

DETERMINING THE FLOW CHARACTERISTICS OF A POWER LAW LIQUID

JAMES R. HILLIER, DALE TING, LISA L. KOPPLIN, MARGARET KOCH, SANTOSH K. GUPTA
University of Wisconsin • Madison, WI 53706

Non-Newtonian liquids present unique problems with respect to their flow behavior. These problems are seldom addressed in undergraduate courses in chemical/mechanical engineering and are possibly covered only through a *single* experiment in one of the laboratory courses. Tjahjadi and Gupta^[1] extended the work of Walawender and Chen^[2] and developed an experimental scheme that illustrates how the apparent viscosity, η , of a pseudoplastic liquid (dilute aqueous solution of Na-CMC) decreases with increasing shear rate, $\dot{\gamma}$. They also suggested performing additional experiments after adding some sodium chloride to the CMC solution, to observe a dramatic decrease in η and relate it to the contraction of the polyelectrolyte molecules in an ionic medium.

Although the results had considerable educational value, the equations used were quite complex and cumbersome to use, with the result that a student obtained little insight into the method of analysis—this limits the value of their experiment.

In the present work (developed as part of the “informal” experiments^[3] at the Summer 2000-I laboratory at the University of Wisconsin-Madison), a much simpler experiment has been developed that uses the easily understood macroscopic energy balance (the engineering Bernoulli equation^[4]) to obtain experimental results.

A 0.07% (by weight) solution of a sodium salt of carboxymethyl cellulose (Na-CMC; weight average molecular weight = 7×10^5 ; DS = 0.9; Aldrich Chemicals, Milwaukee, WI) in deionized water was used for our study. CMC was selected because of its pseudoplastic nature over a range ($1 - 10^5 \text{ s}^{-1}$) of shear rates. In addition, CMC is an inexpensive, nontoxic, biodegradable, water-soluble polymer, commonly used in mining applications, food thickeners, adhesives, and textiles.

The results obtained could also be compared to existing values in the literature^[1] for consistency.

EXPERIMENTAL SET-UP

The experimental set-up is similar to that used for studying the flow characteristics of Newtonian liquids, as described by Crosby.^[5] Flush-mounted glass capillaries (in one case, a copper tube) of different diameters and lengths are used with a drain tank,^[5] as shown in Figure 1. Two different kinds of experimental units were made so as to vary the shear rate over a reasonable range. The detailed dimensions are provided in Table 1.

PROCEDURE

The CMC solution to be used in all the experimental runs was prepared using laboratory-grade carboxymethyl cellulose powder. A solution of 0.07 wt% CMC in deionized wa-

James R. Hillier received his BS degrees from the University of Wisconsin-Madison in Chemical Engineering (2000), Biochemistry (2000), and Molecular Biology (2000). He is currently the Plant Engineer for Equistar Chemicals in Fairport Harbor, OH, while working on a master's degree in polymer engineering and a diploma in disaster management.

Dale Ting received his BS in Chemical Engineering from the University of Wisconsin-Madison in 2000. He is currently working in process development at The Procter and Gamble Co. in Cincinnati, OH.

Lisa Kopplin received a BS in Chemical Engineering from the University of Wisconsin-Madison (2000). She is currently serving as a Project Engineer for General Mills, Inc., in their West Chicago manufacturing facility.

Margaret R. Koch graduated from the University of Wisconsin-Madison with a BS in Chemical Engineering in 2000. She is currently working in Process Development at S.C. Johnson & Son, Racine, WI.

Santosh K. Gupta received his BTech (1968) from I.I.T., Kanpur, and his PhD (1972) from the University of Pennsylvania-Philadelphia. He has been on the faculty of I.I.T., Kanpur, since 1973, and has also been a Visiting Professor at the University of Notre Dame, National University of Singapore, and the University of Wisconsin-Madison. His research interests include polymerization engineering and optimization using AI techniques.

