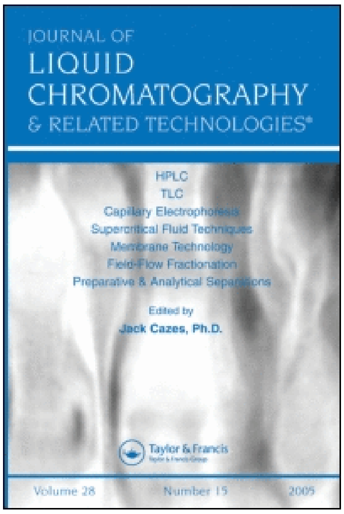

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# Theory of Homopolymer Retention in the Weak Adsorption Limit

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# THEORY OF HOMOPOLYMER RETENTION IN THE WEAK ADSORPTION LIMIT

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## ABSTRACT

The theory of homopolymer fractionation in mixed mobile phase solvent, high performance liquid chromatography (HPLC) developed previously by Boehm, Martire, Armstrong and Bui [12-14] for strongly adsorbed homopolymers is modified for the case where weak polymer adsorption and/or sorption prevails in the stationary phase. A weakly adsorbed homopolymer of degree of polymerization, M, is assumed to consist of a single adsorbed contiguous train of $M^\gamma$ segments where $0 < \gamma < 1$ ($\gamma = 1$ corresponds to strong adsorption) and a tail of $M - M^\gamma$ segments which protrudes into the mobile phase. The analysis predicts that the homopolymer capacity factor, k', depends upon the mobile phase composition, $\phi$, of the better polymer solvent in the vicinity of the critical composition, $\phi_c \equiv \phi_c(M)$, which renders $k' = 1$ for an M-unit homopolymer, according to

$$\ell n\ k' = S(\phi_c(M) - \phi)$$

where the slope, $S = -\partial \ell n k'/\partial \phi_c \sim M^\gamma$. Experimental measurements of S for different chromatographic systems are discussed within the framework of the theory.

## I. INTRODUCTION

Considerable interest exists in the analysis and separation of synthetic macromolecules by high performance liquid chromatography (HPLC). For instance, Armstrong and Bui [1-4] and Snyder and coworkers [5-11] have demonstrated that molecular weight separation of synthetic homopolymers such as polystyrene can be achieved by reversed-phase gradient elution HPLC using a mixed solvent mobile phase such as $MeCl_2/MeOH$ or $THF/H_2O$. In contrast to size exclusion chromatography (SEC), a single reversed phase column can be utilized to separate homopolymers over essentially the entire molecular weight spectrum (oligomer-high polymer) by gradient elution HPLC.

A statistical thermodynamic theory of homopolymer fractionation and its application to gradient elution HPLC has been developed by Boehm, Martire, Armstrong and Bui (hereafter BMAB) to describe the retention behavior of an isolated flexible chainlike homopolymer molecule distributed between a binary mixed mobile phase and an idealized stationary phase of sorbed solvent(s) forming a monolayer on a chemically homogeneous planar surface [12-14]. The BMAB theory assumes that a retained polymer molecule is strongly sorbed in that the number of surface-polymer segment contacts is directly proportional to the degree of polymerization, M. The present investigation seeks to ascertain the modifications required of the original BMAB theory when the retained polymer molecule is weakly sorbed having only a fraction of its M segments in contact with the stationary phase surface monolayer.

Of general interest is the predicted dependence of $\ell nk'$ on mobile phase composition, $\phi$, where k' is the solute capacity factor and $\phi$ is the volume fraction of the better polymer solvent. Of even greater significance are the predicted dependences on M of the critical mobile phase composition, $\phi_c$, at which $k'=1$ ($\ell nk'=0$) and the local slope, $S = -\partial\ell nk'/\partial\phi_c$, of the $\ell nk'$ - $\phi$ isotherm at $\phi = \phi_c$. The $\phi_c$-M and S-M dependences are important components in the BMAB description of homopolymer retention and fractionation and they are experimentally accessible from isocratic $\ell nk'$-$\phi$ measurements performed on several different molecular weight homopolymers on the same HPLC column [15,16,17]. Less reliable estimates of $\phi_c$ and S and their variation with M can also be obtained from gradient elution measurements [16,18,19].

Isocratic measurements of $\ell$nk' - $\phi$ isotherms have been performed for several polystyrene standards of different molecular weights with narrow distributions by several different groups. For example, Lochmüller and McGranaghan [15] have employed both THF/$H_2O$ and $MeCl_2$/ACN mobile phases with a C-8 300 Å mean pore diameter chemically bonded phase; Alihedai et. al. [16] have utilized $MeCl_2$/MeOH mobile phases with both 100 Å and 300 Å mean pore diameter C-18 chemically bonded phases and Northrup et. al. [17] have used both THF/ACN and $MeCl_2$/MeOH mixed mobile phases and a C-4 bimodal pore diameter reversed phase column consisting of a 48%-52% blend of 80 Å and 500 Å silica [20]. Generally a monotonic increase of $\phi_c$ and S with M is observed although variations in the $\phi_c$ - M and especially the S-M dependences have been determined from isocratic measurements performed on these different chromatographic systems. Experimentally one finds that $S \sim M^{\gamma}$ (or $\ell nS \sim \gamma \ell nM$) where the positive exponent, $\gamma$, typically ranges between $0.35 < \gamma < 1$ (see Table 1 which summarizes the experimental data).

The BMAB theory predicts that $\gamma \Rightarrow 1$ as $M \Rightarrow \infty$ if strong polymer sorption prevails on an idealized planar stationary phase surface with a sorbed solvent monolayer compositionally enriched in the better polymer solvent. Experimentally determined values of $\gamma < 1$ suggest that for those chromatographically relevant values of k' where $0 < k' \leq 1$ weak adsorption of the polymeric solute with considerable penetration into the mobile phase may be more realistic physically.

In Sec. II we present a brief summary of the original BMAB theory. In Sec. III a statistical thermodynamic treatment is given for the adsorption behavior of an ideal isolated polymer chain which interacts with a chemically homogeneous adsorption surface with a segment-surface contact free energy, $\epsilon$. The analysis reveals that there is a transition region between the strong adsorption ($\epsilon < 0$) and desorption ($\epsilon > 0$) limits where the average number of polymer segment-surface contacts is proportional to $M^{1/2}$ (rather than M for strong adsorption). The range of $\epsilon$ values over which the transition from strong adsorption to desorption occurs is found to decrease as $M^{-1/2}$.

In Sec. III we also discuss the Monte-Carlo calculations performed by Lal and Stepto [21,22] on the configurational behavior of adsorbed freely rotating polymer lattice chains where excluded volume interactions are included. The average configurational behavior is described in terms of the fraction of segments adsorbed, thickness of the adsorbed layer and the average lengths of train, loop and tail sequences of segments. Under conditions where weak (strong) adsorption prevails it is found that the average number of segment-surface contacts goes as $M^{.58}$ ($M^{1.1}$) for $30 \leq M < 100$. Also for weak adsorption the adsorbed layer was determined to be dominated by the lengths of the tail segments.

In Sec. IV we utilize the results and insights obtained in Sec. III to develop a modified BMAB theory of homopolymer retention which applies under conditions where weak polymer sorption is anticipated. It is assumed that the average configurational behavior of a weakly sorbed chain can be described by a single adsorbed train sequence of $M^\gamma$ segments where $0 < \gamma < 1$ and a single tail of $M-M^\gamma$ segments which extends into the mobile phase. The subsequent analysis predicts that $S \sim M^\gamma$ for large M and that the predicted dependence of $\phi_c$ on M is somewhat sensitive to the assumed behavior of the adsorbed train of $M^\gamma$ segments. However, the basic physical description of the homopolymer retention process and mechanism in the modified BMAB approach remains similar to the original treatment.

Finally in Sec. V we compare and discuss the predictions of the modified BMAB analysis and the experimental results and suggest possible extensions.

## II - SUMMARY OF THE BMAB THEORY OF HOMOPOLYMER RETENTION IN THE STRONG SORPTION LIMIT

The BMAB theory applies statistical thermodynamics to predict the equilibrium distribution of an isolated flexible chainlike homopolymer molecule between a binary solvent mobile phase and an idealized planar stationary phase surface with sorbed solvent(s). The relative phase preference of the polymer molecule depends on M, $\phi$, all possible types of nearest neighbor interactions such as solvent molecule-polymer segment, solvent molecule-solvent molecule, polymer segment-polymer segment, solvent molecule and/or polymer segment-stationary phase surface site, and also the configurational entropy of the flexible polymer molecule in each chromatographic phase. The flexible polymer coil plus the entrained solvent molecules are assumed to behave as a swollen spherical (thin cylindrical) gel in a favorable mobile (stationary) phase environment. Also it is assumed that strong polymer molecule sorption prevails upon retention in the stationary phase with M polymer segment-surface contacts.

