for the terminally anchored interphase relative to its affinity for the solvent which is in contact with the interphase. This partition coefficient is defined by the following expression

$$K_i = \phi_i/\Phi_i \quad (7)$$

K_i is a quantitative measure of the degree of species i partitioning between the solvent, or bulk, phase and the terminally anchored chain interphase. The partition coefficient describes the affinity that a solute feels for the interphase relative to the bulk, or mobile, phase. However, for many applications, such as separations, it is the retention factor for species i, k_i' which is the quantity of concern when the actual process is being considered. The retention factor is simply the product of the partition coefficient and the interphase/bulk phase volume ratio.

$$k_i' = \frac{V_{int}}{V_{bulk}} K_i \quad (8)$$

Here V_{int} is the volume of the interphase and V_{bulk} is the volume of the bulk solution, or mobile phase in the parlance of liquid chromatography. The volume of the interphase is a function of the chain surface density, solvent quality and size, and the size of the terminally anchored chains and is readily calculated as outlined previously. Of course, the volume ratio itself depends upon the geometry of the contacting configuration, in addition to the properties of the interphase. Therefore, it should be possible to design terminally anchored interphases and develop processes

which utilize them to perform given tasks. In this report the design of the stationary phase itself is not considered. The feasibility of using solid spheres coated with a terminally anchored chain interphase as a liquid chromatography interphase will be considered elsewhere.[28] Instead, a representative expression for the volume ratio will be used when considering the retention factor in this report.

$$\frac{V_{\text{int}}}{V_{\text{bulk}}} = \frac{h/2Na}{1-(h/2Na)} \tag{9}$$

This expression yields a volume ratio which has an upper bound of unity and therefore allows one to avoid the situation wherein the bulk, or mobile, phase is essentially eliminated as the terminally anchored interphase reaches its maximum extension. This is an important issue to consider when designing interphases, such as in chromatographic applications, since it will definitely affect the contacting between the interphase and bulk solution and process conditions such as pump capacity.

III. Pure Mobile Phases: Size and Affinity Mediated Chromatography

Consider the case wherein there are a number of species, referred to as i, dissolved within a single majority component, known as the solvent or mobile phase. These species i will display varying degrees of affinity for a given interphase or adsorbent and therefore can be separated on this basis. The theory outlined above allows the determination of a specific species i's affinity for terminally anchored chain interphases regardless of the solvent phase composition. In situations where the minority component species are present in sufficient quantity, the underlying mechanisms of solute retention are sometimes not readily apparent and the equilibria are often complex.[22] This can be observed in Figure 1, where the variation of the interphase volume fraction of species i, ϕ_i, as determined from the equilibrium condition (4) is displayed as a function of the bulk phase volume fraction of species i, Φ_i, for several representative systems. The linear regions of these plots correspond to the situation in which the partition coefficient of species i, K_i, is independent of its bulk phase volume fraction. It is apparent that the extent of the linear regime increases with increasing mobile phase quality and more favorable mobile phase–solute interactions. There is also a critical minority component concentration wherein the terminally anchored chain interphase is greatly swollen by the minority component. This critical concentration is dependent on the mobile phase size and quality and the minority component size and interactions with the mobile phase and terminally anchored chains. It will also depend on the chain surface density.[29] The transition to a minority component swollen interphase becomes more abrupt as the mobile phase quality increases. The highly nonlinear behavior in the poor mobile phase quality cases could be exploited for the removal of priority pollutants from waste streams. However, one should realize that the plots in Figure 1 correspond to the case of $N_i = 5$. For smaller solutes the imbalance between terminally anchored chain and mobile phase interactions would have to be even greater.

However, oftentimes in chromatographic separation processes the situation at hand is one wherein the matrix to be separated consists of some very dilute species i dissolved in a single component mobile phase which will be referred to as species M. As is apparent from Figure 1 under these conditions the following assumptions should hold true

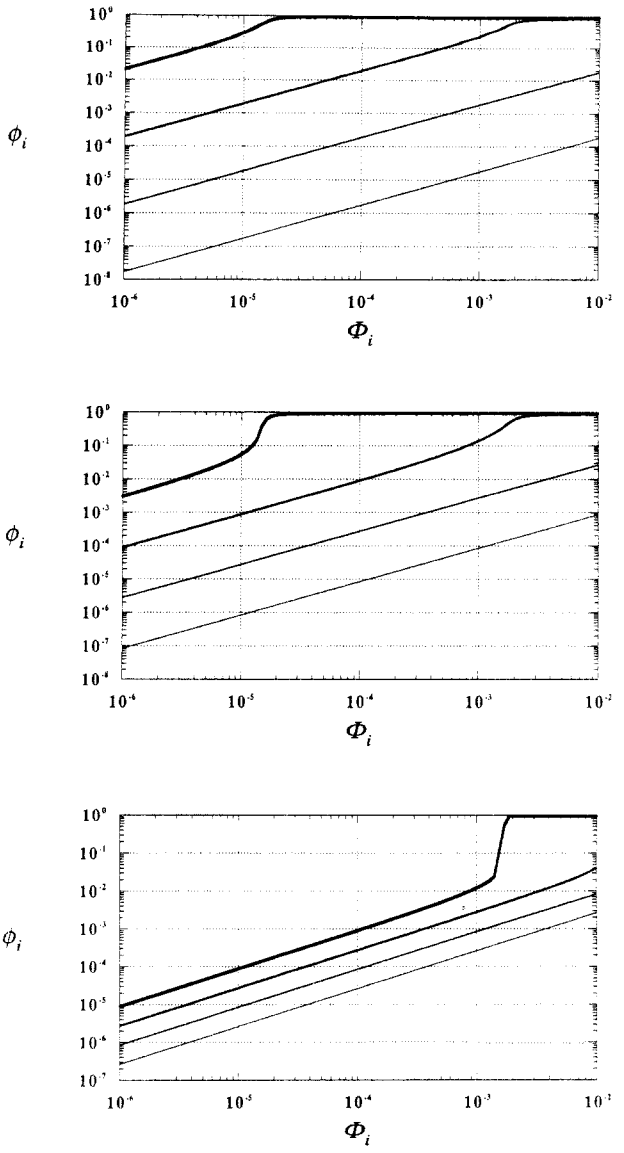

Figure 1. Partitioning of solutes between a pure solvent and a terminally anchored chain interphase: effect of solute bulk phase concentration. The interphase solute concentration, ϕ_i, is shown as a function of its bulk phase concentration, Φ_i, for three solvent conditions: $\chi_{MP} = 2.0$, top; $\chi_{MP} = 1.0$, middle; $\chi_{MP} = 0.0$, bottom. The four solute–mobile phase interaction parameters considered here are $\chi_{iM} = 3.0$, 2.0, 1.0, and 0.0, which correspond to the highest to lowest curves (or thickness to thinnest curves), respectively, in each plot. Here $\chi_{iP} = 0.0$, $N_i = 5$, $N_M = 1$, and $\sigma = 0.01$. All the plots presented in this paper have been calculated from the exact equilibrium expression (4). The approximations made in the text are simply to highlight the physics which are involved.