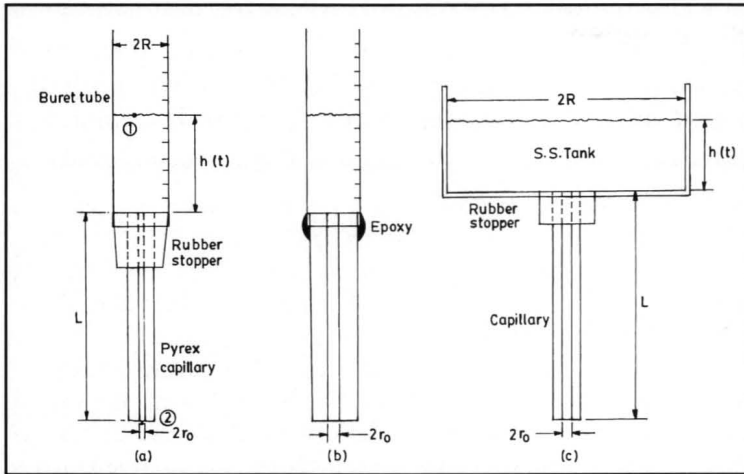


Figure 1. Experimental set-ups for Phases 1 and 2.

a and b, 50 ml graduated tube (buret with lower end cut) connected to aligned glass capillaries, flush-mounted to minimize entrance losses.

c, 5 lit SS tank (diameter - 0.158 m) with sight glass to measure h , used. Glass or Cu capillaries/tubes used. Details provided in Table 1.

TABLE 1
Details of the Experimental Runs

Run No.	Set-Up Used (Fig. No)	$10^3 (2r_0)$ m*	L, m^*	$h (t=0)$ m*	Approx Range of $\dot{\gamma}, s^{-1}$	n^{**}	K^{**} Pa-s ⁿ
1	1a	0.532	0.541	0.0705	69-122	0.809	0.054
2	1a	1.040	0.205	0.20	288-552	0.640	0.0884
3	1a	1.040	0.205	0.20	268-436	0.858	0.7913
4	1a	1.040	0.120	0.20	347-733	0.86	0.04755
5	1a	1.040	0.101	0.20	377-1013	0.62	0.1048
6	1a	1.040	0.101	0.20	358-857	0.70	0.06653
7	1a	1.040	0.055	0.20	535-1619	0.701	0.06599
8	1a	1.040	0.055	0.20	518-1608	0.685	0.07466
9	1a	1.040	0.055	0.46	515-5628	0.639	0.100
10	1a	1.040	0.055	0.46	530-5924	0.633	0.1018
11	1b	1.536	1.216	0.565	318-483	0.839	0.031
12	1b	1.536	1.216	0.57	312-442	1.00	0.012
13	1c (glass)*	2.200	1.279	0.57	513-563	0.311	0.791
14	1c (glass)*	2.720	1.279	0.0705	658-683	0.857	0.026
15	1c (glass)*	2.720	2.279	0.0705	892-965	0.355	0.611
16	1c (Cu)*	3.176	0.610	0.0652	1098-1216	0.507	0.229

* Glass capillary or Cu tube used

+ See Figures 1 a-c

++ See Eq. (2)

ter was prepared well in advance to guarantee the homogeneity of the solutions.^[1] The solution was heated to 30-50°C for about 4 to 8 hours and stirred for over 24 hours. Homogeneity of the solution was confirmed by observing its clarity against a very bright light source.^[1,6]

In each experimental run, a specified amount of polymer solution was added to the holding tank. The initial values, h_0 , of the level of solution in the tank (see Figure 1) are given for the different experimental runs (Table 1). Flow was started, and data on h was recorded over time, t , starting at the calibration mark. This allowed flow patterns to establish so that data would not be altered by flow development. Experimental runs were stopped prior to complete efflux of the liquid from the tank, so as to reduce the significance of end effects.

THEORY

Since CMC solutions behave like pseudoplastics, their apparent viscosities, η , decrease with increasing shear rates, $\dot{\gamma}$. The general dependence of η on $\dot{\gamma}$ is quite complex, but over small ranges of the shear rate, $\dot{\gamma}$, the following power law model^[4,6,7] is followed quite well:

$$\tau = K\dot{\gamma}^n \quad (1)$$

where τ is the shear stress. In Eq. (1), the constant, K , is referred to as the consistency index, and the exponent, n , is the power law index. The apparent viscosity is then given by

$$\eta \equiv \frac{\tau}{\dot{\gamma}} = K\dot{\gamma}^{n-1} \quad (2)$$

A macroscopic (mechanical energy balance for this system^[7, Eq. 5.20] leads to (see Appendix 1 for details)

$$\rho g(L+h) = 2KL \left(\frac{3n+1}{n} \right)^n \frac{v^n}{r_0^{n+1}} \quad (3)$$

In Eq. (3), ρ is the density of the solution, r_0 and L are the (inner) radius and length of the capillary (Figure 1), h is the height of the solution above the capillary entrance at time, t , g is the acceleration due to gravity, and v is the mass-average velocity inside the capillary at time t .

