

FLOW CURVE DETERMINATION FOR NON-NEWTONIAN FLUIDS

A Sequel

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SEVERAL EXPERIMENTS HAVE been described in the literature [1-3] on demonstrating or measuring non-Newtonian effects in the flow of polymer solutions. The importance of these experiments can hardly be overemphasized in view of the fact that in several programs, this may be the only exposure of an undergraduate student to non-Newtonian flow as well as to polymeric systems. It is, therefore, necessary to maximize the learning experience associated with such an experiment. This article describes our efforts to design such an experimental program with the set-up of Walawender and Chen [3], which we found to be most amenable for this purpose.

APPARATUS

We simplified the set-up of Walawender and Chen and did not use their elaborate temperature-control system. Our set-up thus consisted only of a 50 cc. buret connected to a glass capillary through a Tygon tube (see Fig. 1). By doing so, we could have enough parallel set-ups available so that students could take more data on systems during their laboratory session. Several capillaries were made available, having radii of 0.505 and 0.287 mm. (obtained by weighing known lengths of mercury threads in them), and lengths of 20.0, 30.0, and 39.6 cm. The experimental technique was identical to that described by these workers and

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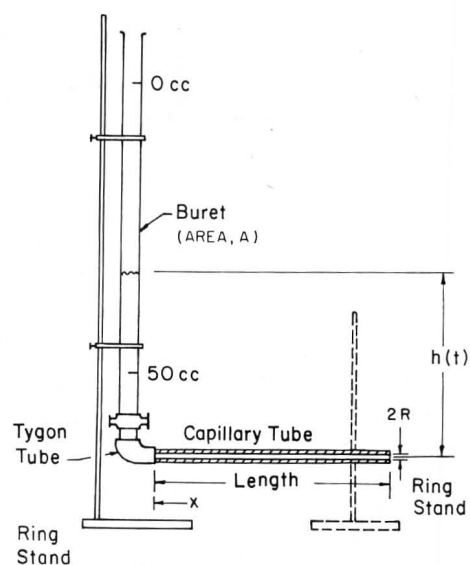


FIGURE 1. The experimental set-up.

consisted of recording the height, $h(t)$, of the meniscus in the buret as a function of time for flow of several solutions through the capillary. This was analyzed to give the apparent viscosity, η_a , as a function of the shear rate, $\dot{\gamma}$.

THEORETICAL

The volume rate of flow, Q , of a *Newtonian* liquid in a horizontal capillary tube under steady, fully developed and laminar conditions, is described by the following equation [4,5]

$$Q = \frac{\pi R^4 (-P')}{8\eta} \quad (1)$$

with

$$-P' = -\frac{dP}{dx} = \text{constant} = \frac{\Delta P}{L} \quad (2)$$

where η , ΔP , L and R are the viscosity, pressure drop across the capillary, length and radius of the capillary, respectively. The pressure drop across the capillary tube in the set-up shown in Fig. 1 is also given by

$$\Delta P = \rho gh(t) \quad (3)$$

where ρ is the liquid density, and g is the acceleration due to gravity. The change of h with respect to time can be expressed as

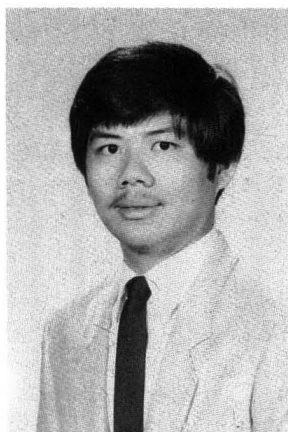
$$\frac{dh(t)}{dt} = -\frac{Q}{A} = -\frac{\pi R^4 [\rho gh(t)]}{8 LA \eta} \quad (4)$$

where A is the cross sectional area of the buret. Integration of Eq. (4) gives

$$\ln [h(t)] = -\frac{\pi R^4 \rho g t}{8 LA \eta} + C \equiv -\frac{B \rho}{\eta} t + C \equiv mt + C \quad (5)$$

where

$$B = \frac{\pi R^4 g}{8 LA} \quad (6)$$



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and

$$m \equiv \frac{d \ln [h(t)]}{dt} = -\frac{B \rho}{\eta} \quad (7)$$

$\log [h(t)]$ vs t plots for such liquids are thus expected to be linear having negative slopes (which may be used to estimate η for Newtonian liquids).

