

THEORY OF GEL PERMEATION CHROMATOGRAPHY.
MECHANISM OF SEPARATION AND THE INFLUENCE OF POLYMER-SORBENT
INTERACTION

J. V. Dawkins

Department of Chemistry, Loughborough University of Technology,
Loughborough, Leicestershire, LE11 3TU, England.

Abstract - The displacement of hydrodynamic volume universal calibration curves to high retention volumes for some polymer-solvent systems in gel permeation chromatography is explained in terms of a network-limited separation consisting of a steric exclusion mechanism and a second mechanism resulting from polymer-sorbent interaction. This treatment is consistent with a thermodynamic interpretation of gel permeation chromatography in which the distribution coefficient (> 1.0) for polymer-sorbent interaction is determined by an enthalpy change for polymer partition or polymer adsorption in the porous packing. Experimental data obtained with crosslinked polystyrene gels and inorganic packings may be represented by the network-limited treatment. Separations in which the distribution coefficient for polymer-sorbent interaction is less than unity correspond to partial exclusion by polymer incompatibility with the sorbent.

INTRODUCTION

Many theoretical models have been proposed for the size separation of polymers with a porous column packing in gel permeation chromatography (GPC). The theories are conveniently classified under two headings - equilibrium models and flow models. Whilst flow mechanisms are important in some experiments, there is abundant evidence indicating that most practical GPC separations are performed close to equilibrium conditions (1,2). The first theories of steric exclusion considered simple geometrical models from which the fraction of pore volume accessible to a solute of given size may be calculated (3). This steric exclusion model is equivalent to the statistical mechanical treatment of the loss in conformational entropy when a macromolecule approaches an inert surface. These thermodynamic theories (1, 4-6) calculate the accessible pore volume in terms of pore size for various models of pore shape and in terms of solute size for both rigid and random coil polymers.

The equilibrium theories predict that the behaviour of all polymers can be represented by a universal size parameter. Experimental GPC results reported by Grubisic, Rempp and Benoit (7) suggested that a plot of log hydrodynamic volume versus retention volume V_R was the same for homopolymers and copolymers separating on crosslinked polystyrene gels with tetrahydrofuran as eluent. Subsequent studies (see the papers cited in reference 8) have confirmed the universal calibration plot of hydrodynamic volume for random coil polymers in eluents such as chloroform, o-dichlorobenzene, and trichlorobenzene, all of which have a solubility parameter δ similar to that of polystyrene. Furthermore, the exponent α in the Mark-Houwink equation is in the range 0.7-0.8 for polystyrene in all four eluents, i.e. the eluent is a good solvent for polystyrene (9). Therefore, the eluent is very compatible with the crosslinked polystyrene gel, and in general solutes do not display preferential affinity for the mobile phase or the stationary phase. Hence, partition (liquid-liquid) and adsorption (liquid-solid) liquid chromatography mechanisms do not influence the steric exclusion separation controlled by solute size.

Although steric exclusion dominates GPC separations, many experiments indicate that the assumption of an inert pore surface is not always valid. For example, early gel filtration experiments with aqueous eluents (3) suggested that some solutes with aromatic groups were retarded on some gels, so that V_R was higher than the value suggested by a steric exclusion mechanism. GPC separations with dimethylformamide (DMF) which is widely used as an eluent for polar synthetic polymers are influenced by polymer-sorbent interaction (10). In particular, the displacement of hydrodynamic volume calibration curves for polystyrene with respect to curves for other polymers in DMF has been observed with separations on crosslinked polystyrene gels (10-14). DMF is a poor solvent for linear polystyrene with α values between 0.60 and 0.64. Consequently, deviations from the universal calibration

plot of hydrodynamic volume for crosslinked polystyrene gels have been observed with organic eluents having α in the range 0.5 - 0.7 and values of δ either less than or greater than that for polystyrene (10-19). In one of the first attempts to show that GPC separations with porous glass were size dependent (20), the plot of log polymer size versus V_R was influenced by eluent polarity. Subsequent studies with inorganic packings have suggested that deviations from the universal calibration plot of hydrodynamic volume are often observed (21).

In this paper, a GPC separation mechanism in which a polymer in an organic eluent separates by the usual dependence of steric exclusion on polymer size and by interaction with the stationary phase is examined. Altgelt and Moore (22) observed that, whilst steric exclusion generally dominates GPC separations, adsorption, partition, and incompatibility mechanisms may result from polymer-sorbent interaction effects. The presence or absence of these secondary mechanisms will be determined by polymer polarity, eluent polarity and polymer-solvent (eluent) interaction.

