# Taylor Dispersion in a Polymer Solution Flowing in a Capillary Tube

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Tracer dispersion in polysaccharide (scleroglucan) solutions flowing through 0.56mm-ID capillary tubes was studied experimentally. In contrast with experiments modeling enhanced recovery processes, the polymer concentration remains constant during a given experiment, while the tracer concentration varies. A preparation procedure giving stable rheological characteristics is described, as well as their dependence on the polymer concentration  $C_p$  (100 mg/L  $\leq C_p \leq 2{,}000$  mg/L). Dispersion measurements are performed with ionic tracers at Péclet numbers between 100 and 2,000. Dispersion coefficient K increases as the square of the Péclet number, showing that the Taylor dispersion mechanism remains dominant. At a constant flow velocity, K decreases by about 75% when  $C_p$  increases from 0 to 2,000 mg/L. This variation is related to the flattening of the velocity profile and can be predicted both with a power-law rheological model and Monte Carlo simulations. The extension of these measurements to heterogeneous porous media is discussed.

#### Introduction

Polymer solutions have extremely widespread applications in domains of the food industry and of petroleum or chemical engineering (de Gennes, 1979; Sorbie, 1991). A key feature is the nonlinear rheological properties of these fluids (Ferry, 1970; Bird et al., 1964, 1977). These properties induce strong variations of the velocity profiles and flow distributions compared to those observed for a Newtonian fluid. In this article, we detect such changes by comparing tracer dispersion in capillary tubes with Newtonian fluids and polymer solutions of different concentrations. The rheological characteristics of the fluid then represent tunable parameters allowing us to investigate the structure of the flow field.

In our experiments, we use ions as a passive tracer. A polymer solution containing a soluble salt displaces another solution with the same polymer concentration but a different salt content. Tracer concentration variations are detected by conductivity measurements. These experiments strongly differ from other modeling oil recovery processes (Sorbie, 1991), in which polymer solutions displace or are displaced by Newtonian fluids. Similar processes have been studied in capillary tubes used for polymer separations (Janca, 1982).

For tracer dispersion in capillary tubes, Taylor dispersion is the dominant mechanism for Newtonian fluids (Taylor, 1953; Aris, 1956). It involves a balance between (a) velocity gradients due to the Poiseuille velocity profile in the tube and (b) molecular diffusion across its section. The former induces a spreading that increases linearly with time; the latter homogenizes the tracer distribution. At times large compared to the characteristic transverse diffusion time:  $\tau_D = R^2/D_m$  (R is the tube radius and  $D_m$  the molecular diffusion constant), one reaches a Gaussian dispersion regime described by the convection-diffusion equation (Dullien, 1991)

$$\frac{\partial C_t}{\partial t} + U \cdot \frac{\partial C_t}{\partial z} = K \frac{\partial^2 C_t}{\partial z^2},\tag{1}$$

where U and  $C_t$  are the average of the flow velocity and the tracer concentration across the tube section, and z is parallel to the tube axis. The longitudinal dispersion coefficient K verifies, for a Newtonian fluid (Aris, 1956),

$$K = \frac{R^2 U^2}{48 D_m} + D_m. {2}$$

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The additive term  $D_m$  represents the effect of pure longitudinal molecular diffusion and is negligible in the range of Péclet numbers corresponding to our experiments.

When the flowing fluid is a shear-thinning polymer solution, the flow profile is no longer parabolic, but flat near the tube axis with larger velocity gradients at the walls. These distortions of the flow profile increase with the polymer concentration: they influence the dispersion process in two ways since both the convective spreading in the central part and the diffusion time across the large velocity gradients near the walls are reduced. These two effects tend to decrease the overall dispersion; we shall verify it both experimentally and numerically.

In the first part of the article, we describe the preparation of the polymer solutions used in the experiments and their rheological characterization, verifying that the solutions have perfectly reproducible and stable properties.

Then we describe dispersion experiments performed in cylindrical capillary tubes with various polymer solutions of different concentrations in a broad range of flow velocities. We observe that the Taylor mechanism remains dominant and that the dispersion coefficient decreases significantly when the polymer concentration increases. This result is derived quantitatively both theoretically assuming a simple power-law rheological characteristic and numerically using flow profiles deduced from the actual rheological curves.

