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Note

Solute-gel interactions in gel permeation chromatography of small molecules in organic media

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Heitz and Kern^{1,2} proposed that the separation mechanism in gel permeation chromatography (GPC) can be considered as a network-limited partition process. In a previous paper³, the following relation was derived for such a mechanism

$$V_R = V_0 + K_D K_p V_i \quad (1)$$

where V_R is the retention volume, V_0 is the interstitial or void volume, V_i is the total volume of solvent within the gel, K_D is the distribution coefficient for steric exclusion, and K_p is the distribution coefficient for solute-gel interactions. For polymers separating solely by steric exclusion, K_p is unity. Then, a plot of the logarithm of hydrodynamic volume versus V_R is the same for random coil polymers in organic media. This was first demonstrated by Grubisic *et al.*⁴ on a semi-logarithmic plot of the product of the intrinsic viscosity $[\eta]$ of the polymer in the GPC eluent and the molecular weight M of the polymer versus V_R . Dawkins and Hemming³ proposed a simple relation between K_D and $[\eta]M$, which, when substituted into eqn. 1, gave

$$(V_R - V_0)/K_p = V_i(-A \log [\eta]M + B) \quad (2)$$

where A and B are constants. Eqn. 2 has been shown to represent solute-gel interactions for polymers in semi-rigid cross-linked polystyrene gels^{3,5,6} and in rigid inorganic packings⁷. Furthermore, the surface area of a porous gel is related to V_i , so that eqn. 2 will represent a network-limited adsorption mechanism as well as a network-limited partition mechanism³.

Smith and Kollmansberger⁸ suggested that the GPC separation of small molecules was determined by the molar volume V_m (cm³/mole). Although the semi-logarithmic plot of V_m versus V_R is now widely accepted, deviations have been reported for some solutes because of solute-gel interactions in the semi-rigid cross-linked polystyrene gels⁹⁻¹². In an earlier paper⁵, the behaviour of toluene and squalene was compared with that of polystyrene and polyisoprene on a semi-logarithmic plot of V_m versus V_R . Application of eqn. 1 to these results showed that the K_p value for polystyrene in cyclohexane gave V_R for toluene in good agreement with the experimental value which was high because of solute-gel interactions³. Consequently, if the

derivation of eqn. 2 is followed but with V_m replacing $[\eta]M$, then for small molecules we obtain

$$(V_R - V_0)/K_p = V_i(-A \log V_m + B) \quad (3)$$

In this communication, GPC data reported by Cazes and Gaskill⁹ for hydrocarbons, glycols and monocarboxylic acids separating on semi-rigid cross-linked polystyrene gel at 130° with *o*-dichlorobenzene as eluent are represented by eqn. 3.

RESULTS

The data given by Cazes and Gaskill⁹ are plotted in Fig. 1. Their experiments were performed with four polystyrene gel columns in series, and from published calibration curves and exclusion limit data¹³, a value of 100 cm³ is reasonable for V_0 . We shall assume that the hydrocarbons separate by steric exclusion alone ($K_p = 1$). It follows that the glycols and monocarboxylic acids separate by steric exclusion and solute-gel interactions ($K_p > 1$). In eqn. 3, V_i , A and B are all constants, so for each value of V_m for the hydrocarbons the value of $(V_R - V_0)$ for the glycols and monocarboxylic acids can be calculated from the value of $(V_R - V_0)_H$ for the hydrocarbons with the relation

$$(V_R - V_0) = K_p(V_R - V_0)_H \quad (4)$$

The lines passing through the experimental data in Fig. 1 correspond to $K_p = 1.09$ (monocarboxylic acids) and $K_p = 1.15$ (glycols) in eqn. 4.

