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ADSORPTION EFFECTS IN THE CHROMATOGRAPHY OF POLYMERS

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SUMMARY

An equilibrium theory of polymer chromatography has been developed by using the model of a gaussian chain in a slit-like pore at arbitrary energies of interaction between the chain unit and the adsorbent and at any ratio of the chain size, R , to the pore width, D . It is shown that five specific regions exist in the chromatographic behaviour of macromolecules, corresponding to different R and D values and different adsorption energies. Analytical expressions for the distribution coefficient, K , have been obtained for each region. The experimental dependences of K on R are discussed.

INTRODUCTION

Most work on the separation and analysis of polymers has involved the use of either gel permeation chromatography (GPC) or adsorption chromatography. These two methods differ in the order of elution of components according to their molecular weights. In the former the separation of macromolecules occurs according to their sizes and the distribution coefficient, K , is less than unity, whereas in the latter $K > 1$ and increases rapidly with molecular weight. Hence, adsorption chromatography can be efficient only for oligomers.

The theory of GPC has been developed in refs. 1 and 2. It is based on the calculation of the free energy change, ΔF , which occurs when the polymer chain enters the adsorbent pores (stationary phase of volume V_p) from the solution (mobile phase) of volume V_0 .

However, it has been demonstrated both experimentally³⁻⁶ and theoretically^{4,7,8} that, except in the case of GPC, a wide range of conditions exists in the chromatography of polymers (as a rule, in mixed solvents) in which weak attractive forces occur between the chain units and the pore surface. In this case $K < 1$, and the elution order is the same as in GPC. When certain "critical" conditions are attained independent both of the pore width and the length of the macromolecules, the distribution coefficient becomes $K = 1$ and all the macromolecules are eluted at the same retention volume, $V_c = V_0 + V_p$. Further change in the conditions (temperature or composition of the binary solvent) leads to inversion of the elution order of the components and to a transition to adsorption chromatography with $K > 1$.

The present paper reports a general theory of chromatography of flexible linear macromolecules which takes account of the existence of adsorption interactions.

In the subsequent discussion the term GPC will be employed as usual for those cases when the pore walls may be considered to be impermeable surfaces. The conditions of weak attraction of units to the pore surface under which the distribution coefficient remains less than unity will be called the "pre-critical region". We also distinguish the "close-to-critical" region in which the value of K is close to unity. In this region the order of component elution according to molecular weight may be different: at $K \lesssim 1$ this order will be the same as in the pre-critical region (as in GPC), whereas at $K \gtrsim 1$ it will change to that obtained in adsorption chromatography. However, as will be shown later, the general types of the dependences of K on the radius, R , and the pore width, D , over the entire "close-to-critical" region are identical. Finally, the conditions under which K is considerably greater than unity will be called the "region of strong adsorption".

THEORETICAL

As in GPC theory^{1,2}, the model of the macromolecule is a gaussian chain consisting of N segments each of length b and mean radius $R = (Nb^2/6)^{1/2}$.

The adsorbent model is a slit-like pore of width $D = 2d$. Let us introduce the probability, $P_N(r)$, for that the end-to-end distance of the gaussian chain is r . In an unlimited (free) volume the probability P_N is given by

$$P_N(r) = (2\sqrt{\pi R})^{-3} \cdot \exp\left[-\left(\frac{r}{2R}\right)^2\right] \quad (1)$$

and obeys the diffusion equation:

$$\nabla^2 P_N - \frac{6}{b^2} \cdot \frac{\partial P_N}{\partial N} = 0 \quad (2)$$

For a chain limited by impermeable walls, the boundary conditions of the walls are added to eqn. 2:

$$P_N|_s = 0 \quad (3)$$

In the case of a chain in a slit-like pore, eqn. 1 remains valid for the coordinates x and y parallel to the slit walls and may easily be integrated. The function $P_N(z)$ for the coordinate z perpendicular to the pore walls is obtained by solving eqns. 2 and 3 and is known from the theory of heat conduction⁹. In refs. 1, 2 this solution was substituted into the expression for the distribution coefficient

$$K = D^{-1} \int_0^D P_N(z) dz \quad (4)$$

to give:

$$K \approx \begin{cases} 1 - \frac{2}{\sqrt{\pi}} \cdot \frac{R}{d} & \text{at } R \ll d \\ \frac{8}{\pi^2} \cdot \exp \left[- \left(\frac{\pi R}{2d} \right)^2 \right] & \text{at } R \gg d \end{cases} \quad (5)$$

Now the short-range adsorption potential near the pore walls will be introduced. As has already been shown¹⁰, the existence of this potential is equivalent to the application of boundary conditions:

$$P_N^{-1} \left. \frac{\partial P_N}{\partial z} \right|_s = H^{-1} \quad (6)$$

The physical meaning of the correlation length, H , has been discussed^{10,11}. In the adsorption region, the value of H is positive and proportional to the average thickness of the layer formed by a long macromolecule on the surface of a planar adsorbent or on the pore walls. The GPC conditions correspond to $(-H) \rightarrow 0$. In this case eqn. 6 is transformed into eqn. 3.

