

CHROM. 5131

SOME VELOCITY PROFILE EFFECTS IN EMPTY TUBES

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SUMMARY

Several investigators have observed that macromolecular solutes deviate from the dispersion behavior predicted on the basis of a parabolic velocity profile. These experimental observations are discussed in the light of numerical computations on unsteady state mass and momentum-transport with concentration-dependent viscosity.

INTRODUCTION

The viscosity of macromolecular solutions is rather sensitive to the molecular weight and concentration of the solute. It seemed desirable to determine the extent to which changes in viscosity might alter the velocity profile of dilute macromolecular solutions during laminar flow in empty tubes and to consider the effect of such changes in the velocity profile on the dispersion of macromolecules. In this paper, some results of a numerical study of this problem are presented. These results are of particular interest in connection with axial dispersion of solute in the injection system of gel permeation chromatographs.

DISPERSION OF SMALL SOLUTE MOLECULES

TAYLOR¹ demonstrated in 1953 that a solute flowing in the laminar regime in a tube is dispersed longitudinally about a plane that moves at the average velocity of the fluid as though it were diffusing about that plane in accordance with Fick's law of molecular diffusion, but with a dispersion coefficient defined by the expression

$$E = \frac{a^2 U^2}{48D} \quad (1)$$

In terms of the flow rate, the longitudinal dispersion coefficient is given by the equivalent expression

$$E = \frac{Q^2}{48\pi^2 a^2 D} \quad (2)$$

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According to these equations, longitudinal dispersion is enhanced by high velocities and large tube diameters and is diminished by large molecular diffusion coefficients.

ARIS² generalized TAYLOR's expression to include extremely slow flows, when molecular diffusion in the axial direction may become significant. When this is the case,

$$E = \frac{a^2 U^2}{48D} + D \quad (3)$$

However, in most practical flow situations, and especially with macromolecular solutes, D is negligible with respect to the first term. ARIS further generalized this expression by substituting a parameter κ for the constant factor $1/48$. The resulting expression for the dispersion coefficient is no longer restricted to a tubular geometry nor to a parabolic velocity profile:

$$E = \kappa \frac{a^2 U^2}{D} + D \quad (4)$$

For a parabolic velocity profile in a tube, $\kappa = 1/48$ as found by TAYLOR. For perfect plug flow, $\kappa = 0$ and there is no dispersion due to flow.

Axial dispersion arises then because of the existence of a velocity profile which causes material at the core of the tube to move faster than the average velocity, while material near the wall moves more slowly than the average velocity. In particular, when a Newtonian fluid of constant density and constant viscosity flows in a tube, material at the centerline moves at twice the average velocity, material in contact with the wall has zero velocity and intermediate velocities define a parabola. In the absence of molecular diffusion, this parabolic velocity profile causes material injected over a short time span to leave the tube over a longer time interval. Solute traveling near the centerline exits early, while material traveling near the wall exits considerably later.

However, when there is appreciable molecular diffusion, the situation is not quite as unfavorable. Near the tip of the velocity front, solute diffuses radially from the core into the more dilute periphery, and is slowed down. Small solute molecules, which have large molecular diffusion coefficients, thus exhibit smaller axial dispersion than they would in the pure convection regime. This is in accordance with the predictions of TAYLOR's equation.

THE DISPERSION OF MACROMOLECULES

ANANTHAKRISHNAN *et al.*³ determined the regions of applicability of the TAYLOR and ARIS equations on a map having as coordinates a dimensionless time parameter ($\tau = Dt/a^2$) and the Peclet number ($N_{Pe} = 2aU/D$). Because of the small molecular diffusion coefficients of macromolecules, the flow of macromolecular solutions tends to be characterized by large Peclet numbers, and convective effects dominate. However, in most practical situations, the time interval involved is such that numerical solutions must be used, since the analytical pure convection solution applies only up to very short times.