In its simplest form, the BMAB theory predicts

$$\ell n\, k' = S(\phi_c - \phi) \equiv |A_1|M(\phi_c - \phi)$$

or

$$k' = \exp[S(\phi_c - \phi)] = \exp[|A_1|M(\phi_c - \phi)] \qquad \text{(II-1)}$$

where $S \equiv -\partial \ell n\, k'/\partial \phi_c = |A_1|M$ and $A_1$ asymptotically approaches a constant value independent of M for large M which is typically negative for chromatographically reasonable selections of the mixed solvents. When sorption of the better polymer solvent onto the stationary phase dominates, the following predictions for $\phi_c$ and $A_1$ result:

$$\phi_c \equiv \phi_c(M) = \phi_c^{\infty} - |a|M^{-1/2} + bM^{-4/5} + c_1M^{-1} + c_2M^{-1}\,\ell nM \qquad \text{(II-2)}$$

and

$$A_1 = X_{12} + X_{13} - X_{23} + dM^{-4/5} + eM^{-1} \qquad \text{(II-3)}$$

Here, $\phi_c^\infty$ ($0 \leq \phi_c^\infty \leq 1$) is the asymptotic limiting value of the critical composition as $M \rightarrow \infty$ and $X_{ij} \equiv \beta c_m(w_{ij} - (w_{ii} + w_{jj})/2)$, (i,j = 1-3) represents the reduced interchange energy (in units of $(\beta c_m)^{-1} \equiv kT/c_m$ where $c_m$ is the mobile phase coordination number) required to form an i-j nearest neighbor pair with energy $w_{ij}$ from i-i and j-j nearest neighbor pairs with energy $w_{ii}$ and $w_{jj}$. The indices 1 and 2 respectively denote the better and poorer mobile phase solvents and 3 corresponds to a monomeric segment of the homopolymeric solute. The quantities a, b, $c_1$, $c_2$, d and e introduced in eqs. (II-2) and (II-3) are independent of M and depend on the interchange energies and weakly upon the mobile phase composition.

Eq. (II-1) indicates that for large M polymers, $k' \equiv \exp[|A_1|M(\phi_c - \phi)]$ undergoes an abrupt transition from a very large to a very low value within a very narrow mobile phase composition range centered at $\phi_c$. Thus a very small change in the mobile phase composition from $\phi_c(1 - \Delta)$ to $\phi_c(1 + \Delta)$ where $\Delta$ is a small positive infinitesimal ($\lim \Delta \rightarrow 0$ as $M \rightarrow \infty$) generates an increasingly abrupt change from very large to very low solute retention as M increases. Eq.(II-2) predicts that $\phi_c$ becomes a monotonically increasing function of M for large M which asymptotically tends to $\phi_c^\infty$ as $M \rightarrow \infty$.

The BMAB analysis indicates that fractionation of homopolymers with respect to M is possible over a wide spectrum of M values (oligomer-high polymer) on a single column provided certain conditions are satisfied: (1) The polymer molecules are flexible; (2) A combination of a good (1) and a poor (2) solvent for the polymer is employed for the mobile phase such that $X_{12} + X_{13} - X_{23} < 0$; (3) The better solvent is preferentially sorbed onto the stationary phase. Fractionation of the higher M homopolymers usually requires gradient elution which commences at an initial mobile phase composition that is less than the critical composition of the lowest molecular weight homopolymer in the sample and the mobile phase composition is then temporally enriched with the better solvent to a value which exceeds the critical composition of the highest M homopolymer present. For very high values of M, $\phi_c$ increases only slightly with M making fractionation more difficult.

In a linear gradient, the temporal variation of the mobile phase composition is

$$\phi(t) = \phi(0) + Bt \quad t \geq 0 \tag{II-4}$$

where $\phi(t)$ ($\phi(0)$) is the mobile phase composition at the column entrance at time t (time t = 0) and B is the rate of increase of the volume fraction of the favorable solvent. The solute retention time, $t_R$, in linear gradient elution and if Eq. (II-1) applies for k' is

$$t_R = t_0 + (|A_1|MB)^{-1} \ln[1 + |A_1|MBt_0 \exp[|A_1|M(\phi_c - \phi(0))]] \tag{II-5}$$

where $t_0$ represents the column dead time. When

$$|A_1|MBt_0 \exp[|A_1|M(\phi_c - \phi(0)] >> 1,$$

eq. (II-5) simplifies to

$$t_R \approx t_0 + (\phi_c - \phi(0))/B + (SB)^{-1} \ln(SBt_0) \tag{II-6}$$

where $S \equiv |A_1|M$. This result can be utilized to determine $\phi_c$ and S by gradient elution measurements provided the linear approximation to $\ln k'$ given by eq.(II-1) is valid over the entire mobile phase composition range where chromatographically significant values of k' are encountered ($10 \geq k' \geq 0.1$) [14]. A linear relationship between $\ln k'$ and $\phi$ over the relevant composition is likely to become more accurate as M increases.

The BMAB theory predicts in general that

$$\ln k' = |A_1|M(\phi_c - \phi) + \sum_{j=2}^{\infty} A_j M(\phi_c - \phi)^j \tag{II-7}$$

where the $A_j$ $j \geq 2$ are monotonically decreasing functions of M which vanish as $M \rightarrow \infty$. Non-linear corrections to $\ell nk'$ appearing in the sum $\sum_{j=2}^{\infty} A_j M(\phi_c - \phi)^j$ contribute whenever the difference $|\phi - \phi_c|$ becomes appreciable and M is sufficiently small so that k' is chromatographically measurable over a considerable composition range.

## III. STATISTICAL THERMODYNAMIC BEHAVIOR OF A CHAINLIKE POLYMER MOLECULE NEAR A PLANAR ADSORPTION SURFACE

Here we consider the statistical thermodynamic behavior of a completely flexible chainlike homopolymer molecule near a chemically homogeneous planar adsorption surface. The polymer chain consists of M freely rotating links each of length b confined to the halfspace $z > 0$ by an impenetrable adsorption surface with which the polymer can interact on a per segment basis. Both the diffusion equation - Green's function approach [23,24] and the Monte Carlo calculations performed by Lal and Stepto [21] for determining the equilibrium configurational behavior of an adsorbed polymer chain will be discussed.

The equilibrium configurations of a flexible homopolymer chain without intrachain interactions can be simulated from the trajectories assumed by a particle undergoing an unrestricted three dimensional random walk [23,24]. This means that the probability density (i.e. Green's function) $G(\underline{r}, 0; M)$ that one end of a chain of M segments is located in a small volume element centered about $\underline{r}$ given that the other end is located at the origin can be obtained by solving a diffusion equation in a local one-particle potential $\beta\phi(r)$ (in units of $\beta^{-1} = kT$)

$$\frac{\partial G(\underline{r},0;M)}{\partial M} = \left(\frac{b^2}{b}\right)\nabla_r^2 G(\underline{r},0;M) - \beta\phi(\underline{r})\,G(r,0;M) \tag{III-1}$$

subject to the initial condition $G(\underline{r},0;M=0) = \delta^3(r) \equiv \delta(x)\delta(y)\delta(z)$. When $\phi(r) = 0$,

$$G(r,0;M) = (3/2\pi Mb^2)^{3/2}\exp[-3r^2/2Mb^2] \qquad \text{(III-2)}$$

which is the familiar Gaussian solution of Eq.(III-1), and it represents the probability density that an ideal chain has an end-to-end separation, r, when it assumes an equilibrium distribution of configurations. The mean square end-to-end separation is $<r^2> = \int_0^\infty 4\pi r^4 G(r,0;M)dr = Mb^2$ and $<r^2>^{1/2} = M^{1/2}b$ where b is the length of a (statistical) segment.

When a chainlike polymer molecule interacts with a surface, the number of accessible configurations is reduced relative to a completely isolated coil. If the interaction between a polymer segment and the surface is a contact potential

$$\beta\phi(r) = \beta\epsilon' b\delta(z) \qquad \text{(III-3)}$$

where $\epsilon'$ has the units of energy and the delta function, $\delta(z)$, has units of reciprocal length, then the probability density for a polymer chain which interacts with the surface is obtained by solving the differential equation

$$\frac{\partial G(\underline{r},0;M)}{\partial M} = \left\{\left(\frac{b^2}{6}\right)\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \beta\epsilon' b\delta(z)\right\} G(\underline{r},0;M) \qquad \text{(III-4)}$$

where for an impenetrable surface $z \geq 0$. It is possible and convenient to remove the constraint that $z > 0$ by including polymer configurations which penetrate through the surface and then removing them by the device of introducing a 'sink' term to the diffusion equation. This loss term has the form $-(\ln \upsilon)b\delta(z)\, G(\underline{r},0;M)$ where $\upsilon$ represents the ratio of the number of ways a given segment of the polymer chain can be generated from a random-walk trajectory starting at the surface to a point above the surface ($z > 0$) (and hence generate an allowed configuration) to the total number of ways the segment could be generated in the absence of the surface. For a completely flexible one-dimensional polymer chain $\upsilon = ½$ [25,26] which means that whenever a chain segment makes contact with the surface the next segment must be diverted away from the surface. For a three dimensional polymer chain whose configurations are simulated by a particle taking a random walk on a cubic lattice, $\upsilon = 5/6$ for a chain which can fold back on itself and $\upsilon = 4/5$ when only one segment is allowed per lattice site.