In the case of a non-Newtonian liquid, the shear stress, τ , is not linearly related to the shear rate, $\dot{\gamma}$, and the 'apparent' viscosity is a function of the shear rate. Weissenberg, Rabinowitsch and Mooney have presented an extremely ingenious method of analyzing experimental data on flow through capillaries under these conditions. Their final equations are given by the following two equations [6,7]

$$\tau_w = \frac{R(\Delta P)}{2L} \quad (8)$$

and

$$\frac{1}{\eta_a(\dot{\gamma}_w)} \equiv \frac{\dot{\gamma}_w}{\tau_w} = \phi_e + \frac{\tau_w}{4} \frac{d\phi_e}{d\tau_w} \quad (9)$$

Here, τ_w and $\dot{\gamma}_w$ are the shear stress and the shear rate at the capillary wall at any time t , and ϕ_e is defined by

$$\phi_e \equiv \frac{4Q}{\pi R^3 \tau_w} = \frac{8QL}{\pi R^4 (\Delta P)} \quad (10)$$

Eq. (3) may still be used to estimate ΔP as a function of time, and the flow rate Q can be easily determined experimentally at different times, using

$$Q = -A \frac{dh(t)}{dt} \quad (11)$$

Thus, both τ_w and ϕ_e can be obtained as functions of time from a *single* experiment on flow through the capillary. Plots of ϕ_e vs τ_w can be made and both η_a and $\dot{\gamma}_w$ can be obtained at any particular time. Thus, the function $\eta_a(\dot{\gamma}_w)$ can be determined. This is identical to $\eta_a(\dot{\gamma})$, since the apparent viscosity is a material property.

Because of errors introduced in computing the slopes in Eq. (9), Walawender and Chen [3] suggested curve-fitting experimental data using

$$h(t) = h_0 \exp\{-kt + (a + bt)^2\} \quad (12)$$

where h_0 is the height of the meniscus at time $t=0$ and k , a and b are constants. The corresponding form of the Weissenberg, Rabinowitsch and Mooney Eq. (9) is then

$$\frac{1}{\eta_a(\dot{\gamma}_w)} = \frac{\dot{\gamma}_w}{\tau_w} = -\frac{m}{B\rho} \left(1 + \frac{1}{4m^2} \frac{dm}{dt} \right) \quad (13)$$

where

$$m \equiv \frac{d(\ln h)}{dt} = -k + 2b(a + bt) \quad (14a)$$

$$\frac{dm}{dt} = 2b^2 \quad (14b)$$

and B is given by Eq. (6).

The method of analysis of experimental data, $h(t)$, on any one system, is to obtain k , a and b by a non-linear curve-fit parameter estimation computer package [8-10], use Eqs. (8) and (3) to give τ_w at any time t , use Eqs. (13) and (14) to give η_a and then get the corresponding $\dot{\gamma}_w$ as τ_w/η_a . The values of τ_w , $\dot{\gamma}_w$ and η_a change with the time, t , and thus, $\eta_a(\dot{\gamma}_w)$ or $\eta_a(\dot{\gamma})$ plot can be obtained from a single experimental run. Our numerical method is a little sensitive to the initial estimates of k , a and b fed into the computer [3] and students gain some valuable experience with convergence problems encountered in numerical procedures.