Finally, we discuss the extension of such experimental approaches to the analysis of the heterogeneities of porous media.

#### Choice and Characterization of Polymer Solution Preparation of polymer solutions

We performed the experiments with a polysaccharide solution of scleroglucan (Elf-Sanofi). Scleroglucan is a neutral polymer with semirigid molecules (Bluhm et al., 1982; Biver, 1986). We chose it because of its nonionic character, which makes its structure and properties nearly independent of the salt content of the solution (Müller et al., 1986). This allows us to perform dispersion experiments with a salt tracer (sodium nitrate, NaNO<sub>3</sub>) detected through conductivity measurements. In aqueous solution, the molecules have the shape of a semiflexible triple helix, that is, their length is about  $10^{-6}$  m, their diameter  $2\times10^{-9}$  m, and their persistence length  $1.8\times10^{-7}$  m. Polymer concentrations range from 100 to 2,000 mg/L. Higher values give unstable and poorly reproducible rheological characteristics, while solutions with polymer concentrations lower than 100 mg/L are almost Newtonian.

The solutions are prepared by letting the polymer dissolve very slowly through mild stirring for several hours, then letting the solution rest for a day, after which it is homogenized for two hours. Then aggregates are eliminated by two successive filtrations through Millipore membranes with respective pore diameters of 5  $\mu$ m and 0.8  $\mu$ m. A low flow rate is used to avoid the deformation or breaking of the microgels and the polymer molecules by an excessive shear. Then a bactericide (NaN<sub>3</sub>) is added to the solution, which is stored under a nitrogen atmosphere.

We use the following filtrability test to verify the quality of the solution and the degree of elimination of the microgels (Chauveteau and Kohler, 1984): when the polymer solution flows slowly through a membrane, the pressure drop across it increases initially and reaches a stable value. The duration and constancy of this plateau region before the pressure increases again are indicators of the stability of the rheology of the solution.

#### Rheological characterization of the solution

Several rheological measurement devices have been used: (a) a Carrimed CSL 100 cone-plate rheometer (shear rates from  $3\times10^{-2}$  to  $500~{\rm s}^{-1}$ ); (b) a low shear 30 coaxial cylinders rheometer (shear rates from  $2\times10^{-2}$  up to  $10^2~{\rm s}^{-1}$ ); and (c) two capillary Teflon tubes with internal diameters of 0.8 and 1.45 mm, respectively (wall shear rates  $\dot{\epsilon}_w$  between 1 and  $10^4~{\rm s}^{-1}$ ). In all cases, we determine the effective viscosity  $\eta_{\rm eff}(\dot{\epsilon})$  equal to the ratio of  $\tau$  (shear stress) to  $\dot{\epsilon}$ . For the coaxial-cylinders and cone-plate rheometers,  $\dot{\epsilon}$  is assumed to be constant in the flow volume.

For capillary tubes, we measure the pressure drop per unit length  $\Delta P/L$  for various tube lengths L in order to correct for entrance effects. The shear stress at the walls is given by  $\tau_w = 0.5 \ R\Delta P/L$ ; then, provided there is a unique relation between  $\tau$  and  $\dot{\epsilon}$  in the fluid, the corresponding shear-rate  $\dot{\epsilon}_w$  verifies (Bird et al., 1964, 1977)

$$\dot{\epsilon}_{w} = -f(\tau_{w}) = -\frac{1}{\pi R^{3}} \left( \frac{dQ}{d\tau_{w}} \tau_{w} + 3Q \right) \tag{3}$$

where Q is the total volume flow rate and  $f(\tau_w)$  is determined from the variation of Q with  $\Delta P$ .

The dependence of  $\eta_{\rm eff}$  on  $\dot{\epsilon}$  measured for the same 2,000 mg/L scleroglucan solution with different techniques is shown in Figure 1. Even though the solution is strongly non-Newtonian, all measurements coincide quite well but for an upward deviation of the cone-plate rheometer curve for  $\dot{\epsilon} > 500~{\rm s}^{-1}$ . We believe that this deviation reflects the additional dissipa-

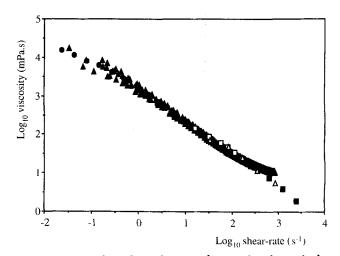


Figure 1. Effective viscosity vs. shear-rate characteristics of a 2,000 mg/L scleroglucan solution.

