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Correlations Between Retention Volume and Molecular Size Parameters in Gel Permeation Chromatography of Small Molecules

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Abstract

Gel permeation columns of Bio Beads S–X8 have been used to provide separation of oligomers and other small organic molecules. Results show successful separations up to molecular weight *c.* 600. The retention times of compounds have been correlated with the largest molecular dimension of the molecules and also with molar volumes.

With polymers of high molecular weight, correlation of gel permeation chromatographic retention volumes with hydrodynamic volume or molecular weight is the usual procedure. However, with small molecules and oligomers, where different structures may be present, a different approach is required. Here retention volume data have been correlated with molar volumes[1] and with the largest molecular dimension of a molecule.[2]

The present results present quantitative data on such correlations. Compounds used in the correlations have been chosen to be of rigid structure and low polarity to minimize solvent–solute interactions. Molar volumes (V_m) were calculated from density and molecular weight and the largest molecular dimension (l) was obtained by direct measurement of scale diagrams. The data used in the correlations are shown in Table 1. These give the following equations and correlation parameters when correlated with retention volume (V_r):

$$V_r = 26{\cdot}76 - 4{\cdot}49 \log V_m \quad (1)$$

correlation coefficient = 0·978; standard deviation = 0·39;

$$V_r = 23{\cdot}29 - 6{\cdot}76 \log l \quad (2)$$

correlation coefficient = 0·968; standard deviation = 0·48.

Though the data give a better fit in equation (1), equation (2) also provides an acceptable correlation. In practice either equation can be used depending on which parameter can be obtained for the material being chromatographed. Solvation of polar species must also be taken into consideration. For example, it has been shown that for phenolic materials in tetrahydrofuran one molecule of solvent must be allowed for each hydroxyl group.[2] Here it would be necessary to use equation (2) since the density, and hence molar volume, of the solvated species would be difficult

[1] Yoshikawa, T., Kimura, K., and Fujimura, S., *J. Appl. Polym. Sci.*, 1973, **16**, 2513.
[2] Duval, M., Bloch, B., and Kohn, S., *J. Appl. Polym. Sci.*, 1972, **15**, 1585.

to obtain. Steric effects of substituents also influence the solvation and solution structure of polar materials.[3] Equation (2) has been used to obtain a calibration plot for components of phenol–formaldehyde resins. Largest molecular dimensions calculated from the equation are compared with those measured from structures.

Table 1. Retention volume and molecular size data

Compound	V_r[A] (ml)	log l (Å)	log V_m (Å^3)
Benzene	17·20±0·05	0·857	2·17
Toluene	16·69±0·15	0·914	2·25
Chlorobenzene	17·15±0·14	0·940	2·23
p-Xylene	16·29±0·15	0·964	2·31
Ethylbenzene	16·51±0·18	0·973	2·31
1,2,4-Trichlorobenzene	16·67±0·20	0·996	2·31
Naphthalene	16·70±0·10	1·079	2·27
Phenanthrene	15·50±0·12	1·228	2·40
2-Phenylnaphthalene	14·70±0·06	1·328	2·51
Polystyrene (M_w = 2025)	11·27±0·03	1·695	3·50

[A] Retention volumes are the mean of two determinations. The deviations from this mean are listed and give rise to a retention volume standard deviation of 0·13 ml.

When agreement is obtained a retention volume can be assigned to the structure and a molecular weight calibration obtained. In this case the components form a homologous series so a molecular weight calibration is feasible. The molecular weight calibration for phenol–formaldehyde resins is shown in Fig. 1. This technique has

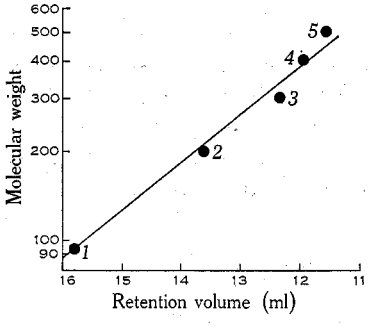

Fig. 1. Calibration plot for phenolic resins: *1*, phenol (mol. wt 94); *2*, two rings (mol. wt 200) (2,2′-methylenediphenol); *3*, three rings (mol. wt 306); *4*, four rings (mol. wt 412), *5*, five rings (mol. wt 518).

been applied to other low molecular weight oligomeric species, e.g. oligomers of dihydroquinolines, where known molecular weight standards are not available. The ability to distinguish between members of a homologous series of oligomers has also been an aid in structure elucidation.

Experimental

A Perkin–Elmer 1240 Gel Permeation Liquid Chromatograph was used with two 1 m by 2·6 mm (i.d.) stainless steel U-shaped columns of Bio Beads S–X8 (Bio Rad Laboratories). The ultraviolet detector was used with a 254 nm filter. Column oven temperature was 50° and solvent degasser temperature 65°. Tetrahydrofuran, fractionally distilled prior to use, was the eluent with a flow rate of 0·5 ml/min. Materials were injected in tetrahydrofuran solution using a 30 μl loop injector.

[3] Coupek, J., Pokorny, S., Jirackova, L., and Pospisil, J., *J. Chromatogr.*, 1973, **75**, 87.

Materials used were laboratory reagent grade, without further purification, since only the retention volume of the peak of the gel permeation curve was required. Polystyrene standard, $M_w = 2025$, was obtained from Waters Associates Inc. A typical phenol–formaldehyde resin of low degree of polymerization was chosen to illustrate the calibration procedure.

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