22. Tennant, B. W., M.S. thesis, Illinois Inst. Technol., Chicago (1952).
23. Townsend, A. A., "The Structure of Turbulent Shear Flow," Cambridge Univ. Press, England (1956).
24. Tsuji, Hiroshi, *J. Phys. Soc. Japan*, **10**, 579 (1955).
25. Uberoi, M. S., and S. Corrsin, *Natl. Advisory Comm. Aeronaut Rept. 1142* (1953).
26. Vermeulen, Theodore, G. M. Williams, and G. E. Langlois, *Chem. Eng. Progr.*, **51**, 85F (1955).
27. von Karman, Theodore, and Leslie Howarth, *Proc. Roy. Soc.*, **A164**, 192 (1938).

Manuscript received November 25, 1964; revision received August 16, 1965; paper accepted August 19, 1965.

A Two-Way Capillary Viscometer

L. S. TZENTIS

Dow Chemical Company, Williamsburg, Virginia

A two-way capillary viscometer for measuring shear rates from <0.01 to $>1{,}000{,}000$ sec.$^{-1}$ at pressure drops up to 1,000 lb./sq.in. has been designed. It consists of a capillary tube mounted vertically between two sample reservoirs, of which the lower one is connected to a mercury manometer. The driving force, gas under pressure in a large tank, is connected to the upper reservoir and the manometer, thus allowing the sample to be moved in either direction through the capillary. The special feature of this viscometer is the indirect automatic measurement of bulk velocity of the fluid sample (3 to 20 cc.) in the capillary tube by means of a mercury manometer.

The precision of measurement of the velocity is one part in four hundred and can be maintained over the whole range of shear rates by the appropriate choice of the ratio of the diameter of the capillary and manometer tube.

Energy losses due to capillary heating and kinetic energy are given in terms of ΔP across the capillary. Couette end effect was found to be 0.3 diam.

A study of the rheology of polyacrylonitrile (PAN) in concentration range of ½ to 10½% PAN shows that the non-Newtonian behavior and elasticity of PAN solution increases rapidly with concentration.

Because of their simplicity, ease of operation, and construction, capillary viscometers have been popular since the days of Hagen and Poiseuille. Detailed information on the types and methods of correlating data for capillary viscometers is readily available (*1*, *2*).

In a capillary viscometer a steady state cannot be established instantaneously. The establishment in the capillary of the final velocity profile of a flowing fluid which is prerequisite for a steady state is delayed by several factors. All occur near or at the contraction made by the capillary joining the reservoir. They are viscous friction at the contraction; the change in kinetic energy of the moving stream entering the capillary; in the isothermal case, the establishment of equilibrium between heat released by friction and heat lost by conduction through the tube walls; and for a viscoelastic fluid, dissipation of energy required to change the shape of the fluid entering the capillary from the reservoir. Corrections for the above factors have to be applied to the data before the true relationship between shear stress and shear rate of the fluid can be established.

One usually avoids most of these corrections by working with capillaries of high L/D ratio to minimize the part of the capillary necessary for the establishment of final velocity profile and, at low shear stresses, to keep the generation of heat due to friction at a minimum. This is fine as long as use of fluids of high viscosities can be avoided. Unfortunately, this is not the case in many modern industries which use polymer solutions of high viscosities.

The two-way capillary viscometer was designed in 1960 in the James River Division of The Dow Chemical Company to investigate the rheological properties of polymer solutions of high viscosities over several decades of shear stress. As the name implies, the two-way capillary viscometer allows one to manipulate the fluid through the capillary in either direction, thus eliminating the need for large samples.

This type of viscometer has been in use since 1950. Westover (*3*) described a capillary rheometer consisting of two rams in opposition at the ends of a capillary with provision for operating at differential pressures up to 25,000 lb./sq. in.

Philippoff (*4*) designed a two-way capillary viscometer with the capillary situated horizontally between two reservoirs. Gas pressure was used to push the fluid alternately between the two reservoirs.

THE TWO-WAY CAPILLARY VISCOMETER

The viscometer, which is immersed in a fluid controlled to within 0.1°C., consists of two stainless steel cylindrical reservoirs (*A*) separated by a capillary (*B*). The reservoirs are screwed into two circular plates (*C*) held together by four screws (see Figure 1). Conical adapters (*D*) at the entrance to the reservoirs minimize entrapment of air bubbles.