SEPARATION MECHANISM

Thermodynamic interpretation

The retention behaviour of a polymer in a porous packing is given in terms of the distribution coefficient K_{GPC} by

$$V_R = V_o + K_{GPC} V_i \quad (1)$$

where V_o is the total volume of the mobile phase, i.e. interstitial or void volume, and V_i is the total volume of the stationary phase, i.e. solvent within the porous packing. The simplest situation to treat theoretically is a separation operating at equilibrium. The standard free energy change ΔG° for the transfer of polymer molecules from the mobile phase to the stationary phase at constant temperature T is related to K_{GPC} by

$$\Delta G^\circ = -k T \ln K_{GPC} \quad (2)$$

where k is Boltzmann's constant.

We consider a GPC separation consisting of two component mechanisms. The primary mechanism involves steric exclusion having a free energy change ΔG_D and the second mechanism, if present, will involve polymer-sorbent interaction having a free energy change ΔG_P . The total standard free energy change then is

$$\Delta G^\circ = \Delta G_D + \Delta G_P \quad (3)$$

Therefore, equations (1) - (3) give

$$V_R = V_o + V_i \exp(-\Delta G_D/kT) \exp(-\Delta G_P/kT) \quad (4)$$

Steric exclusion

For an inert pore surface, the value of ΔG_P will be zero. Statistical mechanical treatments of the steric exclusion mechanism at equilibrium calculate the loss in conformational entropy when a polymer molecule transfers from the mobile phase to a pore within the packing (1, 4-6). The distribution coefficient K_D is defined as the ratio of accessible conformations for polymer within the porous packing to those in the mobile phase. It is assumed that the polymer is a random coil in a theta solvent, i.e. there is no change in the free energy of mixing when the solute transfers from one phase to the other, and that there is no polymer interaction with the inert porous packing, so that other enthalpy and entropy contributions are not considered. Consequently, ΔG_D is given by

$$\Delta G_D = -T\Delta S_D = -kT \ln K_D \quad (5)$$

where ΔS_D is the standard entropy change. Therefore, in the steric exclusion mechanism K_D becomes identical with K_{GPC} . For random coil and rigid polymers, the statistical mechanical interpretation of K_D shows that the separation is determined by the mean molecular projection independent of molecular geometry (2,4,6). The treatment of Giddings et al (6) gives

$$K_D = \exp(-s \bar{L}/2) \quad (6)$$

where \bar{L} is the mean external length or molecular projection, e.g. \bar{L} is equal to the diameter of a sphere, and s is the surface area per unit pore volume.

Experimental evidence that polymer size determines GPC separations was provided by Benoit and co-workers working with crosslinked polystyrene gels (7). They showed that all their

polymers fell on a single curve on a semi-logarithmic plot of the product of $[\eta]$ and M versus V_R , where M is the molecular weight of a polymer and $[\eta]$ is the intrinsic viscosity ($100 \text{ cm}^3/\text{g}$) of the same polymer in the GPC eluent. It can be shown that $[\eta]M$ is proportional to the hydrodynamic volume of a polymer and to the size of a polymer with the Einstein and Flory-Fox equations respectively. Equations (5) and (6) suggest that K_D is independent of temperature, a characteristic of a mechanism controlled by entropy changes. Cooper and Bruzzone (23) have obtained an experimental calibration curve for polystyrene and polyisobutene in trichlorobenzene for porous glass columns at 25 and 150°C . Their separations were dependent solely on hydrodynamic size and were independent of polymer structure, polymer-solvent interaction and temperature. Since trichlorobenzene is a good solvent for both polymers, these results support the view that the separation is controlled by entropy changes and suggest that the free energy of mixing contribution is small compared with the conformational entropy change in the steric exclusion mechanism.

Anderson and Stoddart (24) observed that in the middle of the K_D range theoretical plots of K_D versus the logarithm of polymer size are essentially linear. Therefore, following their procedure and assuming that hydrodynamic volume is the universal size parameter determining a steric exclusion separation, we may write

$$K_D = -A \ln [\eta]M + B \quad (7)$$

where A and B are constants.

Network-limited separation

Separations in which V_R is higher than expected from a steric exclusion mechanism result from polymer-sorbent interactions which must be weak and reversible so that the polymer is not completely retained in the stationary phase. For some polymer-solvent-gel systems, K_D is greater than unity (3), which is inconsistent with a steric exclusion mechanism for which K_D must lie between zero and unity. Our observations for poor and theta solvents as eluents (17-19) suggest that the displacement of the hydrodynamic volume curve for polystyrene with respect to a curve for a polymer separating solely by steric exclusion increases as polymer size decreases, i.e. the larger the volume of the total stationary phase volume accessible to a polymer, the greater the deviation of the polystyrene curve. Consequently, the GPC mechanism can be considered as a network-limited separation, as proposed by Heitz and Kern (25,26).