$$\sum_{i \neq M} \Phi_i \ll 1 \tag{10a}$$

therefore

$$\Phi_M \approx 1 \tag{10b}$$

and by analogy

$$\phi_i \ll 1 \tag{10c}$$

Once these assumptions are made, the partition coefficient for a very dilute species i can be shown to be

$$K_i \cong \exp\left\{-\sigma N_i \mathcal{L}^{-1}\left(\frac{\sigma}{1-\phi_M}\right)\right\} \exp\{N_i(1-\phi_M) \times (\chi_{MP}\phi_M + \chi_{iM} - \chi_{iP} - N_M^{-1})\} = K_{conf}K_{mix} \quad (11)$$

where the mobile phase fraction present in the terminally anchored chain interphase, ϕ_M, is determined from the equilibrium equation for an interphase in contact with a pure solvent since it was assumed that $\Phi_M \approx 1$. This expression was previously derived[5,6,22] and is simply

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{1-\phi_M}\right) + \frac{1}{N_M}(\ln \phi_M + 1 - \phi_M) + \chi_{MP}(1-\phi_M)^2 \cong 0 \quad (12)$$

Here $\cong$ denotes the fact that these expressions are approximations since the small effect of the dilute species i which are present in the system is neglected here.

The simple expression (11) for the partition coefficient under these limiting conditions yields a wealth of insight into the chromatographic properties of terminally anchored chain interphases. This expression is separated into two terms to clarify the two phenomena which influence the partitioning of solutes between the bulk phase and interphase. The first term is due to the configurational constraints that the chains experience due to their terminal anchoring. This term is always less than or equal to unity and therefore reduces the degree of partitioning relative to the value one would expect in the case of free chains. Therefore, terminally anchoring the chains leads to a reduction in solute partitioning and retention. Fortunately, however, it does allow more efficient contacting in separations processes. This attenuation of the partition coefficient due to terminally anchoring the chains was also observed by Marqusee and Dill for their case of short-chain interphase statistical mechanical calculations.[24] The degree of this attenuation is essentially a function of the chain surface density, σ, the solvent quality, and the size of species i under these conditions. The influence of these three factors on the configurational entropy contribution to the partition coefficient is shown in Figure 2. At small chain surface densities the decrease in partitioning due to configurational or steric effects is small due to the fact that the interphase chains are not greatly stretched. As the surface density increases however, the partition coefficient begins to drop rapidly due to the large increase in steric interactions and the subsequent strong chain stretching. The effect of solvent quality is present; however, it is somewhat subtle. The influence of the configurational entropy on the partition coefficient decreases with decreasing solvent quality due to expulsion of mobile phase which occurs as its quality is decreased and which leads to a decrease in the degree of interphase swelling. The influence of the steric effects increases as the solute size increases. This configurational entropy term leads to the expulsion of all species as $\sigma \rightarrow 1$.

The second term accounts for the mixing interactions within the interphase and solvent (*i.e.*, the entropy and enthalpy of mixing). It is apparent that molecules can be potentially separated on the basis of size and affinity. To focus on the influence of solute size on the partitioning behavior, the case of athermal mixing is considered first. Under this condition $\chi_{iM} = \chi_{iP} = \chi_{MP} = 0$ and the partition coefficient is further simplified to

$$K_i = K_{conf} \exp\left\{-\frac{N_i}{N_M}(1-\phi_M)\right\} \quad (13a)$$

It is obvious that the degree of species i partitioning rapidly decreases with increasing species i size, N_i. This is displayed in the uppermost panel of Figure 3. Here the partition coefficient of (13a) has been considered as a function of species i size and the chain surface density. The partition coefficient decreases monotonically with increasing surface density. The magnitude of this attenuation increases as the solute size becomes larger. The critical surface density at which the solutes are essentially expelled from the interphase is also a function of the solute size, with this critical chain surface density decreasing with increasing solute size under these conditions. This size-exclusion mechanism is very sensitive to the solute size even at low surface densities and may provide an excellent means of separating fairly small species of differing size which are of similar chemical composition. The potential of this separation mechanism is shown in the two lower panels of Figure 3, where the retention factor of expressions 8 and 9 is considered for these conditions. Recalling that the retention factor is the product of the partition coefficient and the interphase/mobile phase volume ratio, it is obvious that the retention factor will

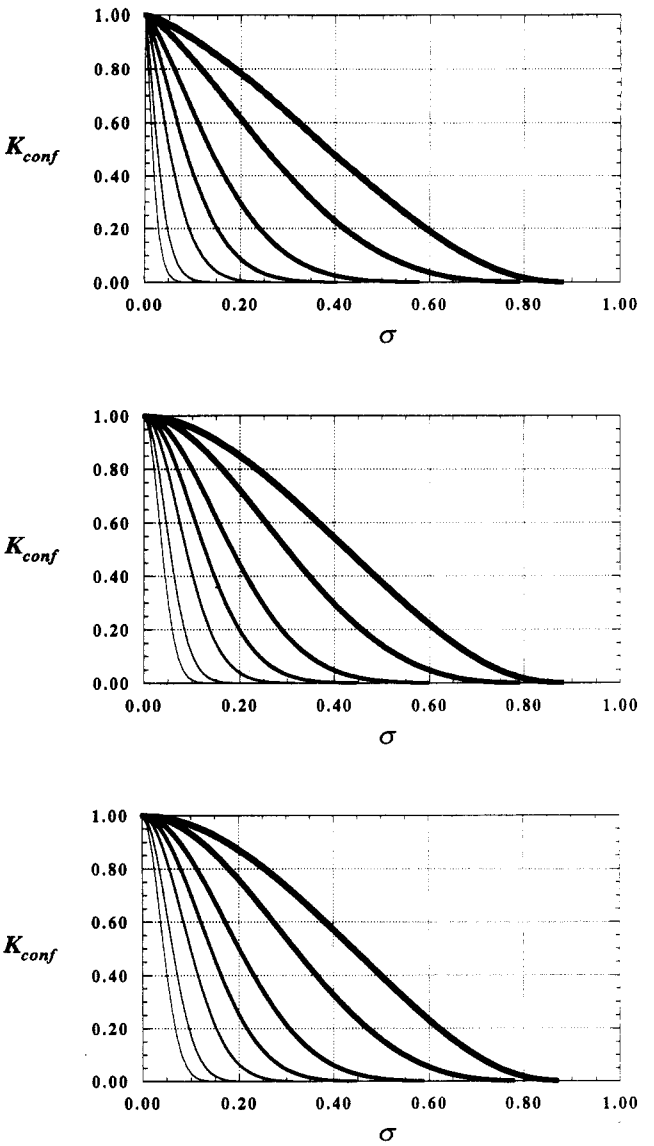

Figure 2. Effect of terminally anchoring the chains on solute partitioning. The configurational contribution to the partition coefficient, K_{conf}, is shown as a function of chain surface density, σ, for three solvent conditions: $\chi_{MP} = 0.0$, top; $\chi_{MP} = 1.0$, middle; $\chi_{MP} = 2.0$, bottom. The seven solute sizes considered here are $N_i = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the highest to lowest curves (or thickest to thinnest curves), respectively, in each plot with $N_M = 1$.