EXPERIMENTAL PROGRAM AND SAMPLE RESULTS

Flow curve measurements were made on carboxymethylcellulose (sodium salt, widely known as CMC) solutions in distilled water. This system is non-toxic and easy to work with. Not only do these polymers exhibit typical pseudoplastic behavior, but, being a polyelectrolyte, they can also be exploited for educational purposes to show the relationship between molecular interactions and viscometric properties [11,12]. Three different molecular weight samples of this polymer, C8758 (low viscosity), C4888 (medium

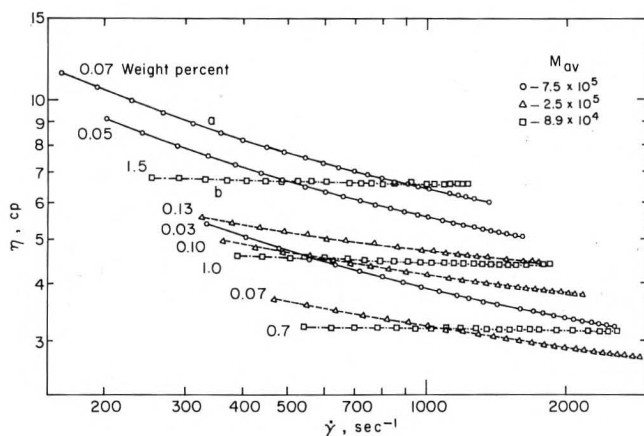


FIGURE 2. Flow curves for three different molecular weight samples of CMC in distilled water (22.8°C). Dia. of capillary = 1.010 mm, Length = 20 cm.

viscosity) and C5013 (high viscosity), having average molecular weights, M_{av} , of about 8.9×10^4 , 2.5×10^5 and 7.5×10^5 respectively (obtained from Sigma Chemical Co., St. Louis), were used to make solutions of concentrations ranging from 0.7% to 1.5% (by weight) for the 'low viscosity', from 0.07%-0.13% for the 'medium viscosity' and from 0.03-0.07% for the 'high viscosity.' This choice of concentrations was made so that inordinately high times of flow through the capillaries are not required. The solutions of the 'high viscosity' polymer had to be stirred for about 45 minutes to attain homogeneity. A good way of checking the homogeneity of the solution was to view it against a bright light and not find any regions having different refractive indices. The experience of making polymer solutions of even such low concentrations as 0.05% is itself quite educational.

Fig. 2 shows a sample set of flow curves for three

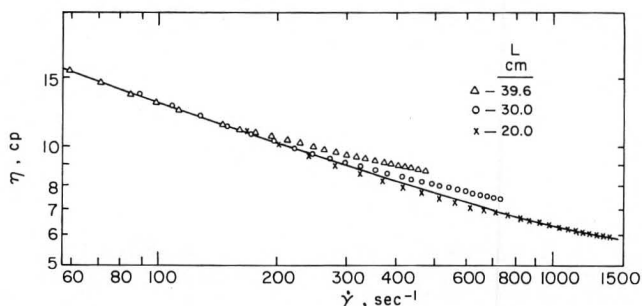


FIGURE 3. Flow curves for the 7.5×10^5 molecular weight CMC sample in distilled water (22.8°C) taken with capillaries of different lengths. Concentration = 0.07%.

concentrations for each of the three CMC samples mentioned above. For the 'high viscosity' sample, the viscosity is observed to fall by a factor of about two over a shear rate range of 200-1500 sec^{-1} . The 'low viscosity' samples, in contrast, show almost Newtonian behavior, at least for the concentrations studied. A comparison of curves a and b in Fig. 2 leads to the significant conclusion that shear-thinning is not always present in polymeric systems, and that two polymeric solutions having the same viscosity at any one shear rate, need not have equal viscosities at a different shear rate. Fig. 2 also illustrates the significant effect of molecular weight on the viscosities at any shear rate. For example, at a shear rate of about 500 sec^{-1} , the viscosity of a 1% solution of a low molecular weight sample of CMC is the same as that of a 0.03% of a high molecular weight sample. In fact, cross plots of η vs concentration (c) or average molecular weight, M_{av} , at any $\dot{\gamma}$, may be made to illustrate these effects. We observed that at $\dot{\gamma} = 500 \text{ sec}^{-1}$, plots