The mass-average velocity of the solution inside the capillary can be obtained using the continuity equation

$$v = \left(\frac{R}{r_0} \right)^2 \left(\frac{-dh}{dt} \right) \quad (4)$$

where R is the inner radius of the drain tank. A second

The primary advantage of the present study is that analysis of the raw data can be performed using equations that are easily understood by juniors in chemical engineering, and standard computer packages can be used . . .

or third degree polynomial can be fitted to data on $h(t)$. This gives excellent values of the coefficient-of-determination of about 0.999 and higher. This polynomial is then used with Eq. (4) to obtain v . Eqs. (3) and (4) can be combined and integrated for Newtonian fluids ($n = 1$) to give the standard^[4] equation for the efflux time for a vertical tank-pipe assembly under laminar-flow conditions. The students find these derivations easier to comprehend (in fact, they can make the derivations themselves) than the equations described by Tjahjadi and Gupta.^[11]

The validity of the assumption of laminar flow should be confirmed by calculating the Reynolds number for the pseudoplastic liquid using^[7; Eq 5.50]

$$Re = 2^{3-n} \left(\frac{n}{3n+1} \right)^n \frac{D^n \rho v^{2-n}}{K} \quad (5)$$

For pseudoplastic flows present in the laminar region, as in this study, the sudden contraction/entrance losses are expected to be negligible.^[1,2] In the more general case where the entrance losses are important, the Bagley correction^[8,9] can be used. This could be a possible avenue of further study for a student.

Equation (3) can be rewritten as

$$\log [\rho g(L+h)] = \log \left[\frac{2KL}{r_0^{n+1}} \left(\frac{3n+1}{n} \right)^n \right] + n \log (v) \quad (6)$$

An appropriate log-log plot of Eq. (6) gives n (= slope). K can then be obtained using n and the intercept, α , using

$$K = \exp \left[\frac{\alpha r_0^{n+1}}{2L} \left(\frac{n}{3n+1} \right)^n \right] \quad (7)$$

Once values are obtained for both n and K , the shear rate (at the wall of the tube, $r = r_0$) can be evaluated using^[4,7; App 1]

$$\dot{\gamma} = \left[\frac{\rho g(L+h)r_0}{2LK} \right]^{1/n} \quad (8)$$

The apparent viscosity, η , can then be evaluated (at *this* wall shear rate) using Eq. (2). Equation (8) assumes that the power law dependence is valid, and so the value of $\dot{\gamma}$ obtained is *inferred* from the data-fitting procedure.

Unfortunately, use of the power law assumption, though helpful in simplifying the experiment at the undergraduate level, can give a false idea of the complexity of the method of analysis routinely used by professional, non-Newtonian

rheologists (who commonly use the Rabinowitsch technique^[6,9]). An alternative procedure of data analysis that is not as difficult and that can be attempted by an undergraduate student, is the use of the Schummer approximation^[10] (described in Appendix 2). Such an analysis preserves, to some extent, the physics of mechanical energy balance and closely follows the steps that would be employed in the professional rheological evaluation of non-Newtonian viscosity. One set of experimental data generated herein is analyzed later to compare the results using the power law and the Schummer approaches.