In conventional liquid chromatography of small molecules (27), an important retention parameter is the capacity factor k' defined by the relation

$$k' = K_P V_i/V_o \quad (8)$$

where K_P is the distribution coefficient for solute partition between the stationary and mobile phases, i.e. the ratio of solute concentration in the stationary phase to that in the mobile phase. For polymers, the fraction of V_i available will depend on solute size and equation (8) must be replaced by

$$k' = K_P K_D V_i/V_o \quad (9)$$

The capacity factor is related to the retention volume V_R by

$$V_R = V_o(1 + k') \quad (10)$$

From equations (9) and (10) we obtain

$$V_R = V_o + K_D K_P V_i \quad (11)$$

which may be compared with equation (1). The derivation of equation (11) assumes a network-limited partition mechanism in which solutes have a different solubility in the mobile phase from that in the solvent held within pores. Alternatively, a network-limited adsorption mechanism may occur when the stationary phase is regarded as the surface area within the pores. For a simple pore structure, the total internal pore volume V_i is related to the surface area S by

$$V_i = \gamma \bar{r} S/2 \quad (12)$$

where \bar{r} is the average pore size of the pore size distribution and γ is a numerical factor which depends on the pore geometry and on the definition of mean pore size (28). We shall therefore assume that S is directly proportional to V_i , so that in equation (11) K_P may describe both partition and adsorption mechanisms. An alternative treatment of a network-limited adsorption mechanism is given elsewhere (18).

Comparison of equations (4), (5) and (11) suggests that K_P is given by

$$K_P = \exp(-\Delta G_P/k T) \quad (13)$$

where K_P is the distribution coefficient for polymer-sorbent interaction and will be greater than unity when polymer is retarded in the stationary phase. In a somewhat simpler thermodynamic interpretation of a network-limited GPC separation (29), it was suggested that K_P is determined by an enthalpy contribution, i.e.

$$\Delta H_P = -k T \ln K_P \quad (14)$$

and the entropy change involved in polymer-sorbent interaction was neglected. Thermodynamic treatments of partition (liquid-liquid) and adsorption (liquid-solid) liquid chromatography have related the distribution coefficient to the heat of transfer of the solute from the mobile phase to the stationary phase (30).

Equation (6) may be substituted into equation (11) to give

$$\ln(V_R - V_O)/K_P = \ln V_i - s \bar{L} / 2 \quad (15)$$

which is similar in form to the expression previously defined for a network-limited adsorption mechanism (18)

$$\ln(V_R - V_O)/K_P = \ln(2/\bar{r}) - R/\bar{r} \quad (16)$$

in which R is the hydrodynamic radius of the polymer. Experimental universal calibrations are plots of $\log [\eta]M$ versus V_R . In order to retain this presentation, equation (7) may be substituted into equation (11) to give

$$(V_R - V_O)/K_P = V_i(B - A \ln [\eta]M) \quad (17)$$

A plot of $\log [\eta]M$ versus the left hand side of equation (17) will represent polymers separating by steric exclusion alone ($K_P = 1$), or polymers separating both by steric exclusion and polymer-sorbent interaction effects ($K_P > 1$). If the value of K_P has been evaluated, then the hydrodynamic volume universal calibration method is applicable provided the retention parameter is changed from V_R to $(V_R - V_O)/K_P$.

RESULTS AND DISCUSSION

Partition - adsorption with polystyrene gels

There is considerable experimental evidence for polystyrene-sorbent interaction for polystyrene in eluents which are poor or theta solvents. Ostocka and Hellman (16) reported a progressive displacement of the plot of $\log [\eta]M$ versus V_R to high V_R as the eluent is changed from chloroform ($\alpha = 0.76$), to tetrahydrofuran ($\alpha = 0.72$), to dioxane ($\alpha = 0.69$), and finally to methyl ethyl ketone ($\alpha = 0.60$), i.e. the displacement increases as polymer-solvent interaction decreases. A similar observation was reported on changing from chloroform to DMF (13) and from tetrahydrofuran to DMF (14). Methyl ethyl ketone and DMF ($\alpha = 0.60 - 0.64$) are poor solvents for polystyrene, and in GPC separations with these eluents the plot of \log hydrodynamic volume versus V_R for polystyrene is displaced to high V_R with respect to a plot for another polymer for which these same eluents are good solvents (13,15). Similar results have been reported for polystyrene at 35°C in the theta solvent cyclohexane (15,17,18). Thus, cyclohexane is a good solvent for polyisoprene and poly(dimethyl siloxane) which follow the same plot of $\log [\eta]M$ versus V_R , whereas the plot for polystyrene is displaced to much higher V_R values (17,18). These results have been successfully represented by equations (16) and (17) as shown in Figure 1. Since K_P (polystyrene) = 1.45, it follows from equation (14) that ΔH_P is negative. This exothermic heat change is explained by polystyrene preferring the polystyrene-like gel environment rather than the mobile phase, because in a theta solvent polystyrene is close to its precipitation temperature. Polymer-solvent and sorbent-eluent interactions are not favourable. The polymer-sorbent interactions correspond to those in forming a condensed state and therefore lead to an exothermic heat change, in like manner to the enthalpy change in multilayer adsorption and capillary condensation in gas adsorption on solids.

