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Study of the flow development of polymer solutions through capillaries*

José Pérez-González[**], **Lourdes de Vargas**[†] and **José Tejero**

Departamento de Ciencia de Materiales, Escuela Superior de Física y Matemáticas
Instituto Politécnico Nacional, Unidad Profesional Adolfo López Mateos
07738 México, D.F.

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Abstract. Flow experiments through capillaries with semirigid and rigid polymers in aqueous solutions were carried out in order to study the dependence of the flow development on the molecular conformation and the length to diameter ratio (L/D), of the capillary at relatively low shear rates. It was found that the apparent viscosity has a strong dependence upon the ratio L/D for a given shear rate, although an asymptotic value is reached. This dependence was reflected in the non-linearity of Bagley's plots. The asymptotic value was attained at lower L/D values for semirigid molecules than for rigid ones, showing the influence of the molecular conformation on the flow field development due to the different modes of relaxation for each type of molecule.

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1. Introduction

The flow of liquids through a capillary tube has been *usually assumed* to be divided into three regions. The first region includes a section where large stresses are developed and a rearrangement of the velocity field takes place, due to the contraction found by the liquid when it enters the capillary tube.

The second one is associated with an *assumed* constant axial pressure gradient in which viscometric measurements can be made. In this region the flow is supposed to be a fully developed steady simple shear flow. Finally the third region is caused by the abrupt change of the boundary conditions at the end of the capillary.

The above assumption could be easily assured if the pressure profile generated along the capillary could be measured. However, there are experimental difficulties to measure the local pressure along the tube. In general only the pressure drop between the capillary ends is measured. It is clear that the influence of end effects is included within the pressure drop.

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[**] CONACyT-scholarship.

[†] COFAA-IPN.

For the case of Newtonian fluids, end effects have been taken into account in the stress determination by assuming an effective capillary length greater than the actual length. For non-Newtonian fluids, several authors have tried to determine the entrance length at which the flow reaches the steady state of simple shear flow by different traditional rheometrical methods of macroscopic character. However, the results differ considerably from one another causing a controversy, an implication of that controversy is that it is not possible to characterize a non-Newtonian fluid by purely traditional rheometrical methods.

The present investigation aims to determine the influence of the geometry of the apparatus and the molecular conformation on the flow of polymer solutions through capillaries.

2. Theory

Measurements of the material properties of polymer solutions can be obtained using different rheometers. One commonly used is the capillary rheometer due to its simplicity.

From the determined flow rate Q, and the pressure drop ΔP, the apparent shear rate $\dot{\gamma}_{\mathrm{app}}$ and the wall shear stress τ_{w} are given by

$$\dot{\gamma}_{\mathrm{app}} = \frac{32Q}{\pi D^3} \tag{1}$$

$$\tau_{\mathrm{w}} = \frac{D\Delta P}{4L} \tag{2}$$

where D is the diameter and L is the capillary length. It is very important to remark here that equations written above were obtained under the assumption that the fluid is homogeneous, the flow is fully developed and there are not wall effects present.

Equation (1) is valid only for Newtonian fluids. In the case of non-Newtonian fluids this equation must be corrected using a method given by Rabinowitsch [1] which will not be considered here.

The correction to the stress due to end effects has been accounted for a Newtonian liquid by assuming an effective capillary length $(L + nD)$, greater than the actual length. Then Eq. (2) takes the form

$$\tau_{\mathrm{wB}} = \frac{\Delta P}{4\left[\frac{L}{D} + \frac{n}{2}\right]} \tag{3}$$

Thus, the pressure drop needed to produce a given shear rate is a linear function of L/D and the value of n can be obtained by extrapolating the plot of ΔP *vs* L/D to $\Delta P = 0$ for a given shear rate. For non-Newtonian fluids E.B. Bagley [2], working with molten polyethylenes, capillaries of L/D values between 1.05 to 15 and shear rates in the range of 5. to 5000 s^{-1}, found that in all cases studied the pressure drop *vs* L/D plots were linear as in the Newtonian case. He concluded that the end correction to the stress could be performed by Eq. (3). This method is generally known as Bagley's correction.