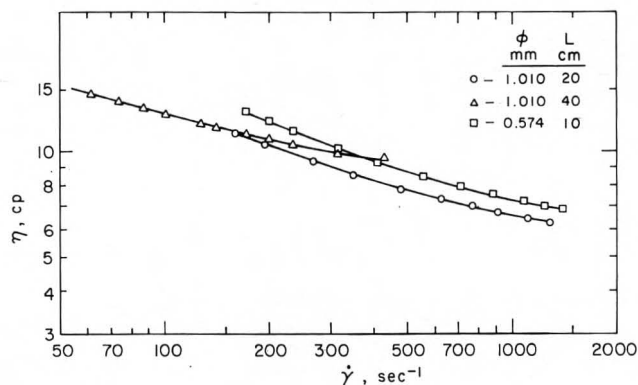


FIGURE 4. Flow curves for the 7.5×10^5 molecular weight CMC sample in distilled water (22.8°C) taken with capillaries of different lengths and diameters. Concentration = 0.0726%.

of η vs (cM_{av}) had slopes about unity (though they did not superpose, both because of free volume effects present at such high dilutions [6,7] and because of the configurational changes associated with different degrees of ionization of the polyelectrolyte in pure water). Students could be advised to read some write-ups on simple molecular theories for the non-Newtonian behavior of polymeric systems [6,7] in order to rationalize some of their data.

Fig. 3 shows data taken on a 0.07% CMC ($M_{av} = 7.5 \times 10^5$) solution in distilled water using capillaries of different lengths. It illustrates the superposition of data, as well as the possibilities offered for extending the range of shear rates which could be studied by use of different capillaries. Fig. 4 shows how similar ex-

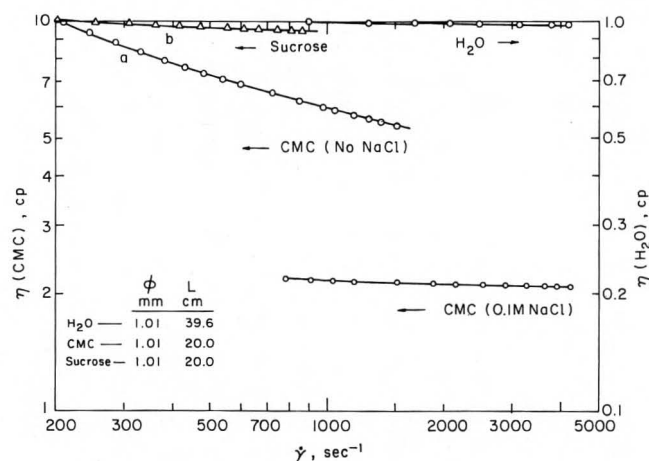


FIGURE 5. Flow curves for water (use right scale for viscosity), for CMC ($M_{av} = 7.5 \times 10^5$, 0.07%) in distilled water and in 0.1M NaCl solution, and for a 50wt% sucrose solution in water. Temperature = 22.8°C .

tension of the range of $\dot{\gamma}$'s results when capillaries of different diameters are used. There is some experimental error in the data reported (about 10%), and there are some additional errors introduced (longest capillary, $\dot{\gamma} \sim 400 \text{ sec}^{-1}$) because of viscous effect in the buret and the Tygon tubing. Lower diameter capillaries of longer dimensions were not tried since they led to very high times of flow and so were not suited for use in the laboratory sessions. However, general trends can easily be inferred from these two figures. It may be mentioned that the low-shear Newtonian region was not reached in our experiments for the high molecular weight samples, and so we failed

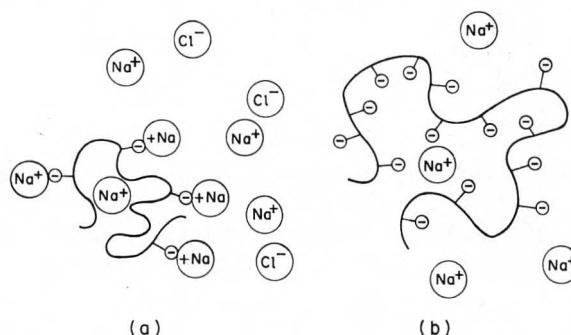


FIGURE 6. (a) A typical molecule of CMC salt in water with 0.1M NaCl (b) in absence of added NaCl.

in our efforts to illustrate how polymer solutions behave as Newtonian fluids till some $\dot{\gamma}$, and then show a drop in viscosity till the second Newtonian region. Use of more sophisticated equipment (*e.g.*, Weissenberg rheogoniometer) could give a more extended range of $\dot{\gamma}$, but their availability is limited only to some chemical engineering departments.