Most macromolecular solutes have molecular diffusion coefficients that are one to two orders of magnitude smaller than those of small solute molecules, and the TAYLOR-ARIS equations, as well as the numerical solution of the convective diffusion equation with a constant velocity profile, predict that macromolecules should be dispersed more than small solute molecules. However, some experimental evidence reported in the literature runs contrary to this expectation. BILLMEYER AND KELLEY⁴ removed all gel columns from a Waters gel permeation chromatographic (GPC) apparatus and studied the dispersion in the injection-detection system for two solutes: a low-molecular-weight solute, *o*-dichlorobenzene (ODCB), dissolved in tetrahydrofuran (THF) and a 0.1% solution of monodisperse polystyrene of molecular weight 160000 also dissolved in THF. They studied the dispersion of both solutes at a number of flow rates and found that in all cases the ODCB was dispersed more than the polystyrene, but they offered no definite explanation for this result. Inasmuch as TAYLOR's equation has been shown to be valid for small molecules by many investigators, one might conclude from KELLEY's experimental results that TAYLOR's equation does not apply for macromolecular solutes during laminar flow in tubes. More recently a considerable amount of valuable experimental data was presented by BIESENBERGER AND OUANO⁵. These authors obtained data on the dispersion in empty tubes of lengths ranging from 18 in. to 285 in. for both step and pulse inputs. Their data include solutions in toluene of *o*-dichlorobenzene and of narrow molecular weight distribution polystyrenes (PS) having molecular weights of 900, 20400, 97200 and 160000. They observed that the concentration and molecular weight of the polymer solute had a profound influence on dispersion in the empty tubing. As the concentration was increased from 0.03 g/dl to 0.6 g/dl, the concentration response to a step input increasingly resembled plug flow. Furthermore, at a given concentration, the behavior approximated plug flow more closely at the higher molecular weight (97200) than at the molecular weight of 20400. Finally, BIESENBERGER AND OUANO found that reducing the tube diameter from 0.1 cm to 0.048 cm yielded a closer approach to plug flow.

NUMERICAL STUDY

A numerical study of the dispersion of macromolecules during laminar flow has recently been completed at the University of Pittsburgh⁶. The results of this study are being reported in detail elsewhere⁷. Only aspects of the study specifically related to GPC injection will be discussed here. A computer program based on the simultaneous unsteady state solution of the convective diffusion equation and of the momentum equation was written and used to simulate the dispersion of a macromolecular solute during flow in a tube. The viscosity of the solution was assumed to follow the Huggins equation:

$$\eta = \eta_s(1 + [\eta]c + k'[\eta]^2c^2) \quad (5)$$

and Newtonian behavior was assumed to apply.

Computations for a step signal of a macromolecular solution displacing pure solvent indicated that the velocity distribution shifts from a parabolic profile to a flatter one as illustrated in Fig. 1. This shift is a transient phenomenon: the profile changes in time as well as along the tube length (Fig. 2). At the front of the step, the

profile flattens with time from a parabolic one to one that is intermediate between fully developed and plug flow. The rate at which this change occurs depends on the solute molecular weight and concentration, as well as on the tube diameter and flow rate. The flattening of the velocity profile is caused by the existence of a significant radial viscosity gradient. When there is such a gradient, the assumptions of constant viscosity and invariant velocity profile introduce error into the dispersion calculations. The concentration gradients, which give rise to viscosity gradients, increase as the Peclet number increases; and in accordance with the Huggins equation, radial concentration gradients give rise to significant viscosity gradients when the product $[\eta]c_0$ of the intrinsic viscosity times the solute concentration is sufficiently large.

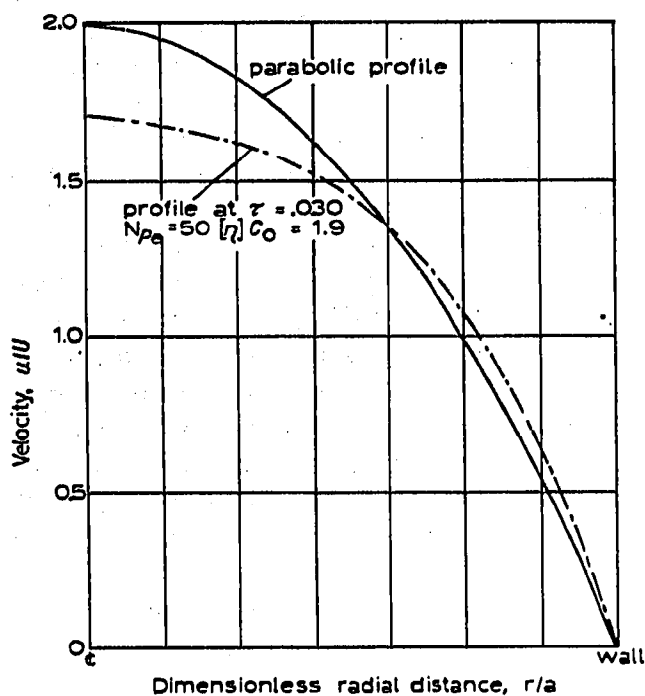


Fig. 1. Velocity profile.