Recent studies have shown that the non-homogeneous flow field leads to an structuration *i.e.*, a correlated inhomogeneous spatial distribution of macromolecules [3–4]. In addition, the configuration of the macromolecules changes in the vicinity of the walls, giving place to a modification of the stress field.

3. Experiment

The capillary rheometer designed in our laboratory consists of a constant hydrostatic head reservoir, an additional small reservoir with 1000 ml capacity, and nine glass capillaries of internal diameter 0.12 ± 0.004 cm and L/D ratios between 5 and 1015, which are attachable to the small reservoir. The ratio between the characteristic length of the reservoir and the internal diameter of the capillary is of the order of 80:1. Several researchers have studied the effect of the contraction on the viscous and elastic behavior of the polymers [5]. As a conclusion of those investigations it is now known that when the contraction is greater than 18:1, the viscoelastic properties of the fluid are independent of the reservoir diameter. Therefore, the effect due to the contraction has been minimized in the apparatus design.

The entrance pressure to the capillaries was changed by varying the height of the constant head. The pressure drop was determined by using a Validyne differential pressure transducer, with an uncertainty of about ± 10 Pa.

The capillaries as well as the small reservoir were kept under a controlled temperature water bath at 26.7 ± 0.2 °C. The diameter of the capillaries were determined with precision of $\pm 0.4\%$ by flow data taken from a Newtonian solution of 95% glycerol in water at 25 °C and compared with a very well calibrated tube [6].

The volumetric flow rate was determined by using an analytic balance and a stopwatch with a precision of 10^{-3} s. The error in the volumetric flow rate was in the order of $10^{-2}\%$. It was observed that when the pressure in the system was changed, the pressure drop stabilized rapidly, but, the volumetric flow rate changed continuously during several minutes until it reached an stationary value. This value was used for all the calculations performed in this work.

The shear rate attained in the experiments varied between 5 to 360 s^{-1}. Polymer aqueous solutions of semirigid and rigid macromolecules of 0.2% concentration were studied. The polymer used in the experiments was Xanthan gum, a polysaccharide of semirigid conformation from which many experimental results are available. The rigid conformation was obtained by adding NaCl in such a way that a 7 pH was obtained [7].

4. Results

The pressure drop between ends of the capillary was measured as a function of the flow rate. From this data the apparent shear rate was determined using equation (1)

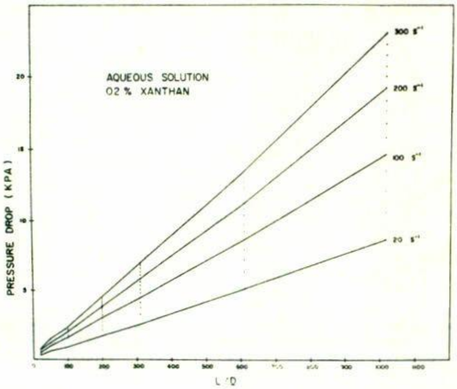

FIGURE 1.

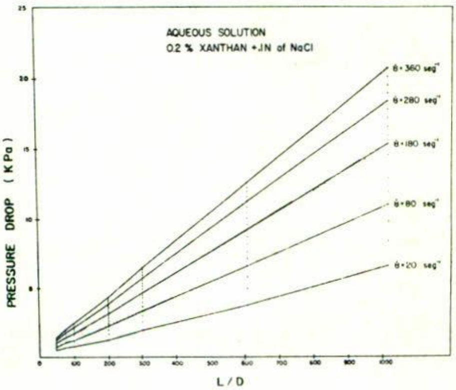

FIGURE 2.