The manometer (*E*), used in bulk velocity determination, which in turn is used to calculate the apparent shear rate, is made from a precision glass capillary held together with four aluminum rods (*F*) as shown in Figure 1. The design puts a minimum of strain on the tube, allowing operation at pressures up to 1,000 lb./sq. in. Two photoelectric cells at a fixed distance apart on the manometer tube are used with a mechanical timer and electromechanical clutch to determine flow time to within 0.001 sec. The distance between the photoelectric cells is determined to 0.01 cm. by means of a cathetometer.

METHOD OF OPERATION

The sample is introduced in the lower reservoir (*A*) of the viscometer, which is then assembled and connected to the manometer (*E*) and nitrogen supply (*J*) as shown in Figure

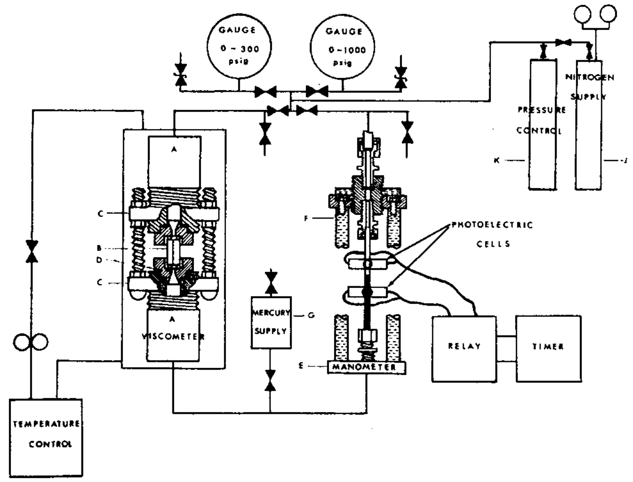

Fig. 1. Schematic diagram of the experimental setup.

1. Low pressure air is applied on the mercury (G), the manometer fluid in the experiment, to fill the manometer (F). The mercury supply (G) is cut off and part of the sample from the lower reservoir is transferred into the upper one by applying pressure on the manometer liquid. The procedure is repeated until about half of the sample is in the upper reservoir.

To minimize the contribution of the manometer liquid to the actual pressure difference across the capillary, the photoelectric cells are adjusted an equal distance above and below the point of hydrostatic equilibrium of the mercury in the manometer. The inset in Figure 2 shows the contribution of mercury to the applied shear stress and the resulting variation in the rate of shear. The cross represents shear stress as calculated from gauge pressure and average shear rate over 3 cm. The difference in shear stress between successive points obtained by means of a cathetometer and a stopwatch is equal to 1 cm. Hg.

To minimize pressure fluctuations, nitrogen (J), the pressure source in these experiments, is introduced into a pressure control tank (K) that has a volume much greater than the actual displacement. During a reading, the supply is cut off and the pressure control tank now at the desired pressure is connected to the viscometer. The pressure is indicated by means of two Heise gauges, range 0 to 300 to 0 to 1,000 lb./sq. in.

Readings are made by applying pressure on the sample in the upper reservoir (A) of the viscometer and by recording the time it takes to move the manometer liquid up through a fixed distance against atmospheric pressure. After each reading, pressure is applied on the mercury in the manometer and the sample is returned to its original position.

TIME ALLOWED BETWEEN READINGS

Following a high pressure reading, a few minutes are allowed between readings so that the heat generated due to frictional effects can be dissipated. The time to allow between readings is found readily from a repeat measurement. At equal stress, a higher velocity is indicated if insufficient time for dissipation of heat was allowed. In cases where the fluid is time dependent, or the sample undergoes chemical changes due to applied shear, an actual temperature measurement is necessary.

INSTRUMENTAL CONSTANTS

The viscometer reservoirs (A) have an I.D. of 0.500 in.; the conical adapters (D), a minimum diameter of 0.250 in. The I.D. of the manometer tube was 132.9 mils and the distance between the photoelectric tubes was ~4 cm. In all the precision capillaries used, the diameter was constant throughout the length. Capillaries of L/D less than 20 were platinum-gold, above that they were glass.

MATERIALS INVESTIGATED

Calibration of the viscometer was made with three Newtonian National Bureau of Standards calibrated oils.