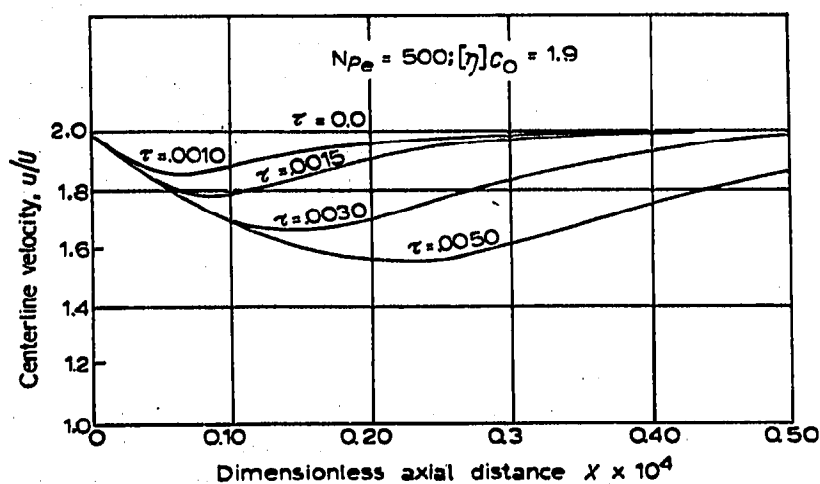


Fig. 2. Velocity profile in a tube of finite length.

Dimensional analysis indicates that the rate at which the velocity profile flattens depends on the Reynolds (N_{Re}) and Schmidt (N_{Sc}) numbers and on the dimensionless product $[\eta]c_0$. When these numbers are sufficiently large, the velocity profile predicted by our computations flattens rapidly and plug flow behavior is approached. At intermediate values, the velocity profile flattens more slowly and reaches an equilibrium value that is nearer to a parabolic profile. At very low Peclet numbers or small $[\eta]c_0$ values, changes in the velocity profile may be negligible.

Table I gives the results of computer simulations of the flow of polymer solutions of several molecular weights and concentrations. The conditions correspond to those used by BIESENBERGER AND OUANO in their experimental work (tube diameter 0.1 cm, flow rate 0.95 cm³/min). The solvent used by these authors was toluene and the solutes were a series of anionic polystyrenes of narrow molecular weight distribution available from the Pressure Chemical Company. Our computations included in addition polystyrene of 860 000 mol. wt.

TABLE I

COMPUTED PERCENT DECREASE IN CENTERLINE VELOCITY DURING FLOW OF POLYSTYRENE SOLUTIONS

<i>Mol. wt.</i>	$[\eta]$	0.15 g/dl	0.30 g/dl	0.60 g/dl
20 400	0.12	0.42		1.66
97 200	0.27	0.94		3.61
160 000	0.34		2.26	4.35
860 000	0.79	2.40	4.70	8.60

Table I shows that there is some decrease in the centerline velocity even at relatively low polymer concentrations and molecular weights. The effect of this flattening of the velocity profile is in qualitative agreement with the results reported by BIESENBERGER AND OUANO. With a parabolic velocity profile and the low molecular diffusion coefficient characteristic of macromolecules, the first solute molecules would be expected to emerge at a dimensionless retention volume of 0.5.

With a flatter velocity profile, the first solute molecules should emerge later, but the rise in concentration should be sharper. These effects are expected to be insignificant at very low molecular weights and small solute concentrations, but should become more significant as solute molecular weight and concentration increase. The calculations also predict that the step input elution curves for the smaller (0.05 cm diameter) tube should break through later and should be steeper than for the larger (0.1 cm diameter) tube. However, even though these results offer a qualitative explanation, these computations do not predict effects of the magnitude observed by BIESENBERGER AND OUANO at these molecular weights and concentrations.

NON-NEWTONIAN EFFECTS

FOX *et al.*⁸ studied the effect of the rate of shear on the viscosity of dilute solutions of polyisobutylene. Their results and those of other investigators indicate that most polymer solutions are Newtonian at very low and very high shear rates, but deviate from Newtonian behavior at intermediate shear values. Such deviations are very important at high molecular weights and moderate to large concentrations,

as shown for instance by SEGAL AND GRAESSLEY⁹ for solutions of polystyrenes in benzene. Deviations from Newtonian behavior at the relatively high shear rates prevailing near the tube wall would reinforce the flattening of the velocity caused by the radial concentration gradient.

For a power law fluid, the laminar velocity profile is given by the expression:

$$u = U \left(\frac{3n + 1}{n + 1} \right) \left[1 - \left(\frac{r}{R} \right)^{\frac{n + 1}{n}} \right] \quad (6)$$

The flow index n is 1.0 for Newtonian fluids, but is less than 1.0 for pseudoplastic polymer solutions.

