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## CONCENTRATION EFFECTS IN GEL PERMEATION CHROMATOGRAPHY

### VI. NON-NEWTONIAN BEHAVIOUR OF POLYMER SOLUTIONS

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#### SUMMARY

Non-Newtonian behaviour has been demonstrated experimentally by using a solution of excluded polystyrene standard as the mobile phase in gel permeation chromatography. A decrease in apparent viscosity of the polymer solution with increasing shear stress was observed under the given conditions. In the range of lower flow-rates, the polymer solution behaved as a Newtonian liquid. The relative viscosity calculated from the slope of the linear part of the graph of pressure *versus* velocity agreed with that calculated from the known concentration of the polystyrene standard. The results are discussed with respect to previous work on concentration effects in gel permeation chromatography.

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#### INTRODUCTION

A systematic study of concentration effects in gel permeation chromatography (GPC), sometimes called exclusion chromatography or size-exclusion chromatography, showed that viscosity phenomena in the interstitial volume played a most important role<sup>1-6</sup>. The change in elution volume with change in concentration of injected polymer solution may, in principle, be due to several contributing processes. When a rigid porous material is used as column packing, the following three main contributions must be taken into account: the contribution of the change in distribution coefficient,  $K_{GPC}$  due to the change in the effective dimensions of the permeating macromolecules with the changing concentration, the contribution of secondary exclusion, and, finally, the contribution of viscosity phenomena in the interstitial volume. Viscosity phenomena and the change in effective dimensions of the permeating macromolecules cause an increase in elution volume with increasing concentration, whereas secondary exclusion causes a decrease in elution volume with increasing concentration. When the molecular weight (MW) of the polymer being investigated is above the exclusion limit of the separation column, only viscosity phenomena are operative; this was studied in our previous paper<sup>2</sup>. It has been postulated that the average elution volume ( $V_{av}$ ) is a linear function of the specific viscosity

( $\eta_{\text{spec}}$ ) of injected polystyrene (PS) standard solutions up to  $\eta_{\text{spec}} \approx 4$  at the lowest flow-rate (0.038 ml/min). In the region of highest specific viscosities,  $\eta_{\text{spec}} \approx 7.3$ , the function ( $V_{\text{av}}$ ) versus  $\eta_{\text{spec}}$  curves down at lower ( $V_{\text{av}}$ ) values. With increasing flow-rate up to 3 ml/min, the curvature is more pronounced and is shifted to a lower  $\eta_{\text{spec}}$  range. A similar dependence on  $\eta_{\text{spec}}$  values has been observed for the width of the chromatogram, characterized by the standard deviation  $\sigma$ . It has been postulated<sup>2</sup> that the experimentally observed phenomena might be explained by non-Newtonian behaviour of concentrated polymer solutions at high shear stress. This high shear stress in flowing polymer solutions results in a decrease in the apparent viscosity, and in GPC experiments may result in a decrease in the change in elution volume due to viscosity phenomena. The decrease in the concentration effects in GPC at high flow-rates (10–30 ml/min) has also been observed by Little *et al.*<sup>7,8</sup> and could be explained by the same mechanism.

In this work, we have tried to verify the hypothesis that polymer solutions flowing through the porous media of GPC columns (or, more generally, in liquid chromatography under commonly used experimental conditions) may exhibit non-Newtonian behaviour and that such behaviour may substantially influence the chromatographic results.

## EXPERIMENTAL

The measurements were carried out with a liquid chromatograph 1084 A (Hewlett-Packard, Palo Alto, Calif., U.S.A.) provided with a sensor measuring the column inlet pressure at the given flow-rate. The column (250 × 4 mm I.D.) was packed with a porous spherical silica gel (Porasil B; Waters Assoc., Milford, Mass., U.S.A.) having a particle diameter of 35–40  $\mu\text{m}$ . The column was sited in a thermostatically controlled water jacket in order to provide constant temperature ( $25 \pm 0.02^\circ$ ). A Knauer Model 2025 differential refractometer (Knauer, Oberursel, G.F.R.) with an 8- $\mu\text{l}$  measuring cell was used as detector. The polystyrene (PS) standard (MW 670,000) had a polydispersity ratio ( $\overline{M}_w/\overline{M}_n$ ) < 1.05 and was supplied by Knauer. Tetrahydrofuran (THF) was distilled from copper(I) chloride and potassium hydroxide under a nitrogen atmosphere. The pure THF or a solution of the PS standard in THF was used as mobile phase in the experiments. The MW of this PS standard is largely above the exclusion limit of the column packing used<sup>2</sup>. The specific viscosity of the prepared PS standard solution in THF was calculated by using the Mark-Houwink equation<sup>9</sup>

$$[\eta] = 1.17 \cdot 10^{-2} M^{0.717} \quad (1)$$

which holds for linear PS in THF at 25°, and, by using the Huggins equation

$$\eta_{\text{spec}} = c[\eta] + c^2[\eta]^2 k_H \quad (2)$$

where  $[\eta]$  is the intrinsic viscosity,  $M$  is the molecular weight,  $c$  is the concentration,  $\eta_{\text{spec}}$  is the specific viscosity, and the Huggins constant,  $k_H = 0.362$  (see ref. 9). Measurement of the pressure corresponding to the given flow-rate was effected in a way such that the variation in pressure with time at constant flow-rate did not exceed