RESULTS AND DISCUSSION

Details of the several experimental set-ups and runs are given in Table 1. These experiments were designed and performed in two phases—Runs 1 and 11 through 16 in Table 1 comprising the first phase, followed by Runs 2-10. The results of the first phase were analyzed and used to help improve the designs for Phase 2. Figure 2 shows data from Phase 1. It demonstrates the decrease of the apparent viscosity with increasing shear rates. Although the viscosity vs. shear rate diagram is incomplete, the shear-thinning effect characteristic of pseudoplastic fluids is quite evident. The straight-line segments on this log-log plot confirm the validity of the power-law model over *small ranges* of shear rate. The data overlap in some regions, which confirms the accuracy of the results. The value of the power law index varies from about 0.3 to 1.0 (see Table 1). The range of shear rates covered extends over almost two decades, and the data appears to fall

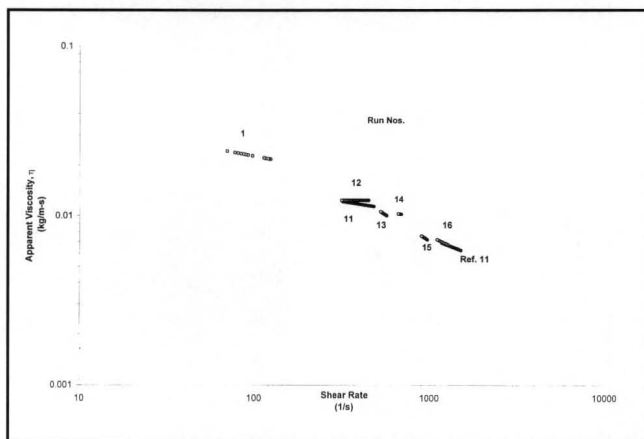


Figure 2. Apparent viscosity vs. shear rate for a 0.07 wt% Na-CMC aqueous solution, assuming power law behavior of the liquid. Phase 1 results shown with Runs indicated. Results from Ref. 11 also shown for comparison. Temperature = 23°C.

on a smooth curve over this range.

The data is also found to be consistent with some earlier work^[11] performed using the same solution, using a stainless steel tank with a copper tube, similar to that used in Run No. 16. Our data is also consistent with the earlier data^[11] on a 0.07 wt% Na-CMC solution having a slightly larger weight-average molecular weight of 7.5×10^5 (the apparent viscosity at 1000 s^{-1} was about 7 cP earlier, and is about the same in Figure 2). The replicability of our results was found to be excellent.

It should be mentioned here that an interesting activity would be to confirm the experimental results obtained here with those using more sophisticated capillary-flow or Couette viscometers available in research laboratories. Use of the former would also illustrate the use of the more exact Rabinowitsch technique of analysis.^[1,9]

The experimental results shown in Figure 2 were then used to design a few additional experiments (Phase 2) so as to ex-

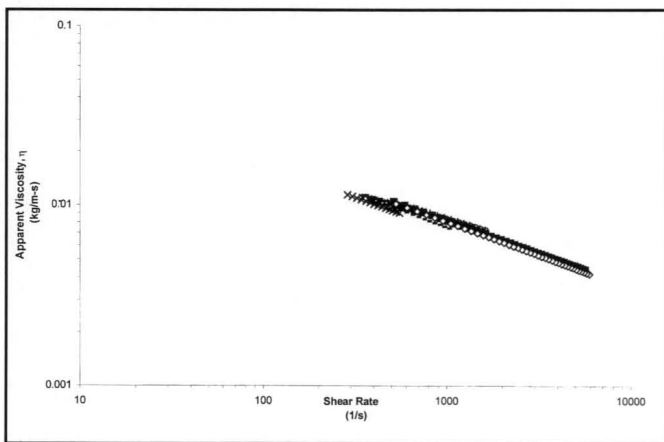


Figure 3. Results for Phase 2, assuming power law behavior of the liquid. Run Nos. 2,3, x; 4, *; 5, -; 6, --; 7, o; 8, +; 9, □; 10 ◇; Temperature = 23 °C.