The modified diffusion equation which incorporates the 'sink' term is congruent to eq. (III-4) when $\epsilon'$ is replaced by

$$\epsilon = \epsilon' - kT\ell n\upsilon \qquad 0<\upsilon\leq 1 \tag{III-5}$$

and with the restriction $z > 0$ removed. The solution of eq.(III-4) with the modification (III-5) subject to the initial condition $G(\underline{r},0;\, M=0) = \delta^3(r)$ gives the probability density $G(\underline{r},0;\, M)$ that an isolated polymer chain of M links without intrachain segment-segment interactions (i.e. excluded volume interactions) has its terminal segment between $\underline{r}$ and $\underline{r} + d\underline{r}$ given that its initial segment is at the origin in contact with the surface.

The behavior of $G(\underline{r},0;\, M)$ depends on $\epsilon$. When $\epsilon < 0$ adsorption of the chain occurs since contact with the surface is energetically favored and overcomes the loss of configurational entropy. If $\epsilon = 0$, that is, $\epsilon' = kT\ell n\upsilon$, the polymer chain behaves as if the surface were absent, and when $\epsilon > 0$, the polymer molecule is essentially desorbed from the surface except for the initial segment which becomes irrelevant for long chains. Once $G(\underline{r},0;M)$ is obtained the canonical partition function, $Q \equiv Q(M, \beta)$, is determined from

$$Q = \int_{z>0} d^3r G(\underline{r},0;M) \tag{III-6}$$

and from Q, the statistical thermodynamic properties of the ideal polymer chain-surface system can be extracted.

The solution of eq.(III-4) with eq. (III-5) is facilitated by taking the Laplace transform of eq. (III-4) with respect to M and then the Fourier transform with respect to the x and y coordinates which are parallel to the plane of the adsorption surface. These transformations convert eq. (III-4) to

$$\left(\frac{b^2}{6}\right)\frac{d^2\bar{G}^*}{dz^2} - \left(\lambda + \left(\frac{b^2}{6}\right)(k_x^2 + k_y^2) + \beta\epsilon b\delta(z)\right)\bar{G}^* = -\delta(z)$$

(III-7)

where

$$\bar{G}^* = \bar{G}^*(k_x, k_y, z; \lambda) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp[i(k_x x + k_y y)]\, G^*(x, y, z; \lambda)$$

(III-8)

and

$$G^* \equiv G^*(x, y, z; \lambda) = \int_0^{\infty} dM e^{-\lambda M}\, G(\underline{r}, 0; M)$$

(III-9)

Eq. (III-7) has the general solution

$$\bar{G}^* = A \exp[-\kappa z]\,\theta(z) + \beta\exp[\kappa z]\,\theta(-z)$$

(III-10)

where $\kappa \equiv \kappa(\lambda,k_x,k_y) = (6b^{-2}(\lambda + (b^2/6)(k_x^2 + k_y^2)))^{1/2}$ has the units of inverse length, A and B are constants, and $\theta(z) = 1$ for $z > 0$ and $\theta(z) = 0$ for $z < 0$ is the Heaviside unit step function. The constants are determined by requiring that $\bar{G}^*$ be continuous at $z = 0$ and that

$$\left(\frac{b^2}{6}\right)\left[\frac{d\bar{G}^*}{dz}\Big|_{z=0^+} - \frac{d\bar{G}^*}{dz}\Big|_{z=0^-}\right] - \beta\epsilon b\bar{G}^*(z=0) + 1 = 0$$

which is obtained by integrating (III-7) across the singularity at z=0. These conditions are satisfied if $A=B=(\kappa b^2/3 + \beta\epsilon b)^{-1}$ and $\overline{G}^*=(\kappa b^2/3 + \beta\epsilon b)^{-1}\{\exp[-\kappa z]\theta(z) + \exp[\kappa z]\theta(-z)\}$.

Performing the inverse Laplace transformation on $\overline{G}^*$ gives

$$\overline{G}=\overline{G}(k_x, k_y, z; M) =$$
$$\exp[-Mb^2(k_x^2+k_y^2)/6]\{(\frac{3}{(2\pi Mb^2)})^{1/2}\exp[-3z^2/2Mb^2]$$

$$-\frac{3\beta\epsilon}{2b}\exp[(\frac{3\beta\epsilon}{b})(z+M\beta\epsilon b/2)]\,erfc((\frac{3}{2Mb^2})^{1/2}(z+Mb\beta\epsilon))\}$$

(III-11)

$$\text{where } erfc(u) = 2\pi^{-1/2}\int_u^\infty e^{-\mu^2}d\mu$$

is the complementary error function.

Taking the inverse Fourier transformation gives

$$G(\underline{r}, 0; M) = (2\pi)^{-2}\int_{-\infty}^{\infty}dk_x\int_{-\infty}^{\infty}dk_y\exp[-i(k_xx+k_yy)]\,G(k_x, k_y, z; M)$$

$$= (\frac{3}{2\pi Mb^2})^{3/2}\exp[-3(x^2+y^2+z^2)/2Mb^2]$$

$$x\{1-\beta\epsilon(\frac{3\pi M}{2})^{1/2}\exp[(\frac{3\beta\epsilon}{b})(z+\frac{M\beta\epsilon b}{2}) + \frac{3z^2}{2Mb^2}]$$
$$x\ erfc((\frac{3}{2Mb^2})^{1/2}(z+Mb\beta\epsilon))\}$$

(III-12)

When $\epsilon \equiv \epsilon'-kT\ell n\upsilon=0$, eq. (III-12) reduces to eq. (III-2) which is the Gaussian distribution for an unperturbed three dimensional polymer coil. When $\beta\epsilon << 0$ which corresponds to strong polymer adsorption the last term on the RHS of eq. (III-12) dominates and as erfc(u) ~ 2 for u→-∞, eq. (III-12) reduces to

$$G(\underline{r},0;M)=\left(\frac{3}{2\pi Mb^2}\right)\frac{3\beta|\epsilon|}{b}\exp\left[\frac{3M(\beta\epsilon)^2}{2}\right]\exp\left[\frac{-3\beta|\epsilon|z}{b}\right]$$
$$x\ \exp\left[-3\left(x^2+y^2\right)/2Mb^2\right]$$

(III-13)

The average thickness of the strongly adsorbed polymer molecule normal to the surface is

$$d\equiv\langle z\rangle=\int d^3r\theta(z)\ \ zG(\underline{r},0;M)\Big/\int d^3r\theta(z)G(\underline{r},0;M)=b/3\beta|\epsilon|$$

(III-14)

The average thickness of the polymer layer varies inversely with $\beta|\epsilon|$ and the polymer assumes configurations in the strong adsorption mode which are closely associated with the surface and the polymer assumes a geometry which resembles a thin cylindrical disc or pancake.

When $\beta\epsilon >> 0$ the asymptotic expansion

$$erfc(u)=\pi^{-1/2}u^{-1}e^{-u^2}$$

for large positive u applies and

$$G(\underline{r},0;M)\Rightarrow\left(\frac{3}{2\pi Mb^2}\right)^2\pi^{1/2}z\exp\left[-3\left(x^2+y^2+z^2\right)/2Mb^2\right]\theta(z)$$

(III-15)

The average value $\langle z\rangle = (M/6)^{1/2}b$ is independent of $\epsilon$ and the polymer molecule assumes dimensions characteristic of a coil removed from the surface.