$\pm 0.1$  MPa. By using pure THF as mobile phase, steady conditions of pressure-flow-rate dependence were attained instantaneously. When the PS solution was used as mobile phase, the pressure was less stable especially at higher flow-rates; this instability effect was probably due to the automatic control unit of the flow-rate in the pumping system used in the liquid chromatograph.

## RESULTS AND DISCUSSION

Newton's law of viscosity expresses the dependence of the shear stress  $\tau$  per unit area on the local velocity gradient,  $dv/dy$ , as

$$\tau = -\mu dv/dy \quad (3)$$

where  $\mu$  is the viscosity of the liquid that is under different conditions of the shear stress constant. Liquids for which  $\mu$  is constant are called Newtonian liquids. For non-Newtonian liquids,

$$\tau = -\eta dv/dy \quad (4)$$

where  $\eta$  is not constant and may be expressed as a function of either  $dv/dy$  or  $\tau$ .

The notation  $\mu$  for the viscosity of Newtonian liquids and  $\eta$  for the apparent viscosity of non-Newtonian liquids is usual in the most physical publications. In the physical chemistry of polymer solutions, it is more common to use  $\eta$  (with corresponding indices) to express various quantities characterizing, *e.g.*, relative viscosity, specific viscosity or intrinsic viscosity, without simultaneous implication of the non-Newtonian character of the given system. In the region over which  $\eta$  decreases with increasing shear stress, the behaviour is termed pseudoplastic; in regions in which  $\eta$  values increase with increasing shear stress, the behaviour is termed dilatant.

The porous interstitial structure of the chromatographic column can be approximated by a statistical system of parallel circular capillaries<sup>10</sup>. For each capillary of given radius  $r$ , it can be shown<sup>11</sup> that

$$\tau = (\Delta P/2L)r \quad (5)$$

where  $\Delta P$  is the pressure drop along the capillary of the length  $L$ . The average shear stress in the column,  $\tau_{av}$ , can be calculated from the expression

$$r_{av} = r_{min.} \int_{min.}^{max.} \varphi(r) dr \quad (6)$$

where  $r_{av}$  is the average radius of the statistical set of capillaries representing the porous packing,  $\varphi(r)$  is the volume fraction of the capillary having the radius,  $r$  and the integral boundaries are the maximum and minimum capillary radii in the system. It then holds that

$$\tau_{av} = \int_0^r r_{av} \tau dr / \int_0^r r_{av} dr \quad (7)$$

From eqn. 5,

$$\tau_{av} = (\Delta P/2L)r_{av} \quad (8)$$

and, by substituting into eqn. 8 from eqn. 4,

$$-(\Delta P/2L)r_{av} = \eta(\dot{\gamma}/dr)_{av} \quad (9)$$

Since the quantities  $2L$  and  $r_{av}$  are constant for the given chromatographic column and express the permeability of the porous interstitial structure, we can write

$$|\Delta P| = \text{const. } \eta(dv/dr)_{av} \quad (10)$$

This equation shows that the change in the measured pressure drop in the column ( $\Delta P$ ) caused by changing the velocity gradient  $(dv/dr)_{av}$  in the column may indicate the possible non-Newtonian character of the mobile phase. The linear velocity,  $v$ , is calculated from the known volumetric flow-rate  $q$ , cross-sectional area of the column  $A$ , and porosity,  $\Phi$ , which is the ratio of the interstitial volume to the whole volume of the column, by using the relationship

$$v = q/(A\Phi) \quad (11)$$

In our experimental arrangement, the pressure at the outlet of the column was always equal to atmospheric. The excess pressure measured at the top of the column was in this case equal to the pressure drop in the column. The dependence of the pressure drop on the linear velocity of the mobile phase is shown in Fig. 1, in which curve a corresponds to pure THF, for which the dependence is linear in the range from 0 to ca. 0.7 cm/sec. At higher linear velocities, the dependence of  $|\Delta P|$  on  $v$  is curvilinear up to higher pressures (this slight curvature is probably due to the partial compressibility of THF), but no published data on the compressibility of THF has been found in order to verify this assumption). The influence of some experimental