It follows from equation (14) that K_P should decrease on raising the temperature because ΔH_P is negative. In addition the magnitude of ΔH_P will change as the temperature of the eluent is raised above the theta temperature because of an increase in polymer-solvent interaction which contributes to the overall enthalpy change. As the eluent becomes a good solvent for the polymer, the solution tends towards an athermal mixture, i.e. a zero heat change. Then, the polystyrene molecules will not display preferential affinity for the gel or the eluent, so that the tendency for polymer retention by interacting with the sorbent is reduced considerably. This behaviour has been confirmed in experimental GPC

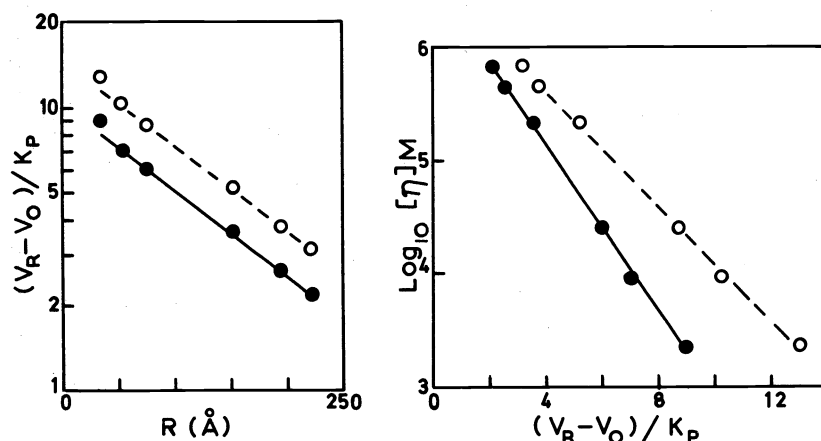


Fig. 1. Plots according to equations (16) and (17) for cyclohexane as eluent at 35°C. O polystyrene ($K_p = 1$); O polystyrene ($K_p = 1.45$); (—) poly(dimethyl siloxane) ($K_p = 1$) and polyisoprene ($K_p = 1$).

separations with poly(dimethyl siloxane) having $K_p = 1$ (steric exclusion) and with polystyrene in trans-decalin which is a good solvent for poly(dimethyl siloxane) ($\alpha = 0.72-0.76$) and a poor solvent for polystyrene at 25°C (19). The displacement of the plot of $\log [\eta]M$ versus V_R for polystyrene is shown to decrease as the temperature is raised (19). The results may be represented by equations (16) and (17), giving the values of K_p shown in Table 1. Kranz, Pohl and Baumann(13) showed that a plot of $\log [\eta]M$ versus V_R for

TABLE 1 Temperature dependence of K_p for polystyrene in trans-decalin

Temperature (°C)	α (Polystyrene)	K_p
25	0.52	1.25
60	0.64	1.2
100	0.67	1.1
138	0.67	1.0

polystyrene in DMF was displaced to high V_R with respect to a plot for polyacrylonitrile ($K_p = 1$). Their results can be represented by equations (16) and (17), giving $K_p = 1.37$ for polystyrene (18). Results with DMF as eluent have suggested that the displacement of curves of $\log [\eta]M$ versus V_R depends on polymer polarity when the eluent is not very compatible with the sorbent(10). Thus, Dubin, Koontz and Wright (10) demonstrated that retardation was in the order polystyrene > poly(methyl acrylate) > poly(vinyl pyrrolidone) > poly(p-nitrostyrene), and they also demonstrated that retardation diminished on raising the temperature for both polystyrene and poly(ethylene oxide) in DMF, which is consistent with a negative enthalpy change for polymer-sorbent interaction.