The configurational partition function for the adsorbed polymer molecule is obtained from eq. (III-6) with G(r,0;M) given by eq. (III-13) and

$$Q \equiv Q(M,\beta) = (1/2)\exp[3M\beta^2\epsilon^2/2]\,erfc\left(\left(\frac{3M}{2}\right)^{1/2}\beta\epsilon\right)$$

(III-16)

The partition function assumes the following limiting forms

$$\beta\epsilon << 0 \qquad Q \sim \exp[3M\beta^2\epsilon^2/2] \qquad \text{(III-17a)}$$

$$\beta\epsilon >> 0 \qquad Q \sim 1/(6\pi M)^{1/2}\beta\epsilon \qquad \text{(III-17b)}$$

$$0 \leq (3M/2)^{1/2}\beta|\epsilon| < 1 \qquad Q \simeq 1/2[1-(6M/\pi)^{1/2}\beta\epsilon] \qquad \text{(III-17c)}$$

The average energy of adsorption in units of kT is calculated from $\beta<E> = -\partial\ell nQ/\partial\ell n\beta$ and has the following limiting forms

$$\beta\epsilon << 0 \qquad \beta<E> \simeq -3M(\beta\epsilon)^2 \qquad \text{(III-18a)}$$

$$\beta\epsilon >> 0 \qquad \beta<E> \simeq 1 \qquad \text{(III-18b)}$$

$$0 \leq (3M/2)^{1/2}\beta|\epsilon| < 1 \qquad \beta<E> \simeq (6M/\pi)^{1/2}\beta\epsilon \qquad \text{(III-18c)}$$

Clearly in the strong adsorption limit where $-\infty < \beta\epsilon << -(2/3M)^{1/2}$, $\beta<E>$ is proportional to the number of chain segments or degree of polymerization, M which indicates that the average number of contacts with the surface, $\overline{C} \equiv \beta<E>/\beta\epsilon$, is also proportional to M. Thus in the limit of strong adsorption, the polymer molecule assumes trainlike configurations which extend over the entire length of the chain and are in contact with the surface.

For $0 \leq \beta|\epsilon| < (2/3M)^{1/2}$ a transition from strong adsorption to desorption occurs and, in this region of weak adsorption which narrows as $M^{-1/2}$, $\overline{C} \propto M^{1/2}$. Also, the probability distribution given by eq. (III-12) reduces to a Gaussian distribution for sufficiently large values of z ($z \geq (2M/3)^{1/2}b$). These results suggest that a weakly adsorbed polymer chain assumes configurations which consist of an adsorbed train of $\sim M^{1/2}$ segments and one or two terminal tails which involve $M-M^{1/2}$ segments which are desorbed from the surface. Finally when $\beta\epsilon >> 0$, $\beta<E> \simeq 1$ becomes independent of M which indicates that only the initial segment is attached to the surface and hence desorption of the remainder of the polymer chain has occurred.

The above results essentially have been obtained by many investigators employing both discrete and continuum (diffusion) models for determining the configurational behavior [27, 28, 29]. This model of an adsorbed polymer chain, however, fails to include excluded volume interactions between chain segments.

Lal and Stepto [21] have performed Monte Carlo calculations of the configurational behavior of an adsorbed polymer chain which include excluded volume interactions. They analyzed freely rotating lattice chains consisting of 30, 50, 75 and 100 bonds adsorbing from athermal solutions onto an impenetrable planar adsorption surface for different adsorption energies which are defined as the energy changes, $\Delta\epsilon_s$, for breaking a segment-solvent interaction to form a segment-surface bond. Strong and weak adsorption were respectively simulated by the selections $\beta\Delta\epsilon_s$=-0.9 and $\beta\Delta\epsilon_s$=-0.5. When the chains are strongly adsorbed they are found to possess extended configurations dominated by trains and loops and short tails. For weak adsorption, however, the chain configurations develop longer tails and the thickness of the adsorbed homopolymer layer is dominated by the lengths of the tails. Indeed, proportionality was obtained between tail length and chain length for the chains investigated (M=30, 50, 75, 100) in the weak adsorption case with about one third of the segments in each tail at all chain lengths.

The average number of contacts, $\overline{C}$, obtained by Lal and Stepto as a function of M (the number of bonds) in their Monte-Carlo calculations satisfy the following relationships obtained by linear regression over the range $30 \leq M \leq 100$ (See TABLE I of ref. 21 )

$$\beta\Delta\epsilon_s=-0.9; \quad \overline{C}=.38\,M^{1.08}; \text{ c.c}=.999 \qquad \text{(III-19a)}$$

$$\beta\Delta\epsilon_s=-0.5; \quad \overline{C}=.99M^{0.582}; \text{ c.c.}=.997 \qquad \text{(III-19b)}$$

where c.c. ≡ correlation coefficient. These results determined from the Monte-Carlo calculations in the strong and weak adsorption limits reinforce and agree rather well with the predictions of the ideal chain-surface analysis based on the diffusion equation.

## IV. MODIFICATION OF THE BMAB THEORY FOR THE CASE OF WEAK POLYMER SOLUTE ADSORPTION IN THE STATIONARY PHASE

Here we apply the insights and results discussed in III to modify the original BMAB theory (see sec. II) when weak polymer adsorption or sorption characterizes its retention in the stationary phase. In general, the configurations of an adsorbed polymer chain can be described in terms of (1) trains which are contiguous sequences of segments in contact with the surface; (2) loops which are successive segments which protrude into the solution or solvent phase and connect adjacent trains, and (3) tails which represent terminal sequences of segments that extend away from the surface into the solvent phase [21,22]. When strong adsorption prevails the chain configurations are dominated by long train sequences connected by loops and short or nonexistent tails with the average number of segment-surface contacts proportional to M. For weak adsorption the chain configurations develop longer tails which determine the thickness of the adsorbed layer and a concomitant decrease in the number and length of the train-loop sequences with an average number of segment-surface contacts proportional to $M^{\gamma}$ where $0<\gamma<1$.

In the subsequent proposed modification of the original BMAB theory to weak polymer sorption, we assume an average configurational behavior which is characterized by a single adsorbed train of $M^{\gamma}$ segments and a single tail of $M-M^{\gamma}$ segments which extends into the mobile phase environment beyond the surface-sorbed solvent monolayer. Thus when a polymer molecule exits from the stationary to the mobile phase (or vice versa) a concomitant displacement of $M^{\gamma}$ monomeric solvent molecules from the mobile to the stationary phase is assumed to occur. Other configurations for the weakly adsorbed homopolymer are viable possibilities such as one which consists of an adsorbed train of $M^{\gamma}$ segments and two tails comprised of a total of $M-M^{\gamma}$ segments which can be apportioned between the tails in $(M-M^{\gamma}+1)/2$ (((M-

$M^{\gamma})/2)+1)$ distinguishable ways if $M$-$M^{\gamma}$ is an odd (even) integer. It turns out, however that if each configuration composed of one train and one or two tails is equally probable, then it suffices for the subsequent analysis to consider the single train-single tail adsorbed configuration since all other configurations of this class will generate the same result. Those configurations for which the $M^{\gamma}$ ($M$-$M^{\gamma}$) segments in contact (not in contact) with the surface appear in multiple train-loop sequences and thus shorter tails are expected to be energetically and entropically less favorable for real polymer chains with definite bond angles and steric hindrances and are not considered in the present investigation.

In ref. [14] (see eq. (22)) the following expression was derived for the capacity factor ($k_3 \Rightarrow k'$) of a chainlike homopolymer solute (component 3) of M monomeric units distributed between a mobile phase (m) consisting of a binary solvent mixture of components 1 and 2 and a stationary phase (s) consisting of a planar chemically homogeneous support surface with a monolayer of sorbed solvents 1 and 2.

$$k_3 \Rightarrow k' = \Phi \; \frac{c_s(c_s-1)^{M-2}}{c_m(c_m-1)^{M-2}} \left(\frac{N_s P_s}{N_m P_m}\right) \frac{(1-M/N_s)^{M-N_s}}{(1-M/N_m)^{M-N_m}}$$

$$\exp\left( (1/2 - g_s)\frac{M^2}{N_s} - (1/2 - g_m)\frac{M^2}{N_m}\right) \left(\sum_{i=1}^{2} f_i\right)^M$$

(IV-1)

where

$$f_i = x_{is}\exp[\beta\Delta e(i,3;s) + ((1-x_{is})(c_s/c_m) - (1-x_{im}))(X_{i3}^m + X_{12}^m - X_{j3}^m)]$$

(IV-2)

($i=1,2$ $j \neq i$). Eq. (IV-1) was derived in the strong adsorption (or sorption) limit where all M units of the homopolymer reside in the surface monolayer when retained in the stationary phase and M (monomeric) solvent molecules are exchanged between chromatographic phases whenever a polymeric solute makes a concomitant transition. In eqs. (IV-1) and/or (IV-2), $\Phi$ represents the phase ratio; $c_a$ ($a \equiv m,s$) represents the coordination number in phase a; $N_a$ ($a \equiv m,s$) denotes the volume (or area) occupied by the polymer molecule and entrained solvent molecules in chromatographic phase a; $P_a \equiv P_a(N_a)$ represents the probability that a polymeric solute molecule and entrained solvent molecules occupies a volume (or area) given by $N_a$; $\beta\Delta e(i,3;s) \equiv \beta(e_{is}-e_{3s}+w_{i3}-w_{ii})$ $i=1,2$ represents the free energy change associated with removing a polymer segment from the stationary phase surface to the mobile phase with the corresponding exchange of a type i ($i=1,2$) solvent molecule; the $e_{is}$ $i=1,2$ and $e_{3s}$ respectively represent the interaction free energy of a type i solvent molecule and a polymer segment with the surface while $w_{ii}$ and $w_{i3}$ $i=1,2$ respectively denote nearest neighbor solvent i-solvent i and solvent i-polymer segment interaction energies; $X_{ij}^{m} \equiv \beta c_m(w_{ij} - (w_{ii} + w_{jj})/2)$ ($i,j=1$-$3$) represents the reduced interchange energy required to form an i-j nearest neighbor pair from an i-i and a j-j nearest neighbor pair; the $x_{ia}$ $i=1,2$ $a=m,s$ represent the volume fractions of solvent component i in phase a; and finally

$$g_a \equiv 1/2 - \sum_{i=1}^{2} x_{ia}X_{i3}^{a} + x_{1a}x_{2a}X_{12}^{a} \quad (x_{ia}+x_{2a}= 1) \quad a \equiv m,s.$$