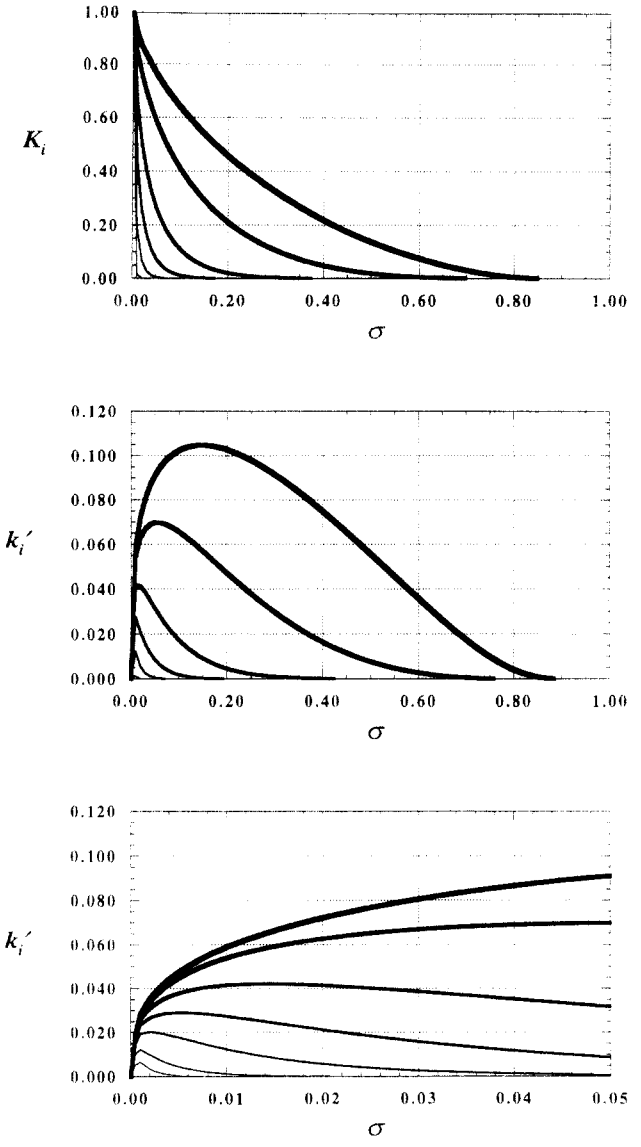

Figure 3. Partitioning and retention of solutes in a terminally anchored chain interphase: size-exclusion mechanism. The partition coefficients, K_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.01$, are shown as a function of surface chain density, σ, for the situation where all $\chi_{ij} = 0$ and $N_M = 1$. The top panel displays the partition coefficient, the middle panel shows the retention factor, and the lowermost panel presents a magnified view of the retention factor at low chain surface density. The seven solute sizes considered here are $N_A = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the highest to lowest curves (or thickest to thinnest curves), respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9).

display a distinctly different behavior than the partition coefficient alone, since the volume ratio is an increasing function of the chain surface density. This will lead to a retention factor which displays a maximum in relation to the chain surface density as is displayed in these two lower panels. Under these athermal conditions the surface density of maximum retention is a strong function of the solute species size, especially for fairly small solutes. The lowermost plot considers the retention factor for low chain surface densities. It is apparent that under these athermal conditions it is most easy to separate fairly small solute species, $1 \leq N_i \leq 10$, rather than large ones and that this separation can be conducted with stationary phases which have a relatively low degree of chain surface density. One should keep in mind that the retention factors reported here are by no means of optimal design as was previously discussed. These retention factors are simply considered to highlight the processes by which this mechanism works. The optimal design of stationary phases will be considered in a subsequent report.[28]

Previously, the case of all athermal interactions within the system was considered and it was observed that this system provides a potentially novel means of size-separating fairly small solutes of similar chemical behavior. Now if only the mobile phase is athermal, $\chi_{MP} = 0$, the partition coefficient becomes

$$K_i = K_{conf} \exp\{N_i(1 - \phi_M)[\chi_{iM} - \chi_{iP} - N_M^{-1}]\} \quad (13b)$$

Here it is apparent that there is a chemical affinity mechanism in addition to the size-exclusion mechanism that was previously discussed. In fact, for situations where $\chi_{iM} > \chi_{iP} + N_M^{-1} + [\sigma/(1 - \phi_M)]\mathcal{L}^{-1}(\sigma/\phi_P)$ a size enhancement effect will be observed. That is, the partition coefficient will increase with increasing solute size under these conditions and is therefore enhanced with increasing solute size. In Figure 4 this size enhancement mechanism is displayed. Here an athermal mobile phase containing dilute solute species, $\Phi_i = 0.001$, in contact with the interphase is considered and the solute–mobile phase and solute–polymer interaction parameters are taken to be 1.168 and 0, respectively (*i.e.*, $\chi_{iM} = 1.168$ and $\chi_{iP} = 0$). However, under the assumptions (10a–c), along with situations in which $K_i \leq 10$, or $\phi_i \leq 0.01$, the only necessary solute interaction information is the difference between the two solute interaction parameters or $\Delta\chi_i = \chi_{iM} - \chi_{iP}$ (see Figure 6). This parameter is the measure of the solute species relative affinity for the mobile phase and the terminally anchored chains. Under the previously outlined conditions a nonzero surface coverage which corresponds to maximum partitioning is observed. This is due to the fact that $[\sigma/(1 - \phi_M)]\mathcal{L}^{-1}(\sigma/\phi_P)$ actually decreases initially as the chain surface density increases and then eventually begins to increase, leading to the exclusion of the solute species i at higher chain surface densities. It is obvious that in the region of size enhancement it is the large solutes which display the largest spread in partitioning behavior. Indeed if one considers the retention factor of the solutes, it is apparent that at low surface densities only the large solutes can be efficiently separated, with the small solutes requiring larger chain surface densities to facilitate their separation under these conditions. Therefore it is possible that this size enhancement mechanism could be used to separate large solutes under similar chromatographic conditions.