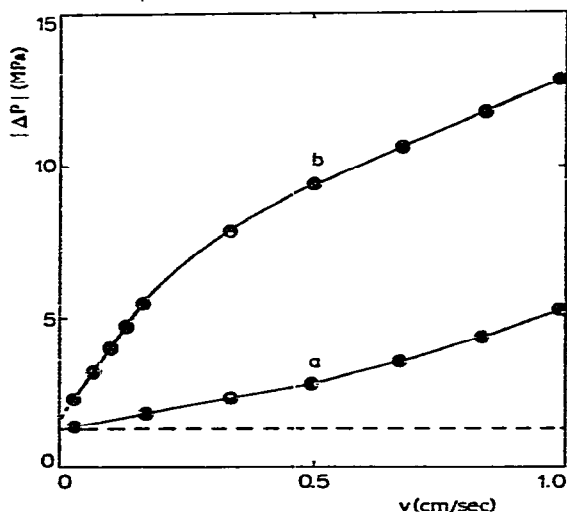


Fig. 1. Dependence of column inlet pressure on the linear velocity of the mobile phase; curve a, pure THF; curve b, solution of PS in THF.

errors, such as the non-linearity of the pressure-gauge response, cannot of course be avoided. The observed curvature could be explained by turbulence. We calculated the Reynolds number (from ref. 10)

$$Re = v d \rho / \mu \quad (12)$$

where  $\rho$  is the fluid density and  $d$  is the average particle diameter of the column packing or another quantity corresponding to the theory of the hydraulic radius.

For our experimental system with pure THF as mobile phase, we obtained an approximate value of 1 for  $Re$  at the maximum velocity ( $c$ ) of 1 cm/sec. According to known literature data, pronounced turbulence can occur<sup>11</sup> in the range  $2 < Re < 2000$ . Thus, in our experiments, there was no remarkable turbulence.

The pressure gauge in our liquid chromatograph exhibited some positive pressure value even at zero flow-rate. This caused the curves a and b on Fig. 1 to cross the  $\Delta P$  axis at approximately the same point, but not to pass through the origin.

Curve b in Fig. 1 shows the dependence of  $\Delta P$  on  $v$  when the solution of the PS standard in THF was used as mobile phase. The concentration of this solution was 1.883% (w/v), which corresponds to a relative viscosity,  $\eta_{rel}$ , of 8.287 [calculated by using the Mark-Houwink equation (eqn. 1) and the Huggins equation (eqn. 2)]. The dependence of  $\Delta P$  on  $v$  when the polymer solution is used as mobile phase is rectilinear from 0 to 0.17 cm/sec, and in this range the PS solution in THF behaves as a Newtonian liquid. The ratio of the slope of the linear part of the curve b to the slope of the curve a in its linear part, expressed as a first derivative,

$$(d\Delta P/dv)_b : (d\Delta P/dv)_a \quad (13)$$

should be equal to the relative viscosity  $\eta_{rel}$  of the PS standard solution with respect to the pure THF as can be seen from eqn. 10. The experimentally determined ratio of the slopes gives  $\eta_{rel} = 8.2$ , which is in good agreement with the value calculated from the known concentration and MW of the PS standard. At higher linear velocities, the graph of  $\Delta P$  versus  $v$  deviated widely from linearity down to lower pressures. This curvature indicates the decrease in the apparent viscosity,  $\eta$ , with increasing shear stress. Thus, the polymer solution obviously exhibits non-Newtonian behaviour in the range of shear stress investigated. According to the literature<sup>12</sup>, this solution should again behave as a Newtonian liquid at higher shear stress, but we do not seem to have reached this higher limit under our experimental conditions.

The dependence of  $\eta$  on the shear stress is a function of MW and the concentration for a given polymer<sup>12</sup>. When higher MWs and higher polymer concentrations are used, non-Newtonian behaviour occurs at lower shear stress values and the relative decrease in  $\eta$  is more pronounced. Our previous results<sup>1-6</sup>, dealing with the systematic investigation of concentration effects in GPC, indicated that viscosity phenomena in the interstitial volume (the hydrodynamic phenomena in its nature) make a predominant contribution to the over-all change in average elution volume, and in the width and shape of the elution curve with change in concentration of the injected polymer solution. The present results show that non-Newtonian behaviour of the polymer solution injected into the column in GPC (or, more generally, in liquid chromatography) obviously participate in the resulting concentration effects. The dependence

of the concentration effects [expressed, e.g., as the change in elution volume with change in concentration ( $dV_e/dc$ )] on the flow-rate of the mobile phase<sup>2,5,7,8</sup> is further experimental evidence of the effect of non-Newtonian behaviour. Since the average concentration and its distribution in the zone moving along the column change because of spreading and separation, the influence of non-Newtonian behaviour during elution changes accordingly. Some quantitative consequences of these phenomena are currently being studied.

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