

Res. Lab. Reprint
1775

GENERAL  **ELECTRIC**
Research Laboratory

EMPERICAL ANALYSIS OF VISCOSITY DATA

By

H. TRACY HALL AND RAYMOND M. FOUSS

SCHENECTADY, NEW YORK

RES. LAB. REPRINT 1775

[Reprinted from the Journal of the American Chemical Society, **73**, 265 (1951).]
 Copyright 1951 by the American Chemical Society and reprinted by permission of the copyright owner.

[Contribution From The Research Laboratory Of The General Electric Company]

Empirical Analysis of Viscosity Dataⁱ

By H. TRACY HALL AND RAYMOND M. FOUSSⁱⁱ

Introduction

The capillary viscometer is essentially a device in which a volume V of liquid flows through a capillary of length l and radius R in t seconds under a pressure of p g./cm.². Using Poiseuille's equation, we may calculate the viscosity η (in poises) by the relationship

$$\eta = \pi gpR^4t/8Vl \quad (1)$$

For a given viscometer, the product pt should be constant if (1) is satisfied; actually, as is well known, the product usually increases as the driving pressure decreases. Three effects, inherent in the design of the viscometer, contribute to this variation: (1) all of the work done by the driving pressure is not dissipated as heat in overcoming viscous friction; (2) flow near the ends of the capillary is not laminar; (3) the volume of liquid which flows from the bulb is not the volume of the dry bulb. Of these, the first is usually the largest correction term for ordinary liquids ($\eta \approx 10^{-2}$) in conventional viscometers. If correction is made for these instrument effects, and the pt product still varies with driving pressure, then we may conclude that the liquid is non-Newtonian, i.e., that $\eta = \eta(p)$. For the usual range of driving pressures (giving average velocity gradients of the order of 10^3 seconds⁻¹), $1/pt$ is linear in p over a much wider range of variables than that corresponding to linearity of pt in $1/t$. We present in this paper an empirical analysis of viscosity data, which permits isolation of the shear-dependent term of the viscosity.

Kinetic Energy and End Effect Corrections.—The liquid leaving the viscometer capillary is travelling with finite velocity; therefore, only part of the work done by the driving pressure overcomes viscous friction within the capillary. The corresponding correction has been accordingly called the

kinetic energy correction. Wilberforce¹ made an important correction to Hagenbach's² first estimate of this quantity and also made an estimate of the end effects on Reynolds's³ analysis of the transition from laminar to turbulent flow. Wilberforce's result may be written

$$\eta = \pi gpR^4t/8Vl - m_p V/8\pi lt \quad (2)$$

$$= \alpha pt - \beta/t \quad (2')$$

If the constant m were unity, the second term on the right then would be the kinetic energy correction, calculated on the assumption that the flow throughout the length of the capillary were laminar; i.e., $m = 1$ corresponds to the case of negligible end effects. Ample experimental evidence shows that, while m is near unity, its actual value is somewhat greater. In other words, practical viscometers have end effects which may not be neglected. A precise calculation of m (or its equivalent) would involve the integration of the Navier-Stokes equation with almost hopelessly complicated boundary conditions. It seems preferable, therefore, to accept (2) as the summary of much experimental evidence and to proceed from this equation as our starting point.

We may consider Equation (2) as a quadratic in $(1/t)$ with the solution

$$1/t = (\eta/2\beta)[(1 + 4\alpha\beta p/\eta^2)1/2 - 1] \quad (3)$$

The variable in the radical is to a close approximation $m_p V/2\pi l\eta t$, which is about $6/t$ for $m \approx 1$, $p \approx 1$, $V = 4$, $l = 10$, $\eta \approx 0.01$. For ordinary work, therefore, we may expand the radical and drop cubic and higher terms; to this approximation

$$1/t = \alpha p/\eta - \alpha^2\beta p^2/\eta^3 \quad (3')$$

¹ L. R. Wilberforce, *Phil. Mag.*, 31, 407 (1891); cf. also G. Barr "Monograph on Viscometry," Oxford University Press, London, 1931, p. 16.

² E. Hagenbach, *Pogg. Ann.*, 109, 385 (1860).

