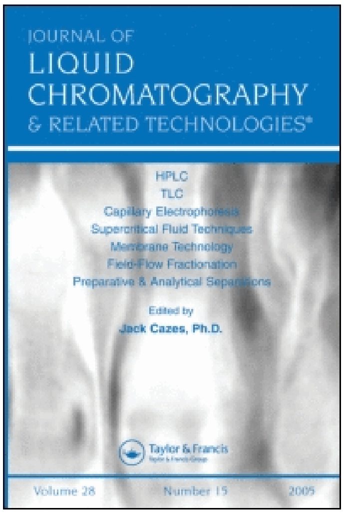

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POLYMER-GEL INTERACTIONS IN GPC WITH ORGANIC ELUENTS *

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ABSTRACT

The displacement of hydrodynamic volume universal calibration curves to high retention volumes for some polymer-solvent systems is explained in terms of a network-limited separation consisting of a steric exclusion mechanism and a second mechanism resulting from polymer-gel interactions. This treatment is consistent with a thermodynamic interpretation of GPC separations in which the distribution coefficient ($\gtrsim 1.0$) for polymer-gel interactions is determined by an enthalpy change for polymer partition or polymer adsorption in the porous packing. Examples of the application of the network-limited treatment to experimental data obtained with crosslinked polystyrene gels and inorganic packings are presented. Network-limited separations in which the distribution coefficient for polymer-gel interactions is less than unity correspond to partial exclusion by polymer incompatibility with the gel. Experimental data for the early elution of poly(vinyl acetate) are consistent with an incompatibility mechanism, giving a dependence of the distribution coefficient for polymer-gel interactions on the molecular weight of poly(vinyl acetate).

INTRODUCTION

Grubisic, Rempp and Benoit (1) showed that a plot of log hydrodynamic volume versus retention volume V_R was the same for

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homopolymers and copolymers separating on crosslinked polystyrene gels in gel permeation chromatography (GPC) with tetrahydrofuran as eluent. Subsequent studies, see the papers cited in reference (2), have confirmed this result with eluents such as chloroform, o-dichlorobenzene and trichlorobenzene, all of which have a solubility parameter δ 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 (3).

Deviations from the universal calibration plot of hydrodynamic volume for crosslinked polystyrene gels have been observed with organic eluents having a in the range 0.5-0.7 and solubility parameters either less than or greater than that for polystyrene (4-9). In one of the first attempts to show that GPC separations with porous glass were size dependent (10), 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, see a recent review (11).

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 (12) observed that whilst steric exclusion generally dominates GPC separations, e.g. the results reviewed in the first paragraph, adsorption, partition and incompatibility mechanisms may result from polymer-gel interaction effects. The presence or absence of these secondary mechanisms will be determined by the polarity of the eluent and of the polymer and by polymer-solvent (eluent) interactions.

SEPARATION MECHANISM

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

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

where V_o is the total volume of 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^o for the transfer of polymer molecules from the mobile phase to the stationary phase at constant temperature T is related to K_{GPC} by

$$\Delta G^o = -kT \ln K_{GPC} \qquad (2)$$

where k is Boltzmann's constant.

We consider a GPC separation consisting of two component mechanisms. The dominant mechanism involves steric exclusion from which it follows that a plot of log polymer size versus V_R is the same for random coil polymers (13), as demonstrated in reference (1). The second mechanism, if present, will involve polymer-gel interactions, so that ΔG^o is given by

$$\Delta G^o = \Delta G_D + \Delta G_p \qquad (3)$$

where ΔG_D is the free energy change for steric exclusion and ΔG_p is the free energy change for polymer-gel interactions. Therefore, equation (1) becomes

$$V_R = V_o + V_i e^{-\Delta G_D/kT} e^{-\Delta G_p/kT} \qquad (4)$$

In a previous paper (14), the retention volume was defined by

$$V_R = V_o + K_D K_p V_i \qquad (5)$$

where K_D is the distribution coefficient for steric exclusion and K_p is the distribution coefficient for polymer-gel interactions. Equation (5) was derived assuming that the GPC mechanism was a network limited separation, as proposed by Heitz and Kern (15,16). Statistical mechanical treatments of the steric exclusion mechanism at equilibrium calculate the loss in conformational entropy ΔS_D when a polymer molecule transfers from the mobile phase to a pore within the packing (13, 17-19). Other entropy and enthalpy contributions to ΔG_D need not be considered.