What if the mobile phase is not athermal? Under these conditions the partition coefficient is given by expression 11. The relevant condition for size enhancement becomes $\chi_{iM} > \chi_{iP} + N_M^{-1} + [\sigma/(1 - \phi_M)]\mathcal{L}^{-1}(\sigma/\phi_P) - \chi_{MP}\phi_M$. When $\chi_{MP} < 0$, such as in the case where the mobile phase may hydrogen-bond with the terminally anchored chains, the size-exclusion mechanism observed under athermal conditions is even more enhanced due to greater interphase swelling by the mobile phase, while any size enhancement effects will be decreased for the same reason. If, however, the mobile phase is a bad solvent for the terminally anchored chains, the size enhancement will be magnified, with the surface coverage corresponding to maximum partitioning shifting to even lower values than that which was observed for the athermal mobile phase case. This phenomenon can be observed in Figure 5 where the case of a bad solvent, $\chi_{MP} = 1$, in contact with the interphase is considered. Here $\Delta\chi_i = 0.715$ in comparison with $\Delta\chi_i = 1.168$ which was considered in the athermal mobile phase case. It can be seen that the relative magnitude of the partitioning effect is the same, while the surface density

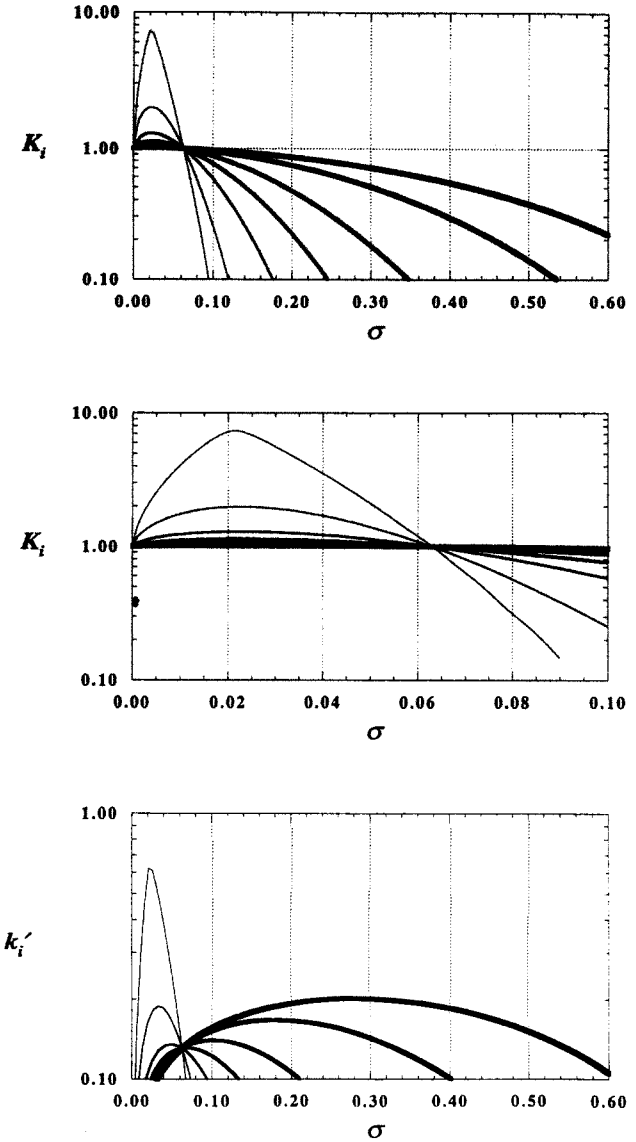

Figure 4. Partitioning and retention of solutes in a terminally anchored chain interphase: size enhancement and exclusion mechanism. The partition coefficients, K_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.001$, are shown as a function of surface chain density, σ, for the situation where $\chi_{MP} = 0.0$, $\chi_{iP} = 0.0$, $\chi_{iM} = 1.168$, and $N_M = 1$. The top panel displays the partition coefficient, the middle panel shows a magnified view of the partition coefficient, and the lowermost panel presents the retention factor. The seven solute sizes considered here are $N_A = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9).

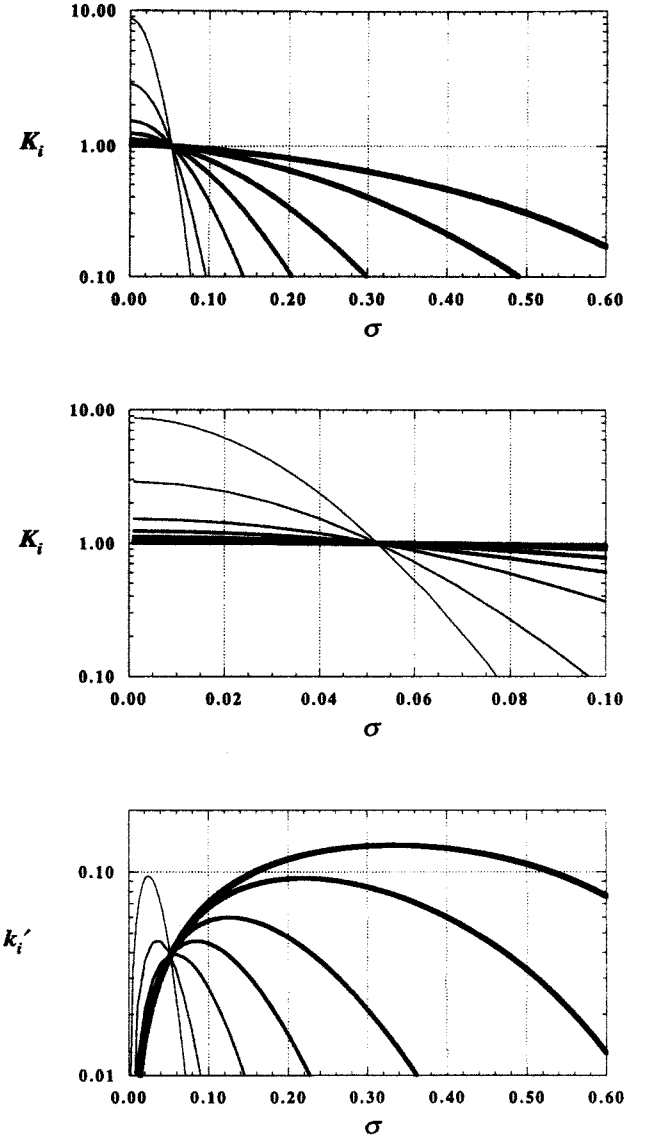

Figure 5. Partitioning and retention of solutes in a terminally anchored chain interphase: size enhancement and exclusion mechanism. The partition coefficients, K_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.001$, are shown as a function of surface chain density, σ, for the situation where $\chi_{MP} = 1.0$, $\chi_{iP} = 0.0$, $\chi_{iM} = 0.715$, and $N_M = 1$. The top panel displays the partition coefficient, the middle panel shows a magnified view of the partition coefficient, and the lowermost panel presents the retention factor. The seven solute sizes considered here are $N_A = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9). Note the difference between this figure and the previous one for very small surface density.

corresponding to maximum partitioning shifts to an extremely small value in comparison with that which was observed in the athermal solvent case. The chain surface density of maximum retention is not much different than that which was found for the athermal case. However, the magnitude of the retention factors is much higher in the athermal case due to the larger degree of interphase swelling, and therefore choice of the mobile phase for any size-enhanced separation will depend on the geometrical nature of the stationary phase and the contacting conditions under consideration.