The differential equation for pure convection

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = 0 \quad (7)$$

with step input boundary conditions, has the solution

$$C_m = \left(1 - \frac{X}{\tau} \right)^{2n/(n+1)} = \left(1 - \frac{x}{\left(\frac{3n + 1}{n + 1} \right) Ut} \right)^{2n/(n+1)} \quad (8)$$

This equation tends to be valid for short tubes, but increasingly large deviations from the pure convection solution are to be expected as the tube length is increased. In deriving eqn. 8, it was assumed that the fluid which is displaced also has flow index n . Fig. 3 shows a plot of this solution for several values of the flow index n .

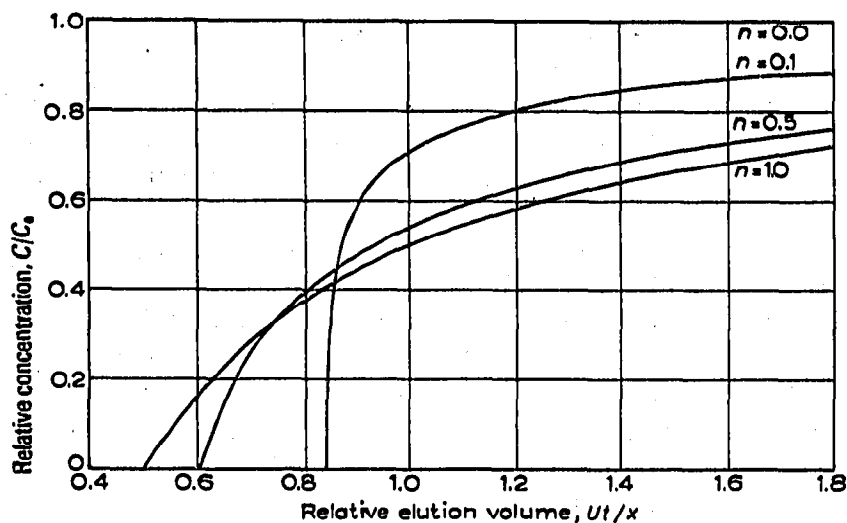


Fig. 3. Pure convection solution.

As the flow index decreases, the behavior of the elution curves is reminiscent of the results obtained by BIESENBERGER AND OUANO at the higher concentrations and molecular weights. However, published data on the shear rate dependence of the viscosity lead to the expectation that higher molecular weights and concentrations would be required for significant non-Newtonian effects. Additional numerical work is in progress at the present time to determine to what extent velocity profile effects might account for the observed anomalies.

With a pulse signal normally used in GPC, the effects are even more complex than for a step signal, as there are two discontinuities in concentration instead of the single discontinuity present with a step. Our computer program has provisions for a pulse input and numerical computations are planned for this type of signal.

CONCLUSIONS

The dispersion of macromolecular solutes during laminar flow in an empty tube has been studied numerically for a step input assuming Newtonian behavior and no chain entanglements. The computations predict a flattening of the velocity profile which provides at least a partial explanation of the experimental results of BILLMEYER AND KELLEY⁴, and of BIESENBERGER AND OUANO⁵. However, the computed decrease in dispersion was of considerably lesser magnitude than the experimental results reported in the literature. Any deviation from Newtonian behavior at high shear rates would cause a further flattening of the velocity profile and a further decrease in dispersion.

NOTATION

a	= tube radius, cm
c	= concentration, g/dl
c_0	= concentration of step signal
C_m	= average concentration over a cross-section
D	= molecular diffusion coefficient, cm ² /sec
E	= axial dispersion coefficient, cm ² /sec
k'	= Huggins constant, dimensionless
n	= flow index, dimensionless
N_{Pe}	= Peclet number, $2aU/D$, dimensionless
N_{Re}	= Reynolds number, $2aU/\nu$, dimensionless
N_{Sc}	= Schmidt number, ν/D , dimensionless
Q	= volumetric flow rate, cm ³ /sec
r	= radial distance from tube centerline, cm
U	= average velocity, cm/sec
u	= velocity, cm/sec
x	= axial distance, cm
X	= dimensionless axial distance, x/aN_{Pe}

GREEK SYMBOLS

η	= viscosity of solution, poises
η_s	= viscosity of solvent, poises
$[\eta]$	= intrinsic viscosity, dimensionless
κ	= factor in ARIS equation, dimensionless
ν	= kinematic viscosity, cm ² /sec (= η/ρ)
τ	= dimensionless time, Dt/a^2

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