Fig. 5 shows data on distilled water and shows its value to match those reported in the literature. Higher length capillaries were necessary to take data on water; otherwise, considerable experimental error would have resulted. This figure also shows the significant lowering of the viscosity of CMC solutions by a factor of 3 to 4 by the addition of NaCl to the solution. This is an excellent illustration of the molecular aspects of polymer rheology. Because of the presence of significant amounts of NaCl, the sodium ions on the polymer molecules do not move out too far into the solution, resulting in very little ionic charge on the macromolecules in such solutions. This is quite different from CMC solutions in water alone, in which the sodium ions of the polymer wander out into the solution, and the polymer has negative charges on its backbone (see Fig. 6). Because of the electrostatic re-

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pulsion between these charges on the flexible polymer molecules, the latter expand and give rise to higher viscosities as well as to non-Newtonian effects. The students are encouraged to read up on more elaborate descriptions [12] of the salt-effect in polyelectrolytes.

Fig. 5 also shows the flow curve for a 50 (wt.%) sucrose solution in distilled water [13]. This solution is Newtonian in the range of shear rates studied and has approximately the same viscosity as the CMC solution (concentration = 0.07%) at the rate of shear of 200 sec^{-1} . The comparison of curves a and b in Fig. 5 brings out the point further and more strongly that two solutions having the same viscosity can still differ significantly in terms of their non-Newtonian characteristics. Students can also interpret these curves in

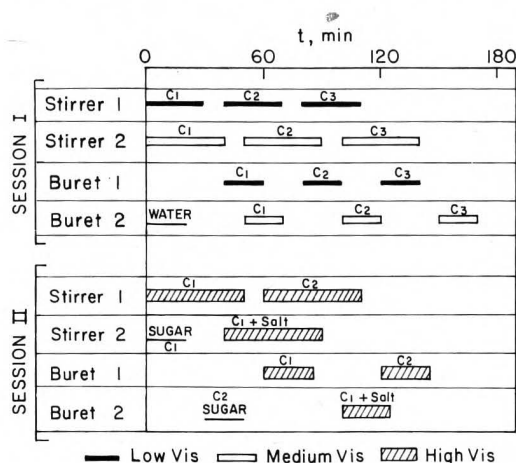


FIGURE 7. A typical plan for two 3-hour laboratory sessions. Remaining time could be used to duplicate same results. C₁, C₂ and C₃ represent different concentrations (see Figs. 2-5).

terms of pressure drops required for achieving a desired flow rate in a pipe.

It has been reported that some CMC solutions are also thixotropic [11], *i.e.*, the viscosity depends on the time elapsed after the shear is applied. This is because the molecules of the polymer could become associated into some type of a macrostructure where the crystalline regions of different molecules aggregate to give higher effective molecular weights and so higher viscosities. These macrostructures could be broken up by various means, *e.g.*, by the application of high shear for some time, leading to thixotropy. We carried out some experiments to illustrate this effect. However, we found that the solutions, after vigorous stir-

ring for one hour and then storing for a week (when the macrostructures could be formed again), exhibited the same η vs $\dot{\gamma}$ behavior as before storing, and so we inferred that thixotropy was absent in our polymer samples. The reason for lack of thixotropy is probably because our samples had a good uniformity of substitution by sodium [11].

CONCLUSIONS

A set of experimental runs on non-Newtonian flow of dilute polymer solutions using an extremely simple set-up has been described, illustrating some important differences between the flow behavior of polymeric systems and common low molecular weight liquids. The program described also enables students to get a grasp of the difficulty in making polymer solutions, as well as gives some experience with convergence problems associated with nonlinear parameter estimation techniques. More results have been reported in this paper than can be obtained in two 3-hour laboratory sessions. The instructor can choose any set out of these. A typical plan for two 3-hour sessions is shown in Fig. 7, wherein the effects of length and radius are omitted. In a single 3-hour session, one could select experiments on three concentrations of the low viscosity CMC, one concentration of the high viscosity polymer, and experiments on sugar solutions and water.

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