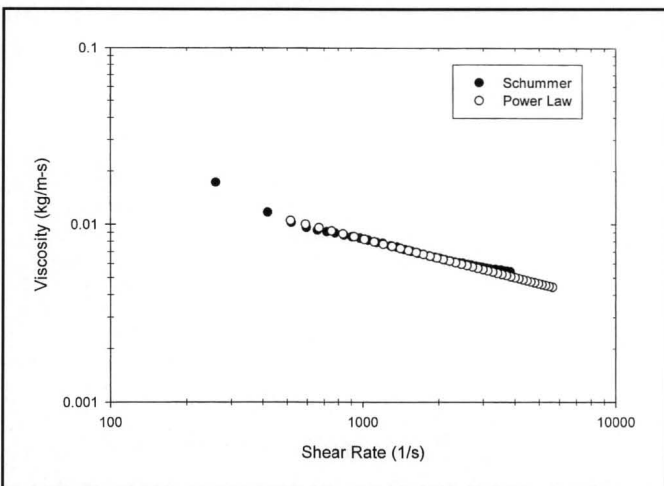


Figure 4. Comparison of η vs $\dot{\gamma}$ obtained assuming power law behavior of the liquid with that using the Schummer correction. Set 9 (Table 1) data used.

tend the range of shear rates. The corresponding plot for the apparent viscosity vs. shear rate for these runs is given in Figure 3, and the values of K and n in Table 1. It was found that the data for the two sets of experimental runs, in the range of shear rates of about 300 to 1000 s^{-1} , superposed very well (these have not been shown since the data points get too cluttered). It is interesting to observe that Runs 9 and 10 give data over a very large range of shear rate, and one could as well use just one or both of these set-ups for a routine laboratory experiment.

It should be emphasized that Eq. (3) is applicable only over small ranges of shear rate (and so over a small range of t , as the meniscus falls). A log-log plot of this equation does not show straight lines for some cases, and one must exercise some judgment to fit the points. Moreover, the viscosity of CMC (a polyelectrolyte) solutions in deionized water is very sensitive to the concentration of *small* amounts of salts that may be present.^[11] The addition of small quantities of NaCl to the solution could help improve the reproducibility of the results substantially, and would help if one were to compare the results obtained by different groups of students taken over several weeks.

Figure 4 shows one set of data (Run 9, Table 1) that has been analyzed using both the power law assumption for the solution as well as the more accurate Schummer technique. The results superpose quite well, but a shift in the curves is quite evident, as discussed in Ref. 10.

CONCLUSIONS

A *simple* experimental set-up was developed to study the decrease of the apparent viscosity of a 0.07% (by weight) aqueous solution of Na-CMC with increasing shear rate. Two experimental units were found that covered a reasonably large range of shear rates of 500 to 6000 s^{-1} . The primary advantage of the present study is that analysis of the raw data can be performed using equations that are easily understood by juniors in chemical engineering, and standard computer packages (*e.g.*, Excel®, etc.) can be used for this purpose.

Additional experimental data can easily be taken after adding sodium chloride to the CMC solution, to study the effect of molecular contraction of the polyelectrolyte.^[11] The results obtained using the power law assumption are compared to more elaborate methods of analysis, and a few additional experiments have been suggested for the more enterprising student.

APPENDIX 1

Details of the Derivation of Eqs. (3) and (8)

The macroscopic mechanical energy balance^[4] is applied

between points 1 and 2 (Figure 1a) with the following assumptions:

- The column is vertical
- The kinetic energies of the liquid at 1 and 2 are negligible
- Entrance or other losses are negligible, and the only losses are due to viscous effects in the capillary

This leads to

$$g(L+h) = \left(\frac{\Delta P}{\rho} \right)_{\text{capillary}} = \frac{2\tau_0}{r_0} \quad (\text{A1.1})$$

where τ_0 is the shear stress at the capillary wall, $r = r_0$, and $(\Delta P)_{\text{capillary}}$ is the pressure drop across the length, L , of the capillary.

A force balance over a control volume of radius, r , and having a differential length, dz , gives^[4]

$$\frac{-dP}{dz} = \frac{2\tau}{r} \quad (\text{A1.2})$$

or

$$\frac{-dP}{dz} = \left(\frac{\Delta P}{L} \right)_{\text{capillary}} = \frac{2\tau_0}{r_0} \quad (\text{A1.3})$$

Equations (A1.2) and (A1.3) give

$$\tau_0 = \tau \left(\frac{r_0}{r} \right) \quad (\text{A1.4})$$

Using the following variation of Eq. (1)

$$\tau = K \left(\frac{-du}{dr} \right)^n \quad (\text{A1.5})$$

where u is the axial velocity at location, r , in Eq. (A1.4), we obtain

$$\dot{\gamma}(r) \equiv \frac{-du}{dr} = \left(\frac{\tau_0}{r_0 K} \right)^{1/n} r^{1/n} \quad (\text{A1.6})$$