³ O. Reynolds, *Phil. Trans.*, 174, 935 (1883).

which immediately leads to the alternative form of (2)

$$1/pt = (\pi g R^4 / 8 V l \eta) - (\pi g^2 R^8 m \rho p / 8^3 V l^3 \eta^3) \quad (4)$$

$$= I - Sp = A/\eta - A' \rho p / \eta^3 \quad (4')$$

Equation (4) states that a Newtonian liquid in a viscometer which needs correction for kinetic energy and end effects will give pt reciprocals linear in the driving pressure; *i.e.*, apparent fluidity is linear in p , and the true value of $1/\eta$ is obtained by extrapolating $(1/pt)$ to zero pressure and dividing by the instrument constant A . This in turn is evaluated by calibration with liquids of known viscosity. Water is usually taken as the standard, with $\eta = 0.008929$ at 25.00° .

Drainage Correction.—Equation (4) was derived on the tacit assumption that V was equal to V_0 , the volume of the dry bulb. This value is correct, if we run into a dry bulb, as recommended by Swindells⁴; if a filled bulb is being drained, however, allowance must be made for the liquid which remains in the bulb, wetting the walls.⁵ We expect the volume of this liquid to be given by

$$\Delta V = a\eta/\rho t \quad (5)$$

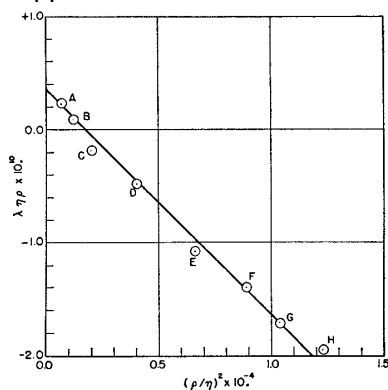


Fig. 1.—Test of Eq. (8): (A) 36.6% of sucrose in water, (B) 32.2% sucrose, (C) 27.7% sucrose, (D) 19.6% sucrose, (E) 91.6 wt. % nitrobenzene in methanol, (F) 80.7 wt. % nitrobenzene in methanol, (G) 72.8 wt. % nitrobenzene in methanol, (H) water.

where a is an empirical constant depending on the geometry of the viscometer bulb. (It may also depend on surface tension of the liquid, but we have insufficient evidence at present to decide this point.) Correcting (1) for ΔV , we see that the coefficient A of (4') becomes

$$A = k/V = k/(V_0 - \Delta V) \quad (6)$$

where V is the volume of liquid which actually passes through the capillary in t sec. Substituting (6) in (4') and dropping higher terms, we obtain

$$1/pt = A/\eta - (A' \rho / \eta^3 - aA^2 / \rho V_0 \eta) p \quad (7)$$

$$= A/\eta - \Lambda p \quad (7')$$

where A now means, $\pi g R^4 / 8 V_0 l$.

Comparison with Experiment.—It will be seen that the slope of the $(1/pt)-p$ plot is made up of two terms of opposite sign, each of which depends explicitly on the viscosity of the test liquid. For liquids of increasing viscosity, therefore, we would expect a reversal of the sign of the slope at high viscosities, when the drainage correction exceeds the Wilberforce correction. This has been observed experimentally, for a series of sucrose-water and nitrobenzene-methanol mixtures, by W. N. Maclay of Yale University, who has kindly made his data available to us. The most direct test of Equation (7) is obtained as follows: we multiply the coefficient Λ by $\eta \rho$ and obtain

$$-\Lambda \eta \rho = aA^2 V_0 - A' (\rho / \eta)^2 \quad (8)$$

In Fig. 1, we show a plot of Maclay's slopes (multiplied by $\eta \rho$) as a function of $(\rho / \eta)^2$. It will be seen that the points average to a straight line as required by Equation (8). From the intercept at $(\rho / \eta)^2 = 0$, we obtain the drainage correction, and from the slope, the Wilberforce coefficient may be evaluated.

It will be noted that a knowledge of the viscosity was necessary in order to carry out the test shown in Fig. 1. Having used these data to determine the (small) drainage correction, we may now test Equation (4) in a completely empirical fashion. In the form (4'), Equation (4) states that the $(1/pt)-p$ plot is linear with intercept I at $p = 0$ and with slope S (assuming no drainage). We may use the result of the extrapolation in Fig. 1 to correct the observed slopes to give values of S

$$S = \Lambda + aA^2 V_0 / \eta \rho \quad (9)$$

The viscosity is readily eliminated between I and S giving

$$I = A(S/A'p)^{1/3} \quad (10)$$

A plot of $\log I$ against $\log S/p$ is shown in Fig. 2 for a variety of systems; the straight line was drawn with a slope of one-third. It will be seen that the points conform closely to the result expected from Equation (10).