Previously, the effect of solute size and chain surface density on the partitioning and retention of the solutes in the terminally anchored chain interphase under various interaction conditions was considered. The effect of the solute–mobile phase and solute–terminally anchored chain interactions is considered more explicitly in Figure 6. The three plots correspond to $\chi_{MP} = 2$, 1, and 0 from top to bottom, respectively. The surface density, $\sigma = 0.05$, mobile phase volume fraction of the solutes species i, $\Phi_i = 0.001$, and solute–chain interaction parameter, $\chi_{iP} = 0$, are the same in all three panels. Under all mobile phase conditions the partitioning of small solutes, $N_i \leq 2$, decreases smoothly with increasing mobile phase–solute affinity. One should recall that for small Φ_i and ϕ_i it is only the difference in solute species interaction parameters that determines the partitioning of the solute species. Only in situations wherein Φ_i or ϕ_i are significant, such as in the nonlinear regions of these plots, is there a need to explicitly account for the individual interaction parameters. It is apparent that within a limited $\Delta\chi_i$ range, which depends on the mobile phase quality, separation of large molecules of fairly similar $\Delta\chi_i$ values may be feasible.

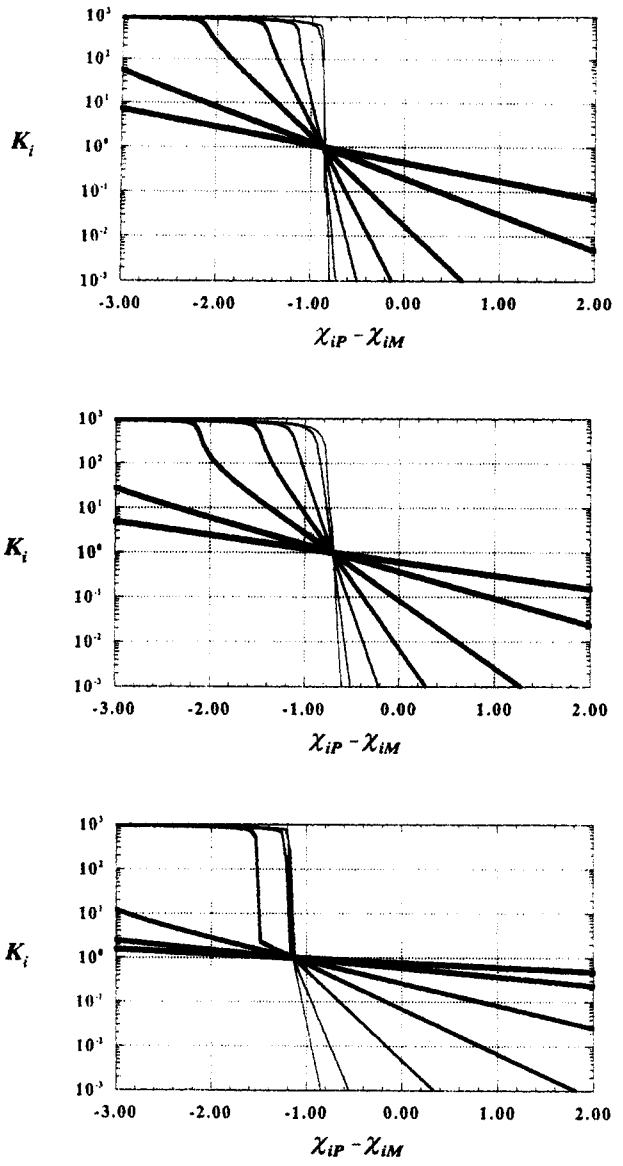

Figure 6. Partitioning of solutes between a pure solvent and a terminally anchored chain interphase: effect of solute interactions. The partition coefficients, K_i, of dilute solute species, $\Phi_i = 0.001$, are shown as a function of solute interaction difference, $\chi_{iP} - \chi_{iM}$, for the situation where $\sigma = 0.05$, $N_M = 1$, $\chi_{iP} = 0$, and $\chi_{MP} = 2.0$, 1.0, and 0.0 from the top panel to the lower panel, respectively. The seven solute sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot.

An interesting observation is that fact that the $\Delta\chi_i$ value which corresponds to a unitary partition coefficient independent of solute size displays a nonmonotonic relation with the mobile phase solvent quality. When $K_i = 1$ $\Delta\chi_i$ is determined by (of course, this is only for the dilute solute assumption and $N_M = 1$ as in Figure 6)

$$\chi_{iP} - \chi_{iM} = \frac{\ln \phi_M + \chi_{MP}(1 - \phi_M)}{1 - \phi_M} \tag{14}$$

since under these conditions it is essentially the mobile phase itself which determines the interphase properties. The nonmonotonic behavior of this property can be observed in Figure 7. This phenomenon allows some control over the $\Delta\chi_i$ region where large molecules are efficiently separated and also the $\Delta\chi_i$ region over which size exclusion and enhancement separations are feasible.

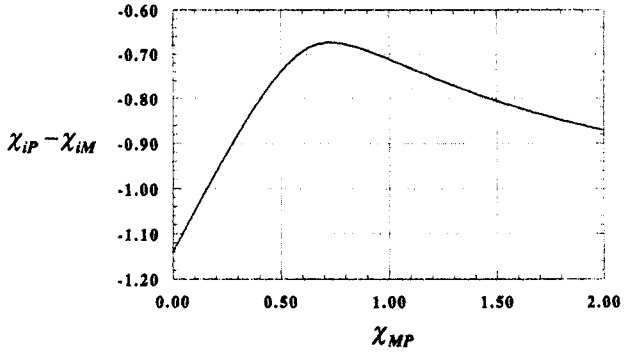

Figure 7. Variation of $\chi_{iP} - \chi_{iM}$ corresponding to $K_i = 1$ with solvent quality. The $\Delta\chi_i = \chi_{iP} - \chi_{iM}$ value corresponding to $K_i = 1$ is shown as a function of the bulk solvent quality with $\sigma = 0.05$ and $N_M = 1$.

IV. Binary Mobile Phases: Gradient Chromatography

Since the stationary phase properties (*i.e.*, chain surface density, chain length, and surface/volume ratio) cannot be varied *in situ*, chromatographic separations are oftentimes enhanced through the use of a binary mobile phase of varying composition. When the mobile phase composition is varied throughout the separation process, the technique is known as gradient chromatography. This approach may also be used to regenerate a terminally anchored chain interphase which has been utilized as an absorbent for a targeted solute species. The solvent, or mobile phase, composition has a strong influence on the equilibrium properties of the terminally anchored chain interphase. Under the assumption of dilute solute species i, the partition coefficient of species i between the terminally anchored chain interphase and a binary mobile phase is given by