■, Capillary tubes; ●; coaxial cylinders rheometer; A, cone-plate rheometer; □, 1.5-mm-ID tube with 900- $\mu$ m-OD beads; A, 1.5-mm-ID tube with 370- $\mu$ m-OD beads. Pure water would correspond to the horizontal line  $\text{Log}_{10}$  ( $\eta_{\text{eff}}(\text{mPa} \cdot \text{s})$ ) = 0.

tion associated with secondary flows appearing at high velocities. These flows are due to unbalanced centrifugal forces generated by the rotation of the cone. For all rheometers,  $\eta_{\rm eff}$  decreases with a power law behavior over a significant range of  $\dot{\epsilon}$  values; however, at the lowest shear rates ( $\dot{\epsilon} \approx 10^{-1} - 10^{-2} \ {\rm s}^{-1}$ ) the onset of a pseudo-Newtonian constant viscosity regime is observed.

In Figure 1, the open symbols correspond to data points obtained in 1.5-mm-ID capillary tubes packed with glass beads of respective diameters (857–1,100  $\mu$ m) and (350–390  $\mu$ m); the beads are cleaned with sulfochromic acid and rinsed with ultrapure water prior to packing. For these experiments, the effective viscosity is taken equal to the ratio of the pressure drop measured for the flow of the polymer solution to that for pure water at the same flow rate. The shear rate at the pore walls is estimated crudely by a parallel channel model, taking into account the spatial pore size variations and is similar to that described by James and McLaren (1975). The quantitative agreement between the  $\eta_r(\dot{\epsilon})$  characteristic obtained with these approximations and that corresponding to other methods may therefore be fortuitous; the important feature is the fact that, despite the complex structure of the flow field in these media, the overall dependence of  $\eta_{\rm eff}$  on  $\dot{\epsilon}$ is the same as for simpler geometries. This contrasts with the viscoelasticity effects observed at some shear rates by James and McLaren (1975) on Polyox solutions in similar geometries. A possible explanation for this is the different conformations of the two molecules (flexible for polyox and semirigid for scleroglucan) that strongly influence the rheological properties (Chauveteau, 1982). The viscoelastic effects may also have been reduced by our filtration procedure and by the large size of the pores of our samples.

We conclude from the preceding results that the rheological characteristics of the scleroglucan solutions are independent of the flow geometry in a range of channel widths from about 100  $\mu$ m up to several mm. This is an encouraging feature for their use as time-independent nonlinear fluids in tracer dispersion experiments.

### Dependence of rheological characteristics on polymer concentration

Figure 2 displays, in the same log-log coordinates as Figure 1, the variation of  $\eta_{\rm eff}$  with  $\dot{\epsilon}$  for several aqueous solutions with scleroglucan concentrations between 100 and 2,000 mg/L. The rheological measurements have been performed with the cone-plate rheometer. As for  $C_p = 2,000$  mg/L, all curves display a power law dependence  $\eta_{\rm eff} \propto \dot{\epsilon}^{n-1}$  ( $\tau \propto \dot{\epsilon}^n$ ) over a broad range of shear rates. The values of the exponent n determined from a regression on the linear part of the curves are shown in Table 1. The dotted straight lines in Figure 2 correspond to this regression, and their slope is n-1. Here n is always between 0 and 1 and is equal to 1 for a Newtonian fluid. The complete rheological curves are well fitted by semiempirical models such as that of Cross (1965), which predicts the following dependence of  $\eta_{\rm eff}$  on  $\dot{\epsilon}$ :

$$\frac{\eta_{\text{eff}} - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (\tau_r \dot{\epsilon})^m}.$$
 (4)

The values of the parameters of Eq. 4  $(\eta_0, \eta_\infty, \tau_r, \text{ and } m)$  are

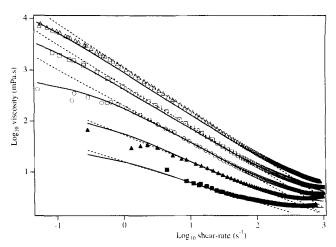


Figure 2. Effective viscosity vs. shear-rate characteristics of scleroglucan solutions of various concentrations.