We seek to modify eq. (IV-1) for k′ to make it applicable when weak homopolymer adsorption (and/or sorption) characterizes the retention behavior in the stationary phase. The weakly adsorbed chain is assumed to consist of a single train of $M^{\gamma}$ segments (actually the nearest integer to $M^{\gamma}$) where $0<\gamma<1$ and then a tail of $M$-$M^{\gamma}$ segments which is desorbed from the surface monolayer and penetrates into the mobile phase. In the present treatment the configurational behavior of the train and tail portions are taken to be independent. Also polymer desorption from the stationary phase is accompanied by the sorption of $M^{\gamma}$ solvent molecules.

The proposed generalization of eq. IV-1 in the weak adsorption case is

$$k' = \Phi \frac{c_s(c_s-1)^{M^\gamma-1}(c_m-1)^{M-M^\gamma-1}N_s^* P_s(N_s^*)\, N_m^* P_m(N_m^*)\ (1-M^\gamma/N_s^*)^{M^\gamma-N_s^*}}{c_m(c_m-1)^{M-2}\ N_m P_m (1-M/N_m)^{M-N_m}}$$

$$X(1-(M-M^\gamma)/N_m^*)^{M-M^\gamma-N_m^*}\ \exp[-(½-g_m)M^2/N_m]$$

$$x\ \exp[(½-g_m)(M-M^\gamma)^2/N_m^* + (½-g_s)(M^\gamma)^2/N_s^*]\ (\sum_{i=1}^{2} f_i)^{M^\gamma}$$

(IV-3)

where $N_s^*$ and $N_m^*$ respectively represent the area and volume occupied by the train and tail portions of the weakly sorbed polymer molecule and entrained solvent molecules and $N_m$ is the volume of the solvent swollen polymer coil in the mobile phase. $N_s^*$, $N_m^*$ and $N_m$ are determined by free energy minimization of the respective polymer train, tail or coil entrained solvent system. The minimization conditions are

$$\frac{\partial \ell n P_s(N_s^*)}{\partial N_s^*} + (N_s^*)^{-1} - \ell n[1-\frac{M^\gamma}{N_s^*}] - \frac{M^\gamma}{N_s^*} - (\frac{M^\gamma}{N_s^*})^2[½-g_s] = 0$$

(IV-4a)

$$\frac{\partial \ell n P_m(N_m^*)}{\partial N_m^*} + (N_m^*)^{-1} - \ell n[1-\frac{(M-M^\gamma)}{N_m^*}] - \frac{(M-M^\gamma)}{N_m^*} - (\frac{M-M^\gamma}{N_m^*})^2[½-g_m] = 0$$

(IV-4b)

and

$$\frac{\partial\ \ell n P_m(N_m)}{\partial N_m} + N_m^{-1} - \ell n[1-M/N_m] - \frac{M}{N_m} - (\frac{M}{N_m})^2[½-g_m] = 0$$

(IV-4c)

Employing the approximations $P_s(N_s^*) \approx M^{-\gamma}\exp[-N_s^*/M^\gamma]$, $P_m(N_m^*) \approx (M-M^\gamma)^{-3/2}$ $\exp[-3N_m^{*2/3}/2(M-M^\gamma)]$ and $P_m(N_m) \approx M^{-3/2}\exp[-3N_m^{2/3}/2M]$ in eqs. (IV-4a)- (IV-

4c), respectively, give $N_s^* = g_s^{1/2} M^{3\gamma/2}$, $N_m^* = g_m^{3/5}(M-M^\gamma)^{9/5}$ and $N_m = g_m^{3/5} M^{9/5}$ and whenever $M^\gamma/N_s^* << 1$, $(M-M^\gamma)/N_m^* << 1$ and $M/N_m << 1$, which corresponds to polymer swelling in good solvent environments. These results for $N_s^*$, $N_m^*$ and $N_m$ are the standard Flory predictions [29, 30, 31] for the dimensions of a solvent swollen cylindrical disc or spherical coil.

Substitution of the above results for $P_s(N_s^*)$, $P_m(N_m^*)$, $P_m(N_m)$, $N_s^*$, $N_m^*$ and $N_m$ into eq. (IV-1) gives after some simplification [e.g. replacing

$$\frac{c_s(c_s-1)^{M^\gamma-1}}{c_m(c_m-1)^{M^\gamma-1}} \; by \; \left(\frac{c_s-1}{c_m-1}\right)^{M^\gamma}$$

for large $M^\gamma$]

$$M^{-\gamma}\ell n k' =$$

$$\ell n\left(\sum_{i=1}^{2} x_{is}\exp\left(\beta\Delta E(i) + \left(\frac{c_s}{c_m}(1-x_{is}) - (1-x_{im})\right)(X_{i3}^m + X_{12}^m + X_{j3}^m)\right)\right)$$

$$-M^{-\gamma/2}(2g_s^{1/2}) + 1/2 M^{-4/5} g_m^{2/5} + M^{-\gamma}\ell n\left[\Phi(1-M^{\gamma-1})^{3/10} M^{\gamma/2} g_s^{1/2}\right] \qquad \text{(IV-5)}$$

where $\beta\Delta E(i) = \beta(\epsilon_{is} - e_{3s} + w_{i3} - w_{ii}) + \ell n[(c_s-1)/(c_m-1)]$ i=1,2. The solvent compositions $x_{im}$ and $x_{is}$ are related by the equilibrium adsorption isotherm of the solvents distributed between the binary solvent mobile phase and the adsorbed surface monolayer, which is [14]

$$x_{1s}(1-x_{1s})^{-1}\exp\left[X_{12}^m \frac{c_s}{c_m}(1-2x_{1s}) + \beta(e_{1s}-e_{2s})\right] =$$

$$x_{1m}(1-x_{1m})^{-1}\exp\left[X_{12}^m(1-2x_{1m}) + \beta(w_{11}-w_{22})/2\right] \qquad \text{(IV-6)}$$

In many applications of interest $\beta(e_{1s}-e_{2s}) << 0$, $\exp[-\beta(e_{1s}-e_{2s})] >> 1$ and $x_{2s} << x_{1s} \simeq 1$ and to an excellent approximation $x_{1s} \simeq u/(1+u)$ and $x_{2s} \simeq (1+u)^{-1}$ where with $x_{1m} \equiv \phi$ and $X_{12} \equiv X_{12}^m$

$$u \equiv u(\phi) = \phi(1-\phi)^{-1}\exp[X_{12}(1-2\phi+c_s/c_m)-\beta(e_{1s}-e_{2s})+\beta(w_{11}-w_{22})/2] \quad \text{(IV-7)}$$

In this approximation eq. (IV-5) can be expressed directly as a function of the mobile phase composition of the better solvent, $\phi$,

$$M^{-\gamma}\ell nk' =$$
$$\ell n[u(1+u)^{-1}\exp\{\beta\Delta E(1)+[\frac{c_s}{c_m}(1+u)^{-1}-1+\phi][X_{12}+X_{13}-X_{23}]\}$$
$$+(1+u)^{-1}\exp\{\beta\Delta E(2)+[\frac{c_s}{c_m}u(1+u)^{-1}-\phi][X_{12}+X_{23}-X_{13}]\}]$$
$$-M^{-\gamma/2}2g_s^{1/2}+1/2M^{-4/5}g_m^{2/5}+M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}M^{\gamma/2}g_s^{1/2}]$$

(IV-8)

where $g_s = 1/2 - (c_s/c_m)[u(1+u)^{-1}X_{13}+(1+u)^{-1}X_{23}-u(1+u)^{-2}X_{12}]$ and we have deleted the 'm' superscript from the $[X_{ij}]$ (i,j,= 1-3).