The interpretation of K_p in terms of an enthalpy change suggests that the presence or absence of polymer-sorbent interactions may be predicted from solubility parameters. The enthalpy change in equation (14) for polymer transfer to the stationary phase can be expressed in terms of δ_1 , δ_2 , and δ_3 for the eluent 1, polymer 2, and crosslinked gel 3 (27). Freeman and Killion (31) have used the expression

$$\ln K_p = \bar{V}_2 [(\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2] / RT + \ln(\bar{V}_3 / \bar{V}_1) \quad (18)$$

where \bar{V} is molar volume and R is the gas constant. They substituted equations (6) and (18) into equation (11) and obtained good agreement between this theoretical equation and experimental GPC data for small molecules. To date, only qualitative predictions have been attempted for polymers. Altgelt and Moore (22) advised that the eluent should have a similar solubility parameter to that for the gel. Adsorption may occur when the solute is more polar than the eluent and partition may occur when the polarity of the eluent is very different from that of the gel and the solute. Several guidelines may be followed in order to minimize polymer-sorbent interaction. When $\delta_2 < \delta_3$, we suggest that K_p will be 1.0 with $\delta_1 > \delta_2$ provided $\delta_1 \approx \delta_3$. This is true for polyethylene separating on polystyrene gel, for which the hydrodynamic volume universal calibration method is well established (8). When $\delta_2 > \delta_3$, we suggest that K_p should be 1.0 with $\delta_1 > \delta_2$. Thus, we found that poly(vinyl pyridine) ($\delta_2 \sim 10.5$) is irreversibly adsorbed on the gel ($\delta_3 = 9.1$) with

chloroform ($\delta_1 = 9.3$) but separates according to steric exclusion ($K_p = 1.0$) with N,N-dimethylacetamide ($\delta_1 = 10.8$) (32). However, polymer-sorbent interaction still occurs with some polar polymers, e.g. DMF ($\delta_1 = 12.1$) (10,14). This emphasises the problems which may arise when it may not be possible to work with GPC eluents which have a solubility parameter similar to that for the gel. When the solute is polystyrene ($\delta_1 = 9.1$) in an eluent such that δ_1 and δ_2 are very different, giving $\alpha < 0.7$, e.g. cyclohexane ($\delta_1 = 8.2$) in Figure 1 and DMF as eluent (10-14), then K_p for polystyrene is greater than unity.

The nature of the mechanism giving rise to $K_p > 1.0$ for polystyrene in poor and theta solvents cannot be defined exactly. The results exhibit characteristics of both partition and adsorption mechanisms. The partition interpretation is substantiated by the observation that retardation is not suppressed by changing the polarity of the eluent, i.e. for cyclohexane ($\delta_1 < \delta_2$) and for DMF ($\delta_1 > \delta_2$). Because the gel surface will be solvated by the eluent and because of the absence of specific adsorption sites, a partition mechanism will arise from the different solubility of polystyrene in the mobile and stationary phases (10,18). On the other hand, the changes in retardation with temperature in Table 1 are not too dissimilar from results reported for the adsorption of some polymers from solution onto non-porous adsorbents (29). These static adsorption experiments in which a polymer solution is mixed with an adsorbent suggest that the extent of adsorption increases as polymer-solvent interaction decreases, provided preferential solvent-adsorbent interactions are absent (33). The representation of GPC data (17-19) over a wide molecular size range by a single value of K_p is consistent with an adsorption mechanism, because studies of polymer adsorption in the absence of size exclusion effects have suggested little or no dependence on molecular weight (33). With highly swollen lightly crosslinked gels, then partition may be the dominant mechanism, as discussed by Lecourtier, Audebert and Quivoron (34).

Adsorption with inorganic packings

Studies of polymer adsorption from solution onto non-porous particles show that the solvent has a considerable influence on the adsorption behaviour (33). First, if the liquid has considerable affinity for the surface, then no polymer is adsorbed. Second, the extent of polymer adsorption increases as polymer-solvent interaction decreases when preferential solvent-adsorbent interactions are absent. The choice of GPC eluent will determine whether irreversible adsorption, i.e. total retention of the polymer in the GPC packing (35), or reversible adsorption, i.e. high V_R , will occur (21). The influence of solvent effects on GPC separations with inorganic packings can be interpreted in terms of the parameters α and δ and in terms of the solvent strength parameter ϵ^0 which represents the interaction energy of an eluent with the packing (36).

Moore and Arrington (20) separated polystyrene by GPC on porous glass with a binary theta solvent mixture of methyl ethyl ketone ($\delta_1 = 9.3$) and isopropanol ($\delta_1 = 11.5$). Polystyrene is apparently not retarded by polymer-sorbent interactions because isopropanol is preferentially adsorbed. On the other hand polystyrene in benzene ($\delta_1 = 9.2$) will separate by steric exclusion and polymer-sorbent interaction because polymer and eluent have similar affinity for the surface sites. Moore and Arrington (20) showed that polystyrene in benzene had a higher V_R than polystyrene in methyl ethyl ketone - isopropanol. The appearance of hydrodynamic volume plots at lower V_R for binary theta solvent mixtures than plots for single good solvents has been confirmed for polystyrene separating on porous silica (37,38). In both these cases, one component in the binary mixture was an alcohol, e.g. methanol or isopropanol, which is more polar than polystyrene. The single solvents, 1,2 dichloroethane ($\delta_1 = 9.8$), benzene ($\delta_1 = 9.2$), chloroform ($\delta_1 = 9.3$) and carbon tetrachloride ($\delta_1 = 8.6$) all have a value of δ_1 similar to that of polystyrene ($\delta_2 = 9.1$), so polystyrene can compete for the surface sites.