 $\Delta,\,2,000$  mg/L;  $\Box$  , 1,500 mg/L;  $\bigcirc$  , 500 mg/L;  $\blacktriangle$  , 200 mg/L;  $\blacksquare$  , 100 mg/L.

also given in Table 1 for the various polymer concentrations used in our experiments. The continuous lines in Figure 2 are obtained by using Eq. 4 with these sets of values (the upward deviation of the data points from the theoretical curve is, as in Figure 1, due to secondary flow effects in the rheometer).

### Reproducibility and influence of control and environmental parameters

We finally verified the reproducibility and stability of the rheological properties. All these control experiments were performed with the 2,000 mg/L solution, which is the most prone to structural modifications and to irreversible rheological changes.

The reproducibility of the flow characteristics from one solution to another is first greatly improved by the filtering process, indeed, the latter reduces from 10% to less than 2% the relative dispersion of the values of the shear stress  $\tau$  at a given shear rate  $\dot{\epsilon}$  and polymer concentration,  $C_p$ . The rheological characteristics of the filtered solutions varied by less than 0.5% over a period of 45 days.

We also estimated the thixotropy of the solution by analyzing plots of  $\tau$  vs.  $\dot{\epsilon}$  obtained by sweeping the whole shear rate range, first in the ascending direction and then in the

Table 1. Variation with the Polymer Concentration of the Experimental Exponent n of the Rheological Law  $\tau = k \dot{\epsilon}^n$ , of the Ratio  $K/K_w$  of the Dispersion Coefficients Computed from Eq. 3 for the Polymer Solution and Water and of the Parameters of the Cross Model Represented by Eq. 4

$C_p$ (mg/L)	n	K/K <sub>w</sub>	$\eta_0$ (Pa·s)	$\eta_{\infty}$ (Pa·s)	$\frac{\tau_r}{(s)}$	m
0	1.00	1.00	n.a.	n.a.	n.a.	n.a.
100	0.60	0.77	0.03	0.0018	0.95	0.74
500	0.50	0.62	0.15	0.00215	2	0.75
1,000	0.29	0.44	0.75	0.0022	4.5	0.78
1,500	0.19	0.28	9.5	0.0027	45	0.80
2,000	0.16	0.23	28	0.0032	54	0.85

descending direction. Different sweep durations were used, but the relative shift between the two curves was never higher than 5%; it is slightly reduced by filtering and by using slower variations of  $\dot{\epsilon}$ . We also compared the rheological properties of the solution before and after it has flown through the capillary tubes used for the experiments. The variations of  $\tau$  for a given shear rate were less than 5%. A final indication of the small influence of the thixotropy of the solution in the experiment is given by the flow measurements on glass bead packings discussed previously. In such systems, much larger and faster shear-rate variations are indeed experienced than in capillary tubes, however, we observed that the viscosity-shear-rate characteristic is weakly perturbed.

As expected, the rheological characteristics depend on temperature: for  $\dot{\epsilon}=1{,}000~\text{s}^{-1},~\tau$  decreases by about 20% when the temperature varies from 25 to 37°C. For that reason, the temperature of the experimental setup was regulated at  $25\pm1^{\circ}\text{C}$ .

Finally, we verified that the solution remained stable and that the relative variation of its rheological characteristics was less than 0.5% when a 10% concentration of NaCl by weight was added. This makes it suitable for dispersion measurements with ionic tracers.

#### Rheological characterization experiments

The study referred to in the section title shows that the rheological properties of our scleroglucane solutions are stable and independent of the environmental parameters. These properties can be considered as simple, nonlinear fluids for flows through channels and porous media with large enough apertures so that elongational viscosity and viscoelasticity effects can be neglected. In the present study we use large capillary tubes (0.56 mm ID), which allow us to avoid these problems.

## **Taylor Dispersion Experiments for Scleroglucan Solutions in Capillary Tubes**

#### Experimental procedure

The dispersion experiments are performed in vertical Teflon capillary tubes that have a length of L = 1.5 m and an internal diameter of 2R = 0.56 mm. Either of two NaNO<sub>3</sub>polymer solutions of salt concentrations of 1 g/L and 1.5 g/L. respectively, is injected at the bottom of the tube by a constant flow-rate syringe pump. A low volume conductivity detector placed at the outlet of the tube allows one to monitor the variations of the salt concentration in the outflowing solution. After abruptly switching the injection from one solution to the other at the initial time (Charlaix et al., 1987a), one monitors subsequent variations of the outlet concentration. The experimental concentration variation at the outlet has an error-function-like shape (Figure 3). The mean delay between the variations at the inlet and the outlet gives the effective tube volume, and the width of the step is related to the dispersion coefficient K.