The last three terms on the RHS of both eq. (IV-5) and (IV-8) depend on M and they vanish as $M \to \infty$. The retention behavior for sufficiently large M solutes depends on whether $M^{-\gamma}\ell nk'$ is positive (high retention) or negative (low retention). A transition from high to low retention is anticipated to occur abruptly for sufficiently large M solutes as $\phi$ is systematically increased. If, for example, when $\phi = \phi_c < 1$, $\ell nk' = 0$, a transition from high to low retention occurs whenever the mobile phase composition changes from $\phi_c(1-\Delta)$ to $\phi_c(1+\Delta)$ where $\Delta \equiv \Delta(M)$ is a small positive number which becomes smaller as M increases. Also, $\phi_c$ depends on M since $M^{-\gamma}\ell nk'$ depends on M and this suggests that fractionation of homopolymers by molecular weight should be viable by gradient elution HPLC [1] and in some systems even isocratic elution [15-17].

In the immediate vicinity of $\phi_c$, where $F(\phi_c) \equiv M^{-\gamma}\ell nk'(\phi_c) = 0$, the capacity factor can be expressed as

$$k' = \exp[M^{\gamma}\sum_{j=1}^{\infty} D_j(\phi-\phi_c)^j]$$

(IV-9)

where $D_j \equiv (j!)^{-1}\partial^j F(\phi_c)/\partial\phi_c^j$. If $|D_j(\phi-\phi_c)^j| << |D_1(\phi-\phi_c)|$ for all $j \geq 2$, then a linear approximation $M^{-\gamma}\ell nk' = D_1(\phi-\phi_c)$ is sufficiently accurate. In general, determining $F(\phi_c)=0$ requires numerical methods as does the evaluation of $D_1$ and if necessary the remaining coefficients $D_j$ for $j \geq 2$. When the stationary phase exhibits a decided preference for the better solvent than $x_{1s} \simeq 1$ which corresponds to $u >> 1$ (strictly $u \to \infty$ as $x_{1s} \to 1$) and (IV-8) reduces to:

$$\overline{F} \equiv M^{-\gamma}\ell n\overline{k}' = \beta\Delta E(1) - (1-\phi)[X_{12}+X_{13}-X_{23}] - M^{-\gamma/2}\, 2\overline{g}_s^{\,1/2}$$
$$+ \tfrac{1}{2}M^{-4/5}g_m^{\,2/5} + M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}M^{\gamma/2}\overline{g}_s^{\,1/2}] \qquad \text{(IV-10)}$$

where $\overline{F}, \ell n\overline{k}'$ and $\overline{g}_s$ indicates that the $x_{1s} \to 1$ or $u \to \infty$ limit has been taken. The mobile phase composition, $\phi_c$, which renders $F(\phi_c)=0$ satisfies

$$\phi_c = \phi_c^{\infty} + (X_{23}-X_{12}-X_{13})^{-1}[-2\overline{g}_s^{\,1/2}M^{-\gamma/2} + \tfrac{1}{2}g_m^{\,2/5}M^{-4/5}$$
$$+ M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}M^{\gamma/2}\overline{g}_s^{\,1/2}]] \qquad \text{(IV-11)}$$

where

$$\phi_c^{\infty} = 1 + (X_{23}-X_{12}-X_{13})^{-1}\beta\Delta E(1) \qquad \text{(IV-12)}$$

A physically meaningful result requires that $-1 \leq (X_{23}-X_{12}-X_{13})^{-1}\beta\Delta E(1) \leq 0$ for $0 \leq \phi_c^{\infty} \leq 1$. Also

$$\overline{D}_1 \equiv \frac{\partial \overline{F}}{\partial \phi_c} = X_{12} + X_{13} - X_{23} + \frac{1}{5}g_m^{-3/5}M^{-4/5}\frac{\partial g_m}{\partial \phi_c} \qquad \text{(IV-13)}$$

$$\overline{D}_j = \frac{1}{j!}\frac{\partial^j \overline{F}}{\partial \phi_c^j} = (j!)^{-1}\left[\frac{1}{2}M^{-4/5}\right]\frac{\partial^j g_m^{2/5}}{\partial \phi_c^j} \quad j \geq 2 \qquad \text{(IV-14)}$$

As $M \to \infty$ $\overline{D}_1 \to X_{12} + X_{13} - X_{23}$ and $\overline{D}_j \to 0$ for all $j \geq 2$. Furthermore, as $M \to \infty$ eq. (IV-10) can be expressed as

$$\overline{F} = M^{-\gamma}\ell n\,\overline{k}' = (X_{23}-X_{12}-X_{13})(\phi_c^{\infty}-\phi) \qquad \text{(IV-15)}$$

When M is large but finite it still remains an excellent approximation to use

$$\overline{F} = M^{-\gamma}\ell n\,\overline{k}' \simeq |\overline{D}_1|(\phi_c-\phi) \qquad \text{(IV-16)}$$

where $\phi_c \equiv \phi_c(M)$ and $\overline{D}_1$ are given by eqs. (IV-11) and (IV-13), respectively. If $X_{23}-X_{13}-X_{12} > 0$, $\phi_c$ is a monotonically increasing function of M which asymptotically approaches $\phi_c^\infty$ as $M \to \infty$. Provided $0 < \phi_c \leq \phi_c^\infty \leq 1$ a transition from high to low solute retention is predicted to occur over a mobile phase composition interval centered about $\phi_c$ which becomes narrower as M increases.

Inspection of eq. (IV-11) reveals that the dependence of $\phi_c$ on M enamates from contributions of the form $-|\bar{a}|M^{-\gamma/2}+\bar{b}M^{-4/5}+\bar{c}M^{-\gamma}\ell nM$ which depend sensitively upon the value of the exponent $\gamma$ $(0<\gamma<1)$. Comparison can be made with eq. (II-2) for the strong adsorption case. Also from the linear approximation for $\ell n\,\bar{k}'$ given by eq. (IV-16) we obtain

$$S = -\partial n\,\bar{k}'/\partial\phi_c = |\bar{D}_1|M^{\gamma}$$

$$\text{or} \qquad \ell nS=\gamma\ell nM+\ell n|D_1| \qquad \text{(IV-17)}$$

This result predicts that measurements of S as a function of M plotted as $\ell n$ S vs. $\ell n$ M should be linear with slope given by the exponent $\gamma$ $(0<\gamma<1)$. Thus the predicted slope of a $\ell n$ S-$\ell n$ M plot becomes smaller when weak adsorption prevails since for strong adsorption $\partial\ell nS/\partial\ell nM \to 1$ when M is large. If $\gamma = 1/2$, which corresponds to an 'ideal' adsorbed chain $\partial\ell nS/\partial\ell nM = 1/2$ for sufficiently large M and $\phi_c=\phi_c^\infty + (X_{23}-X_{13}-X_{12})^{-1}\,[-2\bar{g}_s^{1/2}M^{-1/4}+\tfrac{1}{2}g_m^{2/5}M^{-4/5}+M^{-1/2}\ell n[\Phi M^{1/4}\bar{g}_s^{1/2}(1-M^{-1/2})^{3/10}]]$.

An explicit expression for the retention time, $t_R$, as a function of M for linear gradient elution where $\phi \equiv \phi(t)$ is temporally increased in linear fashion, $\phi(t) = \phi(0)+Bt$, can be obtained readily when $k'=|D_1|M^{-\gamma}(\phi_c-\phi)$ and is

$$t_R = t_o+(|D_1|M^{\gamma}B)^{-1}\ell n[1+|D_1|M^{\gamma}Bt_o\exp[|D_1|M^{\gamma}(\phi_c-\phi(0))]] \qquad \text{(IV-18)}$$

Here $t_o$ is the time required for unretained solute to pass through the column, $\phi(0)$ is the mobile phase composition at the start of the gradient and B is the time rate of change of the composition gradient. Whenever $|D_1|M^{\gamma}Bt_o\exp[|D_1|M^{\gamma}(\phi_c-\phi(0))] >> 1$ eq. (IV-18) reduces to

$$t_R = t_o+B^{-1}(\phi_c-\phi(0))+(|D_1|M^{\gamma}B)^{-1}\ell n(|D_1|M^{\gamma}Bt_o) \qquad \text{(IV-18*)}$$

Clearly for large M and $\phi(0)<\phi_c$, $t_R \simeq t_o+B^{-1}(\phi_c-\phi(0))=t_o+t_c$ where $t_c$ is the time required for the mobile phase composition at the inlet to develop to $\phi_c$ when a linear gradient is sustained. Also, utilization of eq. (IV-18*) allows one to express asymptotically for large M that $\ln t_R \simeq \ell n\, t_R^{\infty} - \text{const.}M^{-\gamma/2}$ where $t_R^{\infty} \equiv t_o + B^{-1}(\phi_c - \phi(0))$.

Equations (IV-18) or (IV-18*) provide a relationship between $t_R$ and M and predict that a very dilute homopolymer mixture can be separated into molecular weight fractions by linear gradient elution HPLC when $\phi(0)$ is less than the critical composition of the lowest M homopolymer present. The order of elution then proceeds successively from the lowest to the highest molecular weight constituent since $\phi_c(M)-\phi(0)$ monotonically increases with M.