and plots of ΔP *vs* L/D at a constant shear rate were obtained for both Xanthan solutions (Figs. 1 and 2). It is clear from the plots that the obtained curves are not straight lines for any of the solutions. In fact, there are three distinguishable regions in each curve. The middle part has a smaller slope than the other two regions. Similar experimental data were found by Jiang, Young and Metzner [8], Cohen and Metzner [9] and Laund and Hirsch [3], although they fitted straight lines through their data according to Bagley. Due to the non-linearity of the obtained flow curves, Bagley's correction was not performed in this work. Instead an apparent viscosity was calculated as

$$\eta_{\mathrm{app}} = \frac{\pi D^4 \Delta P}{128 L Q}$$

and the calculated values were compared for a given shear rate among different capillaries (Figs. 3 and 4). From these figures it can be seen that the value of the

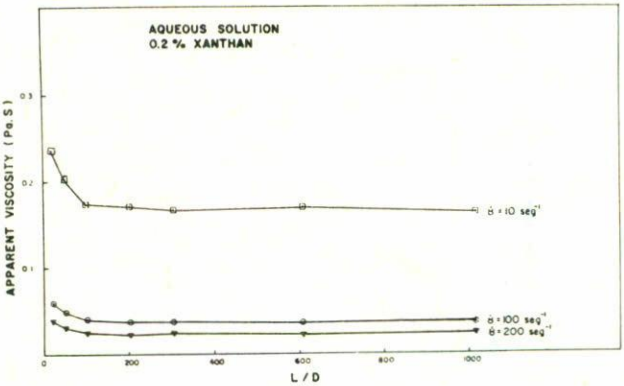

FIGURE 3.

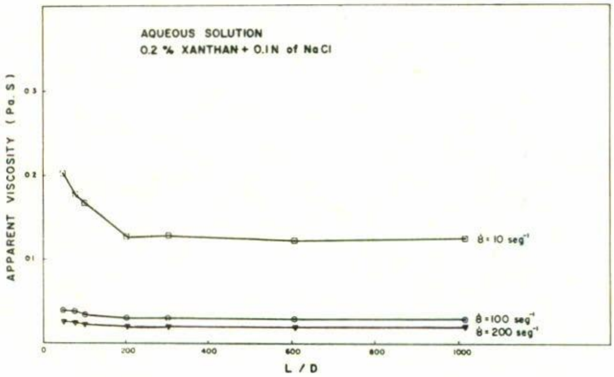

FIGURE 4.

apparent viscosity varies as a function of L/D for each shear rate, and reaches an asymptotic value. The same data are presented in Figs. 5 and 6 as a normalized apparent viscosity defined as the ratio between the viscosity obtained for a capillary of any L/D ratio at a certain shear rate and the asymptotic apparent viscosity value at the same shear rate (this value corresponds to the tube of $L/D = 1015$ for any given shear rate).

There are two observation with respect to these plots. First, the normalized apparent viscosity at a constant shear rate decreases when L/D increases. In general it was observed that the decrease in the normalized apparent viscosity was higher for rigid molecules than for semirigid ones. Second, the normalized value (1 ± 0.03) was reached at lower L/D values for the case of semirigid molecules than in the case of rigid ones.

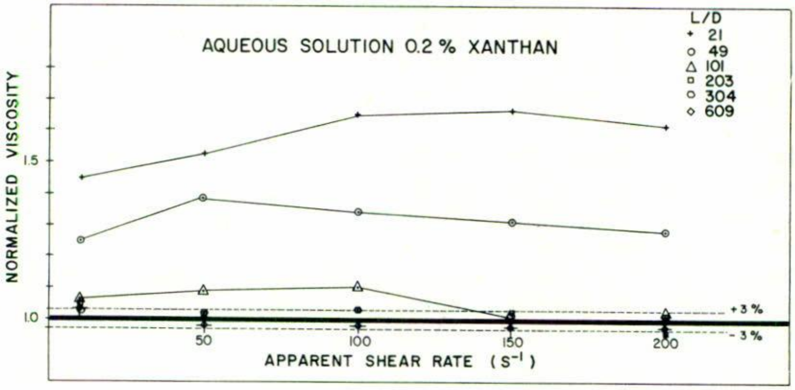

FIGURE 5.