Oil type	Viscosity, poise	Temperature, °C.	Density, g./cc.
H-13	0.06765	25	0.8304
I-14	0.1085	25	0.8339
P-20	419.9	30	0.8865

10.5, 2, and ½% PAN in a concentrated salt solution provided good examples of pseudoplastic fluids.

CORRELATION OF THE DATA

The Rabinowitsch-Mooney (5, 6) equation was used to correlate the data:

$$\left(-\frac{du}{dr}\right)_w = \frac{3}{4}\frac{8V}{D} + 1/4\frac{D\Delta P}{4L}\frac{d(8V/D)}{d(D\Delta P/4L)} \quad (1)$$

Metzner and Reed (7) rearranged this equation

$$\left(-\frac{du}{dr}\right)_w = \frac{3n+1}{4n}\frac{8V}{D} \quad (2)$$

where

$$n = \frac{d\left(\log\dfrac{D\Delta P}{4L}\right)}{d(\log 8V/D)} \quad (3)$$

Equation (2) is particularly well suited to correlate data for the two-way capillary viscometer which gives ΔP and V directly.

Figures 2 and 3 show the shear stress–apparent shear rate relationship for S. V. Oil P-20 and PAN solution as obtained with capillaries of different L/D ratios. The relationship between shear stress and rate of shear in Equation (1) is independent of instrumental constants; therefore, corrections have to be applied to the data obtained with different L/D ratios.

Four corrections will be analyzed: capillary heating, kinetic energy, and Couette and elastic effects. Other possible corrections including that for compressibility were judged much less important and are not treated here.

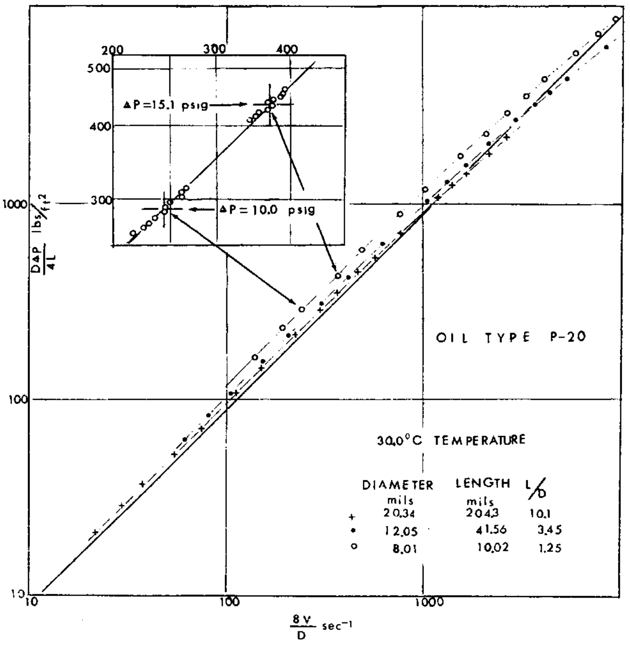

Fig. 2. Uncorrected data for oil P-20.

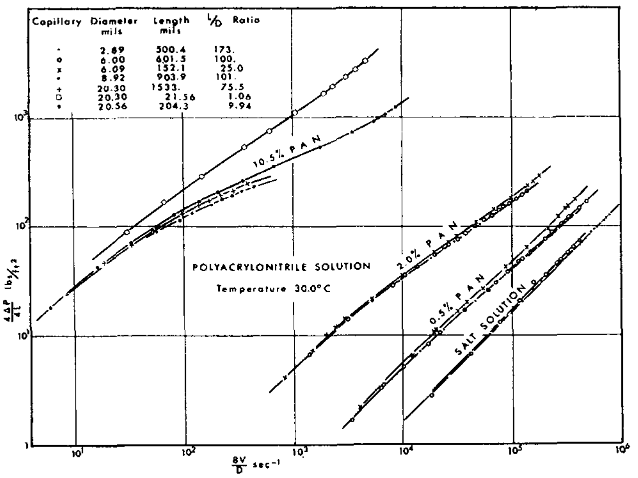

Fig. 3. Uncorrected data for PAN solutions.

CAPILLARY HEATING

Two assumptions will be made: the system is adiabatic, and kinetic energy effects are negligible when heating effects predominate.