If the adsorbed train of $M^{\gamma}$ contiguous segments behaves as a 'rigid' moiety whose dimensions are unaltered by solvent uptake, then eq. (IV-3) for k′ is modified by replacing the factor(s)

$$N_s^* P(N_s^*)\,(1-M^{\gamma}/N_s^*)^{(M^{\gamma}-N_s^*)}\exp((1/2-g_s)M^2/N_s^*)$$

by unity and $k_R'$ becomes

$$k_R' = \Phi\left(\frac{C_s-1}{C_m-1}\right)^{M_{\gamma}} \frac{N_m^* P_m(N_m^*)}{N_m P_m(N_m)} \frac{(1-(M-M^{\gamma})/N_m^*)^{(M-M^{\gamma}-N_m^*)}}{(1-M/N_m)^{(M-N_m)}}$$

$$\times \exp[-(½-g_m)[\frac{M^2}{N_m} - \frac{(M-M^{\gamma})^2}{N_m^*})]\,(\sum_{i=1}^{2} f_i)^{M^{\gamma}}$$

(IV-19)

where $f_i$ is again given by eq. (IV-2) and the 'R' subscript on k′ indicates the rigidity of the adsorbed train. Employing the same approximations for $N_m$, $N_m^*$, $P_m(N_m)$ and $P_m(N_m^*)$ as in eq. (IV-5) for eq. (IV-19) gives after some manipulations which assume $M^{\gamma-1} << 1$:

$$M^{-\gamma}\ell n k_R' = \ell n(\sum_{i=1}^{2} x_{is}\exp[\beta\Delta E(i) - 1 + (\frac{C_s}{C_m}x_{js} - x_{jm})(X_{i3}+X_{12}-X_{j3})])$$

$$+ ½ g_m^{2/5} M^{-4/5} + M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}]$$

(IV-20)

where again $\beta\Delta E(i)=\beta(\epsilon_{is}-e_{3s}+w_{i3}-w_{ii})+\ell n[(c_s-1)/(c_m-1)]$ $i=1,2$ and eq. (IV-6) must be utilized to obtain the $x_{1s}$-$x_{1m}$ adsorption isotherm.

If $x_{1s}\simeq 1$, $x_{2s}\simeq 0$ and $x_{1m}\rightarrow\phi$, eq. (IV-20) simplifies to

$$\overline{F}_R \equiv M^{-\gamma}\ell n\overline{k}_R' = \ell n[\exp[\beta\Delta E(1)-1-(1-\phi)(X_{13}+X_{12}-X_{23})]] + \tfrac{1}{2}g_m^{2/5}M^{-4/5} + M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}] \tag{IV-21}$$

where the 'bar' above the $k_R'$ again indicates the limit $x_{1s}=1$ has been taken. Also $\overline{k}_R'$ may be expressed as

$$\overline{k}_R' = \exp[M^{\gamma}\sum_{j=1}^{\infty}\overline{D}_j(\phi-\phi_c)^j] \tag{IV-22}$$

where $\overline{D}_j \equiv (1/j)(\partial^j\overline{F}_R/\partial\phi_c^j)$ if $\ell n\overline{k}_R'=0$ when $0 \leq \phi = \phi_c \leq 1$. The critical composition is given by the solution of

$$\phi_c=\phi_c^{\infty}+(X_{23}-X_{13}-X_{12})^{-1}[\tfrac{1}{2}M^{-4/5}g_m^{2/5}(\phi_c)+M^{-\gamma}\ell n[\Phi(1-M^{\gamma-1})^{3/10}]] \tag{IV-23}$$

where

$$\phi_c^{\infty} = 1+(X_{23}-X_{13}-X_{12})^{-1}[\beta\Delta E(1)-1] \tag{IV-24}$$

which differs slightly from eqs. (IV-11) and (IV-12). In linear approximation with respect to $\phi_c$-$\phi$, eq. (IV-21) (or IV-22) reduces to

$$M^{-\gamma}\ell n\overline{k}_R' = (\phi_c-\phi)[X_{23}-X_{13}-X_{12}-(1/5)\,g_m^{-3/5}(\phi_c)\frac{\partial g_m}{\partial\phi_c}M^{-4/5}]+O(\phi_c-\phi)^2 \tag{IV-25}$$

and

$$S_R=-\frac{\partial\ell n\overline{k}_R'}{\partial\phi_c}=M^{\gamma}[X_{23}-X_{13}-X_{12}-(1/5)\,M^{-4/5}g_m^{-3/5}(\phi_c)\frac{dg_m}{d\phi_c}] \tag{IV-26}$$

which establishes that $S_R \propto M^{\gamma}$ for sufficiently large M.

## V. DISCUSSION AND COMPARISON OF THEORY AND EXPERIMENTAL RESULTS

Several sets of experimental measurements which can give the dependence of the slope $S = -\partial \ell nk'/\partial \phi_c$ on M have been performed on polystyrene standards using both isocratic and gradient elution HPLC using a variety of mixed solvent combinations and chemically bonded stationary phases of different pore sizes and hydrocarbon chain lengths.

A summary of the experimentally determined S-M results are recorded in Table I along with the mixed mobile phase solvents and the stationary phases employed. Linear regression was utilized to obtain the best empirical fit of the form $\ell nS = \ell n\alpha + \gamma \ell nM$ or $S = \alpha M^{\gamma}$ to the experimental S-M data, where $\alpha$ and $\gamma$ are optimally selected empirical parameters. Inspection of Table I reveals considerable variation in the experimental S-M results which depend upon the mobile phase mixtures, stationary phases, molecular weight range and number of homopolymer solutes utilized and the method(s) used to obtain the S-M data-isocratic or linear gradient elution or some combination thereof.

Whenever possible or feasible, measurements of $S \equiv -\partial \ell nk'/\partial \phi_c$ derived from isocratic measurements of $\ell nk'$-$\phi$ isotherms for a given homopolymeric solute are more reliable than the corresponding linear gradient elution measurements. If the $\ell nk'$-$\phi$ dependence were strictly linear over the relevant mobile phase composition range centered about $\phi_c$, then the isocratic and gradient elution measurements of S and $\phi_c$ should agree. In general such agreement does not occur although it improves as M increases since the transition from high to low retention occurs over a decreasing mobile phase composition range. Specifically for $\phi \sim \phi_c$ linear $\ell nk'$-$\phi$ behavior is observed irrespective of the value of M. However, as $|\phi - \phi_c|$ increases, departures from linearity develop especially for the lower M solutes. These non-linear contributions to $\ell nk'$ for $\phi < \phi_c$ can generate a compositionally averaged gradient determined slope, $S_G$, which overestimates $S = -\partial \ell nk'/\partial \phi_c$ [16].

TABLE I

| Reference | $S = \alpha M^{\gamma}$ | | Solute Molecular Weight Range (kD) | Mobile Phase Solvents | Bonded Stationary Phase (Pore Size Å) |
|---|---|---|---|---|---|
| | $\gamma$ | $\alpha$ | | | |
| 11, 18[a] | 0.50 | 2.25 | 2-233 | $THF/H_2O$ | C-18 (150 Å) |
| 15[b] | 0.654 | 0.472 | 4-300 | $MeCl_2/ACN$ | C-8 (300 Å) |
| 15[b] | 0.669 | 1.03 | 17.5-35 | $THF/H_2O$ | C-8 (300 Å) |
| 16[a] | 0.472 | 3.41 | 2-390 | $MeCl_2/MeOH$ | C-18 (100 Å) |
| 16[a] | 0.517 | 2.03 | 2-390 | $MeCl_2/MeOH$ | C-18 (300 Å) |
| 16[b] | 0.730 | 0.452 | 2-100 | $MeCl_2/MeOH$ | C-18 (100 Å) |
| 16[b] | 0.586 | 0.668 | 2-100 | $MeCl_2/MeOH$ | C-18 (300 Å) |
| 16[c] | 0.732 | 0.446 | 2-390 | $MeCl_2/MeOH$ | C-18 (100 Å) |
| 16[c] | 0.735 | 0.334 | 2-390 | $MeCl_2/MeOH$ | C-18 (300 Å) |
| 16[c] | 0.770 | 0.343 | 17.5-390 | $MeCl_2/MeOH$ | C-18 (100 Å) |
| 16[c] | 0.877 | 0.124 | 17.5-390 | $MeCl_2/MeOH$ | C-18 (300 Å) |
| 16[c] | 0.768 | 0.345 | 50-390 | $MeCl_2/MeOH$ | C-18 (100 Å) |
| 16[c] | 0.994 | 0.0515 | 50-390 | $MeCl_2/MeOH$ | C-18 (300 Å) |
| 17[b] | 0.55 | 0.0054 | 4-390 | THF/ACN | C-4[d] |
| 17[b] | 0.35 | 0.201 | 30.7-390 | $MeCl_2/MeOH$ | C-4[d] |

[a] Gradient elution measurements

[b] Isocratic measurements

[c] Isocratic measurements for 2-100 kD polystyrene samples. Gradient elution measurements for polystyrene samples greater than 100 kD.