Consequently,

$$\Delta S_D = k \ln K_D \qquad (6)$$

In a previous paper (20), it was suggested that K_p is determined by an enthalpy contribution, i.e.

$$\Delta H_p = - kT \ln K_p \qquad (7)$$

and the entropy change involved in polymer-gel interactions 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 (21). It should be possible to apply these treatments to GPC separations of polystyrene ($K_p > 1.0$), reported by the author, since the experimental data are represented over a wide molecular size range by a single value of K_p (8,9,14,20).

In a thermodynamic interpretation of equation (5) (20), it was observed that a positive enthalpy change on transferring solute from the mobile to the stationary phase corresponded to $K_p < 1.0$. Equation (5) will, therefore, explain partial exclusion by incompatibility between a polymeric solute and the gel. However, polymer incompatibility is very dependent on the molecular weight, M, so the dependence of K_p on molecular size must be considered. Consequently, K_p for an incompatibility mechanism resulting from polymer-gel interactions should be given by

$$\Delta G_p = -kT \ln K_p \qquad (8)$$

RESULTS AND DISCUSSION

Universal calibrations are generally plotted in terms of $[\eta]M$ which is proportional to hydrodynamic volume, where $[\eta]$ is the intrinsic viscosity of the polymer in the GPC eluent. Dawkins and Hemming (14) proposed that in the middle of the K_D range the following relation will be valid

$$K_D = -A \log [\eta] M + B \qquad (9)$$

where A and B are constants. Substitution of equation (9) into equation (5) and rearrangement gives

$$(V_R - V_o)/K_p = V_i \ (-A \log [\eta] M + B) \qquad (10)$$

A plot of experimental results according to equation (10) permits the evaluation of K_p.

Partition - Adsorption with Polystyrene Gels

Partition effects may occur whenever the polarity of the eluent is very different from that of the gel and the polymer. For regular solutions, K_p can be calculated from equation (7), since the enthalpy change on 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 organic gel 3, (22). Results for small molecules exhibit good agreement between experiment and calculation (23).

Altgelt and Moore (12) advised that in GPC the eluent should have a similar solubility parameter to that for the gel, but this may not be possible for some polar polymers. Dimethylformamide has been widely used as a GPC eluent for polar polymers, see for example the work of Dubin and co-workers (5, 24, 25) who studied polymer-gel interactions as a function of polymer polarity. These interactions are particularly prevalent for polystyrene ($\delta_2 = \delta_3 = 9.1$) in dimethylformamide ($\delta_1 = 12.1$). For example, Dawkins and Hemming (14) found that K_p for polystyrene in dimethylformamide was 1.37 from a plot of GPC data (7) according to equation (10). This shows that the hydrodynamic volume universal calibration approach based on polystyrene standards is no longer applicable when δ_1 and δ_2 are very different, since a is less than 0.7 when K_p for polystyrene is greater than unity (4-9). Alternatively, universal calibration can be performed with equation (10), as described elsewhere (14).

Several guidelines may be followed in order to minimise polymer-gel interactions. When $\delta_2 < \delta_3$, we suggest that K_p will be 1.0 with $\delta_1 > \delta_2$ provided $\delta_1 \simeq \delta_3$. This is true for polyethylene separating on crosslinked polystyrene gel, for which the hydrodynamic volume universal calibration method is well established(2). 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 ($\delta_1 = 10.8$) (26). However, polymer-gel interactions still occur with some polar polymers, e.g. in N,N-dimethylformamide (24).

The nature of the mechanism giving rise to $K_p > 1.0$ for semi-rigid crosslinked polystyrene gels cannot be defined exactly. As discussed elsewhere (8,14,24), several observations suggest that the mechanism might be partition rather than adsorption. Thus, retardation of polystyrene in poor solvents occurs when $\delta_1 > \delta_2$ and when $\delta_2 > \delta_1$ (14). However, changes in retention behaviour with temperature (9, 24) are not too dissimilar from some results reported for the adsorption of polymers from solution onto non-porous adsorbents (20). With highly swollen lightly crosslinked gels, then partition may be the dominant mechanism, as discussed by Lecourtier, Audebert and Quivoron (27).