$$K_i \cong \exp\left\{-\sigma N_i \mathcal{L}^{-1}\left(\frac{\sigma}{\phi_P}\right)\right\} \exp\{N_i[(\chi_{iM_A} - \chi_{iM_B} - \chi_{M_AM_B} - N_{M_A}^{-1} + N_{M_B}^{-1})\Phi_{M_A} + \chi_{M_AM_B}\Phi_{M_A}^2 + \chi_{iM_B} - \chi_{iP} - N_{M_B}^{-1}]\} \exp\{N_i[(\chi_{M_AP}\phi_P + \chi_{iP} - \chi_{iM_A} + N_{M_A}^{-1})\phi_{M_A} + (\chi_{M_BP}\phi_P + \chi_{iP} - \chi_{iM_B} + N_{M_B}^{-1})\phi_{M_B} + \chi_{M_AM_B}\phi_{M_A}\phi_{M_B}]\}$$
$$= K_{conf}K_{\Phi,mix}K_{\phi,mix} \tag{15}$$

where assumptions 10a and 10c have been made along with

$$\Phi_{M_A} + \Phi_{M_B} \cong 1 \tag{16a}$$

and

$$\phi_P \cong 1 - \phi_{M_A} - \phi_{M_B} \tag{16b}$$

Here M_A and M_B denote mobile phase species A and B, respectively. This expression is much more complex than the analogous one derived for the case of a pure mobile phase. The interphase volume fractions of M_A and M_B can be found as detailed in a previous report.[22] Essentially it is assumed that the very dilute species have very little effect, if any, on the equilibrium properties of the interphase. Previously, it has been noted that the composition of a binary solvent in contact with a terminally anchored chain interphase has a very nonlinear effect on the equilibrium properties of the interphase.[6,10,22] For the special case of equal-sized mobile phase species (*i.e.*, $N_{M_A} = N_{M_B} = N_M$), expression 15 becomes

$$K_i \cong \exp\left\{-\sigma N_i \mathcal{L}^{-1}\left(\frac{\sigma}{\phi_P}\right)\right\}\exp\left\{-\frac{N_i}{N_M}\phi_P\right\}\times$$
$$\exp\{N_i[(\chi_{iM_A} - \chi_{iM_B} - \chi_{M_AM_B})\Phi_{M_A} + \chi_{M_AM_B}\Phi_{M_A}^2 +$$
$$\chi_{iM_B} - \chi_{iP}]\}\ \exp\{N_i[(\chi_{M_AP}\phi_P + \chi_{iP} - \chi_{iM_A})\phi_{M_A} +$$
$$(\chi_{M_BP}\phi_P + \chi_{iP} - \chi_{iM_B})\phi_{M_B} + \chi_{M_AM_B}\phi_{M_A}\phi_{M_B}]\} \quad (17)$$

The first two exponential terms are due to the configurational and mixing entropy, respectively. The entropy of mixing term depends only on the properties of the interphase under these conditions, since the apparent "size" of the mobile phase is independent of its composition. The third and fourth terms are due to the heat of mixing present in the system. The third exponential is determined solely by the properties of the bulk phase, while the final exponential is dependent on the interphase properties. In the limit of pure solvent, Φ_{M_A} or $\Phi_{M_B} \rightarrow 1$, this expression reduces to the one previously found for this case (11). One should also note that the composition of the mobile phase will affect not only the partition coefficient of the solute but also its retention factor, since the mobile phase composition has a strong influence on the interphase thickness and, therefore, on the interphase/mobile phase volume ratio.[6,10,22]

The influence of mobile phase composition on the partitioning and retention of solutes between this mobile, or bulk, phase and the terminally anchored chain interphase is considered in Figures 8–10. Different interaction schemes have been considered in each case. The first case, outlined in the caption to Figure 8, leads to the following dilute solute partition coefficient expression:

$$K_i = K_{conf}\exp\left\{-\frac{N_i}{N_M}\phi_P\right\}\exp\{N_i(\Phi_{M_A} + 1)\}\times$$
$$\exp\{-N_i(2\phi_{M_A} + \phi_{M_B})\} \quad (18)$$

By inspection it is apparent that the partition coefficient should increase with increasing mobile phase A fraction, Φ_{M_A}, with the large solutes rising much faster than the small ones, and indeed that is what is observed in Figure 8. The abrupt swelling of the interphase by large solutes under various mobile phase conditions is also apparent, with the critical Φ_{M_A} at which this swelling occurs decreasing with increasing solute size as one would expect. This behavior yields some insight into the use of these stationary phases as absorption media and also into their subsequent regeneration by changing the solvent quality. These terminally anchored chain interphases may be of use in the recovery of dilute, valuable, or hazardous species. The retention factor under these conditions (ignoring the case of strong interphase swelling by the solute) depends very little on the solvent quality as one would expect since the two mobile phases swell the interphase to the same extent (*i.e.*, $\chi_{M_AP} = \chi_{M_BP} = 0$).

The second case, outlined in the caption to Figure 9, leads to the following dilute solute partition coefficient expression:

$$K_i = K_{conf}\exp\left\{-\frac{N_i}{N_M}\phi_P\right\}\exp\{N_i(\Phi_{M_A} - 1)^2\}\times$$
$$\exp\{-N_i\phi_{M_B}(2\phi_{M_A} + \phi_{M_B})\} \quad (19)$$

By inspection it is apparent that the partition coefficient under these conditions should decrease with increasing mobile phase A fraction, Φ_{M_A}, with the large solutes decreasing much faster than the small ones, and indeed that is what is observed in Figure 9. The abrupt swelling of the interphase by large solutes under various mobile phase conditions, which was present in the case of Figure 8, is not present here. The interphase swelling here is significant at small Φ_{M_A}; however, the transition is not as abrupt as in the previous case. Under these conditions it would prove advantageous to perform large solute separations at low Φ_{M_A}, while separating small solutes at high Φ_{M_A}. This is most easily observed by considering the retention factor, k_i', where it is apparent that while k_i' for large solutes decreases with increasing Φ_{M_A}, k_i' for small solutes actually increases under these conditions. Of course, only one solute specific interaction has been considered here. Complex mixtures would require more detailed study. This variation in retention factor behavior is a result of the fact that the two polymer–mobile phase interaction parameters are distinctly different unlike the

