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

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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 (a 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, Remp 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 $\delta$ similar to that of polystyrene. Furthermore, the exponent $a$ 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 a 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 $\alpha$ in the range $0.5 - 0.7$ and values of $\delta$ 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

$$V_R = V_o + K_{GPC} \frac{V_i}{1}$$

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 $\Delta G^0$ for the transfer of polymer molecules from the mobile phase to the stationary phase at constant temperature $T$ is related to $K_{GPC}$ by

$$\Delta G^0 = -kT \ln K_{GPC}$$

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 $\Delta G_D$ and the second mechanism, if present, will involve polymer-sorbent interaction having a free energy change $\Delta G_p$. The total standard free energy change then is

$$\Delta G^0 = \Delta G_D + \Delta G_p$$

Therefore, equations (1) - (3) give

$$V_R = V_o + V_i \exp\left(-\frac{\Delta G_D}{kT}\right)\exp\left(-\frac{\Delta G_p}{kT}\right)$$

**Steric exclusion**

For an inert pore surface, the value of $\Delta G_p$ 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, $\Delta G_D$ is given by

$$\Delta G_D = -T\Delta S_D = -kT \ln K_D$$

where $\Delta S_D$ 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

$$K_D = \exp\left(-s \frac{L}{2}\right)$$

where $L$ is the mean external length or molecular projection, e.g. $L$ 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 cm²/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

$$K_D = -A \ln [\eta]M + B$$

(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

$$k' = \frac{K_p V_1}{V_o}$$

(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 $V_1$ available will depend on solute size and equation (8) must be replaced by

$$k' = \frac{K_p}{K_D} \frac{V_1}{V_o}$$

(9)

The capacity factor is related to the retention volume $V_R$ by

$$V_R = V_o (1 + k')$$

(10)

From equations (9) and (10) we obtain

$$V_R = V_o + K_D K_p V_1$$

(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 is related to the surface area $S$ by

$$V_i = \gamma \frac{S}{r}$$

(12)

where $r$ is the average pore size of the pore size distribution and $\gamma$ 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

$$K_p = \exp(-\Delta G_p/kT)$$

(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.

$$\Delta H_p = -kT \ln K_p$$

(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

$$\ln(V_R - V_o)/K_p = \ln V_i - s \frac{L}{2}$$

(15)

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

$$\ln(V_R - V_o)/K_p = \ln (2/r) - R/r$$

(16)

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

$$\frac{(V_R - V_o)/K_p}{V_i} = (B - A \ln [nM])$$

(17)

A plot of $\log [nM]$ 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. Otocka and Hellinan (16) reported a progressive displacement of the plot of $\log [nM]$ 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 $\log [nM]$ 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 $\log [nM]$ 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 $\Delta H_p$ 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 $\Delta H_p$ is negative. In addition the magnitude of $\Delta H_p$ 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...
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 $\ln M$ 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 $\ln M$ versus $V_R$ for 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 $\ln M$ 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. Freeman and Killion (31) have used the expression

\[ \ln K_p = \bar{V}_2 \left[ (\delta_2 - \delta_1)^2 - (\delta_2 - \delta_3)^2 \right] / RT + \ln \bar{V}_3 / \bar{V}_1 \] (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. Algelt 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 minimise polymer-sorbent interaction. When $\delta_2 < \delta_3$, we suggest that $K_p$ will be 1.0 with $\delta_1 > \delta_2$ provided $\delta_1 = \delta_3$. This is true for polyethylene separating on polystyrene gel, for which the hydrodynamic volume universal calibration method is well established (18). 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 pyrrolidone) ($\delta_2 \approx 10.5$) 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 ($\delta_1 = 10.5$) (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 eluent is polystyrene ($\delta_1 = 9.1$) in an eluent such that $\delta_1$ and $\delta_2$ 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. from 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 (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).

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 the theta solvent mixtures than plots for single good solvents has been confirmed for polystyrene separating on porous silicas (37,36). 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 $\delta_1$ 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 ($e^2 = 0.87$), 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 ($e^2 = 0.40$) and benzene ($e^2 = 0.32$), 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

$$V_R = V_0 + K_p e^2 f_i$$

(19)
TABLE 2 Values of $K_p$ for polystyrene separating on porous silica

<table>
<thead>
<tr>
<th>Eluent</th>
<th>$c^0$</th>
<th>$I_{NM}$</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol (74.7:25.3, v/v)</td>
<td>0.87</td>
<td>$2.2 \times 10^5$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.0 \times 10^5$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.4 \times 10^5$</td>
<td>1.00</td>
</tr>
<tr>
<td>Benzene/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol (77.8:22.2, v/v)</td>
<td>0.85</td>
<td>$2.2 \times 10^5$</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.0 \times 10^5$</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.4 \times 10^5$</td>
<td>1.03</td>
</tr>
<tr>
<td>Benzene/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.40</td>
<td>$2.2 \times 10^5$</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.0 \times 10^5$</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.4 \times 10^5$</td>
<td>1.16</td>
</tr>
</tbody>
</table>

in which $K_p^0$ 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 $c^0$ 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 Hallman (16) compared the separation on porous glass of polystyrene standards in chloroform ($c^0 = 0.10$), tetrahydrofuran ($c^0 = 0.45$), dioxane ($c^0 = 0.56$) and methyl ethyl ketone ($c^0 = 0.51$). Their plot of log hydrodynamic volume versus $V_R$ suggested that the poorer the solvent for the polymer, e.g. methyl ethyl ketone ($a = 0.6$), 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 Koma (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 $\delta$ and $c^0$. 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 ($c^0 = 0.6$) 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 $\Delta H_\alpha$, corresponding to a positive value of the interaction parameter $\chi^\alpha$ 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)

<table>
<thead>
<tr>
<th>$\eta MJ$</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>374</td>
<td>0.38</td>
</tr>
<tr>
<td>194</td>
<td>0.55</td>
</tr>
<tr>
<td>98.5</td>
<td>0.86</td>
</tr>
</tbody>
</table>

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)

$$\ln K_p = -x_2 \phi_3 (1 + x_2 \phi_3)$$

(20)

where $x_2$ is the degree of polymerisation of the polymer and $\phi_3$ 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**

46. J. V. Dawkins, Polymer 19, 000 (1978).