Berek and co-workers (38) proposed that their results were dependent on polymer adsorption and on preferential adsorption of one component in the binary mixture. If we assume that no polystyrene adsorption onto the packing occurs with the most polar binary mixture, namely chloroform/methanol ($\epsilon^0 = 0.87$), then the plot of log hydrodynamic volume versus V_R corresponds to a separation solely dependent on steric exclusion ($K_p = 1$). For the single solvents chloroform ($\epsilon^0 = 0.40$) and benzene ($\epsilon^0 = 0.32$), polystyrene is separating both by steric exclusion and adsorption ($K_p > 1$). The data of Berek and co-workers (38) have been plotted according to equation (17), giving the values of K_p in Table 2. Studies of polymer adsorption from solution onto non-porous adsorbents suggest only a slight or no dependence of the amount of polymer adsorbed on molecular weight (33). The values for K_p for a given eluent in Table 2 are in reasonable agreement with this behaviour. This method of determining values of K_p can be criticised on the grounds that polymer-sorbent interaction may still be present even for a polar eluent such as a mixture of chloroform and methanol. It may then be preferable to modify equation (11), as suggested by Campos and Figueruelo (39), to

$$V_R = V_0 + K_D K_P^0 f V_i \quad (19)$$

TABLE 2 Values of K_p for polystyrene separating on porous silica

Eluent	ϵ°	$[\eta]M$	K_p
Chloroform/ Methanol (74.7:25.3, v/v)	0.87	$\left\{ \begin{array}{l} 2.2 \times 10^5 \\ 1.0 \times 10^5 \\ 0.4 \times 10^5 \end{array} \right.$	$\left. \begin{array}{l} 1.00 \\ 1.00 \\ 1.00 \end{array} \right\}$
Benzene/ Methanol (77.8:22.2, v/v)	0.85	$\left\{ \begin{array}{l} 2.2 \times 10^5 \\ 1.0 \times 10^5 \\ 0.4 \times 10^5 \end{array} \right.$	$\left. \begin{array}{l} 1.07 \\ 1.04 \\ 1.03 \end{array} \right\}$
Benzene	0.32	$\left\{ \begin{array}{l} 2.2 \times 10^5 \\ 1.0 \times 10^5 \\ 0.4 \times 10^5 \end{array} \right.$	$\left. \begin{array}{l} 1.22 \\ 1.15 \\ 1.16 \end{array} \right\}$
Chloroform	0.40		

in which K_p° represents polymer-sorbent interaction for a polymer-eluent-sorbent reference system and f is a coefficient showing the deviation in the K_p value of a new system with respect to that of the reference system. According to this approach the K_p values in Table 2 must then be regarded as f values. Equation (19) has satisfactorily explained the changes in the elution of polystyrene in mixed eluents in terms of polymer-sorbent, solvent-sorbent and polymer-solvent interactions (39).

The results in Table 2 suggest that polymer-sorbent interaction for inorganic packings decreases as eluent polarity increases because of the higher affinity of the eluent for the surface of the pores. The dependence of polymer-sorbent interaction on polymer-solvent interaction may be studied with eluents having about the same polarity, in the absence of specific eluent - adsorbent interactions. For single liquids as eluents with ϵ° in the range 0.40 - 0.56, deviations from the universal plot of log hydrodynamic volume versus V_R have been reported for polystyrene in poor solvents (15,16). Otocka and Hellman (16) compared the separation on porous glass of polystyrene standards in chloroform ($\epsilon^{\circ} = 0.40$), tetrahydrofuran ($\epsilon^{\circ} = 0.45$), dioxane ($\epsilon^{\circ} = 0.56$) and methyl ethyl ketone ($\epsilon^{\circ} = 0.51$). Their plot of log hydrodynamic volume versus V_R suggested that the poorer the solvent for the polymer, e.g. methyl ethyl ketone ($\alpha = 0.6$), the greater the displacement of the plot to high V_R . The same trend for porous glass is evident in the results of Iwama and Homma (15) for polystyrene in the non-polar theta solvent cyclohexane compared with the eluents methyl ethyl ketone (poor solvent) and tetrahydrofuran (good solvent). Although these results can be interpreted in terms of a separation operating by steric exclusion and adsorption mechanisms in which the degree of polystyrene adsorption becomes more prevalent as polymer-solvent interaction decreases, this may not be true when the eluents have different polarities as judged by values of δ_1 and ϵ° . Kotera, Furusawa and Okamoto (40) observed that polystyrene separating on porous glass followed the same hydrodynamic volume calibration curve with diethylmalonate (theta solvent) and tetrahydrofuran as eluents. The tendency for increased adsorption from the theta solvent is balanced by the greater affinity of diethylmalonate ($\epsilon^{\circ} \approx 0.6$) for the packing compared to tetrahydrofuran.