This can be integrated from $r = r_0$ ($\tau = \tau_0$) to $r = r$ ($\tau = \tau$) to give

$$u(r) = \left(\frac{\tau_0}{Kr_0} \right)^{1/n} \frac{r_0^{1/n+1} - r^{1/n+1}}{1 + \frac{1}{n}} \quad (\text{A1.7})$$

Equation (A1.7) can easily be integrated over $0 \leq r \leq r_0$ to give the mass average velocity, v , as

$$v = r_0 \left(\frac{\tau_0}{K} \right)^{1/n} \frac{1}{3 + \frac{1}{n}} \quad (\text{A1.8})$$

which can be rearranged (and Eq. A1.1 used) to give

$$\tau_0 = \frac{Kv^n}{r_0^n} \left(\frac{3n+1}{n} \right)^n = \frac{r_0}{2} \left(\frac{\Delta P}{L} \right)_{\text{capillary}} \quad (\text{A1.9})$$

Equation (A1.9) can be combined with Eq. (A1.1) to give Eq. (3).

Equation (A1.6) can be simplified to give

$$\dot{\gamma}(r) = \left(\frac{\tau_0 r}{Kr_0} \right)^{1/n} \left(\frac{\rho g(L+h)}{2LK} r \right)^{1/n} \quad (\text{A1.10})$$

which leads to Eq. (8) (with $r = r_0$).

APPENDIX 2

Details of the Schummer Approximation^[10]

The apparent shear rate $\dot{\gamma}_{\text{ap}}$, and the apparent viscosity, η_{ap} , are defined^[10] by

$$\dot{\gamma}_{\text{ap}} = \frac{4v}{r_0} = \frac{4Q}{\pi r_0^3} \quad (\text{a})$$

$$\eta_{\text{ap}} \equiv \frac{\tau_0}{\dot{\gamma}_{\text{ap}}} = \frac{r_0^2 \rho g(L+h)}{8vL} \quad (\text{b}) \quad (\text{A2.1})$$

Schummer states that the “true” shear rate, $\dot{\gamma}$, corresponding to $\dot{\gamma}_{\text{ap}}$ (at which the viscosity is equal to η_{ap}) is given by

$$\dot{\gamma} = 0.83 \dot{\gamma}_{\text{ap}} = \frac{3.32v}{r_0} \quad (\text{A2.2})$$

The experimental data can be used to give the average velocity, v , in the capillary, as a function of time. This can be used with Eqs. (A2.1b) and (A2.2) to evaluate η_{ap} and the “true” (or the corresponding) shear rate, $\dot{\gamma}$, to give a more accurate plot of η vs $\dot{\gamma}$.

REFERENCES

1. Tjahjadi, M., and S.K. Gupta, *Chem. Eng. Ed.*, **20**, 84 (1986)
2. Walawender, W.P., and T.Y. Chen, *Chem. Eng. Ed.*, **9**, 10 (1975)
3. Sather, G.A., and J. Coca, *Chem. Eng. Ed.*, **22**, 140 (1988)
4. Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, 2nd ed., John Wiley and Sons, New York, NY (2001)
5. Crosby, E.J., *Experiments in Transport Phenomena*, Department of Chemical Engineering, University of Wisconsin, Madison, WI (1961)
6. Kumar, A., and S.K. Gupta, *Fundamentals of Polymer Science and Engineering*, Tata McGraw Hill, New Delhi, India (1978)
7. McCabe, W.L., J.C. Smith, and P. Harriot, *Unit Operations of Chemical Engineering*, 5th ed., McGraw Hill, New York, NY (1993)
8. Bagley, E.B., *J. Appl. Phys.*, **28**, 624 (1957)
9. McKelvey, J.M., *Polymer Processing*, John Wiley and Sons, New York, NY (1962)
10. Dealy, J.M., and K.F. Wisbrun, *Melt Rheology and Its Role in Plastics Processing*, van Nostrand Reinhold, New York, NY (1990)
11. Zhang, J., J. Jenkins, B. Linden, and A. Kristopeit, *UW-Madison Transport Lab Memo*, Madison, WI (2000) □