When $H^{-1} \rightarrow 0$, the boundary conditions are obtained from eqn. 6:

$$\left. \frac{\partial P_N}{\partial z} \right|_s = 0 \quad (7)$$

Eqn. 7 is used in the theory of the behaviour of macromolecules under the critical conditions¹⁰⁻¹³. In experimental work the value of H may be changed, for example, by varying the eluent composition or the temperature.

Boundary conditions (eqn. 6) have been employed in refs. 12, 13 to describe the adsorption of gaussian chains on the plane, and in ref. 11 to develop the theory of chromatography. The results of those studies agree with those obtained in refs. 14-16 in which a lattice model of the chain was used and the interaction between the chain units and the pore walls was established directly by introducing the short-range potential, ε . A comparison of refs. 11-13 and refs. 14-16 has made it possible to obtain the relationship between H and ε over the entire range of $-\varepsilon < -\varepsilon_c$ ¹¹. Near the critical conditions, in accordance with ref. 10, we obtain

$$H \approx b (\varepsilon_c - \varepsilon)^{-1} \quad (8)$$

where $-\varepsilon_c$ is the critical energy at which the entropy losses of the chain and the energy gain due to adsorption of units on the adsorbent surface are exactly compensated.

The general solution of eqns. 2 and 6 has been obtained in the theory of heat conduction⁹. The substitution of this solution into eqn. 4 gives

$$K(\lambda, g) = \sum_{i=1}^{\infty} \frac{2\lambda^2 \cdot \exp[-(g\alpha_i)^2]}{\alpha_i^2 [\lambda(\lambda + 1) + \alpha_i^2]} \quad (9)$$

where $g = R/d$, $\lambda = -d/H$ and the eigenvalues α_i are the roots of the characteristic equation:

$$\alpha \cdot \operatorname{tg} \alpha = \lambda \quad (10)$$

Distribution coefficient and diagram of regions

Fig. 1 shows the dependence of the distribution coefficient K on the ratio of the chain size to the slit size, R/d , calculated from eqns. 9 and 10 at different values of the parameter $\lambda^{-1} = -H/d$.

The asymptotic formulae for K at $-\lambda \gg 1$ (in the adsorption region), at $\lambda \approx 0$ (in the close-to-critical region) and at $\lambda \gg 1$ (in the pre-critical region) have been obtained previously¹¹. Expressions for the density profile of units inside the pores and for the fraction of units adsorbed were also reported¹¹. These results make it possible to describe the chromatographic behaviour of polymers of different molecular weights (chain size R) in adsorbents with wide ($d > R$) and narrow ($d < R$) pores and at different polymer-adsorbent interaction energies (parameter H). It is convenient to discuss this behaviour using a diagram with five specific regions (Fig. 2): strong adsorption (A), the close-to-critical regions for wide pore (CW) and narrow pore (CN) adsorbents and the pre-critical (GPC-like) regions for narrow and wide pores (PN and PW).

Let us consider the manifestation of these regions in the dependence of K on R (Fig. 1). We begin with the adsorption region (small H values), curve 6. This curve is described by:

$$K \approx 2 \frac{H}{d} \cdot \exp \left[\left(\frac{R}{H} \right)^2 \right] \quad (11)$$

As already indicated, the parameter H in the region of strong adsorption represents the effective thickness of adsorption layers formed on the pore walls. In wide pores

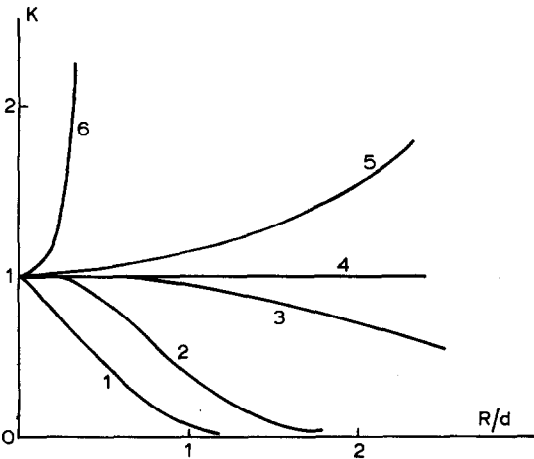


Fig. 1. Distribution coefficient, K , of a flexible gaussian chain vs. the ratio of the chain radius, R , to the pore half-width, d , at various values of the adsorption interaction parameter, $H/d = 50(1)$, $3(2)$, $0.1(3)$, $0(4)$, $-0.1(5)$ and $-3(6)$.