An alternative representation of the experimental data is to plot $\log V_m$ versus

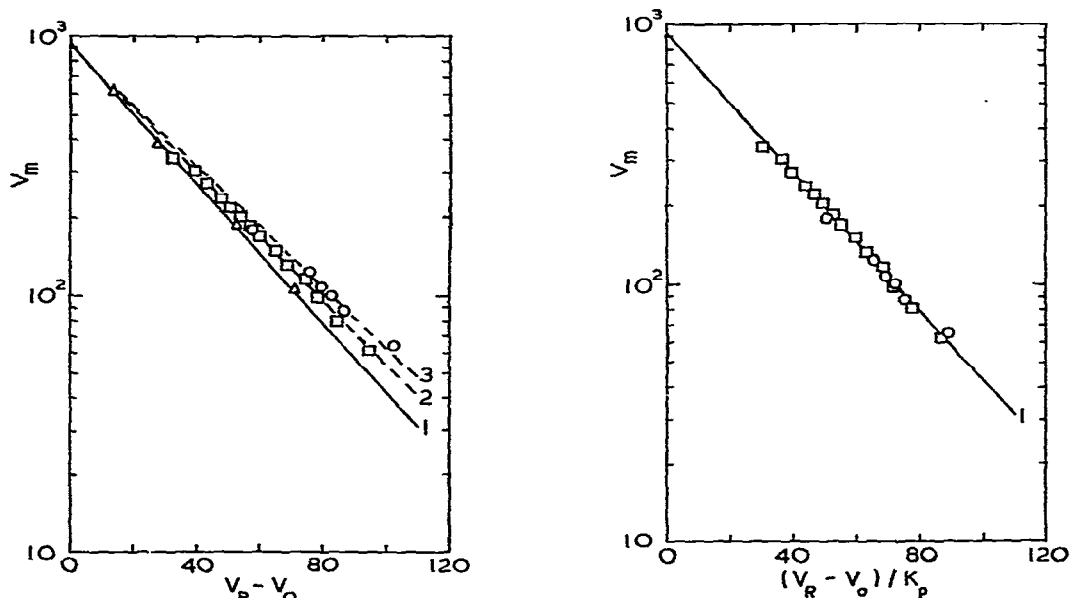


Fig. 1. V_m versus $V_R - V_0$ for the GPC data from ref. 9. Δ = Hydrocarbons; \square = monocarboxylic acids; \circ = glycols; 1 = hydrocarbons ($K_p = 1$); 2 = monocarboxylic acids, from eqn. 4 ($K_p = 1.09$); 3 = glycols, from eqn. 4 ($K_p = 1.15$).

Fig. 2. V_m versus $(V_R - V_0)/K_p$ according to eqn. 3 for the GPC data from ref. 9. 1 = Hydrocarbons ($K_p = 1$); \square = monocarboxylic acids ($K_p = 1.09$); \circ = glycols ($K_p = 1.15$).

the left-hand side of eqn. 3, taking $K_p = 1$ (hydrocarbons), $K_p = 1.09$ (monocarboxylic acids), and $K_p = 1.15$ (glycols). It is concluded from Fig. 2 that a network-limited separation mechanism and eqn. 3 satisfactorily predict the retention behaviour of small molecules which exhibit solute-gel interactions.

DISCUSSION

It has been shown that eqn. 1 follows from a thermodynamic interpretation of the GPC separation mechanism¹⁴. The value of K_p at equilibrium is given by

$$K_p = e^{-\Delta H^0/kT} \quad (5)$$

where ΔH^0 is the standard enthalpy change on solute transfer to the pore surface in the gel, k is Boltzmann's constant, and T is temperature. The values of K_p (>1) in Figs. 1 and 2 assume that ΔH^0 is independent of molecular size. For very small molecules, this assumption may be approximate. An even better representation of the data in Figs. 1 and 2 may be obtained with K_p values depending on solute size, in particular for the glycols.

Thermodynamic theories for a partition mechanism have been discussed by Lecourtier *et al.*¹⁵ who proposed an expression for V_R containing a distribution coefficient for steric exclusion and a partition coefficient. This relation is derived for a gel phase consisting of a swollen network of lightly cross-linked chains. The data in Fig. 1 were obtained with semi-rigid gels which are highly cross-linked and exhibit little swelling. An expression containing distribution coefficients for steric exclusion and adsorption was proposed by Aurenge *et al.*¹⁶ to explain the high V_R values for some small molecules. However, they did not consider the thermodynamics of their separations.

It has been suggested that GPC may be used to determine molar volumes of small molecules from a calibration curve established with *n*-alkanes as standards¹⁷. This approach requires that K_p is unity. The presence of solute-gel interactions which are more likely for polar solutes, depending on the polarity of the GPC eluent, will invalidate values of molar volumes obtained from hydrocarbon standards.

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