Using the Wilberforce values of I and S , as given in Equation (4) to eliminate R , we obtain the equation

$$\rho / \eta = (8\pi l / m V_0) (S / I^2) \quad (11)$$

⁴ J. F. Swindells, *J. Colloid Sci.*, 2, 183 (1947).

⁵ G. Jones and R. E. Stauffer, *THIS JOURNAL*, 59, 1630 (1937); R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, 4, 97 (1949).

In Fig. 3, ρ/η is plotted against S/l^2 . The points may be averaged by a straight line through the origin, from which we obtain $m = 1.15$ for $l = 11.0$ cm. and $V_0 = 4.02$ cc. It should perhaps be mentioned that the scattering of the points in

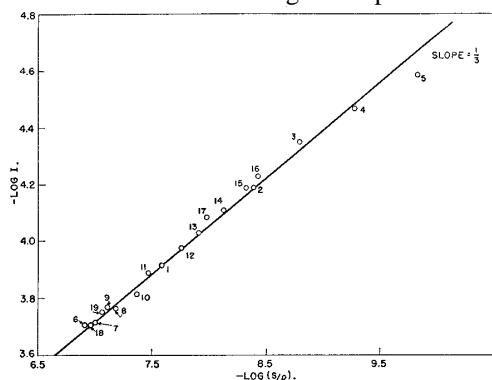


Fig. 2.—Plot of $\log l$ vs. $\log S/\rho$ for various liquids: 1, H_2O ; 2, 19.6% sucrose; 3, 27.7% sucrose; 4, 32.3% sucrose; 5, 36.6% sucrose; 6, MeOH; 7, 5.4% $PhNO_2$ in MeOH; 8, 22.5% $PhNO_2$ in MeOH; 9, 24.5% $PhNO_2$ in MeOH; 10, 38.6% $PhNO_2$ in MeOH; 11, 55.6% $PhNO_2$ in MeOH; 12, 72.8% $PhNO_2$ in MeOH; 13, 80.7% $PhNO_2$ in MeOH; 14, 91.6% $PhNO_2$ in MeOH; 15, 98.0% $PhNO_2$ in MeOH; 16, $PhNO_2$; 17, EtOH; 18, PhMe; 19, $MeNO_2$.

Fig. 3 is within the experimental error of determining a slope, where the total change in apparent viscosity over our pressure range was of the order of only one per cent.

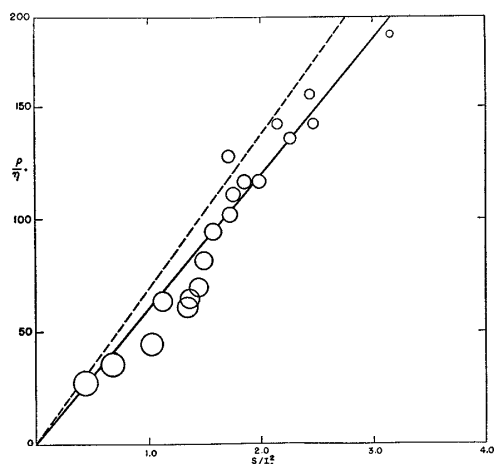


Fig. 3.—Test of Equation (11): dotted line, $m = 1$.

Structural Viscosity.—Solutions of polymers, especially at higher concentrations or at high molecular weights, or when the polymer carries an electrostatic charge, usually show a dependence of apparent viscosity on the rate of shear.⁶⁷ Extrapolation to zero rate of shear on the Bingham plot is generally impossible, because the pt -($1/t$) plots are frequently curved. However

($1/pt$)- p curves for several systems investigated are linear. We are indebted to R. A. Mock of the Sterling Chemistry Laboratory of Yale University for the data of Fig. 4, which gives the ($1/pt$)- p plots for a series of solutions of polyvinylpyridine in methanol. The polymer has a molecular weight of the order of 10^6 . Its intrinsic viscosity $[\eta]$ equals 4.5. As will be seen, the data fall on straight lines for all the systems and we may extrapolate to $p = 0$, thus obtaining viscosity values characteristic of the polymer and independent of the viscometer.