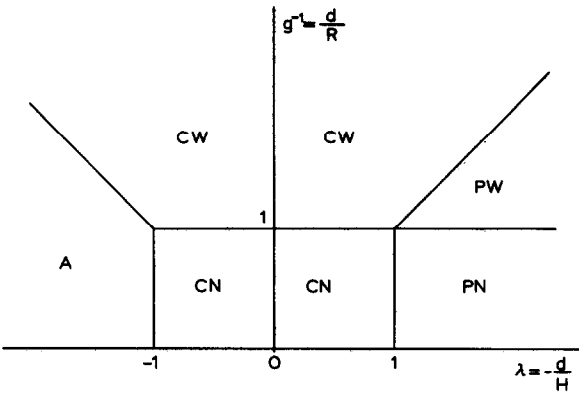


Fig. 2. Diagram of the behaviour of a flexible gaussian chain in a slit-like pore. The regions of adsorption (A), the "close-to-critical" region for the narrow (CN) and wide (CW) pores and the pre-critical regions in narrow (PN) and wide (PW) pores are shown.

these layers are formed by different macromolecules. In narrow pores, in principle, a single chain can pass from one wall to another forming a "bridge" between them. However, the probability of such bridge formation decreases rapidly with increasing d and with increasing attractive forces between the chain units and pore walls (with decreasing H). Eqn. 11 shows that the chromatographic method permits the experimental determination of the thickness of these layers. The region of strong adsorption is defined by the inequalities $H < d$ in narrow pores or $H < R$ in wide pores (Fig. 2).

When the attraction of units to the pore walls becomes weaker, the thickness of the adsorption layers increases, so that in narrow pores the two distinctly separate layers will begin to merge. This effect corresponds to the transition to the close-to-critical region (CN), where:

$$K \approx \left[1 + \frac{1}{45} \left(\frac{d}{H} \right)^2 \right]^{-1} \cdot \exp \left(\frac{R^2}{dH} + \frac{R^2}{3H^2} \right) \quad (12)$$

In wide pores the transition to the close-to-critical region occurs at $H \gtrsim R$, and the distribution coefficient in the CW region takes the form:

$$K \approx 1 + \frac{R^2}{dH} + \frac{2}{3\sqrt{\pi}} \cdot \frac{R^2}{dH^2} \quad (13)$$

The close-to-critical region contains the critical conditions $H^{-1} = 0$ for which $K = 1$ (line 4 in Fig. 1).

The negative values of H correspond to attractive forces weaker than the critical level. In this case, $K < 1$, but the dependences 12 and 13 retain their form until the conditions $|H| > d$ in narrow pores or $|H| > R$ in wide pores pertain (cf., curves 3 and 5 in Fig. 1).

If the attraction of units to the pore walls decreases ($|H|$ decreases), passage into the GPC-like, pre-critical region occurs (curve 2 in Fig. 1). In wide pores (PW) the distribution coefficient is given by:

$$K \approx 1 - d^{-1} \left(\frac{2}{\sqrt{\pi}} R - |H| \right) \quad (14)$$

This equation may be considered as the effective decrease in the chain size by the value $|H|$ (*cf.*, eqn. 5).

On the other hand, in narrow pores (region PN) weak attraction of units to the walls is reflected in the distribution coefficient as an effective increase in the pore width by the value $|H|$:

$$K \approx \exp \left\{ - \left[\frac{\pi R}{2(d + |H|)} \right]^2 \right\} \quad (15)$$

If we move from the top to the bottom in the diagram (Fig. 2), we pass through the regions CW \rightarrow PW \rightarrow PN. Accordingly, curve 2 in Fig. 1 exhibits three parts: quadratic dependence, eqn. 13, linear dependence, eqn. 14 and exponential dependence, eqn. 15. The parameter $|H|$ for the system under investigation can be determined from the linear dependence.

Finally, curve 1 in Fig. 1 corresponds to the GPC case and is described by the well known dependences 5. The transition from one type of dependence to another corresponds to movement from the top to the bottom in the diagram through the regions PW \rightarrow PN at $\lambda \gg 1$. The condition $R \approx d$ serves as a boundary between the different types of dependences in GPC.

DISCUSSION

For all chromatographic regions, the experimental dependences of the distribution coefficient, K , on the size of the molecules, R , have been obtained^{3,4} by varying the composition of the binary solvent and the temperature. The deviation from the GPC relationships (eqn. 5) due to weak attraction of the chain units to the adsorbent surface (pre-critical conditions) has been observed^{5,6}.

When discussing the influence of these effects on the distribution coefficient K , Dawkins and Hemming¹⁷ suggested that K may be represented as the product

$$K = K_e K_a \quad (16)$$

where K_e is the distribution coefficient of the macromolecule in the case of GPC and K_a is independent of R and d and is determined only by the energy of interaction between the unit and the adsorbent. On the other hand, Bakoš *et al.*⁶ considered that

$$K = K_e + K_a + K_p \quad (17)$$

and it has been suggested that K_a and K_p be used in the expressions borrowed from the liquid-solid adsorption chromatography and liquid-liquid partition chromatography of low-molecular-weight compounds. In both cases the "polymer effect" is

evidently contained only in the K_c value and hence the dependence of K on R/d is given by eqn. 5. However, experimental data⁵ on the chromatography of polystyrenes in binary solvents (methyl ethyl ketone–heptane) contradict these suggestions.

The general trend of the dependence obtained in ref. 5 is analogous to that of curve 2 in Fig. 1 and is described by eqns. 14 and 15.

It would be of interest to carry out precise chromatographic experiments varying the polymer–adsorbent interactions in order to see whether their results confirm the theory discussed above.

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