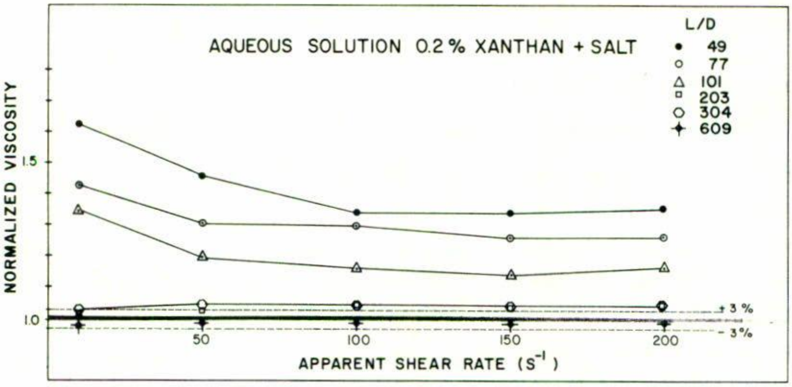

FIGURE 6.

5. Discussion

The non-linearity of the curves presented in figures 1 and 2 does not permit to make the Bagley's correction, because it is not clear in which region the correction should be performed.

The first region of the curves, that corresponds to very short capillaries, can be interpreted as the one in which the velocity field rearrangements are taking place and end effects are dominant. Therefore, there is not any region in the tube in which the flow is fully developed, in other words, it does not exist a long enough region with a constant pressure gradient, so Bagley's correction can not be performed.

The second region may be due to the influence of relaxation effects on the rheological properties of the solution. The relaxation times depend on the internal degrees of rotational freedom of macromolecules. These times are longer for rigid molecules than those of semirigid ones when they are subjected to a transient shear or elongational flow field [10,11]. Experimental results obtained by Chow and Fuller [12] showed that under a shear step the relaxation times are longer for rigid Xanthan molecules than for semirigid ones, which support the statement made above and the fact that the asymptotic value is reached at lower L/D for semirigid molecules.

The highest decrease in the normalized viscosity as a function of L/D for rigid molecules as compared to semirigid ones at a constant shear rate may be due to slip and wall effects in agreement with de Vargas and Manero [6] who showed that these effects are greater for rigid molecules.

The usual theory is based on the flow of a fluid with a constant concentration, *i.e.*, independent of the position and time. This theory does not take into account molecular conformation and its possible influence on the flow field development due to apparatus geometry. Therefore it is clear that the obtained results in this work can not be explained by the usual theory.

6. Conclusions

The principal results of this work are summarized in the following points:

1. The plots ΔP *vs* L/D are not linear for both polymer solutions.
2. The apparent viscosity for a given shear rate decreases as L/D increases and reaches an asymptotic value.
3. The variation of the apparent viscosity as a function of L/D for a given shear rate, is large and it is possible that in addition to end effects there were other phenomena taking place as slip and wall effects.
4. The change in the viscosity, for a given shear rate and L/D, depends on macromolecule conformation. This shows the importance of the molecular internal degree of freedom for the flow development.

Acknowledgments

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Resumen. Se realizaron experimentos de flujo a través de capilares con soluciones acuosas de polímeros rígidos y semirígidos con el fin de estudiar la dependencia del desarrollo del flujo con respecto a la conformación de las macromoléculas y la razón longitud a diámetro del capilar (L/D), a velocidades de deformación relativamente bajas. Se encontró que la viscosidad aparente tiene una fuerte dependencia de la razón L/D para una rapidez de deformación dada, aun cuando se alcanza un valor asintótico. Esta dependencia se refleja en la no linealidad de las gráficas de Bagley. El valor asintótico fue alcanzado a valores más bajos de L/D para las moléculas semirígidas que para las rígidas, mostrando la influencia de la conformación molecular en el desarrollo del campo de flujo debido a los diferentes modos de relajación para cada tipo de moléculas.