This measurement may be perturbed by gravitation-driven instabilities that are due to vertical concentration gradients and by secondary flows in curved tubes (Ermin-Erdogan and Chatwin, 1967). These effects are important for large diameters and low viscosity fluids. We therefore used straight verti-

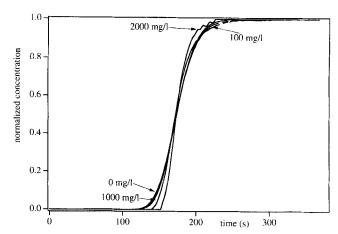


Figure 3. Experimental dispersion curves for water and water-polymer solutions.

cal small-diameter tubes and verified that the dispersion coefficient for pure water is identical when the lighter fluid is either below or above the heavier one.

We also verified that entrance effects at the inlet of the tube were negligible by comparing dispersion coefficients measured for 1.5-m-long tubes to those obtained for shorter ones. These values are identical for pure water and we assumed, for polymer solutions, that the entrance effect would be still smaller since the velocity profiles are flatter.

#### Experimental dispersion at various polymer concentration

Experimental curves obtained at the same Péclet number Pe = 2,000 with scleroglucan solutions of polymer concentrations 0, 100, 1,000 and 2,000 mg/L are shown in Figure 3. Concentration variation fronts are markedly sharper for the two most concentrated polymer solutions ( $C_n = 1,000$  and 2,000 mg/L) than for pure water  $(C_p = 0)$  or for  $C_p = 100$ mg/L. This confirms qualitatively that the flattening of the velocity profile at high polymer concentrations reduces the Taylor dispersion coefficient. This also confirms the theoretical expectation that, even for viscous concentrated solutions, the molecular diffusion coefficient  $D_m$  of ions in water is not strongly modified. If  $1/D_m$  were proportional to the macroscopic viscosity, as is the case for pure liquids, the Taylor dispersion coefficient would increase according to Eq. 2. In the rest of the article,  $D_m$  is therefore taken equal to the value  $1.15 \times 10^{-9}$  m<sup>2</sup>/s for pure water.

## Experimental variations of the longitudinal Taylor dispersion coefficient for non-Newtonian polymer solutions

The "Gaussian" dispersion coefficient  $K_g$  is determined by fitting the experimental curves to solutions of the Gaussian convection-diffusion equation, Eq. 1 (Charlaix et al., 1987a). The fit is excellent, with no trace of tail effects, which indicates that no complexation of ions on the polymer molecules or the aggregates occurs.  $K_g$  is determined within  $\pm 7\%$ .

Figure 4a displays the variation of the ratio  $K_g/U^2$ , with the Péclet number  $100 \le Pe = UR/D_m \le 2{,}000$  for various polymer solutions  $(0 \le C_p \le 2{,}000 \text{ mg/L})$ . For pure water,  $K_{rw}/U^2$  is constant and of the order of 1.4 s  $(\pm 5\%)$ , in

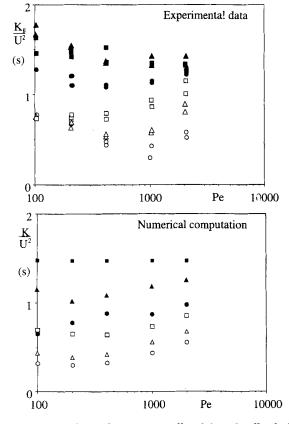


Figure 4. Variation of the normalized longitudinal dispersion coefficient  $K/U^2$  with the Péclet number  $Pe = UR/D_m$ .

(a) Experimental data; (b) numerical computations.  $\blacksquare$ , pure water;  $\triangle$ , 100 mg/L;  $\bigcirc$ , 500 mg/L;  $\square$ , 1,000 mg/L;  $\triangle$ , 1,500 mg/L;  $\bigcirc$ , 2,000 mg/L.

agreement with the theoretical value  $R^2/48D_m = 1.42$  s. For all polymer solutions,  $K_g/U^2$  is also about constant within  $\pm 15\%$ , although there seems to be a shallow minimum in some curves ( $Pe \cong 500-1,000$ ). Although, for  $C_p = 100$  mg/L,  $K_g/U^2$  is close to the pure water value (and even slightly higher at low velocities), it decreases steadily for higher polymer concentrations.