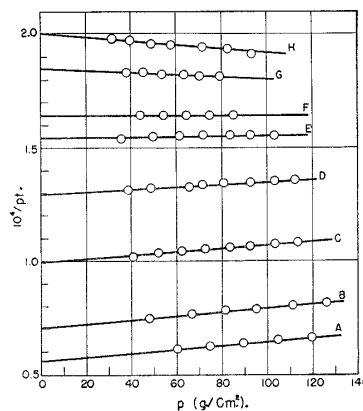


Fig. 4.—($1/pt$)- p plots for a series of solutions of polyvinylpyridine in methanol. The concentration of polyvinylpyridine in g./100 ml. is as follows: (A) 0.3378, (B) 0.2637, (C) 0.1678, (D) 0.0979, (E) 0.0593, (F) 0.0452, (G) 0.0184, (H) 0.0000.

Still more important, we may now use Eq. (7) to obtain some information regarding the dependence of viscosity of polymers on rate of shear. Suppose we assume that Eq. (7) gives the dependence of apparent viscosity on pressure as far as drainage, end effect and kinetic energy corrections are concerned. Then any remaining dependence must be due to change of polymer viscosity increment with rate of shear. A test of this hypothesis is shown in Fig. 5. The dotted line is the ideal dependence of $\Delta\eta\rho$ on $(\rho/\eta)^2$ obtained by our calibration liquids. The circles show the dependence of the observed $S\eta\rho$ products for the polymer solutions of Fig. 4, where S is the slope from this figure. The difference between observed and ideal slopes will, by hypothesis, depend on change with pressure of the contribution of the solute to viscosity.

We now proceed to an analysis of this proposal. Let z be the reduced viscosity

$$(\eta - \eta_0)/\eta_0 = (\eta_r - 1) = \eta_{sp} = zc \quad (12)$$

where η is solution viscosity at pressure p and concentration c , η_0 is solvent viscosity, η_r is relative viscosity and η_{sp} is specific viscosity. Let z_∞ represent the reduced viscosity at

⁶ H. Mark, J. Appl. Phys., 12, 41 (1941).

⁷ R. M. Fuoss and U. P. Strauss, Ann. N. Y. Acad. Sci., 51, 836 (1949).

concentration c at zero rate of shear (zero pressure or infinite time). To avoid double subscripts, let j be the limit approached by the relative viscosity at zero rate of shear

$$j = \lim (\eta_r)_{P=0} = \eta_\infty/\eta_0 \quad (13)$$

so that $j - 1 = z_\infty c$. Let η_∞ be the solution viscosity at the same limit. Now the contribution of the polymer to solution viscosity will be expected to change with changing velocity

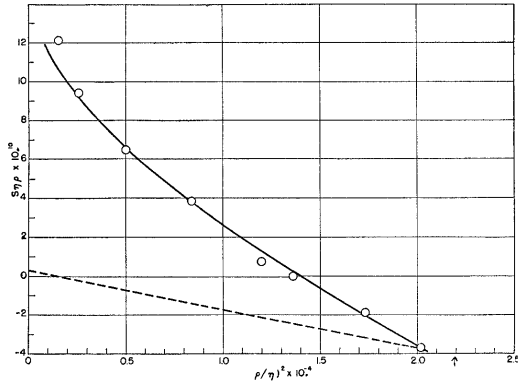


Fig. 5.—The dependence of the observed $S\eta\rho$ products on $(\rho/\eta)^2$ for the polymer solutions of Fig. 4 where S is the slope from this figure. The dotted line is the ideal dependence of $\lambda\eta\rho$ on $(\eta/\rho)^2$ i.e., as far as drainage and kinetic energy corrections are concerned.

gradient, which is, in turn, proportional to driving pressure. High rates of shear could both elongate the polymer coil and orient the ellipsoid hydrodynamically equivalent to the coil, which would tend to decrease viscosity; we, therefore, make the assumption that in first approximation

$$z = z(p) = z_\infty (1 - kp) \quad (14)$$

where k is an arbitrary constant. From (12)

$$\eta = \eta_0 (1 + zc)$$

Substituting (14) into the above expression, and using the abbreviations defined in the preceding paragraph, we find

$$\eta = \eta_\infty (1 - [j - 1] kp/j) \quad (15)$$

Approximating $(1 - x)^{-1}$ as $(1 + x)$ in the equation for reciprocal viscosity, we obtain

$$\begin{aligned} 1/pt &= A_0/\eta - \Lambda p \\ &= A_0/\eta_\infty - \Lambda p + (A_0 q k/\eta_0) p \end{aligned} \quad (16)$$