Polymer retardation and irreversible polymer adsorption in inorganic packings may be reduced (21). From the previous observations the choice of eluent is important. A liquid must be a good solvent for the polymer and must be more polar than the polymer. If the eluent is not very polar because of polymer solubility considerations, small quantities of an adsorption-active substance may be added to the eluent in order to suppress adsorption (41). Many GPC studies have been performed with inorganic packings which have been treated by silanisation (21). However, this may not be suitable for all polymer-eluent pairs. Dubin, Koontz and Wright (10) obtained universal calibration curves for polystyrene, poly(methyl acrylate), poly(ethylene oxide) and poly(p-nitrostyrene) in DMF with untreated porous glass. The hydrodynamic volume curves for these polymers in DMF with silanised porous glass did not superimpose, the displacement of each curve decreasing as polymer polarity increased. This suggests that in very polar media hydrophobic polymer-sorbent interactions may occur. Even very polar eluents may not be suitable for some polymers with untreated silica; for example, poly(vinyl pyrrolidone) in DMF is irreversibly retained in porous glass because of hydrogen bonding (10).

Incompatibility with polystyrene gels

The observations of the early elution of some polymers may be explained by polymer incompatibility with the gel (22,42-45). A positive value of ΔH_p , corresponding to a positive value of the interaction parameter χ_{23} between polymer and sorbent, leads to a value of K_p below unity in equation (14). A polymer exhibiting repulsive interactions on

transferring to the stationary phase will have a plot of log hydrodynamic volume versus V_R displaced to low V_R . Consequently, equations (11) and (17) should represent a separation involving steric exclusion and partial exclusion by incompatibility between polymer and sorbent. Data (43) for polystyrene and poly(vinyl acetate) in tetrachloroethylene have been plotted according to equation (17) (46). Polystyrene is assumed to separate by steric exclusion alone ($K_p = 1$) and values of K_p for poly(vinyl acetate) are given in Table 3.

TABLE 3 Values of K_p for poly(vinyl acetate)

$[\eta]M$	K_p
374	0.38
194	0.55
98.5	0.86

The decrease in K_p as molecular size increases can be predicted from a thermodynamic interpretation of K_p , using equation (13) rather than equation (14). This approach leads to (46)

$$\ln K_p = -x_2 \phi_3 (1 + \chi_{23}) \quad (20)$$

where x_2 is the degree of polymerisation of the polymer and ϕ_3 is the volume fraction of gel. The values of K_p in Table 3 are in the direction predicted by equation (20). An alternative thermodynamic treatment of partial exclusion by polymer incompatibility has been reported (45).

CONCLUSIONS

GPC separations of polymers involving a steric exclusion mechanism and polymer-sorbent interaction are represented satisfactorily by a network-limited mechanism. Partition, adsorption and incompatibility effects resulting from polymer-sorbent interaction can be represented. The distribution coefficient for polymer-sorbent interaction can be given a thermodynamic interpretation.