[d] Bimodal pore diameter column composed of a 48% 80 Å and 52% 500 Å mixed silica support surface.

The first S-M measurements on a series of polystyrene homopolymers were performed by Snyder and coworkers using $THF/H_2O$ mixed mobile phases and a 150 Å mean pore diameter C-18 chemically bonded phase and linear gradient elution HPLC [11, 18]. They obtained the empirical fit $S_G = 2.25\ M^{.50}$ where the subscript 'G' denotes gradient elution. The best linear regression fits to the $S_G$-M measurements obtained by Alihedai et. al. on polystyrene solutes ranging from 2-390 kD using gradient elution HPLC with $MeCl_2/MeOH$ mixed mobile phases and either a 100 Å or 300 Å mean pore size diameter C-18 stationary are $S_G = 3.41\ M^{.472}$ (c.c. = 0.982) and $S_G = 2.03\ M^{.517}$ (c.c. = 0.977), respectively. These results compare favorably with those of Snyder et. al. although different chromatographic phases were utilized.

Measurement of S for any M taken from isocratic $\ell nk'$-$\phi$ measurements in the vicinity of and including $\phi_c(M)$ are more reliable and Alihedai et. al. [16] obtained the following best linear regression fits for solutes between 2 - 100 kD; $S = 0.452\ M^{.730}$ (c.c. = 0.993) and $S = 0.668\ M^{.586}$ (c.c. = 0.995) for the 100 Å and 300 Å C-18 columns respectively using $MeCl_2$/MeOH mobile phases. For comparison the isocratic measurements of the slopes of $\ell nk'$-$\phi$ isotherms reported by Lochmüller and McGranaghan [15] for five polystyrene solute samples with molecular weights between 4 kD and 300 kD eluted with $MeCl_2$/ACN mobile phases and a C-8 bonded phase of 300 Å mean pore diameter can be fit by linear regression to $S = 0.472\ M^{.654}$ (c.c = 0.994). Also their isocratic measurements of the slopes for three polystyrene solute samples of 4, 17.5 and 35 kD using THF/$H_2O$ mobile phases and a 300 Å C-8 bonded phase can be represented by $S = 1.03\ M^{.669}$ (c.c. = 0.993).

When the isocratic measurements performed by Alidhedai e. al. in $MeCl_2$/MeOH mobile phases for 2-100 kD polystyrene standards are supplemented by gradient elution determined $S_G$ for 233 kD and 390 kD polystyrene solute standards, then $S = .446\ M^{.732}$ (c.c. = 0.994) for the 100 Å C-18 column and $S = .334\ M^{.735}$ (c.c. = 0.980) for the 300 Å C-18 column. Also recorded in Table I are the linear best fits of the isocratic S-M data reported in [16] for smaller sets of solute standards which include the highest molecular weights studied. The exponent $\gamma$ in the best fit of the form $S = \alpha M^{\gamma}$ tends to increase towards unity for the 300 Å C-18 column when the set of polystyrene standards is limited to molecular weights between 50 kD and 390 kD. This perhaps suggests that strong adsorption may be the dominant mode of retention for these higher M solutes.

Utilization of $MeCl_2$/MeOH mobile phases with a C-18 column tends to generate $\ell nk'$-$\phi$ isotherms which change rather abruptly from high to low retention over a narrow composition range about $\phi_c(M)$ even for the lower M polystyrenes. As a result, isocratic measurements of the $\ell nk'$-$\phi$ isotherms in the vicinity of $\phi_c(M)$ become extremely difficult and uncertain for $M > 10^3$ (i.e., mol. wt. > 100 kD) polystyrenes. Northrup et. al. [17] observed, however, that by selecting THF/ACN mobile phases and a bimodal pore size C-4 stationary phase [20], isocratic measurements of $\ell nk'$-$\phi$ isotherms for five polystyrene standards with 4 kD $\leq$ mol. wt. $\leq$ 390 kD were possible. These isocratic measurements lead to the linear regression best fit $S = .0054\ M^{.55}$ (c.c. = .997). Northrup et. al. [17] also utilized $MeCl_2$/MeOH mobile phases along with the same C-4 bimodal stationary phase to obtain $\ell nk'$-$\phi$ isotherms isocratically for the same five polystyrene standards. Their corresponding best linear regression fit is $S = .201\ M^{.35}$ (c.c. = .973) for the four highest molecular weights (30, 50, 100 and 390 kD). These results are obtained from lower capacity columns and none of the isocratic $\ell nk'$-$\phi$ measurements involved the region where $\ell nk' \geq 0$ and thus did not include compositions where $\phi \leq \phi_c(M)$. Hence the relevant $\phi$ range for determination of $S \equiv -\partial \ell nk'/\partial \phi_c$ was not probed directly by the measurements and only values of S extrapolated to the relevant composition, $\phi_c(M)$, from higher compositions $\phi > \phi_c(M)$ for each solute were obtained.

The experimentally determined S-M behaviors exhibit considerable variation and clearly depend on the chromatographic conditions and the range of M values probed. The values of the exponent $\gamma$ in the relationship $S \sim M^\gamma$ were obtained from linear regression fits to the various experimental measurements and have been found to range between $0.35 \leq \gamma < 1$ with most of the results confined to the range $0.5 < \gamma < 0.75$. These results suggest that the polymeric solutes are generally weakly adsorbed and/or sorbed in the stationary phase with a considerable portion of the solute penetrating into the mobile phase environment over the composition range of chromatographic significance where $0 < k' \leq 10$. The experimental results for $\gamma$ agree reasonably well with the theoretical estimates $\gamma = ½$ for an ideal adsorbed chain and $\gamma = 0.582$ [21] for the Monte-Carlo generated adsorbed chains with excluded volume interactions included. The modified BMAB theory introduced in the previous section predicts that S ~ $M^\gamma$ where $M^\gamma$ corresponds to the number (to the nearest integer) of polymer segments sorbed contiguously as a single train sequence onto the idealized stationary phase monolayer. The case $\gamma = 1$ corresponds to the strong adsorption limit treated in the original BMAB analysis.

A more realistic model of the adsorption surface which explicitly incorporates the pore structure and the bonded alkyl chains would clearly be a desirable improvement of the BMAB theory. It is anticipated that configurations where trains of adsorbed segments reside in neighboring pores connected by a loop or bridge sequence of segments protruding into the mobile phase might contribute significantly to the retention in real systems, especially for large M solutes and small diameter pores. Despite its shortcomings, however, the present model does suggest that consideration of weak adsorbed and/or sorbed states can rationalize the numerous experimental observations from many chromatographic systems that S ~ $M^\gamma$ where $\gamma < 1$ rather than the strong adsorption prediction that S ~ M for sufficiently large M.

Since the $\phi_c$ - M dependence is predicted to depend on the exponent $\gamma$, this dependence also correlates with the extent of sorption of the polymeric solute in the stationary phase especially for the lower M solutes. The $\phi_c$ - M dependence on $\gamma$ is sensitive to whether the adsorbed train sequence is solvent swollen or is better characterized as a rigid chain skeleton which is more likely for smaller M.

For chromatographic conditions where $k' >> 1$ homopolymer retention is anticipated to be determined by strong adsorption. However, under chromatographic conditions where $0 < k' < 1$ weaker adsorption modes are more likely to dominate. The transition from strong to weak adsorption behavior for large M homopolymers may be abrupt or rather gradual functions of $\phi$ depending upon the chromatographic system involved. An abrupt transition for a fixed M solute is more likely to occur if the mobile phase consists of a mixture of a good and relatively poor solvent for the polymeric solute, and there exists a strong preference for sorption of the better solvent and a preference for the solute in the stationary phase. Mixed mobile phases of $MeCl_2$/MeOH and THF/$H_2O$ and well end-capped C-18 chemically bonded stationary phases tend to exhibit increasingly abrupt transitions from high to low retention as M increases which suggests strong polymer adsorption for $\phi < \phi_c(M)$ and weaker adsorption for $\phi > \phi_c(M)$. If, however, the mobile phase solvents have similar affinities for the polymeric solute and the stationary phase exhibits only slight preference for the better solvent and has lower capacity for the solute, then low retention $0 < k' < 1$ may prevail over a considerable range of $\phi$ and weak adsorption of the polymeric solute is anticipated. The THF/ACN mixed mobile phase and C-4 stationary phase utilized by Northrup et. al. [17] represents a chromatographic system where weak polymer sorption behavior is likely to dominate. Indeed isocratic $\ell nk'$-$\phi$ measurements have been performed directly for polystyrene standards up to 390 kD with this system.

Finally it should be mentioned that explicit *a priori* determination of the actual mobile and stationary phase conditions which lead to weak homopolymer adsorption is beyond the scope of the present investigation.

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