The first assumption suggests that all the mechanical energy is converted into heat and none is dissipated through the walls of the capillary in the time interval of a reading. This is reasonable in view of the small L/D ratios in the case of the metal capillaries and insulating properties of the glass in the long ones. An alternative to this assumption would be an isothermal condition at the wall of the capillary. From Toor's (8) excellent treatment of this case, it is clear that even at the most favorable conditions L/D ratios of over 300 are necessary just to reach a steady state velocity profile for 10.5% PAN solution and S. V. Oil P-20.

Use of L/D ratios, above 300, with reasonably small capillary diameters, is not practical due to very high pressure drops that will be encountered with polymer solution of high viscosity at shear stresses of interest.

The second assumption, that of ignoring the kinetic energy when capillary heating predominates, is quite accurate for solutions of high viscosity. With the aid of Figure 5, it is easy to see how negligible the contribution of kinetic energy is when compared to the pressure drop required to achieve the particular shear rate in S. V. Oil P-20 or 10.5% PAN solution.

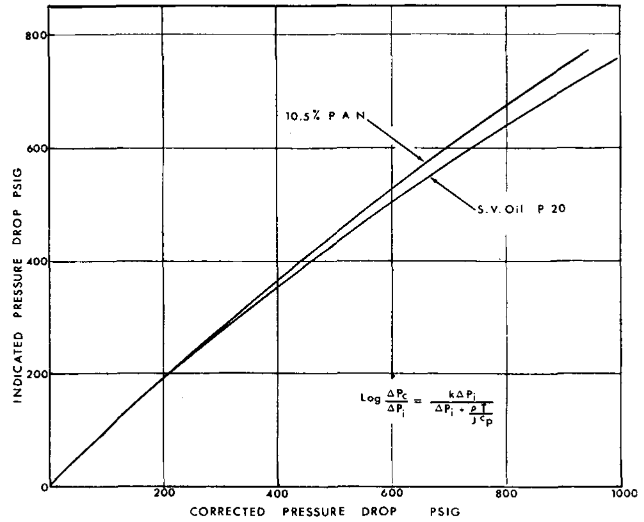

Fig. 4. Capillary heating in terms of pressure drop across the capillary tube.

From Bernoulli's theory for fluid flow

$$\int v dp - F = 0 \tag{4}$$

$$F = v\Delta P \tag{5}$$

if

$$F = QJ \text{ and } Q = c_p \Delta t \tag{6}$$

$$\Delta t = \frac{v\Delta p}{Jc_p} \tag{7}$$

The viscosity-temperature relationship in a narrow temperature range can be represented by

$$\log \mu = \frac{A}{T} + B \tag{8}$$

Conversion of mechanical energy into heat by molecular friction will raise the temperature of the fluid and decrease the viscosity. Labeling the decreased viscosity as μ_2 and the original viscosity as μ_1, one obtains

$$\log \mu_1 - \log \mu_2 = \frac{A}{T_1} - \frac{A}{T_2} = \frac{A(T_2 - T_1)}{T_1 T_2} \tag{9}$$

Substituting Equation (7) into (9) and simplifying further by noting that $T_2 = T_1 + \frac{v\Delta p_2}{Jc_p}$, one gets

$$\log \frac{\mu_1}{\mu_2} = \frac{Av\Delta p_2}{T_1\left(T_1 + \frac{v\Delta P_2}{Jc_p}\right)Jc_p} \tag{11}$$

We are interested here in the ΔP correction and not viscosity; therefore, since corrections will be made at constant shear rate, Equation (11) can be written as

$$\log \frac{\Delta P_1}{\Delta P_2} = \frac{Av\Delta P_2}{T_1\left(T_1 + \frac{v\Delta P_2}{Jc_p}\right)Jc_p} \tag{12}$$

For S. V. Oil P-20, A was determined to be 3404.8°C.$^{-1}$ and c_p was estimated from reference 9 to be 0.45 B.t.u./(lb.)(°F.).

At 30°C. the Equation for S. V. Oil P-20 reduces to

$$\log \frac{\Delta P_1}{\Delta P_2} = \frac{11.23\,\Delta P_2}{\Delta P_2 + 73.404} \tag{13}$$

For 10.5% PAN, A is 2256.8, $c_p = 0.50$, and at 30°C. Equation (12) becomes

$$\log \frac{\Delta P_1}{\Delta P_2} = \frac{7.44\,\Delta P_2}{\Delta P_2 + 66{,}000} \tag{14}$$

Equations (13) and (14) are represented graphically in Figure 4.