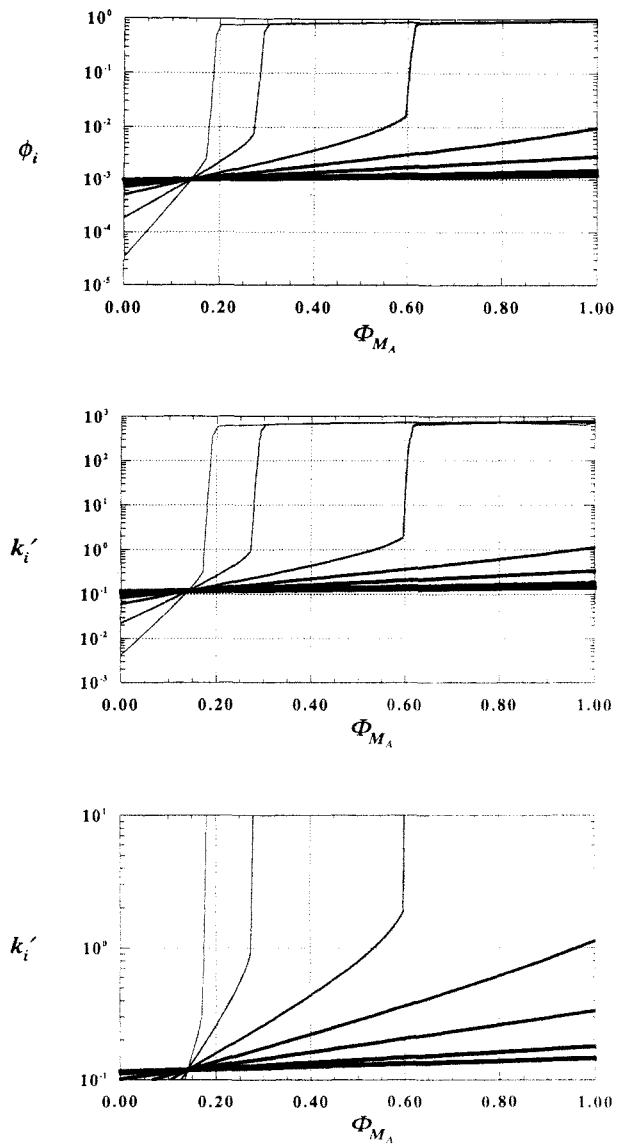

Figure 8. Partitioning and retention of solutes in a terminally anchored chain interphase: binary solvents and gradient chromatography. The interphase solute concentrations, ϕ_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.001$, are shown as a function of mobile phase composition, Φ_{M_A}, for the situation where $\chi_{M_AP} = 0$, $\chi_{M_BP} = 0$, $\chi_{M_AM_B} = 0$, $\chi_{iM_A} = 2$, $\chi_{iM_B} = 1$, $\chi_{iP} = 0$, $\sigma = 0.05$, and $N_M = 1$. The top panel displays the interphase solute concentration, the middle panel shows the retention factor, and the lowermost panel presents a magnified view of the retention factor. The seven solute sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9).

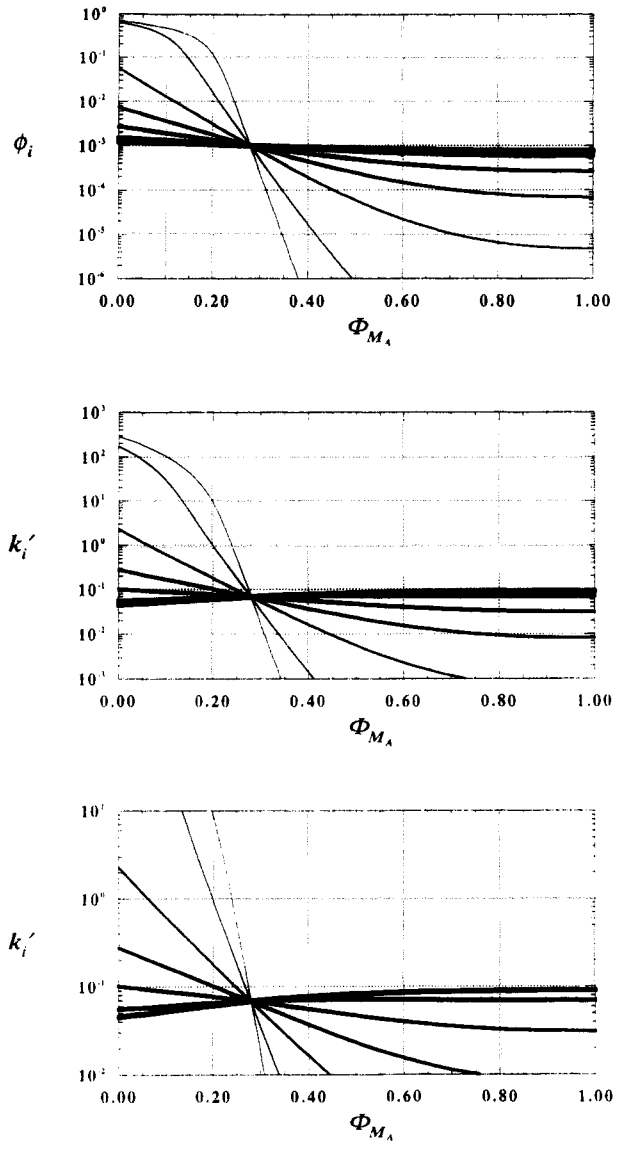

Figure 9. Partitioning and retention of solutes in a terminally anchored chain interphase: binary solvents and gradient chromatography. The interphase solute concentrations, ϕ_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.001$, are shown as a function of mobile phase composition, Φ_{M_A}, for the situation where $\chi_{M_AP} = 0$, $\chi_{M_BP} = 1$, $\chi_{M_AM_B} = 1$, $\chi_{iM_A} = 0$, $\chi_{iM_B} = 1$, $\chi_{iP} = 0$, $\sigma = 0.05$, and $N_M = 1$. The top panel displays the interphase solute concentration, the middle panel shows the retention factor, and the lowermost panel presents a magnified view of the retention factor. The seven solute sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9).

previously considered situation.

The third case, outlined in the caption to Figure 10, leads to the following dilute solute partition coefficient expression:

$$K_i = K_{conf} \exp\left\{-\frac{N_i}{N_M}\phi_P\right\} \exp\{N_i(\Phi_{M_A}^2 - 1)\} \times \exp\{-N_i\phi_{M_B}(2\phi_{M_A} + \phi_{M_B} - 2)\} \quad (20)$$

By inspection it is apparent that the partition coefficient should increase with increasing mobile phase A fraction, Φ_{M_A}, with the large solutes increasing much faster than the small ones, and indeed that is what is observed in Figure 10. There is no extensive interphase swelling under these conditions. Under these conditions it would prove advantageous to perform large solute separations at high