This reduction is displayed in Figure 5a, in which  $K_g/K_{gw}$  is plotted as a function of the exponent (1-n), used in this case to characterize the degree of nonlinearity of the fluid. The curves obtained at different Péclet numbers are very similar (the values for Pe = 2,000 are slightly larger). In all cases,  $K_g/K_{gw}$  decreases by a factor of 3 between  $C_p = 0$  and 2,000 mg/L.

## Numerical Computation of the Taylor Dispersion Coefficient

## Theoretical expression of the Taylor dispersion coefficient for a non-Newtonian power law fluid

The Taylor approximation (Taylor, 1953) for the determination of the dispersion coefficient in a capillary tube with a laminar flow is easily adapted to time-independent fluids with nonlinear rheological characteristics. This amounts to a generalization of the local Fick's law  $\mathbf{f} = -D_m$  grad  $c_t$  into a

macroscopic relation  $F = -K\partial C_t/\partial z - (\mathbf{f} \text{ and } F \text{ are, respectively, the local diffusion flux and its average across a tube section, <math>c_t$  and  $C_t$  are the local and the mean concentration, K is the Taylor dispersion coefficient). Assuming a quasi-stationary tracer concentration distribution moving at the mean fluid velocity U and of a longitudinal concentration gradient  $\partial c_t/\partial z$  constant with the distance r to the tube axis z, one obtains

$$K = \frac{2}{D_m R^2} \int_0^R \frac{1}{r} \left( \int_0^r \xi(v_z(\xi) - U) \, d\xi \right)^2 dr \tag{5}$$

in which  $v_z(\xi)$  is the axial velocity for  $r = \xi$ . One verifies that Eq. 5 reduces to the classical Taylor expression, Eq. 2, for a parabolic Poiseuille velocity profile. Longitudinal molecular diffusion results in an additive term of the order of  $D_m$  in Eq. 3 (Aris, 1956). It can be neglected in our experiments, for which the Péclet number is high ( $\ge 100$ ).

Let us now analyze the case of power law fluids for which the shear stress  $\tau_{rz}$  is related to the shear rate  $\dot{\epsilon} = \partial v_z/\partial r$  by  $\tau_{rz} = k \dot{\epsilon}^n$ . Assuming a one-dimensional flow with only one nonzero velocity component, one readily computes the flow velocity profile  $v_z(r)$  from the equation of motion of the fluid. Using Eq. 5 to determine the longitudinal Taylor dispersion coefficient K, one obtains:

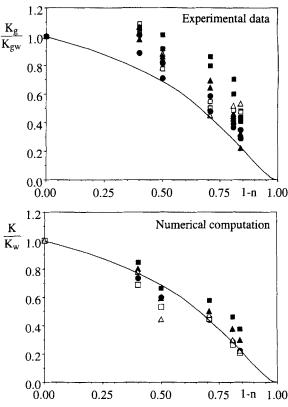


Figure 5. Dependence of the normalized dispersion coefficient  $K/K_w$  on the exponent 1-n characterizing the deviation from a Newtonian behavior.

(a) Experimental data; (b) numerical computations.  $\blacksquare$ , Pe = 2,000;  $\triangle$ , Pe = 1,000;  $\bigcirc$ , Pe = 500;  $\Box$ , Pe = 250;  $\triangle$ , Pe = 100. The continuous line is deduced from Eq. 6.

$$K = \frac{R^2 U^2}{2D_m} \frac{n^2}{(1+3n)(1+5n)} \,. \tag{6}$$

For n = 1 (Newtonian fluid), Eq. 6 reduces to the high Péclet number limit of Eq. 2 (the corresponding value of K for pure water will be referred to as  $K_w$ ).

The values of  $K/K_w$  given by Eq. 6 are independent of U and correspond to the dotted lines in Figure 5a and b. These values decrease with n, and therefore with the polymer concentration, as observed experimentally. The relative variation has the right order of magnitude and qualitative shape, although it is larger than the observations by about 10-20%. This indicates that flow profile variations indeed explain the decrease of the Taylor dispersion coefficients for shear-thinning, non-Newtonian fluids.