KINETIC ENERGY CORRECTION

The kinetic energy in units of pressure drop can be expressed as

$$\text{K. E.} = \frac{\rho V^2}{\alpha g_c} \tag{15}$$

but, since

$$V = \frac{(\text{S.R.})D}{8} \tag{16}$$

$$\text{K.E.} = \frac{\rho(\text{S.R.})^2 D^2}{64\, g_c\, \alpha} \tag{17}$$

where

$$\alpha = \frac{(4n+2)(5n+3)}{3(3n+1)^2} \text{ (reference } \mathit{10}) \qquad (18)$$

for Newtonian fluids $n = 1$ and $\alpha = 1$.

Figure 5 shows the kinetic energy correction as a function of shear rate with capillary diameter and fluid density as parameters.

COUETTE CORRECTION

Couette correction, otherwise known as the end effect, is due to converging stream lines at the entrance into the capillary, creating a region of excessive pressure drop. The correction can be determined in terms of capillary diameters by plotting the pressure drop vs. L/D ratio of several capillaries at constant rate of shear. S. V. oil P-20 data shown in Figure 2 were used to determine the Couette correction of 0.3 diam. This is in line with values reported by Oka (*11*).

ELASTICITY

The elasticity of the fluid can be expressed as a function of shear rate in terms of number of diameters that has to be added to the length of the capillary. This method, introduced by Bagley (*12*), is essentially that of Couette. The difference between the two methods is that the Couette correction is independent of shear rate (this was checked for the salt solution, an inelastic liquid, at shear rates up to 500,000 sec.$^{-1}$), whereas the elastic correction is a function of it (Figure 6).

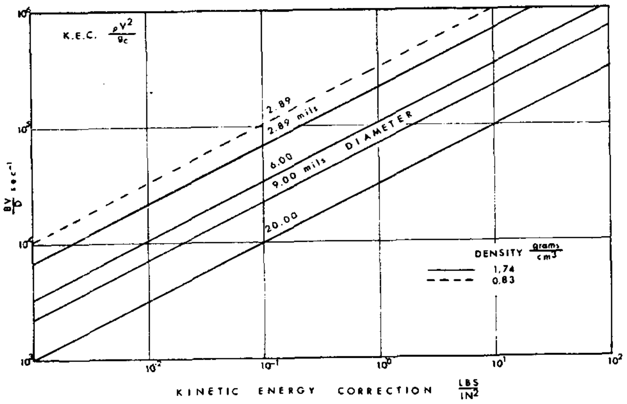

Fig. 5. Kinetic energy effects in terms of pressure drop across the capillary tube.

It is important to remember that it is necessary to correct the raw data for capillary heating and kinetic energy before determining the elastic correction. Values that are as much as twice as high can be attributed to the elasticity of the fluid if this is not done.

CALIBRATION OF THE VISCOMETER

The low viscosity calibration fluids H-13 and I-14 required only kinetic energy corrections which were quantitatively small. The reason for this is easily seen from Figure 5. The low density of the oils and the small diameter of the capillary used decrease the contribution of the K. E., which becomes an appreciable fraction of the total pressure drop only at shear rates above 100,000 sec.$^{-1}$. The Couette correction of 0.3 diam. was added to the length of the capillary. This correction was also very minor for the low viscosity fluids because of the high L/D ratio of the capillary.

The third oil, P-20, required both Couette and capillary heating corrections. Kinetic energy effects were negligible.

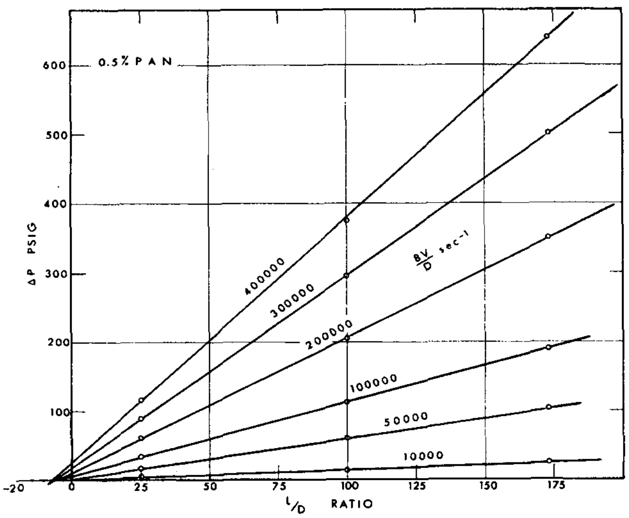

Fig. 6. Elasticity correction (*m*) for 0.5% PAN solutions.