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 (11). First, if the liquid has considerable affinity for the surface, then no polymer is adsorbed. Second, if preferential solvent-adsorbent interactions are absent, then the extent of adsorption increases as polymer-solvent interaction decreases. The choice of GPC eluent will determine whether irreversible adsorption, i.e. total retention of the polymer in the GPC packing, or reversible adsorption, i.e. high V_R, will occur (28). The influence of solvent effects on GPC separations with inorganic packings can be interpreted in terms of the parameters a, δ and the solvent strength parameter ε^0 which represents the interaction energy of an eluent with the packing (29).

Moore and Arrington (10) separated polystyrene by GPC on porous glass with a binary theta solvent mixture of butanone

(δ_1 = 9.3) and isopropanol (δ_1 = 11.5). Polystyrene is not retarded by polymer-gel interactions because isopropanol is preferentially adsorbed. On the other hand polystyrene in benzene (δ_1 = 9.2) will separate by steric exclusion and polymer-gel interactions because polymer and eluent have similar affinity for the surface sites. Moore and Arrington (10) showed that polystyrene in benzene had a higher V_R than polystyrene in butanone-isopropanol. Similar observations on polystyrene, separating on porous silica, in the eluents chloroform (δ_1 = 9.3)-methanol (δ_1 = 14.5), benzene-methanol, benzene and chloroform have been reported by Berek and co-workers (30). The results of Berek and co-workers have been interpreted in terms of equation (10), see the values for K_p in Table 1 (11). It was assumed that no polystyrene adsorption (K_p = 1) onto the packing occurs with the most polar binary mixture (ε^0 = 0.87). For the other eluents, polystyrene is separating by steric exclusion and adsorption (K_p > 1). Studies of polymer adsorption from solution onto non-

TABLE 1

K_p Values for Polystyrene (11)

Eluent	ε^0	$[\eta]M$	K_p
Chloroform/			
Methanol	0.87	2.2×10^5	1.00
(74.7:25.3,v/v)		1.0×10^5	1.00
		0.4×10^5	1.00
Benzene/			
Methanol	0.85	2.2×10^5	1.07
(77.8:22.2,v/v)		1.0×10^5	1.04
		0.4×10^5	1.03
Benzene	0.32	2.2×10^5	1.22
Chloroform	0.40	1.0×10^5	1.15
		0.4×10^5	1.16

porous adsorbents suggest only a slight or no dependence of the amount of polymer adsorbed on molecular weight. The values for K_p for a given eluent in Table 1 are in reasonable agreement with this behaviour.

The results in Table 1 suggest therefore that polymer adsorption in the GPC packing decreases as eluent polarity increases. The dependence of the extent of adsorption on polymer-solvent interactions may be studied with eluents having about the same polarity, in the absence of specific eluent-adsorbent interactions. For eluents with ε^o in the range 0.40-0.56 as poor solvents for polystyrene, deviations from the universal hydrodynamic volume plot have been reported for separations with porous glass (4,6). These results are 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 interactions decrease. Polymer adsorption on silica in terms of polymer-solvent, polymer-gel, and solvent-gel interactions has been interpreted by an extension of equation (5) (31).

Incompatibility with Polystyrene Gels

Altgelt has observed the early elution of some polymers in GPC, suggesting partial exclusion because polymer is incompatible with the gel (12,32,33). Data (33) for polystyrene and poly (vinyl acetate) in tetrachloroethylene separating on crosslinked polystyrene gels have been plotted according to equation (10)(34). 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 2. A thermodynamic interpretation of ΔG_p in equation (8) for partial exclusion by polymer incompatibility with the gel has shown that ln K_p is linearly proportional to -M, i.e. K_p decreases as molecular size increases (34). The values of K_p in Table 2 are in the direction predicted by the theoretical treatment for partial exclusion by polymer incompatibility.

TABLE 2

K_p Values for Poly(vinyl acetate)(34)

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

CONCLUSIONS

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

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