### Numerical computation of the Taylor dispersion coefficient for polymer solutions used in the experiments

To quantitatively confirm these results, we computed numerically the flow profile  $v_z(r)$  in the capillary tube by integrating the equation of motion, using the complete actual rheological characteristic  $\tau_{rz}(\partial v_z/\partial r)$  measured experimentally (Figure 2). Then K is obtained by another numerical integration using Eq. 5 and values of  $v_z(r)$  computed at 500 different distances r from the axis. We computed  $K/K_w$  for all experimental values of the longitudinal pressure gradient and for the rheological characteristics corresponding to all polymer concentration values actually used in the experiment.

The variations with the Péclet number of the ratios  $K/U^2$ obtained with this procedure are shown in Figure 4b for several polymer concentrations: the weak dependence on Pe is in good quantitative agreement with the experimental observations, although  $K/U^2$  seems to increase slightly with the Péclet number. A similar conclusion is reached by comparing Figures 5a and b, in which the ratio  $K/K_w$  is plotted as a function of the parameter 1-n (equal to 0 for Newtonian fluid). The same strong decrease by a factor of 2.5-3 is observed between solutions of concentrations 0 mg/L and 2,000 mg/L, both in the experimental and numerical curves. The numerical curves at the highest Péclet numbers also give dispersion coefficients that are slightly larger than those predicted for power law fluids (Eq. 10) for the three most concentrated solutions. This is expected since the actual experimental viscosity used in the numerical computation varies more slowly with the shear rate than an ideal power law, particularly at low and high shear rates.

#### **Discussion and Conclusions**

In the present work we have shown the feasibility of tracer dispersion measurements using polymer solutions as a carrier fluid with nonlinear rheological characteristics. Scleroglucan solutions with reproducible and stable rheological properties insensitive to moderate shear rates have been prepared; sodium ions do not modify the structure of the polymer and do not complex on it, so they can be used as passive tracers. We have demonstrated experimentally that Taylor dispersion in capillary tubes is very sensitive to flow profile changes due to the fluid rheology. The flattening of the flow profiles for a shear-thinning polymer solution results in a decrease by a

factor of 2.5 to 3 of the dispersion coefficient for 2,000 mg/L solutions. These variations follow well both theoretical predictions, assuming power-law rheological characteristics and computations based on the actual velocity profile calculated from the complete rheological curves. Let us point out that similar effects have been predicted theoretically for liquid chromatography in capillary tubes using electroosmotic flows (Martin et al., 1985).

One interesting future development of such measurements is their extension to porous media for which dispersion is mostly associated to velocity variations from one pore to another (Dullien, 1991; Koch and Brady, 1985). For shear-thinning fluids, velocity contrasts inside the porous medium as well as the disorder of the flow field should be increased. Such effects will be particularly important when the distribution of the permeability of individual flow channels and of local flow velocities is very broad. Then, most of the flow takes place through a subset of the flow channels including the largest ones (Charlaix et al., 1987b). In such media, tracer dispersion is largely determined by the structure of the sublattice and the diffusive or convective exchange between slow and fast channels (de Arcangelis et al., 1986). We then expect tracer dispersion to be strongly modified for nonlinear fluids (Chaplain et al., 1992). Let us also point out that a great deal of theoretical work has been devoted to representations of the transport properties of plastic or nonlinear fluids in porous media (Adler and Brenner, 1984; Sorbie, 1991; Vradis and Protopapas, 1993).

In conclusion, dispersion measurements in which the polymer content is kept constant and only the tracer concentration is varied provide a powerful nonlinear probe of the structure of complex flow systems; it will be particularly well adapted to porous media. Although dispersion is a macroscopic measurement associated with global transit times of tracer particles, its nonlocal nature makes it sensitive to the local flow structures. One particularly interesting feature is the fact that the degree of nonlinearity can be tuned by changing the polymer concentration.

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#### Notation

m = characteristic exponent in Cross model

 $\eta_0$  = zero shear-rate limit viscosity in Cross model

 $\eta_{\infty}$  = high shear-rate limit viscosity in Cross model

 $\tau_r$  = characteristic relaxation time in Cross model

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