where

$$q = (j - 1)/j^2 \quad (17)$$

Eq. (16) is of the form

$$1/pt = A_0/\eta_\infty + (k - \Lambda)p \quad (18)$$

where

$$K = A_0 q k/\eta_0. \quad (19)$$

In other words, a polymer solution which is non-Newtonian will give in first approximation a linear $(1/pt)-p$ plot with a slope dependent on concentration and molecular weight. The test of our assumption is to see whether the dependence of the slopes of Fig. 4 on concentration is given by Eq. (19); $q = q(C)$ by definition. The

experimental values of K are obtained by correcting the observed slopes S for drainage, end effects and kinetic energy according to Eq. (7). These corrections are read off the dotted line of Fig. 5. We then plot the values of K against Aq/η_0 where experimental extrapolated values of j (cf. Eq. (13)) were used to compute q by means of Eq. (17). The points of Fig. 6 lie on a straight line through the origin and from the slope we find for the shear coefficient $k = 1.67 \times 10^{-3}$. For a polystyrene with molecular weight 670,000 and intrinsic viscosity 2.27 in toluene, $k = 0.36 \times 10^{-3}$. For the latter material, measurement of viscosity in an Ostwald viscometer, where the average driving pressure is about 10 g./sq. cm., would give an apparent viscosity which was 0.36% too low (if shear dependence of solute viscosity were the only cause of apparent variation of viscosity with pressure).

We may now reverse the procedure, having a numerical value for k , and compute theoretical $S\rho\eta$ values for the systems of Fig. 4. The solid curve of Fig. 5 is computed on the basis of a single arbitrary constant k . The curve reproduces the observed values well within the experimental error of determining slopes from point-wise data.

As implied above, the slopes depend both on concentration and on molecular weight, because

$$z_\infty = [\eta] + k'[\eta]^2 c, \quad (20)$$

and

$$[\eta] = KM\alpha \quad (21)$$

By extrapolating $(1/pt)-p$ plots to zero pressure, we obtain reduced viscosities which are characteristic of the polymer molecule at rest. It should be emphasized that these are the values which should be extrapolated to zero concentration in order to obtain a true intrinsic viscosity which will be independent of the conditions of the viscosity measurements.

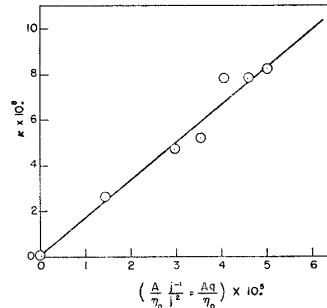


Fig. 6.—Experimental test of Eq. (19): data obtained from Fig. 4.

The shear constant k of Eq. (14) is, of course, an apparatus constant, because a given pressure produces a smaller velocity gradient in a

smaller capillary for given V , l and η , since the flow time is increased (Table I of Ref. 9). If we combine Kroepelin's formula⁸ for the average velocity gradient β in a capillary

$$\beta = 8V/3\pi R^3 \quad (22)$$

with Eq. (1), we have, to an approximation accurate enough for a correction term

$$p = 3l\eta\beta/gr \quad (23)$$

and Eq. (14) becomes

$$z = z_\infty (1 - 3kl\eta\beta/gr) = z_\infty (1 - s\beta) \quad (24)$$

where the shear constant s , defined as change of reduced viscosity with velocity gradient, is seen to be

$$s = (3l\eta/gr)k \quad (25)$$

Summary

1. The Wilberforce equation, which includes kinetic energy and end effect corrections for capillary viscometers, can be rearranged to an equation in which apparent fluidity is linear in driving pressure. An additional term, also linear in pressure, is produced by drainage errors. A method is described for the experimental evaluation of these corrections.

2. Polystyrene and polyvinylpyridine solutions exhibit a fluidity which varies linearly with pressure, after the above corrections have been made. This residual variation is ascribed to a distortion and/or orientation of the polymer molecule. Analysis of the data permits description of the shear dependence in terms of a single arbitrary constant k , the shear constant. At a pressure p , the intrinsic viscosity of a polymer is

$$[\eta] \propto (1 - kp)$$

SCHENECTADY, NEW YORK

RECEIVED MAY 9, 1950

ⁱ Presented at the Schenectady Meeting of the National Academy of Sciences, October 1950.

ⁱⁱ Yale University, New Haven, Conn.

⁸ H. Kroepelin, Kolloid Z. 47, 294 (1929).