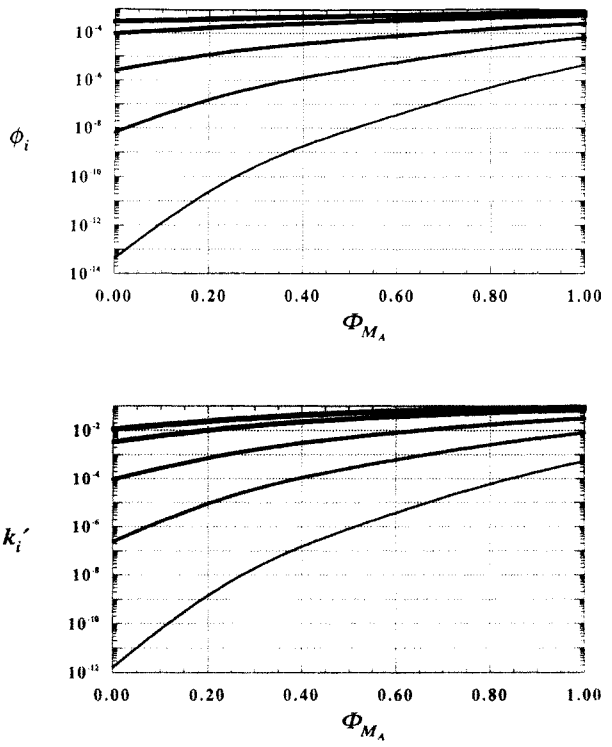

Figure 10. Partitioning and retention of solutes in a terminally anchored chain interphase: binary solvents and gradient chromatography. The interphase solute concentrations, ϕ_i, and retention factors, k_i', of dilute solute species, $\Phi_i = 0.001$, are shown as a function of mobile phase composition, Φ_{M_A}, for the situation where $\chi_{M_AP} = 0$, $\chi_{M_BP} = 1$, $\chi_{M_AM_B} = 1$, $\chi_{iM_A} = 1$, $\chi_{iM_B} = 0$, $\chi_{iP} = 1$, $\sigma = 0.05$, and $N_M = 1$. The top panel displays the interphase solute concentration and the bottom panel shows the retention factor. The seven solute sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the thickest to thinnest curves, respectively, in each plot. The retention factor was calculated as outlined in the text (see expressions 8 and 9).

Φ_{M_A}, while separating small solutes at low Φ_{M_A}. This is in direct opposition with respect to the previously encountered example (see Figure 9), which makes sense in light of the fact that these are almost directly opposite conditions. Of course, once again, only one solute-specific interaction has been considered here. Complex mixtures would require more detailed study.

The use of gradient chromatography and terminally anchored chain interphases to facilitate a separation is illustrated in Figure 11. Here three situations have been considered. All three cases are such that $\Delta\chi_i^{M_A} = \chi_{iM_A} - \chi_{iP} = 0.2$, although the χ_{ij}'s are different. Two of the cases, thin line and vertical tick marks, also satisfy the condition $\Delta\chi_i^{M_B} = \chi_{iM_B} - \chi_{iP} = 0.4$ although the χ_{ij}'s are also different. Under these conditions there is essentially no separation (they are nearly coincident), which is not surprising in light of the fact that at these dilute conditions (*i.e.*, $\Phi_i = 0.001$ and $K_i < 1$) it is really the $\Delta\chi_i$'s which will determine the extent of separation, not the individual χ_{ij}'s. This can be most easily observed by rewriting expression 17 in the following form:

$$K_i \cong \exp\left\{-\sigma N_i \mathcal{L}^{-1}\left(\frac{\sigma}{\phi_P}\right)\right\} \exp\left\{-\frac{N_i}{N_M}\phi_P\right\} \times \exp\{N_i[(\Delta\chi_i^{M_A} - \Delta\chi_i^{M_B} - \chi_{M_AM_B})\Phi_{M_A} + \chi_{M_AM_B}\Phi_{M_A}^2 + \Delta\chi_i^{M_B}]\} \exp\{N_i[(\chi_{M_AP}\phi_P - \Delta\chi_i^{M_A})\phi_{M_A} + (\chi_{M_BP}\phi_P - \Delta\chi_i^{M_B})\phi_{M_B} + \chi_{M_AM_B}\phi_{M_A}\phi_{M_B}]\} \quad (21)$$

where the dependence of the partition coefficient on the

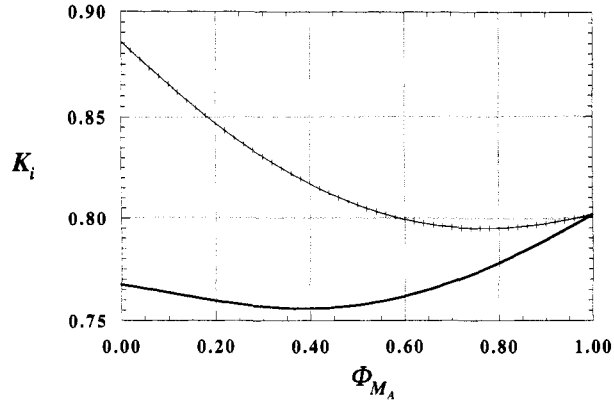

Figure 11. Separation of solutes by gradient chromatography. The partition coefficient, K_i, is shown as a function of mobile phase composition, Φ_{M_A}, for various solutes with $\chi_{M_AP} = 0$, $\chi_{M_BP} = 0.5$, $\chi_{M_AM_B} = 1$, $N_i = N_M = 1$, $\Phi_i = 0.001$, and $\sigma = 0.05$. The thin curve corresponds to $\chi_{iM_A} = 0.2$, $\chi_{iM_B} = 0.4$, and $\chi_{iP} = 0.0$; the vertical ticks correspond to $\chi_{iM_A} = 0.5$, $\chi_{iM_B} = 0.7$, and $\chi_{iP} = 0.3$; and the thick line corresponds to $\chi_{iM_A} = 0.5$, $\chi_{iM_B} = 0.3$, and $\chi_{iP} = 0.3$.

$\Delta\chi_i$'s is much more clearly denoted. Just as in the case of pure mobile phases in the dilute solute regime, separation of equal-sized molecules requires differing $\Delta\chi_i$'s for at least one of the solvents. This is shown by the thick line in Figure 11, where $\Delta\chi_i^{M_B} = \chi_{iM_B} - \chi_{iP} = 0.0$, not 0.4. Here it is observed that the degree of separation increases with decreasing Φ_{M_A} as one would expect. Therefore, to separate similar-sized molecules with gradient techniques differing $\Delta\chi_i$'s are required.

V. Summary and Conclusions

A previously developed, Flory-type mean-field analysis[22] of the mixing of a multicomponent, polydisperse solvent with an interphase of terminally anchored chains of finite extensibility has been utilized in the determination of the chromatographic properties of terminally anchored chain interphases. Due to its simplicity and inherent limitations, this approach provides only a qualitative description of solute partitioning and retention. However, this simple model should prove useful in determining the general equilibrium properties of these interphase–solvent systems. In the limit of dilute solute species this approach led to simple, analytical expressions which describe the partitioning and retention of solute molecules in the interphase. The partitioning and retention of the solute molecules were found to depend explicitly on the surface density of the terminally anchored chains, solvent strength, terminally anchored chain length, solute size, and the various interactions among the species present. Both size exclusion and size enhancement effects were observed. The former may prove to be advantageous in the separation of small molecules, while the latter are applicable to the separation of large molecules in an analogous manner. It was observed that similar-sized molecules require differing affinities, whether a pure or binary (gradient) mobile phase is utilized, leading to affinity-based separations. Highly nonlinear absorption regimes were also observed and may prove useful in the recovery of priority solutes from dilute solution, since it may prove possible to regenerate them simply by changing the mobile phase quality. It was also demonstrated that the chromatographic properties of terminally anchored chain interphases are controlled not only by their partitioning behavior but also by their retention behavior. The retention behavior was shown to be strongly influenced by the solvent phase conditions. Consideration of both solute partitioning and retention should allow the design of terminally anchored interphase systems which will prove advantageous in achieving a desired separation.

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