The Couette correction is quite important in this case because of the low L/D ratio of the capillaries used. The capillary heating correction amounted to 25% of the pressure drop at 600 lb./sq. in. The corrected data fall on a single line as shown in Figure 8. Either the pseudoplastic behavior of the oil at higher shear stresses or the failure at these high shear stresses of the assumptions made concerning capillary heating is responsible for data deviating from 45-deg. line around a shear rate of 3,000 sec.$^{-1}$

The actual Newtonian viscosity of oil P-20 indicated by the data is ~ 7.5% higher than the calibration value of 419.9 poise at 30°C. This difference is probably due to the age of the sample used (about 2 yr.).

None of the three types of oil showed elastic effects.

RHEOLOGY OF PAN

As far as corrections for PAN in a salt solution were concerned, the data fell into two categories: the dilute solution of (½ and 2% PAN) where kinetic effects predominated, and the concentrated solution (10.5% PAN) where capillary heating effects were dominant.

The data from capillaries of different L/D ratio corrected for capillary heating, kinetic energy, Couette, and elasticity did indeed fall on unified lines as shown in Figure 7. The slopes of the curves in Figure 7 are the pseudoplasticity constants, which were used to determine the

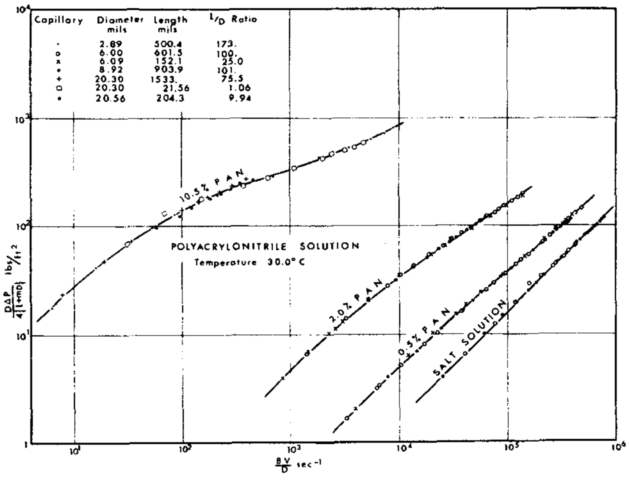

Fig. 7. Shear stress–apparent shear rate for PAN solutions.

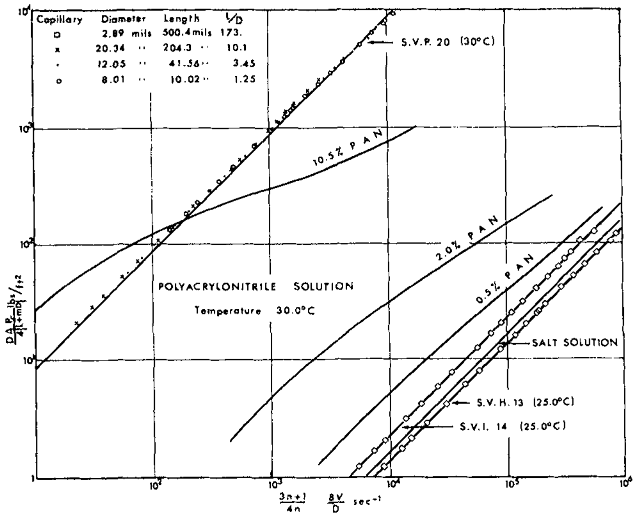

Fig. 8. Shear stress at the wall–shear rate at the wall for S.V. oils and PAN solutions.

relationship between shear stress at the wall with shear rate at the wall for PAN solution (Figure 8). Finally, the pseudoplasticity constant and the elastic correction for the above solution are shown as functions of shear rate in Figure 9.

CONCLUSIONS

Only at low shear stress and shear rates do the uncorrected data from capillary viscometers represent the true rheological behavior of the fluid. Corrections for capillary heating of high viscosity fluids at high shear stress, kinetic energy at high shear rates, Couette end effect for low L/D ratio capillaries, and entrance effects for elastic fluids are necessary if the true relationship between stress and rate of shear over several decades is desired. In this paper, convenient methods for applying the above corrections to data from capillary viscometers are given.