REFERENCES

1. E. F. Casassa, *J. Phys. Chem.* **75**, 3929 (1971).
2. M. E. Van Kreveland and N. Van Der Hoed, *J. Chromatogr.* **83**, 111 (1973).
3. For references, see H. Determann, *Gel Chromatography*, Springer-Verlag, Berlin (1969), Chap. 3.
4. E. F. Casassa, *J. Polym. Sci. B5*, 773 (1967); *Separation Sci.* **6**, 305 (1971); *Macromolecules* **9**, 182 (1976).
5. E. F. Casassa and Y. Tagami, *Macromolecules* **2**, 14 (1969).
6. J. C. Giddings, E. Kucera, C. P. Russell and M. N. Myers, *J. Phys. Chem.* **72**, 4397 (1968).
7. Z. Grubisic, P. Rempp and H. Benoit, *J. Polym. Sci. B5*, 753 (1967).
8. W. V. Smith, *Rubb. Chem. Technol.* **45**, 667 (1972).
9. J. V. Dawkins, J. W. Maddock and D. Coupe, *J. Polym. Sci., Part A-2*, **8**, 1803 (1970).
10. P. L. Dubin, S. Koontz and K. L. Wright, *J. Polym. Sci., Polym. Chem.*, **15**, 2047 (1977).
11. R. M. Scream and R. W. Seemann, *Appl. Polym. Symp.* **8**, 81 (1969).
12. M. Zinbo and J. L. Parsons, *J. Chromatogr.* **55**, 55 (1971).
13. D. Kranz, U. Pohl and H. Baumann, *Angew. Makromol. Chem.* **26**, 67 (1972).
14. P. L. Dubin and K. L. Wright, *Polym. Preprints* **15**, 673 (1974).
15. M. Iwama and T. Homma, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)* **74**, 277 (1971).
16. E. P. Otocka and M. Y. Hellman, *J. Polym. Sci., Polym. Lett.* **12**, 331 (1974).
17. J. V. Dawkins and M. Hemming, *Makromol. Chem.* **176**, 1777 (1975).
18. J. V. Dawkins and M. Hemming, *Makromol. Chem.* **176**, 1795 (1975).
19. J. V. Dawkins and M. Hemming, *Makromol. Chem.* **176**, 1815 (1975).
20. J. C. Moore and M. C. Arrington, Paper presented at the Third International GPC Seminar, Geneva, May (1966).
21. J. V. Dawkins, in *Chromatography of Synthetic and Biological Polymers Volume 1* (R. Epton ed.), Ellis Horwood, Chichester, England (1978), p. 30.
22. K. H. Altgelt and J. C. Moore, in *Polymer Fractionation* (M. J. R. Cantow ed.), Academic Press, New York, (1967), Chap. B.4.
23. A. R. Cooper and A. R. Bruzzone, *J. Polym. Sci., Polym. Phys.*, **11**, 1423 (1973).
24. D. M. W. Anderson and J. F. Stoddart, *Anal. Chim. Acta.* **34**, 401 (1966).
25. W. Heitz and W. Kern, *Angew. Makromol. Chem.* **1**, 150 (1967).

26. W. Heitz, Ber. Bunsenges Phys. Chem. 77, 210 (1973); Z. Anal. Chem. 277, 323 (1975).
27. J. J. Kirkland, Modern Practice of Liquid Chromatography, Wiley-Interscience, New York, (1971).
28. D. H. Everett, The Structure and Properties of Porous Materials (D. H. Everett and F. S. Stone ed.), Proceedings Tenth Symposium of the Colston Research Society, Butterworths, London, (1958), p. 95.
29. J. V. Dawkins, J. Polym. Sci., Polym. Phys., 14, 569 (1976).
30. J. N. Done, J. H. Knox and J. Loheac, Applications of High-speed Liquid Chromatography, Wiley, New York (1974).
31. D. H. Freeman and D. Killion, J. Polym. Sci., Polym. Phys., 15, 2047 (1977).
32. J. V. Dawkins and M. Hemming, Polymer, 16, 554 (1975).
33. Y. S. Lipatov and L. M. Sergeeva, Adsorption of Polymers, Wiley, New York (1974).
34. J. Lecourtier, R. Audebert and C. Quivoron, J. Chromatogr. 121, 173 (1976).
35. G. W. Longman, G. D. Wignall, M. Hemming and J. V. Dawkins, Colloid Polym. Sci. 252, 298 (1974).
36. L. R. Snyder, Principles of Adsorption Chromatography, Dekker, New York (1968).
37. H. A. Swenson, H. M. Kaustinen and K. E. Almin, J. Polym. Sci. B9, 261 (1971).
38. D. Berek, D. Bakos, T. Bleha and L. Soltés, Makromol. Chem. 176, 391 (1975).
39. A. Campos and J. E. Figueruelo, Makromol. Chem. 178, 3249 (1977).
40. A. Kotera, K. Furusawa and K. Okamoto, Rep. Prog. Polym. Phys. Japan 16, 69 (1973).
41. S. P. Zhdanov, B. G. Belenkii, P. P. Nefedov, E. V. Koromaldi and M. A. Kuznetsova, J. Chromatogr. 77, 149 (1973).
42. K. H. Altgelt, Makromol. Chem. 88, 75 (1965).
43. K. H. Altgelt, Separation Sci. 5, 777 (1970).
44. A. G. Ogston and P. Silpananta, Biochem. J. 116, 171 (1970).
45. B. G. Belenkii, L. Z. Vilenchik, V. V. Nesterov, V. J. Kolegov and S. Ya. Frenkel, J. Chromatogr. 109, 233 (1975).
46. J. V. Dawkins, Polymer 19, 000 (1978).