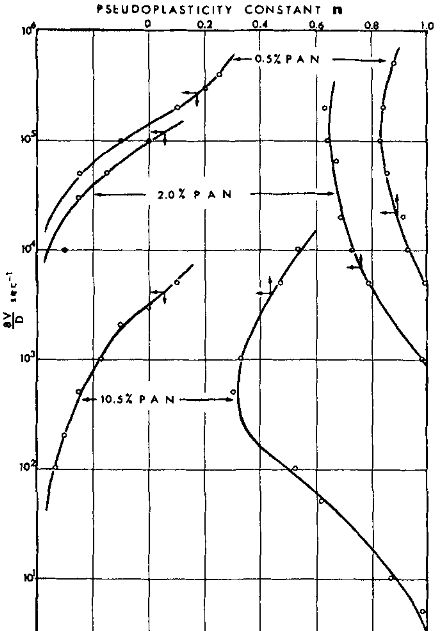

Fig. 9. Elastic correction and pseudoplasticity constant as a function of shear rate for PAN solutions.

The two-way capillary viscometer has been shown to be a suitable instrument for investigation of rheological properties of both Newtonian and non-Newtonian liquids of low and high viscosity over many decades of shear rate. The novel feature of the viscometer, a mercury manometer, allows one to measure automatically, with a precision of one part in four hundred, the bulk velocity of the fluid sample over a wide range of shear rate.

ACKNOWLEDGMENT

The author is indebted to R. D. Crozier for moral support and many helpful suggestions.

NOTATION

A = constant, °C.
B = constant
C_p = specific heat at constant pressure, B.t.u./(lb.$_m$) (°F.)
D = diameter of capillary, mil
F = frictional force, lb.$_f$
g_c = dimensional conversion factor, 32.2 (ft.)(lb.$_m$)/sec.^{2}) (lb.$_f$)
K.E. = kinetic energy
K.E.C. = kinetic energy correction, lb./sq. in. gauge
L = length of the capillary, mil
J = mechanical equivalent of heat, (ft.)(lb.)/B.t.u.
m = elastic correction in equivalent diameters of the capillary
n = pseudoplasticity constant
ΔP = total pressure drop across capillary, lb./sq. in. gauge
ΔP_c = pressure drop corrected, lb./sq. in. gauge
ΔP_i = pressure drop indicated, lb./sq. in. gauge
Q = heat, B.t.u./(lb.$_m$)
S.R. = bulk shear rate, sec.$^{-1}$
S.S. = shear stress, lb./sq. ft.
t = temperature, °C.
T = absolute temperature, °K.
$\left.\frac{du}{dr}\right|_w$ = shear rate at the wall, sec.$^{-1}$
v = specific volume, cc./g.
V = bulk velocity, cm./sec.
α = function of n
ρ = density, g./cc.
μ = viscosity, poise

LITERATURE CITED

1. Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," Interscience, New York (1963).
2. Reiner, Marcus, "Deformation, Strain and Flow," Interscience, New York (1960).
3. Westover, R. F., *SPE Tech. Paper 6, Paper 80* (1950).
4. Phillipoff, Wladimir, *Trans. Am. Soc. Lubricating Engrs.*, **1**, 82 (1958).
5. Rabinowitsch, B., *Z. Phys. Chem.*, **A145** (1929).
6. Mooney, Melvin, *J. Rheol.*, **2**, 2 (April, 1931).
7. Metzner, A. B., and J. C. Reed, *A.I.Ch.E. J.*, **1**, 434 (1955).
8. Toor, H. L., *Trans. Soc. Rheol.*, **1** (1957).
9. "Natural Gasoline Supply Men's Association Engineering Data Book," 6 ed., p. 133, Tulsa, Okla. (1951).
10. Metzner, A. B., "Advances in Chemical Engineering," Vol. 1, Academic Press, New York (1956).
11. Oka, S., "Rheology,' Vol. 3, F. R. Eirinch, ed., Academic Press, New York (1960).
12. Bagley, E. B., *J. Appl. Phys.*, **28**, 5 (May, 1957).

Manuscript received March 22, 1965; revision received August 5, 1965; paper accepted August 9, 1965.